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**GEOLOGICAL AND MEDICAL SCIENCES
FOR A SAFER ENVIRONMENT**

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Volume 2



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PREFACE

This volume contains the abstract of the scientific contributions presented to GeoMed2011, the 4th International Conference on Medical Geology, held in Bari (Italy) from 20 to 25 September 2011. The meeting was organized by *the Italian Chapter of the International Medical Geology Association (IMGGA)* and the *Associazione Italiana per lo Studio delle Argille – onlus (AISA, the Italian Association for the Study of Clays)*, on behalf of the IMGGA). Part I includes the contributions submitted as oral presentations, Part II includes the poster contributions.

The scientific program of the meeting included 4 plenary lectures, 148 oral and 119 poster contributions. All the contributions were revised by 74 international experts, many of them being the conveners of the 20 sessions dealing with the five themes of the Conference: *Biominerals & Biomaterials; Environmental Toxicology & Epidemiology; Minerals & Environment; Air, Soil & Water Pollution & Quality; Risk Assessment & Communication*. Our sincere thanks go to these colleagues who devoted their time to the GeoMed2011.

Our heartfelt thanks go to the many people who worked hard to organize the scientific and social events as well as to the Institutions and business enterprises which supported the meeting. We owe a special thank-you to the delegates, more than 230 coming from 49 Countries, who contributed to make this meeting of the International Medical Geology Association a memorable event.

Saverio Fiore
Chair, GeoMed2011

PLENARY LECTURES

HEALTH AND EARTH MEDICAL GEOLOGY BUILDING A SAFER ENVIRONMENT

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Emerging diseases commonly present the medical community with many difficult problems. In addition, emerging disciplines may offer the medical community new opportunities to address a range of health problems. One such emerging discipline is Medical Geology.1-4 Medical Geology can be considered as a complement of environmental medicine dealing with the impacts of the natural geologic materials and processes (that is, the natural environment) on the incidence and spatial/temporal distributions of human (and other animal) diseases. As one of the selected topics highlighted during the International Year of Planet Earth (2007-2009), medical geology is aimed at improving interdisciplinary interactions among earth and public health scientists, providing the basis for innovative and exciting research that can lead to new discoveries and greater knowledge. Among the environmental health problems that medical scientists are working with the geosciences community are: exposure to toxic levels of trace elements such as arsenic, cadmium, mercury and uranium; trace element deficiencies; exposure to natural dusts and to radioactivity, and naturally occurring organic compounds in drinking water. Analytical characterization of naturally-occurring trace elements and toxic organic compounds in ground water is helping to explain patterns of diseases such as arseniasis, fluorosis, and Balkan Endemic Nephropathy – a condition leading to end-stage kidney failure. Satellites and geographic information systems are being used to monitor the movement of large dust clouds moving across oceans carrying toxic metals and pathogenic microbes that may kill coral and may cause asthma. Regionally, dust exposure can affect broad regions such as the dust stirred up by earthquakes in the arid regions of the southwestern U.S. and northern Mexico. This dust carries spores of a fungus (*Coccidioides immitus*) that cause Valley Fever, a potentially fatal respiratory condition. Although the consequences of this type of exposure are not fully understood, modern medical and environmental techniques offer promise of developing innovative solutions to prevent or minimize exposure to potentially deleterious natural environmental pollutants and processes. In this presentation, we provide an overview and examples of some of the health problems being addressed by medical geologists dealing with exposure to natural materials and environmental processes.

Keywords: health, Earth, Medical Geology

ARSENIC IN DRINKING WATER CAUSES MULTIPLE HEALTH HAZARDS: AN EMERGING ENVIRONMENTAL PANDEMIC

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Arsenic is a ubiquitous element in the crust of the earth. It is transported in the environment mainly by water. Although arsenic is one of the oldest poisons identified and used in ancient time, the systemic health hazards of long-term exposure to arsenic in drinking water have been intensively investigated only since 1960s. Arsenic in drinking water has been well documented to cause multiple health hazards including characteristic skin lesions (hyperpigmentation and/or depigmentation, palmar hyperkeratosis, Bowen's disease and skin cancers), blackfoot disease, ischemic heart disease, cerebral infarction, peripheral vascular disease, microvascular diseases, abnormal peripheral microcirculation, carotid atherosclerosis, QT prolongation in electrocardiography, hypertension, goiter, diabetes mellitus, posterior subcapsular lens opacity, pterygium, slow neural conduction, retarded neurobehavioral development, erectile dysfunction, as well as cancers of the lung, kidney, bladder, liver and prostate. Several biomarkers of susceptibility to arsenic-induced health effects have been identified. They include arsenic methylation capability, folate and carotenoids intake, and genetic polymorphisms of enzymes involved in xenobiotic metabolism, DNA repair, and oxidative stress. Further exploration of gene-environment and gene-gene interactions on the development of arsenic-induced health hazards is in urgent need. The cancer risk associated with arsenic in drinking water in Taiwan has been analyzed to set up the maximal contamination level of arsenic in drinking water by the World Health Organization and Environment Protection Agency of the USA. According to the WHO Guidelines for Drinking-Water Quality, 0.01 mg/L was established as a provisional guideline value for arsenic. The guideline is intended for use as a basis for the development of national standards in the context of local environmental, social, economic, and cultural conditions. Due to the rapid growth of human population, severe surface water pollution, global warming and climate change, more and more world populations are using groundwater as the main drinking water source. The global disease burden of chronic arsenic poisoning from drinking groundwater has significantly expanded from few confined endemic areas to a pandemic environmental calamity all over the world in the late 20th century. The number of victims exposed to arsenic from drinking water is rapidly increasing. Hundreds of millions of people are living in areas where the arsenic content in drinking water exceeds the maximal contamination level recommended by the World Health Organization.

Keywords: arsenic, drinking water, cancer

ANTIBACTERIAL CLAYS AND THEIR POTENTIAL FOR MEDICINAL APPLICATIONS

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In this era when many bacteria have developed antibiotic resistance, and may produce more harmful toxins as a defense mechanism (e.g. Shiga-toxin), investigation of natural alternative antibacterials is of paramount importance. Natural clays have been used for healing since the earliest recorded history, but their medicinal properties have largely not been scientifically recognized. Medicinal and therapeutic uses of clays have been documented based on the extraordinary absorptive/adsorptive properties of clay minerals and the health benefits recognized in aiding digestive processes or cleansing and protecting the skin. Kaolins adhere to the gastrointestinal mucosa as a protective coating, or absorb and rid the body of dissolved toxins, bacteria, and viruses. While the ability to absorb water and organic matter is a common attribute of many smectites, certain clays were identified that do not physically adhere to bacteria, but are antibacterial against a broad spectrum of human pathogens including antibiotic resistant strains. French green clays (rich in Fe-smectite) were used clinically for healing Buruli ulcer, a necrotizing fasciitis ('flesh-eating' infection) caused by *Mycobacterium ulcerans*. Clinical work by Line Brunet de Courssou (Williams et al., 2004) highlighted the potential medicinal use for natural clays. Since then other clay deposits have been identified containing minerals that are bactericidal. These clays are important because they may reveal an alternative antibacterial mechanism to those commonly employed by antibiotics, leading to an economical treatment for skin infections, especially in global areas with limited hospitals and medical resources.

Analysis of the chemical interaction occurring at the clay mineral - bacterial interface is being explored and will be pertinent in understanding the mechanism by which the clay minerals can inhibit bacterial growth. Initial investigations show that various natural clays can have no effect on microbial growth, enhance microbial growth or completely inhibit growth. Therefore, it is important to identify the common components of natural clays that exhibit an antibacterial effect.

A comparison was made of the depositional environments, mineralogies and chemistries of several antibacterial clays that kill a broad spectrum of human pathogens. Results suggest that bactericide results from a chemical reaction, which may disrupt an essential physiological function of the bacteria. Common properties of the antibacterial clays include:

- (1) Natural antibacterial clays contain nano-scale (<200 nm) illite-smectite crystals, which provide an extensive and reactive surface for biogeochemical interactions.
- (2) Each clay contains minerals with reduced Fe and other transition metals that may play a role in the antibacterial process by producing reactive oxygen or nitrogen or sulfur species that potentially degrade organic components critical to cell survival.
- (3) The antibacterial agent is soluble at extreme pH (<4 or >10) and low oxidation state.
- (4) There is no physical attraction of the clay to bacteria, and without water there is no antibacterial effect. Therefore the antibacterial mechanism involves solution components and chemical reactions affecting the cell wall or metabolic functions.

(5) Aqueous clay leachates are antibacterial initially, but lose their effect on bacteria as the solution becomes oxidized. This points to an important role of the clay in buffering the solution chemistry to conditions that promote solubility of transition metals involved in the antibacterial reaction.

Experiments were conducted using *E. coli* grown to log phase (10^7 cells/cfu) in Luria broth, then rinsed and treated with the aqueous leachate of antibacterial clay. After 24 hrs, the bacteria were prepared by rinsing one aliquot in distilled-deionized water and another in EDTA-oxalate solution, which removes metals from the exterior cell envelope. Chemical analyses of the *E. coli* killed by the aqueous leachates were compared to the untreated control population. Results show that intracellular concentrations of Fe and P are elevated relative to controls. Phosphorus uptake by the cells supports a regulatory role of polyphosphate or phospholipids in controlling Fe(II). Fenton reaction products can degrade critical cell components, but we deduced that extracellular processes do not cause cell death. Rather, Fe(II) overwhelms outer membrane regulatory proteins and is oxidized when it enters the cell, precipitating Fe(III) and producing lethal hydroxyl radicals.



Photo collage showing the progressive healing of Buruli ulcer using French green clay. The clay crystals shown are 200nm diameter hexagonal structures. The cell image shown is of *E. coli* treated with antibacterial clay leachate for 24 hrs (from Williams et al., Environmental Science and Technology, 2011).

Keywords: clays, bacteria, Medical Geology

ENVIRONMENTAL HEALTH RISK OF THE FUKUSHIMA NUCLEAR POWER PLANT ACCIDENT

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A massive earthquake with a magnitude of 9.0, so-called ‘the Tohoku Pacific Earthquake’, occurred on 14:46 March 11, 2011. The ensuing enormous Tsunami struck the north-east coast area of Japan and caused tremendous damage. The earthquake and tsunami attacked the reactors of the Fukushima Dai-ichi nuclear power plant (1F) operated by the Tokyo Electric Power Company (TEPCO) and four reactors (Unit 1 to 4) were seriously damaged. As results, a large amount of radionuclides such as ^{131}I , ^{134}Cs and ^{137}Cs was released to the atmospheric and marine environment. The total released radioactivity is estimated to be 0.37~0.63 million TBq, which corresponds to the major accident (level 7) according to the rating of the International Nuclear and Radiological Event Scale (INES).

Soon after the accident, a radiation monitor at the 1F main gate (about 1.0 km west from Unit 2) indicated high dose rates up to more than 12mSv h^{-1} on March 15 when both explosion in Unit 2 and fire in Unit 4 occurred coincidentally. On the same day, the dose rate in Fukushima city at 61km north west from 1F recorded more than $20\mu\text{Sv h}^{-1}$; the level decreased and now reached stable around $1.5\mu\text{Sv h}^{-1}$.

Screening for local residents near 1F was performed by Fukushima prefecture using portable GM survey meters. The initial screening level was set as 13,000cpm and raised to 100,000cpm. The contamination levels of 30 residents were above the screening level, though they became much lower after decontamination. Nearly 200,000 people (about 10% population in Fukushima prefecture) have taken screening tests by the end of May.

On March 15, the local headquarter issued a direction to administer the stable iodine (KI) during evacuation from the evacuation area (20km radius) to the prefecture Governor and the heads of cities, towns and villages. At the end of March, 1,080 children (~15years old) near the evacuation zone were tested for thyroid gland exposure and it was found that the I-131 levels in thyroid are within safe limits.

Whereas, the Prime Minister directed evacuation of the residents within the 20km radius from 1F (Unit 1). At the end of May, the area within 20 km radius from 1F have been defined as ‘no-entry zone’, other designated areas as ‘planned evacuation zone’, and some areas between 20 and 30 km radius of 1F as ‘emergency evacuation preparation area’.

Japanese government and Fukushima prefectural organization have inspected radioactivity in food and, from March 23, have restricted distribution of food that fails to meet provisional regulation values (e.g. 300Bq kg^{-1} for ^{131}I and 200Bq kg^{-1} for ^{134}Cs or ^{137}Cs in drinking water, milk, dairy products). Continuous, enhanced monitoring and regular inspections are necessary to reduce the anxiety of residents.

Keywords: Fukushima, nuclear power plant, radionuclide, dose, risk

ORAL SESSIONS

**GEOCHEMICAL EVALUATION OF HEAVY METAL
CONCENTRATION OF AMBIENT PARTICULATE MATTER
(PM10) AND SOILS OF SELECTED AREAS IN LAGOS
METROPOLIS, NIGERIA**

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Recent studies have pointed to evidence that coarse particle in the air as well as heavy metal contents of soils could be significant contributor to respiratory and cardiovascular diseases. This study was aimed at determining the metallic constituents of particulate matter and soils of part of Lagos Metropolis and their potential environmental significance. Thirty (30) PM10 samples were collected using High Air Volume Sampler (#1500) with cellulose filter disk while twenty five (25) composite soil samples were collected from the study area. All the samples were digested and the extract analysed for their metals contents using Inductively Coupled Plasma-Mass Spectrometry. The pH of the soil samples ranges from 5.6-8.8 and the Electrical Conductivity ranges 206- 1353 $\mu\text{S}/\text{cm}$. The result of soil analysis in ppm revealed the following ranges of composition: Cu (20-156), Pb (35-938), Zn (50-170), Ni (10-52), Cr (38-114), Co (5-26), Mn (173-1049), V (30-195), Sr (40-220), Ba (55-844), and Th (16-97). The following metal concentration values were obtained (in ppm) for the particulate samples: Zn (4.747.5), Mn (5.0-20.0), Sr (3.6 - 6.1), Ba (1.5- 8.1), Cu (1.8-13.7), Pb (1.0-5.0), Cr (1.0-2.0), V (0.5-1.7) and Zr (0.6-1.3). The various result showed significant enrichment for most of the metals when compared with their calculated background value. Further evaluation of the result indicated that contamination occurred mostly in densely populated and areas of high commercial activity. Reasonable high levels were also observed in the samples collected along the major highways where traffic is quite intense.

Keywords: heavy metals, PM10 samples, contamination

THE HEALTH IMPLICATION OF URANIUM (U) AND THORIUM (Th) CONTAMINATION OF SOILS FROM THE YOUNGER GRANITE COMPLEX OF JOS PLATEAU, NORTH CENTRAL NIGERIA

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Soil samples of the Younger Granite complex from the Jos Plateau were analyzed for U and Th using inductively coupled plasma mass spectrometer (ICP-MS), after a total digestion. Cassiterite mining is on-going on the Jos Plateau. The objective of the study was to determine the concentration of radioactive elements in soils of an area known for its high levels of radiation. Statistical analysis of the results showed that U and Th were present at the contamination level, based on the calculated indices of geo-accumulation (Igeo), and the enrichment factor (EF). Radioactivity causes gene mutation and cancer in man and within the area of study are observed congenital birth defects common among populations exposed to high radioactivity; and also skin cancer and hepatitis. The major sources of the radioactivity are both geologic and anthropogenic. Multidisciplinary studies of the health impact of the radioactive elements contamination of soils in the study community can lead to new diagnosis and therapy.

Keywords: uranium and thorium, soils, jos plateau, health

RISK ANALYSIS OF THE BAGNOLI BROWNFIELD SITE: ASSESSMENT OF THE THREAT FOR THE HEALTH OF LOCAL POPULATION

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Bagnoli (Naples) is located along the south-eastern coastal sector of the Campi Flegrei volcanic area. Campi Flegrei are characterized by a large presence of magmatic alkaline rocks and thermal waters, generally enriched in potential toxic metals (e.g., As, Pb, Cd). An industrial settlement for steel works (ILVA) has been present in the Bagnoli area for about 100 years. After the ILVA shut down, the brownfield area underwent remediation. The brownfield is characterized by the large presence of industrial filling, scums and slags overlaying natural volcanic soils. A number of topsoil (at a depth < 1 m from the surface), subsoil (at a depth > di 1 m from the surface) and groundwater samples was collected over the brownfield area to be analyzed and to produce concentration data for potential toxic elements (As, Cd, Cu, Hg, Pb, Zn), PAHs and PCBs. Studies (De Vivo and Lima, 2008. In: *Environmental Geochemistry: Site characterization, Data analysis and Case histories*, Elsevier, 355–3859; Tarzia et al., 2002. *Geochemistry: Explor.-Environ.-Analysis*, 2, 45-56) demonstrated that metals found in the brownfield area derive from both former industrial activities and hydrothermal processes producing enrichments of As and other toxic elements in the superficial environment. On the other hand, PAH and PCBs, as opposed to the metallic elements, are totally anthropogenic. Risks maps, compiled on the base of Italian legislation (D. Lgs. 152/06), show that all the toxic elements and compounds, often exceed the trigger and action limits all over the brownfield area. Thus a risk analysis was performed to assess the threat for the health of population living in the surroundings of the brownfield. After developing an hydrogeological model of the area, the risk analysis was carried out on soils and waters following the official Italian guidelines for risk analysis on contaminated site (APAT, 2008). Results given by the second level (quantitative) risk analysis showed that over 25 years average exposure of 100.000 human beings, a strong increase of cancer cases should be expected (up to 600 cases) compared to the normal expectancy. As expected, most of the risk is due to organic compounds such PAHs and PCBs.

Keywords: Bagnoli brownfield, risk analysis, organic compounds

ADSORPTION OF AFLATOXIN B1 ON THE LOCAL NATURAL ZEOLITE

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The human diet contains a wide variety of natural carcinogens. Aflatoxins, a group of potent mycotoxins with mutagenic, carcinogenic, teratogenic, hepatotoxic and immunosuppressive properties, are of particular importance because of their adverse effects on animal and human health. Aflatoxin B1 (afB1) is the most toxic and most prevalent compound. In the study, natural zeolite originated from Gördes region of the Turkey was investigated for its ability to adsorb afB1 in simulated human digestion solutions. It is aimed to determine the mechanism of the aflatoxin adsorption for biological applications. For this, the characterization of the adsorbent was performed and adsorption experiments were conducted. The theoretical cation exchange capacity was determined as 2.08 meq/g. The equilibrium time was determined as 120 min based on the experiments performed at a fixed afB1 concentration of 2 ppm, adsorbent dose/solution of 25 mg/10 mL, solution pH of 7.4, at 37 °C, and at an agitation speed of 130 rpm as a function of contact time. The experimental adsorption equilibrium data obtained for initial afB1 concentrations (in the range of 0 - 2 ppm) were fitted to the Langmuir, Freundlich, and Langmuir-Freundlich (Sips) adsorption equilibrium models. The experimental adsorption equilibrium data fitted better to Sips equation than to other equations, due to the fact that this model has three adjusting parameters as compared to the Langmuir and Freundlich models with two parameters. Effect of different parameters (temperature, solution pH, adsorbent/solution ratio, initial afB1 concentration, agitation speed, adsorbent particle size) on the amount of afB1 adsorbed at equilibrium was tested. The adsorption capacity did not significantly affected by the adsorption temperature. Slight increase in the equilibrium adsorption capacity of the zeolite for afB1 at the lower solution pH can be explained by the change of the zeolite surface with the pH. The amount of afB1 adsorbed at equilibrium decreased as the zeolite particle size increased. This confirmed that the adsorption occurs on the external surface of the zeolite particle as expected regarding the size of afB1 molecule which is larger than the pore size of the zeolite. afB1 adsorption rate was increased at equilibrium with the increase in agitation speed. As the zeolite dose increased, while volume of the adsorption solution was kept constant, the adsorption capacity of the zeolite decreased.

Keywords: aflatoxin, adsorption, natural zeolite

MAIZE CROPS IN MINING ZONES OF MÉXICO. A THREAT TO HUMAN HEALTH?

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Corn products are one of the bases of Mexican diet. Safe maize crops become then a relevant health issue. Unfortunately not all crop fields are located in pollutant-free areas. Green house studies of the development and heavy metal's absorption of maize plants (*Zea mays* L. cv H-515) rose in tailings, and soils collected at various distances from mining wastes (two of them actually used for maize cultivation) were carried out. Plants were harvested and evaluated for physical parameters such as weight, stem and leaves length, and number of leaves. Concentrations of Zn, Pb, Fe, Cu, As and Cd were measured in the respective soil and plant parts. As expected, the highest metals' concentrations were determined in plants grown in the tailings. Heavy metals contents in soils were: Fe>Zn>Pb>As>Cu> Cd. Higher concentrations were found in roots with respect to aerial plant parts. After 70 days growth in one of the experiments, range concentrations in roots varied as: Zn (54.7 to 3555 mg/kg), Pb (11.1 to 320 mg/kg), Cu (10.4 to 90.1 mg/kg), Cd (1.3 to 55 mg/kg), and As (0.1 to 0.4 mg/kg). The highest bioconcentration factors were determined for Cd and Zn. Although As reached the lowest concentrations in roots, it presented a high translocation factor. Grains collected from other experiment reflected this fact with concentrations up to 0.4 mg/kg As. Clear differences were found in plants weight and development according to the degree of contamination of their respective soil. Results show the need to avoid maize rising in sites close to mining wastes.

Keywords: maize, mining, As and heavy metals

WHEN VOLCANIC WATERS ARE BENEFICIAL TO HEALTH

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The Copahue volcano is situated in the province of Neuquén near the border between Argentina and Chile. It is a stratovolcano, the only one that remains active in the Argentina Patagonia, where remains fumaroles, pots, flue pipes and emerge hot springs and natural muds used, since more than one hundred years, with therapeutic purposes in the health spa station named like the volcano. The objectives of this study were collect and analyze the eleven volcanic mineral waters (Mate, Sulfurosa, Limón, Vichy, Volcán, Ferruginosa, Circuito, Baños externos, Laguna verde, Laguna Sulfurosa y Laguna del Chanco) used in balneotherapy and mud therapy in Copahue Spa. The result shows that from the point of view of the Medical Hydrology, nine of them are hyperthermal. Six have a mineralization less than one thousand mg/L: Two are sulphur mineral water, five are sulphated, and three are bicarbonated; one is CO₂ rich water and one is ferruginous. The skin effects of these waters are anti inflammatory and antiseptics and are used in the treatment of chronic eczema, psoriasis, acne, also in skin burns after-effects. The waters administrated by respiratory way, have mucolytic action, fluidising effects, decreasing the viscosity of mucous secretions, are indicated in recurrent infections, cold, prolonged suppuration, hypertrophic and purulent chronic inflammatory of the airway mucosa, associates or not with an allergic status with chronic infections. Finally, the waters are used in Degenerative Chronic Rheumatisms, chondral ageing, Rheumatoid Arthritis, Sjögren's Syndrome, Reiter's Syndrome, Psoriatic Arthropaty, Soft Tissue Nonarticular Rheumatism, in example, Periarthritis, Myalgias, Myositis, Tendonitis, Tenosynovitis, Neuralgias, Neuritis, Fibromyalgia, Bursitis, Fasciitis, cellulitis and post traumatic after-effects.

Keywords: mineral water, mud therapy-spa treatment, copahue

REMOVAL OF TEXTILE DYES FROM WASTE WATER OF KIFFRY TEXTILE FACTORY USING NATURAL CLAY OF THE REGION

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Two types of Kiffry clays (Brown clay and Yellow clay) were characterized. Chemical compositions were analyzed by XRF and ICP techniques. The XRD pattern of the samples shows that the samples are of mixed layered type of illite/smectite structure, contaminated with various percentage of kaolinite. The highest percentage of smectite is present in Brown clay sample which is obvious from the relative peak high and peak area at (001) ($2\theta = 6.9$) of smectite compared to kaolinite and illite.

The method of methylene blue adsorption has been used for the determination of specific surface area (SSA) and cation exchange capacity (CEC). The SSA were 83.93 and 83.1 m²/g, and CEC were 28.5 and 28.0 mmol/g for Brown and Yellow clays respectively.

Most of synthetic organic chemicals compounds (e.g., dyes) are potential or known human carcinogens and are of considerable health concern, even at low concentrations. Methods for decolorization have therefore become important in recent years. Adsorptions of a textile dye of Kiffry textile factory from aqueous solutions at 25°C by natural Brown and Yellow clays of Kiffry region have been studied. The equilibrium time was found to be 35 min. The data was found that Langmuir isotherm model fits the data very well for dye adsorption on both clays.

Keywords: Kiffry clay, textile dye, adsorption

X-RAY MICRODIFFRACTION AND URINE: A NEW ANALYSIS METHOD OF CRYSTALLURIA

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The qualitative and quantitative analysis of crystalluria have clinical significance in the diagnosis and prognosis of urolithiasis. Optical methods used on a routine basis can fail the correct identification of crystal materials for several reasons, such as the small grains size of crystals or the morphological convergence of different crystal species. The aim of this research is to provide an new accurate methodology to better analyze the crystalluria in patients with renal stone disease. Subjects for study were selected on the basis of pre-determined criteria: 8 patients with lithiasis disease hospitalized at the San Carlo Hospital (Potenza); 3 healthy subjects with no history of renal calculi. The procedure involves an urine collection, the separation of the solid residual by centrifugation, and its analysis by X-ray diffraction. Since very low amount of solid residual is obtained from each patient, a microdiffractometer was used instead of a more conventional instrument. The X-ray spectrum obtained from the sample and from a known standard was processed by Rietveld method in order to quantify crystalline species and the amorphous component. The proposed methodology has two main advantages: i) to properly identify the crystalline phases in the urine, according the crystallographic criteria, that are not biased by grain size, morphology or any other optical interferences due to dust, organic coatings or others; ii) accurately quantify both crystalline and amorphous components of the urine. The temperature of urine collection and the solid residual conservation represent critical phases of this methodology.

Keywords: urinary crystals, XRD

ANALYSES METHODS OF CRYSTALLURIA

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Urine is an extremely complicated solution with variable composition. Various crystals are seen in human urine. Oxalate, phosphate, uric acid and urate crystals are generally seen in urinary calculi. The qualitative and quantitative analysis of these crystals have clinical significance in the diagnosis and prognosis of urinary calculi formation (urolithiasis). Unfortunately little has been done for the analysis of crystals in urine.

Currently, the study of urinary crystals is performed by referring to the European Guidelines for examining urine, where the centrifugation of urine is recommended. The procedure is completed by the resuspension of sediment for analysis at the phase-contrast microscope with polarizer. The study of Gai and Lanfranco [2007] show that the major nephrology centers have a variety of methods of preparation of urine for analysis, especially in terms of time and spin speed. In order to perform a correct qualitative and quantitative analysis of the sediment, different alternative methods have been developed: chemical analysis, infrared spectroscopy and Xray diffraction.

The X-ray method has many advantages which can be summarized in an easy sample preparation, automation of the measure, the semi-automatic evaluation of the diffractometric reflection through simple software, the exact differentiation of all crystalline phases and the possibility of obtain quantitative estimates of abundance of the phases (see the review edited by Bish & Post [1989]). Conversely, it has some disadvantages, mainly due to the amount of sample needed (tenshundreds of milligrams, that quite often are not available) and to the possible orientation of the crystals. However these problems can, be overcome by using the microdiffraction analysis.

Microdiffractometers have an X-ray beam of very small diameter (tens of micron) and a sample holder that rotate around 2 axes during the measure, in order to get a random orientations of the crystals respect to the incident beam.

Such an arrangement of the instrument give the additional advantage of single crystal analysis (as well as bulk dust), and not requirement of pre-treatment, such as grinding or complex positioning of the specimens.

Keywords: urinary crystals, XRD

ORGANO-CLAYS AND NANOSPONGES FOR ACQUIFER BIOREMEDIATION: ADSORPTION AND DEGRADATION OF TRICLOPYR

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The environmental problems associated with the presence of pesticides in the soil and in ground water are becoming increasingly more important. Many compounds are not retained by soil colloids and tend to be carried by water seepage to the water table. Moreover, the likelihood of ground water being contaminated is increased by the low degradability of the molecules. To avoid this problem, mitigation techniques have been proposed that consist in creating barriers made of suitable materials to facilitate the adsorption and degradation of the pollutants. Recent studies have suggested that organo-clays have a high water decontamination potential due to the fact that they can adsorb considerable quantities of organic compounds. Nano sponges are hyper cross-linked polymers based on cyclo-dextrins. They can include a large quantity of molecules of suitable polarity and dimension. Preliminary studies have shown that nano sponges can adsorb pesticides with different polarities. The work aims at evaluating the capacity of some organo-clays and one nano sponge to adsorb the herbicide, triclopyr. Triclopyr was chosen because it is a good example of a moderately mobile, leachable, molecule. The rate of degradation of the molecule in the soil, with and without the presence of the materials under examination, was also determined. Both the organo-clays and the nano sponges adsorbed more than 90% of the herbicide. When added to the soil, the materials accelerated the degradation of triclopyr. These results lead us to suggest that they be used in creating reactive barriers for the remediation of soils and aquifers.

Keywords: nanosponges, organoclays, pesticides

SURVEY OF AEOLIAN AIRBORNE DUST OVER IRAN FROM THE POINT OF VIEW GEOCHEMISTRY AND MINERALOGY (CASE STUDY: WESTERN IRAN AND NORTH OF PERSIAN GULF AND SEA OF MOKRAN)

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This research aims to show the characteristics and particle-related pollution of massive dust storms reaching Iran and North of Persian Gulf and Sea of Mokran. Satellite images have shown that these Aeolian dust storms originate in Arabian countries in Middle East and North of Africa continent. We have conducted numbers of analysis to reveal the particle size analysis, SEM, XRD, and ICP-MS for the detection of the most important source areas with regard to radioactive, heavy and toxic trace elements. Analyses for pesticides were also performed by HPLC and microorganisms diffusion was evaluated. Result has revealed that the most dangerous source areas of dust storms reaching Iran are located in Iraq country and war implications by turns have the worst effect on Iraqi environment, natural resources and human health. Soon after dust storm, Iran country was affected by toxic, radioactive elements, pesticides and microorganisms (bacteria, fungus, viruses), which could be a source of human diseases and soil pollution, and negatively influence the forest and plant communities.

Keywords: geochemistry & mineralogy of dust, radioactive and trace elements of dust, Iran, Persian Gulf, Sea of Mokran

HIGH SILICA ZEOLITE Y FOR EMBEDDING SULFONAMIDE ANTIBIOTICS: AN AFFORDABLE MATERIAL FOR WATER CLEAN-UP AND DRUG DELIVERY

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Sulfonamide antibiotics are persistent pollutants of aquatic bodies, known to induce high levels of bacterial resistance. The adsorption of ten sulfonamides into a high silica zeolite Y with cage window sizes comparable to sulfonamide dimensions was studied in order to clean-up water polluted with sulfa drugs. At maximal solubility, nine sulfonamides were almost completely (>90%) and quickly ($t < 1$ min) removed from water by zeolite. With the exception of sulfanilamide which showed scarce affinity for zeolite Y (3% zeolite DW), the other sulfa drugs adsorbed at 26% zeolite DW on average. The presence of sulfonamides inside the cage was revealed by unit cell parameter variations and structural deformations obtained by X-ray structure analyses carried out using the Rietveld method on exhausted zeolite. For all the host-guest systems, the close vicinity of antibiotic aromatic moieties and their substituents with zeolite framework was evidenced by multidimensional and multinuclear SS-NMR and in situ FTIR spectroscopies and confirmed by ab initio computational modelling. Sulfonamides with the lowest steric hindrance (namely sulfadiazine, sulfathiazole and sulfapyridine) form H-bonded dimers inside zeolite cage. Multiple weak H-bonds and van der Waals type interactions between antibiotics and zeolite are responsible for the irreversible extraction from water of all the examined drugs. Lastly, the most stable tautomeric form of each antibiotic adsorbed into zeolite was identified. The sulfonamide amount loaded into zeolite Y is remarkably high to consider this material affordable not only for clean-up but also for drug delivery issue.

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Keywords: adsorption, host-guest & guest-guest interactions, sulfonamide, Tautomerism

FLUORIDE RICH ROCKS AND ITS IMPACT ON GROUNDWATER QUALITY

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Groundwater pollution due to natural factors has been witnessed in many parts of the world. Arsenic, iron and fluoride are few of the ions which make the groundwater unsuitable for consumption due to natural conditions of a particular region. This study focused on assessing the probable reasons for the presence of higher or lower concentration of fluoride in groundwater of Nalgonda district, Andhra Pradesh, India. Groundwater samples were collected from March 2008 to January 2010 once every two months. Fluoride concentration in the groundwater samples was determined using ion chromatography. Nearly 500 groundwater samples were collected during this study. Groundwater in this region contained fluoride between 0.07 and 8.8 mg/L. Bureau of Indian Standards and World Health Organisation has put forth that the suitable range for fluoride for drinking is 0.6 to 1.5 mg/L. Fluoride concentration of up to 0.6 mg/l is required for human body as it will help to have stronger teeth and bones. But consumption of water with fluoride above 1.5 mg/L results in acute to chronic dental fluorosis and prolonged exposure will lead to skeletal fluorosis which causes weakness and bending of the bones. As per these standards, 20% of the groundwater samples were below 0.6 mg/L and 33% were above the maximum permissible limit of 1.5 mg/L. Earlier studies have shown that the granitic rocks of Nalgonda region possess fluoride content higher than that of world average of granitic rocks. Hence, weathering of these granitic rocks is the cause for the higher concentration of fluoride in groundwater of this area. Apart from these agrochemicals and evapotranspiration also contribute to some extent for high fluoride concentration. As ingestion of high fluoride has a long term effect on human health it is essential to monitor its concentration in groundwater used for drinking periodically and take measures to keep them within the permissible range of 0.6 to 1.5 mg/L. In this area, as the source is natural pertaining to inherent rocks of this region, it is better to adopt artificial recharge such as rainwater harvesting as a groundwater management measure to hold on to the fluoride concentration within the standard limits.

Keywords: fluoride, groundwater, granitic rocks

ASSESSMENT OF DUST EMISSIONS AT NELLIS DUNES RECREATION AREA, NEVADA, USA: PRELUDE TO A HUMAN HEALTH RISK ASSESSMENT

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In the USA, the largest single source of both PM₁₀ and PM_{2.5} is road dust (EPA, 2005). For over 40 years, the Nellis Dunes Recreation Area (NDRA) has been heavily used for off-road vehicle (ORV) recreation with an estimated 300,000+ drivers per year (Goossens and Buck, 2009). A map of NDRA was created and contains 17 surface units based on textural composition, surface crusts, rock cover, and vegetation (McLaurin et al., 2011). Natural and ORV-generated dust emissions were measured. Wind erosion is greatest in the sandy areas, ORV emissions are greatest in the silty and rock-covered areas. Emissions from ORV activities increase exponentially with driving speed, and are highest for 4wheelers. On an annual basis, ORV-generated emissions equal natural dust emissions. Dust containing palygorskite is of concern because it commonly crystallizes in an asbestiform morphology and is found in all but 2 map units. Extremely high concentrations of naturally-occurring arsenic were found. To our knowledge, no previous study has reported As concentrations in airborne dust from natural surfaces as high as those found in this study: PM₁₀ up to 290 ppm; PM₆₀ up to 312 ppm. Water-soluble arsenic is as high as 14.7 ppm. Emission rates for arsenic were calculated for all surface units. Sandy areas have the potential to emit the greatest amount of arsenic-containing dust during windy conditions, whereas specific silt, rock-covered, and silty sand units have the highest arsenic emissions during ORV activities. In vivo experiments were conducted in mice to examine the immunotoxicological and histopathological effects following 3 daily exposures to dust samples from 3 map units. Suppression of humoral immunity and splenic T-lymphocytes were the most sensitive parameters affected. Toxicology and human exposure data will be collected to define site-specific parameters for probabilistic modeling of human health risks.

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Keywords: dust, arsenic, palygorskite

IDENTIFICATION OF MAGNETIC PARTICULATES IN ROAD DUST ACCUMULATED ON ROADSIDE SNOW USING MAGNETIC, GEOCHEMICAL AND MICRO-MORPHOLOGICAL ANALYSES

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Road traffic is considered a significant emission source of anthropogenic particulates in urban areas. A strong connection exists between long-term exposure to urban air pollution and respiratory diseases, coronary atherosclerosis, and increased cancer and mortality risks. Dust discharged into the air by road traffic, contains strongly magnetic, iron-rich particles, which are commonly associated with heavy metal concentrations. This compels current studies to monitor vehicle-derived magnetic particles using fast and cost-efficient techniques such as magnetic measurements. In this study magnetic methods combined with geochemical and micro-morphological analyses were applied to examine road dust extracted from snow, collected near a busy urban highway and a low traffic road in a rural environment (southern Finland). Significant differences in horizontal distribution of mass specific magnetic susceptibility were observed for both sites. Furthermore, the magnetic methods revealed that coarse-grained, multi-domain (MD) magnetite is the primary magnetic mineral. Two groups of anthropogenic particulates were identified in the studied road dust samples: (1) iron-rich spherules (diameter~2–70 micrometres) and (2) angular-shaped particles (d~1–300 micrometres) mostly composed of Fe, Ni, Cr, Cu and Zn. The spherule-shaped particles occur mostly in emissions from industrial activities and residential wood combustion, while the angular-shaped particles are derived from vehicle emissions. Additionally, fine-grained (d<2 micrometres) tungsten-rich particles were identified in the road dust from both sites, possibly derived from the abrasion of tyre studs. A decreasing trend in magnetic susceptibility and selected trace elements with increasing distance from the road edge was observed in the investigated road dust samples. This study demonstrates that the combination of magnetic, geochemical and micro-morphological methods may be applied as an effective tool in monitoring vehicle-derived particulates, especially those posing serious threats to human health.

Keywords: vehicle emissions, magnetic properties, geochemical analyses

IMPACT OF 2010 MERAPI VOLCANIC ASH ERUPTION IN INDONESIA FOR WATER SUPPLIES

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The 2010 eruptions of Merapi Volcano in Indonesia, began in late October 2010 when Merapi Volcano in Central Java, Indonesia began an increasingly violent series of eruptions that continued into November. Beside respiratory health effect to human health, volcanic ash may result in short-term physical and chemical changes in water quality. The addition of volcanic ash to water supplies can lead to a change in water quality. The most common ash-contamination problems result from a change in turbidity and acidity, but these usually last a few hours to a few days unless the ash fall occurs for prolonged periods of time. For longer period, the effect of pyroclastic flow was also suspected to effect of surface water, in fact the material of pyroclastic flow consist of fresh volcanic material which can carry a variety of metals and other potentially-pathogenic trace elements. In this study, thirty water samples were obtained from several water supplies including groundwater, surface water, waterworks company, and spring, which collected on the day after eruption. The result showed that some of some water samples has been contaminated by volcanic ash. Some parameters including Total Suspended Solid, Color, pH, Iron, Mangan, Nitrate, Lead, Cadmium, Selenium were detected above the threshold. Especially for Selenium, it was considered high and the source of selenium was considered from sulfur composition in volcanic ash sample. On the other hand, the impact of pyroclastic flow for water supplies has been carried out, by sampling five location of surface water in two month after eruption. Water quality data obtained from several rivers in study area indicated Iron, pH, turbidity and Total Suspended Solid were above the threshold. In particular, the suspension of ash in water can block intake filters and cause wear and tear on components of water treatment plants due to its abrasive and corrosive nature. High turbidity levels can compromise the effectiveness of disinfection of pathogenic microorganisms. Other effects are high water demand for cleanup depleting water storage in reservoirs, and the leaching of soluble components, particularly acidity, into receiving waters.

Keywords: volcanic ash, water supplies

ARSENIC EXPOSURE IN LATIN AMERICA BY DRINKING WATER: EXPERIENCES FROM 14 COUNTRIES

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In Latin America, the problem of arsenic (As) contamination of groundwater and to less extent of surface water is known from 14 out of 20 countries comprising Argentina, Bolivia, Brazil, Chile, Colombia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Peru and Uruguay.

The occurrence of As in drinking water and related health effects were identified in the 1910s in Bellville (Córdoba province, Argentina) but recent studies in mummies from northern Chile proved that the impact of chronic arsenicosis affected human populations already 7000 years ago. Arsenic contamination was detected for the first time in 10 Latin American countries only within the last 10-15 years. It has been roughly estimated that at least 4.5 million people in Latin America are chronically exposed to high levels of As ($>50\mu\text{g/L}$), and at least 14 million if we consider the WHO provisional drinking water standard ($10\mu\text{g/L}$). Health effects due to chronic exposure to As from drinking water comprise internal and external cancers, reproductive outcomes, and childhood cognitive function, etc.

In Latin America, As in the water resources is predominantly of geogenic origin; in most cases it is mobilized from Tertiary to recent volcanic rocks and their weathering products. In the Andean mountain range, oxidation of sulfide minerals is the primary mobilization process. Rivers originating in the Andes, transport As to the more densely populated lowlands (e.g. Rímac river in Peru and Pilcomayo river in Bolivia). In the Andes and the Central American and Mexican mountain ranges, As-rich geothermal waters locally contaminate fresh water resources. In alluvial aquifers, As is mobilized from Fe, Al and Mn oxyhydroxides (secondary As sources) under oxidizing or slightly reducing conditions (e.g. Chacopampean Plain Argentina and many sites in Mexico).

Although the As problem has been known since one century; the problem has not received enough attention by national authorities or international cooperation agencies to mitigate the problem. Furthermore, the rural people are often unaware of the situation and/or dependent on As-contaminated water as their only drinking water resource. Thus, although suitable remediation methods were developed (e.g., solar oxidation methods, phytoremediation, use of natural materials as adsorbents for As removal) they were mostly tested only on laboratory scale, and only few pilot studies on field scale exist even today.

Keywords: geogenic arsenic, Latin America, drinking water

THE IMPACT OF VOLCANIC EMISSIONS ON ETNA'S SNOW COVER

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Volcanoes are one of the major natural sources of several trace elements to the atmosphere: They contribute to atmospheric pollution by increasing the amount of reactive and greenhouse gases and aerosols. In particular, Mt. Etna is considered to be, on longterm average, the major global atmospheric point source of many environmental harmful compounds. Their emission occurs either through continuous passive degassing from open-conduit activity or through sporadic paroxysmal eruptive activity, in the form of gases, aerosols or particulate. For several months during the year (generally December-May), the summit of Mt. Etna is under a thick blanket of snow. This huge reservoir of frozen water, interacting with the volcanic plume, accumulates a great quantity of volcanogenic elements during the winter. Samples of snow were collected at different distances from summit craters along an 8 km radial transects, in the 2006 and 2007 winters. Each snow sample was analyzed for 37 elements in the laboratory using IC, ICP-OES and ICP-MS techniques. The impact of volcanic emissions is clearly detectable considering the opposite trends of pH and TDS (total dissolved solid) measured in snow samples with increasing distance from their "source". The pH values range from 1.7 on the rim of the summit craters up to 7.6 at a distance of about 8 km, and TDS ranges from diluted samples (few mg/l) at distal sites, up to extremely concentrated samples (500 - 3500 mg/l) close to the emission vents. The acidity in precipitation around the volcano depends mainly on the concentrations of volcanogenic acid forming ions (SO₂, HCl and HF), as well as on concentrations of mainly geogenic alkaline species, which may eventually neutralize the acidity. Regarding metals concentrations, there are orders of magnitude of difference between the different sites with decreasing values from the crater's rim up to the farthest sites (5-8 km from craters). In particular three groups of elements were extremely enriched (many orders of magnitude higher) at the summit craters with respect to the distal samples: Halogens (Br, Cl, F, I) and S ascribable to volcanic gas contribution; Al, Fe and Ti deriving from magmatic silicate particulate; and elements such as Se, Cu, As, Bi, Cd, Tl, Pb and Hg which are highly mobile in the high temperature volcanic environment.

Keywords: snow chemistry, trace elements

CLIMATE CHANGE, FAMINE CRISIS, CHOLERA OUTBREAK AND EMERGENCY RELIEF RESPONSE IN CHAD

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In Chad, rainy season usually stretches from April to October. In northern regions it is shorter, in southern longer. From 1960 to 2006, United Nations' official records report mean country rainfalls at 120 mm per year. 1990 was the driest year (92 mm), 1994 the wettest one (160 mm). All over 2009 and early 2010 rainfalls dropped so sharply that in some areas of northern and western regions, such as Kanem and Barh-El-Gazal, it was almost 0. Drought caused the overall animal and cereal production to drop down to 34% of 2008's. In 2009, epidemiological surveys settled the proportion of severe (SAM) and moderate acute malnutrition (MAM) in under five children at 4 and 19 %. Emergency was declared. UNICEF, WFP, non-profit organizations and European institutes put in place a relief response by setting-up therapeutical feeding centres (CNT), targeting SAM affected children with negative appetite test and/or infectious complications, ambulatory feeding centres (CNA), targeting SAM affected children with positive appetite test and with no infectious complications up, and supplementary feeding centres (CNS), targeting the MAM affected children. In CNTs and CNAs, this relief operation gave some good results (deaths < 1%, drop-outs < 10%, cured/improved children > 88%). Such results may estimatedly have saved the lives of about 10 children per 1000 per year out of an overall reported under 5 mortality rate of 209. However, an epidemiological survey, carried out from July to September 2010, gave no evidence of improvement of SAM and MAM proportions in children population. Such results support the idea that the input of children shifting from healthy conditions into MAM and SAM remains untouched and CNS network is still insufficient. Meanwhile, wells got dry because of the low level of underground water. Lake Chad shrank a lot and left behind mildly salted water made ponds, animals and people make a promiscuous use of. Thereafter, outbreaks of cholera and other water-borne diseases spread in remote communities which were settled either on-shore besides the lake and offshore in small islands. A structured response was put in place by: a) supplying drinkable water tanks from outside; b) drilling additional deep wells; c) setting-up cholera treatment centres. However, these relief operations were not enough for cholera controlling until social communication and education about hazardousness in drinking water from ponds was not put in place consistently.

Keywords: climate change, famine crisis

**BIONANOCOMPOSITES BASED ON NATURAL POLYMERS
AND NANOCCLAYS. AN EXTENDED PHYSICO-CHEMICAL
STUDY TO EVIDENCE THE ROLE OF THE POLYMER
NATURE AND THE NANOCCLAY SHAPE**

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This study was developed along the idea that the combination of biopolymers, derived from renewable resources, and nanofillers, environmentally friendly, may form a new family of hybrid materials at low cost, namely bionanocomposites, with excellent and unique properties. To this aim, as polymeric matrices were selected two pectins (with different degrees of methyl esterification) and hydroxypropyl cellulose; as fillers two nanoclays with dissimilar shape were chosen, i.e. halloysite (nanotubes) and laponite RD (nanodisks). The casting method was used for the nanocomposites preparation. A very good compatibility between the biopolymer and the nanoclay allowed us to obtain a good dispersion of the filler into the polymeric matrix. These systems were studied in both the aqueous and the solid state from the physico-chemical view-point in dependence of the composition of both components. The thermodynamic studies (Isothermal Titration Calorimetry, Differential Scanning Calorimetry and densitometry) and the structural (Dynamic Light Scattering) characterizations on the aqueous mixtures were able to discriminate the interactions, which control the adsorption of the biopolymer onto the solid substrate. The gained insights were useful to interpret the microscopic structure of the nanocomposites highlighted by scanning electron microscopy, optical transparency and percolation theory. Moreover, the dynamic mechanical analysis allowed us to determine the tensile and the rheological properties. The surface features were explored through the contact angle measurements while the thermal stability through the thermogravimetric experiments. The attained fundamental knowledge represents a solid basic point for designing new hybrid nanostructures for specific purposes

Keywords: surface properties, tensile properties, thermal stability

GEOLOGY AND HEALTH: THE HIGHLY CARCINOGENIC ERIONITE MINERAL AND THE NEED FOR A RISK ASSESSMENT IN ITALY

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Erionite is a mineral belonging to the zeolite family (hydrated aluminotectosilicates) distinguished by the dominant extra-framework cation (erionite-Ca, K and Na). A small number of zeolite species may develop asbestiform crystalline habit, for example mordenite, mazzite, roggianite, erionite and offretite. In Europe there are no systematic studies on the distribution of erionite or similar fibrous zeolites in the environment, even if some minerals of the zeolite family have been actively exploited and used in recent decades. Erionite has been classified as highly carcinogenic (Class 1) by the WHO. It is up to 800 times more carcinogenic than asbestos fibres, and in particular it can cause mesothelioma, a nearly-always fatal disease. On the other hand, little is known about the toxicity of other fibrous zeolites, commonly intergrown with erionite. In Italy the knowledge of the epidemiology of mesothelioma linked to erionite is extremely scarce; while the mesothelioma cases attributed to asbestos exposure are well known and recorded, domestic cases from exposure to airborne erionite fibers are still to be inferred. The correctly recognized erionite findings occur in volcanic deposits (pyroclastics and lavas), which have been subject to alteration processes under a specific range of P, T and pH. The mineral has been reported in a few Italian outcrops, but a systematic geological mapping of erionite-bearing deposits is still not available. We carried out first preliminary investigations and sampling in selected areas in Tertiary volcanic rocks. The first mineralogical investigations by means of XRPD, SEM-EDS and OM confirmed the presence of small amounts of erionite and abundant fibrous offretite in vugs of basaltic rocks. Intergrowths and overgrowths with other minerals are quite common and the morphological-chemical similarities among these zeolites pose a special analytical problem with the need of combining different techniques. An effective risk assessment in Italy will require coordinated actions from governative agencies, local health authorities, Universities and research centres, in order to: i) realize an extensive mapping of the erionite occurrence in the Italian zeolite deposits; ii) carry out air monitoring in areas of intense zeolites exploitation; iii) activate a dedicated taskforce internal to the Italian mesothelioma register for epidemiologic surveillance; iv) release a sampling and determination protocol for airborne erionite.

Keywords: erionite

SOURCE RECOGNITION OF INHALED ATMOSPHERIC PARTICLES ACCORDING TO GEOCHEMICAL AND STATISTICAL EVALUATIONS OF TRACE ELEMENT SIGNATURES

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During 2001 the Mount Etna had a large eruption producing a large amount of pyroclastic products consisting of a mixture of glass, minerals and soluble salt materials (SAF) encrusting solid particles. Inhalation of the finest of these materials induced pulmonary diseases in people living in subjected areas and gave us the possibility to collect bronchoalveolar lavages (BAL) from people in care in Catania hospitals. Concentrations of several trace elements measured in these BAL fluids (BALF) evidence strong enrichments in several trace elements compared to reference values. Related enrichments factors, calculated with respect to composition of volcanic ejecta (EFASH), show similar values in BALF and in SAF for V, Cr, Fe, Cu, As, lanthanides (apart from Ce), Pb and U, suggesting that these elements have originated by leaching of finest inhaled volcanic particles. EF values calculated with respect to Upper Continental Crust (EFUCC) for Co and Mn resulting close to 1 similarly indicate that these elements are probably released in human lungs from inhaled particles of non-volcanic, lithogenic nature. On the contrary, both EFASH and EFUCC values calculated for other investigated trace elements suggest the occurrence of further sources of inhaled solids, probably from anthropogenic sources. To test this hypothesis EF values of the latter elements with respect to a typical road dust composition (EFRD) have been calculated and this origin is strongly suggested for Ni, Cu, Cd and Pb. But La, Ce and Y EFRD values remain unexplained in terms of parent material and a further anthropogenic origin for these elements can be invoked probably originated by fluid catalytic converters used during hydrocarbon refinery activities, that are usually characterised by high Y, La and Ce contents. Statistical evaluation of BALF compositions according to Principal Component Analysis corroborates above mentioned suggestions identifying three main components in the variance space: the first one (46% of the variance) grouping the same elements previously attributed to the volcanic origin (except Pb), the second one (27% of the variance) grouping Ni, Cd, Y, La and Ce and a third component (12% of the variance) identified by Co, Ni, Cu, Pb and, secondarily, La and Ce. These results show that statistical and geochemical assessment of BALF analyses are together able to identify suspended atmospheric solids in the environment recognising mixtures of natural and anthropogenic products.

Keywords: bronchoalveolar fluids, lanthanides

ATMOSPHERIC DUST AND OTHER PARTICULATES DEFINING THE RISKS FROM A MEDICAL GEOLOGY PERSPECTIVE

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It has been estimated that as much as 2 billion tonnes of dust is entrained in the atmosphere per annum. Exposure to dust in the open environment is usually accepted as a fact of life, while exposure to dust in the workplace is regulated to a greater or lesser degree in many countries. While the impacts of dust from industrial processes on human health is well recognized and widely regulated, less attention has been paid to dust from geological sources and to less visually obvious finer particulates. This is, perhaps, due to information being widely scattered in scientific papers with few, if any, widely accessible syntheses of the key facts. Also, research is in many respects at an early stage because of practical difficulties of observing, monitoring and sampling diffuse aerosols in the complexly moving atmospheric column. However, dust performs an important function in the atmosphere, with individual particles acting as nucleation centers for droplets that become precipitation (rain, snow etc) that is essential to life and geomorphological processes. Deposited dust may also, in time, add beneficially to soil formation. There is a need to promulgate present knowledge more widely and to identify matters that need more research in order to address the impacts on people, agriculture, livestock and the natural environment. An important step in elucidating the role of atmospheric dusts and health is to facilitate cooperation among geologists, environmental scientists, and medical specialists (including epidemiologists), to characterize the properties of contaminants, their dispersal, and the toxicological pathways of the elements they transport. Of relevance is the emerging field of Medical Geology which is aimed at assessing the impacts of natural environmental risk factors and processes on animal and human health. This presentation stresses the global scale of the problem, which is under-evaluated and under-reported in terms on environmental management and health implications.

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Keywords: arsenic, beneficial therapeutic, environmental poison

ARSENIC – A BENEFICIAL THERAPEUTIC AND AN ENVIRONMENTAL POISON

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Arsenic is a ubiquitous element in the earth's crust with a crustal average of about 2 mg/kg but with concentrations in clastic sedimentary rocks as high as 500 mg/kg. Arsenic is transported mainly by water, although other natural and anthropogenic sources of exposure to arsenic, including volcanic emissions, forest and agricultural fires, pressure treated wood, mining and smelting activities, and burning of arsenic-rich coal, are of increasing concern. The history of arsenic is double-edged –n-dash it has a beneficial or medicinal aspect and a detrimental or poisonous aspect. In medicine, arsenicals were used in the Greek and Roman civilizations to treat a wide range of ailments. In the 1930s arsenic trioxide was the main therapeutic agent in the treatment of chronic myeloid leukemia. Later in the 20th Century, arsenic trioxide was introduced as an anticancer agent in China for the treatment of acute promyelocytic leukemia (APL). In the US, the use of arsenic trioxide in medicine has been approved by the FDA for the treatment of patients with relapsed or refractory APL. As an environmental poison, acute and chronic health effects of inorganic arsenic exposure in humans have been described from contaminated drinking water and food. An example of the breadth and severity of health problems caused by exposure to arsenic can be found in Guizhou Province, P. R. China where villagers used coal with arsenic concentrations as high as 35,000 mg/kg in a residential setting. Exposure to arsenic resulted from ingestion of crops dried over coal fires, ingestion of arsenic-rich dust, and inhalation of indoor air polluted by the arsenic mobilized by coal combustion. Tens of thousands of people in the region consequently suffered from chronic arsenic poisoning. Those affected exhibited typical symptoms of arsenic poisoning including hyperpigmentation, hypopigmentation, hyperkeratosis, Bowen's disease, and squamous cell carcinoma.

Keywords: arsenic, beneficial therapeutic, environmental poison

THE RESEARCH OF ADSORPTION/DESORPTION BEHAVIOR BETWEEN CLAY MINERALS AND ANTIBIOTIC- TETRACYCLINE

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The livestock industry on Taiwan is well-developed, and due to in a subtropical region, temperature and humidity of the environment cause the bacteria growth in livestock farms, so antibiotics are often used in the treatment to prevent from the diseases of livestock and poultry. These excreta produced by the livestock containing antibiotics could affect rivers, lakes, groundwater, and other water bodies, through runoff and infiltration. So, a good sorbent that can remove the tetracycline (TC) from the aqueous environment is necessary to be developed.

Our research carried out to study the behaviour between the TC and montmorillonite such as SWy-2, SAz-1, SHCa-1 and SYn-1. The experimental result demonstrated that (1) the kinetic adsorption isotherm agrees with the pseudo-second order model and approaches at the maximum adsorption capacity in 2 hours; (2) it follows a Langmuir adsorption isotherm with the maximum adsorption amounts of 355 mg/g, 460 mg/g, 350 mg/g, 170 mg/g at pH=4~5; (3) the intercalation of TC makes the d-spacing of swelling clays become the full width at half maximum (FWHM) with a stack of 2 to 3 layers, indicating that after the intercalation, the TC can decrease the clay crystallinity. (4) Depending upon the nature of the swelling clay minerals and the TC concentration, the intercalation process could be transitional, involving the occurrence of mechanical mixtures, materials of intermediate layer thicknesses, and/or mixed layering of different ordering states.

It is concluded the montmorillonite can be a good sorbent to removal of tetracycline from water due to the maximum adsorption, compared to the clay minerals such as, rectorite, palygorskite, illite and kaolinite.

Keywords: kinetic, adsorption, desorption

TISSUE MINERALIZATION OF HYDROXYAPATITE

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Apatite/hydroxyapatite, one of the most widely distributed minerals in the world, exists in both sedimentary and organic environments. Although the crystallographic structure and chemical information of apatite minerals is well documented, an understanding of the formation/transformation mechanism at the microscopic level remains unclear. This paper presents the (bio)mineralization of hydroxyapatite in both natural and laboratory environments using an electron microscopy approach with an emphasis on the mineral/substrate interface.

Previous examination of hydroxyapatite's role in the development of tesserae of shark skeletons have found morphologically and elementally distinctions in the mineralized and unmineralized phases of tesserae. Both SEM and TEM images of collagen fibers illustrated the formation of tesserae and mineralization of tissue. Cross-sectional EM study revealed that isolated mineralized phases were embedded in the unmineralized tissue and hydroxyapatite crystals have been observed "walking" out from the mineral border onto the variously mineralized fibers. Electron diffraction and HRTEM images indicate that prismatic cartilage was composed of nanocrystalline hydroxyapatite. Microchemical analysis using EDS also showed a dramatic increase of Ca and P at the mineralization front while S gradually decreased.

The formation of hydroxylapatite in synthetic tissue was examined in the laboratory for bone implant integration. SEM images show that the osteoblastic culture on the acidetched Ti disk had a fibrous network with small globular structures. The cross-sectional TEM study shows a layer of well-mineralized tissue developed on the Ti substrate. The mineralized tissue consists of fibrous and platy minerals composed of Ca and P, and has the diffraction characteristic typical of hydroxylapatite. Tissue cultured remotely from the Ti layer appeared amorphous. The numerous short-range ordered fringes observed in HRTEM, indicate the presence of poorly defined nanocrystallites, which in turn infers the onset of crystallization had occurred in the tissue. The mineralization behavior of hydroxyapatite in different parts of tissue demonstrate that Ti had a positive effect on the process of tissue mineralization.

Keywords: biomineralization, tissue mineralization, hydroxyapatite, electron microscopy

**TRANSFORMATION, TRANSLOCATION DYNAMICS &
METABOLISM OF CHLORPYRIFOS IN PLANT & ANIMAL**

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INFRARED AND RAMAN STUDIES OF BIOAPATITE DEPOSITS IN HUMAN HEART VALVES

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The carbonate group is an important constituent of bioapatite, a calcium phosphate close to hydroxyapatite, main constituent of bone and dental enamel. $[\text{CO}_3]^{2-}$ can occupy two different sites in the structure (type A and B), and seems to control the growth, evolution, morphology, and physical properties of synthetic nano-carbonated hydroxyapatite [1]. Infrared and Raman spectroscopy were used to evaluate the carbonate substitution in pathological bioapatite from patients undergoing valvular replacement caused by severe aortic and mitral stenoses [2]. FTIR spectra were collected in the 4000-400 cm^{-1} spectral range using a PerkinElmer System 2000, while Raman spectra in the range 4000-200 cm^{-1} using a Horiba Jobin-Yvon LabRam Confocal Microscope at a resolution of about 3 cm^{-1} . The 3- PO_4 IR mode appears as an intense band at 1023 cm^{-1} , a shoulder at 1059 cm^{-1} , and a third band at 1104 cm^{-1} . The asymmetric stretch vibration mode (3) of CO_3 is represented by four bands at 1418, 1450, 1471, 1503 cm^{-1} while the out-of-plane bending mode (2) of CO_3 by the band at 872 cm^{-1} . This characteristic IR signature seems to be typical of Na-bearing type A-B carbonate apatite [3]. The band at 1503 cm^{-1} could indicate the accommodation of the carbonate group in a second channel position (Type A2) usually present in carbonate apatite synthesized at high-pressure [4]. On the contrary the Raman band at 1071 cm^{-1} , observed in all spectra and due to 1- CO_3 , is specific of $[\text{CO}_3]^{2-}$ substituting $[\text{PO}_4]^{3-}$ (type B) and the band observed at 961 cm^{-1} due to 1- PO_4 mode is in agreement with the shift assigned to 1- PO_4 mode for bone and synthetic type B carbonate apatite with different carbonate contents [5]. The height and area of many of the Raman peaks are strongly correlated with weight percent carbonate. The ratio of peak area at 1071 cm^{-1} and peak area at 961 cm^{-1} was used to determine the percentage of carbonate in the analyzed samples, as described by Awonusi et al. [6]. Values obtained (4.5-7.0 %) are in good agreement with those of biological apatite from bone.

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Keywords: bioapatite, FTIR, Raman

DIETARY EXPOSURE TO INORGANIC ARSENIC IN AREAS WITH ELEVATED LEVELS OF GEOGENIC ARSENIC IN LATIUM (CENTRAL ITALY)

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In Latium (central Italy), arsenic concentrations exceeding the regulatory limit of 10 µg/L for drinking water have been found in groundwater from a large area of old volcanic activity. At least in part of the area, high arsenic concentrations have been detected also in topsoil and subsoil and we recently showed that geogenic arsenic in agricultural soils is largely phytoavailable and enters the food chain at some sites. As a result, local population may be exposed to inorganic arsenic via water and also through consumption of food with higher than background arsenic concentrations. In order to assess dietary exposure to inorganic arsenic and identify the main contributors to the exposure, an integrated approach was adopted combining biomarkers of exposure, arsenic speciation (by HPLC-ICP-MS) in local food and duplicate diets, and a study of the impact of As-rich water in food processing and cooking. Total arsenic in toenails and speciated urinary arsenic (by HPLC-ICP-MS) were used as biomarkers of inorganic arsenic exposure. All subjects involved in the study provided samples of the water(s) used for drinking and cooking as well as detailed information on water use and smoking habits. Cooking experiments were done at relevant water arsenic concentrations and food processing was studied by sampling water, flour, and bread from local bakers. The intake contribution from food and water was investigated and the long-term exposure to inorganic arsenic assessed by toenail arsenic concentrations. The results are discussed in the light of the recent EFSA's assessment of inorganic arsenic exposure from food and water in European countries.

