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Preventing Recalcitrant **O**rganic **M**obile Industrial chemicals for **C**ircular **E**conomy in the soil-sediment-water **S**ystem

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D2.2 – Characterization of PFAS and chlorinated solvent contamination in two aquifers in Spain*

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Executive Summary

The aim of this deliverable is the description and characterisation of the Case Study #7 foreseen in the Grant Agreement of PROMISCES. At an early stage of the project execution, the site foreseen in the proposal was reconsidered since the aquifer under consideration was not contaminated with PFAS anymore, but only with chlorinated solvents. For this reason, the partners decided to investigate an additional aquifer potentially contaminated with PFAS. In this way, the investigation has been conducted in 2 sites, the originally considered site contaminated due to diffuse pollution from a waste treatment facility and other industrial sources (Site 1), and a second one likely to be contaminated with PFAS due to fire-fighting training practices (Site 2).

Characterisation of Site 1 has shown an industrial groundwater pollution in the water flow direction. Conductivity and other physicochemical parameters such as sodium, potassium or nitrates increased along with the concentration of volatile organic compounds (VOCs). Twenty out of the 59 screened VOCs were identified in polluted groundwater wells with concentrations ranging from 0.1 µg/L to 8 µg/L. Trichloroethylene and tetrachloroethene were the most abundant chlorinated solvents reaching values above the EU Directive for drinking water 2020/2184.

Characterisation of Site 2 has shown the presence of 19 PFAS, including the new 6:2 FTSA (fluorotelomer sulfonate), in groundwater as well as in soils. The analyses have revealed the presence of, not only the most recalcitrant compounds, such as PFOS or PFOA (both banned in the industry after their inclusion in Annex B and A, respectively, of the Stockholm Convention on POPs, and also included in the Water Framework Directive), but also new compounds used as substitutes. As a result, the aquifer remediation treatments contemplated in PROMISCES will focus on the compounds (VOCs and PFAS) identified as most relevant in the present deliverable as well as in Site 2 for the field remediation testing.

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1 Introduction

Aquifers are very important as source of drinking water. However, in many cases they suffer from overexploitation and/or chemical contamination. In the framework of the H2020 project PROMISCES, this issue is addressed in Case Study #7, which is carried out in two sites located in Spain. Two sites, instead of one as originally foreseen, have been investigated because the PFAS content investigated during the first characterization of the site was found to be lower than expected in the work plan. For this reason, the partners decided to investigate an additional aquifer potentially contaminated with higher PFAS content. In this way, the investigation in this subtask (2.2.2) has been conducted in 2 sites: Site 1 affected by diffuse pollution from a waste treatment facility and other industrial sources, and Site 2 affected by fire-fighting training practices.

The subsoil characterization of these two sites, which has been performed by ESOLVE, Eurecat and IDAEA-CSIC is summarized in the present report. The results of this characterization will form the basis for the development of tasks 2.2. and 2.3. in WP2 and task 3.4. in WP3.

The objectives of the characterisation were the following:

- Identification of the local geology to further model the transport of PFAS from soil to groundwater in Task 2.3. (WP2)
- Identification of the most abundant and frequently detected PFAS and chlorinated solvents occurring in the groundwater of Case Study #7 to further assess remediation technologies in Subtask 3.4.1 (WP3)
- Identification of the most polluted groundwater wells for field testing of the selected degradation treatments in Subtask 3.4.2 (WP3).

2 Site description

Case study #7 is composed of two independent sites situated in the north of Spain. One of the sites is an aquifer polluted by chlorinated solvents coming from diffuse pollution of the surrounding industrial activities (Site 1), while the other is an aquifer affected by perfluorinated compounds (PFAS) from aqueous film forming foams used in fire-fighting activities (Site 2).

The first site (Site 1) has an extension of 15,300 m². The subsoil of the site consists mainly of silt. This lithology presents different proportions of sand and clay depending on the depth. Between 7 and 8 meters deep, a layer of gravel with silty sand appears, very permeable. With respect to the groundwater dynamics, the direction of the maximum hydraulic gradient is to the southwest, and groundwater depth ranges from 5.5 to 6.5 m.

The second site (Site 2) has an area of 4,050 m². The site lays over alluvial and colluvial Quaternary sediments. These detrital sediments lay unconformably over the bedrock, which is basically formed by fractured granodiorite and granite with narrow porphyritic dykes. From top to bottom a sequence of permeable and impermeable layers is found. The aquifer bottom is around 10m depth, where unweathered granite starts to appear. Based on the lithological description, we can consider the main groundwater bearing unit is formed by detrital sediments and weathered bedrock high hydraulic conductivity due to intergranular porosity. A second unit will be represented by the non-

weathered bedrock with secondary porosity along the fractures network through which water flows. Groundwater depth at the site ranges between 5.5 to 6.0 m.

In the framework of WP2, Site 2 will be the case study used to obtain experimental data to calibrate and validate a model to simulate the transport of PFAS in groundwater. In the framework of WP3, remediation treatment tests at bench-scale will be performed with groundwater from both aquifers to address contamination from two different pollutant classes, but the field testing will be only done in the PFAS-polluted aquifer (Site 2).

2.1 Chlorinated solvent polluted aquifer (Site 1)

The occurrence of chlorinated solvents in this site comes from the diffuse pollution of the surrounding industries via soil/groundwater. This small plot of about one hectare is paved. It has a total of six wells: one groundwater well (called Pozo, Figure 1), and five smaller monitoring wells (MW2, MW6, MW7, MW14 and MW18). The groundwater gradient direction in this site is predominantly from the NE to the SW. Groundwater depth ranges from 5.5 to 6.5 m.

Near this plot, in 2019, there was a hazardous waste treatment plant fire incident that required the employment of PFAS-containing Aqueous Film Forming Foams (AFFF). As a result, for some time the aquifer exhibited some PFAS concentrations in addition to the chlorinated solvents. However, from September 2021 (just before the start of the present project), PFAS concentrations in all groundwater wells are below the detection limits. For this reason and considering that the site is currently involved in a judicial process and the authorities do not allow any intervention on the site, it was decided to add a second site to the Case study #7, named here as Site 2. Since the remediation treatment at full scale will be performed on Site 2, not full geological characterization or hydraulic conductivity tests have been performed in Site 1.

