

UPWATER

UNDERSTANDING GROUNDWATER POLLUTION TO PROTECT AND
ENHANCE WATERQUALITY

DELIVERABLE D2.1 MONITORING PLAN



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CONTENT

Executive Summary.....	6
1. SAMPLING METHODOLOGIES AND FREQUENCY OF DEPLOYMENT.....	7
2. CASE STUDIES.....	9
2.1 STENGÅRDEN (DENMARK).....	9
2.2 BESÒS (SPAIN).....	12
2.3 ATHENS (GREECE).....	20
3. References.....	29



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LIST OF ABBREVIATIONS

Abbreviation	Definition
ACA	Catalan Water Agency
Agbar	Aigües de Barcelona
AMB	The metropolitan Area
ANSTO	Australian Nuclear Science and Technology Organisation.
AU	Aarhus University.
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
BR	Barcelona Regional Agencia Metropolitana de Desenvolupament. Urbanístic d'infrastructures SA.
CC	Climate change
CoV	Coronavirus
CPS	Ceramic passive sampler
CS	Case study
CSIA	Compound specific isotope analysis
CSIC	Agencia Estatal Consejo superior de Investigaciones Científicas.
DGT	Diffusive Gradients in Thin Films
DI	Direct Injection
DMA	Differential Mobility Analyzer
EYDAP	Athens Water Supply and Sewerage Company.
EV	Enterovirus
FC	Future City Foundation
FNCA	Fundación Nueva Cultura del Agua.
GAC	Granular activated carbon
GC	Gas chromatography
GW	Groundwater
HAdV	Human Adenovirus
HEV	Hepatitis E virus
HPLC	High-Performance Liquid Chromatography
IAV	Influenza A virus
IDAEA	Institute of Environmental Assessment and Water Research.
INERIS	Institut National de L'Environnement Industriel et des Risques.



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IR	Isotope Ratio
JCPyV	JC Polyomavirus
MBBR	Moving Bed Biofilm Reactor
MS	Mass Spectrometry
NBS	Nature Based Solutions
NGS	Next Generation Sequencing
NoV	Norovirus
NTUA	National Technical University of Athens.
PAHs	Polycyclic aromatic hydrocarbons
PFAS	Per- and polyfluoroalkyl substances
PMMoV	Pepper Mild Mottle Virus
qPCR	Quantitative Polymerase Chain Reaction
SPE	Solid Phase Extraction
TARH	Terra, Ambiente e Recursos Hidricos Lda.
UB	Universitat de Barcelona.
UPWATER	Understanding groundwater Pollution to protect and enhance WATER quality.
UWA	University of Western Australia
VAE	Vacuum-Assisted Evaporation
VPS	Viral Passive Samplers



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EXECUTIVE SUMMARY

This document describes the outcome of Task 2.5 'Monitoring Plan' within the UPWATER project (Understanding groundwater Pollution to protect and enhance WATER quality, Horizon Europe project N° 101081807). The UPWATER project has three case study sites; one in Denmark (Stengården dumpsite), Spain (Besòs river) & Greece (Athens), respectively. The CS are affected by different sources of pollution that adversely affect the quality of the local groundwater (GW). In the Danish case study, the GW is impacted by pesticide wastes, whereas in the Spanish and Greek CS, the GW is primarily polluted as a result of urban and industrial activities.

To protect GW resources, it is important to design effective monitoring plans that allow the evaluation of the geographical and temporal distribution of contaminants and to tailor site-specific mitigation strategies. The here presented monitoring plan contains the background contamination at each case study and has a site-specific emphasis both with respect to the pollutants to be monitored, the deployed analytical methods and the mitigation approach. The monitoring strategy includes the analysis of organic contaminants, metals and viral pathogens, and is based on the periodic monitoring (every 3 months) of GW contaminants for a period of 12-18 months, depending on the case study, to determine any patterns and time trends in the pollution. Traditional grab sampling will be contrasted to passive sampling techniques so that the latter can be validated and implemented in future studies. While grab sampling allows the punctual analysis of contaminants, passive sampling will deliver time integrated concentrations of GW contaminants, thus excluding day to day variabilities and enabling a more representative procedure. Three types of passive samplers will be deployed in the case studies:

- Ceramic Passive Samplers (CPS) for the analysis of organic contaminants
- Diffusive Gradients in Thin Films (DGTs) for the analysis of metals
- Viral passive samplers (VPS) for the analysis of water pathogens

This deliverable contains the first results of initial sampling campaigns (T4.1) and meets milestone 3 of the UPWATER project (monitoring plan for the individual CS). The current version of the deliverable is a revised version which includes monitoring of Per- and polyfluoroalkyl substances (PFAS) for the Besòs and Athens with CPS in addition to application of DGTs for monitoring of metals in Stengården.



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1. SAMPLING METHODOLOGIES AND FREQUENCY OF DEPLOYMENT

Passive sampling for the analysis of water contaminants is an established technique although its deployment for GW monitoring still requires method validation to ensure its performance. The UPWATER project will validate three types of passive samplers for GW monitoring: Ceramic Passive Samplers (CPS), Diffusive Gradients in Thin Films (DGT) and Viral Passive Samplers (VPS).

Ceramic Passive Samplers: As CPS allow high enrichment factors, the use of CPS will promote integrated sampling to have representative information on the contaminants present in GW, allowing the detection of a large number of contaminants. CPS will also minimize the number of grab samples and thus, the time and costs related to monitoring.

