The meaning of the spatial and temporal heterogeneity of the turnover processes for the prognosis of nitrate concentrations in the groundwater is discussed.The depth profiles of nitrate concentrations and groundwater age are presented, as well as soil investigations (physical and chemical) and investigations of the turnover of nitrate. The common view of all raised information leads to a vertical zoning of the turnover of nitrate in groundwater. In a flow- and transport model different land use scenarios were simulated taking into consideration the consumption of reactive material in groundwater. The results show the partial significant influences on the quality of raw water.

Schlüsselwörter: Nitrat, Grundwasser, Heterogenität, Nitratabbau, Denitrifikation
Keywords: nitrate, groundwater, heterogeneity, nitrate turnover, denitrification

11. Denitrification in Groundwater – Results from Investigations in two Austrian Case Study Regions (Ch. Schilling, A. P. Blaschke, D. Gutknecht, H. Kroiss, J. O. Skøien & M. Zessner)

11.1. Introduction

In the second half of the past century, bioavailability of nitrogen due to fertiliser application in terrestrial ecosystems increased considerably. Advancements in agricultural and residential development resulted in serious ecological problems by massive point and diffuse loads of nitrogen (and phosphorus) to groundwater and surface waters. Oxygen depletion and excessive algae blooms (eutrophication) in surface and coastal water bodies were recognised (L. B. Mee, 1992) and raised the awareness and the necessity for a sustainable management of nutrient sources. To derive measures for an effective management of nitrogen (and phosphorus) emissions from catchments, the main sources of emissions and the emission pathways to the surface waters have to be identified with consideration of all transformation and retention processes at the catchment scale.

The daNUbs project EVK-CT-2000-00051 (2-2001/1-2005) "Nutrient Management in the Danube River Basin and its Impact on the Black Sea" (H. Kroiss, 2005) focussed on the identification of the main sources and pathways of nitrogen and phosphorus emissions from subcatchments and their impacts on the Western Black Sea. In frame of the daNUbs project, investigations were carried out in two Austrian case study regions, the Ybbs and the Wulka catchment. Both catchments were selected forwards representing different conditions within the Austrian part of the Danube basin in terms of climate, hydrology, geology and land use practices. Water and nutrient balance calculations were performed using different models. Since in-situ measurements of denitrification rates in soil and groundwater are highly uncertain, denitrification in groundwater can be identified establishing nitrogen balances at the catchment scale. That denitrification in groundwater is an important process reducing diffuse nitrogen loads to surface waters significantly, could be shown using groundwater and surface water quality data for both catchments and will be presented in this paper. As a consequence, reflection of denitrification processes in groundwater in modelling approaches estimating nitrogen emissions to surface waters is a requirement for correct estimations at the catchment scale.

11.2. Methods

Groundwater and surface water quality was observed in the Ybbs and the Wulka catchment for the period 2001 to 2003. Additionally, existing observations from the beginning of 1994 were used to evaluate the groundwater and surface water quality in terms of nitrogen transformation and transport at the catchment scale. Water balance calculations were performed using the conceptual continuous time model SWAT 2000 (J. G. Arnold et al., 1999). Mean water balances were calculated with daily time step on the subcatchment level for the period 1992 to1999 and 1991 to 2000, for the Wulka catchment and the Ybbs catchment respectively. Emphasis was on identification of main water balance components in respect to morphological and climatic conditions as well as on individual catchment-specific contribution of runoff components to the river discharge.

Nitrogen emissions from both catchments were calculated using the empirical emission model MONERIS (H. Behrendt et al., 1999) with focus on identification of main emission pathways. Calculated total nitrogen emissions to the surface waters were compared to calculated loads from nitrogen surplus and to observed nitrogen instream river loads to identify nitrogen losses in groundwater and surface water by denitrification.