Keywords: inorganic arsenic dietary exposure, biomarkers of exposure, speciation

ARSENIC IN MINE-IMPACTED SEDIMENTS: CHARACTERIZATION, BIOAVAILABILITY, AND MOBILITY

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Fifty years of gold mining in Yellowknife on the Great Slave Lake, Canada, has resulted in a huge unresolved arsenic contamination problem in the area. Microorganisms surviving in that environment could play a significant role in redox transformations of arsenic species leading to their mobilization from sediments. The focus of our study was the quantification of two target genes in sediment samples: *arsC* and *aroA*, which are, respectively, responsible for arsenate reduction and arsenite oxidation. Quantitative real-time PCR was used to monitoring the capacity for arsenic mobilization by microbes. The amplifiable DNA for analysis of both genes was purified directly from samples by a process developed to prevent heavy metal, cyanide and chloride inhibition of enzymes in qPCR analyses. Surface sediment samples obtained from Baker Creek, which receives water from the Giant Mine tailings ponds contain from 500 to 158x10⁴ *aroA* gene copies per 1 ng total DNA, but very low numbers for the *arsC* gene, indicating that the mobility of arsenic in this environment should be low. A 2006 report revealed that arsenic, iron, and manganese concentrations in Long Lake on the Quinsam Coal Mine property were considerably elevated over provincial guidelines. There was some evidence for effects on the local benthic community. The citizens of Campbell River BC, concerned about the future of the local fishery, requested the Canadian Water Network to investigate further. We now report that the arsenic concentrations in Long Lake sediments can reach 650 mg/kg, well above background levels in the area. Statistical analysis of the analytical data from surrounding sediments, soils, and coal residues shows that the sediments in Long Lake have a unique composition. The arsenic is bound to iron oxides (XANES and X-ray studies) and is bioavailable to the indicator species *Corophium volutator* (mud shrimp). A seep into Long Lake from the mine's residue storage area was identified as one source of the contamination. Short term caged mussel studies showed that the arsenic concentration increased in mussels collected from a reference site when placed in Long Lake. Long term monitoring of the arsenic concentration in mussels in the Quinsam River indicates that an abrupt increase occurred around the year 2000 from 3 mg/L to around 8 mg/L.

Keywords: arsenic, sediment, bioavailability

SULFUR GAS MONITORING IN VOLCANIC/GEOTHERMAL AREAS WITH PASSIVE SAMPLERS: HUMAN HEALTH IMPLICATIONS

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Volcanic and geothermal areas are one of the major natural sources of sulphur gases to the atmosphere. Hydrogen sulphide (H₂S) is a toxic gas mainly associated to geothermal systems while sulphur dioxide (SO₂) is released in huge quantities from volcanoes characterized by open conduit activity. Apart from being one of the most impressive geodynamic expressions, volcanoes are also an important tourist attraction. During the summer season the number of tourists visiting the crateric areas each day is on average many tens at Stromboli, hundreds at Vulcano, Santorini and Nisyros and thousands at Etna. Touristic exploitation of active volcanic areas cannot exempt from warranting a reasonable security to the visiting persons. But while many risks in these areas have been since long time considered, gas hazard, a very subtle risk, is often disregarded. The atmospheric concentrations and dispersion pattern of naturally emitted SO₂ were measured at three volcanoes of southern Italy (Etna, Vulcano and Stromboli) while that of H₂S at four volcanic/geothermal areas of Greece (Sousaki, Milos, Santorini and Nisyros). Measurements were made with a network of passive samplers positioned at about 1.5 m above the ground, which gave time-integrated values for periods from few days to 1 month. Samplers were placed in zones of the volcanoes with high tourist frequentation. Measured concentrations and dispersion pattern depend on the strength of the source (craters, fumaroles), meteorological conditions and geomorphology of the area. At Etna, Vulcano, Stromboli and Nisyros measured concentrations reach values that are absolutely dangerous to people affected by bronchial asthma or lung diseases. But considering that these are average values over periods from few days up to one month, concentrations could have reached much higher peak values dangerous also to healthy people. The present study evidences a peculiar volcanic risk connected to the touristic exploitation of volcanic areas. Such risk is particularly enhanced at Etna where elderly and not perfectly healthy people can easily reach, with cableway and off-road vehicles, areas with dangerous SO₂ concentrations.

Keywords: sulphur gases, passive samplers

MINERALOGICAL FACTORS AFFECTING THE POTENTIAL TOXICITY OF VOLCANIC ASH

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Multidisciplinary research into volcanic ash as a respiratory health hazard arose from the eruption of Mt. St. Helens (MSH), USA in 1980 and has returned to mainstream prominence in the wake of the recent Eyjafjallajökull, Iceland eruption in 2010. Exposure to ash is known to trigger acute respiratory diseases, such as asthma and bronchitis, and has the potential to instigate chronic diseases if the particles are sufficiently fine to deposit in the alveolar region of the lungs. One suspected disease-causing mechanism arises from the existence of crystalline silica in volcanic ash, specifically as cristobalite, which is classed as a human carcinogen. Recently, we have established that the potential toxicity of volcanic ash is likely to vary depending on the type and style of eruption. Dome-forming eruptions in particular tend to generate substantial quantities of crystalline silica, which crystallises as the lava dome slowly cools. An inherent feature of domes is their instability, resulting in collapse and the generation of respirable cristobalite-rich ash. The effects of structure and composition on volcanic cristobalite toxicity are ill-defined as the physiological burden has only been sufficiently studied at one location; Soufrière Hills volcano (SHV), Montserrat. Here we present results from a systematic characterisation of the mineralogical properties of crystalline silica from a suite of volcanic locations. To further define the disease-causing potential of ash and to elucidate the properties responsible for adverse biological responses, the abundance, purity, crystallographic form, and crystal shape of volcanic silica were determined using XRD, electron microprobe, SEM, and Raman spectroscopy. As with previous observations at SHV, the cristobalite is found within the groundmass as well as growing into vugs in dome rock, in both platy and euhedral forms. The composition is impure, containing traces of other cations such as aluminium (up to 3 wt%). The quantity of cristobalite differs between volcanic settings due to variability in activity and duration of dome growth. Collating mineralogical results from MSH, SHV, Merapi, Unzen, and Santiaguito will provide insights into the global respiratory hazard posed by volcanic ash. As higher levels of cristobalite in ash raise concerns about the onset of chronic, injurious disease following exposure, it will be possible to recognize hazards based on existing settings and significantly aid risk mitigation.

Keywords: ash, cristobalite, toxicity

DIETARY EXPOSURE TO INORGANIC ARSENIC IN AREAS WITH ELEVATED LEVELS OF GEOGENIC ARSENIC IN LATIUM (CENTRAL ITALY)

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In Latium (central Italy), arsenic concentrations exceeding the regulatory limit of 10 µg/L for drinking water have been found in groundwater from a large area of old volcanic activity. At least in part of the area, high arsenic concentrations have been detected also in topsoil and subsoil and we recently showed that geogenic arsenic in agricultural soils is largely phytoavailable and enters the food chain at some sites. As a result, local population may be exposed to inorganic arsenic via water and also through consumption of food with higher than background arsenic concentrations. In order to assess dietary exposure to inorganic arsenic and identify the main contributors to the exposure, an integrated approach was adopted combining biomarkers of exposure, arsenic speciation (by HPLC-ICP-MS) in local food and duplicate diets, and a study of the impact of As-rich water in food processing and cooking. Total arsenic in toenails and speciated urinary arsenic (by HPLC-ICP-MS) were used as biomarkers of inorganic arsenic exposure. All subjects involved in the study provided samples of the water(s) used for drinking and cooking as well as detailed information on water use and smoking habits. Cooking experiments were done at relevant water arsenic concentrations and food processing was studied by sampling water, flour, and bread from local bakers. The intake contribution from food and water was investigated and the long-term exposure to inorganic arsenic assessed by toenail arsenic concentrations. The results are discussed in the light of the recent EFSA's assessment of inorganic arsenic exposure from food and water in European countries.

Keywords: inorganic arsenic dietary exposure, biomarkers of exposure, speciation

ARSENIC IN MINE-IMPACTED SEDIMENTS: CHARACTERIZATION, BIOAVAILABILITY, AND MOBILITY

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Fifty years of gold mining in Yellowknife on the Great Slave Lake, Canada, has resulted in a huge unresolved arsenic contamination problem in the area. Microorganisms surviving in that environment could play a significant role in redox transformations of arsenic species leading to their mobilization from sediments. The focus of our study was the quantification of two target genes in sediment samples: *arsC* and *aroA*, which are, respectively, responsible for arsenate reduction and arsenite oxidation. Quantitative real-time PCR was used to monitoring the capacity for arsenic mobilization by microbes. The amplifiable DNA for analysis of both genes was purified directly from samples by a process developed to prevent heavy metal, cyanide and chloride inhibition of enzymes in qPCR analyses. Surface sediment samples obtained from Baker Creek, which receives water from the Giant Mine tailings ponds contain from 500 to 158x10⁴ *aroA* gene copies per 1 ng total DNA, but very low numbers for the *arsC* gene, indicating that the mobility of arsenic in this environment should be low. A 2006 report revealed that arsenic, iron, and manganese concentrations in Long Lake on the Quinsam Coal Mine property were considerably elevated over provincial guidelines. There was some evidence for effects on the local benthic community. The citizens of Campbell River BC, concerned about the future of the local fishery, requested the Canadian Water Network to investigate further. We now report that the arsenic concentrations in Long Lake sediments can reach 650 mg/kg, well above background levels in the area. Statistical analysis of the analytical data from surrounding sediments, soils, and coal residues shows that the sediments in Long Lake have a unique composition. The arsenic is bound to iron oxides (XANES and X-ray studies) and is bioavailable to the indicator species *Corophium volutator* (mud shrimp). A seep into Long Lake from the mine's residue storage area was identified as one source of the contamination. Short term caged mussel studies showed that the arsenic concentration increased in mussels collected from a reference site when placed in Long Lake. Long term monitoring of the arsenic concentration in mussels in the Quinsam River indicates that an abrupt increase occurred around the year 2000 from 3 mg/L to around 8 mg/L.

Keywords: arsenic, sediment, bioavailability

NATURALLY OCCURRING ARSENIC AND RADIOACTIVITY IN THE NEAPOLITAN VOLCANIC PROVINCE AS A SOURCE OF A POTENTIAL HAZARD FOR HUMAN HEALTH

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The Neapolitan Province is located in the Campania Region, along the Tyrrhenian coastline, in one of the most densely populated active volcanic areas of the Earth. More than 3 million people inhabit the 1171 sq km area including Napoli city. The geology of the area is prevalently represented by volcanics, erupted from the Upper Pleistocene to Recent by Mt. Somma-Vesuvius on the east, by Ischia and Campi Flegrei volcanic fields on the west and by different ignimbrite eruptions (Campanian Ignimbrites) originated by fissural volcanic activities developed along fractures activated in the Campanian plain. Geochemical studies carried out on soils of the Neapolitan Volcanic Province (NVP) showed that soils are naturally enriched in As and its background values range between 10 and 19 mg/kg. Concentrations rise up to 150 mg/kg in correspondence with areas where ascent of geothermal fluids occur on the surface such as the Bagnoli brownfield area, the Pozzuoli and the Flegrean Littoral (Cicchella et al., 2005. *GEEA*, 5, 29–40.). Due to its volcanic nature, the whole NVP territory is also characterized by a natural radioactivity which basically is 2-3 times higher than the areas of Campania region where volcanics are not present or where they are present as a thin pyroclastic layer: total radioactivity ($E > 0.40$ MeV) is generally < 40 Bq over silico-clastic and carbonatic deposits of the inland areas and > 120 Bq in the provincial area of Napoli, where the Mt. Somma-Vesuvius and Campi Flegrei volcanic complexes occur (Lima et al., 2005. *Appl. Geoch.*, 20, 611-625). Distribution of As and natural radioactivity data obtained for the NVP have been spatially compared with cancer mortality data distribution (Montella et al., 1996. *Lega Italiana per la Lotta contro i Tumori, Istituto Nazionale Tumori, Napoli*) to evaluate if any correlation occurs between geochemical and epidemiological data (Albanese et al., 2008. In: *Environmental Geochemistry: Site characterization, Data analysis and Case histories*, Elsevier, 391-404). As matter of the fact, in the NVP the mortality rate for leukemia is higher than the regional average suggesting the existence of a potential relationship with the natural occurring radioactivity. Furthermore, liver cancer is also well correlated with As-rich areas, although such a correlation by no means implies that the naturally occurring As is a primary cause of this increased cancer risk.

Keywords: arsenic, radioactivity, cancer risk

CHARACTERIZATION OF MESOTHELIOMA INDUCING MINERAL ERIONITE BY TEM-EDS-SAED: SARIHIDIR VILLAGE, CAPADOCIA, TURKEY

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Sarihidir village of Cappadocia, Turkey have history of very high mesothelioma rate among the villagers. Erionite series, zeolite group minerals, which are known to induce mesothelioma, has been characterized by using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), powder x-ray diffraction (XRD), and inductively coupled plasma-mass spectroscopy (ICP-MS). Transmission Electron Microscopy (TEM) – EDS – Selected Area Electron Diffraction (SAED) is powerful set of techniques for quantitative characterization of erionite series minerals. In this study, TEM used for characterization of individual mineral structure and cross-sectional morphology, EDS used for mineral chemistry, and SAED for crystal structure verification. For parts of the requirements of quantitative mineral characterization, balance error test (E % < 10) and Mg-content test (Mg < 0.80) were performed on TEM-EDS results. Among the 60 analyses: 11 passed on E% test (18.3 %), 33 passed on Mg-content test (55 %), only 3 passed both E% and Mg-content tests (5 %). This shows the difficulty of obtaining quantitatively characterized erionite results. Formulas of erionite which passed both E % and Mg-content tests are presented. All three erionites that passed both tests are identified as erionite-K, which supports the previous SEM-EDS results by Dogan et al., 2006. Erionite passing both E % and Mg content tests and their proposed formulas are given:

Sample ID E % Mg Species Formula

2006-8.27	0.67	Erionite-K	K4.35	Ca0.98	Na0.26	Mg0.67	Si28.58	Al6.58	Fe0.58
2335-7.58	0.69	Erionite-K	K2.96	Ca1.81	Na0.37	Mg0.69	Si28.15	Al7.00	Fe0.70
2615-2.44	0.29	Erionite-K	K1.97	Ca1.92	Na0.14	Mg0.29	Si29.36	Al6.15	Fe0.52

Keywords: mesothelioma, erionite, quantitative mineralogy

MESOTHELIOMA INDUCING MINERALS IN CAPPADOCIA: COMPLETE MINERAL CHARACTERIZATION BY SEM-EDS-XRD

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Residents of the three “meso” villages of Cappadocia, Turkey have history of very high percentages of malignant mesothelioma (MM) as both malignant pleural mesothelioma (MPM) and malignant peritoneal mesothelioma (MPEM). Unfortunately, most houses in these villages were made from volcanic tuffs obtained from nearby sources, which are contaminated with erionite series minerals, the most carcinogenic minerals known and listed as a Group-I carcinogen for humans. Some of these villages moved to the new locations. For example, many villagers from Sarihidir were carried construction materials from their “old” houses to the “new” village and used them as construction materials either in their new houses or as garden walls. In this study, complete mineralogy of the rocks – not just erionite – have been investigated in detail and hoping that this could be a model for future investigations in quantitative mineralogy-mesothelioma relationships. The following minerals are observed: (i) Zeolite group minerals include erionite, clinoptilolite, chabazite, mordenite, faujasite, stilbite, phillipsite, epistilbite, laumontite, and paulingite; (ii) Clay minerals include montmorillonite, illite, rectorite, nontronite, and beidellite; (iii) Other rock forming minerals include: (a) silica: quartz, tridymite; (b) carbonates: calcite, dolomite, vaterite; (c) micas: biotite, lepidolite, vermiculite, phlogopite, zinnwaldite, muscovite; (d) feldspars: albite, andesine, anorthite, labradorite, bytownite, orthoclase, sanidine, anorthoclase; (e) feldspatoid: analcime; (f) evaporitics: gypsum, anhydrite, halite; (g) others: sepiolite, palygorskite, jarosite, volcanskoite, fayalite, enstatite, clinochlore, magadiite, wilhendersonite, swinefordite, antigorite, and alunite. Erionite is present in all samples collected from “meso” and “non-meso” houses. Erionite is observed in garden wall rocks of the public primary school and coffee house – the daily meeting places of the “New” Sarihidir village people. This shows that the villagers are still being exposed to erionite, although presumably in smaller quantities than at the “Old” Sarihidir village.

Keywords: erionite, mesothelioma, Cappadocia

THE GOLD MINING LEGACY: A GEOCHEMICAL HISTORY OF THE VICTORIAN GOLDFIELDS WITH EMPHASIS ON OUR ARSENIC HERITAGE

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The mineral riches of the gold fields region of Victoria, Australia, have contributed to the nations wealth and development. The region retains unique artefacts, buildings and landscape features that help explain the past to future generations and provides testimony to a rich cultural past. This landscape is also a source of environmental contamination with metals such as arsenic, mercury, antimony and lead in elevated concentrations in many media.

Assessment and management of contaminants in soils, mine waste, vegetation (both indigenous and introduced) and animal (human and other) requires both acknowledgement of the complex behaviour of the contaminant and the reservoir or media. Definitions of backgrounds become complex, the history of a site is key and the potential impact on human health worthy of discussion.

Surface soil sampling reveals highly elevated metalloid values with up to 16,600 mg/kg arsenic. Public land, accessible to all, frequently returns values in excess of 1000 mg/kg arsenic with the water soluble component approaching 3% of this value. Drinking water usually meets WHO and Australian standards but water bodies used for recreation and irrigation record values up to 2.83 mg/L arsenic. Indigenous vegetation records up to 6.86 mg/kg dry weight arsenic and vegetables can prosper in 800 mg/kg arsenic soils. Domestic vegetable gardens returned produce in excess of the 1 mg/kg dry weight guideline.

This paper summarises historical and new data from this significant gold producing domain and postulates the need for clear advice to residence of the region. On a global scale the levels reported are modest but the potential for multiple contaminated media leading to ingestion by humans is high. The issue of low level but long term exposure is discussed in the context of confounding factors. The risk to our population needs to be considered and appropriate public health debates should ensue.

Keywords: arsenic, ecosystem

ADVERSE HEALTH IMPACTS OF MINING ACTIVITIES

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Potential human health risks occur at most stages of mining life cycle, from exploration through to mine closure, and may result from both surface and subsurface mines, large and small-scale mining operations, whether located in remote locations or adjacent to towns, in pristine or degraded environments, and at all climatic zones and geomorphologically diverse areas. The mining sector comprises different activities including exploration, extraction, beneficiation e.g., crushing, screening, washing, and flotation. Other mining activities include the use of explosives, the use of chemicals, waste disposal, and Traffic of heavy equipments. It is now well documented that those mining activities have proven to have significant health impacts on the mine workers and adverse environmental impacts on the surrounding environment. The health of miners can be significantly deteriorated because of the long term and systematic exposure, ingestion, inhalation, and skin direct contact with toxic heavy metals, radionuclides, acidic drainage, and toxic chemicals e.g. cyanide, mercury or other toxic materials. Inhalation of dust and air particulate matters (PM10) are among the significant pathways into the human body of carcinogenic pollutants such as asbestos fine fibers. Asbestos and coal mining are among the activities that have produced mining related diseases such as pneumoconiosis including Asbestosis, Pleural plaques, Malignant mesothelioma, Black lung, and Anthracosis. Other mining related diseases include, Silicosis, Dental and Skeletal Fluorosis, Talcosis. Hyperpigmentation, Keratosis, and skin cancer are common diseases related to chronic arsenic exposure. Chronic health impacts can also result from other processes that are related to the mining activities such as soil and water pollution, due to the migration of contaminants from the site through the physical dispersion of particles by erosion and weathering, or from chemical dispersion such as acid rock drainage or leachate from mine wastes and tailings. Exposure to heat, noise and vibration can also impose adverse health impacts. Thus the range of mining impacts on miners health can be permanent and, in some cases, lead to fatalities. Unless proper measures and best available technologies and best environmental practices are applied to mitigate the possible health effects caused by mining activities, the health risk situations might extend far beyond the boundaries of the mine site.

Keywords: health impacts, mining activities

CUMULATIVE RISK ASSESSMENT OF LEAD, CHROMIUM AND ZINC IN GROUNDWATER AND DRINKING WATER: A CASE STUDY FROM PORT-AU-PRINCE, HAITI

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Drinking water can be considered as a complex mixture that consists of tens, hundreds or thousands of chemicals of which the composition is qualitatively and quantitatively not fully known. In Port-au-Prince, groundwater pollution by contaminants from waste disposal sites and industrial wastewater is a well-known environmental issue and poses a substantial risk to local resource users. The presence of heavy metals (chrome, nickel and lead) has been identified in water from this environmental media. Concentrations of lead [40 µg/L], Nickel [250 µg/L] and Chromium [470 µg/L] greater than the respective threshold value of these metals in drinking water, were measured in groundwater. Studies on human exposures to chemicals and associated health effects in drinking water allow to major chemical risks, particularly for children, relating to Pb(II), Cr(III), Cr(VI) and Ni(II) contained in the groundwater. However, this research has been only conducted on single chemicals. The aims of this study were (i) to carry out a brief review of to health impact from exposure to chemical mixtures in order (ii) to evaluate the cumulative risk assessment of heavy metals for human health in drinking water. Hazard index evaluation method (HI) has been used to assess the health mixture effects of the selected heavy metals on hepatic, renal organs on the groundwater consumers. A more-than-additive joint toxic action ($HI > 1$) has been obtained for the hazard index (HI) calculation of the 3 metals on both target organs. These results require monitoring in order to understand and manage the cumulative human health risk by heavy metals in Port-au-Prince's drinking water.

Keywords: heavy metals, drinking water, cumulative risk assessment

BIOACCESSIBILITY OF Pb IN URBAN SOILS AND INFLUENCE OF TEMPORAL VARIATION AND SOIL PARTICLES SIZE RELEVANT TO INGESTION

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Since the ingestion of soil particles is great source of human exposure to a variety of metals, it is essential to understand its toxicity to assess the risks they bring to health. Physiologically based extraction tests, or bioaccessibility test, which simulates sequentially the chemicals conditions encountered in the human stomach and intestine are widely employed to determine the amount of metals that is absorbed by the human body if contaminated soil is ingested [1]. Metal chosen in this work was Pb, an indicator of environmental pollution due to its history of use. The soils used in this study were collected in São Paulo, for a period of 8-months in five locations with different traffic to investigate their influences on the bioaccessibility of Pb. São Paulo was chosen because this city is considered as one of the main cities in Brazil, its population and economic growth allowed that the pollution, caused mainly for vehicles and industries, reached critical levels. Due to these anthropogenic activities, the toxic metal content, as lead, is generally high. Intake of urban soil can thereby result in significant amounts of the adults' and children's daily metal intake. The samples were sieved in order to separate soil particle fractions representing deliberate (<2 mm) and involuntary (<53 µm) soil ingestion by children, as well as a third size fraction of 53-100 µm representing soil that is easily transported by suspension. Quantification measurements were performed by ET AAS. Concentration of Pb in all samples' fraction were above reference value for São Paulo State (17 mg/kg), with maximum values of 322,4±1,7 mg/kg (Ibirapuera Park), 214,2±9,3 mg/kg (Sumaré Ave.), 227,36±1,2 mg/kg (Marginal Ave.), 120,20±3,6 mg/kg (Paulista Ave.) and 47,24±0,6 mg/kg (Nove de Julho Ave.). The bioaccessibility of Pb ranged from 7,1% to 77,8% in gastric fluid, and 1,9% to 64,8% in intestinal fluid. Changes in bioaccessibility were a function of soil particles size, in the order crescent 2mm<10053µm<53µm in gastric fluid and the opposite for intestinal fluid, and depends of temporal variation (driving style, traffic volume, matrix composts and climate conditions).

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Keywords: bioaccessibility of Pb, urban soil, ET AAS

POSSIBLE EFFECTS OF MINERALIZATION AND LITHOLOGICAL INTERACTION ON NATURAL WATER

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This paper studies the possible effects of mineralization and water-Lithological interaction on natural water of J. Ed Dair – J. Dumbeir and Mazroub areas, North Kordofan State-Western Sudan. Surface and underground samples were collected from different localities in wet and dry seasons in Ed Dair –Dumbeir area and in dry season only from Mazroub area. Physical and Chemical analysis have been done in different laboratories according to A.P.H.A standard methods. Seasonal variation of physico-chemical properties in j. Ed –Dair area has been illustrated by drawing seasonal variation graphs and by comparing the data with W.H.O Standard. Spatial distribution maps of all elements in Ed Dair area have been drawn. The same tests have been done for Mazroub area. Analytical work in Ed Dair area in wet and dry season show that the constituents which significantly affect health of human being are not within the recommended value limits of the WHO guidelines, but still below the Maximum Values, except for fluorite and Cadmium in some localities which increase from these limits. Water samples from Mazroub area exceed limits of the maximum values of the W.H.O guidelines The suitability of the waters for irrigation purposes has been also studied in the tow studied areas. Assessment of water chemistry was investigated by using different statistical techniques such as X-Y plot, correlation, factor analysis and cluster analysis. Interactions of groundwater with the lithological unit suggested by geochemical modeling.

Keywords: North Kordofan State, mineralization, geochemical modeling

BIOMONITORING GENOTOXICITY IN THERMOELECTRIC POWER PLANT WORKERS EXPOSED TO VOLATILE ORGANIC COMPOUNDS OF FUEL-OIL

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On a daily basis, several occupational groups may be highly exposed to petroleum derivatives, which are potentially genotoxic. In thermoelectric power plants, workers are exposed to volatile organic compounds (VOCs) released during the combustion of fuel used to run the turbine-generators. The present study was designed to examine the genotoxic effects of occupational exposure to VOCs in workers from a thermoelectric power plant, using the micronucleus assay with exfoliated buccal epithelial cells. A total of 44 exposed workers and 47 non-exposed individuals were recruited. The former group was mainly exposed during the transportation of fuel oil and naphtha and the maintenance of turbines and engines. For each individual, 1000 buccal epithelial cells, stained according to the Feulgen method, were analyzed for the frequency of micronucleated cells and cells with other nuclear anomalies (pyknosis, karyorrhexis, and karyolysis). Information on life-style factors and an informed consent were obtained from each participant. Significant differences ($p < 0.001$) in the median frequencies of micronucleated cells (1.8 vs. 0.2) and cells with other nuclear anomalies (82.4 vs. 58.3) were observed between VOC-exposed and non-exposed individuals. The analyzed confounding factors (age, smoking, alcohol, and mouthwash) did not show any significant association with the frequency of micronucleated cells, while age was found significantly associated with the frequency of cells with other nuclear anomalies. To our knowledge, this is the first report linking VOCs' exposure to potential genotoxic effects in buccal epithelial cells of thermoelectric power plant workers.

Keywords: micronuclei, volatile organic compounds (VOCs), occupational health

TRACE ELEMENT INVESTIGATIONS IN KIDNEY STONES: A PILOT CASE IN BASILICATA (SOUTHERN ITALY)

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Trace elements have been found in kidney stones. Their role in lithogenesis is debated. They may be involved in crystal induction depending on the particular relations between metals and solutes able to crystallize in urine. It is common knowledge that kidney stone is one of the most common health problems in the world and that it is strictly connected with environmental factors. It is important to highlight that kidney stones containing trace elements could be considered as environmental pollution markers. Our study aimed at assessing the content of trace elements in kidney stones collected among the Basilicata (southern Italy) inhabitants. 48 kidney stones composed of calcium oxalate, calcium phosphates, uric acid, cystine and a mixture of these were analyzed for the content of specific chemical elements either involved in the kidney stone crystallization process (Ca, Mg, K, Zn, Fe, Cu, Mn) or potentially toxic (Pb, Cr) by AAS, ICP, and a SEM microanalysis was carried out on petrographic thin sections. This study confirms the presence of some foreign elements in the kidney stone structure. Three main findings emerge from the results: 1)most kidney stones collected have high concentrations of elements such as K, Cu and Mg and a low content of Fe when compared to the results obtained from other researches; 2)appreciable amounts are found in inorganic phases (calcium oxalate e phosphates), whereas only Zn content is higher in organic phases (uric acid and cystine); 3)among calcium-containing stones (more abundant), the calcium-phosphate ones contain greater amounts of trace elements than the calcium-oxalate ones, and among the calciumoxalate ones weddellite retains more trace elements than whewellite. Furthermore, the results show that the concentration of Zn, Cu, Fe, Pb and Cr is greater than that of a standard diet ingestion, therefore varying amounts of these elements may be attributed to their enrichment in the diet of the inhabitants of polluted areas.

Keywords: trace elements, kidney stones

THE COMPOSITION OF KIDNEY STONES: COMPOSITIONAL FEATURES AND ENVIRONMENTAL INFLUENCE ON BASILICATA (SOUTHERN ITALY) CASE STUDY

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The aims of this study are to analyze the geo-environmental factors, which can influence the kidney stones formation and identify the main types of kidney stones to be found in Basilicata, through a chemical-mineralogical and petro-morphologic study. A three-year-long epidemiological study was carried out in order to identify the prevalent nephrolithiasis. A representative sample of the Basilicata inhabitants hospitalized at San Carlo Regional Health Service Trust in Potenza was chosen in order to find out their dietary and behavioural habits through the submission of a questionnaire during the observation period. In order to identify a statistical relation between a supposed factor (or exposition to a certain factor) and the development of kidney stones in Basilicata, parameters of statistical association will be determined: Odds ratio. A morphological and compositional characterization together with the use of integrated techniques - optical and scanning electron microscopy and X-ray powder diffraction - were performed on more than 80 kidney stones collected in three years. Some thin petrographic sections were obtained for a representative number of bigger kidney stones. The amount of some chemical elements specifically involved in the kidney stone crystallization process (Ca, Mg) or potentially toxic (Pb, Cr) was found by means of optical and atomic absorption spectrometry. This scientific activity is a first example of Italian study of kidney stones carried out at regional level with a multidisciplinary approach which made it possible significant achievements in the field of human health protection. This morpho-compositional data are useful for classifying each type of kidney stone, and, therefore, each patient in more than 30 different subgroups characterized by specific etiologic factors necessary to determine the treatment and disease prevention, especially in the presence of mixed stones requiring proper intervention for each mineral phase present. Kidney stones, being so widely spread in many stone types, can be considered as markers to evaluate the presence of trace elements, especially those potentially toxic, in human body as well as in the environment. Several kinds of kidney stones with a new mineral assemblage have been found and this represents a further step forward in understanding this widespread disease and stimulates further research.

Keywords: kidney stones, classification and composition, environmental influence

DISTRIBUTION OF ARSENIC IN SPRING WATERS FROM TWO BASINS ASSOCIATED TO MESSEJANA PLASENCIA DYKE (AMBLÉS AND CORNEJA VALLEYS, SPAIN)

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The Central Iberic Zone (Central System, Spain) is principally composed of schists, greywackes, and granitoides and it is a geotectonic area with significant mineralization. In the northern sector the mountains of the Central System are in contact with Tertiary sediments of the Duero basin and other smaller basins, where high concentrations of arsenic are known to occur (Sahún et al. 2004, García-Sánchez et al. 2005, Giménez et al. 2010). Forty-seven spring waters have been sampled in two pull-apart basins associated to Messejana Plasencia Dyke: Amblés and Corneja Valleys. Electrical conductivity, pH, ORP, and temperature were determined in the field. Major and some minor (As, B, F, Li, Sr) ions, and SiO₂ have been analyzed in the laboratory. Most of the waters have been classified as bicarbonate (80%). Chloride waters represent only 15% of total. Nitrate concentrations reach very high values in some samples. For cations there are no significant differences. Results demonstrate that spring waters from Amblés have higher levels of salinity than those collected in Corneja Valleys, but in both cases arsenic levels are generally low. Most of the samples have levels below 5 µg/L, and samples with arsenic levels higher than this value have been found in only two points of Corneja Valley. In two points from Amblés Valley hydrogeotoxicity by arsenic is higher than 1 (HGTAs>1, Giménez et al. 2010). Waters are usually oxic waters with pH levels around 7. Dissolved arsenic concentrations could be explained by silicate weathering processes and the influence of deep groundwaters. Further study will be necessary to determine whether the arsenic occurrences are linked mainly to water-rock interactions, structural features or anthropogenic contamination.

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Keywords: arsenic, hydrogeotoxicity, Central System (Spain)

RISK-BASED REGIONAL RANKING OF HEALTH ENVIRONMENTAL STRESSORS

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The EU Health and Environment Action Plan (2004) highlights that more integrated and effective information and tools are required to support environmental health policies. In this context, there is a need for screening approaches to address detailed health risk and impact assessment towards the most critical stressors and scenarios. The identification in a regional context of the priority chemical contaminants to be further investigated, according to their risk for human health, is indeed a challenging task. To this aim, in the frame of the FP6 European Project 2-FUN (Full-chain and UNcertainty Approaches for Assessing Health Risks in FUture ENvironmental Scenarios) a “Risk-based Tool for the Regional Ranking of Environmental Chemical Stressors” has been developed, aimed at supporting decision-makers in the identification of priority environmental contaminants, as well as priority areas, to be further assessed. The tool implements a methodology based on a Weight-of-Evidence approach, integrating three types of information, identified as “Lines-of-Evidence”, i.e.: 1) LoE “Environmental Contamination”, including data on chemical contamination of environmental matrices in the region and informing thus about potential population exposure; 2) LoE “Intake”, including results from biomonitoring campaigns (i.e., chemicals concentrations in human biological matrices) and supporting the knowledge on actual population exposure to chemicals; 3) LoE “Observed Effects”, including information on the incidence of health outcomes associated to environmental exposure to chemicals. A Multi-Criteria Decision Analysis methodology was developed to support the integration of information related to the three LoEs for each chemical and associated health outcomes. The tool allows to rank chemical stressors at the regional level as well as within each sub-area (e.g. counties). Moreover, it supports the identification of priority sub-areas within the region, where environmental and health data suggest possible health effects and thus more investigation efforts are needed. Results of a testing application to the region of Flanders (Belgium) will be presented. In the application, data on soil contamination by metals and organic contaminants are integrated with data on exposure biomarkers and data on health effects measured in adolescents within the frame of the biomonitoring campaign realized by the Flemish Centre of Expertise for Environment and Health in the period 2002-2006.

Keywords: chemicals ranking, health risks, biomonitoring

GROUNDWATER GEOCHEMISTRY, QUALITY AND ITS IMPACT ON HUMAN HEALTH: FIELD BASED DENTAL FLUOROSIS ASSESSMENT IN THE MAIN ETHIOPIAN RIFT

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This study aims to investigate the link between geology, water quality and health impacts on rural communities in the Main Ethiopian Rift (MER) who rely on the local groundwater as drinking water source. The local population is affected by dental and skeletal fluorosis as an estimated 8 million are exposed to high fluoride groundwater. Of 50 studied groundwater wells, 48 (96%) exceed the permissible fluoride limit of 1.5 mg/L prescribed by WHO. The fluoride contents in the groundwater (mean: 9.2 ± 9.6 mg/L) are associated with other toxic elements such as As, U, V, Mo and B. Particularly, 54% of the investigated groundwater wells show As concentrations above the WHO recommended limit of 10 µg/L. Leaching experiments of the MER rhyolitic rocks and their weathered sediments were shown high concentrations of F, As, Mo and U in leachates, suggesting that the local sediments represent the main source for toxic elements. The health impact was evaluated based on two approaches (1) field observation of the various degrees of dental fluorosis and collection of supplementary interview data (n=73 individuals) including gender, age, water consumption, diet, water sources for drinking; and (2) sampling of biomarkers (toenails and fingernails) for analyses of bioaccumulation of toxic elements. Preliminary data confirm that observational occurrences of prevalence and severity of dental fluorosis (normal-mild-moderate-severe) increase with fluoride concentrations in groundwater. Consequently, the data suggest that higher fluoride concentrations in groundwater are associated with an advanced degree of fluorosis among individuals who consume the groundwater as their primary drinking water. Based on the field dental health assessments, two major areas that are adversely affected by dental fluorosis (“hot spots”) were identified. Given water constraints the rural communities are mainly restricted to agricultural products such as maize, teff (Ethiopia’s indigenous cereal), and wheat. Dairy products are barely available. Thus, in addition to water quality, poor nutrition and diets (calcium and vitamin D deficiency) are plausibly contributed in aggravating the impact of fluoride on the health of the people. At the next phase of the research, the presence of other contaminants is examined with evaluation of their specific health impacts. This pilot study integrates water geochemistry and field-based epidemiology can be similarly applied to other sectors of the East African Rift.

Keywords: aqueous geochemistry, fluorosis assessment in Ethiopian Rift, human nails

GEOSTATISTICS: A COMMON LINK BETWEEN MEDICAL GEOGRAPHY, MATHEMATICAL GEOLOGY, AND MEDICAL GEOLOGY

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Geostatistics provides a set of statistical tools for the analysis of data distributed in space and time. It allows the description of spatial patterns in the data, the incorporation of multiple sources of information in the mapping of attributes, the modeling of the spatial uncertainty and its propagation through decision-making. Since its development in the mining industry, geostatistics has emerged as the primary tool for spatial data analysis in various fields, ranging from earth and atmospheric sciences, to agriculture, soil science, environmental studies, and more recently exposure assessment. In the last few years, these tools have been tailored to the field of medical geography or spatial epidemiology, which is concerned with the study of spatial patterns of disease incidence and mortality and the identification of potential “causes” of disease, such as environmental exposure or sociodemographic factor.

Data available for human health studies fall within two main categories: individual-level data (e.g. location of patients and controls) or aggregated data (e.g. cancer rates recorded at county or ZIP code level). Although none of these datasets falls within the category of “geostatistical data” as classically defined in the spatial statistics literature, geostatistics offers a promising alternative to common methods for analysing spatial point processes and lattice data. One of the most challenging tasks in environmental epidemiology is the analysis and synthesis of data collected at different scales and over different spatial supports. For example, one might want to explore relationships between health outcomes aggregated to the ZIP code level, census-tract demographic covariates, and exposure data measured at a few point locations. Geostatistics provides a theoretical framework for performing the various types of changes of support, while providing a measure of the reliability of the predictions.

This paper provides an overview of geostatistical methods available for the analysis of geological and health data, with a focus on the issue of error propagation, that is how the uncertainty in input data (e.g. arsenic concentrations) translates into uncertainty about model outputs (e.g. risk of cancer). Methods for uncertainty propagation, such as Monte-Carlo analysis, are critical for estimating uncertainties associated with spatially-based policies in the area of environmental health, and in dealing effectively with risks.

Keywords: uncertainty, interpolation, cancer

CALCIUM PHOSPHATE RENAL CALCULI: FINE STRUCTURE, COMPOSITION, AND MECHANISM OF FORMATION

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Chemical composition of non-homogeneous phosphate stones should be related to the conditions prevailing during the formation of each individual part. The object of this communication is to provide detail study of phosphate stone composition on micro- and macro-scale.

Fine inner structure, chemical and phase composition of 10 phosphate calculi from different patients were determined by chemical (wet) analysis, observation by scanning microscope, semi-quantitative determination of Ca, Mg, P and C by energy dispersive X-ray and to X-ray diffraction.

Eight calculi are formed by amorphous calcium phosphate and two by hydroxyapatite. Magnesium was inversely related to Ca/P ratio. Chemical composition of solid phase, in specific areas, varies in wide limits, i.e. composition of calculus interior is highly inhomogeneous on microscale.

All studied calculi contain an abundance of organic matter incorporated in their volume; the content of carbon is a double of the calcium content in molar quantities. Phosphate renal calculi with the low Ca/P molar ratio predominantly consist of amorphous calcium phosphate whereas these with the high Ca/P molar ratio are composed of poorly crystalline hydroxyapatite which can be partially carbonated. Magnesium may be an inhibitor of HAP formation from urine. Abundant organic matter incorporated into calculus volume indicates its decisive role at stone formation. Variable point composition of stones implies widely varying conditions during their development. The following mechanism of phosphate stone formation is considered: organic debris accumulated in kidney cavities serves as a template for formation of a solid phosphatic concretion from supersaturated urine (at urine pH values above 6.2) through heterogeneous nucleation processes.

Keywords: phosphate calculi, structure and composition, etiology

A TOXICOLOGICAL APPROACH TO ENVIRONMENTAL EDUCATION IN CHEMICAL SCIENCES: EXPLORING A NEW FIELD OF STUDY

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Chemistry, with all its scientific and technological applications, is a protagonist of the various processes of contamination, as well as of its detection, prevention and control. Toxicology, which emerged historically as the “Science of Poisons”, has been widening its scope of study as a consequence of recognizing that “problems such as atmospheric pollution, the destruction of ecosystems or the disappearance of species have a serious impact on human beings...” (1). Nowadays it includes multiple areas, most of them directly or indirectly linked to the environmental problems: Environmental Toxicology, Ecotoxicology, Medical Geology are already common topics. Toxicology is essentially the interdisciplinary science that studies the adverse effects of chemical substances on living organisms. In Uruguay, the Faculty of Chemistry, together with areas of the Faculties of Science and Engineering, is the main university institution devoted to the formation of professionals and researchers in Chemical Sciences and their diverse applications. Due to the responsibility of chemical substances in the affectation of the environment, a solid environmental background is imperatively required for all students of these faculties in the present context.

Toxicology, Chemistry and Environment are nowadays thoroughly intertwined as regards, for example, the impact of chemicals on the health of all living organisms. In the Faculty of Chemistry of the University of the Republic in Uruguay, the former course of “Chemical Toxicology” has been substituted and widened by four new courses at present. Beyond the particular characteristics of each course and their relationships with the “environmental issue”, there is a need to explore and expand the environmental perspective to the same fundamentals of Toxicology.

In this study we want to present, through the example of our Toxicology courses and our research practice, the emerging need to make a deeper reflection about Environmental Education, in order to prevent the risk of just applying a stereotyped label of “environmental”. At the same time, we intend to show the particular ability of Chemical Toxicology to facilitate the integration of the environmental perspective to the curricular contents of our university teaching.

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Keywords: environmental education, chemistry, toxicology

WATER QUALITY ANALYSIS OF HEAVY METALS As, Cd, Cu, Pb, AND Hg FROM ETANG SAUMATRE LAKE IN HAITI

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Etang Saumtre (Lac Azuie) in Haiti is a saline lake on the border between Haiti and the Dominican Republic. This lake will soon be facing a population increase of thousands of people as a result of the recent January 2010 earthquake. These people will be using the wells surrounding the Etang Saumatre for drinking water and domestic purposes. Etang Saumatre is also an important resource for subsistence fishers, feeding 25,111 people annually. It is important that water quality in the lake and groundwater be investigated in order to ensure that the resources are sufficient for human consumption. Moreover we need to better understand the connections between the lake and groundwater system to potentially mitigate any possible health concerns. Water samples were taken from Etang Saumatre and surrounding wells and the dissolved concentrations of arsenic, cadmium, copper, lead, and mercury were determined by ICP-MS. These heavy metals, known to be most hazardous to human health, are considered toxic at certain concentrations according to World Health Organization's Drinking Water Quality Standards (2008). The results showed that the concentrations of these metals were above the toxic level in most of the sampling sites. The results for cadmium, lead, and mercury also showed that there were similar concentrations between the groundwater wells and the lower depths of the lake which would provide evidence for groundwater flow into the lake.

Keywords: water quality, heavy metals

THE RESPIRATORY HEALTH HAZARDS OF VOLCANIC ASH: A REVIEW OF CURRENT KNOWLEDGE FROM A MINERALOGICAL AND TOXICOLOGICAL PERSPECTIVE

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Following the eruption of Mt St Helens, USA, in 1980, it was recognised that volcanic ash had the propensity to cause acute and chronic respiratory disease. In particular, the presence of cristobalite, a form of crystalline silica, was of concern as it may cause silicosis and is a carcinogen. Despite a number of epidemiological, clinical, toxicological and mineralogical studies at Mt St Helens, the overall hazard of the ash remains unclear, particularly as exposure was fairly limited.

Dedicated research on the respiratory health hazards of volcanic ash resumed in 1995 following the onset of eruptions at Soufrière Hills, Montserrat (still ongoing today) where, in addition to abundant crystalline silica, it was recognised that reactive iron on the particle surfaces could provide a mechanism for toxicity. Here we present a summary of detailed studies done by our group and collaborators on ash from the Soufrière Hills eruptions, as well as Chaitén (Chile), Vesuvius and Etna (Italy), Sakurajima (Japan), Rabaul (Papua New Guinea), Merapi (Indonesia) and Eyjafjallajökull (Iceland), which have erupted a range of ash compositions (mafic to highly silicic).

Our analyses have shown that volcanic ash erupted from the collapse of lava domes is the most hazardous in terms of cristobalite content but also that efficient fragmentation in dome-collapse pyroclastic flows generates abundant inhalable material. Particularly fine ash is also during interaction between fresh magma and water (phreatomagmatic activity) e.g. at Mt Vesuvius in AD79. Basaltic eruptions usually generate coarser ash but the high iron content of the magma correlates with increased iron-catalysed surface reactivity (measured through generation of the deleterious hydroxyl radical). Many volcanoes produce fibre-like particles but we have only observed these as rare occurrences amongst 'normal' angular, blocky ash particles.

In recent years we have included toxicological assessment within our 'rapid analysis' protocol. To date our results concur with the overall view of more detailed studies at Mt St Helens and Soufrière Hills: the ash is not as toxic as expected given the presence of cristobalite. Fundamental research on the properties of the cristobalite has found that the cristobalite's toxicity may be impaired because of substituted cations (particularly Al) in the crystal structure and because the surfaces of cristobalite particles may be occluded by coatings of glass or adhered mineral grains.

Keywords: volcanic ash, health

COAL-RELATED HEALTH ISSUES IN CHINA: PAST, PRESENT, AND FUTURE

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P.R. China is the world's oldest and largest producer and user of coal. Coal mining and coal use has left a long legacy of safety and health problems. In the past, millions of rural villages using coal in residential environments have suffered serious health problems such as arseniasis, fluorosis, selenosis, and probably mercury poisoning, in addition to lung cancer likely caused by mobilization of fine-grained quartz particles. Emissions from old coal burning power plants have contributed to country-wide air pollution resulting in widespread respiratory and related health problems. Although many of these problems have been diminished through education, medical attention, improved technology, and increased standard of living, many health issues still remain. Among these are: Black Lung disease that impacts thousands of coal miners each year; the health effects of prolonged heat exposure as coal mining extends deeper into the earth; uncontrolled coal fires mobilize toxic elements and toxic organic compounds that impact the coal miners and nearby villagers; the use of toxic trace element rich coal alternatives such as stone coal and oil shale. Future coal-related health issue may include the effects of drinking water that has been in communication with low-rank coal deposits and other long-term, low-level exposure to particulates, trace elements, organic compounds, acid gases, etc. mobilized by coal mining, transportation, combustion, and coal byproduct use and disposal. Collaboration between the geoscientist, medical community, and the coal mining industry will be critical in recognizing these more subtle health issues and devising practical solutions.

Keywords: coal, trace elements, human health

INVESTIGATION OF SNAIL POPULATION DYNAMICS FOR SCHISTOSOMIASIS TRANSMISSION CONTROL USING STRONTIUM ISOTOPE TRACERS

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Schistosomiasis, which is the second-most prevalent tropical disease affecting two-hundred million people annually world-wide, is caused by infections of parasitic worms of the genus *Schistosoma*, which use snails of the genus *Oncomelania* as intermediate hosts for maturation before contaminating freshwater. Lake and marshland regions of China continue to have problems with human schistosomiasis infection, which can be partially attributed to the inability to control snail populations in an environmentally sensitive manner. The parasite maturation process in a snail is required for the schistosomes to be capable of penetrating a mammalian host. The study and control of snail populations, therefore, is a key aspect for reducing human infection rates. This research project focuses on snail population dynamics (specifically population origin) using strontium isotopes in snail shells as a tracing mechanism. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) are commonly used as a tracer for water-rock interactions because the ratio observed in a water is inherited from the source rocks with which it contacts. Studies that have been conducted on tracking the movement patterns of fish using $^{87}\text{Sr}/^{86}\text{Sr}$ in otoliths (ear bones) indicate that the use of strontium isotopes as a tracer for snails would be valid because of the composition and formation similarities between snail shells and fish otoliths, coupled with significant variations of $^{87}\text{Sr}/^{86}\text{Sr}$ in the source waters throughout the region. The goals of this research are (1) to prove a relationship exists between strontium isotopes in water and snail shells by sampling from locations of varying $^{87}\text{Sr}/^{86}\text{Sr}$, and then testing the most recent formed shell material (shell aperture) for $^{87}\text{Sr}/^{86}\text{Sr}$ and comparing to the water where the sample was collected, and (2) to determine the origin of snail populations in the Chinese Lakes of Poyang and Dongting (known for endemic schistosomiasis) by testing shell samples from the lakes for $^{87}\text{Sr}/^{86}\text{Sr}$ in the oldest shell material (shell apex) and comparing to different source waters in the region. This talk will present the preliminary research findings, including the relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ in snail shells and source waters.

Keywords: schistosomiasis, strontium isotopes

VINYL CHLORIDE CONTAMINATION IN AQUIFERS AT U.S. NPL SITES CORRELATED WITH INCIDENCE OF LIVER CANCER

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National Priority List (NPL) sites designated by the U.S. Environmental Protection Agency (USEPA) as having vinyl chloride monomer (VCM) contamination in nearby ground-water aquifers pose an excess cancer risk to residents in the vicinity. The target organ for vinyl chloride is the liver, as indicated by higher incidences of liver cancer for workers in plants polymerizing polyvinyl chloride (PVC). PVC sludge wastes containing some un-polymerized VCM were disposed indiscriminately, infiltrating permeable substrate to contaminate local aquifers. Some dumping was sanctioned by government regulators, who, before the 1980s, did not recognize the carcinogenicity of VCM and did not demand containment of the leachate. Residents drank the VCM-contaminated water from their wells until health dangers were realized starting in the 1980s. Now, thirty years later, higher incidences of liver cancer have been recorded in these areas.

VCM contamination (USEPA data) was compared with liver cancer incidence (Center for Disease Control and Prevention (CDC) data) in several U.S. states. Of the ca. 1300 NPL sites, 524 have VCM as the contaminant of concern. Data were evaluated considering possible exposure scenarios. When plotted, a linear trend was noted indicating increasing rates of liver cancer incidence compared with the location of nearby VCM contamination at NPL sites. The U.S. states studied, Maryland, Delaware, Pennsylvania, Ohio, Massachusetts, New Jersey, and Washington State, all showed this correlation.

Although other causes of liver cancer could be responsible, namely arsenic, diabetes, cirrhosis of the liver, and heredity, nevertheless, it would be prudent to limit ingestion of ground water down gradient from NPL sites having VCM. Private wells are normally not regularly tested for VCM or other organic contaminants. Public wells are normally not tested regularly for VCM unless a problem is anticipated. Even when tested for VCM, the analytical detection limit is normally higher than needed to assure health protection. The Maximum Contaminant Level (MCL) for VCM used by the USEPA as a standard for public water supply testing is 2 ug/L, whereas an excess cancer risk of one in 100,000 is possible with a concentration of 0.24 to 0.48 ug/L.

This study underscores the potential danger of long-term ingestion of water from aquifers in areas that have VCM concentrations, even at levels that meet drinking-water standards.

Keywords: vinyl chloride, liver cancer, NPL sites

MINERALOGICAL CONTROLS ON LEAD BIOACCESSIBILITY IN TAILINGS DUST

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One of the main risks that exposed and unvegetated tailings pose to human health is airborne dust that may be inhaled or ingested. In the case of Pb-bearing dust, both particle size and the identity of the Pb-hosting minerals affect the degree of risk. Finer dusts (<5µm diameter) have a higher potential of being ingested deeper into the human lung causing possible tissue damage and toxic effects. We have collected size-fractionated airborne dust and near-surface tailings at New Calumet Mine, Quebec, Canada, a former Pb and Zn producing mine. The project is intended to evaluate and improve methods for risk assessment of abandoned and unvegetated mine waste based on mineralogical speciation and bioaccessibility testing. The most bioaccessible Pb compounds are PbCO₃ (cerussite), Pb₃(CO₃)₂(OH)₂ (hydrocerussite) and PbO, followed by PbSO₄ (anglesite), PbS (galena) and Pb₅(PO₄)₃Cl (pyromorphite) (Plumlee and others, 2006). Airborne dust samples were collected on the tailings piles using a PIXE (Particle Induced X-ray Emission) Cascade Impactor which separates aerosol fractions onto nine impactor stages ranging from 16µm to 0.06µm. These stages were then analysed by PIXE to obtain elemental concentrations. Bulk samples of the tailings were collected for bioaccessibility tests as well as for total metal content, grain size distribution, and Pb speciation using ESEM (Environmental Scanning Electron Microscope) techniques. Both airborne dust and bulk tailings samples underwent synchrotron microanalysis including microXRD (micro X-ray Diffraction) for identification of microcrystalline compounds and microXRF (micro X-ray Fluorescence) for element mapping and metal ratio evaluation. The bioaccessibility tests involved gastric and pulmonary leaching of metals by simulated body fluids. Despite extensive oxidation of iron sulphide minerals in the near-surface tailings, galena persists as the most abundant Pb-bearing phase. However, rims of hydrocerussite forming alteration rims on some galena grains have been identified by ESEM, microXRD and microXRF. Element mapping also indicates a correlation of Pb with Cl and Fe suggesting that additional Pb may be hosted in Fe oxyhydroxides and pyromorphite.

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Keywords: tailings, dust, bioaccessibility

CHARACTERIZATION OF INDIVIDUAL PARTICLES IN DUST SAMPLES

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A comprehensive understanding of the risk associated with metal-bearing dust includes identification of the solid phases hosting the metals. Synchrotron microanalysis can provide information on elemental concentrations, crystal structure and oxidation state of individual particles, and distinguish anthropogenic from geogenic sources. At abandoned gold mines in Nova Scotia, windblown and vehicle-raised dust was collected in seven aerodynamically fractionated size ranges (0.5 to 16 µm) using a cascade impactor deployed at three tailings fields. All three sites are used for recreational activities and off-road vehicles were racing on the tailings at two mines during sample collection. MicroXRD of individual particles was used to identify Fe-As⁵⁺ weathering products including scorodite (FeAsO₄•2H₂O) and amorphous hydrous ferric arsenate. Microanalysis was applied to house dust and garden soil from a single urban home in Ottawa, Canada with the purpose of distinguishing metal associated with soil particles from metal associated with indoor consumer products. Element correlations (via XRF mapping) and microXRD prove to be the most valuable tools. In the living room, Pb is associated with Mn and Fe hydroxide and phosphate minerals, similar to particles identified in the garden soil. However, in the bedrooms, Pb-based and non-Pb paint pigments as well as gypsum, bassanite and portland cement indicate in-home renovation. Zinc is present as zincite and wurtzite, constituents of the pigment lithophone, and also in metallic form. A principal advantage of synchrotron-based microanalysis is that little or no sample preparation is needed and thus there is little risk of post-sampling modification.

Keywords: tailings dust, house dust, synchrotron microanalysis

BIOACCUMULATION AND DISTRIBUTION OF ARSENIC IN AQUACULTURAL FISH RAISED IN CONTAMINATED GROUNDWATER: POTENTIAL RISKS FOR HUMAN INTAKE

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Aquacultural tilapia (*Oreochromis mossambicus L.*) and shrimp (*Penaeus monodon L.*) from groundwater-cultured ponds in southwestern Taiwan (Budai, Yichu and Beimen) were analyzed to estimate the arsenic (As) bioaccumulation and the potential health risk to human intake. Most of the aquacultural ponds exhibited higher arsenic concentrations than the government-mandated safe limit ($50 \mu\text{g L}^{-1}$) of Taiwan. Arsenic concentrations in tilapia in Budai ($0.33\text{-}1.58 \text{ mg kg}^{-1}$) were found to be higher than those in Yichu ($0.791.07 \text{ mg kg}^{-1}$) and Beimen ($0.73\text{-}0.78 \text{ mg kg}^{-1}$). Mean arsenic concentration in shrimp was found $0.36 \pm 0.01 \text{ mg kg}^{-1}$ in Beimen. Bioaccumulation of arsenic in tilapia is highly correlated ($r^2=0.80$) with arsenic concentration of pond water. Arsenic concentration in total fish is also highly correlated with that in bone ($r^2=0.98$), head ($r^2=0.97$) and tissue ($r^2=0.96$). Among three different arsenic species studied, organic species of DMA (dimethyle arsenic acid sodium salt) was found higher relative to inorganic species of As(III) and As(V). The bio-concentration factors (BCFs) of fish were 10.3 to 22.1. The values of TR (target cancer risk) for all fish were very high (2.9×10^{-4} to 13.9×10^{-4}) in comparison to the USEPA safe standard (1×10^{-6}). The THQ (Target Hazard Quotient) values were also very high (1.5-7.2) in comparison to the USEPA safe standard (1.0). These results suggest that the local inhabitants in this region were subjected to arsenic exposure at levels known to cause carcinogenic and non-carcinogenic health effects.

Keywords: groundwater arsenic, tilapia, bioaccumulation

EFFECTS OF EXPERIMENTAL METHYLMERCURY INTOXICATION: QUANTIFYING THE APOPTOTIC PROCESS IN BRAIN

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Methyl mercury (MeHg) is a widespread environmental pollutant that is characterized as a substance with potent toxic effects on the central nervous system (CNS). We have previously shown that MeHg infusion for 90 min. induces an immediate and significant elevation of extracellular glutamate levels (Juárez et al. 2001). In addition, the same concentrations that induce an increase in extracellular glutamate levels induce cell death by apoptosis, involving the NMDA receptor (Juárez et al., 2005). The aim of this study was to determine if these concentrations induce neuronal death in brain by apoptosis. Fifteen female Wistar rats (n=5) were administered with MeHg at doses of 2, 4 and 6 mg/kg body weight by esophageal tube for three weeks, on a daily basis, control group only water was administered. Animals were weighed at the beginning and end of the experiment. At the end of exposure, animals were perfused via intracardiac saline and PBS buffer solution with 4% paraformaldehyde, the brain and cerebellum were placed in a fixative solution to preserve them until their inclusion in paraffin. Tissues were cut by 7 microns thick and apoptosis in them was determined in situ using TUNEL immunohistochemistry assay. Animals that were given the highest dose, showed of apoptotic cells in the frontal cortex and cerebellum, these animals showed a significant weight loss compared to animals that were given lower doses which showed no evidence of apoptosis, suggesting that in cases of exposure to low doses of MeHg that do not significantly alter the animal metabolism in which apoptosis does not occur.

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Keywords: methylmercury, brain, apoptosis

DIFFUSION OF SUPPORTED PHOSPHOLIPID BILAYER MEMBRANES ON THE SURFACE OF B-ORIENTED MFI FILM WITH CONTROLLED SURFACE ROUGHNESS

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Supported phospholipid bilayer membranes (SPBs) are extensively investigated as models of cell membranes [1]. The effect of interaction of SPB with support surface on SPB diffusion was often addressed. Variety of non-porous supports with smooth surfaces like mica, silica, etc. has been already used. Application of porous supports is rather rare (cf. [2] and references therein). The b-oriented MFI film grown on stainless steel (bMFI/SS) with controlled surface roughness is used in present study. The main advantage of this support is its simplicity. Moreover, further modification of the b-MFI/SS surface and interface region is rather straightforward, which enables tailoring the properties of the film surface in desired manner.

Mixed 1,2-palmitoyl-oleoyl-sn-glycero-3-phosphocholine (POPC) / 1,2-palmitoyl-oleoyl-sn-glycero-3-phosphoserine (POPS) (4:1 mol:mol) lipid vesicles labeled with Bodipy C12-HPC (2-(4,4-difluoro-5,7-dimethyl-4-bora-3a,4a-diazas-indacene-3-dodecanoyl)-1-hexadecanoyl-sn-glycero-3-phosphocholine) were deposited on b-MFI/SS. Creation of SPB was confirmed using fluorescence microscopy combined with fluorescence correlation spectroscopy (FCS). Using the synthesis according [3] with modified conditions and post-synthetic treatments the series of b-MFI/SS samples with various surface roughness was prepared. The zeolite support prepared by one step hydrothermal treatment is composed mainly from the monolayer of b-oriented overgrown crystals with small amounts of inserted a-oriented ones. The b-oriented zeolite surface with minimized concentration of the a-oriented MFI crystals exhibits roughness typically 50 nm. The overall support surface roughness is tuned by changing the concentration of the a-oriented surface crystals (a ~100 nm). The effect of thus introduced roughness of support surface on SPBs – b-MFI/SS film interaction is investigated using fluorescence. Diffusion of SPB measured with FCS was found to be affected by surface roughness of b-MFI/SS. SPBs lateral diffusion on surface with prevailing roughness of 50 nm was about two times faster ($D = 3.5 \text{ m}^2/\text{s}$) than the one on the surface with 100 nm roughness ($D = 2.4 \text{ m}^2/\text{s}$).

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Keywords: phospholipid bilayer membranes, surface roughness

HUMAN EXPOSURE TO ARSENIC FROM DRINKING WATER AND ASSOCIATION WITH SKIN LESIONS

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The widespread incidence of chronic arsenicosis in the Bengal Delta has led to intensive research on arsenic (As) enrichment in groundwater. West Bengal, India is well known for severe As contamination, with large numbers of exposed individuals within the Gangetic Plain. Present study aimed to determine the degree of severity of As exposure from drinking As- enriched groundwater (50 µg/L) in the part of Gangetic Plain (Barasat, West Bengal). Association between As exposure and skin lesions (keratosis and melanosis) has been evaluated. Randomly selected subjects were used to determine As accumulations in hair, nail and urine in relation to chronic As exposure via drinking water. Arsenical dermatosis, keratosis and melanosis were investigated by medical evaluation and field survey. Arsenic in hair, nail, and urine was found to be positively correlated with As in drinking water. An association between As exposure and prevalence of keratosis and melanosis was also observed. The accumulation of As in hair, nail and urine was dependent on the age of the individuals. An association of As exposure from drinking water was observed with a risk of keratosis and melanosis among surveyed population in studied area. The level of As accumulations in hair, nail and urine highlighted the degree of severity of As exposure in the Bengal Delta region. Accumulations of As in hair, nail and urine were dependent on gender, age of the individuals and the rate of As intake through different exposure routes.

