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Combining passive sampling with suspect and non-target screening (NTS) to monitor groundwater quality

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Report

Combining passive sampling with suspect and non-target screening (NTS) to monitor groundwater quality

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Management samenvatting

Combinatie van passive sampling met non-target screening helpt bij vroegtijdige detectie van grondwaterverontreinigingen

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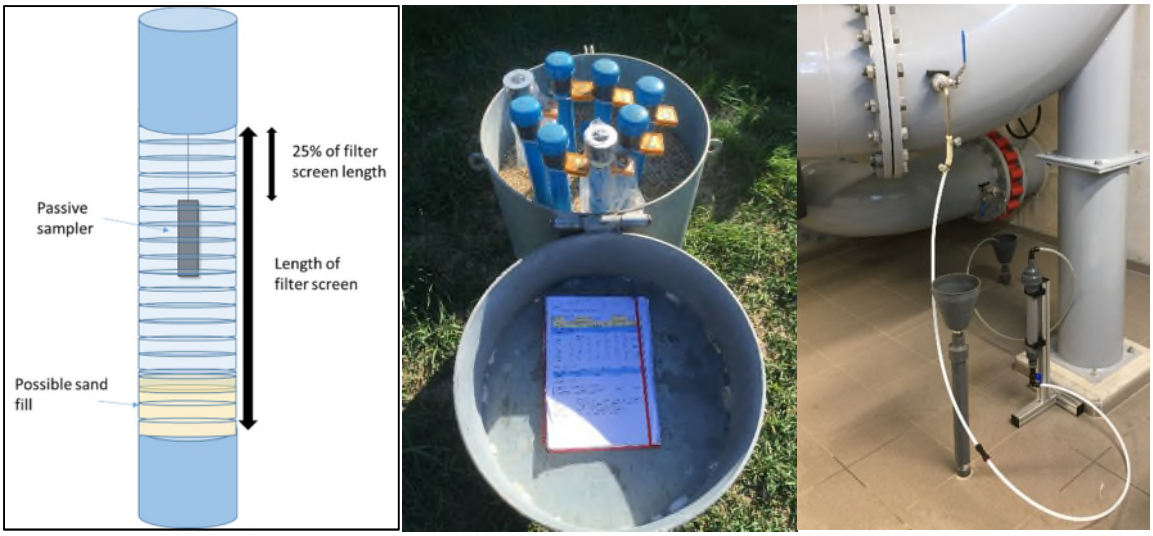
Suspect en non-target screening (NTS) is een bekende techniek om te identificeren welke stoffen (features) aanwezig zijn in watermonsters. Tijdens een pilot op pompstation Lith bleek dat er 20 keer meer stoffen in het grondwater zijn aangetroffen door NTS te combineren met *passive sampling*. De combinatie van *passive sampling* en NTS kan daarom een nuttige aanvulling vormen op de huidige grondwatermonitoringsprogramma's van drinkwaterbedrijven. Deze combinatie van technieken maakt het namelijk mogelijk om in een vroeg stadium te identificeren welke stoffen potentieel problematisch zijn voor de toekomstige ruwwaterkwaliteit. Dit biedt meer ruimte om maatregelen tijdig in gang te zetten. De geïdentificeerde stoffen kunnen bovendien worden toegevoegd aan de reguliere monitoring middels conventionele doelstofanalyse.



Links: Conceptuele weergave van een passive sampler in een monitoringsput. Midden: Monitoringsput met daarin twee passive samplers op verschillende dieptes. Rechts: flow cell met daarin een passive sampler aangesloten op de hoge druk leiding voor het meten van de ruwwaterkwaliteit

Belang: toenemende druk op grondwater vereist alertere kwaliteitsmonitoring

Grondwater vormt wereldwijd een belangrijke bron voor de drinkwaterproductie. De kwaliteit van het grondwater staat echter onder toenemende druk doordat er een veelvoud aan antropogene stoffen in het milieu terechtkomt. Monitoring vindt meestal plaats middels doelstofanalyse, maar dit heeft als belangrijke tekortkoming dat slechts een zeer beperkt aantal stoffen wordt bemeten. Mogelijk blijven veel verontreinigingen hierdoor buiten beeld of worden ze onnodig laat geïdentificeerd. Het beter kunnen detecteren en anticiperen op toekomstige verontreinigingen in ruw water vereist dus een alertere grondwatermonitoringsaanpak.

Aanpak: toepassing van *passive sampling* voor grondwatermonitoring

Afgelopen jaren zijn verschillende studies uitgevoerd naar de afzonderlijke toepassing van NTS en passive sampling in waarnemingsputten. NTS maakt het mogelijk om veel meer, vaak onbekende stoffen, te identificeren vergeleken met doelstofanalyse. Nadeel is dat de methode nog weinig gevoelig is (hoge detectielimiet). Met passive sampling kunnen stoffen al bij lagere concentraties gedetecteerd worden door deze te concentreren in een *sorbent.* Maar de techniek wordt meestal slechts toegepast op een beperkt aan tal stoffen (doelstofanalyse).

In dit onderzoek zijn de sterke punten van beide gecombineerd en toegepast op zowel waarnemingsputten als het gecombineerde ruwe water van pompstation Lith (Brabant Water). Hiertoe is een speciale flow-cel ontwikkeld. Daarnaast zijn als referentie steekmonsters genomen (grab samples) op dezelfde locaties. Alle grondwatermonsters zijn geanalyseerd met en *suspect en non-target screening* (NTS)-methode. Tot slot zijn suspect analyses uitgevoerd om inzicht te krijgen in de aanwezigheid van toxische stoffen.

Resultaten: Met passive sampling detecteert NTS 20 keer meer stoffen

Toepassing van NTS op de *passive samples* leverde in sommige locaties bijna 20 keer zoveel stoffen op als NTS op de steekmonsters. Bovendien kon aan de hand van de eerder ontwikkelde prioriteringsaanpak (Brunner et al., 2019) een reeks potentieel toxische verbindingen worden geïdentificeerd die met de conventionele doelstofanalyse onopgemerkt bleven. Het onderzoek laat dus zien dat *passive sampling*, in combinatie met *NTS*, sneller leidt tot de detectie van chemicaliën.

Toepassing: *passive sampling* in combinatie met *NTS* als onderdeel van monitoringstrategieën

De resultaten van dit onderzoek tonen aan dat *passive sampling* in combinatie met *NTS* een veel breder scala aan chemische stoffen kan detecteren, waarvan sommige potentieel toxisch zijn. Dit is een sterke verbetering ten opzichte van het conventionele meetprogramma, waarmee zo'n breed scala niet wordt gemeten. Het grote scala aan stoffen, in combinatie met de gevoeligheid van de methode, maakt het mogelijk sneller te anticiperen en reageren op de bedreigingen voor een grondwaterwinning. De resultaten van de passive sampling kunnen bovendien helpen om de routinematige monitoring via doelstofanalyse regelmatig te verbeteren en uit te breiden met de stoffen die een actuele een bedreiging vormen. De ontwikkelde aanpak heeft dan ook een belangrijke toegevoegde waarde voor de monitoring van grondwaterbronnen.

Belangrijke vervolgstappen zijn het doorontwikkelen van deze methode voor zeer polaire stoffen en het ijken van de passive samplers met in-situ calibraties om ook concentraties af te kunnen leiden.

Rapport

Dit onderzoek is beschreven in het rapport ***Passive sampling and suspect and non-target screening (NTS) to monitor groundwater quality*** (BTO-2021.001).

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Contents

1 Introduction

The BTO project "Early Warning Systems for the quality monitoring of water resources for drinking water production" focuses on evaluating new techniques that can potentially improve current early warning systems (EWS) used to monitor the quality of ground- and surface water used for drinking water production. From this literature review, passive sampling was identified as a promising method to improve early detection of a wide range of substances in sources for drinking water, in particular groundwater (Been & Beernink, 2019). Passive sampling is per se not a monitoring technique but rather a (time-integrated) sampling approach. The latter point is what makes it particularly interesting for monitoring purposes as it allows to monitor the presence of potential contaminants in drinking water sources over longer periods of time, hence also at lower concentrations, rather than providing only a snapshot of the chemical composition, as is the case with conventional grab sampling approaches. Given the limited spatial and temporal monitoring data, passive sampling represents an interesting addition to complete our current view about occurrence of contaminants in drinking water sources.

Groundwater is the most important source for drinking water in the Netherlands and also on a global scale essential as a source for drinking water production (Giordano et al., 2009; Vewin, 2017). Groundwater quality can be affected by e.g. salinization (e.g. in coastal zones), agricultural activities and other users of the subsurface (e.g. geothermal energy) (van der Aa et al., 2014; van Loon et al., 2019). To verify suitable groundwater quality and as an early warning signal for deterioration of the groundwater quality monitoring of the groundwater is needed. Conventionally, grab samples are taken from A) monitoring wells in the proximity of the groundwater abstraction site and B) from the raw water mix that enters the treatment facility on a scheduled basis (e.g. each 2 months). Large data gaps are therefore present in the monitoring system (both in time and spatially), and it is likely that not all pollutants are being measured (Been & Beernink, 2019).

An alternative approach to conventional grab sampling is provided by passive sampling, which relies on the use of *in situ* sampling devices that are deployed in the exposure medium and selectively accumulate contaminants on a sorbent. The type of sorbent used determines the substances measured by the passive sampling device; for instance, the ion-exchange Strata X-AW, TiO2, and Oasis® HLB (divinylbenzene/N-vinylpyrrolidone copolymer) have been used for the determination of polyfluoroalkyl substances (PFASs), glyphosate, and polar organic compounds in groundwater, respectively (Fauvelle et al., 2017; Kaserzon et al., 2019; Soulier et al., 2016). After exposure, contaminants accumulated on the sorbent are extracted and analysed with a suitable analytical technique. Due to their ability to pre-concentrate contaminants, passive sampling devices provide lower detection limits compared to conventional grab sampling. In addition, passive sampling extracts are generally free of substances which could contribute to matrix effects due to the ability of the sorbents to selectively accumulate substances based on their physicochemical properties. These features make passive sampling a desirable approach for monitoring harmful chemicals in drinking and groundwater, in particular when these are present at low concentration. Recently, Deltares published a report in which passive samplers were deployed to monitor the presence of crop protection chemicals, pharmaceuticals and volatile organic compounds in groundwater aquifers of WML (de Weert, 2019). In their study, three different types of samplers were employed, namely for hydrophobic (e.g., silicone rubbers), hydrophilic (i.e., Empore® (3M) and Atlantic® (Biotage) disks) and volatile organic compounds (e.g., polydimethylsiloxane (PDMS)). With respect to monitoring polar compounds, Atlantic disks are the most appropriate among those tested in the abovementioned study because they use an HLB polymer, which allows to cover a broad range of polarities (i.e., logKow). The authors also considered using POCIS and Speedisk sorbents, however commercially available devices are too large for deployment in monitoring wells (de Weert, 2019). The authors also used performance reference compounds (PRCs), which were added to the silicone rubber passive samplers to determine the volume of water sampled and can hence be used to estimate concentrations. PRC

results from silicone rubbers was used to extrapolate the volume sampled by the passive samplers for hydrophilic compounds. This was done because PRCs cannot be used directly with Empore and Atlantic disks because they are too strongly adsorbed on the material (de Weert, 2019). After deployment and extraction, the passive samplers were analysed using targeted methods, in particular gas and liquid chromatography coupled to tandem mass spectrometry (i.e., GC-MS and LC-MS/MS). While targeted methods are very effective to detect trace amounts of potentially harmful substances, these approaches are limited with respect to the number of chemicals that can be traced. In particular because they require prior knowledge about which chemicals to analyse. Another study (de Weert, 2020), looked at the possibility of combining passive sampling with suspect and non-target screening to extend the number of chemicals which can be detected at groundwater abstraction points, however, to the authors' knowledge, the study is still ongoing or results have not been published yet.

Suspect and non-target screening (NTS) using high-resolution mass spectrometry (HRMS) has been increasingly used to monitor groundwater quality as it allows to detect the presence of suspected compounds which are not only part of the routine monitoring (i.e., "known unknowns"), but also to detect and identify unexpected and previously unknown chemicals (i.e., "unknown unknowns"). However, while great technological improvements have been done in recent years, HRMS instruments are still characterized by lower sensitivities compared to targeted approaches. Preconcentration methods (e.g., solid-phase extraction) are sometimes employed to overcome these limitations, however these are time consuming and might increase matrix effects.

