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Nitrogen and organic compounds correlations in groundwater from the aquifer in a semi-island (Curonian Spit, Lithuania)

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Anthropogenic activities are a major source of groundwater contamination in semi-island regions, and evaluation methods developed for inland sites may not be appropriate for coastal sites. We investigated the feasibility of diversity a nitrate-affected groundwater source-fate system in a semi-island environment using comparative methods. The study site was a groundwater well-field in Neringa, Lithuania, where nitrogen compounds obtained in groundwater had increased from the origin thereafter treatment plants. We used ammonium ions and ammonium nitrogen / organic compounds ratios and direct evaluation of total nitrogen concentration to show that biological processes occurred in both source area and water treatment, and could increase nitrogen concentrations over time. The nitrogen compounds and organic carbon compounds rate was changing water quality from the place of origin aquifer, offering a possible means of preventing diversity of the nitrogen compounds by controlling reacting rate over the site. We conclude that biological processes are the real reason of nitrogen compounds diversity at this type of site.

Key words: groundwater, nitrogen compounds, denitrification, organic compounds, water quality

INTRODUCTION

The groundwater of Neringa, on the south-eastern Baltic Sea coast, is the only source of drinking water for Nida, Preila–Pervalka and Juodkrantė settlements situated on sandy belt that is under constant threat of natural and anthropogenic impact. Due to the low hydrological and biological activity of groundwater ecosystems, adverse effects of natural and anthropogenic activities can persist for much longer time periods in semi-islands than in inland water sources (Klimas and Gregorauskas, 2002). Groundwater abstraction has an influence on migration of contaminants, activates saltwater intrusions into pumped aquifers. In the above mentioned reference it is stated that one of the main indicators is an increased nitrate concentration. Similar findings were provided by Holman et al. (2005) following validation of an intrinsic groundwater pollution vulnerability methodology using a national nitrate database based upon nitrate concentrations from 1 108 boreholes throughout England and Wales. As a result, today water supply specialists face a circumstance of past environmental damage to many water bodies of surroundings of semi-islands that must be remediated to restore the water quality and protect human health (Valentukeviciene and Rimeika, 2007). Similar findings appear in scientific articles from different countries around the world. It was found out that nitrate compounds of the coastal aquifer results from point sources such as cesspools and infiltration from agricultural use of nitrate fertilizers in the Gaza Strip (Abu Maila et al., 2004). The results of scientific research by Omar Ali Al-Khashman (2007) indicate that the inorganic

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constituents of groundwater were influenced by natural and anthropogenic sources and show that some of the springs were highly polluted with nitrate at Petra region in the southern part of Jordan. Similar findings were published about Brazil's groundwater quality inorganic parameters by Boaventura and Saboia de Freitas (2005).

In semi-island environments, the water balance inevitably favors the leaching of pollutants into groundwater or runoff into surface waters. The leaching of pollutants was investigated with evaluation of the effect of highways and local activities on the quality of underground water in Ogun State, Nigeria (Odukoya et al., 2010. Therefore, many large-scale attempts to remove contaminated wastewater and storm-water have focused on engineered strategies such as treatment and / or removal and dilute and / or re-use to remove the pollutants from the environment, but these methods can cause further environmental damage in fragile semi-islands (Klimas and Gregorauskas, 2002). A different strategy is possible in semi-islands where potential water sources for human use exceed an acceptable pollution level (Valentukeviciene and Albrektiene, 2012). In humid climates, the groundwater status of the semi-islands largely determines whether the water balance favors recharge or discharge (Valentukeviciene and Rimeika, 2006). Hence, in some cases the movement of pollutants in arid climates can be controlled by controlling the water balance with sustainable use (Vandenbohede et al., 2008). We report the results of case studies designed to evaluate nitrogen compounds attenuation as a remedial strategy for the nitrate contaminated shallow groundwater and alluvial aquifer in the semi-island ecosystem at a former resort-tourism site near the well-field.

