



Hydrogeological processes and geological settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystem

Deliverable 8.3

European interlaboratory testing of emerging organic compounds in groundwater

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1 INTRODUCTION AND OBJECTIVES

The work package 8 of the HOVER project, within the GeoERA programme of research, concerns effective monitoring of emerging contaminants in groundwater. The aim is to develop and validate methods for assessing the quality of groundwater with a specific focus on Emerging Organic Compounds (EOCs). This work package develops consistent approaches to GW monitoring for EOCs in groundwater in terms of sampling, site selection, monitoring frequency and methodology (including analytical techniques) and ensures it is effective and data are comparable across the range of European geological and environmental settings.

Sampling and analytical methodologies are strong obstacles associated to new challenges linked to emerging contaminants. The main objective of the action reported in this report was to compare data on emerging contaminants obtained by different laboratories across Europe. For that it was initially planned to organize an interlaboratory test on emerging contaminants in groundwater samples. Due to the coronavirus outbreak, it was not possible to mobilise all the laboratories initially targeted.

As there were not enough labs involved in this action, it has been reoriented on a comparison on different groundwater sampling locations, with different qualities of water and different concentration levels of emerging contaminants. This exercise allows to have an initial assessment of the difficulties associated with the prospect of integrating emerging organic compounds in the regular monitoring of groundwater on an EU scale.

In addition to the originally stated goal, an attempt was made to qualify the influence of sampling conditions on sampling results. This was made on an example of one case study and shall also be treated as an initial assessment pointing out at difficulties that may significantly impact on sampling results.

2 MATERIAL AND METHODS

Two studies were undertaken in preparation of this report. The first was focused on comparison of analytical results obtained from the same case study sites but from different laboratories and the second was focused on one study sites, where different sampling protocols were applied. In this part materials and methods of both exercises are described.

2.1 Comparison Study

2.1.1 Sampling sites

Four sampling sites were selected for the comparison study exercise, due to previous studies highlighting the occurrence of molecules of interest in groundwater: one sampling site in Slovenia, one sampling site in Poland and 2 sampling sites in the Netherlands. The groundwater sampling sites are briefly described hereafter.

2.1.1.1 Slovenian groundwater sampling site



Figure 1: Location of the Slovenian groundwater sampling site

Location: situated near landfill (X (Gauss-Kruger): 5459394; Y (G-K): 5098792; Z 294,274 m).

Land use: urban

Type of borehole: piezometer (1999)

Depth: 12 m

Screen: 5 – 11 m b.g.l

Geology: intergranular aquifer (Quaternary)

Age: < 20 y

Detected compounds:

- Year 2017 (research of pesticides, carbamazepine, propyphenazone and caffeine). Carbamazepine and propyphenazone concentrations observed in March 2017 are reported in Table 1.

Table 1: Carbamazepine and propyphenazone at the Slovenian sampling site in March 2017

Date	Time of pumping	Carbamazepine (ng/L)	Propyphenazone (ng/L)
21.03.2017	After 7 min	325	81
21.03.2017	After 32 min	330	83
21.03.2017	After 62 min	349	87
21.03.2017	After 122 min	364	87
21.03.2017	After 182 min	347	86

- Year 2019, research of pharmaceuticals and benzotriazoles, Table 2.

Table 2: Pharmaceuticals and benzotriazoles at the Slovenian sampling site in June 2019

Date: 20.6.2019	Concentration (ng/L)
4-methyl-1H-benzotriazole	540
1H-benzotriazole	4900
5-methyl-1H-benzotriazole	140
Diclofenac	3800
Caffeine	35
Cetoprofen	11000
Carbamazepine	230
Salbutamol	110
Salicylic acid	360
Acetilsalicylic acid	470

2.1.1.2 Polish groundwater sampling site

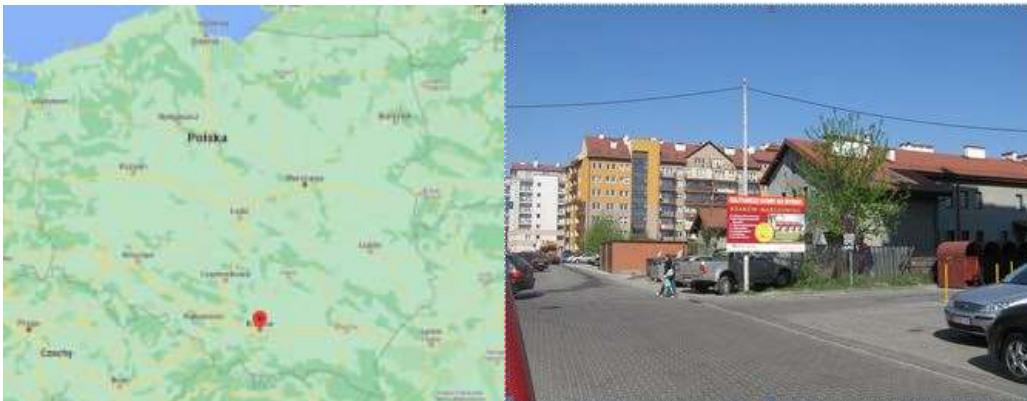


Figure 2: Location of the Polish groundwater sampling site

Location: situated in city centre, in close proximity to a hospital

Land use: urban

Type of borehole: piezometer (1992)

Depth: 21,5 m

Screen: 14,5-19,5 m b.g.l.