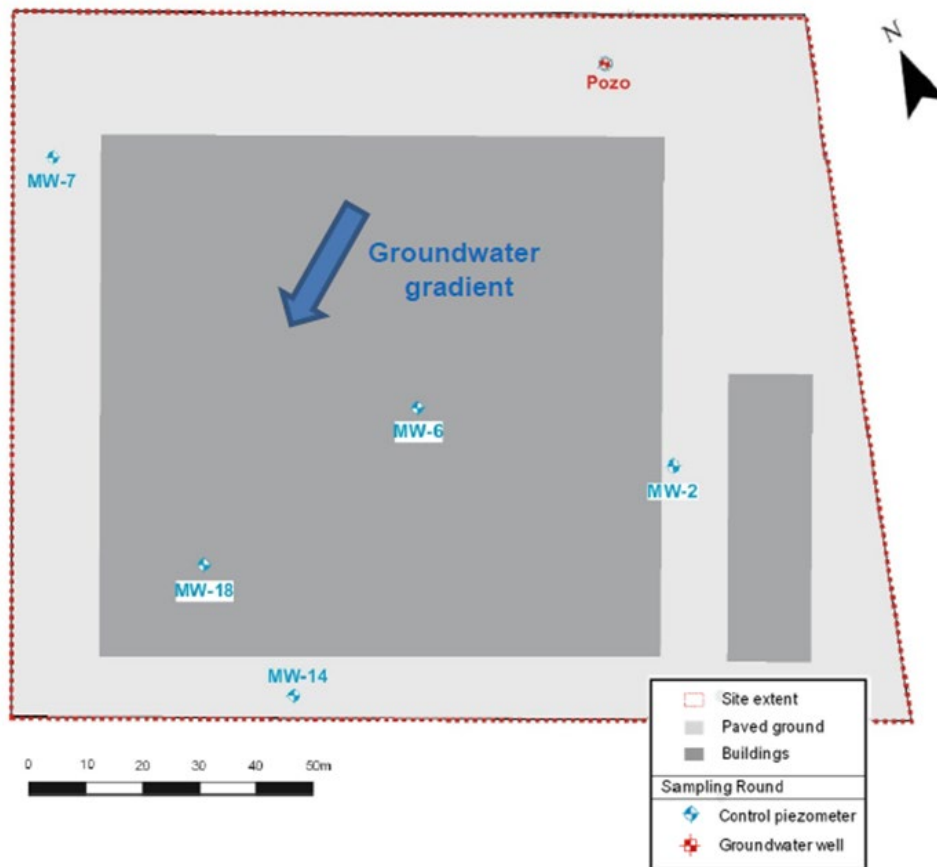


Figure 1: Site 1 layout showing the groundwater sampling points and water flow direction

2.2 PFAS polluted aquifer (Site 2)

This small plot is about 4000 m² and 50% of its surface is concrete paved (see Figure 2). PFAS-containing AFFF are employed here in fire-fighting training activities. The site had no known use until the 1990's, when the current activity started. Fire-fighting training activities have been conducted at this site since the 1990's, with an approximate frequency of one or two training activities per month. Fire-fighting training areas are potential sources of PFAS contamination because many fire suppressants contain Aqueous Film-Forming Foams (AFFF). These substances have been documented to be a source of PFAS contamination at airports and military bases (Mueller & Yingying, 2020). This site is partially paved, allowing the infiltration of these substances to soil and groundwater.

Active release areas in Figure 2 are the places where the AFFF are currently being used, while the abandoned release area is the place formerly used. A total of 6 wells (MW01 to MW06) were drilled and installed between September and November 2021 jointly with the frame of another EU-funded project, the [LIFE SOuRCE](#). All wells reached around 10 m depth. Four wells were drilled in the active areas (MW01, MW02, MW03, MW04), one downstream the active area (MW05) and one in the abandoned release area (MW06). The groundwater gradient direction is predominantly from the NW to the SE.

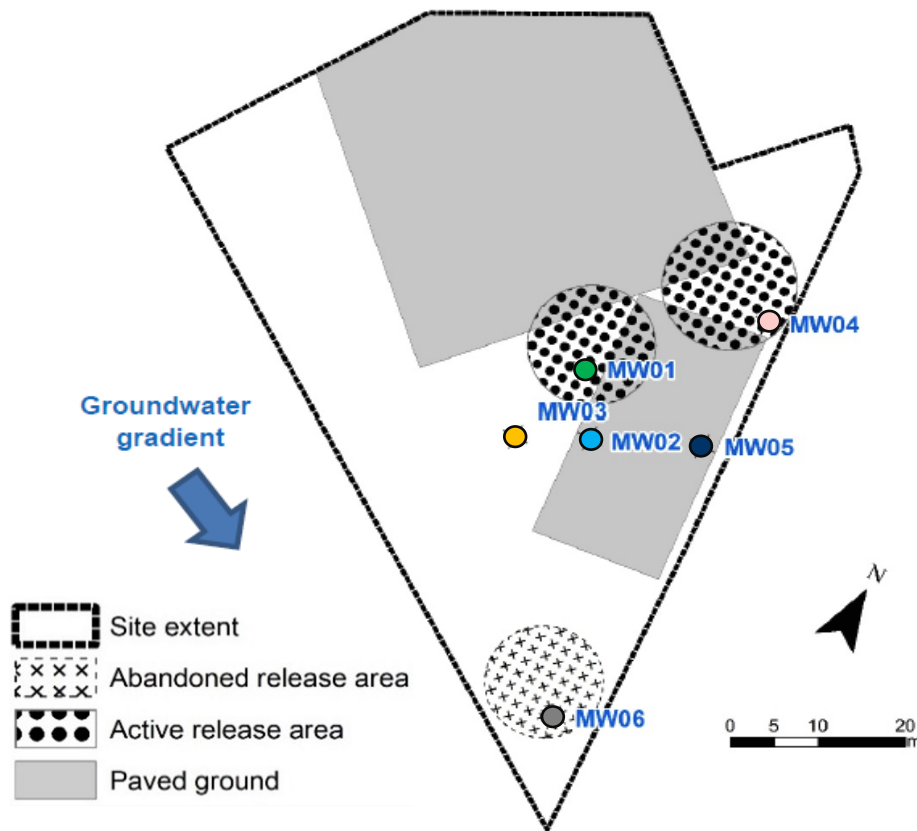


Figure 2: Site 2 layout showing the groundwater sampling points and water flow direction

3 Methodology

3.1 Drilling methodology

A total of 6 monitoring wells (MW01 to MW06) were drilled and installed at Site 2 between September and November 2021, jointly with the tasks conducted in the framework of [LIFE SOuRCE](#). MW01 to MW03 were drilled in September 2021, and MW04 to MW06 were drilled in November 2021. ESOLVE consultants supervised all the drilling and construction process of wells. The groundwater monitoring wells were constructed as described below:

- Rotary drilling technique was used. Drilling diameters were 128 mm (MW04 to MW06) and 152 mm (MW01 to MW03). Cores were recovered continuously from grade to the total depth of boring completion and disposed in PFAS-free plastic boxes for visual characterization, logging and sampling by an on-site geologist. Soil cores were screened for VOCs using a PID, and selected samples were submitted for laboratory analyses. All wells reached 10 m depth, where nearly unweathered granite is found, therefore considered the aquifer bottom.

- Using 102 mm (MW01 to MW03) and 76 mm (MW04 to MW06) diameter polyvinyl chloride (PVC) casing slots (well screens). A minimum of 1 m-thick sealing top (cement at the top, bentonite below) was installed.
- Appropriately sized silica gravel pack was installed in the annular space around the screened interval, generally extended from bottom to 1.7m deep.
- The well annulus was filled with 0.5-1.0 m of bentonite pellets to provide a seal above the gravel pack. Bentonite pellets were slightly hydrate
- Portland cement grout was placed at the top of the well to seal.

3.2 Sampling

Groundwater samples were taken from the chlorinated solvent polluted aquifer (Site 1, MW2, MW6, MW14 and “Pozo”) and the PFAS polluted aquifer (Site 2, 6 monitoring wells MW01-06) on 01/02/22 and 02/02/22. Different clean containers were used depending on the subsequent analyses. Samples for metals, cations and anions were collected in 250 mL HDPE bottles. Samples for total organic carbon (TOC) were collected in 50 mL Falcon tubes. Groundwater for the analyses of chlorinated solvents and benzene, toluene, ethylbenzene and xylene (BTEX) was sampled in triplicate in 40 mL glass vials. Groundwater for the analyses of PFAS was collected in 1 L PET bottles.

