

Template of Mid-Term Progress Report

Water Joint Programming Initiative 2018 Joint Call

Closing the water cycle gap - Sustainable management of water resources

This Template should be used by the Project Coordinator for the reporting of the project. <u>This template does not substitute national regulations</u>





2018 Joint Call Mid-Term Progress Report Closing the water cycle gap - Sustainable management of water resources

Tools and criteria for URBAN groundWATer management" "URBANWAT"

This document must be filled in by the project coordinator with the help of its project partners and must be sent to the WaterWorks2017 Follow-up Secretariat by **30/10/2020** (for Consortium URBANWAT).

The WaterWorks2017 Follow-Up Secretariat will ensure distribution to the concerned national funding agencies. The project coordinator is responsible for sending a copy of the report to its partners.





PROJECT TITLE AND ACRONYM

Author of this report (Coordinator): Carlos Ayora Ibañez, Enric Vázquez, Laura Scheiber and Rotman Criollo Date of submission: 31/10/2020 E-mail: cayora I@gmail.com Project Website: in construction Project code: WaterWorks2017-URBANWAT

Duration of project: 30 month Start date: 01/09/2019

End date: 01/03/2022

Period covered by this report: 12 month



I. Publishable Summary Maximum I page

According to EU projections (2050), half of the population is expected to live in cities, one of the zones with the highest water demand and an important source of pollutants. Considering the increasing pressure on water world-wide, a better knowledge for urban groundwater management is needed URBANWAT is financed by the EU Commission under the call "Closing the Water Cycle Gap". The aims of this project is to propose improved tools and criteria for groundwater management in urban areas to ensure the sustainability of urban water resources, define their potential uses and their risks by an integrative and innovative approach. The research will involve a multidisciplinary approach including the description of the natural state of the hydrological cycle, development of particle tracer technology to determine contaminant flow paths and, the detection of pollutants: water quality parameters, pollutants of emerging concern (CECs) and microorganisms (viruses).

To achieve that, URBANWAT proposes to use novel approaches based on liquid chromatography high resolution mass spectrometry to achieve the following goals: (i) to identify differences in degradation in different anoxic conditions using CECs as indicators of contamination and their transformation products (TPs) as indicators of degradability; (ii) to analyse fate and transport of selected contaminants in the soil-plant as a remediation system using selected infrastructures; (iii) to understand and determine the movement of the contaminants applying encapsulated DNAtagged nanoparticles as tracer; To do so, column experiments will be performed. Moreover, metagenomic-based methodologies (iv) to explore the presence of emergent viruses in groundwater samples applying viral metagenomics. Viral concentration methods from water samples will be optimized in this study.

The main expected output will be an integrated approach for urban groundwater management using monitoring, measuring and modeling, like an integrated numerical modeling of the water cycle and their contaminants to better manage the water resources in urban areas, innovative tracers to really measure, and finally to have a better monitoring of urban water systems due to improved analysis protocols.

2. Work Performed and the Results achieved during the reporting period

Maximum 10 pages.

Please attach any deliverables produced and information on milestones achieved during the reporting period of this report.

a. Scientific and technological progress

WP1. Inorganic chemical, CECs sampling and analyses of groundwater

Task I.I Field campaign

From July 6 to 17, 2020, the first field campaign was carried out (the date of this campaign was affected by COVID-19) in which groundwater samples were taken in 50 points distributed



throughout Barcelona and 5 samples wastewater. Samples were taken to analyze major elements, traces, REEs, stable water isotopes and EOCs.

Now we are waiting to receive the analytical results of the WPI to be able to start managing this information and knowing the distribution of the different pollutants in the waters of the Barcelona city.

We are expansed and improved an existing platform to integrate all data from a geo-spatial database. Specifically, the database contained all the information on organic chemistry and has been expanded to integrate the organic components that we are going to analyze in this project.

We are developed the deliverable DI.I protocol for groundwater sampling (attached in this document).

<u>Task 1.2 Development of new analytical methodologies combining polar chromatography with HRMS</u> for the determination of PMOCs in groundwater

We are still evaluating the extraction methodology of PMOCS from groundwater with a multilayer cartridges composed Oasis HLB + WAX+ WCX + Bond elute PPL to simultaneously retain less polar, acid, basic and more polar analytes respectively. In this regard, due to the importance of ensuring a more effective extraction of analytes with very low Log D values, it is proposed to evaluate two elution procedures by SPE with multilayer cartridges. In addition, we are evaluating their retention in analytical columns designed for the retention polar compounds and also we already performed the evaluation of the detection method in target for more than 150 high polar compounds by LC-MS/MS (Thermo Quantiva QqQ) and LC-HRMS/MS (Q-Orbitrap).

Task 1.3 Evaluation of the transformation of polar compounds.

This task will be started in January 2021 checking the transformation products in the samples from the first campaign

WP2. Microbiological sampling and analyses of groundwater

Task 2.1. Optimization of viral concentration and detection methods for identification of viruses in groundwater samples

In order to detect viruses in groundwater samples, a new rapid (2h) large volume concentration (LVC) method, based on Polysulfone Hollow fiver membranes (Rexeed 25A 30KDa) with wet foam elution cans, was coupled with a Centricon® Plus-70 (30KDa) ultrafilter. By using both devices, the viral particles present in 50 litres of water could be concentrated into a final volume of 250-500ul. Based on the UB group's background, the method was compared with the one-step skimmed milk flocculation (SMF) protocol (10L), and with the ultrafiltration with Rexeed or Centricon alone. The methods performed equally well with groundwater samples, but LCV increased 123x times the volume analysed compared to the other three procedures. When testing naturally occurring viruses in groundwater samples (NoV GI and GII), the LCV increased the sensitivity of the quantification assay and higher viral concentrations were reported.



Artificially spiked samples (including human adenoviruses, coxsakievirusB5, and the bacteriophages phi174 and MS2), were filtrated and eluted with two different elution cans (Tween20/PBS and Tween20/Tris). Percentage of recoveries were significantly higher when using Tween20/Tris both in cell culture titration and qPCR quantification.

A standard operational procedure (SOP) using Rexeed 25A and Centricon Plus-70 ultrafiltration devices for LVC of viruses from groundwater samples has been produced (Deliverable D2. lattaches in this document).

Task 2.2. Analysis of samples collected in the points 1, 2, 3 and 4 described above for Classical Fecal Indicators (E. coli and Intestinal enterococci), human and animal viral indicators as well as relevant viral pathogens

The sampling plan, initially organized in march 2020, was moved at the end of July 2020. Eight wastewater samples and 8 groundwater samples were collected all over the city of Barcelona. Four different sites were selected: a high and a medium populated site, an area impacted by industrial activity and a riverside location. All samples were concentrated and quickly tested for the present of the new SARS-CoV-2 virus. No presence of the virus causing the COVID-19 pandemic was detected in the samples collected in July 2020. Human adenoviruses and JC polyomaviruses, pathogens and indicators of the levels of human fecal pollution, were quantified at mean concentration values typically reported in this type of water samples.

WP. 3 Identification of the origin and behaviour of contaminants present in the hydrological cycle

This work package has not yet started to be developed since it is necessary to have all the analytical results of the field campaign for its development. The work is expected to begin during the month of November according to the information provided by the laboratories.

WP4. Application of environmental-friendly DNA-tagged nanoparticles for measuring mobility of pollutants.