At many resort sites, wastewater containing organic compounds, ammonium, nitrate, nitrite, amines are easily transported into the shallow groundwater zone and often into underlying deep aquifers. No correlation was found between the geochemical evaluation and the particular geological layer, differences variation of nitrate concentrations were near ten times in some cases (Carreira et al., 2010). The fluorescence properties of dissolved organic matter (DOM) in groundwater in the Permian limestone of northeast England were determined from six monitoring boreholes in the environs of Darlington, County Durham, northeast England (Baker and Lamont-Black, 2001). Different characteristics and origin of dissolved organic carbon were investigated (Routh et al., 2001) in Yegua ground water in Brazos County, Texas. The research on carbon biochemistry of ground water in southwest China was carried out by Si-Liang Li et al. (2005).

Nitrate is mobile in supplied water and can be dangerous to humans at low levels (De Roos et al., 2003; Ward et al., 2007). Drinking water nitrate exposure (>10 years with average nitrate >5 mg/L) was associated with increased colon cancer risk among subgroups of inhabitants with low vitamin C intake and high meat intake (De Roos et al., 2003). Eskiocak et al. (2005) stated the effects of taking chronic nitrate by drinking water on thyroid functions and morphology of inhabitants in related areas. Nitrate in community water supplies and risk of childhood type 1 diabetes were evaluated in Sardinia, Italy (Muntoni et al., 2006).

Nida settlement is one of the very few former resort sites on the Baltic Sea coast of Lithuania, nearly+ all of which are in semi-island area in Neringa Region. The contaminated site at Nida well-field consists of a source area, which is the site where nitrogen compounds originally leached into the soil from the natural and anthropogenic activities, and contamination wastewater which is moving away from the source area in the deep aquifer. The use of groundwater was investigated to help remediate nitrate in the source area and over the water treatment plant. The remediation strategy for the source area (Valentukeviciene and Albrektiene, 2012) was to enhance biological treatment by establishing and using different rate of organic carbon, nitrogen compounds and related substances (the dominant pollutants at the site).

The strategy for remediating the nitrogen compounds was to promote the growth of forming biomass and useful microorganisms growing over the aquifer to slow the migration of nitrogen compounds away from the source area (Tenokuchi et al., 2006), and allowing natural biological processes to remove nitrate from the water over time. Enhanced biological processes by bacteria could reduce water treatment costs and, if they are controlled into the groundwater, could transform nitrogen compounds from the aquifer,

slowing or preventing nitrate fate. Prevention of the transformation of natural organic compounds by using well-field boreholes markedly increased ammonium concentration and clogging in water treatment equipment over the relatively short start-up within few months. However, it was uncertain whether biological processes in the source area could be sustained over time, whether natural organic compounds occurred to a significant extent in the water and whether short filtration rate and prolonged stagnation over the water supply system were actually provided into the water treatment plant. Sorption processes can be useful with elimination strategy of removal ammonium ions from treated water (Mazeikiene et al., 2010). The present study addressed those major aims: the report on ammonium / organic compounds rates in the source area due to biological processes induced by organic carbon over a two-year period; the report on case studies of groundwater organic compounds conducted to determine the limiting factors for biological processes in the source area.

MATERIALS AND METHODS

Nida water-field is located in Neringa Region in Curonian Spit southeast of the Baltic Sea coast, Lithuania in a pine tree forest, dune-and-swale environment on the semi-island (Fig. 1).

Average annual precipitation is approximately 80 mm, arriving as spring, summer or autumn rains or winter snow and rain. High level of shallow groundwater was obtained on excavated site near the groundwater boreholes field (Fig. 2).

Fig. 1. Groundwater field with the top cover of borehole

Fig. 2. High level of shallow groundwater at excavated site near the boreholes field

The source area at the site covers all length between the Baltic Sea coast and Curonian Lagoon near the area where wastewater outlets were situated and where drilled boreholes were constructed to extract groundwater from the deep aquifer. The water treatment equipment and some pipelines were removed during the initial renovation of the site to remove iron, manganese and nitrogen compounds. The remaining well-field consists of fine sand overlying gravel layer with silt, clay and sandy loam on the bottom layers. The groundwater was contaminated by nitrogen compounds during the possible infiltration through the sand layer and is the apparent source of nitrogen contamination in the stand-by boreholes. Although ammonium is the main contaminant of concern at the site as it is transformed in the water treatment plant, nitrate is also present in the groundwater and was assayed in this study.