Hence, the goal of this study was to evaluate the added value of combining passive sampling and NTS to monitor the quality of groundwater in comparison to conventional grab sampling and targeted analysis. Particular focus was set on polar chemicals, which are known to be more problematic for drinking water production because of their recalcitrance to removal during drinking water treatment processes. For this purpose, two groundwater monitoring wells and two groundwater pumping stations at the drinking water abstraction point of Lith (currently operated by Brabant Water) were investigated. Moreover, a dedicated sampler casing and a device to sample water from pressurized pipes were developed and implemented in this study. This study aims at evaluating the possibility of using passive sampling in combination with NTS for early detection of potential chemical contaminations in groundwater.

Three potential main advantages that were specifically evaluated for the use of passive sampling combined with NTS compared to either conventional grab sampling or passive sampling coupled to targeted analyses:

- Obtain a time-integrated overview of pollutants present in groundwater sources;
- Detect trace level contaminants which are currently not part of routine monitoring;
- Screen for a broad range of polar chemicals without being limited by prior knowledge about which chemicals to analyse.

2 Materials and methods

2.1 Case study

The passive samplers were tested at a drinking water production location of drinking water company Brabant Water (BW). This production location consists of 8 groundwater wells which are activated irregularly, on average 3 to 4 wells are active at once continuously. Around the pumping wells, monitoring wells are placed at varying depths and distances from the abstraction wells. Two of these monitoring wells were monitored with the passive samplers at two depths, resulting in 4 measurement locations. Next to this, two locations were chosen for the flow cell measurements. One abstraction well, that was manually adjusted so that it was active during the entire measurement period and the raw water mix (mix of the active groundwater wells). Pictures of the field work can be found in Appendix I.I, I.II and I.III.

2.1.1 Monitoring locations

Two monitoring wells were chosen that are measured frequently in the standard monitoring procedure of the water company. One monitoring well was placed north ('monitoring well north') of the pumping wells (300m distance) and one location placed west ('monitoring well west') of the pumping wells at 150m distance from the pumping wells (Figure 1). Based on both the field samples (e.g. pH, EC, temperature) and the measured grab samples it is concluded that 3 out of 4 monitoring wells are not leaky. Monitoring well 0348-pf04 (deep screen of Monitoring well North) however shows an increase of electrical conductance (Dutch: EGV) during the cleaning of the well before deployment of the passive sampler, which could point to a leaky well (Appendix IV). The passive sampling results could probably also clarify this. Nevertheless, the pre-defined monitoring wells were used for the passive sampling measurements because measuring other/more substances due to a leaky well might also be an interesting result. The raw drinking water is measured at two locations in the system, directly from one of the pumping wells, and, from the combined flow of active pumping wells called the 'raw water' (Figure 1). Additional information about the geohydrology of the monitoring locations is provided in Appendix VI.

Figure 1: Overview of the case study site with the 4 measured locations. Dashed line indicates locations where the developed flow cells were employed. For each monitoring well a deep and shallow screen was used to be measured, resulting in a total of 4 monitoring well measurement locations.

2.2 Passive sampler

Because monitoring wells are an essential part in the early warning system for groundwater sources for drinking water production, the passive sampler should be usable in all types of monitoring wells. In the Netherlands the size of monitoring wells can differ, but the smallest diameter most commonly used is 1 inch. To the best of our knowledge, commercially available passive sampler casings are generally larger, hence a custom casing was designed in the context of this study.

2.2.1 Sampler casing

The casing was made of stainless steel and consists of three parts as shown in Figure 2. The main body of the casing has a 2mm deep notch on each side where two sorbent pads can be placed (more details are about the sorbent used are provided below). Once the sorbent pad is placed on the casing, a stainless-steel cover is screwed on each side of the main body to keep the sorbent in place. The top and bottom of the casing have a hole to connect a locking pen, which itself was connected to a stainless-steel wire to hang the casing during deployment in monitoring wells or flow cells (more details below). In the case of groundwater monitoring wells, the length of the wire was chosen so that the passive sampler hangs at the depth of the filter (see Figure 5). The other end of the wire was connected to the top of the well casing and sealed with a plastic cap to ensure that no water can enter the well (Appendix I.II). All materials (i.e., casing, wire, locking pen, screws) were thoroughly cleaned with ultrapure water, MeOH and acetone prior to deployment.

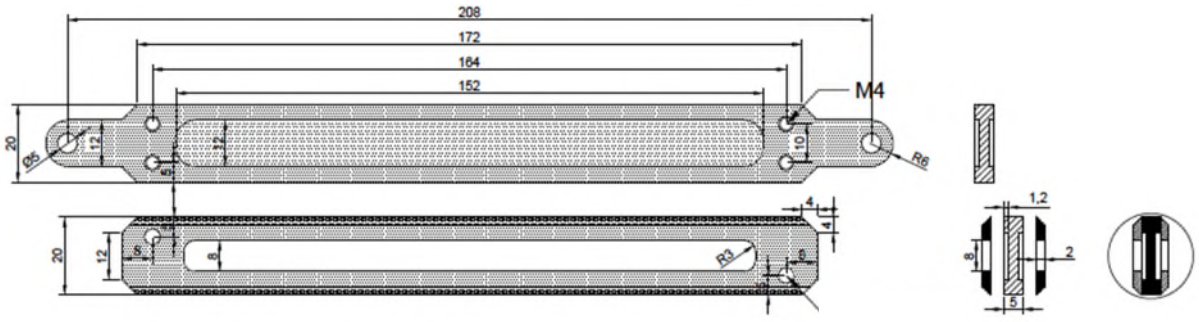

Figure 2: Scheme of the designed casing for the passive samplers. Surface area of the well to place the sorbent is approximately 182.4 cm2. Sorbent exposed area (after cover is placed) is equal to 121.6 cm2.

2.2.2 Flow cells

This study also aimed at deploying passive samplers to monitor the quality of water at two groundwater pumping stations (additional details about the specifications of the pumping stations are provided below). To avoid having to introduce the passive samplers into pressurized pipes, a device was developed which allows to deviate part of the water stream from the pressurized pipe to the passive sampler. The device, referred to as a “flow cell”, consisted of a sealed PVC cylinder (2.5 cm radius, 40cm length) in which the sampler casing can be hanged (see Figure 3). The bottom part of the flow cell was equipped with a connector, to which a Teflon tubing (10 mm ID) was attached. The latter was then connected to the sampling faucet on the pressurized pipe. The top part of the flow cell was equipped with a similar Teflon tubing used to evacuate the water after it flowed through the flow cell. Prior to deployment, all flow cells were cleaned with approximately 50L of ultrapure water. Subsequently, the flow cells were cleaned with MeOH and acetone. Similarly, all tubing and connectors were thoroughly cleaned with ultrapure water, MeOH and acetone prior to deployment.

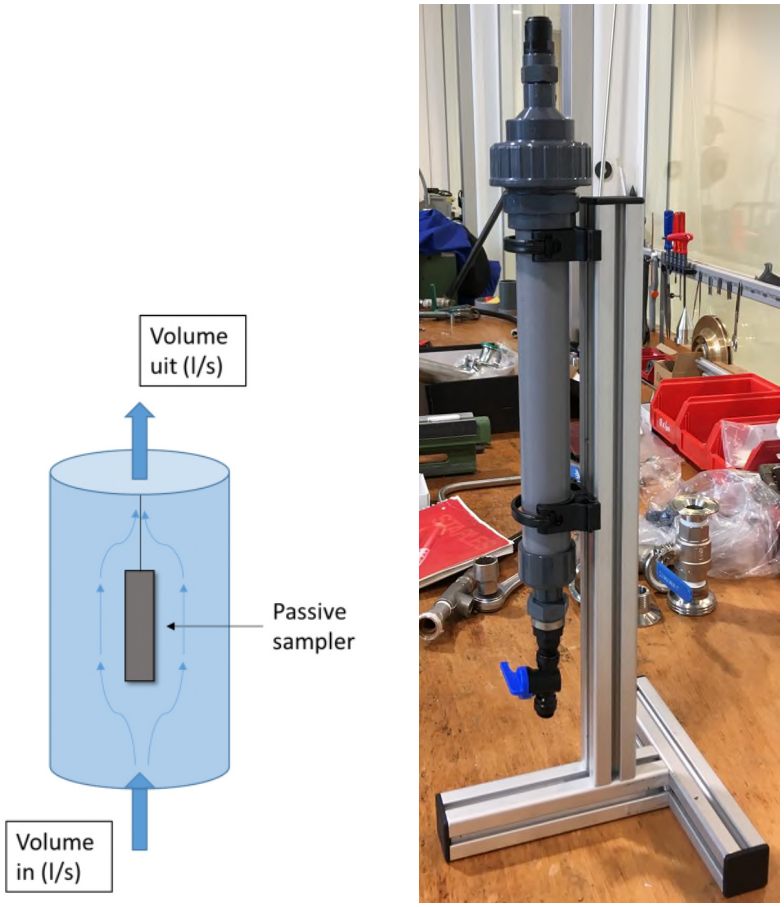

Figure 3: Right: schematic representation of the flow cell used in combination with the passive sampler. Left: picture of the flow cell on its stand.

2.2.3 Sorbent

Hydrophilic lipophilic balance (HLB) was used as a sorbent in the context of this study. HLB consists of vinyl pyrrolidone divinylbenzene copolymer with polar functionalities (see Figure 4) which is commonly used to extract a wide range of acidic and basic (i.e., polar), as well as neutral compounds in water samples (Mills et al., 2014). HLB was purchased as custom made of 10 x 20 cm pads (Affinisep, France), which were cut with razor blades to fit the size of the dedicated compartment on each side of the passive sampler casing. Each pad had a surface area of approximately 182.4 cm2 while the exposed area (after placing the cover) was equal to approximately 121.6 cm2 (see Figure 2). After being prepared and placed on the casings, the samplers were placed in sealed glass bottles previously cleaned with water, MeOH and acetone and stored at 4°C and in the dark until deployment. All equipment used to prepare the sorbent pads was thoroughly cleaned with ultrapure water, MeOH and acetone prior to usage.

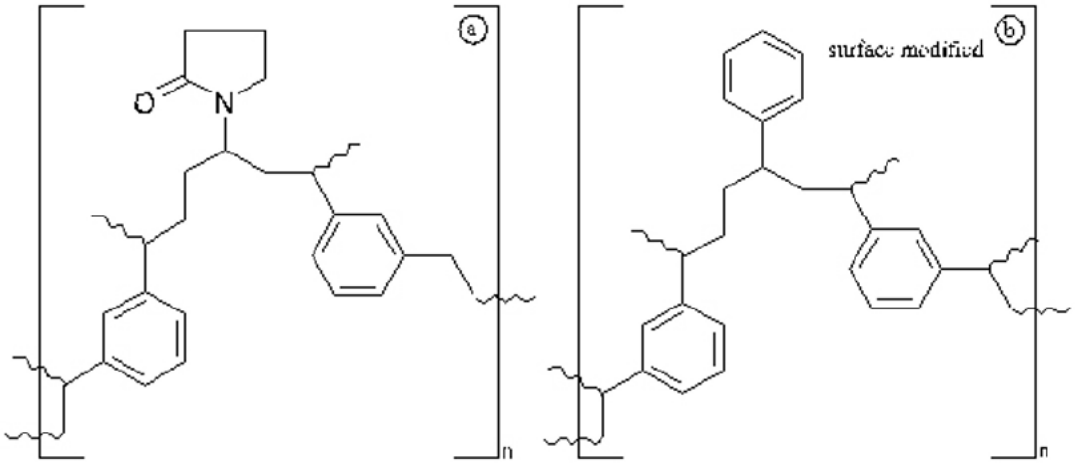

Figure 4: Structure of the HLB polymer, i.e. vinyl-pyrrolidone-divinylbenzene (Qureshi et al., 2011).

