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CONFERENCE PROCEEDINGS

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Pollution of Urban Groundwater by Emerging Contaminants in Kharkiv region, Ukraine

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Abstract
The article is presented the contamination data by emerging contaminants in a shallow urban groundwater and forest groundwater located in Kharkiv region, Ukraine. The emerging contaminants as mainly illicit drugs were used as trace anthropogenic recharge tool of groundwater. Elevated the presence of emerging pollutants in most of urban springs confirmed the mixing of urban groundwater with sewage leakages in some springs. The contribution of sewage leakages leads to the urban groundwater contamination by emerging compounds that increase the risk for environmental and human health reducing its potential as pure drinking water source.

Keywords
Urban springs; pharmaceuticals; illicit drugs; emerging contaminants; groundwater

INTRODUCTION

Nowadays, one of important source of drinking water worldwide is considered as groundwater (WWAP 2015). Especially, the part of groundwater as a primary drinking water source is growing due to the deterioration of surface water quality and quantity under influence of climate variability, contamination and re-allocation of surface run-off (FAO 2011, WWAP 2015). Groundwater as a source of drinking water might become more important even in those areas where it had not been used in the past. In virtue of following regulations (EU WFD 2000, Groundwater Directive 2006) surface water and groundwater quality has been improved in European Union (EU) (European Commission, 2012). Nevertheless, many countries that share the transboundary surface water and aquifers in Europe, for example Ukraine, still have a high concern on low quality and quantity of available groundwater resources due to ongoing and increasing pollutions and due to the lack of appropriate regulations (Vystavna, 2018a,b).

Contemporaneously, groundwater use for drinking supply is strongly dependent on seasonality of recharge conditions, meteorological events and contaminations (Quevauviller 2007; Griebler, 2010; Taylor 2012; Havril, 2018). Evaluation of contamination of urban aquifers can be complex tasks for groundwater management as the data on recharge, mixing and transformation of chemical compounds is generally difficult to obtain in a short-term period (Healy, 2010). Sometimes, these resources are not available for groundwater management, mainly in developing countries (WWAP, 2015). Organic compounds, particularly pharmaceuticals, have been used to determine the sewage contribution in groundwater (Jurado, 2012; Schaider, 2016; Yin, 2019) and water residence time (Lapworth, 2018). The presence of such compounds in ground waters is great concern because it's cause of serious public health risk (Samojlenko, 2014).

This study was performed in a highly urbanized area, the Kharkiv city, located in East Ukraine where local population intensively use groundwater as an alternative to tap water as a drinking source (Vystavna, 2017a). The area of research is also located in a zone with a risk of military activity, where groundwater could be considered as an important strategic drinking water source. The proposed shallow aquifer was studied before to understand the general contamination status (Vystavna, 2017a; Vystavna, 2015), knowledge on water quality variation is highly limited that determines the direction of our research.

The aim of this research was to determine the estimation of groundwater contamination of urban areas by emerging contaminants. The objective of the study was: to trace and qualitatively determine of the mixing of groundwater with anthropogenic components such as sewage leakages.

Research of catchments

Five urban (T1, S2, N3, Y4 and P5) and one peri-urban forest (O6) groundwater sites were selected for the purpose of this study (Figure 1).