Keywords: arsenic exposure, groundwater, skin lesions

FAST IDENTIFICATION OF SAHARAN DUST MINERAL CONTRIBUTIONS TO URBAN ATMOSPHERE USING ATR-FTIR SPECTROSCOPY

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Atmospheric particulate matter (PM) is one of the most important environmental problems due to its adverse effects on human health, building materials, atmosphere, and several components of the environment. Size segregated airborne PM have been gaining importance for having better explanation of its harmful effects, chemical compositions and origins. Inhalable airborne particles can be classified into different groups, mainly fine (PM_{2.5}) and coarse (PM_{2.5-10}) fractions, because they have specific sources and characteristics. As it is widely accepted, PM_{2.5} emissions are very risky to create chronic effects since they are small enough to penetrate into the deeper sections of human respiratory system, even into the lungs and blood. In addition, some recent studies showed that the highest association rise in respiratory symptoms (e.g., asthma) admissions correlated with the increase in PM_{2.5-10}. In recent studies, the impacts of the Saharan originated dust storm were highlighted during transitional periods in Istanbul, Turkey, but no chemical analyses were included. It is very difficult to detect and collect PM samples for Saharan contribution event in a megacity (Istanbul) atmosphere which was located significantly far from the source; it requires a prior meteorological analysis supported by transportation models. Characterization of atmospheric particles can be done by several analytical techniques including single element methods, multielement methods, spectroscopic and microscopic techniques, UV-detection or mass spectrometric detection, and single-particle analytical techniques. Previously some researchers performed FTIR based analysis on airborne aerosol samples. FTIR coupled with ATR, is a new technique developed recently and there are only few examples of recent studies, to our knowledge, which are subjected to quantification or qualification of chemicals species of aerosol samples. Main aim of this study is to use ATR-FTIR analysis method for fast identification of mineral contributions originated from a Saharan dust storm on a megacity (Istanbul) atmosphere, where the anthropogenic contributions are high. Typical differences in the spectra of background dust loads and Saharan dust storm episodes are discussed. This study has a particular importance as being one of the first attempts to qualify the contributions of Saharan dust storms over Istanbul atmosphere using ground base measurements.

Keywords: airborne metals, atmospheric chemistry, air pollution

PRELIMINARY RESULTS OF MINERALOGIC AND GEOCHEMICAL PROPERTIES OF ZEOLITE OCCURRENCES IN AROUND OF KULU (KONYA) AND HAYMANA (ANKARA)

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Pyroclastic rocks which occurred from explosive volcanism and spread in Lower Miocene lacustrine and fluvial environments in the region. They contain various amounts of zeolite minerals, the formation of which is related to an interaction of volcanic material or detrital clays with saline alkaline lake water and groundwater. Some zeolite, e.g., clinoptilolite (mean Si/Al: 4.40), chabazite and erionite were determined in tuff/tuffite layers while analcime, montmorillonite, illite, dolomite, calcite and rarely gypsum minerals were observed in clay layers. Clinoptilolite and chabazite minerals observed as nearly pure minerals in tuffite layers. The zeolite minerals compose 10–95% of the rocks. Economically the deposit may be of great importance for Turkey, considering its enormous zeolitized outcrop area. Chabazites are mainly Na-chabazites and clinoptilolites are generally Ca-clinoptilolite. Erionites Structural Mg in erionites is mainly lower than 0.80 and Si/Al ratios is 3.76. Previously there is no study related to zeolite occurrences and deposits in the investigation area. Mineral formulae and mineral types of zeolite minerals were calculated by using of microprobe and EDS analyses. And also, it is known that erionite is dangerous for environmental health. The areal distribution of the zeolite minerals covers an area of about 40 km². Erionite is a human and animal carcinogen and one of the most toxic minerals known. Erionite deposits have been reported in many countries and three villages of Cappadocia, Turkey; however, it is only in the area erionite occurrence is first determined in the region. The environmental exposure to erionite has not been demonstrated yet but there is three villages are settled on the zeolitic tuffs.

Keywords: zeolite, erionite, health

**CHARACTERISTICS OF HEAVY METAL CONTAMINATION
OF SURFACE WATERS FROM ABANDONED SULFIDE
MINES AND THEIR TAILINGS IN AROUND OF
ESPIYE (GIRESUN, TURKEY)**

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The investigated area in the west of the Eastern Pontides, NE Turkey represents the eastern part of the metallogenic province of the Black Sea. This province contains over 400 massive and vein-type Cu–Zn–Pb deposits and occurrences. The chemical properties of effluent from mine sites were characterized by very low pH of <2.0 and high levels of TDS and EC. Furthermore, the waters contained elevated levels especially of Cd, Cu, Fe, Mn, Pb, Zn, As, Ni, Al and SO₄²⁻. The lowest concentrations were measured for Be, Cs, Mo, Ga, Cr, V, Cl, Be and most of REEs. Increases in As, Cu, Pb, Cd, Zn and Fe concentrations were noticed at and around the mine areas. These metals are continuously dispersed downstream and downslope from the tailings and mines by clastic movement through wind and water. Because of the existence of sulfides in the tailings, water samples from the tailings site and around the mines were very acidic with a pH of 2.60, have high total dissolved solids (TDS) of 1870 mg/L and measured electric conductivity (EC) at about 2.550 µS/cm. These samples also have up to 58, 29.500, 18.7, 13.153, 181, 27 mg/L and 513, 63, 1.707 g/L of Cd, Cu, Pb, Zn, As, Ni, and Fe, Al (g/L) and SO₄²⁻, respectively. In the main river at 200m away from interference, the pH is 8.10 and EC is 277 µS/cm, and the element concentrations are 5.5, 17, 1.9, 13.7, 1.8, 0.3 658, 1.9 and 51. The results obtained from this study show that all the spring and almost stream water sources had one or more trace metal level in concentration above the acceptable limits set by the WHO for drinking water. The stream and main river waters have been used as drinking water in the region. Cd, As, Fe and partially Pb and Zn content are above the WHO permissible limits for drinking water. And also, the stream water have been used in agriculture and animal husbandry. This suggests a risk to the population given the toxicity of these metals and the fact that especially the stream and partially river waters are the only sources of potable water in this environment. Precautionary actions should be considered in order to prevent the dispersion of pollutants and avoid population exposures.

Keywords: NE Turkey, heavy metal, contamination

METAL SULFIDE FORMATION IN THE HUMAN INTESTINE: POTENTIAL FOR NEW INSIGHT INTO MICROBIAL SULFATE REDUCTION

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The geochemical importance of dissimilatory sulfate reduction in the formation of diagenetic iron sulfides in sedimentary environments is generally accepted. Sulfate-reducing prokaryotes (SRP) gain energy by transferring electrons from organic substrates and hydrogen to sulfate. The end-product of sulfate reduction, hydrogen sulfide, tends to combine with a range of metals to form metal sulfides with extremely low solubility constants. This microbial process has proved to be of key importance in the treatment of various industrial wastewaters and acid mine drainage. The environmentally important SRP are also recognized to be normal constituents of gut microbiota in humans and animals. Some potentially adverse health implications of sulfidogenic bacteria are attributed to the cytotoxic effect of hydrogen sulphide. Several reports suggest that SRP activity in the large intestine may be implicated in inflammatory bowel disease and ulcerative colitis. Sulfidogenic anaerobes have also been postulated as aetiological agents in a number of diseases such as cholecystitis, brain and abdominal abscesses, rheumatic disease, and bacteraemia (reviewed in Macfarlane et al., 2007). Little attention has been paid to the possible effects of metal sulfide formation by SRP inhabiting the large intestine. We consider two plausible mechanisms for SRP impact on human health via the formation of sulfides. (I) SRP may substantially reduce the bioavailability of essential metals, such as iron and copper, by precipitating them in the form of insoluble sulfides; (II) SRP can produce potentially harmful nano-crystals of metal sulfide. Our study of SRP-produced copper sulfides, isolated from natural environments and human faeces, illustrates the hypothesised routes. A new anaerobic spore-forming sulfidogenic Firmicute was isolated from human faeces. Scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDAX) revealed that copper and sulfur were the main constituents of the solid precipitate produced by the strain. Transmission electron microscopy (TEM) analysis revealed that sulfate-reducers belonging to both major phylogenetic groups harboring SRP (i.e., Deltaproteobacteria and spore-forming Firmicutes) produced nano-sized particles when cultivated under elevated metal concentrations. We acknowledge support from the Russian Ministry of Education and Science under the “Kadry” programme, the RF President grant to AG and RFFResearch Grant 09-04-99138-r_ofi.

Keywords: microbial sulfate reduction, iron/copper sulfides, SEM/TEM

ENVIRONMENTAL GEOCHEMICAL PROBLEMS IN HUNGARY

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The most important environmental–geochemical problems in Hungary is coming from the lack of certain elements rather than having too much from them. From the literature that is known that the bigger part of the country suffer from the lack of I, Se and Mo, and this results already some health consequences. The geochemical exploration of the Geological Institute of Hungary made clear, that the territory of the country is not uniform, but 4 regions can be divided. In the bigger part of the central (2.) region the Cu, Zn and other essential elements show lower concentration than the minimum necessary for plants. Searching the geological reasons, it was found, that the purpose of this is the lime accumulation, which is typical in this region. In the ice–age, when the precipitation was fewer than nowadays and the vegetation set the soil less, the wind blew the dust of carbonate rocks covered the main part of the Transdanubian Midmountain far away, and it was deposited mixed with loess and wind-blown sand. The crystalline limestone- and dolomite dust gradually dissolve in the unsaturated zone and it precipitates in the pores as amorphous carbonate. In the superficial loose sediments Ca, Mg, Sr (and Ba) accumulate among the cations, and CO₃ (SO₄ and PO₄ too) among the anions, all the other elements are crowded out, so the micro-nutrient supply of the soil became deficient. Other kind of problems occur in the eastern (4.) region which was separated because of the mining–heavy-industrial contamination of the area, so there are more non-ferrous metals, mainly Cd, and the concentration of that is significantly over the contamination limit value.

Keywords: geochemistry, environment, Hungary

MICROELEMENT COMPOSITION AND STRUCTURE OF HUMAN TOOTH TISSUE BIOMINERAL PHASE

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Bone and tooth biomineral phase can accumulate from environment trace elements, particularly heavy metals. Chemical composition and properties of tooth biomineral component reflect physiological peculiarities of organism functions and can give important information for ecological monitoring of residence region. In many regions of Russia pathological processes in hard tooth tissue of different etiology (increased abrasion, caries lesions, tooth hypersensitivity, etc.) are closely connected with negative ecological situation, especially in Urals region. The aim of present work was to study by inductively coupled plasma – mass-spectrometry (ICP-MS) and Raman spectroscopy the microelement composition and structure of human tooth tissues and its alteration due to progressing of diseases, e.g. increased tooth abrasion and caries. Teeth of different degree of integrity were studied – intact, carious of various depth and localization and also with increased abrasion. All ICP-MS measurements were made by ELAN 9000 (PerkinElmer). A method of layer-by-layer dissolution by acid etching of tooth enamel was developed. Laser ablation sampling of teeth surfaces with Cetac LSX500 was performed as well. Raman spectra were obtained by LabRAM (Horiba Scientific). Groups of trace elements concentrating in intact and affected enamel in different ways were separated; element incorporation features depended on a degree of tooth tissue integrity. Diseased teeth had contained the microelements in lesser concentrations as compared with intact teeth. The majority of them represented essential microelements (e.g. Cr, Co, Ni, Mn, Zn, As, Se), micro-quantities of which are known to be a part of enzyme composition of human organism. Bone inorganic and organic phase conversion during pathological processes was examined: degree of bone apatite crystallinity, mineral-organic ratio, carbonate-ion relative concentration and its inter-positional distribution were calculated.

Keywords: hydroxyapatite, Raman spectroscopy, microelemental composition.

HI-TECH-METAL LITHIUM IN THE NATURAL ENVIRONMENT AND HEALTH ISSUES

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Hi-tech-metals are classified as strategic metals within the EU. They are important for the development of new technological applications and advanced consumer products. Hi-techmetals include antimony, beryllium, cobalt, gallium, germanium, indium, iridium, lithium, niobium, platinum, palladium, rhodium, ruthenium, tantalum and certain rare earth metals. There is only a limited amount of information available about the potential exposure to hitech-metals in natural environment. Lithium (Li) occurs naturally trace amounts in the minerals of rocks and soils, and in aquatic environments. The major dietary sources of Li are drinking water and edible vegetables. The pharmaceutical use of lithium in the treatment of bipolar disorders is well known. There have been suggestions that low-Li in drinking water may be associated with behavioral abnormalities, the risk of suicide, and coronary heart disease among others. Evident geographical variation in the incidence of diseases mentioned above and Li concentration in ground water exists in Finland. This study was conducted to investigate the Li concentrations in the humus layer and edible mushrooms. A total of 70 humus samples and 80 mushroom samples were collected from a 5 km² study area near the abandoned Luikonlahti mine (which was in operation from 1968-1983) in eastern Finland. The total concentration of Li in humus ranged from 0.25 to 12.80 mg/kg with the median value of 1.77 mg/kg. The available fraction of Li (ammonium acetate extraction) ranged from 0.03 to 0.24 mg/kg with the median value of 0.03 mg/kg. Li concentrations of all edible mushroom samples were below the detection limit value (< 0.1 mg/kg). Generally, Li is considered easily available to plants although there are large differences in the ability of different plant species to take up Li. There are few studies dealing with the Li concentrations in edible mushrooms. Different mushroom taxa seem to show differences in their ability to accumulate Li. The results of our study indicated that Li originates from stable silicate minerals and insoluble Li seemed not to end up in food chains via mushrooms studied. Because drinking water seems to be the main source of Li, geomedical studies assessing potential associations between various health parameters on individuals or groups and the Li concentration in ground water are warranted.

Keywords: hi-tech-metals

ENVIRONMENTAL DISTRIBUTION OF TRACE METALS IN THE BIU VOLCANIC PROVINCE NIGERIA: EXPOSURE AND ASSOCIATED HEALTH PROBLEMS

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The Biu volcanic province constitutes one of the largest volcanic provinces in Nigeria. It marks the structural culmination between the Benue and the Chad sedimentary basins. The province covers a superficial area of 5000Km² with a thickness of 250m. Geochemical analysis of the volcanic soil revealed the complete leaching of the major elements (Fe₂O₃, CaO, K₂O, MgO, MnO, TiO₂) from the surface soil probably into water sources. This may explain the extremely high CaO and K₂O levels especially in the stream water where they display values of 348mg/l and 36 mg/l as against 200 mg/l to 12 mg/l respectively of WHO admissible limits for drinking water. The accumulation of transition metals in the soil (Co 84-111ppm; Cr: 230-443 ppm); Ni: 169-237 ppm) is geogenic derived from the weathering of the host basaltic rock. Cr, Ni, and Cu do not easily form soluble ions in solution explaining why they display lower levels below their respective WHO admissible limits for drinking water. The absence in the soil profile and the extremely higher values of Potentially Harmful Elements (PHEs) (As, Se, Sb, and Cd) in the spring and stream water as opposed to the lower values in the wells and borehole water suggest their extreme solubility, the leaching and transportation of these elements from deep sources. The higher values of Zn and Pb (10-40 ppm and 246-496 ppm respectively) 4x their average abundance in basalts, could be explained like for Co, Cr, Ni, by their absorption and retention in clay minerals structure. The over-exposure to Potentially Harmful Elements through the ingestion of water and food could have adverse health hazards. Few of the inhabitants show manifestations of nail deformity and hyperpigmentation of the skin and hand palms. Others present various forms of skin diseases which all could be attributed to exposure to As and Se toxicity.

Keywords: volcanic province, potential harmful elements, health hazards

CHEMICAL PHYSICAL CHARACTERIZATION OF INORGANIC CRYSTALS IN HUMAN SYNOVIAL LIQUID

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Synovial fluid accumulates in the joint cavity in different conditions; this work outlines the data from those analyses that help in their differential and definitive diagnosis. The gross appearance of the fluid can provide a quick bedside orientation with regard to the amount of inflammation present in the joint: totally transparent synovial fluid originates in noninflammatory conditions of which osteoarthritis is the most common and the amount of turbidity grossly relates to the amount of inflammation. Most turbid to purulent fluids usually come from infected joints, but exceptions are not uncommon. The presence of these conditions and this ion in high concentration within the synovial fluid, can lead to formation and the precipitation of inorganic crystals of different shape and nature. Some examples are certainly represented by crystals of monosodium urate, calcium pyrophosphate dihydrate crystals and hydroxyapatite nanocrystals. The presence of these crystals determine the pathological onset of arthritis annoying for the patient. This work aims to study different synovial fluids from patients suffering from arthritic pain, to isolate the inorganic part in it present and study the nature and morphology through with different analytical methods, like scanning electron microscopy (SEM), transmission electron microscopy (TEM), Infrared analysis (FT-IR) and X-Ray Diffraction (XRD). The focus of this investigation has focused primarily on hydroxyapatite nano-crystals [1] and their size, morphology, structure, crystallinity degree, surface area and diseases related to them. In this way is possible to have a complete characterization of inorganic crystals found into synovial fluids and try to think of a cure that conflict and obstacles to the formation of these crystals.

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Keywords: inorganic crystal, hydroxyapatite, synovial fluid

POTENTIAL HUMAN HEALTH EFFECTS OF ENVIRONMENTAL FACTORS AT LOCAL AND EUROPEAN LEVELS: DEVELOPMENT OF AIR QUALITY AND THERMAL STRESS INDEXES

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In the framework of the European project PASODOBLE (FP7), we set up downstream information services by combining environmental and health data with a view to support the health care community and to improve vulnerable people welfare. Indeed there is a profound relationship between human health, well-being and environmental parameters such as air pollution levels and heat. The main objectives are to establish correlations between environmental parameters, exposure of populations and their reactivity, to develop and validate air quality and thermal stress indexes and to construct a prediction model of these sanitary indexes. Those risk indicators, based on those recommended by organisations such as WHO and by local and national authorities, are then tested and analysed to reach a common methodology. These indexes will be implemented on 3 European sites: Greece (Athens and Thessaloniki), the Netherlands and “Provence Alpes Côte d’Azur” (South East of France). The selected region and cities are among the most affected by the atmospheric pollution in Europe. The Athens and Thessaloniki urban areas are among the most densely populated cities in Greece, which suffered severe air pollution problems during the last decades, mostly related to PM10 levels. The air quality, combined with the strong hot season of the Mediterranean climate, is known to be one of the worse in Europe, especially in summer, and leads to serious sanitary concerns. The service aims to provide up-to-date, detailed information on air quality and thermal discomfort. The air quality risk index is based on the Relative Risk associated with short-term exposure to common air pollutants and takes into account the possible adverse effects in line with the coexistence of all the pollutants. This information will be then pushed to health professionals for a validation and to check the usefulness of the information to them. Once validated and quality checked, the risk indicators will be provided to doctors that will disseminate the information to their patients. Depending on the gravity of the pathology of the vulnerable people, the risk index can be misinterpreted by the patient. Therefore, it must be first given to doctors and not directly to the patients. Training sessions, implemented by the European Medical Association, on the use and interpretation of this risk index will be then organized for doctors to be able to give the proper information with associated recommendations to their patients.

Keywords: health effects, environmental index

ARSENIC ENRICHMENT IN SURFACE WATER AND SOIL IN YARLUNG TSANGPO AND SINGE TSANGPO DRAINAGES IN TIBET, CHINA

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The average soil arsenic concentration was reported to be 18.7 mg/kg based on a survey of 205 samples in Tibet. This is considerably higher than the commonly cited crustal background value of 10 mg/kg of As for soil, and is unlikely due to anthropogenic pollution. To investigate the origin of this geochemical anomaly in soil arsenic, water (n=80), stream sediment (n=69), soil (n=79) and rock (n=58) samples were collected from the Yarlung Tsangpo (upstream of Brahmaputra) and Singe Tsangpo (upstream of Indus) drainage basins in June 2008.

Arsenic enrichment is pronounced in the Singe Tsangpo drainage basin. The average arsenic concentration in soil, stream sediment and stream water is 44±26 mg/kg (n=33), 42±40 mg/kg (n=37) and 58±69 µg/L (n=39), respectively. In the Yarlung Tsangpo drainage, the average arsenic concentration in soil, stream sediment and stream water is 30±33 mg/kg (n=23), 28±11 mg/kg (n=28) and 11±16 µg/L (n=30), respectively. The average concentration of arsenic in upstream water of Yarlung Tsangpo River is 38±28 µg/L (n=5), and is much higher than the value of 5±3 µg/L (n=23) downstream. The high background concentration of arsenic in soil of this area may be associated to the broad distribution of ophiolite melange and meta-sedimentary sequences containing shale, phyllite and schist that may be rich in arsenic. However, the average concentrations of As in rocks from Singe Tsangpo and Yarlung Tsangpo are 11.2±9.2 (n=27) and 9.2±14.0 (n=23) respectively and the maximum concentration is 35±6 mg/kg in metamorphic breccia. It is likely that soil As enrichment results from the weathering process of rocks.

Water from other sources sampled in Tibet also show As enrichment. Water from two hot springs contain 5985 µg/L and 3842 µg/L arsenic. A dug well (about 2 m depth) is found to contain 195 µg/L As. The average arsenic concentration of salt lake water is 1947±3619 µg/L (n=8, range 40-10626 µg/L), but a fresh water lake has 21 µg/L arsenic. The positive correlation between [As] and [Na]⁺[K] in water samples indicates that arsenic enrichment in water from the Singe Tsangpo and the upstream of the Yarlung Tsangpo may be associated with the salt lakes or hot springs in these drainage basins.

As enrichment in the water and sediment in Singe Tsangpo and upper Yarlung Tsangpo drainages may pose a potential risk of endemic arseniasis for the residents in this area.

Keywords: arsenic, enrichment, Tibet

ISOTOPE RATIOS, ENVIRONMENTAL PROCESSES AND DEPLETED URANIUM EXPOSURE ASSESSMENT

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Between 1958 and 1982 depleted uranium (DU) metal was processed at a National Lead plant in Colonie, NY, USA. Combustion of scrap metal resulted in emissions of uranium particulates. The ATSDR concluded that these emissions could have increased the risk of certain health effects for Colonie residents [1].

Parrish et al. [2] demonstrated that it is possible to detect the excretion of DU with urine more than 22 years after inhalation exposure. Isotope ratios demonstrate that an exposed population exists at Colonie, whereas significant exposure was not common amongst Gulf War Veterans. Thus analytical techniques developed in geochemistry laboratories offer medical researchers evidence to underpin proposed investigations into the health effects of DU exposure.

High precision isotope ratios obtained by MC-ICP-MS also provide evidence for the origin of the DU processed at Colonie [3, 4]. This information helps to constrain the timing of likely exposures to between 1967 and 1982. The sensitivity and ion counting options of the Neptune plus with Jet Interface improves the analytical precision that is possible from the very small analyte quantities that are available in bioassay and individual particulate samples.

EXAFS data and SEM images reveal the mineralogy of the particulate contamination. These properties control how the material will behave in the environment and also in the lungs of exposed individuals [5]. It is possible to trace the environmental processes that control the distribution of depleted uranium contamination in soils using lower precision isotope ratios obtained by quadrupole ICP-MS. This is illustrated by soil profiles and contamination maps of the area surrounding the former NLI site [6]. The isotopically distinct composition of the depleted uranium allows for the quantification of the degree of contamination relative to the variable background concentrations of natural uranium present in environmental samples.

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Keywords: uranium

COMMON GEOCHEMICAL AND MINERALOGICAL CHARACTERISTICS AMONG ANTIBACTERIAL CLAY DEPOSITS

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Clays have been known for their medicinal properties since prehistory, and now they are used in pharmaceutical and cosmetic preparations due to their sorption capacity and rheological properties. Less understood is their effectiveness as bactericides, in part due to the fact that not all healing clays are antibacterial and in part due to their great mineral and chemical diversity. Williams et al. 2008 conducted a pilot study on two French clays to determine a scientific basis for the antibacterial effect observed against *Mycobacterium ulceran*. One of the clays was a broad-spectrum antimicrobial, even against antibiotic resistant bacteria. However the other clay enhanced bacterial growth. Antibacterial testing against a Gram-negative (*E. coli*) and a Gram-negative (*B. subtilis*) allowed identification of four more antibacterial clays from different parts of the world. In this work we used methods from clinical microbiology, geology and geochemistry to compare the antibacterial action of these clays. First we assessed and compared the depositional environments, mineralogy, and key physical (surface properties) and geochemical variables of the antibacterial clays to non-antibacterial clays to identify variables that could be involved in the bactericide. We manipulated the chemical composition of the samples to determine any change in antibacterial effectiveness. Results suggest that illite/smectite rich samples with reduced Fe phases are common to the antibacterial clays. Recently we discovered a clay that showed inhibition of cell viability on *E. coli* but not in *B. subtilis*. Because these organisms differ in their cell-wall structure, the different response to the clay helps us elucidate a particular mechanism. We believe that the antibacterial activity is controlled by the extremely large surface area of the minerals, surface charge and available metal species toxic to bacteria. Understanding what makes a clay antibacterial could be useful for exploration of these medicinal-mineral resources, and finding new sources of natural drugs to treat infectious diseases.

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Keywords: clay minerals, antibacterial

MINERALIZED DUST EXPOSURE IN THE MIDDLE EAST: POTENTIAL HEALTH RISKS FROM METALS AND MICROBIAL PATHOGENS

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In the Middle East, dust and sand storms are a persistent problem delivering significant amounts of mineralized particulates via inhalation into the mouth, nasal pharynx, and lungs. The health risks of this dust inhalation are presently being studied but accurate characterization is lacking. Experiments were designed to study the chemical composition, mineral content, or microbial flora of Kuwaiti and Iraqi dust for its potential to cause adverse human health effects. Multiple site samples were collected and chemical and physical characterization including particle size distribution and inorganic analysis was conducted, followed by analysis and identification of biologic flora to include bacteria, fungi and viruses. Data indicates that the mineralized dust is composed of calcium carbonate over a matrix of metallic silicate nanocrystals containing a variety of trace and heavy metals constituting ~3 % of the PM10 particles by weight, of which ~1% is bioaccessible aluminum and reactive iron, each. Microbial analysis reveals a significant biodiversity of bacteria of which ~25 % are known pathogens. Of the microbes identified, several have hemolytical properties and most have significant antibiotic resistance. Viral analysis indicates a tremendous amount of virions with a large percent of RNA viruses. The level of total suspended particle mass at PM10 constitutes an excessive exposure micro-particulates including PM 2.5. Reported data on cell culture and animal studies have indicated a high level of toxicity to these dust particles. Taken together, these data suggest that at the level of dust exposure commonly found in the Middle East (i.e., Iraq, Kuwait, and Afghanistan), in addition to the microbial and metal content, mineralized dust constitutes a significant health risk, both acute and chronic, to deployed troops and native inhabitants.

Keywords: mineralized dust, metals and microbial pathogens

NATURAL OCCURRING ASBESTOS IN ITALY

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Naturally Occurring Asbestos means asbestos presence of geological origin, in rocks or their alteration products, outcropping or buried, with asbestos minerals content varying and not definable in advance. In Italy NOA are quite distributed in all National territory and particularly well known are the cases of Balangero (ex asbestos mine, Piedmont Region), Ophiolites Quarries in Emilia Romagna, Lombardy and Piedmont Region, Biancavilla (Sicily), etc. A National Program to map the Asbestos occurrence has been funded and started in 2001 (L. 93/2001, D.M. 101/2003). The Italian asbestos mapping have to be realized distinguishing 4 different categories: 1-2-4 dedicated to factories, buildings, and landfills with asbestos and one (category 3) for Natural Occurring Asbestos:

- Mining activities, in use or disused, processing of rocks and minerals containing or not containing asbestos in areas where the presence of asbestos is known.
- Rocky masses which are characterized by the presence of asbestos.

The areas identified as NOA are mainly concentrated in central and northern Italy, and they do provide an outline of the main Italian risk situations. Limited areas with risk outcrops are also in Calabria, Basilicata and Sicily Regions, although not yet officially mapped according to the Italian Decree n° 101/2003. Most of the data so far acquired and officially sent by the regions, is related to mining activities in use or disused (former mines for asbestos extraction, quarries for ornamental stones extraction, quarries for inert materials extraction). There are still big gaps about natural outcrops mapping with no economic use, or of some outcrops came from local works (roads, earthworks etc.). This paper reports the updated map data on a national scale with close examination on some well-known situations (mining activities in Lombardy and Emilia Romagna). The collected data allow for a fairly complete picture of situations at greatest risk that could be used as comparison in European and international scale. We also highlight the need to implement this database with minor situations. Finally, we underline the lack of funds and national guidelines both to complete the mapping and to implement any possible remediation and restoration of the territory.

Keywords: asbestos, NOA

BIOMONITORING AND BIOMARKERS OF LEAD EXPOSURE: EXPERIENCE IN URUGUAY

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Medical Geology among other Environmental Health disciplines, requires the use of biomarkers to assess human and other sensitive environmental exposure to trace elements and toxic chemical pollutants. This is also applied to sensitive living species in the ecosystems. The need for human biomonitoring data in public health risk assessment can play an important role in establishing relationships between a specific human health effect and a specific chemical exposure. Animals can also suffer from diseases owing to element deficiency or toxicity, and may be even develop early serious health problems before they occur in humans.

Lead (Pb) is an example of a well known bioavailable toxic chemical pollutant in the environment, thus it can be absorbed and cause adverse health effects on susceptible living organisms. In Uruguay, this environmental problem became of public concern on 2001, and it is being multidisplinarly approached since then.

The biomonitoring for lead human exposure reflects an individual's current body burden, which is a function of recent and/or past exposure activities. Lead in whole blood (BLL, B-Pb) is mainly used for assessment of lead exposure, both for screening, biomonitoring and diagnostic purposes. B-Pb is still the most reliable indicator as it has been fully interpreted and validated in the scientific literature to be routinely used to assess lead exposure. Several alternative biomarkers that may aid diagnosis of the extent of Pb exposure include Pb determinations in plasma/serum, saliva, bone, teeth, feces, and urine. However, none of these matrices has gained convincing acceptance as an alternative to lead in whole blood owing to many confounding variables.

This work highlights the importance of lead biomonitoring of human and animal populations illustrated by the Uruguayan experience. The applications of alternative environmental lead exposure biomarkers and the main aspects of B-Pb as the predominant biological biomarker to environmental lead exposure are explained. Uruguayan studies in human populations (infants, children, adults, workers) and animals (dogs) lead studies are reviewed to show the incidence of different variables on human B-Pb, and the fact that animals can be "sentinels" of environmental lead health hazards in human is also demonstrated.

Keywords: biomarkers and biomonitoring, blood lead levels, Uruguay

FACING ARSENIC ENVIRONMENTAL AND HEALTH ISSUES IN URUGUAY WITH A MEDICAL GEOLOGY APPROACH

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Scientific research has been recently conducted in Uruguay to study the presence of geogenic arsenic (As) in groundwater and preliminary results, showed As levels above those recommended by WHO for drinking water (10 µg/L) in different aquifers of the country. For example, in a study on Raigon aquifer, water samples showed an arsenic concentration range from 1,4 to 24,2 µg/L with a median of 14,2 µg/L while in other study, the median, maximum and minimum As concentrations determined in several acquifers (Mercedes, de la Costa) have been 16.9, 58.0 and 0.1 µg/L, respectively. Besides, As concentrations between 4,9 and 116 µg/L in water samples from thermal corridor of Uruguay river, were published recently.

Several laws and decrees regulate water sources quality and the drinking water is supplied only by a state company that is controlled by a state regulation institute, being As new recommended levels < 20 µg/L. In a 6 years period study of those data assessment, As concentration in drinking water samples taken from different areas of the country, showed an increase from not detectable to quantified levels.

The risk of the Uruguayan population consuming this water has not yet been estimated, so it is important to develop systematic studies to assess population's chronic exposure to inorganic arsenic through drinking water and health impacts. This environmental health issue is now becoming a matter of concern with a medical geology approach, as similar aims research teams and experts from geosciences and biosciences, joined to face those arsenic exposure risks problems.

As a consequence, several multidisciplinary studies have been developed, focusing on arsenic geological and toxicological aspects. For this purpose, analytical and speciation methodologies were optimized and validated for arsenic analysis in water and urine, as available tools in Uruguay. Arsenic biomonitoring and determination of urine metabolites of general population and exposed workers, are currently ongoing research studies. Those environmental and health arsenic issues in Uruguay, are reviewed in this work, to show the recent advances in this Medical Geology subject in our country.

Keywords: arsenic, medical geology, Uruguay

RISK FACTORS IN URINARY CALCULI

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The formation of stone in urine environment consists of the precipitation as solid phase of poorly soluble salts. This is the basis for a classification of Nephrolithiasis which includes: calcium stones (calcium oxalate and phosphate), uric acid, cystine, infections stones (struvite and carbonate apatite), rare stones (2-8 dihydroxyadenine, xantine, drugs). The corresponding risk factors are peculiar of each type of renal calculi, as listed: Calcium oxalate (Hypercalciuria, Hyperoxaluria, hypocitraturia), Calcium phosphate (Hypercalciuria, hypocitraturia, alkaline pH), Uric acid (Acidic pH, hyperuricosuria), Cystine (Cystinuria), Infection stones (Alkaline pH induced by urease). Stone formation is only possible in supersaturated urine with respect to the solid phase, and this condition applies to some but not all type of renal stones (cystine stones, uric acid, struvite). Conversely, in the most frequent calcium nephrolithiasis, it is believed risk derive from an alteration of the ratio between promoters and inhibitors in urines. Main inhibitors are classified into ionic (citrate and magnesium) and macromolecular (glycosaminoglycans, Tamm-Horsfall glycoprotein, nephrocalcin, etc). In the clinical practice evaluation of risk factors is carried out on urine samples which are analyzed for components of the stones, inhibitors (ionic) and pertinent urine species to be used in the calculation of state of saturation. Therefore, renal stone formation can be viewed as the outcome of systemic metabolic derangements, either primary or secondary to favouring pathologies (i.e. primary hyperparathyroidism). In the last years the role of the kidney has been re-evaluated, emphasizing the interaction between crystals and renal tubular epithelia, mediated by inflammation, oxidative stress, tissue injury. However, these hypotheses do not have any practical utilization.

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Keywords: urinary calculi, state of saturation, hypercalciuria, hyperoxaluria, hypocitraturia

DUST FROM MINERAL EXTRACTION: REGULATION OF EMISSIONS IN THE UNITED KINGDOM

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Quarrying in the UK is principally for aggregates but also for coal and industrial minerals. Dust arises at all stages of quarrying and from old partly vegetated tips left by 18th to early 20th century metalliferous mining. Environmental permits set out operating conditions to protect air quality and surface water. Air quality legislation sets limit values for Pb, Cd, As, Ni, and Hg. If air quality objectives are unlikely to be met an action plan is prepared. Local authorities must identify contaminated land, establish what remediation is required, who is responsible for it and ensure that remediation takes place. Planning determines when, where and how development should take place. Local planning policy documents identify land allocations for extraction, criteria for determining planning applications, and measures for enforcing conditions. Policies are subjected to sustainability appraisal (including strategic environmental assessment). Planning applications should conform to local planning policies. If proposed development might cause significant environmental harm environmental impact assessment (EIA) is required to assess likely impacts and propose mitigation and monitoring measures as a basis for planning conditions. Health and Safety legislation and regulations protect the workforce at, and visitors to, sites setting out exposure limits. The local authority is responsible for investigating nuisances that cause unacceptable annoyance to the public. A notice can be issued requiring operations to stop. Minimisation of dust emissions depends on good design and management of sites. Principles of good site management include thinking ahead, reacting quickly to problems and training.

Keywords: mineral dust, regulation, environmental permits, planning, health and safety, public nuisance

PARTICIPATIVE RISK COMMUNICATION AS AN IMPORTANT TOOL IN MEDICAL GEOLOGY STUDIES

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Risk situations related to brownfield sites, contaminated lands and exposed groups to toxic substances are common in South America. In some of these situations there is a lack of institutional response to the risks and consequences coupled with a failure to communicate the risks to those affected. Drawing on empirical research in 4 Latin American communities exposed to lead contamination, we investigated what strategies of Risk Communication (RC) have been used by researchers to communicate the risks of contamination, and possible impacts of these strategies. Considering that risk situations of contaminated lands are characterized by uncertainty/controversy, and their residents are in a collective stress situation because of the physical conditions in their neighborhood and possible impacts on their health, in our study we argue for the need of participative RC in Medical Geology studies. Participative RC is based on cultural/social elements, trust, open dialogue and collective learning process to implement policies for mitigating risks and for a sustainable future. However, the analysis of these cases suggests that the efforts of RC have focused only on information transmission and public persuasion. In 2 Brazilian cases (Adrianópolis-Southeastern, and Santo Amaro-Northeastern), researchers who are involved in Medical Geology studies on contamination were concerned about communicating with people; however they did not have a systematic and grounded RC plan. In Bauru (Southeastern, BR) and La Teja (Montevideo, UR) multidisciplinary teams were created to handle contamination, and communicate the risks. RC plans included meetings with locals and communication with the media. Nonetheless, we observed that scientific uncertainties/controversies and a lack of information frustrated the plans. In all cases we noted that RC did not promote an open dialogue, and a discussion about life styles of locals. As a consequence, affected public have the perception that research results have not been properly released, and there is a prevalent understanding (by assorted actors) that environmental/health research is not being undertaken for the public good. These experiences endorsed a need for a debate about participative RC between Medical Geology researchers. The challenges of risk assessment/management highlight the call for improving communication in order to favor dialogue/partnership between those who assess the risks and those who live with the risks.

Keywords: risk communication, contaminated lands, South America

RISK GOVERNANCE: A NEW APPROACH TO HANDLE GEOHAZARDS AND ENVIRONMENTAL AND CLIMATE CHANGES

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Environmental and climate changes are part of a new set of risks that are characterized by incomplete understanding of their causes and consequences, by the fact of being incalculable, impossible to compensate, and often invisible, uncontrollable and irreversible (Beck, 1992, 1995). The challenges these risks pose are shifting because of evolving patterns of vulnerability and limitations of existing approaches to mitigating or reducing risks (Walker, 2010). Recent examples of environmental and climate changes, such as floods and landslides in different countries (including Brazil), have highlighted that established models of risk assessment/management and ways of thinking and acting over geohazards may not be sufficient for mitigating risks. Official authorities and experts, including Medical Geology researchers, have noted that dealing with these risks requires specialized knowledge to recognize and measure them; meanwhile it demands a collective and participative process to handle them – particularly considering that events associated with environmental and climate changes have highlighted that individual perceptions have an important role in ways in which individual attitudes and actions of mitigation/adaptation are defined and practiced (Hogan and Marandola Jr, 2009). For geohazards associated with environmental and climate changes the Risk Governance (RG) approach have become increasingly important. RG is a collective learning process to implement policies for mitigating risks and for a sustainable future, which involves representatives of all actor groups (scientists, affected public, authorities, agencies), and takes account of the social/cultural factors that influence individualized and collective answers to risks. RG includes scientific assessments of the risks to human health and the environment, and scientific assessment of related concerns, as well as social and economic implications (Renn, 2008). Considering all challenges involved with studies on geohazards and environmental and climate changes, we endorse a need for a debate about RG between Medical Geology researchers. We encourage thinking that the risk assessment/management require co-design the framing of the problem in an open and effective dialogue with different actor groups; recognize the limits of expert knowledge and the importance of the lay knowledge to generate a common understanding of the magnitude of the risk, as well as the potential risk management options.

Keywords: risk governance, climate change, environmental changes

EVIDENCES OF COMPETITIVE ADSORPTION OF HYDROCARBONS INTO AN HYDROPHOBIC ZSM-5

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Volatile organic compounds and hydrocarbons constitute a significant fraction of the hazardous air and water pollution. Research on hydrocarbon removal has been mainly focussed on single components from air matrix, whereas the studies involving aqueous dilute solutions are few. However, in most environmental applications, these pollutants are present in the form of mixtures in very dilute aqueous solution. In this study, we report on evidence of 1,2-dichloroethane (DCE), methyl tert-butyl-ether (MTBE) and toluene (TOL) adsorption into ZSM-5 zeolite. A combined diffractometric and gas chromatographic study was used to: 1) investigate the adsorptive properties of ZSM-5; 2) characterise its structure after the adsorption of selected contaminants; 3) localise the organic species in the zeolite pores; 4) compare the adsorption data for a mixture of these contaminants with concentrations in the ppb and ppm range. The ZSM-5 sample is a commercial adsorbent, (SiO₂/Al₂O₃ =280), purchased by Zeolyst International. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction -Gas Chromatography. XRD powder patterns were collected on ZSM-5 before and after adsorption on a Bruker D8 Advance diffractometer. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C/min. The experimental results prove that the kinetic of adsorption of all components is fast and indicates that competition exists between the organic compounds at low cosolute concentrations. Rietveld refinements indicate that the relevant incorporation of DCE, MTBE and TOL in the ZSM-5 causes significant increase of all unit cell parameters in comparison to those of the untreated material as well as strong distortions of the channel systems where the contaminants are hosted. The very favourable adsorption kinetics along with the effective and highly irreversible adsorption of DCE, MTBE and TOL molecules into zeolite ZSM-5 pores make this cheap and environmental friendly material a tool with interesting applications for the removal of hydrocarbons from wastewater.

Keywords: hydrophobic zeolite, competitive adsorption, hydrocarbons

ADSORPTION OF PHARMACEUTICALS FROM DILUTE AQUEOUS SOLUTIONS INTO SYNTHETIC BETA ZEOLITE

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Domestic and commercial wastewaters contain a variety of organic wastewater contaminants such as pharmaceuticals and personal care products. These compounds undergo incomplete removal in wastewater treatment plants and they are found in the surface waters receiving the effluents of these plants. The aim of this work is to investigate the capability of beta zeolite in removing three test molecules Hydrochlorothiazide (HTZ) Ketoprofene (HTP) and Diclofenac (DCF), respectively. All of these drugs are ubiquitous contaminants in the sewage waters, in particular HTZ is not effectively removed by conventional activated sludge treatment and membrane bioreactors (MBRs) [1]. Three beta zeolites with different silica alumina ratio (36/36 and 25 respectively) were purchased in their protonated forms (Tosoh Corporation), in order to investigate the role of hydrophobicity on the retention. Kinetics and adsorption isotherm batch data obtained via HPLC-DAD prove that beta zeolite with SAR equal to 36 has a higher adsorbent capacity than that with SAR equal to 360 when both HTP and HTZ are considered. Thermogravimetric analysis (TGA) revealed that the amount of pharmaceuticals embedded in the beta framework is strongly related to the SAR value, thus confirming a higher adsorption of HTZ on low SAR beta. Finally, a comparison of the X-ray diffraction patterns of untreated and exhausted samples shows relevant differences both in the intensity and position of the diffraction peaks, indicating that the beta crystal structure was markedly modified by the pharmaceuticals adsorption experiment. In conclusion, the experimental results demonstrated that SAR plays an important role in determining the adsorption capacity of zeolites employed as adsorbent materials. The high adsorption properties were attributed to the large hydrophobic surface area and the regular-shaped, open and interconnected three-dimensional pore structure of the zeolite. For these reasons, the Beta zeolites are efficient in removing drugs from wastewater and in particular polar drugs.

[1] Radjenovic', J.; Petrovic', M.; Barceló, D. *Water Research (Oxford)* 2009 Vol. 43 No. 3 pp. 831-841

Keywords: beta zeolite, adsorption, pharmaceuticals

ASBESTOS RELATED PATHOLOGIES AMONG RESIDENT POPULATION ON CALABRIA-LUCANIA BORDER WITH ENVIRONMENTAL AND OCCUPATIONAL EXPOSURE TO TREMOLITE

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Along with the mapping of areas on the Calabria-Lucania line presenting outcrops of serpentinite and metabasites rocks, containing tremolite, a group of geologists from the CNR of Tito Scalo (PZ) has undertaken an environmental monitoring of tremolite airborne fibres, showing an exposure up to 5 ff/l. A multidisciplinary workgroup in a Consensus Conference has scheduled an epidemiological-health surveillance on the involved population aiming to assess the prevalence of asbestos related diseases due to environmental and occupational asbestos exposure. The resident population of Lauria and Castelluccio Superiore cities was recruited for the current study on a voluntary basis. The health surveillance protocol included an occupational medicine physical examination along with lung function tests for each resident person above 18 years old. Moreover, people living in the area from more than 20 years performed chest X-ray in double projection with ILO-BIT reading in double blind test along with a visit of a pulmonologist. 699 residents voluntarily joined the health surveillance protocol. Results show people affected with asbestos related pulmonary and pleural pathologies, both benign and malignant. Among these, it has to be highlighted the presence of 2 malignant pleural mesothelioma and 1 lung cancer cases. Consistently with data coming from the literature, the frequency of benign and malignant pleural pathologies is related to the environmental asbestos exposure, which lasts since their birth. Soil movements in construction and agriculture sectors determine a risk of tremolite occupational exposure which can be correlated with types of pulmonary diseases discovered.

Keywords: natural occurring asbestos, asbestos related pathologies, environmental and occupational exposure

PLEURAL MALIGNANT MESOTHELIOMA AMONG RESIDENT POPULATION IN AREAS WITH NATURAL OCCURRING ASBESTOS ON CALABRIA-LUCANIA BORDER

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The researches following the signalling of three Mesothelioma outbreaks occurred among people living in areas near to Lagonegro, Lucania, without any evident asbestos exposure, have led to the discovery of naturally occurring asbestos. The geologists group belonging to the Institute of Methodologies for Environmental Analysis of CNR, Tito Scalo (PZ), carried out the geological and mineralogical characterization of the southern area of Lucania, showing the presence of natural outcrops of serpentinite and metabasites rocks, containing tremolite (type of asbestos). The same group has carried out an in-depth monitoring of asbestos fibres in the airborne particulate, thanks to the use of SEM/EDS. The aim of the study was to assess the role of the exposure to naturally occurring asbestos as the cause of malignant mesothelioma in people living in Lucania area, polluted by tremolite fibres. Building on such analysis, outbreaks occurred in areas with natural outcrops of rocks containing tremolite were extracted from the Lucania Mesothelioma Register. For the selected cases, a thorough analysis about asbestos exposure was conducted. To date, the Lucania Mesothelioma Register accounts for 90 cases, 17 of which arose among people living in areas with outcrops of ophiolites. In 11 of these cases (9 men and 2 women), it was assessed a definite exposure to tremolite fibres; 2 cases were due to environmental exposure, while the remaining 9 cases were caused by working environment exposure in productive sectors as the construction, agriculture or farming ones. In these sectors, indeed, movements of the soil containing asbestiform minerals lead to occupational exposure to tremolite fibres above natural levels. Six cases were classified as unknown asbestos exposure.

Keywords: natural occurring asbestos, malignant pleural mesothelioma, environmental and occupational exposure

PREDICTION OF MAXIMUM POSSIBLE TSUNAMI FLOODING AIMED TO THE REDACTION OF PREVENTION, MITIGATION AND INTERVENTION PLANS

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Tsunami impact is known to leave a devastating mark on coastal areas; the recent experience of the February 11, 2011 Japan Tsunami, due to the high density of human settlements, showed that the effects of an unforeseeable tsunami can be unimaginably catastrophic. In order to safeguard continued human activity in case of an impact from extreme events, it is essential to actively search for monitor suspect areas and develop models that provide forecasting, warning and pre- and post-events managing instruments. In fact the implementation of mathematical models correspond realistically to the complexity of processes that occur during coastal inundation. The mathematical models were used to obtain the run up and the landward flooding limit produced by future tsunamis. Numerical models that simulate the potential of tsunamis have been produced; they are based on differential equations with particular boundary conditions according to the local coastal features. In particular, Hills & Mader's formula enables us to calculate the inland flooding limit of a tsunami. The results depend from the values of the n Manning's, corresponding to the hydraulic roughness. This formula has been recently modified for sloping rocky coasts; in spite of this, it is strongly influenced by Manning's number. In function of different surface materials, many authors use different roughness coefficient values and quite often they are not the same. As a consequence, the use of the Hills & Mader equation is not always rigorous. Furthermore, the value does not remain constant over time in the same place, due to vegetation overgrowth and/or urban development and variations of flow conditions. As a consequence it is possible to obtain an evaluation of the present roughness. Our aims have been: i) develop a method to obtain a real Manning coefficient based on Terrestrial Laser Scanner and LIDAR topographical data; ii) test the method in study areas with evidence of a past tsunami impact; iii) present scenarios of possible depreciable future tsunami inundations.

Keywords: tsunami, coastal hazard, coastal risk

ASSESSMENT OF INDIVIDUAL EXPOSURE DOSE IN HIGH BACKGROUND RADIATION AREA OF TAMIL NADU, INDIA

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South coast of India is known as the high-level background radiation area (HBRA) mainly due to the emission from beach sands that contain natural radionuclides as components of the mineral monazite. The rich deposit of monazite unevenly distributes in longer than 100 km along the coastal belt of Tamil Nadu and Kerala where inhabitants commonly live and work. In our previous study, the HPGe radiation detector identified 6 nuclides of thorium series, 4 nuclides of uranium series, and 2 nuclides belonging to actinium series in the sand samples from three different HBRA spots of the coast of Tamil Nadu. Here we conducted the individual dose assessment based on personal and indoor ambient doses of inhabitants in Tamil Nadu by using RPL glass dosimetry system for the first time. Measurement of individual and indoor ambient dose was conducted for 87 local inhabitants and in their dwellings in southern Tamil Nadu, consisting of 67 subjects from 24 villages in HBRA and 20 subjects from 12 villages in control area. Subjects were asked to wear a RPL glass dosimeter as a necklace all day long except the sleeping period. Another dosimeter for ambient dose monitoring was hung from the ceiling of the dwelling at 2m high from the floor. Measurement by a glass-tip dosimeter was performed for around 14 days, and then both individual and ambient dose assessment in a measuring period was converted to an annual dose (mSv/y). The doses for all test subjects were subtracted by the average reading in Nagercoil, the largest city in southern Tamil Nadu. A linear correlation was observed between ambient and individual personal doses for all 87 inhabitants with a correlation cofactor of 0.7653 and a slope of 0.7464 for a linear regression line. This is in good consistency with the study conducted in Kerala that obtained a slope of 0.7169 in a regression line of comparison between personal doses measured by the OSL dosimeters and estimated external doses by scintillometers. The averaged individual dose of all HBRA subjects was 2.09 mSv/y, whereas no detectable individual dose was found in control subjects. Among villages, subjects in Chinnavillai were exhibited the highest average dose of 7.17mSv/y ranging from 2.79 to 14.17 mSv/y. The person who received 14.17 mSv/y, the highest dose among all subjects, was a housewife and her lifetime cumulative dose was estimated as 921.05 mSv based on the update life expectancy data for female Indian in recent statistics by WHO.

Keywords: high background radiation, Tamil Nadu, individual exposure dose

MINERALOGICAL ANALYSIS AND GEOCHEMICAL CHARACTERIZATION OF EXOGENIC AND ENDOGENIC PARTICLES IN EXPLANTED LUNG AND HILAR LYMPH NODE TISSUE

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Scanning electron microscopy and x-ray microanalysis were used to image and analyze particles in the explanted lung and hilar lymph node tissue of a New York City firefighter who was exposed to World Trade Center (WTC) dust. The patient was diagnosed with idiopathic pulmonary fibrosis in 2006, and underwent a successful lung transplant in July 2008. Results presented here are part of a larger study in collaboration with the Columbia University College of Physicians and Surgeons and New York City Fire Department to identify particulate matter and other anomalies in lung tissue that might be attributable to exposures at the WTC site.

Lung and hilar lymph node tissue samples were prepared by fixing in formalin and mounting in paraffin. Electron microscopy samples were prepared by thick sectioning using a tissue slicer. Slices of tissue were mounted on conductive carbon tape for analysis. Samples were imaged and analyzed in variable pressure mode in standard and field emission electron microscopes. Particles were counted and probable mineralogy was determined by stoichiometry.

Results showed clear differences in relative phase abundance between lung and lymph node. Both tissue types had a variety of minerals and other phases, such as feldspars, clays, silica-rich particles, iron and iron-titanium oxides, glasses, and various unidentified phases. However, within the node, silica-rich phases, predominately quartz, were much more abundant than other phases. These results suggest different physiological processes were at work in the two tissue types, and potentially include different mixtures of physical clearance, particle dissolution and precipitation of new particles. Particles identified in the lung tissue are inhaled exogenic or altered exogenic particles. Particles in the hilar lymph nodes represent inhaled particles that have been transported from the lung parenchyma via pulmonary lymphatics, and deposited in the hilar lymph nodes. Other particles, including calcite crystals and a layered aluminosilicate phase, identified near and at the margin of the node appear to be forming in place. Further studies including chemical speciation and reaction path modeling should provide insights into geochemical-physiological processes within the lung and how the body deals with exposures such as those encountered at the WTC disaster site.

Keywords: dust, lymph node tissue

NATURALLY OCCURRING ARSENIC OCCURRENCE IN GROUNDWATER AND BIOMARKER ASSESSMENT IN EXPOSED POPULATIONS FROM NORTH CAROLINA, USA

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Naturally occurring arsenic (As) contamination of drinking water from private wells is a health concern in the United States as the Safe Drinking Water Act regulations do not include private wells. Homeowners using private wells in areas where As concentrations are naturally elevated are at an increased health risk compared to those who consume regulated municipally supplied water. While high levels of As exposure cause acute symptoms, evaluating the symptoms and diseases directly associated with intermediate levels, but exceeding the Maximum Contaminant Level threshold (10 µg/L), are problematic due to the long latency period between chronic exposure and disease occurrence. Understanding the correlation between intermediate levels of As exposure and actual disease outcomes is difficult but important in order to evaluate the health implications of long-term consumption of As-bearing drinking water.

This study is focused in As-rich groundwater from Union County in North Carolina, which is part of the Piedmont region of the southeastern USA. The study aims to evaluate the distribution of As in the local groundwater and to investigate how different As levels in drinking water from unregulated private wells affect the health of the local population. In order to understand the population exposure, human keratin in the form of toenails were used as a biomarker of exposure. The data show that the distribution of As in the groundwater is directly associated with the aquifer lithology, as higher As concentrations are found in wells located in meta-volcanic rocks. The data also show large variations in As concentrations varying from concentrations near zero to 130 µg/L, probably reflecting the heterogeneity of the fracture network of the local aquifer system. In about 20% of the wells, As occurs as As-(III) species, while As-(V) is the predominate species in the others, which infer that reducing conditions control As speciation and could pose addition risks to human health. Preliminary data from well water-nail pairs reveal a statistically significant correlation, in which the male and children sub-populations seem to be most sensitive to As accumulation in the nail. This suggests that this method could be used in assessing the effect of low-level exposure on human population prior to disease occurrence.

Keywords: arsenic, groundwater, health

A PHYSICO-CHEMICAL ASSESSMENT OF THE POTENTIAL RESPIRATORY HEALTH HAZARD OF QUARRIED VOLCANIC DEPOSITS

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The potential respiratory health hazard of volcanic ash is routinely studied but little is known about the respiratory hazard of quarried volcanic deposits, either as loose, clastic deposits or freshly blasted lavas. Quarrying of both deposit types may expose workers to fine particulate and subsequent processing of material may reactivate particle surfaces, thereby affecting their potential toxicity.

Here we explore whether quarried volcanic particulate can potentially cause respiratory disease; either through reactivated surfaces on aged deposits or formation of new particulate from blasted lava which might pose a similar hazard to fragmented, erupted ash. Such quarrying is of economic importance and here, samples collected from New Zealand (tephrite, trachybasalt, basaltic andesite, dacite and rhyolite), Montserrat (andesite) and Greece (rhyolite) are presented. Grain size analyses of particulate generated from solidified lava flows indicated that the finest particles were produced as a result of drilling (carried out prior to blasting); however, in all magma types, processed (finished) product also contained significant quantities of respirable material. SEM analyses confirm that the morphology of particles can be altered by the method of processing. Crystalline silica quantification was determined by XRD and showed that the Montserratian samples contained the greatest quantities (up to 16 wt.% quartz), with the basaltic and rhyolitic samples containing much lower levels. Preliminary surface reactivity analyses indicate a trend between magma type and hydroxyl radical generation, with magmas richer in iron generally generating more radicals. Further surface reactivity tests and leachate experiments are currently in progress. This trans-disciplinary research will incorporate mineralogical characterisation with risk assessment of the quarries visited, providing them with information useful for potentially shaping policy on occupational exposure.

Keywords: volcanic, health, hazard

ENVIRONMENTAL IMPACTS OF COPPER MINING IN THE MIDUK AREA

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The accurate estimation of metal bioavailability in soils is becoming more important in ecological risk assessment. In this study, 60 soil samples at two depths (0-5 cm and 15-20 cm) in the vicinity of Miduk Porphyry Copper Mine, Kerman Province, Iran, were analyzed for total concentration of 45 elements. To determine the bioavailability of various heavy metal forms, sequential extraction analysis (Tessier procedure, 1997) was carried out. In order to study the relationship between the metal concentration in soil and underlying bedrock and finding the geogenic source of pollution in soil, 20 rock samples were analyzed for total concentration of 45 elements. 20 thin sections of rocks were prepared from different rock types of Miduk area to study alteration zones and mineralogy of rock units. Average concentration of Ag, As, Cd, Cu, Ni and Pb in soil samples are 0.88, 28.57, 0.6, 482.69, 53.05 and 122.3 mgkg⁻¹, respectively. The results of sequential extraction analysis show that more than 66% of Cu is bound to Fe-Mn oxides fraction. The highest As content is leached from residual fraction (48.6%). The following average mobility sequence was observed: Mg > Cd > Mo > Ag > Ni > Zn > Cu > Cr > Pb > As > Fe. In order to assess the possible bioaccumulation of these elements, the roots and the overground parts of 3 plant species (Astragalus: Fabaceae, Acanthophyllum: Caryophyllaceae, Artemisia aucheri: Asteraceae) were collected, analyzed and compared with geochemical distribution of elements in soil. The highest transfer factor (Tf) in the plant species is found for Cd, Mo, Cu, and the lowest is for Cr, Co and Al. High levels of As, Cu and Ag in soil samples poses a potential risk in the area. Results highlighted the need for continuous monitoring of elements in Miduk area to prevent the serious environmental and pollution problems in the future.

Keywords: miduk porphyry copper mine, Iran, trace element, soil, sequential extraction, plant, rock

MORPHOLOGY AND COMPOSITION OF A PEDIATRIC SIALOLITH: AN ELECTRON MICROPROBE AND RAMAN SPECTROSCOPY INVESTIGATION

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The term sialolithiasis refers to the formation of crystallized particles known as salivary calculi or sialoliths in the submandibular gland and in the glandula parotis, especially in the so called Whartons's and Stensen's ducts, respectively. The etiology of these calculi is poorly known as well as the precise mechanism of their formation. However the most important factors controlling the development of sialoliths are: 1) presence of bacteria, 2) viscosity and pH of saliva, 3) anatomy of the Whartons's duct and 4) relatively high concentration of Ca in saliva. Therefore, characterization of morphology and chemical composition of the sialoliths is important to define the most appropriate medical treatment of the patients and to prevent further formation of sialolithiasis. Sialolithiasis is a common disease in middle-aged patients, affecting about 1.2 % of population. In children, this entity is rare and it is estimated that the pediatric population represents only 3% of all cases of sialolithiasis. The aim of this contribution was to investigate by electron microprobe and Raman spectroscopy a sialolith formed in the Whartons's duct of an 11 years old patient. The studied sialolith, about 2 mm in size, is white in color and has a rounded shape. It consists of a core composed of small particles (about 2 microns in size), containing S, Cl, P, K, Ca and Na (only qualitatively analyzed), rimmed with a phase of Ca, P and O (only semi-quantitatively analyzed). This compound is banded like agates and shows a zoning of several thin layers, few microns across, characterized by different distribution among Ca, P and O. It also forms crystalline and mammillary aggregates and botryoidal clusters of radiating crystals. The phase contains Cl and S, up to 0.26 and 0.53 wt%, respectively. F content is negligible, ranging between 0 and 0.11 wt%. REE, U and Th, that generally can be detected in apatite occurring in natural rocks, are absent in the analyzed sialolith. Based on the semi-quantitative analyses, it was not possible to classify whether the compound is apatite or brushite, isoclasite and monetite. Therefore, we analyzed it using Raman spectroscopy. The obtained spectrum shows no discernible scattering bands over the range of 150–2000 cm⁻¹, but its shape indicates a fluorescence effect, suggesting that the studied compound is an amorphous or poorly crystalline phase.

Keywords: sialoliths, microprobe, Raman

AREA AND VOLUME CALCULATION OF PROPOSED URANIUM TAILINGS POND, SERIPALLY, NALGONDA DISTRICT, ANDHRA PRADESH, INDIA

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Uranium mill tailings may cause hydrogeological contamination by its radioactive ore residue and the chemicals added during the ore processing. Radium, present in the tailings, is leached out along by the atmospheric water, and toxic chemical rich water added during milling. This can contaminate the surface and ground water in the neighboring tailings pond area. Substantial uranium reserves have been identified at Lambapur-Peddagattu region in Nalgonda district of Andhra Pradesh and UCIL is in the process of obtaining clearances for construction of three underground and one open pit mines in the area and a processing plant at Seripally, 52 km away from the mine site. The design of tailings pond choice is primarily dependent upon natural topography, site conditions, and economic factors. The design of the proposed tailings dam depends on the geomorphology of the Valley. Because costs are often directly related to the amount of fill material used in the dam or embankment (i.e., its size), major savings can be realized by minimizing the size of the dam and by maximizing the use of local materials, particularly the tailings themselves. In this study, the purpose is to calculate the surface area and volume of proposed tailings with digital terrain models analyses derived from geographical information systems in order to reduce costs. Topography map (1:25,000) surveyed by GSI and high resolution remote sensing image (LISS IV) are the main and basic data resource for this research. Area of Interest (AOI) of proposed tailings pond is derived from remote sensing image, which contains 2 dimension (2D) information, and therefore calculation of 2D area of proposed tailing pond can be acquired. The proposed tailings pond is estimated to occupy about 80 hector in the vicinity of Mudigonda forests. The valley surface elevation starts from 305m to 410m. The slurry volume was estimated to ranged from 140975.62 to 8818455.38 cubic meters, and surface area was estimated to ranged from 156282.040 to 890137.040 square meters based on one meter to 18 m bund construction. Calculating area and volume, and using these calculations in the phase of determining various choices within the planning process, considerably reduces the expenses and the time spent on the plans and projects of waste disposal. These calculations should be taken into consideration before the tailings pond is constructed.

Keywords: area and volume calculation, uranium tailings pond, Seripally, India

USE OF BIO-ORGANIC MATTER FROM URBAN WASTES TO PREVENT THE LEACHING OF HERBICIDES TO GROUND WATER

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The herbicides terbuthylazine and metolachlor, often applied as mixture, are widely used to control many annual grasses and broad-leaved weeds. Several studies report that both the herbicides have been found in ground water at concentrations above the authorized limits. The aim of the present study was to test the capacity of the soluble (SBO) and insoluble (IOR) fractions deriving from urban wastes of different origin to reduce the leaching of the herbicides by promoting adsorption processes. The urban waste were different origin composts and sludges which humic-like soluble fraction (SBO) was obtained by basic extraction. SBO have shown promise as chemical auxiliaries for a number of technological applications in the chemical industry and in environmental remediation while the solid residue (IOR) of extraction could found useful applications in agricultural and environmental fields. Adsorption studies were performed on a silt loam soil, (pH 7.8, 0.8 % OC) mixed with different amounts (2 to 16 %) of SBO and IOR. Suspensions of samples of amended soil in aqueous solution of the herbicides were equilibrated for 24 h at 25 °C. The amount of herbicide left in solution was determined by LC-MS. The extent of adsorption of both the herbicides on the non amended soil was about 25 % of the applied amount. This value increased at increasing amount of SBO and IOR to up to 80 %. The results confirm that the studied organic materials, exhibiting affinity to both soil surfaces and organic molecules, could improve adsorption of herbicides on soil aggregates, slowing down their release in the soil solution, therefore reducing their dispersion in the environment.

