Regional monitoring of temporal changes in groundwater quality

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Abstract Changes in agricultural practices are expected to affect groundwater quality by changing loads of nutrients and salts in the recharging groundwater. Regional monitoring networks installed to register those changes often fail to produce convincing evidence. This study presents an approach to evaluate and prove the effects of increasing and decreasing agricultural pollution on groundwater quality using a combination of trend analysis on time series and concentration–depth profiles. To reveal trends that might have become obscured by chemical reactions, additional semi-conservative parameters were introduced that are less sensitive to those reactions. Significant trends in the sampled groundwater were matched with the temporal changes of manure loads in recharging groundwater, using a groundwater age distribution that was verified using tritium concentrations. For the Noord-Brabant example, trends in the nutrient concentrations were not detected using a trend analysis. However, evidence for the increase of solute concentrations due to increasing manure loads was found for the semi-conservative parameter "oxidation capacity". The study shows that it is possible to identify significant trends for groups of wells sampled from area-types sharing common characteristics.

Key words conservative and reactive transport; groundwater quality monitoring; nitrate; time series; travel time

INTRODUCTION

In general, groundwater quality monitoring networks fulfil their task, demonstrating differences between areas with specific land use and soil types and indicating proportions of polluted groundwater at a given time (Reijnders *et al.*, 1998). However, evidence for temporal changes in nutrient concentrations in larger areas can seldom be found (e.g. Reijnders *et al.*, 1998). The probable reasons are: (a) the long travel times of groundwater to the well screen, (b) the obscuring, attenuating or retarding effect of physical and chemical processes on solute breakthrough, and (c) the spatial variability of contaminant concentrations in recharge, the hydrological residence time, and the reactive properties of the aquifer sediments.

Figure 1 shows a conceptual example of the concentration response in a monitoring well to a linear increase of the manure load given a 15-year hydrological residence time from the recharge point. For a conservative water-quality parameter, a linear trend will be observed beginning 15 years later. However, retarding or degrading processes tend to extend the response time and hence the associated monitoring period

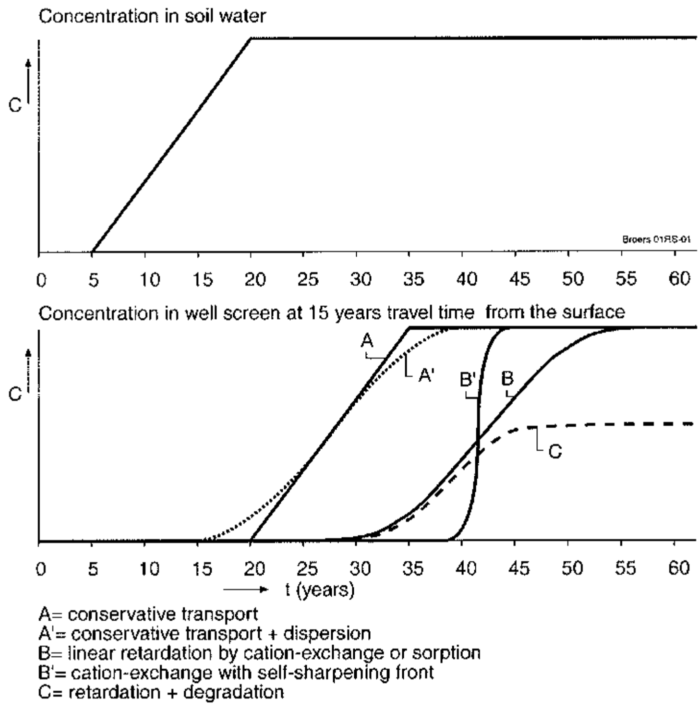

Fig. 1 The hydrochemical response of groundwater to a linear increase of the manure loads given a 15-year hydrological residence time from the recharge point.

needed to detect the changes in concentration for non-conservative parameters. Reactive processes may even transform the linear trend into a step trend. The nutrients N, P and K are known to behave non-conservatively in groundwater; each is influenced by different hydro-geochemical processes (Griffioen & Broers, 1999). The example shows that groundwater travel times and possible subsurface reactions should be evaluated to explain the trends in the monitoring data.