As a quality control measurement, for each site one transportation blank and one equipment blank were performed. The first consisted of reagent water that was carried through the sampling and handling to check on contamination from external sources. The second consisted of ultrapure water that passed through all the sampling equipment to determine the possible contamination during the sampling process. The operators wore PFAS-free clothes and gloves, and precautions were taken to avoid cross-contamination.

Soil samples from two monitoring wells in Site 2 were taken after their drilling: MW4 on 08/11/21 and MW5 on 09/11/21. Three subsamples of each soil core were selected for the following soil analyses: granulometry, porosity, bulk density, humidity, total organic carbon, sulfur and sulphate, carbonates, elemental analysis, and X-ray diffraction (XRD). These subsamples corresponded to the unsaturated zone (2.70–2.90 m), the groundwater level zone (5.0–5.1 m) and the saturated zone (9–9.15 m), respectively.

3.3 Physico-chemical analyses in groundwater

Groundwater level and physico-chemical parameters (pH, conductivity, dissolved oxygen and redox) were measured in-situ by Esolve personnel. pH, conductivity, dissolved oxygen, and redox were measured with a portable multimeter equipped with specific probes. Suspended matter was determined after filtration of 200 mL of water with a membrane filter (0.45 μm) and weighting the retained solids after drying at 105°C. Total organic carbon was analyzed by a TOC analyzer (Schimadzu TOC 5050A). Cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and anions (Br^- , Cl^- , PO_4^{3-} , NO_3^- , SO_4^{3-}) were analyzed by ionic chromatography (Dionex Thermo Scientific Aquion and Dionex 2100 CC, respectively). Bicarbonate content was estimated from Ca^{2+} and Mg^{2+} concentrations.

3.4 Physico-chemical analyses in soil

Granulometry was determined on dried soil by separating the different granulometric fractions by manual sieving. Soil was sieved to a fraction < 2 mm to perform the rest of the analyses. Bulk

density, particle density and porosity were measured following the methods described in Klute (1986). Humidity was calculated by drying the soil at 105°C and calculating the weight loss. Total organic carbon, sulfide and sulphate content were determined with a carbon/sulfur analyzer (Leco CS744). Carbonates content was estimated by thermogravimetric analysis. Si, Ca and Mg content was determined by X-Ray Fluorescence (XRF), while the rest of elements (Al, Fe, K, Mn, Na, Ni, Cu and V) were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after acid digestion. X-Ray Diffraction (XRD) was performed to identify the main mineral phases.

3.5 Analysis of chlorinated solvents

Groundwater samples from Site 1 (Figure 1) were analyzed by IDAEA-CSIC for chlorinated solvents using a Purge-and-Trap (PT) technique coupled with gas chromatography (GC) with a mass spectrometer (MS) instrument. The PT manually dispensed 10 mL of the water sample or a standard solution. The samples placed in the vial were purged for 11 min by a stream of helium at 40 mL/min and trapped in an adsorbent. After desorption at 250 °C for 4 min, the volatile organic compounds were transferred directly into a Trace GC coupled to a MS equipped with a CP-Select 624 CB capillary column (60 m x 250 µm x 1.4 µm). The column was set at 40 °C during 10 min, ramped 50–150 °C at 5 °C/min, and to 210 °C at 15 °C/min, this temperature was held for 10 min. The injector was operated in split mode and helium was used as carrier gas.

The MS was operated in full-scan acquisition mode in the m/z 35-380 Da range. Quantification was performed by the internal calibration method using fluorobenzene, 4-bromofluorobenzene and 1,2-dichloroethane- d_4 as internal standards. Nine-point calibration curves were prepared using deionized water just before instrumental analysis. The following 59 volatile organic compounds (VOCs) were determined in groundwater samples: dichlorodifluoromethane, chloromethane, vinyl chloride, bromomethane, chloroethane, trichlorofluoromethane, 1,1-dichloroethylene, methylene chloride, trans-1,2-dichloroethylene, 1,1-dichloroethane, 2,2-dichloropropane, cis-1,2-dichloroethylene, bromochloromethane, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, 1,1-dichloropropylene, benzene, 1,2-dichloroethane, trichloroethylene, 1,2-dichloropropane, dibromomethane, bromodichloromethane, cis-1,3-dichloropropylene, toluene, trans-1,3-dichloropropylene, 1,1,2-trichloroethane, tetrachloroethylene, 1,3-dichloropropane, dibromochloromethane, 1,2-dibromoethane, chlorobenzene, 1,1,1,2-tetrachloroethane, ethylbenzene, m-xylene/p-xylene, o-xylene, styrene, bromoform, isopropylbenzene, bromobenzene, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane, n-propylbenzene, 2-chlorotoluene, 1,3,5-trimethylbenzene, 4-chlorotoluene, tert-butylbenzene, 1,2,4-trimethylbenzene, sec-butylbenzene, 1,3-dichlorobenzene, 4-isopropyltoluene, 1,4-dichlorobenzene, n-butylbenzene, 1,2-dichlorobenzene, 1,2-dibromo-3-chloropropane, 1,2,4-trichlorobenzene, hexachlorobutadiene, naphthalene, 1,2,3-trichlorobenzene.

3.6 Analysis of PFAS

Analysis of PFAS in the groundwater samples from Site 2 (Figure 2) was performed by IDAEA-CSIC using solid phase extraction (SPE) followed by liquid-chromatography coupled to high resolution quadrupole-Orbitrap mass spectrometry (LC-HRMS) according to the methodology developed in the group (Llorca et al. 2012a). Water samples (500 mL) were first spiked with a mixture of surrogate internal standards (mixture of labelled PFASs) in methanol (10 µL of the mix at 100 ng/mL). Then, the samples were extracted and pre-concentrated by SPE using Oasis WAX 3cc cartridges. The final eluates (collected in PP tubes) were evaporated under a gentle stream of nitrogen and reconstituted in 100 µL of water:methanol (9:1). In order to monitor any cross contamination, each

extraction batch was accompanied with a blank consisting of HPLC water spiked with the surrogate internal standards.

Soil samples from Site 2 were extracted by SPE according to the methodology described by Llorca et al. (2012b). One g of each sample was settled in a PP tube, spiked with 20 µL of the surrogate internal standard mix and, then, extracted with 10 mL of methanol by ultrasonic assisted extraction for 1h. The extracts were centrifuged at 2500 rpm at room temperature for 10 min and the supernatant evaporated under a gentle stream of nitrogen. Finally, the samples were reconstituted in 100 µL of water:methanol (9:1). In order to monitor any cross contamination, each extraction batch was accompanied with a blank consisting of a PP empty tube spiked with the surrogate internal standards.

In both cases (water and soil samples) the analysis of PFAS was carried out by LC-HRMS using an Hypersil GOLD PFP analytical column and an electrospray ionization source (ESI) working under negative conditions. Data acquisition was done in full scan mode (100-1000 Da) working at FWHM of 70000 and, in parallel, in data dependent scan of the MS of the PFAS parent ions. The whole system was controlled by Xcalibur 3.0 software. Quantification of the samples was performed with QualBrowser from Xcalibur software.

4 Site characterization results

4.1 Chlorinated solvent polluted aquifer (Site 1)

4.1.1 Groundwater flow investigation

The site has an extension of 15,300 m². Lithology consists mainly of silt with different proportions of sand and clay depending on the depth. Between 7 and 8 meters deep, a layer of gravel with silty sand appears, very permeable.

Groundwater depth ranges from 5.5 to 6.5 m and the direction of Maximum hydraulic gradient is to the southwest.