Keywords: terbuthylazine, metolachlor, herbicides

CAN GEOPHAGIA IMPROVE MEDICAL AND NUTRITIONAL DEFICIENCIES OF GEOPHAGIC INDIVIDUALS? A CASE OF GEOPHAGIA IN EASTERN CAPE PROVINCE, SOUTH AFRICA

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Deliberate ingestion of soils (Geophagia) is widely practiced in several countries across continents including Africa (South Africa, Cameroon, Democratic Republic of Congo, Nigeria, Swaziland, Tanzania and Uganda), Asia (China, India, Guatemala, New Guinea, Philippines, and Thailand) and the Americas. The ingestion of soils and clays has never been satisfactorily understood and explained, but studies have pointed to nutrient deficiency as the main cause, especially among pregnant and lactating women. Several studies have however revealed the practice to be common in non pregnant females and a few males. The ability of the soils to satisfy the requirement of the geophagic individual is influenced by its properties. In this study a survey was carried out to investigate the reasons behind the practice of geophagia, in the Eastern Cape Province of South Africa and to appreciate the physical and chemical properties of the soils ingested in the light of the reasons advanced to justify the practice. Information on type, colour, and quantity of geophagic materials ingested, frequency of ingestion, and reason for ingestion was obtained through the administration of a questionnaire. Geophagic clayey soils were collected from different areas around the Province and their physicochemical properties (texture, pH, cation exchange capacity) and chemical properties (major and trace elements, and total carbon) determined. Results indicate geophagia to be mostly common among single women between the ages of 21 – 40. The soils eaten were described as clays, stones, soil and soft soil having a gritty, silky or powdery feel. About 20g of the preferred soil was consumed at least once a day for a variety of reasons that were mainly medical, nutritional and cultural. The soils varied in their properties with pH values of between 5 and 9, and CEC values that were indicative of the presence of primary rather than secondary clay minerals. Low total carbon content in the geophagy soils indicated that the CEC was derived mainly from the minerals contained in the soil. It is worth noting that geophagia was most common in women in their child bearing age. Contributions to the recommended dietary requirements of the geophagic individual from the ingested clay are reported. The implications of the physicochemical and chemical properties of the soil on the various reasons advanced to justify their ingestion are also discussed.

Keywords: iron absorption, particle size, nutrient supplementation

HEAVY METALS AND PATHOGEN LOAD IN VEGETABLES GROWN ON SLUDGE-AMENDED SOIL: THE ROLE OF SOIL TYPE

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Sewage sludge has been, and is still being used to improve agricultural yields in many countries around the world. However, the popularity of sludge as soil amendment has been affected by concerns related to possible uptake of heavy metals and pathogens from sludge-amended soils. As a result, guidelines for maximum concentration of heavy metals, and load fecal coliforms in sludge destined for agricultural use exist in many countries. These guidelines consider sludge heavy metals and pathogen load only but studies have indicated that several factors interplay to determine the bioavailability of heavy metals in sludge-amended soils and their uptake by crops. Similarly the microbiological risk of growing vegetables on sludge-amended soils depends on several a factor among which is the ability of the soil to sustain the pathogen. Both bioavailability of heavy metals and survival of pathogens in sludge-amended soils are influenced by soil physical, chemical and mineralogical properties which vary with soil orders. Soil type may play a significant role in the bioavailability of heavy metals to plants grown on sludge-amended soils, as well as the load of *Escherichia coli* (a fecal coliform) in plants grown. This study investigated the role of soil type in the bioavailability of heavy metals (cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc) in four soil orders amended with sludge, and their uptake by spinach and carrots grown on these soils. It also aimed at identifying the soil order that presented the highest health risk with regards to the presence of *E coli* in the vegetables grown. Sludge of different ages (three months and three years) were applied to four different soil types at volume/volume percent ratio of 5:95, 10:90, 20:80 and 40:60 sludge:soil. Spinach and carrots were grown for nine and thirteen weeks respectively, after which they were harvested and the concentrations of the heavy metals and load of fecal coliforms and *E. coli* in the vegetables determined. Results indicated significant differences in uptake of heavy metals by both vegetables from the different soils. Survival of fecal coliforms in the soils also varied with soil and sludge application rates. The role of soil type in the bioavailability of heavy metals and presence of *E coli* in the vegetables is discussed. Results emphasize the need to consider soil types in the design of guidelines for sewage sludge use in agriculture.

Keywords: luvisols, vertisols, soil mineralogy

ENVIRONMENTAL COBALT AND HEALTH

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Cobalt, like other metals, is unevenly distributed in the natural environment. Cobalt is an essential trace element for humans and animals and an integral part of vitamin B12. However, when too much cobalt is taken into the human body, harmful health effects can occur. Severe Co contamination of soil is relatively uncommon but mining, smelting and industrial processing may all cause Co contamination.

Cobalt is one of the hi-tech-metals that EU has listed as critical metal, which refers commodities that are highly important to industry and society, and whose availability is subject to risk and uncertainty. The possible increase in mining and processing of Co makes it important to highlight studies on the geochemical circulation of Co and its distribution in the food chain. Soil contamination and remediation requirements must be assessed if the concentration of Co in soil exceeds the threshold value of 20 mg/kg, according to the Government Decree on the Assessment of Soil Contamination and Remediation Needs in Finland.

In Finland Co has been mined and produced in some polymetallic sulfide mines. However, there have been few investigations performed under field conditions on the availability and transfer of Co in the soil-plant system in the mining environment. In this study we investigated Co concentrations in the topmost soil (humus layer) and in wild edible mushrooms in the Luikonlahti Cu-Zn-Co mining district in eastern Finland. The soil contamination threshold value for Co was exceeded in the humus layer for the distance of about 500 m around the concentrating mill area. The total concentration of Co in humus ranged from 2.55 to 133 mg/kg. Available fraction of Co (ammonium acetate extraction) ranged from 0.68 to 23.3 mg/kg. The Co concentration in wild mushrooms depended greatly on taxa. Concentrations of Co in *Boletus edulis* grown in the studied mining area ranged from < 0.05 to 2,6 mg/kg with a median value of 0.87 mg/kg dry weight. In our previous study *Boletus edulis* grown in non-polluted collection sites Co ranged from 0.05 to 0.15 with a median of 0.08 mg/kg. The daily intake for Co considered safe according to legal standards is 1.4 mg/day. Rough calculation reveals that one kilogram of fresh *Boletus edulis* grown in the studied mining area would contain c. 18% of the given daily limit for Co.

Keywords: cobalt, environment of mine

OUTLINE OF NATURAL ZEOLITE MINERALS OCCURRING INSIDE THE TAKAMATSU CRATER DISTRICT IN SHIKOKU, JAPAN

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Recently we found a new locality of small size zeolite minerals in the hydrothermally altered volcanic tuff inside the Takamatsu crater district in Shikoku, Japan. The purposes of this study are to elucidate the geological significance as a special locality and to define the standard value of this occurrence. We find some small size zeolite minerals occurring in the vein-lets of the whitish wall rock inside the Takamatsu Crater. By the analytical results using XRD and SEM, we determined some zeolite minerals, which look like mordenite or gismondine. Additionally, by the water quality purification using our outside experimental facilities with 15m pool, we have elucidated that these natural zeolites are clearly effective to adsorb ammonium ions and to remove colitis germs. This study area is still now on geologically discussions and we have investigated for more than ten years to elucidate the genesis or the formation process of this area. We have considered the occurrence of this area as follows that; firstly there occurred a lot of active volcanic formations and then much of small mountains were formed around, secondly they were suffered by an extra-terrestrial matter such as a falling of iron meteorites, and finally the surface of those mountains were weathered and eroded by wind and rain. There might be a catastrophe like an active volcanic eruption or earthquake.

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Keywords: Takamatsu Crater district, the water quality purification, remove colitis germs

PRESENCE OF MULTIDRUG-RESISTANT ORGANISMS IN AQUATIC ENVIRONMENT: WHAT IS ITS IMPLICATION ON HUMAN HEALTH?

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Antimicrobials are used in not only health care facilities but also households. Some antimicrobials are excreted as unmetabolized products, contaminating the aquatic environment through sewage. For instance, 87% of the administered dose of levofloxacin (LVFX) was excreted unchanged in the urine within 48 hours [1]. Consequently, these excreted antimicrobials might have contributed to the emergence of multidrug-resistant organisms (MDROs) in the aquatic environment. Objective: This study aims to show the status of MDRO emergence in aquatic environment in Japan and discuss its implication. In 2009, depending on the location of water-treatment plants, 10 water samples were collected from Tama River (length: 138 km) in Tokyo. A total of 120 colonies of gram-negative bacilli were isolated. Bacterial species were identified and antimicrobial susceptibility tests (16 antimicrobials) were performed. The outcome measures were (1) percentage of drug-resistant strains among the isolated bacteria; (2) critical MDROs such as those resistant to imipenem (IPM) and quinolones or IPM and cephalosporins; and (3) antimicrobial concentration at sample collection sites. The antimicrobial concentration was less than the detection limit, except for amoxicillin and sulfamethoxazole-trimethoprim. Of the 120 isolates, 106 were resistant to at least 3 antimicrobials, including the undetectable ones. Of the 25 strains resistant to IPM, 6 were also resistant to ciprofloxacin/LVFX, 17 were resistant to at least 1 of the tested cephalosporins (cefazolin, ceftriaxone, cefuroxime, and cefotaxime), and 2 were resistant to all. The isolated bacteria showed resistance to antimicrobials whose concentrations were undetectable by LC-MS. Human health is threatened by MDROs. Primary exposure to MDROs might be recreational activity in an aquatic environment, and these MDROs possibly circulate in the community via infected people. Our results suggest the need to develop a monitoring system for MDROs in aquatic environment. Although the primary problem is ‘the excreted antimicrobials’; technically, it may not be wise to monitor the antimicrobial concentration. Funding Source(s): Japan Society for the Promotion of Science

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Keywords: multidrug-resistant organisms, antimicrobials, aquatic environment

GEOCHEMICAL EVALUATION OF IMPACTS OF URBANIZATION ON SOILS AND DUSTS IN AKURE AND BENIN CITY METROPOLIS, NIGERIA

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This study is aimed at determining the spatial distribution of heavy metals in the soils and road dusts of the study areas. A systematic sampling of soil and dust from Akure and Benin City metropolis was undertaken. Composite top soil samples, road dusts and dusts samples from filling stations were collected from major roads traversing the cities. Eighty-two (82) top soil samples, Sixty two (62) road dust samples and eleven (11) samples from filling stations were collected. All the samples were air dried at room temperature and disaggregated were digested using hot aqua regia and subsequently analysed for elemental contents using Inductively Coupled Plasma Emission Spectrometry (ICP-OES). The results of the analysis on Akure samples revealed the following range of values pH (6.6 - 7.9); Total Dissolved Solids (96.2-3276); EC (148-5040 μ S/cm); Cu (10-71ppm); Pb (12-158ppm); Zn (25-552ppm); Ni (5-32ppm); Cr (10-76ppm); Co (6-22ppm); Th (3-23ppm); Cd (0.5-1.5ppm); Ba (54-261ppm); Mo (1-3ppm) and V(26-72ppm). For the dusts the following trends were observed: Cu (35-147ppm); Pb (52-487ppm); Zn (118-876ppm); Cr (48-162ppm); Co (6-19ppm); Th (17-25ppm); Cd (0.7-1.4ppm); V (50-132ppm); Mo(1-6ppm)and Ba (65-145ppm). The results of the analysed samples from Benin City showed the following trends: pH (5.5 to 7.8); Electrical Conductivity (37.0-860.0?S/cm) and TDS (24.0-328.25mg/L). The elemental composition revealed the following trends: Cu (4-1125ppm); Pb (9-2889ppm); Zn (29- 5022ppm); Ni (2-52ppm); Co (1-12ppm); Mn (53-132ppm); Th (3-12ppm); Sr (4-969ppm); Cd(Below Detection Limit, BDL-27.2ppm); Sb (5-12ppm); V (17-108ppm); La (3-13ppm); Cr (15-90ppm), Ba (6-530ppm) and As (BDL-6ppm). The geochemical and geo-accumulation index maps produced showed large variability in the spatial distributions of elements in topsoil and dust respectively as well as their pollution status. Further evaluation of the results using contamination indices revealed that soils and dusts from areas that are densely populated with considerable commercial activities are significantly enriched in metals with considerable impact on quality of the environmental media analysed.

Keywords: urbanization, contamination indices, pollutants

ARSENIC, CADMIUM, COPPER AND LEAD IN ATMOSPHERIC PARTICULATE MATTER IN THE CENTRAL REGION OF SÃO PAULO STATE, BRAZIL

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Trace elements in urban particulate matter have been of concern to the environmental agencies worldwide because of their direct adverse effects on the waters, ecosystems, and also on human health. Metals/metalloids such as arsenic, cadmium, copper and lead are of particular concern because of their prevalence, persistence in the environment and potential chronic toxicity. A total of ten sets of particulate samples, each in a 7 day period, were obtained in both dry and humid period, in Araraquara city. The region is one of the most important sugar cane harvested in São Paulo State, Brazil. A 12-stage micro-orifice uniform deposit impactor (MOUDI) was used to collect particulate matter (PM). Polycarbonate filter substrates were used on all stages, and at a flow rate of 28.0 l min⁻¹ the 50% cut off diameters (D50) were (mm) 18.6, 10.2, 6.4, 3.2, 1.9, 1.0, 0.58, 0.33, 0.19, 0.1 and 0.063. The filters and samples were weighted on a microbalance that was readable to 1 mg. The sample masses of size fractions PM_{6.4-10.2}, PM_{3.2-6.4} and PM_{0.33-0.58} accounted for 10-18%, 13-20% and 12-32% of the total, respectively. Samples were digested in HNO₃:HCl 3:1, and further analyzed by ICP-MS. The experimental protocol used in this study was validated using standard reference material (NIST 1648a). The medium concentration in dry and humid period were respectively (ng m⁻³): As(1.57, 0.44), Cd (1.20, 0.79), Cu (4.96, 2.57) and Pb (3.67, 2.12). Seasonal variation showed higher values of trace elements for samples collected in the dry period. That variation represents the impact of meteorological conditions, which can change the concentration level of aerosol and its chemical composition by aerosol transport. In order to evaluate the medium concentration in the dry period, the 12-stage was organized in (µm): PM_{>10.0}, PM_{10.0-2.0}, PM_{<2.0}. The element concentrations for those categories were (ng m⁻³): As (0.77, 0.18, 0.68), Cd (0.26, 0.21, 0.73) Cu (0.57, 1.94, 2.45) and Pb (0.19, 0.76, 2.71). In general, PM_{<2.0} yielded higher concentrations for these elements, except for As. It is well known that fine particles are usually formed by combustion or gas-to-particle conversions and can be rich in toxic metals/metalloids, as well as sulphate, ammonium and nitrate ions. The measured distributions are believed to result from a combination of processes including local anthropogenic and natural sources, long-range transport and resuspension.

Keywords: particulate matter, trace elements, ICP-MS

BIOGEOCHEMICAL PROCESSES AND METHYLMERCURY PRODUCTION IN FRESHWATER WETLANDS

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Mercury is the number one contaminant issue worldwide in terms of the number of sites affected. Mercury contamination of the environment has increased since the industrial revolution through release of this volatile metal into the atmosphere from various anthropogenic sources. Human health is primarily impacted by consumption of fish containing high levels of mercury, mostly in the form of neurotoxic and bioaccumulative methylmercury (MeHg). MeHg may cause neurological impairment and cardiovascular impairment. Minamata disease is a neurological disorder caused by extreme MeHg exposures. Neurological damage in developing fetuses is a particular concern. All fifty U.S. states now have fish consumption advisories for MeHg, and it remains a concern worldwide. MeHg also poses a threat to piscivorous wildlife through endocrine disruption and neurologic effects, resulting in gradual population declines.

Mercury is a problem in medical geology because biogeochemical processes in the environment convert inorganic mercury from anthropogenic sources into MeHg. The Everglades, Florida has some of the highest levels of MeHg in fish in the USA. We have been investigating the environmental conditions promoting MeHg production and bioaccumulation in this large wetland ecosystem. Obligate anaerobes, including sulfatereducing and iron-reducing bacteria are responsible for methylating inorganic mercury. Wetlands are particularly important habitats for MeHg production as anoxic sediments provide the environmental conditions that support anaerobic metabolism. In many respects the Everglades is an ideal environment for MeHg production due to: (1) extensive wetland area, (2) high inorganic mercury deposition, (3) sulfate contamination from agricultural runoff, and (4) high dissolved organic carbon (DOC) content. Sulfate contamination is 60100 times levels present prior to development and stimulates microbial sulfate reduction and MeHg production in the Everglades. The relationship between sulfur and MeHg production is complex, however, with stimulation by sulfate and inhibition by sulfide. DOC plays a key role by binding and stabilizing inorganic mercury and transporting it to sites of methylation. This presentation will summarize the results of more than ten years of study of the biogeochemical basis of MeHg production in freshwater wetlands, as well as presenting some recent data on MeHg production in coastal areas.

Keywords: mercury, wetlands, biogeochemical processes

ASPHODELLUS FISTULOSUS TOLERANCE TO ARSENIC WITH RELATION TO THE SPECIATION IN SOILS DISTURBED BY MINING ACTIVITIES

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Mining generates large quantities of waste, such is the case of the mining district of Cerro de San Pedro, San Luis Potosí, Mexico. The waste generates acid mine drainage; therefore, releasing potentially toxic elements (PTE) such as arsenic. By cause of this a methodology has been implemented that facilitates the discernment of the interaction of the PTE on the soil as well in the biota. Total concentrations of As in rhizospheric soils of *Asphodellus fistulosus* are in intervals from 216 to 1017 mg/kg, which exceed the allowable limit both in agricultural use soils and industrial use soils established in Mexican legislation as well as guidelines in the UK, France and Argentina having as maximum allowable limits of As 22 and 260 mg/kg, 20 and 500 mg/kg, 37 and 120 mg/kg, 20 and 50 mg/kg, respectively. In this study, As was quantified in roots and leaves of *As. fistulosus* getting higher bioaccumulation in roots. The quantification was performed by acid digestion in a closed system. Has been determinated the arsenic chemical speciation for the purpose to understand the behavior of metals, as well as mobility and bioavailability in the environment, the speciation was determined by evaluating the geochemical fractions presents in the rhizospheric soils, the main fractions considered were anionic exchangeable, bound to carbonates, bound to iron and manganese oxides, and differed from the fraction not available as the residual fraction and bound with sulfides. Bioaccumulation of As in *As. fistulosus* was correlated with bioaccessibility and geochemical speciation in rhizospheric soils. The phytoavailability in rhizospheric soil was performed by extraction with a solution of low molecular weight organic acids (C2C4), and correlated the results with the pH, redox potential and carbonates content in soils. This methodology has been integrated to provide an alternative diagnostic evaluation and environmental impact in plant species that have shown tolerance to acid mine drainage and sites with high concentrations of arsenic.

Keywords: phytoavailability, arsenic, rhizospheric soil

IRON TOPOCHEMISTRY, SURFACE REACTIVITY AND IN VITRO TOXICITY OF AMPHIBOLE ASBESTOS

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The in vitro toxicity of asbestos tremolite from Italy and USA localities and UICC crocidolite was investigated on human alveolar A549 cell line. Chemical reactivity of the same fibrous samples was studied in relation to Fe content, oxidation state and structural coordination, with the aim to correlate Fe topochemistry to the observed cell toxicity. Direct correlation between fibers Fe²⁺ at the exposed M(1) and M(2) sites and their chemical reactivity was established. However, the relationship with cell toxicity is not straightforward: UICC crocidolite has Fe content and chemical reactivity largely higher than that of tremolite samples, but all have comparable in vitro toxic potential. Results obtained evidenced that Fe topochemistry is certainly a primary factor, but not the only one, in asbestos-induced cell toxicity.

Keywords: amphibole asbestos, iron topochemistry, surface reactivity

EFFECT OF LEAD LEVELS IN BREAST MILK ON ESTIMATED INFANT INTAKE OF LEAD

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Breast milk is the first food for infants and it serves as the major nutrient source for biological functions and growth during the early stages of life. For that reason, infant exposure to lead through breast milk is of special concern. Lead is neurotoxic and may cause mental deficiency, movement disorders, kidney dysfunction, and abnormal perception, especially during fetal growth and development. However, lead concentrations in breast milk in this study are low and comparable to those found in other studies. A Hazard Index (HI) exceeding 1.0 indicates that infant consuming breast milk has a potential health risk. In the present study, the HI ranged from 0.055 to 0.329. It means that the body burden of lead in the infants was not affected by consume of breast milk.

Keywords: breast milk, lead levels, hazard index

SOIL ARSENIC AND MELANOMA: IS THERE A LINK?

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Arsenic may act as a cocarcinogen in conjunction with ultraviolet radiation resulting in non-melanocytic skin cancers. Arsenic uptake from soil around historical gold mining activity during childhood is established and we sought to investigate possible links between soil arsenic level and melanoma risk in the larger population.

Preparatory to applying spatial epidemiological techniques to estimate these associations, spatial empirical Bayes (SEB) smoothed standardized incidence ratios (SIRs) for melanoma, and two soil arsenic exposure metrics, were derived for 61 statistical local areas (SLAs) in Victoria's goldfields.

We applied spatial autoregressive modelling to estimate associations, taking into account socioeconomic disadvantage (SED), modelled as a dichotomised score, such that SLAs with scores below the median Victorian value were classified as more disadvantaged. Interactions between SED and exposure metrics were investigated. The connectivity matrix for SLAs incorporated in conditional autoregressive (CAR) models was based on adjacency of SLA boundaries. To assess the robustness of findings, we also stratified SLAs by quintiles of exposure metric 1, estimated aggregate SIRs by gender and SED category, and calculated relative risk (RR) as the ratio of the SIR in the uppermost quintile relative to the lowest quintile.

SEB smoothed SIRs for male melanoma increased by 0.05 (95% CI, 0.01 - 0.08) per 2.7 fold increase in exposure metric 1, when adjusted for SED and an easterly trend, and for female melanoma, by 0.05 (95% CI, 0.02 - 0.09) in more disadvantaged areas, adjusted for a northerly trend. In more disadvantaged areas with high soil arsenic, excess risk of melanoma was observed for males (RR 1.52 [95% CI, 1.25-1.85]) and females (RR 1.29 [95% CI, 1.08-1.55]).

This ecological study found that elevated soil arsenic levels are associated with a small but significant increase in melanoma risk over a twenty year period in socioeconomically disadvantaged areas. Inferences from group-level analysis cannot be assumed to apply at individual-level, and the study was not able to account for other melanoma risk factors or other possible sources of arsenic but these findings suggest that elevated soil arsenic levels may be linked with melanoma. In a country such as Australia where elevated rates of melanoma development are recorded, this finding has significant public health implications.

Keywords: arsenic, skin cancer

THE ROLE OF ENERGY EXTERNAL COSTS FOR A COMPREHENSIVE EVALUATION OF SUSTAINABLE ENERGY STRATEGIES

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As well known, pollutants emissions released by energy-related activities are transported in the atmosphere causing health and environmental damages. These external damages are responsible of indirect costs for the society that usually are not taken into account in the commodities' prices. In recent years the scientific community deployed many efforts to assess energy externalities, as well as to give guidance for supporting the design of internalisation measures. The ExternE methodology, developed under a EU-funded ExternE project series, represents the main reference to estimate the external costs of energy technologies, providing generalised values (Euro/ton of emission) per country for the most important pollutants. A subsequent fundamental step is to integrate the external costs into a partial equilibrium model to individuate sustainable development patterns that reduce the overall environmental damages of human activities and take into account these energy-related hidden costs. The IEA-ETSAP makes available a sound modelling framework to combine into an unique platform the economic, environmental and energy-technology data in order to better understand the behaviour of energy systems, to plan their optimal development over a medium-long term horizon, and thus to provide direct, usable inputs to the formulation and evaluation of energy policies in the overall framework of sustainability. In particular, the TIMES models' generator allows developing flexible and detailed energy-technology- models on different spatial scales to perform an in-depth characterisation of the analysed energy system, from demand to supply side, and to explore contrasting scenarios representing the potential development of the energy panorama over the time horizon according to the take up of different policy measures (resources and technology availability, pollutant emissions reduction, renewable share, etc.). The integration of externalities into this modelling framework set up thus an innovative tool to support policy-oriented multidisciplinary investigations, aimed at achieving a sustainable resource management notably taking account of the economic, environmental and social dimensions of energy policies. Selected scenario results concerning the NEEDS-Italy model will be presented to illustrate the expected role of different energy sources and energy related-externalities in the definition of air quality policies.

Keywords: energy system model, external costs

RESPONDING TO THE 2010 NIGERIAN LEAD POISONING OUTBREAK LINKED TO ARTISANAL GOLD ORE PROCESSING: CONTRIBUTIONS FROM THE EARTH SCIENCES

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In spring 2010, a pattern of ongoing childhood deaths (up to 400) and illness (355+) was noted by Medecins Sans Frontieres (MSF) in villages of Zamfara State, Nigeria, and was determined to be due to lead (Pb) poisoning. The cause was artisanal gold ore processing, which had recently been mechanized. Gold ores are first hand crushed, then pulverized in a flourmill (the recent mechanization), then washed and the gold extracted by amalgamation. In May 2010, US CDC deployed a rapid response team to two of the hardest-hit villages, to help assess the extent of the problem, understand exposure pathways and evaluate mitigation options. MSF and CDC found unprecedented levels of acute lead poisoning, particularly in young children, with blood lead levels nearly as high as 400 µg/dl; >10 µg/dl is indicative of lead poisoning. The CDC/ATSDR team collected many samples, including raw and ground ores, soils, waters, and dust sweep samples. The USGS is working with CDC to determine mineralogical and geochemical characteristics of the samples, to assist in understanding exposure pathways, assessing other villages for similar contamination, mitigating exposures, and cleaning up contaminated areas.

Mineralogical analyses show the ores are lightly to moderately oxidized quartz veins. Primary Pb sulfide (which is not bioaccessible) is present from 1 to ~30 vol% in ore samples. Weathering prior to mining created a complex secondary Pb mineral assemblage dominated by highly bioaccessible Pb carbonate, with lesser Pb phosphate, oxide, sulfate, vanadate, and tungstate minerals. The same Pb minerals are abundant in dust sweep samples collected from eating areas of many family compounds where the ores were processed, indicating severe processing-related contamination and a logical exposure route via hand/mouth transmission and incidental ingestion. Bulk Pb concentrations in sweep samples are up to 12 wt %, with most indicated to be bioaccessible by physiologically based extraction tests using simulated gastric fluids. Bulk mercury (Hg) is also high in sweep samples (up to 60 ppm), due to contamination from Hg lost during amalgamation; some is water-soluble and bioaccessible in simulated gastric fluids. Dermal Hg uptake during amalgamation, Hg inhalation during amalgam smelting, and Hg contamination of soils, water wells, and waterways (with conversion to more bioavailable and toxic methyl Hg) may also be problematic from a health perspective in addition to the Pb poisoning.

TOXICOLOGICALLY RELEVANT CHARACTERISTICS OF ATMOSPHERIC PARTICULATE MATTER FROM DIVERSE GEOGENIC, GEOANTHROPOGENIC, AND ANTHROPOGENIC SOURCES

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The air humans breathe, depending upon where they are, what they are doing, and many other factors, can contain a complex mix of airborne particulate matter (PM) derived from myriad sources. Over the past decade, our USGS project has collaborated with many colleagues in the earth and health sciences to measure toxicologically relevant mineralogical, physical, geochemical, biosolubility, bioaccessibility, and bioreactivity characteristics of diverse PM types or sources. These include a spectrum of geogenic (produced from the Earth by natural processes), geanthropogenic (produced from natural sources by processes that are modified, enhanced, or contaminated by human activities) and anthropogenic (produced by human activities) PM and PM sources; all have either been shown or speculated to cause adverse health impacts. Our project's results help public health experts understand better the nature of diverse PM exposures, and therefore potential health impacts.

Diverse PM types (many desert dusts, glacial dusts, wildfire ash, volcanic ash, dusts transported between continents) can have abundant respirable particles (<2.5 μm , PM_{2.5}) that may contribute to respiratory and related cardiovascular health problems due to their abundance, mineralogy, geochemistry, biosolubility, and bioreactivity. Some PM types can cause irritation of dermal, ocular, and respiratory tissues because they contain acutely bioreactive, caustic alkali minerals (wildfire ash, concrete particles in building collapse dusts, cement dusts, coal fly ash) or caustic acid minerals (soluble metal sulfate salts in coal dusts or weathering sulfidic mine wastes; volcanic ash; urban PM). Many PM types contain potentially toxic elements that are bioaccessible in simulated lung or gastric fluids, such as: wildfire ash and ash from burned buildings (Cr[VI], As, Pb, Sb, Mn, Cu, Zn); dusts from building collapse (Pb, Sb, Zn, Cu, Cr[VI]); coal fly ash (Pb, Tl, As, Cd, V, Cr[VI], Cu, Zn); dusts from metal mine wastes and PM from sulfide smelting, mercury ore roasting, or artisanal gold amalgamation (Pb, Hg, As, Cd, Cu, Zn, Mn, others); and volcanic ash (F, Mo, Mn, Cu, Zn). Oxidative stress and toxicity in the lungs may result from inhalation of PM that release Fe, Mn, and other redox-sensitive elements either acutely in high concentrations (ie biosoluble iron sulfates and bioreactive sulfides in mine wastes or coal dusts) or chronically in lower concentrations (biodurable volcanic ash, asbestos, etc.).

Keywords: atmospheric particulate

MOLECULAR SIMULATION STUDY OF LDH INTERCALATED WITH PORPHYRINS

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Molecular calculations were used for structure analysis of various intercalated layered structures of layer double hydroxides (LDH) with different porphyrin anions. Simulations bring a detailed insight into the structure arrangement of the interlayer space and on the surface. We can analyze mutual interactions between inorganic layers and organic species, their charge distribution, energy characteristics, distribution function, influence of water on the stability of structure. Simulations were done in Cerius2 and Materials Studio modelling environment. Resultant calculated structures were carefully derived on the base of experimental results and presented models are in a good agreement with them. Knowledge of structure - properties relationship is crucial for explanation of physical properties of inorganic-organic hybrid materials [1].

Quantum mechanics and molecular modeling calculations combined with X-ray diffraction, thermogravimetry and electron density measurements were used for structure analysis of (i) Mg-Al LDH intercalated with [5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS)], (ii) Zn²⁺-Al LDH intercalated with porphyrin anions [Zn(II)-5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin – (ZnTPPS)] and (iii) both types of LDH intercalated with Pd-TPPS and Pd-TPPC (carboxyphenyl). The high crystallinity achieved upon hydrothermal treatment allowed us to give further insights into the interlayer structural arrangement of porphyrin guests. Porphyrins intercalated into LDH are producers of singlet oxygen with sufficient long lifetime. So, these hybrid materials create antibacterial environment [1] and are usable in medicine applications.

[1] Kovár P., Pospíšil, M., Káfuková, E., Lang, K., Kovanda F., Journal of Molecular Modeling, 2010, 16, 223-233.

Keywords: porphyrin, LDH, molecular simulations

MATURATION OF PORTUGUESE GEOMATERIALS FOR PELOOTHERAPY APPLICATION

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Maturation process is a complex and multifactorial process that allows the improvement of the quality of the material and endows the mud with organic substances produced by microorganisms developed during the process. Time of maturation, light exposure, stirring procedures, temperature and raw material properties, for instance, have influence on the characteristics of the final mud, the peloid. We designed a maturation survey in order to study the effects of maturation on the properties of some Portuguese geomaterials. Two natural mud samples from São Miguel (Azores) and one natural Portuguese bentonite were submitted to maturation during 120 days. Azorean samples and bentonite were sieved at <63 µm and <90 µm, respectively, and kept covered by a layer of mineral water during the entire process at 20 °C. The abiotic conditions were restricted to natural and artificial light and bimonthly stirring procedures. Mineralogical, chemical and physical analyses were performed before and after the maturation period to raw materials and final mud. Virgin muds are finely grained (above 80% of <63 µm fraction), and reveal a composition consisting mainly of alunite, feldspars, quartz and amorphous aluminosilicates; kaolinite is the main clay mineral. Bentonite shows over 71% of <63 µm fraction and mineralogical composition consisting mainly of smectite, feldspars and calcite. Chemical composition analysis of samples reveals high content on SiO₂, Al₂O₃, Fe₂O₃, K₂O, Na₂O and TiO₂. Bentonite sample presents higher percentage of Fe, Ca and Mg than Azorean muds, instead volcanic materials are richer on S and K. Slightly enrichment on Na and Ca was detected on samples after maturation. According to the results some properties such as cation exchange capacity, exchangeable cations and cooling kinetics were improved by maturation. The bicarbonated-sodium type of mineral water used for maturation seems to influence some of these properties.

Keywords: healing geomaterials, maturation, pelotherapy

DISSOLUTION OF SMECTITE IN SYNTHETIC LUNG FLUIDS. ROLE OF ORGANIC LIGANDS AND BIODURABILITY

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The World Health Organization has identified smectites as having the potential to produce moderate fibrosis in the lungs following long-term exposure (1). Harmful effects may be dependent on the dissolution rate in lung fluids. The aim of this study is to determinate the smectite dissolution rates in saline solutions that mimic synthetic lung fluids (SLF) to gain knowledge about the residence time of the inhaled clay particles in the human body.

Dissolution rates of K-montmorillonite were measured in modified Gamble's solutions at pH 4 (macrophages) and 7.5 (interstitial fluids) at 37°C in stirred flow-through reactors. The particle size, measured by transmission electron microscopy, was of 500 nm in diameter. The effect of organic acids was investigated through the addition of lactate, citrate and glycine (0.15, 1.5, 15 mmol L⁻¹).

The results showed that the addition of lactate or glycine does not markedly affect the montmorillonite dissolution rates at pH 4 irrespective of their concentration. However, at pH 7.5 there exists a slight inhibitory effect of lactate on the dissolution, probably due to a reduction in the number of reactive surface sites caused by lactate adsorption onto the montmorillonite surface. However, citrate enhances the dissolution rate by 0.5 orders of magnitude at pH 4 and more than one order of magnitude at pH 7.5, thus indicating the prevalence of the ligand-promoted over the proton-promoted dissolution mechanism under these experimental conditions. The enhancement of the dissolution rate in acidic citrate solution likely comes from the formation of surface complexes between the ligand and the edge surface of montmorillonite. In neutral conditions the effect may be also due to the decrease of the activity of Al⁺³ by formation of aqueous Al-Citrate complexes.

The kinetic data were used to estimate the reduction in size of an inhaled clay particle. At pH 7.5, a particle of 500 nm in diameter could be reduced 25% in presence of citrate whereas the reduction in saline solution would only be 10% after 10 years.

[1] WHO (2005) Bentonite, kaolin and selected minerals. Environmental Health Criteria 231, pp. 1-174.

Keywords: montmorillonite, dissolution, biodurability

ARSENIC AND THEIR ENVIRONMENTAL IMPACTS ON SOILS AND CROPS IN THREE SUB-BASINS OF BOLIVIAN ALTIPLANO

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The Altiplano is an endorheic basin in the Central Andes of Bolivia located between the Western and Eastern Cordilleras. Since the early Quaternary, the Altiplano has always been occupied by lakes, but these have not always had the same extent as the present day lakes. The present lake system on the Altiplano is the result of the evolution of a more ancient system which began from the lower Pleistocene, with the transition at the end of the Pliocene from a relatively warm climate to a cool damp climate. The size of the lakes is directly related to the recession of glaciers at the start of the interglacial periods. In Bolivia, there are very few comprehensive studies so far on As and other trace element (TE) contamination of water resources from geogenic sources or anthropogenic activities and their impact soils and crops. The present study attempts to understand the relationship between water used for irrigation which has caused to enrichment of the soils with As and other TE and subsequent uptake by crops in the area around Poopó Lake. Sampling was carried out during 2008 in three mining areas viz. Coriviri, Ventaimedia and Poopó, which included surface water and groundwater, soil and crops [beans (*Vicia faba*), potato (*Solanum tuberosum*), barley (*Hordeum vulgare*) and alfalfa (*Medicago sativa*)]. The similar distribution of surface water and groundwater samples on Piper plots suggest that a narrow variations hydrochemical facies which is predominantly Ca-Mg-HCO₃ type. The Eh values reveal that arsenate (AsV) is the principal aqueous species in groundwater and surface water with almost same As-species. The soil samples are characterized higher total TE concentrations and lower values of Fe/S can be observed in the floodplain. Arsenic concentrations in soils were higher (13.0—40.0 mg/kg), compared by unimpacted soil and there are in the same order than those of the crustal median values. Crops contain relatively higher As concentrations and lower Cu, Zn and Pb concentrations as compared to the literature. Principal Component Analysis shows that the TE concentrations in the crop do not relate to the TE contents of the soils. This possibly means that the TEs in the soils are not significantly bioavailable and bulk of the transfer of TE to the crops seems to take place from the water used for irrigation.

Keywords: trace element, crops, Bolivian Altiplano

SUITABILITY OF PORTUGUESE CLAYS FOR MEDICAL HYDROLOGY APPLICATIONS

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In Portugal, there is an old tradition in using clayey materials for therapeutic purposes. They are applied at several beaches of the Atlantic coast, in the form of clay-sea water mixtures to treat skin and rheumatic diseases. During many generations, they have been applied without scientific studies that prove their therapeutic validity. In the last decade, the Portuguese scientific community has become increasingly more interested in assessing the properties that make clayey materials suitable for therapeutic purposes. The abundance of clayey formations and the established practices of medical hydrology in our country turned this interest into a new perspective of application. A group of clayey materials which was recently considered suitable for medical hydrology applications is presented. They include different clays (in age and origin) collected from well-known formations, in some cases outcropping at beaches where empirical applications occur. To determine their suitability for therapy, compositional, physicochemical, thermal and rheological properties were assessed. To assess their composition, conventional techniques were used (XRD, XRF and Sedigraph analysis). Physicochemical properties (cation exchange and specific surface) were estimated using the ammonium acetate and BET methods. Plasticity and abrasivity indices were assessed using Atterberg limits and Einlechner abrasion tests. Thermal properties (specific heat and cooling kinetics) were determined using DSC and cooling curves analysis. Pharmacotechnical tests estimated the rheological properties (flowability and viscosity). The most relevant characteristics were: high phyllosilicates content, abundant smectite, illite and kaolinite, and safe hazardous concentrations. Samples showed moderate capacity to exchange Ca^{2+} , high plasticity and low abrasivity together with high specific heat and slow cooling kinetics. They evidenced fair flowability and were promising to formulate viscous dispersions. Because the majority of the assessed characteristics are in accordance with those presented by clay materials applied in spa (Carretero et al., 2006; Veniale et al., 2007) the studied clays were considered suitable for medical hydrology applications.

[1] Carretero, M.I., Gomes, C.S.F., and Tateo, F. (2006). Handbook of Clay Science, Chapter Clays and human health. Elsevier, Amsterdam, Nederland.

[2] Veniale, F., Bettero, A., Jobstraibizer, P.G., Setti, M. (2007). Thermal muds: Perspectives of innovations. Applied Clay Science, 36:141-147.

Keywords: healing clays, therapeutic validity, suitable properties

ENVIRONMENTAL ASSESSMENT OF Pb, As AND Cr CONCENTRATIONS IN TOPSOIL, GROUND-LEVEL DUST AND MOSS FROM URBAN PLAYGROUNDS, PUBLIC GARDENS AND PARKS FROM LISBON, PORTUGAL

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This study presents results from a project untitled “Geochemical survey of Lisbon urban soils: a baseline for future human health studies”. Fifty one topsoil and 50 ground-level dust samples were collected in playgrounds, schoolyards, urban parks and public gardens. At each site, 1 uncontaminated moss transplant was fixed to a horizontal tree limb, which remained in situ for a period of 6 months. Soil were sieved to the <2 mm (usually used in environmental studies) and <250 µm (usually used in bioaccessibility testing) soil fractions. Dust samples were sieved to the <500 µm fraction. Total concentrations of potentially harmful elements (PHE) were determined by ICP-MS. Concentrations of PHE in the soil, one of the important pathways of exposure, were compared with those in dust and in moss. Oral bioaccessibility testing for As, Cr and Pb was carried out using the Unified Bioaccessibility Method, validated by the Barge group. For Cr, the spatial distribution of total concentrations is similar in both soil fractions; higher Cr concentrations occur in the soils of the Volcanic Complex of Lisbon; previous studies indicate that these are residual, in situ soils, and the source of Cr is mostly geogenic; Cr in dusts indicate that Lisbon airport is a source of Cr but the biomonitors show that the major atmospheric inputs of Cr in the urban environment occur downtown; bioaccessibility estimates have the same range in the gastric(G) and gastric-intestinal (GI) phases, but samples with higher bioaccessible Cr are not the same in both phases, indicating that the soil properties control Cr dissolution in both compartments. Lead also shows a similar distribution of total concentrations in both soil fractions and shows that higher Pb levels occur downtown; dust and in biomonitors have considerably higher Pb concentrations than soil but the spatial distribution is similar, indicating an atmospheric contribution for Pb in the soil; bioaccessibility estimates are significantly higher in the G phase and the higher estimates occur in a small garden near a petrol station, and in a playground. In the urban environment of Lisbon As occurs in low concentrations; the spatial distribution of As total concentrations is slightly different between soil fractions and markedly different for dusts and biomonitors; bioaccessibility estimates have the same range of values in the G and GI phases and, unlike Cr, higher bioaccessibility estimates occur in the same samples in both phases.

Keywords: urban soil, potentially harmful elements

THE CONTROL EXERT BY SOIL MINERALOGY IN THE MOBILITY OF POTENTIALLY HARMFUL ELEMENTS TO HUMAN HEALTH IN THE URBAN SOILS OF LISBON, PORTUGAL

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This study aims seeking relations between topsoil mineralogy and geochemistry to assess the importance of minerals in the fixation of potentially harmful element (PHE) in soils of urban spaces frequently used by children. In the urban environment the heterogeneities between sites are high and metal sources, metal distribution among the soil phases, soil physic-chemical properties and, consequently, metal mobility and bioavailability, are site-specific. This study is crucial to understand results on metal fractionation and bioaccessibility estimates for some PHE in the urban soils. Lisbon has an area of 284 km², 521 774 inhabitants and is divided in 53 districts. The smaller are near the Tagus River and those with a higher population and housing density, a predominance of old buildings, narrow and steep roads, and a high traffic density. The majority of public gardens and playgrounds of the city are located in this area. Topsoil was collected at 51 sites (public parks and gardens, playgrounds and schools). Total concentrations of PHE were determined by ICP-MS in all samples and 26 were selected for mineralogical analyses that were carried out by XRD. The soil clay fraction (<2µm) was also studied by XRD. The microanalysis of soil particles was carried out by SEM. The mineralogy of the 26 soil samples is siliceous (quartz, feldspars and phyllosilicates) but some show significant amounts of carbonates. In the clay fraction, illite, smectite and kaolinite are the most common minerals. In order to seek the relationships between soil mineralogy and geochemistry, linear regression, principal components analysis and cluster analysis were used. The results show that illite is correlated with Pb and calcite with S, indicating that clays and carbonates in the soil may be the main phases in the fixation of these elements. Smectite seems to control the fixation of Ni, Cr and V in soils of the volcanic complex of Lisbon. The results from SEM analysis partly confirm these results. The EDX spectrum of a calcite grain with Si, S, Cl and K in its composition shows a Zn particle at the surface. A possible interpretation is that some calcite particles may be neoformed in the urban soil, incorporating in its structure metallic cations like S, acting as a sink for traffic related S. SEM analysis of the soil clay fraction shows Ni particles at the surface of smectite grains, which supports the hypothesis that smectite is controlling the fixation of Ni in the surface environment.

Keywords: urban soil, soil mineralogy, clays

NATURALLY OCCURRING ASBESTOS IN SERPENTINITE QUARRIES: A CASE STUDY IN VALMALENCO, CENTRAL ALPS, NORTHERN ITALY

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Serpentinites are renowned ornamental and dimension stones, characterized by a wide variety of green shades and by interesting technical properties, such as high compressive strength and durability. They are produced in the Malenco Valley, Central Alps (northern Italy, Sondrio) where the geological set-up is dominated by the ultramafic Malenco massif. Good quality long fibre chrysotile asbestos was also produced in this alpine district since the XIX century: little mines acquired importance in the years preceding the WW2, with maximum exploitation during war years (1940-1945). Some serpentinite quarries “cross” at times tunnels of the old asbestos mines: the chrysotile veins (some cm in thickness) are concentrated along the main fractures, that at present time “guide” the serpentinite extraction. These chrysotile veins are fairly common especially in the Val Lanterna area, associated to an important ENE-WSW striking fracture and hydrothermal vein system. Workers’ exposure during quarrying and processing can not be ruled out and must be assessed according to national laws. From 2004 to nowadays, the INAIL Regional Management of Lombardia – supported by the Central Contarp, with the collaboration of University of Milan-Bicocca – carried out extensive monitoring campaigns both in quarries and in manufacturing laboratories. More than 500 samples divided between massive rock/vein and airborne dust samples were collected during the 2005-2008 surveys. Airborne personal and environmental samples were analyzed by means of phase-contrast microscopy (PCM) and SEM-EDS at the INAIL-CONTARP laboratories, whereas the massive samples were studied at the laboratories of the University of Milano-Bicocca (SEM-EDS, XRPD, PLM, IR). Geological and geostructural mapping of the chrysotile veins was also performed by the University, in order to characterize and quantify the “asbestos content” in every quarry. Prevention actions were planned on the basis of the analytical results, and are still in progress: drilling technologies, dust suction and water abatement were tested in the field, under coordinated supervision of the local authorities, procedural and organizational solutions are implemented both in the quarries and in the manufacturing sites. Employers and workers are trained appropriately according to the law. A specific method for monitoring NOA exposure in these workplaces will be soon released.

Keywords: asbestos, serpentinite

GEOLOGICAL RISK ASSESSMENT OF EXPOSURE TO CHEMICAL ELEMENTS FOR ENVIRONMENTAL HEALTH IN THE ARAÇUAÍ PEGMATITE DISTRICT OF ITINGA MINAS GERAIS, BRAZIL

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The research was performed in a mineral district where there are several lithium ferrous pegmatites. The geological and geochemical studies of the area and toxicological results in three risk groups as follows: Metasediments of Macaúbas Group and Salinas Formation occur in the area, as well as aluminous granites (Teixeirinha and Quati) mainly formed by quartz, feldspars, muscovite, biotite, sillimanite, andalusite, cordierite and tourmaline; The 51 drainage and untreated water supply samples, from approximately 80% of the area, were analyzed and results showed Al values from 0.200 to 0.928 ppm, exceeding the Health Ministry and CONAMA recommended levels; The 3.1% Al average content in 46 soil samples is also high as compared with the 1.7% Al in soils from 08 Minas Gerais drainage basins and the 0.96% Al average value in 39 stream sediment samples show results relatively close to the 0.88% Al found in stream sediments of the cited basins; Analyses of 12 samples of vegetables (cucumber, mustard, onions, cabbage and bell pepper) showed an average of 1059 mg/kg Al; The Igrejinha and Fazenda Velha communities (Araçuaí Municipality), where 133 people were subjected to plasma analyses, revealed 68% are with Al values above 03 g/L, up to this value is considered normal by the ATSDR (2008), 49% of the people have >10µg/L, 10% of the population >60µg/L, 4% >100µg/L and 2% >200µg/L. And in a group of 16 people receiving dialysis, 94% of this population is above 03µg/L of Al, 75% >10µg/L, 44% >60µg/L, 25% >100µg/L and 19% >200µg/L. The results show that the Al absorbed by the Igrejinha and Fazenda Velha populations is of natural origin, with the exposure path: rock-soil-water-food. It is estimated that in the study area 3200 people living on the river banks of the Jequitinhonha tributaries, especially the Piauí Creek, are exposed to Al, which can cause adverse health effects such as neurological diseases, osteoporosis and renal, pulmonary and liver failure. Clinical and epidemiological studies related to Al exposure are recommended for this region and medical geology studies for areas where enterprises, such as mining, are proposed, which can cause impacts to human health and the environment. It is important to carry out this work before establishing the new development, during its operation and following deactivation.

Keywords: geological risks, environmental, health

**MINERAL COMPOSITION OF ATMOSPHERIC DUST IN
SANTIAGO ISLAND, REPUBLIC OF CAPE VERDE:
PRELIMINARY RESULTS OF CVDUST PROJECT**

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Mineral dust produced from windblown soils and deserts is one of the largest contributors to the global aerosol loading and has strong impacts on regional and global climates, long-term climate trends as well as marine and terrestrial ecosystems. Knowledge of the compositions of atmospheric dust is pertinent to understanding its impact on human health. Epidemiological studies have consistently shown an association between Air Particulate Matter pollution and the number of deaths from cancer and cardiovascular and respiratory diseases. African dust is a special case in that it is comprised almost entirely of inorganic materials and the concentration of pollutant species is relatively low. Cape Verde is located in an area of massive dust transport from land to ocean, and is thus ideal to set up sampling devices that will able the characterization and the quantification of the dust transported from Africa. The main objectives of CV-Dust project are: 1) to characterize the chemical and mineralogical composition of dust transported from Africa by setting up an orchestra of aerosol sampling devices in the strategic archipelago of Cape Verde; 2) to identify the sources of particles in Cape Verde by using receptor models; 3) to elucidate the role Saharan dust may play in the degradation of Cape Verde air quality; 4) to model processes governing dust production, transport, interaction with the radiation field and removal from the atmosphere. The project is a joint initiative of Aveiro University and Technological and Nuclear Institute (Lisbon, Portugal), together with the Cape Verde University and the support of the Cape Verde Atmospheric Observatory. Aerosol sampling is being performed at Praia airport during one year and mineralogical composition is being studied by X-ray diffraction, TEM and Scanning electron microscopy. Structural (crystallochemical) formulas will be computed from XRD and SEM – EDAX analytical data. Major phases identified in all samples, regardless of the season, include various silicates and aluminosilicates, carbonates, sulphates, phosphates, oxides and hydroxides. The identification of the main sources and origins of the particles sampled in the archipelago will be carried out by integrating complementary tools such as Principal Component Analysis, Positive Matrix Factorization, Chemical Mass Balance, Multilinear Regression Analysis, Air Mass Back trajectories analyses, meteorological data and particle size segregate analysis.

Keywords: mineral dust, X-ray diffraction, Cape Verde

SEA WATER MATURATION OF HEALING CLAYS: MIOCENE SMECTITIC CLAYS FROM LISBON REGION (PORTUGAL)

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Maturation is a complex process affected by several factors, such as water temperature, light exposure and mixing procedures that determine the final mud characteristics. There have been some indications that peloid quality is also affected by granulometry, mineralogy and physico-chemistry of the raw material and geochemistry of the water. Some researches evidenced that water retention, consistency, bioadhesiveness, ease of handling, pleasant sensation while applied to the skin, cooling kinetics and exchange capacity through mud/skin interface are important features for the formulation of peloids that can be modified through maturation with salt water.

In Portugal, treatments with natural (geological) muds are done outdoors (“in situ”) in sites located near the seaside as the cases of Consolação Beach (Peniche), Meco Beach (Costa da Caparica), Parede Beach (Oeiras) e Burgau Beach (Lagos), generally mixing local clays with sea water. Our aim is to evaluate the effects of clay maturation with sea water on mineralogical and chemical composition as well as on physical and technological properties of these clays.

We have studied samples from Miocene smectitic clays outcropping south of Lisbon, forming cliffs on very popular beaches. Mineralogical composition was assessed by XRD analysis. Chemical composition was analysed by XRF. Grain size distribution was assessed using wet sieving and a X-ray grain size analyser. Properties of these clays such as: particle size distribution, cation exchange capacity, specific surface area, expandability, plasticity, viscosity, abrasivity, pH, cooling rate, specific heat and heat diffusiveness had been assessed. All samples were sieved at 63 µm before the maturation procedures. Small tanks (ca 1.3 dm³) were filled with mud and covered by a layer of sea water during the process (ratio 5:1). Tanks were kept uncovered during the experiment. Two different subsamples were submitted to maturation, one during 30 days, the other during 60 days, in a controlled room temperature (about 21°C during the day and 18°C at night). Only slightly geochemical and mineralogical modifications occurred probably due to the weathering of primary minerals, but significant changes on technological properties (particle size distribution, cation exchange capacity, plasticity, abrasivity and cooling rates) were detected.

Keywords: healing clays, salt water maturation, pelotherapy

GENOTOXIC BIOMONITORING OF HUMANS INHABITING A VOLCANICALLY ACTIVE ENVIRONMENT

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The micronucleus assay in exfoliated buccal cells is a minimally invasive method for monitoring human populations exposed to mutagenic agents. The present study was designed to evaluate whether chronic exposure to a volcanically active environment might result in genotoxic effects in human oral epithelial cells. A study group of 120 individuals inhabiting a volcanically active environment (Furnas village) and a reference group of 122 individuals inhabiting a village without historical records of active volcanism (Santo António village) were examined in this study. Individuals from Furnas village inhabit a volcanically active environment marked by several degassing manifestations, including fumarolic fields, thermal and cold CO₂ springs and soil diffuse degassing areas. For each individual, 1000 buccal epithelial cells, stained according to the Feulgen method, were analyzed for the frequency of micronucleated cells and cells with other nuclear anomalies (pyknosis, karyorrhexis and karyolysis). Information on life-style factors and an informed consent were obtained from each participant. Significant differences ($p < 0.001$) in the median frequencies of micronucleated cells (4.3 vs. 1.7) and cells with other nuclear anomalies (23.5 vs. 7.7) were observed between exposed and non-exposed individuals. The risk of having a high frequency of micronucleated cells was increased 5.43 fold (95% CI = 2.8 to 10.6, $P < 0.001$) in exposed individuals compared to non-exposed. No significant association was observed between cells with micronuclei and age, gender, smoking, consumption of alcohol or use of mouthwash elixir. The higher genotoxic risk of individuals inhabiting a volcanically active environment is for the first time clearly highlighted by this biomonitoring study. Given that micronucleated cells in oral epithelia are recognized as a predictive biomarker of cancer risk within a population of healthy subjects, these findings could contribute to explain the high incidence rates of lip, oral cavity and pharynx cancers previously referred for Furnas village inhabitants.

Keywords: micronuclei, volcanism, human biomonitoring

METAL CONCENTRATION IN SEDIMENTS OF LAGUNA DE BUSTILLOS IN MEXICO; IMPLICATIONS ON HUMAN HEALTH

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The Laguna de Bustillos is an important aquatic ecosystem in the state of Chihuahua, Mexico. Previous research has shown that the water in this laguna has been contaminated with metals; therefore, it was hypothesized that sediments could be also contaminated. The objective was to determine the concentration of heavy metals in sediments of this ecosystem. Twenty-eight sampling points were randomly selected throughout the Laguna's area and two sediment samples were obtained at each point; 0-15 cm and 15-30 cm depth. A total of 56 sediments samples were collected. Of the total 28 sampling points, seven points represented the area close to a panel's industry discharge (PI), seven points represented the area close to the discharge of the city of Cuauhtemoc (C), seven points represented the area close to the Mennonite's colonies discharges (MC) and seven points represented the area close to local communities named ejidos (E). The statistical analysis used a factorial treatment design of 4x2; where factor A was the sampling point with four levels (PI, C, MC and E) and factor B was the depth with two levels; 0-15 and 15-30 cm. The differences were noted using a 0.05 significance level. The following parameters were determined; pH, EC, and the subsequent 17 metals; Ag, As, Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, and Zn were quantified in a Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) 2100 Perkin Emer. In all parameters, significance due to sampling points was found but no differences were noted for either sampling depth or the interaction. The pH varied from 9.1 in C to 8.6 in CM. The EC ranged from 0.38 ms in PI to 0.14 ms in CM. The elements that exceeded the amount in sediments were Ag with 2.76 mg k⁻¹ in PI, Al with 13.03 mg k⁻¹ in E, As with 15.72 mg k⁻¹ in CM, B with 19.31 mg k⁻¹ in PI, Ca with 80,118 mg k⁻¹ in PI, Cd with 1.23 mg k⁻¹ in PI, Cr with 46.14 mg k⁻¹ in C, Cu with 19.76 mg k⁻¹ in E, Fe with 12,943 mg k⁻¹ in C, K with 4,490 mg k⁻¹ in E, Mg with 8,061 mg k⁻¹ in E, Mn with 337.03 mg k⁻¹ in C, Na with 3,072 mg k⁻¹ in PI, Ni with 31.51 mg k⁻¹ in E and C, Pb with 5.65 mg k⁻¹ in CI, Si with 180.79 mg k⁻¹ in C, and Zn with 41.88 mg k⁻¹ in PI. The concentration of some elements were found in levels that can cause damage to the ecosystem both short and long term and could represent a potential health hazard due to human consumption of fish from this aquatic reservoir.

Keywords: metals, sediments, laguna Bustillos, Mexico

INTERACTION OF COSMIC RADIATION WITH THE SURFACE OF THE EARTH

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The Institute of Radiation Protection is part of the German Helmholtz Center for Environmental Health. Among other goals, the center aims at investigation of environmental parameters that affect human health. Because the field of ionising particles produced by interaction of primary cosmic radiation with the molecules of the atmosphere does have the potential to be carcinogenic to humans, much effort is being made to quantify the radiation dose to cockpit and cabin crew. These efforts include calculations (e.g. we are developing and using the EPCARD code to calculate air crew doses) and measurements (e.g. we are running two Bonner Sphere Spectrometers, one at the Environmental Research Station Schneefernerhaus on the Zugspitze mountain at 2650 m above sea level, Germany, the other in Ny-Alesund on Spitsbergen, close to the magnetic North Pole, at sea level). While these measurements basically aim at experimental validation of calculated doses to air crew at flight altitudes, the interaction of cosmic radiation with the surface of the Earth turns out to complicate the situation.

In the present paper, it is demonstrated how the atmosphere–lithosphere interface influences the secondary field of cosmic radiation. Special emphasis is placed on secondary neutrons from cosmic radiation (which add significantly to total dose from cosmic radiation). It is shown that changes in neutron intensity may be due to changes in solar activity (Forbush decreases), but also due to changes in environmental parameters (neutron fluence oscillations). Methods are discussed that allow discrimination between both sources of neutron intensity changes. As an example, the period in September 2005 is discussed that includes the most recent large Forbush decrease.

Keywords: cosmic radiation, surface of the Earth

**ENERGY AND WATER RESOURCES: UNDERSTANDING THE
IMPACT OF COAL COMBUSTION RESIDUES ON THE
ENVIRONMENT BY EVALUATING THE EFFECTS OF THE
2008 COAL ASH SPILL IN TENNESSEE, USA**

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Coal is a major source of energy, providing 41% of the world's electricity, resulting in 125 million tons of coal combustion residues (CCRs) produced each year. CCRs are enriched in trace metals (e.g. Hg, As, Se, Sr), and while 30% of CCRs in the US are utilized in beneficial re-use applications, 70% are disposed of in ash impoundments and landfills. The environmental impact of CCRs is manifested by surface water and/or groundwater contamination, which can severely impact the water resources and thus the health of nearby populations. An investigation of the environmental impacts of the largest coal ash spill in the US history at the Tennessee Valley Authority (TVA) coal fired power plant in Kingston, TN has revealed that CCRs release contaminants into the environment and mobilization of the contaminants depends on the coal ash types, pH, and redox conditions of the ambient environment. Systematic monitoring of the quality of water and sediments in downstream segments of the Emory and Clinch Rivers near the TVA spill site has shown that the interaction of CCRs with natural river water mobilizes leachable coal ash contaminants (LCACs) such as boron, arsenic, selenium, strontium, and barium. Several distinctive patterns have also been revealed: (1) surface waters in areas of restricted water exchange show high LCAC levels (e.g., As: 9- 95 µg/L) (2) downstream diluted Emory and Clinch Rivers show low LCAC concentrations below the US EPA maximum contaminant level (As=10 µg/L), but with levels (e.g., As ~4 µg/L) above the baseline of the upstream rivers; and (3) porewater extracted from bottom sediments of the downstream Emory and Clinch Rivers with significantly high LCAC levels (e.g., As 9-285 µg/L). The high levels of LCACs measured in porewater could help explain the higher LCAC concentrations measured in the fish collected at the spill site. Our field and leaching experimental data show that boron is a sensitive indicator for CCR contaminant leaching, with boron content up to 1276 µg/L in pore water relative to the upstream river water (6 to 9 µg/L) and $\delta^{11}\text{B}$ values of -12‰ and -16‰ (relative to NIST951). This isotopic composition is significantly different from that of meteoric boron and provides a novel tool to trace the CCR leachate in the environment. The spill was an unexpected event, but provided an opportunity to understand the environmental impacts of coal combustion.

Keywords: coal combustion residue CCR, coal, coal ash

EFFECT OF SILICATE-SURFACES IN AEROSOL PARTICLES ON THE OXIDATION OF ATMOSPHERIC FORMIC ACID. A QUANTUM CHEMISTRY INVESTIGATION

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Heterogeneous reactions of atmospheric volatile organic compounds (VOCs) on aerosol particles may play an important role in atmospheric chemistry. Silicate particles are present in air-borne mineral dust in atmospheric aerosols, and radical reactions can be different with the presence of these mineral particles. The formic acid (HCOOH) is the most abundant carboxylic acid in the troposphere. Atmospheric HCOOH influences pH dependent chemical reactions in clouds and is a major acidic component of rain. Humans are exposed to formic acid in ambient air and food, as well as via inhalation and dermal contact. In the presence of atmospheric aerosols, the reactivity of adsorbed formic acid with OH free radicals is expected to be different than the one in the gas phase. The adsorption of formic acid molecule on models of silicate surface is studied with quantummechanical methods. The effects of this adsorption on the spectroscopic properties of this system are also analysed reproducing the experimental results and predicting new insights for future research. The reaction of hydroxyl free radical with formic acid adsorbed on silicate surface was studied. The mechanism and kinetics have been determined focusing on the oxidation pathway. The presence of mineral surface catalyses the reaction decreasing the activation free energy and silicates act as a sink of these organic pollutants.