Geology: intergranular aquifer (Quaternary)

Detected compounds:

2016: estrone 16ng/l, 17-alfa-estradiol 61ng/l, diclofenac 10ng/l, ibuprofen <MQL, carbamazepine 13ng/l, sulfamethoxazole 2ng/l, sulfapyridine 3ng/l

2.1.1.3 Dutch groundwater sampling sites

Pilot site well 106, filter 1



Figure 3: Location of the Dutch site no 1 - well 106

Location: rural GPS 5.7843038°; 51.6209362°

Land use: agricultural

Type of borehole: piezometer

Screen: 8-10 m b.g.l.

Geology: intergranular aquifer (Quaternary)

Age dating: 1 year

Detected compounds: In previous sampling campaigns by the Province of North Brabant, carbamazepine and bisphenol A were detected out of the 20 selected emerging contaminants (note: not all 20 selected molecules were analysed).

Well 106 is located in Landhorst, in the Province of North Brabant (Figure 3). In a recent study, age dating results helped to identify areas in which water from the river Meuse recharges groundwater. The first screen of well 106 (106_1) is one of the wells that show signals of Meuse water recharge (Kivits et al. 2019).

Pilot site Spring n.020



Figure 4: Location of the Dutch site no 1 - Spring n.020

Location: rural GPS 5.821643°; 50.8811272°

Land use: forest

Type of borehole: spring

Mean travel time: 13 years

Detected compounds: In 2018 TNO sampled this spring and analysed it on 29 veterinary antibiotics. From this package of 29 antibiotics, the following molecules overlap with the HOVER task 8.3 molecule list: azithromycin, carbamazepine, clarithromycin, erythromycin, sulfamethoxazole and trimethoprim were analysed. Only carbamazepine was found.

Spring n.020 is located in the most southern part of the Netherlands nearby Valkenburg in the Province of Limburg (Figure 4). The spring is situated in a small forest area on a hillside next to a more elevated agricultural field. A recent study, in which nitrate concentrations in Dutch chalk springs were forecasted using tritium-based travel time distributions, shows that only a young

model (~13 years) fits the tritium results (Van Vliet and Broers, 2019). The nitrate concentrations were high (250 mgNO₃/l) and are decreasing, but they are still higher than 50 mgNO₃/l.

2.1.2 List of compounds

Participants were asked to provide a list of compounds they are able to analyze in groundwater samples. Depending on participants, the lists of analyzed compounds were different, varying from 17 to more than 140 emerging contaminants, representing more than 150 individual molecules. These lists have been cross compared to select emerging organic compounds that could have been analyzed by all participating laboratories, with LOQs compatible with the expected concentrations in selected groundwater sampling sites. The final lists consisted of a total of 13 emerging organic compounds (Table 3).

Table 3: List of emerging compounds retained for the comparison

substances	CAS number
4-Nonylphenol	104-40-5
Atenolol	29122-68-7
Bezafibrate	41859-67-0
Bisphenol A	80-05-7
Caffein	58-08-2
Carbamazepine	298-46-4
Diclofenac	15307-86-5
Fenofibrate	49562-28-9
Gemfibrozil	25812-30-0
Metoprolol	37350-58-6
Paracetamol	103-90-2
Sulfamethoxazole	723-46-6
Trimethoprim	738-70-5

2.1.3 Sampling strategy

Each groundwater samples were collected in duplicates for each site and for each laboratory, in association with a field blank. Thus 3 samples (A, B and Blc) were taken on every site to be send to the 4 participating laboratories.

Samples were collected when water physico-chemical parameters have become constant. That means that observation boreholes were cleaned by pumping out at least 3 volumes of stagnant water from a well prior to sampling. The field blank was taken by pouring demineralized water into a sampling bottle provided by a lab, immediately after taking a groundwater sample. Only LAB_1 provided its own clean water for field blanks. There was no specific order in the bottles filling depending on laboratories. The Table 4 shows the field physico-chemical parameters when sampling the 4 groundwater sites.

Table 4: Groundwater sampling sites field physico-chemical parameters.

Field physico-chemical parameters					
location	Date	pH	Temp (°C)	EC (µS/cm)	O ₂ (mg/l)
NL_020	07/12/2020	7.47	10.9	830	8.67
NL_106	07/12/2020	7.68	13.6	551	0.03
POL	02/12/2020	6.71	12.8	1208	1.72
SLO	01/12/2020	7.08	14.7	1117	0.24

The bottles were stored in cool boxes with freezer packs immediately after sampling. The cool boxes were sent to participating laboratories the same day or the day after sampling. For one lab, bottles had to be frozen after sampling before sending back to the laboratory. They were kept frozen until all the bottles from the three different countries had arrived.

2.1.4 Participating laboratories and analytical methods

The exercise simulates the implementation of a prospective campaign in groundwater. Each participant had to find a laboratory for the sampling of emerging compound as it would do in the case of a regular sampling campaign, like the watch list monitoring campaign for example. Some participants launched a public tender, while others used their own research laboratory. Contrary to a real interlaboratory study, here, laboratories were not informed they were participating to a comparison exercise. Thus, the results can be considered as representative of a regular exploratory campaign in groundwater.

There were 4 participating countries, with 5 laboratories. Participating country A requested 2 laboratories for the study. Both took in charge a part of the list of molecules in a complementary way. Thus, in order to simplify the presentation of the result in the report, these two labs have been merged into one.

