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 8.5

Proposal and recommendations for monitoring emerging pollutants in EU groundwater

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TABLE OF CONTENTS

1 INTRODUCTION

Emerging pollutants are substances detected or expected to be detected in the environment, but are not routinely included in groundwater resource protection regulations and whose fate, behaviour and toxicological effects are poorly understood. Examples include pharmaceuticals, personal care products and perfluorinated compounds (e.g. PFOS/PFOA) and biocides that are not regulated in GW (excluding pesticides). They are not unique by comparison with regulated pollutants with respect to monitoring (e.g. in terms of sampling and analytical issues). An emerging compound is not “by definition” a compound that has inherent complexity or that necessarily leads to sampling or analytical difficulties. In some cases, emerging compounds can be much easier to monitor than historical/regulated compounds. Therefore, by default, classical or standardised methods of sampling or of analysis can often be applied.

What characterizes emerging pollutants is often, by definition, the absence of information on some technical, analytical aspects which can lead to significant issues in terms of quality, reliability of results (risk of field or lab contaminations, stability in samples…). Other aspects of these substances of “recent interest” are sometimes the lack of analytical tools like commercial analytical standards, in particular deuterated standards, Certified Reference Materials or Proficiency Testing schemes.

More and more, in addition to classical industrial/agricultural pollutants (pesticides etc.) emerging compounds include daily life products (like personal care products), which are ubiquitous and raise questions about the risks of cumulative contamination.

This reports objective is to review key aspects related to the choice of sampling sites, sampling and analytical operations that might impact reliability of the monitoring of emerging substances. Beyond the questions which are specifically linked to the emerging nature of these new compounds, it turns out that the establishment of monitoring of these emerging compounds brings to light more traditional monitoring questions such as, the concepts of the definition of limit of quantification and its meaning, estimation of uncertainty or difficulties with interpretation of the data and more generally the need of harmonized rules for method validation.

2 SAMPLING SITES

2.1 Groundwater monitoring network sampling design

Emerging compounds form, by definition, an heterogeneous family in term of use pattern and behaviour in the environment, and the choice of sampling sites is of great importance when establishing a network dedicated to the monitoring of these chemicals in groundwater. Different strategies can be chosen to select groundwater sampling sites, depending on the type and diversity of the compounds monitired, the number of sites potentially monitored (available ressources), the size of the area under investigation and the objective of the study. Bunting et al., 2021, mentionned that various scales of study are required to understand aspects of EOC's occurrence.

Large-scale studies offer an insight into spatial occurrence and trends in EOCs, and allow researchers to understand how widespread or diffuse a particular EOC is in the groundwater system, this aspect will be an important consideration for regulating EOCs in the future. National-scale studies are important to gather evidence about EOC's in groundwater across Europe, and will help to define threshold values and a regulatory framework. But these types of study require a large organisational element, and organisation, are difficult to implement and expensive.

Smaller scale studies are primarily used to understand temporal variability and specific hot-spots where EOC contamination may be more likely to occur. Although the majority of studies are still focused on point sources, in areas where EOC's have previously been detected or known to have been released. Practically, this helps to direct the study and keeps costs down. Targeted studies are often employed where EOC's have been detected in the past, due to the presence of a current or previous structure or environmental setting. The study may then screen for a larger range of compounds to determine the scale of the contamination of groundwater in this area

Even if there are an increasing number of regional and national studies (Lopez et al., 2015, Manamsa et al., 2016, Brueller et al., 2018) the number of large-scale studies, and those with a large number of analytes, are still relatively low, owing to the high cost of screening and the logistical complexity of screening for large numbers of compounds. Increased quantification of EOC's in groundwater is still needed to aid the development of threshold values. However, it is important to continue large scale scoping studies which are invaluable for assessing the occurrence of EOC's in groundwater bodies across a range of environmental settings.

2.2 Influence of GW sites settings

The determination of natural and anthropogenic factors that influence the content of the emerging organic contaminant (EOC) in GW is very important. Sampling campaigns/networks need to be defined taking into account characteristics of sampling sites, their recharge areas and analyses planned. Information collected is the basis for compiling the database for further statistical analysis and interpretation of sampling results.

The general list of information that is required to be gathered from a sampling site (after Mezga, 2014) consists of:

Geographical information - land use (paste and current)

- Sampling site location
- *CORINE land cover* data is used for specification of natural and anthropogenic influence on the recharge area of sampled groundwater. The CORINE categories should be divided into groups for example natural, urban and agriculture.
- Potential sources of pollution, diffuse sources (agricultural land use, sludge spreading areas) and point sources (current and historical industrial sites, cities, waste water treatment plant, landfill…)

Groundwater well characteristics

- Borehole type (observation well, pumping well, spring…)
- Borehole design (depth, borehole log, borehole construction such as screen depth and length)

Geological and Hydrogeological settings

- Lithological characteristics of a borehole
- Characteristics of an aquifer (type, porosity, transmissivity, etc.)
- Thickness of unsaturated / saturated zones and an assessment of confinment
- Local/regional hydrodynamics (water level, flow pathways, links to surface water)
- Hydrogeological situation: discharge, recharge or intermediate area.

These metadata are of great importance for a comprehensive interpretation of EOCs groundwater concentrations. Depending on the objective of the monitoring, some of the above should be explored in more detail. For example, the former and current land uses should be described in detail in the case of a pressure-impact characterization. To determine the origin and transport of organic pollutants in intergranular aquifers, Mezga 2014 and Koroša 2019 paid particular attention to the identification and characterization of recharge areas for which specific methods were developed depending on the type of aquifers. For data analysis at EU level, some data will need to be generalized and standardized.

2.3 Age dating and monitoring of emerging contaminants

Several published studies have employed residence dating methods to assess organic contamination in groundwater systems, most notably in early work for pesticide investigations (e.g., Lapworth et al., 2006; Baran et al., 2009). It follows that this framework could also be useful for understanding the risks of EOC contamination in groundwater. For example, Barnes et al. (2008) found that groundwater samples from shallower wells had significantly greater numbers of different wastewater indicator compounds (including pharmaceuticals) detected, compared to deeper wells, which supports the hypothesis that residence times may be useful indicators of contaminant risk.