4.1.2 Groundwater (GW) chemical characterization

The groundwater physical-chemical characterization showed high conductivity values in sampling wells MW-6 and MW-14 (57.6 and 11.6 respectively) with a pH around 5.4, Eh of 69.2 and 158.7 mv, respectively, and TOC lower than 50 mg/L. High conductivity is due to industrial co-contaminants such as Zinc. Sampling wells MW-2 and "Pozo" showed a pH around 7.4, with a conductivity of 1 ms/cm, Eh of 65.9 and -68.5, respectively, and TOC equal to 3 and <2 mg/L, respectively (Table 1 and Table 2). On the other hand, chemical analysis of the sampling wells MW-6 and MW-14 showed an increase of all monitored ions, especially chloride and metals such as Fe, Ni and Cu, which can act as catalysts in the proposed advanced oxidation processes (Table 2 and Table 3).

Table 1: In situ parameters measured in Site 1

Sample name	Depth	Temperature	pH	Conductivity	O2	Eh
	(m)	(°C)		(mS/cm)	(mg/L)	(mV)
Well "Pozo"	6.21	16.8	7.40	0.42	2.38	65.9
MW-2	7.19	16.3	7.49	1.44	0.82	-68.5
MW-6	7.325	17.3	5.21	57.60	1.33	69.2
MW-14	7.415	19.1	5.52	11.68	5.32	158.7

Table 2: Groundwater physical-chemical characterization of the chlorinated solvent polluted aquifer (Site 1). All values are expressed in mg/L

Sample name	TSS	TOC	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Br ⁻	Cl ⁻	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Well "Pozo"	15	<2	44	2	19	11	<0.1	72	<0.1	0.6	5.1	71
MW-2	979	3	104	20	14	139	<0.2	212	<0.2	0.8	109	209
MW-6	2336	<50	5820	521	41	244	<20	24600	<20	216	81	-
MW-14	103	<10	1990	175	12	186	<2.0	5410	<2.0	259	128	-
MW Field Blank Site 1	<1.5	<50	<0.5	<0.25	<0.1	<0.1	<0.1	<0.25	<0.1	<0.5	<0.4	-
MW Transport Blank Site 1	<1.5	<1	<0.5	<0.25	<0.1	<0.1	<0.1	<0.25	<0.1	<0.5	<0.4	-

Table 3: Groundwater metals occurrence in Site 1. All values are expressed in µg/L

Sample name	Cd	Co	Pb	Zn	Fe	Ni	V	Cu	Ba	Mn	As
Well "Pozo"	<1	2	<5	1970	<50	<5	<0.5	<5	432	3510	<1
MW-2	<1	5	<5	110	360	8	<0.5	<5	550	4420	7
MW-6	302	990	83	3091000	1842000	6930	<5	3050	1830	116000	<10
MW-14	42	226	24	267000	3950	782	<5	170	498	34400	<10
MW Field Blank	<0.5	<0.5	<2.5	<25	<25	<2.5	<0.25	<2.5	<1	<1	<0.5
MW Transport Blank	<0.5	<0.5	<2.5	<25	<25	<2.5	<0.25	<2.5	<1	<1	<0.5

As for the chlorinated solvents (and other VOCs), 20 out of the 59 studied chemicals were identified in the samples analyzed (Table 4). The extraction wells that showed the greatest concentration of VOCs were those in which the conductivity and other ions were greater. The most abundant chlorinated solvents were trichloroethylene (TCE) and tetrachloroethylene (perchloroethylene, PCE), with concentration levels between 0.3 and 8 µg/L, followed by other VOCs such as chloromethane, dichloroethylene, or BTEX. PFAS were not detected in the MW6 sample analyzed.

Table 4: Chlorinated solvents and other VOCs detected (in at least one sampling point) and concentrations measured in Site 1. HPLC and MW_BE indicate laboratory and sampling blanks, respectively

	LOD	LOQ	HPLC	MW_BE	MW_2	POZO	MW_14	MW_6
Compounds	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
CHLOROMETHANE	0.053	0.177	<LOD	<LOD	<LOD	<LOD	<LOD	1.354
CIS-1,2-DICHLOROETHYLENE	0.012	0.041	<LOD	<LOD	<LOD	<LOD	0.844	0.450
CHLOROFORM	0.090	0.300	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD
BENZENE	0.011	0.036	<LOD	<LOD	<LOD	<LOD	<LOD	0,665
TRICHLOROETHYLENE	0.020	0.065	<LOD	<LOD	<LOD	<LOD	7.808	2,864
TOLUENE	0.059	0.196	<LOD	<LOD	<LOD	<LOD	0.202	1.959
TETRACHLOROETHYLENE	0.046	0.153	<LOD	<LOD	<LOD	<LOD	6.332	0.283
ETHYLBENZENE	0.004	0.014	<LOD	<LOD	<LOD	<LOD	<LOD	0.874
M-XYLENE/P-XYLENE	0.004	0.012	<LOD	<LOD	<LOD	<LOD	<LOD	0.669
O-XYLENE	0.003	0.010	<LOD	<LOD	<LOD	<LOD	<LOD	1.483
1,3,5-TRIMETHYLBENZENE	0.004	0.015	<LOD	<LOD	<LOD	<LOD	<LOD	0.312
1,2,4-TRIMETHYLBENZENE	0.004	0.013	<LOD	<LOD	<LOD	<LOD	<LOD	0.601
1,2-DICHLOROBENZENE	0.003	0.010	<LOD	<LOD	0.275	<LOD	<LOD	<LOD
NAPHTHALENE	0.011	0.037	<LOD	<LOD	<LOD	<LOD	<LOD	0.257

4.2 PFAS polluted aquifer (Site 2)

4.2.1 Local geology

The local geology was only studied in Site 2 since it is the case study that will be used for the modelling and the remediation implementation.

Borehole drilling until 10 m deep provided detailed local information about the site's geology. The detected lithologies were, from top to bottom, the following:

- Anthropic fill. The most superficial unit, with a thickness ranging from 0.15 m (concrete pavement in MW06) to 3.3 m (MW02). It comprises a wide range of lithologies due to its

man-made nature, from pebbles and gravel to silty sand and a concrete pavement on surface. Ceramic remains (bricks) can be observed at some locations.

- Silty sand (or sandy silt) with occasional gravel, reaching depths between 3.6 m (MW03) and 4.2m (MW02). Brownish, compact. Vegetal and gastropod remains can be observed at some locations.
- Medium-coarse sand. This unit was only observed at MW02 (4.2 to 4.4 m depth) and MW03 (from 3.5 to 3.9 m depth). Quite loose, it had scarce silt and some gravel.
- Gravel, pebbles and cobbles. The top of this layer could be found between 3.7 m deep (MW01) and 4.4 m deep (MW02). The bottom was detected between 6.0 m deep (MW04) and 8.5 m deep (MW06). Its thickness ranged from 2.5 m to 5 m. It usually had a 30 to 40% sandy matrix. At points MW01 and MW05, a layer with less sandy matrix and higher proportions of pebbles and cobbles was detected at the middle section of this unit. At MW02 and MW04, a layer of silty sand was encountered in the middle of this unit (reaching a thickness of 2 m at MW04). This is the first water-bearing unit encountered, with a general groundwater table being at 5.6 to 5.9 m deep during the drilling campaigns. It also constitutes the most permeable unit.
- A couple of very thin layers (whitish compact sandy silt, and pebbles and cobbles in white gravel) were found at MW01 only.
- Silty and clayey, thin sand layers. Finer grain sizes were observed at the bottom of the before mentioned gravel unit in all boreholes except MW05. Although it can be up to 2 m thick, in most locations it hardly reached a thickness of 0.5 m. This layer usually was red-brown colored and had white loose gravel from decomposed granite. At 10 m deep, this was the last encountered unit at points MW01, MW04 and MW06.
- Clayey gravel with pebbles and cobbles. The top of this layer could be found at 7.5 m or deeper in all boreholes except MW01 and MW06. It had a high loose content of decomposed granite. Whitish color. At some points it is less than 0.5 m thick. At 10 m deep, it was the last encountered layer at points MW02, MW03 and MW05.