Based on preliminary concentrations of the concern contaminants detected in GW (in the ng/L range), it was decided that 3 months deployment for the CPS would be good to have high enrichment factors. Two CPS (duplicate samples) will be deployed in each well (20 wells in Besòs, 15 in Athens and 6 in Stengården) for a period of 3 months each, and during the 18 months monitoring as stipulated in the project. In total, 6 sampling campaigns will be carried out during the 18 months of monitoring, which should allow seasonal variations to be detected with the CPS. To validate the procedure, at the beginning of each season, we will collect a grab sample to compare the results among both sampling methods. This comparison will allow validating the CPS in real field conditions. CPS will be done to analyze contaminants of emerging concern and perfluoro alkyl substances (PFAS).

Diffusive Gradients in Thin Films: According to expected concentrations (in the ng/L - ug/L range) in GW, the plan is to deploy DGTs for 1 to 2 weeks to detect labile concentrations of metals. Firstly, we need a validation test that will consist in a preliminary campaign in Besòs to confirm concentrations and deployment times. After that, we will deploy 2 DGTs to get duplicate samples in each well (20 wells in Besòs and 15 in Athens) for a maximum period of 2 weeks each, and during the 18 months monitoring as stipulated in the project.

Viral passive samplers: will be developed by selecting the best sorbent and contact time between sampling material and the water sample. We plan to deploy VPS underwater for a period between 2 and 15 days for further viral nucleic acid extraction, specific quantitative polymerase chain reaction (qPCR) detection and Next Generation Sequencing (NGS) of the groundwater virome using specific probe panels to capture specific viral families of interest (e.g. human fecal pollution indicators (HAdV and JCPyV), pathogens traditionally associated to groundwater fecal contamination (NoV and EV) and viral pathogens with potential zoonotic transmission (CoV, IAV, HEV).

The validation of analysis of the contaminants captured on the different kind of passive samplers will be done using either direct injection or vacuum assisted extraction and requires:

- **Solid Phase Extraction (SPE)** and **vacuum-assisted evaporation (VAE)** for the grab-sample preparation, and
- **Liquid Chromatography coupled to Mass Spectrometry (HPLC-MS/MS)** for detection.



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Direct injection (DI) will be performed when the concentration of the pollutants is high, e.g., in the Danish CS. The methods will be optimized and validated to deliver concentrations of contaminants from both grab and passive sampling for assessing the concentration patterns, removal, degradation and sorption. These high throughput methods will enable to tackle hundreds of samples, even though, considerable labor and skill is needed.

Compound specific isotope ratio analysis (CSIA) will be deployed to contribute to source apportionment¹ and to help distinguish the degradation processes of contaminants of Emerging Concern (CECs). CSIA is a compound specific method but has a low sensitivity (high limits of detection). UPWATER will provide a novel and validated strategy to use CSIA on CPS time-integrated samples as contaminants will be preconcentrated directly on the CPS. Validation tests will be performed coupling CSIA of CECs with extraction from both grab samples and CPS, to check that no artefacts (e.g., change in isotope ratios) during laboratory sample manipulation will be produced and to validate the use of CSIA with CPS. Once validated, this CPS-CSIA approach will be used for determining isotope ratios of selected CECs in the extracts obtained from CPS deployed during 3 months in selected wells from the Besòs and the Stengården sites. CSIA will also be performed in selected grab samples to compare the results among both sampling methods.

Isotopic analysis of inorganic dissolved solutes (e.g., ¹⁵N, ³⁴S, ¹⁸O, ¹¹B, etc.) will be performed in grab groundwater samples from the Besòs and the Athens sites (10-20 sampling points in 3 sampling campaigns for both cases). These analyses will be used for source apportionment and elucidation of contaminant transformation processes. These results will also be used for improving hydrogeological and hydrochemical conceptual models of each study site, by coupling them with water stable isotopes (¹⁸O, ²H).

¹ An efficient approach for improving GW quality that identifies and tracks the source of a given contaminant by elucidating qualitatively and quantitatively the link between emission source and GW occurrence



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2. CASE STUDIES

2.1 STENGÅRDEN (DENMARK)

Main efforts at Stengården dumpsite will go into developing a biobased approach for removing the main pollutants of the site (pesticides from production residues dumped in the last century). Thus, the emphasis will be on establishing and optimizing two consecutive reactors (MBBR and Biofilter), resulting in the determination of the removal rate, reaction kinetics and reaction mechanisms.

This will be supported by determinations of concentrations in the GW to support the modelling and determine the success of the removal efforts initiated by UPWATER. The region of Sjælland is developing considerable efforts to remove the main pollutants with currently available technologies, i.e., sorption to granular activated carbon (GAC). This approach works fine, but is a) costly, b) energy intensive (regeneration of the GAC) and c) the water on site seems to have other compounds (ions or detergents) that interacts with GAC, decreasing the sorption capacity of the GAC considerably.

HPLC-MS/MS analysis will be done by AU, Isotope ratio analysis by UB, passive sampling by CSIC. Table 1 shows the compounds to be monitored in the Stengården case study site. Table 2 details the sampling frequency. Figure 1 and Table 3 indicate the position of the groundwater wells to be monitored at Stengården.

Table 1. Compound list for Stengården (Denmark). ⁽¹⁾: Analysis of isotope ratios (CSIA) will be subject to detected CECs concentrations and to the results of the validation tests, +: will be included in monitoring.

