

What is the origin of the phosphorous? Quantification of sources and pathways for phosphorus and sediment losses in an agricultural dominated catchment

Introduction

The use of models for assessments of spatial and temporal variability of flow of P, but also sediments and nitrogen (N) was investigated, with focus on the possible added value of intense monitoring, increased efforts to include local information, as well as local vs. regional model calibration. Also fingerprinting techniques for assessments of sources to sediments was investigated and the potential of the use of ^{18}O isotope ratios in water to reduce uncertainties of water flow paths in hydrological models was assessed.

Another objective was to investigate if the oxygen isotope ratios in dissolved inorganic phosphate in riverine surface water can be used to distinguish between phosphorus (P) originating from agricultural runoff and from rural sewage effluents during different periods of the year.

Materials and methods

Monitoring of N, P, Si and suspended sediments was carried out in a larger catchment (162 km²). In this catchment, also collection of material to be analysed for "fingerprinting" of sources of sediments was made. A sediment trap construction was developed for this purpose.

In order to investigate if the temporal variation in stream water isotope signature can be related to the relative contributions of the different sources of phosphate, repeated samplings of the $\delta^{18}\text{O}$ composition of PO_4^{3-} were made in a small (7.3 km²) agricultural catchment which received anthropogenic phosphorus inputs from mixed agricultural sources and from rural sewage. To cover different seasons and water flow dynamics, sampling was made in the outlet of the small agricultural catchment, as well as from field drainage wells and sewers.

In the small catchment, a monitoring programme for sampling of $\delta^{18}\text{O}_w$ (in streamwater, drainage wells and precipitation), PO_4^{3-} , and tot-P (in streamwater and drainage wells) was implemented. Sampling was made 1-2 times per month in 3 years at 6 sites in the catchment in order to cover all seasons as well as different flow dynamics. Selection of timing for monitoring was made with the help of the hydrological forecast tool WebHyPro. In one upstream sub-surface drainage well and at the outlet of the catchment, time frequent monitoring (2 hours) was carried out during snowmelt and rainfall events.

The hydrological catchment model HYPE was set up with various spatial and temporal resolutions, with validation against monitored data, in order to assess if and how incorporation of local databases and local calibration could reduce uncertainty.

Results

The assessments based on the HYPE model setups showed that inclusion of local information only to a very limited extent improved model performance regarding temporal and spatial variability. Neither did the possibility to improve model performance by using an hourly time step instead of a daily significantly improve results, with exception of inclusion of local meteorological information. Use of local calibration instead of regionally set parameter did significantly improve model results. The use of $\delta^{18}\text{O}_w$ in model calibration made it possible

to limit model uncertainty by defining model parameter setups that reflected flow pathways corresponding to the dynamics of $\delta^{18}\text{O}_w$ in the riverine water.

The fingerprinting analyses revealed significant differences in signal between different landscape components. Studies to assess the integrated signal in the river from sediments trapped in the river in the larger of the two studied catchments will be finalized in December 2013.

The oxygen yield from the $\delta^{18}\text{O}_P$ analysis was within the acceptable range. Samples within the acceptable range were regarded as representing PO_4^{3-} that precipitated as Ag_3PO_4 . Only a few samples were close to the equilibrium line. Thus the measured $\delta^{18}\text{O}_P$ can be assumed to reflect the isotope signature of different P sources. This is a prerequisite to apply this tool for quantification of the contribution from different sources. The significant deviation from equilibrium values can be explained by a short residence time of DIP in the stream water. There were two distinct sources for dissolved inorganic phosphate in the streamwater (i) geological background, i.e. phosphate mobilized from mineral phosphate with $\delta^{18}\text{O}_P$ values of +6 to +9 ‰, and phosphate released from septic tank systems with higher $\delta^{18}\text{O}_P$ values, ranging from approximately +13 to +16‰. In addition a third source was identified, consisting of phosphate originating from fertilizers added to agricultural fields and cycled in the upper soil horizon.

Discussion and conclusions

With regard to the modelling based studies, the main conclusion is that model results of P and other nutrients only to a limited extent are improved by inclusion of more detailed local data, compared to when using nationally available databases. Neither decreasing the time step in the model from a daily to an hourly time step did significantly increase model performance. Local calibration and use of very local meteorological information did, however, generally increase the performance of the model. This reflects that, with the exception of the added value of local meteorological information, it rather is the complexity of processes than the limitation in databases that is the main cause of uncertainty. Combination of monitoring, tracer studies, modelling and expert judgements is therefore recommended in order to make judgements as a basis for decisions related to local water management aiming to reduce emissions of P and other nutrients.

The potential to use $\delta^{18}\text{O}_P$ in the differentiation of P sources within small catchments with short riverine transit times of DIP was demonstrated. We conclude that the $\delta^{18}\text{O}_P$ in the stream water of the study catchment reflects the signature of different sources being mixed in the stream. The data confirmed the relative importance of rural sewage during summer low-flow periods. In addition, the significant variation in the isotope signature in drainage water phosphate, particularly in wells or occasions where an impact from manure or sewage was suspected, or in connection to snowmelt events, suggests that the method can be a useful way of quantifying the contribution from different sources. For samples containing large amounts of organic matter, it is recommended to use a different extraction procedure to avoid contamination by oxygen originating from other sources than phosphate.

Publications

Rönnberg, R. 2012. Identifiering av fosfatfosfors käll- och flödesfördelning i ett litet jordbruksområde (Identification of phosphate phosphorus source and flow paths in a small agricultural catchment. Examensarbete (Exam thesis) , Institutionen för Geovetenskaper, Luft-, vatten- och landskapslära, Uppsala universitet. ISSN 1401-5765

Tonderski, K.S, Andersson, L., Ahlgren, J., Rönnberg, R., Schönberg, R., Taubald, H. Using $\delta^{18}\text{O}$ in phosphate as a tracer for catchment phosphorus sources. Submitted to Environmental Science and technology in November 2013.

Two papers that will be included in Andreas Milvers licenciate thesis (Institute for Earth Science, University of Gothenburg; to be defended in spring 2014) are available as manuscripts:

Andersson, L, Milver, A., Johanesson, K., Lindström, G., and Tonderski, K. Understanding of spatial variability for nutrient transport from models and monitoring – what is our message to water managers?

Andersson, Rönnberg, R., Johanesson, K., Lindström, G., and Tonderski, K. Modelling of water and phosphorus flows from a small agricultural catchment - evaluation of the possibility to increase model performance by the use of local data and local calibration.

In addition, a paper based on linking $\delta^{18}\text{O}$ in streamwater and fingerprinting to catchment modelling is planned to be finalized in 2014.