Fram and Belitz (2011) used a combination of groundwater tritium activity and selected pharmaceutical (n=14) and pesticide analysis to assess the vulnerability of groundwater in California, USA. Pharmaceutical compounds were detected in 3.3% of the 855 samples containing modern groundwater (tritium activity > 0.2 TU). Of the 28 samples with detections of pharmaceutical compounds, 86% also contained pesticides at concentrations greater than the highest MDL used during the period of study, 71% also contained VOCs other than THMs (primarily solvents), and 61% also contained THMs.

A study by Sorensen et al (2015) was one of the first published studies to combine the use of modern residence time tracers (CFCs and SF_6) and broad screening for EOCs to assess the vulnerability of the deeper karstic bedrock aquifer beneath Kabwe, Zambia. Bulk residence times of 10–30 years and a large fraction of more modern water suggest the bedrock aquifer could potentially be at risk from the ingress of a range of modern organic compounds; yet the number of observed compounds is low. This supported a recent groundwater vulnerability assessment of the bedrock aquifer, which concluded that the bedrock aquifer was not at risk currently, due to the extensive overlying clay-rich superficials which were likely to provide a significant barrier to contamination migration (Museteka, 2013).

Lapworth et al (2018) employed the use of CFCs, SF_6 and broad screening LCMS-QTOF to assess EOC contamination in the sedimentary aquifer beneath Varanasi, India. Groundwater residence tracer profiles match the depth trends observed for the EOCs and other micro-organic contaminants and strongly suggest a significant component of younger groundwater at depth, even at sites which are cased out below 100 m and are completed at depths of 200 m.

Moreau et al (2019) took this concept a step further by including the use of groundwater ages in a stratified sampling design. This study in New Zealand found that EOC detections occurred across young (1–11 yrs), intermediate (11–50 yrs) and old (50–250 yrs) groundwaters, with higher concentrations and more types of EOCs detected at sites in the youngest age category.

Also, in the Netherlands groundwater age dating is used in groundwater quality monitoring (Kivits et al 2019a and 2019b). In GeoERA HOVER D5.3, it is shown for a Dutch pilot area how the occurrence of pesticides was related to the groundwater age tracer and land use (Ascott et al, 2020).

In this pilot area, data was used from Monitoring Networks for the WFD in the Sand-Meuse region. The wells of this network have all been sampled for 3H/3He during campaigns in 2001, 2008/2009 and recently in 2017/2018 (Kivits et al, 2019b). Using 3H/3He age dating, information is obtained about saturated zone travel times and groundwater ages, which enables the data produced to be used for forensics of past land use inputs (Visser et al. 2007; Visser et al. 2009). The pesticides concentrations were related to infiltration years (subtracting age of the sample from the year of sampling itself) and results are presented in jitter and boxplots (see Figure 2.1 for an example of desphenyl-chloridazon).

Desphenyl-chloridazon is a metabolite of chloridazon. Chloridazon has been permitted in the Netherlands since the early 1990's and was found in the groundwater since then. Figure 1 shows that desphenyl-chloridazon was frequently found in agricultural areas in water from the infiltration periods 1990-2000, 2000-2010 and 2010-2020. Ascott et al (2020) concluded that the majority of pesticide hits were observed in the youngest infiltration year classes (2000-2010 and 2010-2020) and in agriculture areas.

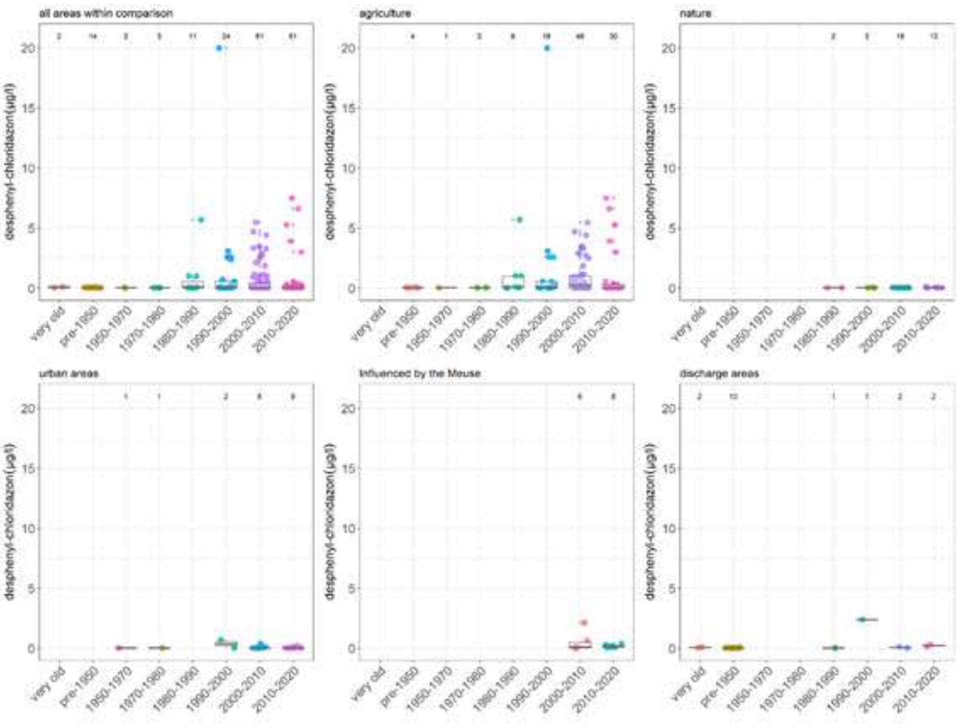


Figure 1: Jitter and boxplots of desphenyl-chloridazon (µq/l) per infiltration year class based on tracer ages for several land types: all areas within comparison, agriculture, nature, urban areas, areas influenced by the Meuse and discharge areas (Ascott et al, 2020).

The same methodology is useful to study the transport of emerging contaminants (see e.g., Kivits et al 2018) and Figure 2 for emerging contaminant carbamazepine. Carbamazepine is only found in the most recent infiltration years (2010-2020) and in areas in which Meuse water recharges groundwater. Screen 106_1, sampled for the interlab test in HOVER D8.3 (Togola et al., 2021), is one of the screens in this homogeneous area type. Carbamazepine was also detected in the interlab test samples as expected.