Keywords: airborne mineral dust, formic acid, modelling

ADSORPTION OF SULFONAMIDES ON PHYLLOSILICATE SURFACES AS MODELS OF SLOW RELEASE NANOMATERIALS BY DIFFERENT THEORETICAL APPROACHES

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Phyllosilicates can be considered as natural nanomaterials that can be functionalized for therapeutic slow release of drugs. Sulfamides form a great group of antibiotics widely used since decades for human therapeutics and in veterinary for intensive livestock production. The efficiency of the administration of these drugs is very low and the presence of these antibiotics and their derivatives in soil can alter the bacterial resistance to animals and humans through the soil, water and food chains. Therefore, it is important to search environmental-friendly slow-release nanomaterials, in order to overcome these problems. Then, it is important to investigate the adsorption of these drugs on the surfaces of these nanomaterials. The adsorption of sulfonamides, Sulfamethoxypyridazine and Sulfamethoxypyrimidine, as models of sulfonamides, on pyrophyllite surface of (001) plane have been investigated by means of empirical interatomic potentials and quantummechanical methods based on Hartree-Fock and Density Functional Theory (DFT) approximations. Molecular Dynamic simulations have been also performed for this adsorption exploring the different configurations that these sulfonamides can adopt with respect to the surface. The adsorption energy calculated with different methods are compared and discussed on the application of empirical potentials and DFT methods for describing the weak interactions of this adsorption.

Keywords: modelling, adsorption, phyllosilicates

PROPOSED CLASSIFICATION OF OPHIOLITES DEPOSITS AND USE OF MATERIALS EXTRACTED ACCORDING TO THEIR CONTENT OF ASBESTOS

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As it is widely known and studied in ophiolites (ultramafic rocks of intrusive magmatic origin, partially altered or metamorphosed) asbestos fibres may be found in the form of pockets and small veins (those typical of alpine ophiolites, very rare in Apennines) and distributed within the fractures. Mining, quarrying and processing could release a number of asbestos fibers into the environment, that needs to implement preventative measures of workers protection and local population. The methods of control of the extracted materials are carried over from the Ministerial Decree (DM) 14/05/1996, which defines criteria for the classification and the use of "green stone" according to their content of asbestos. The excavation is allowed under a certain danger level as defined by the amount of asbestos released from the rocks, where the value of Release Index must be $Ir < 0.1$. In addition to this law (exclusive to the ophiolites quarry sector) we can find the provisions of health and safety at work in Legislative Decree n. 81/2009. It stipulates specific analytical measures and controls over all work environments at risk for the presence of asbestos. The law identifies the permissible exposure limit (defined as "VL" Value Limit), beyond which they must take appropriate precautionary measures. Various objections were raised over the correct application of the Ministerial Decree 5/14/1996, in particular relate to the real meaning of Ir (Release Index). The real ophiolitic danger is related to the chance of rocking crumbler during extraction and subsequent work phases since it is during these activities that rocks can more easily release asbestos fibres. These considerations were already included in the studies carried out by the Emilia-Romagna Region (Il Progetto Regionale Pietre Verdi - 2004). It proposes a new classification of the ophiolites deposits based on a simple but direct measurement of the release index (called AR "asbestos free or releasable") taken before and during the mining activities related to the types of products produced by the quarry.

Keywords: ophiolites deposits

SPATIAL ESTIMATION OF SOIL SAMPLES ACCORDING TO HARMFUL EFFECTS ON HUMAN HEALTH: THE CASE OF PANASQUEIRA MINE (CENTRAL PORTUGAL)

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Mining activity is one of the main industrial activities that produce more residues, left in piles or tailings dam, subject to weathering, leading to the production of acid mine drainage (ADM) that consequently affects the surrounding environment (namely soils and the local population). The beneficiation process at Panasqueira Mine have given rise, during a long production period, to a large amount of sulphide-rich waste, contained in several tailing ponds, two of them located nearby S. Francisco de Assis Village. AMD evidences associated with sulphides leaching, with low pH and high metal contents, were noticed and also measured in streams closer to the mine. The local community subsists on agriculture and cattle breeding. When soil quality became compromised it affects all the food chain, from the soil itself, prone to be absorbed and/or ingested; to plants, that apart from nutrients also capture heavy metals; to cattle fed locally until the population that consumes vegetables and meat from local production. The assessment of soil contamination in this area is then of most importance. A new two-step methodology for soil sample categorization according to harmful effects on human health is proposed, based on Geostatistics (Multivariate Data Analysis). The first step comprises the combined use of Principal Component Analysis (PCA) and Correspondence Analysis (CA). PCA was applied to a data set of 75 soil samples and respective chemical analysis which allowed distinguishing between geological and anthropogenic origins of the elements, giving rise to the identification of the contaminant group of chemical elements that act in this area. Once identified the contaminant group, a complete disjunctive matrix of the data is built classifying each sample, for each element, as Clean (above the average local background level - analysis of 20 soil samples located upstream of the mining area), in need of Reclamation (above the guide level for agriculture soils) or in need of Intervention (if sample value is between mean local background and guide level). The referred matrix is then submitted to a CA, which has the advantage of projecting variables and samples in the same factorial space enabling to extract a hierarchy of samples according to their contamination level. The second step concerns the spatial estimation of soil samples based on the categorisation previously established. For that a Multiphase approach based on Kriging was used.

Keywords: soil pollution, multivariate analysis, spatial estimation

**KINETICS, THERMODYNAMICS AND ADSORPTION
ISOTHERMS OF REMOVAL OF HEAVY METAL IONS (Cu²⁺
AND Pb²⁺) USING KURDISTAN/KIFFRY CLAY**

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Local clay sample of Kiffry region was analyzed for its chemical composition by XRF, the SSA and CEC were found to be 77.8 m²/g and 21.54 mmole/100g respectively using methylene blue method. Adsorption characteristics of Cu⁺² and Pb⁺² on the clay surface were studied. Optimum initial pH was found to be 6.5 and 6 for Cu⁺² and Pb⁺² respectively. Adsorption capacity were studied to be increased from 12.28 to 256 mg/g for Cu⁺² and 12.47 to 529 mg/g for Pb⁺² as metal ion concentration increased and the removal percentage decreases from 86 % to 28.45% and 99.5% to 53.6 % for both Cu⁺² and Pb⁺² respectively as volume/mass ratio (v/m) increases from 250 ml/g to 2500 ml/g. The adsorption isotherms show that Langmuir isotherm is best fitted than other isotherm models and the kinetic of the sorption were analyzed to be of the second order, the activation energy was found to be about 40KJ/mole for both metal ions. The thermodynamic parameters, standard Gibb's free energy (G°), standard enthalpy (H°) and standard entropy (S°) calculated for both metals using the Langmuir constants (KL) for metal ion sorption on the clay.

Keywords: removal of heavy metal ion, Kiffry clay, adsorption isotherms

GROUNDWATER QUALITY ASSESSMENT AND HUMAN HEALTH IN THE SOUTH CHENNAI COASTAL AQUIFER, INDIA

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Coastal aquifer south of Chennai, India is bounded by salt/sewerage contaminated water on all four sides: the Bay of Bengal in the east, a canal in the west, and the Adyar river and Muttukadu estuary in the north and south, respectively. Environmental and ecological imbalance is arising in this area due to over exploitation of groundwater by private wells due to increase in settlements, hotels, tourism and industrial activities. Exploitation of groundwater is often not matched by rainfall recharge which promotes seawater intrusion. In the year 2002, the government brought an act that makes rainwater harvesting mandatory for all buildings in this area. The objective of this study is to determine the groundwater quality of this region. Groundwater samples were collected from 50 wells once in three months from August 2008 to May 2009. Groundwater level, Electrical conductivity, pH, ORP and temperature of samples were measured in-situ. The concentrations of major and minor ions were determined by titration and ion chromatography. Groundwater qualities based on the measured concentrations were compared with recommended drinking water limits based on the Bureau of Indian Standards and the World Health Organisation. Various thematic layers were prepared and an overlay analysis was carried out by using weighing method. Groundwater quality index map prepared indicate the influence of salinisation and anthropogenic activities in the northern part of the study area and marginal in southern part due to aquaculture activities.

Keywords: groundwater quality, Health impact assessment, overlay analysis, Chennai, India

COMPARISON OF TWO ADSORPTION MECHANISMS FOR SMALL SIZED MOLECULES ONTO ZEOLITES IN VIEW OF UREMIC TOXIN REMOVAL

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The adsorption properties of zeolites for uremic toxins have been investigated in view of selective removal of such molecules from physiological solutions at 37°C. These investigations were performed in order to explore alternative methods to blood purification by dialysis in case of renal failure. Two zeolite structure types have been retained, each of them showing selective adsorption properties for creatinine (a free soluble uremic toxin molecule) and p-cresol (a partially protein bound uremic toxin molecule), respectively. MFI type zeolites, anhydrous Silicalite 1 and Na-ZSM-5 were synthesized and employed for the adsorption of p-cresol. Two modified commercial MORdenite type zeolites (different Si/Al ratios) were used containing Na⁺ and H⁺ as charge compensating cations. Adsorption isotherms- and microcalorimetric measurements in pure water, in physiological buffer solution (D-PBS) as well as in D-PBS containing Bovine Serum Albumine in physiological concentrations, were performed. While affinity for p-cresol vs. the MFIs is mainly modified by the cation presence in the void system, spectroscopic investigations (MAS-NMR), XRD with Rietveld refinement, and Monte-Carlo simulations confirmed a physisorption mechanism. Concerning MOR, only the H⁺-Mordenites show high and selective chemisorption for creatinine (confirmed by MAS-NMR), however, influenced by the composition of the liquid. Both adsorption mechanisms are compared and discussed in detail.

Keywords: uremic toxin removal, zeolites, adsorption

SOIL GEOCHEMISTRY AND CANCER - A CASE OF MEDICAL GEOLOGY, ISRAEL

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The natural geochemical background of the north-western part of Israel (The Haifa district) is governed by element associations depicting common heavy minerals, carbonates and clays, volcanic rocks (Mg, Cr, Co, V, Ni, Mo), phosphate-rich cherts and cherts (P, Zn, U, As, Cd) and barium-rich limestones. In the course of a detailed geochemical survey, few locations in which soils were locally polluted mainly with Cr, Zn and Cd were identified. The city of Haifa and its suburbs is located within the surveyed area, along with major industrial facilities that emit hundreds of tons of metals into the air per year. The soils in these vicinities are characterized by an accumulation of various trace metals (As, Cd, Pb, Sb, Mo, Mn) as a result of long-term discharge from numerous industries and deposition following transportation by runoff and prevailing weather systems. The use of isotopic ratios of lead ($^{206}\text{Pb}/^{207}\text{Pb}$) pointed out a steel plant as one source for some metal pollutants in the area. Thus, the buildup of these trace metals in soils can serve as a proxy for evaluating the exposure of inhabitants in the area to pollutants of anthropogenic origin. An assessment of cancer occurrence in the Haifa district vs. the rest of Israel (1:1 ratio) was carried out, based on an historical prospective study of 175,704 citizens of the Haifa district who participated in the Israeli Central Bureau of Statistics (CBS) 1995 census and followed-up until 2007. The hazard ratio (HR) for cancer incidence was calculated across a wide variety of socio-demographic variables, demonstrating an increased risk of developing cancer in the Haifa district comparing with the rest of Israel (HR=1.12, 95% CI: 1.08-1.23, $p<0.001$). Smoking rates in the Haifa district did not explain the increased cancer incidence. Calculating the average concentration for each trace metal in every census block and linking it to the home address of participants in the cancer study suggested a trend of increased risk of cancer incidence (HR 1.12, 95% CI: 1-1.28, $p = 0.053$) in cadmium-rich areas after adjusting for demographic variables.

Keywords: geochemistry, cancer, cadmium

ENRICHMENT OF ARSENIC IN QUATERNARY SEDIMENTS FROM ANKALESHWAR AREA, INDIA: INFLUENCE OF ANTHROPOGENIC ACTIVITIES

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Arsenic contamination is well known in Bengal, India and some of the eastern and central regions of the country. The enrichment of Arsenic in the western region of the country in general and quaternary sediments of Ankaleshwar area, Gujarat, India, in particular, has been reported for the first time in the present article. The study on soil contamination has been undertaken in Ankaleshwar, which is one of the biggest industrial townships of India. About 25 near-surface sediment/ soil samples were collected from top 10 cm, representing entire study area and 5 profile samples in order to study the vertical distribution of Arsenic in the sediments. The finer fractions (<63 μ) were used to analyze for arsenic (As), using X-ray fluorescence spectrometer (XRF). The sediment samples were compared with the upper continental crust representing in the UCC normalized plots and standard shale to find the geo-accumulation index (I-geo) as well as pollution index (Pi). Almost all samples exhibit substantial enrichment of arsenic and those around industrial areas show significantly higher values of it. The data reveals that the soil resources in the region, particularly around the industries, urban areas, agricultural lands and effluent carrying streams are considerably contaminated, exhibiting elevated levels of As. The arsenic contamination of the sediments has posed intensive stresses and pollution risks to the quality of groundwater resources of the area, besides immediate perils for human health and ecosystem. The study emphasizes the need to mitigate the intensity of arsenic pollution and to maintain the productivity of soil resources on which majority of local population depends for livelihood.

Keywords: Ankaleshwar, Quaternary sediments, arsenic pollution

**INVESTIGATION OF THE EFFECT OF ADDING NATURAL
ZEOLITE TO SOLID WASTE LANDFILL CLAY LINER FOR
ADSORPTION OF MN AND ZN IONS IN LEACHATE**

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Penetration of landfill leachate into subsurface due to various pollutants is one of the most problematic issues for soil and water in the environment. Generally, solid waste landfills consist of a compacted clay liner (CCL) for prevention of groundwaters pollution with leachate. The capability of CCL for pollution control and the enhancement of its characteristics for better performance have been investigated by a number of researchers, recently. A study has been conducted to investigate the influence of zeolite in combination with kaolinite for Zinc (Zn) and Manganese (Mn) removal from leachate and the possibility of reduction of clay layer thickness. Laboratory experiments have been conducted in a plexy glass column with inside diameter and height, 15 and 50 cm, respectively. Synthetic leachate has been synthesized by distilled water and Zn and Mn salts. Combination of zeolite and Kaolinite could increase heavy metals removal more than 90 percent. The results exhibit that by addition of 3-9% of zeolite to Kaolinite, the required thickness of the CCL can be reduced significantly.

Keywords: zeolite, kaolinite, heavy metal

NATURAL ARSENIC IN NORTHERN SWEDEN A RISK ASSESSMENT

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Arsenic (As) is an old poison that has made a “comeback” especially as a chronic toxicant in drinking water coming from groundwater sources. There are three mechanisms that mobilize arsenic into water, a high pH decreasing adsorption of anions, oxidation of sulphides and reduction of ferric compounds. The redox dependence in combination with the low permissible limits for water means that even moderate amounts of arsenic in soils and rocks could pose an environmental risk. In Northern Sweden large areas are underlain by metasediments containing about 1 % S. This project has investigated the cycling of arsenic in metasediment areas and in tills overlying them. The media taken into consideration are water, plants and the aquatic fauna like macroinvertebrates and fish.

Till rich in sulphidic metasediments oxidize and an accumulation of the released arsenic can be seen in the B-horizons of the podsols. In wetland ferric reduction raises the arsenic content in groundwater up to 100 µg/L as compared to the permissible limit for drinking water which is 10 µg/L. After discharge into drainages and streams the released ferrous iron oxidizes and the ferric precipitates may contain as much as 0.5 % As and sandy sediments 200-500 mg/kg As. Larger streams and lakes have above background concentrations of As and a number of lakes have in the order of 5-9 µg/L As. Wetland plants do show elevated As but only the silica rich *Equisetum* spp. have largely elevated content up to 30 mg/kg. Presumably the uptake of arsenic occurs via similar mechanisms as for silica. The silica rich and crispy *Equisetum* spp. is not palatable for wild grazing animals like reindeers and mooses. In macroinvertebrates and fish arsenic has been speciated into As(III), As(V), MMA, DMA and arsenobetain. The data for macroinvertebrates are somewhat difficult to decipher presumably due to problems in extraction. Fish show predominantly organic arsenic and can be considered suitable for consumption.

Thus the overall assessment is that in spite of strikingly high concentrations in sediments and in groundwater the As does not represent a great environmental risk. Only wetland groundwater is a risk if used for water supply when high in Fe and As.

Keywords: arsenic, toxicity, fish

COMPOSITIONAL PROFILES OF POLYCYCLIC AROMATIC HYDROCARBONS IN HIGHER PLANTS USING MULTIVARIATE ANALYSIS TECHNIQUES

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Thirty six higher plants sampled from oil exploration sites in Niger Delta, Nigeria were analyzed with gas chromatography–mass spectrometry to determine the occurrence, distribution and compositional profiles of polycyclic aromatic hydrocarbons (PAHs). The 28PAH ranged from 335 to 3094 ng/g. Higher PAHs concentrations were observed in the plants when compared with the soils and sediments concentrations with predominance of 2 and 3 ring PAHs. Multiple linear regression (MLR) and principal component regression (PCR) were used in predicting the soil PAHs concentrations based on the concentrations of PAHs obtained in plant species collected from the same locations, the results showed that non woody plants gave more reliable predictions. The Principal Component Analysis (PCA) shows the plants in all the locations do not maintain a particular pattern in their total PAHs concentrations. The differing physiological characteristics and maturity in the plants could be responsible for the observed patterns. Similarly, the PCA recognised three main clusters in the PAHs distribution among the plant samples from all locations; the distinct dissimilar molecular masses, density and solubility might be responsible for the observed pattern exhibited by the PAHs.

Keywords: higher plants, polycyclic aromatic hydrocarbons, principal component analysis

IN SITU TERRESTRIAL GAMMA RADIATION IN SEVATTUR–SAMALPATTI CARBONATITE COMPLEXES, TAMIL NADU, INDIA

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Natural radioactivity in rocks is caused principally by primordial radionuclides, such as ²³⁸U, ²³⁵U, ²³²Th, and to a lesser extent by ⁴⁰K and ⁸⁷Rb. Concentration of these radioactive elements could result in the anomalous values of terrestrial gamma radiation. Even though the radiation from these naturally sources are generally low, it may cause health problems. The geology of the area plays a major role in the concentration and distribution pattern of these elements. Hence a study of in situ terrestrial gamma radiation levels and distribution of dose rates in parts of the Sevattur–Samalpatti carbonatite complexes, Tamil Nadu, India has been taken up using a portable radiation survey meter. Correlation between gamma level of soils and the underlying rocks suggest that soils are in situ and they are derived from these rocks. The highest level of radiation is recorded from Sevattur in Carbonatite rocks and soil over these rocks. The carbonatites are poorly exposed and seen as isolated mounds and boulders as well as linear dykes, veins and lenses within pyroxenite and syenite. Carbonatites from Sevattur contain pyrochlore and apatite with calcite. The rocks contain 0.5% (Nb,Ta)₂O₅ and 10.% P₂O₅. The pyrochlore (uraniferous type) is in metamic state and is disseminated. The pyrochlore minerals contain 19.30% of U₃O₈. Hence the radiation is high. The Samalpatti carbonatites have very low radiation. The Samalpatti carbonatites are mainly sovite and silicocarbonatite. Calcite is the most prominent mineral with minor abundance of dolomite. Grossularite, chlorite, scapolite, diopside and barkevikite are present in the silicocarbonatites. In Onnarakai, riebeckite sovite, riebeckite ferroan sovite and ferroan carbonatitic breccia with abundant opaque minerals and ilmenite–rutile are present. The radioactive elements are very less in the carbonatites and hence the in situ Gamma radiation is not high in this carbonatite complex. Next to Carbonatites, Syenites and then followed by pegmatites, gneisses and pyroxenites have higher concentration in Sevattur. In Samalpatti very low radiation values were recorded in dunites and serpentinites. The dose equivalents and effective dose rates are well in excess of 1mSv/yr maximum permissible limits in sevattur areas, suggesting a reasonably good chance of radiation hazards in these places. People living in these areas should therefore be made aware of the potential radiation related health problems.

Keywords: natural radioactivity, carbonatites

SOURCE AND HEALTH EFFECTS OF FLUORIDE IN LAMPHUN PROVINCE, THAILAND

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Lamphun Province is located in the Chiang Mai Basin, Thailand. During the last couple of decades, the water demand in Lamphun Province has increased because of rapid industrial development and population increase. Numerous small-scale water supply systems using groundwater have been developed in sub-urban communities to meet the burgeoning demands. However, groundwater contains high fluoride up to 16mgF/L, which brought about dental and skeletal fluorosis among the residents. Thai Government installed RO membrane plants for the removal of fluoride from groundwater; and RO-filtered water is bottled and delivered to each household. Thanks to this effort, the fluoride levels in their drinking water have decreased significantly to the concentrations below the Thai Standard of 0.7 mgF/L. It was found in our survey, however, that the urinary fluoride levels are still high among the residents because many of them use fluoride-containing water, i.e. piped water supply and private well water, for cooking. Because the local people cannot pay for bottled water for all their water uses, it is very important to get the local people involved to come up with the water supply and water use planning to minimize the risks arising from ingestion of fluoride-laden waters with the lowest expenditure of their households. For this purpose, the fluoride contents of various water sources, such as village water supply systems, shallow and deep groundwaters, rain water and bottled water, were measured and the distribution of fluoride concentration in groundwater was made to identify possible geological sources of fluoride. In addition, the health impact of fluoride was investigated in collaboration with the local dentists. We visited local junior high schools to identify the dental fluorosis and took urine samples from them. There was a correlation between urinary levels of fluoride and dental fluorosis. The major source of fluoride was identified as their cooking water by interview survey.

Keywords: fluoride, dental fluorosis, urine

PESTICIDE FATE IN THE ENVIRONMENT AND STRATEGIES OF MITIGATION

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The pesticide distribution among the different environmental compartments is quite complex and affected by pesticide chemio-dynamic properties. The soil/water partition coefficient K_{oc} , the pesticide half life DT_{50} , the air/water partition coefficient K_H (Henry's constant), the octanol/water partition coefficient $\log K_{ow}$ are the most important parameters affecting the pesticide environmental behaviour. In the environment pesticides are distributed in liquid, solid and gaseous phase; their presence in solid phase (for example in sediment or soil) is due to adsorption phenomena that control the distribution in the other phases, while their most mobile portion is located in liquid and gaseous phases. This portion is available for microbial degradation and for vertical or lateral transfer related to ground and surface water contamination. Generally, the solid phase retention minimises the pesticide mobility risk, but makes pesticide disappearance more difficult. Transformation can allow formation of metabolites under the action of chemical, photochemical, biological processes. The life time of pesticides and their persistence in the environment are conditioned by their reactivity versus abiotic processes (photolysis, hydrolysis, redox reactions) or biotic processes (biodegradation, conjugation, metabolisation). Pesticides either in solution or adsorbed on the soil solid phase may undergo a chemical degradation by oxidation or photolysis induced or catalysed by soil components. The abiotic degradation is often incomplete and leads to intermediate substrates for biological reactions. The biotransformation is a complex process requiring several steps and sometimes generating metabolites more polar, soluble, even more toxic than the parent compound due to bacteria, fungi, algae. The biodegradation requires the pesticide bioavailability (function of water solubility, adsorption coefficient K_d and capacity of bacteria to reach adsorption sites) and a sufficient microbial growth. Mitigation of environment contamination can be obtained with biological or management strategies. Among biological mitigation strategy wetlands (natural and artificial), vegetated filter strip and biobed are emerging system. Among management strategies agronomic practices as rotation, reduction of application rate, improved distribution system (nozzles or spray boomer), calibration of spray equipment, improved plant protection products formulation are common practice.

Keywords: pesticides, environmental repartition, environmental mitigation

EPIDEMIOLOGY OF URINARY STONES IN ITALY AND EUROPE

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Urolithiasis may be considered a chronic disease owing to the high recurrence rate and because it is frequently aggravated by congenital or acquired metabolic deficiencies. Therefore it is correctly estimated by the prevalence rate, that is the number of cases of the disease in a given population and includes all the patients who have experienced at least one episode of urolithiasis in their lives.

Measurement of the prevalence rate is carried out on randomised samples of the general population and tends to increase as a function of the age of the population, in proportion as the number of cases increases.

In the course of the last 100 years, there has been a gradual increase in the prevalence of reno-ureteral stone disease, typical of adult age and featuring mainly calcium oxalate.

Endemic infantile vesical calculosis, due to malnutrition with calculi composed of ammonium urate and calcium oxalate, is still present in some areas of undeveloped countries but its prevalence is decreasing in proportion as social conditions gradually improve.

The general prevalence rate range 1-15%. The potential risk factors for stone formation are both genetic and environmental (climate, diet, life-style and working activity).

Keywords: epidemiology, urinary stones

PHYSICO-CHEMICAL AND TRACE ELEMENT GEOCHEMISTRY OF SWARNA RIVER, SOUTHWEST COAST OF INDIA: A BASELINE STUDY

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The Swarna river, a small tropical river (80 km length) flowing in the southwest coast of India forms a major source of water for domestic use to a million inhabitants of Udupi district, Karnataka. The river flows through the sub-urban region with no major industries found in the present time but are likely in the near future as the area is fast developing with expansion in education and industrial sectors. This would result in higher freshwater withdrawal within the river basin due to population amplification. The river discharges annually 16,512 m³ of water into the Arabian Sea, of which significant part is being discharged during the monsoon. The paper presents the preliminary results on the spatial and temporal (monthly scale) variability of trace elements along with physico-chemical parameters in the Swarna River for a period of six months. The river water is neutral to mildly basic in nature. The specific conductance which controls the partitioning behaviour of trace elements ranges from 23.3 to 44.5 μ S/cm. Dissolved oxygen which defines the redox condition in water ranges from 6.96 to 8.75 mg/L. Major part of the river basin consists of silicate rocks like granite gneiss, dolerite dyke and laterite¹. No studies have been made yet on the dissolved and suspended metal concentrations in the Swarna river and groundwater in the region, even as one million people use it for drinking purposes. The uptake of bio-available (dissolved) trace elements would affect the physiological functions of humans and other organisms. As the large community in this region depends on the freshwater of Swarna river, there is an urgent need to study the trace element geochemistry of this west flowing river for better water management and sustainable development. Preliminary results of the trace metal measurements are expected in March 2011.

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Keywords: tropical river, trace element, toxicity

HALLOYSITE CLAY NANOTUBES AS CARRIERS FOR SUSTAINED DRUG DELIVERY

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One way to utilize the high functionality and stability of bio-related materials is to create hybrids consisting of materials of biological origin and inorganic materials. Halloysite, a polymorph of Kaolinite, with predominantly hollow tubular structure in the submicron range [1-3] is an economically viable raw material that can be mined as a raw mineral. Halloysite nanotubes (HNTs) are efficient nano-containers capable of entrapping a number of active agents [2] within the inner lumen, followed by their retention and slow release [3]. Halloysite is a green environmentally friendly material available in commercial quantities. The lumen of the halloysite tube accommodates globular protein diameters, allowing their entrapment while retaining their activity for use in biocatalysis. In this work a combination of high resolution imaging techniques such as TEM, SEM and SFM have been employed to elucidate the structure. We have also investigated their viscoelastic properties and performed cytotoxicity assays utilizing neoplastic cell lines. The results indicate that halloysite nanotubes were readily uptaken by neoplastic cells and exhibit a high level of biocompatibility [4]. To confirm their possible biomedical use as therapeutic nanocarriers we successfully encapsulated bioactive compounds and studied their anti-neoplastic effect into model cancer cell lines. Preliminary in vivo study will be also highlighted.

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Keywords: halloysite clay nanotubes, nanocarriers, cancer

GENETIC OF CALCIUM KIDNEY STONES

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Calcium nephrolithiasis is one of the most prevalent uronephrologic disorders in the western countries. Studies in families and twins evidenced a genetic predisposition to calcium nephrolithiasis.

Family-based or case-control studies of single-candidate genes evidenced the possible involvement of calcium-sensing receptor (CASR), vitamin D receptor (VDR), and osteopontin (OPN) gene polymorphisms (SNPs) in stone formation.

The only high-throughput genome-wide association study identified claudin 14 (CLDN14) gene as a possible major gene of nephrolithiasis.

Specific phenotypes were related with these genes: normocitraturia with CASR gene SNPs, hypocitraturia and severe clinical course with VDR gene SNPs, and hypercalciuria with CLDN14 gene SNPs.

The pathogenetic weight of these genes remains unclear, but an alteration of their expression may occur in stone formers.

Technological advances and accurate clinical examination may get new insight about the genetic basis of nephrolithiasis.

Keywords: nephrolithiasis, hydrophilic clay-affinitive

RISK AND BENEFIT ASSESSMENT OF TRACE AND MAJOR ELEMENTS DETECTED IN HONEY OF DIFFERENT ORIGINS

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Honey is a natural product consumed as food and used as an active component in medicine and cosmetology. From the perspective of environmental science determination of trace and major elements in honey can be valuable tool for following issues: (a) benefit assessment of detected major element and micronutrient involvement in food chain, (b) risk assessment of detected potentially toxic trace element contamination or involvement in food chain, (c) assessment of sitespecific environmental impacts and other influences on the product formation. These problems are in a scope of interest because honey is a foodstuff mostly consumed without any processing and the chemical composition of honey is not constant and equal due to its geographical of botanical origin, and also can be dependent on the site and time specificclimatecharacteristic. Current study was performed by analyzing more than 70 honey samples that were collected from markets and groceries all over Latvia. Honey samples were analyzed by using flame atomic absorption spectrometry methods and inductively coupled plasma mass spectrometry. For sample pre-treatment various techniques were tested for example dry ashing, wet digestion by concentrated nitric acid or simple sample dissolution in warm water. Overall it was possible to determine 5 major elements (Ca, Fe, K, Mg, Na) and a range of trace elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn). The results reveal that the main major elements detected in honey are potassium and calcium. Content of major elements substantially depend upon botanical origin of honey. Trace element analysis is particularly useful for the identification of potentially toxic elements and can reflect impact of site-specific anthropogenic pollution. Risk and benefit assessment of trace and major elements in honey of different origins was performed in larger scale than concerning Latvia only. Available studies of honey analysis all over European countries were summarized. It was discovered that trace and major element content varies in a wide range in honey samples with different geographical origin. Within the scope of awareness heavy metals (Pb, Cd, Cr) are important due to their potential risk for human health but such elements as Mn, Cu, Zn, Fe, K can be brought forward as beneficial elements.

Keywords: honey, trace and major elements, environmental contamination

RACE, TEMPERATURE AND WATER HARDNESS FACTORS AND DISTRIBUTION OF URINARY STONES, IN THE KHUZESTAN PROVINCE, IRAN

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Urinary stone diseases in the Khuzestan province, in the southwest of Iran is growing and it required extensive studies on various factors of the urinary stones formation in this province.

In this research, in addition to distribution of urinary stones in different areas of province, the role of bio (race), climate (temperature) and geology (water hardness) factors in urinary stones diversity has been studied. Mineralogical studied using XRD showed that collected samples can be divided in to three mineralogical groups: uric acid, calcium oxalate and phosphate.

The results show that, arab's and persian' (lores tribes) races urinary stones according to their mineralogy, have a same variation pattern. Also the results which attained from temperature effect investigation on the mineralogy of urinary stones, confirms that from Mediterranean sub-humid climates (north-eastern area of the provience) to warm and dry climates (south and southwest area of the province), oxalate stones and urate stones concentration decreases and increases respectively. For instance in some warm and dry climates which have the highest annual average temperature (25°C), uric acid stones are the only mineralogy phases.

Finally, with comparing water hardness level of different areas of the Khuzestan province with mineralogy of collected samples, conclude that despite of positive correlation in some regions, there is no obvious correlations in general and it needs much more researches.

Keywords: urinary stone, Khuzestan, Iran

INFLUENCES OF TRAFFIC POLLUTION ON SPATIAL DISTRIBUTION OF HEAVY METALS IN ROADSIDE SOILS

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Soils on the roadside can receive pollutants from traffic sources including historical use of leaded petrol, tear and wear of tyres and other parts of vehicles, as well as paint of road marks. This study investigates the levels and spatial distribution of heavy metal pollution in roadside soils sampled from several locations in Galway and Dublin in Ireland. Results from a roadside sports ground showed clear influences of traffic pollution on soils adjacent to a busy road, and such pollution is reduced by the presence of a bush fence on another side. Based on the results from a park with a large green area, the spatial range of traffic pollution could reach about 30 meters inside the park, and the influences mainly demonstrated an exponential relationship with the distance away from the road. It was found that leaded paint can increase Pb concentrations of roadside soils in a couple of meters. Roadside barriers can alleviate the influences of heavy metal pollution from traffic on roadside soils.

Keywords: soil, heavy metals, traffic pollution

POSTER SESSIONS

INVESTIGATION ON ARSENIC CONCENTRATION IN WATER AND SEDIMENT SAMPLES AROUND THE ABANDONED TORGHABEH GOLD DEPOSIT, NE IRAN

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Abandoned Torghabeh gold mine is located about 10 km at west of Mashhad, Khorasan Razavi province, NE Iran. The main ore mineralization is arsenopyrite ± pyrite ± gold ± quartz. Torghabe district is one of the most beautiful places in the province with many fruit orchards, so investigation on arsenic concentration in water and sediment at this restrict seems to be essential. Arsenic concentration in 6 water and 12 sediment samples of drainage basin were analyzed by atomic absorption. The concentration of arsenic was determined between 0.1-8.2 µg/l. It is lower than WHO (2008) standard limit. Arsenic concentration in sediment samples range from 2.87-23.15 mg/kg. Based on US EPA (2004) the standard limit of arsenic in sediments and soil at residential and industrial area are 0.39 mg/kg and 1.69 mg/kg, respectively. So all of the sediments in this district seems to be contaminated. XRD results show that the most frequent minerals in the sediments are quartz, calcite, albite, clinocllore ferroan and muscovite. In sediment with the higher content of As(>20 mg/kg) calcite was appear in the XRD results, but albite and muscovite are more frequent in the sediment with lower As content(<5 mg/kg). It should be concluded that calcite is one of the adsorbent minerals for arsenic at the sediments. It needs more detail mineralogical investigation.

Keywords: arsenic, Torghabe, Iran

TREATED WASTEWATER INFILTRATION IN CONSTRUCTED PONDS AT PAPHOS DISTRICT, CYPRUS

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Paphos is the smallest city of Southern Cyprus; however during the last decade population has increased extremely. One of the most important environmental issues that Paphos municipality has to deal in this new era is the sewage which produces 4,895,000 m³/yr of wastewater. After close consideration with Water Development Department (WDD), and taking into account the groundwater table drop over the last fifty years, Paphos municipality proceeded with the construction of an Urban Wastewater Treatment Plants. The treated effluent is used for the enrichment of Ezousa Aquifer by entering twenty two shallow ponds which lie along Ezousa River. Afterwards water is pumped from the groundwater and discharges it in to an existing channel, which connects the Asprokremmos dam with agricultural land in Paphos. Treated sewage effluent quality is continuously assessed in terms of salinity, heavy metals, persistent organic compounds and microbiota, to optimize the quality of the downstream groundwater used for local irrigation. Guideline limits on the treated wastewater quality are in agreement with the Cypriot wastewater reuse standards and they are stricter than those proposed by the World Health Organization (WHO). We are going to present all physical parameters of the aquifer enrichment facilities, including geological and hydrological properties of the aquifer. Also we will present the quality of the treated sewage effluent and the groundwater prior and after the treated effluent infiltration.

Keywords: wastewater, infiltration, re-use water

DIVERSE RESPONSE OF WILD AND MUTANT STRAINS OF DROSOPHILA MELANOGASTER TO SOLANACEAE ALKALOIDS

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In our previous reports we showed that Solanaceae alkaloids have ovicidal effect, together with repellent activity against *Spodoptera exigua* moths, cause negative chemotaxy of *Dugesia gonocephala* flatworms and have cardioinhibitory effect on *Zophobas atratus* beetles. *Drosophila melanogaster* is one of the most useful laboratory models to test acute and subacute reproductive toxicity for insects. We examined the effect of Solanaceae extracts on three strains of *D. melanogaster*: wild type, white strain (sex-linked mutation) and sephia strain (autosomal mutation). The experiment was carried out under laboratory conditions at a temperature of 20+/-2 °C and 60+/-5% relative humidity. Insects laid eggs on the agar substratum containing various concentrations of extracts. Then, larval development (number of individuals, ratio of development) was evaluated. Subsequent generation of imagoes was transmitted to the next control vials and the insects were allowed to copulate and lay eggs. The three exposed strains revealed various responses to the stressor. Larval development revealed bimodal action of extracts for wild type population. Higher concentrations speeded up the development, while the lower ones – slowed it down. We think that such an effect could be caused by two factors: either extract affected hormonal balance or larvae were able to detect higher concentrations of Solanaceae extracts, while the lower ones were under the threshold level. Therefore, in case of the higher concentrations, larvae try to escape from toxic substratum and to moult quicker. Wild type showed concentration-dependant final toxicity, with high correlation coefficient (-0.8507) between extract concentration and survival ratio of imagoes, whereas both mutants showed lower correlation coefficients (-0.1619 and -0.6704 for white and sephia strain, respectively). However, they showed higher, not concentration-dependant mortality, than wild type. White mutant flies were more susceptible to the alkaloids as compared to sephia mutant flies. The next generation, exposed to control substratum, showed bimodal reproductive effects of extracts. Imagoes cultured with higher concentrations of extracts laid more eggs than those which were exposed to lower concentrations. Perhaps, the extract causes epistatic regulation of reproduction. To sum up, tested extract has promising insecticidal activity, especially that it can be used in relatively low concentrations.

Keywords: Solanaceae alkaloids, *Drosophila melanogaster*, reproductive toxicity

SOLANACEAE EXTRACTS AFFECT DEVELOPMENT AND REPRODUCTION OF SPODOPTERA EXIGUA MOTHS

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Specialized chemicals derived from different plants have been projected as weapons for pest control plan as they are shown to function as general toxicant, growth and reproductive inhibitors, repellents or oviposition-deterrents. They influence also physiological processes in insects. These compounds are mainly plants secondary metabolites, and some of them are already used as alternative to traditional chemical compounds currently applied as pesticides. Nowadays, numerous tests and bioassays are used to estimate biological activity or toxicity of different plant extracts. To evaluate the effects of Solanaceae extracts on *Spodoptera exigua* moths we developed several low cost and easy bioassays. They check for the effect of tested substances on all developmental stages: eggs, larvae, pupae and imagoes. Moreover, they let us to examine the lethal and sublethal effects. Several alterations, like reproductive, teratogenic, behavioural, physiological and developmental disturbances can be observed. The effects of extracts on various developmental insect stages were tested by adding the solution of tested substance to the nutrient (for larvae) or immersing the pupae into the plant extract solution. To test reproductive effects, pupae were placed in suitable chambers. After pupation, adult females laid eggs on extract-soaked substratum or the control one. The number of eggs and hatching success are determined and compared. To test ovicidal effects, pieces of paper with packets of eggs are immersed in a solution of the toxic chemical. Again, hatching success was checked. Then, teratogenicity is documented, inhibition-concentration curves, correlation factors and inhibition concentration values are determined. Our tests revealed, that Solanaceae extract may have possible ovicidal effect, at least in some range of concentrations. Moreover, females preferred extract-free substratum for egg-lying than the tested substratum. Also imagoes, which developed from extractexposed pupae, laid less eggs and their hatching success was decreased. In conclusion, our studies clearly indicate that the described bioassays can be used to evaluate the biological actions of plant extracts. Moreover, they can be useful in explanation of the toxic action of various substances and show the possible way of their application. Next, Solanaceae extracts and possibly alkaloids they contain, seem to be a promising agents, which can be used as agrochemical for plant protection.

Keywords: glycoalkaloids, sublethal effects, insects

AN ECOLOGICAL RISK ASSESSMENT ON COASTAL SEA SEDIMENTS AT THE BAGNOLI BROWNFIELD SITE (ITALY)

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The Bagnoli brownfield site, one of the largest Italian dismantled industrial areas undergoing remediation, is located in the western sector of the urban territory of the city of Naples (Southern Italy) inside the active volcanic field of Campi Flegrei. The remediation project, funded by the Italian government, started in 1996 in the brownfield site; viceversa only monitoring activities have been carried out on the coastal area sea sediments facing the brownfield site. A total of 384 sea sediment samples were collected from 128 boreholes at different depths (0–20 cm, 20–30 cm, 30–50 cm, 100–120 cm, 150–180 cm, 180–200 cm, 280–300 cm, and 380–400 cm) down the seabed along the coastline. Analyzed samples show that the coastal area facing the brownfield site is strongly contaminated by both metals, whose distribution seems to be controlled by the grain size of the sediments, and by organic compounds (PAHs and PCBs). Geochemical mapping and R-mode factor score analysis allowed us to identify the ground waters, emanating from the brownfield site to the sea across an artificial structure (“Colmata a mare”) limited by two piers and filled by scum, slag and landfill material, as the main source of contaminants. Groundwater metal contamination was proven to be mostly dependent on a natural hydrothermal enrichment process related to the volcanic activity of Campi Flegrei (De Vivo and Lima, 2008. In: *Environmental Geochemistry: Site characterization, Data analysis and Case histories*, Elsevier, 355–3859), whereas PAHs and PCBs, which occur well above the concentration levels permitted by the Italian Law, are undoubtedly anthropogenic. Generic Hazard Quotient (HQ) (maximum measured pollutant concentration divided by a selected reference value representing the predicted “no effect concentration”) has been calculated for As, Cd, Cr, Hg, Ni, Pb, PAHs and PCBs in seabed sediments (0–20 sampling depth) with the aim of performing an Ecological Risk Assessment (ERA). Result obtained showed that the Bagnoli brownfield site coastal sea sediments are always characterized by HQ > 1 up to the remarkable values of 14,737 and 1,666 respectively for PAHs and PCBs. Since the higher the HQ, the more frequent adverse ecological effects are expected, a remediation project should be planned, as a priority, the PAHs and PCBs occurring in the sea sediments next to the coastline, since the area in the summer time is crowded by family and children.

Keywords: sea sediments, ecological risk assessment, Campi Flegrei

CHARACTERIZATION OF THE IMPACT CAUSED BY THE DISCHARGES OF A WASTEWATER TREATMENT PLANT INTO A FLUVIAL LEISURE AREA - A PORTUGUESE EXAMPLE

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The Ocreza River is a Portuguese river that has its source in the Gardunha chain, inner center of Portugal, at 1160 m altitude and stretches for 80 km until it drains into the Tagus River. It has several creeks and tributaries along which there are several river beaches and lakes that are used for recreational activities. The impact of several wastewater treatment plants discharges on water quality must be monitored and controlled, because of its crucial role on local communities' health.

This paper focuses on the Póvoa wastewater treatment plant which discharges into the Ramalhoso River, a tributary of the river Ocreza. Twelve water samples were collected between the wastewater treatment plant discharge and the Ocreza river confluence, and were georeferenced. The first point is located upstream to the discharge point, the second one in the discharge point and all the other samples are located downstream of secondary inflows at approximately equal distances. Sampling campaigns were conducted during three different hydrological periods in 2010: rainy winter (January), intermediate conditions (March) and dry season (June). For all campaigns and sampled points a field flow measurement was done. The following chemical parameters were also analyzed: (BOD) biochemical oxygen demand, (DO) dissolved oxygen concentration, dry residue, P_{total}, N_{total}; pH, temperature and microbiological parameters. The dissolved oxygen concentration (DO), biochemical oxygen demand (BOD) and the microbiological parameters were used as indicators for the presence of organic matter in the body of water, and as parameters for evaluating the environmental pollution.

A coupled hydrodynamic and water dispersion model was used to simulate the pollution in the Ocreza River due to sewage effluent. The QUAL2kv2 software was used to construct a water quality model. The simulation results are consistent with field observations and demonstrate that the model has been correctly calibrated. The model is suitable for evaluating the environmental impact of sewage effluent on Ocreza River from the wastewater treatment plant inflows, allowing feasibility studies of different treatment schemes and the development of specific monitoring activities.

Keywords: wastewater plant discharges, water quality model, numerical simulation

DEVELOPMENT OF ARSENIC ANALYTICAL METHODOLOGIES IN WATER AND URINE BY Hg-AAS FOR ROUTINE DETERMINATIONS IN URUGUAY

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Environmental arsenic (As) levels in water resources have not yet been taken into account to systematically assess population's exposure and health impacts in Uruguay. However, new environmental and occupational regulations have been recently established and there are special needs of developing analytical tools to assess As levels and speciation in water resources, urine and determination of metabolites in exposed populations. Natural low As concentrations require highly sensitive techniques and no ICP-MS is available in this country, so a simple method for routine determinations of total and inorganic arsenic in natural water and urine is proposed and validated. It is based on a flow system with detection by hydride generation (Varian VGA77) - atomic absorption spectrometry (HG-AAS). The sample treatment for total As was optimized for water and urine using sulfuric acid and potassium persulfate for the elimination of organic matter, and potassium iodide and hydrochloric acid for the reduction of As(V) to As(III). For inorganic As determination, only the reduction was carried out. Detection and quantification limits were 0.08 μgL^{-1} and 0.26 μgL^{-1} respectively, linear range was up to 10 μgL^{-1} . Accuracy was evaluated as recovery from analysis of a reference material provided by Mexico's Centro Nacional de Metrología (CENAM) for proficiency testing, with recoveries in the range 95% -115% for natural water, and by spiking various urine samples, with recoveries in the range 90-110%. Precision (repeatability, RSD%) was better than 10% for both water and urine samples. Arsenic recommended limits are: for drinking water < 10 μgL^{-1} for total arsenic (WHO, Guidelines for Drinking-Water Quality) and for urine, < 35 μgL^{-1} on occupational exposed workers (ACGIH-BEI®) and 10-20 μgL^{-1} on general population (ATSDR, As Tox-Profile). If those levels are considered as reference, the proposed methods are suitable for this purpose. In conclusion, the figures of merit of these methodologies, are appropriate for routine monitoring of total and inorganic As in water and urine, according to international recommendations and Uruguayan regulations.

Keywords: arsenic in water and urine, hydride generation, Uruguay

IMPACT OF TARANTO INDUSTRIAL AREA ON THE AIR QUALITY OF THE URBAN AREA

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Industrialization, urbanization and economic growth have resulted in a profound deterioration of air quality. The growing interest about particulate matter (PM) is due to its dangerous consequences on human health, in fact several epidemiological studies have shown the negative effects of PM on human health such as respiratory and cardiovascular disease, neurotoxic effects and cancer. In particular PM may be the carrier of acidic or toxic species, deeply into the lung and can cause oxidative stress and local pulmonary and systemic inflammatory responses. Heavy metals are important and well known pollutants that have been identified in several environmental matrices world-wide. They are potentially toxic, even at low exposure levels, and they're mainly emitted by anthropogenic sources. This pollutants locally emitted, undergo dilution with ambient air and various types of transformations during the transport process. The information about the vertical diffusive properties of the low layers of the atmosphere and the weather data could be a useful tool to identify the transport and dispersion of pollutants locally emitted. 'Fugitive emission' campaign was performed from 15th April to 6th May 2010 in three different sites around the iron and steel pole of Taranto (Apulia Region, South of Italy). The main interest on Taranto is due to the presence of several activities of high impact as very wide industrial area close to the town and the numerous maritime and military activities in the harbor area. The aim of the campaign was to triangulate in the neighbourhood of the examined site on the basis of the direction of the wind in order to determine the impact of the local emissive source on the surrounding areas and on the citizen human health. The preliminary analysis of collected data for all three sites, showed that when the wind direction allowed the transport from the plant to one of the considered receptor site, iron (Fe), manganese (Mn), Arsenic (As) and zinc (Zn) concentrations are greater than those observed in other two sites. Moreover, in these days the Mn concentration exceeded the EPA threshold limit (50 ng m⁻³) and Arsenic concentration exceeded the limit set by Directive 2004/107/CE (6 ng m⁻³).

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Keywords: aerosol characterization, industrial aerosols, metals

SPATIAL DISTRIBUTION OF ABUSE DRUGS IN HUMID AREAS

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The presence of abuse drugs in surface waters of rivers, lakes, marsh, etc are indicatives of human activity, and may denote a lack in the purification of urban wastewaters. In some cases, found levels of these substances can be used for estimation of the population's consume. Drugs of abuse are excreted mainly as metabolites through human waste, and only traces or small quantities can be found unaltered in soils and waters. Due to the limited number of research studies in this field, there is scarce understanding of the environmental occurrence, transport and fate for these compounds and it is also not known the effects of the permanent exposure of aquatic organisms to these toxics. Coastal marshes are one of the most important Mediterranean type ecosystems, which have suffered during the last decades an important demotion due to the intensification of agriculture and the construction of infrastructures. Pego-Oliva marsh is a good example of that. For this reason we selected this area, of approx. 1,290 ha, to assess the levels of drugs of abuse through the analysis of twenty-three water samples taken in this wetland. A previously developed analytical method for the simultaneous determination of 14 drugs of abuse and their metabolites in surface waters, using solid-phase extraction (SPE) and liquid chromatography tandem mass spectrometry (LC-MS/MS) was utilized. Several isotope-labelled internal standards were included in the method as a way to compensate the matrix effects, for a better quantification. Ecstasy, amphetamine, metamphetamine, MDA, ketamine, THC-COOH (the main metabolite of the THC), cocaine and their main metabolites (benzoylecgonine and ecgonine methyl ester), methadone, morphine and 6-acetylmorphine were found at concentrations in the range of 0.2 ng/L until 20.4 µg/L. It was impossible to establish an origin of the drugs or the levels of consumption in the population of the surrounding areas due to that the marsh receive waters from different sources like Gallinera, Molineel, Bullent and Racons rivers, which could bring contaminated waters from long distances, as well as the presence of springs.

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Keywords: emerging contaminants, wetlands, drugs of abuse

IMPACTS OF URBAN POLLUTION ON UNDERPRIVILEGED POPULATION HEALTH: A CASE STUDY OF THE CITY OF ANTANANARIVO, CENTRAL MADAGASCAR

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The problems of economic growth, social and educational development, urbanization and low protection of the environment are recognized in the city of Antananarivo. These are acute in urban areas and impact on public health, poverty alleviation and sustainable development. The rural-urban migration activated by the search for increased incomes has resulted in the concentration of large populations in relatively small areas under poor conditions of sanitation. These areas are at risk of geological and environmental disasters and pose huge problems for waste management, supply of raw materials, water use and air quality. Thus, there are some illnesses due to the bad qualities of air, soil, water and hindrances due to the disruptions in the majority of the underprivileged population. Therefore, the impact of the pollution has reached a disturbing magnitude and is arousing public awareness. This paper examines the geogenic and anthropogenic sources, characterizes components of the pollution load and their health effects, and suggests practical guidelines for attaining useful solutions to the problem. Mass education and effective solid waste management must be involved in preventive remedial measures.

Keywords: urban pollution, impacts on health, underprivileged population

MEDICAL GEOLOGY IN MADAGASCAR: PRELIMINARY REVIEW

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Madagascar is an island in south-west Indian Ocean, with an area of 581540 square kilometer and having a population of over 20 million spread over 24 Regions and a territory with varied geological domain. The land-water ecosystem developed in response to geological, geochemical and hydrodynamic processes vary from place to place. Thus, the distribution and the concentrations of various natural elements also vary. Areas of excess or deficient concentration of essential trace elements and heavy metals related to health are therefore not well defined. On the other hand, geogenic processes leading to health hazards have now been established in a few countries of the world but these processes are not well known by scientific community in Madagascar. The relationship between medical treatment and geology and studies on aspects of Medical Geology in the country are rare and sparse. Many geoscientists are not totally convinced that geology can solve problems related to human health. Hot springs are included in the concept. Heavy metals and other constituents in hot spring waters can be very useful for health but sometimes also toxic for human health. Madagascar's hot springs have been utilized for bathing from ancient times mainly for medical and convalescent purposes. Therefore, the different properties and the impacts on human health of water springs are described in this chapter. An important point to note is that no systematic studies have been carried out to establish geological linkage with diseases; nevertheless, case histories of endemic diseases are reported from different parts of the island. Two major endemic diseases on account of geogenic reasons are related to deficiency concentrations of magnesium and calcium.

Keywords: Mg, cardiovascular disease, hot springs

AIR POLLUTION AND THE NEED FOR REMEDIAL MEASURES IN ANTANANARIVO

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The problems of urbanization, population explosion and the increased use of automobiles are well known in Antananarivo. The impact of the pollution in the vicinity of overcrowded cities and from industrial effluents and automobile exhausts becomes very common. Natural or geogenic sources of pollution include weathering of mineral deposits, brush burning and windblown dusts. The sources of atmospheric pollution are industrial emissions from fossil fuel combustion, and power plants, usually located within or at the precincts of the urban areas. The major sources of heavy metal pollution are anthropogenic that include those associated with fossil fuel and coal combustion, industrial effluents, solid waste disposal, fertilizers and mining or metal processing. In Antananarivo, among the heavy metals, the most serious effect of pollution is presently associated with lead (Pb) emission from gasoline combustion by automobiles that would account for about 80% of atmospheric pollution. At present, the impact of the pollutants is confined mostly to the urban centers with large populations, high traffic density and consumer-oriented industries. Most of gases are toxic and carcinogenic. Major components of particulate matter include also smoke, dust, fog and mist. This preview chapter focuses mainly on the critical issues of these urban pollutions and proposes useful solutions to the problem that include: reduction in the sources of heavy metal through bans on the use of Pb-containing products such as leaded gasoline, reduce/eliminate pollutants at source, prevent pollutants from entering the environment, etc.

Keywords: heavy metal, air pollution, useful solutions

STUDY OF THE MEDICAL GEOLOGY AND GEO HAZARDS IN WESTERN IRAN

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This research, based on the study of medical geology in Sanginabad region. Sanginabad which is part of the Sanandaj-Sirjan structural zone, in west Iran. The Sanandaj-Sirjan Zone (SSZ) is located between the central Iran block and the Zagros Fold-Thrust Belt and is a part of the Zagros orogen. The water in Sanadaj and Bijar area is polluted by metal and semimetal components. Lifetime decreasing, getting cancer and large number of kidney disease are the main problems that have been reported amongst inhabitants because of the polluted water with these components. The basic researches in Sanandaj area started from 2003-2004 with identification the high risk regions from the normal risk regions. The first step of the sampling was started on the surface waters and underground waters in small scale but with wide range at the surface. These samples obtained better indexes and data from the rocks and soils samples. According to the data from rocks and soils specimens, we can find the source of this anomaly and high potential risk area in that region. By a totally overview we notice the additions of some metal and semimetal elements in the structural units on the region. The lithology of Bijar region is composed of igneous, metamorphic and sedimentary rocks. The igneous rocks are being a part of The Urumieh-Dokhtar Magmatic Assemblage that forms a distinct linear intrusive-extrusive complex, which extends along the entire length of Zagros orogen, with a width of over 4 km. The Urumieh-Dokhtar Magmatic Assemblage contains various lithologic units including Diorites, gabbros, granodiorites, granite bodies of different size, widely distributed basaltic Lava flows, trachybasalts, ignimbrites and pyroclastic rocks, mostly tuffs and agglomerates.

According to the volcanism activities we have mineralization that formed from southeast (Dashkasan mine) to northwest (zarshuran mine). the main minerals of this mines are including gold (Au), realgar (AsS), orpiment (As₂S₃), Stenonite (Sb₂S₃) and Cinnabar (HgS) that have increased the Hg, Sb, As elements enormity at this region. Sweet water deposits (travertine) that are belong to quaternary is distributed at the whole of region. These deposits of porous travertine sediments specified with yellowish white color. The hydrothermal activities are related with new volcanism of the region. devolatilization of the lower magmas have brought the arsenic to the hydrothermal system then entered to the groundwaters.

Keywords: Medical Geology, geo-hazards, Environmental Geology

NATURAL, INCIDENTAL AND MANUFACTURED NANOPARTICLES IN THE ENVIRONMENT: BEHAVIOR, FATE, BIOAVAILABILITY, RISK ASSESSMENT AND HEALTH EFFECTS

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The distinctions between naturally occurring, incidental, and manufactured NPs are often blurred. Naturally occurring NPs are ubiquitous, distributed throughout the atmosphere, oceans, soil systems, terrestrial water systems, and in most living organisms. They are even present in the deep Earth, and throughout the solar system and interplanetary space. The number of simple and complex manufactured nanomaterials (NMs), and their uses, have been growing tremendously in last years. Incidental NP inputs to the environment have risen dramatically since the beginning of the Industrial Revolution due to manufacturing emissions and the combustion of fossil fuels. For example, incidental CNTs and other fullerene-related nanocrystals have been reported to originate from propane stoves, wood fires, burning tires, and other sources, and fullerene C60 has been found in geologic deposits, candle soot, and meteorites. Large-scale production of engineered NMs presents the possibility that organisms and ecosystems may be exposed to new levels and qualities of substances with unknown consequences. It is essential to manage risks associated with different nanoparticles exposure to differentiate the relative importance of manufactured, natural, and incidental sources of NMs at each step of the material's life cycle and understand the processes that govern NM transport, persistence, bioavailability, and toxicity. So, the aim of this paper is to illustrate the fate and interactions of nanomaterials in complex environmental contexts to assess exposure and possible harm, also in order to assess the specific effects of NPs in the workplace.

Keywords: nanoparticles, ecotoxicity

HUMAN KIDNEY STONE STUDIES BY SEM/EDX AND LA-ICP-MS METHODS

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In this paper we describe the compositional and morphological characteristics of nine human kidney stones.

The study has been conducted using different analytical techniques: X-ray diffraction, Scanning Electron Microscopy, EDX analysis and LA-ICP-MS analysis. These different analytical methodologies allowed us the identification of the crystalline components; the morphological analysis and the determination of major and trace element composition.

Four of the nine samples were embedded on resin and cut to obtain a thin section to be studied by optical microscopy and by LA-ICP-MS; another part of the samples were used to analyze them with scanning electron microscopy (SEM) coupled with an energy dispersive X-ray spectrometer (EDX, Link 10000). Powder was analyzed by FTIR spectroscopy and X-ray diffraction. All the kidney stones studied show millimetric dimensions and characteristic red-brown colour, in particular, the stones studied were composed of pure calcium oxalate monohydrate and calcium oxalate dehydrate respectively whewellite, ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), and weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) as the dominant phase, which are the most common kinds of mineral phases composing human kidney stones. Six stones are composed of numerous small spherulites and each spherulite shows a strongly pronounced concentric lamination with a great number of crystallite growth around a nucleus of variable nature, on the contrary the other three samples show a structure a rose.

The aim of this work was to carry out interdisciplinary studies in order to describe composition, morphology and the possibility to individuate, by trace elements composition, the correlation between the disease and the environmental pollution. The significance and role of trace elements in renal stones has been studied by LA-ICP-MS. However trace elements are distributed in human tissue in very low concentration, they play a significant role in most biological processes, previous studies show that the concentration of trace elements, such as Zn, Sr, Fe, and Cu, in renal stones depends on their chemical composition, but the existence of toxic elements such as lead in organisms may be caused either by environmental pollution.

Keywords: kidney stones, SEM-EDX, LA-ICP-MS

COPAHUE, ARGENTINA: MUD MATURATION FOR ITS POSSIBLE APPLICATION IN HUMAN HEALTH

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Copahue volcano is situated in the province of Neuquén, Argentina. Several geothermal features like hot springs, ponds and fumaroles, occur in the surroundings of Villa Copahue. The associated geothermal system causes the occurrence of singular thermal muds with important presence of sulphur and clay minerals. In this place an international-level thermal complex, Copahue Thermal Center (CTC), was developed for therapeutic treatments under medical supervision. These peloids are extensively used for the treatment of several rheumatic, muscle, neurological and dermatological pathologies. The natural mud have a composition rich in sulfur, as well as clay minerals kaolinite and smectite type, which are in contact with a highly acidic liquid phase with high salt content and dissolved gases (Baschini, et al 2010). These muds, a nonrenewable resource, are used and discarded causing a strong impact on the system. The objective of this study was carried out an experimental maturation of muds in the CTC, from regional clay minerals and acid water of the place, in order to obtain similar materials, in composition and properties, to the natural ones. An Experimental Station (ES) was built with a wooden container with about 4000 L of capacity, where kaolinite and smectite (in proportions 75:25) from regional deposits were mixed with natural thermal acidic waters. The pH value of the system was about 3 and the temperature was about 55C during all the experience. At different times for a period of 1 year samples from the ES were taken and analyzed. The properties evaluated were cationic exchange capacity, specific surface, Atterberg limits, kinetic cooling and color. The best properties of the muds in relation to these parameters were achieved at the third and fourth months from the beginning of the process. SEM, XRD and Infrared techniques were used to evaluate the maturation evolution. The results showed a good cementation of the material and the gradual incorporation of sulfur into the system. The results showed that the maturation process of muds can be produced, in a period of four months, a material with very good properties for therapeutic use.

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Keywords: muds, maturation

MUDS AND SALTS FROM LAGUNA MAR CHIQUITA (OR MAR DE ANSENUZA), CÓRDOBA, ARGENTINA: NATURAL MATERIALS WITH THERAPEUTIC POTENTIAL USE

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The Laguna Mar Chiquita, located in Cordoba's province, Argentina, is the largest saline lake in South America, with a variable surface between 2,000 to 6,000 km². Lake level fluctuations are associated to climate changes (dry or wet period) at middle latitudes in south eastern South America (Piovano et al, 2002, Troin et al, 2010). During the last 50' and 60' the mud collected from the bottom of the lake was extensively used for topical application over the skin and the salts precipitated in the coast were used for domiciliary baths. Subsequent water level increases (decades of the 70, 80, 90) diminish the possibility of using these materials. However, during the last decade the decline of water levels has increased the potential for reuse of muds and salt deposits of this lake. The aim of this study was to characterize the composition of the muds and salts obtained from this lake and its coast. Nine solid samples and one water sample from Laguna Mar Chiquita were collected around Miramar, the unique coastal town. The salinity of the water, 28 to 360 g/L like minimum and maximum reported, has reached in the last decades values as low as 33 g/L, with salt contents above 60 g/L at the present. The predominant dissolved anion was chloride while sodium was the most important cation. Sulphate was present in minor proportions in the water but it was the most important anion in the precipitated salts. The pH was neutral or slightly alkaline. XRD diagrams showed a predominance of sodium chloride in the water of the lake, while the entire coastline displayed predominant deposits of calcium carbonate and minerals like calcite, gibbsite, eugsterite and thenardite. The dominant composition of the mud, with possible therapeutic application, was a mixture of illite like predominant phyllosilicate, quartz, plagioclase, feldspar, muscovite, calcite and halite. The thermograms obtained from mud samples showed typical endothermic peaks associated to the inorganic materials and exothermic ones attributed to the presence of organic matter. Waters and muds from Laguna Mar Chiquita showed significant similarity to those from the Mar Menor, Murcia, Spain (Carretero et al, 2010), place in which widely promoted tourism is related to the use of muds with therapeutic purposes.