Since April 2020 two novel DNA encapsulated microparticles have been designed and produced. So far in total 4 different DNA tags have been used per microparticle-type. These microparticles have a new type of iron-core with higher magnetic moment allowing for better separation and make use of ds DNA in stead of ss DNA. The particles are encapsulated using silicium dioxide coating to shield the DNA from the environmental conditions. Consequently, physical and chemical stability tests have been performed in the lab and analysis protocols developed and tested. After summer the mass balance of particle recovery is closed (all particles can be recovered from a water sample.).

The new DNA encapsulated particles have been used in sand tank experiments (length 100 cm) and compared to NaCl tracer experiments. The results show identical arrival time for the peak concentration in the sand tank experiment.

The final report (D4.1) has seen some delays but is expected end of 2020.



WP 5. Proposed remediation of runoff water contamination and evaluation of the ecotoxicological risk

In WP5, it was planned to define and select the soil-water-(plants) continuum for the future column experiments (D5.1). Nevertheless, the Covid-19 pandemic significantly delayed this task. Indeed, before selected the material for the column experiments, field campaigns were needed to sample different type of soils in the Barcelona city area. This task has been delayed due to the confining period and then the prohibition of traveling from one country to other and the restriction of field campaign. Consequently, the soil excavation has only been performed at the end of September 2020. Two different zones in Barcelona city area have been sampled and in each zone, two different depths have been selected in order to have various permeable properties as well as sorption characteristics for emergent contaminants due to the mineral composition. Moreover, for each zone, already contaminated soils have been sampled as an analogous/control sample to be compared later with the post-mortem soil extracted from the column experiments. The second deliverable due in WP5 is the 5.2 about the development of the experiment setup. Rationally, without soils the experiments could not be developed. Nevertheless, the methodology for the batch experiments has been established and validated with other soil materials as part of another project funded in the 2018 joint call (Maradentro). The methodology already validated will be easily applied for the UrbanWat project and is described in the deliverable 5.2. Moreover, a large literature study has been done and column experimental procedure has been decided from the previous study. The design of the column experimental setup is almost finish and described in the D5.2 (Deliverable D5.2 attached in this document).

WP 6. Testing real-scale test facility Delft University of Technology.

This part of the project is scheduled for the second phase of the project. Due to the delays as consequence of the COVID19 pademic, these experiments are foreseen in the second part of 2021

b. Collaboration, coordination and mobility

Due to covid-19 pandemic, the mobility has been clearly affected. Nevertheless, online meeting in particular between CNRS partner and CSIC-chemists for one hand and between CNRS and Delft Univ. for another hand have been organized in order to plan and manage the water chemistry data and the protocol for column experiments. Moreover, the CNRS partners as well as the CSIC are part of another JPI project funded in the 2018 joint call named Maradentro. We jointly developed the methodology for batch experiments.

There has been direct collaboration between the groundwater group (IDAEA), the environmental chemistry group (IDAEA) and the microbiology group (UB), especially to coordinate and carry out the sampling campaign.



On the other hand, the groundwater group (IDAEA) has also collaborated with the CNRS and TUD groups by providing them soil samples from the Barcelona study area so that these two groups can carry out laboratory work. Due to the current situation (COVID-19), these samples could not be sent until the beginning of this past October, so this has also delayed the start of laboratory work.

c. Impact and knowledge output

URBANWAT project has had a considerable impact within the scientific community, since 4 scientific papers have been published in journals with a high impact index, 1 project report in an open access journal (in process, under review) and 2 international congresses (AGU 2019 and EGU 2020) have disseminate of the project and the outcomes obtained.

3. Table of Deliverables

Please indicate whether the planned deliverables are completed, delayed or readjusted. Explain any changes/difficulties encountered and solutions adopted. Please add/delete rows, as necessary in the table below.

Deliverable name	Lead partner (country)	Date of delivery (dd/mm/yyyy)	Changes, difficulties encountered and new solutions adopted
WPI			
D1.1 Protocol for groundwater sampling	CSIC	Month 6	
D1.3 Report on occurrence of PMOCs in groundwater; D1.4 Assessment of PMOCs degradation in groundwaters	UB (Spain)	Month 20	Due to some delay due the Covid pandemic, the method is still in validation.
WP2			
D2.1 A SOP of an optimized method for viral concentration from groundwater samples	UB (Spain)	Month 10	Uploaded on the website intranet to be shared among partners
WP4			
D4.1 Report: artificial DNA trace	TUD	Month 15	Is expected end 2020
WP5			



Deliverable name	Lead partner (country)	Date of delivery (dd/mm/yyyy)	Changes, difficulties encountered and new solutions adopted
D5.1 list of soil-water-plants continuum that will be tested	CNRS	Month 7	Due to a delay in receiving the soil materials, the final selection of the continuum water-soil-plants could not be decided. Nevertheless, the reception of the soil is planned for October 15th and the full analyses and batch tests will be performed before the end of 2020.
D5.2 Development of the experimental setup	CNRS	Month 9	This deliverable should be delayed for 31/12/2020. This delay is due to the Covid-19 pandemic. The batch experiments methodology is defined and the column one is under development. The column should be built for the end of the year. Part of this deliverable it has been given month 12.

4. Budget review

Please include a budget breakdown here, i.e. how the funding has been used so far.





5. Consortium Meetings

Please list below the Consortium meetings which took place during the reporting period, by filling in the table below. Add/delete rows as necessary in the table below.

Ν	Date	Location	Attending	Purpose/ main issues/main decisions?
0			partners	
•	Septem ber 19 th and 20 th 2019	Barcelona https://twitter.com/ID AEA_CSIC/status/1175 742588042776578	partners CSIC, TUD, UB, CNRS	Kick-off meeting AGENDA September 19 th – Aula de seminario A 12:00 - 12:30 Arrival of partners, reception with some snacks 12:45 – 13:00 Coordinator's Welcome Lunch 15:00 – 16:00 Partners oral presentation (15 min about your research group +15min how your group will contribute to URBANWATER
				project) 15:00-15:30 Evironmental Chemistry Group (ECG-CSIC) 15:30-16:00 Centre National de la Recherche Scientifique (CNRS)



				 16:00-16:30 Coffee Break 16:30-17:00 Department of Water management of Delft University of Technology (TUD) 17:00-17:30 Laboratory of Viruses Contaminant of Water and Food, Department of Genetics, Microbiology and Statistics of the Barcelona University (UB). 17:30-18:00 Hydrogeology Group of CSIC (HG-CSIC)
				20:30 Social dinner
				September 20 ¹¹¹ – Aula de seminario A
				9:30 Web portal status, URBANWAT logo, diffusion activities
				10:00 Rain storm about how involve the stakeholders
				10:30 Publications rules, congresses, etc
				11:00 Coffee break
				11:30 Planning short courses (what, how, where),
				11:30 Mobility activities PhD works
				12:00 Workshop Barcelona and TUDelft
				12:30 Chronogram
				13:00 Lunch
				Open discussion and summary
	Septem		CSIC, UB,	The objective of the meeting was to introduce the new members of the
2	ber 29 th	ONLINE MEETING	CNRS,	project, review the project chronogram, explain what has been
	2020		TUD	progressed in the project and plan what remains to be done.