Compound	CAS no	Backgrd min (µg/L)	Backgrd max (µg/L)	Methods	Isotope ratio ⁽¹⁾	Passive sampling
4-Chlor-2-methylphenol	1570-64-5	0.17	0.36	Direct HPLC-MS/MS	+	+
4-Chlorophenoxy-propionic acid (4-CPP)	3307-39-9	1.7	8.1	Direct HPLC-MS/MS	?	+
4-chloro-2-methylphenol sulfate	2801487-84-1	?	?	Direct HPLC-MS/MS		
4-chloro catechol	2138-22-9	?	?	Direct HPLC-MS/MS		+
Dichlorprop	120-36-5	0.1	4.1	Direct HPLC-MS/MS	+	+
Mecoprop	93-65-2	1	8.7	Direct HPLC-MS/MS	+	+
2,6-Dichlorbenzamide	2008-58-4	0.1	0.36	Direct HPLC-MS/MS		
Trace metals aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium,	-	-	-	ICP-MS / DMA (for Hg)	-	+



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cobalt, copper, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, uranium						
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Table 2. Sampling frequency for Stengården dumpsite (Denmark)

	Parameters	N° of sample points	Expected n° of sampling campaigns	Total numbers of samples	Comments
Lab reactors					
	Grab samples	12	24	288	AU
	Isotope ratio (CSIA of CECs)	-	-	-	Sampling: AU Samplers: CSIC
Pilots					
	Grab samples	5	Approx. 104	520	AU
	Isotope ratio (CSIA of CECs)	3	5	15 (total number of analyses 60)	10-15 samples × 3-4 compounds Sampling: AU Determination: UB
	Passive sampling (CPS)	5	Approx. 6	20	Sampling : AU Samplers: CSIC
	Passive sampling (DGT)	5 (1 inlet, 4 outlet)	Approx. 3	30	Sampling: AU Samplers: CSIC
Groundwater					
	Grab samples	10	2	20	AU
	Isotope ratio (CSIA of CECs)	2	3	6 (total number of analyses 10)	5 samples × 1-2 compounds Sampling: AU Analysis: UB
	Passive sampling (CPS)	10	2	20	Sampling: AU Samplers: CSIC



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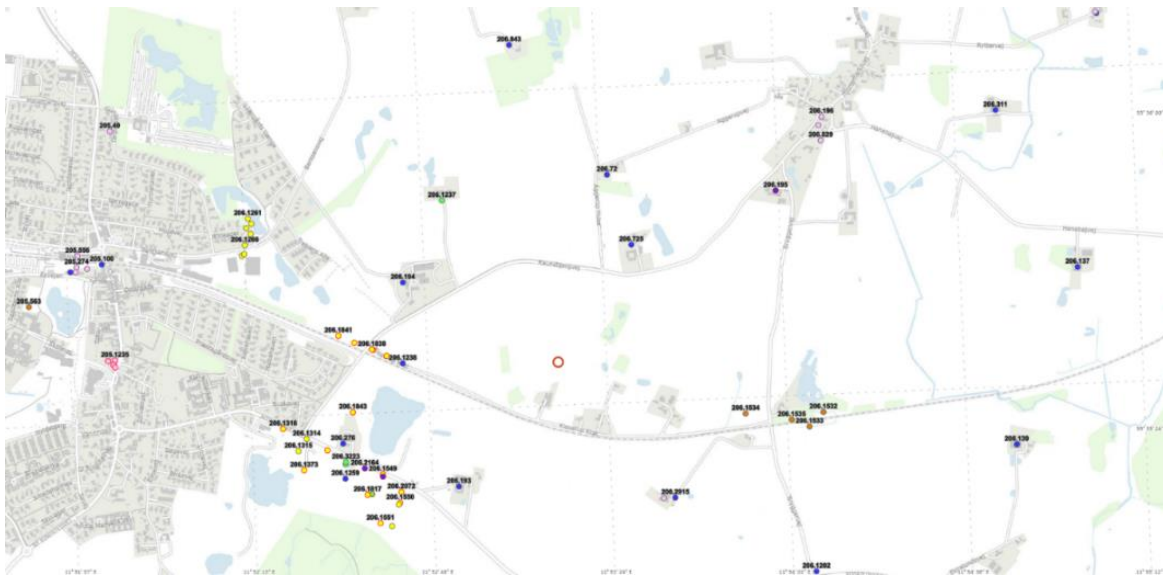


Figure 1. Map of the Stengården dump site sampling points (GEUS, 2023)

Table 3. Wells for groundwater monitoring at Stengården dump site (GEUS, 2023)

Well n°	Co-ordinate EUREF89 format	Depth [m]
206.1841	681.166,48 , 6.164.476,67	54
206.1839	681.222,86 , 6.164.451,63	50
206.1838	681.285,12 , 6.164.428,3	58
206.1840	681.336,95 , 6.164.405,67	54
206.1238	681.394,24 , 6.164.379,38	49
206.1316	680.971,44 , 6.164.148,28	20
206.1843	681.218 , 6.164.207	55
206.1822	681.035 , 6.163.409	40
206.1817	681.270 , 6.163.916	28
206.2073	681.379,9 , 6.163.881,2	25
206.2163	681.323,86 , 6.163.980,49	26
206.2164	681.259,94 , 6.164.008,99	26



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2.2 BESÒS (SPAIN)

Surface infiltration water is heavily polluted with CECs and ammonia in the Besòs river catchment. UPWATER will develop and assess novel biobased technologies (NBS) based on circular biobased systems to protect the Besòs aquifer against pollution. The NBS will first be validated at lab-scale and then upscaled and replicated in the Besòs river catchment by the utility stakeholders (The metropolitan Area (AMB), Catalan Water Agency (ACA)). UPWATER will also evaluate the innovative combination of passive monitoring and transport modelling approaches to identify sources and emission pathways of pollutants from surface water to GW which will enable the assessment of human and environmental risks at different temporal and spatial scales. Tables 4 and 5 show the compounds, and virus' and metals, respectively, to be monitored in the Besòs case study site. Table 6 details the sampling frequency. Figure 2 and Table 7 indicate the position of the groundwater wells to be monitored in Besòs.

