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D. Vione, B. Ravizzoli, E. Rinaldi, F. Pettinato, R. I. Olariu, C. Arsene. Studies Regarding Groundwater Quality at Rural Sites. 1. Estimation of the Anthropic Factor Impact by Complementary Chemical Analyses. *Rev. Chim.* **2009**, *60*, 237-240.

Studies Regarding Groundwater Quality at Rural Sites. 1. Estimation of the Anthropic Factor Impact by Complementary Chemical Analyses.

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Groundwater in the village of Letcani, NE Romania, was monitored during 2005-2006. It yielded very elevated levels of nitrate, NO_3^- (up to 64 times the health guidelines), most likely the consequence of traditional agricultural techniques (use of manure as fertiliser) and of the lack of a sewers network. Boron, possibly contained in fertilisers, and sulphate of geological origin were also present in elevated concentration.

INTRODUCTION

The quality of the environment as a whole is mainly determined by the interaction between natural and anthropogenic factors. Pollution of different environmental compartments is a serious problem, especially in the developing countries. Furthermore there is an essential need to monitor groundwater quality in different regions of the world, because it may provide a safe source of drinking water and supplies an important medium for the monitoring of environmental changes.[1]

The chemical composition of groundwater is a measure of its suitability as a source of water for human and animal consumption, irrigation, and for industrial and other purposes. Groundwater quality reflects normally the inputs from different compartments such as atmosphere and soil or from pollutant sources such as agriculture, domestic and industrial wastes.[2,3]

Groundwater follows through the subsurface a variety of pathways and, normally, its influence on surface water quality is highly site specific (mainly due to specific groundwater chemistry).

The present work reports on data from a programme initiated in order to evaluate the effects and processes of anthropogenic perturbations on groundwater at a local scale. Based on the very elevated concentration of nitrate (NO_3^-), as determined in the groundwater of the investigated area (up to 64 times higher than the health-based guideline level of 50 mg NO_3^- L^{-1}), considerations are made on the high potential risk of the nitrate level for the population health. Analysis of other chemical parameters (sulphate, SO_4^{2-}, magnesium, Mg^{2+}, calcium, Ca^{2+}, trace metals and possible organic contaminants, *i.e.* pesticides) allows better discrimination between anthropogenic and natural contribution to the groundwater quality in the area.

RESULTS AND DISCUSSION

Samples of groundwater, over a period of 18 months (2005-2006), were collected in the surroundings of the Iasi town, in the rural village of Letcani, northeastern Romania. The location of the sampling sites is shown in Fig. 1. All the sites are traditional wells that are still used by local people for irrigation and/or drinking purposes, with the single exception of well 3. The investigated wells are ranging in depth from 3 m to 10 m.

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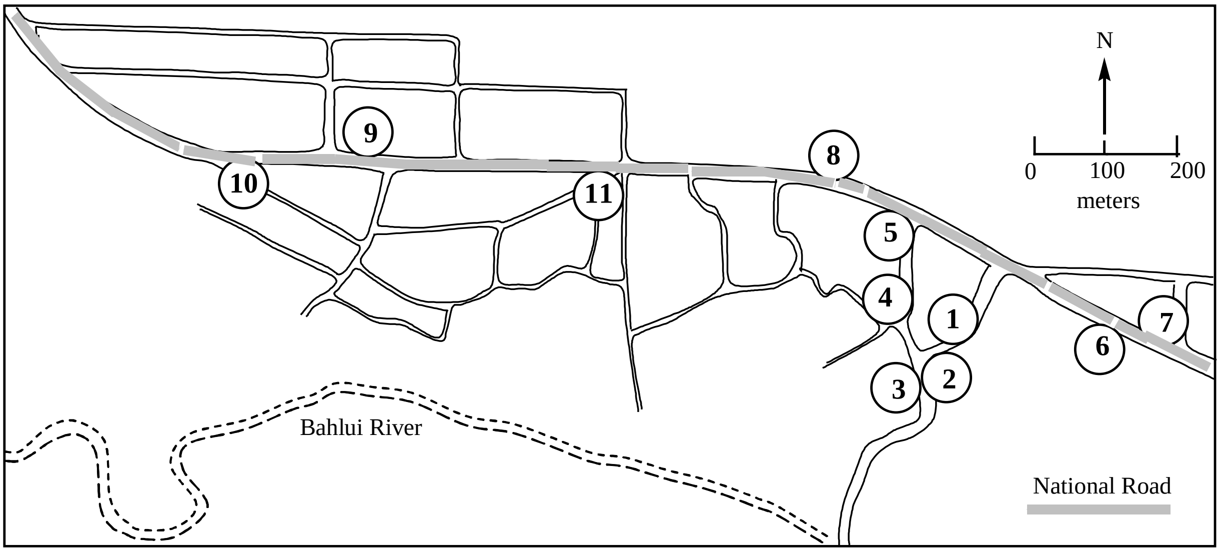

