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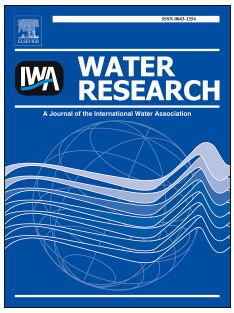

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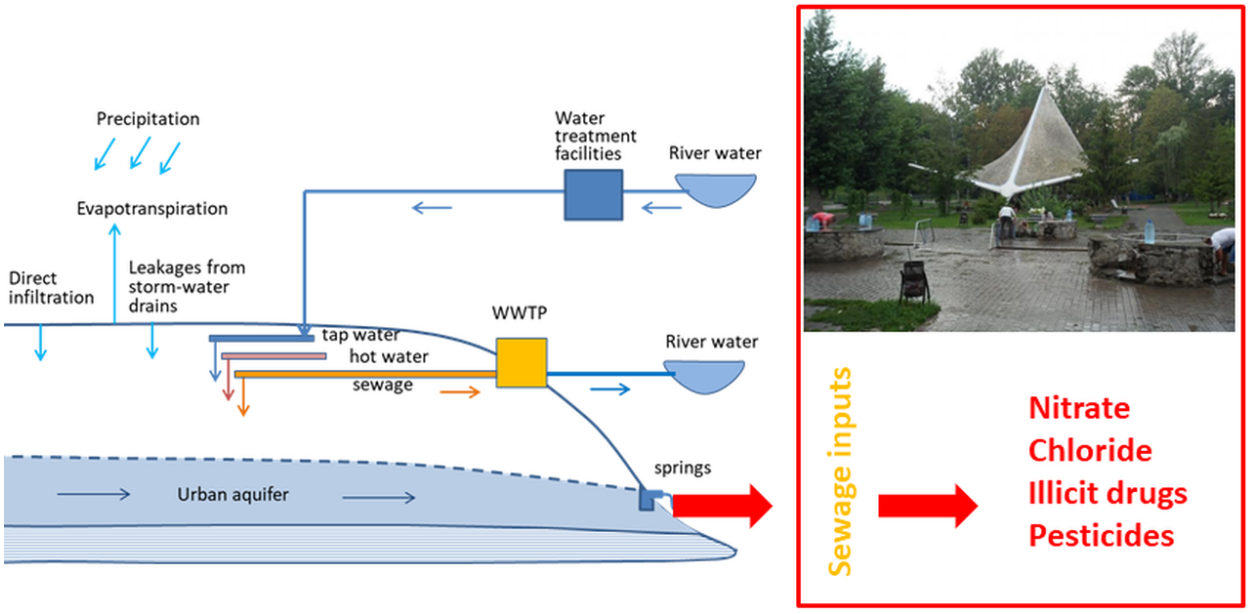

Multi-tracing of recharge seasonality and contamination in groundwater: a tool for urban water resource management

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Abstract

In this study, sources of recharge and contamination in urban groundwater and in groundwater underneath a forest in the same aquifer were determined and compared. Data on hydro-chemical parameters and stable isotopes of water were collected in urban and forest springs in the Kharkiv region, Ukraine, over a period of 12 months. Groundwater transit time and precipitation contribution were calculated using hydrogeological data and stable isotopes of water to delineate groundwater recharge conditions. Hydro-chemical data, stable isotopes and emerging contaminants were used to trace anthropogenic groundwater recharge and

approximate sewage and tap water contributions to the aquifer. The results indicated that each spring had unique isotopic signatures that could be explained by recharge conditions, groundwater residence time, and specific mixing patterns with sewage and water leaks. Elevated nitrate content, stable isotopes of nitrate, and the presence of emerging pollutants (mainly illicit drugs) in most of the urban springs confirmed mixing of urban groundwater with sewage leaks. These leaks amounted to up to 25% of total recharge and exhibited seasonal variations in some springs. Overall, the results show that urban groundwater receives variable seasonal contributions of anthropogenic components that increase the risk to the environment and human health, and reduce its usability for drinking water production. The multi-tracing approach presented can be useful for other cities worldwide that have similar problems of poor water management and inadequate sewage and water supply infrastructure.

Keywords: urban hydrology; stable isotopes; emerging compounds; aquifer; nitrate; pesticide.

1. Introduction

Groundwater is an important source of drinking water worldwide and its role is growing due to deterioration of surface water quality and quantity under the impact of climate variability, contamination, and run-off re-allocation (FAO 2011, WWAP 2015). Surface water and groundwater quality has been improved in the European Union (EU) (European Commission 2012), mainly due to a number of water regulations (i.e., EU WFD 2000, Groundwater Directive 2006). However, in many countries that share transboundary EU surface water and aquifers, for example Ukraine, there is great concern regarding the low quality and quantity of available groundwater resources because of ongoing and increasing

contamination (Yakovlev et al. 2015), and a lack of appropriate environmental regulations (Vystavna et al. 2018a,b).

Drinking water supply from groundwater depends strongly on the seasonality of recharge, climate, and contamination (Griebler et al. 2010; Taylor 2012). Thus groundwater management is a complex task requiring multiple tools, including hydrogeological and hydro-chemical models (Healy and Scanlon 2010; Manna et al. 2016). This in turn often requires exhaustive databases and detailed descriptions of environmental conditions, and/or direct measurements using advanced infrastructures and equipment (Herrmann et al. 2015). In many cases, such resources are not available in developing countries (WWAP 2015). Another approach is to study physical (environmental isotopes) (Barrett et al. 1999; Vystavna et al. 2018c) and hydro-chemical (inorganic and organic) tracers (Fenech et al. 2012) that can provide information on groundwater recharge and contamination at a reasonable cost in a short time (Yin et al. 2019). The stable isotopes of water, i.e., oxygen-18 (^{18}O) and deuterium (^{2}H), have been found to be efficient tracers for describing groundwater recharge, water origin, age, and pathways (Ettayfi et al. 2012; Tipple et al. 2017). The stable isotopes of nitrate (^{18}O and ^{15}N) have been widely applied to trace nitrate (NO_3) contamination sources (Urresti et al. 2015; Archana et al. 2018; Taufiq et al. 2019). Organic compounds, particularly pharmaceuticals, have been used to determine the sewage contribution to groundwater (Schaider et al. 2016; McCance et al. 2018; Castiglioni et al. 2019). However, a multi-tracing approach that includes physical, organic, and inorganic chemical tracers for assessing the urban water cycle has not been fully investigated. For example, a combination of these methods has not been used previously to identify recharge and contamination seasonality in shallow alluvial aquifers located in a temperate climate. Thus the present study had the following objectives: (i) to describe recharge conditions in urban and forest groundwater

catchments; (ii) to evaluate hydro-chemical parameters and stable isotopes in groundwater; and (iii) to trace and quantify mixing of groundwater with sewage and tap water leaks.

The novelty of the research lies in the sophisticated application of multiple tracers (stable isotopes of water and nitrates, conventional hydro-chemical parameters, and emerging pollutants) in parallel with conventional approaches (hydro-geochemical models, multivariate statistics) to determine the seasonality of groundwater recharge and contamination with water and land uses. In the study, urban and natural (forested) groundwater catchments (located in presumably similar climate and hydro-geological settings) were compared. The study area was the densely populated city of Kharkiv (1.4 million inhabitants) in Eastern Ukraine, where groundwater is used as an alternative to tap water (Vystavna et al. 2017). The study area has limited local runoff and is located in a zone under risk of military action. Therefore, groundwater is considered an important strategic drinking water source that can potentially replace tap water in an emergency. The shallow aquifer selected for the analysis has been studied previously in terms of general contamination status and hydrogeological conditions (Yakovlev et al. 2015; Vystavna et al. 2017), but knowledge of the seasonality of recharge and water quality variation in the aquifer was lacking.

2. Studied catchments

Five urban (T1, S2, N3, Y4, and P5) and one peri-urban forested (O6) groundwater sites were selected for this study. All sites are located in the forest-steppe zone of the temperate continental climate area, with average annual precipitation of 521 mm and average annual air temperature of +9.1°C (2005-2017; Kharkiv airport World Meteorological Organization (WMO) station, ID 34300). During the sampling period (October 2016-September 2017), total precipitation was 18% lower (426 mm) than the long-term average, indicating a dry hydrological period. Cold season precipitation (November-April) accounted

for ~70% of total precipitation during the sampling period. From April to October (warm season), evapotranspiration usually exceeds precipitation in the region.

Groundwater was studied where it emerges at the surface as springs (Figure 1a). The urban springs were fitted with outflow tubes and the forest spring flowed into an open pit discharging outflowing groundwater. The maximum elevation at the spring outflows ranged from 113-123 m a.s.l. in the urban catchment to 140 m a.s.l. in the forested catchment. The most recent sediment layers (up to 120 m thick) are composed predominantly of permeable materials (sands and loams) of Quaternary, Neogene, and Paleogene origin, but with some spot inclusions of clay in upper layers (Geological Survey 2007). Springs are fed from fractured fine-grained sandstones and siltstones of the Eocene age. The depth to the aquifer is 2-36 m below the surface and the average hydraulic conductivity of the saturated zone is 2×10^{-4} m s^{-1}. The aquifer can be considered a homogeneous system in which the watertable is adapted to the topography and is recharged by precipitation and anthropogenic sources (Geological Survey 2007; Vystavna et al. 2017). Hydrogeological cross-sections are shown in Supplementary Material.