Table 4. Compound list for organic contaminants in Besòs (Spain). ⁽¹⁾: Analysis of isotope ratios (CSIA) will be subject to detected CECs concentrations and to the results of the validation tests. ? Indicates that background concentrations are unknown.

Compound	CAS n°	Backgrd min (µg/L)	Backgrd max (µg/L)	Methods	Isotope ratio ⁽¹⁾	Passive sampling
Dichlorprop	120-36-5	?	?	SPE-LC-HRMS	+	+
Mecoprop	93-65-2	?	?	SPE-LC-HRMS	+	+
MCPA	94-74-6	?	?	SPE-LC-HRMS	+	+
Atrazine	1912-24-	?	?	SPE-LC-HRMS	+	+
4-Chlor-2-methylphenol	1570-64-5	?	?	SPE-LC-HRMS	+	+
4-Chlorophenoxy-propionic acid (4-CPP)	3307-39-9	?	?	SPE-LC-HRMS	?	+
1H-Benzotriazole	95-14-7	0.09	1.1	VAE-LC-HRMS	+	+
5-methyl-benzotriazole	136-85-6	<LOQ	0.77	VAE-LC-HRMS	+	+
Sucralose	56038-13-2	0.6	9.0	VAE-LC-HRMS	+	+
Bisphenol A	80-05-7	0.001	1.4	VAE -LC-HRMS	+	+



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Diclofenac	15307-86-5	0.01	0.02	VAE -LC-HRMS	+	+
Furosemide	54-31-9	0.000	0.5	VAE -LC-HRMS	?	+
Gemfibrozil	25812-30-0	0.000	0.6	VAE-LC-HR-MS	+	+
Iopamidol	60166-93-0	1.2	3.9	VAE -LC-HR-MS	?	+
Lamotrigine	84057-84-1	0.014	0.8	VAE -LC-HR-MS	+	+
Valsartan	137862-53-4	0.003	1.3	VAE -LC-HR-MS	+	+
Valsartan Acid	164265-78-5	0.004	0.02	VAE -LC-HR-MS	?	+
Perfluoro-n-butanoic acid (PFBA)	375-22-4	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-pentanoic acid (PFPeA)	2706-90-3	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-hexanoic acid (PFHxA)	307-24-4	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-heptanoic acid (PFHpA)	375-85-9	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-octanoic acid (PFOA)	335-67-1	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-nonanoic acid (PFNA)	375-95-1	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-decanoic acid (PFDA)	335-76-2	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-undecanoic acid (PFUdA)	2058-94-8	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-dodecanoic acid (PFDoA)	307-55-1	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-tridecanoic acid (PFTrDA)	72629-94-8	?	?	SPE-LC-HRMS	-	+
Perfluoro-n-tetradecanoic acid (PFTeDA)	376-06-7	?	?	SPE-LC-HRMS	-	+
N-methylperfluorooctanesulfonamidoacetic acid (N-MeFOSSA)	2355-31-9	?	?	SPE-LC-HRMS	-	+



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N-ethylperfluorooctanesulfonamidoacetic acid (N-EtFOSSA)	2991-50-6	?	?	VAE -LC-HRMS	-	+
Potassium perfluoro-1-butanefluorobutanesulfonate (PFBS)	29420-49-3	?	?	VAE -LC-HRMS	-	+
Sodium perfluoro-1-pentanesulfonate (PFPeS)	630402-22-1	?	?	VAE -LC-HRMS	-	+
Potassium perfluorohexanesulfonate (PFHxS)	3871-99-6	?	?	VAE -LC-HRMS	-	+
Sodium perfluoro-1-heptanesulfonate (PFHpS)	21934-50-9	?	?	VAE -LC-HRMS	-	+
Potassium perfluorooctanesulfonate (PFOS)	2795-39-3	?	?	VAE -LC-HRMS	-	+
Sodium perfluoro-1-nonanesulfonate (PFNS)	98789-57-2	?	?	VAE -LC-HRMS	-	+
Sodium perfluoro-1-decanesulfonate (PFDS)	2806-15-7	?	?	VAE -LC-HRMS	-	+
Sodium perfluoro-1-dodecanesulfonate (PFDoS)	2806-15-7	?	?	VAE -LC-HRMS	-	+
Sodium 1H,1H,2H,2H-perfluorohexanesulfonate (4:2FTS)	27619-93-8	?	?	VAE -LC-HRMS	-	+
Sodium 1H,1H,2H,2H-perfluorohexanesulfonate (6:2FTS)	27619-94-9	?	?	VAE -LC-HRMS	-	+
Sodium 1H,1H,2H,2H-perfluorohexanesulfonate (8:2FTS)	27619-93-8	?	?	VAE -LC-HRMS	-	+



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Table 5. Compound list for pathogens, trace metals and inorganic dissolved solutes in Besòs (Spain).