Fig. 1 - Position of the sampling locations in Letcani, Iasi county, NE Romania.

Nitrate

The monitoring of nitrate in groundwater yielded very elevated values, ranging from 94.1±7.2 (well 4, January 2006) to 3220.0±247.9 mg NO_3^- L^{-1} (well 3, June 2006). The reported errors are standard deviations of measures made at least in triplicate.

Fig. 2 shows the trend of nitrate in different wells (1-7) during the year 2005. It is apparent a seasonal variation with a maximum around May-July in the majority of the cases, which is compatible with increased microbial activity in soil during summer that would lead to enhanced oxidation of organic nitrogen. Note that wells 8-11 were added in 2006 to the monitoring programme and yielded nitrate values in the range 150-750 mg NO_3^- L^{-1}. Additionally, the nitrate values in wells 1-7 during 2006 were included in the 94-3220 mg NO_3^- L^{-1} range.

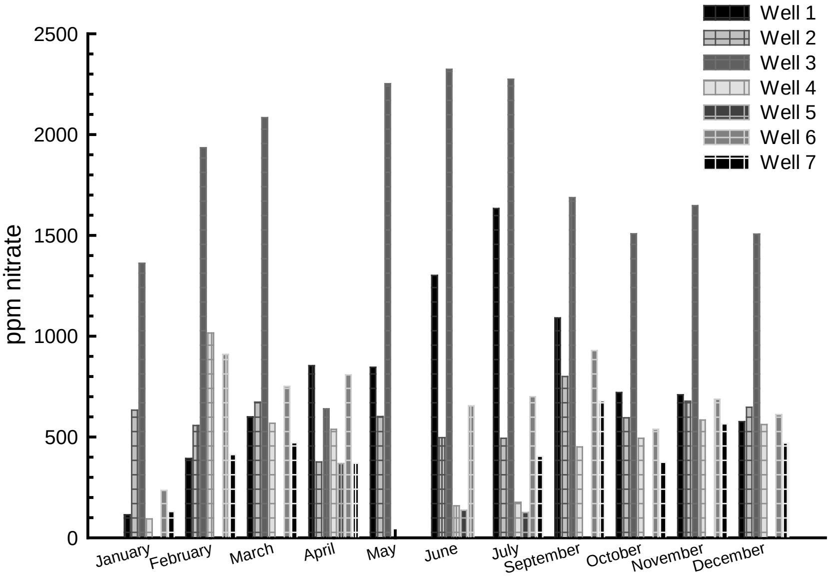

Fig. 2 - Time and spatial trend of nitrate in Letcani groundwater (2005 data).

Precipitation cannot account for the occurrence of such elevated nitrate concentration in groundwater, because the nitrate levels in rainwater in Iasi are in the range 0.22 - 12.1 mg NO_3^- L^{-1}.[4] Extensive use of nitrate fertilisers has been reported to cause groundwater contamination in other locations, but the resulting nitrate levels were much lower.[5] Furthermore, the low-technology agricultural techniques that are mainly adopted in the Letcani area are unlikely to make very extensive use of nitrate salts. Accordingly, considering also the seasonal trend of nitrate, microbial processing of organic nitrogen from human and animal wastes, including manure, is the most likely NO_3^- source to groundwater in Letcani.