Not all participants have their internal laboratory, therefore some surveys needed to cooperate with private subcontractors. Thus, it was not possible to obtain all the detailed information for the comparison of methods. All laboratories applied the same general methodologies for analyzing emerging organic compounds. Solid phase extraction, allowing reconcentration of analytes from groundwater samples was used by all labs. For analysis, all labs applied liquid chromatography/tandem mass spectrometry methods for quantification.

2.2 Influence of pumping protocols on sampling results

Protocols for groundwater sampling are generally established and regulated. ISO 5667-11:2009 Water Quality – Sampling - Part 11: Guidance on sampling of groundwaters is the current international standard in force, which informs of the necessary considerations when planning and undertaking groundwater sampling to survey the quality of groundwater. The standard specifies types of pumps that are recommended for sampling specific chemical compounds. It is generally accepted that sampling for typical groundwater chemicals such as major ions and trace metals does not require much consideration while sampling as pumping rates and location of a

pump shall not have much influence the results. When undertaking large sampling campaigns, practicality of sampling has to also be taken into accounts and for this reason the most common approach for sampling is to use submersible impeller pumps or inertial pumps. Location of the pump as well as pumping rate may however influence the representatively of a water sample and hence the result of sampling. Modelling study by McMillan et al. (2014) have confirmed that pumping rate, its location along the screen as well as intrinsic characteristic of an aquifer and screen length play a role in homogeneity of a water sample. In general when sampling low permeability aquifers or have short screen lengths, pumping rate have little influence on sample representative as large drawn dawns cause mixing of water when pumping, causing the sample to be homogeneous and representing the entire screen length as well as the surrounding aquifer. Sampling protocols will have more influence when sampling deeper boreholes with long screens that are located in more productive aquifers, where flow rate will decide whether the sample represents only the filter depth (discrete samples), its close vicinity (low-flow pumping methods) or aquifer surrounding a borehole (high-flow pumping methods).

As highlighted in the ISO 5667-11:2009 norm, different groundwater parameters are sensitive to a sampling device used (Table 5). Discrete depth samplers, bladder pumps and inertial pumps are most suitable for groundwater sampling and the most commonly used inertial pumps have limitations to be used for sampling for dissolved gasses and TOX. Emerging contaminants are a new group of contaminants, for which limited sampling recommendations are available. Therefore, in this study we have conducted an experiment to see if a sampling device and sampling strategy may have an influence on sampling results.

Table 5: A guide to the suitability of sampling methods for different groundwater parameters, after ISO 5667-11:2009

Sampling device	Groundwater parameter													
	✓ - suitable; (✓) – limites suitability; ✖ - generally not suitable													
	EC	pH	Alkalinity	Redox (Eh)	Major ions	Trace metals	Nitrates	Dissolved gasses	Non-VOCs	VOCs	TOC	TOX	Microbiology	EOCs
Depth sampler – bailer (open)	✓	✖	✓	✖	✓	✓	✓	✖	✓	✖	✓	✖	✓	?
Discrete depth sampler – bailer (closed) or shut-in-sampler	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	?
Inertial pump	✓	✓	✓	✓	✓	✓	✓	✖	✓	✓	✓	✖	✓	?
Bladder pump	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	?
Gas-drive pump	✓	✖	✖	✖	✓	✓	✓	✖	✓	✖	✖	✖	✖	?
Gas-lift pump	✓	✖	✖	✖	✓	✓	✓	✖	✖	✖	✖	✖	✖	?
Submersible impeller pump	✓	✓	(✓)	(✓)	✓	✓	✓	(✓)	✓	(✓)	(✓)	(✓)	(✓)	?
Suction (surface) pump	✓	✖	✓	✖	✓	✓	✓	✖	✓	✖	✖	✖	✓	?

EC – electric conductivity

VOC – volatile organic compounds

TOC – total organic carbon

TOX – total organic halogen

EOCs – emerging organic contaminants

2.2.1 Experiment settings

The experiment was performed on one of the sites used in the comparison study, on site located in Poland. The site has been included in sampling for emerging contaminants in 2016 (Kuczyńska A., 2017) and in 2020 (within GeoERA project).

Sampling performed in 2016 revealed presence of the following ECs in a groundwater sample: estrone (16 ng/l), 17-alfa-estradiol (61 ng/l), diclofenac (10 ng/l), carbamazepine (13 ng/l), sulfamethoxazole (2 ng/l) and sulfapyridine (3 ng/l). In 2020, a groundwater sample taken contained 4-Nonylophenol (205 ng/l), sulfametoazole (9,5 ng/l), and carbamazepine (9 ng/l).

For the experiment performed in 2021, 12 groundwater samples were taken, two for each sampling scenarios A-E¹, plus 2 blank samples (*Table 6*). Sampling scenarios A-E were defined to distinguish differences in sampling protocols. In scenarios A and E, water samples were taken using a discrete sampler of 1 m length and a volume of 1 l. In scenarios B-D a submersible pump was used and this was used at low (B, C) and high (D) flow rates and different depth of a pump; B- at the top of the screen, C- in the middle of the screen and D – above the screen. Each water sample contained three 1 l green glass bottles.

Prior to performing scenario B, three volumes of water was removed from the borehole. All bottles were rinsed with sample water three times prior to taking a water sample for analysis. All samples were analysed for a total of 150 pharmaceuticals.