Groundwater residence time distributions were calculated based on a modified approach (D. Tarbaton, 1997) using interpolated groundwater surface information. Based on calculated groundwater residence times distributions, nitrogen emissions by groundwater to the surface water with consideration of denitrification using reported half life times (see F. Wendland & R. Kunkel, 1999) could be estimated at the catchment scale for the Ybbs and the Wulka catchment.

11.3. Results and discussion

Groundwater observation wells have been grouped in respect to their distances to the surface water. Following the groundwater flow along the flowpath towards the surface water, total inorganic nitrogen (TIN) concentrations in groundwater decreased significantly from areas with large distances to the surface water (> 100 m distance) towards riparian, surface water near groundwater (< 100 m distance) in both catchments (Tab. 11.1). Further decreasing TIN concentrations were observed from riparian groundwater to the concentrations, which were observed in surface water. Since observed chloride concentrations of the Wulka catchment remained constant, decreases in TIN concentrations from groundwater to surface water can be attributed to denitrification in groundwater and partly in surface water. For the Ybbs catchment, chloride concentrations decreased from groundwater to surface water as well indicating reduction in TIN levels beside denitrification in groundwater (and surface water) by dilution with surface water low in TIN levels from upstream catchment areas. Generally, TIN and chloride levels in groundwater and surface water of the Ybbs catchment were considerably lower (Tab. 11.1) compared to those observed in the groundwater and surface water of the Wulka catchment. Water balance calculations

Tab. 11.1: Observed mean total inorganic nitrogen (TIN) and chloride (Cl) concentrations in groundwater and surface water of the Ybbs and the Wulka catchment (1994 to 2003).
Gemessene mittlere Konzentrationen des gesamten anorganischen Stickstoffs (TIN) und Chlorids (Cl) im Grund- und Oberflächenwasser der Einzugsgebiete Ybbs und Wulka (1994 bis 2003).

Location of observation point	YBBS		WULKA	
	TIN [mg N/l]	Cl [mg/l]	TIN [mg N/l]	Cl [mg/l]
Groundwater wells with > 100 m distance to surface water	7.0	9.9	22.3	56
Groundwater wells with < 100 m distance to surface water	2.4	7.2	7.4	48
Surface water	1.4	3.6	5.6	50

indicated remarkable differences in mean annual precipitation and groundwater recharge, respectively between the Ybbs catchment (1377 mm · a^{-1} and 494 mm · a^{-1}) and the Wulka catchment (699 mm · a^{-1} and 118 mm · a^{-1}). Elevated annual groundwater recharge of the Ybbs catchment results in dilution of nitrogen concentrations in percolation water as well as in lower substrate availability (nitrate) for subsurface denitrification (compared to the Wulka catchment). Additionally, groundwater residence time in the Ybbs catchment is likely to be considerably lower due to larger subsurface specific discharges.

Load calculations and emission estimations supported these assumptions. Despite lower TIN levels in groundwater, due to larger groundwater recharge nitrogen emissions to the surface water of the Ybbs catchment exceeded the calculated emissions to the surface water of the Wulka catchment approximately by factor 4 (Fig. 11.1, grey bars). Since both catchments are characterised by almost equal area-specific nitrogen surpluses, nitrogen losses in soil and groundwater of the Wulka catchment by denitrification are considerably larger.

Differences between calculated nitrogen emissions to surface water and observed instream nitrogen load indicated nitrogen losses via denitrification in river (Fig. 11.1), what is compared to denitrification in soil and groundwater of minor importance in both catchments. Calculated groundwater residence time distributions for selected parts of both catchments confirmed, that the Ybbs catchment is characterised in average by noticeably shorter groundwater residence times in comparison to the Wulka catchment. This fact gave evidence that also denitrification in groundwater of the Ybbs catchment is less compared to denitrification in groundwater of the Wulka catchment. For both catchments it could be shown, that particularly areas with short distances to the surface water and low groundwater residence times (< 9 to 10 years) are responsible for most of the nitrogen emissions (> 90 % of total nitrogen emissions), which are emitted by groundwater to the surface water. Using a half life time of