Overall, nitrate in Letcani groundwater exceeded by up to 64 times the health-based guideline level of 50 mg NO_3^- L^{-1}.[5] Such a value, mainly motivated by the methaemoglobinaemia risk in babies, suggests that Letcani groundwater can be dangerous for babies and not completely without risk for adults also. It would constitute a striking example of the impact of traditional agricultural activities and lifestyle (e.g. the use of manure and the absence of a proper sewers network), often referred to as “natural”, on both the environment and the human communities. From the point of view of human health, the problem of nitrate does not compensate for the limited or no use of pesticides in the area (*vide infra*), which in turn constitutes one of the main environmental problems linked with modern agricultural techniques.

Furthermore, nitrate levels thus elevated can also cause significant photochemical reactions when groundwater is drawn to the surface for agricultural purposes and exposed to sunlight: substantial photogeneration of $^\bullet OH$ radicals [6-8] and the production of nitrating agents in the form of nitrogen dioxide ($^\bullet NO_2$), with possible formation of toxic and potentially mutagenic aromatic nitroderivatives,[8-11] are the main reactions involved.

Organic compounds

Within organic constituents, pesticides, polycyclic aromatic hydrocarbons, aliphatic hydrocarbons and organohalogenated compounds were investigated. No traces of pesticides (<0.05 μg L^{-1}), polycyclic aromatic hydrocarbons (PAHs, <0.005 μg L^{-1}), aliphatic hydrocarbons (<50 μg L^{-1}) and halogenated hydrocarbons (<0.1 μg L^{-1}) could be detected in the groundwater samples under study. This confirms the general impression that agriculture in the area follows traditional techniques, and allows exclusion of a significant role of possible fuel spills that could take place during the maintenance of agricultural equipment or vehicles.

Hardness, Barium, Boron

The hardness of the studied groundwater samples was relatively high: the sum of $[Ca^{2+}] + [Mg^{2+}]$ as $CaCO_3$ was in the range 500-1600 mg L^{-1} (equivalent to 50-160 °F), considerably higher compared to the usual drinking water range of 10-500 mg L^{-1}. Interestingly, in the Letcani area Mg dominates over Ca, and levels of 100-200 mg Mg L^{-1} were observed, which is rather unusual.[5] These levels are most likely connected with the abundance of Mg (and Ca at a lesser extent) minerals in soil. Overall, with hardness levels consistently above 500 mg $CaCO_3$ L^{-1} (>50°F), all the unpleasant though health-irrelevant effects connected with elevated water hardness are expected to occur in the Letcani area.

Among other inorganic constituents that were found in the samples at relatively elevated concentration there were Ba and B. Ba was found in all the samples, usually in the 30-60 μg L^{-1} range, with some samples reaching 80-90. In a single case (well 8) it was found a value of 223±2 μg L^{-1}. Though not very usual, such levels are of no health concern because they are relatively distant from the 700 μg L^{-1} guideline value.[5] Barium is very likely of geological origin as an impurity of Ca and Mg minerals. Boron was in the range of 550-1000 μg L^{-1}. It could be of geological origin, but at these levels it is also reported to occur because of the application of B-containing fertilisers [5] and, being above the guideline value of 300 μg L^{-1}, it might cause gastrointestinal irritation. Such an effect could further be enforced by the contemporary presence of elevated sulphate levels (*vide infra*).

Zn values in the 5-800 μg L^{-1} range, of no health concern, could be attributed to the extensive use of galvanised iron plate as roof cover. In single samples it was detected the presence of Cu and Cr, much below the guideline values,[5] which could be attributed to corrosion of the well material. The levels of As, with a maximum of 8.5±0.1 μg L^{-1} (well n° 7), were generally around 1 μg L^{-1} and in all the cases below 10 μg L^{-1}, thus of no health concern. At these levels the possible As origin could be geological.[5]