4.2.2 Groundwater flow investigation

All head measurements from both drilling campaigns are listed in Annex I. These measurements were collected after a minimum of 72 hours interval from the last well development to avoid undesired pumping interferences.

Non-Aqueous Phase Liquid (NAPL) was not detected at any location. Foam formation was not detected at any sampling location. No chemical odors or sheen (iridescences) were noted in groundwater samples or purge water. Groundwater was noted as clear and colorless.

A piezometric surface map showing the interpolated groundwater contours and the inferred groundwater flow direction is presented in Figure 3. Collected data from November 2021 shows a maximum hydraulic gradient direction towards the East. The average gradient is approximately 1.5%. Data from September 2021 also fits with these results.

Hydraulic tests were carried out at 5 wells (MW01 to MW05) to estimate site-scale hydraulic conductivity (K). This parameterization will help designing a correct pumping system for groundwater treatment.

Data shows that MW01 is the most permeable well with $K=1.3\text{m/d}$. MW02, MW03 and MW05 have medium permeabilities ranging from 0.55 to 0.67 m/d. The less permeable well, with difference, is MW04 with $K=3.1 \cdot 10^{-4}$ m/d. These observations fit with detected geology during drilling works.

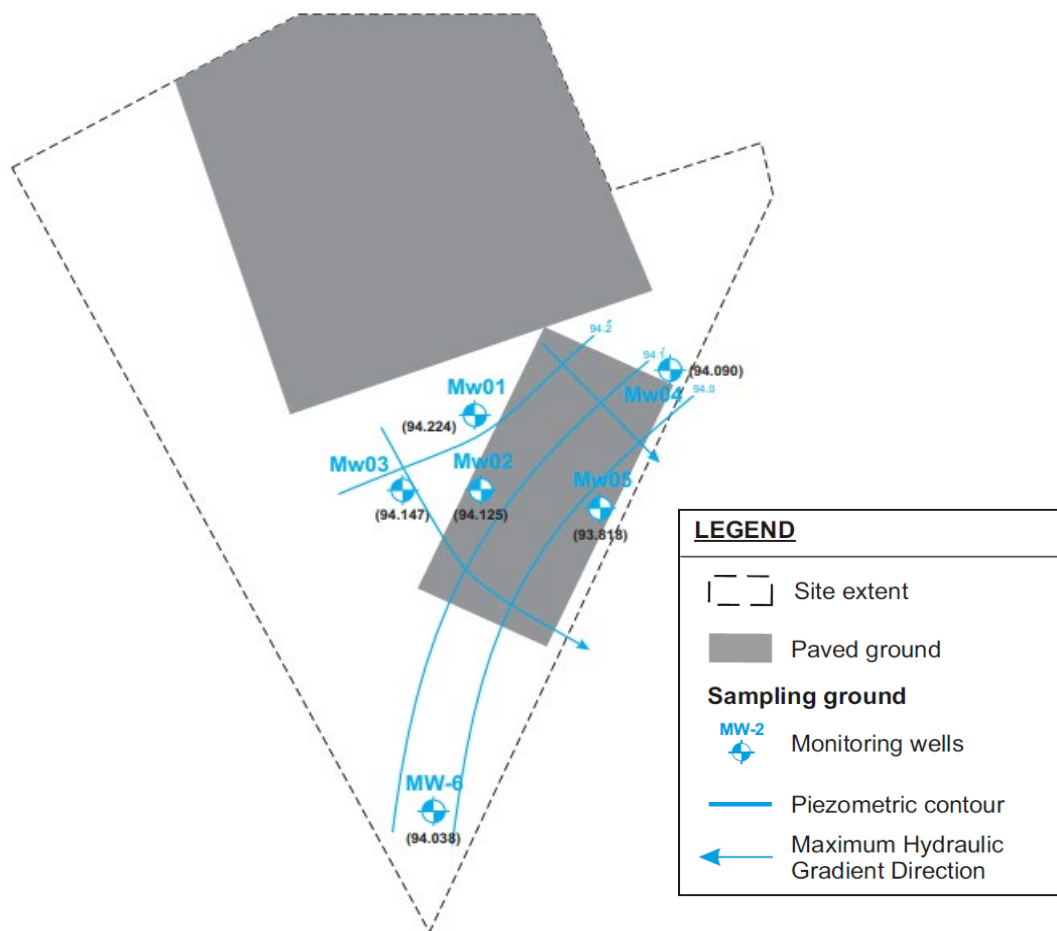


Figure 3: Piezometric surface map showing the interpolated groundwater contours and the inferred groundwater flow direction in Site 2

4.2.3 Groundwater analytical characterization

The groundwater physical-chemical characterization showed a pH around 7 or slightly below in all sampled wells, conductivities between 355 and 915 $\mu\text{S}/\text{cm}$, dissolved oxygen up to 1.93 mg/L, Eh between 93 and 143 mV, and TOC between 2 and 6 mg/L (Tables 5 and 6). On the other hand, the chemical analysis of these samples showed little presence of metals and it did not evidence pollution by hydrocarbons or organochlorines. However, the analysis of PFAS evidenced the presence of 19 compounds at concentrations higher than the limit of quantification (LOQ). As it is shown in Table 7, these PFAS were carboxylic acids (PFCA), sulfonic acids (PFSA) and fluorotelomer sulfonates (FTSA). Total PFAS concentration range from 45 ng/L to 126 $\mu\text{g}/\text{L}$ whereas the maximum carbon chain was of 12 carbons. On the other hand, new PFAS including 6:2 diPAP, 8:2 diPAP, ADONA, EtFOSA, EtFOSAA, FOSAA, MeFOSAA, MeFOSA, HFPO-DA (Gen-X), PFMOAA, PFMOPrA, PFMOBA, PFO2HxA, PFO3OA and PFO4DA were not detected.

Table 5: In situ parameters measured in Site 2

Sample name	GW Depth	Temperature	pH	Conductivity	O2	Eh
	(m)*	(°C)		(uS/cm)	(mg/L)	(mV)
MW01	5.91	17.5	6.86	692	1.74	136.7
MW02	6.15	16.3	6.87	643	1.93	142.4
MW03	6.605	17.4	6.82	915	1.86	120
MW04	5.87	17.2	6.89	906	1.86	146
MW05	6.353	18.1	6.89	616	1.64	92.6
MW06	5.945	16.2	7.56	355	1.17	112.5

*Meters below ground surface.