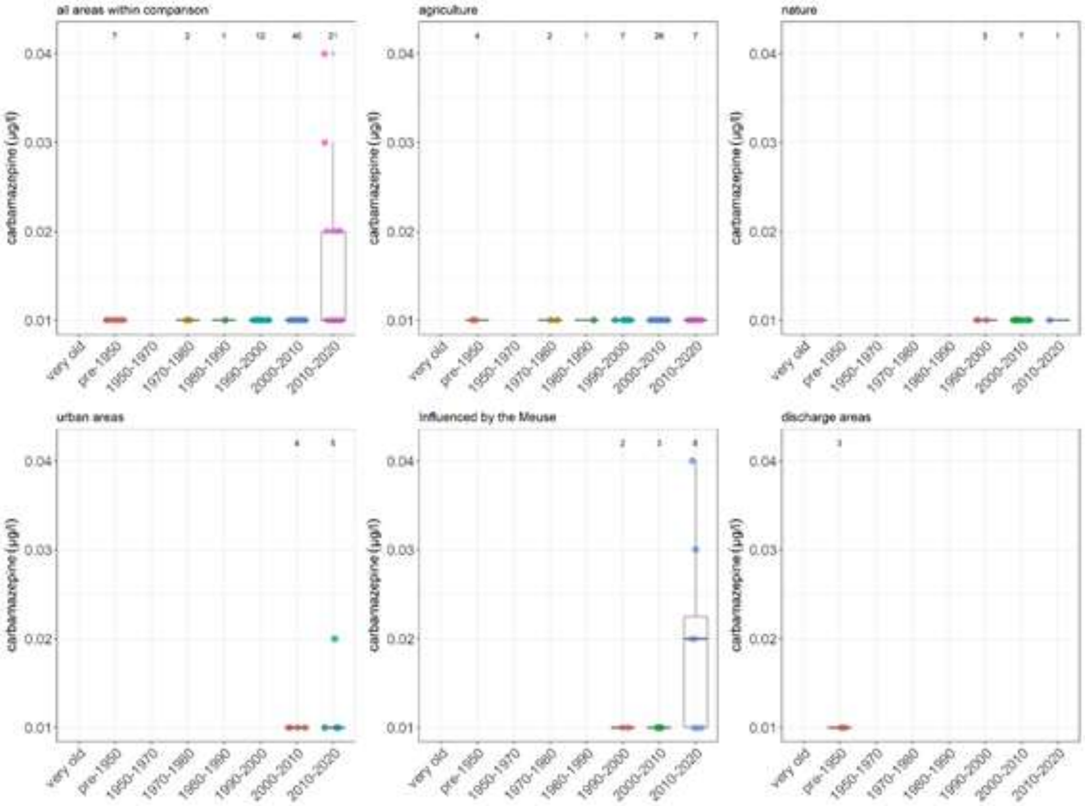


Figure 2: Jitters and boxplots of carbamazepine (µq/l) per infiltration year class based on tracer ages for several land types: all areas within comparison, agriculture, nature, urban areas, areas influenced by the Meuse and discharge areas.

The aim of the study of Kivits et al (2018) was to characterize the presence of antibiotics under agricultural fields in relation to groundwater age and the processes that may control their fate in a groundwater environment. Ten multi-level wells with in total 46 filters were sampled, focusing on relatively young, previously age-dated groundwater below agricultural fields. The antibiotics were found at all measured depths down to 23 m and in groundwater up to 40 years old. These findings reflect the known application history of antibiotics in the Dutch veterinary system and indicate that leaching of antibiotics from agricultural fields on which manure is applied is a pathway for pollution of the aquatic environment.

3 SAMPLING

3.1 Risk of contamination in the field

3.1.1 General aspects on field practices

An increasing number of monitored pollutants come from industrial products that are used on a very large scale, on a daily basis or in domestic practices (for example personal care products, medicines, plastics). These products are sometimes incorporated into a lot of equipment and commonly used materials (plastics). This results in great difficulties in controlling the risks of contamination, whether in laboratories but also increasingly in field during sampling or handling. These risks may come from the equipment, but in many cases from the operators themselves.

In addition, very significant and progressive improvements in analytical techniques now make it possible to achieve extremely low limits of quantification. In order to ensure the quality of the results across the entire monitoring chain, it is necessary that sampling practices evolve simultaneously and that they gain in rigor and quality so as not to degrade the gains in analytical performance.

In order to control the risks of contamination, rigorous quality control (QC) of sampling needs to be conducted both in the field and in the laboratory. Moreover, rigorous sampling practice should be applied:

- Sampling personnel should avoid using products containing compound of interest to prevent secondary contamination of samples at sampling (e.g., drinking coffee and consuming other products containing caffeine).
- Equipment should also be checked regarding risk of contamination. Blanks of the whole sampling chain included.

The main compounds that can cause risks of contamination among substances currently monitored are (see case studies below):

- Plasticizers: phthalates (DEP, DiBP for example), bisphenol A, N-butylbenzenesulfonamide
- Personal care product: diclofenac, galaxolide, paraben
- Other: caffeine

For all these compounds, quality controls ("field blank" type) must be set up on a regular basis either to test the equipment (pump, pipes, flasks, filters, etc.) or to test the practices of the operators.

For operators, field blanks may be prepared from ultrapure water that was sequentially transferred from one bottle to another at a sampling site.

In the context of groundwater sampling, blanks' testing for equipment (pumps, tubing, ...) are not easy (more difficult than for surface water sampling) and therefore not well documented. For most of compounds purging time seems sufficient to prevent cross contamination. But it is not always the case and hydrophobic compounds or compounds that are part of material may cause contamination. Therefore, it is recommended to regularly perform blank tests on the whole sampling chain.

International standard exists on quality assurance and quality control on sampling and should be applied (ISO 5667-14). Beyond the realisation of these internal quality control, the organisation of intercomparison for sampling is a very useful tool to evaluate the impact of sampling practice on data quality and especially to evaluate risks of contamination (see case study for metals). These intercomparisons are technically difficult to conceive for the groundwater context but they are very rich and instructive.

Good practice in sampling groundwater is to have a dedicated equipment for the specific environmental context, different from one used for industrial context. However, it is good practice to clean sampling material prior to use. With respect to emerging contaminants, it seems that there is a need to progress on these cleaning/rinsing methods and for example to exchange on various practices.