Table 6: Experimental sampling scenarios applied for the study

Sampling scenario	Sampling device	Depth of sampling device [b.g.l]	Relation of sampling depth to screen length	Sampling rate [m ³ /l]	Temperature [°C]	pH [-]	Electric Conductivity [µS/cm]
A	Discrete sampler	18.45	Bottom	n/a	13.7	6.90	1215
B	submersible pump	15.2	Top	0,03	15.4	6.91	1125
C	submersible pump	17.7	Lower Middle	0,03	16.0	6.90	1180
D	submersible pump	11.7	Above	1,2	13.45	7.01	1129
E	Discrete sampler	18.45	Bottom	n/a	15.0	6.99	1210

¹ Numerical results represent mean values
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Figure 5: Taking water samples with a discrete sampler and with a submersible pump.

3 RESULTS

3.1 Results on comparison of concentrations of common compounds

3.1.1 General observations

Heterogeneity in the restitution from laboratories led to apply systematic correction to all results. Therefore, it was decided to apply systematic expanded uncertainties of 30% for all measurements, independently to the laboratory and the measured concentrations. Lab 1 to 3 calculated uncertainties based on validation of the analytical method (including repeatability and reproducibility) since lab 4 expressed uncertainties as RSD on triplicates. Limits of quantification reported by the labs are presented in all figures, even though the calculation method was not the same for all labs which partly explains the large variations between labs.

Each lab made duplicates which are for the most part consistent, just like field blanks. The inconsistencies are highlighted for each molecule independently.

Results are sometimes very discordant between labs, without systematic lower or stronger errors: variability depends on samples or on molecules.

3.1.2 Results per molecule

For **4-nonylphenol**, results presented in Figure 6 are comparable between labs, except for Lab 1 which quantified systematically lower value than other labs.

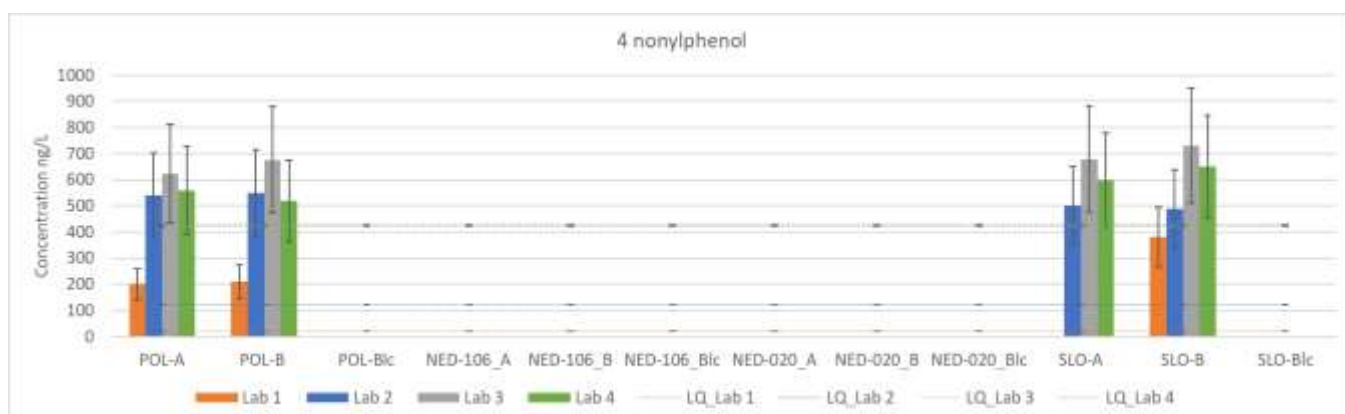


Figure 6: Comparison of 4-nonylphenol analysis.

Bisphenol A is well known to be an ubiquitous compound, that led to difficulty to maintain clean lab blanks. As shown in Figure 7, in our exercise, Lab 3 has encountered a systematic pollution that forced it to revalue upwards the classical LOQ (from 0,05 to 0,15 $\mu\text{g/L}$). Nevertheless, the result observed in sample 106-A, just above the corrected LOQ seems to be an artefact.

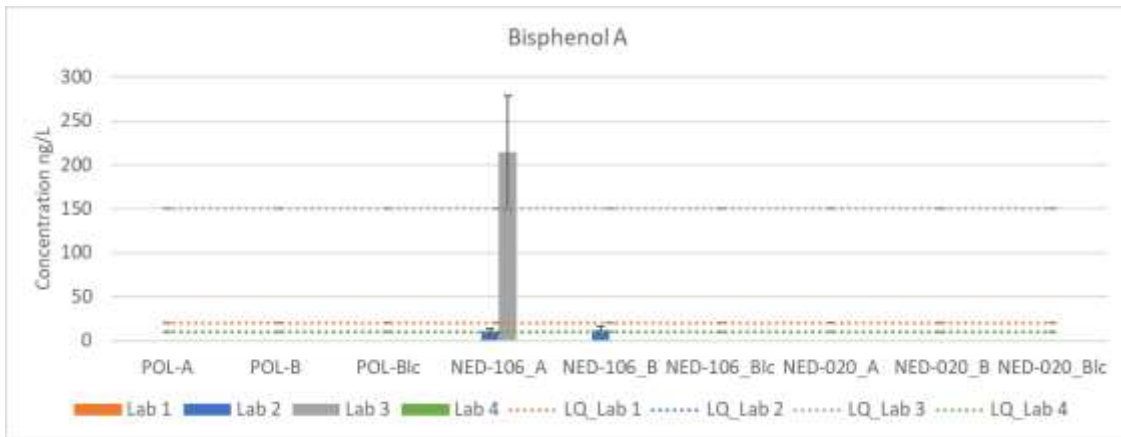


Figure 7: Comparison of bisphenol A analysis of samples POL, NED-106 and NED-020

At higher concentration of Bisphenol A in samples (SLO A and B), results in Figure 8 become more comparable between labs, except for LAB-1.