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Keywords: saline lake, mud, salts

XRD AND FESEM CHARACTERIZATION OF CRYSTALLITES AND PARTICLES OF FINE POWDERS FROM KAOLIN PROCESSING

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The commonly measured aspects of airborne particles are grouped (Klein, 1993) as: 1) Morphological; grain size, shape, habit (aspect ratio, fibrous nature) evaluated by high magnification optical microscopy, SEM, TEM. 2) Chemical composition; usually evaluated by EDS attached to TEM or SEM. 3) Structural information, produced from electron diffraction or structure images. These techniques among other including X-ray diffraction (XRD) are now used to analyze the finer particles in earth systems (Hochella et al, 2008). XRD quantitative analysis of silica crystalline phases in airborne particulate in industrial and urban environment was extensively discussed by Smidt (1992) and it is a standard technique (OSHA Method ID-142, 1996; NIOSH Method 7500, INSHT MTA/MA 056/A06) Silicates and phyllosilicates are frequent mineral components of natural and anthropogenic atmospheric dust, as result of the processes involved in the comminution size (e.g. weathering or other natural processes, and milling or other industrial processes) and show microstructural characteristics (crystallite size, shape and strain, size distribution, strain distribution, crystallite aggregation) that can be analysed by XRD microstructural methods These methods are successfully used for silicates and sheet silicates. Dimensions of particles of these materials often range in the nanometric scale, and thus accurate characterization is of great technological interest, having also implications considering human health. Some examples concerning XRD microstructural methods are referred to industrial minerals, focusing on the statistic value of these techniques, where results correspond to thousands of effective particles. New results are provided concerning kaolinite produced both by hydrothermal synthesis and high energy milling of reference kaolinites. Voigt function and Warren-Averbach methods are used, and their results are compared with results of analysis of images from TEM, FESEM and AFM. The found average crystallite sizes for hydrothermal kaolinites are in the range 18.4 - 29.4 nm. Electronic microscopy observations are in good agreement with XRD data, following the trends observed for average crystallite size and CSDs width when particle thickness (corresponding to the crystallographic direction studied by XRD) is measured with statistical significance.

Keywords: powder X-ray diffraction, dust, size

INAIL RISK INSURANCE FOR ASBESTOSIS IN ROAD AND RAIL YARDS IN BIANCAVILLA AREA

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At the end of the nineties, in the area of Biancavilla (CT), a village on SE slope of Etna volcano, it was observed an excess of cases of pleural mesothelioma in the population than the national average. Afterwards, survey of the Institute for Prevention and Occupational Safety (ISPESL) in Rome confirmed that cases of mesothelioma were related to an environmental exposure to asbestiform fibers of a mineral called fluoride-edenite, resulting from a metamorphic process on basaltic rocks outcropping in Mount Calvario; this material had been widely mined from the mount and other sites and used in civil engineering. The natural fibrous mineral has ideal formula $\text{NaCa}_2\text{Mg}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2$, structure of prismatic amphibole and intermediate composition between tremolite and actinolite; it is not defined as “asbestos” although it has a similar potentially of health hazard when inhaled. During the 2000s, Italian Worker's Compensation Authority (INAIL) Sicily - Technical Consultancy Risk Assessment and Prevention (CONTARP) conducted some investigations concerning the potential occupational exposures to fluoride-edenite fibers into road and rail building sites in Biancavilla. The main issue was to assess the possible asbestosis risk to insuring purpose. The building sites regarded: urgent interventions to make an urbanized area safe and the works to renovate the railway Paternò-Adrano. Starting from the special regulations for the asbestosis risk (D.P.R. 1124/1965) and discussing about the interest of INAIL connected to building sites, in this paper the authors explain the technical-analytical method used in Biancavilla: from the characterization of sites in terms of location, type of work, tasks, equipment, organizational measures, prevention and protection of workers, up to the results obtained from the analytical detection (SEM - EDS) on bulk and dust samples, collected with personal sampler, compared with the analytical data of other Corporations engaged in the monitoring of airborne fibers in the territory (according to the program of ISPESL and ISS - National Institute of Health). INAIL's investigations led to say there were not concentrations of asbestos or asbestiform fibers so high to oblige to insure workers against the specific risk of asbestosis. However, a health risk from exposure to asbestiform fibers could not be excluded.

Keywords: asbestosis in road

APPLICATION OF ZEOLITE SYNTHESIZED FROM FLY ASH FOR THE REMOVAL OF Pb

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In the last few years many water purification processes have been developed and most of them are based on the utilization of low-cost materials with high pollutant-removal efficiency. Among these, zeolites are good and largely used adsorbent materials. They are hydrated aluminosilicate minerals with a three-dimensional open structure which makes them very useful for solving the mobility of toxic elements thanks to their ability to exchange cations, their large surface area and their typical porous structure. These minerals can be synthesized from different source materials and fly ash, a by-product of coal combustion waste, is one of the most used.

In this study, we have carried out column absorption tests to determine the Pb sorption behaviour of zeolite synthesized at a low temperature (60°C) from an Italian coal fly ash. Different amounts of zeolitic material ranging from 10 to 60 g were used with standard solutions containing 10 mg/L of Pb (ion concentration). The solid samples were characterized by X-ray diffraction and scanning electron microscopy. The cation exchange capacity (CEC) was also estimated. The filtered water solutions were analyzed by inductively-coupled plasma spectrometry (ICP-MS).

The synthetic zeolitic material shows a substantial ability to remove heavy metal (average 97%) from contaminated aqueous solutions. Pb concentration already decreases when using 10 g of zeolite. The increasing Na concentrations in the leachate documents that the toxic element is exchanged with Na⁺ ions. The results also indicate that the amount of Pb removed from solutions does not change significantly with the increasing amount of zeolite and the sorption process already occurs within the first minutes of contact with the contaminated solution.

The results obtained encourage a possible utilization of zeolite formed from waste material with an inexpensive and advantageous method..

Keywords: Pb-contaminated water, zeolite, fly ash

EVALUATION OF THE ARSENIC EFFECTS ON C. ELEGANS MODEL SYSTEM

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Arsenic is a highly toxic element that can be found in the environment. Particularly its presence in food composites is a serious risk for both humans and animals. The main source of exposure is arsenic-contaminated groundwater used in agriculture to irrigate crops, which could potentially lead arsenic entering in food chain. Epidemiologic studies have shown a significant association between the consumption of arsenic through drinking water and cancers of the skin, lung, bladder, liver, and kidney, neurologic disease, cardiovascular disease, as well as other non-malignant diseases. There are several techniques for assessing changes in gene expression: the DNA microarray and, most recently, the study of MicroRNA (miRNAs) for the detection of early indicators in various diseases. MiRNAs are a novel class of small noncoding RNAs that modulate the expression of genes at the post-transcriptional level. These small molecules have been shown to be involved in cancer, apoptosis, and cell metabolism. In vivo studies were performed in *C.elegans* model system in order to evaluate arsenic effect on microRNA profiles. We investigated changes in miRNA expression profiles in *C.elegans* at two different time-points (6 and 24 hours) after exposure at different concentrations of sodium arsenite (0, 0.1, 0.5 mM). At first, we focused our attention to some miRNA families homologous to humans. Preliminary results show an effect of arsenic on the profiles of miRNA expression; in particular we observed an up-regulation of some microRNAs such as *lin-4* (*mir125* counterpart in humans), *let-7* (human homologue *let 7, d, e, a, i, b*), *mir57* (*mir-100, mir-99* counterpart in human), *mir-234* (human homologue *mir-137*), which were found to be up-regulated in some conditions of stress as reported in a recent study of Simone et al, 2009. The up-regulation of these microRNAs, caused by the treatment with sodium arsenite, could confirm the hypothesis that the oxidative stress underlies the mechanism of exposure to this xenobiotic, and that miRNAs play an important role on cellular response to genotoxic oxidative stress.

This investigation received financial support from the joint project of the Italian Ministry of Health and the ISPEL entitled "Development and application of innovative methodologies and techniques for risk assessment and health effects in occupational and environmental exposures (20082011)"Project 6, Scientific Coordinator: dr Elena Sturchio.

Keywords: *C. elegans*, microRNAs, arsenic exposure

EVALUATION OF HEALTH IMPACT IN AN OPEN-PIT MINING AREA IN CATAMARCA, ARGENTINA

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Mining industry in Catamarca (CAT), a province in NW Argentina, has grown over the past decade. As a result, concerns regarding environmental and health impact have risen in the local community. The present work is aiming at assessing the impact on health from mining in Bajos de la Alumbra, a gold and copper open-pit mine in CAT. This study involved evaluation of on-site safety and health hazards in mine employees; during this work river water quality analysis was performed on, both upstream and downstream water samples. Interviews with hospital staff and neighbors in four towns near the mine were done to analyze effects on health of the population. Comparison of CAT cancer and mortality rates to national levels was also done to assess potential increased risk. We also performed a field study at Amanao, a settlement located 17 km from the mine involving clinical examination and complementary studies of 57 individuals > 15 years old (>90% of the population). No health hazards in mine employees were reported, nor did injuries surpass expected trauma rates. The upstream water quality showed elevated pH, high calcium and sulphate concentrations and contained strontium (indicating natural source from sedimentary rocks). Calcium and sulphate concentrations downstream remained elevated making water unsuitable for drinking. Hospital staff at neighboring towns reported no significant changes in the epidemiologic profile of local communities. Similarly neighbors did not report diseases as a result of contaminated water usage. Incidence rates for breast, prostate, kidney cancers and lymphomas were significantly higher in CAT than national rates. In children lymphoma, central nervous system and liver cancer rates were higher in CAT than average national rates. Both in adults and in children, increased cancer rates corresponded predominantly to the central region of the province, distant from the mining area. Cancer mortality rates in CAT were comparable to rates in other regions in Argentina, cardiovascular diseases were the leading cause of death both in CAT and nationwide. In Amanao infections (hydatidosis, brucellosis, trypanosomiasis) and hypertension were the most common diseases, however lung and skin diseases were not prevalent. Despite contamination claims from anti-mining groups, in this initial surveillance study we found no evidence that mining activities increased risk of disease in the general population.

Keywords: mining, health, impact

REMOVAL OF PHENOLS FROM WATER BY USE OF LAYERED DOUBLE HYDROXIDES

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This work is devoted to studies of processes of sorption of phenols by synthetic clay minerals of different composition. Solving the problem of preventing contamination of the environment depends on the successful solution of the problem of industrial wastewater from pollutants, especially from phenols. Therefore becomes more urgent problem of pollution of natural waters, the growth in waste water and the search for effective methods of cleaning them. The purpose of work is the search for new anionic sorbents. The application of this sorbent would allow to effectively remove of phenols from wastewater. The most promising sorbents are sorbents based on double hydroxides of metals with the structure hydrotalcite. They are cheap, accessible and effective, universal sorbents, and they have a high absorption capacity, resistance to environmental stress and can serve as excellent carriers for fixing on the surface of various compounds with their modification. The using of clay minerals with 2:1 structure type the changing value of the basal interlayered distances are very effective. Water molecules, as well as the positive and negative ions can be adsorb in interlayer space of these minerals. Therefore it is possible to place large ions between layers and forming columns. So we can create a system of pores where various small molecules can be placed. The pores size resulting in the intercalation process are about several tenths of nanometers. The samples were synthesized with the following ratios of cations in the matrix. The specific surface of LDHs was determined by low-temperature nitrogen adsorption chromatographic method with subsequent processing of the results obtained by BET method. The change of interlayer distance in LDHs after the adsorption of phenol, were investigated. Adsorption capacity of the obtained sorbents was investigated in the reaction of phenols with LDHs different composition of general formula $MgxAl_y(OH)_z$ with varying degrees of isomorphous substitution. During the adsorption the amount of adsorbed phenol from the aqueous phase were fixed. The kinetic parameters of ion-exchange were studied.

Keywords: phenols

POLLUTION OF WATER RELATED WITH AN ABANDONED URANIUM MINE AND HEALTH EFFECTS

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The Vale de Abrutiga uranium mine is located close to the reservoir of the Aguieira dam. The mine is an open pit and the tailings and rejected ore were deposited on permeable ground, and are not covered by vegetation. The open pit mine was closed, filled with water, and a lake was formed. The newly formed acid waters caused dissolution of metals and flowed to the reservoir of the Aguieira dam. Drainage waters from the open pit lake, mine tailings and rejected ore have pH values close to 2.5, high conductivity, and high concentration of U, SO₄²⁻, Zn, Fe, Mn, Ra and Cu, and groundwater shows high conductivity and contamination of U, Fe, Mn and Ra. Exposure to U can result in both chemical and radiological toxicity, for which the lung and the kidneys are the main target organs. The major chemical effect is kidney toxicity, causing damage to the kidney cells, and even kidney failure and death. Human exposure to U-radiation, and its compounds, increases the possibility of developing cancer during their lifetime. Correlation between radon exposure and lung cancer in the U-miners is well documented. Inhalation, injection, ingestion or body exposure to Ra can cause cancer and other body disorders. Manganese in excess is toxic. Recent studies suggested a connection between Mn inhalation and central nervous system toxicity in rats. A form of Parkinson's Disease-type neurodegeneration called "manganism" has been linked to manganese exposure. Excessive intake of iron can damage the cells of the gastrointestinal tract directly, and can enter the bloodstream by damaging the cells that would regulate its entry. Once there, it causes damage to cells in the heart, liver, etc. Too much ingested zinc can promote deficiency in other dietary minerals. In toxicity, copper can inhibit the enzyme dihydrophil hydratase, an enzyme involved in haemopoiesis. Most Cr(VI) compounds are irritating to eyes, skin and mucous membranes. Chronic exposure to Cr (VI) compounds can cause permanent eye injury. Chromium(VI) is an established human carcinogen.

Keywords: abandoned uranium mine, contaminated waters, health effects

CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF ETNEAN VOLCANIC EMISSIONS USING ACTIVE BIOMONITORING TECHNIQUE (MOSS-BAGS)

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Biomonitoring may be defined as the use of organisms and biomaterials (biomonitors) to obtain information on certain characteristics of a particular medium (atmosphere, hydrosphere etc.). In particular, mosses accumulate large amounts of trace metals, making them good bioaccumulators to estimate atmospheric pollution. The moss-bags technique, introduced in the early 1970', has become very popular. Such active biomonitoring technique is particularly useful in highly polluted areas and has been extensively used in industrial and/or urban areas to examine deposition patterns and to recognize point sources of pollution. The main objective of this study, which represents the first application of the moss-bags technique in an active volcanic area, was to test its efficacy in such environment. Complementary objectives were: to determine the different behaviour and the areal dispersion of volcanogenic elements emitted from Mt. Etna; to characterize the morphology and mineralogy of particles transported in the plume-system, basing on microscopy investigation. A mixture of Sphagnum species was picked in a clean area, treated in laboratory (rinsed, dried and packed) and exposed in field for 1 month. Sites were chosen considering the prevailing wind at Mt. Etna's summit. Milled samples were analysed for major and trace elements concentrations, after microwave digestion (HNO₃ + H₂O₂), by ICP-MS and ICP-OES techniques. Morphology and mineralogy of volcanic particulate were investigated by using a SEM with EDS. Analyses clearly showed the efficacy of the moss-bags technique also in this peculiar environment. Several elements were strongly enriched in the mosses exposed to the volcanic emissions. The highest enrichment was measured close to the summit crater, but evidences of metals bioaccumulation were also found in downwind sites, at several km from the volcanic source. The accumulation factor (exposed/unexposed moss) allowed us to distinguish a group of elements (Tl, Bi, Se, Cu, As, Cd, S), which are highly mobile in the high temperature volcanic environment. Also alkali metals showed a significant increase in their concentrations, probably because of their affinity for the halide species carried by the volcanic plume. Microscopic observations evidenced sulphate and halide crystals on particles trapped by the mosses. Mosses exposed at sites directly fumigated by the volcanic plume showed crystal growth also directly on the moss surface.

Keywords: biomonitoring, moss-bags, trace elements

PRECIPITATION OF STRUVITE BY SOIL BACTERIA AND ITS POSSIBLE IMPLICATIONS IN HUMAN HEALTH

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Struvite ($\text{NH}_4\text{MgPO}_4 \times 6\text{H}_2\text{O}$) is biomineralized by soil bacteria in cultures *in vitro* but this mineral has rarely been described in natural soils. Struvite is abundant in materials from animal excrements (guano, animal manure, "ornithogenic soils" of the Antarctic tundra etc.). It also precipitates in waste-water treatment plants, where it causes problems by obstructing piping and conduits. The discharge of purified residual waters, which are often rich in N and P, constitutes an environmental problem in that it brings about the eutrophication of rivers, lakes and reservoirs. Thus considerable research has been conducted into the possibility of increasing the precipitation of struvite in residual waters. Furthermore, nitrogen in the form of NO_3^- in drinking waters is a threat to human health because of its possible relationship with infantile methaemoglobinaemia and stomach cancer.

In this study we investigated the formation of struvite by soil bacteria from the A and C horizons of two Spanish saline soils. These bacteria were cultivated *in vitro* in culture media deriving from 1:1 extracts of the horizons and artificial saline solutions. In all culture media sufficient quantities of crystals appeared to be isolated and analysed by means of XRD and SEM-EDX. The crystals were mainly of aragonite, magnesium-calcite, and struvite. Nevertheless, neither in the fine-earth fraction (<2 mm) of the horizons nor in the accumulations of secondary soil carbonates (nodules and carbonate crusts) were any phosphates detected. Thus we may hypothesize that struvite is a metastable soil mineral, forming possibly in micro-sites and in seasonal periods with high bacterial activity and is subsequently dissolved by biological or inorganic mechanisms and thus becomes available as a nutrients source for the plants and/or microorganisms.

Metastable soil struvite has a buffering effect and would prevent the leaching of nitrogen to water, either on the surface or at depth. In addition to nitrogen, struvite contains phosphorus and magnesium and therefore it connects the biogeochemical cycles of all these elements and has the same buffering effect for P and Mg.

This study was supported by project CGL2008-04456/BTE of the Spanish Ministry for Education and Science.

Keywords: struvite

GEOPHARMACY: TEACHING MEDICAL GEOLOGY IN PHARMACEUTICAL SCIENCES

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Since 1850 in the Spanish Pharmacy Faculties the students learn a subject called Applied Geology to the Pharmacy (Geopharmacy) in which they can study: a) Principles of crystallography, with emphasis on the formation of crystals, including the crystallization of biological macromolecules, and the study of polymorphism of pharmaceutical products (mineral or not). b) Properties of minerals that affect the pharmaceutical use of crystalline substances. c) Minerals used in Pharmacy as active ingredients and/or excipients, with emphasis on the study of the phyllosilicates (clay minerals). d) Toxic effects of minerals, mainly those with asbestiform morphology, being common contaminants of phyllosilicates with use in Pharmacy. e) Human biomineralization, focusing on bones, teeth and lithiasis. f) Suitability of minerals for pharmaceutical and cosmetic use, according to the Pharmacopoeia. Undoubtedly, Geopharmacy is a scientific field belonging to Medical Geology. Geopharmacy knowledge contributes significantly to the professional development of future pharmacist. For example, crystal formation is a major activity in the pharmaceutical industry, since most of the products are crystalline. Furthermore, the physicochemical conditions of crystal formation can induce precipitation of the different polymorphs. The pharmaceutical polymorphism (broader in concept, that purely crystallographic) has a strong interest in Pharmacy from the point of view of therapeutic actions and economic level, where patents may be different if it is different polymorphs. About the crystallization of biological macromolecules, we can say that the majority of recent Nobel prizes in Biochemistry and even in Medicine are related to research involving the study of macromolecular crystals and the use of advanced crystallographic techniques has allowed discovering for example, reaction mechanisms in the process of genetic transcription and operation of ribosomes. However, Geopharmacy has disappeared as a compulsory subject in the Spanish Universities to the adaptation of curricula to the European Higher Education Space (Bologna Process) and only in some Pharmacy Faculties (for example, Granada) will be taught as optional.

Keywords: geopharmacy

RESIDENTIAL RADON AND THE RISK OF MALIGNITY: THE CASE OF LAGES PINTADAS CITY, NORTHEASTERN BRAZIL

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The Lages Pintadas city (Northeastern-Brazil) has presented an unusually high incidence of different cancer types in contrast to other neighboring municipalities. Metamorphosed rocks of granitic composition and pegmatite form this region. We make a pilot research aims to provide the Lages Pintadas city actions in the environmental and public health field as regards the distribution of the carcinogenic agent radon and decay products in urban and rural areas. Residential radon is the most important environmental risk factor for lung cancer. The Indoor radon measurement was making with long-term passive radon detectors (E-PERM® by RADELEC INC.), Gross gamma radiation with RS-125 spectrometer with NaI crystal (TERRAPLUS). We present the results from 110 Long-term passive radon detectors installed in 100 dwellings (mainly-bedrooms) in Lages Pintadas city. The survey was performed during two periods of five months on the dry season (December-April). All dwelling are without ceilings and have ceramic roofs, while the floor is tiled or cemented. The choice of different dwellings was random. For the two periods, the GM for Indoor-Radon were 358 Bq/m³ (SD: 823; range 20-3723; MED: 376). In the first measured period the data range: 15-4055 Bq/m³ (MED: 368; GM: 381; SD: 940) but in the second measured period, the data are less scattered and range: 20-36391 Bq/m³ (MED: 323; GM: 294; SD: 777). Consequently, all dwellings exceed the WHO action level of 100 Bq/m³ for indoor radon. The gamma radiation level was also checked in each dwelling (range; 16-109 nGray/h; MED: 83; GM: 139; SD: 17), this data was considered normal. Our results show that for the Lages Pintadas city the indoor-radon are high and further and more extensive research is needed.

Keywords: residential radon, natural radioactivity, northeastern Brazil

INVESTIGATION OF MOLECULAR MODIFICATIONS BY FTIR AND FTNIR SPECTROSCOPY

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Arsenic (As), a naturally occurring metalloid, is the principal contaminant of soil, water and food especially in some eastern countries such as Bangladesh, India and China. As concentrations ranging between 25-80 g l⁻¹ higher than the limits set by law (10 g l⁻¹), have recently found in drinking water (network and groundwater) in some Italian regions, including Lazio (central Italy). The main exposure route to iAs is dietary. Arsenic-contaminated groundwater is often used in agriculture to irrigate crops for food and animal consumption, which could potentially lead arsenic entering in human food chain. Arsenic is not an essential element for plants and its over-concentration in the soil can generate toxicity phenomena. Its translocation from soil to plant constitutes one of the main human exposure ways. Inorganic arsenic (iAs) is a non-threshold, class 1 carcinogen and iAs species are thought to be more toxic than the organic ones (oAs). Epidemiologic studies have shown a significant association between the consumption of arsenic through drinking water and cancers of the skin, lung, bladder, liver, and kidney, neurologic disease, cardiovascular disease, as well as other nonmalignant diseases. The aim of this work is to evaluate, respect to the control sample, the effects of different arsenate concentrations in *Vicia faba* seedlings by FTIR and FTNIR spectroscopy. FTNIR is a spectroscopic technique that uses the near-infrared region of the electromagnetic spectrum from 800 nm to 2500 nm. FTNIR is primarily used in medical diagnostics, also has been used outside of the medical field, food and agrochemical quality control, and combustion research, as well as cognitive neuroscience research. Furthermore, *V. faba* seedlings exposed to the same As different concentrations were used to evaluate the phytotoxic and genotoxic effects by comet assay. Preliminary results obtained by the two spectroscopic techniques show the effects caused by arsenate mainly related to molecular modifications determined by the chemical interactions of As with the biomolecules (i.e. carbohydrates, proteins and nucleic acids) of plant. The genotoxicity test shows significative results as As may be responsible for DNA damage. One of the mechanisms by which DNA damage can be induced by As might be oxidative stress in *V. faba*.

Keywords: FTIR and FTNIR spectroscopy, genotoxicity tests, arsenic exposure

PORTLAND CEMENT AND HEALTH IMPACTS

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Portland Cement is basically a finely ground cement clinker mixed with a small amount of calcium sulfate dehydrate. It is obtained by heating to a high temperature a mixture of substances such as limestone, sand, clay and shale. It is a light gray or white powder. Cement dusts are produced during blasting of raw materials, grinding of cement clinker and packaging or loading of finished cement.

Although this material is widely used in building and construction works as an important ingredient in concrete products, very scarce information on health effects of the particulate air pollution from cement factories, is available. However, most cement dusts chemical elements are potentially harmful to the environmental biota in general and children are the most susceptible affected human populations.

Some of the dangerous elements of cement dust include: Particulate Matter (PM_{2.5} & PM₁₀), lead, arsenic, chromium VI and chromium III, mercury, manganese, cadmium, crystalline silica among others.

It is well known that when Portland Cement, contacts with moisture in eyes or on skin, or when mixed with water, it becomes highly caustic (pH >12) and will damage or burn the eyes or skin. Inhalation may cause irritation and lung disease as well. Low levels toxic metals chronic exposure are other health issues to take into account.

Uruguay has several Portland Cement kilns in different parts of the country and there are only few studies on occupational exposure assessment .

This work describes the main health risks of populations living near a cement kiln and of occupationally exposed workers. Risk assessment and safety conditions are explained with special emphasis on minimizing toxic effects of cement pollutants.

We conclude that there must be a concern on risk management not only for health prevention but also for the environment protection in cement quarrying sites and around cement factories.

Keywords: portland cement, health, environment

BIOGEOCHEMICAL MAPPING OF PHYTOAVAILABLE ARSENIC, CADMIUM AND LEAD IN ITALIAN AGRICULTURAL SOILS

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The geographical distribution of phytoavailable arsenic, cadmium and lead in Italian agricultural soils was investigated using wheat as a test plant. More than seven hundred samples of wheat grains were collected in the majority of Italian agricultural areas and pooled into composite samples, homogeneous with respect to geographical origin and wheat variety. Representative samples were obtained by applying pre-established criteria for the collection of individual samples and their grouping into composite samples. The number of individual samples was proportional to the surface under cultivation in each region, and only the prevailing wheat varieties in each growing area were selected. Arsenic, cadmium and lead concentrations were determined by ICP-MS after grain cleaning, grinding and closed-vessel microwave digestion of the resulting flour. Geographical variability of arsenic, cadmium and lead concentrations in wheat was studied considering the provinces (i.e., administrative districts) as reference areas. The spread of element concentrations was high and appeared to be related to spatial variability associated with geochemical and environmental factors. Since this apparent spatial variability could be biased by the temporal variability of element levels, i.e. year-to-year fluctuations of element concentrations in wheat at each location, a 3-year longitudinal study on 7 wheat cultivars grown in 22 areas of central and northern Italy was carried out. Average year-to-year variations in element levels were low, demonstrating a minor bias due to the specific sampling year. These results show that mapping of phytoavailable arsenic, cadmium and lead in agricultural soils can be done by measuring arsenic concentration in representative samples of wheat grains. The biogeochemical maps were obtained by calculating the deciles of mp distribution, where mp represents the arithmetic mean of element concentrations in wheat for each province. The relations between the different elements were investigated and are discussed as well

Keywords: biogeochemical mapping of agricultural soils, phytoavailable arsenic, cadmium and lead, wheat

GENE EXPRESSION, HOMEOSTASIS AND APOPTOTIC PROCESSES IN TWO HEPATOBLASTOMA CELL LINES TREATED WITH AS(III) AND AS(V)

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The gene expression profiles of apoptosis-related genes and the cellular homeostasis of two hepatoblastoma cell lines (HepG2 and Hep3B) treated with different amount of As(III) and As(V) have been studied. The expression of a panel of 96 apoptosis-related genes has been investigated using TaqMan low density arrays (TLDA), while the expression of selected proteins has been studied by Western blotting. A detailed bioinformatics analysis has been also performed to obtain the statistically relevant biological processes and pathways.

HepG2 and Hep3B hepatoblastoma cell lines have peculiar and distinct properties since HepG2 constitutively express p53 while Hep3B cells are p53-deficient. We therefore focused the interest on p53-dependent apoptosis genes and their likely downstream effects in related pathways.

In this contribution we will report and discuss our results showing that As(III) and As(V) species induce a different response in terms of cytotoxicity, proliferation and induction of apoptosis.

Keywords: homeostasis and apoptotic processes

ELEVATED TRACE METALS AND REE CONTENTS IN THE CO₂-RICH GROUNDWATERS OF FLORINA (N. GREECE) A NATURAL ANALOGUE OF CARBON STORAGE SYSTEMS

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The Florina basin, being the main commercial source of CO₂ in Greece, represents a good natural analogue for the study of the impact of geologic carbon storage. It is part of a NNW-SSE trending graben filled with ~600 m Plio-Pleistocene fluvial and lacustrine deposits. The area is characterized by the upflow of great quantities of geogenic CO₂ probably associated to presently extinct Quaternary volcanic activity. The gas originates mainly from crustal sources but has also a minor (~10%) mantle contribution. This strong upflow of nearly pure CO₂ can be recognized in industrially exploitable gas reservoirs, high pCO₂ shallow groundwaters and surface gas manifestations. But the increased CO₂ content has a deleterious impact on groundwater quality. Due to the increased aggressiveness of the low-pH CO₂-rich waters with respect to the aquifer rocks, EU drinking water limits are exceeded for many parameters (e.g. Electric conductivity, pH, Na, SO₄, F, Al, B, Ba, Fe, Mn and Ni). Considering the additional impact of widespread agricultural activities, which is recognizable in sometimes elevated nitrate contents, only few of the sampled waters (4 out of 40) could be used for potable purposes. Aquifer waters are also characterized by high REE contents with ΣREE up to ~12 µg/l. Shale-normalized profiles show positive La and Y anomalies and Ce negative anomalies probably indicating a main derivation from iron oxyhydroxide dissolution. The positive Eu anomaly evidences also carbonate dissolution while the enrichment in HREE is probably due to the abundant presence of bicarbonate, which increases HREE solubility through complexation. Future developments of carbon capture and storage programs in the nearby sedimentary basin of Ptolemais and Servia have to carefully take in account the possible deterioration of their groundwater resources due to CO₂ leaks from the storage reservoirs.

Keywords: trace elements, REE, CCS natural analogues

MALIGNANT PLEURAL MESOTHELIOMA FROM SUBJECTS WITH SIMILAR PROFESSIONAL ASBESTOS EXPOSURE

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Malignant Pleural Mesothelioma (MPM) is an aggressive tumour, whose main aetiology is the long-term exposure to asbestos fibres. The diagnostic procedure of MPM is difficult and often requiring invasive approaches: therefore it is clinically important to find accurate markers for MPM by new non-invasive methods that may facilitate the diagnostic process and identify patients at an earlier stage. In the present study the exhaled breath of 13 patients with histology established diagnosis of MPM, 13 subjects with long-term certified professional exposure to asbestos (EXP), and 13 healthy subjects without exposure to asbestos (HC) were analysed. An analytical procedure to determine volatile organic compounds by sampling of exhaled air on a bed of solid sorbent and TD-GC-MS analysis was developed in order to identify the compounds capable of discriminating among the three groups. The application of univariate (ANOVA) and multivariate statistical treatments (PCA, DFA and CP-ANN) showed that cyclopentane and cyclohexane were the dominant variables able to discriminate among the three groups. In particular it was found that cyclohexane is the only compound able to differentiate MPM group from the other two; therefore it can be a possible marker of MPM. Cyclopentane is the dominant compound in the discrimination between EXP and the other groups (MPM and HC), then it can be considered a good indicator for long-term asbestos exposure. This result suggests the need of frequent and thorough checks on EXP subjects in order to constantly monitor their health and then possibly to study the evolution of MPM over time.

Keywords: malignant pleural mesothelioma, biomarkers

HEALTH RISK ASSESSMENT IN UNEXPECTED CONTAMINATION WITH A COMBINATION OF CARCINOGENIC AGENTS

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The focus of the case study reported herein is a brownfield site (formerly a filling station) located in a residential area of Pesaro (central Italy). Field surveys were conducted and contamination by oil compounds (benzene, toluene, ethylbenzene, and xylene - BTEX) and hydrocarbons, both at the ground surface and in the groundwater, was found. The concentration of benzene (maximum allowable limit (MAL) 1 g/L) was found to be 60 g/l. Surprisingly, very high concentrations (2792 g/l vs. an MAL of 1 g/L) of the chlorinated solvent tetrachloroethylene (TCE), unrelated to the filling station, were also detected over an extensive area. Several wells have been drilled in this area to irrigate flower and kitchen gardens. Groundwater withdrawal for domestic purposes was forbidden as soon as the TCE contamination was detected. Decontamination (with a minimum benzene target set at 13 g/l) and urban requalification (to allow for the construction of a residential building) proceeded simultaneously. A health risk assessment (HRA) was carried out in accordance with Legislative decree 152/06 integrating BTEX, hydrocarbon TCE and chlorinated solvents HRAs. Since HRA of some carcinogenic agents includes only the long term incremental risk and does not account for short term health risk, no criteria are available to estimate the overall health risk for local residents while work is in progress. Meanwhile, owing to poor coordination between environmental and public health professionals, workers have not been undergoing biological monitoring (measurement of TCE in urine). The decontamination activities have also enabled the temporary protection of the aquifer from further contamination by chlorinated solvents. The clearing of both BTEX hydrocarbons and chlorinated solvents is proceeding on schedule (benzene is down to 36 g/l and TCE in well samples to 204 g/L). To conclude, as a result of this experience the project was expanded to include another public area where, unlike in the former, the polluter can't be clearly identified. This extension has been realized thanks to the collaboration between several public entities that obtained the necessary resources. Finally, this methodology has already been applied to several other sites with work already under way. However, the assessment and management of the health implications of environmental contamination still need to be improved.

Keywords: health risk assessment

MERCURY DISTRIBUTION IN DEEP-SEA SEDIMENTS OF THE MEDITERRANEAN SEA

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The Mediterranean is a semi-closed basin connected to the world oceans through the narrow and shallow Strait of Gibraltar. The sill at the Strait of Sicily divides the basin into an Eastern and Western Basin. The sediments of the Mediterranean are deposited on top of an extremely thick layer of evaporates, formed during the so-called Messinian Salinity Crisis whose origin was found to be dominantly tectonic. The sediments are characterized by a low organic content (>1 wt.%) and oxygen is present in the whole water column down to the bottom. It was found that total mercury concentrations in off-shore marine sediments of the Mediterranean Sea are, on average 0.5 nmol g⁻¹, twice as high as the supposed world-wide natural background. The observed enrichment is mainly the consequence of the world's largest cinnabar deposits and surficial and submarine volcanic and geothermal activity. It was estimated that approximately 65% of the world's Hg resources are located in the Mediterranean area. Most of the research on Mediterranean bottom sediments was performed in coastal areas, but data on mercury species in Mediterranean deep-sea cores is still lacking. This study represents a systematic research performed on Hg determination in deep-sea cores sediments. The vertical profiles of mercury in sediment were investigated in detail to elucidate the temporal behavior of this metal. Sediment samples were collected with a box corer from ten sites during an oceanographic sampling campaign aboard the Italian research vessel Urania in July 2006 in the Eastern and Western basins of the Mediterranean. The results of the study revealed that Hg concentrations ranged from not detected to 0.161 mg Kg⁻¹ d.w.. Hg concentrations in sediment profiles were not uniform. In most cores the concentrations decreased from the surface and at a depth of 10 cm the concentrations varied between not detected and 0.039 mg Kg⁻¹ d.w. and were within the range of values of the earth's crust. These results are in good agreement with the concentrations of Hg determined in the deep cores collected in the Eastern and Western Mediterranean (Ogrinc et al., 2007).

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Keywords: mercury, mediterranean sea, sediments

GERMANIUM GEOCHEMISTRY IN MINERAL GROUNDWATER FROM MOUNTAIN AREAS OF SOUTHERN POLAND - A CASE STUDY OF ITS AFFINITY TO OTHER ELEMENTS

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Germanium commonly demonstrates silicon-like geochemistry, and is used as a tracer of petrogenetic processes leading to (re)crystallization of rocks in mantle, metamorphic, magmatic environments. Ge-geochemistry is also very promising in tracing low temperature events. In continental crust, mean Ge content is 1.4 ppm and mean Ge:Si molal ratio of 1.7E-6. In groundwater, the highest Ge content is usually found in geothermal aquifers, which occur in reactive silicates-rich bedrocks. Germanium evokes the rousing interest also in biology and medicine. In some countries, Ge-rich mineral waters are applied in balneotherapy, or are accessible as a bottled waters. The Ge-Si relationship becomes particularly interesting to study in Ge- or Si-rich groundwater. Geochemical study revealed increased Ge content in mineral waters of the Sudetes and the Bieszczady mountains, Southern Poland. In the Sudetes (SM) two main types of medicinal waters used in balneotherapy occur: lowenthalpy CO₂-rich waters, and thermal SO₄-HCO₃ waters with F, H₂S and Rn. Both types are enriched in Ge with respect to crust composition. The Ge and Si concentrations are of 0.03 – 10.25 ppb (mean 1.88 ppb), and of 4.34 – 43.66 ppm (mean 21.35 ppm), respectively. The Ge content in SM correlates with Si, depends mainly on water temperature and reactivity of silicates, and show Ge:Si ratio from 1.2E-6 to 218E-6 (mean 34E-6). In the Bieszczady (range of the Carpathians), mineral waters (BM) are currently studied at site where low-enthalpy CO₂-rich HCO₃-Cl-Na (with increased H₂S, B) waters are planned to use for balneotherapy. The BM show Ge content higher than in SM, and a different Ge-Si pattern. The Ge and Si content in BM are of 0.08 – 35.8 ppb (mean 7.4 ppb), and of 1.75 – 8.82 ppm (mean 4.6 ppm), respectively. The maximum Ge content in the BM is the highest one which have been found hitherto in groundwater of Poland, and is at the same level as Ge content in thermal waters of the world. The Ge:Si ratio in BM varies from 11.4E-6 to 2692E-6 (mean 611E-6). In sedimentary rocks of BM area, accessory sulphide minerals (pyrite, marcasite, sphalerite, galena, realgar, orpiment) occur. In BM, Ge does not show correlation with Si, Zn, or Fe, but it correlates positively with As, what suggests that orpiment is the dominant Ge-source mineral phase in this environment. Study of BM indicate that Ge-rich water might be also found in low-enthalpy environments in bedrock, which is enriched in sulphides.

Keywords: germanium, silicon, mineral water

ASSESSMENT OF GROUNDWATER AVAILABILITY, WATER QUALITY, AND HABITAT OF THE ÉTANG SAUMÂTRE REGION, HAITI FOLLOWING THE 01-12-2010 EARTHQUAKE

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Étang Saumâtre is a brackish lake located in the southeast region of Haiti, ~45 km from Port-au-Prince. An essential source of irrigation and drinking water for the populations of Thomazeau, Ganthier, and Fond Parisien are freshwater springs and shallow wells tapping the complex, fractured aquifer system surrounding Étang Saumâtre. Thus, the present study is particularly timely in that we will not only assess direct effects of the 01-12-2010 earthquake on the lake and surrounding groundwater system but also provide vital baseline data for monitoring the future impact of natural and anthropogenic changes on groundwater quality and the lake ecosystem. We present physical and chemical hydrologic and sediment data for the lake and its surrounding aquifers to classify Étang Saumâtre and its recharge zone. Specifically we present an analysis of stable isotopes, C, H, and O and the trace element chemistry. We will pay particular attention to the trace elements which can reveal unique insights into water-rock interactions in saline systems. Sediment samples (1cm intervals) and particulate material will be used to evaluate grain size, sedimentation characteristics, and mineralogy. In addition, we will determine the age of sediments in order to monitor the history of sedimentation rate. Water samples will be analyzed for a subset of dissolved gases (i.e. CFC, SF₆, He, Ne, Ar, radon, N₂, CO₂, CH₄), and age dating techniques (3H/3He and radiogenic 4He) will be used to construct a model for hydrological transport rate and regional flow for the region surrounding Étang Saumâtre. This model will include sub-lacustrine (groundwater discharge vs. deep water fractured flow) inputs to the lake. Bearing in mind that any significant reduction in annual fish production at Étang Saumâtre due to quake-induced disturbance of the ecosystem may exacerbate the already precarious health situation of communities living in its vicinity, it is critical that as part of the broader research focused on water quality that we assess the impact of the quake on Étang Saumâtre in terms of the ability to sustain a productive fishery. These data are vital to the development of a management plan to protect the livelihood of fishers and maintaining the health of the communities surrounding the lake.

Keywords: water, irrigation, human health

BASES AND CATION EXCHANGE CAPACITY IN PELOIDS MATURED WITH MINERAL WATERS FROM THE PROVINCE OF GRANADA (SPAIN)

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The use of peloids in balneotherapy is a healing method that helps in the treatment of chronic diseases or elderly people, significantly improving their disease and reducing the doses needed in the administration of medications. The maturation of peloids is necessary to improve and stabilize its therapeutic properties. Maturation is a complex process that usually occur between 60 days and 2 years, and that depends on solid and liquid phases. During this process, due to temperature, time, water content, pH, and homogenization, peloid become a mature final product. Many authors have studied this process and they conclude in changes on physical and chemical characteristics of thermal mud, increasing the volume of rehydration and improve its thermal properties. Furthermore, maturation generated metabolites of some colonizing organisms, which are considered responsible for its anti-inflammatory action. Our research group has studied the ultramicrofabric of peloids with scanning electron microscope to observe their development during the maturation process. The behavior of peloids as ionic mediators on human skin may be due to some of their physicochemical properties, such as exchange bases (calcium, magnesium, sodium and potassium) and cation exchange capacity. The aim of this work is to study the exchange bases and cation exchange capacity of peloids prepared with mineral water from different springs and spas of Granada (Alicún de las Torres, Zújar Graena, La Malahá and Lanjarón) and bidistilled water; the maturation time was one, three and six months. The solid phase was a mixture of kaolin-bentonite in proportion 9:1 (w:w). The value of cation exchange capacity increases in most of peloids with respect to the solid phase (not mixed with mineral water) and also increases with the maturation time. This fact would be related to the evolution of peloid fabric during the maturation process, which could increase the cation exchange positions on the clay sheets. With regard to the exchange bases, we have observed that their values are highly related to the mineral water used.

Keywords: peloids

SINGLE-PARTICLE ANALYSIS OF ATMOSPHERIC INORGANIC AEROSOL IN THE BASILICATA REGION (SOUTHERN ITALY)

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150 samples of airborne particulate matter (PM10) were collected from April 2007 to July 2008 in four different areas of the Basilicata region (southern Italy). A total of about 150.000 particles was analyzed by a Field Emission Scanning Electron Microscope equipped with an Energy-Dispersive Spectrometer (FESEM-EDS). The data set was reduced by INCA Feature software using mineralogical criteria. Eight particle groups were identified among which Silicate, Sulfur and Industrial particles were found to be the most abundant. Allumosilicates are by far the most common type of particles even if a part of these can be spherical-shaped fly ash particles. The industrial area of Potenza, characterized by metallurgic industries, seems to affect significantly the high presence of metal particles (mainly Fe-Zn spinels) found in many samples analyzed. The anthropogenic pressure given by Na, Cl and Na-S particles found both in the Lavello and Matera samples is likely to be linked to combustion processes from waste dumps or incinerators situated in these areas. The Viggiano area is episodically characterized by high concentrations of calcium sulphates and S-only particles as well as a significant presence of siliceous nanospheric particles aggregate. The Viggiano sampling station is situated close to a big oil rig which is likely to be the major cause of the presence of these particles in the atmosphere. Significant differences were found in the particulate concentration and composition of the samples collected in different seasons and different parts of the day. In summer crustal particles are the most abundant, while in winter both sulfur-rich particles and industrial particles are the most abundant, especially during the nighttimes due to climatic conditions (atmospheric stability, thermal inversion etc.). Sulfur-rich particles are more concentrated during the daytime because of solar radiation and anthropic emissions.

Keywords: single-particle analysis , airborne, Scanning Electron Microscopy

ASSESSMENT OF MERCURY LEVEL IN CANNED FISHES (TUNA AND BONITO). INFLUENCE OF THE TECHNOLOGY AND TOXICOLOGICAL RISK

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Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine fishes. Mercury is a known human toxicant and the primary sources of mercury contamination in man are through eating fish. The aim of this study was the determination of the mercury content in samples of canned tuna (*Thunnus thynnus*) and canned bonito (*Sarda sarda*), and in fresh fish. It was carried out the statistical analysis of the factors that influence its accumulation (packing, preparation and commercial brand), and the evaluation of the toxicological risk due to its consumption 110 samples, commercialized in Galicia (Spain), were subjected to digestion, in acid medium on a microwave station. The determination of mercury content was performed by inductively coupled plasma mass spectrometry (ICP-MS). As results, considering the studied presentations (packing), the order for the mercury content was: fresh > canned > glass container. The glass presentation was the least contaminated with average value of 0.3111 µg/g wet weight. According to the preparation type, levels of mercury were: oil ~ natural > pickle. As for the commercial brands, statistically significant differences were not observed, and “Albo” showed the lowest contents. The results of this study indicate that tuna and bonito fishes have concentrations below the permissible FAO/WHO levels for this toxic metal (1 µg/g), except in two samples of fresh tuna that exceeded this limit. In general, taking in account the participation of tuna and bonito, in Spanish diet and the mercury concentrations in this study, a consumption of these species, canned and fresh, does not represent a toxicological risk, except for pregnant women.

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Keywords: mercury, canned fishes, technology

WORKERS' ASBESTOS EXPOSURE ASSESSMENT IN QUARRYING THE GREENSTONES (OPHIOLITES) IN THE PARMA PROVINCE

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In the province of Parma we count the highest number of active Greenstones quarries. A regional survey was carried out in the years 2002-2004 in order to analyze the extracted materials and to define the workers' exposure to asbestos. In 2009-2010 a new survey was conducted to refine the research. The investigated productive sector has in total a few dozens of employees, seasonally working. The Apennine ophiolitic materials are peculiar ones, the simultaneous presence of fibrous and non fibrous serpentine makes an interesting comparison between different microscopic analytical methods. The 11 mining sites are homogeneous in types of activities (with the exception related to the use of explosive charges in a single slot). In 4 sites there was a monitoring of the workers assigned to the typical works in a quarry: excavator and wheel loaders driver, truck driver and manager of the mill. We can make considerations on the characterization of tasks even if we have a limited number of samples. The sampling was performed in accordance with the methodology established by UNI EN 589/97. We collected 13 samples of a personal nature (Cp), corresponding to n. 7 exposures for an entire work shift, as indicated by the WHO 1997 method. The filters were analyzed in phase contrast optical microscopy - PCOM for comparison with the limit value (LV), concentration in ff / cc and / or ff / liter and Scanning Electron Microscopy – SEM, both to compare the two methods and to verify the extent of the presence of asbestos fibers. The personal exposure data were statistically processed to determine the applicability of the standard UNI EN 689/97: log-normal distribution, GSD, homogeneity of the investigated group and, by the software application ALTREX we calculated the probability exceeding the LV (% Pn) with its confidence interval. Regressions were performed for comparisons between analytical methods as well as counts of total fibers and asbestos fibers. The results of the survey, concerning occupational exposures, point out that the process of extraction of green stones must be kept under control (ORANGE situation in accordance with Appendix D of the UNI EN 689/97), but above all, they suggest to think about the operative method of mining and quarrying and the intended use of the extracted materials (coarse pieces rather than crushed and powder).

Keywords: asbestos, ophiolites

SIMULTANEOUS DETERMINATION OF PHARMACEUTICAL COMPOUNDS IN ENVIRONMENTAL SAMPLES BY SPE AND GC-MS

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Pharmaceuticals are a new class of widespread environmental pollutants. These compounds and their bioactive metabolites can be continually introduced to the aquatic environment as complex mixtures through industrial discharges, effluents from sewage treatment plants (STEP), aquaculture and livestock farming or leaching of landfills. The sewage system is an important key point to control the environmental contamination, but treatment plants are often unable to remove efficiently a substantial part of the pharmaceuticals. Therefore several pharmaceuticals persist in the treated water and contaminate the environment reaching levels ranged from ng L⁻¹ to g L⁻¹. Nevertheless, their presence in the aquatic environment and their impact on aquatic biota and on human health have not been adequately studied yet, although there is some experimental evidence that pharmaceuticals may cause harmful effects such as morphological and metabolic alterations on aquatic species and induction of antibiotic-resistance in aquatic pathogenic bacteria. The purpose of this study was to present a simple procedure for simultaneous determination of ibuprofen, caffeine, diclofenac, paracetamol and ketoprofen at trace level (ng L⁻¹) in environmental samples using Solid Phase Extraction (SPE) preconcentration, followed by derivatization with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) and gas chromatography–mass spectrometry (GC–MS) analysis. SPE was carried out with WCX cartridge while extraction volumes were 500 mL for the Waste Water Treatment Plant (WWTP) and 1000 mL for natural water samples. The LODs of individual compounds, determined by calculating the standard deviation of five replicate analyses, ranged from 0.8 ng L⁻¹ (caffeine) to 2.8 ng L⁻¹ (ketoprofen) for tap water, while for wastewater LODs increased by a factor of 10. In order to evaluate the reliability of the method, it has been applied to the analysis of different water samples: surface water taken from Galeso River, Battentieri River and D'Aiedda Channel (Mar Piccolo basin of Taranto); surface sea waters influenced by urbanization (taken from Mar Grande basin of Taranto); wastewater coming from a WWTP effluent (about 100.000 P.E.); drinking water. Results obtained showed that concentrations varied from not detectable value for surface waters to several hundreds of nanograms per liter for WWTP, confirming the suitability of the method for multi-residue analysis of different environmental matrices.

Keywords: pharmaceutical compounds, SPE extraction

THE EFFECTS OF COLEMANITE ON TESTICULAR IN RATS

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Borate minerals are one of the most important and strategic minerals for their use as antiknock agents in gasoline, medicine, antiseptic, preservative agent and as a washing cleansing. Borate mine operations are very important to facilitate the development of a predictive capability for the environmental behavior of borate and similar mineral deposits and landfills for future use. Colemanite is one of the most important boron minerals used for production of boric acid. In some studies, it was reported that high dose of boric acid exposure produces testicular lesions in adult rats. The aim of this study is to investigate whether the effect of colemanite on testicular in rats. Sixteen male wistar rats (body weight 200-250 g) were used in the experiments. They were randomly divided into four groups. The first group was used as a control. The other groups were high-dose colemanite, lowdose colemanite, and high boron dose. High-dose colemanite (164.8 mg/kg day), low-dose colemanite (4.12 mg/kg day), and high boron dose (80 mg/kg day) were given through oral gavage once daily for 4 weeks. The control group was given distilled water. The first blood samples were taken before beginning the study and the second samples obtained 4 weeks later. Serum FSH, LH, inhibin B, and SHBG levels were measured by ELISA in all groups. Testis tissues were examined by light microscope. The rat apoptosis RT² profiler PCR array (SA Biosciences TM) was used to evaluate the expression profiles of 84 key genes which are strongly related with programmed cell death. There were no notable changes of seminiferous tubules, basal laminas, and leydig cells of the rats in all groups. There is no significant difference between the values of basal FSH, LH, inhibin B and 4 weeks after colemanite administration. There is also no significant difference apoptotic genes expression levels in testes tissue of rats between groups. This study is found that the colemanite has not formed testicular damage dependent on dose and duration. More comprehensive studies are needed on this subject.

Keywords: boron, reproductive disorders, colemanite miners

HIGH RESOLUTION MAPPING OF METAL CONTAMINATION IN AN URBAN SPORTSGROUND (GALWAY, IRELAND) USING ORDINARY COKRIGING WITH MAGNETIC SUSCEPTIBILITY DATA

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Lead contamination in soils poses a serious threat to human health and in particular, children playing on a lead polluted urban sportsground are potentially at risk to metal exposure. The production of maps for metal distribution in urban soils is important for both understanding the geochemical processes involved and the implementation of related environmental management policies. The aim of this study was to generate maps of metal (Cu, Pb and Zn) distribution at increased resolution in a contaminated urban sportsground (South Park, Galway) in Ireland. This study was carried out using the geostatistical technique of ordinary cokriging with magnetic susceptibility (MS) as a covariate. The MS was examined at a grid density of 10×10 m. Soil samples were collected at a lower density on a 20×20 m grid and the metal content was determined using a portable X-ray fluorescence (P-XRF) system. Strong positive correlations were found between MS and concentrations of Cu, Pb and Zn in the soil. The ordinary cokriging method allowed for the enhanced estimation of map values when the distribution of a secondary variable (MS) is sampled more intensely than the primary variable of interest (concentrations of Pb, Cu and Zn). Validation results demonstrated that the cokriging predictions facilitated the generation of more accurate prediction maps for metal concentration (Cu, Pb and Zn) using MS data, rather than maps produced using metal concentrations alone with ordinary kriging. Prediction maps of individual metal contaminants (Cu, Pb and Zn) were also produced for comparative purposes.

Keywords: metal contamination, magnetic susceptibility, geostatistics

HEAVY METALS IN THE SURROUNDING WATER AND SEDIMENTS OF TAILING DAM OF SASA MINE

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Discharge of contaminated water associated with the storage of slag flotation in the tailing dam, represent a serious environmental problem that affects both surface and groundwater.

Water and sediments samples were analyzed for heavy metals in the vicinity of the Sasa Mine, along the Kamenicka and Bregalnica rivers flows into the Vardar River. The investigation results showed high concentrations of certain heavy metals (Mn, Zn, Cd, Pb and Cu) in water and sediments that pass or derived from the vicinity of the mine Sasa. The concentrations of this metals are highest near tailing dam of SASA mine. Going to the inflow into the Lake Kalimanci concentration of these metals are reduced to almost clean water and sediments at the exit of the Lake. This may indicate that standing water in the Lake resulted in the sedimentation of the heavy metals.

Keywords: heavy metal, water, sediments

ARE PELOIDS MEDICINES?

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Certain types of mud have been used worldwide for ages for healing and cosmetic purposes. To some of these types of mud the name peloid had been attributed for the first time in 1933 to encompass the different terms employed in different languages for the natural sediments that in an adequate wet state were used for therapeutic purposes. However, on the last decades the literature on therapeutic and cosmetic muds and peloids appears to be pretty confused, for some authors mud and peloid, and consequently mud therapy and pelotherapy are considered synonymous, for others they are not so. Therefore, effectively, what is a mud? What is a natural peloid? Is any type of mud a natural peloid? What is a peloid? What types of healing mud and natural peloids are known and how are they individually defined? What distinguishes mud therapy from pelotherapy? Are peloids medicines? These questions and the corresponding responses will be dealt with and discussed in the present paper. Peloids, as a rule, undergo a more or less complex manipulation or engineering process; therefore, their healing properties could be attributed not only to the natural components they bear, but also to any other natural or artificial compounds that could be created or added in order to respond to a particular function. Both natural peloids and peloids are being used under medical counseling and accompanying in Health Resort Medicine or Spa Therapy Centers. Although still requiring more scientific evidence there are sufficient clinical evidence on specialized literature, showing at least the short-term benefits of peloids. Such benefits are being attributed to a combination of factors, and within these mechanical, thermal and chemical effects. Clinical evidence based on epidemiological emphasizes the benefits of pelotherapy on degenerative and inflammatory rheumatism taking advantage of peloids analgesic, anti-inflammatory, anti-oxidant and anti-microbial there is evidence of positive effects of peloids on dermatological affections, especially on psoriasis and on skin care functions (cleansing, degreasing, exfoliating, hydrating, tonifying, and reaffirming).

Keywords: peloids, spa therapy, skin care

SPECIATION OF Mo(VI) OXYANIONS IN NATURAL WATERS

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Molybdenum is an essential trace element, whose mobility is highly dependent on the hydrological cycle. In most conditions prevailing in natural waters, Mo(VI) anions are the only thermodynamically stable soluble species. So, the speciation and concentration of the main anionic components are important in determining its bioavailability and environmental impact. Its chemical speciation in natural aquatic scenarios has been poorly studied mostly because molybdenum biological relevance has been only recently acknowledged. In this work we report the potentiometric study of oxyanions of Mo(VI) and their interaction with some other metal ions: Na⁺, K⁺, Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺, Cu²⁺, Zn²⁺ and Cd²⁺. Experimental conditions were chosen to simulate the natural waters media (20.0 °C, low ionic strength, 0.15 M). The results show that, in the absence of metal ions, MoO₄²⁻ is the predominant species for pH values above 4.4. The formation of the protonated forms of MoO₄²⁻ and of the polynuclear species only occurs for acidic conditions. For samples containing low molybdenum concentrations, such as those normally encountered in natural waters, HMoO₄⁺ predominates from pH 3.6 to pH 4.4 and H₂MoO₄ is the most abundant species below pH 3.6. Polymeric species [Mo₈O₂₆]⁴⁻ and [Mo₇O₂₄]⁶⁻ appear only when the total molybdenum concentration is greater than 1 mM, being of no relevance in natural waters. The stoichiometry and the stability constants of the formed species in the presence of metal ions were also measured. Cation charge has a major influence on the thermodynamic equilibria: while interaction with the monovalent ions is negligible, the M²⁺ cations are bound to anionic molybdenum species to a considerable extent. For total molybdenum concentration below 1 mM, the predominant form of molybdenum (VI) is still MoO₄²⁻ above pH 4.4, with a variable percentage of [M(MoO₄)], depending on the metal ion concentration. As the pH value becomes lower than 4.4, the most abundant species become [M(HMoO₄)]. For example, 10⁻⁷ M Mo(VI) in the presence of mean natural waters concentrations of Ca²⁺ (16.5 mM) shows the predominance of [Ca(MoO₄)] for pH values above 4.4, and [Ca(HMoO₄)]⁺ for more acidic media. So, results show that in conditions simulating natural waters, availability of soluble anionic molybdate species is strongly influenced by pH media and the presence of +2 metal ions.

Keywords: natural waters, speciation, molybdates

PT-BASED ANTI-CANCER TREATMENTS - A GEOCHEMICAL PERSPECTIVE ON BIOCHEMICAL INTERACTIONS

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Metabolism of platinum (Pt)-based anticancer drugs begins as soon as it enters the blood stream. Though doses, on average, range from 150 mg/m² to 400 mg/m² only about 1% of the cisplatin that enters the cell actually binds to DNA. The mode of action of cisplatin and other Pt-based anticancer drugs is well known as are the associated toxicologic impacts and long-term health impacts (late effects). Understanding the geochemical behavior of Pt and other metals reveals potential deleterious interactions between Pt, Cd, and Zn. These potential interactions merit significant attention given the late effects associated with Pt-based treatments. This presentation discusses on the potential interactions of Pt and essential metals as well as explores the utility of Hg, Cd, and Cr as homologs to evaluate the processes associated with late effects and long-term Pt circulation.

Keywords: (Pt)-based anticancer drugs

IODINE IN GROUNDWATER AND HUMAN HEALTH IN DENMARK

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Increasing awareness of the importance of medical geology in Denmark has resulted in initiation of a project on iodine in the hydrological cycle and human health. The presentation will give a detailed description of the new project and preliminary results will be presented. Endocrinological research has shown that both a too high and a too low iodine intake are important for the incidence of a number of diseases related to the function of the thyroid gland (e.g. Laurberg et al., 2003). In Denmark geographical differences in iodine intake are partly caused by different iodine contents in drinking water (Laurberg et al., 2003). As a consequence the Danish population receives iodized table salt. Danish drinking water supply relies entirely on groundwater. The content of iodine in groundwater is affected by atmospheric deposition, desorption from sediments and geochemical reactions in the hydrological cycle. Therefore there is a need for investigations of iodine in the whole hydrological cycle in order to elucidate the geographical differences in iodine uptake from drinking water. A Danish 3-years project has just been initiated (2011-2013) aiming to study the variations in iodine bioavailability in groundwater and to evaluate the human health effect. The project includes the iodine cycle from precipitation over soil water, groundwater and finally to tap water.

The project consists of: 1.) Statistical designed sampling and analytical methods development for quantification of inorganic and organic iodine species under different hydro-geochemical conditions in Denmark 2.) Interpretation of existing iodine groundwater-data in the Danish geo-database JUPITER 3.) Testing of advanced methods (e.g. synchrotron generated K-edge XANES) for determination of the specific organic and inorganic iodine species 4.) Evaluation of the geographical distribution of iodine in groundwater and human health.

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Keywords: iodine, thyroid gland, biogeochemistry

NATURAL AND ANTHROPOGENIC POLLUTANTS IN LAKE SEDIMENTS IN HANOI CITY

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There are many lakes and ponds that are the remains of paleo river channels of the Red River in Hanoi city. A number of these water areas have decreased with urbanization. According with unplanned reclamations, many water areas have lost surface outflow. On the other hand, untreated waste waters from households flow into these water areas. Also, groundwater that is one of the main resources of water supply in Hanoi city has high concentrations of metallic elements (e.g. Fe, Mn, As) and NH₄. Origin of these metallic elements is considered to be rocks that are distributed in the upstream area of the Red River. Therefore, these water areas have been contaminated by not only natural pollutants but also anthropogenic pollutants. However, it is estimated that the sediments in these water areas absorb, concentrate and decompose a part of pollutants. The objective of this study is to clarify the function of the lake sediments from the view point of solute transport with water cycle. We collected water samples and sediment core samples from the four small lakes that were distributed in suburban areas of Hanoi city and abstracted pore water from the sediments by centrifuge. Chemical components such as major dissolved ions, metallic elements and TOC of pore water and sediments were analyzed. Results of analysis suggested that the sediments absorb and concentrate the most of metallic elements. These lakes were in oligo-aerobic condition due to eutrophication that was induced by inflow of untreated waste water. EN.H.E. calculated from the result of ORP of the sediments in these lakes that were composed of silt or clay showed positive value. Also, concentrations of Fe²⁺ in the pore water were very low. Therefore, Fe in the pore water and the sediments was considered to exist as Fe(OH)₃ and absorb the metallic elements such as As. On the other hand, concentration of NH₄⁺ in the pore water increased with depth. It was estimated that organic substances were decomposed in the sediments. In this presentation, we will show the depth profiles of chemical properties of the pore water and the sediments and discuss about the behavior of pollutants in the sediments.

Keywords: urbanization, pollution, water area

CHANGING WATER ENVIRONMENTS: THE INTERACTION BETWEEN VITICULTURE, WATER USAGE AND SEDIMENTS

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The Sunraysia district in South Eastern Australia has been a viticulture centre for over a hundred years. The soils, within the grape districts of the Murray Basin, have been subjected to flood and aerial irrigation methods for over a century although recently the move towards less water intensive methods has been encouraged. The identification of salinity issues associated with irrigation were first identified in the 1940's and a system of subsurface drainage was placed below the vineyards to manage the perched water table, reduce potential salinity issues and allow the continuation of successful grape growing in the region. The drainage system remains in place and essential for salinity and nutrient management however the appearance of crystalline blockages within the network is of concern. An investigation has been carried out on the nature and composition of the blockages. This presentation explores the "secrets" unlocked from within the calcitic sediments that are contained in the terra cotta subsurface drainage system first laid down during the early 20th century. The crystalline blockage material was subjected to chemical and mineralogy analysis revealing a history of chemical capture. The examination of the sediments, accumulating for 80 years, present a history and insight into the nature of the chemicals that have lodged in the drainage system over time and include fungicides, soil enhancers, growth promoting elements applied to the grapevines during the growing season. The examination of the sediment provides us with a picture of the types of minerals/materials that were present during the times when drainage waters were discharged directly into the iconic Murray River. The significance of this discharge is evidenced by usage with 3,780GJ extracted from the river annually. Salinity and nutrification are known and ongoing problems.