Compound	Backgrd min	Backgrd max	Methods	Isotope ratio	Passive sampling
Viral indicators and pathogens	10 genome copies /L	1000 genome copies /L	Specific quantitative PCR	-	PMMoV, JCPyV, HAdV, EV, NoV
Trace metals aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, uranium	-	-	ICP-MS / DMA (for Hg)	-	DGT
Isotopes of inorganic dissolved solutes (NO ₃ , SO ₄ , B, DIC) and water isotopes (¹⁸ O, ² H)	-	-	IRMS coupled to peripherals	+	-



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Table 6. Sampling frequency for the Besòs site (Spain).

Parameters	N° of sample points	of	Expected n° of sampling campaigns	Total number of samples	Comments
Lab reactors					
Grab samples	20		3	60	3 bioelectrochemical designs (×3) + 3 root mat designs (×3). + 1 combined prototype (×1). All configurations will be tested by triplicate and inlet and outlet samples will be collected. CSIC (20 sampling points x 3 sampling campaigns).
Isotope ratio (CSIA of CECs)	3		3	9 grab samples × 2 compounds (total = 18)	Only for the final prototype: UB
Pilot (NBS)					
Grab samples	4		6	24 organics + 12 metals	Inlet, intermediate sampling point and outlet from the NBS, but also surface water from the river (sampling points=4). All sampling points will be monitored every 2 months for 12 months. CSIC
Isotope ratio (CSIA of CECs)	4		6	24 samples × 2 compounds (total = 48)	UB
Passive sampling (CPS and DGTs)	4		6	24×3 (replicates): 72 passive samplers for CPS and 72 for DGT	12-months monitoring. Sites: inlet, intermediate point, effluent and surface river water (4 sampling points × every two months). CSIC
Inorganic isotopes	2		5	A total of 50 analyses	10 samples × 5 analyses (water isotopes, SO ₄ , NO ₃ , B, DIC) CSIC, UB
Groundwater					
Grab samples	20		6	Grab samples 20 sites ×1 sample ×6 campaigns = 120 samples	CSIC



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				(every 3 months in 18 months)	
	Passive sampling (CPs) Table 4 Table 5	20	6	Passive samplers 20 sites × 2 CPS × 6 campaigns = 240 samples	CSIC
	Isotope ratio of (CSIA of CECs)	3	3	9 samples × 1 compound (total=9)	UB
	Passive sampling (DGTs)	20	6	Passive samplers 20 sites × 2 DGT × 6 campaigns = 240 samples	CSIC
	Passive sampling (VPS)	2	16 samples during wet season and 16 samples during dry season.	A total of 32 viral passive samplers to obtain 32 samples.	6 viral qPCR analyses [3 viral MST tools: HAdV, JCPyV, PMMoV; 2 human viral pathogens: EV and NoV and 1 virus with zoonotic potential: HEV, IAV or CoV (to be decided according to the clinical data reported at the time of sampling)] 1 NGS run per season and sampling point (2 seasons × 2 points) a total of 192 qPCR analyses and 4 NGS sequencing data. UB
	Inorganic isotopes	10-20	3	A total of 200 analyses (including both GW and surface water)	50 samples × 3 analyses (water isotopes, SO ₄ , NO ₃) and 25 samples × 2 analyses (B, DIC) CSIC, UB



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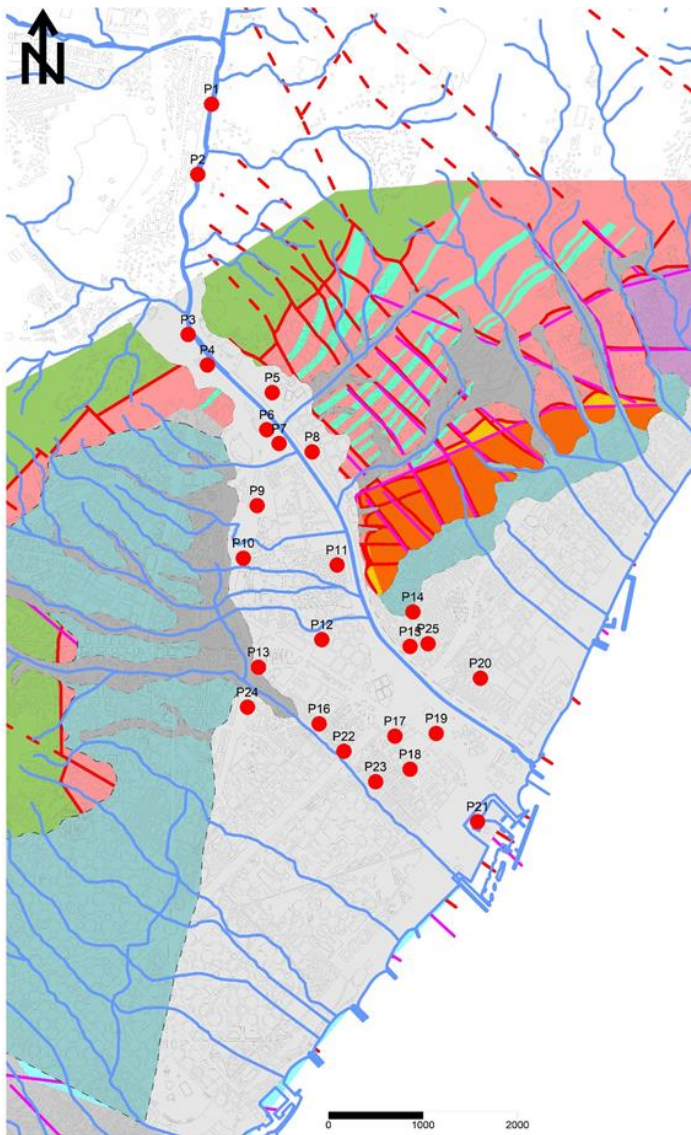


Figure 2. Map of the Besòs (Spain) GW sampling points (red). Scale in meters.



