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Nitrates in springs and rivers of East Ukraine: Distribution, contamination and fluxes

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ABSTRACT

Spatial and temporal variation of nitrate concentrations has been studied in 4 rivers and 21 springs of the transboundary (Russia/Ukraine) Seversky Donets watershed in eastern regions of Ukraine – Kharkiv, Donetsk and Lugansk oblasts. Samples have been taken from 13 sites on the Lopan, Udy, Oskol and Seversky Donets rivers together with springs on left and right river banks between August 2013 and May 2014 and analysed on major ions and nitrates. Water temperature, pH, electrical conductivity, redox potential have been measured on site. The results showed high spatial and temporal variability of nitrate concentration in both surface and groundwater. The hydrogeological settings, seasonal trends and human impact were major factors influencing nitrates mobility and accumulation in contaminated springs, which contributed to surface water pollution. Mean nitrate concentrations were 26.7 mg L^{-1} (C.V. = 92%) in springs and 6.9 mg L^{-1} (C.V. = 114%) in rivers. The nitrate fluxes from springs to rivers were estimated at ca. 3 t km^{-2} annually. About 1/5 of spring water samples were characterized with higher nitrate concentrations than limits recommended by WHO and National Drinking Water Standards (Ukraine). Springs have been classified according to nitrate concentration and enrichment as high, moderate and low contaminated.

1. Introduction

The nitrate contamination of natural water is rising worldwide (Katz et al., 2004; Stuart et al., 2011; Stone and Edmunds, 2014) that leads to water supply difficulties, pollution of drinking water and spread of nitrate-related diseases (Canter, 1997).

Nitrates enter natural water with various non-point and point sources (Katz et al., 2004); their accumulation and mobility are strongly controlled by denitrification (Jahangir et al., 2012) and dilution. The nitrate contamination is found to be dependent on land use patterns, geological, hydrological and climate conditions. Anthropogenic sources of nitrates are mainly leakages from sewage systems (Schultz et al., 1979; Robson and Neal, 1997; Stuart et al., 2011), storages of fertilizers, manure (Iqbal, 2002), landfills (Ding et al., 2001), industrial and municipal discharges, run-off from urban and agricultural areas (Ako et al., 2014). Nitrates in surface and groundwater pose environmental and human health concern as they change the nutrient balance in aquatic systems (Jahangir et al., 2012) and even may have cancerogenic properties (Ward et al., 2005; Ako et al., 2014). The World Health Organization (WHO, 2008) has promulgated a guideline of a maximum of 50 mg L^{-1} of nitrates in drinking water.

As nitrate ion is mobile in the environment, it is necessary to know nitrates inputs and pathways in both surface and groundwater and to understand the transport processes in each compartment of water basin (Flipo et al., 2007), including springs.

Springs provide sources of potable water and possess ecological, recreational and cultural values. At the same time they represent transition from groundwater to surface water and directly reflect the state of groundwater in the aquifers (Boy-Roura et al., 2013). Groundwater is an important water resource in East Ukraine and accounts up to 20% of total water supply in the region. Nowadays, the groundwater extraction in this part of Ukraine is ca. 1570 thousand m^3 per day, where 44% is used for drinking and households supply, 11.5% – for industrial supply, 0.6% – on irrigation and the rest (ca. 44%) is used for the mining drainage purposes.

Nitrates occurrence and dynamics in springs were analysed in several studies (Burg and Heaton, 1998; Katz et al., 2001, 2004; Boy-Roura et al., 2013; Ako et al., 2014) in which nitrate ions were considered as an indicator of nitrogen pollution. However, most of these studies described only large discharge springs located mainly in karst systems, and a little attention was paid to small discharge

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springs (Boy-Roura et al., 2013), associated with unconsolidated rock formations that are particular features of aquifers in the east part of Ukraine.

The objective of this study was to find the patterns of nitrate distribution in surface and groundwater, identify natural and anthropogenic factors influencing nitrate contamination in springs and streams in the transboundary (Russia/Ukraine) watershed with different geological features, land uses and anthropogenic effects. We also intended to estimate contributions from anthropogenic and natural sources of nitrate contamination at the watershed level by calculating nitrate fluxes from recharge areas.

2. Study area and methods

2.1. Description of the study area

The Seversky Donets basin (54,520 km^2 in the territory of Ukraine) is the largest watershed of Northeast and East Ukraine, being extensively used for drinking, industrial and agricultural water supply. This river is a main receiver of treated wastewaters from Kharkiv, Lugansk and Donetsk regions (ca. 8 M people with average density of 200 persons per km^2). The river network consists of 425 streams with the length of more than 10 km and 11 rivers with the length of more than 100 km. The soil surface elevation ranges from 24 to 345 m a.s.l. We studied Seversky Donets (SD) watershed with its major transboundary sub-basins of the rivers Udy and Oskol within limits of Ukraine (Fig. 1).

