



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

Authors and affiliation:

Togola, A.^[BRGM], **Lopez, B.**^[BRGM], **Kuczyńska, A.**^[PGI-NRI], **Koroša, A.**^[GeoZS], **Mali, N.**^[GeoZS], **Rosenqvist, L.**^[SGU], **van Vliet, M.E.**^[TNO], **Lapworth, D.J.**^[BGS], **Wyszomierski, M.**^[PGI-NRI]

E-mail of lead author:
a.togola@brgm.fr

Version: 20-10-2021

This report is part of a project that has received funding by the European Union's Horizon 2020 research and innovation programme under grant agreement number 731166.



Deliverable Data	
Deliverable number	D8.3
Dissemination level	Public
Deliverable name	Supporting documents
Work package	WP8
Lead WP/Deliverable beneficiary	BRGM

Deliverable status		
Submitted (Author(s))	29/10/2021	Anne Togola
Verified (WP leader)	30/10/2021	Benjamin Lopez
Approved (Coordinator)	30/10/2021	Laurence Gourcy

This report is part of a project that has received funding by the European Union's Horizon 2020 research and innovation programme under grant agreement number 731166. Scientific work is co-funded by the Geological Surveys and national funds allocated for science within the period 2018-2022.

TABLE OF CONTENTS

1	INTRODUCTION AND OBJECTIVES	3
2	MATERIAL AND METHODS	4
2.1	Sampling sites	4
2.1.1	Slovenian groundwater sampling site	4
2.1.2	Polish groundwater sampling site.....	5
2.1.3	Dutch groundwater sampling sites.....	6
2.2	List of compounds.....	7
2.3	Sampling strategy	8
2.4	Participating laboratories and analytical methods.....	9
3	RESULTS	10
3.1	Results on common compounds	10
3.1.1	General observations.....	10
3.1.2	Results per molecule.....	10
3.2	sampling tests.....	15
4	DISCUSSIONS AND RECOMMENDATION	16
4.1	Need for harmonization	16
4.2	Need for interlab exercises.....	16
4.3	Impact on results and interpretation	16
5	REFERENCES.....	17

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 a first assessment of the difficulties associated with the prospect of integrating emerging organic compounds in the regular monitoring of groundwater.

2 MATERIAL AND METHODS

2.1 Sampling sites

Four sampling sites were selected for the 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 Slovenian groundwater sampling site



Figure 1: Location of the Slovenian groundwater sampling site

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

Land use: urban

Type of borehole: piezometer (1999)

Depth: 12 m

Screen: 5 – 11 m

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 slavenian sampling site in March 2017

Date	Time of pumping	Carbamazepine (µg/L)	Propyphenazone (µg/L)
21.03.2017	After 7 min	0.325	0.081
21.03.2017	After 32 min	0.330	0.083
21.03.2017	After 62 min	0.349	0.087
21.03.2017	After 122 min	0.364	0.087
21.03.2017	After 182 min	0.347	0.086

- 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 (µg/L)
4-methyl-1H-benzotriazole	0.54
1H-benzotriazole	4.9
5-methyl-1H-benzotriazole	0.14
Diclofenac	3.8
Caffeine	0.035
Cetoprofen	11
Carbamazepine	0.23
Salbutamol	0.011
Salicylic acid	0.036
Acetilsalicylic acid	0.047

2.1.2 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

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

2.1.3 Dutch groundwater sampling sites

Pilot site well 106, filter 1

Well 106 is located in Landhorst, in the Province of North Brabant. 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). Table 3 shows the coordinates, filter number, the depth ranges in m below surface level and the apparent groundwater age.

Table 3: Description well 106, filter 1

Well ID	Filter No	GPS Latitude	GPS Longitude	Depth top of screen (m below surface)	Depth bottom of screen (m below surface)	Well type (O=observation, P=pumping)	Apparent Age (y)
106	1	5.7843038°	51.6209362°	8	10	O	1



Figure 3: Location well 106

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).

Pilot site Spring n.020

Spring n.020 is located in the most southern part of the Netherlands nearby Valkenburg in the Province of Limburg (see Table 4 and 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.

Table 4: Description Spring n.020

Spring ID	GPS Latitude	GPS Longitude	Mean Travel Time (MTT) (y)
n.020	5.821643°	50.8811272°	13



Figure 4: Location Spring n.020

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.