6. Stakeholder/Industry Engagement

Maximum I page

Different stakeholders from each study site have been engaged within the project. For instance, the stakeholders from Barcelona City Council are involved in the design and performance of the field campaign. Since the beginning of the project, BCASA (a company created by the Barcelona city council that is in charge of managing the entire water cycle of the city) has been in collaboration. A first meeting was held with BCASA to present the project on January 28, 2019 at BCASA's headquarters and BCASA has also played a key role in planning the sampling campaign, since they have presented us with a proposal for sampling points. and their operators have accompanied us and helped us during the field campaign (beginning July 6, ending July 17, 2020). During different meetings the steering committee of the project together with technicians related with the water cycle of the city decided locations where field measurements can be done. These points are representatives of the subsurface of the city. All the information compiled and generated had been exchanged to complete the common conceptual model of the subsurface behaviour in the city. This improvement of the outcomes can be the analysis of groundwater levels variation during the construction of high-speed train (AVE) or the future analysis of the sea water intrusion in the city.



https://docplayer.es/189680481-Participacion-y-colaboracion-en-proyectos-r-d-i-que-investigan-sobre-sarscov-2-en-el-ciclo-del-agua.html

- 7. List of Publications produced by the Project Open Access
- List all presentations, posters, and publications in scientific, peer-reviewed journals derived from this project, separating those in preparation, those in review and those accepted or in press.
- Provide websites and/or electronic copies of the key ones.
- Indicate all the co-authors for each publication.
- Order publications per date (chronologically) and for each year by alphabetical order.

Metadata on all project publications are required to be submitted as part of the final reporting. This will be done via the **Open Data & Open Access platform**, available at: <u>http://opendata.waterjpi.eu/</u> (also accessible from the bar menu of the Water JPI website).

	Peer-reviewed journals	I. Rusiñol M., Martínez-Puchol S., Forés E., Itarte M., Girones
	,	R., Bofill-Mas S. Concentration of coronavirus and other
		potentially pandemic enveloped virus from wastewater.
		Current Opinion in Environmental Science & Health. 2020,
		17:21 – 28. https://doi.org/10.1016/j.coesh.2020.08.002
		2. Bofill-Mas S. and Rusiñol M. Recent trends on methods for
		the concentration of viruses from water samples. Current
		Opinion in Environmental Science & Health. 2020, 16:7-13.
		https://doi.org/10.1016/j.coesh.2020.01.006
		3. Labad, F.; Manjarres, D, Montemurro, N; Pérez, S Analytical
		method development for the extraction and detection of
		PMOCS using a multilayer cartridge and HRMS in natural
		waters, in preparation
International		4. A. Jurado; S. Bofill-Mas; E. Vázquez-Suñé; E. Pujades; R.
		Girones; M. Rusiñol (2019) Occurrence of pathogens in the
		river–groundwater interface in a losing river stretch (Besòs
		River Delta, Spain). SCIENCE OF THE TOTAL
		ENVIRONMENT 696 (2019) 134028,
		doi: 10.1016/j.scitotenv.2019.134028
		5. Magnetic Nanoparticles to Unique DNA Tracers – Effect of
		Functionalization on Physico-Chemical Properties. (submitted)
	Books or chapters in	I. I. Foppen, JW and TA Bogaard (2019): Application –
	books	Water treatment/Water management. Chapter 11 In
		"Fabrication and Application of Nanomaterial". Ed. Sulalit
		Bandyopadhyay. McGraw-Hill Education; I edition (June 7,
		2019). ISBN-13: 978-1260132236



	Communications (presentations, posters)	 AGU 2019 (Poster presentation). URBANWAT_ Tools and criteria for URBAN groundWATer management. Scheiber Pagès, Laura ;Vázquez Suñé, Enric ;Bogaard, Thom ;Bofill Mas, Sílvia ;Perez Solsonés, Sandra ;Ginebreda Martí, Antoni ;Luquot, Linda ;Rusiñol, Marta ;Criollo, Rotman EGU 2020 (Poster presentation). URBANWAT_ Tools and
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National	Peer-reviewed journals	1. 2. 3.
(separate lists for each	Books or chapters in books	1. 2. 3.
Thationality)	Communications (presentations, posters)	1. 2. 3.
	Popular articles	1. 2. 3.
Dissemination initiatives	Popularconferences	1. 2. 3.
	Others	1. 2. 3.

8. Knowledge output transfer

For each of the Knowledge Output arising from the project so far, please complete the following table.

Short Title	Concentration of coronavirus and other potentially pandemic enveloped virus from wastewater.
Knowledge Output Description	As the novel SARS-CoV-2 was detected in faeces, environ- mental researchers have been using centrifugal ultrafiltration, polyethylene glycol precipitation and aluminium hydroxide flocculation to describe its presence in wastewater samples. High recoveries (up to 65%) are described with electronegative filtration when



	using surrogate viruses, but few literature reports recovery efficiencies using accurate quantification of enveloped viruses. Considering that every single virus will have a different behaviour during viral concentration, it is recommended to use an enveloped virus, and if possible, a betacoronaviruses as murine hepatitis virus, as a surrogate. In this review, we show new data from a newly available technology that provides a quick ultrafiltration protocol for SARS- CoV-2. Wastewater surveillance is an efficient system for
	the evaluation of the relative prevalence of SARS- CoV-2 infections in a community, and there is the
	need of using reliable concentration methods for
	an accurate and sensitive quantification of the
Knowledge Type	virus in water.
I The second sec	scientific publication
Link to Knowledge Output	https://doi.org/10.1016/j.coesh.2020.08.002
Sectors & Subsectors	Emissions on d Water Dourse
Find Lison	Emissions and water Reuse
	Scientific Community
IPR	n/a
Policy-Relevance	The recently published review is intended to be a
If the Knowledge Output is relevant to the WFD or	guide for wastewater quality managers that need
why	to adapt water quality directives to the new
,	coronavirus scenario.
Status	finalized
Short Title	Recent trends on methods for the concentration
	of viruses from water samples.
Knowledge Output Description	Relevant studies on waterborne viral occurrence published in the past 2 years have been analysed showing that most of them were performed in surface waters and wastewater. Viruses were concentrated from surface water samples by applying, mainly, electronegative filtration or ultrafiltration combined with PEG precipitation, centrifugation, or centrifugal ultrafiltration, whereas for wastewater, most authors used flocculation/precipitation. Main novelties include monolithic filtration/chromatography and ultrafiltration-based new approaches as well as methods deployable in the field. Considering