The land uses in Kharkiv city (total area 307 km^2), where the five urban springs (T1-P5) are located, include residential (55% of total area), industrial (16.5%), vegetated areas (20%), and traffic networks. The population density is 3200-27,400 per km^2 (for details, see Supplementary Material). The urban water supply is provided predominantly (97%) by two sources of surface water: (i) the Seversky Donets River, around 40 km from the city (85% of the total drinking water supply) and (ii) the man-made Dnipro-Donbass channel, starting around 130 km from the city and carrying water from the Dnipro River to the Seversky Donets River basin. Two water treatment plants are located within the urban area. The centralized drinking water supply from deep groundwater wells (up to 800 m depth) comprises just 3% of the total supply and is limited to two small neighborhoods (18,200

inhabitants; 6.64 km^2) not located within the study area. Pressurized water supply pipes are placed at 0-5 m below the terrain. Urban wastewater is collected by shallow and deep mains, and undergoes mechanical and biological treatment at the city's wastewater treatment plant (WWTP) (550,000 m^3 d^{-1}). The treated wastewater is discharged into the Lopan and Udy Rivers (Figure 1a,b). Around 20% of urban households are not connected to the urban sewerage network and instead use pit latrines and septic tanks, which can leak into the shallow groundwater. At present, the sanitary infrastructure in Kharkiv city is in a state of disrepair, resulting in numerous and frequent leaks (around 24% of total water supply), a problem that cannot be eliminated in the short term (KP Voda 2017).

Catchment O6 drains a forest-dominated landscape without agricultural land use and only negligible urbanization (residential buildings and roads account for <9% of the total drained area). The forest vegetation is typical forest-steppe oak woodlands on a rolling plain terrain with grey and dark-grey forest soils. Besides forestry, catchment O6 is used mainly for outdoor recreation.

3. Methods

3.1 Meteorological and hydrogeological parameters

Meteorological data (daily air temperature, relative humidity, precipitation) for the period 2015-2017 were obtained from Kharkiv WMO station. Potential pan evapotranspiration was calculated based on mean monthly air temperature and humidity, according to a method adapted by Romanenko (1961) for the climate and soil conditions of Ukraine.

Spring catchment areas were delineated according to upstream boundaries of water lines measured on local hydrogeological maps (Geological Survey 2007). The remaining uncertainty in groundwater flow direction was handled by including a 20° shift of the

auxiliary water flow line on both sides, as proposed by Ferrante et al. (2015).

Minimum water transit time was estimated based on the velocity of vertical infiltration flow at the spring outflows, taking into account the thickness of upper sediment layers and the hydraulic conductivity of the vadose zone. Maximum water transit time was estimated based on the velocity of the lateral groundwater flow at the most remote catchment area boundary, considering the orography, groundwater flow direction, and hydrogeological structures (Geological Survey 2007). Detailed calculations are presented in Supplementary Material.

3.2 Sampling and analysis

Monthly precipitation (October 2015-September 2017) was sampled at the Kharkiv Global Network of Isotopes in Precipitation (GNIP) station (49.5615°N/36.1208°E, 101 m a.s.l., located 3 km from Kharkiv WMO station) coordinated by the International Atomic Energy Agency (IAEA), using a commercial evaporation-free precipitation collector with a submerged capillary tube (PALMEX®, Croatia). Groundwater was sampled monthly for hydrological variables and stable isotopes of water, and on five occasions from October 2016 to September 2017 for hydro-chemical parameters. Discharge in springs was measured at the time of sampling, using a stopwatch and a calibrated container. Simultaneously, groundwater temperature was measured using a mercury thermometer, while pH, electrical conductivity (EC), and redox potential (ORP) were measured using HI-98130 Multiparameter and H-98121 Pocket pH and ORP tester (Hanna Instruments®).

Tap water samples were collected from two drinking water supply schemes. The first site represented the part of urban tap water network supplied by the Dnipro-Donbass channel (one sample in October 2016). The second represented the part of the network where water comes from the Seversky Donets River (six bi-monthly samples October 2016-September 2017) (Figure 1b). The purpose was to check whether tap water of different origins had

similar isotopic composition. A sample of the sewage influent to the WWTP was taken simultaneously with the tap water sample in September 2017, in order to compare their isotopic composition (Figure 1b).

Unfiltered water samples for analysis of major ions and nitrate were collected in 500-mL plastic bottles and analyzed by the potentiometric method (Vystavna et al. 2017). The difference between two replicates was less than 5%. For analysis of stable isotopes of water ($\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O), water samples were collected in 50-mL high-density polyethylene bottles and analyzed using the laser instrument Picarro L2120-*i*. Each sample was analyzed at least twice, with seven injections per vial. The results were compared with those for internal laboratory standards calibrated against primary reference materials, and were expressed per mille (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW). The typical precision, expressed as the one-year variance in an internal control standard, didn't exceed ±0.1‰ and ±1.0‰ for $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O, respectively.

Water samples for analysis of stable isotopes of nitrate ($\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3) were collected in October 2016 and September 2017. These samples were filtered (0.22 μm) in the field and transferred to plastic bottles (50 mL). Nitrate isotope analysis was carried out by the denitrifier method (Sigman et al. 2001; Casciotti et al. 2002), whereby nitrate was converted to N_2O and an isotope ratio mass spectrometer (GasbenchII/delta V plus, Thermo Fisher Scientific®, USA) is used for simultaneous determination of $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3. The results were compared with those for internal laboratory standards calibrated against primary reference materials, and were expressed as ‰ relative to the standards AIR for $\delta^{15}N$-NO_3 and V-SMOW for $\delta^{18}O$-NO_3. Typical precision, expressed as the one-year variance in an internal control standard, was better than ±0.6‰ for $\delta^{15}N$-NO_3 and ±0.4‰ for $\delta^{18}O$-NO_3.

Groundwater samples (1-L amber glass bottles) for non-targeted analysis of emerging compounds were collected in September 2017. The screening of chemicals was based on an exact mass in an open access library (over 2,000 compounds) by liquid chromatography quadrupole time-of-flight mass spectrometry (LS-Q-TOF-MS) coupled to an Accela 1250 LC pump (Thermo Fisher Scientific®) and an HTS XT-CTC autosampler (CTC Analytics AG®, Switzerland), operated using Xcalibur software (Thermo Fisher Scientific®). A Hypersil gold aQ column (50 mm × 2.1 mm ID × 5 µm particles; Thermo Fisher Scientific®) was used for chromatographic separation. Details of sample preparation can be found in Supplementary Material.

Results on the presence of the most likely compounds were selected according to the following criteria: i) error between theoretical and experimental exact mass <5 ppm; ii) difference in isotopic pattern between theoretical and experimental <10%; iii) identification of the compounds using comparison of the spectrum obtained with the theoretical spectrum, based on the exact mass library with probability >70% (Library Score), where the score takes into account the isotopic distribution, mass accuracy, and mass/spectra, with values close to 100 showing the most likely elemental composition; and iv) retention time (error <5%). Because of the nature of the screening analysis, exact concentrations could not be determined.

3.3 Data analyses

The relative ion composition for each sampling site was plotted in diagrams according to Stiff (1951) and the isometric log-ratio (ilr)-ion according to Shelton (2018). The environmental data were tested for normal distribution. When the distribution was skewed, the data were transformed logarithmically (Legendre and Legendre 2012). Principal component analysis (PCA) was used to plot isotope and hydro-geochemical characteristics per site and month. In a second PCA with time-averaged isotope and hydro-geochemical

characteristics per site, the presence/absence in the springs of a range of emerging organic compounds, such as drugs, pesticides, and food compounds from one-off measurements, was fitted using the procedure "envfit" (Oksanen et al. 2018). All calculations were performed in R 3.3.5 (R Core Team 2018). Detailed information on the statistical analyses is provided in Supplementary Material.

The local meteoric water line (LMWL) (October 2015-September 2017, n=24) was constructed by the reduced major axis method (Crawford et al. 2014). The equation obtained was compared with the global meteoric water line (GMWL), described as $\delta^2H = 8 \times \delta^{18}O + 10$ by Craig (1961). Isotopic composition of springs, sewage, and tap water was plotted against the LMWL, to examine relative variation and differences in isotopic composition of hydrological components. Deuterium excess (d-excess = $\delta^2H - 8 \times \delta^{18}O$) was used as an indicator of non-equilibrium conditions, which occur during evaporation as water with d-excess <10‰ is presumed to undergo evaporation (Dansgaard 1964).

A two-component mixing model (Unnikrishna et al. 2002) was used to estimate the contribution of precipitation from warm (May-October) and cold (November-April) periods of the year, based on annual flow-weighted $\delta^{18}O$-H_2O value in springs and in cold and warm precipitation (calculations shown in Supplementary Material).

The groundwater transit time was estimated according to Herrmann et al. (2015):

$$\tau_r = \frac{\sqrt{\frac{1}{f^2} - 1}}{2\pi} \qquad (1)$$

where τ_r is the groundwater transit time in years and f is the ratio of $\delta^{18}O$-H_2O amplitude in groundwater flow to that in precipitation. The transit time was estimated by two approaches: (i) using the amplitude of $\delta^{18}O$-H_2O for the 12-month study period; and (ii) using the amplitude of $\delta^{18}O$-H_2O taken only for the cold period, assuming selective recharge (Vystavna et al. 2018c). A first rough approximation of groundwater transit time at the study sites was

calculated assuming that the isotopic lapse rate was insignificant due to the small differences in elevation between catchments.