2.2 List of compounds

Participants has been asked for the list of compounds they are able to analyze in groundwater samples. Depending on participants, the lists of analyzed compounds were different, 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 analyzed by all the laboratories, with LoQ compatible with the expected concentrations in selected groundwater sampling sites. At the end, 13 emerging organic compounds listed in Table 5 have been selected for the exercise.

Table 5: 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

2.3 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) have been sampled on each site to be send to all the 4 participating laboratories.

Samples were collected when water physico-chemical parameters have become constant. That means that wells were pumped at least 3 volumes of stagnant water from the well prior to sampling. The field blank consisted in bottles filled with demineralized water from the lab immediately after groundwater sampling. 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 6 shows the field physico-chemical parameters when sampling the 4 groundwater sites.

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

Table 6: Groundwater sampling sites field physico-chemical parameters.

Field physico-chemical parameters					
location	Date	pH	Temp (°C)	EC (uS/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

2.4 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 in one.

As all participants don't have their internal laboratory, some are 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.

3 RESULTS

3.1 Results on 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 5 are comparable between labs, except for Lab 1 who quantified systematically lower value than other labs.

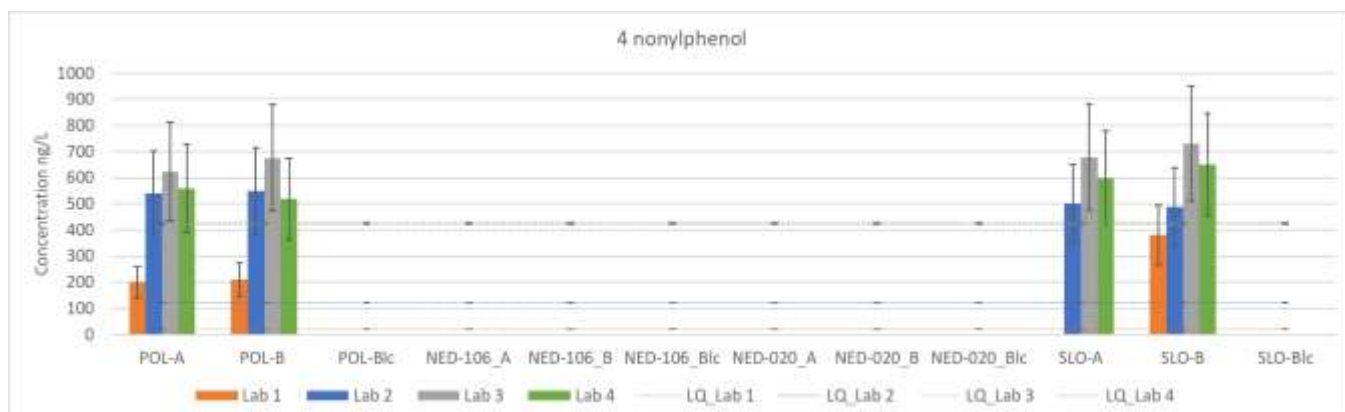


Figure 5: Comparison of 4-nonylphenol analysis.

Bisphenol A is well known to be an ubiquitous compound, that led to difficulty to maintain clean lab blanks. As shown in Figure 6, in our exercise, Lab 3 has encountered a systematic pollution that forced it to revalue upwards the classical LOQ (from 50 to 150 ng/L). Nevertheless, the result observed in sample 106-A, just above the corrected LOQ seems to be an artefact.

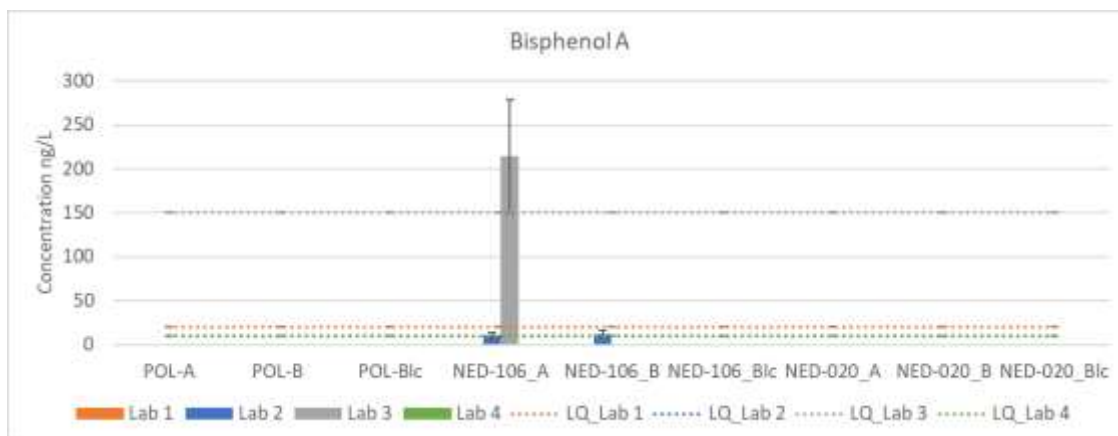


Figure 6: Comparison of bisphenol A analysis of samples POL, NED-106 and NED-020

At higher concentration of Bisphenol A in samples (SLO A and B), results in Figure 7 become more comparable between labs, except for LAB-1.