Table 6: Groundwater physical-chemical characterization of the PFAS polluted aquifer (Site 2). All values are expressed in mg/L

Sample name	TSS	TOC	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Br ⁻	Cl ⁻	PO4 ³⁻	NO3 ⁻	SO4 ²⁻	HCO3 ⁻
MW01	860	3	81	16	3	34	0.2	45	<0.1	22	42	164
MW02	546	2	66	13	3	30	0.2	44	<0.1	21	37	133
MW03	2908	2	107	25	3	40	0.3	49	<0.2	15	50	226
MW04	988	6	110	28	2.9	33	<0.2	34	<0.2	0.7	21	238
MW05	2906	2	71	12	3	31	0.2	44	<0.1	18	33	138
MW06	3720	<2	33	7	3	21	<0.1	25	<0.1	5.1	23	68
MW Field Blank	<1.5	<2	<0.5	<0.25	<0.1	<0.1	<0.1	<0.25	<0.1	<0.5	<0.4	NA
MW Transport Blank	<1.5	<1	<0.5	<0.25	<0.1	<0.1	<0.1	<0.25	<0.1	<0.5	<0.4	NA

Table 7: Groundwater metals occurrence in Site 2. All values are expressed in µg/L

Sample name	Cd	Co	Pb	Zn	Fe	Ni	V	Cu	Ba	Mn	As
MW01	<1	<1	<5	101	<50	<5	<0.5	<5	144	102	<1
MW02	<1	<1	<5	<50	<50	<5	<0.5	<5	117	8	<1
MW03	<1	2	<5	<50	<50	3	<0.5	<5	169	179	<1
MW04	<1	6	<5	<50	<50	11	<0.5	<5	198	1470	2
MW05	<1	3	<5	<50	95	<5	<0.5	<5	109	254	<1
MW06	<1	<1	<5	<50	<50	<5	<0.5	<5	80	2	<1
MW Field Blank	<0.5	<0.5	<2.5	<25	<25	<2.5	<0.25	<2.5	<1	<1	<0.5
MW Transport Blank	<0.5	<0.5	<2.5	<25	<25	<2.5	<0.25	<2.5	<1	<1	<0.5

Table 8: Concentrations of PFAS detected in groundwater samples from Site 2, and method limits of detection (MLOD) and quantification (MLOQ), all expressed in ng/L

	MLOD	MLOQ	MW01	MW02	MW03	MW04	MW05	MW06	MWD	MWB1	MWB2
PFBA	0.042	0.14	240.38	50.32	27.22	1247.32	98.31	2.27	0.19	< MLOD	< MLOQ
PFPeA	0.042	0.14	1185.19	291.33	125.77	112071.37	1049.13	9.87	< MLOD	0.15	< MLOQ
PFHxA	0.045	0.15	1069.55	234.89	132.45	9137.00	790.79	6.83	< MLOD	1.09	< MLOQ
PFHpA	0.048	0.16	400.23	93.73	30.35	1548.99	338.14	6.05	< MLOD	1.28	< MLOD
PFOA	0.045	0.15	47.12	30.76	15.12	504.23	57.62	6.02	< MLOQ	0.45	< MLOQ
PFNA	0.039	0.13	3.52	8.24	1.78	66.94	3.88	0.36	0.18	1.23	0.77
PFDA	0.297	0.99	2.95	5.02	< MLOQ	62.47	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ
PFUnA	0.363	1.21	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ	2.89	< MLOQ
PFDoA	0.504	1.68	< MLOQ	< MLOQ	< MLOQ	< MLOD	< MLOD	< MLOQ	< MLOD	< MLOQ	< MLOD
PFTeDA	0.504	1.68	< MLOQ	< MLOD	< MLOQ	< MLOD	< MLOD	< MLOD	< MLOQ	65.27	5.73
PFTeDA	1.632	5.44	< MLOD	< MLOD	< MLOQ	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD
PFHxDA	0.624	2.08	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD
PFODA	1.488	4.96	< MLOD	< MLOD	< MLOQ	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD
PFBS	0.093	0.31	36.62	17.75	9.38	128.84	48.32	3.72	2.36	1.74	2.49
PFPeS	0.09	0.30	34.10	7.09	1.29	148.77	39.34	0.41	< MLOD	< MLOQ	< MLOQ
PFHxS	0.093	0.31	411.50	83.30	10.00	889.69	244.69	4.18	0.39	3.88	< MLOQ
PFHpS	0.12	0.40	6.78	6.48	< MLOQ	37.52	10.95	< MLOQ	< MLOD	< MLOQ	< MLOQ
PFOS	0.111	0.37	413.61	1098.24	104.27	444.74	97.42	5.91	0.79	53.60	< MLOQ
PFNS	0.147	0.49	2.30	7.16	0.53	1.70	< MLOQ	< MLOQ	< MLOD	< MLOQ	< MLOD
PFDS	0.138	0.46	1.14	2.35	< MLOD	< MLOQ	< MLOD	< MLOD	< MLOD	< MLOQ	< MLOD
PFDoS	0.327	1.09	< MLOD	< MLOQ	< MLOQ	1.22	< MLOD	< MLOD	< MLOD	< MLOD	1.36
10:2 FTSA / H4-PFDoDS	0.327	1.09	6.29	3.20	2.55	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD
4:2 FTSA / H4-PFHxS	0.093	0.31	2.87	< MLOD	< MLOD	3.22	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD
6:2 FTSA / H4-PFOS	0.111	0.37	58.21	33.38	48.66	213.07	15.79	< MLOD	< MLOD	< MLOD	< MLOD
8:2 FTSA / H4-PFDeS	0.138	0.46	8.54	15.08	9.78	23.42	0.83	< MLOD	< MLOD	0.47	< MLOD

4.2.4 Soil analytical characterization

The physical-chemical characterization of the soil showed that, in terms of granulometry, it is predominantly gravel and sand fractions with a low content of silt (< 50 μm) and clays (< 2 μm) (Figure 4 and Annex II). Soil bulk density is 1.43 g/mL in average for all samples, with particle density of 2.72 g/mL and 46% of porosity (Annex III). The main mineral phases are quartz, feldspars, and some clay minerals (illite, chlorite, kaolinite....) (Annex IV), with a low organic carbon (0.25%) and no presence of inorganic carbon (Annex V). Furthermore, it has a moderate content of iron with traces of Ni, Cu, and V, which can act as catalysts in oxidation processes reactions (Table 9). Thermogravimetric analysis showed no carbonate content.