3.1.2 Case studies on sample contamination

Since 2013 Aquaref (www.aquaref.fr), French National Reference Laboratory for water monitoring has been conducting studies to test the risks of contamination during sampling operations for the main families of substances at stake. These studies concern groundwater but also surface water. Results from surface water sampling studies can, to some extent, be applied to groundwater in terms of handling samples in the field. Some conclusions of these studies are provided below. It is very important to mention that these studies relate to a level of limit of quantification practiced at the French level at the time of the studies and that the conclusions can be modified for lower limits of quantification.

3.1.2.1 Phtalates and alkylphenols

Ghestem et al. (2012) conducted tests to determine the potential impact of the type of tubing used in pumping groundwater on phtalates monitoring data. These compounds are often part of composition of many plastics that are used in tubing material for groundwater sampling operations. In this report seven phtalates compounds have been studied with a LOQ of 20 ng/l. The main objective of these tests was to determine the potential contamination introduced by four types of tubing of different origins and natures (Teflon, PVC with or without phtalates, low cost tubing). The results show, thanks to the purge time of the piezometer, a low impact of the type of tubing used for most of the substances, with exception of the substance DiBP (diisobutylphtalate) for which contamination seems to occur with certain types of pipe (low cost tubing) up to 80 ng/l. Except for the DiBP all sampling conducted on the site led to results below the limits of quantification.

Moreau et al. (2015) showed that contamination could occur for 4-nonylphenol during sampling with one old PVC tubing. Concentrations up to 100-150 ng/l in excess with Teflon or new PVC tubing have been observed.

3.1.2.2 Diclofenac

Ferret & al (2018) studied risks of contamination for diclofenac during handling in fields. During this study, two campaigns were performed: The first, in the laboratory, concerned to test various quality controls (blanks, spike etc.), and second on site at a reference monitoring station to test the impact of on the results. Results showed a contamination when sampling operators used anti-inflammation cream containing diclofenac. The non-respect of the application method (e.g. washing hands after application) showed a systematic contamination of samples: quantified values were between 0,022 µg/L and 0,094 µg/L, which are greater than the French mandatory LOQ (0,01 µg/L). Even if the application method was respected, some samples were found slightly contaminated with diclofenac, with quantified values between 0,004 and 0,017 µg/L. All tests were made with nitrile gloves. However, wearing nitrile gloves do not eliviate this risk of contamination.

3.1.2.3 Galaxolide

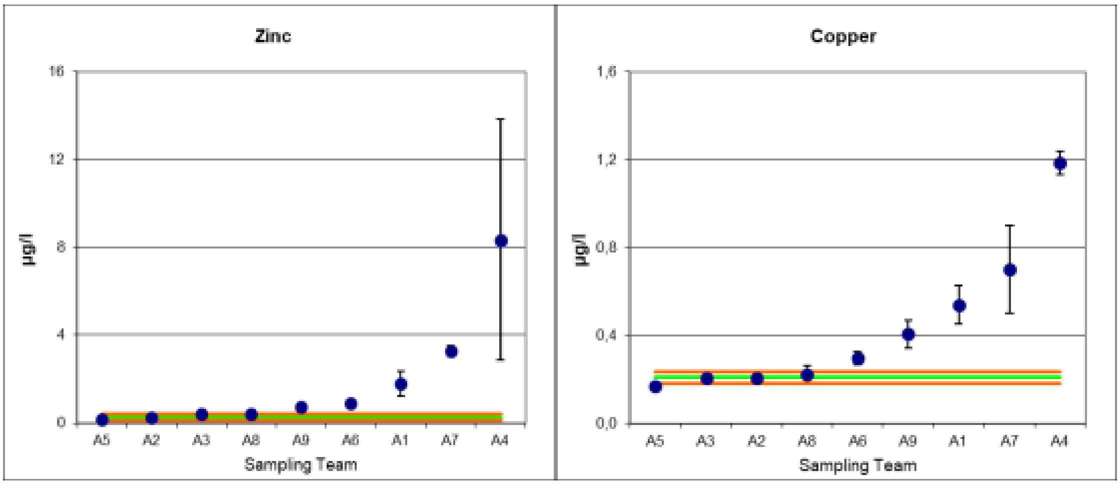
Moreau et al. (2017) performed sampling when a commercial hand cream containing 500 mg/kg of galaxolide has been used. The trials were performed by 2 operators, with different equipment, with or without applying hand cream, and with or without wearing nitrile gloves. The aim was also to evaluate the risk when the sampling conditions are not optimal. All « blank samples» and all samples analyzed after cream application and wearing nitrile gloves lead to very low concentration (below 10ng/L). However, after cream application and without wearing nitrile gloves, contaminations between 10 and 30 ng/L (below but close to the regulatory limit) were obtained.

3.1.2.4 Paraben

Paraben are widely used in the composition of cosmetic products, food and medicines. In the work of Ferret et al. (2015), several sampling campaigns were realized, on a station of reference. Results showed a real contamination when operators (sampling and / or analysis) used cosmetics and / or body care products containing parabens. Quantified values could reach concentrations greater than 900 ng /l, values above regulatory LOQ (30 ng /l). This impact concerned methylparaben, ethyl paraben and propyl paraben. The use of nitrile gloves by operators has reduced the contamination, but is not sufficient to totally eliminate it (quantification around 50-100 ng/l can still occur). However, despite the care taken for the preparation of experiment plan, in some cases the source of contamination is difficult to identify (contamination during the analytical step, operator contamination, contamination of gloves, equipment contamination etc).

3.1.2.5 Metals

Most metals are not considered as emerging compounds. The following example just illustrates how field intercomparisons can bring useful results in order to identify bias on sampling. Ghestem et a.l (2009) organised an intercomparison on groundwater sampling. It took place at a piezometer for the duration of one week. Nine teams of samplers carried out field work according to their routine procedure and duplicate samples taken to analyse well-defined chemical parameters (nitrates, pesticides, volatiles compound, metals). For each sample two analyses were carried out. Most of the results show a good agreement between the results of the different teams. The only parameters for which the effect linked to the sampler was predominant were for trace elements such as Cu, Zn (see below). For these elements, contamination of the samples during sampling has been clearly identified. The origins of these contaminations can be multiple (tubing, intermediate material, etc.). The main origin of contamination which has been identified is the presence of brass in the sampling chain (team n°4). Similar such intercomparison has been organised in 2021 on emerging compounds like phtalates, paraben, alklphenols, ... Results will be published in end 2021. Preliminary results show good results regarding the absence of global contamination over all participants for the compounds mentioned above. Very rare contaminations have however been observed for galaxolide, caffeine, diisobutylphtalate.