This study presents an improved approach to evaluate and verify the effects of increasing and decreasing agricultural pollution on groundwater quality. The approach includes the evaluation of the groundwater age and the non-conservative behaviour of the chemical parameters, and combines concentration–depth profiles and time series trend analysis. The results are illustrated using examples from the Dutch province of Noord-Brabant, one of the areas in Europe most affected by agricultural pollution.

METHODS

Temporal changes can be identified from a trend analysis of time-series data measured at a specific depth and a comparison of solute concentrations at different depths at a specific time. The approach combines the two data sources for area-types with homogeneous land use, geohydrological situation, and soil characteristics.

Time series trend analysis

The objective of the trend analysis is to identify the area-types where significant concentration changes have occurred during the monitoring period. The monitoring data consists of the 1984–1998 annual groundwater sampling of well screens at two depth intervals (5–15 and 15–30 m below land surface). The data were considered to be a random sample of groundwater quality in the area-types. Time series of the median, 25 and 75 percentile, and maximum and minimum concentrations in the area-types were used for the trend analysis. The time series were checked for changes in the detection limits and the sampling and analysis procedures. Significant trends in the time series of the sample statistics were identified using the non-parametric Mann-Kendall trend test. The trend slope and 95% confidence intervals were computed using the Kendall-Theil robust line method (Helsel & Hirsch, 1992).

Concentration–depth profiles and conservative prediction

Changes in groundwater composition can also be derived from concentration–depth data, assuming a certain groundwater age distribution and conservative transport. Concentration changes with depth were assessed using box plots of the measured concentrations in a certain area-type at 5–15 and 15–30 m depth.

A conservative transport prediction was made that transforms the historical input of solutes in recharging groundwater into a concentration–depth forecast. The prediction is based on an assumption of the groundwater age distribution. In recharge areas, a simple age distribution can be expected, constrained by the amount of groundwater recharge (N), the porosity (ε), and aquifer thickness (T) following Raats (1981):

$$t_z = \frac{\varepsilon T}{N} \ln\left(\frac{T}{T-z}\right) \tag{1}$$

where t_z is the age at depth z. The age distribution was checked using tritium concentrations in the wells sampled.

The concentration–depth forecast was compared with the measured concentrations summarized in the box plots (concentrations at fixed moment in time) and the significant trends found using time series analysis (concentration changes at fixed locations).

Use of semi-conservative parameters

In regular trend analyses only concentrations of the solutes that are of direct interest, like nutrients N, P and K, are investigated (e.g. Reijnders *et al.*, 1998). The breakthrough of those reactive solutes can easily be retarded or attenuated by hydro-geochemical processes. We propose the additional use of parameters that are less sensitive to subsurface reactions and refer to them as "semi-conservative" parameters. For instance, oxidation capacity (OXC) behaves conservatively during the process of nitrate reduction by pyrite oxidation. Oxidation capacity was defined as the sum of

NO_3 and SO_4 in electro-equivalents per litre. The sum of cations can also be used as a semi-conservative parameter when cation-exchange processes dominate the transport of the cations and mineral dissolution processes do not occur. The semi-conservative parameters were used in the time series and concentration–depth analysis.

RESULTS

The approach is illustrated for area-types with intensive livestock breeding in the Pleistocene sandy areas of Noord-Brabant. The upper geology of those areas consists of fluvial sandy deposits overlain by a thin layer of aeolian cover-sands and fluvio-periglacial deposits. The land use of the chosen area-types is characterized by alternating maize and grassland. Average N-loads in those areas have increased from 1960 to 1990 because of increasing use of manure and fertiliser (Fig. 2). Distinction was made between recharge areas and drained areas, containing 13 and 22 wells, respectively. Tritium concentrations in the recharge area-type indicate an average groundwater recharge of about 0.25 m year^{-1}, yielding a groundwater age of about 30 years at 22 m depth. The tritium concentrations in the drained area-type indicate less groundwater recharge and a larger age variation than the recharge areas. The conservative predictions were based on time series of the input of nutrients and salts from atmospheric deposition, fertiliser and animal manure (van der Grift & van Beek, 1996). Crop uptake and harvesting was calculated following Beekman (1998). The leaching of nitrate was corrected for denitrification in the unsaturated zone on the basis of the groundwater level regime according to Beekman (1998). Parameters used for the predictions are listed in Table 1.