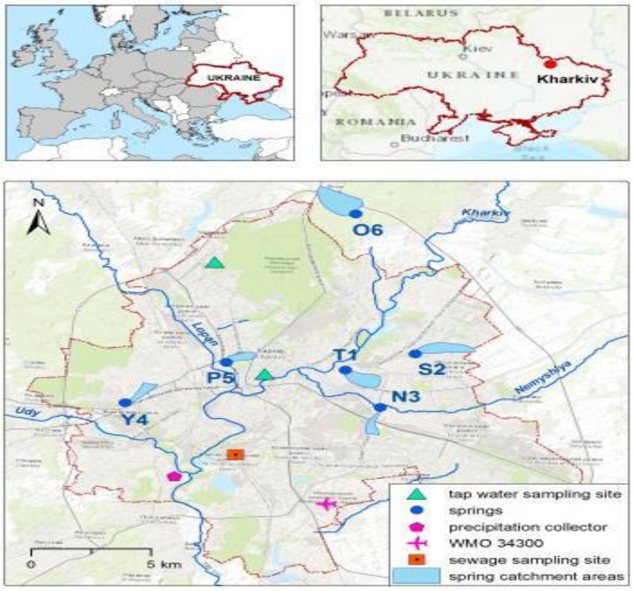

Figure 1. The location of sampling area and sites

The maximum elevation at the spring outflows ranged from 113 to 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. 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} (Vystavna, 2019).

The catchments of urban and forest are located in temperate continental climate conditions of Kharkiv region. The average annual precipitation is 521 mm, and the average annual air temperature is 9.1°C (the Kharkiv world meteorological station WMO ID 34300, 2005-2017).

Urban wastewaters are collected by sewer pipes (shallow and deep mains), treated by mechanical and biological processes in two wastewater treatment plants (WWTP) and discharged into Lopan and Udy Rivers. The WWTP 'Dikanivka' processes 80 % of urban wastewater (550,000 m^3 d^{-1}). About 24 % of population has no connection to urban sewerage network and use pit latrines and septic tanks. Built during the Soviet period, to date, urban water and sewerage infrastructure of the Kharkiv city has deteriorated and causes numerous leakages (24 % of the total water supply) which cannot be eliminated in the short term (KP Voda 2017).

The forest spring (O6) catchment drains a forest-dominated landscape. The catchment is situated in a peri-urban area featuring no agricultural land use and rather negligible urbanization (residential buildings and roads account for less than 9 % of the total drained area).

METHODS AND ANALYSIS

Groundwater samples (1L amber glass bottles) for 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 2000 compounds) by Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry (LC-QTOF) (Thermo Fisher Scientific, San Jose, CA, USA) coupled to an Accela 1250 LC pump (Thermo Fisher Scientific) and an HTS XT-CTC autosampler (CTC Analytics AG, Zwingen, Switzerland), operated using Xcalibur software (Thermo Fisher Scientific, San Jose, CA, USA). A Hypersil gold aQ column (50 mm × 2.1 mm ID × 5 μm particles; Thermo Fisher Scientific) was used for the chromatographic separation. Purified water was prepared using a Milli-Q Advantage system, including an ultraviolet radiation source (Millipore, Billerica, USA). LC/MS grade Formic acid (Sigma-Aldrich, Steinheim, Germany) (at 0.1 %) and acetonitrile, methanol (Merck (Darmstadt, Germany) with 0.1 % (vol/vol) were used to prepare the mobile chromatographic phases. Samples were pretreated by solid phase extraction (SPE) with a pre-concentration factor of 500. Si-C18 and polymeric Strata X extraction cartridges (500 mg per 6 mL) were from Supelco (Bellefonte, PA, USA) and Phenomenex (Torrance, CA, USA), respectively. A PHM 240 Model pH-meter (Radiometer, Copenhagen, Denmark) with combined glass electrode was used for sample pH adjustment. The SPE extraction procedure was performed by modifying a validated method previously reported (Santos, 2005). Two sorbents (Si-C18 and Strata X) were used for this procedure. Spiked ultrapure water of 1000 mL (for the optimization step) or real filtered sample of 500–1000 mL (for the validation step) was transferred to the SPE cartridges through a Teflon tube at a flow rate of about 10 mL min^{-1}, using a Supelco 12-port vacuum manifold system (Bellefonte, PA, USA) connected to a vacuum pump. Before elution, the cartridges were rinsed by 10 mL of methanol/water (5/95, v/v) followed by 10 mL of n-hexane applied to the top of the cartridge (Santos, 2005). Two different solvents (methanol and acetone) were tested as eluent phase at a flow rate of about 1 mL min^{-1}. The elute was evaporated in a flask by a Rotavapor (Büchi, Flawil, Switzerland) to reach a final volume of few milliliters and then it was quantitatively transferred into a conical bottom glass vial. Finally, the solvent was evaporated under a gentle stream of nitrogen leaving only a small, concentrated quantity. The residue was reconstituted with 0.5 mL of acetonitrile/water (45/55, v/v) of which 50 μL was injected into the column. Because of the nature of the screening analysis, exact concentrations could not be determined.