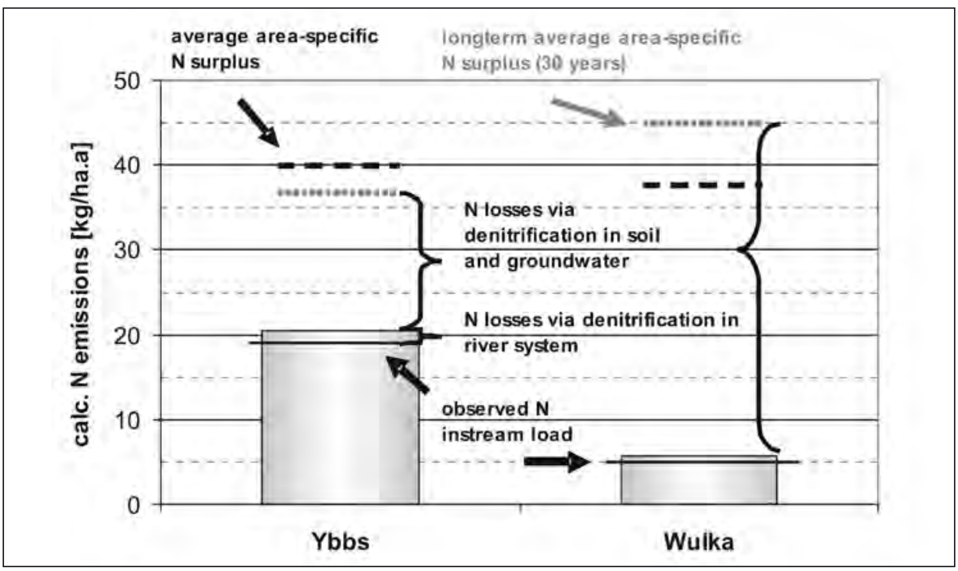

Fig. 11.1: Calculated nitrogen emissions (in kg/ha · a) to the surface water using the MONERIS model for the Ybbs catchment and the Wulka catchment.
Berechnete Stickstoffeinträge (in kg/ha · a) in das Oberflächenwasser anhand von MONERIS für die Einzugsgebiete Ybbs und Wulka.

four years to characterise denitrification resulted in calculated diffuse emissions, which were comparable to calculated diffuse nitrogen emissions using the MONERIS model as well as to load calculations from observation for the Wulka catchment. For the Ybbs catchment, calculated diffuse nitrogen emissions were underestimated using a half life time of four years, what indicated once more less denitrification in the groundwater of the Ybbs catchment.

11.4. Conclusions

Investigations in the Ybbs and the Wulka catchment provided information about comprehensive connections between catchment hydrology and morphology, observable concentration levels in groundwater and surface water and consequently, the magnitude of emission being contributed to surface waters. Denitrification in groundwater could be observed in both catchments, but site specific denitrification in groundwater is a function of local environmental conditions and differs considerably between the Ybbs and the Wulka catchment. Groundwater residence times are the result of hydrological and hydrogeological conditions and largely determine nitrogen fluxes through biologically active micro sites, in which conditions are favourable for denitrification to prevail.

Using modelling approaches to estimate nitrogen emissions at the catchment scale, denitrification in groundwater is a crucial process determining the level of diffuse nitrogen emissions to surface waters, and therefore it has to be considered and implemented in modelling approaches conveniently. Knowing about the spatially diverse contributions of catchment areas to diffuse nitrogen emissions to surface waters, strategies can be derived for a sustainable management of agricultural areas without affecting surface water nitrogen loads. In contrast, particularly areas under agricultural use and with large distances to surface waters are highly vulnerable in respect to elevated nitrogen concentrations in groundwater. So, sustainable management of catchment areas has to take into account both aspects of water protection depending on protection goals focussing either on groundwater and/or on surface water protection.

