



Inorganic nitrogen inventory in a lowland heterogeneous agricultural field: implications for groundwater quality monitoring and assessment

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The inorganic nitrogen leaching from agriculture can have a severe and long-lasting effect on groundwater quality and it can also affect surface water quality since the contaminated groundwater can be discharged into drains in reclaimed lowland territories, like in the Po river delta. These lands lie below the actual sea level, thus they are continuously drained by pumping stations which collect the water from a capillary distributed network of channels and ditches. A complicating factor in understanding and quantify the effective leaching of nitrogen from agricultural fertilizers is the background ammonium presence in the sub-soils, due to peat layers, which provide a natural source of organic nitrogen slowly mineralized into ammonium. This implies that the geochemical inventory of ammonium-bearing sediments in peaty soils and sediments has an important control for the future development of groundwater quality in these areas. To estimate the mass of inorganic nitrogen present within the unsaturated zone below agricultural fields, a 6 ha wide site was characterized with high resolution core depth profiles. Cores were analyzed for inorganic nitrogen content (nitrate, nitrite and ammonium) and for bromide, used as nonreactive tracer. The soils and sediments within the site are highly heterogeneous, since many sedimentological environments overlapped during the last few centuries, creating vertical and lateral facies heteropies. These facies heteropies were reconstructed in a GIS environment via grain size analysis, soil organic matter content and detailed stratigraphic logs. The vertical distribution of inorganic nitrogen species is nitrate prevalent in the first meter of soil, where oxic condition prevailed (also induced by tillage and drains); ammonium is the major nitrogen species from 1 to 4 m below ground level. Where buried sandy sediments (paleochannels) are present beneath 1 m below ground level, nitrate can penetrate slightly deeper in the unsaturated zone. Nitrite is detected only in the oxic portion of the unsaturated zone, suggesting that denitrification takes place. Elevated ammonium, chloride and bromide contents are directly related with non-drained peaty sediments (lying below drains elevation), confirming their natural origin. Sharp vertical gradients were found between nitrate and ammonium/bromide, confirming that the recharge only affects the first meter of soil. The ammonium nitrogen inventory in the studied area is more than double with respect to nitrate nitrogen, and even two orders of magnitude higher than nitrite nitrogen. The impact of data quality and resolution on the derived inventory was investigated by varying the size of the considered subset of geological and geochemical data. We found that geological data resolution is less significant with respect to geochemical data. The large presence of ammonium-bearing sediments in these lowland territories makes very challenging to assess nitrogen pollution from agricultural activities, such as fertilizer spreading, but this natural source should be taken into account when groundwater monitoring campaigns are performed.