RESULTS

The identified chemicals have been divided into three principal groups: drugs (D) (caffeine, nikethamide, riluzole, phenazone, pilocarpine, pergolide, ajmaline, carbamazepine, moxonidine, dihydrocodeine, sulfathiazole, papaverine, pentedrone and aripriprazole), pesticides (P) (dodine, chlordimeform, atrazine, simazine and butraline), and food compounds (FC) (chanoclavine, kojic acid as an additive and alternariol as a mycotoxin). The details are presented in Table 1.

Table 1. Detection, physico-chemical properties of emerging compounds in groundwater

Compound	T1	S2	N3	Y4	P5	O6	Log K_{ow}	Group	Application
Caffeine	+	+	-	-	+	-	-0.07	D	stimulant, food additive
Dodine	-	-	-	+	-	-	1.15	P	fungicide, applied for the plant protection
Nikethamide	+	-	-	+	-	-	0.33	D	stimulant, illicit drug
Riluzole	-	-	-	+	-	-	2.3	D	antidepressant, anti-convulsion
Chanoclavine	+	+	+	-	+	-	2.14	FC	tricyclic ergot alkaloid (ergoline)
Phenazone	+	-	+	+	-	-	0.38	D	analgesic, nonsteroidal anti-inflammatory, antipyretic
Alternariol	+	+	+	-	-	-	2.37	FC	mycotoxin as secondary metabolites produced by filamentous fungi in crops or during storage, transport and processing of food and feed commodities
Pilocarpine	+	+	-	+	+	+	1.1	D	alkaloid, to treat increased pressure inside the eye and dry mouth
Pergolide	+	-	-	+	-	-	4	D	ergoline-based dopamine receptor agonist used for treatment of Parkinson's disease
Ajmaline	+	-	-	-	-	-	1.81	D	alkaloid, antiarrhythmic agent
Chlordimeform	+	-	+	+	+	-	2.89	P	acaricide active mainly against motile forms of mites and ticks, banned by UN Rotterdam Convention 1998
Kojic acid	+	-	-	-	-	-	0.64	FC	additive, used in food and cosmetics to preserve or change colours of substances
Atrazine	-	+	-	-	-	-	2.61	P	herbicide, banned by EU Directive 91/414/CEE
Carbamazepine	-	-	+	-	-	-	2.45	D	antidepressant
Simazine	-	-	+	-	-	-	2.18	P	Herbicide of the triazine class, banned in EU (EU Directive 91/414/CEE)
Moxonidine	-	-	+	-	-	-	n.f.	D	new-generation centrally acting antihypertensive drug licensed for treatment of mild to moderate essential hypertension
Dihydrocodeine	-	-	+	-	-	-	0.6	D	semi-synthetic opioid analgesic prescribed for pain or severe dyspnoea, or as an antitussive
Sulfathiazole	-	-	-	+	-	-	0.05	D	organosulfur compound used as a short-acting sulfa drug
Butralin	-	-	-	+	+	-	4.93	P	herbicide, mainly applied as a plant-growth regulator on tobacco fields, banned by EU Directive 91/414/CEE
Papaverine	-	-	-	+	-	-	2.95	D	opiate alkaloid isolated from plant Papaver somniferum and produced synthetically, illicit drug
DEET (Pentedrone)	-	-	-	-	+	-	n.f.	D	stimulant of cathinone class that has been sold as designer drug,
Aripriprazole	-	-	-	-	+	-	5.3	D	antipsychotic, primarily used in the treatment of schizophrenia and bipolar disorder

+/- means detected/not detected in the groundwater site; n.f.-not found

All detected drugs in this study could be the results of abuse and some are illicit drugs usage. The most frequently detected drug (in 5 out of 6 springs) was the alkaloid pilocarpine (prescribed to treat increased pressure inside the eye and dry mouth) which was found even in the forest spring. The food compound chanoclavine and the pesticide chlordimeform were detected in 4 out of 6 studied springs. Caffeine, the analgesic phenazone and the mycotoxin alternariol were found in 3 out of 6 studied springs. Other compounds were found in 1 or 2 sites. However, each spring was characterized by a distinct group of detected compounds according to the principal component analysis (PCA) ordination (Figure 2) (Vystavna et al., 2019).