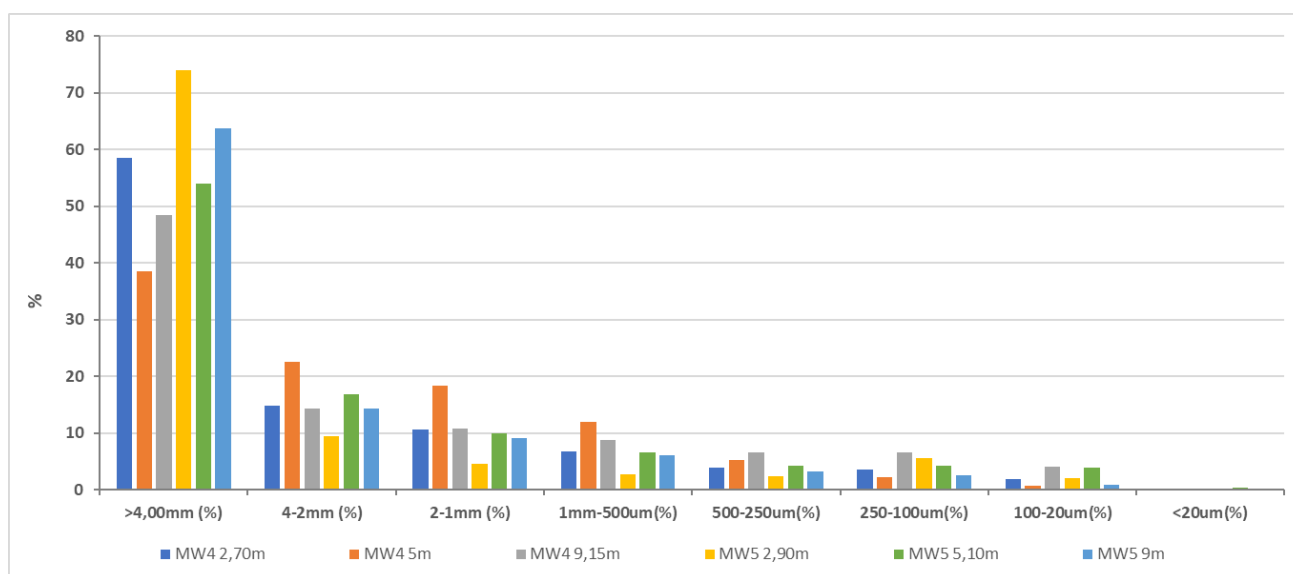


Figure 4: Granulometry of the Site 2 soil

Table 9: Soil moisture and metals at Site 2. Dry sample 105 C

Sample name	Moisture	Al	Si	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn
	%													
MW4 2.7m	12.66	5.420	16.272	0.016	1.975	<LOD	0.535	0.008	0.019	0.058	3.758	0.004	0.003	0.014
MW4 5m	3.36	6.003	14.745	0.011	2.082	<LOD	0.405	0.005	0.021	0.068	3.507	0.005	0.002	0.014
MW4 9.15m	6.29	6.099	16.885	0.008	2.510	0.548	0.387	0.010	0.020	0.091	3.177	0.004	0.004	0.013
MW5 2.9m	18.56	5.204	18.000	0.020	1.890	<LOD	0.517	0.008	0.015	0.055	3.670	0.005	0.003	0.012
MW5 5.10m	3.87	5.919	17.522	0.009	2.268	<LOD	0.419	0.007	0.018	0.048	4.058	0.004	0.003	0.015
MW5 9m	9.11	5.881	15.186	0.009	2.494	0,061	0.486	0.015	0.018	0.079	4.009	0.005	0.005	0.021
Blank		1.008	1.706	<LOD	<LOD	0,127	<LOD	<LOD	0.036	0.022	0.126	0.003	<LOD	0.003

Regarding the analysis of PFAS, the soil contained 11 compounds at higher concentrations than the MLOQ; all belonging to the same chemical classes found in water (carboxylic acids (PFCA), sulfonic acids (PFSA) and fluorotelomer sulfonates (FTSA) (Table 10). The PFAS detected contain a maximum chain length of 9 carbons and, generally, it has been observed that long-chain PFAS are retained on the unsaturated zone due to the air-water partitioning coefficient. Furthermore, the concentration of PFAS decreases towards the bottom of the aquifer, while short-chain increase, probably because of the degradation of long-chain PFAS that could be degraded, such as FTSA. Finally, other new emerging PFAS such as 10:2 FTSA / H4-PFDoDS, 8:2 FTSA / H4-PFDeS, 4:2 FTSA / H4-PFHxS, 6:2 diPAP, 8:2 diPAP, ADONA, EtFOSA, EtFOSAA, FOSAA, MeFOSAA, MeFOSA, HFPO-DA (Gen-X), PFMOAA, PFMOPrA, PFMObA, PFO2HxA, PFO3OA and PFO4DA were not detected.

Table 10: Concentrations of PFAS in soils of Site 2 and method limits of detection (MLOD) and quantification (MLOQ), all expressed in ng/g

	MLOD	MLOQ	MW5 9m	MW5 5.10m	MW4 2.70m	MW4 9.15m	MW5 2.90m	MW4 5m
PFBS	0.093	0.31	2.23	<MLOQ	<MLOQ	2.86	<MLOQ	<MLOQ
PFPeS	0.075	0.25	<MLOD	<MLOQ	<MLOQ	<MLOD	0.27	<MLOQ
PFHxS	0.03	0.10	<MLOQ	0.62	0.36	<MLOQ	2.76	0.15
PFHpS	0.12	0.40	<MLOQ	<MLOQ	1.65	<MLOD	1.59	1.34
PFOS	0.111	0.37	<MLOQ	<MLOQ	17.80	<MLOQ	<MLOQ	<MLOQ
FOSA	0.24	0.80	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFNS	0.267	0.89	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFDS	0.18	0.60	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFDoS	0.327	1.09	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFBA	0.423	1.41	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ
PFPeA	0.15	0.50	<MLOD	0.73	2.16	0.53	1.69	1.04
PFHxA	0.159	0.53	<MLOQ	0.93	1.79	<MLOQ	1.84	0.64
PFHpA	0.108	0.36	<MLOQ	<MLOQ	0.54	<MLOQ	0.95	<MLOQ
PFOA	0.066	0.22	1.00	0.93	2.03	0.76	3.76	<MLOQ
PFNA	0.039	0.13	<MLOQ	<MLOQ	0.59	<MLOQ	<MLOQ	<MLOQ
PFDA	0.417	1.39	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ
PFUnA	0.363	1.21	<MLOQ	<MLOD	<MLOD	<MLOQ	<MLOQ	<MLOQ
PFDoA	0.504	1.68	<MLOD	<MLOD	<MLOQ	<MLOD	<MLOQ	<MLOD
PFTTrDA	0.504	1.68	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFTeDA	0.432	1.44	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFHxDA	0.624	2.08	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
PFODA	1.488	4.96	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
6:2 FTSA / H4-PFOS	0.3	1.00	<MLOQ	2.47	6.33	<MLOQ	3.98	<MLOQ

5 Discussion

In the two monitored sites the impact of industrial activities on the groundwater quality has been easily detected by the increase of conductivity and other ions such as Na, K or nitrates. The water flow direction allowed us to draw the contamination plume in both sites. The increase in the concentration of these general quality parameters runs parallel with an increase of PMTs such as chlorinated solvents in Site 1 and PFAS in Site 2.

In Site 1, the most abundant chlorinated solvents were PCE and TCE, with concentration levels up to 8 µg/L. The sum of the concentration of these two compounds in the sampling well MW-14 was above the threshold of 10 µg/L set by the DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2020 on the quality of water intended for human consumption. The great abundance of these two compounds is in agreement with the fact that they have been extensively used in a variety of industrial applications, but also due to their persistence in soil and groundwater (Kueper et al., 2914). Although the concentration levels of TCE and PCE were greater in MW14 than in MW6, MW6 showed the presence of 14 VOCs whereas only 4 of them were detected in MW14. Among VOCs identified in MW6, BTEX and chloromethane prevailed. This, together with the location of the sampling point in the middle of the building (Fig 1), suggests that this was probably the site where the main industrial spill took place.

In Site 2, PFAS were identified in both groundwater and soil samples, where the detected compounds include PFCA, PFSA and FTSA. The concentrations in waters were up to 112 µg/L for PFPeA and followed for the banned PFOS. In the case of soils, the concentrations reached 17.8 ng/g for PFOS followed for 6:2 FTSA, PFHpS, PFBS and PFHxS due to their tendency to be adsorbed.