In the article by Klimas and Gregorauskas (2002) the monitoring data was generalized on the basis of groundwater quality in the source area. The monitoring size and location was based on an initial survey of groundwater nitrate and ammonium concentrations, and it was subsequently determined that contamination extended beyond the system of the water treatment and supply.

Approximately 280 water samplings interspersed with additional samples were examined in boreholes at water fields between the Baltic Sea and Curonian Lagoon within Curonian Spit. The

field was investigated using a start-up system, 8 hours a day, at a target rate of total treated water capacities approximately 75 m^3 h^{-1} during the first stage (from August to March) beginning in 2007. Results through 2007–2009 were presented in start-up reports. In 2008 and 2009, due to reduced nitrogen compounds removal, improvement was applied only occasionally to keep plant working and did not exceed 11 m^3 h^{-1}. During the second period, the water treatment plant was operated 11 m^3 h^{-1} and the water retention time was till 80 h. Groundwater was supplied with approximately 12 h and 80 h of stagnation periods per borehole from a well-field of Nida.

From 2007 to 2008 and 2008 to 2009, water quality measurements were obtained daily, August to March, using ISO, EN and Lithuanian Standard Methods. Water quality was measured at water inlet in boreholes pipes installed in the pumping stations. The sample tap locations were distributed in a grid pattern over the site. The automatic pH meter was calibrated and operated as described by the instruction manual.

Nitrogen compounds concentration was monitored in water treatment plants of each day except weekends by measuring the ammonium and nitrate, nitrite of groundwater to ensure water quality following EU and Lithuanian national requirements. Every 5th day (2007–2009) all indicators (total iron, ammonium, nitrate, and nitrite) in each sample were measured (ca. 6–7 measurements per month). The dependency between ammonium concentrations and nitrate, nitrite was determined each stage for a subsample of 5–10 indicators encompassing the range of water treatment equipment in the plant, and used to evaluate nitrification and / or denitrification possibilities for the entire groundwater. Amines concentration was measured in groundwater and treated water samples from the plant harvested for 1 L sampling containers made of dark glass. Thereafter 500 mL of water sample were added with 1 g of EDTA (Fluka, 03699). General conditions of chromatographic analysis with HPLC-HP 1200 Agilent FLD-HP 1200 Agilent: column- 250 x 3.0 mm, 5 µm; Gemini 5u C18, Phenomenex; eluent A – HPLC water, eluent B – acetonitrile.

Denitrification was assayed in groundwater from working and standing-by boreholes by the production of pumped out water using the nitrogen compounds ratio technique. Boreholes complexes are the last stage of the conversion of nitrogen compounds, resulting in the accumulation of nitrogen in the biomass, which can be assayed by organic nitrogen concentrations (Valentukeviciene and Albrektiene, 2012). Triplicate water samples (1L) were taken daily (with exception of weekends and holidays) from groundwater water boreholes outlets sampling taps at all locations within the water fields area. All water samples were analyzed in laboratory at JSC "Klaipėdos Vanduo" under standard protocols. The effect of organic carbon compounds enrichment on nitrogen compounds removal was tested on bio-membranes blocks taken at consideration with re-growth biomass following fouling and blockage. Water samples were taken to laboratory in refrigerated containers and assayed with or without additional aeration. Water samples were transported to the laboratory in screw cap, septa-sealed, 1000 ml glass bottles at approximately 2 hours.

Commercially available water quality tests (Merck, Germany) at verified concentrations were used to measure nitrogen compounds concentrations on site. Water quality was evaluated in triplicate samples for each chemical indicator (ammonium ions, nitrite, nitrate, total nitrogen, and organic nitrogen, Chemical Oxygen Demand using COD_{Cr} and COD_{Mn} methods).

RESULTS AND DISCUSSION

Nitrogen compounds concentrations were measured following monitoring requirements in the Baltic Sea and Curonian Lagoon water. Since Lithuania joined the European Union in 2004 till nowadays total nitrogen concentration in the Baltic Sea water was approximately up to 0.5 mg/L, and higher concentrations up to 2.5 mg/l were obtained in Curonian Lagoon water (Fig. 3).