2.3 Groundwater monitoring wells

2.3.1 Deployment of passive samplers

Casings were attached to a stainless-steel wire and deployed at the pre-defined depth. The length of the wire was set so that the passive sampler attached 25% beneath the top of the filter that was measured (Figure 5). This was done by checking the distance between the top of the monitoring well and the top/bottom depth of the screen that was being measured (
Table 2).

The wire was attached to the top of the well. Before deployment of the passive sampler, the monitoring well was flushed clean and grab samples were taken. This process is done following a pre-defined protocol (Appendix I.IV). Basically, the protocol ensures that the proper parameters are measured during the cleaning of the well to A) check if the well is (not) leaky[1] and B) to make sure that the groundwater well is flushed clean when starting the measurements. In total, the total volume of the well is pumped minimally 3 times out of the well to clean the well. During and after flushing of the monitoring well grab samples were collected. This ensures that the water quality being measured in the well represents the water quality of the groundwater around the well. During the deployment of the passive sampler it is expected that the water inside the well is representative for the water quality in the surrounding of the well screen. How large the representative aquifer volume actually is depends on the movement of the groundwater (e.g. regional groundwater flow, due to drinking water abstraction). In principle, only the grab sample taken after the flushing of the tube were analysed and used to compare to the passive sampler results. However, if the well seems to be leaky, the grab sample that was taken during the flushing can also be analysed.

The depth of the screens that were being measured were based on the depth of the screens of the abstraction wells (~20 to 50m depth). The screens are situated in the formation of “Beegden” and the formation of “Sterksel”. The upper monitoring screen that is measured at the two locations is therefore higher in the subsurface, the deep screen is at the same depth as the abstraction (Appendix I.VI). If we assume that most pollutants come from the ground level, it is expected that more pollutants can be found in the upper well screen. The measurements took place in the beginning of 2020, the passive samplers were deployed for ~2 months (Table 1).

Table 1 The measurement period of the passive samplers (~2 months).

Name of location	Deployment of passive samplers	End date
B45B0348-pf1	20-2-2020	22-4-2020
B45B0348-pf4	20-2-2020	22-4-2020

[1] When a well is leaky water from the ground level can enter the well at the top and seep to the depth of the well filter screen

B45B0334-pf3	21-2-2020	22-4-2020
B45B0334-pf6	21-2-2020	22-4-2020

Table 2 Code, depth and steel wire length for the 4 groundwater monitoring well locations

Well code	Screen number	Ground level (m +NAP)	Top monitoring well (m +ground level)	Screen length (m)	Depth top screen (m - top monitoring well)	Depth bottom screen (m – top monitoring well)	Calculated length of steel wire (m)
B45B0334	3	2.32	0.83	2	-5.55	-7.55	6.05
B45B0334	6	2.32	0.82	2	-22.64	-24.64	23.14
B45B0348	1	2.77	0.75	1	-4.73	-5.73	4.98
B45B0348	4	2.77	0.75	1	-25.83	-26.83	26.08

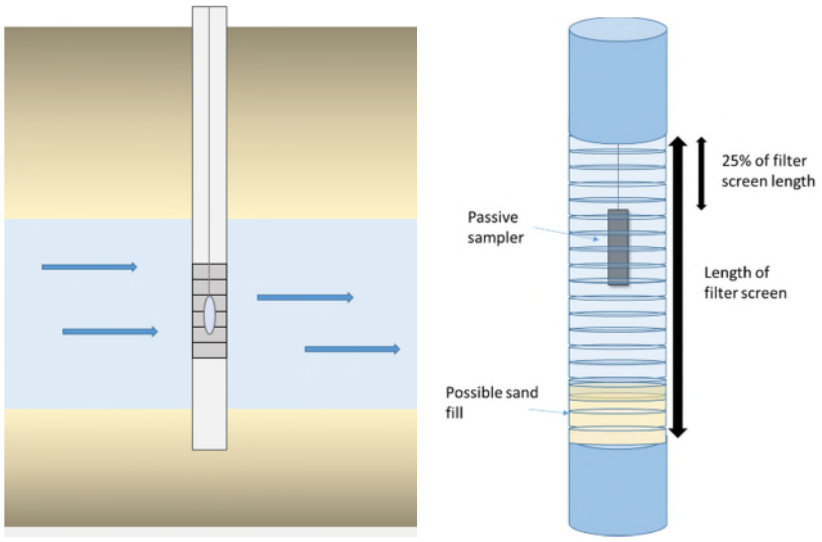

Figure 5: Left: passive sampler in a groundwater monitoring well. Right: schematization of the passive sampler inside the well tube and positioning relative to the well screen.

2.3.2 Blanks

In order to account for potential contamination of the passive sampler during handling and field deployment, a blank was used. This is a sampler (i.e., casing and sorbent prepared as described above) which has undergone all the steps involved in the sampling process except for deployment in the well. A single field blank was used for all four monitoring wells. During deployment of the samplers in the monitoring wells, the field blank was removed from the glass bottles and exposed to the surrounding air during the whole process. The same procedure was then repeated for deployment at the next monitoring well. Finally, when samplers were being retrieved from the wells after deployment, the blank was again exposed to the air during the procedure. This was repeated for each well. Between deployment and collection and after passive samplers have been retrieved from the monitoring wells, the blank was stored at -20°C.

2.3.3 Grab samples

Grab samples were collected for all locations. Grab samples were collected before and after deployment of the passive samplers in amber glass bottles previously rinsed with ultrapure water, MeOH and acetone. Grab samples

were stored at -20°C immediately after collection and were thawed on the day of analysis. Blank grab samples consisted of the abovementioned glass bottles filled with ultrapure water.

2.4 Groundwater pumping stations

2.4.1 Deployment of flow cells

To measure the water that has already been extracted from the source (in this case groundwater), flow cells described previously have been used. Part of the water stream was tapped from the bulk stream and deviated to a flow cell containing a passive sampler. The passive sampler was deployed in the centre of the flow-cell which resulted in a continuous flow around all sides of the passive sampler as illustrated in Figure 3. The measurements were done for a minimum of 24 hours (Table 3). Output flow speed from the sampling tap was adjusted to 1-2 L/min, as measured in duplicate with a simple bucket filling test. This results in a flow speed of approximately 2-3 cm/s inside the flow cell. The latter flow was chosen as it did not cause any damage to the sorbent material. The total flow that flowed through the installation was for the raw water mix 2.3 m^3 and for the pumping well 2.4 m^3, Table 3.

Table 3: Field data of the two flow cell measurements

Location	Start Date/time	End Date/time	Total time (hours)	Flow speed (l/min)	Total flow (m^3)	Comments
Pumping well	18-05-2020 09:30	19-05-2020 13:30	27	1.5	2.43	*Diesel engine during deployment*
Raw water	18-05-2020 11:00	19-05-2020 14:00	26	1.45	2.262	

2.4.2 Blanks

Similarly to the blank for the groundwater monitoring wells, the blank consisted of a passive sampler (i.e., casing and sorbent) which was exposed to the air at the location during installation of the flow cell. This was repeated when samplers were collected after deployment. After having been exposed to the environment, the blank passive sampler was introduced in a clean flow cell to take into account also potential contaminants from materials in the latter. The flow cell with the blank passive sampler was then filled with ultrapure water and sealed. It was then placed on a benchtop shaker and agitated for 3 consecutive days at 20 rotations/min. After 3 days (total 96.5 hours) the blank passive sampler was retrieved and stored as actual samples at -20°C until extraction and analysis.

2.5 Sample preparation and analysis

2.5.1 Grab samples

Grab samples were collected in amber glass bottles previously rinsed with ultrapure water, MeOH and acetone. After collection, all samples (including blanks) were stored at -20°C until analysis. On the day of analysis, samples were thawed and spiked with an internal standard solution containing atrazine-d5, benzotriazole-d4 and bentazone-d6 at a final concentration of 1 µg/L. Samples were subsequently filtered through 0.2µm nylon filters and transferred to 1 mL amber glass vials for analysis. All samples were prepared and analysed in triplicates.

2.5.2 Passive samplers

After collection, passive samplers and field blanks were left on their casings and stored in glass bottles at -20°C until analysis. On the day of analysis, sorbent pads were removed from the casing and placed in pre-cleaned glass tubes. Both pads (one on each side of the casing) were placed in the same tube. Subsequently, sorbents were spiked with internal standards (as for grab samples, final concentration in the extracts of 1 µg/L) directly in the glass tubes. 5 mL of MeOH were then added to the tubes and these were then vortexed for 2 min. The 5 mL MeOH were then

transferred to a second clean glass tube and the procedure was repeated one more time. Finally, the 10 mL of MeOH were evaporated to dryness under a gentle flow of nitrogen and reconstituted in 1 mL ultrapure water.

2.5.3 Non-target screening analysis (NTS)

Analysis of both grab and passive sampler extracts were performed using a Tribrid Orbitrap Fusion (ThermoFisher Scientific, Bremen, Germany) equipped with a heated electrospray ionization source operated in positive and negative ionisation mode. Chromatographic separation was achieved using a Vanquish HPLC system (ThermoFisher) equipped with a XBridge BEH C18 XP column (150 mm × 2.1 mm I.D., particle size 2.5 µm, Waters, Etten-Leur, The Netherlands) in combination with a 2.0 mm × 2.1 mm I.D. Phenomenex SecurityGuard Ultra column (Phenomenex, Torrance, USA), maintained at 25°C. Ultrapure water and acetonitrile with 0.05% formic acid were used as mobile phases. The gradient was linearly increased from 95% and 5% acetonitrile to 100% acetonitrile over 25min, which was then held constant for 4 min before switching back to initial conditions. Calibration of the mass spectrometer was performed in both positive and negative ionisation mode using a calibration solution (Pierce) to ensure a mass error below 2 ppm. Evaporator and capillary temperature were set to 300°C, source voltage were set to 3000 V and -2500 V for positive and negative ionisation, respectively, while the RF lens was set to 50%. Full high-resolution mass spectra were recorded from 80 to 1300 m/z with a resolution of 120,000 FWHM. A 5 ppm window was used for quadrupole isolation. Acquisition was performed in data dependent acquisition (DDA) with high collision dissociation (HCD) stepped collision energy (CE) of 20, 35 and 50% at 15,000 FWHM. Injection volume was 100µL and each sample was analysed in triplicate. Solvent blanks were injected every 5-10 samples to ensure no carry over and IS signal stability.

2.5.4 Routine (Targeted) method

Routine analysis of samples was carried out by Aqualab Zuid following their standardized and validated LC-MS/MS method which targets 69 known contaminants. These analyses were performed only on grab samples, not on passive samplers, which were analysed only using the previously described NTS method.

2.6 Data analysis

Compound Discover 3.1 (ThermoFisher) was used for peak picking, componentization and suspect screening. The workflow used in Compound Discover, as well as the databases used for suspect screening, are reported in Figure 6. The term *feature* is commonly used in NTS and refers to the accurate mass (expressed in Dalton (Da) or as mass-to-charge ratio (m/z)) of a detected compound, its retention time (expressed in minutes and referring to the time needed for a compound to elute from the chromatographic column) and intensity (corresponding to the peak area of the measured signal, which is correlated to the concentration of compound in the analysed sample). In the context of this work, the latter definition of feature will be used. The feature list compiled by Compound Discover, consisting of accurate mass and retention times, intensity as peak area, attributed molecular formula and suspect screening outputs (e.g., whether a match was found with one of the used databases) were exported as comma separated values for further processing in R (RStudio Team, 2020). Prior to exploratory analysis, features were grouped by sample type and location. Subsequently, features whose group mean intensity was < 10x solvent blanks were removed. Furthermore, features whose coefficient of variation was above 15% within a given group were also removed. Finally, a principal component analysis (PCA) was performed to investigate all samples together (i.e., passive samplers from monitoring wells, grab samples from monitoring wells, passive samplers from flow cells and grab samples from pressurized pipes). Prior to PCA analysis, features whose group mean intensity was < 10x field blanks were removed. The data was scaled to unit variance prior to the PCA. Subsequently, a comparison of feature intensity was performed, by calculating the sum of all features (in samples and blanks) for each group, to determine the contribution of features in field blanks to the overall intensity of features. Additional PCAs were then computed (i.e., after blank subtraction and scaling to unit variance) per individual group to investigate group-specific differences among samples.