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Table 7. Wells for groundwater monitoring for Besòs (Spain)

Well n°	Co-ordinate X (UTM) EUREF89 format	Co-ordinate Y (UTM) EUREF89 format
P1	432559	4592769
P2	432413	4592026
P3	432311	4590336
P4	432516	4590015
P5	433202	4589724
P6	433143	4589330
P7	433275	4589184
P8	433625	4589097
P9	433041	4588528
P10	432895	4587975
P11	433888	4587902
P12	433727	4587115
P13	433056	4586823
P14	434690	4587406
P15	434661	4587042
P16	433698	4586226
P17	434500	4586095
P18	434661	4585745
P19	434938	4586124
P20	435405	4586707
P21	435376	4585191
P22	433960	4585934
P23	434296	4585614
P24	432939	4586401
P25	434851	4587071



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2.3 ATHENS (GREECE)

On this site UPWATER envisages identifying the main hydrogeochemical processes within a multilayered urban aquifer system with respect to diffuse and point GW contamination sources, originating from surface and unsaturated zone activities. This research targets to identify the interactions between different hydrologic zones, such as: (a) surface and saturated zone (i.e. surface water from Kifisos river that percolates to the GW table and/or downward movement of surface contaminants from typical urban land uses e.g. parking areas, roads, parks etc.), (b) unsaturated and saturated zone (e.g. leaking contaminants from sewer network and/or GW recharge from leaking water supply and stormwater network); and (c) the impacts on the marine ecosystem which is the final acceptor of all the above points and diffuse submarine GW discharge. For the realization of the above, UPWATER will use the following contaminant tracers: Impacts from gasoline, petrol and related products through stormwater (BTEX, PAH), impacts from sewer network: pharmaceuticals, anti-corrosives, PFAS, etc. (see Table 8). Table 9 details the sampling frequency for these contaminants. Figure 3 and Table 10 indicate the position of the groundwater wells to be monitored in Athens.

NTUA will be able to analyze BTEX and PAH by using GC-MS/MS (Laboratory of Analytical Chemistry at NTUA). Although there is a high uncertainty with respect to the occurrence of these contaminants in the underlying upper aquifer layers, mainly due to their limited mobility within porous media, elevated concentrations are expected in the unsaturated zone where intensive infiltration of stormwater takes place at specific parts of the study area (including the pilot site). The outcome of the first sampling will be used to decide on continuation or discontinuation.

As there is high uncertainty of expected concentrations for the sewer marker compounds, UPWATER will follow an iterative process.

AU and CSIC will support NTUA with the analyses of 30 and 40 samples, respectively, for a range of contaminants detected in the first sampling campaign (see Table 8). Table 8 focusses on compounds, expected in high concentrations in wastewater and with expected low sorption and high persistence. Based on the results of this initial campaign, a total of approximately 180 samples from the various campaigns will be collected and analyzed at CSIC, AU and NTUA.

UB will analyze isotope ratios of inorganic dissolved solutes (NO_3 , SO_4 , B, DIC) and water isotopes (^{18}O , ^2H) in 50 groundwater and surface water samples.



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Table 8. Compound list for the Athens case study (Greece). +: included in monitoring, ¹⁾ For initial testing
²⁾ For further analysis. ?: No data available (especially in groundwater)

Compound	CAS n°	Backgrd (µg/L) in wastewater	Backgrd (µg/L) in GW	Method	Isotope ratio	Passive sampling	Responsible
1H-Benzotriazole	95-14-7	10	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
5-Methyl 1H Benzotriazole	136-85-6	10	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Diclofenac	15307-86-5	1	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Carbamazepine	298-46-4	1	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Gabapentin	60142-96-3	20	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Diatrizoic acid	117-96-4	20	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Iohexol	66108-95-0	20	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Iopromide	73334-07-3	20	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Iomeprol	78649-41-9	20	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Losartan	114798-26-4	5	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Metoprolol	37350-58-6	3	?	Direct HPLC-MS/MS	-	-	AU ¹⁾ ; NTUA ²⁾
Caffeine	58-08-2	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹⁾ ; NTUA ²⁾



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Diclofenac	15307-86-5	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Gemfibrozil	25812-30-0	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Diazepam	439-14-5	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Oxazepam	604-75-1	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Mirtazapine	61337-67-5	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Amphetamine	300-62-9	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Sucralose	56038-13-2	?	?	VAE - LC-HR-MS	-	+	IDAEA ¹ ; NTUA ²
Benzene	71-43-2	?	?	GC-MS	-	-	NTUA ²
Toluene	108-88-3	?	?	GC-MS	-	-	NTUA ²
Ethylbenzene	100-41-4	?	?	GC-MS	-	-	NTUA ²
Xylene	1330-20-7	?	?	GC-MS	-	-	NTUA ²
Napthalene	99 91-20-3	?	?	GC-MS	-	-	NTUA ²
Acenaphthylene	208-96-8	?	?	GC-MS	-	-	NTUA ²
Acenaphthene	83-32-9	?	?	GC-MS	-	-	NTUA ²
Fluorene	86-73-7	?	?	GC-MS	-	-	NTUA ²
Phenanthrene	85-01-8	?	?	GC-MS	-	-	NTUA ²
Anthracene	120-12-7	?	?	GC-MS	-	-	NTUA ²
Fluorathene	206-44-0	?	?	GC-MS	-	-	NTUA ²



