Origin and effects of nitrogen pollution in groundwater traced by $\delta^{15}N_{-NO3}$ and $\delta^{18}O_{-NO3}$: the case of Abidjan (Ivory Coast)

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Abstract. Groundwater resources of area of Abidjan are heavily impacted by nitrate pollution. A survey on 13 wells providing drinking water to the city was conducted in 2005, considering stable isotopes of the water molecule and of dissolved compounds (^{13}C and ^{15}N), major and trace elements. Nitrogen isotopes allow to define the origin of nitrate contamination, mainly from urban sewage, and the processes controlling its distribution. This information, coupled to hydrogeology and groundwater geochemistry highlights major changes in groundwater quality. Nitrate content is associated to an increased acidity of poorly buffered solutions in a geochemically open system and therefore is not affected by denitrification. Dissolved inorganic carbon confirms an input from organic matter decomposition, related to both pollution and diagenesis. This geochemical evolution is observed in both Quaternary and Continental Terminal aquifers, and is independent on depth. The comparison with previous hydrochemical data suggests a rapid decline in groundwater quality.

1. Introduction

Groundwater contamination by nitrates is frequently observed in West Africa, and is reported for Burkina-Faso[1] Niger [2, 3] Benin [4] and Senegal [5] especially close to urban area. Several origins have been suggested including urbanisation, deforestation and peri-urban agricultural development.

In the Abidjan region, high dissolved nitrate concentrations may be found also at 100 m depth [6]. Numerous pollution sources and causes have been suggested, among which increasing and deregulated urbanisation. In Abidjan, only 30% of the population is connected to the sewage network, discharging used water into the Ebrie lagoon [7, 8]. In addition, the system is affected by chronicle malfunctioning of purification plants and by the unregulated interconnection with the rainwater drain. On the other hand, peri-urban area and peripheral cities are characterised by the total absence of a sewage network, and the diffuse presence of individual of leaking wells and septic tanks.

Aquifers from the Continental Terminal and Quaternary formations host young and vulnerable waters as indicated by bacteriological studies evidencing the common presence of *Escherichia coli* [9].

2. Geological setting

The Abidjan region is located in southern Ivory Coast (West Africa), facing the Guinea Gulf. This region constitutes the central part of a coastal sedimentary basin, between the latitudes of 5°70 and 6°00 N and the longitudes of 3°30 and 4°30 W. The coastal basin represents 3% of the Ivory Coast surface.