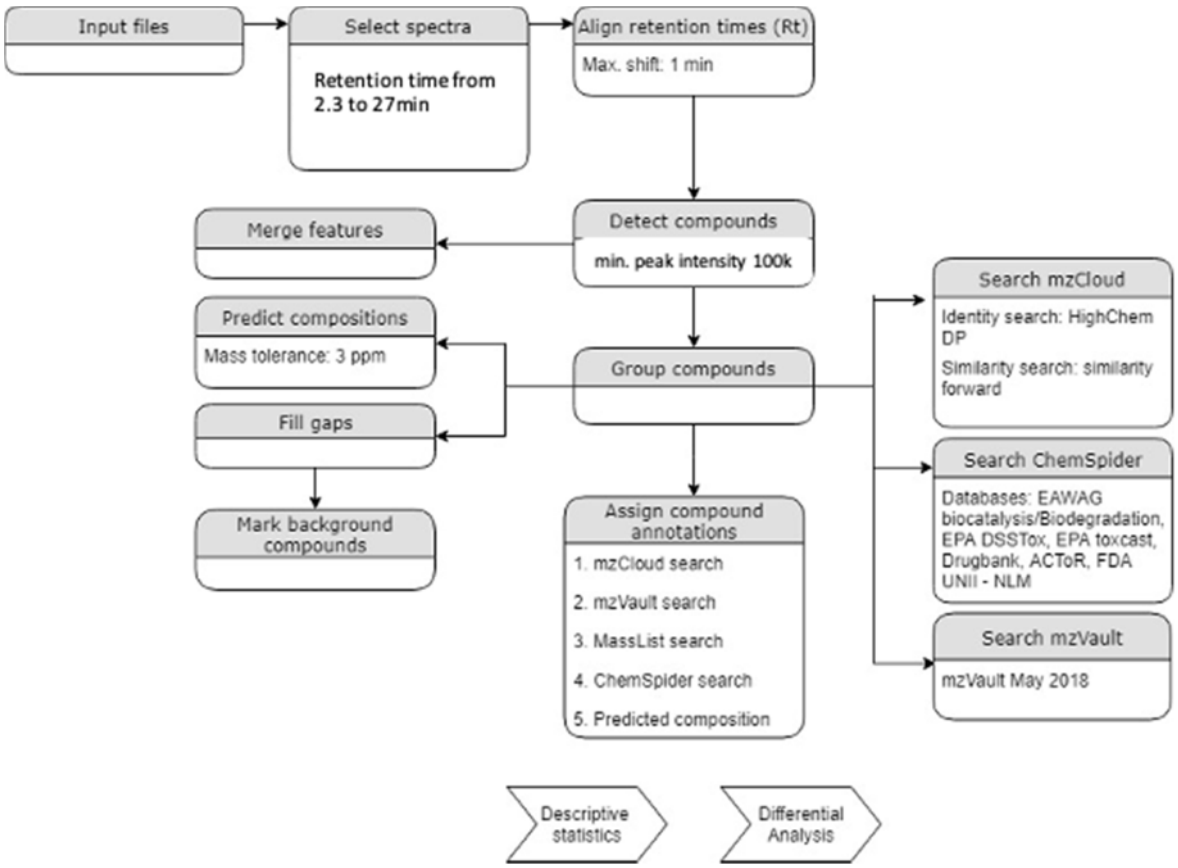

Figure 6: Workflow used for data processing in Compound Discover 3.1.

Differences in *m/z* and retention times (Rt) between features detected in passive samplers and their corresponding grab samples were investigated by means of violin plots (after blank subtraction). Furthermore, the number of features for which an MS2 triggered, as well as the scores from the *mzCloud* search, were compared among the various groups. *mzCloud* scores, which range from 0 to 100, provide an indication of the match between the MS2 spectra of a feature detected in a sample and the MS2 spectra from the library. Scores above 70 can be considered as a probable identification of the actual molecule (equivalent to a level 3 identification, out of 4 levels, according to Schymanski et al. 2014 (Schymanski et al., 2014)). *mzCloud* outputs were further investigated, in particular for features with a score ≥ 70, the logKow (experimental and/or predicted) of the tentatively identified molecule was looked up in the EPI Suite™ (US EPA, 2015). These were then used to compare the polarity of features among the various sample types (i.e., passive vs grab samples) and locations.

2.7 Toxicity assessment

Finally, using the CAS number found in the EPI Suite™, information about the potential toxicity of features with an *mzCloud* search score ≥ 70 was searched. For this purpose, the approach developed by (Brunner et al., 2019) was used. The latter relies on retrieving half maximal effective concentration (EC50) of water relevant compounds from the ToxCast database of the US EPA (United States Environmental Protection Agency, 2018), which contains EC50 values for thousands of compounds which have been tested with hundreds of different bioassays. EC50 provide an indication of the potency of compounds, which can in turn be used for prioritization of features which require further attention and monitoring. Following the approach developed by (Brunner et al., 2019), focus was set on assays which cover endpoints for water-relevant compounds, namely xenobiotic metabolism, modulation of

hormone systems, reactivity, stress response, reproduction and development, cell viability, thyroid toxicity, neurotoxicity, and PPAR receptor activation. The complete list of relevant bioassays can be found in (Brunner et al., 2019).

3 Results and discussion

3.1 Non-target screening

The first step in the evaluation of the results from NTS analyses consisted in determining the influence that features detected in field blanks have on all features. For this purpose, the intensity of features detected in each sample was summed to obtain an overview of their contribution to the overall intensity of measured features (see Figure 7). Not surprisingly, the overall intensity of features detected in passive samplers deployed in groundwater wells was substantially higher compared to the other locations. The sum of intensities from features detected in the field blank from the groundwater wells were approximately ⅓ to ¼ of the total intensity from deployed samplers, both in positive and negative ionisation. Whilst this is an important contribution, highlighting the need to use field blanks, it illustrates that there are features is still an important number of features which appeared only in samples. The field blank from the pumping station (i.e., flow cell) was characterized by some particularly intense features which are visible in negative ionisation mode. These could be due to the material flow cells are made of (i.e., PVC), which might release some compounds which contribute to the signal measured in the blank. With respect to grab samples, the intensity of detected features was clearly substantially lower compared to the corresponding passive samplers, both for positive and negative ionisation. The sum of features intensities in grab blanks was equivalent to that of actual samples, suggesting the presence of important contributions in the blanks.

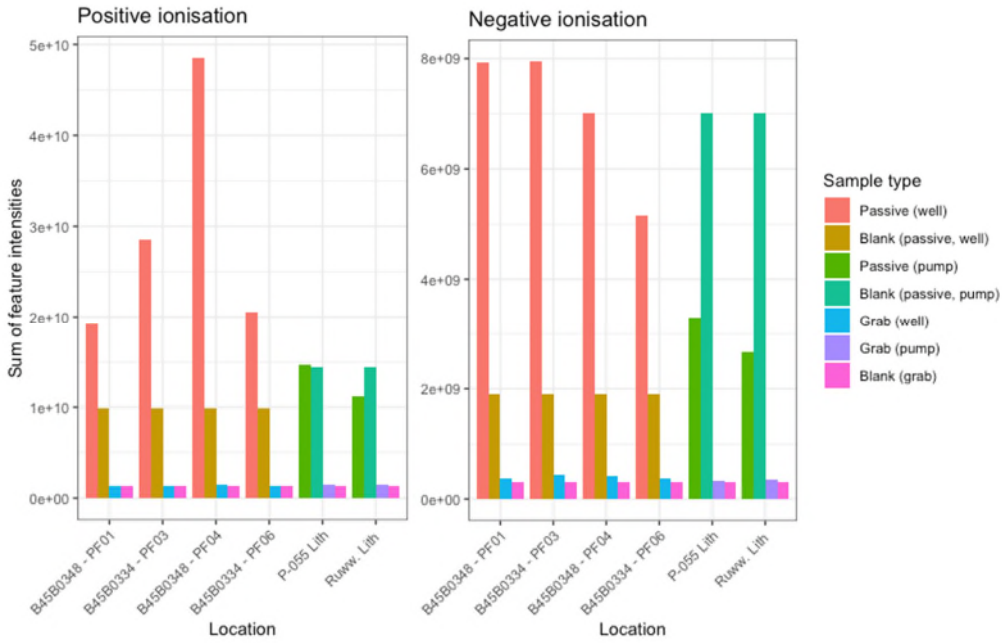

Figure 7: For each sample, the intensity of all features was summed and compared among the different samples to evaluate their contribution. This is done particularly to compare the signal obtained from blanks. For instance, for passive samplers deployed in pumping stations (i.e., flow cells), there are features with very high intensity.

As described previously, features which did not have a mean intensity per group (i.e., sample type and location) of at least 10 times that of the corresponding field blank, were removed for further processing. An overview of the number of detected features, number of triggered MS2 and outputs of searches in *mzCloud* are reported in Table 4. As can be seen, after blank subtraction, a large number of features were still detected in passive samplers, both in groundwater wells and at pumping stations. In both cases, these were at least an order of magnitude higher compared to the number of features detected in grab samples. For a large number of the detected features, an

MS2 acquisition was triggered, which allows to compare the obtained MS2 spectra with available databases and provide a tentative identification of the actual compound. In the context of this study, emphasis was put on matches with *mzCloud*, in particular on the number of features having a score above 70, as reported in Table 4. These are particularly relevant because features having such scores have a likely chance of being correctly identified. The ratio between the number of features with a score > 70 and the total number of detected features (after blank subtraction) did not differ particularly between passive samplers and corresponding grabs. However, in absolute terms, the large number of features with a high score obtained with passive samplers clearly has an advantage in terms of identifying potential contaminants.

*Table 4: Overview of results from NTS. Features samples indicates the number of features detected in samples after subtraction of features found also in blanks (if their intensity was not at least 10x that in measured in the blank). Features blanks indicates features detected in blanks. Number of MS2 refers to the number of MS2 spectra (i.e., fragmentation) which were recorded. mzCloud score refers to the number of features with a match score above or below 70 and the number of features that did not have a match with mzCloud. *For monitoring wells and pumping stations, the same blank (i.e., ultrapure water) was used, hence the same number of features detected in the blank.*

Ionisation mode	Location	Sample type	Features		Number of MS2	*mzCloud* score > 70	*mzCloud* score < 70	Lack of match with *mzCloud*
			Samples	Blanks				
Positive	Groundwater wells	Passive sampler	8940	3873	4693	460	299	7731
		Grab	219	*494	152	26	11	182
	Pumping stations	Passive sampler	977	3823	594	45	22	910
		Grab	74	*494	37	3	3	68
Negative	Groundwater wells	Passive sampler	5239	1221	4085	241	186	4812
		Grab	334	*205	301	23	14	297
	Pumping stations	Passive sampler	1321	1637	1038	44	39	1238
		Grab	183	*205	159	12	6	165

3.1.1 Groundwater monitoring wells

Following the exploratory analysis of all samples and locations, a more thorough investigation was performed among passive samplers and grabs collected in monitoring wells. Results are reported as PCA plots in Figure 9. the previously highlighted difference between PF04 and the other monitoring wells remains clearly visible. Interestingly, when looking at grab samples, which were collected before and after deploying the passive samplers, a clear difference can be seen in the grab sample of PF04 before deployment, while this does not seem to be the case in the sample collected after. As mentioned previously, this could be due to a leakage or the effect of pumping in the well to collect the grab sample. Results from targeted analysis seem to confirm the former hypothesis, as will be discussed later. Interestingly, while the differences between PF04 and the other wells are still clearly visible in the analysis results of the passive sampler in negative ionisation, this is not the case for the grab samples which appear to be closely grouped. More important differences are visible in grab samples of PF03 and PF01. However, when observing grab samples, it can be seen that quite some variability is visible between collection periods. This might suggest that, although groundwater velocity is expected to be very low, changes in quality can occur also at timescales of months. Because of the time-integrative characteristic of passive samplers, they capture this variability unlike grab samples.