6 Conclusions

In view of the monitoring results shown above, Site 1 is highly polluted with PCE and TCE (0.2 to 8 µg/L), whereas Site 2 is polluted with PFAS, especially with the highly mobile PFPeA (0.009 to 112 µg/L) and PFOS (0.79 ng/L to 1.1 µg/L) in groundwaters, and PFOS (17.8 ng/g), 6:2 FTSA (2.47 – 6.33 ng/L), and the rest of sulfonic acids (ranging from 0.36 ng/g for PFHxS to 2.86 ng/g for PFBS) in soils. These compounds are considered under the Groundwater Directive (2006/118/EEC) in the Groundwater Watch List. In addition, the concentrations detected in Site 2 were much higher than the limit levels established in the Drinking Water Directive 2020/2184, where the limit for the sum of 20 individual PFAS is 0.1 µg/L. These PMTs have therefore been selected for the development and assessment of the remediation treatments in Task 3.4. The groundwater profile of the concentration of these PMTs was drawn in the groundwater and the most polluted groundwater wells were identified (MW-14 in Site 1 and MW04 in Site 2). Besides the concentration of PMTs, our results also highlight the increase in concentration of other physicochemical parameters such as conductivity, sodium, potassium, nitrates or sulfates, which will need to be taken into account in the development and optimization of the remediation treatments at lab scale (WP3).

7 Literature

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Annexes

Annex I: Groundwater depths and piezometric head

Well name	Z Reference (m)	GW depth (m)*	Head (m)
<i>September 6, 2021</i>			
MW01	99.964	5.955	94.009
MW02	100.000	6.215	93.785
MW03	99.957	8.640	91.317
<i>November 16, 2021</i>			
MW01	99.964	5.740	94.224
MW02	100.000	5.875	94.125
MW03	99.957	5.810	94.147
MW04	100.050	5.960	94.090
MW05	100.008	6.190	93.818
MW06	99.618	5.580	94.038

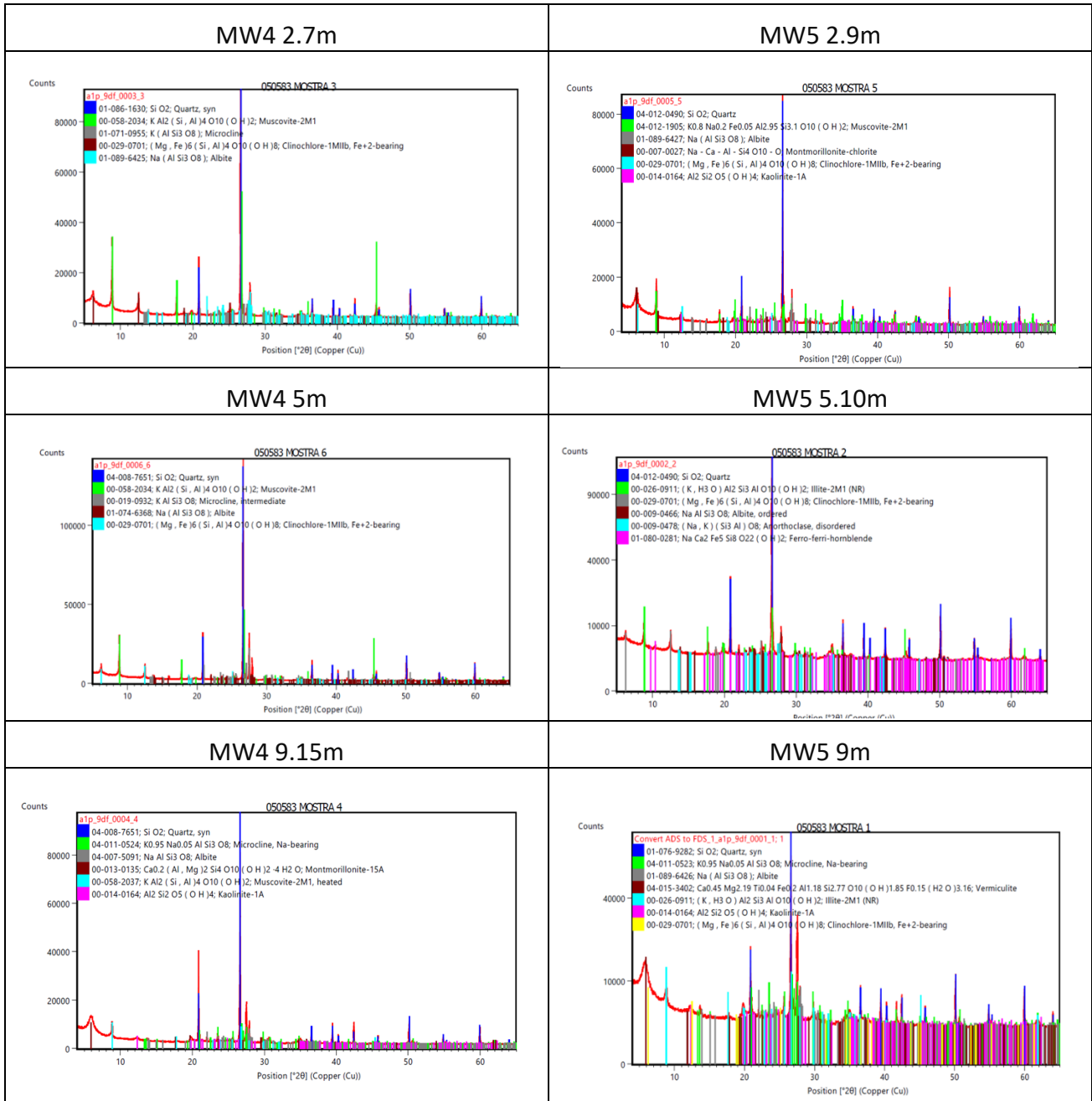
*Meters below ground surface.

Annex II: Site 2 soil granulometry.

Dry Sample 105°C	Sieve/Granulometry							
	4	2	1	0.5	0.25	0.1	0.02	0.001
	>4 mm (%)	4-2mm (%)	2-1mm (%)	1mm- 500µm (%)	500-250 µm (%)	250-100 µm (%)	100-20 µm (%)	<20µm (%)
MW4 2.70m	58.48	14.77	10.62	6.77	3.91	3.64	1.85	0.04
MW4 5m	38.53	22.58	18.34	12.06	5.25	2.3	0.8	0.06
MW4 9.15m	48.47	14.26	10.88	8.82	6.6	6.53	4.06	0.3
MW5 2.90m	73.92	9.45	4.67	2.73	2.36	5.62	2.07	0.11
MW5 5.10m	53.92	16.88	9.94	6.56	4.21	4.21	3.9	0.31
MW5 9m	63.71	14.38	9.05	6.02	3.31	2.62	0.88	0.06

Annex III: Site 2 soil characterization in terms of bulk and particle density and porosity.

Dry sample 105°C and sieve <2mm	Bulk Density	Particle Density	Porosity
	g/mL	g/mL	%
MW4 2.70m	1.29	3.50	63.20
MW4 5m	1.48	2.19	32.70
MW4 9.15m	1.49	2.47	39.80
MW5 2.90m	1.28	2.50	48.70
MW5 5.10m	1.77	2.96	40.10
MW5 9m	1.27	2.72	53.20

Annex IV: Site 2 soil XRD figures.


Annex V: Site 2 soil physical-chemical characterization.

Dry sample 60 °C & sieved < 2 mm	Moisture 60°C	(TOC) C	S	SO4	Inorganic C
	%	%	%	%	%
MW4 2.7m	13.7	0.5423	0.014	0.041	n.d
MW4 5m	3.81	0.0657	0.003	0.008	n.d
MW4 9.15m	5.18	0.4920	0.002	0.005	n.d
MW5 2.9m	17.25	0.1420	0.004	0.011	n.d
MW5 5.10m	4.52	0.0665	0.003	0.008	n.d
MW5 9m	8.13	0.1860	0.001	0.003	n.d