The chloride (Cl^-) concentration and $\delta^{18}O$-H_2O were used to separate the annual contributions of tap water and sewage leaks to urban groundwater, using the ternary mixing model (Grimmeisen et al. 2017; Vystavna et al. 2018d):

$$(f_1+f_2+f_3) \times [Cl^-, \delta^{18}O]_{ub} = f_1 \times [Cl^-, \delta^{18}O]_{gw} + f_2 \times [Cl^-, \delta^{18}O]_{tw} + f_3 \times [Cl^-, \delta^{18}O]_{sw} \quad (2)$$

where Cl^-_{ub} and $\delta^{18}O_{ub}$ [mg L^{-1}, ‰] are flow-weighted chloride concentration and $\delta^{18}O$-H_2O in urban springs; Cl^-_{gw} and $\delta^{18}O_{gw}$ [mg L^{-1}, ‰] are flow-weighted chloride concentration and $\delta^{18}O$-H_2O in the forest spring; Cl^-_{tw} and $\delta^{18}O_{gw}$ [mg L^{-1}, ‰] are average chloride concentration and $\delta^{18}O$-H_2O in tap water; and Cl^-_{sw} and $\delta^{18}O_{gw}$ [mg L^{-1}, ‰] are chloride concentration and $\delta^{18}O$-H_2O in sewage. Chloride concentration in sewage was considered stable and equal to the average of 350 mg L^{-1} (City Council 2010). The $\delta^{18}O$-H_2O in tap water was used for sewage, assuming similar origin of these waters (Vystavna et al. 2018d). The values f_1, f_2, and f_3 are the fractions of natural recharge, water supply, and sewage leaks, respectively, with the sum of f_1, f_2 and f_3 equal to 1.

To separate seasonal contribution of sewage leaks (f_1) from other possible recharge sources (f_2), measured $\delta^{18}O$-H_2O and Cl^- concentration were used as tracers in the binary model (Vystavna et al. 2018d):

$$(f_1+f_2) \times [Cl^-, \delta^{18}O]_{ub} = f_1 \times [Cl^-, \delta^{18}O]_{sw} + f_2 \times [Cl^-, \delta^{18}O]_{gw} \quad (3)$$

The simultaneous use of Cl^- and $\delta^{18}O$-H_2O enabled differentiation between inputs from sewage and road de-icing salt. Both these sources have a high chloride content, but de-icing salt enters the groundwater mainly with snowmelt, which has lower isotopic signature than sewage. Moreover, street runoff is mostly collected by the urban drainage and storm water system. Binary and ternary models were processed using the MIX Program v1.0 (Vázquez-

Suñé et al. 2010). The $\delta^{15}N\text{-}NO_3$ vs. $\delta^{18}O\text{-}NO_3$ linear regression plot was used to determine the dominant sources of nitrate in groundwater (Kendall 1998).

4. Results

4.1 Stable isotopes of water in precipitation

Between October 2015 and September 2017, the isotope concentrations in precipitation were highly variable, with extreme lows in November 2016. The amount-weighted average $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ in precipitation was -9.2‰ and -64.5‰, respectively. Annual amplitude of $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ in precipitation was 8.7‰ and 63.3‰, respectively (details in Supplementary Material). On a monthly scale, the oxygen and hydrogen stable isotopes in precipitation correlated well with average annual air temperature (Pearson coefficient $r>0.77$, $p<0.01$, $n=24$), but not with precipitation amount ($r<0.5$). The equation obtained for the LMWL was: $\delta^{2}H = 7.61 \times \delta^{18}O + 4.88$.

The urban sites T1 and Y4 and the forest site O6 had relatively similar isotopic range, but differing d-excess values (7.1‰, 9.9‰, and 8.4‰, respectively). Site N3 showed slightly higher isotopic values than the group of urban springs. Site S2 had the lowest and site P5 the highest isotopic values among the springs (Figure 2). According to the simultaneously taken samples, tap water from the Dnipro-Donbass channel was slightly enriched in isotopes compared with tap water from the Seversky Donets River. The isotopic composition of tap water was more seasonally variable than that of groundwater, with lower d-excess values and higher isotopic values, giving a regression line with a clear evaporation signal reflecting the surface water origin. The isotopic values of S2, N3, and P5 were well aligned with the tap water regression line (Figure 2). Simultaneously taken samples of sewage and tap water had similar isotopic composition, with standard deviation <5%.

4.2 Precipitation contribution and groundwater transit time

The annual amplitude of $\delta^{18}O$-H_2O in groundwater differed slightly between sites, ranging from 0.1‰ to 0.3‰. The contribution of warm and cold precipitation to groundwater recharge was comparable between springs, with a marked dominance (>83%) of cold precipitation. Groundwater transit time was comparable for sites N3, Y4, P5, and O6, but slightly shorter for S2 and twice as long for site T1 (Table 1).

Table 1. Precipitation contribution, groundwater transit time, and recharge at the five urban sites (T1, S2, N3, Y4, and P5) and the forest site (O6)

Site ID	Cold precipitation contribution %	Warm precipitation contribution %	Groundwater transit time, years				Estimated recharge		
			Hydro-geological method (based on filtration and recharge area)	Isotopic method based on:		According to the position of extreme $\delta^{18}O$-H_2O values	Natural recharge f_1, %	Recharge by tap water leaks f_2, %	Recharge by sewage leaks f_3, %
				Annual amplitude of $\delta^{18}O$-H_2O	Amplitude of $\delta^{18}O$-H_2O in the cold period				
T1	89	11	0.4–26	14	1.7	Not detectable	76	0	24
S2	93	7	0.9–18	5	0.6	0.7	89	8	3
N3	87	13	0.3–4.7	7	0.8	0.8	70	13	17
Y4	91	9	0.3–3.3	7	0.8	Not detectable	82	4	14
P5	83	17	0.3–3.8	5	0.7	0.7	55	34	11
O6	90	10	0.3–5.1	7	0.7	0.7*	100*	0*	0*

*Assumed according to the position of the extreme isotopic value and selected calculation method.

4.3 Major ion composition

The groundwater was near neutral or slightly acidic, with pH values between 6.1 and 7.4. Redox potential ranged from oxidizing to reducing conditions (from +287 to -117 mV), while EC varied between 950 and 1540 μS cm^{-1} in the urban springs, but was lower (740 to 900 μS cm^{-1}) in the forest spring. Total dissolved solids (TDS) ranged from 861 to 1170 mg L^{-1} in the urban springs and from 632 to 732 mg L^{-1} in the forest spring. HCO_3^- concentration ranged from 230 to 480 mg L^{-1} in both urban and forest springs. Average Cl^- concentration in urban springs (74±30 mg L^{-1}) was approximately twice that in the forest spring (25±14 mg L^{-1}). Average SO_4^{2-} and Na^+ concentrations were notably higher (280±100 mg L^{-1} and 124±35 mg L^{-1}, respectively) in urban springs than in the forest spring (65±10

mg L^{-1} and 39±3 mg L^{-1}, respectively). The Ca^{2+}, Mg^{2+}, and K^{+} concentrations were comparable between urban and forest springs (Figure 3a). However, HCO_3^- and SO_4^{2-} were the dominant ions in the urban springs, while HCO_3^- and Ca^{2+} dominated in the forest spring (Figure 3a). Tap water had highly variable ion concentrations, particularly for HCO_3^-, Cl^-, SO_4^{2-}, and Na^+ (Figure 3a). Its dominant ion composition was comparable to that of urban groundwater. Sewage was characterized by higher SO_4^{2-}, Cl^-, and Na^+ concentrations compared with groundwater and tap water (Figure 3a). Samples from the forest spring O6, and to a lesser degree from urban spring Y4 and tap water, were of the HCO_3^- type. Sewage, and to a lesser extent urban spring S2, tap water, and then springs N3 and T1, were of the Na^+ + K^+ type. The samples were best distinguished based on the ratio Cl^- + SO_4^{2-} to HCO_3^- (Figure 3b). The measured variables are shown in Supplementary Material.

Multivariate statistical analysis showed that, in terms of isotope and hydro-chemical water composition, the springs T1, N3, Y4, and P5 were also similar over time, with gradually increasing EC from Y4 to P5, N3, and T1 (Figure 4). In contrast, the forest spring O6 plotted separately, towards the lowest concentrations of ions and EC. Urban spring S2 plotted at another extreme, with the lowest isotope ratios and the highest concentrations of inter-correlated SO_4^{2-} and Na^+. Tap water was even farther along the first axis, which was mostly positively correlated with EC and TDS. Thus, the general order was: tap water, the natural spring O6, urban springs Y4 and S2, then P5 and T1, and finally N3 (Figure 4).

4.4 Nitrate contamination, contribution of sewage and tap water leaks

Nitrate concentrations showed high variability, ranging from 0.3 to 90 mg L^{-1} in the urban springs and from 0.3 to 7 mg L^{-1} in the forest spring, and with noticeable NO_3^- enrichment (5- to 10-fold) in urban groundwater. Except at site T1, the maximum nitrate concentrations were observed in March and June (Figure 5). Stable isotopes of nitrate in the

springs were within the range reported for NO_3^- derived from sewage and manure (Figure 6). Sites T1 and Y4 displayed high variation in $\delta^{18}O$-NO_3. However, the variation in $\delta^{15}N$-NO_3 values was lower at all sites. At most urban springs (T1, N3, Y4, and P5), stable isotopes of nitrate, particularly $\delta^{18}O$-NO_3, tended towards enrichment with increasing NO_3^- concentration (Figure 6).

The sewage contribution at sites T1 and N3 was estimated to be 19-24% and showed less seasonal variation than in the other urban springs (Figure 5). At sites Y4 and P5, the sewage contribution was lowest in October 2016 and highest in December 2016. At P5, the sewage contribution was positively related to discharge. At site S2, the sewage contribution was less than 3% (Figure 5). The annual contribution of tap water leaks to urban groundwater recharge was highly variable between sites, with the maximum estimated for P5 (34%). Site S2 showed the lowest recharge from sewage and tap water leaks among the urban springs (Table 1).

