DECIPHERING SPATIAL AND TEMPORAL PATTERNS OF NITRATE IN A GROUNDWATER-DOMINATED AGRICULTURAL CATCHMENT

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Introduction

The ecological status of rivers and of their recipient seas is adversely affected by nutrient releases associated with agriculture and domestic wastewaters. Since riverine inputs constitute the dominant pathway of nitrate pollution to the Baltic Sea the management of eutrophication in this brackish inland sea relies on mitigation actions undertaken by the bordering states in river basins in line with the Water Framework Directive. Consideration of the subsurface nitrate pathways and of groundwater – surface water interactions is a prerequisite for the understanding of nitrate pollution in catchments. The coupled effects of the hydrological and biogeochemical processes in groundwater and watercourses give rise to spatial (longitudinal) and temporal (seasonal, diurnal and runoff controlled) patterns in riverine nitrate concentrations and fluxes. The presented work aims at identification and explanation of these patterns in the Kocinka river catchment whose watercourses reveal high concentrations of this agricultural pollutant. Results of this work are relevant for actions undertaken to mitigate nitrate pollution in river basins.

Samples and methods

The Kocinka catchment is located to the north of Częstochowa in the Odra River basin. Snapshot samplings for determination of the chemical and isotopic ($\delta^{18}O$, $\delta^{2}H$) composition of river water were conducted between spring 2014 to summer 2017. Groundwaters feeding the river were sampled in springs and shallow observation wells adjacent to the river channel. Water temperature, electric conductivity pH and dissolved oxygen concentrations were determined in situ. Nitrate concentrations were determined by spectrophotometry and ion selective electrode. Discharge was determined from water stages recorded continuously in the lowest reach of the river. Precipitation was measured and collected for the isotopic analyses in Biała, in the upper part of the catchment.

Results

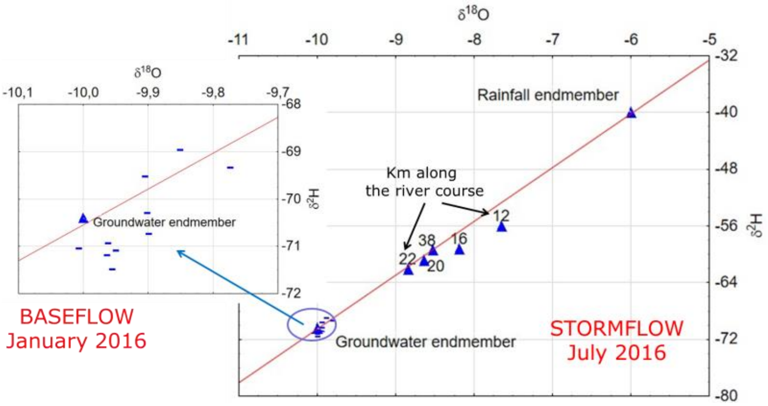

Figure 1. *Isotopic composition of the Kocinka River at two extreme flow conditions. Red line represents the Local Meteoric Water Line.*

The longitudinal patterns of both the electrical conductivity and isotopic composition indicate that groundwater is the main component of the streamflow contributing between 60% during an extreme stormflow event to virtually 100% during baseflow conditions. Concentrated and diffuse groundwater inflows feed the river down to the 22 km. Isotopic signatures of river water (Fig. 1) showed that the contribution of groundwater to the streamflow increased between 12 to 22 km and decreased further downstream due to mixing between the groundwater and fast runoff derived from recent rainfall. The mixing occurred along the Local Meteoric Water Line that represents the $\delta^{18}O$ - $\delta^{2}H$ relationship in local precipitation. The deviation of the isotopic compositions for the 12 and 16 km from the LMWL reflects the isotopic modification of river water in a large through-flow pond through which most of the Kocinka streamflow is diverted. The prolonged residence times of water in the pond influence also river water quality leading, from early spring to late autumn, to significant reduction of nitrate concentrations. For baseflow conditions, the blown-up part of the graph shows clustering of river water samples close to the groundwater isotopic signatures, which indicates that the streamflow was dominated by groundwater inflows to the river.
The longitudinal patterns of nitrate concentrations are partly controlled by groundwater inflows which are highly polluted in the upper part and moderately polluted in the middle part of the catchment. Fig. 2 exemplifies these trends for one of the sampling campaigns. Contributions of the highly polluted groundwater endmember (not shown on the plot) replenished nitrate concentrations downstream the pond where nitrate removal occurs. Downstream 16 km the river is fed by the moderately polluted groundwater, which results in the reduction of nitrate concentrations. Further decrease of concentrations downstream 22 km might be due to nitrate removal in the semi-natural reach of the river but also due to dilution with recent rainfall, as the isotopic signatures suggest. Nitrate removal and dilution with fast runoff result in summer minima and winter maxima of nitrate concentrations.

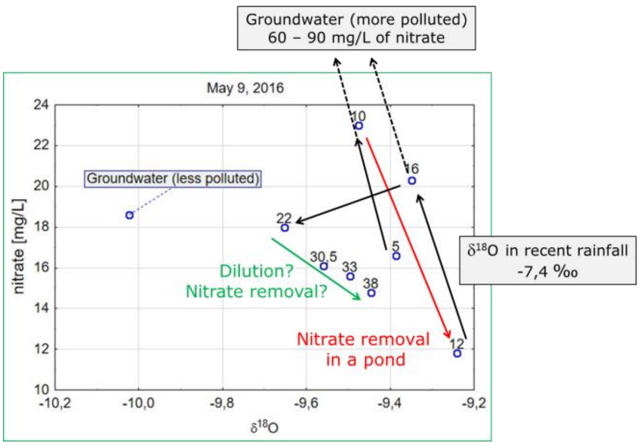

Figure 2. *Longitudinal changes in nitrate concentrations plotted against the $\delta^{18}O$ of river water. Numbers at circles denote km from the river source.*

Conclusions

Groundwater inflows control not only the streamflow but also nitrate concentrations in the Kocinka River catchment. Significant nitrate removal occurs only in the through-flow pond. Reduction of nitrate export from the catchment relies on the mitigation of nitrate pollution in the Częstochowa aquifer. Ponding of river water is the only viable option for the in-stream mitigation.

Acknowledgements

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