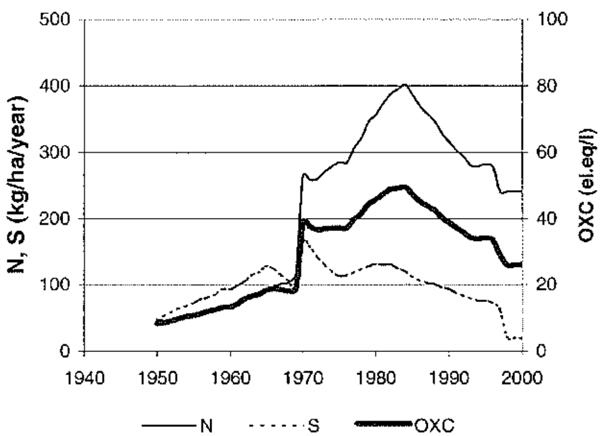

Fig. 2 The temporal variations associated with the 1950–1990 increase in nitrogen and sulphur loads (corrected for crop uptake) and resulting OXC concentrations in area-types with intensive livestock breeding.

Nitrate Time series analysis for the 1984–1998 monitoring period yielded no significant trends for the nutrient concentrations of N, P, and K in the two area-types. Nitrate concentrations decreased markedly from 5–15 m to 15–30 m depth (Fig. 3(a and b).

Table 1 Parameters for conservative predictions.

	Recharge N (m day^{-1})	Porosity ε	Aquifer thickness T (m)	Reduction factor*
Recharge areas	0.25	0.35	75	0.75
Drained areas	0.175–0.25	0.35	50–75	0.5

* Reduction factor for denitrification in the unsaturated zone.

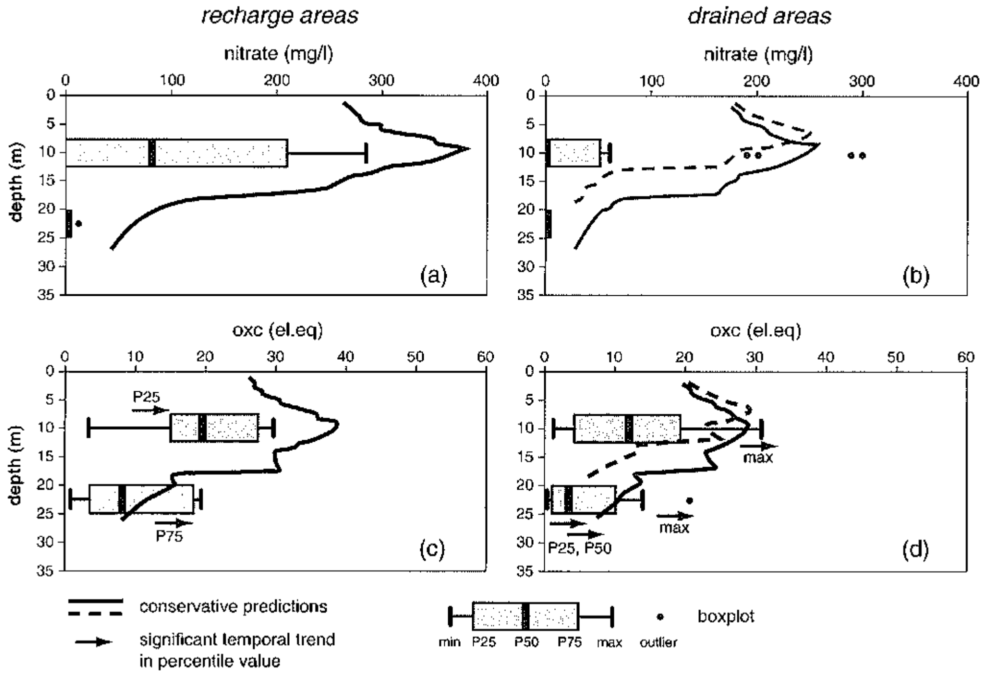

Fig. 3 Concentration–depth profiles; box plots (1998), conservative predictions (for 1998), and significant trends for nitrate (a and b) and OXC (c and d) in recharge areas and drained areas. Arrows denote the direction of the significant temporal trends over the period 1984–1998.