Sulphate

The concentration values of sulphate in the samples were relatively high, up to 600 mg L^{-1}, while according to drinking water guidelines their concentration should not exceed 250-500 mg L^{-1}.**[5]** The occurrence of sulphate in groundwater might be due to precipitation or to release from rock and soil. In the latter case sulphate would mainly be present as $CaSO_4$ or $MgSO_4$, and correlation between SO_4^{2-} and Ca^{2+} or Mg^{2+} should be expected. Indeed, statistically significant correlation could be found between sulphate and Mg^{2+}, and between sulphate and Ca^{2+} + Mg^{2+}. The geological origin of sulphate is also confirmed by the much lower values detected in rainwater, which were in the 0.61-11.20 mg L^{-1} range.**[4]**

CONCLUSIONS

The present paper presents data on groundwater chemical characteristics in the village of Letcani, NE Romania. Sampling has been undertaken during 2005-2006. Nitrate, sulphate, hardness, calcium, magnesium and organics (such as pesticides, aliphatic and polycyclic aromatic hydrocarbons, organohalogenated compounds) are among the investigated chemical parameters. The chemical monitoring yielded very elevated levels of nitrate, NO_3^-, most likely as a result of traditional agricultural techniques (use of manure as fertiliser) and of the lack of a sewers network. Natural origin of nitrate (release from soil) is not excluded. Sulphate, assigned as of geological origin, was also present in elevated concentration. Among the investigated trace elements, boron due to its high concentration may be of some environmental and human heath concern.

EXPERIMENTAL

Sampling. Measures were taken to prevent the loss of analytes from the samples and any cross contamination. Sampling equipment was cleaned in the laboratory with detergent, rinsed first in clean water and finally thoroughly washed in deionised water for at least three times. Samples have been collected with a monthly frequency and stored under refrigeration until analysis.

Nitrate monitoring. For experimental convenience the monitoring of nitrate was carried out by UV-VIS spectrophotometry, measuring sample absorbance at 200 nm (optical path length 1 cm). As instrument it was used a CINTRA 10e UV-vis spectrophotometer, with a wavelength range of 190-1200 nm. To enable proper absorbance measurements it was necessary to dilute the samples in the ratio 1:250. Significant correlation between sample absorbance at 200 nm (A_{200nm}) and the concentration of nitrate determined by ion chromatography ($[NO_3^-]$) has been found for lake water in Piedmont, NW Italy, where $[NO_3^-] \leq 0.1$ mM.**[7]** Even better correlation could be expected for the groundwater samples under study, where nitrate is at least an order of magnitude more concentrated, and in fact the corresponding correlation plot yielded $A_{200nm} = 0.450\ [NO_3^-] - 0.035$, where $[NO_3^-]$ denotes the nitrate concentration determined by ion chromatography, with excellent linearity ($r^2 = 0.99996$).

Ion chromatography determinations. Cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}) were quantified in some samples by ion chromatography using a Dionex DX 500 Ion Chromatograph, equipped with Rheodyne injector (20 μL sample loop), LC 30 chromatography oven, GP 40 gradient pump, and ED 40 electrochemical detector operated in conductivity mode. Details of analytical operations are reported elsewhere.**[7]**

Determination of organic compounds. Samples for **pesticide** analysis were extracted with SPE cartridges (J.T. Baker n° 7650-07) containing 500 mg C18 phase and 200 mg of styrene-divinylbenzene resin. The cartridges were previously rinsed with 5 mL ethyl acetate, conditioned with 5 mL methanol and then with 5 mL bidistilled water. An amount of 1 L sample was added with 5 mL methanol and flown through the cartridge at 10 mL min^{-1}. It followed washing with water and drying under nitrogen flow. Extraction was carried out with 10 mL ethyl acetate, the extract was evaporated to dryness and then redissolved in 500 μL hexane containing the internal standard (fenchlorphos). An aliquot of this solution (1 μL) was injected in pulsed splitless mode (injector temperature 250 °C) into an Agilent 5975 gas chromatograph interfaced to a quadrupole mass spectrometer (quadrupole GC-MS), equipped with a 30 m Supelco PTE^{TM}5 capillary column (0.25 mm ID, 0.25 μm film thickness). The temperature programme was as follows: initial oven temperature 40°C (1 min), then to 160°C at 35°C min^{-1}, to 190°C at 2°C min^{-1}, to 250°C at 10°C min^{-1}, stay at 250 °C for 5 min. Gas carrier (He) flow was 1.2 mL min^{-1}, and MS data acquisition in Selected Ion Monitoring (SIM) mode. The method allows the detection of 30 pesticides within the same run.