Result of sampling intercomparison exercice on groundwater (X-axis : reference of the sampling team; Y-axis : concentration in the sample; error bars correspond to the variation of duplicate sampling)

3.1.3 Recommendations to reduce the risk of field and lab contamination of samples

- Make field operators aware of the risks of contamination for certain families of emerging pollutants, due to both the equipment used and the operator (personnal care products, medicines).
- Gloves are essential when handling samples and vials in field. However, for some substances it is not sufficient to guarantee the absence of contamination. Hand washing and then rinsing with clean water seems essential to limit the risks of contamination, especially for personnal care products.
- Generalize the implementation of rigorous quality control for sampling in application, for example, of the ISO 5667-14 standard. These quality controls are generally already implemented in structures accredited according to ISO 17025.
- Continue to acquire knowledge on the risks of contamination, for example through the organization of intercomparison exercises or through dedicated studies.

3.2 Stability of substances in samples

3.2.1 General aspects on stability of substances in water samples

The reliability of monitoring results for water samples is strongly dependent on the transport conditions and by the delay between sampling and analysis especially for pollutants that have a low stability. The normative requirements and the requirements transcribed in the calls for tenders are strong. In operational conditions, difficulties in applying regulatory and normative texts were raised. This concerns both compliance with a temperature of 5 ° C ± 3 ° C when transporting samples, but also compliance with the delay before analysis (for organic compounds it is often of 24 or 48h).

For “legacy” and already regulated pollutants, the stability data are generally known and make it possible to reliably define requirements for laboratories in terms of delay before analysis. For emerging pollutants, these data are often rare or absent. However, they seem essential to know in order, if necessary, to include these pollutants on regulatory or prospective lists. In France, only a few substances have unfortunately been investigated in groundwater or in water for human consumption despite their low stability in water ; the search for metabolites should have been favored (eg: captan, folpel, etc.). Therefore, it seems necessary to ensure that a new substance of interest has sufficient stability for the monitoring data to be exploitable, reliable. Otherwise, rapid identification of metabolites should be preferred.

Moreover stability data should be quickly implemented in guidelines and standards (e.g. ISO 5667-3) applied in a common way by all labs, especially in the framework of accreditation scheme, to assure comparability of practice and of monitoring data on this specific point.

The methodology of stability studies at international or European level has always been very heterogeneous and the results to conclude on stability are therefore very difficult to compare and there is an urgent need to improve this situation. Recently French standardisation committee has proposed to ISO committee a guide dedicated to stability studies. It was accepted and it will soon be published as : *ISO 5667-25 - Water quality — Sampling — Part 25: Guideline on the validation of the preservation time of water samples*. This guidance should improve the comparability of these stability data.

3.2.2 Case studies on stability of substances in water samples

3.2.2.1 Evaluation of stability of samples for various EOC after sampling

Parabene

Assoumani et al. (2018) have studied the stability in water of 4 parabens (Methylparaben, Ethylparaben, Propylparaben and Butylparaben). For the study of the stability of parabens, a preliminary study was carried out on mineral water (Evian water) and surface water, spiked at 200 ng / L for each paraben, to identify a means of stabilizing the concentrations. The results showed that acidification to pH = 3 (with nitric acid and formic acid) and freezing stabilized the concentrations of the parabens tested in these waters for 7 days. Then, a stability study was carried out, as part of an interlaboratory test, with spiked surface water stabilized with two acids (ascorbic acid and nitric acid). Nitric acid kept paraben concentrations constant for 7 days at 5 ± 3 ° C (with a maximum allowable instability of 20%).

Various emerging compounds

Moreau et al. (2016) studied the stability in water of 11 “emerging” pollutants. The substances are caffeine, anticorrosive substances (benzotriazole and tolyltriazole), plasticizer (bisphenol A), and pharmaceutical substances: carbamazepine and paracetamol, preservatives for body treatment substances: triclosan, triclocarban and parabens (methyl, ethyl, propyl). The trials were done on 2 surface waters, and 2 concentration levels.

Considering this chosen stability criteria, caffeine, bisphenol A, triclosan, triclocarban, benzotriazole, paracetamol and carbamazepine were stable for 4 days in the 4 studied conditions. For tolyltriazole, data were not sufficient to conclude either way. In the case of parabens, a very high decrease in concentration with time has been evidenced in one of the samples (from 40% to 60% decrease between sampling and day 1).

Pesticides

A stability study was carried out in 2015 by Moreau et al. (2016). This study provided information on the stability of 46 pesticides in water samples, as well as on the influence of temperature and, to a lesser extent, the content of suspended solids.

With a stability criteria of less than 20%, 8 molecules appear unstable 3 days for the 2 temperatures, these are 4.4 dichlorobenzophenone, biphenyl, captan, chlorothalonil, dichlorvos, disulfoton, folpel and terbuphos. Two molecules appear stable for 3 days at 5 ± 3 ° C but unstable at 20 ° C. These are cypermethrin and deltamethrin. All the other substances appear stable for 3 days for the 2 temperatures and the 2 matrices tested. Figure 3 shows the results for 3 contrasted pesticides.

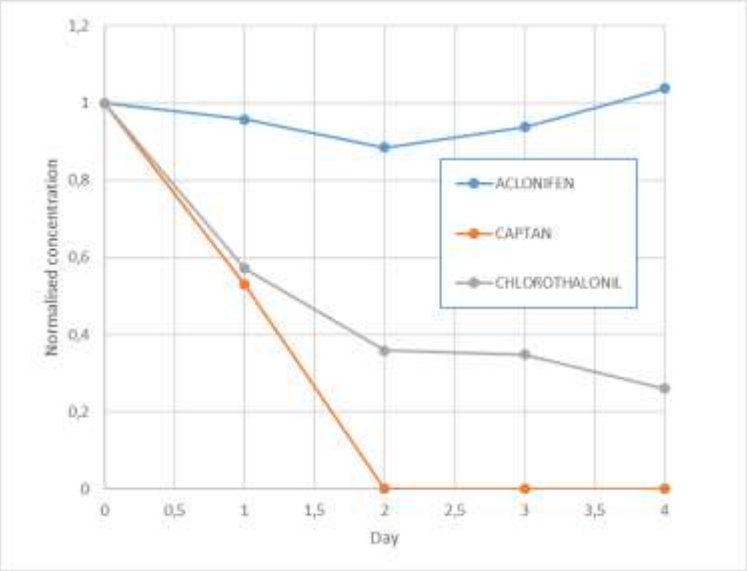


Figure 3: Stability of 3 pesticides in surface water (x-axis : day between spike of sample and analysis; y-axis : normalised concentration)