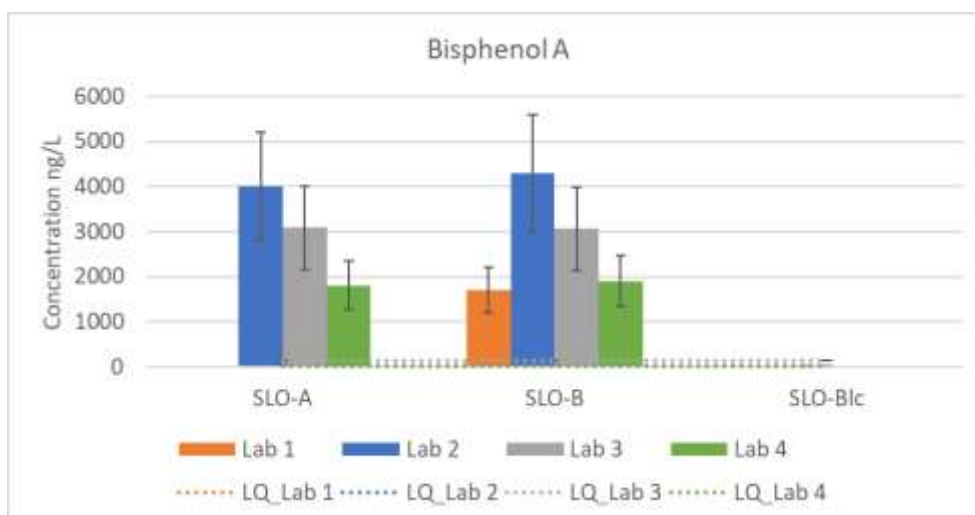


Figure 7: Comparison of bisphenol A analysis of samples SLO

Values measured for caffeine, Figure 8, 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.

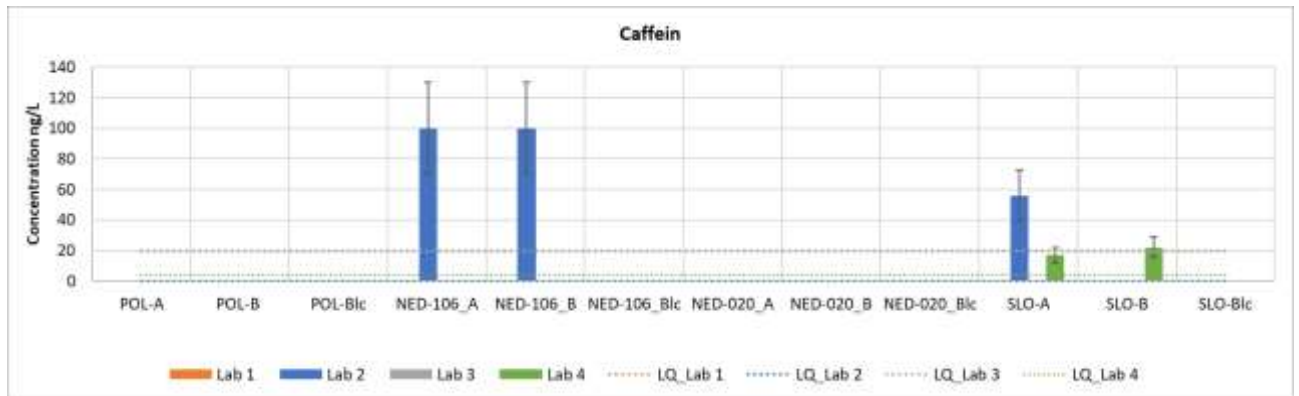


Figure 8: Comparison of caffeine analysis

Results on carbamazepine shown in Figure 9 depend on the samples. On POL and NED-106 samples, results are comparable between 3 Labs (1/3/4) when LAB 2 provided higher values. Previous measurements of carbamazepine at site NED-106 are consistent with the results of lab 1,3 and 4. On SLO, the divergent result is given by LAB 1. This variability is very important and not clearly understandable, as carbamazepine is not known as a difficult molecule to analyse.