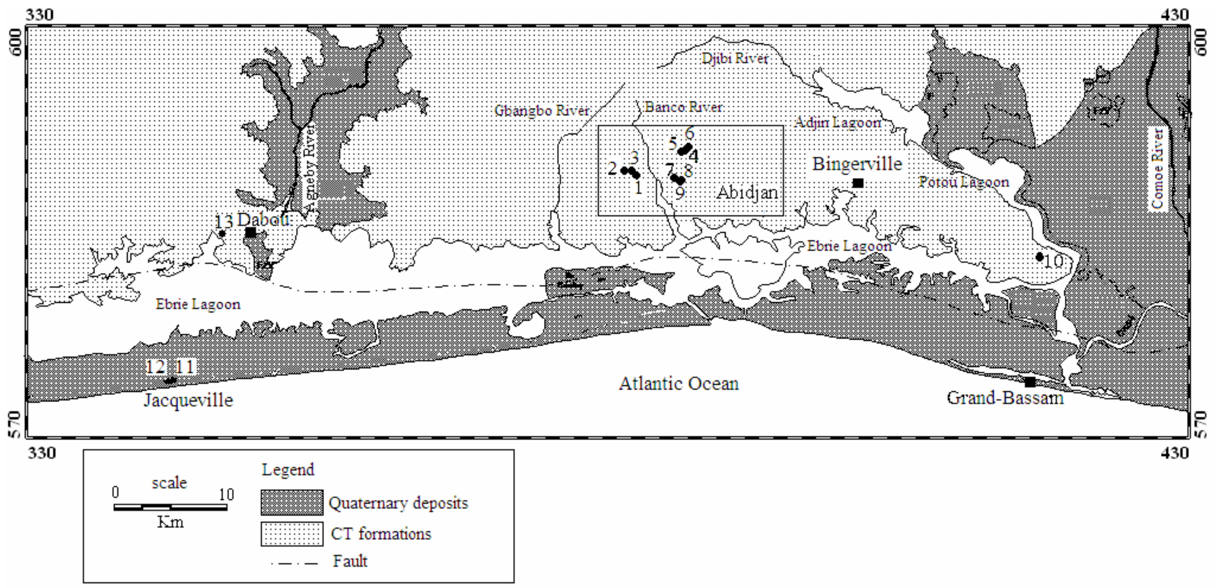

FIG. 1. Geological setting of the investigated region and sample location

West Africa, form the Sahel down to the Gulf of Guinea, is affected by monsoon type rainfall and squall lines. The climatic regime in the Abidjan region is humid and warm with fourth distinct seasons. The vegetation is a clear forest near the coastline and becomes dense further in the continent.

Three aquifers may be distinguished within the sedimentary basin:

- The Quaternary formations (Q), located in the southern part of Ebrie Lagoon, reach a maximum thickness of 140 m and show permeability ranging from $4*10^{-5}$ to 10^{-3} m/s. These formations host the Oogolian et Nouakchottian aquifers, located respectively in coarse and fine-to-medium grained marine sands. These aquifers are very sensitive to pollution, their piezometric level being very close to the land surface.
- The Continental Terminal formations (CT) are Mio-Pliocenic deposits mainly constituted by sands, clays, sandstones and indurate lateritic layers. They are located to the north of Ebrie Lagoon and display a maximum thickness of 160 m. These formations host the aquifer tapped for domestic purposes in the Abidjan area. Its permeability ranges form 10^{-6} to10^{-3} m s^{-1} and it shows a great transmissivity, between 30 10^{-2} m^2 s^{-1} and 20 10^{-2} m^2 s^{-1}[10][12]
- The Upper Cretaceous formation is constituted by poorly fractured calcareous rocks mixed with coarse sand. This reservoir is exploited by the Société Africaine d'exploitation d'Eau Minérale (SADEM) for the production of bottled water. This aquifer is poorly known in term of geometry, volume of pumped water and static level.

The bed rock of the studied area is constituted by the Precambrian crystalline basement.

Due to their relevance as drinking water resource for the Abidjan region, only the CT and Q aquifers have been considered in this study. Previous work has shown that unpolluted groundwater from CT displays low values of pH (3.5-5.4) and mineralization (EC between 20 and 55µS cm^{-1}). Water from the Q aquifer also shows low pH values (3.8-6.6) but is characterised by a relatively higher mineralization (140-225 µS cm^{-1}) [6].. As a consequence of acidic pH, pCO_2 varies between $10^{-2,40}$ et $10^{-0.6}$ atm (*vs* atmospheric $pCO_2 = 10^{-3.5}$ atm). The comparison between $\delta^{13}C$ of DIC and $\delta^{13}C$ of soil gas has shown that dissolved carbon is acquired during transit through the unsaturated zone in an geochemically open system. Tritium and carbon-14 contents indicate that the low mineralization of groundwater is due to the short time of contact and the total absence of carbonates in the aquifer bedrock [6]. Higher conductivities and mineralization are related to groundwater pollution by nitrates and/or chlorides.

3. Materials and methods

The investigation has been conducted on 12 groundwater samples which are exploited by the Société de Distribution d'Eau de Côte d'Ivoire (SODECI) for human consumption and one private well; eleven samples tap the Continental Terminal and two the Quaternary aquifers. Well depths range from 10 to 118 m. All samples have nitrate concentration higher than 10 mg/l.
The pH, redox potential, alkalinity (by HCl titration) and conductivity were in most cases measured in situ. Chemical analyses were performed at the University of Pavia, by ion chromatography and ICP-MS. All reported values have ionic balance within 5%. Samples for stable isotope analysis were collected and prepared according to standard procedures [13]. All gases were analysed on a Finningan™ MAT 250 Mass Spectrometer at ISO4 s.s., Turin, Italy.