	future climate change impacts, more studies on viral occurrence in groundwater, seawater, and reclaimed water are needed as well as
	standardized methods in view of future
	regulations comprising analysis of viral
Knowledge Type	scientific publication
	-
Link to Knowledge Output	https://doi.org/10.1016/j.coesh.2020.01.006
Sectors & Subsectors	Emissions and Water Reuse
End User	Environmental Managers & Monitoring Scientific Community
IPR	n/a
Policy-Relevance	The comprehensive review on the current applied
any other related Directives, please list and explain	methods for virus concentration, and further
why	detection, in water samples is a check list of
	regulations derived from WFD
Status	finalized
Short Title	Occurrence of pathogens in the river-
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	point located at 380 m from the river in the absence of FIB. The presence of human viral contamination may represent a risk for the use of groundwater as a drinking water source. Further research is needed to understand the dynamics of pathogens in river-groundwater interface over long time periods and a wide range of flow conditions (wet and dry periods) since the urban groundwater of this aquifer might be a valuable drinking water resource in Barcelona especially during drought periods. The methodology followed in this research can be applied to other urban aquifers with similar purposes since the
	scarcity and contamination of freshwater
Knowledge Type	scientific publication
Link to Knowledge Output	doi: 10.1016/j.scitotenv.2019.134028
Sectors & Subsectors	Hydrology and chemistry
End User	Environmental Managers & Monitoring Scientific Community
IPR	n/a
Policy-Relevance If the Knowledge Output is relevant to the WFD or any other related Directives, please list and explain why	These improvements underlies the crucial importance of clean water and sanitation with a stand-alone Sustainable Development Goal dedicated to ensuring 'access to water and sanitation for all'. For instance, improvements on Water Framework Directives.
Status	finalized
Short Title	Magnetic Nanoparticles to Unique DNA Tracers – Effect of Functionalization on Physico- Chemical Properties
Knowledge Output Description	Limited number of potential tracers such as salts, isotopes and dyes, make study of hydrological processes a challenge. Traditional tracers find limited use due to lack of multipoint tracing and background noise, among others. DNA based tracers have been shown to have great potential enabling synthesis of ideally unlimited number of unique tracers besides being environmentally friendly, highly sensitive and capable of multipoint tracing. To prevent unintentional losses in the environment during application and easy recovery for analysis, we hereby report DNA encapsulation in silica containing magnetic cores



	(iron oxide) of two different shapes – spheres and
	using co-precipitation or thermal decomposition
	Physica chamical properties such as size, zota
	notontial atc of the iron oxide nanoparticles have
	been entimized for different ligende and
	surfactors Managert for the first time the effect
	surfactants. We report for the first time the effect
	of surface coating on the magnetic properties of
	the iron oxide nanoparticles at each stage of
	functionalization, culminating in silica shells.
	Efficiency of encapsulation of three different
	dsDINA molecules has been studied using
	quantitative polymerase chain reaction (qPCR).
	Our results show that our DNA based magnetic
	tracers can be used for hydrological monitoring
	with easy recoverability and high signal
	amplification.
Knowledge Type	scientific publication
Link to Knowledge Output	DOI: 10.21203/rs.3.rs-84463/v1
Sectors & Subsectors	Water management and quality
End User	Environmental Managers
IPR	n/a
Policy-Relevance	
If the Knowledge Output is relevant to the WFD or	
any other related Directives, please list and explain	
why	
Status	submitted
Short litle	Chapter 11 "Fabrication and Application of Nanomaterial".
Knowledge Output Description	Comprehensive coverage of the fabrication of
	nanomaterials from a chemical engineering
	perspective.
	This practical chemical engineering work serves
	as an in-depth introduction to the synthesis,
	characterization, and functionalization of
	nanomaterials using solution-based methods.
	You will explore specific applications, including
	targeted drug delivery, hydrological tracing,
	water purification, and catalysis.
	Fabrication and Application of
	Nanomaterials offers clear explanations and



	state-of-the-art techniques, both in situ and post modifications. You will master the techniques for
	synthesis and applications of fabricated
	nanomaterials through concise theory, numerical
	problems, and recent case studies from industry
	and academia.
Knowledge Type	Book chapter
Link to Knowledge Output	
Sectors & Subsectors	Water treatment/Water management
End User	Environmental Managers
IPR	n/a
Policy-Relevance	
If the Knowledge Output is relevant to the WFD or	
any other related Directives, please list and explain why	
Status	Finalized
Short Title	URBANWAT_ Tools and criteria for URBAN
	groundWATer management
Knowledge Output Description	According to EU projections (2050), half of the
	population is expected to live in cities, one of the
	zones with the highest water demand and an
	increasing pressure on water world-wide a better
	knowledge for urban groundwater management
	is needed URBANWAT is financed by the EU
	Commission under the call "Closing the Water
	Cycle Gap". The aims of this project is to propose
	improved tools and criteria for groundwater
	management in urban areas to ensure the
	sustainability of urban water resources, define
	integrative and innovative approach. The
	research will involve a multidisciplinary
	approach including the description of the natural
	state of the hydrological cycle, development of
	particle tracer technology to determine
	contaminant flow paths and, the detection of
	pollutants: water quality parameters, pollutants
	of emerging concern (CECs) and microorganisms
	(viruses).



	To achieve that, URBANWAT proposes to use		
	novel approaches based on liquid		
	chromatography high resolution mass		
	spectrometry to achieve the following goals: (i) to		
	identify differences in degradation in different		
	anoxic conditions using CECs as indicators of		
	contamination and their transformation products		
	(TPs) as indicators of degradability; (ii) to analyse		
	fate and transport of selected contaminants in the		
	soil-plant as a remediation system using selected		
	infrastructures; (iii) to understand and determine		
	the movement of the contaminants applying		
	encapsulated DNA-tagged nanoparticles as		
	tracer; To do so, column experiments will be		
	performed. Moreover, metagenomic-based		
	methodologies (iv) to explore the presence of		
	emergent viruses in groundwater samples		
	applying viral metagenomics. Viral concentration		
	methods from water samples will be optimized in		
	this study.		
Knowledge Type	Poster congress		
Link to Knowledge Output			
Sectors & Subsectors	Urban groundwater management		
End User	Environmental Managers		
IPR	n/a		
Policy-Relevance			
If the Knowledge Output is relevant to the WFD or			
any other related Directives, please list and explain			
why			
Status	Finalized		

9. Open Data

In relation to Open Data, the funded projects will be requested to submit metadata on all the resources directly generated by the project, as well as additional information on how these data will be exploited, if and how data will be made accessible for verification and re-use, and how it will be curated and preserved. Metadata on all project resources are required to be submitted as part of the final reporting. This will be done via the **Open Data & Open Access platform**, available at: <u>http://opendata.waterjpi.eu/</u> (also accessible from the bar menu of the Water JPI website).



Data compiled and generated during the first year of the project will be available. Hence, some information is already uploaded in some open journal repositories such as the supplementary material enclosed in the paper https://doi.org/10.1016/j.coesh.2020.01.006. Other information already published will be available for the scientific and technician communities.

- 10. Problems Encountered during Project Implementation
- Please indicate if any problems were encountered during the Project Implementation.
- Did any of the partners find difficulties related to the grant agreement, the availability of funds at national level or other similar issues not specifically related to the technical part of the project?

For the all the partners, a total confinement period has been imposed to everybody from March, 15th to May, 11th 2020. After May, 11th a partial confinement was still imposed, and a more regular situation has been established since September 2020. Consequently, very few tasks have been achieved during this period and even after as we were depending of other partners from the consortium where the national situation concerning the Covid-19 pandemic was different.

II. Suggestions for improvement regarding project implementation?

There are no suggestions for improvements on the project implementation since all the delays are because of the COVID-19 pandemic.