Keywords: water quality, sedimentary record

A MINERALOGICAL AND TOXICOLOGICAL ASSESSMENT OF THE HEALTH HAZARD OF ASH FROM THE 2010 MERAPI ERUPTION

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Mt. Merapi, Java is amongst the most active volcanoes in Indonesia and lies immediately north of the major city of Yogyakarta. The volcano commonly erupts viscous lava, forming an unstable dome in the crater. However, on 26 October 2010, a major explosive eruption began, with pyroclastic density currents (PDC) damaging nearby villages. Volcanic ash deposition was widespread but activity decreased around 9 November with cessation of ashfall by the end of November. With influx of ash from lahars and the history of mining of deposits in the region, it is likely that ash will continue to affect communities over the coming years. Following media reports of wide-spread respiratory health problems and the fact that people were returning to ash-covered homes, we launched an assessment of the risk of susceptible people developing respiratory diseases, such as asthma and silicosis, and associated diseases such as tuberculosis.

20 samples of fresh ash were sent to the UK and also collected by us (ash, lahar and PDC deposits) in early December 2010, when air quality assessment was also carried out. The ashfall from Merapi varies in the amount of respirable (< 4 µm diameter) ash (1.4 - 15.6 vol. %, typically < 10 vol. %, by laser diffraction). This range is typical of that observed in other explosive eruptions. The finest sample was erupted during the initial explosions on 26 October and its fineness may be attributable to the disruption and disintegration of an existing dome as values are in line with those seen in dome-collapse eruptions. The ash resulting from PDC, collected in people's houses, is also very fine-grained with two samples having 19 vol. % < 4 µm material. However, the sample collected from a lahar deposit (which might be mined at a later date) contained no respirable particles. The amount of crystalline silica varied amongst samples. Most samples contained 3-6 wt. % cristobalite (by XRD-PSD), typical of an explosive eruption at a dome-forming volcano (cristobalite is produced primarily in volcanic domes or through alteration of the edifice) although 3 samples contained 9-10 wt. % cristobalite. The quartz content of the ash was negligible (as magmatic quartz phenocrysts are not dominant minerals in trachybasaltic/andesitic rocks). Haemolysis assays were negative. Other analyses are ongoing at time of writing. The results will add to our currently limited knowledge on the health impacts of ash in volcanic crises in low-income economies.

Keywords: volcanic ash, health, Merapi

EVALUATION OF URINARY ARSENIC IN CHILDREN AND THEIR MOTHERS LIVING NEAR AN INDUSTRIAL COMPLEX (ESTARREJA, PORTUGAL)

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The Chemical Complex of Estarreja (CQE), one of the most important poles of the Portuguese chemical industry, is located in the north littoral of Portugal and has been operating for more than seven decades. The CQE is composed of several chemical industries which are recognized as important inputs of heavy metals into the environment. The most important inputs are chiefly related to past industrial activities, namely, the production of sulphuric acid from arsenopyrite roasting (e.g. As, Cu, Ni, Pb and Zn) and from a chloralkali plant (Hg). Nowadays the situation is different (EEC legislation), but for a long time the liquid industrial effluents have been discharged to the sewage outlet coming from the factories, and the solid wastes were deposited in the soil without prior treatment. These soils are mostly permeable, sandy soils with low humus content, often used as pasture and agricultural land. Recent studies (Inácio et al, 2010) show high levels of arsenic in soils (above 10,000 mg kg⁻¹) and forage plants (maximum concentrations in green shoots are 255 mg kg⁻¹) of this area. However, there are no studies in order to investigate possible relationships to public health problems. The main purpose of this study was to evaluate the urinary arsenic levels in local residents. The data were collected in January 2011 from 85 children aged 7 to 14, and their mothers, from the Estarreja area (parish of Beduído and Veiros) and from a reference area (Vagos, parish of Ouca). The parish of Ouca, located 40 km south of Estarreja, was selected as the reference area since it has no significant industry, but has a similar geology, pedology and population lifestyle. 95% of the individuals selected live in these places for more than five years and more than 50% live there for more than twenty years. The data presented were collected from questionnaires and from the first morning urine samples. The preliminary results show that, with the exception of a few cases in Estarreja children, deserving further studies, urinary arsenic levels are generally similar to those reported for the general population in European countries (Fillol et al, 2010).

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Keywords: urinary arsenic, human health, children

A STUDY OF THE RELEASE OF ASPIRIN FROM MODIFIED SURFACE OF THE NATURAL CLINOPTILOLITE

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Zeolites as porous materials with well-ordered structures attract a great attention for storage and release of organic guest molecules. In this study, clinoptilolite rich natural zeolite (NZ) from south region of Serbia has been investigated as a carrier for controlled release of aspirin. Immobilization of aspirin on NZ was performed by adsorption. In order to improve the adsorption ability of clinoptilolite, NZ was treated with cationic surfactant benzalkonium chloride (BC). BC was used to modify the NZ surface from partial monolayer to a bilayer coverage. Adsorption of aspirin was performed using 500 and 1000 g ml⁻¹ aspirin solutions. It has been found that the NZ with bilayer BC coverage (NZ-BC) exhibits the highest aspirin uptake. Aspirin delivery from the NZ-BC displays two stages. The first one occurs rather sharply, about 40% within first 15 minutes. Afterwards, the release proceeds more gradually. About 50% of the immobilized aspirin was delivered from the NZ-BC during 6 hours. Release profile indicates that the delivery is controlled by a diffusion process in the first stage, whereas the electrostatic interaction between the carboxylic groups of aspirin and ammonium cations from BC are predominant in the second stage.

Keywords: clinoptilolite, aspirin, controlled release

ASSESSMENT OF INHERENT TOXICITY OF CERTAIN ROCKS AND ITS IMPACT ON HUMAN HEALTH – A STUDY AT PAMBAR RIVER SUB – BASIN, NW TAMIL NADU, INDIA

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Minerals present in the rocks will be differing from their physical and chemical properties and this determines the intensity of impact of inherent toxicity of rock. The essence of rocks will be seen readily in soil and groundwater by weathering and rock – water interaction in aquifers, respectively. By studying these elements the inherent quality of rocks and transformation of this to the environment can be understood. Therefore a study was conducted in Pambar River Sub – Basin, NW Tamil Nadu, India, to see the interaction of rock with water and soil and the impingement of these natural components on human health. Samples of groundwater, rock and soil from several locations of the basin were collected and analyzed for chemical composition. Ion chromatography was used to cognize the composition of groundwater; similarly, EDAX analysis evidenced the chemistry of rocks and soils. The essential ion that decides the quality of groundwater is Fluoride. The presence of fluoride at different quantities has different effects on human health. The desirable range of fluoride in drinkingwater is 0.6 to 1.5 mg/l (BIS, 1992). In the study area most of the groundwater is offered with fluoride ion above 1.5 mg/l up to 3.85 mg/l, by the rocks and fractures that form the aquifer system. Analysis of rock indicates the abundance of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$) mineral with 20% calcium, 9.5% phosphate and chlorine 2.3%, in the Carbonatite intrusion which leads to the concentration of fluoride in groundwater. The intake of fluoridated water affects the human health by driving them to dental and skeletal fluorosis. In the study area children below the age of 10 years and people who are residing there for generations are displaying dental fluorosis. And also, the groundwater in the area is hard to very hard because of higher amount of Calcium and Magnesium ions in groundwater, because of release of these ions from calcites and pyroxenes in the rocks of different origin. Accession of more amount of calcium has lead to development of kidney stones. There is another way of transformation of the ions to human health and that is intake of food products that are cultivated in the soil resulted from weathering of the rocks. The analysis of the components in vegetables and spices grown in the area are showing dominance of the minerals which are dominant in the soils. Even though several studies were conducted in the area to delineate the result of rocks and water on human health this is a comprehensive study of all the aspects of impact of rock through various components to human health and has proved the contribution of rocks to human health in various ways.

Keywords: toxicity

A STUDY ON HYDROGEOCHEMISTRY OF GROUNDWATER IN THE CHAHAR FARSAKH, SOUTH- EAST OF BIRJAND, IRAN

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In order to make an appraisal of the hydrogeochemical specifications of the groundwater in south-east of Birjand, Iran a selection of about 9 water sources including qanat and spring was made in Chahar Farsakh area. Physical parameters such as Total Dissolved Solids (TDS), EC, pH, hardness and major ion concentrations of groundwater samples were taken into consideration. Hydrogeochemical data suggest that the groundwater is mostly Cl-SO₄ type. Aquifer materials varying from limestone to alluvial sediments. In the case of TDS, there is a considerable amount of dissolved ions in the water samples. Total hardness (TH) based on the CaCO₃ of groundwater widely varies from 1445.87 to 259.6 (mg/l). High TDS and TH values of the samples indicate the presence of the saline groundwater system that should be consider as a great health concern in the study area.

Keywords: groundwater, total dissolved solids, Chahar Farsakh

COLIPHAGES DETECTION BY PCR AS A FECAL INDICATOR IN WATER

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Human pathogens, which are excreted with human and animal feces, can be cause an infection to human through water sources. Coliphage detection can be useful to monitor water sources as an indicator in a fecal analysis because many waterborne pathogens are enteric viruses and coliphages have some similarities for life cycle and characteristics with enteric viruses. Fecal samples were collected from each 10 human, cows, and chickens, respectively, in 2010. In these fecal samples, coliphage concentration was determined by plaque assay. Viral DNAs were extracted from water and fecal samples, and presence of coliphage was determined by PCR, followed by sequence analysis of the amplicons. The mean concentration of coliphages in cows were 3.7 plaque forming units (PFU)/g, and in chickens were 4.8 PFU/g., whereas coliphages were not detected from 7 of 10 human fecal samples. In cow and chicken samples, 27 of 38 (71.0%) and 12 of 48 (25.0%) plaques were positive for somatic coliphage, respectively. However, all plaques were negative in human fecal samples. Compared with those available in the GenBank databases using the NCBI BLAST program, 9 of 10 plaques from cow were closely related to coliphage NC6 (nucleotide accession no. DQ079907) which is one of Microviridae G4-like strains, and all 6 plaques were related to coliphage NC28 (nucleotide accession no. DQ079875) belongs to Microviridae -like strains. These results suggested that viral contamination from feces of cows and chickens can be easily detected with coliphages, Microviridae group, by PCR assay. In this context, coliphages, Microviridae group, can be proposed as a fecal indicator for specific animals in water environments.

Keywords: enteric virus; coliphage; fecal indicator, cow, chicken, PCR assay

EYJAFJALLAJÖKULL VOLCANIC ASH: INFLUENCE ON PM 2.5 MEASUREMENTS IN SOUTHERN ITALY

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The strong eruptions of the Eyjafjallajökull volcano (Southern Iceland) on 14th April 2010 produced injection in atmosphere of volcanic ash particles that reached Southern Italy on 20 April. In order to evaluate the falling of the volcanic ash particles onto the ground at a long distance from the eruptive centre, PM2.5 in-situ measurements were performed at the Istituto di Metodologie per l'Analisi Ambientale of the National Research Council of Italy (IMAA -CNR, Tito Scalo - Southern Italy) from 20th to 26th April 2010. Concentration of PM2.5, chemical composition, mineralogical and morphological features of the PM2.5 particles collected during the passage of the volcanic ash were investigated. Results show that PM2.5 and Al, Ca, Fe, K, Mg, Mn and Ti daily concentrations were characterized by an increasing pattern during the first days of sampling. Field Emission Scanning Electron Microscope (FESEM) observations revealed the presence of volcanic ash particles in PM2.5 samples. Complex secondary aerosols that could be related to Eyjafjallajökull volcanic emissions were found in the fine fraction (Feret Diameter 0.8µm). Moreover, volcanic ash particles were also found in the coarser fraction: they are mainly composed by mixtures of different minerals strictly connected to basaltic-to-andesitic magmas and characterised by Energy Dispersive X-ray Spectrometer (EDS) spectra always and are signed by the presence of sulfur. Finally, SEM-observed volcanic particles show the presence on their surfaces of very little particles that can be condensate phases of soluble components mainly derived from the oxidation and hydration of sulphurous anhydride released during eruptions.

Keywords: volcanic ash, chemical composition, SEM

RAPID ASSESSMENT PROGRAM (RAP) IN A SUBURBAN WETLAND IN MEXICO

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The objective was to conduct a Rapid Assessment Program (RAP) in a wetland located in Villahermosa, Tabasco, Mexico. This water reservoir is located at the College of Biological Sciences at the Juarez Autonomous University of Tabasco. This wetland is a potential area for study and a source of research practices for Tabasco's students. The great landscape on the grounds of the university is also of great value. The study analyzed the water quality in two artificial reservoirs (A and B) that were sampled in June and December. The following variables were measured; depth, temperature, pH, transparency, DO, SO, EC, turbidity, total solids, nitrates, total phosphorous, total phosphorous in sediment, chlorophyll, DBO and fecal coliformes. Using these variables, a Water Quality Index (WQI) was calculated. An inventory of both aquatic and terrestrial flora and fauna was recorded. The results showed that the water quality in B reservoir was lower during both the June and December samples. It was especially low in June, where a WQI of 41 was calculated. Consequently, some species which are contamination indicators were present in this ecosystem such as, the Pomacea flagellate and others of the dipteran order. Moreover, some flora species, which are also indicators of pollution, were present like Pistia stratiotes and Salvinia auriculata. Eight classes of fauna were recorded. Eighty-six species of wild birds dominated this aquatic ecosystem followed by reptiles with 36 species. The lowest classes were the gastropod (5), crustacean (2), insect (7) and arachnidan (1). Eleven species are in the risk category according to the Mexican Norm concerning the protection of flora and fauna, including the fish Gambusia yucatanana which is an endemic of the Grijalva-Usumacinta hydraulic ecosystem. This aquatic ecosystem has ornamental, medical and fruit plants. It is also important to point out that we found the specie Dieffenbachia seguine, which is under special protection status.

Keywords: wetlands, RAP, urban reservoir

FISH AS BIOLOGICAL HEALTH INDICATORS IN AN AQUATIC POND IN VILLAHERMOSA, TABASCO MEXICO

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The objective was to obtain biological indicators in an aquatic pond located in Villahermosa, Tabasco, Mexico. Fish assemblages were investigated and in the most dominant species, the standard length (SL), total moisture weight (TMW), condition factor (CF), hepatic somatic index (HSI), gonad somatic index (GSI) and finally, prevalence (P) and abundance of parasites (A) were measured to the nearest millimeter. Five fish species were captured on June 16, 2010 (J) and seven on December 8, 2010 (D). The *Parachromis friedrichsthalii* was the most dominant species. About 56% were male (M) and 33% females (F) in the J samples while in the D samples, about 28% were M and 71% were F. The SL for the species captured in J was 22.14±2.30 cm for M and 20.4±2.95 cm for F. For those species captured in D, the SL for M was 19.62±0.57 cm and 20.03±1.77 cm for F. The TMW was 170.42±46.82 g for M and 123.63±33.12 g for F for those species captured in J, while in the D samples the average was 142.6±6.67 g for M and 123.63±33.12 g for F. The CF variable was 0.02±0.0014 for M and 0.01±0.0025 for F in the J samples while in the D samples, the M obtained 0.02±0.0008 and 0.01±0.0018 in F species. The GSI varied from 3.75±3.04 in F species to 0.61±0.66 in M species during J and from -0.45±0.4327 in F species to -1.588±0.909 in M species during D samples. During the J samples, M obtained 1.46±0.6 and F 1.76±0.12 of the HIS variable. While in D, -0.98±0.196 was noted for M and -1.223±0.832 for F. In J samples, two nematode species were noted; the *Spiroxys* genus had 67% of P and it had a high A of (75). The *Contraecaecum* genus (Type 1) presented low P with 22% as well as low A with 0.56. In comparison, during the D samples two nematode species were noted as well as one Cestode parasite, one Copepod parasite and one Protozoan parasite. The *Spiroxys* sp presented about 92.86% of P and the A was also high with 85.64. The *contraecaecum* sp presented high P with 71.43%; but low A with 2.86. The *Posthodiplostomum* sp had low P with 7.14% and low A with 0.029. The *Plerocercoid* sp presented low P with 35.71% and low A with 4.43. The *Ergasilus* sp presented low P with 14.29% and low A with 1.21. The *Henneguya* sp had low P with 21.43% and low A with 0.86. In general, the biological indicators showed low water quality and the presence of parasites in the fish that could be potentially harmful to humans that consume this product.

Keywords: fish, biological indicators, tropical areas

DIFFERENT PHYSIOLOGICAL EFFECTS OF PLANT-DERIVED GLYCOALKALOID EXTRACTS ON INSECTS

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Many plants in the Solanaceae family contain glycoalkaloids. They are produced by the plants as natural defence factors against animals, insects and fungi that might attack them. For this reason they are considered to be used in pest control, as alternative to traditional chemical compounds. Unlike conventional insecticides, which are based mainly on a single active compound, plant-derived insecticides comprise an array of chemical compounds which indicate pleiotropic activities, affecting both behavioural and physiological processes in insects. However, our knowledge of the physiological activities of glycoalkaloids in insects is limited. To evaluate the physiological effects of plant extracts on the insect heart contraction and the haemolymph circulation *in vitro* and *in vivo* heart bioassays were performed. *In vitro* studies have showed that potato glycoalkaloid extract inhibits the contractions of the semiisolated heart of *Zophobas atratus* adult beetles, but was inactive on adults of *Tenebrio molitor* and *Leptinotarsa decemlineata*, and *Spodoptera exigua* larvae. Injections of glycol alkaloid extract to 1-day old pupae of *Zophobas atratus*, caused major disorders in the heartbeat alternations and rhythmicity and the myocardium contraction frequency. In the third hour after injection, a decrease in the amplitude contractions were observed. Furthermore, the changes in duration of the heart activity phases (anterograde and retrograde) were indicated. All cardiotropic effects of the glycoalkaloid extracts were entirely reversible in the *Zophobas atratus* pupae. Topical application of the same extract on 1-day old pupae of *Spodoptera exigua* have showed different effects. It increased the heart contraction frequency, in all phases of the heart activity up to 24 hours after exposition. These are the first reported activities of glycoalkaloids on insects' physiology.

Keywords: glycoalkaloids, cardiotropic effects, insects

STUDY OF SOIL'S QUARTZ GRAINS AS A SOURCE OF POTENTIAL AIR POLLUTION

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The presence of substances and mineral particles in the air may be harmful to health when are inhaled repeatedly. Among these substances, small particles of crystalline silica (<5 µm) are recognized. Potentially, the soil is a medium of input of particles into the atmosphere by deflation and transport (movement) by the wind. Among the great diversity of soil mineral particles, the quartz is abundant and is shown from macroscopic sizes up to silt size (50-2 µm) and even up to clay size (<2 µm), making it as material for take into account in environmental toxicity studies. Classically, it had been considered a mineral of low chemical reactivity but new studies about soil, by our Research Group, have questioned this paradigm (Spanish Ministry of Science and Innovation project no CGL2009–10671 “Revisión del paradigma de la inalterabilidad del cuarzo en suelos mediterráneos”). In this paper we propose the use of a methodology for the study of quartz grains in soils as a potential source of disease by repeated inhalation of those mineral particles. The methodology is based on a specific process by pretreatment of quartz grains of fine sand (50-250 µm) and silt (50-2 µm) fractions, detailed observation with SEM (with coupled EDX) of statistically selected grains, followed by classification in morphotypes, imaging analysis and statistical interpretation of results, with the final establishment of relative harmfulness indexes. This multi-technique has been applied to the quartz mineral from surface horizons of five modal soils from the most characteristic landscapes from the vicinity of the Granada's city.

Keywords: air pollution, quartz mineral

**MINERAL SPRING WATER IN VICTORIA, AUSTRALIA:
POTENTIAL HEALTH IMPLICATIONS OF NATURALLY
OCCURRING ARSENIC AND ANTIMONY SULPHIDES LINKED
TO A MINING AFFECTED LANDSCAPE**

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Significant global consumption of spring and mineral water is fuelled by its perceived therapeutic and medicinal qualities, cultural habits and taste. The Central Victorian Mineral Springs Region, Australia comprises around 100 naturally flowing artesian springs that have high CO₂ content and exhibit distinctive tastes. The area has a rich settlement history by miners in the 1850's and the first commercial operations of a health resort in 1895. The landscapes were affected by gold mining activities and the occurrence of with geographically proximal mine waste, mullock heaps or tailings.

Surface and subsurface sampling reveals highly elevated metalloid values in soil and rock specimens. For example, arsenic and antimony concentrations of up to 2250 mg kg⁻¹ and 32 mg kg⁻¹ respectively are recorded. The arsenic concentration is more than 50 times that of the WHO guideline for soils (40 mg kg⁻¹). These and other metalloids have similar chemical behaviour, geochemistry and potentially significant toxicity if mobilised. The potential for aquifer contamination by surface and near-surface naturally occurring metalloids is considered.

Over the last ten years, repeated mineral springs sampling has revealed elevated metalloid values. In 2003, a maximum of 0.038 mg/L of arsenic was recorded at a popular tourist spring which is in excess of the Australian Drinking Water Guideline (0.007 mg/L). Recent sampling has confirmed elevated levels at several sites and for a variety of metalloids. This is of concern because long term exposure to arsenic in drinking water is implicated in bladder, lung and skin cancer, and other cancers. It is also implicated in non-cancer diseases such as diabetes mellitus, hypertension, and cardiovascular diseases. Despite the known elevated levels, mineral water source points remain accessible to the public with some springs actively promoting the therapeutic benefits of the waters. Given that some consumers seek out the waters for their medicinal properties it follows that they may already affect health negatively or health compromised. The risk to these consumers needs to be considered and appropriate and verified analyses made available to the public.

Keywords: mineral springs, metals, health

ADSORPTION AND DEGRADATION OF SULFACHLOROPYRIDAZINE SULFONAMIDE ANTIBIOTIC INTO A HIGH SILICA MORDENITE

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Despite their well-know ability to induce high level of bacterial resistance, persistent sulfonamide antibiotics have been using in veterinary medicine without paying attention in handling and confining contaminated manure and sewage disposal. Owing to their acidic nature, sulfonamides concentrate in anionic form in water bodies where they can remain unchanged for long periods of time. In this study the removal of sulfachloropyridazine sulphonamide (SC) from water by adsorption in a high silica mordenite zeolite (MOR) with channel window dimension comparable to that of the antibiotic was investigated. The adsorption of sulfachloropyridazine by mordenite was completed within 4 h with the maximal amount of adsorbed antibiotic of 18% zeolite dry weight. The adsorption kinetics performed at room temperature and 65°C highlighted an unfavourable temperature effect. The desorption trials conducted on exhausted mordenite elucidated the irreversibility of the adsorption process. Diffractometric data allowed us to obtain clear evidences of the embedding of sulfachloropyridazine into mordenite channels as well as to exactly localize the organic species in the structure. The relevant incorporation of SC in MOR structure is confirmed by a variations of unit cell parameters as well as a remarkable deformation in the dimensions of the channel systems, when compared with the parent zeolite. The most evident effect was the lowering of Cmc_m real symmetry of the parent MOR to Cmc₂₁ after adsorption of SC. On the whole, Rietveld refinement revealed the incorporation of 2.0 sulfonamide molecules within the MOR framework, in very good agreement the saturation capacity determined by the adsorption isotherm. Upon adsorption on silanol sites of mordenite, sulfachloropyridazine was degraded to a new product identified as 4-amino-N-(6-hydroxyl-3-pyridazinyl)benzene sulfonamide. The byproduct was not formed in the absence of mordenite.

Keywords: sulfachloropyridazine, adsorption, degradation

ESSENTIAL OIL TO REDUCE THE PESTICIDES USE

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Agricultural pesticides are an heterogeneous compounds group used to protect crops against biotic and abiotic diseases. Pesticides have an high intrinsic toxicity that determines adverse effects to human health and environment. Current studies show that some pesticides are potential endocrine disruptors with pseudo-hormonal activities that interfere with the reproductive process on exposed workers. Especially in greenhouses female workers are particularly exposed to chemical risk directly for the use of pesticides and in some cases following to the inappropriate use of personal protective equipment. Studies carried out on primigravious greenhouse workers have indeed shown that there is a probable link between women's exposure to pesticides and the occurrence of reproductive disorders (reduced fecundability ratio, spontaneous abortion or preterm delivery, prolonged time-to-pregnancy and birth defects). Directive 2009/128/EC of 21 October 2009, establishing "a framework for Community action to achieve sustainable use of pesticides", proposes to reduce risks and impacts on human health and the environment and promotes use of integrated pest management techniques and agricultural alternatives to pesticides. Adoption of national plans by the Member States which, according to their specific agricultural and environmental conditions, will set up their quantitative targets to "reduce dependency on the pesticides use". To protect workers, reduce production costs and get healthier crops and less environmental impact is therefore necessary to address alternative or complementary phytoiatric practice to reduce pesticides use. In recent years is growing interest in using allelopathic mechanisms in agriculture, (direct or indirect, beneficial or harmful to a plant on another, through production of chemical compounds released into the environment). Our study proposes to test, in open-field and in greenhouse, a formulation based on essential oils, for common weeds control, to reduce level of risk greenhouse workers, consumer and environment.

Keywords: essential oils, endocrine disruptors, sustainable use of pesticides

**PRELIMINARY INVESTIGATIONS OF SOME FIBROUS
ZEOLITES WHICH MAY CAUSE ADVERSE HEALTH
EFFECTS: A CASE STUDY FROM VOLCANIC ROCKS OF
NORTHERN ITALY**

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Zeolites are secondary minerals occurring in volcanic rocks, whose genesis require high alkalinity, low temperature and low pressure conditions, due to diagenetic, deuteritic or hydrothermal processes. Among zeolites, fibrous erionite represents a well-known health hazard. Exposures to erionite fibers can cause adverse health effects identical to those of asbestos, including mesothelioma. For this reason, erionite is the only zeolite which was classified as a human carcinogen, although there may be other fibrous zeolites should not be considered intrinsically safe. Despite of the lack of epidemiological information on populations exposed to natural asbestiform minerals other than asbestos and erionite, experimental results suggest that, if breathed, all mineral fibers of similar size, habit, and biopersistence may carry the same risks for humans. In Italy, very few occurrences of fibrous zeolites was reported, but the widespread zeolitization processes of most italian volcanic deposits could suggest the local presence of such hazardous mineral, often associated with other non-hazardous and commercially exploited zeolites. In the Northern Italy a huge amount of volcanic rocks are often deeply weathered and show veins and vesicles frequently filled by secondary minerals such as hydrous silicates, silica and nonsilicates. Preliminary investigations indicate that the most common silicates are zeolites, including some fibrous species (erionite, offretite, and natrolite). Considering that the exposure to fibrous zeolites can be assumed as dangerous where anthropic activities such as quarrying or building/restructuring activities are in progress, the identification and quantification of the possible presence of these health-threatening minerals should be the first step of a risk assessment process.

Keywords: fibrous zeolite, Italy

DETERMINATION OF ACARICIDE RESIDUES IN BEESWAX

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The beeswax can contain pollutants lipophilic. These may come from the environment and beekeeping practices. The main pollutants found in beeswax are chemicals from beekeeping practices, while those arising from the ecosystem seem to be less important.

Currently acaricides are necessary on a regular basis to control Varroa. Investigations carried out in Europe show that the concentration of acaricides in the beeswax increases as the number of applications of these products is increasing and decreases very slowly in the case of a reduced use of them. In the U.S. beekeepers have noted negative consequences such as the inability of bees to generate queens or a sharp increase in their turnover rate. Many studies have been carried out to determine sub-lethal effects of acaricides in colonies of *Apis mellifera*. In Argentina the recovery of beeswax and the production of beeswax printed for commercial use is high, so it is necessary to assess the presence of acaricides' residues. We have developed a technique to detect the presence of several acaricides such as Cumaphós, Fluvalinate and Flumethrin, according to the methodology described by Jiménez et al (2005). The results show that 87% of beeswax printed exhibit residues of Cumaphós and the 37.5% of Fluvalinate. All samples that presented residues of Fluvalinate showed also residues of Cumaphós. Cumaphós residues were detected in 62.5% of beeswax recovery, Fluvalinate residues in the 37.5% and only 25% of beeswax recovery presented both the acaricides. Flumethrin residues were not detected in any sample of beeswax.

The rational behind of Cumaphós variations in the samples is the continuous application of acaricides by the beekeepers, and the accumulation of their residues from year to year in beeswax. The Fluvalinate, a pyrethroid acaricide, is not longer used in beekeeping and its presence can be due to the heavy applications made in the past and to its high persistency in beeswax. The results highlight the presence of lipophilic acaricides in beeswax and the need to analyze the effects that these products can cause in the bees colonies.

[1] Jiménez, J.; Bernal, J; Nozal, M.; Martín, M. 2005. Residues of organic contaminants in beeswax. Eur. Lipid. Sci. Technol. 107: 896-902.

Keywords: beeswax, acaricides, Varroa

CHROMIUM ACCUMULATION IN WILD EDIBLE MUSHROOMS: UPTAKE AND TOXICITY

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The environmental pollution has increased notably the interest to the fungi for its accumulation capacity of heavy metals. Chromium can be considered even a trace element, but in excessive dose is a toxic for health. The aim of this work was to provide the accumulation capacity (bioconcentration or bioexclusion) of chromium in fruit bodies of some edible mushrooms, in relation to some factors: substrate (soil acidity and organic matter content), species and ecology (mycorrhizal and saprophyte), and morphological portion (hymenophore and rest of the fruit body), and finally the evaluation of the toxicological risk derivative from its consumption. 167 edible mushroom samples of 22 species and 50 soil growing samples of forest upper soil horizon, from two differentiated zones in reason of greater or smaller pollution in the province of Lugo (Galicia, Spain) were collected. Fungi samples were divided in two anatomical portions, hymenophore and the rest of the fruit body, processed by wet digestion in the acid medium and analyzed its chrome content by ICP-OES. The obtained data were treated statistically through the Program SPSS version 19.0. As result, more accumulator species were: *Lycoperdon utrifforme* (5.76 ppm), *Coprinus comatus* (5.38 ppm) and *Agaricus campestris* (5.22 ppm). *Cantharellus cibarius* (0.726 ppm) and *Tricholoma portentosum* (0.885 ppm) accumulated chrome in minor quantity. There were not statistically significant differences between chromium levels in hymenophore and in the rest of the fruit bodies but there were for the ecology factor between mycorrhizal and saprophytic species. All mushroom species were bioexclusors of chromium (BCF < 0.5) in relation to the soil growing the mushroom. Organic matter and pH do not show a significant influence on the accumulation of chromium in the studied species. From the toxicological point of view, taking into account the participation of the mushrooms in the human diet, it can be considered that its chrome contribution, it does not suppose risk for the health of the consumer.

Keywords: chromium, mushrooms, bioconcentration factors

POTENTIALLY CONTAMINATED SITES AT SOMMA-VESUVIUS COMPLEX

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In 2009, the fluoro-edenite was discovered for the first time in Somma-Vesuvius complex, in ejectas from Le Novelle Quarry, Ercolano town. The fluoroedenite is a calcic amphibole that forms the extreme end of the series edenite-fluoro-edenite. It has different morphologies such as prismatic, acicular and fibrous and was discovered in 2000 in the town of Biancavilla, located at the slopes of Etna volcano. The discovery was linked to the observation of a significant increase of mortality from pleural mesothelioma, a disease known to be related to the inhalation of asbestos fibers. It was felt that the cause of that phenomenon could be a natural factor which turned out to be just the fluoro-edenite. Subsequent investigations demonstrated the pathogenicity of fluoro-edenite in fibrous habit. The Ministerial Decree n. 101/2003 requires the mapping realization of the areas affected by the presence of asbestos. At present the possible presence of fluoro-edenite in fibrous habit at Somma-Vesuvius complex and its possible spread has not yet investigated. Since 1995, with the creation of the National Park of Vesuvius, it's prohibited sampling for any use in that area. So it is difficult to carry out investigations on fluoro-edenite. In the Federico II University of Naples there is, however, an important collection of samples from Vesuvius: the Vesuvius Collection of the Real Museo Mineralogico. The collection boasts more than 3500 samples (minerals, lava) and about 400 ejectas, on which new investigations can be made. Recent mineralogical studies on ejectas found different types of amphiboles: tschermakite, Mg-horneblenda, pargasite, fluoropargasite and potassium-rich fluoro-magnesiohastingsites. These minerals have acicular habit, and sometimes the fluoropargasite crystals show fibrous habit. Further investigations should be conducted to understand what is the actual spread of fibrous amphiboles in rocks from Somma-Vesuvius volcanic complex and to understand what is their real danger for the population.

Keywords: fibrous amphiboles, fluoro-edenite, Somma-Vesuvius complex

ARSENIC(III) ADSORPTION FROM AQUEOUS SOLUTION BY USING FE(III)-LOADED XAD-8 RESIN IMPREGNATED WITH DEHPA

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Arsenic forms highly toxic chemicals thereby rising epidemiological problems to human health. The paper presents a novel support for arsenic (III) adsorption and its removal from aqueous solutions. The support is new solvent-impregnated resins (SIR) which is capable of selective adsorption and can be considered as an alternative adsorbent materials. SIR were obtained by impregnating Amberlite XAD-8 with di(2-ethylhexyl)phosphoric acid (DEHPA) as extractant and ethylic alcohol as solvent by dry impregnation method. In view of arsenic (III) adsorption the DEHPA-impregnated XAD-8 resin was loaded with Fe(III) ions. In order to establish the adsorption performance of the material, the influence of different physicochemical parameters (pH, contact time, ratio S:L and initial concentration of arsenic) was investigated. The maximum adsorption capacity of the material towards As(III) was determined through equilibrium studies using Langmuir and Freundlich isotherm models. The thermodynamic studies allowed us to determine thermodynamic parameters H_0 and S_0 . The kinetic studies were performed using the pseudo-first order and pseudo-second order kinetic models.

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Keywords: arsenic, adsorption, SIR

HEAVY METALS CONTENT IN URBAN SOILS OF ISFAHAN, CENTRAL IRAN

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Various heavy metals have been reported as dangerous agents to the human health and wildlife when they occur in the environment at high concentrations. The environmental exposure to heavy metals is a well-known risk factor for cancer. Cadmium and lead compounds are classified as human carcinogens by several regulatory agencies. Gastrointestinal cancers (GI Ca) are common malignancies all over the world. Twenty five percent of all cancer-related deaths are attributed to GI Ca. We investigated levels of two different heavy metals (Cd, Pb) in soils of Lenjanat region in Isfahan province, Central Iran where intensive agriculture surrounded by different industries like steel and cement making factories and mining. According to database, many people suffered from gastrointestinal cancers in this region. Two hundred topsoil samples (0–20 cm depth) were collected from agricultural and non-agricultural soils of the region and analyzed for heavy metals. Results showed that the amount of heavy metals decreased with increasing the distance from the factories. The concentration of Pb and Cd was more than 55 and 5 mg kg⁻¹, respectively. The total Cd concentration in most of the samples exceeded the suggested Swiss thresholds (0.8 mg kg⁻¹). It seems that aerosols originated from industries and mining activities are the main sources for heavy metals in agricultural soils of the area. Thus, analyzing heavy metal contents in dust could provide us a better insight to solve the problem.

Keywords: heavy metals, gastrointestinal cancers, soil pollution

ELECTRON MICROPROBE STUDY ON INCLUSIONS IN GALLSTONE: PRELIMINARY RESULTS

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In this work we present the preliminary data obtained by electron microprobe analyses on small particles included in a gallstone. The studied gallstone, yellow-brownish in colour, has a rounded shape with a diameter of about 2 cm. It was surgically extracted from a female patient, 72 years old. The gallstone was longitudinally sectioned and two pieces were obtained. One of them was polished and, prior to examination by electron microprobe, the polished surface was carbon coated. Wavelength dispersive qualitative analyses, carried out in the groundmass, revealed the presence only of oxygen. However, another lighter element that can not be detected by electron microprobe, such as H, can be present. This observation suggests that the gallstone is probably composed of cholesterol. The polished surface of the gallstone was examined by electron microscope, which allowed the finding of several particles included in the groundmass. These inclusions have an irregular shape, with a size variable from about 10 up to 60 microns. According to the energy dispersive system qualitative analyses, most of them consist of pure Ca. However several compounds containing S, Cl, K, Ca, Mg, Na and Si in different proportion have been also identified. In these latter compounds also tiny particles (less than 10 microns) of nicely shaped crystals of Ca and irregular spot of Cu have been found. Our data, although preliminary, suggest that electron microprobe can be considered an efficient tool to investigate gallstones, with special regards to their inclusions and, as a consequence, to evaluate the presence of certain elements.

Keywords: gallstone, inclusions

QUALITY OF FORMATION WATER FROM THE NIGERIAN OIL FIELDS FOR BALNEOTHERAPY

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The 21st century medicine seeks to offer Medicare at lower, more affordable rates. The need to create more access to health care delivery, and explore more therapeutic options informed the desire to undertake a research with an interdisciplinary outlook, linking geology and medicine.

Standard sampling laboratory procedures were applied to the formation water samples collected from oil companies in the Niger Delta in set between longitudes 30E - 90E and latitudes 40301N - 50201N. Results reveal favourable conditions for balneotherapy, climatotherapy, and other associated therapies within and around the Niger Delta area. Preponderant medicinal water types include mineral, hypothermal, alkaline, chlorosodic, iodinated, brominated, fluorinated, lithic and borous waters. Prospects for development in the health and economic sectors of the nation (Nigeria) through this resource are reassuring.

Keywords: balneotherapy, balneology, climatotherapy

NATURAL ENVIRONMENTAL RADIOACTIVITY IN VALIZAS RESORT, ROCHA, URUGUAY

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The Uruguayan east coast has a very rich ecosystem and a variety of mineral resources such as black sand ores, with 7 million tons of heavy minerals evaluated in the Aguas Dulces area. These ores are composed by 50% of ilmenite, 20% of magnetite, 5% of zircon, 1% of rutile and 0.6 % of monazite. As a result of this, all the radionuclides which belonging to the 238-U and 232-Th series are present in the Uruguayan east coast. The objective of this work is to evaluate how the natural radioactive contaminants transfer from the sand to other compartments. Samples were taken from Valizas Resort (34° 20' 31,42" S and 53° 47' 19,47" W). Total alpha and beta activity was measured using a Analyzing miniscaler Ratemeter model PRS-5 with a sample compartment STB-3, in sand, sea and fresh water, and plants. All samples were previously treated as follows. Sand was dried, water was evaporated and coast plant was calcinated. Background, sand, seawater and fresh water residues, vegetation ashes and a 238U standard were measured. Some representative values of the specific activity obtained are 445 + 193 (dpm/L) for sea water, 7,2 + 1,7 (dpm/L) for fresh water near the coast, 5,8 + 2,0 (dpm/L) for fresh water far from the coast 20,9 + 3,0 (dpm/g) for sand and 0,7 + 0,5 (dpm/g) for plants. The transfer coefficients are $2,1 \times 10^{-3}$ for sea water, $3,4 \times 10^{-4}$ for fresh water near the coast, $2,8 \times 10^{-4}$ far from the coast and $3,3 \times 10^{-2}$ for plants. From the specific activity and the transfer coefficients obtained, we can conclude that natural radioactive contaminants move from the sand to other compartments. The sea water has 13 times the maximum permissible specific activity for drinking water (33 dpm/L) whereas the fresh water value is below the intervention level. The transfer coefficient from sand to plant is the highest; the value obtained is in the order of results reported in the literature. Future work will be focused on determining naturally occurring radionuclide by gamma and alpha spectroscopy, in order to identify specific radionuclide transfer coefficient.

Keywords: natural radioactivity, soil-to plant transfer, black sands

EXAMINATION OF ELIMINATIONS OF VOC AND MOISTURE WITH ZEOLITES QUICKLY REACTIVATED BY MICROWAVE HEATING

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It was examined whether VOC (volatile organic compounds) and moisture were effectively eliminated with zeolite quickly reactivated by microwave heating (MWH, $f=2.45\text{GHz}$). Ethyl alcohol and toluene were used as VOC, and pelletized Na-X, Na-LSX and Na-Y zeolites and AC (active carbon) were examined as adsorbent for VOC. Adsorption properties were measured in a bag containing adsorbent of 5g and VOC of 1000-4000 ppm in air, and an efficiency of adsorption was an order of $\text{AC} > \text{Na-Y} > \text{Na-LSX} > \text{Na-X}$. Both Na-LSX and Na-X could adsorb VOC but caused desorption of VOC in an intermediate stage due to moisture. A mixture of $\text{Na-X} + \text{AC} = 2.5\text{g} + 2.5\text{g}$ caused no desorption. In MWH, temperature rise was an order of $\text{Na-LSX} > \text{Na-X} > \text{Na-Y}$. AC caused sparks during MW irradiation. A pelletized mixture of $\text{Na-X} : \text{AC} = 1 : 1$ caused no sparks but the pellet was too fragile to handle. Since each adsorbent showed a reverse aptitude for the adsorption of VOC and MWH, a simultaneous use of Na-X and AC was examined. A breakthrough curve of adsorption bed with $\text{Na-X} + \text{AC} = 200\text{g} + 200\text{g}$ was measured for methyl alcohol in air. After the breakthrough, Na-X was heated to ca. 570K by MWH (500W \times 15 min). Such a cycle was repeated twice, and the breakthrough curves were compared with each other. A beginning of breakthrough slightly became earlier after the second MWH than the first MWH. For toluene, a similar tendency was observed in the breakthrough curves. It was considered that a reactivation temperature by MWH was high, VOC partly decomposed and pores in zeolite were partially blocked by carbon generated from VOC. To eliminate moisture at low cost, natural zeolite (and Na-X for reference) was examined. Both natural zeolite (NZ) and Na-X of 1.5kg were fully hydrated in a container and reactivated by MWH (1000W \times 30min). This cycle was repeated 30 times, and changes of adsorption capacity C with the number of treatment n were investigated. NZ was heated up to ca. 530K by MWH and Na-X up to ca. 570K. C for both zeolites linearly decreased with increasing n , and its dependence of NZ on n was expressed by $C_n/C_0 = 1 - 2.27 \times 10^{-3}n$ and that of Na-X $C_n/C_0 = 1 - 3.27 \times 10^{-3}n$, where C_n denotes C after n th treatment. When a life of adsorbent is defined as n_l at $C_{n_l}/C_0 = 0.5$, the life of NZ is $n_l = 220$ and that of Na-X is $n_l = 152$. Dried NZ of 1kg can eliminate moisture of 19.3kg by its life in the present conditions. The result indicates that the use of NZ together with MWH is promise for the elimination of moisture.

Keywords: VOC, moisture, zeolite

URANIUM CONCENTRATION ON AGRICULTURAL SOILS NEAR CUNHA BAIXA MINE (PORTUGAL CENTRE-NORTH) AFTER A SEASONAL PERIOD OF IRRIGATION

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As in many European countries, Portugal had a legacy of former uranium mining sites surrounded or located near villages where the agriculture and livestock pastures frequently take places. This is the case of Cunha Baixa, one of the most important mines exploited (1970-1993) in the center-north of Portugal. Preliminary assessments of the impact resulting from the mining operations reported that in the surrounding mine area, surface and groundwater quality was affected throughout the mine site. As the Cunha Baixa inhabitants grow their own crops, vegetables and fruits and use shallow water pumped from wells for irrigation, it is an important issue to know the effect of this practice on soils and plants. This investigation presents and compares the results of uranium (total and soil available fractions) in a field experiment carried out in the dry season in two uranium enriched agricultural soils (U total: 21 to 60 mg/kg and 95 to 156 mg/kg in soils A and B, respectively) before and after a long period of irrigation (6 months). During this period, in different soil plots were cultivated beans (*Phaseolus vulgaris* L.) and potatoes (*Solanum tuberosum* L.) and following lettuces (*Lactuca sativa* L.) and beans. Local agricultural practices were followed and the crops were watered, according to irrigation needs, with two different water qualities: low and high total dissolved uranium concentration (< 20 mg U/L and 940 to 1040 mg U/L, respectively). At the end of the field experiments in soil plots A and B cultivated with beans and after with lettuce the total uranium content did not change significantly. Otherwise, in soil plots cultivated with potato and after with beans total uranium content increased 2 to 3 fold. These behavior was observed whatever dissolved uranium content in irrigation water. In general, the uranium available soil fractions were small and did not show appreciable differences when compared to the beginning of the experiments. The cultivated plant species in these soils shown to be able to uptake and retain uranium in the edible tissues, particularly in lettuce leaves (204-282 mg U/kg fresh weight). The results of this work highlight the needs to understand the uranium transfer in the soil-water-plant agricultural system. This knowledge is crucial as it concerns with both the chemical and the radiotoxic effects on the health of human inhabitants of former uranium mine sites by inhalation of soil particles and intake of uranium enriched food.

Keywords: uranium, agricultural soils, irrigation water

LEMNOS EARTH: QUALITY AND SUITABILITY FOR MEDICINAL USES

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In the Ancient Greek period, mud materials (Lemnos Earth) were used for medicinal uses (e.g. as antiseptic cataplasms, to cure skin afflictions, as cicatrisers, as a cure for snake bites). Hippocrates, Aristotle and others, produced classifications of medicinal earths. Most of these materials are clays, given different names depending on various factors including origin, differences in their mineralogical composition and properties. For example, Terra Samia, T. Sigillata, T. Lemnia, T. Cimolia, T. Sono / ptica, T. Eretria, T. Negra, etc (Beck 1996; Giammatteo et al., 1997).

At present, clay minerals used for therapeutic purposes are basically smectites, palygorskite, kaolinite and talc. In order to determine the quality of Lemnos Earth, its suitability and efficiency for medicinal uses a series of samples were collected and studied by various techniques. The mineralogical composition of the material was determined using XRD and SEM and it was found to be rich in smectite and specifically in Ca-montmorillonite. The chemical analyses of major trace elements and REE, as well as the determination of a series of physical properties such as CEC and BET, show that the material was suitable and effective for therapeutic purposes but prolonged use of the material could cause serial health problems.

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Keywords: lemnos earth, medicinal uses, ca-montmorillonite

IBERULITES: COMPLEX AEROSOLS. POSSIBLE SHUTTLES FOR THE TRANSPORT OF BIOLOGICAL MATERIALS

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The iberulites are a special type of atmospheric microspherulites formed in the troposphere under certain conditions and finally fall to the Earth's surface. Their average size is about 100 microns. Its name comes from where they were discovered: the Iberian Peninsula. Iberulites are co-associations with axial geometry and pinkish colour, consisting of mineral grains and noncrystalline components, structured around a core of coarse particles with a smectitic cover and a single vortex. They are formed in the troposphere by complex dustwater-gas interactions. The interactions between water drops and aerosols (dust) from the Sahara, create complex hydrodynamic conditions that cause water-dust drops, which are the precursors of iberulites. Precursor drops fall to lower levels of the troposphere and that involves the coalescence process, drying and the formation of a vortex. The core of iberulites consists mainly of grains of calcite, quartz, feldspar and dolomite. The cover is composed of clay minerals, sulfates, chlorides and amorphous silica, some of these minerals are neoformed. The overflight of areas with volcanic emissions containing sulfur (the Canary and the Azores islands) incorporates SO₂ on the surface of the iberulites. With the humidity SO₂ is converted into sulfuric acid which attacks the minerals in the cover producing new minerals (alunite-jarosite and gypsum mainly). Subsequently, the descent into the marine boundary layer (MBL) of the Atlantic Iberian-Moroccan induces the incorporation of marine salts, planktonic organisms and other biological specimens such as brochosomes, bacteria and viruses. The iberulites are large aerosol particles very fragile and brittle formed by many small-sized mineral grains, which can be inhaled into the respiratory tract. It is during the summer months when more amount of Saharan dust reaching southern Europe and iberulites are part of this dust. The adverse health effects associated with exposure to dust include chronic obstructive pulmonary disease, exacerbation of asthma and allergy, fibrosis, slower lung development in children, and lung cancer. Recently there has been observed a close correlation between Saharan dust intrusions and child and senile mortality.

Keywords: iberulites, biological materials

THE INFLUENCE OF CONNECTED URBAN AND OF EMERGING AGRICULTURAL SURFACE WATER FLOWS IN THE PRESENCE CONTAMINANTS (PHARMACEUTICAL COMPOUNDS) IN PROTECTED NATURAL WETLANDS

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The Mediterranean wetlands are unique in biological diversity and they offer multiple benefits constituting a great water reserve for the planet and to produce biomass and nutrients for the trophic chain. However, the increasing human impact and the socio-economic development of the last decades have produced important losses in these ecosystems. To study the impact of urban and traditional agricultural landscapes on natural protected wetlands new holistic and multidisciplinary approaches are necessary. In this work are methodology based in the combination of environmental forensic procedures under which different techniques, (such as Liquid chromatography-mass spectrometry analysis of 16 water samples to determine 17 domestic use pharmaceutical compounds, aerial photographs and ortophotos to map surfaces water flows and Geographical Information Systems to integrate information from different sources and to establish the territorial implications of water flows and emerging contaminants from urban systems to open water in protected natural wetlands) are combined. The work has been developed in the Natural Park of La Albufera (Valencia, Spain), which includes a coastal lagoon, marshlands, dunes and pinewoods, surrounded by rice fields in its not urbanized part. In spite of this great ecological value, it suffers impacts derived from the high human and industrial occupation, and of the hydrological contributions from the connected irrigation systems. Result shows that after treatment, the presence of 12 pharmaceutical compounds is detected in the majority of the water samples analysed. Urban agglomerations and population concentration are determinants in the number or pharmaceutical and concentrations detected. Further, the traditional irrigation drainage systems are determinant in the surface water flows from the urban systems to the natural environments. In that later case they act as interconnection mechanisms from urban landscapes to the natural open waters in the protected Natural Park. Thus, further studies are needed to determine trends and rates of emerging contaminants inflows and the impacts into the wetland water and habitats to developed effective protection policies.

Keywords: environmental health, environmental forensics, Mediterranean wetlands

Zn, Pb AND As ORAL BIOACCESSIBILITY OF LISBON URBAN SOILS

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Ingestion of dust or soil particles could pose a potential health risk due to long-term potentially harmful elements (PHE) exposure. Fourteen urban topsoil samples (public gardens and parks, playgrounds) were used to estimate the human oral bioaccessibility of Zn, Pb and As. The bioaccessibility testing was carried out through the Unified Bioaccessibility Method (UBM), validated by the Bioaccessibility Research Group of Europe (BARGE). Reference soils (NIST SRM 2711a and BGS 102), blanks and duplicated soils samples were used in order to assess the precision of the results. The comparison with the BARGE inter-laboratory values show a good precision and accuracy of the data produced by the UBM method. In the gastric phase (G), the bioaccessible fractions of Zn, Pb and As are in the ranges 31-246 mg/kg, 47-197 mg/kg and 0.86-4.78 mg/kg, respectively, and 3.3-50.5 mg/kg, 0.4-21 mg/kg and 0.98-4.39 mg/kg, respectively, for the gastrointestinal (GI) phase. Similarly to the results obtained by the BARGE group, bioaccessibility estimates for As are similar in both phases but that is a significant decrease in bioaccessible Pb and Zn in the GI phase. The different trends in Zn and Pb bioaccessibility between simulated G and GI phases are likely to be related to pH of each phase, by possible reactions with soil matrix components and potential ligands in the extracted solutions. For risk assessment purposes and as a protective measure of human health, this study uses the bioaccessibility estimates of the G phase. Significant positive correlations were observed between bioaccessible estimates in the G phase and total PHE concentrations. Linear regression analysis shows that oral bioaccessibility is affected by some physico-chemical soil parameters. In these soils, illite and smectite play an important role in the fixation of PHE in the soil. The spatial distribution of the samples shows that: higher values of bioaccessible Pb are related to high traffic and historical gardens; higher values of bioaccessible As are related with the fertilizers used; higher bioaccessibility estimates for Zn occur in samples 16, 33 and 14, respectively a schoolyard (fertilizers), a small garden near a petrol station (tyre wear) and a public park (probably a crematorium). The unified test presents some valuable data for risk assessment. Indeed, the incorporation of oral bioaccessible concentrations into risk estimations could give more realistic information for health risk assessment.

Keywords: oral bioaccessibility, potentially harmful elements, urban soil

A DIFFERENT PERSPECTIVE ON ORAL BIOACCESSIBILITY OF Cu, Zn AND Cr IN LISBON AND NORTHAMPTON URBAN SOILS

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The most common potential harmful elements (PHE) for human health are As, Cd, Cr, Cu, Pb and Zn. Incidental soil ingestion by children is an important exposure pathway for assessing public health risks associated with exposure to PHE contaminated soils. Children spend more time playing outdoors and through their hand-to-mouth actions are particularly vulnerable to the risk posed by PHE. However, some of these PHEs are essential for the metabolism of living organisms, children included. Elements such as Cr, Cu, and Zn are required by organisms at low levels but become toxic at some higher levels of exposure. This study compares the quality of urban soils from two cities (Lisbon and Northampton) in terms of their content in essential elements to human health. The methodology used is based on the results of oral bioaccessibility testing, which was carried out using the UBM Barge method. Bioaccessibility estimates are in the range of 31-246 mg/kg for Zn, 0.33-2.43 mg/kg for Cr and 2.7-51.7 for Cu in the soils of Lisbon and 6.1-95.4 mg/kg for Zn, 0.33-65.1 mg/kg for Cr and 3.6-36.5 for Cu in the soils of Northampton. Soil ingestion studies have been performed for exposure and risk assessment purposes and the US EPA has recommended values of 0.2 g/day and suggests that a reasonable ingestion rate for children with pica is 10 g/day. Considering the maximum bioaccessibility estimate (more critical due to eventual toxicity) and the Recommended Daily Intake (RDI) for children aged from 1-8 years old, the results show that: for Zn, a child needs to ingest about 49 g/day of Lisbon soil and 125 g/day of Northampton soil to reach the necessary RDI requirements; for Cu, the amount of soil needed is 9 g/day for Lisbon and 12 g/day for Northampton to fulfil the dietary Cu requirements; for Cr, a child needs to ingest about 6 g/day of Lisbon soil and 0.23 g/day of Northampton soil to reach the RDI. This is a very straightforward and broad-brush approach and it doesn't take into account factors such as: soil is only one source of these elements in a child's diet; the finest soil fractions are suspended and easily inhaled; absorption of elements from soil is modified by the presence of food in the gastrointestinal tract. However, it allows for comparison of the soil composition and quality in terms of essential element concentration. Bioaccessible Cr in Northampton soil raises some concern since a soil ingestion of 0.9 g/day would reach the toxicity level for young children.

Keywords: bioaccessibility, essential elements, urban soils

**DEVELOPMENT OF AN ANTI-CELLULITE PELOID
CONTAINING BENTONITE OF PORTO SANTO ISLAND,
MADEIRA ARCHIPELAGO**

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The relevant properties of bentonite and biogenic carbonate sand of Porto Santo Island, Madeira archipelago have been investigated in order to use these materials for therapeutic applications and topical use in local spas and Geomedicine centers. The aim of this work was to design an anti-cellulite peloid using bentonite (smectite rich clay) from Porto Santo and two plant extracts (Horse Chestnut Extract and Ivy Extract). The application of hot peloid causes the enlargement of pores facilitates the absorption of cosmetic ingredients to deeper layers of the epidermis is absorbent and moisturizing. Its use is recommended for initial treatment of lipodystrophies and slows down the development process of cellulite due to its ability to stimulate the venous and lymphatic circulation and its anti-inflammatory effect.

In this study, formulations containing 20% of bentonite <180 microns and 10% of plant extracts were prepared. Viscosity and texture analysis of the peloid, as well as the firmness and adhesiveness, were performed. The viscosity tests were performed in a rotating viscometer Brookfield DV-E (Germany).

To evaluate the effectiveness of the developed peloid, centimeter measurements and skin biometric techniques (with Multiprobe Adapter Systems MPA® from Courage & Khazaka) were used before and after peloid application on thigh and arm of human volunteers. After 20 minutes of hot peloid application an increase of skin hydration, a slight increase of skin pH and no skin irritation were observed at the application sites. The appropriate characteristics of consistency and adhesiveness and the results obtained in the centimeter measurements and biometric techniques suggest that the developed peloid has anti-cellulitis potential.

Keywords: peloid, bentonite, cellulite

EFFICACY OF EXFOLIANT FORMULATIONS CONTAINING BIOGENIC CARBONATE SAND FROM PORTO SANTO ISLAND, MADEIRA ARCHIPELAGO

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Particular types of sand are used worldwide in therapeutic applications. Biogenic carbonate sand of the island of Porto Santo, in Madeira archipelago has been used over the years by man in the form of sand-baths. According to medical reports and public recognition, it have been used locally for many years with apparent success for the treatment of osteo-articular and muscular diseases. Exfoliation is a procedure that aims to accelerate the cutaneous process of cellular renovation by the use of keratolitic substances. This is a way in which the skin acquires a more youthful and renewed aspect. In this study hydrogels with exfoliant properties, containing biogenic carbonate sand were developed. Several granulometric fractions of sand were used in products for application as exfoliants in face, body and feet, respectively. Biogenic carbonate sand of Porto Santo shows platy shape and low hardness (3 in the Mohs' scale) but still high enough to be able to act as effective exfoliating agent. Viscosity of prepared gels was evaluated at 20°C with a rotation viscosimeter. Texture analyses were performed using a Texturometer and the maximum force (firmness) and the negative area (adhesiveness) were calculated. In order to test their exfoliant efficacy, gels were also applied on the skin of several human volunteers, and skin microrelief parameters were evaluated using non-invasive biometric techniques. All the prepared gels presented refluidificant behaviour without tixotropy. Viscosity increased with the increase in the size of sand particles incorporated in the gels. They also showed appropriate firmness and adhesiveness properties convenient for topical application and exfoliation, causing an improvement of skin appearance. Gels containing Porto Santo sand showed suitable consistency and good exfoliant properties. Depending on the granulometry of the incorporated sand, it is possible to obtain products able to produce exfoliation in different anatomic regions of skin as demonstrated by biometric measurements.

Keywords: biogenic carbonate sand, exfoliant, efficacy

OCCUPATIONAL EXPOSURE EVALUATION OF WORKERS OF PORTLAND CEMENT INDUSTRY IN URUGUAY

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Portland cement is a light gray or white powder used as a building material in the production of concrete with strong adhesive properties when mixed with water. Employees who work with Portland cement are at risk of developing skin problems, ranging from mild and brief to severe and chronic. Portland cement becomes highly caustic (pH>12) when it is in contact with moisture in eyes or on skin, or when mixed with water, and will damage or burn the eyes or skin. Inhalation may cause irritation to the moist mucous membranes of the nose, throat and upper respiratory system or may cause or may aggravate certain lung diseases or conditions. The produced cement is composed of calcium, silicium, aluminium, manganese and ferrous oxides, sulphates and other materials, mostly water. The aim of this work is to evaluate occupational exposure of workers of three uruguayan Portland cement plants. 46 personal and zone airborne samples were collected in plants 1, 2 and 3 and analyzed to determine occupational exposure. Samples of total and respirable dust were collected according to NIOSH 1 methods 0500 and 0600. 2010 ACGIH TLV'S 2 were considered as reference values being 1 mg/m³ for respirable Portland cement dust and 10 mg/m³ for total dust (PNOS 3). It was also considered 50 % of the TLV value as action level. We found that in Plant 1: 50 % of the samples were above the TLV value and 25 % exceeded del action level. In Plant 2: 43 % > TLV and 21% > action level. In Plant 3: 38 % > TLV and 8 % > action level. We discuss the reasons we observed that could lead to this results and conclude that there is a need of improving working conditions. Important measures should be taken to prevent occupational exposure including recommendations for the workers involved and the authorities of the industry. Meanwhile we emphasize that at some workplaces PPE4 should be used: 1) NIOSH: National Institute of Occupational Safety and Health;m; 2) ACGIH TLV'S: American Conference of Governmental Industrial Hygienists- Threshold Limit Values; 3) PNOS: Particulate Not Otherwise Specified; 4) PPE: Personal Protection Equipment.

Keywords: portland cement, occupational exposure, dust

CONTAMINATION OF ENVIRONMENT OF HEAVY METALS: HONEY AS A SENSITIVE INDICATOR

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Honey is a quick, safe and natural energy giver because its simple sugar is quickly absorbed into the blood stream, honey is an easily digestible foodstuff containing a range of nutritiously important complementary elements. Besides a high content of a range of saccharides, there are also organic acids, amino acids, mineral matters, colors, aromatic substances and a trace amount of fats. The contribution of minerals is relatively low and normally accounts for 0.1 – 0.2 % of nectar honeys. Analysis of honey for trace elements content is necessary in food quality control as well in the monitoring of the bee environment. The goal of this preliminary study was mainly to evaluate the effectiveness of honeys as biological indicator and in particular, this work gives increasing attention to specific mineral elements as Cd, Pb, Cr and As, expression of environmental pollution. Cd, Pb, Cr and As were determined by using Atomic Absorption Spectrometry in seventy-eight honey samples from nine geographical areas all over Southern Italy and from five different botanical origins: chestnut (*Castanea sativa*), sulla (*Hedysarum* spp.), multiflora, citrus (*Citrus* spp.), and eucalyptus (*Eucalyptus* spp.). The data collected were subjected to analysis of variance (ANOVA). The results show that our samples did not have traces of As as the concentration was below detection limits. The levels of Cr ranged between 0.32 and 1.02 ppm, with a mean value of 0.71 ppm. In particular, honey from areas 2, 3 and 7 presented the significantly higher average value. The average content of Cd in honeys from the areas studied was of 0.013 ppm. The average level of Pb in the our campioni è stato pari a 0.3 ppm. Honeys from area 2 presented the highest content of Pb (0.90 ppm, $P < 0.05$), followed by honeys from areas 7 and 1 have presented values of Pb of 0.34 and 0.33 ppm, respectively ($P < 0.05$), while in the other areas this element has showed value lowest, < 0.17 ppm. These production areas are characterized by high anthropogenic presence and industrialization. The concentrations of heavy metals in honey and the variability due to differences in such factors as floral source, foraging range, entrapment of atmospheric aerosols by flowers, season and time of year, rainfall, etc., and the easy availability of honey make it a sensitive indicator of the environmental pollution.