4. Results

Results confirm the general characteristics of groundwater from the Abidjan region: very low mineralization (E.C. between 69 and 331 µS cm^{-1}), acidic pH (4.0-5.3), with sodium and chloride as dominant ions. Nevertheless, nitrates range from 10 to more than 100 mg/l in samples with the highest conductivity, suggesting a major contribution to groundwater mineralisation. SiO_2 content is uniformly set at about 10 mg/l. Among trace elements, Al^{3+} is very high, and exceeds the drinking water standards for several samples. Traces of B and P were also detected. A good correlation between all chemical parameters is observed, suggesting the presence of a dominant mineralization process.

Stable isotopes of the water molecule agree with the results of previous studies, which indicate for both aquifers a local recharge form rain water. $\delta^{13}C$ values range from -15.39 to -23.08‰ *vs* PDB. Despite the wide range of nitrate concentrations, $\delta^{15}N$ and $\delta^{18}O$ range respectively form 9.55 to 12.55 ‰ *vs* AIR and from 6.3 to 10.7 ‰ *vs* SMOW.

5. Discussion

5.1. Origin of groundwater pollution

The isotopic composition of dissolved nitrates has been plotted in the classical $\delta^{15}N$ vs $\delta^{18}O$ (Fig. 2) diagram, where the position of the composition fields has been adjusted taking into account the isotopic composition local waters ($\delta^{18}O \approx$ -2.6‰). For most nitrates an origin from septic system effluents can be evoked. This observation may be further confirmed by the close relationship between dissolved nitrate content and isotopic composition (Fig. 3) which indicates that most of the contamination has a positive $\delta^{15}N$, typical of animal and human waste. Increase in dissolved nitrates is associated to an increase in sulphate, chloride, bromine and to detectable amounts of B, all typical contaminants for used water. A similar tendency is also observed for the Q aquifer.

No denitrification seems to occur despite the elevated depth of collection for most samples, around 100 m. A direct relationship between $\delta^{15}N$ of DIN and $\delta^{13}C$ of DIC is observed (Fig. 3). The more negative values of $\delta^{13}C$ in low nitrate water could correspond to a decomposition of organic matter transported from the surface, indicating that the downward migration of dissolved nitrates is very rapid and occurs in a system which is geochemically open to oxygen.