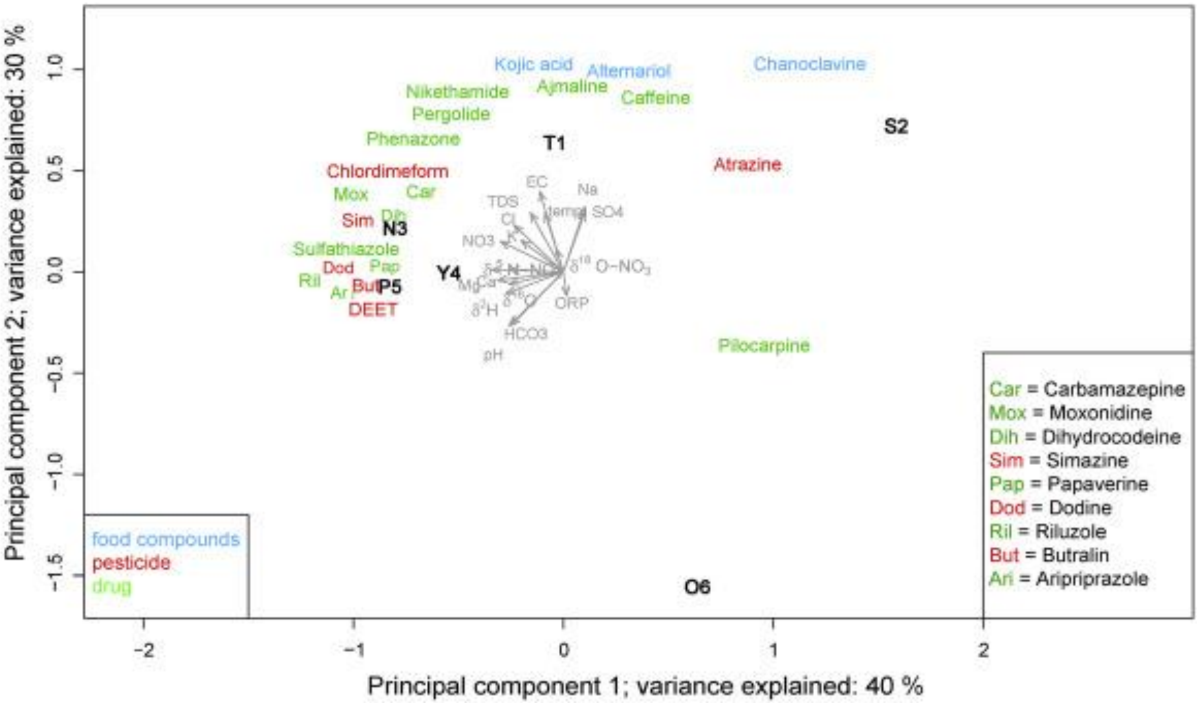

Figure 2. Principal component analysis (PCA) plots of presence of emerging compounds in groundwater samples (Vystavna, 2019) (average of all measurements over the whole sampling period)

Measured characteristics are labeled in grey. In violet: fitted correlation (Oksanen, 2018) of the presence/ absence of a number of household/agricultural chemicals and pharmaceuticals. The first two axes are plotted; their cumulative proportion of explained variance amounted to 0.75.

Site T1 was most correlated with the alkaloid ajmaline, the stimulant caffeine and two food compounds that tended towards the positive y axis and correlated well with Na^+ and SO_4^{2-}. Site S2 was most correlated with the pesticide atrazine. N3, Y4 and P5 were most correlated with drugs such as papaverine, dihydrocodeine and carbamazepine. N3 was also correlated with pesticide simazine. Four pesticides tended towards negative x, and one pesticide, atrazine, along the positive x axis (Figure 2).