The study area belongs to the East-European Precambrian platform with Archean-Proterozoic crystalline basement. The basement is covered with sedimentary formations of variable thickness and geological age consisting of clastic deposits (sands, sandstones, clays, siltstones and mudstones) and carbonate rocks (limestone and chalk).

Within the study area the surficial geology up to 120 m of depth is composed mostly of permeable and loose sedimentary materials: sands, loams and clayey loams of Quaternary, Neogene and Paleogene ages. The Seversky Donets and Oskol riverbeds in the upper reaches are underlain by Upper Cretaceous marls and chalk (sampling points SD01 and OS01). The middle-reaches of Udy, Lopan and Seversky Donets rivers relate to consolidated Middle Paleogene formations of sand- and siltstones (sampling points U01–U05, L01–L03 and SD02). From the city of Izyum, Seversky Donets enters the Donetsk Folded Belt, which stands out for its complicated geological structures. Here the riverbed cuts into Lower Cretaceous sandstones, Jurassic, Permian and Carboniferous sandstones, clays and limestone (sampling points OS02, SD03–SD05).

From hydrogeological point of view, the study area belongs to the Dnieper-Donets Artesian Basin (total area is 165,000 km^2). The shallowest aquifer in this basin occurs at 5–30 m below the day surface depending on landscape position and geological conditions. Water-saturated zone consists predominantly of Quaternary loams, sandy loams and alluvial sands, Oligocene and Eocene sandstone and fissured Cenomanian – Lower Cretaceous chalk and marl. These formations outcrop on the surface on the western slopes of the steep river valleys and ravines (Vystavna et al., submitted for publication).

The SD drainage area is situated in the Eurasian forest–steppe and steppe natural zones and characterized by mean annual temperature of 7.0 °C (absolute minimum − 41 °C, absolute maximum + 42 °C), mean January temperature of −5 °C, mean July temperature of +21 °C, and annual precipitation from 470 to 540 mm (Vystavna et al., 2012a, 2012b) with the long-term mean annual precipitation of 519 mm (Vasenko et al., 2006). Soils in SD watershed are mainly clayey at highlands and sandy at river floodplains.

Generally, land uses of the studied catchment are agriculture (77%), forestry (13%) and settlements (4%). Agricultural lands include arable lands (61%), pastures (10%) and others (29% – orchards, farms, etc.) Annual input of inorganic fertilizers on arable lands is up to 50–60 kg ha^{-1} almost 70% of which are nitrate fertilizers. Organic fertilizers are applied only at 1% of arable lands with annual amount of 0.4 t ha^{-1}.

Different parts of the basin have different land use patterns and anthropogenic impacts. The upper part of SD basin within Ukrainian territory is represented with agricultural (60%), forestry (11%), and industrial (2%) land uses featuring numerous rural

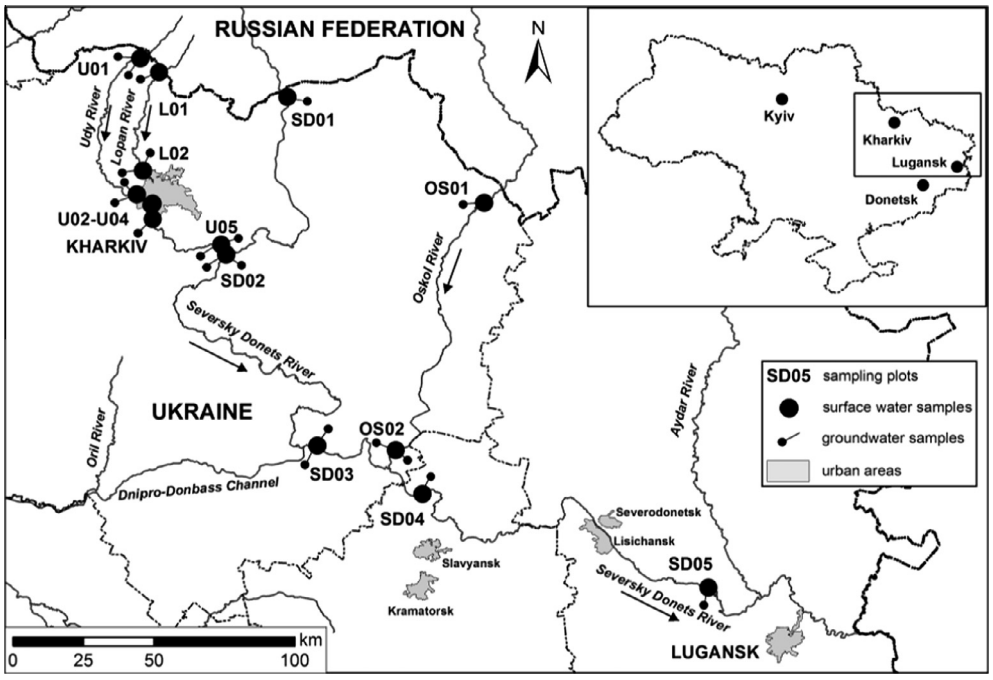

Fig. 1. Study area and sampling sites.