Following the conservative transport prediction for the recharge areas, the nitrate front should occur deeper (Fig. 3(a)). Thus, the observed sharp decrease in nitrate concentrations with depth should be attributed to reduction of nitrate, probably by the oxidation of organic matter or iron sulphides. Consequently, the trend analysis of the time series of the nitrate concentrations failed.

Oxidation capacity The conservative predictions correspond much better with the measured concentrations for OXC than for nitrate. Contrary to nitrate, significant temporal trends were found for the sample statistics of OXC (e.g. Fig. 4). The significant temporal increase in the OXC concentration is clearest for the deeper screens, i.e. between 15–30 m (arrows in Fig. 3(c and d)). This is feasible, since the concentrations are expected to increase as the OXC peak of 1985 has not arrived yet at the deeper screens. Still, the observed OXC concentrations are somewhat lower than the conservative prediction. This suggests nitrate reduction by organic matter occurring in the saturated or unsaturated zone, in addition to the reduction by sulphides. Contrary to the reduction by sulphides, the reduction by organic matter does lower the OXC.

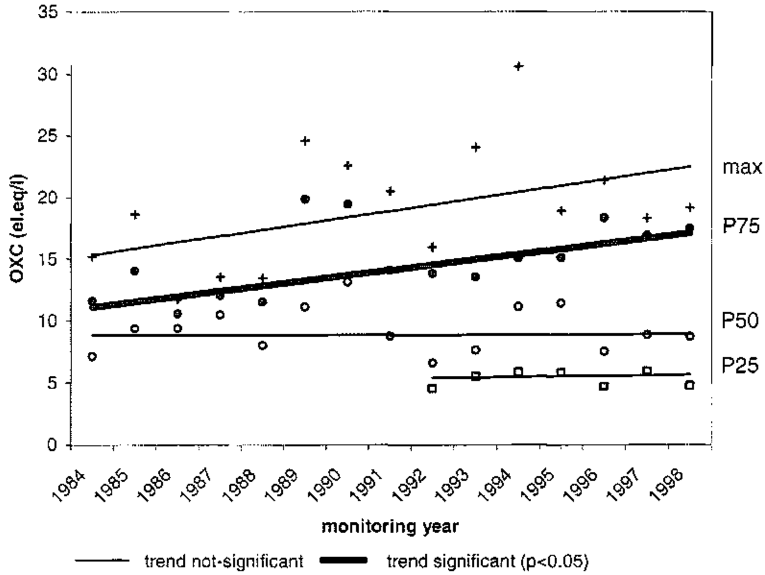

Fig. 4 Time series analysis of sample statistics of the area-type "intensive livestock breeding in recharge areas" at 15–30 m depth.

DISCUSSION AND CONCLUSIONS

The complementary use of time series data and fixed-time data of different depth yields additional value compared to the individual methods. Time series analysis alone might fail to reliably detect groundwater quality changes because non-conservative behaviour limits the breakthrough of the solutes. Often, the monitoring design (e.g. sampling depth and frequency) implicitly assumed conservative transport. Therefore, the use of semi-conservative parameters helps to prove the impact of changes in nutrient loads on groundwater quality. Moreover, time series analysis does not make use of all of the information available, and is sensitive to changes in laboratory and field methods. In fact, changes in laboratories, detection limits and field methods over the period 1980–1998 have had serious effects on the quality of the time series of the national and regional monitoring networks in The Netherlands (e.g. Frapporti, 1994; Venema et al., 2000). However, the interpretation of concentration–depth data relies on estimates of the groundwater age distribution. Tritium measurements can be used to reduce this source of uncertainty in some cases.

The comparison of a conservative prediction of the concentration profiles with the measured data yields indications of the hydro-geochemical processes, such as retardation and (bio)degradation. For example, the significant trends in OXC at larger depth should be attributed to increasing sulphate levels that are caused by pyrite oxidation with nitrate reduction. We conclude that the combined use of conservative predictions, nutrient concentrations and concentrations of semi-conservative parameters helps to understand and verify the impact of agricultural practices on groundwater quality.

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