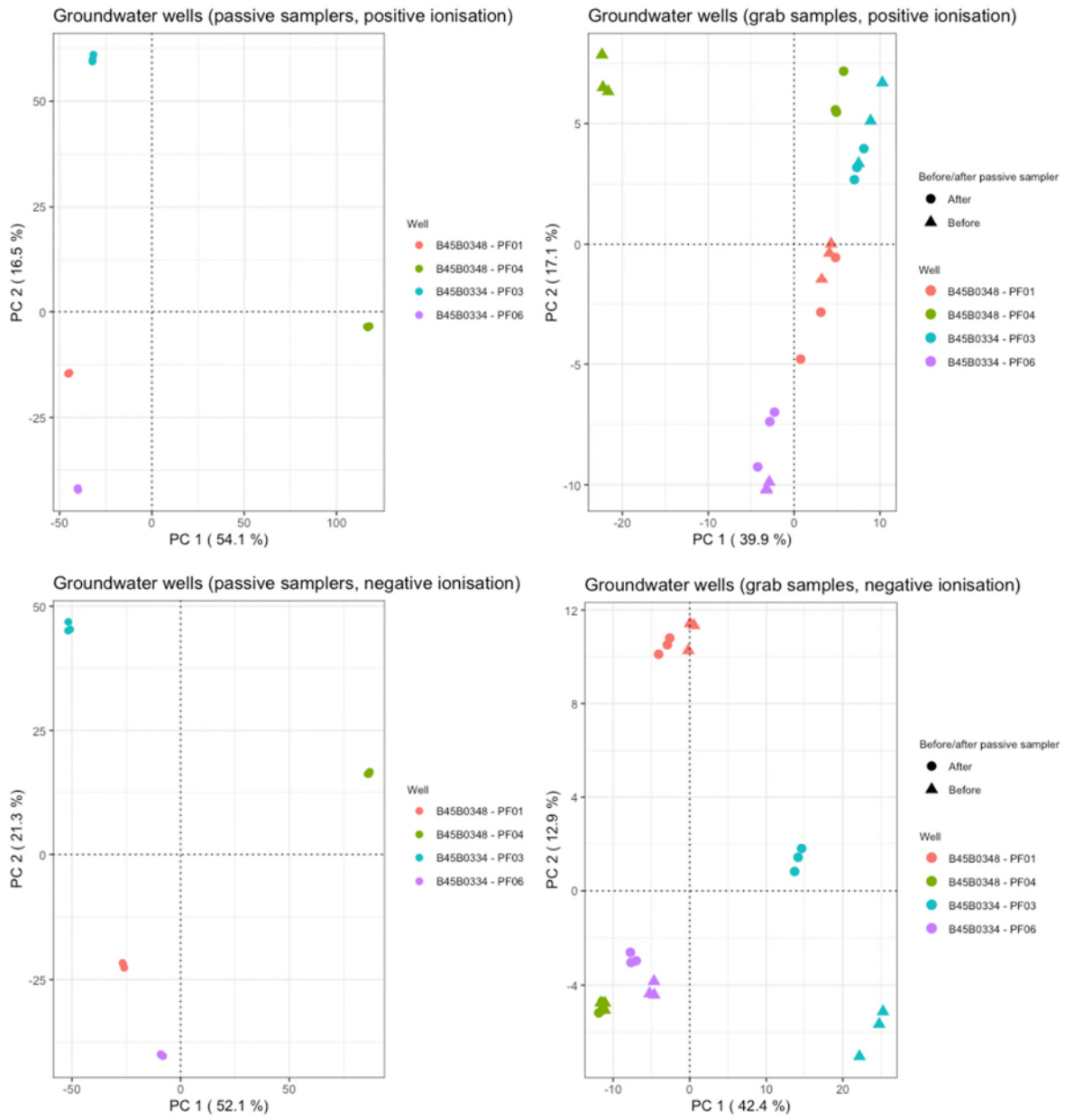

Figure 8: PCA of passive samplers (left) and grab samples (right) collected in groundwater monitoring wells in positive (above) and negative (below) ionisation. Before/after indicates whether the grab sample was collected before or after deployment of the passive sampler.

Differences in retention time and molecular weight of features detected in the different samples were also investigated (see Figure 10). The proportion of features having higher retention times in passive samplers is higher compared to grab samples. This is due to the fact that HLB is a universal sorbent which, besides acidic and basic (i.e., polar) compounds, will also retain more neutral and hydrophobic chemicals which are not detected in grab samples due to their low concentration and/or tendency to adsorb onto suspend solids. This pattern however was less clear in negative ionisation, given that the majority of features detected in grab samples had retention times around 10 min. With respect to the molecular weight of detected features, no particular difference could be observed between passive samplers and grab samples, besides that the former had a higher number of features with MW > 400 Da.

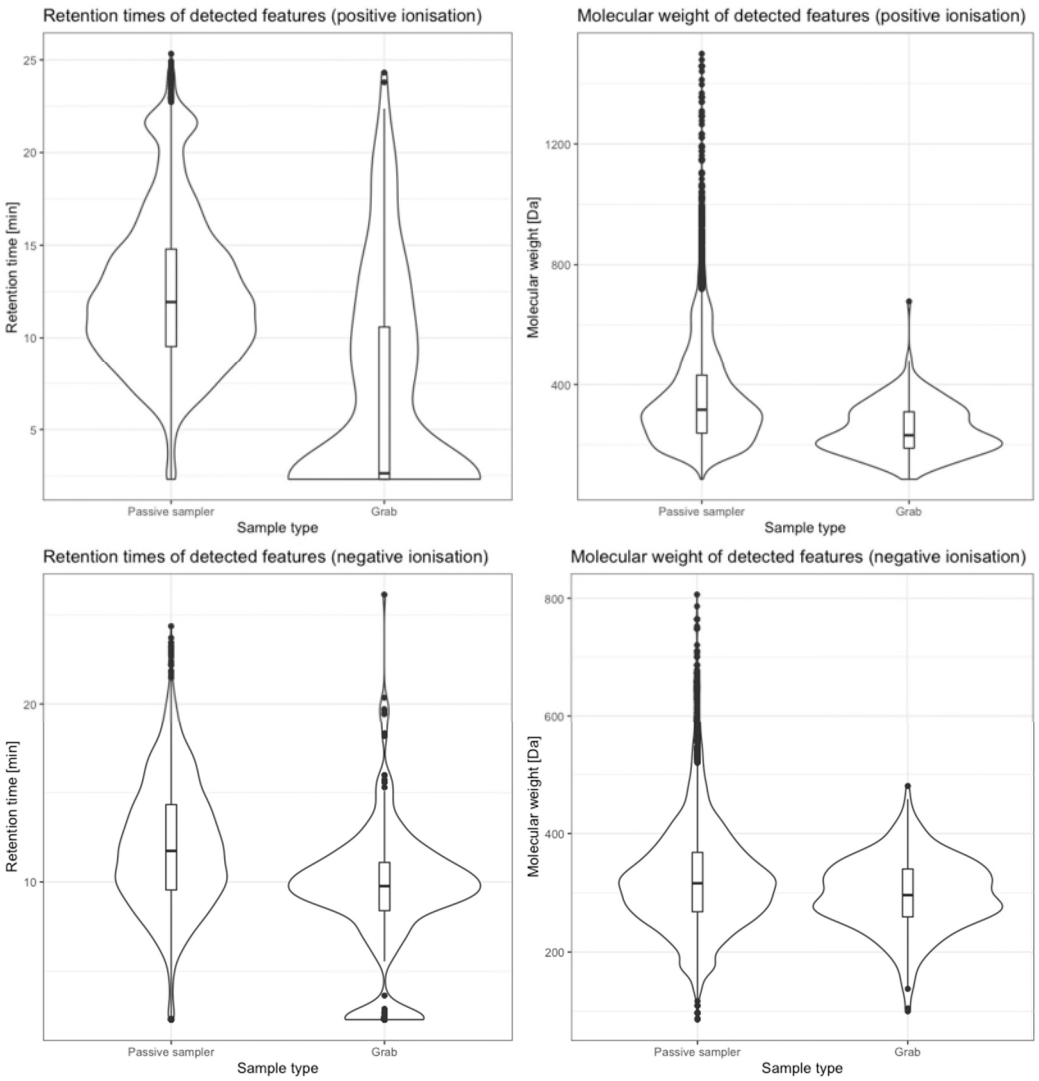

Figure 9: Retention times (min) and molecular weights (Da) for all features detected in passive samplers and grab samples collected in groundwater monitoring wells.

3.1.2 Pumping stations

Similarly to groundwater monitoring wells, an exploratory analysis of differences between passive samplers (i.e., flow cells) and grab samples was carried out using PCA (see Figure 11). The first main difference between which can be observed is between the replicate injections of the passive sampler installed at *Pump Lith*. In fact, the three replicates appear to be scattered compared to the replicates of the passive sampler from *Ruw Lith*. However, quite some differences among replicates are also visible among the grab samples. These could be due to an inhomogeneity of the samples.

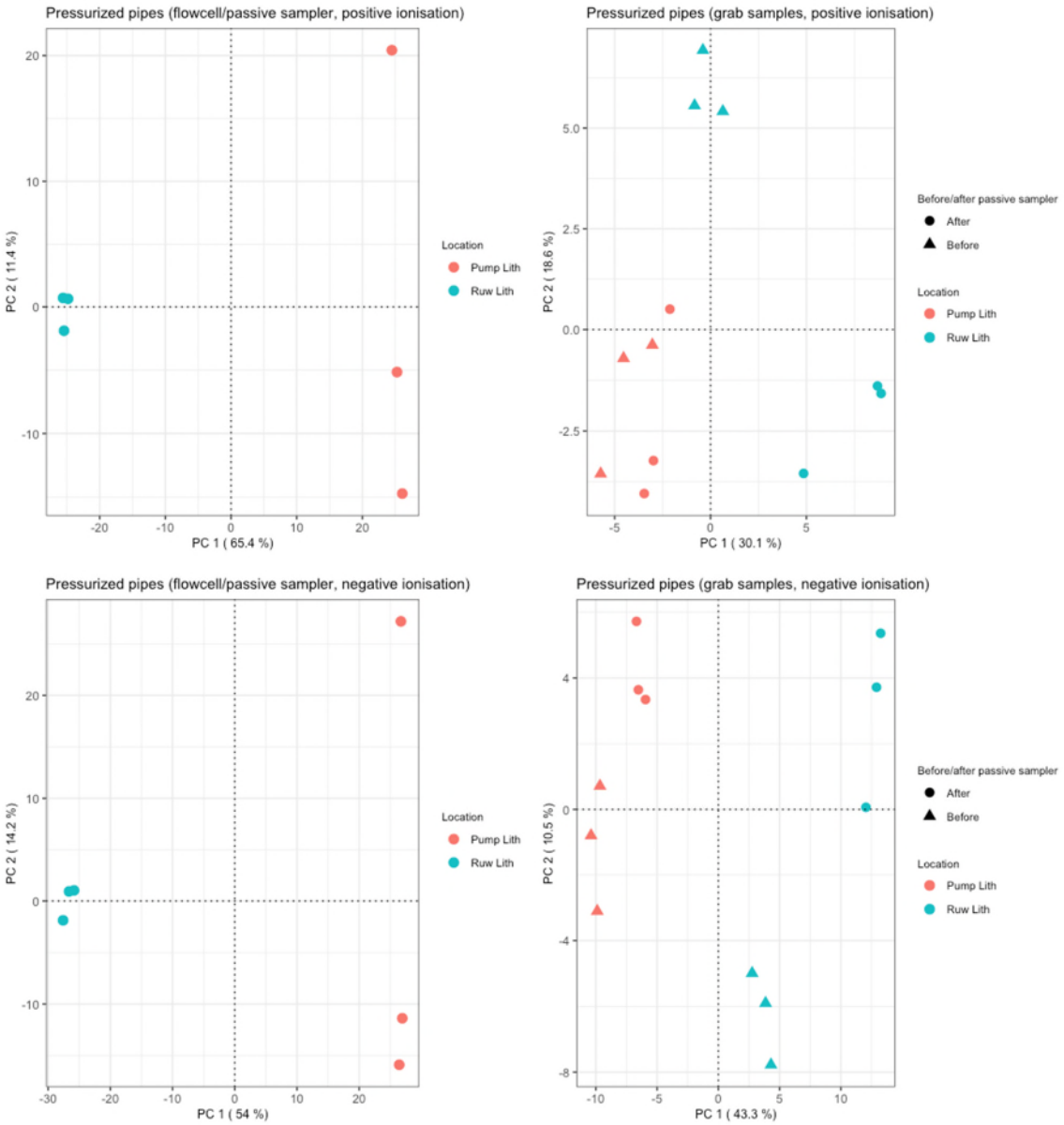

Figure 10: PCA of passive samplers (left) and grab samples (right) collected in pumping stations in positive (above) and negative (below) ionisation. Before/after indicates whether the grab sample was collected before or after deployment of the passive sampler.