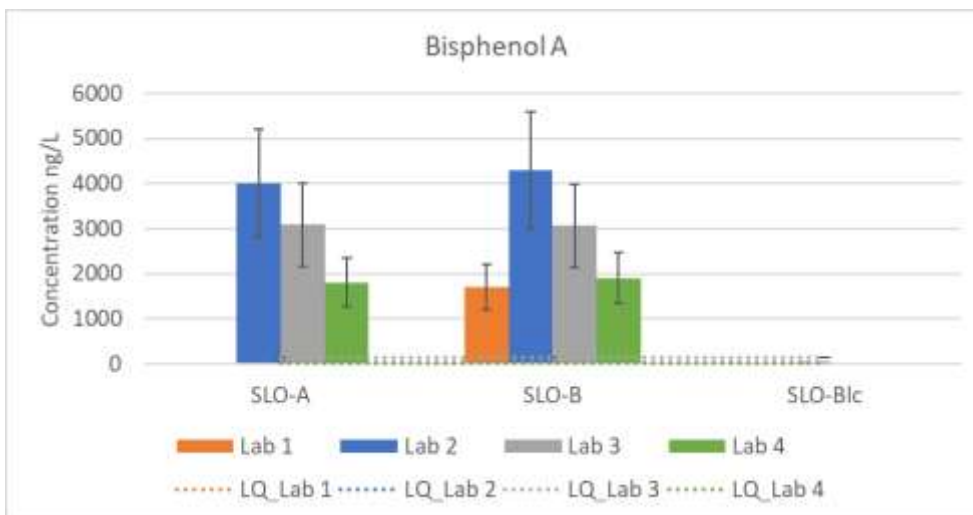


Figure 8: Comparison of bisphenol A analysis of samples SLO

Values measured for **caffeine**, Figure 9, in NED-106 samples by LAB-2 are consistent between replicates, but seem to be nevertheless an artefact, as other labs cannot measure caffeine, even if LOQs should allow its quantification. As ubiquitous contaminant, these results can potentially be explained by a contamination in the lab. Hypothesis of a contamination on the field is contradicted by the fact that all field blanks are clean. Results in SLO samples are consistent: LAB-3, with higher LOQ cannot detect caffeine as LAB-4.

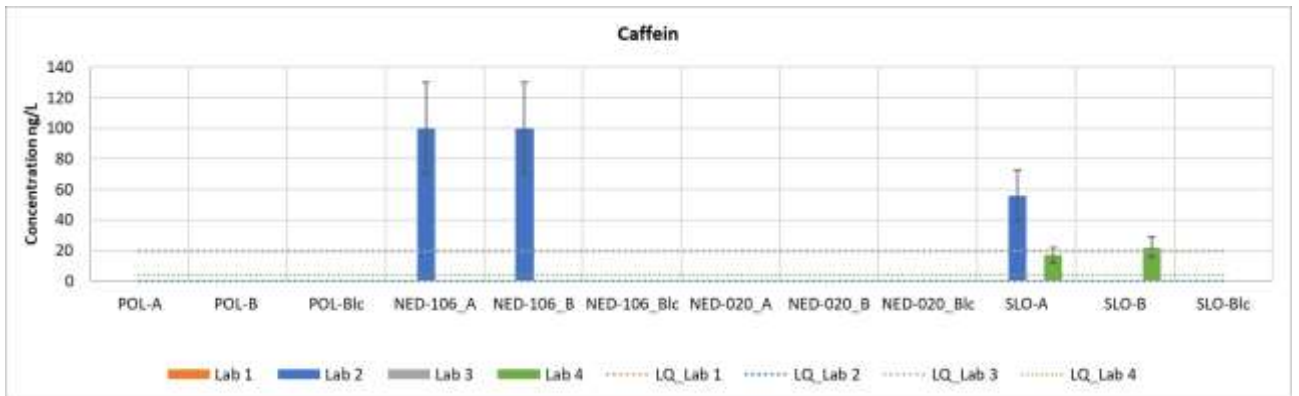


Figure 9: Comparison of caffeine analysis

Results of **carbamazepin** shown in Figure 10 depend on the samples. On POL and NED-106 samples, results are comparable between 3 Labs (1/3/4), however LAB 2 provided higher values. Previous measurements of carbamazepin at site NED-106 are consistent with the results of lab 1,3 and 4. On SLO samples, the divergent result is given by LAB 1. This variability is very important and not clearly understandable, as carbamazepin is not known as a difficult molecule to analyse.