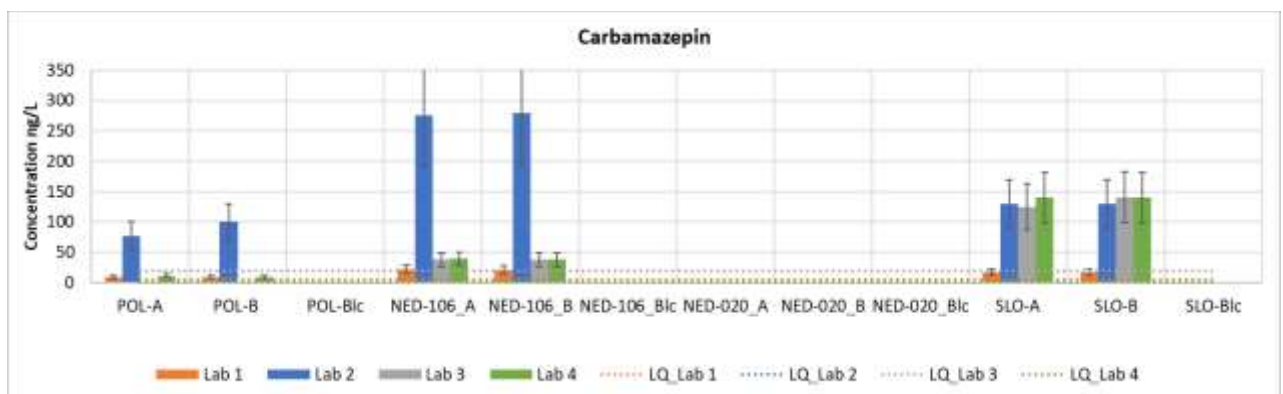


Figure 9: Comparison of carbamazepine analysis.

The comparison of diclofenac analysis by the 4 laboratories is visible in Figure 10. 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.

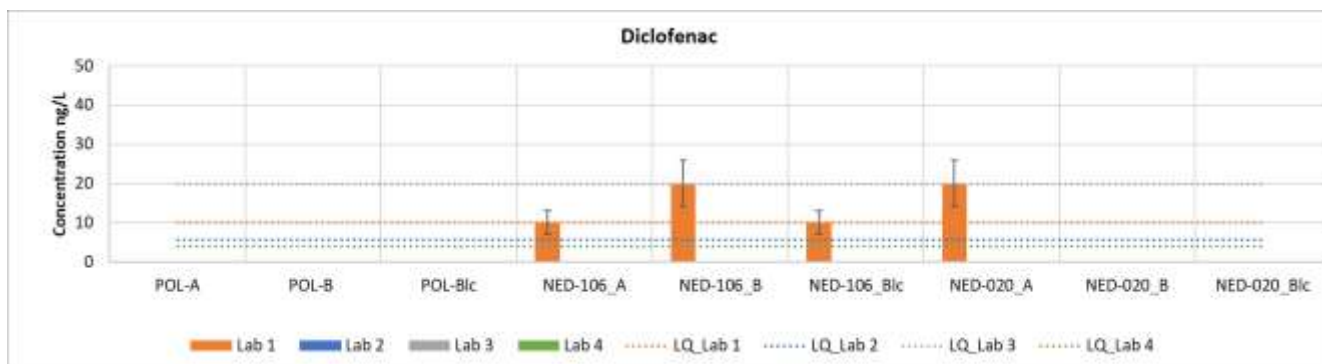


Figure 10: Comparison of diclofenac analysis of samples POL, NED-106 and NED-020.

Results from sample SLO in Figure 11 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.