Similarly to monitoring wells, the proportion of features with longer retention is higher in passive (flow cells) compared to grab samples from pressurized pipes (see Figure 12). Once again, this difference was less obvious in negative ionisation as the media retention time was around 12 and 10 min for passive samplers and grabs, respectively. As discussed previously, this is most likely due to the characteristics of the sorbent used in the passive samplers, which besides polar compounds, also allows to concentrate neutral and more hydrophobic chemicals. In terms of molecular weights, the median in passive samplers was around 350-400 Da, while this was around 250 Da for grab samples in positive ionisation and 300 Da in negative ionisation.

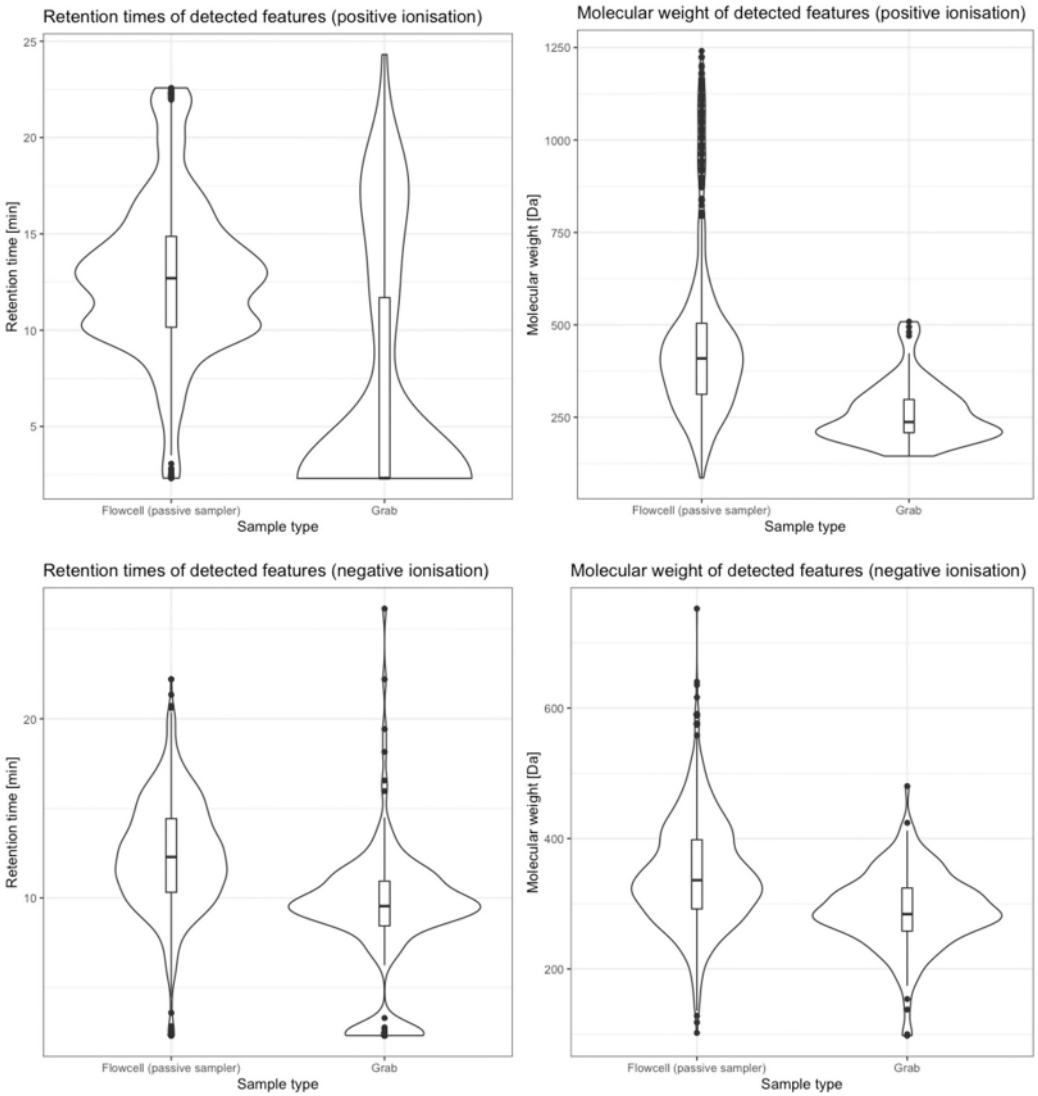

Figure 11: Retention times (min) and molecular weights (Da) for all features detected in passive samplers and grab samples collected in pumping stations.

3.2 Prioritization and toxicity

In Table 4, the number of features having a *mzCloud* score above 70 were reported. These features were further selected for prioritization given that they have a high likelihood of corresponding to the assigned compound from the database. CAS numbers of features were retrieved from the EPI Suite database, together with octanol-water partition coefficients (logKow), to obtain an idea of the polarity of detected features in the various sample types. The distribution of logKow are reported in Figure 13. In agreement with what was already found when comparing retention times of features between passive samplers and the corresponding grab samples, features found in the former appear to have higher logKow and hence be less polar compared to features detected in grab samples. However this is less obvious in negative ionisation given that medians logKow between passive samplers and grabs are in the same range. Nevertheless, it should be noted that logKow were not available for all features with a *mzCloud* score above 70, thus only an indicative overview of the polarity of detected features can be obtained. In future studies it will be highly interesting to deploy passive samplers with different sorbents, for instance weak anionic and cationic exchange resins to determine if a broader range of polar chemicals can be detected. From a

drinking water perspective these are of particular interest as they are expected to be more difficult to remove during treatment processes. These should be combined also to alternative types of chromatographic conditions, such as hydrophilic interaction liquid chromatography (HILIC) or mixed-mode resins, to ensure that highly polar compounds can be retained, detected and identified (Reemtsma et al., 2016).

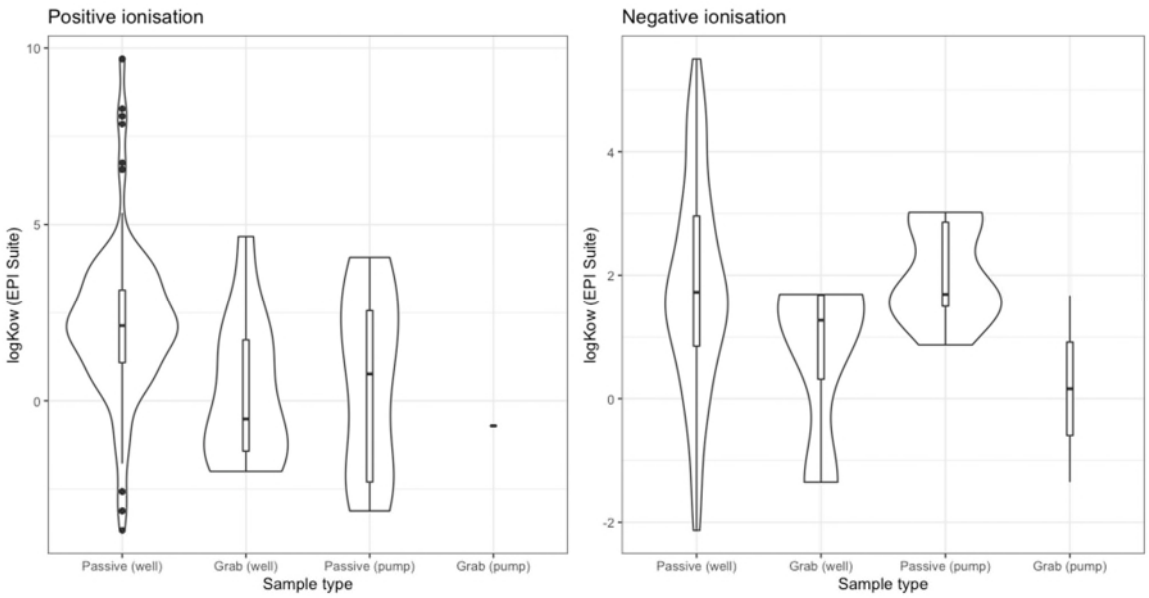

Figure 12: LogKow of features found in EPI Suite.

Toxicity information of tentatively identified features (having a *mzCloud* score above 70) was searched using the ToxCast repository from the US EPA, which contains EC50 values for thousands of compounds. EC50 values derived from bioassays measuring relevant endpoints (as described in section 2.6), can be used as indicators of potential human toxicity. For passive samplers deployed in groundwater wells, for 56 and 37 features in positive and negative ionisation, respectively, an EC50 value could be retrieved from the ToxCast repository. For grab samples, 5 and 4 features in positive and negative ionisation, respectively. For passive samplers deployed in pumping stations, EC50 values 8 and 6 features could be found, while for grab samples one for one feature in negative ionisation. Out of the total 117 features for which an EC50 value could be found, 37 features were prioritized based on their potential toxicity for humans, as shown in Table 5. It should be noted that to avoid having a too long table, for passive samplers collected in the monitoring wells, only features whose EC50 was below or equal 0.01 (i.e., low concentrations trigger an effect and hence these substances can be considered as potent with respect to the measured endpoint) were reported in Table 5. The complete overview of all features having a *mzCloud* score > 70 is provided in the Supporting Information. When comparing the number of prioritized features, a larger number could be selected from passive samplers, in particular from those which were deployed in groundwater wells. Slightly fewer were selected from passive samplers used in the pumping stations, yet these were also deployed for approximately one day, while in wells samplers were exposed for 60 days. Nevertheless, even if they were deployed for only 24h, passive samplers in pumping stations clearly allowed the detection of a larger number of potentially relevant features compared to grab samples. Among the detected features, those having high intensities (i.e., supposedly present in non-negligible concentrations), low logKow (i.e., polar and hence more difficult to remove) and low EC50 (i.e., high potency) are of particular interest. For instance, metolachlor ESA, a transformation product of the herbicide metolachlor, and bentazone were detected in the collected samples. Metolachlor ESA is currently not part of the routine targeted analyses. Bentazone is part of the targeted method and was reportedly detected at concentrations ranging from 0.025 (Ruw Lith) to 0.5 µg/L (PF01). The possible presence of 2-methyl-4,6-

dinitrophenol, which is being used as an herbicide, was also detected in passive samplers collected from the monitoring wells. Various dinitrophenols are included in the targeted method, however none was detected, while 2-methyl-4,6-dinitrophenol specifically is not part of the targeted method. Another relevant compound which is potentially present in various samples is 2-mercaptobenzothiazole, which has been identified as a potential carcinogenic (Sorahan, 2009), yet is currently not part of the routine monitoring method. The detected and prioritized features could be formally identified and if their presence, or that of analogue compounds (e.g., isomers), is formally confirmed through the analysis of a reference standard, then they should be included in routine monitoring programs and their concentration monitored over time.

Table 5: Overview of prioritized features. LogKow is the predicted octanol-water partition coefficient while LogKow (exp) is the empirical value.

