

ASSESSMENT OF BIOGEOCHEMICAL PROCESSES INVOLVED IN NH₄⁺ AND NO₃⁻ ATTENUATION PROCESSES. EVIDENCES FROM DIFFUSE AND POINT SOURCE CONTAMINATION SITES BY A MULTI-ISOTOPIC APPROACH

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Increasing anthropogenic loading of reactive nitrogen (N) along the N cascade in the environment raises many concerns for drinking water quality, human health, freshwater ecosystems and coastal water degradation.

High-resolution vertical isotope data ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{15}\text{N}_{\text{NH}_4}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{13}\text{C}_{\text{DIC}}$) have been adopted to gaining insights into N species origins, fate and related attenuation processes in groundwater. Evidences from an anthropogenic impacted alluvial coastal aquifer (ACA) and a septic system plume (SSP) are presented as indicative of diffuse and point source contamination, respectively. Common stand-points for both sites relies on groundwater reducing conditions and elevated ammonium concentrations (up to 68.25 mgNL⁻¹ for the ACA and 40.61 mgNL⁻¹ for the SSP).

Groundwater in the ACA is characterized by high DOC, DIC and sulphate concentrations but low to moderate methane content. $\delta^{15}\text{N}$ results suggested a geogenic source for the elevated ammonium in the ACA, originating by the mineralization of N-organic rich fine sediments (1÷3‰) while nitrate derives by septic effluent leaching (12÷15‰). Attenuation processes of ammonium are ruled by dilution and by nitrification, witnessed by the $\delta^{15}\text{N}_{\text{NH}_4}$ enrichment (~7‰). The positive correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ agreed with the occurrence of heterotrophic denitrification. In the shallow part of the aquifer, $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ data highlight that oxidation of pyrite occurs but is not necessarily linked to nitrate removal. At the bottom of the aquifer, sulphate depletion together with sulphur and oxygen isotopes enrichment, testifies that sulphate reduction occurs via anaerobic methanotrophy (-40.4‰) coupled with sulphate reduction.

A well-characterized cross section in the SSP showed chloride remarkably uniform across the plume, suggesting that it is composed of straight sewage and excluding dilution effects. The total N in the septic tank is present as ammonium (40.54 mgNL⁻¹) which is abruptly attenuated at the bottom of the plume and at distal monitoring locations. Conversely, nitrate, here a by-product, significantly increases downgradient the source zone revealing peak values in the upper fringe of the plume (58.01 mgNL⁻¹). N and oxygen isotope signals ($^{15}\text{N}_{\text{NH}_4}$, $^{15}\text{N}_{\text{NO}_3}$,

$^{18}\text{O}_{\text{NO}_3}$) suggest that multiple attenuation processes take place in the SSP: (i) nitrification in the unsaturated zone and shallow part of the plume, where high nitrate concentration is accompanied by depleted $\delta^{15}\text{N}_{\text{NO}_3}$ (57.50 mgNL⁻¹ and -3.2‰, respectively), (ii) denitrification where nitrate concentration decreases (<1 mgNL⁻¹) with an enrichment trend for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ (up to 44.8‰ and 26.8‰, respectively). Moreover, isotopes signals demonstrate that anammox activity is associated with N natural attenuation for which a concurrent enrichment of ^{15}N in both nitrate and ammonium is observed (up to 40‰).

From a comparison of the two investigated sites is apparent the variety of biogeochemical processes that can occur in the subsurface, which can be untangled only by using a complete suite of hydrogeochemical analyses (major and minor water species and stable water isotopes) coupled with high resolution multi-level sampling techniques. This study remarks the advantage of stable isotopes as a tool for tracing origin and attenuation processes in N cycle, especially in complex hydrogeological setting where steep geochemical reactions overlap.