Deliverables



URBANWAT Tools and criteria for URBAN groundwater management

Protocol for groundwater sampling

Deliverable No.	1.1
Version	3
Version Date	06/03/2020
Author(s)	Laura Scheiber, Rotman Criollo, Enric Vázquez, Sandra Pérez, Silvia Bofill



Content

1.	Introdu	uction	.3
	1.1 Wł	ny groundwater sampling?	.3
2.	Groun	dwater Hydrogeochemistry and National Water Quality Guidelines	.3
	2.1	Groundwater hydrogeochemistry	.3
	2.2	Caracterísitcas físico -qímicas	.4
	2.3	Water quality guidelines	.5
	2.4	Preparation and logistics	.8
	2.4.	1 Sampling plan	.8
	2.4.	2 Distribution of sampling points1	0
	2.4.	3 Criteria for sampling1	1
	2.4.	4 Difficulties in sampling1	2
3	Purę	ge and sampling conditions1	2
	3.1	Pumping and sampling equipment1	2
	3.2	Sampling containers1	3
	3.3	Bore purging method	4
	3.4	Groundwater Sampling Methods	5
	3.5	Hydrogeochemical sampling1	8
4.	Sampl	e Identification, Transport and Storage1	9
	4.1 La	belling and sample identification1	9
	4.2 Ch	ain of custody1	9
	4.3 Tra	ansport and storage1	9
5	Safe	ety and health2	20
6	Res	ponsibilities	20

1. Introduction

1.1 Why groundwater sampling?

This guide aims to provide information to be able to carry out standardized groundwater sampling, which ensures the representativeness of the samples, as well as their preservation in the most appropriate conditions.

The main objective of this document is to set up the procedure and technical requirements of the personnel, material and instruments related to the taking of samples, transportation and preservation of groundwater destined for chemical analysis.

It should be noted that for the writing of this guide, the recommendations included in the official methods have been followed, whenever possible; when these do not exist, proposals by renowned organizations (BRGM, EPA, etc.) or based on the experience of the authors have been considered.

2. Groundwater Hydrogeochemistry and National Water Quality Guidelines

2.1 Groundwater hydrogeochemistry

Groundwater contains a wide variety of substances at different concentrations.

Most of these substances are dissolved in ionic form as simple ions (cations or anions eg Na⁺, Ca²⁺, Cl⁻) or complex ions (eg SO₄²⁻, HCO₃⁻). Another part of these substances is found in a non-ionic molecular form, frequently in equilibrium with ionic species, such as carbonic acid H₂CO₃⁻. The gases are generally dissolved.

The chemical composition of groundwater is mainly the net result of a set of chemical reactions between the water and the ground through which it circulates, including both the solid phase (minerals) and the gases and organic matter present in it.

Most of the soluble components in groundwater come from soluble minerals in soils and sedimentary rocks. A much smaller part has an atmospheric origin and can also come from surface water bodies.

The solutes present in groundwater are incorporated into it during all phases of the hydrological cycle, starting with the atmospheric phase (rain).

In most groundwater, 95% of the ions are represented by a few major ionic species: cations and the anions. But in groundwater we can also find minority components, which represent less than 1% of the total ionic content and trace elements, which are those found in concentrations less than 0.0001 mg / L.

Mayor components

Anions: Chloride (Cl⁻), Sulfate (SO₄²⁻), Bicarbonate (HCO₃⁻).

Cations: Sodium (Na⁺), Calcium (Ca²⁺), Magnesium (Mg²⁺)

Nitrate (NO_{3}^{-}), carbonate (CO_{3}^{2-}) and potassium (K⁺)

Minor components

They represent less than 1% of the total ionic content. ex. Fe²⁺, F⁻, K⁺, Sr²⁺

Trace components

They are generally found in concentrations less than 0.0001 mg / L. ex. As, Cr, Pb, Cu, Zn, etc.

Fundamental gases

Carbon dioxide (CO_2) and dissolved oxygen (O_2) , although they are not frequently analyzed in groundwater.

The normal sequence of a 'young' water, of recent infiltration, is:

Ca²⁺> Mg²⁺> Na⁺

 $HCO_{3}^{-} > SO_{4}^{2} > CI^{-}$

after a long time of residence, you tend to invest to:

 $Na^+ > Mg^{2+} > Ca^{2+}$

 $CI^{-} > SO_4^{2-} > HCO_3^{-}$

Some chemical alterations can be due to:

- Interaction with atmospheric air
- Volatilization losses
- Interference with coating material
- Biological processes (Biodegradation)
- Pollution from the surface
- Mix of waters

2.2 CARACTERÍSITCAS FÍSICO -QÍMICAS

TEMPERATURE:

Calorific potential referred to a certain origin.

It is measured in °C and °F.

Groundwater: temperature very little variable and responds to the annual average of the atmospheric temperatures of the place, increasing in the product of the depth by the geothermal gradient (1°C every 33 m).

CONDUCTIVITY:

Ability of a water to conduct electricity.

It is measured in microsiemens / cm (uS / cm) or micromhos / cm (umhos / cm).

It grows with the temperature and a reference is taken (18°C or 25°C). It grows 2% at / $^{\circ}$ C with increasing temperature.

It grows with the content of dissolved ions.

It varies from 100 to 2000 uS / cm at 18°C in fresh water, and can reach up to 100,000 in brines.

HYDROGENION CONCENTRATION, pH

In general, the pH of natural waters remains between 6.5 and 8, although exceptionally it can vary between 3 and 11.

PH plays an important role in many biogeochemical processes in natural groundwater (carbon balance, redox processes, etc.).

2.3 Water quality guidelines

The Drinking Water Directive (Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption) concerns the quality of water intended for human consumption. Its objective is to protect human health from adverse effects of any contamination of water intended for human consumption by ensuring that it is wholesome and clean. The consolidated text of the Directive with its latest amendments including Commission Directive (EU) 2015/1787 of 6 October 2015 can be found in the Directory of European Union consolidated legislation.

The Directive laid down the essential quality standards at EU level. Add up to of 48 microbiological, chemical and indicator parameters must be monitored and tested routinely. In general, World Health Organization's guidelines for drinking water and the opinion of the Commission's Scientific Advisory Committee are used as the scientific basis for the quality standards in the drinking water.

Microbiological parameters			
PARAMETER PARAMETRIC VALUE (Number/100 mL)			
Escherichia coli (E. coli)	0		
Enterococos 0			
Chemical parameters			
Acrylamide	0.10 μg/L * ^{Note 1}		
Antimony	5.0 μg/L		
Arsenic	10 μg/L		
Bencene	1.0 μg/L		

URBANWAT. Tools and criteria for grounWATer management DELIVERABLE: Protocol for groundwater sampling

Benzo pyrene	0.001 μg/L
Boron	1.0 mg/L
Bromate	10 μg/L* ^{Note 2}
Cadmium	5.0 μg/L
Chrome	50 μg/L* ^{Note 3}
Copper	2.0 mg/L* ^{Note 3}
Cyanide	50 μg/L
1,2-Dichloroethane	3.0 μg/L
Epichlorohydrin	0.1 µg/L* ^{Note 1}
Fluoride	1.5 mg/L
Lead	10 μ g/L* ^{Note 3 and 4}
Mercury	1.0 μg/L
Nickel	20 μg/L* ^{Note 3}
Nitrate	50 mg/L * ^{Note 5}
Nitrite	0.5 mg/L* ^{Note 5}
Pesticides	$0.1 \mu g/L^{*Note 6 and 7}$
Total pesticides	$0.5 \mu g/L^{*Note 6 and 8}$
Aromatic polycyclic hydrocarbons	0.1 µg/L* ^{Note 9}
Selenium	10 μg/L
Tetrachloroethene and trichloroethene	10 μg/L
Trihalomethane	100 µg/L* ^{Note 10}