Ionisation	Location	Sample type	Name	Formula	Monoisotopic mass	CAS	Log Kow	Log Kow (exp)	EC50 [µM]	Endpoint
Positive	Wells	Passive samplers	Triphenylphosphine oxide	C18 H15 O P	278.0861	791-28-6			4.7E-03	general.cell.viability
			2-Mercaptobenzothiazole	C7 H5 N S2	166.9863	149-30-4	1.83		8.0E-03	general.cell.viability
			Benzotriazole	C6 H5 N3	119.0483	95-14-7			8.4E-05	general.cell.viability
			Tributylamine	C12 H27 N	185.2143	102-82-9	4.46		8.0E-03	general.cell.viability
			2,6-Di-tert-butyl-1,4-benzoquinone	C14 H20 O2	220.1463	719-22-2	4.07	4.42	7.9E-05	general.cell.viability
			Docosahexaenoic acid ethyl ester	C24 H36 O2	338.3185	112-86-7	9.69		4.6E-05	general.cell.viability
			N,N,4-Trimethylaniline	C9 H13 N	135.1048	99-97-8	2.72	2.81	8.0E-03	general.cell.viability
			Carvone	C10 H14 O	150.1045	99-49-0			7.7E-03	general.cell.viability
			Epitestosterone	C19 H28 O2	288.2089	481-30-1	3.27	3.32	7.2E-04	Hormone.mediated
			Bis(2-ethylhexyl) amine	C16 H35 N	241.2770	106-20-7	6.56		1.5E-05	general.cell.viability
Negative	Wells	Passive samplers	Dodecyl sulfate	C12 H26 O4 S	288.1371	151-21-3			6.9E-03	Stress.responses
			2-Methyl-4,6-dinitrophenol	C7 H6 N2 O5	198.0277	534-52-1	2.27	2.13	2.2E-03	Stress.responses
			Paracetamol	C8 H9 N O2	151.0633	103-90-2	0.27	0.46	8.0E-03	general.cell.viability
			Paracetamol	C8 H9 N O2	151.0633	103-90-2	0.27	0.46	8.0E-03	general.cell.viability
			Gallic acid	C7 H6 O5	170.0215	149-91-7	0.86	0.7	5.0E-06	PPAR
			2,6-di-tert-Butylphenol	C14 H22 O	206.1671	128-39-2	4.48	4.92	1.4E-05	general.cell.viability
Positive	Wells	Grab samples	2-Mercaptobenzothiazole	C7 H5 N S2	220.1463	149-30-4	1.83		8.0E-03	general.cell.viability
			(S)-Nicotine	C10 H14 N2	312.2089	54-11-5	1	1.17	7.1E-01	Xenobiotic.metabolism
			2,2-Dithiobis(benzothiazole)	C14 H8 N2 S4	346.2144	120-78-5	4.66		1.0E+01	Reactivity
			Metolachlor ESA	C15 H23 N O5 S	174.0793	171118-09-5	1.69		2.5E+01	Hormone.mediated
			Thymine	C5 H6 N2 O2	329.1297	65-71-4	-0.32	-0.62	8.3E+01	Xenobiotic.metabolism
Negative	Wells	Grab samples	Bentazone	C10 H12 N2 O3 S	329.1297	25057-89-0	1.67	2.34	8.2E-02	Stress.responses
			Dimethenamid ESA	C12 H19 N O5 S2	240.0569	205939-58-8			4.4E+01	Xenobiotic.metabolism
			Metolachlor ESA	C15 H23 N O5 S	321.0705	171118-09-5	1.69		2.5E+01	Hormone.mediated
			Dimethenamid ESA	C12 H19 N O5 S2	166.0266	205939-58-8			4.4E+01	Xenobiotic.metabolism

Positive	Pumping station	Passive samplers	2,6-Di-tert-butyl-1,4-benzoquinone	C14 H20 O2	329.1297	719-22-2	4.07	4.42	7.9E-05	general.cell.viability
			Norgestrel	C21 H28 O2	142.0185	797-63-7	3.48		1.4E-03	Hormone.mediated
			Corticosterone	C21 H30 O4	166.9863	50-22-6	1.99	1.94	2.5E-03	Hormone.mediated
			Edaravone	C10 H10 N2 O	162.1157	89-25-8	2.56		7.9E+00	Stress.responses
			Metolachlor ESA	C15 H23 N O5 S	331.9570	171118-09-5	1.69		2.5E+01	Hormone.mediated
Negative	Pumping station	Passive samplers	Metolachlor ESA	C15 H23 N O5 S	329.1297	171118-09-5	1.69		2.5E+01	Hormone.mediated
			Bentazone	C10 H12 N2 O3 S	126.0429	25057-89-0	1.67	2.34	8.2E-02	Stress.responses
			Dimethenamid ESA	C12 H19 N O5 S2	240.0569	205939-58-8			4.4E+01	Xenobiotic.metabolism
			Isophthalic acid	C8 H6 O4	321.0705	121-91-5	1.76	1.66	8.5E-02	Stress.responses
			Metolachlor ESA	C15 H23 N O5 S	329.1297	171118-09-5	1.69		2.5E+01	Hormone.mediated
			4-Chloro-3-methylphenol	C7 H7 Cl O	321.0705	59-50-7	2.7	3.1	1.5E+01	Stress.responses
		Grab sample	Bentazone	C10 H12 N2 O3 S	240.0569	25057-89-0	1.67	2.34	8.2E-02	Stress.responses

Although the compounds listed in Table 5 have not been formally identified through the comparison with a reference standard, their prioritization and the fact that various of the annotated compounds are not present in the current monitoring method, illustrates the advantage of combining passive sampling and NTS to monitor groundwater quality. Whilst some compounds could be detected in both passive and grab samples, suggesting that these might be present at non-negligible concentrations, still a large fraction of the prioritized features were only detected in passive samplers. Based on the results of the analysis and information from the literature, an additional selection can be made to determine features which should be formally identified by analysing a reference standard. From an early warning perspective, being able to detect and identify new contaminants at trace concentrations is highly relevant as these might be indicative of future contaminations which would have not been detected otherwise. As discussed previously, HLB is a reliable and robust sorbent commonly used as to extract a broad range of chemicals, both polar (i.e., acidic and basic) and more hydrophobic (i.e., neutral). However, because of its universal character, it is not as efficient as for instance mixed-mode cation or anion exchange resins (e.g., Oasis® MCX and Oasis® WAX), to extract extremely polar positively or negatively charged compounds. For this reason, the implementation of specific cationic and anionic exchange sorbents in addition to HLB should be contemplated as it would allow to cover an even broader range of potentially problematic compounds for drinking water production. Moreover, the present study only focused on qualitative differences among sampled sites, however if field calibrations of passive samplers are performed to determine uptake rates, then quantitative results could be produced. Nevertheless, even if only qualitative data is provided, this can be used to detect the presence of previously unknown compounds which can then be added to routine monitoring programs to closely follow their concentration in groundwater aquifers.

4 Conclusions

4.1 Conclusions

A dedicated passive sampler casing for groundwater monitoring wells as well as a device to sample from pressurized pipes in pumping stations were developed for this study. Passive samplers were deployed for 60 days in groundwater wells and for 24h in pumping stations. The comparison between number of detected features and number of matches with the used databases clearly illustrates that through the use of passive samplers, a much larger number of trace compounds, ranging from polar to more hydrophobic ones, can be detected. In fact, even after removal of background features detected in the blanks, more than 14,000 features (both positive and negative ionisation) were detected in passive samplers deployed in groundwater monitoring wells, compared to 550 in grab samples. Similarly, 2,300 features were detected in passive samplers deployed at pumping stations compared to 260 in grab samples. Approximately 820 of the features detected in passive samplers had a match with the *mzCloud* database above 70, which is a strong indication that they have been correctly identified. In the case of grab samples, only around 60 features had such a score. The detected features were further investigated to determine if certain compounds could be prioritized based on their potential toxicity for humans. This further selection highlighted the potential presence of various compounds which are currently not part of routine monitoring programs and which, because of their physico-chemical characteristics, in particular a low logKow, could be particularly problematic from a removal perspective. These results clearly show that the combination passive sampling and NTS allows to detect and prioritize features which are not to be part of the current routine monitoring method, which involves the analysis and quantification of 69 priority compounds using LC-MS/MS.

PCA showed that substantial differences could be observed between monitoring wells, these were visible both in passive samplers and in grab samples. While for PF04, this could be due to a leakage which causes contaminated water from shallower aquifers to reach deeper levels, these findings illustrate that the chemical profile of water in the different parts of the aquifer can differ significantly. Hence, focussing on a limited number of chemicals as is the case for current routine monitoring approaches might not be sufficient to capture all contaminants potentially present. These differences are even more obvious when looking at results from the analysis of passive samplers, as they allow to detect a larger number of compounds.

The integrative characteristics of passive samplers are of particular interest because they allow to cumulate chemicals over time and hence provide a more comprehensive picture of water quality. In terms of cost-effectiveness, passive sampling is more expensive compared to conventional grab sampling. In particular because sorbents need to be purchased, particular attention needs to be given to cleaning all gear and avoiding contaminations. However, extraction of retrieved sorbents is straight forward. Furthermore, while the deployment and collection of one sampler is more expensive compared to collecting one grab sample, the latter covers only a limited period of time and is limited with respect to detection of trace level compounds. The result of the analysis of passive samplers will be indicative of the average water quality in the aquifer for a longer period, providing a more comprehensive picture of water quality in the investigated source. Nevertheless, based on the obtained results we strongly advise to always collect a grab sampler before and after deployment of the sampler to ensure that all potential influences are taken into account (e.g., leakage from shallower layers).

4.2 Recommendations

This research illustrates that passive sampling combined with NTS is a promising approach to monitor groundwater quality as it allows to detect the presence of a broad range of chemicals at low concentrations. This is of particular importance from an early warning perspective as potential contamination plumes can be detected earlier, and

corrective measures can be implemented sooner. Based on the findings from this research we can formulate the following recommendations:

- Passive samplers combined with NTS is a useful addition to conventional monitoring of groundwater quality with targeted analysis of grab samples, since this allows identification of a much broader range of chemicals at lower detection limits;

- We recommend that passive sampling and NTS are applied periodically to identify new compounds which are currently not part of routine monitoring. The findings can be used to update routine targeted monitoring by addition of new compounds;

To enhance the efficiency of passive sampling, we recommend that future research is aimed at:

- Deployment of additional sorbents (e.g., WAX and MCX) in combination to HLB to cover a broader range of (highly) polar chemicals (e.g., ultra-short chain PFAS) which are particularly problematic for drinking water production. If needed, sorbents specific for more hydrophobic compounds can also be used;

- In-situ calibration of passive samplers, as this allows to obtain quantitative data from deployed samplers without additional analysis of grab samples;

Finally, Passive samplers as developed and implemented in this study are not limited to groundwater monitoring but can be used to assess the quality of surface water (both from aquifers, abstraction points, pumping stations or across the treatment train).

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I Appendix

I.I Passive samplers

Figure 13: Passive samplers ready for deployment.

I.II Groundwater well measurements

Figure 14: Left: Passive sampler going into a groundwater well for sampling. Right: finished installation of the undeep and deep passive sampler (sealed steel rings).

I.III Pumping stations

Figure 15: Flow cell installed at one of the pumping stations.