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Pyrene	129-00-0	?	?	GC-MS	-	-	NTUA ²⁾
Benzodiazepines	12794-10-4	?	?	GC-MS	-	-	NTUA ²⁾
Perfluoro-n-butanoic acid (PFBA)	375-22-4	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-pentanoic acid (PFPeA)	2706-90-3	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-hexanoic acid (PFHxA)	307-24-4	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-heptanoic acid (PFHpA)	375-85-9	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-octanoic acid (PFOA)	335-67-1	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-nonanoic acid (PFNA)	375-95-1	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-decanoic acid (PFDA)	335-76-2	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-undecanoic acid (PFUdA)	2058-94-8	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-dodecanoic acid (PFDoA)	307-55-1	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-tridecanoic acid (PFTTrDA)	72629-94-8	?	?	VAE LC- HRMS	-	+	IDAEA
Perfluoro-n-tetradecanoic acid (PFTeDA)	376-06-7	?	?	VAE LC- HRMS	-	+	IDAEA
N-methylperfluorooctanesulfonamidoacetic acid (N-MeFOSSA)	2355-31-9	?	?	VAE LC- HRMS	-	+	IDAEA



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N-ethylperfluorooctanesulfonamide acetic acid (N-EtFOSSA)	2991-50-6	?	?	VAE LC- HRMS	-	-	+	IDAEA
Potassium perfluoro-1-butanesulfonate (PFBS)	29420-49-3	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium perfluoro-1-pentanesulfonate (PFPeS)	630402-22-1	?	?	VAE LC- HRMS	-	-	+	IDAEA
Potassium perfluorohexanesulfonate (PFHxS)	3871-99-6	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium perfluoro-1-heptanesulfonate (PFHpS)	21934-50-9	?	?	VAE LC- HRMS	-	-	+	IDAEA
Potassium perfluorooctanesulfonate (PFOS)	2795-39-3	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium perfluoro-1-nonanesulfonate (PFNS)	98789-57-2	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium perfluoro-1-decanesulfonate (PFDS)	2806-15-7	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium perfluoro-1-dodecanesulfonate (PFDoS)	2806-15-7	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium 1H,1H,2H,2H-perfluorohexanesulfonate (4:2FTS)	27619-93-8	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium 1H,1H,2H,2H-perfluorohexanesulfonate (6:2FTS)	27619-94-9	?	?	VAE LC- HRMS	-	-	+	IDAEA
Sodium 1H,1H,2H,2H-perfluorohexanesulfonate (8:2FTS)	27619-93-8	?	?	VAE LC- HRMS	-	-	+	IDAEA
Viral indicators and pathogens	-	1000 genome copies/L		Specific quantitative PCR			PMMoV, JCPyV, HAdV, EV, NoV	UB



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Isotopes of inorganic dissolved solutes (NO ₃ , SO ₄ , B, DIC) and water isotopes	-	-		IRMS coupled to peripherals	+	-	UB
Trace metals aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, uranium	-	?	?	ICP-MS / DMA (for Hg)	-	DGT	IDAEA ¹ ; NTUA ²



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Table 9. Sampling frequency for the Athens site (Greece).

parameters	N° of sample points	Expected n° of sampling campaigns	Total number of samples	Comments
Pilot (NBS)				
Passive sampling (CPS)	3	6	3 sites × 2 samplers × 6 campaigns= 36	CSIC
Passive sampling (DGTs)	3	6	3 sites × 2 samplers × 6 campaigns= 36	CSIC
Inorganic isotopes	2	5	A total of 50 analyses	10 samples × 5 analyses (water isotopes, UB) (SO4, NO3, B, DIC, NTUA)
Groundwater				
Grab samples	15	2		AU and IDAEA for initial testing
Passive sampling (CPS)	15	6	15 sites × 2 CPS × 6 campaigns = 180 samples	
Passive sampling (DGTs)	15	6	15 sites × 2 DGT × 6 campaigns= 180 samples	
Passive sampling (VPS)	2	16 samples during wet season and 16 samples during dry season.	A total of 16 viral passive samplers to obtain 16 samples.	6 viral qPCR analyses [3 viral MST tools: HAdV, JCPyV, PMMoV; 2 human viral pathogens: EV and NoV and 1 virus with zoonotic potential: HEV, IAV or CoV (to be decided according to the clinical data reported at the time of sampling)] 1 NGS run per season and sampling point (2 seasons x 2 points) a total of 192 qPCR analyses and 2 NGS sequencing data. UB
Inorganic isotopes	10-20	3	A total of 200 analyses (including both GW and surface water)	50 samples × 3 analyses (water isotopes, SO4, NO3) and 25 samples × 2 analyses (B, DIC) NTUA, UB