4.5 Emerging contaminants in groundwater

The emerging contaminants detected in groundwater were divided into three groups: drugs (caffeine, nikethamide, riluzole, phenazone, pilocarpine, pergolide, ajmaline, carbamazepine, moxonidine, dihydrocodeine, sulfathiazole, papaverine, and aripriprazole), pesticides (DEET (pentedrone), dodine, chlordimeform, atrazine, simazine, and butraline), and food compounds (alternariol (a mycotoxin), chanoclavine and kojic acid (food additives) (details of use and properties are shown in Supplementary Material). All of the drugs detected can be abused and some are illicit drugs. The most frequently detected drug (in five of the six springs studied) was the alkaloid pilocarpine, which was found even in the forest spring. Chanoclavine and chlordimeform were detected in four springs. Caffeine, phenazone, and alternariol were found in three springs. Other compounds were found at one or two sites. Each

spring was characterized by a distinct group of detected compounds according to the PCA ordination (Figure 7). The stimulant caffeine and food compounds tended towards the positive y axis and correlated well with Na^+ and SO_4^{2-}. Four pesticides and most of the drugs detected tended towards the negative x axis and correlated well with $\delta^{15}N\text{-}NO_3$, Cl^-, and NO_3^-. Atrazine and pilocarpine were more along the positive x axis (Figure 7).

5. Discussion

5.1 Urban groundwater recharge

By complementing hydrogeological modeling with tracing of stable isotopes in water, we were able to delineate natural and anthropogenic recharge of the shallow aquifer studied. The results indicate that both urban and forest springs in the study area are selectively recharged by cold precipitation (Table 1). This is typical for the temperate continental climate, where evapotranspiration can be 2- to 3-fold higher than precipitation amount, which reduces natural recharge during the warm period (Vystavna et al. 2018c). Consequently, the $\delta^{18}O\text{-}H_2O$ amplitude in cold precipitation was found to be a more realistic parameter for estimating groundwater transit time than the amplitude in annual precipitation (Table 1), and this might apply to other sites with a continental climate. In some springs (S2, N3, and P5), the estimated transit time was similar to that determined from naturally occurring isotopic extremes (Table 1). Exceptionally low isotopic composition of precipitation in November 2016 was associated with isotopically depleted Arctic air masses and locally recycled moisture exceeding evaporation according to the Hybrid Single Particle Langarian Integrated Trajectory model (details in Supplementary Material). With its high amount, combined with above-zero air temperature and low evapotranspiration, November precipitation was efficient in recharging groundwater, which explains the unusually low isotopic composition in some urban springs

(S2, N3, and P5) (Figure 5). Therefore, natural $\delta^{18}O$-H_2O extremes in precipitation were used as natural tracers to confirm the estimated groundwater transit time (Table 1).

The hydrogeological method for estimating groundwater transit time cannot be highly accurate due to limited availability of hydrogeological data (Healy and Scalton 2010). However, it gives a preliminary range of the possible water age in the aquifer. Our findings confirm the validity of the model used (Eq.1) in estimating regional groundwater transit time, and also highlight potential applications of isotopic extremes in hydrogeological studies.

Since isotopic and chemical signatures differed between hydrological components, it was possible to estimate anthropogenic recharge by applying binary and ternary mixing models. In the present case, tap water and sewage had lower d-excess than warm precipitation, indicating that likely mixing with tap water and sewage decreased the d-excess of urban springs compared with the natural recharge conditions (Figure 2). We found a discrepancy between the contributions of precipitation, tap water, and sewage leaks, signifying that natural recharge of springs in Kharkiv city can be limited to large hydrological events occurring in the cold period (Table 1). Similar mechanisms can be expected to operate in other temperate, dry-summer areas with inadequate water management. Tap water and sewage leaks have been found to contribute to urban groundwater recharge, changing the hydrological function of groundwater and influencing its contamination status, as found in many previous studies (Chen et al. 2008; Houhou et al. 2010; Tubau et al. 2017). The method for quantification of tap water leaks into groundwater applied in the present study was based in principle on distinct isotopic signatures of urban hydrological components that are generally valid for regions where drinking water supply derives from surface water. Thus, this method should generally be applicable to many regions in Eastern and Central Europe, particularly in post-Soviet countries (Moldova, Ukraine, Belarus, and Russian Federation) with similar problems in urban water resource management.

5.2 Urban groundwater contamination

Isotope composition and changes in this over time clearly distinguished the forest spring from urban groundwater, but stable isotopes of water were not able to trace groundwater contamination and its origin. However, the additional chemical variables measured (EC, TDS, Cl^-, Na^+, and NO_3^- concentrations) revealed the influence of anthropogenic activities in urban springs (Figures 3a and 6). This confirms findings in other studies in different regions (Schmidt et al. 2007; Ettayfi et al. 2012; Grimmeisen et al. 2017). The general hydro-chemical trend in our study was from the forest spring O6 to urban sites Y4 and S2, further to sites P5 and T1, and then N3 (Figure 4). Spatially and seasonally highly variable nitrate contamination (Figure 5) was likely controlled by different nitrate source and hydrological processes. Nitrate in soil can originate from leaky pit latrines and septic tanks, but also from soil nitrification (Nikolenko et al. 2018). At sites T1 and S2, the nitrate concentration decreased with increasing flow, indicating dilution. In the other springs, including that at the forest site, the nitrate concentration increased with increasing flow (Figure 5). A reason may be that oversaturated soil can release accumulated nitrate when the water level changes. Ensuing nitrate contamination in groundwater has been observed e.g., in Western France (Aquilina et al. 2012). In the present study, analysis of stable isotopes of nitrate confirmed that sewage leaks can be the principal source of nitrate accumulation in the soil (Figure 6), as we also found in an earlier study (Vystavna et al. 2017). Mineralization and subsequent nitrification of the organic soil N-pool could be a source of nitrate, particularly at the forest site, but it was not clearly distinguished in the $\delta^{15}N\text{-}NO_3$ vs. $\delta^{18}O\text{-}NO_3$ bi-plot (Figure 6). Without additional tracers (e.g., boron; Kendall 1998), stable isotopes of nitrate are not able to discriminate manure, which can be a nitrate source in the forest catchment (dumping of animal excrement) and at site P5 (potential leaks from a zoological park). However, sewage leaks were traceable by human drugs and food compounds in urban springs

(Figure 7). The highest diversity of drugs and food compounds was found in those springs that also showed the highest sewage contribution (T1, N3, Y4, and P5). The relationship observed between the non-persistent chemicals caffeine and food compounds, and some ions (SO_4^{2-} and Na^+) indicates that these emerging compounds continually enter T1 with raw sewage, likely from mains. However, the positive relationship between persistent drugs, pesticides, and NO_3^- at N3, Y4, and P5 may point to sewage leaks from pit latrines rather than sewage mains (Figure 7). Some persistent pesticides and food compounds were detected at sites with negligible sewage contribution (urban site S2 and forest site O6). This suggests accumulation over time (Jurado et al. 2012).

Overall, our results indicate that organic tracers can be useful in confirming sewage contribution to urban groundwater, but also in differentiating raw sewage inputs from those derived from pit latrines and septic tanks. The resulting influence on groundwater quality threatens its usability as a drinking water source (Schmidt et al. 2017) and likely influences the biotic community (Di Lorenzo et al. 2019). These will be considered as additional indicators of urban impact in our future research.

6. Conclusions

By combining stable isotopes of water with hydrogeological calculations, we were able to describe recharge conditions in urban and forest groundwater catchments that clearly indicate strong seasonal patterns of groundwater, to evaluate groundwater contamination in urban areas, and to quantify mixing of groundwater with sewage and tap water leaks. Data on emerging compounds supported our conclusions on spatially distinct types of anthropogenic recharge and helped to distinguish between contamination of urban groundwater with raw sewage from defective mains and with leaks from pit latrines and septic tanks. Since groundwater, particularly at shallow depth, can be heavily influenced by seasonal patterns of

recharge and land use, seasonal monitoring is important (or even essential) in order to reach useful conclusions on the patterns shaping water quality and thus the usability as a drinking water resource. High nitrate contamination of urban springs and the presence of potentially toxic emerging compounds indicate health risks associated with the use of the urban springs studied as drinking water sources. This poses crucial challenges for future planning of resource allocation.

Combining physical (isotopes) and chemical (major ions and emerging compounds) analyses proved useful in determining and quantifying hydrological and hydro-chemical processes in the urban subsurface. This multi-tracing method provides an integrative and comprehensive view of the regional hydrological cycle, which can be helpful for improving urban water management. Having been tested in a major Eastern European city, the proposed tool can be particularly useful for cities suffering from similar problems of poor water management and inadequate sewage and water supply infrastructure.

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References

Aquilina L., Vergnaud-Ayraud V., Labasque T., Bour O., Molénat J., Ruiz L., de Montety V., De Ridder J., Roques C., Longuevergne L., 2012. Nitrate dynamics in agricultural

catchments deduced from groundwater dating and long-term nitrate monitoring in surface- and groundwaters. Science of the Total Environment 435–436, 167–178.

Archana A., Thibodeau B., Geeraert N., Xu M.N., Kao S.-J., Baker D.M., 2018. Nitrogen sources and cycling revealed by dual isotopes of nitrate in a complex urbanized environment. Water Research 142, 459–470.

Barrett M.H., Hiscock K.M., Pedley S., Lerner D.N., Tellam J.H., French M.J., 1999. Marker species for identifying urban groundwater recharge sources: a review and case study in Nottingham, UK. Water Research 33 (14), 3083–3097.

Casciotti K.L., Sigman D.M., Hastings M.G., Böhlke J.K., Hilkert A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Analytical Chemistry 74, 4905–4912.

Castiglioni S., Davoli E., Riva F., Palmiotto M., Camporini P., Manenti A., Zuccato E., 2018. Mass balance of emerging contaminants in the water cycle of a highly urbanized and industrialized area of Italy. Water Research 131, 287–298.

Chen Q., Qu J., Liu R., Li W., 2008. Rule-based model for aging-induced leakage from water supply pipe network in Beijing City. China Water & Wastewater 24(11), 52–56 (in Chinese with English abstract).