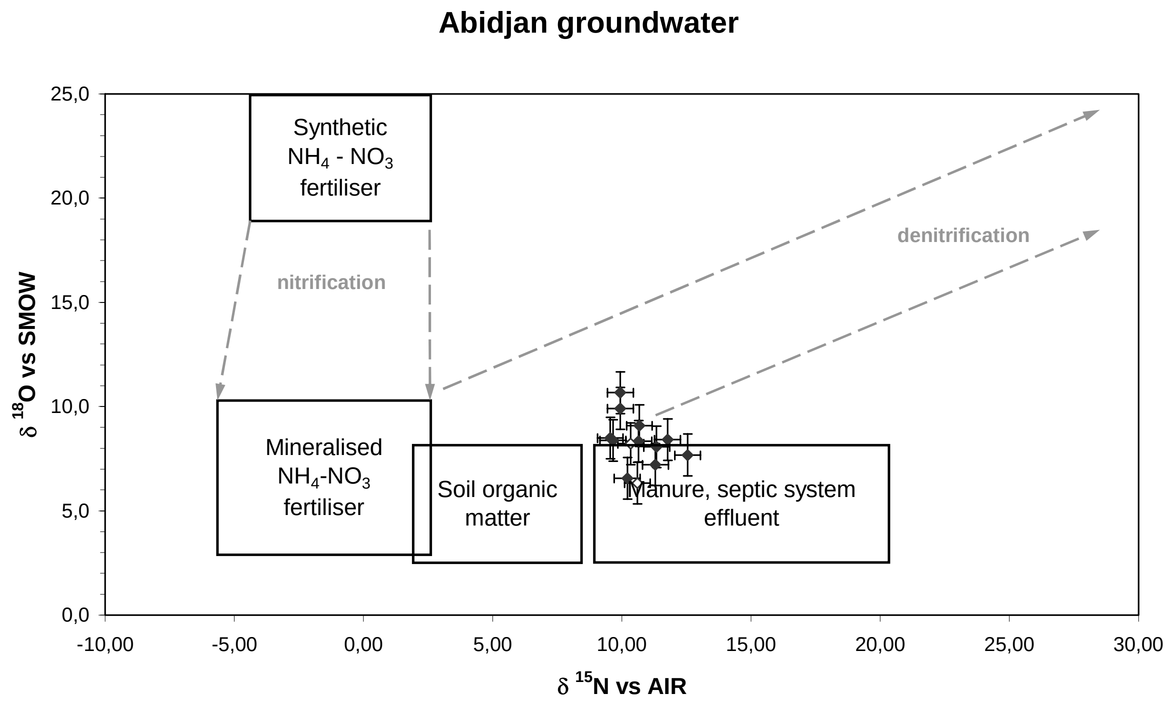

FIG. 2. Isotopic composition of dissolved nitrates in Abidjan groundwater. Empty diamonds: Q aquifer; full diamonds: CT aquifer

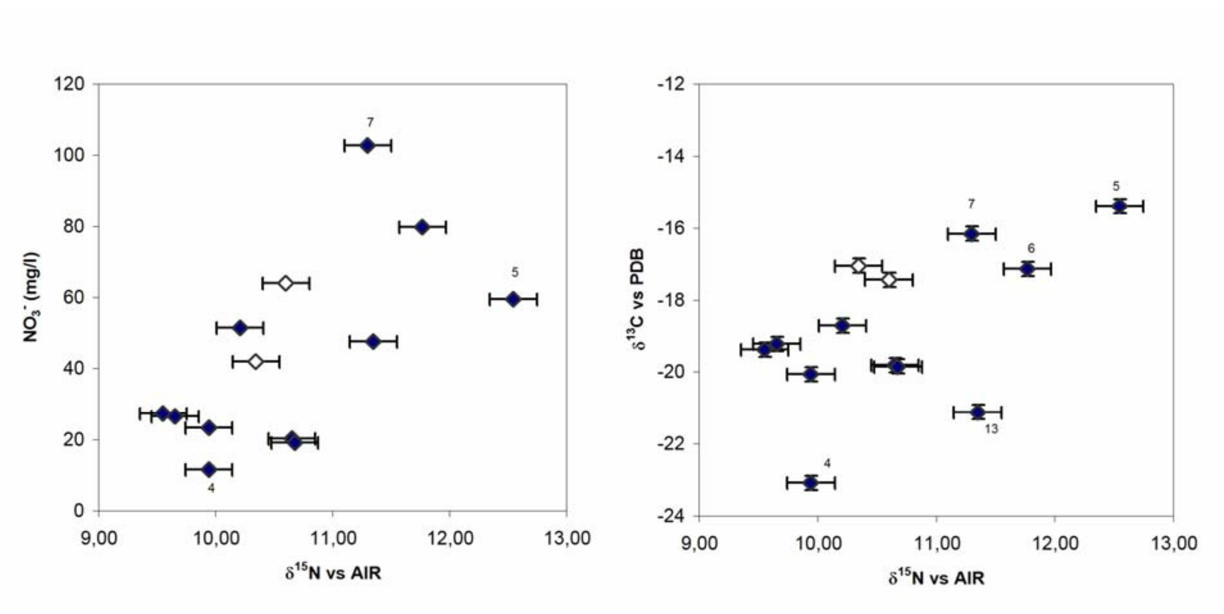

FIG. 3. Nitrate concentration and $\delta^{13}C$ of DIC vs $\delta^{15}N$ of DIN. Empty diamonds: Q aquifer; full diamonds: CT aquifer

