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Role of shallow groundwater in nitrate and herbicide transport in the Kervidy agricultural catchment (Brittany, France)

JEROME MOLENAT & CHANTAL GASCUEL-ODOUX

UMR Sol Agronomie et Spatialisation, Institut National de la Recherche Agronomique, Route de Saint Brieuc, F-35042 Rennes, France
e-mail: molenat@roazhon.inra.fr

Abstract The objective of this study was to investigate shallow groundwater transport of nitrate and herbicides to a stream in an agricultural catchment. Nitrate and some herbicide concentrations were monitored in shallow groundwater and stream water of the Kervidy catchment (5 km^2) located in French Brittany. Also, flow and the nitrate transport from groundwater to the stream were modelled. Results indicate that groundwater in the saprolite is a major store of nitrate due to relatively long hydrological residence times (up to three years). Also, some of the herbicides, particularly the triazines, moved rapidly through the soil to the groundwater suggesting that herbicides can be routed through the soils to the stream as groundwater discharge.

Key words agricultural pollution; Brittany France; herbicide; nitrate; residence times; shallow groundwater

INTRODUCTION

Brittany, the western region of France, has been concerned about water quality degradation for more than two decades. In Brittany, nitrate concentrations at all stream water monitoring sites equalled or exceeded 40 mg $NO_3^- l^{-1}$ in 1998. Pesticide pollution of stream water is also a growing issue. An accurate understanding of nitrate and pesticide transport within catchments is needed by policy makers and land-use managers to develop and implement better land-use and agricultural management practices. The objectives of the experimental and modelling study reported herein is to identify the main flow paths controlling nitrate transport from the root zone to the stream. The general hydrology of Brittany is dominated by shallow groundwater. Consequently, we studied the groundwater chemistry on three hillslopes of the Kervidy catchment (France) during non-storm periods for two years. Then, we developed and tested a two-dimensional flow and nitrate transport model for one of the hillslopes to get a preliminary estimate of nitrate travel times. Also, we sampled the groundwater to assess the occurrence of herbicides in groundwater.

MATERIAL AND METHODS

Experimental site, field study and sampling strategy

The 5-km^2 Kervidy catchment is a sub-catchment of the Naizin catchment, situated in central French Brittany (Fig. 1). The climate is humid (909 mm annual average precipitation) and

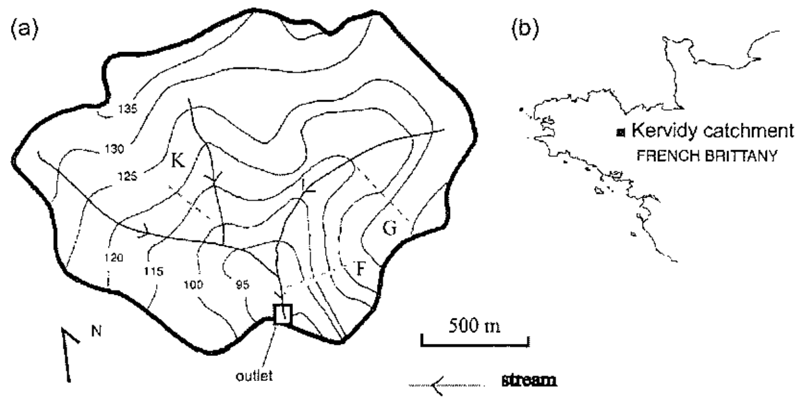

Fig. 1 Map (a) and location (b) of the Kervidy catchment showing the three studied hillslopes called F, G, and K.

temperate. Land is mainly used for intensive agriculture (maize and wheat). Annual nitrogen excess ranged from 185 to 196 kg N ha^{-1} during the last decade (Bouraoui *et al.*, 1999). The aquifer underlying the catchment is composed of three layers: a thin soil cover, a weathered shale, and a fissured shale. Fifteen piezometers were installed along three hillslopes for sampling of the weathered aquifer (Fig. 1). A 40-m deep piezometer was installed close to the catchment outlet to sample water in the fissured shale. A gauge station and a weather station provided continuous stream discharge and hourly rainfall, respectively.

Groundwater samples in hillslope K and stream samples were collected fortnightly from January 1997 to December 1999, for nitrate and sulphate (Molénat *et al.*, 2001), as well as Rare Earth Element analysis (Dia *et al.*, 2000). Groundwater in hillslopes G and F were sampled for one year beginning in December 1998. One sample from the 40 m deep piezometer was collected in February 1998. Redox potential and pH were measured in the field. A sample aliquot was filtered and analysed for anion concentration by ion chromatography. Samples were also collected for herbicides analysis. Nitrate concentrations are reported as mg l^{-1} as NO_3^-. Samples were collected every two weeks during spring 1998, winter 1999, and spring 1998, each of which was preceded by herbicide applications. Samples were analysed by gas chromatography for atrazine (which is applied to maize in spring), atrazine metabolites, and isoproturon (applied to wheat in winter).