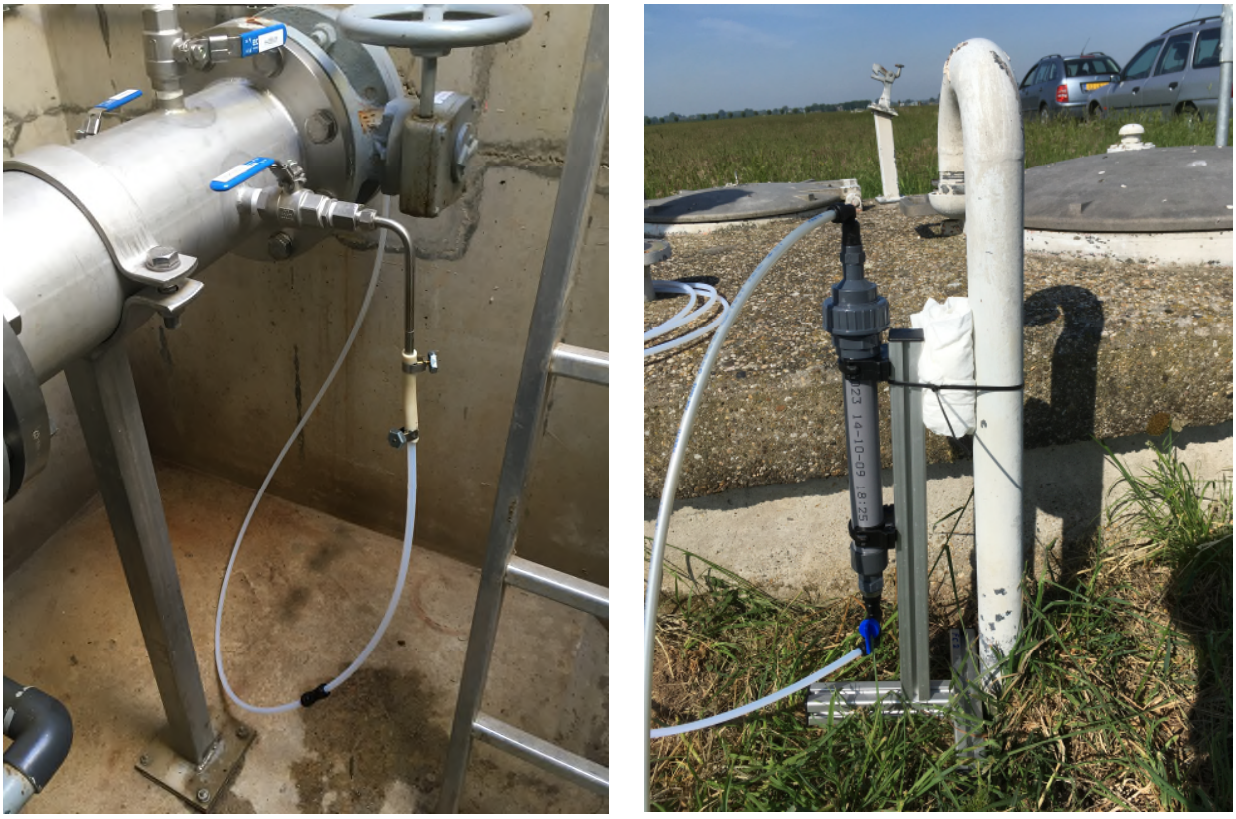


Figure 16: Measuring groundwater abstraction well. Left: connection to the abstraction well. Right: above ground installation

I.IV Measurement protocol for groundwater monitoring wells

Peilbuis	….	Inhangdiepte pomp	……. m			Naam		…….
Filter nr.	…..					Organisatie		…….
aantal verversingen	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]	Monster pakket
Dag 1 (inhangen passive sampler) Datum	……							
10%	….	….	….	….	….	….	….	
25%	….	….	….	….	….	….	….	
50%	….	….	….	….	….	….	….	C(reserve) + A
75%	….	….	….	….	….	….	….	
100%	….	….	….	….	….	….	….	
150%	….	….	….	….	….	….	….	C (reserve)
200%	….	….	….	….	….	….	….	
250%	….	….	….	….	….	….	….	C (reserve)
300% *	….	….	….	….	….	….	….	A,C,D
350%	….	….	….	….	….	….	….	C (reserve)
Inhangen passive sampler								
Dag 60 (ophalen passive sampler) Datum	……							
Ophalen passive sampler								D
Vervolgens schoonpompen en grab-sample nemen								
300% *	….	….	….	….	….	….	….	C,D

(*) Pomp langer door als pH, EGV niet stabiel

pakket A	BW/AQZ	Cl
pakket B	BW/AQZ	SO4, HCO3, NO3, Al, Br, Na, K, Ca,Mg, Fe, Mn, NH4, DOC, CH4
pakket C	BW/AQZ	doelstofanalyse op ….(zelfde pakket als vorige meetronde)…..
(reserve)	BW/AQZ	alleen analyseren indien peilbuis lek
pakket D	KWR	Non-Target Screening & suspect-analyse
Passive Sampler	KWR	Non-Target Screening & suspect-analyse

I.V Results of the cleaning protocol measurements for the groundwater wells

Well B45B0334

Put	B45B0334-pf3				Naam		Stijn Beernink	
Filter nr.	3				Organisatie		KWR	
Diepte	6 m							
Diameter	2 duims							
meting nr	Datum 21-2-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
10% meting		09:28	0.57	0.5	5.3	775	1.24	676
25% meting		09:30	1.4	0.5	6.5	778	0.61	674
50% meting		09:33	2.8	0.5	7.1	769	0.42	676
75% meting		09:39	4.2	0.5	6.77	766	0.42	677
100% meting		09:43	5.7	0.5	7	765	0.37	678
150% meting		09:52	8.5	0.5	7.2	766	0.34	678
200% meting		10:02	11.4	0.5	7.3	765	0.34	678
250% meting		10:12	14.2	0.5	7.4	766	0.34	678
300% meting		10:24	17.1	0.5	7.5	761	0.38	679
350% meting		10:37	19.9	0.5	8	760	0.46	679
NHANGEN PASSIVE SAMPLER								
JITHALEN PASSIVE SAMPLER								
meting nr	Datum 22-4-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
300%		10:00:00	16	12	12.7	841	0.91	6.65

Put	B45B0334-pf6				Naam		Stijn Beernink	
Filter nr.	6				Organisatie		KWR	
Diepte	23 m							
Diameter	2 duims							
meting nr	Datum 21-2-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
10% meting		11:33	2.7	0.5	8.2	421	1.03	7.3
25% meting		11:39	5.6	0.5	8.6	425	0.8	7.29
50% meting		11:42	11.8	0.5	8.6	427	0.7	7.29
75% meting		11:45	17.4	0.5	8.6	427	0.7	7.29
100% meting		11:47	22.7	12	8.4	428	0.64	7.29
150% meting		11:50	32.5	12	8.5	428	0.6	7.29
200% meting		11:54	45.4	12	8.5	429	0.58	7.29
250% meting		11:57	57.2	12	8.4	430	0.54	7.28
300% meting		12:01	68.1	12	8.4	430	0.52	7.28
350% meting		12:08	79.2	12	8.7	431	0.52	7.28
INHANGEN PASSIVE SAMPLER								
UITHALEN PASSIVE SAMPLER								
meting nr	Datum 22-4-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
300%	11:00		69	12	12.5	408	0.69	7.4

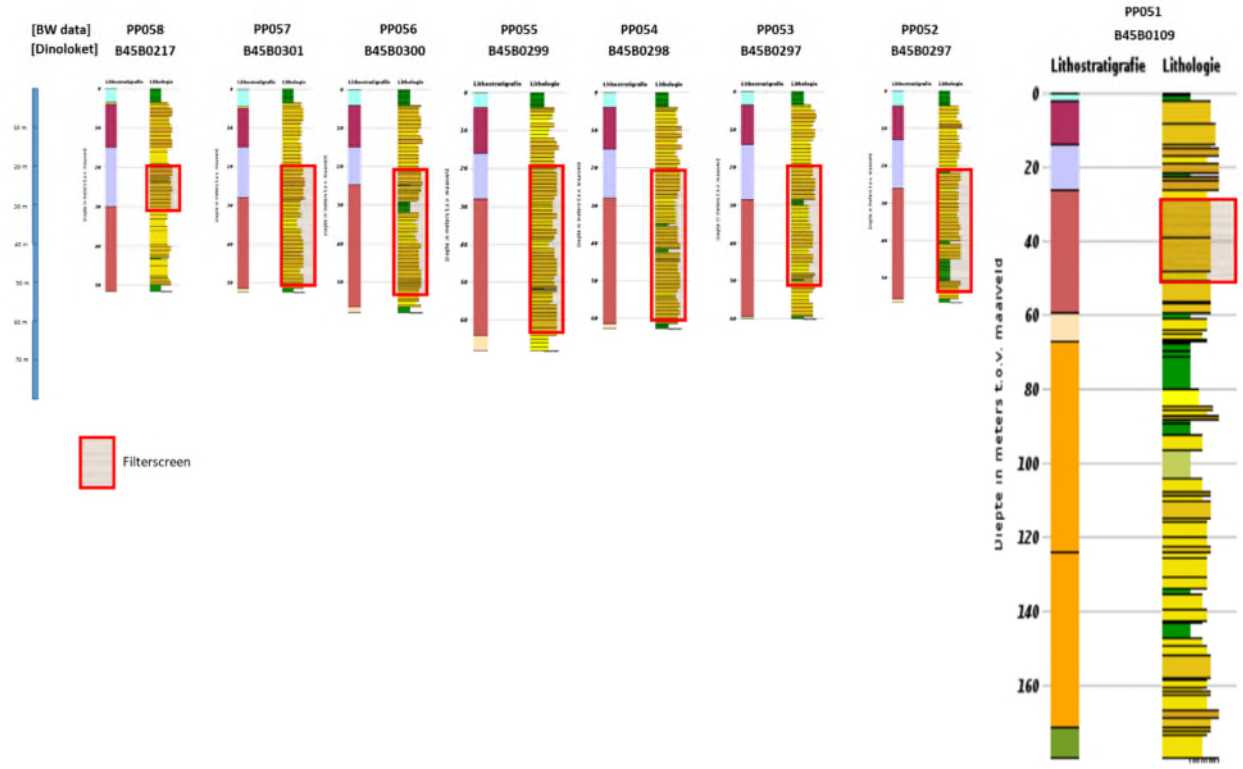
Well B45B0348

Put	B45B0348-pf1				Naam		Stijn Beernink	
Filter nr.	1				Organisatie		KWR	
Diepte	5 m							
Diameter	2 duims							
meting nr	Datum 20-2-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
10% meting		09:29	0.5	0.4	8.9	782	1.49	6.73
25% meting		09:32	1.2	0.4	9.1	783	0.84	6.7
50% meting		09:35	2.1	0.4	9.3	783	0.63	6.68
75% meting		09:40	3	0.4	9.3	790	0.57	6.69
100% meting		09:44	4.2	0.3	9.3	795	0.49	6.69
150% meting		09:52	6.6	0.3	9.4	775	0.46	6.68
200% meting		10:00	8.4	0.3	9.4	798	0.45	6.68
250% meting		10:08	9.75	0.3	9.5	799	0.41	6.69
300% meting		10:15	12.6	0.3	9.5	801	0.46	6.69
350% meting		10:26	14.8	0.3	9.7	802	0.4	6.68
INHANGEN PASSIVE SAMPLER								
UITHALEN PASSIVE SAMPLER								
meting nr	Datum 22-4-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
300%		09:00:00	12	12 l/min	11.5	759	0.64	6.7

Put	B45B0348-pf4				Naam		Stijn Beernink	
Filter nr.	4				Organisatie		KWR	
Diepte	26 m							
Diameter	2 duims							
meting nr	Datum 20-2-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
10% meting		x	x	x	x	x	x	x
25% meting		x	x	x	x	x	x	x
50% meting		10:57	12.5	12l/min	9.5	306	4.12	7.04
75% meting		11:03	19	12l/min	9.3	332	1.77	7.1
100% meting		11:06	25	12l/min	9.4	339	1.23	7.09
150% meting		11:10	32.5	12l/min	9.2	338	1.21	7.07
200% meting		11:20	50	12l/min	9.1	348	0.67	7.11
250% meting		11:27	62.5	12l/min	9.3	350	0.5	7.12
300% meting		11:34	75	12l/min	9.4	349	0.7	7.11
350% meting		11:41	87.5	12l/min	9.4	349	0.66	7.11
INHANGEN PASSIVE SAMPLER								
UITHALEN PASSIVE SAMPLER								
meting nr	Datum 22-4-2020	tijdstip	Verpompt [Liter]	Debiet [L/min]	T [Celcius]	EGV [S/m]	O2 [mg/l]	pH [-]
300%		09:30	75	12l/min	11.9	207	0.88	7.01

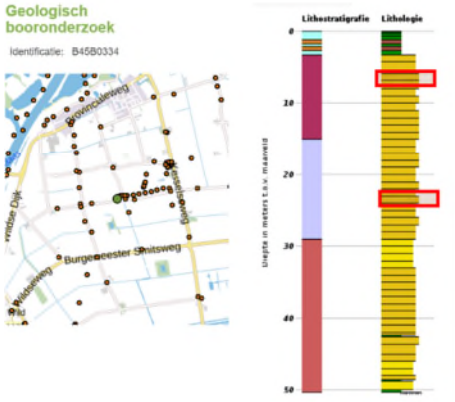
I.VI Geohydrological characteristics of the monitoring and abstraction wells

Abstraction wells – screens are indicated with red box



Monitoring wells – measured screens are indicated with red box

- B45B0334



B45B0348