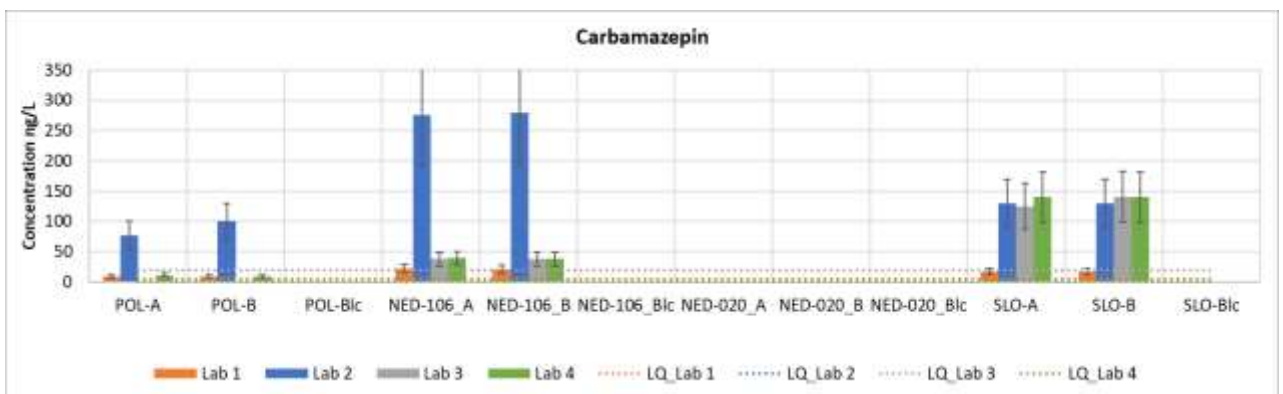


Figure 10: Comparison of carbamazepin analysis.

The comparison of **diclofenac** analysis by the 4 laboratories is presented in Figure 11 and Figure 12. Diclofenac illustrates well the complexity of interpreting and understanding variations between labs. Results on samples POL, NED-106 and NED-020 show quantification by only one lab, LAB 1, even if LOQ of LAB 2 and LAB 4 should allow its quantification. Considering the contamination of the associated blank, results from the lab can potentially be attributed to a contamination, but not occurring in the field: In this case, all labs should have measured this contamination.

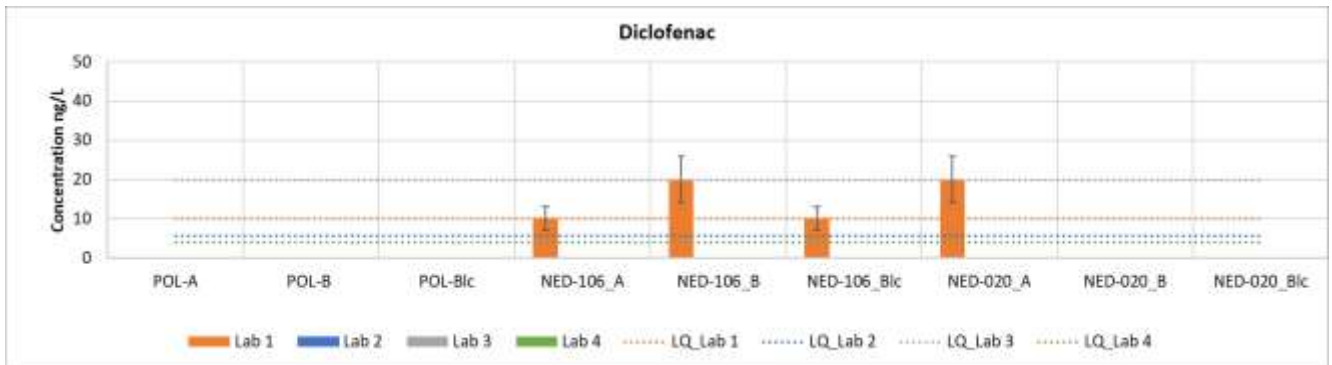


Figure 11: Comparison of diclofenac analysis of samples POL, NED-106 and NED-020.

Results from sample SLO in Figure 12 are different. Despite clean field blank, all labs measured high concentrations of diclofenac, all with consistency in duplicate, but with high differences between labs, that cannot be attributed to analytical uncertainty.

In a previous campaign in 2019, diclofenac was quantified around 4 µg/L., A high concentration like 270 µg/L had not been measured before. However, the sample site is impacted by landfill leachate that can lead to high concentration of emerging contaminants.

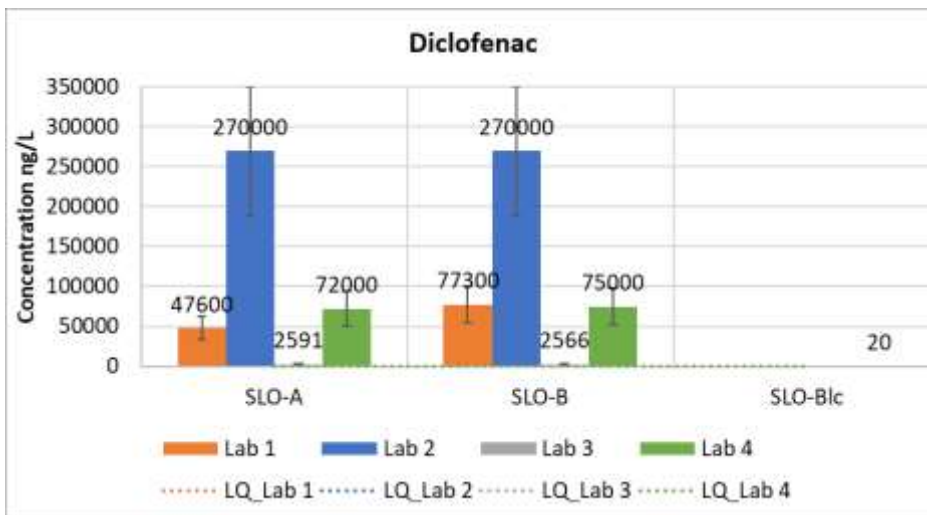


Figure 12: Comparison of diclofenac analysis of samples SLO.