Groundwater modelling

We developed and tested a two-dimensional model of flow and nitrate transport in the groundwater for one of the hillslopes using MODFLOW and MT3D. The model allowed us to test flow and transport hypotheses that were conceived from the field observations, and to estimate groundwater travel times. For this preliminary work, the groundwater flow was modelled under steady-state conditions corresponding to winter conditions. Groundwater recharge was set at 2 mm day^{-1} uniformly over the entire hillslope and evapotranspiration was assumed to be insignificant. The nitrate concentration in recharge was set at 100 mg l^{-1}, the expected current value. From an initial uniform concentration of 20 mg l^{-1}, the spatial and temporal distribution of groundwater nitrate concentrations were computed until equilibrium was reached. Denitrification was represented as a first order reaction.

RESULTS AND DISCUSSION

Groundwater chemistry

In time, the groundwater displayed only small temporal variations of nitrate and sulphate concentrations. In space, the nitrate and sulphate concentrations in the weathered aquifer displayed the same spatial pattern along the three hillslopes. Nitrate concentrations decreased from upslope to downslope whereas sulphate concentrations increased from upslope to downslope (Fig. 2). Upslope and downslope nitrate concentrations ranged from 100 to 180 mg l^{-1} and from 40 to 80 mg l^{-1}, respectively. Sulphate concentrations were less than 1 mg l^{-1} in the upslope piezometers and ranged from 14 to 28 mg l^{-1} downslope. pH also displayed a downslope gradient from 5 to nearly 7. In contrast, the redox potential was constant along each hillslope at around 400 mV. In the fissured aquifer, nitrate and sulphate concentrations were much lower than in the shallower groundwater, 2.8 mg l^{-1} and 20.8 mg l^{-1}, respectively.

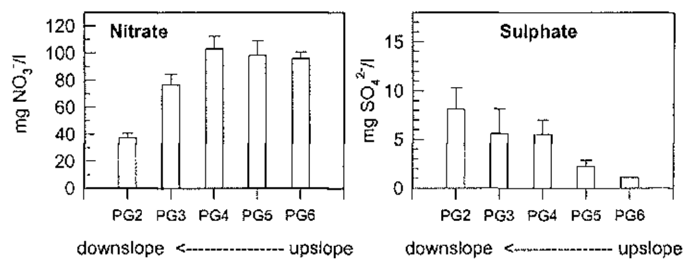

Fig. 2 Annual mean nitrate and sulphate concentrations along hillslope G in the Kervidy catchment. The PGs are the piezometers.

The weathered aquifer is a large hydrological reservoir of nitrate, and at 450 kg ha^{-1}, which is twice the nitrogen excess and 5–9 times the annual stream water nitrate flux (50 and 80 kg N ha^{-1} in 1996–1997 and 1997–1998, respectively) (Molénat *et al.*, 2001). The weathered aquifer, therefore, is an important store of nitrate in the catchment, of which annual stream water nitrate export is only 11% to 18% of the nitrate stored in the groundwater. The nitrate concentrations in the stream are controlled by the water table in the weathered groundwater (Molénat *et al.*, 2001). The mixing of the low nitrate concentration water of the shale aquifer with the shallow groundwater explains the distinct spatial pattern in the weathered aquifer chemistry. Low nitrate concentrations in this aquifer may result from autotrophic denitrification and the oxidation of pyrite (FeS_2) in shale and the production of sulphate (Pauwels, 1994). So upward flows from the deep aquifer to the weathered aquifer would explain both the nitrate and sulphate distributions in the weathered aquifer.

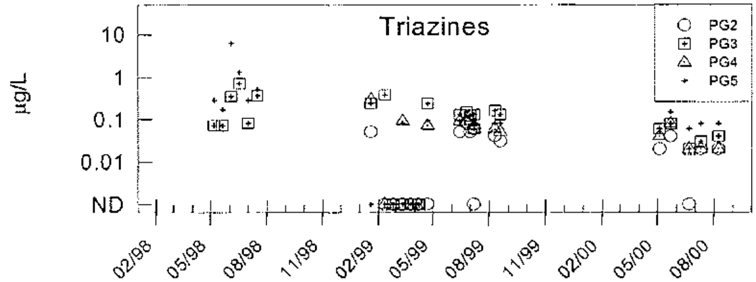

Fig. 3 Triazine concentrations in piezometers along transect G in the Kervidy catchment (ND = not detected). Downslope direction goes from PG5 to PG2.