Note 1: The value of the parameter refers to the residual monomeric concentration in water, calculated according to the characteristics of the maximum migration of the corresponding polymer in contact with water. Note 2: Where possible without affecting disinfection, Member States should strive for a lower value. For the waters referred to in letters a), b) and d) of paragraph 1 of article 6, the value shall be fulfilled, at most, ten calendar years from the date of entry into force of this Directive. For the period from the fifth to the tenth year after the entry into force of this Directive, the parametric value of bromate shall be 25 μ g / I. Note 3: The value applies to a sample of water intended for human consumption, obtained by a suitable sampling method (1) at the tap and collected in such a way that it is representative of an average weekly value ingested by consumers. Where appropriate, the sampling and control methods shall be carried out in a harmonized manner, to be established in accordance with Article 7 (4). Member States shall take into account the presence of peak values that may cause adverse effects on human health. Note 4: For the waters referred to in letters a), b) and d) of section 1 of article 6, the value will be fulfilled, at most, fifteen calendar years from the date of entry into force of the present Directive. For the period between the fifth and the fifteenth year after the entry into force of this Directive, the value of the lead parameter will be 25 μ g / I. Member States shall ensure that all appropriate measures are taken to reduce the concentration of lead in water intended for human consumption as much as possible for the period necessary to meet the value of this parameter. In implementing the measures necessary to meet this value, Member States will progressively prioritize areas with the highest concentrations of lead in water intended for human consumption. Note 5: Member States shall ensure that the figure of 0.10 mg / I for nitrites is respected when leaving the water treatment facilities and the condition that [nitrate] / 50 + [nitrite] / 3 # 1, where the brackets mean concentrations in mg / I for nitrate (NO3) and for nitrite (NO2). Note 6: "Pesticides" mean: organic insecticides, organic herbicides, organic fungicides, organic nematocides, organic acaricides, organic algaecides, organic rodenticides, organic molluscicides, related products (among others, regulators growth) and their relevant metabolites and degradation and reaction products. Only those pesticides that are likely to be

present in a given supply need to be controlled. Note 7: The parameter value applies to each of the pesticides. For aldrin, dieldrin, heptachlor, and heptachlorepoxide, the parametric value is 0.030 µg / I. Note 8: "Total pesticides" means the sum of all pesticides detected and quantified in the control procedure. Note 9: The specified compounds are: - benzo (b) fluoranthene benzo (k) fluoranthene - benzo (ghe) perylene - indene (1,2,3-cd) pyrene. Note 10: Where possible without affecting disinfection, Member States should seek to obtain a lower value. The specified compounds chloroform, bromoform, dibromochloromethane. are: bromodichloromethane. For the waters referred to in letters a), b) and d) of paragraph 1 of article 6, the value shall be met, at most, ten calendar years from the date of entry into force of this Directive. For the period from the fifth to the tenth year after the entry into force of this Directive, the parametric value of total THMs shall be $150 \mu g / I$.

Indicators parameters			
PARAMETER	PARAMETRIC VALUE (Number/100 mL)		
Aluminium	200 μg/L		
Amonium	0.5 mg/L		
Chloride	250 mg/L * ^{Note 1}		
Clostridium perfringens	0 number/100mL ^{*Note 2}		
Colour	Acceptable to consumers and no abnormal		
	changes		
Conductivity	2500 μS/cm (20ºC)* ^{Note 1}		
Hydrogen ion concentration	\geq 6.5 and \leq 9.5 ^{*Note 1 and 3}		
Iron	200 μg/L		
Manganese	50 μg/L		
Odor	Acceptable to consumers and no abnormal		
	changes		
Sulfate	250 mg/L ^{*Note 1}		
Sodium	200 mg/L		
Flavour	Acceptable to consumers and no abnormal		
	changes		
Colony count at 22ºC	no abnormal changes		
Coliform bacteria	0 number/100mL* ^{Note 5}		
Total Organic Carbon (TOC)	no abnormal changes* ^{Note 6}		
Turbidity	Acceptable to consumers and no abnormal changes *Note 7		

Note 1: The water must not contain corrosive substances. **Note 2**: This parameter needs to be measured only if the water comes totally or partially from surface water. In the event of noncompliance with this parameter value, the affected Member State shall investigate the supply to ensure that the presence of pathogenic micro-organisms such as cryptosporidium does not give rise to any potential danger to human health. Member States shall include in their report the results of all such investigations, in accordance with Article 13 (2). **Note 3**: For still water packed in bottles or other containers, the minimum value may be reduced to 4.5 pH units. For water packed in bottles or other containers that is naturally rich in carbon dioxide or with artificial addition of it, the minimum value may be lower. **Note 4**: It is not necessary to measure this parameter if the TOC parameter is analyzed. **Note 5**: For waters packed in bottles or other containers, the unit is number / 250 ml. **Note 6**: It is not necessary to measure this parameter for supplies of less than 10,000 m³ per day. **Note 7**: In the case of surface water treatment, Member States should try to achieve a parametric value of no more than 1.0 NTU (nephelometric turbidity units) in the water leaving the treatment facilities. **Note 8**: The periodicity of the control will be indicated later, in Annex II. **Note 9:** Excluding tritium, potassium, radon, and radon decay products. The periodicity of the control, the control methods and the most suitable places for taking samples will be indicated later in Annex II. **Note 10:** The proposals required by Notes 8 and 9 on the periodicity of the control, the control methods and the most suitable places for the control points indicated in Annex II will be adopted in accordance with the procedure established in Article 12 In preparing such proposals, the Commission shall take into consideration inter alia the relevant provisions in accordance with the existing legislation or the appropriate control programs including the results of the control derived from them. The Commission shall present such proposals no later than 18 months after the date referred to in Article 18 of this Directive. 2. Member States do not need to monitor drinking water for tritium or radioactivity in order to establish the total indicative dose when they consider that on the basis of other controls carried out the levels of tritium or the total indicative dose of water are they are well below the parametric value. In that case, it will communicate the reasons for its decision to the Commission, including the results of those other controls carried out.

2.4 Preparation and logistics

2.4.1 Sampling plan

Before monitoring, a sampling plan must be designed taking into account: (1) Objectives of the sampling and elements to analyze; (2) Characterization of the aquifers to be sampled; (3) Location (x, y, z) of the points to be sampled; (4) Know the constructive characteristics of the wells to be sampled; (5) Type and size of samples; (6) Techniques and instruments for in situ determinations; (7)

Sampling techniques; (8) Sample preservation procedure and (9) Sampling schedule.

It is important to have a field spreadsheet for each well where at least the following information must be included

- Constructive profile of the well to be monitored
- Well site identification
- Name of the technicians who perform the sampling
- Sampling date
- Data logging and purge time
- Blowdown flow
- Volume of water purged
- On-site parameter measurement log
- Record the appearance of water after purging
- Samples collected

All the following procedures may not be necessary for each sampling event. Use those procedures aplicable to your sampling plan or customize this list.