For **gemfibrozil**, Figure 13 results are consistent between labs on NED-106 samples. However, that is not the case on SLO samples: the measurement from LAB 2 should have been confirmed by other labs considering their LOQs.

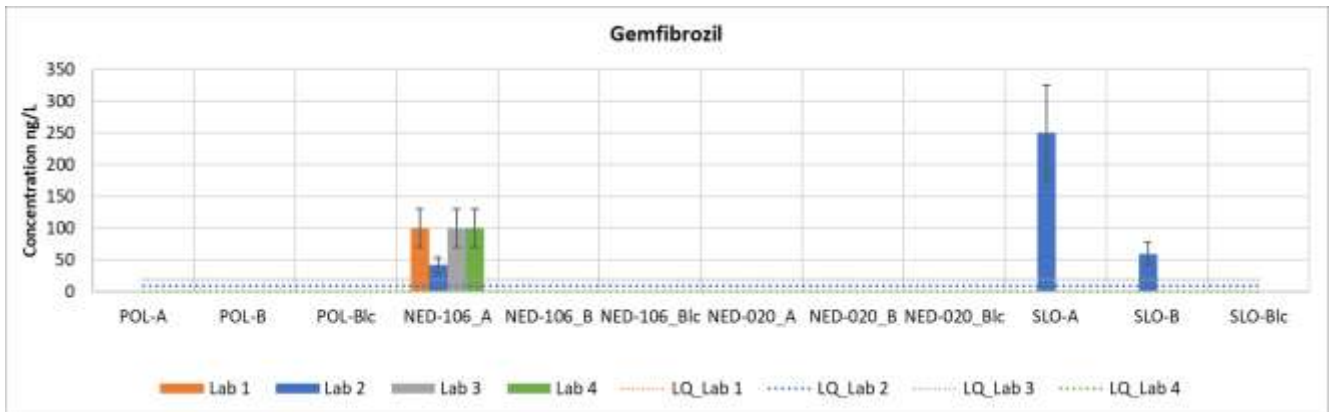


Figure 13: Comparison of gemfibrozil analysis.

Data for **sulfamethoxazole** are highly comparable between labs for POL and NED-106 samples as it is shown in Figure 14.

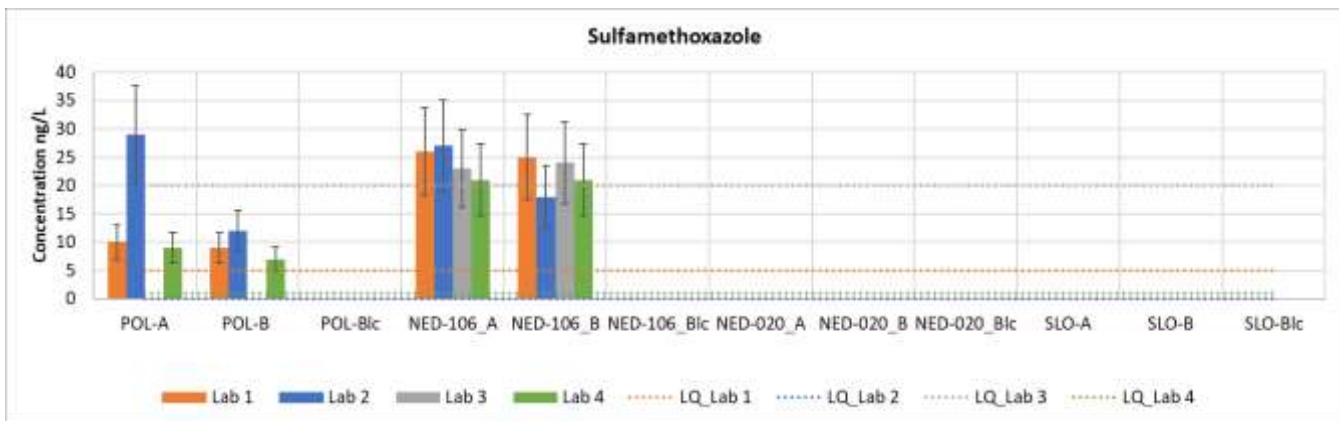


Figure 14: Comparison of sulfamethoxazole analysis.

For **trimethoprim** (Figure 15) quantifications by LAB 2 are not confirmed by the other labs, even if LOQ permitted the quantification.

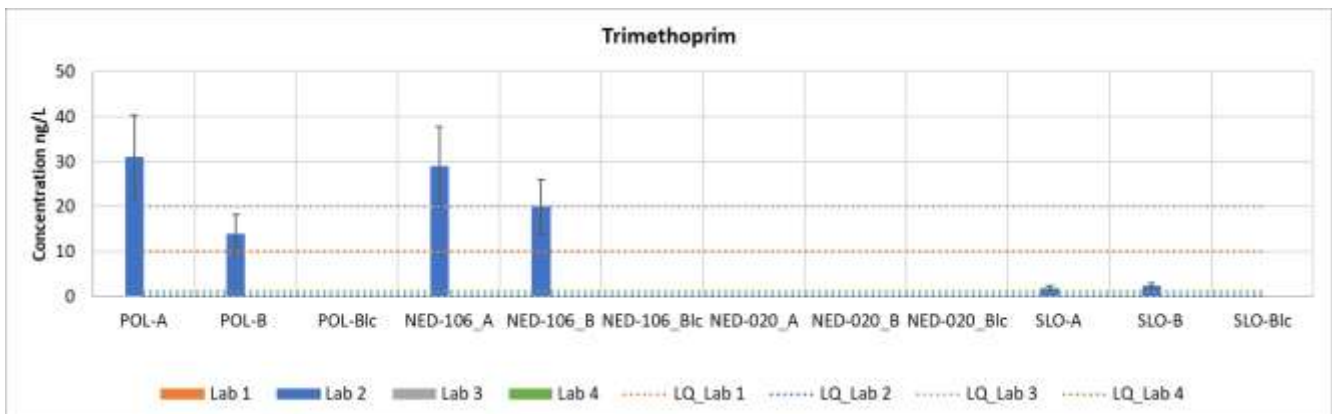


Figure 15: Comparison of trimethoprim analysis.