The analysis of **chlorinated hydrocarbons** was carried out by purge and trap-GC-MS, using a Varian Archon autosampler connected to a Tekmar Velocity XPT purge&trap apparatus, interfaced to a Varian CP3800 gas chromatograph equipped with a 60 m DB624 capillary column (0.25 mm ID, 1.4 μm film thickness) and a Saturn 2200 ion-trap mass spectrometer. Samples were stored at 10°C into the autosampler before analysis. Then 5 mL sample were injected into the sparger where they underwent He stripping for 11 min at room temperature. Volatile substances were adsorbed on a Supelco Vocarb 4000 trap, then the trap was heated at 240-250°C and the desorbed species transferred to the GC column. The temperature programme was as follows: initial oven temperature 35°C (8 min), then to 160°C at 10°C min^{-1}, stay at 160°C for 12 min, to 200°C at 20°C min^{-1}, stay at 200°C for 7.5 min. Gas carrier (He) flow was 1.2 mL min^{-1}, MS data acquisition in Full Scan mode. The method allows detection of 37 chlorinated and 17 aromatic hydrocarbons within a single run.

Samples (1 L each) for the determination of **polycyclic aromatic hydrocarbons** were added with 5 mL methanol and underwent extraction with a Baker n° 7020-06 SPE cartridge, containing 500 mg C18 phase. The cartridge was previously washed with 10 mL dichloromethane, then conditioned with 10 mL methanol. After cartridge washing with ultrapure water, the sample was flown at around 10 mL min^{-1}. The cartridge was then let to dry and eluted with 10 mL dichloromethane. The extract was concentrated to 100 μL with a gentle flow of high-purity nitrogen, and dissolved in acetonitrile up to a final volume of 1 mL. After sonication, it was injected into a High Pressure Liquid Chromatograph with Fluorescence detection. The adopted instrument was a Jasco HPLC equipped with a 100 μL sample loop, Supelcosil LC-PAH column (25 cm length, 0.46 cm diameter), and Jasco fluorimetric detector. Eluent flow rate was 1.2 mL min^{-1}. It was adopted the following binary gradient (A = CH_3CN, B = water): 40% A for 5 min, up to 100% A in 25 min, hold 100% A for 15 min, down to 40% A in 5 min. The excitation and emission wavelengths of the fluorimetric detector were programmed to vary according to the retention time of the target PAHs (11 detected in a single run).

Samples for the analysis of **total hydrocarbons** (200 mL) were acidified with HCl and underwent liquid-liquid extraction with 20 mL 1,1,2-trichloro-1,1,2-trifluoroethane (freon 113) in a separatory funnel. The organic phase was purified on silica gel, and an aliquot introduced in the measurement cell of a Perkin Elmer Spectrum One IR spectrophotometer. The quantification was based on the absorbance of the sample in the frequency region of 3015-2800 cm^{-1}.

Trace metals analysis. Samples were stored at 4°C in polyethylene bottles and acidified with 1% nitric acid. Sample aliquots were then injected by nebulisation into a Perkin Elmer ELAN 6100 ICP-MS, equipped with a quadrupole mass spectrometer. The measurement range was (μg L^{-1}): 5.0-100 for Al and Cu, 20-100 for Ba, 0.4-50 for Be, 1.0-50 for As and Sb, 2.0-50 for Se and Pb, 4.0-50 for Ni, 5.0-50 for Co, Cr, V and Mn, 0.1-10 for Cd, 0.2-10 for Tl, 100-500 for B.

ACKNOWLEDGEMENTS. The authors acknowledge support from the Scientific and Technological agreement 2006-2008 between Italy and Romania within the EQUILIBRIAAS-PRO project, and from the CLG NATO Programme No. 982287.

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