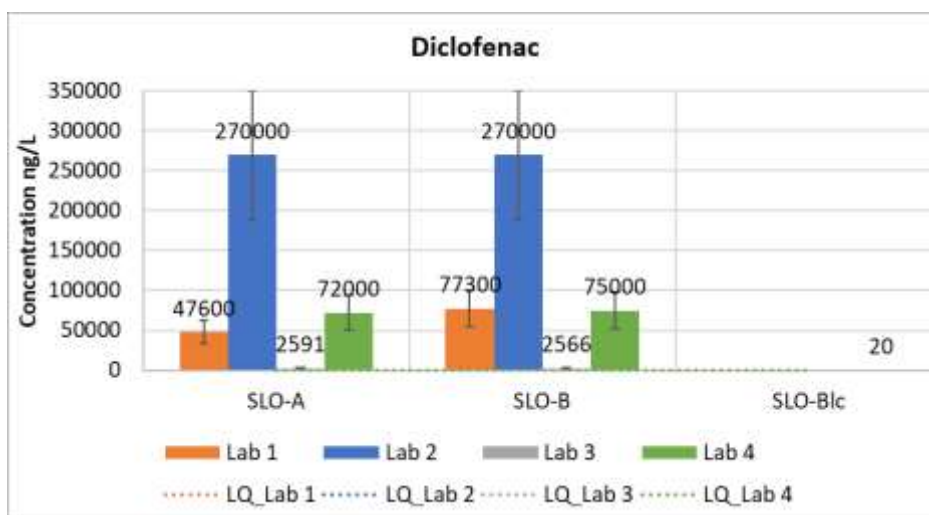


Figure 11: Comparison of diclofenac analysis of samples SLO.

For gemfibrozil, Figure 12, while results are consistent between labs on NED-106 samples. That is not the case on SLO samples: the measurement of LAB 2 should have been confirmed by other labs considering their LOQs.

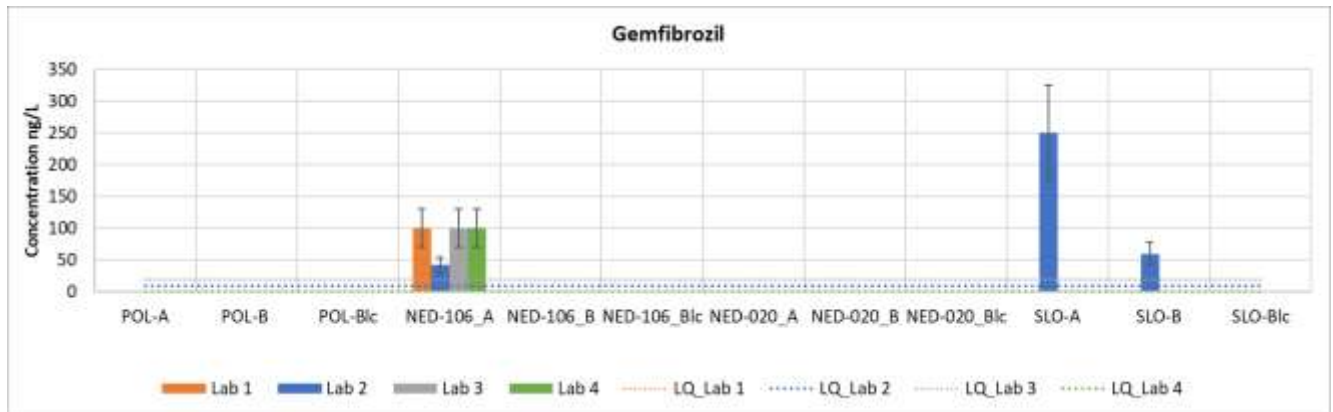


Figure 12: Comparison of gemfibrozil analysis.

Data for sulfamethoxazole are highly comparable between labs on POL and NED-106 samples as it is shown in Figure 13.