5.2. Effects of groundwater pollution

The acidity associated with nitrate pollution is generally buffered by the presence of carbonates in the aquifer matrix, this phenomenon increasing water hardness and TDS [14]. In the case of the CT and Q aquifers, the absence of carbonates and the fast infiltration rate result in a shift of groundwater towards more acidic pH, as shown in Fig.4. The increased acidity promotes the hydrolysis of matrix silicates, releasing major and trace cations in the solution. This justifies the observed correlation between trace elements and DIN content, even for elements wich are not generally derived form the surface (e.g. Rb). The enhancement of silicate weathering is not evidenced by the SiO_2 content as water is generally saturated with respect to chalcedony, but rather by Al^{3+} which is not limited in solubility, and shows a marked tenedency to increase, reaching contents exceeding drinking water standards.

Sample 5 generally does not follow the depicted trends; it should be noted though that this sample shows the highest contents of all contaminants and the less acidic pH of the whole data set. Previous studies evidence in this well the presence of ammonia and bacterial contamination [15]. Sample 13 is a private well, only 10 m deep, and is located to the East of the main investigated area. The well is positionned at a lower altitude with respect to the village and is close to an uncontrolled landfill.

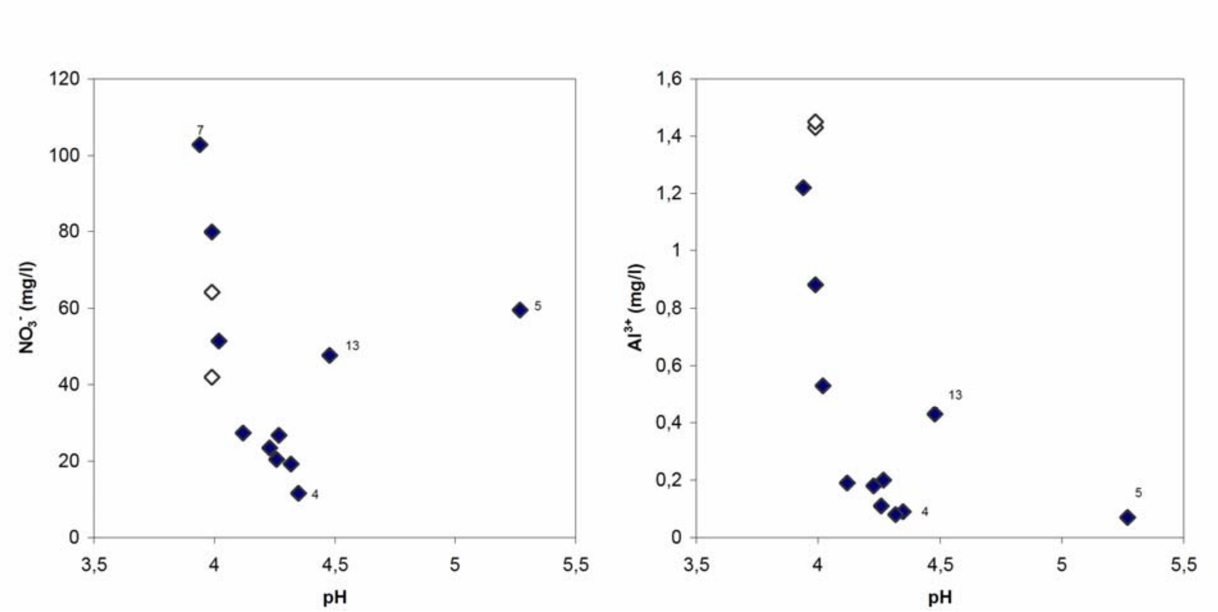

FIG. 4. Geochemical response of the water-rock system to the acidic perturbation induced by dissolved nitrates. Empty diamonds: Q aquifer; full diamonds: CT aquifer

6. Conclusion

Stable isotopes of DIN allowed to evidence the origin of dissolved nitrates in groundwater from the Abidjan area and indicate the mechanisms of infiltration. In addition the study evidenced the major perturbation induced by the addition of nitrates to the water-rock equilibrium.
The comparison with previous hydrochemical and isotopic data [6] suggests that this geochemical evolution is very rapid and leading to a dramatic decline in groundwater quality.

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