City Council, 2010. The declaration of the Kharkiv City Council No. 321 from 8.09.2010 on the discharge of raw wastewater in the municipal sewage system.

Craig H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703.

Crawford J., Hughes C.E., Lykoudis S., 2014. Alternative least squares methods for determining the meteoric water line, demonstrated using GNIP data. Journal of Hydrology 519 (Part B), 2331–2340.

Dansgaard W., 1964. Stable isotopes in precipitation. Tellus 16, 436–468.

Di Lorenzo, T., Di Marzio W.D., Fiasca B., Galassi D.M.P., Korbel K., Iepure S., Pereira J.L., Reboleira A.S.P.S., Schmidt S.I., Hose G.C., 2019. Recommendations for ecotoxicity testing with stygobiotic species in the framework of groundwater environmental risk assessment. Science of the Total Environment 681, 292-304.

EEA, 2002. Nitrate concentration in groundwater. Retrieved from European Environment Agency: http://www.eea.europa.eu/data-and-maps/figures/nitrate-concentration-in-groundwater.

Ettayfi N., Bouchaou L., Michelot J.L., Tagma T., Warner N., Boutaleb S., Massault M., Lgourna Z., Vengosh A., 2012. Geochemical and isotopic (oxygen, hydrogen, carbon, strontium) constraints for the origin, salinity, and residence time of groundwater from a carbonate aquifer in the Western Anti-Atlas Mountains, Morocco. Journal of Hydrology 438–439, 97–111.

European Commission, 2012: A Blueprint to Safeguard Europe's Water Resources. Communication from the commission to the European parliament, the Council, the European economic and social committee and the committee of the regions. Brussels, Belgium.

EU WFD, 2000. Directive 2000/60/EC of the European Parliament and of the Council of the 23 October 2000: establishing framework for the community action in the field of water policy. Official Journal of European Commission L327, 321–371.

FAO, 2011. The state of the world’s land and water resources for food and agriculture (SOLAW) – Managing systems at risk. Food and Agriculture Organization of the United Nations, Rome and Earthscan, London.

Fenech C., Rock L., Nolan K., Tobin J., Morrissey A., 2012. The potential for a suite of isotope and chemical markers to differentiate sources of nitrate contamination: a review. Water Research 46 (7), 2023–2041.

Ferrante M., Mazzetti E., Fiori A., Burini M., Fioriti B., Mazzoni A., Schirò G., Vacca G., Brunone B., Meniconi S., Capponi C., 2015. Delineation of Wellhead Protection Areas in the Umbria region. 2. Validation of the Proposed Procedure. Procedia Environmental Sciences 25, 96–103.

Geological Survey, 2007. Supplementary report to geological map of Ukraine, scale 1:200000, sheets M-37-XIII (Kharkiv). Printed in Kharkiv, Ukraine.

Grimmeisen F., Lehmann M.F., Liesch T., Goeppert N., Klinger J., Zopfi J., Goldscheider N., 2017. Isotopic constraints on water source mixing, network leakage and contamination in an urban groundwater system. Science of the Total Environment 583, 202–213.

Groundwater Directive, 2006. European Commission, COM(2003)550.

Healy R.W., Scanlon B.R., 2010. Estimating Groundwater Recharge. Cambridge University Press, Cambridge, New York.

Herrmann F., Keller L., Kunkel R.,Vereecken H.,Wendland F., 2015. Determination of spatially differentiated water balance components including groundwater recharge on the Federal State level – a case study using the mGROWA model in North Rhine-Westphalia (Germany). Journal of Hydrology: Regional Studies 4 (Part B), 294–312.

Houhou J., Lartiges B.S., France-Lanord C., Guilmette C., Poix S., Mustin C., 2010. Isotopic tracing of clear water sources in an urban sewer: A combined water and dissolved sulfate stable isotope approach. Water Research 44 (1), 256–266.

Jurado A., Vazquez-Sune E., Carrera J., Lopez de Alda M., Pujades E., Barcelo D., 2012. Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a Europe context. Science of the Total Environment 440, 82–94.

Kendall C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall C, McDonnell JJ (eds) Isotope tracers in catchment hydrology. Elsevier, Amsterdam, 839 pp.

Legendre P., Legendre, L., 2012. Numerical ecology. Elsevier.

Manna F., Cherry J.A., McWhorter D.B., Parker B.L., 2016. Groundwater recharge assessment in an upland sandstone aquifer of southern California. Journal of Hydrology 541 (Part B), 787–799.

McCance W., Jones O.A.H., Edwards M., Surapaneni A., Chadalavada S., Currell M., 2018. Contaminants of Emerging Concern as novel groundwater tracers for delineating wastewater impacts in urban and peri-urban areas. Water Research 146, 118–133.

Nikolenko O., Jurado A., Borges A., Knoller K., Brouyer S., 2018. Isotopic composition of nitrogen species in groundwater under agricultural areas: A review. Science of the Total Environment 621, 1415–1432.

Oksanen F., Blanchet F.G., Friendly M.,Kindt R., Legendre P., McGlinn D., Minchin P.R., O'Hara R. B., Simpson G.L., Solymos P., Stevens M.H.H., Szoecs E., Wagner H., 2018. Vegan: Community Ecology Package. R package version 2.5-2. https://CRAN.R-project.org/package=vegan.

R Core Team, 2018. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/.

Romanenko V.A., 1961. Computation of the autumn soil moisture using a universal relationship for a large area. Procedia of the Ukrainian Hydrometeorological Research Institute, No. 3, Kiev, Ukraine.

Santos J.L., Aparicio I., Alonso E., Callejòn M., 2005. Simultaneous determination of pharmaceutically active compounds in wastewater samples by solid phase extraction and high-performance liquid chromatography with diode array and fluorescence detectors. Analitica Chimica Acta 550, 116–122.

Schaider L.A., Ackerman J.M., Rudel R.A., 2016. Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer. Science of the Total Environment 547, 470–481.

Schmidt S.I., Cuthbert M.O., Schwientek M., 2017. Towards an integrated understanding of how micro scale processes shape groundwater ecosystem functions. Science of the Total Environment 592, 215–227.

Schmidt S.I., Hahn H.J., Hatton T.J., Humphreys W.F., 2007. Do faunal assemblages reflect the exchange intensity in groundwater zones? Hydrobiologia 583, 1–19.

Shelton J.L., Engle M.A., Buccianti A., Blondes M.S., 2018. The isometric log-ratio (ilr)-ion plot: A proposed alternative to the Piper diagram. Journal of Geochemical Exploration 190, 130–141.

Sigman D.M., Casciotti K.L., Andreani M., Barford C., Galanter M., Böhlke J.K., 2001.A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Analytical Chemistry 73, 4145–4153.

Stiff Jr. H. A., 1951. The interpretation of chemical water analysis by means of patterns. Journal of Petroleum Technology 3, 15–17.

Taufiq A., Effendi A.J., Iskandar I., Hosono T., Hutasoit L.M., 2019. Controlling factors and driving mechanisms of nitrate contamination in groundwater system of Bandung Basin, Indonesia, deduced by combined use of stable isotope ratios, CFC age dating, and socioeconomic parameters. Water Research 148, 292–305.

Taylor R.G., Scanlon B., Döll P., Rodell M., van Beek R., Wada Y., Longuevergne L., Leblanc M., Famiglietti J.S., Edmunds M., Konikow L., Green T.R., Chen J., Taniguchi M., Bierkens M.F.P., MacDonald A., Fan Y., Maxwell R.M., Yechieli Y., Gurdak J.J., Allen D.M., Shamsudduha M., Hiscock K., Yeh P.J.-F., Holman I., Treidel H., 2012. Ground water and climate change. Nature Climate Change 3, 322–329.

Tipple B.J., Jameel Y., Chau T.H., Mancuso C.J., Bowen G.J., Dufour A., Chesson L.A., Ehleringer J.R., 2017. Stable hydrogen and oxygen isotopes of tap water reveal structure of

the San Francisco Bay Area's water system and adjustments during a major drought. Water Research 119, 212–224.

Tubau I., Vázquez-Suñé E., Carrera J., Valhondo C., Criollo R., 2017. Quantification of groundwater recharge in urban environments. Science of the Total Environment 592, 391–402.

Unnikrishna P.V., McDonnell J.J., Kendall C., 2002. Isotope variations in a Sierra Nevada snowpack and their relation to meltwater. Journal of Hydrology 260 (1–4), 38–57.

Urresti B., Vadillo I., Jiménez P., Soler A., Sánchez D., Carrasco F., 2015. Application of stable isotopes ($\delta^{34}S$-SO_4, $\delta^{18}O$-SO_4, $\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3) to determine natural background and contamination sources in the Guadalhorce River Basin (southern Spain). Science of the Total Environment 506–507, 46–57.

Vázquez-Suñé E., Carrera J., Tubau I., Sánchez-Vila X., Soler A., 2010. An approach to identify urban groundwater recharge. Hydrological Earth System Science 14(10), 2085–2097.

Vystavna Y., Diadin D., Yakovlev V., Hejzlar J., Vadillo I., Huneau F., Lehmann M.F., 2017. Nitrate contamination in a shallow urban aquifer in East Ukraine: Evidence from hydrochemical, stable nitrate isotope, and land use analysis. Environmental Earth Sciences 76 (13), No. 463.

Vystavna Y., Cherkashyna M., van der Valk M.R., 2018a. Water laws of Georgia, Moldova and Ukraine: current problems and integration with the EU legislation. Water International 43 (3), 424–435.