LOGISTICS	 Organize for location get to with the land/home/facility proprietor and inhabitants (Permission/notification to land/home owner/tenant). Directions to the site and site access roads/site access keys Contact names_addresses and phone
	 Contact names, addresses and phone numbers list
	 Site map showing well locations

DOCUMENTATION AND REFERENCE MATERIALS	 Sampling and analysis plan and health and safety plan Well Specific Field Sheet and Field Procedures <u>Documentation sheet</u> Well and boring logs Field note book and waterproof pens Clipboard with waterproof cover Chain of custody forms and other sample tracking forms Camera and film 		
LABORATORY ARRANGEMENTS	 Select a qualified laboratory to perform the sample analysis. Check that the laboratory (and subcontracted lab) is certified to perform the required analysis. Make sure you have sufficient numbers, types, and volumes of sample containers get extras! Discuss sample preservation, holding time, shipping requirements with the laboratory. Inform the laboratory of the date and number of samples you will send. Familiarize yourself with chain of custody and other sample tracking procedures. 		
SITE HISTORY	Review past water quality data to determine the well sampling order.		
PURGING AND SAMPLING EQUIPMENT	Pump or bailer and accessories Battery for sampling pump Sample containers. B ring extra. Water proof labels/tags Filters and elements for the preservation of the sample as acids Gloves		
FIELD MEASUREMENTS AND EQUIPMENT	Water level measuring instrument Temperature instrument Conductivity meter and calibration standards pH meter, buffer solutions (pH 4, 7 and 10) Dissolved oxygen meter Eh meter		

	All meters fully charged and operational; spare batteries Closed flow through cell Inspect the equipment for defects, loose bolts, frayed wiring, etc Check that all equipment is properly decontaminated and stored for transport. Fill out the Well Specific Field Sheet as much as possible before heading out to the field		
DECONTAMINATION EQUIPMENT	Non-phosphate cleaner and scrub brushes Wash and rinse tubs or buckets and wastewater containers		
SAMPLE PRESERVATION AND SHIPPING	 Sample preservatives, transfer pipettes Coolers sufficiently large to hold all samples. Crushed or cubed ice (frozen cold packs discouraged, need temp. blank) Bubble wrap, ZiplockTM bags or equivalent to protect sample containers 		
TOOLS AND MISCELLANEOUS	 Additional locks, keys for wells, flashlight, rain gear, etc. Adjustable wrench, screw drivers, hammer, scissors, knife, duct tape, etc. Plastic garbage bags for contaminated waste 		
HEALTH AND PERSONAL PROTECTIVE EQUIPMENT	 Safety glasses and/or splash shield Inner and outer gloves (compatible for contaminants) Hard hat and steel toed boots First aid kit and eye wash kit Reflective vest Safety helmet 		

2.4.2 Distribution of sampling points

The purpose and scope of the sampling must be assessed before sampling. A key issue is spatial distribution, that is, the number and distribution of wells and boreholes to be incorporated into the campaign. This decision is prior to sampling, and therefore belongs to the preparation group. But there is another aspect of interest: the vertical component of wells and boreholes, which is often not properly incorporated into

hydrogeological studies. For this reason, it has been considered appropriate to include the spatial distribution in the section on purge and sampling conditions.

In general, the inclusion of the vertical component in sampling is recommended. The final decision will depend on several factors: equipment of the well / well, existence of lithological column, tubing that penetrates various formations, construction quality of the well / well, etc. The following criteria are adopted:

• If there are perforations with point piezometers penetrating different formations, they will always be chosen as they provide more accurate information on the state of the aquifer.

• If it is possible to use shutters and the knowledge of the lithology is adequate (lithological column and construction characteristics are available), these wells / boreholes will be used to carry out the sampling.

• In all other cases (lack of basic information, inappropriate facilities, interest in the overall state of the aquifer), vertical distribution will not be taken into account.

2.4.3 Criteria for sampling

When a sample of groundwater is extracted, as it rises and is brought to the surface, it is exposed to physicochemical conditions different from those in the aquifer. Some species, particularly those included in carbonate and redox reactions, may experience changes in contact with air, room temperature, and atmospheric pressure.

The sampling sequence or order is not arbitrary, but must be based on the sensitivity of the various parameters to environmental changes introduced by the same purge and sampling operation, which, let us remember, represents a remarkable alteration of natural conditions.

Taking these considerations into account, the following sampling order has been established:

1. Measurement of the piezometric level

Before starting the sampling, itself, the piezometric level must be recorded. It will almost always be done using a level probe with a light detector and, ideally, with the same probe for all wells / boreholes. This gives the depth of the water, which must be measured from the nozzle. It is essential to clean the probe after reading to avoid contamination of samples from other wells.

2. Field parameters

Field parameters include temperature, pH, redox or Eh potential, electrical conductivity, dissolved oxygen, turbidity, and alkalinity. These parameters are as important as those in the laboratory, but must be measured appropriately and quickly in the field to prevent changes in contact with air, ambient temperature, and atmospheric pressure. These are non-conservative features of groundwater. In addition, these parameters have an added value, as they are very valuable to indicate that stabilization has occurred during pumping. Stabilization (understood as 3 approximately constant readings of temperature, pH, Eh, with measurements taken every 2 minutes) is synonymous with representative groundwater and therefore indicates the time at which the sample.

The measurements will always be made in a shady place, preventing the sun from directly impacting the water and the electrodes. It is very important to always protect the electrodes from dust and sun. If the electrodes have overheated, they must be immersed in the container, with the groundwater, to return to thermal equilibrium.

3. Metals

Common metal protocols suggest the desirability of filtering water before sampling, as significant concentrations of it may be associated with colloidal and fine particles in suspension. However, in principle, the option of not filtering is adopted when it is intended to estimate the overall risk of water pollution - without differentiating the distribution into phases.

To maintain the solubility conditions of groundwater, acid (usually nitric acid) must be added to keep the pH below 2.

4. Inorganic

The term inorganic encompasses: basic anions and cations, nitrogen compounds (ammonium and nitrites, in addition to nitrates) and sulfides.

5. Organic

Encompasses any chemical compound that contains carbon, forming carbon-carbon and carbon-hydrogen bonds.

6. Microbiology

Microbiological determinations require special care in avoiding artificial contamination during the sampling process. It is very common for abnormal values to be obtained due to inadequate sampling, even if a container is conveniently sterilized by the laboratory. In this case, it should be filled only up to the neck of the bottle, avoid artificial aeration and any contact with the tube or sampling material, and obviously use a sterilized sampler.

2.4.4 Difficulties in sampling

Common deficiencies or errors that lead to a wrong or inadequate interpretation of the condition of the groundwater in the aquifer:

- Hydrogeological complexity: ignorance of the System, lack of trained technicians
- Physicochemical modification of the sample (errors in sampling, handling, preservation and / or transportation.
- Problems associated with drilling and / or monitoring wells (Lack of construction project, construction deficiencies, etc)

3 Purge and sampling conditions

3.1 Pumping and sampling equipment

In sampling, it is intended to determine the quality of groundwater in the environment closest to the point considered and at a specific time or moment, not the quality of water stored inside a well, which can take a long time stagnant or immobilized inside.

The purpose of the purge is to dislodge stagnant water in the well in order to obtain representative samples from the aquifer.

The operation is carried out after the measurement of the water level, and the volume to be extracted is variable, although it is common to evacuate three times the well volume.

As an indication that the water is representative aquifer stability can be determined easy to measure parameters such as pH, conductivity or temperature.

If the purge process is not performed or is done incorrectly the samples lose representativeness, so it should be included in the file field a notation about the time of purge and the volume of water withdrawn.