Keywords: honey, heavy metal

HIDROGEOCHEMICAL CONSIDERATIONS AND RELATIONSHIP WITH THE ENVIRONMENTAL HEALTH IN THE UPPER PARANÁ RIVER, PORTO RICO REGION, BRAZIL

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In the present work, it was studied several aspects of the hydrogeochemical of the Mutum Islands and Porto Rico, as well as its surroundings in the upper Paraná River, Brazil. The downstream of the dams of Porto Primavera and Rosana were also studied, because these tanks have had influenced the water quality and river dynamics. Samples of the Paraná river channel were collected, as well as ponds internal Mutum Islands and Porto Rico. The samples were collected in low water period, the month of August and during the flood, March. Si, Mg, Mn, Ca, Sr, Ni, Fe, Zn, Pb, Cd, P, Cr, Al, Ba, Co and Cu were analyzed by Emission Spectrometry with Power Inductive Coupled Plasma (ICP-AES). The concentrations of the elements in the low water period were: Fe=11.27 mg L⁻¹, Mg=2.72 mg L⁻¹, Ca=6.42 mg L⁻¹, Mn=1.28 mg L⁻¹, Cd=0.005 mg L⁻¹, Cu=0.007 mg L⁻¹, Ba=0.17 mg L⁻¹, Co=0.011 mg L⁻¹, Zn=0.43 mg L⁻¹, Pb=0.14 mg L⁻¹ and Al=7.22 mg L⁻¹. The concentrations of Al, Pb, Zn and Cd are higher than stipulated by CONAMA Resolution 357 (maximum of 0.1 mg L⁻¹, 0.01 mg L⁻¹, 0.18 mg L⁻¹ and 0.001 mg L⁻¹, respectively). These results are indicating a contamination related to human activities, possibly because the use of chemicals or the release of wastewater in the region. In the period of flooding the metal concentrations were below the low water period. Ni (0.038 mg L⁻¹) concentration was also higher than CONAMA Resolution 357 (max. 0.025 mg L⁻¹), which could also be related to pesticides. The lowest pH values found are located in isolated ponds. However, high rates hydro-geochemical could be responsible for some infectious diseases, intestinal and respiratory in the Porto Rico region (Brazil). Since some chemicals including metals such as Al, Zn, Cr and Pb cause diseases of the respiratory system (chronic lower airway, chronic obstructive pulmonary disease and pneumonia) and others such as Mn, Pb, Co and Hg cause gastrointestinal problems (gastroenteritis). Data of the System of Health (DATASUS) indicate that the Porto Rico region (PRR) showed higher levels of diseases than those of the State of the Paraná in Brazil (PB). The diseases of the digestive system (PB=8% and PRR=15% of the local people), respiratory system (PB=18% and PRR=27% of the local people) and genitourinary system (PB=6% and PRR=25% of the local people) presents different patterns.

Keywords: Paraná River (Brazil), hydro-geochemical, environmental health

**DEVELOPMENT OF AN EXPERT SYSTEM FOR OPTIMIZING
THE EVALUATION AND SELECTION OF RISK BASED
APPROACHES AND TECHNOLOGIES FOR BROWNFIELD
REHABILITATION: PERSPECTIVES FROM TIMBRE
PROJECT**

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Brownfield regeneration plays a key role in sustainable land use management. The 7th Framework Programme project TIMBRE (Tailored Improvement of Brownfield Regeneration in Europe) starts from the observation, that many useful and innovative remediation technologies as well as methods to support risk assessment and decision making processes for an optimized brownfields' regeneration have been developed, but are only rarely applied using their full potential. Identified obstacles for an effective regeneration are (i) the abundance of strategies, tools, documented case studies and remediation technologies available at the EU level as well as (ii) the difficulties in adapting them to cultural, regional and site-specific requirements. TIMBRE's main objective is to overcome these barriers by providing brownfields' owners, local authorities and stakeholders with a web-based problem- and target-oriented customizable decision support toolbox. This contribution features the methodological approach and designed activities of TIMBRE Work Package 1 that focuses on the development of a web-based Expert System. As a crucial part of the TIMBRE toolbox this online information centre will provide access to proven state of the art solutions for brownfield regeneration. This requires the collection, analysis and classification of accessible literature, methodologies and tools. Particular efforts will be devoted to collect and review the ecological and human health risk assessment and management methodologies and tools recognizing their key role for the evaluation and rehabilitation of brownfields. The Expert System will offer a multi-criteria methodology for the evaluation and ranking of the collected information providing end-users with the most suitable instruments for each phase of the brownfield regeneration process. Results will be tailored to the site-specific needs taking the local priorities and requirements into account. This approach involves local experts, site owners, public authorities and engineering companies in the definition of evaluation criteria.

Keywords: brownfields, risk assessment, expert systems

STRUCTURE, COMPOSITION AND FORMATION MECHANISM OF AORTIC VALVE CALCIFIC DEPOSITS

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The structure and chemical composition of valve calcific deposits were investigated. The deposits were chosen arbitrarily and subjected to chemical analysis, observation with scanning electron microscope, semi-quantitative determination of Ca, Mg, Na, K, P and C elements by energy dispersive X-ray, X-ray diffraction and Fourier transform infrared spectroscopy.

These deposits were found to have non-uniform internal structures composed of layers of a structureless aspidinic inorganic material, substantial amounts of voluminous organic material and in a few samples small spheres were also present. Two groups of deposits with distinctly different chemical compositions were identified: one group with a low Ca/P molar ratio (1.59) and the other group with a high (1.82) Ca/P molar ratio.

The deposits belonging to the group with a low Ca/P molar ratio contained higher concentration of magnesium and consisted of increased amount of amorphous calcium phosphate. The deposits with a high Ca/P molar ratio contained low concentration of magnesium and consisted predominantly of carbonated hydroxyapatite. The inorganic material was identified as a poorly crystalline carbonate hydroxyapatite containing molecular water with the average formula $\text{Ca}_{9.1}\text{Mg}_{0.4}(\text{Na,K})(\text{PO}_4)_{5.8}(\text{CO}_3)_{0.3}(\text{OH})_2$.

The actual chemical composition of the apatitic solid phase varied not only from deposit to deposit but also within the same deposit. The non-uniform internal structure of the deposits, the occasional presence of spherical particles and the variable composition between specific areas of the individual deposits indicate that their formation did not proceed under constant conditions. The organic debris formed as a consequence of injured tissue, acted as an inducer of calcium phosphate crystallization through heterogeneous nucleation processes.

Keywords: aortic valve calcific deposits, chemical analysis, EDAX, SEM, FT-IR, X-ray diffraction

BIOREMEDIATION OF SOIL IMPACTS BY MINING ACTIVITIES BY MICROBIAL SULFATE REDUCTION

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Mining-metallurgical industry is an important income source for many countries. Unfortunately, mineral extraction operations represent pollution sources that have been associated with environmental receptors alterations that cause health problems in surrounding population. Lead concentrations ranging from 1300 to 2100 mg kg⁻¹ or as high as 7000 mg kg⁻¹, has been reported in surface soils near to copper, lead and zinc foundries. Actually there are mining wastes and smelter slag deposits containing high amounts of lead and heavy metals that have not been reported and therefore their environmental impact also have not been evaluated. Principal stabilization technology is a cost-effective biological treatment, which emphasizes use of sulfate-reducing bacteria (SRB), to produce products with lower solubility compared to other treatment techniques.. In this work, we studied a sample of soil impacted by emissions from a copper smelter and mine wastes, whose Pb concentrations is 5533.3 mg kg⁻¹ that exceeded the allowable limit established in the Mexican law. The biostabilization was developed using a microbial consortium with sulfate-reduction activity previously isolated from soil with a high degree of lead bioaccessible called JH. To evaluate efficiency of this consortium, changes in mineral fractions of Pb speciation (water-soluble, carbonate-bound, iron-manganese-oxide bound, organic matter and sulphide-bound and residual) on three soil profiles a column was packed with this soil in a closed batch system. After biological treatment the soil lead mineralogical speciations and the lead bioaccessible fractions modifications were determined. Tests of soil stabilization showed a Pb removal of 55%, which represent an overall decrease with respect to the bioaccessibility of 27%.

Keywords: bioaccessibility, sulfate-reducing, biostabilization

QUALIFICATION OF PORTUGUESE MINEROMEDICINAL WATERS FOR PELOOTHERAPY

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Portugal has a significant historical background in what concerns the use of geological resources for therapeutic purposes. Clays and mineral waters are abundant and empirically used in the form of hydrothermal muds, for the treatment of muscular, rheumatic and skin diseases. Nowadays, Portuguese spas are still requested for thermal treatments due to the peculiar physico-chemical characteristics of its mineral waters. In the last decade, various publications studied the influence of different types of mineral waters in treatments combining the therapeutic effects of clays and minero-medicinal waters (Sánchez et al., 2002; Veniale et al., 2004; Gámiz et al., 2009). In this study, several mineral waters were collected from springs/wells located at Portuguese spas or traditional healing baths commonly used for the treatment of skin and musculo-skeletal disorders. We aimed at their geochemical characterization in order to select a group of suitable minero-medicinal waters to be used in the formulation of peloids. The concentrations of major cations and trace elements were determined using an inductively coupled plasma-atomic emission spectrometry method (ICP-MS) at ACME Anal. ISO 9002 Accredited Lab - Canada. The geostandard WASTWATR3 was used by ACME to check the validity and reproducibility of the results. Data analysis was performed using Piper diagram and Principal Component Analysis (PCA). Different hydrochemical types were obtained for the studied waters, the results showing a large range of chemical characteristics and diverse water types.

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Keywords: hydrothermal muds, minero-medicinal water, hydrochemical type

MICRO-RAMAN SPECTROSCOPY AND VP-SEM/EDS TECHNIQUE APPLIED TO THE CHARACTERIZATION OF INORGANIC PARTICLES, FIBRES AND ASBESTOS BODIES IN HISTOLOGICAL SECTIONS USED FOR RESPIRATORY DISEASE DIAGNOSES

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The correlation between inhaled fibrous material, in particular the mineral phases defined by the law as “asbestos”, and diseases of the respiratory system - asbestosis, mesothelioma, pulmonary carcinoma - is largely demonstrated by a large scientific literature. Previous work carried out in our laboratories proved that micro-Raman spectroscopy is a technique able to recognize crystalline phases on untreated samples. In particular recently micro-Raman spectroscopy has been coupled with VP-SEM/EDS- Variable Pressure Scanning Electron Microscopy with annexed Energy Dispersive Spectroscopy - to characterize, without digestion of the biological matrix, particles/fibres directly in the histological sections used for the medical diagnoses. A methodology allowing the characterization of the same particle/fibre under the two techniques has been developed. Thin sections of lung tissue and pleural plaque from patients affected by the above respiratory diseases have been studied. All the inorganic phases, fibrous or not, and the “asbestos bodies”, observed under the optical microscope, has been undergone to spectroscopic, using 632.8 nm laser beam as excitation source, and morphological-chemical study under VP-SEM/EDS. The results are presented and discussed.

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Keywords: micro-Raman spectroscopy, asbestos bodies, histological sections

**GRAZING OF EQUUS CABALLUS (THE HORSE/PONY) IN THE
GOLDFIELDS REGION OF VICTORIA, AUSTRALIA: DOES
ELEVATED METALS IN THE SOIL TRANSLATE TO
ELEVATED BODY BURDEN IN THE ANIMAL?**

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The Goldfields region of Victoria, Australia has naturally elevated metalloid levels that have been further concentrated by mining activities. Values up to 3,490mg/kg As are recorded in the Ballarat region with 3.1mg/kg recorded as water soluble. The area has been extensively mined for gold (more than 13.2 million ounces extracted), but in recent times has been a site of significant growth and urban development. Materials from past mining activities are distributed throughout the regional city of Ballarat and, at its periphery, grazing of horses is common practice and consistent with the rural lifestyle that draws people to the region.

A cross-sectional and statistically selective study targeting the horse and their grazing field was devised to investigate metalloid bioavailability and uptake. Using human toenail material as a model, we analysed hoof horn material (n=65) and collected 45 soil samples (including mine waste and tailings material) from the fields. The outermost hoof material was discarded and extensive washing was required before digestion and analysis via ICPMS and ICP-OES.

Mine waste material from horse paddocks ranged in arsenic value of from 0.4-4320mg/kg. Soil material ranged from 0.5-59.6 mg/kg arsenic and hoof horn arsenic concentration ranged from 0.2 to 1.6mg/kg with all samples presenting detectable arsenic. Other elements associated naturally with gold mining activities and materials are similarly elevated.

The presence of arsenic and other metals in hoof horn support the premise that metals are bioavailable to the horse. Statistical results show a weak but statistically significant correlation ($p = 0.013$) between arsenic concentration in soils and hoof horn. Limited base line data for hoof horn material is available but if comparison to human models is valid, it is postulated that the levels detected are significant.

Keywords: Equus caballus, hoof horn, arsenic

CADMIUM LEVELS IN LIVER AND KIDNEY OF RAZORBILL AND COMMON MURRE AFFECTED BY THE PRESTIGE OIL TANKER SPILL

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The oil spilled by the sinking of the Prestige oil tanker, due to its low quality, contains high levels of heavy metals (Balseiro et al., 2005). This disaster resulted in the deaths of about 300 000 seabirds (SGO, 2005), finding fuel in the digestive system of some of them.

For the purpose of this study we collected 29 razorbills (*Alca torda*) and 55 commons murre (*Uria aalge*) between December 2002 and February 2003 from the Recovery Center of Oleiros (A Coruña - NW Spain). In marine birds necropsied, liver and kidney samples were subjected to digestion, in acid medium, into a microwave station and the determination of cadmium concentration was performed by inductively coupled plasma mass spectrometry (ICP-MS). The results, expressed in dry weight, show ranges of cadmium in liver of razorbills and murre ranging from 0.25-2.93 ppm and 0.26 to 52.56 ppm, and the averages were 1.16 ppm and 2.48 ppm, respectively. For the kidney, also in razorbills and murre we establish ranges between 0.43 to 8.59 ppm and 0.61 to 62.30 ppm, with averages of 2.55 and 5.20 ppm, respectively. The analysis of variance shows a statistically significant difference ($p < 0.01$) between the two species, with the highest levels of cadmium in common murre than razorbills in both kidney and liver, those levels were also higher in kidney than in liver. In conclusion, the levels of cadmium detected in both species of birds are very high compared with other studies (Pérez López et al., 2006), this may be due to bioaccumulation of metal in oil spills (Burger et al., 1992). Acknowledgement: This work was financially supported by Xunta de Galicia (INCITE08PXB261087PR).

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Keywords: cadmium, oil, seabirds

PROCESSING CLAY AS EFFECTIVE DRUG FOR CURING OF DIGESTIVE INFECTIOUS DISEASE

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In this research, the Purification and enrichment of clay minerals by zinc to be done by initiative methods of Iranian research group for the first time

For this studies ,we used calcium bentonite clays which is collected from Alteration volcanic ash. and then exactly studied them on view of microbiology and geochemical. Thus we recognized type of useful and harmful microbe and percent each of mineral content .Then eliminated harmful microbes and useless elements from clay samples and enriched them by zinc micromineral powder about 30 percent by initiative methods of research group. As know the zinc is one of important micromineral for body that participate in structure more of 100 Enzyme and shortage zinc is a serious problem in cycle of digestive infectious disease .thus by using this new medicinal compound as powder and tablet with a glass of water can electively remove microbe of infectious disease without any trouble and also can cure shortage of zinc in body. The specifications new medicinal compound is as follow: Color = light gray, Odor = Flat, Moisture = 0.010 %, pH = 8.1; Mesh size = #200 Mesh and mineral content is Zn, Se, Ti, Fe , Ca, Mg, Na, Al, K, silica.

Keywords: processing, clay , drug , infectious disease

THE POWER OF CLEAN, LIVING SOIL ON REMOVAL OF ENVIRONMENTAL CONTAMINATION

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Based on studies done, the soil has a lot of microorganism which can eradicate pathogenic organisms from the environment . If there was not such power in the soil, our globe would very soon be changed to a pool of infective agents. So, not only the clean-living soil is not infective but also acts as a detergent and regarding this power it could be used instead of water (water carries the microbes, but the soil kills the pathogenic microbes). The clean living soil has very important role to clean our environment (on base of 3 reason): 1) cleaning superficial soil from contaminations; 2) cleaning of the underground water resources; 3) cleaning of the air pollution. Many research could be done, to approve the cleaning power of the soil: 1) the contaminated water goes into the earth then, the clean, wholesome water, as a spring water comes out of the earth; 2) the microbial, physical and chemical air pollution is removed when it blows as the wind on soil specially in the spring; 3) sunshine radiation on the superficial soil could activate the titanium dioxide (TiO₂) which kills the pathogenic microbes like T.B. bacilli; 4) the animal which are familiar with the nature cure their diseases with the soil in sunshine; 5) there is plant roots in the soil (with its microbiological flora) so that even one pathological microbe cannot come up the plant stem; 6) industrialization of the cities deprives us of the cleaning power of the soil so the living environment can be contaminated and exposed the people to different diseases. In this article we speak in detail about the soil factors which clean our living environment and factors which contaminate the soil from traditional, religious, experimental point of view. In final this is our messages to the world people: 1) as it was common in the old era our body and the air should be familiar with the clean living soil and the nature; 2) if we like to benefit from the environmental, cleaning power of the soil we should let the air blow as the wind on the soil and the sun shine radiation to the earth; 3) we should avoid anything which cut the contact of the superficial soil to be expose to the air, rain, and the sunshine; 4) leaning ability of the soil is several time greater in the windy, rainy, shiny spring season.

Keywords: power, clean - living soil, removal

**DISSOLUTION KINETICS OF TREMOLITE IN MIMICKED
LUNG FLUIDS. EFFECT OF CITRATE AND OXALATE.
PART 1: MACROSCOPIC STUDY**

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Toxicological studies show that interactions between fibrous material and biological environment are strongly dependent on both geometry and crystal chemistry of mineral fibers. Geochemical (in vitro) experiments are essential to understand clearance mechanisms of inhaled particles by human body. The aim of this study is to evaluate tremolite dissolution rates in mimicked human-body conditions, including citrate and oxalate as a proxy for organic acids in alveolar fluids. The effect of citrate and oxalate on the dissolution rate was measured at 37°C in non-stirred flow-through reactors, using modified Gamble's solutions at pH 4 (macrophages), 7.4 (interstitial fluids) and 5.5 (intermediate check point) containing 0, 0.15, 1.5 and 15 mM of citrate or oxalate. Tremolite from Sierra Nevada (Granada, Spain) was used as a starting material. The logarithm of dissolution rates calculated from Si concentration in the output solutions without organic ligands depend on pH, decreasing when the pH increases from -12.01 (pH 4) to -13.04 (pH 7.4) mol/g·s. Measured Mg/Si ratio shows a preferential release of Mg²⁺ at acid pH decreasing drastically at basic pH. The presence of both ligands enhances dissolution rates at every pH, increasing when the ligand concentration increases until reach approximate one order of magnitude for the highest concentration. Citrate produces a stronger effect as a catalyst than oxalate, mainly at more acidic pHs. The measured Mg/Si ratio in solution is modified by the presence of ligands due to the formation of aqueous complexes or the precipitation of magnesium salts. These results suggest that the ligand-promoted dissolution mechanism promoted needs to be considered in order to quantify asbestos degradation in biological conditions. More studies are necessary to evaluate the species in solution, their interaction with the mineral surface and their role in the dissolution process(es). In this sense electron microscope studies of the solids obtained in these experiments can help us to monitor the changes in fiber morphology induced by the alteration reaction.

Keywords: tremolite, dissolution rate, dissolution mechanism

**DISSOLUTION KINETICS OF TREMOLITE IN MIMICKED
LUNG FLUIDS. EFFECT OF CITRATE AND OXALATE.
PART 2: MICROSCOPIC STUDY**

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The increasing concern of the scientific community about ultrafine particles, from different nature, and their harmful effects for human health make necessary to complement classic degradation studies with morphologic studies that help to monitor particle size distribution and identify the most dangerous ones. The aim of this study is to analyze and compare the changes in tremolite particles before and after dissolution in mimicked alveolar fluids, including citrate and oxalate as a proxy for organic acids. Tremolite particles were altered at 37°C for 2 months in non-stirred flow-through reactors, using modified Gamble's solutions at pH 4 (macrophages) and 7.4 (interstitial fluids) without and with organic acids (15 mM citrate or oxalate). After the alteration samples were deposited on carbon stubs and then coated with a carbon film for SEM study. The raw tremolite is composed of a wide range of fibrous particles (10-340 µm in length): big fibers (length:diameter ratio L/D >10, 20-30 µm diameter D), thin and long fibers (L/D >50, aprox. 5 µm D), cleavage fragments (L/D 2-3, aprox. 30 µm D) and fine particles (<20 µm L, <4 µm D) that are the most abundant. At pH 4, particle surface smooths out and the amount of fine particles decreases significantly. However at pH 7, cleavage fragments with irregular terminations become the most abundant particle type and their surface is extensively etched following c axis direction. Big fibers are almost absent. Ligands produce a decrease in the abundance of big fibers and a prevalence of cleavage fragments. Surface etching is intense, both along cleavage planes and perpendicular to c axis, where the coalesce of etch pits generates cracks. This phenomenon was more developed in oxalate than in citrate solutions. These results suggest that two mechanisms of particle breakage coexist during the process of dissolution. Fibers length decreases by splitting parallel to the main cleavage plane (fiber longitudinal direction), with developments of kinks along the fibers. Coalescence of etch pits perpendicular to c axis induces breakage and particle shortening, particularly intense in the presence of ligands.

Keywords: tremolite, SEM, dissolution mechanism

EMISSIONS OF HARMFUL ELEMENTS AND ORGANIC POLLUTANTS FROM SMALL SCALE WOOD COMBUSTION SYSTEMS

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The application of wood as a heat supplier may reduce the greenhouse gas effect, the shortage of fossil energy sources and the dependency from fossil fuels. Wood combustion in Europe is widely applied e.g. for residential heating in stoves and boilers. About 14 Million out of 40 Million households in Germany own small-scale wood-burning furnaces. We investigated how the air quality changes due to the emissions of harmful elements and organic pollutants during wood combustion. Especially compounds bound on fine (<1µm) and ultrafine (<0.1µm) particles or gaseous compounds may enter the alveoli of the lung and trespass into the blood.

Methods Some systematic burning experiments with wood pellets, chips and logs were performed by using state-of-the-art small-scale combustion systems. The wood-burning furnaces tested already hold optimized emission characteristics. To collect the hazardous fly ash, an innovative filter holder consisting of PTFE with a 150mm diameter is used in our study. It guarantees sufficient material for the analysis and assures a low contamination background.

Results **Heavy metals:** To get a reliable reconstruction of element fluxes for input/output balances, we analyzed beside the wood samples all the originating ashes e.g. grate ash, heat exchanger ash and fly ash. The element amounts of Cd, Zn, Sn, Tl, Pb, Bi, and Sb contained in the ashes were 10-80 % lower than their amounts contained in the fuel even if emission reduction facilities such as a flue gas condenser or an electrostatic precipitator were installed. This takes effect in all automatically fuelled furnaces. This insufficient retention suggests that portions of these elements are quasi-gaseous and can leave the furnaces as gas or as very fine nucleated particles and are presumably able to trespass cell membranes. **Organic pollutants:** The concentration of organic compounds strongly depends on the kind of the fuel, the furnace and on the combustion conditions. The emission of the pollutant PAH (especially Benzo(a)pyrene) is below detection limit in the wood pellet boiler, is increasing in the wood- chip furnace and is above a factor 100 higher in a wood log fuelled fireplaces indicating inappropriate conditions for complete oxidation. This is very critical because 6 Million fireplaces exist alone in Germany. Other organic parameters such as levoglucosane, abietic acid and oxidized PAH show a similar trend. An effective reduction of the emissions is necessary.

Keywords: wood burning, heavy metal emission, organic pollutant emission

SOIL QUALITY, SOIL HEALTH, HUMAN HEALTH

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The paper, Soil: their implication to human health (a review by Abrahams, 2002)¹ highlights the important role of soil as geofactor in the relationship of many human diseases with the environment. Soils affect human health in two ways: directly or indirectly. The direct way is by ingestion (voluntary or involuntary), inhalation and dermal absorption. The indirect form occurs when the soil affects the atmosphere, hydrosphere or biosphere, and changes in these media affect human health, via air, water or food. When analyzing the direct and indirect effects of soils on human health is demonstrated that these effects are related to the following soil properties: a) retention capacity of elements and molecules including water, related to the amount and type of colloidal particles; b) the activity of soil organisms that can metabolize or inactivate elements and molecules; c) the spatial organization of solid particles (structure) at macro, micro and ultramicro levels, which regulates fluid transport in soil, and d) the soil resilience.

Soil quality considers the soil's capacity, within land use and ecosystem boundaries, to carry out its functions of biogeochemical cycling, partitioning of water, storage, release, buffering, and energy partitioning. A minimum data set of quantitative indicators for assessing the soil quality includes physical (texture, depth, porosity, and water retention), chemical (organic matter, pH, electrical conductivity, extractable N, P, and K), and biological (microbial biomass and soil respiration) characteristics. These characteristics reflect the same properties mentioned above.

Farmers' field diagnosis of soil health, a more integrative term preferred by farmers to soil quality, uses qualitative and sensory indicators. They include description of the plough layer (e.g. earthworms, erosion, tillage ease, feel, or smell), plants (crop appearance, seed germination, and roots), animals (animal health and wildlife), and surface water appearance.

Linkages between soil quality and plant, animal and human health as well as the perception of soil as a living, dynamic organism that functions holistically rather than as inanimate object have led to use synonymously the terms soil quality and soil health.

For all the foregoing, we conclude that when assessing the soil quality (or health) also is considering the influence of soil on human health.

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Keywords: soil, health

DEVELOPMENT, CHARACTERIZATION AND COMPARATIVE STUDY OF SILICONE-BASED FORMULATIONS CONTAINING BOTH POTASSIUM MICA AND TITANIUM DIOXIDE

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Micas are an important group of phyllosilicate minerals. Micas are extensively used in skin care and preventive medicine products as ultraviolet inorganic filters to provide skin protection, shine and softness. On the other hand, silicones are harmless, emollient, non occlusive and water repellent excipients. The aim of this study was the development and characterization of silicone emulsions and gels containing mica comparatively to the same silicone-based formulations containing titanium dioxide (TiO₂). Water/silicone emulsions and silicone gels containing mica (5%, w/w) of different particle sizes (SVP <125 m and SVR > 125 m) or the same percentage of TiO₂ were prepared by conventional techniques and submitted to texture, rheological and accelerated physical stability studies. The in vitro evaluation of the sun protection factor (SPF) was also performed by spreading 1mg/cm² of each formulation in roughened polymethylmethacrylate (PMMA) plates. Then, UV-spectra from 290nm to 400nm were obtained using a spectrophotometer. Accelerated stability studies showed that silicone gels containing mica remained stable after 3 cycles (30 min) of centrifugation at 3000 rpm. For the other formulations tested, sedimentation of mica has occurred. All the emulsion and gel formulations presented refluidificant behaviour, however, emulsions with mica or TiO₂ showed lower viscosity than gels. Besides, silicone formulations containing mica showed significantly higher values of firmness and adhesiveness comparatively to formulations with titanium dioxide. The SPF values of formulations containing mica were significantly lower than those obtained with TiO₂ formulations. Although silicone-based formulations containing potassium mica have shown good physical and mechanical characteristics for application on the skin, the SPF values (spectroscopic reflecting component) were lower than those obtained with TiO₂ bearing formulations, which means that a higher percentage of mica should be incorporated in the corresponding formulations.

Keywords: potassium mica, titanium dioxide, silicones

WATER PURIFICATION BY USING DIFFERENT ORGANOCLAY COMPLEXES

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The cleaning up of contaminated water is one of the most difficult and expensive goal in environmental engineering. Clay minerals are the most important inorganic components in soil for sorption of contaminants, but without modification are ineffective stable sorbents for contaminant compounds. The treatment with surfactants changes the surface properties from hydrophilic to hydrophobic and greatly increases the basal spacing of the layers. [1-4]. This new material, named organoclay, is used in some environmental applications as the removal of contaminants from polluted waters offering a promising device in decontamination planning and environmental remediation. Several routes can be employed to modify clays and clay minerals [5]. Ion exchange with alkylammonium ions is wellknown and the preferential method to prepare organoclays, but clays and clay minerals can also be modified with biomolecules, like proteins, enzymes, amino acids, peptides, etc. [6]. With the aim to develop an effective, safety and economic matrix capable of removing organic contaminants from water for animal and human consumption we compared the behaviour of two organoclays realized by using natural montmorillonite (MMT) and octadecyl-trimethyl-ammonium bromide and bovine serum albumin as surfactants. Tribenuron-methyl a highly active herbicide was used as contaminant test. Tribenuron-methyl solutions containing both the active ingredient and its degradation derivative were tested. Basal spacing (d001) of the unmodified and modified clay mineral was determined by X-ray diffraction (XRD), following drying at 25°C. The herbicide retention by MMT and the surfactant-modified MMT was measured by LC/MS. The results of XRD and chemical analyses confirmed the potentiality in the environmental field of both modified clays. The effectiveness of tribenuron-methyl adsorption coupled with the complete removal of its derivative gives account of the usefulness of organoclay systems for the elimination of this kind of pollutant from water in cleaning processes.

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Keywords: organoclay, ODTMA, albumine

METAL RICH AIRBORNE PARTICULATE MATTERS IN SURFACE SOILS OF ANGREN-ALMALYK MINING- INDUSTRIAL AREA, UZBEKISTAN

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Distribution and morphology of atmospheric particles on soil surface along the deposition gradient in Angren-Almalyk mining industrial area was main focus of this study. Soil samples were collected along two downwind transects at 22 sampling locations (in 2-km intervals) from the soil surface. The fine grained fraction (0,63mm) was subjected to gravity separation and fractioned into (i) a heavy and (ii) a light minerals. The heavy mineral fractions were embedded in epoxy-resin based briquettes. Element mappings were performed with the polished and carbon-coated thin sections using JEOL microprobe. A lot of grains and spherical particles with bright contrast appeared in the microprobe scans indicating heavy metal-rich chemistry. Spherical particles dominated in soil samples collected near the metal smelting and coal firing sites. Angular sulphide ore minerals (pyrite, galena, chalcopyrite, and sphalerite) were dominant in samples collected near the mining wastes depositories. The morphology and internal microstructure of spherical particles in heavy mineral fraction of soil samples from the Almalyk indicates a pre-existing molten phase, probably emitted by an inefficient air pollution control technique of the smelter. In subsamples of this transect spherical particles can be divided in: pure metal particles (Cu, Zn, Al), metal-rich cores with silicate rims, small spherical metal sulphide or oxide particles within larger heterogeneous glassy particles, well organized particles with dendrite structure. Elemental composition of spherical particles in soils from Angren is very poor (almost all of them has elevated content of Fe oxide with less Si, Al, Mn, Ca). In some particles less contents of Pb, Cu and S were observed. Spherical particles in Angren soils can be divided into 3 groups: a) well organized massive dendrite particles with Fe oxide in light growing crystals and matrix containing Si, Al, Ca, Fe; b) homogenous spherical particles without any structures; c) small microscopic particles coated Fe oxide. Ore mineral particles are mainly hematite, titan-magnetite, magnetite and very less pyrite particles. Many of them covered with secondary ore minerals as Fe hydroxide and carbonates. Calcareous condition of soils in studied areas can stabilize atmospheric particles and prolong their weathering process by covering them with carbonate material. Obtained data can give a new insight into solubility and bioavailability of heavy metals in polluted soils.

Keywords: airborne metal-rich particles, heavy metals in soil surface, environmental impact assessment

CONTAMINATION OF MARINE ORGANISMS (MOLLUSKS AND FISH) IN TARANTO GULF IN RELATION TO MERCURY SPECIATION IN SEDIMENTS

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Contamination of marine organisms with toxic chemicals, such as mercury and its compounds, has been intensively studied in recent years, due to the fact that these contaminants are persistent, toxic, tend to bioaccumulate, and pose human and ecosystem risks. In sediments, inorganic mercury may also be converted by bacterial activity into methylmercury, the most toxic chemical species which may cause the permanent harm to the central nervous system, such as behavioural disorders and deficiencies in immune system and development. The aim of this work was to determine the concentration of total mercury (THg) and methylmercury (Me-Hg) in the sediments and in different edible tissues of bivalve molluscs (*Mytilus galloprovincialis*, *Chlamys varia*), gastropod molluscs (*Hexaplex trunculus*) and fish (*Symphodus melops*) collected at 5 sites from Taranto coastal environment, in order to investigate contamination level and public health risks associated with consuming fish and seafood harvested from this area. Moreover the goal of this study was also to estimate the weekly intake and compare it with the provisional tolerable weekly intake (PTWI) recommended by the European Food Safety Authority (EFSA, 2004). Total mercury (THg) and methylmercury (Me-Hg) concentrations in sediments ranged from 0.036 to 7.730 mg/Kg d.w. (mean: 2.777 mg/Kg d.w.) and from 1 to 40 µg/Kg d.w. (mean: 11 µg/Kg d.w.) respectively. In mollusks THg concentrations ranged from not detectable to 1870 µg/kg d.w. while in fish from 324 to 1740 µg/kg d.w. Me-Hg, concentrations in fish ranged from 190 to 1040 µg/kg d.w. and from not detectable to 1321 µg/kg d.w. in mollusks. THg in examined marine organisms exceeded the maximum level fixed by the EC Decision (0.5 mg/Kg w.w.) solely in gastropod mollusks *Hexaplex t.*. The estimated weekly intake for THg and Me-Hg was in many cases over the PTWI established by EFSA for all edible species, and in less measure for *Mytilus g.* especially in children. In this perspective, it is imperative that continuous monitoring of mercury and methylmercury levels in all foods be done, with crucial attention to seafood, considered a primary vector of these substances for human.

EFSA (European and Food Safety Authority). 2004. Opinion of the Scientific Panel on Contaminants in the Food Chain on a request from the Commission related to mercury and methylmercury in food (Request N° EFSA-Q-2003-030) (adopted on 24 February 2004). The EFSA J. 34, 1-14.

Keywords: mercury, methylmercury, sea food

CLAY THERMOTHERAPY

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Heating of clay can be indirectly and directly. Indirect is pure conduction process. Direct heat can diffuse through the cream-based clay that is applied spreading, dipping in waterbased clay and inhalation of steam heating the particles of clay-volatile aerosols. Action of heat causes the skin irritation receptors, causing reflex mechanism, via parasympathetic, there is vazodilation of arterioles, capillaries and venues. At the same time, the reflex mechanism, starts to grow blood vessels in depth. In some cases, such as fresh injury without bleeding, so. bruises need refrigeration. Clay in the form of creams is very efficient treatment possible consequences of stroke, when used immediately after the attack. Mosquito bites and some insects cause local heating of tissue from swelling. For conduction heating using thermoclay which returns for three minutes in a microwave oven and wrapped in cloth applied to the neck, spine, abdomen and others. Of particular importance is the elimination of gases that accumulate in the colon. Diffusion heating involves smearing a cream made with clay, which contains hot pepper extract. It is used for rheumatism. Clay in the form of creams can be an indicator of some problems in the body. That part of clay that had stopped last points to some disorder. Thus, acne and pimples, bruises and back had stopped. Important diagnostics of the spinal column. Aqueous solution of clay, sea salts and extracts of plants is being converted to ultrasound generator lights acting inhalation. All proposed methods will be practically demonstrated.

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Keywords: clay, thermotherapy, gel

ROLE OF BENTONITE CLAY IN THE ECOLOGY OF THE HUMAN BODY

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Ecology of the organism is a scientific field study of the processes in the human body, their interconnection and coordination. Based on biochemical, thermophysical, electrodynamic, fluid dynamic, and membrane separation processes in biosystems. It takes knowledge of physiology and anatomy, but from the point of biophysics, the refore knowledge of the mutual influence of physiological and anatomical structure of the organism. You also need knowledge of engineering principles biofluide, electrodynamics, thermodynamics, and biochemistry of basic processes in the body. Contemporary ecology deals with all kinds of food and other products that are consumed and their combination, and special features - additives. Specifically deals with some pharmaceutical and cosmetic products and their toxic effects on the body. Clay as pristine material in all civilizations has played a major role in maintaining the equilibrium of human health. Its application was from food, through spreading, making the courts, to immersion in water. Properties of bentonite clay as toothpaste, put to death for drinking water, soap, shampoo, powder and unified with some plants, to modern nanomaterials is constantly being updated in a variety of products to maintain the quality of human life. The analysis of emulsion, dispersion, electrical, thermo, ion exchange and other features of bentonite clay

Keywords: ecology human body, bentonite clay, thermodynamic

^{226}Ra , ^{232}Th AND ^{40}K RADIONUCLIDE MEASUREMENTS IN SOIL SAMPLES OF HUNGARY

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Radionuclides of ^{226}Ra , ^{232}Th and ^{40}K are found in all soils and rocks. Their distribution is more frequent in the upper continental crust than in the other spheres of the Earth because of their highly incompatible property. The worldwide average radionuclide concentrations in soils for ^{226}Ra , ^{232}Th and ^{40}K are 32 Bq/kg, 45 Bq/kg and 412 Bq/kg, respectively. These radionuclides and their daughter isotopes have direct effect on the human through their radiation in the nature environment. We collected soil samples from the upper 0-30 cm layer of the soils to define the ^{226}Ra , ^{232}Th and ^{40}K radionuclide concentrations. In Pest County 34 samples from 34 localities (16 on loess and 18 on sand), in Zsámbék basin (Pest and Komárom-Esztergom counties) 10 samples from 10 localities (all on loess), at Kvägöszls (SW-Hungary) 4 samples from 3 localities (on red sandstone) and in Pál-völgyi Cave (Budapest) 5 samples (4 on limestone and 1 on marl) have been collected and then studied their activity concentrations for ^{226}Ra , ^{232}Th and ^{40}K by use of HPGe gamma-spectroscopy technique. The main aim of our study is to relate the measured activity concentrations to the soil type and their source rock type from which the soils developed. The average ^{226}Ra , ^{232}Th and ^{40}K activity concentrations were 32 ± 3 Bq/kg, 20 ± 2 Bq/kg and 256 ± 26 Bq/kg in the soil samples of Pest County where the loess has greater values (^{226}Ra : 43 ± 4 Bq/kg; ^{232}Th : 26 ± 3 Bq/kg; ^{40}K : 220 ± 23 Bq/kg) than sand (^{226}Ra : 25 ± 3 Bq/kg; ^{232}Th : 16 ± 2 Bq/kg; ^{40}K : 310 ± 28 Bq/kg). In Zsámbék basin the average values for loess are: ^{226}Ra : 31 ± 4 Bq/kg; ^{232}Th : 22 ± 4 Bq/kg; ^{40}K : 280 ± 56 Bq/kg. The average ^{226}Ra activity concentration is 80 ± 37 Bq/kg in the sandstone of Kvägöszls where a former uranium mine operated. In Pál-völgyi Cave the average activity concentrations are ^{226}Ra : 31 ± 6 Bq/kg, ^{232}Th : 26 ± 5 Bq/kg, ^{40}K : 291 ± 65 Bq/kg for limestone and ^{226}Ra : 32 ± 4 Bq/kg, ^{232}Th : 26 ± 1 Bq/kg, ^{40}K : 315 ± 9 Bq/kg for marl. In concluding, the average ^{226}Ra , ^{232}Th and ^{40}K activity concentrations in the studied soil and rock samples are within the average worldwide range, however soils developed on loess show higher values than those on sand.

Keywords: radionuclides, soils, Hungary

BALKAN ENDEMIC NEPHROPATHY: THE COMPLEX EQUATION OF MULTIFACTORIAL ETIOLOGY

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A fatal kidney disease, Balkan endemic nephropathy (BEN) has been plaguing certain geographically restricted rural areas of the Balkan Peninsula for decades. More than 50 years have passed since the initial medical description of the disease and although its etiology is still unclear several advances have been recently made in unraveling some potential causative factors. A phytotoxin, called aristolochic acid (AA) and produced by the plant *Aristolochia clematitis* (birthwort) has been proposed to be responsible for the kidney failure and the associated urothelial cancers and more recent data has pointed to the presence of biomarkers (DNA-AA adducts) of previous exposure to aristolochic acid of BEN patients. However, such adducts can be the mere consequence of the presence of *Aristolochia clematitis* in high abundance in the endemic, but as well in nonendemic, areas. However, the exposure pathway to AA is unclear. Wheat flour contamination with the toxin has been proposed but if this is true or not it is still an open question, as long as similar contamination and similar exposure pathways may potentially occur in many other places around the world, where BEN is not present. *Aristolochia clematitis* could be an important risk factor for BEN in a genetically susceptible population, but an additional, geographically confined, agent has to contribute in a synergistic or additive way to the etiology of the disease. Our original proposal was that Pliocene lignite deposits, present in and around the endemic areas would provide the geographic character of the disease. The Pliocene lignites are immature coals, capable of leaching large amounts of potentially nephrotoxic and carcinogenic organics that are transported into the water sources used by the villagers. Such low and high molecular weight compounds, may set up the stage for other toxins, like AA, to reach a threshold effect in causing BEN, in a multifactorial disease induction pattern. Extracts of Pliocene lignites from endemic area and high molecular weight organic concentrates of endemic water samples are able to inhibit kidney cell growth and induce cell death at higher concentrations. Other effects include expression downregulation and intracellular reorganization of actin and stimulation of multidrug resistance protein 1 expression. All these effects may sensitize kidney cells and make them more susceptible to additional environmental insults, resulting in the BEN phenotype.

Keywords: Balkan, endemic, nephropathy.

EXPOSURE TO TERRESTRIAL GAMMA RADIATION IN WESTERN SWEDEN

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After excluding contribution from radon 42% of the average effective dose from natural background radiation comes from terrestrial gamma radiation (TGR) in Sweden. In western Sweden, in the county of Vastra Gotaland, the TGR is high and originates mainly from granite, but the county has also areas with low TGR (0-500 nGy/h). This study aims to investigate the distribution of TGR in relation to the population (population-weighted average). Data for the study comes from the database at the Swedish Geological Survey and is based on aerial measurements. The digital database has unique measurements for each 200 x 200 meter grid for uranium, thorium and potassium, respectively. With conversion factors for the three nuclides, the TGR can be calculated in nGy/h. Each individual in Vastra Gotaland (n=1.5 million) was retrieved from the population registry with the dwelling coordinates. Using the Geographical Information System the coordinates of the individual's home was matched with the level of TGR. Then the TGR for each municipality was calculated as 1) an average of the grid cells (surface-weighted average) and 2) the population-weighted average, respectively.

The population-weighted average of TGR for the county of Vastra Gotaland was 56 nGy/h. There was a tendency of higher population-weighted municipality average compared to the surface-weighted average i.e. the population distribution was skewed towards regions with higher TGR. In the 49 municipalities the median populationweighted average was 55 nGy/h, Sotenas had the highest 118 nGy/h and the Trollhattan municipality had the lowest average of 37 nGy/h. In our study we found that the population-weighted average of TGR for the municipalities in Vastra Gotaland was higher than the surface-weighted average. This is probably a random phenomenon, but important to keep in mind when designing and evaluating ecological studies.

Keywords: terrestrial gamma radiation, epidemiology, Geographical Information System

CHEMICAL, MINERALOGICAL AND MORPHOLOGICAL CHARACTERIZATION OF FINE AEROSOL PARTICLES (PM 2.5) IN A SOUTHERN ITALIAN SITE

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The current increasing interest in the study of fine aerosol particles (e.g., PM_{2.5}) is due to the identification of adverse effects on human health, environment and climate (IPCC, 2007; WHO, 2007). In particular, the increase in the aerosol particle levels is one of the major causes of atmospheric pollution in urban and industrial areas mainly due to the health dangerous effects they have on human health. These effects are related both to the concentration levels and the chemical-mineralogical composition of the aerosol particles which are influenced in their turn by emission sources and atmospheric transformation processes. In the light of this, studies directed towards the characterisation of aerosol particles can help the improvement of air quality control strategies as well as the prevention and mitigation of the negative effect on the human health and life quality. In this context PM_{2.5} in-situ measurements were performed at the Istituto di Metodologie per l'Analisi Ambientale of the National Research Council of Italy (IMAA- CNR, Tito Scalo - Southern Italy) from April to July 2010. The PM_{2.5} concentration, chemical composition, mineralogical and morphological features of the PM_{2.5} particles collected were analysed. Particular attention was paid to chemical elements (e.g., chromium, lead) and minerals (e.g., silica polymorphs, metal oxides) that may pose severe risks to health.

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Keywords: aerosol particles, minerals

MESOTHELIOMA EPIDEMIC IN CAPPADOCIA/TURKEY: GEOLOGICAL MAPPING AS BASIS OF RISK ASSESSMENTS

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A mesothelioma epidemic known since 1978 causes > 50 % of all deaths in three villages in Cappadocia [1, 2]. The high mortality was shown to be linked to the chronic dust exposure to Erionite, $(K_2, Ca, Na)_2[Al_4Si_{14}O_{36}] \cdot 15(H_2O)$, which is known to be a human carcinogen and was detected in the dust of the villages [3]. Erionite is commonly found worldwide in altered silicic tuffs in saline lacustrine sediments [4]. However, except for Cappadocia, nowhere else Erionite exposure could be linked to such a high mortality. Recent studies in Cappadocia [5] revealed, that mesothelioma caused by Erionite may be genetically predisposed. The landscape of central Cappadocia is characterized by ignimbrites and fall-out tuffs of Miocene age (11-5.5 Ma) [6, 7]. The ignimbrites are dominantly non-welded and cover an area of 10.000 km². Most of the traditional houses were dug as dwellings into the soft, non-welded ignimbrites. Recent houses are built with carved blocks of the ignimbrites, most often unplastered. Inhabitants are thus continuously exposed to dust of tuffs since infancy. Our field studies indicate, that three depositional environments can be distinguished on/in which the ignimbrites came to rest: (a) lacustrine basin (Paleo-Ürgüp-Basin), (b) laharic depositional fans within the Nevşehir Plateau and (c) erosional surfaces [6]. Results show, that the lateral distribution of Erionite is restricted; it only occurs in patches within those tuffs that were deposited in lacustrine environments. Within the ERASMUS program we thus started mapping the depositional facies of sediments directly underlying the base of each ignimbrite in cooperation with the universities of Nide and Sivas. The results indicate, that only the two ignimbrites younger than 7 Ma in age overlay terrestrial sediments. Ignimbrites between 10 and 7 Ma in age overlay lacustrine sediments only in the north. The emplacement facies of ignimbrites older than 10 Ma have not been studied yet. The facies maps indicate variable southward extension of the Paleo-Ürgüp-Basin onto the laharic paleo-plaines exposed in the recent Nevşehir Plateau.

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Keywords: mesothelioma, erionite, geological mapping

USE OF REGIONAL GEOCHEMICAL PROSPECTING OF FLUORINE IN SUB-BASINS OF THE MIDDLE PART OF THE SÃO FRANCISCO RIVER, NORTH OF MINAS GERAIS/BRAZIL

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The Multiuse Geochemical Project is a national/regional prospecting research, carried out since 2007 by the Geological Survey of Brazil (CPRM), aiming to outline behavior patterns of 53 chemical elements in stream sediments and soils, and 34 ions in surface waters. Drainages sampled held in an area of 200 km² and the soil grid was 25 x 25 km. In the studied area total fluorine in sediments and soils as well as fluoride in surface water was analyzed. Samples collected: 345 of sediments, 290 of surface waters and 85 of soils. Average and maximum values obtained for F respectively 376 and 1720ppm for soils, 320 and 1076ppm for sediments and 0.20 and 1.02 mg/L for surface waters. The predominant geology of the studied area is a rhythmic subhorizontal Neoproterozoic sequence formed by pelites and interposed limestones, varying in thickness from a few to dozen meters. At the Eastern Northern occur granites, sandstones, gnaisses, bifs and sienites. Previous work carried out on part of the studied area shows the presence of fluoride in groundwater and its inter-relation with cases of dental fluorosis, indicating the fluorite as source of F occurring in limestones of the Bambui Group (BG) (Velasquez, 2007). In the State of Paraná, there were defined areas with fluoride levels in surface waters above 0.25 mg/L (maximum 0.957 mg/L) encompassing regions with occurrences of fluorosis in Itambaracá city (Licht, 2006). The extensive distribution of these F curves for soil, sediments and superficial water in such high grade compared to the previous ones, indicate that probably there is another source of fluorine, coming from the metasediments of the Bambui Group added to high levels of fluoride present in limestones, responsible for the enrichment of fluoride levels in the superficial water. The results of this survey clearly show the areas that should be the target of further detailed studies and show the relevance of this CPRM Project. Licht, O.A.B. 2006 – Geoquímica Multielementar de Superfície na Delimitação de riscos e impactos ambientais, estado do Paraná, Brasil – www.cprm.gov.br/publique/media/Painel34.pdf acesso:11/01/2011. Velasquez, L.N.M. et al. 2007 – Investigação hidrogeológica de Flúor em aquíferos carbonáticos do médio São Francisco-MG e epidemiologia da fluorose dentária associada. Relatório final CTHidro 01/2003. 139p.

Keywords: geochemical survey, fluorine, dental fluorosis

MORTALITY RATES FOR ALL CAUSES, ALL TUMORS, AND LUNG CANCER IN THE FORMER INDUSTRIAL AREA OF BAGNOLI AND FUORIGROTTA, NAPLES, FROM 2001 TO 2007: PRELIMINARY DATA

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Mortality data represent a useful marker for population health assessment. Besides, diseases of the respiratory system are particularly relevant in evaluating the long term effects on health among people exposed to industrial pollutants, either occupationally or environmentally. This is precisely the situation of residents in Bagnoli and Fuorigrotta districts, two areas of Naples located in contiguity with the former industrial site of Bagnoli-Coroglio. The aim of the present work was to compare mortality rates for all causes, all cancers, and lung cancers, as observed in people living in Bagnoli and Fuorigrotta with those of the entire population of Naples for the years 2001 to 2007. Mortality data were extrapolated from the mortality register of ASL Napoli 1 centro, Servizio di Epidemiologia e Prevenzione. The following endpoints were taken into account for each of the studied diseases: total number of cases, crude and standardized mortality rates divided by gender, with confidence limits at 95%. Data were not truncated by age because of the low number of cases recorded. Standardization was carried out based on data recorded for the national population (2001 census). Standardized mortality rates (SMR) for the overall period, in males and females, for all causes, all cancers and lung cancers were lower in Bagnoli and Fuorigrotta than in Naples. Throughout the entire period, rates for all causes were constant, in males and females, in Naples and Fuorigrotta and constant or slightly decreasing in Bagnoli. Standardized rates for all cancers in males are constant in the whole Naples municipality, slightly decreasing in Fuorigrotta, and highly decreasing in Bagnoli, while they were constant in females in all three cases. Lung cancer rates in males were constant in Naples and decreasing in Fuorigrotta and, particularly since 2003, in Bagnoli. In females lung cancer rates seem to be slightly increasing in Naples, steady in Fuorigrotta and very variable in Bagnoli, with spikes in 2002, 2004, and 2006, thus showing an opposite trend according to gender in this areas. To improve the epidemiological significance of these results it will be helpful to calculate the SMR for the same data after truncating by age, and to compare them with those obtained from other districts located in close contiguity with other, current or past, industrial areas of Naples (e.g. Barra-Ponticelli-San Giovanni eastern suburbs).

Keywords: mortality rates, lung cancer, industrial pollutants

PREFORMULATIVE STUDY OF CLAYEY SAMPLES TO BE USED AS HEALTH CARE MATERIALS

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Medical geology is a multidisciplinary scientific field shared by specialists of distinct areas and scientific domains, dealing with the relationships between the geological environment and health in humans, animals and plants. Health effects of minerals may be negative (being responsible of health problems) or positive (being used in health care products). Within minerals, clay minerals, the essential constituents of clays, are frequently related to positive health effects because of their interaction with biological systems (1). Clays are effectively used in the treatment of several diseases (2). In particular, these mineral materials are currently used in drug delivery systems (3-4). They are also used in conventional medicines and cosmetics, once some specifications regarding safety and efficacy are complied by the natural material (5). Some specific pharmaceutical test must be fulfilled by the candidate clay material before consider it as a pharmaceutical substance. These tests give information about the safety and technical properties of the material to be used in a specific function (for example, as active or inactive ingredient of a given formulation) and are a fundamental part of the preformulation studies (6-7). With these premises, two natural clayey samples from southern Spain and Southern Italy were studied to determine their suitability as pharmaceutical raw materials. Mineralogical and chemical studies were carried out and specific preformulative assays were also made, including powder micromeritics and flow, volumetric density, gel forming capacity and swelling. The measured properties allowed establishing the feasibility of the studied samples to be used in cosmetics or therapeutic formulations. When necessary, formulations should also include some other rheological additive and commercial clayey materials were proposed.

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Keywords: clay, preformulation, health care products

USE OF CLAYEY SAMPLES IN THERMAL THERAPEUTIC MUDS

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Clays are frequently used in topical health products (with therapeutics or cosmetics purposes) because of the special properties of their water suspensions (1-2). A particularly interesting employ of clays to promote health is their use in complementary and alternative medicine (CAM) products. Beside their employ by some important non allopathic medical systems as Ayurvedic medicine and traditional Chinese medicine, they are also frequently used in some complementary treatments of conventional medicine, as fundamental ingredients of thermal muds used in medical hydrology. With this purposes, hydrothermal or hydrothermalized pastes produced by primary or secondary mixing of clayey (geo)materials with salty thermo-mineral waters, are topically applied (3). These therapeutic agents are named peloids and the treatment pelotherapy. Composition, preparation, quality and suitability of the peloids should be exhaustively studied as they are health care products. Thermal muds are nowadays frequently prepared by mixing clayey raw materials with mineral thermal waters and as semisolid health care products; preparation, characterization and clinical use of these products must be considered under the pharmaceutical point of view (4-6). With these premises, three different clayey materials mainly constituted of kaolinite, palygorskite or smectites were extemporaneous mixed with thermal water from Graena thermal station (Granada, Spain). The constituent and resultant water/solid systems were characterized and compared with similar suspensions in purified water. The results allowed determining the possibilities of these samples to be used as thermal muds.

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Keywords: CAM, thermal muds, clay

“MECHANOCHEMICAL RETENTION” OF CADMIUM IN DIOCTAHEDRAL AND TRIOCTAHEDRAL SMECTITES

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The presence of heavy metals in the environment is a potential risk for water and soil quality due to their toxicity to plant, animals and human life. Lots of technologies and treatments have been developed to remove them from aqueous solutions. Several natural and synthetic sorbents have been employed for such aim. Among them, clay minerals have revealed highly potentials in such applications due to their low cost, availability, and low toxicity. Mechanochemical processes allow to activate chemical reactions by inducing different kinds of mechanical stress and without any other energy supply. This study investigated the effect of dry milling on the ability of dioctahedral and trioctahedral smectites to immobilize heavy metals cations. To this purpose a dioctahedral smectite “bentolite L” and a trioctahedral one “laponite RD” were ground with six distinct amount of cadmium chloride in dry conditions by means of zirconia planetary ball mill. Increasing milling time and Cd/clay minerals mass ratio were selected for experimental tests whereas grinding energy and ball to powder ratio were hold to constant value. Cadmium immobilization degree was evaluated by ICP/OES analysis and expressed by the leachable fraction of Cd ions. Two different leaching procedures were adopted: the first one with deionised water and the second one with 1 M MgCl₂ solution. Time depending experiments pointed out an increased Cd retention as time increases for both bentolite L and laponite RD. Long time experiments (24 h) showed otherwise that, at the same milling regimes and Cd/clay minerals mass ratio, laponite RD exhibits stronger Cd retention capability than bentolite. Mechanical treatment, depending on time and different mass ratio, induced the increase of retention efficiency. The mechanisms at bases of the “mechanochemical retention” of cadmium by both clay minerals were also characterized by means of solid state and surfaces characterization techniques such as FTIR and XPS of the clay minerals cadmium spiked mixtures, before and after grinding.

Keywords: mechanochemistry, cadmium, clay minerals

MAJOR AND TRACE ELEMENTS COMPOSITION OF THE URINARY STONES, KHUZESTAN PROVINCE, IRAN

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Due to increasing of urinary stones in Khuzestan province (southwest of Iran), this study is carried out to determine the chemical composition of urinary stones in this area. In this way 10 samples from main hospitals of the province were collected for mineralogical and geochemical analysis. Geochemical data using XRF show that CaO, MgO and P₂O₅ have the most distribution in compare of other major oxides. The most important elements in urinary stones are: Zr=135.5, Cu= 33.4, Zn= 47.4, Sr= 174.6, Cl= 558.6. The distribution of these elements is very low compared with the results of the studies carried out in other parts of the Middle East such as Jordan. Regarding the presence of Mg in Phosphorate minerals (such as Niahite and Struvite), positive correlation between MgO and P₂O₅ can be result of high tendency of Mg in participating in the Phosphorate phase. The negative correlation between P₂O₅ and CaO is also significant. It goes that each of the phases of P₂O₅ and CaO usually exist in the phosphorate and calcic minerals and are hardly found together in a high amount. The positive correlation between P₂O₅ and Sr is also significant. Other elements show no significant correlation with other major oxides. The high amount of Cu and Zr in uric acids and the positive correlation between these two is also significant. The high amount of Zr in uric acid minerals, due to the immobility of this element, and high value of Zr in the environment (food and water). But With attention to the concentration of copper in uric acid minerals (formation in PH<6) and the positive correlation between Cu and LOI ((Loss On Ignition), it is very likely that the copper sediment is resulted from the Presence of Organic compounds such as C (formation of CO₃). Finally, this study conclude that distribution of elements in the urinary stones is not just due to geochemical factors, but, according to specific environmental, mineralogical, and biological conditions.

Keywords: urinary stones, Khuzestan, Iran

EFFECTS OF PLASTICIZERS ON HUMAN (TK6) LYMPHOBLAST CELLS

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The main objective of this study is to determine and compare the toxicity and mechanism of damage of the phthalates Di-ethylhexyl (DEHP) and its principal metabolites, Mono-ethylhexyl (MEHP) and 2-Ethyl-1-Hexanol (EH) on the TK-6 human lymphoblastic cell line. Phthalates are a family of compounds used widely in the manufacturing industry. The exposure of humans to these compounds can result from the use of personal care products, paint, inks, rubber, dry cleaning and plasticizers. The metabolite EH is an organic alcohol produced in the cells as result of the biotransformation of di-ethylhexyl phthalate (DEHP). Phthalates are considered estrogen disrupters and effects on the reproductive and respiratory systems have also been reported however, the effects of phthalates on the immune system are limited. For the cell toxicity assays TK6 cells were cultured on 12.5cm² flasks with modified RPMI 1640 culture media with 10% FBS, and incubated at 37°C with 5% CO₂. TK-6 cells were exposed to DEHP, MEHP and EH at doses ranging from 5µM, to 350µM for 48 and 72 hours. TK6 cells viability Inhibition Concentration (IC₅₀) was assessed by the Trypan Blue exclusion protocol. The IC50 was later used to determine additional damage to the mitochondrial membrane and generation of reactive oxygen species (ROS). Mitochondrial membrane permeabilization and ROS generation were measured by implementation of the Mito PT™ (Immunochemistry) assay and the reagent DCFH-DA respectively. Results clearly demonstrated the capacity of these phthalates to inhibit cell growth on human lymphoblast with IC₅₀s of 234 µM, 196 µM and 75nM for DEHP, MEHP and EH respectively. Perturbation of the mitochondrial membrane permeability was also observed as well as generation of ROS for DEHP and MEHP. The metabolite EH presented little damage to the mitochondrial membrane and no generation of ROS in comparison with the controls. The study strongly suggests apoptosis as the mechanism of cell damage for DEHP and EMHP but not for EH. Future experiments will be performed to evaluate autophagy as the cell death mechanism for EH. The study indicates the effect that these ubiquitous compounds can have in cell of the human immune system.

Keywords: lymphoblast cells

A CONTRIBUTION TO THE STUDY OF PATHOLOGICAL BIOMINERALIZATION OF AORTIC VALVES

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In this study we aimed to the analysis of pathological biomineralization (PB) of explanted human aortic valves during cardiosurgery indicated for their stenosis. The aortic valve stenosis is the most frequently operated valve dysfunction at present. An inorganic analysis (and photodocumentation) of 20 explanted aortic valves was carried out using a polarizing microscope, electron microscope (BSE), infrared spectroscopy (IR), Cameca electron microprobe, X-ray analysis to provide a qualitative determination of inorganic substances in aortic valves. Imaging by low-velocity electrons was applied in the case of one sample.

Using these methods was proved that the most common inorganic substances in pathologically mineralized parts of the valves are phosphorus and calcium in the form of hydroxylapatite. Fluorine is less common, being represented by fluorapatite and hydroxylfluorapatite. The content of inorganic component in the degeneratively altered valves ranges from 65 to 90 wt. %. In each of the 20 samples, polarizing and electron microscopy proved that the mineralization process is a multi-stage one, and is equivalent to the process of bone reconstruction. At the same time, test analyses using X-ray fluorescence analysis and IR spectroscopy were performed: they verified the determination of inorganic substances in the explanted aortic valves. Orientation study by IR spectroscopy revealed that outer layers of the degenerated valve tissues contain an organic component with peptide bonds close to polyamides with an admixture of fatty acids and, in the central part, calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$.

In a set of 20 samples, pathological biomineralization of altered aortic valves was proved to be characterized – from the viewpoint of inorganic chemistry – by multistage formation of a mass of hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), to a lesser degree by fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and hydroxylfluorapatite.

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Keyword: biomineralization aortic valves

THE ROLE OF MAFIC AND ULTRAMAFIC ROCKS IN THE CONTAMINATION OF WATERS AND SOILS: A CASE STUDY IN THE KOHISTAN REGION OF NORTHERN PAKISTAN

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Mafic and ultramafic rocks are enriched in minerals such as olivine and pyroxene and are, therefore, having high concentrations of Ca, Mg, Fe, Cr, Ni, Mn, Co, Cd. The weathering of these rocks gives a variety of soils known as ultramafic or serpentine soil. Uptake by the plants, growing on these soils and leaching of metals into the percolating water could be of great environmental concern. Macro and trace metal contamination represents one of the most burning threats to soil ecosystem, as well as human health due to their sever effects and toxicity. In Pakistan mafic and ultramafic rocks are well exposed in the Kohistan region where the Indus Suture Zone (ISZ) represents the thrusting of the Indian plate underneath the Kohistan island arc. In order to investigate the effects of mafic and ultramafic rocks on the ecosystem of Kohistan region, the geochemical investigations of the waters, soils and plants of the region were carried out during this study. The macro (Na, K, Ca, Mg, Fe and Mn) and trace (Cu, Pb, Zn, Cd, Cr, Ni and Co) element concentrations were analyzed in water, soil and wild plant samples collected from mafic and ultramafic horizons in the Jijal, Dubair and Alpuri areas of Kohistan region. In the water samples collected from Kohistan region, all the physical parameters, anions and majority of heavy metal concentrations were found within the permissible limits set by world health organization (WHO). However, Pb, Zn, Cd, Ni and As showed higher concentrations than their respective permissible limits in 29%, 6%, 7%, 2% and 2% water samples, respectively. Heavy metal concentrations were evaluated for non-carcinogenic risk such as chronic daily intake (CDI), hazard quotient (HQ) and cancer risk (CR). The noncarcinogenic risk HQ were <1 for all the HMs except As. This level of contamination revealed a low chronic risk and medium cancer risk when compared with US-EPA guidelines. The soil samples of the study area showed significant ($P < 0.05$) contamination level of various heavy metals, while plants had greater variability in the metal uptakes from the serpentine soil. The multifold enrichment factor of Cr, Ni, Co and Cu in *B. lyceum*, *S. jacquimonthi* and *R. hastatus* of the plant species suggested that these plants have the ability to uptake and accumulate high concentrations of metals. This high accumulation of these toxic metals such as Cr and Ni, may pose potential threats to local community of Kohistan region after entering into human food chains.

Keywords: mafic and ultramafic rocks, contamination of waters, Pakistan

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