For other compounds: paracetamol, metoprolol, fenofibrate, bezafibrate and atenolol, no quantification occurred in any participating labs.

3.2 Results of the influence of pumping rate on sampling results

Results revealed presence of 6 different compounds, including Bisfenol A, 4-Nonylphenol, Caffeine, Cotinine, Carbamazepine and Epoxycarbamazepine, (Table 7).

Table 7: Sampling results for selected ECs

		Sampling scenario		A	B	C	D	E
		Date	Dec 2020	Jul 2021				
			HIGH FLOW	DISCRETE SAMPLER	LOW FLOW		HIGH FLOW	DISCRETE SAMPLER
		Temp [°C]	12,8	13,7	15,4	16	13,45	15
		pH	6,71	6,9	6,91	6,9	7,01	6,99
		EC [µS/cm]	1208	1215	1125	1180	1129	1210
		pumping rate [m³/l]	0,5	n/a	0,03	0,03	1,2	n/a
		sampling depth [b.g.l]	10,08	18,45	15,2	17,7	11,7	18,45
No.	Parameter	LOQ (ng/l)	Concentration (ng/l)					
1	Bisphenol A	20				145		
2	4-Nonylphenol	20	209		535	665	275	59,5
3	Caffeine	20				35		
4	Sulfamethoxazole	5	9,5					
5	Cotinine	5			9	12		11
6	Carbamazepine	5	9	21	23,5	19	23	19,5
7	Epoxycarbamazepine	20					5	

Only two molecules: 4-Nonylphenol and Carbamazepine have repeated results in two campaigns, in December 2020 and July 2021. Results for 4-Nonylphenol show high variability in concentrations between different sampling scenarios, with much higher values pumped at low flows and in deeper placement of the pump. 4-Nonylphenol is a viscous liquid with restricted water solubility (logKow = 5.76, <https://pubchem.ncbi.nlm.nih.gov>). Due to its chemical properties it tends to adsorb to organic matter/soil. Slower, low flow pumping results in more than a double concentration of this compound in water samples (535-665 ng/l) that when pumping with high flow rate and the pump located above the screen length (209-275 ng/l). There was no 4-Nonylphenol in a water sample withdrawn from the well using a discrete sampler at the beginning of the experiment, and there was little concentration of it at the end of the experiment, using the same sampling device. In contrast, carbamazepine for which Log Kow is 2.45 (<https://pubchem.ncbi.nlm.nih.gov>) revealed stable concentrations throughout the entire experiment (19-23.5 ng/l), with its metabolite epoxycarbamazepine to occur at the end of pumping at high rate. Epoxycarbamazepine is more toxic than carbamazepine. The highest number of contaminants was found in a sample taken in low flow pumping conditions with the

pump placed in the lower part of the screen. Following geoinsight.com such conditions are best for taking a sample representative directly from the screen area, where natural groundwater horizontal flow is the biggest.

4 DISCUSSIONS AND RECOMMENDATION

The reported experiments cannot be considered as statistically significant, however they provide important insights to problems that require more research and deeper analysis in the field of ECs' monitoring.

The study on laboratory analysis comparison proved that work on emerging contaminants is demanding and requires engagement of laboratories before planning site investigations. Analytical protocols and lack of internal standards for some parameters may significantly impact results and cause their heterogeneity. This in turns questions the general reliability of results and may put a shade on policies that are currently developed in the area of emerging contaminants. More effort should be put towards harmonization of analytical procedures and protocols to guarantee stability and comparability of results.

Observed differences proved the need for further and more extensive tests not only on simple matrix (natural water with low DOC content, range of molecules concentration in the linearity range of all labs etc.) but also more complex matrices should be experienced to reinforce the competence of the participating labs.

Some discrepancies between results seem to be related to the specificity of the matrices (SLO) with high DOC content and high amount of emerging contaminants. Lot of labs are not used to handling this type of samples, especially when they are identified as "groundwater". In general, for these types of samples, more related to wastewater samples, labs apply other methodologies, such as an initial dilution of sample before the extraction step. For this reason, labs shall be engaged and informed about sample matrices to apply methods most suitable for given situations.

For comparability of results on larger scale studies, such as monitoring of emerging substances on a European scale, specific analytical methods related to the aims of monitoring are required. This is especially important if results of such monitoring are used for defining regulations in the area of groundwater monitoring and management.

Quality control procedures, both in-situ and laboratory may be vital for the interpretation of results, hence good practice guidance documents would benefit the process of EC monitoring implementation.

The second experiment performed throughout this work highlighted potential uncertainties that may result from application of different sampling procedures. Further work is required on sampling protocols to ensure sampling results are reliable and comparable between study sites.

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