Vystavna Y., Frkova Z., Celle-Jeanton H., Diadin D., Huneau F., Steinmann M., Crini N., Loup C., 2018b. Priority substances and emerging pollutants in urban rivers in Ukraine: Occurrence, fluxes and loading to transboundary European Union watersheds. Science of the Total Environment 637–638C, 1358–1362

Vystavna Y., Huneau F., Diadin D., 2018c. Defining a stable isotope framework for isotope hydrology applications (precipitation, surface and groundwater) for East Ukraine. Isotopes in Environmental and Health Studies 2(54), 147–167.

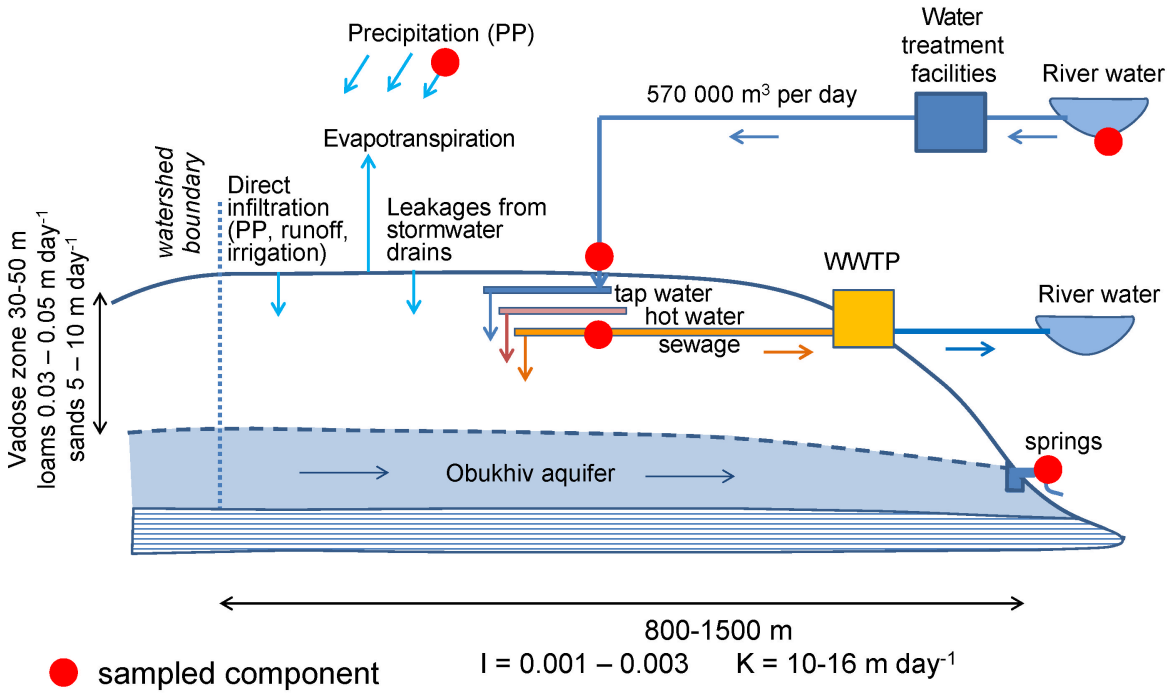
Vystavna Y., Diadin D., Rossi P.M., Gusyev M., Hejzlar J., Mehdizadeh R., Huneau F., 2018d. Quantification of water and sewage leakages from urban infrastructure into a shallow aquifer in East Ukraine. Environmental Earth Sciences 77, No. 748.

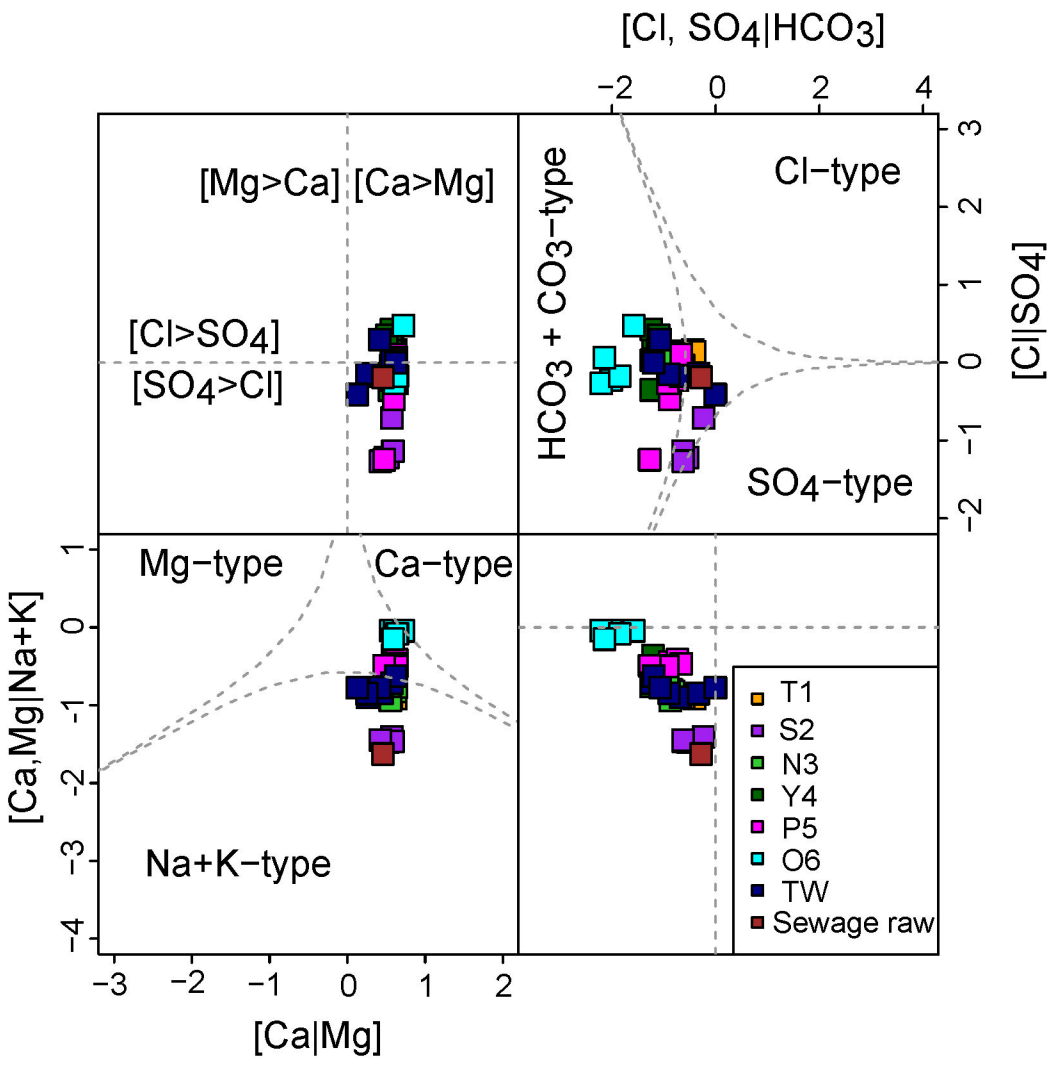
WWAP, 2015. United Nations World Water Assessment Programme. The United Nations World Water Development Report 2015: Water for a Sustainable World. Paris, UNESCO. https://www.un-igrac.org/sites/default/files/resources/files/Groundwater%20overview%20-%20Making%20the%20invisible%20visible_Print.pdf

Yakovlev V., Vystavna Y., Diadin D., Vergeles Y., 2015. Nitrates in springs and rivers of East Ukraine: distribution, contamination and fluxes. Applied Geochemistry 53, 71–78.

Yin H., Xie M., Zhang L., Huang J., Xu Z., Li H., Jiang R., Wang R., Zeng X., 2019. Identification of sewage markers to indicate sources of contamination: Low cost options for misconnected non-stormwater source tracking in stormwater systems. Science of the Total Environment 648, 125–134.