Natural nitrogen compounds concentrations in groundwater can be obtained in low and high concentrations and organic compounds – relatively high (Valentukeviciene, Rimeika, 2007). Groundwater quality indicators based on long term monitoring observation results are generalized below following I, II, and III horizons.

I horizon: Fe_{total} 0.5–1.0 mg/l, Mn – 0.05–0.1 mg/l, ammonium ions concentrations – 0.5–1.0 mg/l, COD_{Mn} 3.0–6.0 mgO_2/l.

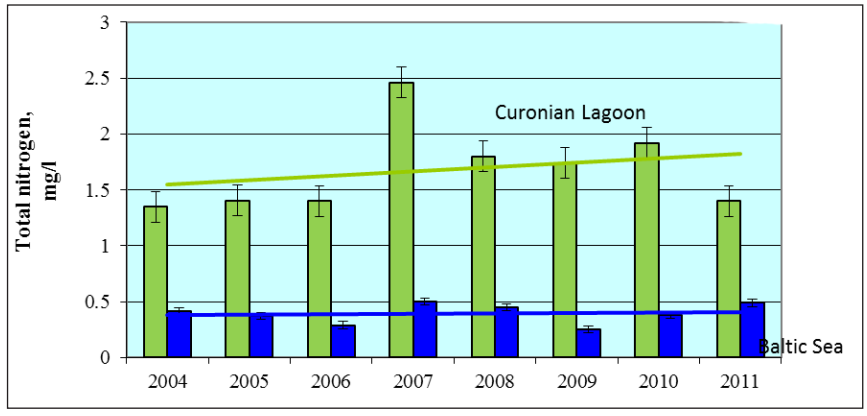

Fig. 3. Medium annual concentration of total nitrogen in the Baltic Sea and Curonian Lagoon water

II horizon: Fe_{total} 15.0–25.0 mg/l, Mn – 0.1–0.9 mg/l, ammonium ions concentrations – 1.0–10.0 mg/l, humous acids – 1.0–3.0 mg/l, fulvic acids – 0.5–2.5 mg/l, COD_{Mn} 20.0–30.0 mgO_2/l.

III horizon: Fe_{total} 1.0–10.0 mg/l, Mn – 0.1–0.6 mg/l, ammonium ions concentrations – 1.0–8.0 mg/l, humous acids – 0.2–2.0 mg/l , fulvic acids – 0.5–2.5 mg/l, COD_{Mn} 8.0–16.0 mgO_2/l.

Nitrogen compounds interactions with organic compounds possibilities were also evaluated in this research. Several groundwater boreholes in Neringa Region (Curonian Spit) are characterized by high ammonium ions concentrations which in some cases are higher than 0.5 mg/l the maximum limit accepted by Lithuanian Hygiene Norm for drinking water, in dependency with increased organic compounds concentrations expressed by Chemical Oxygen Demand (COD_{Mn}). Obtained dependency is presented in Fig. 4, it can be explained by destruction process of biological decay in groundwater, when ammonium ions are some kind of residual by the end of process.

The results also showed that measured COD_{Mn} and ammonium ions concentrations (C_{ammon}) were obtained at a level of first order regression following the 1st equation.

$$COD_{Mn}=-0.735\ ln\ (C_{ammon})+7.89 \quad (1)$$

In case when ammonium concentrations are represented using ammonium nitrogen, the dependency with COD can be obtained if COD_{Cr} indicator is used (Fig. 5). The explanation of this kind of dependency can be followed by oxidation

