

## Redox controls on denitrification at the soil–aquifer interface

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The onset of large-scale groundwater abstraction in the 1960s for drinking water production has resulted in a significant lowering of the watertable, at the study site in the eastern part of the Netherlands. Here, zones with upward seepage of anoxic groundwater the decreased and the surface load of nitrate increased due to intensified agricultural activities.

This study focuses on the effects of this increased oxidant loading on the chemistry of the subsurface and the controlling redox processes. So far, oxygen and nitrate concentrations are being buffered by the reductive properties within the soil and aquifer matrix within the upper fifteen meters of the subsurface. In this zone, the decline in nitrate is mirrored by a decrease in soil-derived dissolved organic matter (DOM) and nitrite concentrations, pointing to active denitrification. However, DOM alone cannot account for the observed oxidant decrease.

An unsuspected source of additional reduction capacity was found in the presence of a shallow ferrous iron-bearing carbonate phase [1]. Isotopic and elemental investigation of this phase indicated that it precipitated from alkaline Fe(II)-containing groundwater. The well-known and widespread occurrence of ironhydroxide accumulations in the sandy soils of this area originated from the source of upward seeping deeper anoxic groundwater.

To quantify the importance of the identified oxidant buffering reactions, oxidation studies were performed on sediments and groundwater from various depths. It was found that 90% of DOM was oxidized within the soil zone, that 10% of the remaining fraction did not degrade in the aquifer. Excitation–emission fluorescence spectroscopy on DOM samples indicated a largely humic/fulvic composition with only little changes with the various degradation extents. Sediment incubations confirmed that the identified carbonate phase was sufficiently reactivity to contribute to the observed denitrification.

This study is a clear illustration of the how the interplay between chemical processes in aquifer and soil control the chemistry of groundwater.

### Reference

[1] N. Hartog, J. Griffioen, P.F. van Bergen, *Chem. Geology* (2004) <http://dx.doi.org/10.1016/j.chemgeo.2004.11.006>

## Evapoconcentration not an indicator of nitrate in Kansas ground water

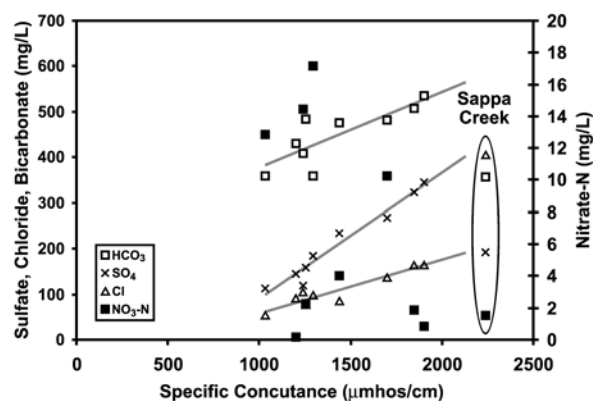
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Nitrate source determination in an area with a calcareous silt/clay vadose zone and high salinity groundwater due to evapoconcentration precludes the use of  $\text{NO}_3/\text{Cl}$  ratios for quantifying denitrification processes or identifying animal waste sources. In northwest Kansas, groundwater was evaluated using  $\text{SO}_4/\text{Cl}$  ratios, anion trends, and the  $\delta^{15}\text{N}$  natural abundance isotope method to identify sources of heightened nitrate concentrations in drinking water.

An increasing trend of anion concentration with specific conductance is typical of evapoconcentration enrichment of ground water as is shown in the figure below.  $\text{SO}_4/\text{Cl}$  ratios and mixing curves also suggest that evapoconcentration occurred. Sappa Creek, which flows through the study area, shows the impact of increased salinity possibly due to water softeners, sewage treatment outfall, or runoff from adjoining farmland and a golf course.



Nitrate-N values do not appear to be related to evapoconcentration enrichment processes (see figure). Nitrate sources included primarily fertilizer with some animal waste. Possible enrichment in  $^{15}\text{N}$  associated with processes involving calcareous silt/clay soils and/or denitrification enrichment affected observed isotope values at wells where no apparent animal waste sources exist. The presence of a very depleted  $\delta^{15}\text{N}$  value, low nitrate, and reducing water chemistry suggests that areas of limited biological activity exist even when the general water chemistry is impacted with measurable nitrate.