3.2.2.2 Stability of EOC in the aquifer

Koroša et al. (2020) studied the determination of mass transport in the unsaturated zone of coarse-gravel aquifer and its hydraulic properties as well as the study of transport processes of three pharmaceuticals (propyphenazone, caffeine and carbamazepine). Based on the obtained data of the unsaturated zone, the parameters of sorption (Kd) and degradation (µ, T1/2) of selected pharmaceutical were determined. Caffeine has the lowest sorption capacity (mean Kd = 0.027 L*kg-1) but decays rapidly (maximum T1/2 = 69.31 days). Sorption coefficient of propyphenazone is higher (Kd = 0.07 Lkg-1) and its degradation is slower compared to caffeine (highest T1/2 = 92.42 days). The parameters for carbamazepine could not be determined using an advection dispersion equation, which suggests more complex transport mechanisms for the compound.

3.2.3 Recommendations regarding stability of substances in water samples

- Include the criteria of substances stability among the priorisation criteria for regulation of new emerging compounds and if necessary, plan stability tests in lab to acquire data.

- Harmonization between laboratory practices for the setting of stability tests is needed. The new ISO standard ISO 5667-25 could be a good starting point for this and it needs to be implemented quickly in laboratories.

4 ANALYSIS

4.1 Different Analytical Methods

4.1.1 Classical Target methods

Analytical methods for identification and quantification of EOCs in groundwater have mostly focused on multi-residue analysis to enable rapid and sensitive simultaneous determination. The expected concentration are mainly in the low ng/L range; therefore, pre-concentration is mandatory.

The majority of established methods for the analysis of pharmaceuticals in surface waters published in recent years comprise solid-phase extraction (SPE) in combination with liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Verlicchi et al. 2014; Roberts et al. 2016; Bade et al. 2015; Patrolecco et al. 2015; Mirasole et al. 2016). Liquid chromatography combined with time-of-flight mass spectrometry (LC-QTOF-MS) has been used for nontargeted analysis of pharmaceuticals (Bade et al. 2015); gas chromatography instead of liquid chromatography is also sometimes used (Deng et al. 2003; Roberts et al. 2016; Togola and Budzinski 2008). Although gas chromatography (GC) is less commonly used as a separation method, it is suitable for non-polar, volatile substances, as well as for substances that can be converted to volatile ones by the derivatization process. The main advantage of GC is that the method is less sensitive to the substances present in the matrix, and its disadvantage is the demanding and time-consuming sample preparation (Auersperger et al., 2005; Comerton et al., 2009; Buchberger, 2011; Mali et al., 2017).

4.1.2 Screening methods with High Resolution Mass Spectrometry

High-resolution mass spectrometry techniques make it now possible to obtain a fingerprint that tends to take into account all of the substances present in a given sample. It is therefore a particularly powerful technique that could change monitoring practices in future years. Of course, this fingerprint (and the related compounds) depends on the type of chromatography used (GC or LC) and the extraction conditions. But it remains that these techniques allow access to an exceptional amount of information on the substances present in a sample, and in particular on the emerging substances it contains. The search for these compounds (not a priori identified) is called "non-targeted" analysis.

Work on "non-targeted" analysis has grown significantly in recent years in many areas related to the measurement of micropollutants (Bade et al., 2015; IKSR, 2015; Ruff et al., 2015; Schlabach et al., 2013; Schymanski et al. 2014a; Schymanski et al., 2014b; Schymanski et al., 2015). Thus, this type of activity has particularly developed widely in the field of food analysis. In the environmental field, much work is now focused on improving knowledge for the implementation of this technique. At European level, some of the main players in this field are part of the NORMAN network (https://www.norman-network.net/). Most of NORMAN's activities within the framework of the physicochemical analyses component are currently dedicated to this theme.

Most of the current applications of the technique relate to its use in the context of campaigns intended to identify new compounds to be monitored. HRMS has great advantages for this purpose. It allows:

- A search by the "targeted / suspect screening" approach of any large list of molecules established before or after the acquisition of the chemical fingerprint.
- Research in samples previously analyzed and whose fingerprint has been properly banked. A "recent" molecule of interest (that is to say brought to light by new analyzes or new knowledge) can thus be searched in samples / extracts analyzed beforehand and initially processed to respond to a list not including this molecule.
- A search by “non-targeted” approach, allowing the structural identification of the molecules present in the sample. This approach can be particularly long and complex.

The great power of these new approaches is the possibility of being able to set up retrospective “analyzes”. The possibility of being able to search in a set of already banked mass spectra, the presence of a newly identified compound allows better reactivity at lower cost (for a first qualitative approach, no need for a new sampling campaign / d 'to analyse). The overall set of samples may be partially exploited depending on local specificities. Being able to answer different questions from a set of banked data makes it possible to predict (temporally and spatially) the number of stations monitored which can be operated differently depending on the problem posed.

The contributions of these new technologies for surveillance nevertheless go hand in hand with an increase in analytical complexity compared to current techniques. The novelty of these approaches leads to a lack of validation of methodologies, an absence of a methodological guide. It should also be noted that HRMS methods may prove to be less sensitive than current targeted methods, because by definition less specific. Molecules requiring very low detection limits may not be able to be observed (eg hormones). Finally, the effect of the preparation of the extract must be considered because this step can operate a selection on certain molecules which are nevertheless present in the sample (Togola et al., 2015).

4.1.3 Passive sampling as a tool for identifying CECs in groundwater

The presence of contaminants of emerging concern (CECs) in the groundwater results also in an increasing demand for sensitive and reliable monitoring tools. In the groundwater, there is a high possibility that CECs are present in concentrations below the limit of quantification (LOQ), and several of them below the limit of detection (LOD) at ppt and sub-ppt levels. The assessment of water quality requires also developments in appropriate sampling technology. Passive sampling has been proved as a useful monitoring tool also for CECs in the groundwater (Mali et al., 2017; Pinasseau et al. 2019; Caban et al., 2021). It allows continuous monitoring over an extended time period and determining time-weighted average water concentrations of contaminant. Compared to the classical sampling methods, the cost for analysis of the passive sampler is lower, due to the relatively simple sample treatment, limited matrix interferences, and considerably lower detection limits. With such sampling technique, we can also determine a big range of unknown and unspecified compounds in groundwater.