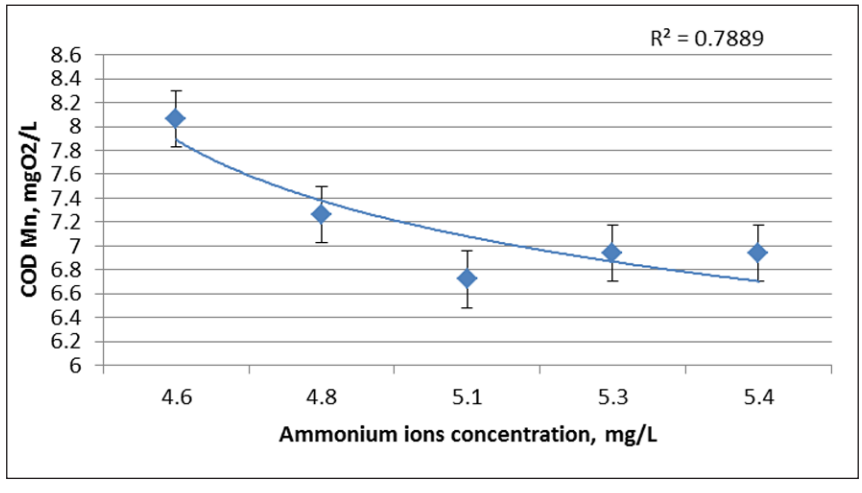

Fig. 4. Ammonium ions concentration dependency on COD_{Mn} in groundwater from boreholes

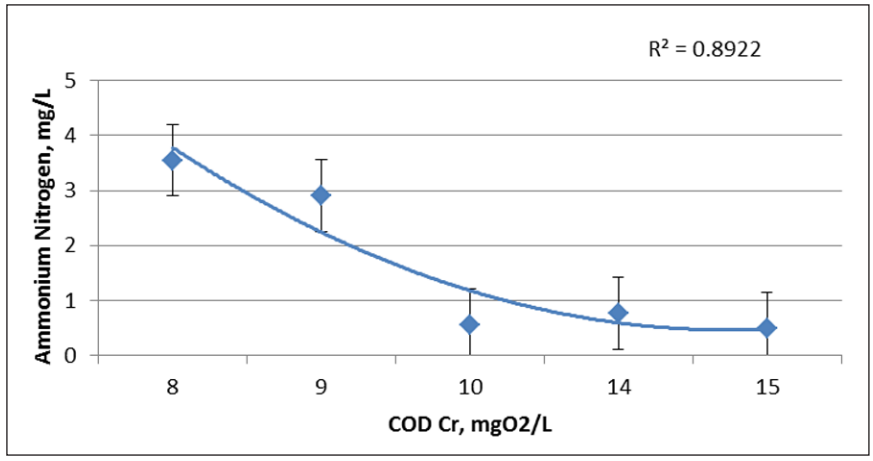

Fig. 5. Ammonium nitrogen concentration dependency on COD_{Cr} in groundwater from boreholes

results when using dichromate solution it is nearly 98% of total organic compounds, using permanganate solution oxidation results approximately 70% of organic matter.

In the first order logarithmic regression after the initial data was statistically evaluated, i. e. the 2nd equation was obtained, using COD_{Cr} and ammonium nitrogen concentrations (C_{AN}).

$$C_{AN}=-2.13\ ln\ (COD_{Cr})+3.69 \quad (2)$$

Some previous research dealt with the existence of correlations between both the main factors affecting the groundwater nitrogen compounds and those which influence the contamination risk and the ammonium concentrations in groundwater, as well as between organic compounds and the amount of nitrogen compounds in the boreholes water. The correlation between nitrate concentration in groundwater and parameters affecting aquifer intrinsic vulnerability was investigated by Debernardi et al. (2008). The results of these correlations are scientifically and practically controversial; some findings are similar to the previous research (Valentukeviciene, Albrektiene, 2012). In some cases there are reliable correlations (Fig. 6) between different parameters of nitrogen compounds, in others (ammonium ions, nitrite, and nitrate) there are no significant correlations.

It was found that after evaluation of nitrogen compounds the exponential dependency of total nitrogen concentrations (C_{TN}) on ammonium