Isoproturon, and triazines (atrazine and all its metabolites) in the weathered aquifer were highly variable in time and space without displaying any specific pattern (Fig. 3). Of the 69 samples collected during the two year collection period, atrazine and diethyl-atrazine (DEA), one of the main atrazine metabolites, were detected in 24 and 16 samples, respectively. Nine of the atrazine samples and 14 of the DEA samples had concentrations greater than 0.1 $\mu g\ l^{-1}$, the EC limit for drinking water. Isoproturon was detected in four samples of the 53 analysed, three of them having concentrations greater than 0.1 $\mu g\ l^{-1}$. Some herbicides, such as triazine, can move rapidly to and with the groundwater to the stream, as observed for shallow groundwater in the Kervidy catchment. In contrast to isoproturon, triazines seem to be soluble and persistent enough in soils for movement to shallow groundwater to occur. The occurrence of herbicides in groundwater depends directly on the agricultural practices (timing, location, and rate of herbicide application), the specific characteristics of the compounds in soils (persistence and mobility), and the mechanisms and rate of movement in the unsaturated zone (amount and timing of rainfall, and depths to groundwater). All these factors make herbicide recharge much more variable in time and in space than nitrate recharge. The recharge variability results in a temporally variable herbicide contamination along the hillslope.

Modelling: flow paths and residence time

Despite the simplicity of our model, no large discrepancy appeared between the simulated hydraulic heads and the observed ones (RMSE = 1.5 m). The major difference between predicted and observed hydraulic heads occurred upslope with a difference of 2.9 m. The simulated nitrate concentrations along the hillslope also were similar to those observed in the piezometers (RMSE = 12 mg l^{-1}). Simulations displayed an upslope gradient as in the field. However, the simulated decrease along the hillslope was less pronounced than the observed one. In the model, nitrate concentration decreases are caused by upward flows from the deep denitrified groundwater (Fig. 4), which is consistent with the observations. Travel times in the groundwater along the hillslope vary markedly depending on where the solutes enter the groundwater (Fig. 4). When solutes enter the groundwater in the 40% lowermost part of the hillslope, the travel times are shorter than one year. The travel time of a solute

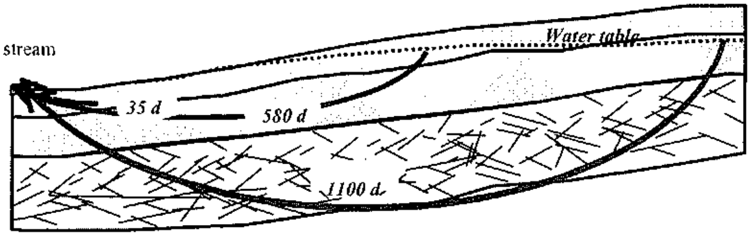

Fig. 4 Flow paths and residence times of water inferred by numerical modelling along hillslope G in the Kervidy catchment.

entering the upper 60% of the hillslope was 1–3 years. The travel times are underestimated because they were computed for winter conditions when hydraulic gradients are the largest and because molecular diffusion between mobile water and immobile water was not represented in the model. Furthermore, solute movement in the vadose zone, which was not considered in the study, also may be long.

CONCLUDING REMARKS

One main result of our study is that shallow groundwater in weathered bedrock can be a major nitrate store in the catchment. Nitrate recharge occurs all year on the hillslope and the groundwater is characterized by large residence times. From an operational perspective, it will take many years to reduce nitrate leaching and the decrease of nitrate concentrations in streams following any remedial measures, including zero future fertiliser applications. The study also shows that significant herbicide concentrations can occur in groundwater. However, herbicide concentrations, unlike nitrate concentrations, do not appear to follow any spatial or temporal pattern, which may be explained by the variability in time and in space of herbicide recharge.

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REFERENCES

Bouraoui, F., Turpin, N. & Boerlen, P. (1999) Trend analysis of nutrient concentrations and loads in surface water in an intensive fertilized watershed. *J. Environ. Qual.* **28**, 1878–1885.

Dia, A., Gruau, G., Olivié-Lauquet, G., Riou, C., Molénat, J. & Curmi, P. (2000) The distribution of rare earth elements in groundwaters: assessing the role of source-rock composition, redox changes and colloidal particles. *Geochimica et Cosmochimica Acta* **64**, 4131–4151.

Cheverry, C. (1998) *Agriculture Intensive et Qualité des Eaux*. INRA Editions, France.

Molénat, J., Durand, P., Gascuel-Odoux, C., Davy, P. & Gruau, P. (2001) Mechanisms of nitrate transfer from soil to stream in an agricultural watershed of French Brittany. *Water Air and Soil Pollution* (in press).

Pauwels, H. (1994) Natural denitrification in groundwater in the presence of pyrite: preliminary results obtained at Naizin (Brittany, France). *Mineral. Mag.* **58A**, 696–697.