4.2 Risk of contamination in the lab

In the same way as for sampling operations (see 3.1), analytical operations can be source of contamination, in particular for families of substances found in products, materials of common use (plasticizers, body care products ,…).

In the laboratory, the control of these risks is essential to guarantee the quality of results. As for sampling, it involves performing internal quality control and in particular blank or duplicate analysis at each chromatographic run.

4.3 Precise reference of the substances to be monitored / analytical standards

4.3.1 General aspects on the identification of substances to analyse for in groundwater

The clear identification of the substance or of the parameter that has to be monitored appears for a non-specialist as a quite an easy task. But from an analytical point of view, it is more and more an important challenge due to the complexity of some new substances, and sometimes due to the evolution of analytical methods (which now can identify, in some cases, different forms of a substance that were not identified before). Moreover, in some cases there may be confusion between the forms sold or marketed and the chemical forms that the laboratory will have to analyse.

Before a new substance is added to a monitoring campaign, or to a list of regulatory compounds, it appears necessary to include a step of chemical/analytical validation by chemical experts. This step will have the objective to define as precisely as possible the molecule to be monitored and especially the relevant form from the laboratory point of view.

This step should also guaranty better exchange of data at European level by assuring that one substance will have the same reference in all countries. This could require some common conventional rules regarding the definition of substance in the database: it is for example the case for acid/saline forms, enantiomeric forms, … (eg : perfluorooctane sulfonate or perfluorooctane sulfonic acid, metolachlor vs S metolachlor, …).

4.3.2 Case studies on the identification of substances to look for in groundwater

4.3.2.1 Nonylphenols

The first EQS directive (2008/105/CE) listed priority substances and set Environmental Quality Standards for surface water. In its 2008 version the family of alkylphenols has been added, with in particular the substance 4-nonylphenol to which has been associated the CAS number 104-40-5 and an EQS of 0.3 (annual average). The alkylphenol family is a family which includes both linear and branched forms. Linear forms are not relevant from an environmental point of view. However, the form added in the version 2008 of the directive is linear nonylphenol. Therefore, under the same term of 4-nonylphenol but with an imprecision on CAS number, many monitoring data have been acquired and turned out to be irrelevant. The directive was modified in 2013 (2013/39/UE) and the CAS number was changed, now referring to para-branched forms.

(CAS 84852-15-3). However before this correction, chemical status assessment has probably been biased.

4.3.2.2 Metolachlor and S Metolachlor

Some pesticides are composed of several enantiomeric forms (same molecule but with different geometric forms), which can have very different efficacy on crops. Approvals are given on a case-by-case basis, on products incorporating all the enantiomeric forms or more specifically on products enriched with the more efficient enantiomer. Some products, mixtures of various enantiomeric forms, are sometimes replaced several years later by products enriched with the most effective enantiomer. This is the case with metolachlor which has been replaced by the product of commercial name “S metolachlor”.

Monitoring of “S metolachlor” can lead to ambiguities between maintaining monitoring of the total metolachlor form or the very specific measurement of the S enantiomeric form of metolachlor. These ambiguities and the lack of rules on this point can lead to confusion in the databases and to a lack of comparability in the data.

4.3.3 Recommendations for identifying the right substances to look for in groundwater

- In the framework of emerging compounds monitoring, include chemical expertise in the definition of the parameters to be analysed by laboratories

- To assure a better coherence of European and international database, harmonization and therefore conventional rules seems necessary for the definition of some chemical substances

5 OTHER ANALYTICAL ASPECTS

5.1 Limit of quantification

The European Directive 2009/90/EC aims to provide an assurance and quality control framework for analyses carried out in monitoring programs linked to the European Water Framework Directive (WFD).

This directive imposes in particular requirements concerning the performance of the analytical methods to be used for the WFD. Other requirements relate to laboratory quality assurance systems as well as the quality controls to be applied (interlaboratory tests and reference materials). The two main performance criteria mentioned are:

- The method's limit of quantification must be less than 30% of the environmental quality standard (EQS)
- The uncertainty in the EQS must be less than 50% (k = 2).

In addition to the strict requirement of the Directive, the issues linked to the concept of limit of quantification are very important. This is a method performance criterion:

- which can potentially be an element of competition between laboratories,
- which is often a contractual element between client and laboratory,
- which constitutes very important information for the quality of the result (the uncertainty is particularly high around this concentration)

In general also, environmental concentrations are often very close to the limits of quantification, hence the importance of mastering this notion and the performance of the method at these levels. Especially, the estimation of limit of quantification has a great impact in environmental monitoring data through the calculation of frequency of quantification, which is an important parameter of assessment on emerging compounds.

Unfortunately, the notion of "limit of quantification" is a poorly defined notion (Mermet 2008). Many different definitions exist as well as many estimation methods. Directive 2009/90/EC proposes a definition resulting from a consensus but which not allow a harmonization of practices on this point.

Schematically, two main “methods” are applied :

- One method is based on the determination of standard deviations on blank samples or on the evaluation of the signal-to-noise ratio. Generally this method doesn’t give any information on trueness /biais at the LOQ level and so give no information on a minimum level of uncertainty that could be necessary.
- Other methods use spiked samples at the target LOQ and confirm that a given level of accuracy (biais and precision) can be achieved at this level.

More harmonization of this notion seems necessary. The recent revised standard CEN/TS 16800 “Guideline for the validation of physico-chemical analytical methods” has made a step forward by presenting these two main approach and by proposing a way to differentiate them.

One important point to assure representativity of the LOQ parameter is that its estimation should be done through experimental tests on samples representative of the future monitoring and not on deionised water.

5.2 Quality control

To ensure the reliability of analytical results, laboratories must perform complete and detailed validations of the analytical methods they have developed. In the same way as for the limit of quantification, this validation must be carried out:

- According to standardized methods which make it possible in particular to estimate the fundamental parameters of a method, namely trueness and precision.
- On samples representative of future samples to be analyzed.

After this initial implementation, laboratories must also set up internal (blank, replicate, …) and external quality controls. This is a requirement of accreditation scheme according to ISO 170215. External quality controls based on “references” external to the laboratory are particularly important as they allow faster progress towards data comparability by limiting method effects between laboratories.

