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Development of miniaturized submersible fluorometers for the detection of aromatic hydrocarbons in marine waters

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Polycyclic aromatic hydrocarbons (PAHs) are among the most widespread organic contaminants in aquatic environments. Due to their physico-chemical properties, PAHs are persistent and mobile, can strongly bioaccumulate in food chains and are harmful to living organisms. They are thus recognized by various international organizations as priority contaminants and are included in the list of 45 priority regulated substances by the European Union. Because of their aromatic structure, PAHs are "optically active" and have inherent fluorescence properties in the ultraviolet (UV) spectral domain (200-400 nm). Therefore, UV fluorescence spectroscopy has been successfully used to develop PAH sensors (i.e. UV fluorometers). Currently, five UV submersible fluorometers are commercially available for in situ measurements of PAHs: EnviroFlu-HC (TriOS Optical Sensors, Germany), Hydrocarbon Fluorometer (Sea & Sun Technology, Germany), HydroC TM / PAH (CONTROS, Germany), UviLux AquaTracka (Chelsea Technology Group, UK) and Cyclops-7 (Turner Designs, US). These UV fluorometers are all dedicated to the measurement of phenanthrene (λ Ex / λ Em: 255/360 nm), one of the most abundant and fluorescent PAHs found in the aquatic environment.

In this study, we developed original, miniaturized submersible fluorometers based on deep UV light-emitting diodes (LEDs) for simultaneous measurements of two PAHs of interest: the MiniFluo-UV 1 for the detection of phenanthrene (PHE, at λ Ex / λ Em: 255/360 nm) and naphthalene (NAP, at λ Ex / λ Em: 270/340 nm), and the MiniFluo-UV 2 for the detection of fluorene (FLU, at λ Ex / λ Em: 255/315 nm) and pyrene (PYR, at λ Ex / λ Em: 270/380 nm). The MiniFluo-UV sensors have several features: measurements of two PAHs at the same time, small size (puck format, 80 x 60 mm), very low energy consumption (500 mW at 12V), LED monitoring, analog and numerical communication modes. The two MiniFluo-UV sensors were first tested in the laboratory: 1) on standard solutions of PHE, NAP, FLU and PYR in the range 0.1-100 μ g 1-1 and 2) on a water soluble fraction (WSF) of crude oil diluted in 0.2 μ m filtered seawater (0 to 50% of WSF in seawater). Then, the MiniFluo-UV sensors were mounted onto a conductivity temperature depth (CTD) vertical profiler and tested at sea. Several profiles were performed in the Bay of Marseilles, in different harbours and hydrocarbon-impacted sites. The MiniFluo-UV measurements performed in the laboratory and in the field were associated with spectrofluorometric (EEM/PARAFAC) and/or chromatographic (GC-MS) analyses. The result obtained show that the MiniFluo-UV are pertinent and efficient tool for monitoring hydrocarbon pollutions in the marine environment.

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