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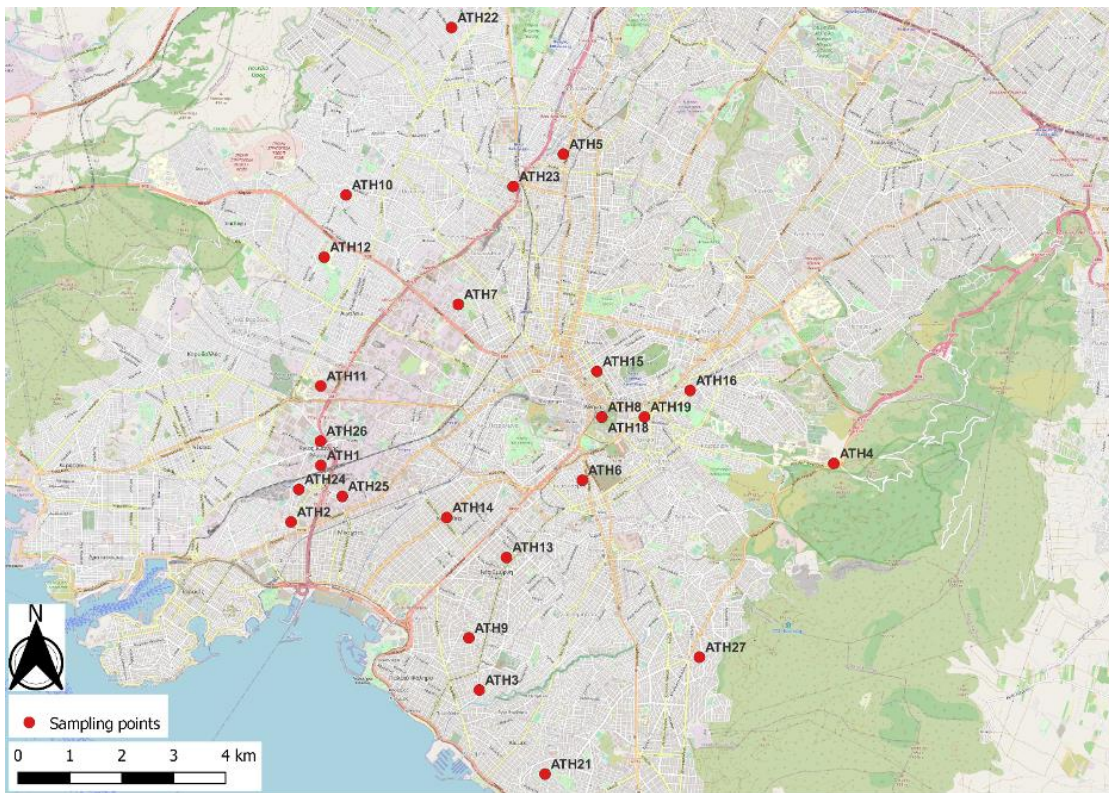


Figure 3. Map of Athens (Greece) site GW sampling points.



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Table 10. Wells for groundwater monitoring for Athens (Greece).

Well n°	Co-ordinate N EUREF89 format	Co-ordinate E EUREF89 format
ATH1	471321.9	4201700
ATH2	470747.1	4200610
ATH3	474374.1	4197373
ATH4	481203.2	4201738
ATH5	475992.3	4207700
ATH6	476357.4	4201416
ATH7	473969.8	4204806
ATH8	476734.7	4202634
ATH9	474172.9	4198378
ATH10	471808.9	4206912
ATH11	471318.4	4203233
ATH12	471387.5	4205714
ATH13	474897.8	4199928
ATH14	473745.7	4200694
ATH15	476639.6	4203512
ATH16	478433.9	4203146
ATH17	476734.7	4202634
ATH18	476734.7	4202634
ATH19	477555.1	4202634
ATH20	476734.7	4202634
ATH21	475641	4195753
ATH22	473838.8	4210140
ATH23	475026.1	4207076
ATH24	470899	4201238
ATH25	471736	4201104
ATH26	471314	4202168
ATH27	478612.5	4198004



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LIST OF FIGURES

Figure 1. Map of the Stengården dump site sampling points (GEUS, 2023).....	11
Figure 2. Map of the Besòs (Spain) GW sampling points (red). Scale in meters.	18
Figure 3. Map of Athens (Greece) site GW sampling points.....	27



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LIST OF TABLES

Table 1. Compound list for Stengården. ⁽¹⁾ : Analysis of isotope ratios (CSIA) will be subject to detected CECs concentrations and to the results of the validation tests, +: will be included in monitoring.	9
Table 2. Sampling frequency for the Stengården dumpsite (Denmark).....	10
Table 3. Wells for groundwater monitoring at Stengården dump site (GEUS, 2023)	11
Table 4. Compound list for organic contaminants in Besòs (Spain). ⁽¹⁾ : Analysis of isotope ratios (CSIA) will be subject to detected CECs concentrations and to the results of the validation tests. ? Indicates that background concentrations are unknown.	12
Table 5. Compound list for pathogens, trace metals and inorganic dissolved solutes in Besòs (Spain).	15
Table 6. Sampling frequency for the Besòs site (Spain).....	16
Table 7. Wells for groundwater monitoring for Besòs (Spain).....	19
Table 8. Compound list for the Athens (Greece) case study. +: included in monitoring, ¹⁾ For initial testing ²⁾ For further analysis. ?: No data available (especially in groundwater)	21
Table 9. Sampling frequency for the Athens site (Greece).....	26
Table 10. Wells for groundwater monitoring for Athens (Greece).....	28



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