Summary

In frame of the daNUbs project EVK-CT-2000-00051 (2-2001/1-2005) "Nutrient Management in the Danube River Basin and its Impact on the Black Sea" investigations were carried out in two selected Austrian case study regions, the Ybbs catchment and the Wulka catchment. Denitrification in groundwater could be observed based on nitrogen surplus assessments in relation to groundwater and surface water quality observations. Differences between the selected case study regions in respect to nitrogen fluxes and denitrification activity could be attributed to hydrogeological circumstances, which were characterised by water balance calculations using the conceptual SWAT 2000 model. Using the empirical emission model MONERIS the total nitrogen emissions were calculated for both case study areas with consideration of the individual emission pathways.

An approach was developed for the calculation of diffuse nitrogen emissions to surface water with consideration of denitrification processes in the groundwater based on calculated groundwater residence times. This approach enabled the identification of catchment areas, which are responsible for most of diffuse nitrogen emissions to the surface water and which are therefore highly sensitive in terms of controlling diffuse nitrogen emissions to the receiving coastal waters of the Black Sea. These areas could be clearly distinguished from areas, which are important for local groundwater protection and revealed the contrarious effects of measures related to specific protection goals with focus on either the reduction of nitrogen levels in groundwater or the reduction of nitrogen emissions to surface waters.

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Zusammenfassung

Im Rahmen des daNUbs-Projektes EVK-CT-2000-00051 (2-2001/1-2005) „Nutrient Management in the Danube River Basin and its Impact on the Black Sea“ wurden Untersuchungen in zwei ausgewählten österreichischen Einzugsgebieten, dem Ybbs-Einzugsgebiet und dem Wulka-Einzugsgebiet, durchgeführt. Denitrifikation im Grundwasser konnte anhand von Messungen der Grundwasser- und Fließgewässergüte im Verhältnis zu berechneten Nährstoffbilanzen festgestellt werden. Unterschiede zwischen beiden Gebieten in Hinblick auf die emittierten Stickstofffrachten sowie auf Denitrifikationsraten im Grundwasser wurden maßgeblich durch die lokalen, hydrologischen und hydrogeologischen Bedingungen in den Einzugsgebieten beeinflusst. Die hydrologischen Verhältnisse in beiden Gebieten wurden mit dem konzeptionellen Modell SWAT 2000 charakterisiert. Das empirische Emissionsmodell MONERIS wurde zur Berechnung der Gesamtstickstoffemissionen aus den Einzugsgebieten in die Fließgewässer mit Berücksichtigung der jeweiligen Emissionspfade verwendet.

Es wurde ein flächendifferenzierter Ansatz zur Abschätzung diffuser Stickstoffemissionen mit Berücksichtigung von Denitrifikationsprozessen im Grundwasser basierend auf berechneten Grundwasseraufenthaltszeiten entwickelt. Dieser Ansatz erlaubte die Identifikation von Flächen, welche maßgeblich zu diffusen Stickstoffemissionen in die Fließgewässer beitragen. Diese Flächen sind von maßgebender Bedeutung für die Einflussnahme auf Stickstoffemissionen, welche über die Fließgewässer bis in die Küstengewässer und das Schwarze Meer transportiert werden. Diese Flächen konnten klar von denen abgegrenzt werden, welche für den lokalen Grundwasserschutz von Bedeutung sind und verdeutlichten die gegensätzliche Relevanz der Flächen für Maßnahmen, welche entweder auf eine Reduktion der Stickstoffkonzentrationen im Grundwasser oder auf eine Reduktion der Stickstoffemissionen in das Schwarze Meer abzielen.

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Keywords: denitrification in groundwater, water balance, nitrogen emissions, groundwater residence time

Schlüsselwörter: Denitrifikation im Grundwasser, Wasserbilanz, Stickstoffemissionen, Verweilzeit des Grundwassers