List of figures

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S2
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Y4
P5
O6
TW
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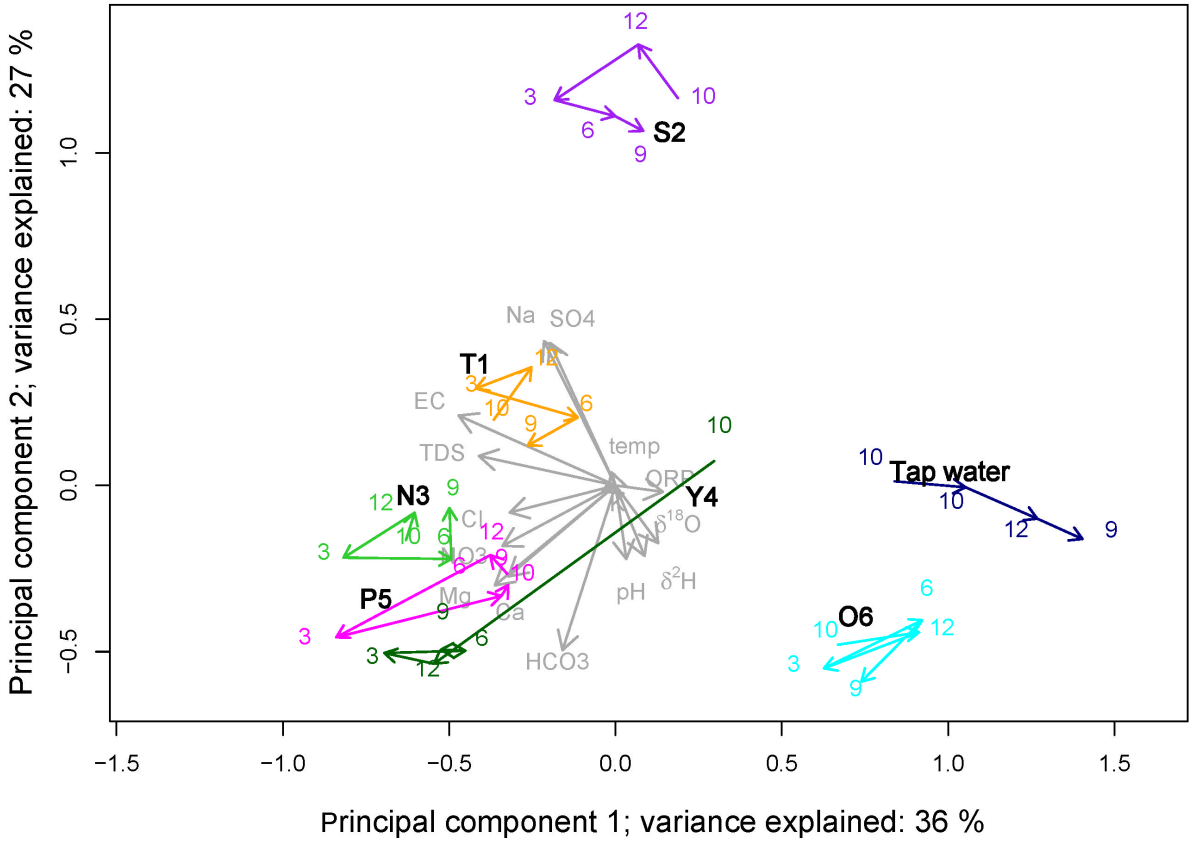
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S2
T1
N3
P5
Y4
O6
Tap water
Na
SO4
EC
TDS
temp
ORP
Cl
NO3
Mg
Ca
pH
HCO3
δ18O
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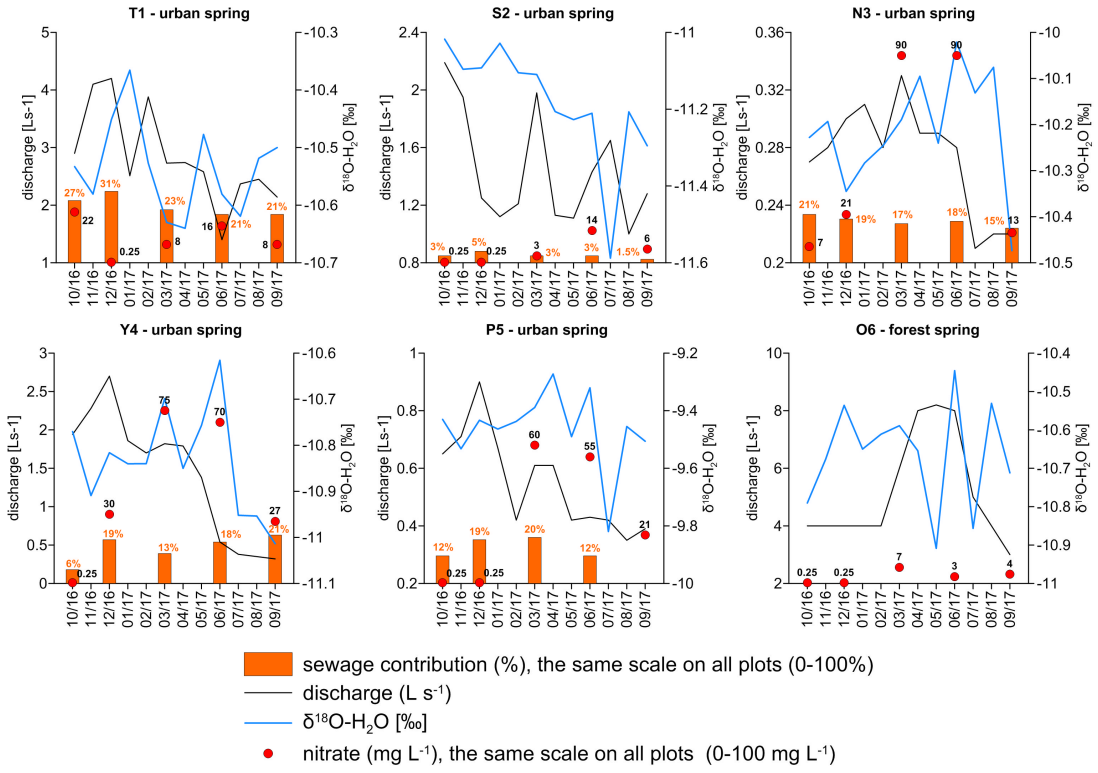
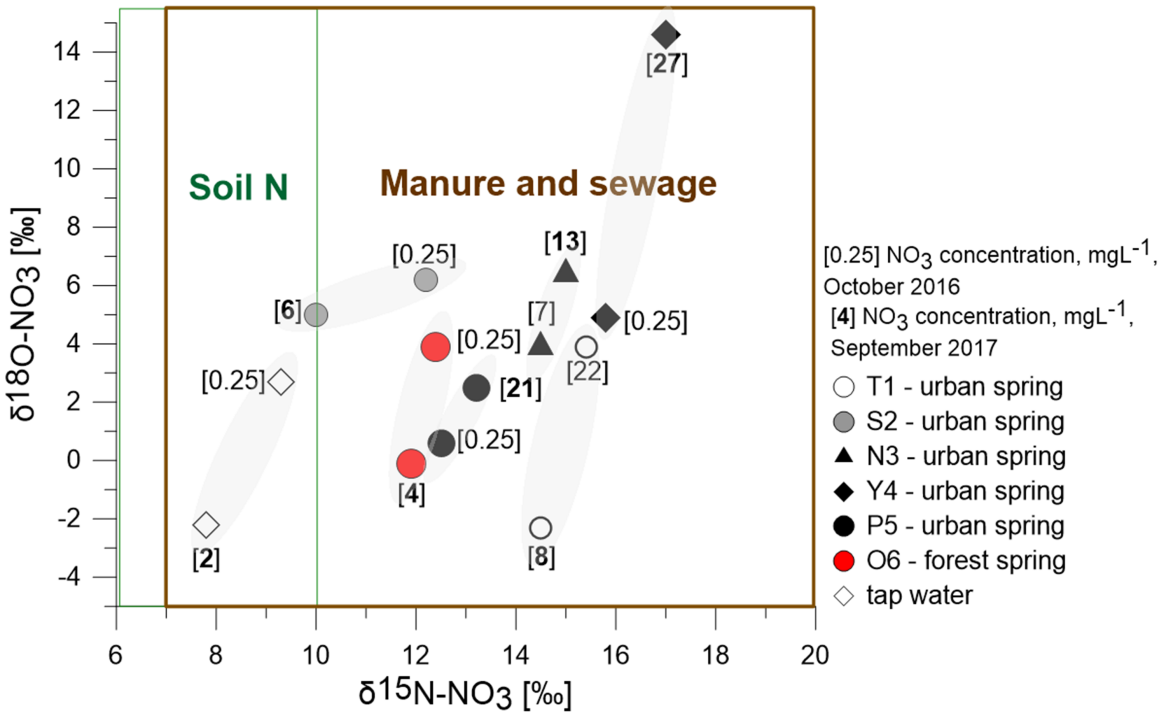
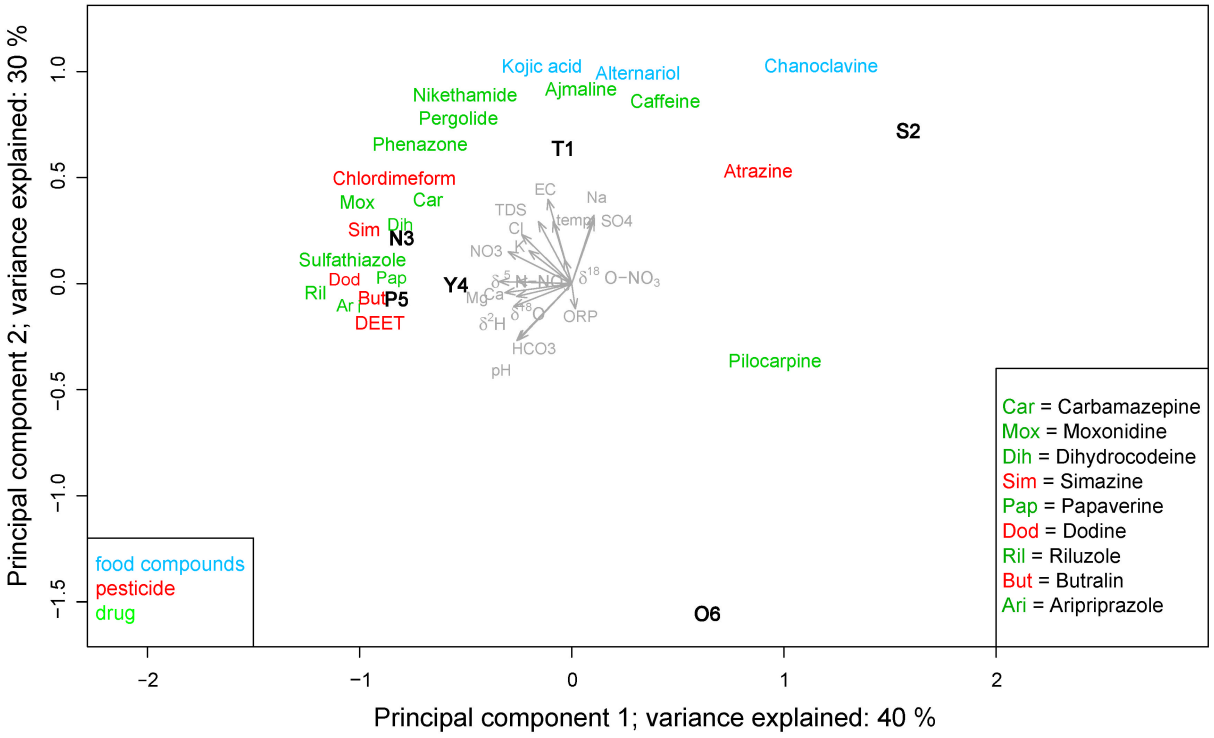
1.5