DISCUSSIONS

The impact of anthropogenic land use was reflected by the presence of drugs, pesticides and food compounds in urban springs (Figure 2). The highest diversity of drugs and food compounds was found in springs with the high sewage contribution (T1, N3, Y4 and P5). The relation between the non persistent chemicals caffeine, food compounds indicates that these emerging compounds continuously enter T1 with raw sewage likely from mains. However, the presence the persistent drugs at N3, Y4 and P5 may point to sewage leakages from pit latrines. Some persistent pesticides and food compounds were detected at sites with negligible sewage contribution (urban S2 and forest O6).

CONCLUSIONS

This research is showed that urbanization changes sources and recharges of urban groundwater composition and their pollutions. It has significant influence even on peri-urban springs. Such kind of monitoring is therefore important for contamination status for controlling the shaping water quality and thus the usability as a drinking water resource. High contamination of urban springs with potentially toxic emerging compounds indicated the health risk associated with the use of urban spring as drinking water sources.

REFERENCES

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.

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. COM(2012) 673 final. SWD(2012) 381 final and SWD(2012) 382 final. Brussels, Belgium.

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

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 *J. European Comm*., 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.

Griebler, C., Stein, H., Kellermann, C., Berkhoff, S., Brielmann, H., Schmidt, S., Selesi, D., Steube, C., Fuchs, A., Hahn, H. J. (2010) Ecological assessment of groundwater ecosystems - Vision or illusion? *Ecological Engineering*, **36**, 1174-1190.

Havril, T., Tóth, Á., Molson, J. W., Galsa, A., Mádl-Szőnyi, J. (2018) Impacts of predicted climate change on groundwater flow systems: Can wetlands disappear due to recharge reduction? *Journal of Hydrology*, **563**, 1169-1180.

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

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.

Lapworth, D. J., Das, P., Shaw, A., Mukherjee, A., Civil, W., Petersen, J. O., Gooddy, D. C., Wakefield, O., Finlayson, A., Krishan, G., Sengupta, P., MacDonald, A. M. (2018) Deep urban groundwater vulnerability in India revealed through the use of emerging organic contaminants and residence time tracers. *Environmental Pollution*, **240**, 938-949.

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. [online] https://CRAN.R-project.org/package=vegan.

Quevauviller, P. (2007) General introduction: the need to protect groundwater. In: Groundwater Science and Policy - An International Overview (ed. Quevauviller P). *RSC Publishing*,. 3-18.

Samojlenko, N.N., Ermakovich, I.A. (2014) Effect of pharmaceuticals and their derivatives on the environment. *Water and Ecology: Problems and Solutions*, **2**, 78-87.

Santos, J. L., Aparicio, I., Alonso, E., Callejòn, M. (2005) Simultaneous determination of pharmaceutically active compounds in wastewater samples by solid phase extraction and highperformance 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.

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.

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

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-storm water source tracking in storm water systems. *Science of the Total Environment,* **648**, 125-134.

Vystavna, Y., Diadin, D., Yakovlev, V., Hejzlar, J., Vadillo, I., Huneau, F., Lehmann, M. F. (2017a) 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), 463.

Vystavna, Y., Diadin, D., Grynenko, V., Yakovlev, V., Vergeles, Y., Huneau, F., Rossi, P., Hejzlar, J., Knöller, K. (2017b) Determination of dominant sources of nitrate contamination in transboundary (Russia/Ukraine) catchment with heterogeneous land use. *Environmental Monitoring and Assessment,* **189**, 509.

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., Schmidt, S., Diadin, D., Rossi, P., Vergeles, Y., Erostate, M., Yermakovych, I.,Yakovlev, V., Knoller, K., Vadillo, I. (2019). Multi-tracing of recharge seasonality and contamination in urban groundwater. *Water Research,* **161**, 413-422.