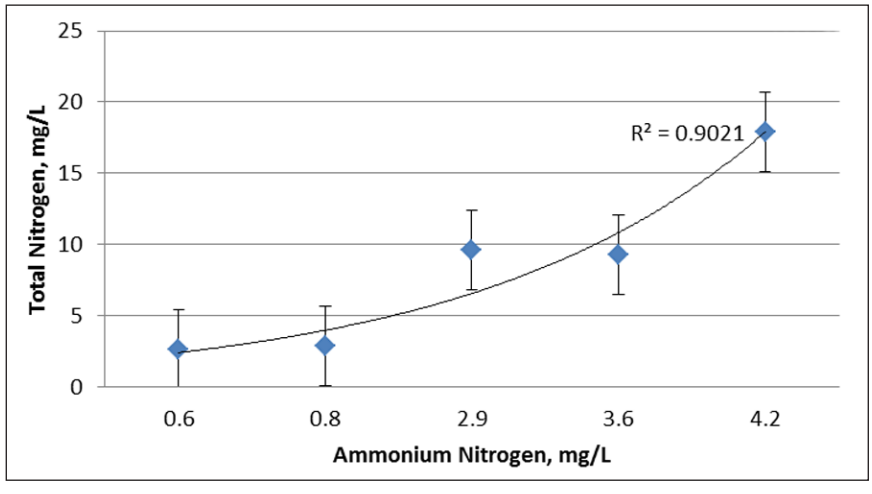

Fig. 6. Total nitrogen concentrations dependency on ammonium nitrogen concentrations in groundwater from boreholes

nitrogen concentrations (C_{an}) occurred (the 3rd equation).

$$C_{Ntotal}=1.454e^{0.5Can} \quad (3)$$

Thereafter statistical analyses were completed and the only reliable correlations were obtained between: ammonium nitrogen – total nitrogen, ammonium nitrogen – COD_{Cr}; ammonium ions concentrations – COD_{Mn}.
No correlation was obtained between amines, other nitrogen compounds – BOD_7; ammonium nitrogen-organic nitrogen and ammonium ions concentrations-nitrites, nitrates.

CONCLUSIONS

The investigated nitrogen compounds of groundwater from a water-field horizon situated in Curonian Spit National Park are very sensitive to the influence of the presence of organic compounds.

The analysis shows that nitrogen compounds are generally in ammonium nitrogen form and partially in a complex organic substance form. The concentrations of nitrites and nitrates residuals that remained were without any significant changes. Nitrogen compounds need to be monitored by related methods in correlation with organic compounds.

The results of the performed investigations demonstrate that nitrogen compounds from groundwater can be reduced by using organic compounds removal technologies (slow sand filtration processes). When analysis was carried out under the conditions of conventional control, the borehole filter susceptibility to fouling by the biological layer was higher than under the conditions of organic compounds control. Both results from the tested nitrogen and organic compounds were strongly influenced by groundwater saturation with biological by-products from the surrounding environment. It can be concluded that the process investigated can be beneficial and effective in solving issues encountered in relatively small semi-island water treatment and supply works.

Such processes still need to be proved in a more extensive research study, but as shown in the preliminary results, it could be applied as a basic scenario.

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AZOTO IR ORGANINIŲ JUNGINIŲ KORELIACIJA PUSIASALIO (KURŠIŲ NERIJA, LIETUVA) POŽEMINIO VANDENINGO SLUOKSNIO VANDENYJE

S a n t r a u k a

Antropogeninė veikla yra pagrindinis požeminio vandens taršos šaltinis pusiasalių (nerijų) teritorijose, todėl vertinimo metodai, sukurti vidinėms (žemyninėms) teritorijoms, gali būti netinkami pakrančių teritorijoms. Tyrėme nitratais paveiktų požeminio vandens šaltinių sąveikos sistemą pusiasalio (nerijos) aplinkoje naudodami lyginamuosius metodus. Tyrimų vieta – požeminio vandens gręžiniai Neringos mieste, kuriame azoto junginių koncentracijos požeminiame vandenyje padidėjo įrengus vandens ruošimo įrenginius. Vertinome amonio jonų ir amonio azoto / organinių junginių rodiklius, taip pat bendro azoto koncentraciją, siekdami parodyti, kad biologiniai procesai vyko šaltinio bei vandens ruošimo vietoje ir galėjo padidinti azoto koncentracijas. Derinami azoto junginių ir organinės anglies junginių kiekiai keitė vandens kokybės parametrus, taip buvo atskleisti būdai, kaip galima užkirsti kelią azoto junginių koncentracijos didėjimui vykdant kontroliuojamas chemines reakcijas.

Darome išvadą, kad biologiniai procesai iš tiesų lemia azoto junginių pasiskirstymą tokio tipo teritorijoje.

Raktažodžiai: požeminis vanduo, azoto junginiai, organiniai junginiai, denitrifikacija, vandens kokybė