Principal component 2; variance explained: 30 %
Principal component 1; variance explained: 40 %
Kojic acid
Alternariol
Chanoclavine
Nikethamide
Ajmaline
Caffeine
Pergolide
Phenazone
T1
S2
Atrazine
Chlordimeform
Mox
Car
Sim
Dih
N3
Sulfathiazole
Dod
Pap
Ril
But
P5
Ar
DEET
Y4
EC
Na
TDS
Cl
temp
SO4
NO3
K
δ18 O−NO3
Mg
Ca
δ2H
δ18O
ORP
HCO3
pH
Pilocarpine
O6
food compounds
pesticide
drug
Car = Carbamazepine
Mox = Moxonidine
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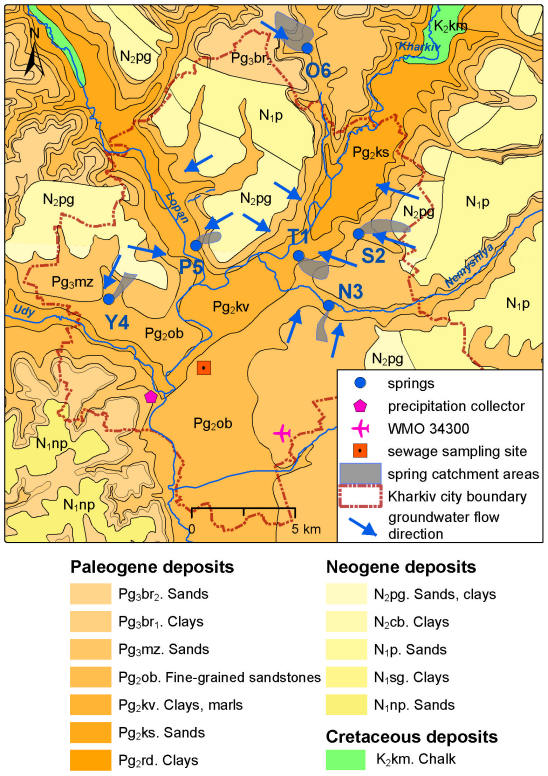
Sim = Simazine
Pap = Papaverine
Dod = Dodine
Ril = Riluzole
But = Butralin
Ari = Aripriprazole



Paleogene deposits

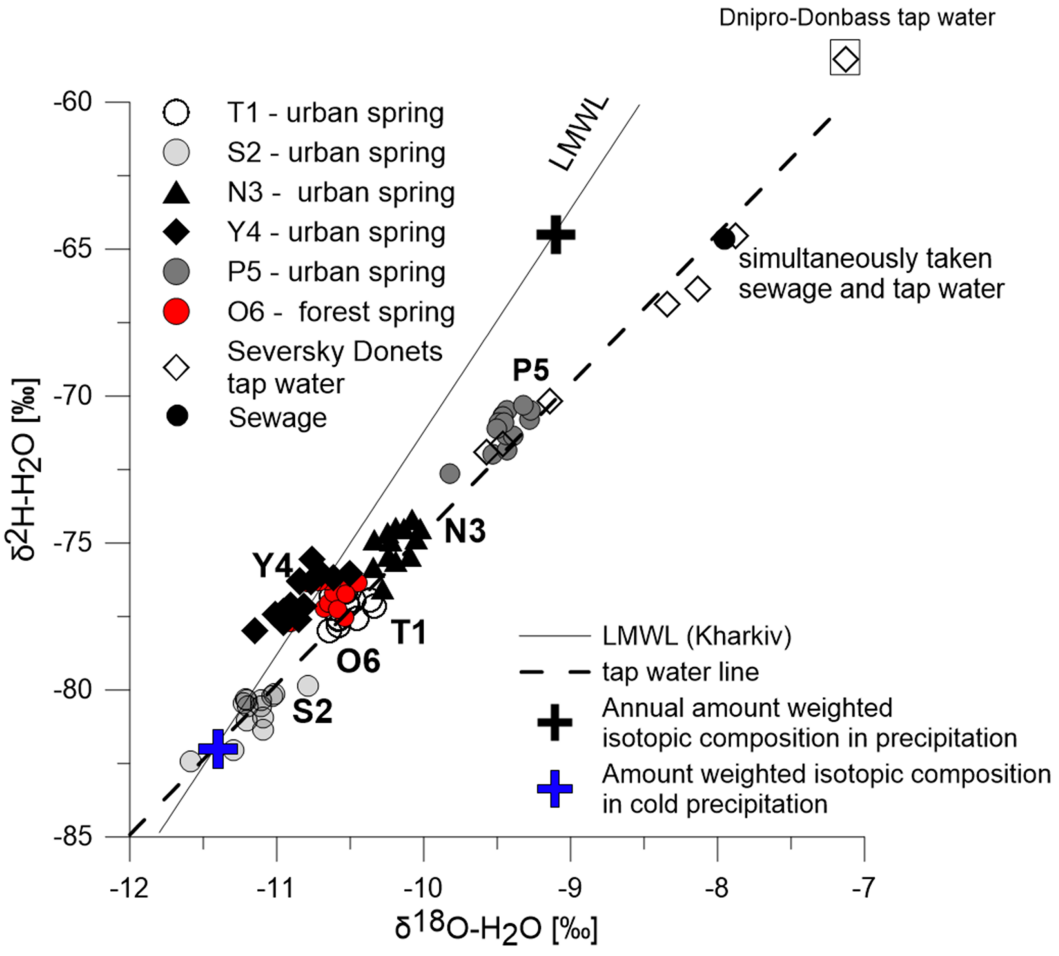
- Pg_3br_2. Sands
- Pg_3br_1. Clays
- Pg_3mz. Sands
- Pg_2ob. Fine-grained sandstones
- Pg_2kv. Clays, marls
- Pg_2ks. Sands
- Pg_2rd. Clays

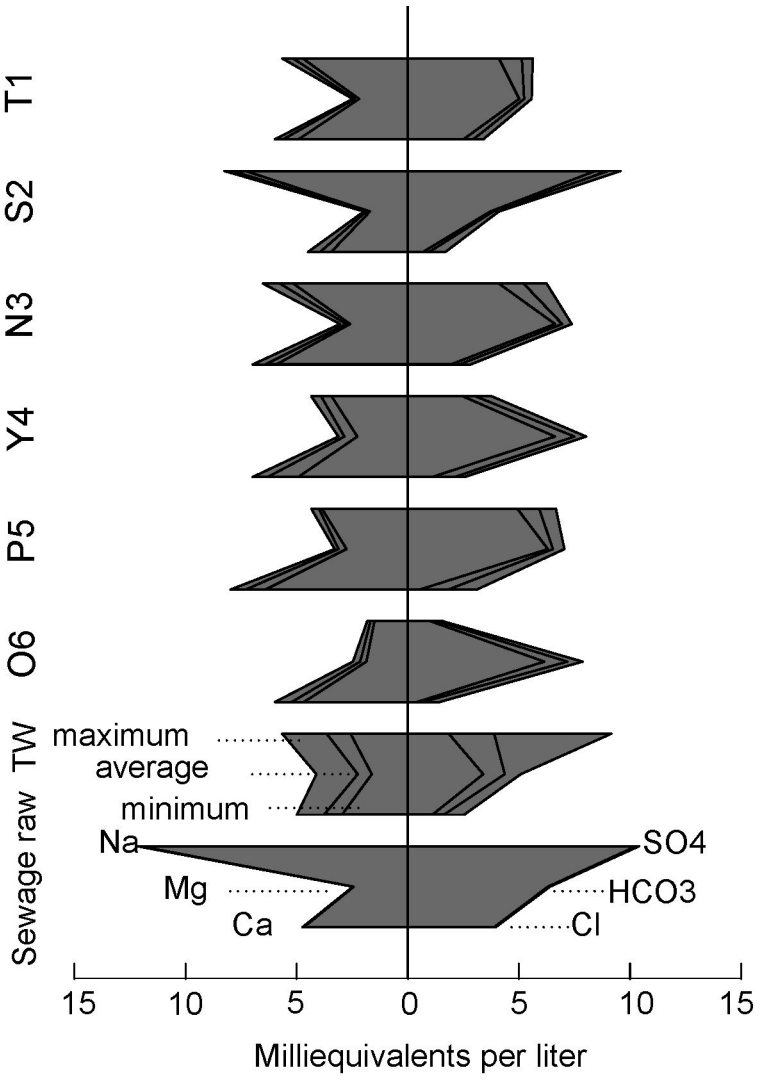
Neogene deposits

- N_2pg. Sands, clays
- N_2cb. Clays
- N_1p. Sands
- N_1sg. Clays
- N_1np. Sands

Cretaceous deposits

- K_2km. Chalk


Dnipro-Donbass tap water
T1 - urban spring
S2 - urban spring
N3 - urban spring
Y4 - urban spring
P5 - urban spring
O6 - forest spring
Seversky Donets tap water
Sewage
LMWL
simultaneously taken sewage and tap water
P5
N3
Y4
T1
O6
S2
LMWL (Kharkiv)
tap water line
Annual amount weighted isotopic composition in precipitation
Amount weighted isotopic composition in cold precipitation
δ2H-H2O [‰]
δ18O-H2O [‰]
-60
-65
-70
-75
-80
-85
-12
-11
-10
-9
-8
-7



Highlights:

Urban groundwater quality is highly impacted by sewage inputs

Stable isotopes and emerging contaminants traced sewage leakages to groundwater

Sewage contribution and nitrate content varied seasonally in urban groundwater

Natural $\delta^{18}O$ extremes in precipitation reflected estimated groundwater transit time

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Declarations of interest: none