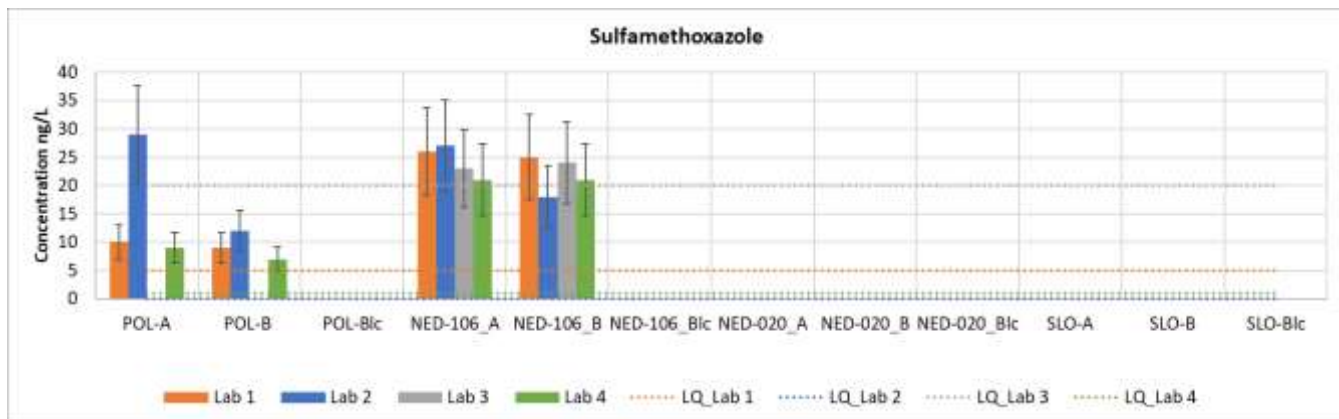


Figure 13: Comparison of sulfamethoxazole analysis.

For trimethoprim (Figure 14) quantifications by LAB 2 are not confirmed by the other labs, even if LOQ permitted the quantification.

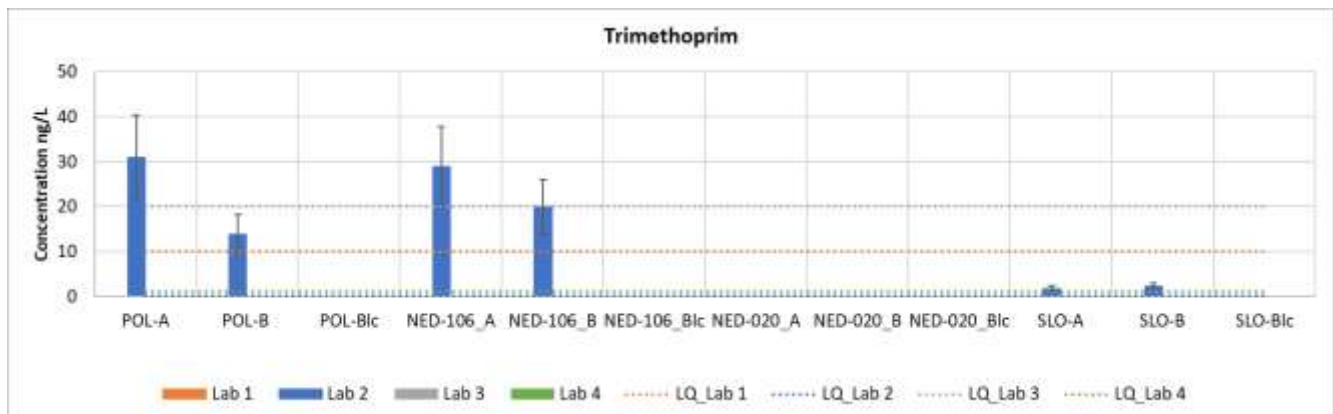


Figure 14: Comparison of trimethoprim analysis.

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

3.2 sampling tests

4 DISCUSSIONS AND RECOMMENDATION

4.1 Need for harmonization

Comparison of samples is difficult because of the heterogeneity in the reported value – uncertainties, LOQ ..).

Work on emerging contaminants is more difficult because of no /few interlab exercises,

Lack of internal standards for some compounds.

4.2 Need for interlab exercises

The reported study cannot be considered as an interlab because of not enough involved labs to determine a reference value for each compounds.

⇒ Need for interlab test

Need for interlab exercise but not only on simple matrix (natural water with low DOC content, range of molecules concentration in the linearity range of all labs etc.): more complex matrices should be experienced to reinforce the competence of the participating labs.

⇒ Reinforcement of QA/QC in the lab

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 type of samples, more related to wastewater samples, labs apply other methodologies, such as an initial dilution of sample before the extraction step.

4.3 Impact on results and interpretation

Clearly specify that we need to require specific analytical methods related to the aims of the monitoring campaign!

Ask the lab QA/QC information (such as uncertainties) to take into account this information in the interpretation!

And don't forget to qualify also the sampling uncertainties.

5 REFERENCES

Kivits, Tano, Hans Peter Broers & Mariëlle van Vliet 2019. Dateren grondwater van het Provinciaal Meetnet Grondwaterkwaliteit Noord-Brabant. Inzicht in de toestand en trends van 12 indicatoren van de grondwaterkwaliteit. Rapport TNO 2019 R11094, TNO, Utrecht.

Van Vliet, Mariëlle & Hans Peter Broers (2019). Reistijdverdelingen en nitraatprognoses voor 15 bronnen in het KRW-meetnet Krijt-Maas op basis van metingen van tritium in 2001, 2009 en 2017. TNO 2019 R11581, TNO, Utrecht.