These external quality controls are mainly of 2 types:

- Certified reference materials. This type of material exists quite regularly for solid matrices but, in the case of the water matrix and therefore of groundwater, it is almost non-existent for organic compounds because of the difficulties linked to the stability of these substances.
- Interlaboratory tests which allow, on the same sample, to verify the results obtained by different laboratories

Interlaboratory tests are therefore particularly important tools for making progress at a national or European level on the reliability of water analysis results and also, for contractors, to know the dispersion of results that they can expect from the profession of laboratories on a given parameter, beyond the uncertainty provided by the laboratory.

With regard to so-called emerging pollutants, these tests are most often absent and laboratories must therefore be satisfied with internal controls of their results. This situation is not at all satisfactory and can be a source, as already indicated, of differences between methods or laboratories.

Therefore it appears essential that the stakeholders in charge of monitoring campaigns on this type of substance can facilitate or ensure the implementation of this type of test at national or European level. The faster this implementation, the more limited the risk of outliers or non-comparable data will be.

5.3 Uncertainty

The notion of uncertainty can cover many aspects, from the compound recovery when analysing the concentrations of emerging compound in lab, to the sampling uncertainties. The point is that it is important to bear in mind that it is not possible to consider an emerging compounds concentration value in groundwater without taking into account a significant percentage of error, especially for results reported closed to the limit of quantification.

5.3.1 Analytical compound recovery

First, it may cover the uncertainty of the results of the analysis. These uncertainty estimates, even if they remain complex, are now well managed by laboratories according to well-established normative standards (GUM, ISO 11352, etc.). For some emerging compounds that are difficult to analyse, uncertainties level up to 60-70% (k=2) can be observed in interlaboratory exercise. Near limits of quantification such level of uncertainties are classically observed. These levels, especially for emerging compounds for which there are few available data, need to be taken into account by river basin managers when evaluating trend, comparing results coming from two laboratories or from two different sites sampled at different times. Comparing results without reliable information on uncertainty is challenging.

Laboratories accredited according to the NF EN ISO 17025 standard have the obligation to be able to provide their customers with uncertainty assessments. The way in which uncertainties are presented is particularly important in order to avoid sources of confusion. Thus, an uncertainty must always be related to a concentration level (uncertainties increase when the concentrations are close to the limits of quantification) and an uncertainty must always be accompanied by information on the coverage coefficient used (as a general rule a coefficient of 2 is used for a probability of 95%).

5.3.2 Sampling uncertainties

Uncertainty can also relate to sampling uncertainties which are much more difficult to estimate. Very little data is therefore available to date to assess these uncertainties.

Finally, the estimates may relate to the indicators used by managers through the notion of the level of confidence associated with these estimates and in particular with the assessment of the chemical state of water bodies. This estimate of the confidence level of the chemical state assessment is currently carried out more or less empirically or expertly by the people in charge of European reporting. There is in fact no nationally defined method and the parameters to be taken into account for its estimation are now essentially qualitative. While these parameters appear to be quite relevant for estimating the overall confidence level of the condition assessment exercise, they are nevertheless insufficient and must be supplemented by information on the statistical uncertainties associated with the calculations of the annual mean and detection frequency estimators. It is indeed important for managers to have information on the uncertainties relating to the estimators of the chemical state of the bodies of groundwater that they calculate.

Croiset et al. (2016) have proposed a method in order to estimate the uncertainties relating to the calculations of the average of the annual means (Mma) and of the frequency of exceeding the threshold value (Fd) according to the behavior of the chemical element studied, the uncertainty associated with the measurements and the sampling schedule. The method followed is based on the generation of virtual chronicles, the parameters of which are known and mastered. The estimators Mma and Fd were calculated on these time series and the variability of these results as a function of the variation of the parameters defining the chronicles was investigated. The results show that the uncertainties associated with the calculation of the Mma and the frequency of exceeding the threshold can be particularly high, and therefore the assessment of the chemical status can be biased; they can also help the manager when establishing a monitoring program, to optimize monitoring according to the characteristics of each water point. A graphical interface named Hypst-R has been developed.

6 CONCLUSION

The objective of this report is to identify key points relating to the monitoring of groundwater (sampling and analysis) by focusing on the monitoring of emerging compounds. What emerging compounds have in common with regard to monitoring is that, by definition, these pollutants are often poorly described, some of their characteristics relating to sampling or analysis are poorly known. In order to ensure from the beginning of monitoring that the data will be reliable and interpretable, it is important to specify these characteristics as quickly as possible.

In recent years, sampling has been recognized as a key point in the measurement chain and for its quality. More and more pollutants are commonly used pollutants in domestic life such as body care products, plasticisers. These pollutants therefore pose important questions related to risk of contamination and therefore anomalies in the results. These risks can occur in the lab but also on the field during sampling. It is therefore recommended that the sampling teams should be informed of these risks and that they regularly set up quality controls to identify and control for them.

The delay between sampling and analysis is also an important parameter. Some pollutants are not very stable in water samples and require rapid analyses and / or monitoring of metabolites. Taking into account the stability characteristics of the new substances to be monitored is an important parameter for setting the requirements for laboratories and checking that degradation products are not more relevant to monitor.

Regarding analysis, new methods using high-resolution mass spectrometry and allowing the acquisition of a complete "fingerprint" of a sample are methods of the future, particularly for the monitoring of emerging pollutants. In fact, they make possible the acquisition of information on the sample in a non-targeted way and then, if necessary, via retrospective analyses, the search for the presence of substances from a large list of pollutants in a "screening" approach. It is also possible to search a posteriori for a new substance of emerging interest.

Especially for new contaminants, the chemical expertise of laboratory staff is necessary for a good definition of the parameters to be analyzed. For certain types of substances, common rules should also be set to facilitate data exchange at European level by ensuring that the same names and protocols are used in the different countries.

Finally, the validation of analytical methods remain, for emerging pollutants as for other pollutants, important elements of the quality of the results. Progress in the harmonization of limit of quantification concepts which directly impact the estimates of quantification frequencies particularly used by managers, still seems necessary. In addition, it is necessary, especially for emerging pollutants that all the concerned actors (stakeholders, laboratories) mobilize so that external quality controls such as inter-laboratory tests are put in place very quickly. They significantly improve the comparability of data.

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