Excessive pumping can cause:

- Pronounced drops, with turbulent flow, not being representative samples (volatilization, oxidation or precipitation of pollutants may occur.
- Cloudy water
- Alter the direction of migration of pollutants

There are several strategies for purging wells and boreholes. Existing protocols take into account the characteristics of tubing of the aquifer, ie the response to the purge action.



3.2 Sampling containers

The containers must keep the sample in identical conditions they had when they went collected, without adding or subtracting components or modify the physical or chemical state of existing ones, in particular they must meet the following terms:

- ✓ Do not release organic matter, elements alkalis, boron, silica and others that contaminate the Water.
- ✓ The adsorption exerted by the walls on the components present in the sample must be minimal.
- ✓ Container material must not react chemically with the constituents of the sample.
- Sample containers in which are going to determine microbiological parameters must be sterile and contain no residual agent used in its sterilization or release growth inhibiting or enhancing substances bacterial.
- ✓ The closure system must be hermetic. The choice of the packaging material has a great importance, because on some occasions can interact with the

sample by altering noticeably its characteristics. Normal soda glass tends to dissolve, increasing the concentration of sodium and silica in water. Borosilicate glass containers (pyrex) tend to slowly leach amounts appreciable manganese, lead, zinc and arsenic. Finally, the phosphates are adsorbed and desorbed of certain types of glass. Most plastic containers can give the water organic substances that interfere with the analysis of pesticides and other compounds. Furthermore, propylene containers are porous so that losses can occur by evaporation. Many plastics are permeable to gases and most to CO.

The capacity of the containers will be adapted to the needs of the laboratory. The containers will be new (never reuse bottles), made of polypropylene or PVC and hermetically sealed.

The caps of the containers must ensure a hermetic closure and not react with the components of the water. Stoppers made of a material similar to that of the bottles will be used, taking into account that the glass ones should not be used with highly alkaline materials as they adhere easily.

Avoid touching the inside of the caps when handling the containers when collecting the samples.

3.3 Bore purging method

• PURGA VOLUMEN DETERMINADO

The flow rate for filling the bottles should not exceed 250mL / min, for organic substances and 500mL / min for inorganic substances.

The equipment for taking the sample should be introduced and removed slowly and cautiously in the well.

Advantage:

Can be used by various teams

Does not require chemical measurements to perform the purge

Does not require continuous control of physical-chemical parameters

Limitations:

Generates a larger volume of water

It does not apply in the middle of low hydraulic conductivity.

• LOW FLOW PURGE

The objective is to achieve hydraulic stabilization as quickly as possible, avoiding mixing of the water and considering that only the water from the filtering portion is pumped.

The time of the purge volume is determined by the hydraulic stability and the physicalchemical parameters, indicative of the groundwater quality.

In low flow blowdown the volume of water drawn from the well is reduced by up to 30%.

It reduces turbidity problems, since it reduces the disturbances caused in the water column of the well and the formation.

The lower the flow rate during the purge, the better the control of descent and turbidity.

Flow rates are determined for each well based on the drop values. In practice flow rates of 250 to 500mL / min are used. It should not exceed 1L / min, to avoid mobilization of solids in the formation.

Advantage:

Minimize purge volume Turbidity is reduced Greater control in the sample <u>Limitations:</u> Instrument calibration in the field.

Can't use bailers

Using the pumps can cause disturbances inside the well

• PURGE USING SHUTTERS

Procedure used for the purging and punctual sampling of the groundwater, at determined depths, where it is intended to isolate a section to be sampled.

Advantage:

Minimize the volume of water purged.

In wells with a multilayer filtering section, it allows to isolate each section or fractured areas.

Collection of specific samples.

Limitations:

Requires specialized technicians

Cannot be used with bailers

3.4 Groundwater Sampling Methods

Procedures for chemical sampling and analysis should be uniform to ensure the comparability of analysis results from very distant control points, which will have been sampled by different people and using various sampling systems, in addition of analyzed in different laboratories.

Operations prior to the collection of samples.

The first step prior to a groundwater sampling campaign consists of carrying out a series of fine-tuning operations on the materials and equipment for taking samples.

Preparation of field documentation: cartography, manuals for use and calibration of equipment, field notebooks, labels. As far as possible, the records of the wells or equivalent information (diameter, depth, location sketch, etc.) will be obtained.

Review of the status of the sampling equipment, function check, battery status, and spare material (batteries, calibration standards, preservatives, demineralized water, filters, etc.).

Cleaning of all equipment to be used. The material will be washed with detergent, and it will be rinsed three times with running water and twice with deionized water.

The plastic material, except the sample collection bottles that will be new, is cleaned with HCl or HNO3, and they are flushed with water and deionized water.

The electrodes are washed with deionized water, dried and stored in their corresponding solutions if necessary.

Labeling and referencing of the bottles. It will be done preferably with adhesive labels or indelible marker (waterproof), before taking samples. In case of using adhesive labels, it is advisable to cover the label with a transparent plastic adhesive strip that prevents damage due to humidity. It is recommended to label the bottle cap as well. Avoid naming samples with long references. It is better to have a number or letter and number, and write down the correspondence with its official reference or toponym in the field notebook.

Both manual samplers and pumps will be washed after the operation, to avoid cross contamination in other wells. Depending on the construction materials of these devices, their cleaning will be adapted to the manufacturers' instructions.

Filling the containers.

As a general rule the containers will be filled to the brim trying not to leave a camera of air between the water and the closing plug. However, in containers containing samples for microbiological analysis shall to have enough air chamber to be able to shake and homogenize the sample avoiding contamination accidental.

Taking method.

Samples will preferably be taken by submersible pump pumping. The submersible pumps must be properly washed after taking each sample.

Unless otherwise indicated, the mouth of the pump or the sampler will be located in front of the section of well that is open or, if there are several, the one that is presumed more permeable.

The pumps will be purged before proceeding to take the sample, letting the borehole water flow through it to carry away possible remains of previous samples, at least 3/4 times the content of the pump and pipes. The samplers will be filled and emptied with the water from the point to be sampled at least 3 times before collecting the final samples.

If the catchment is equipped and the introduction of a sampling system is not possible, the water must be collected from the tap closest to the borehole. The sample will be representative of the water extracted from the catchment, but not necessarily of that belonging to a certain level or depth of intake. If the pump is not running when the sample is to be taken, just let the water run through the tap for 5-10 minutes to displace the water contained in the pipe, after it has been started.

The field record will always reflect the method of sampling, as well as whether it was taken at the tap, and the pumping time, in order to pump the same period in subsequent sampling.

Groundwater level measurements

Before starting sampling, the piezometric level must be measured. It is advisable to do this by means of a level probe with acoustic or light detector and, ideally, with the same probe for all wells / boreholes. This gives the depth to the water level, which must be measured from the curb or altimetric reference.

Once the level has been measured in many points of the aquifer, the piezometric map can be represented, which would be the map of the distribution of the piezometric level of the entire aquifer. From this map it is possible to know how the waters of the aquifer flow: direction, intensity and gradient. Therefore, a piezometric map is similar to a topographic map of the groundwater level. In this way, the water flow will occur perpendicular to the level curves (isopieces) from the highest to the lowest.

It is essential to clean the probe after reading to avoid contamination of samples from other wells.

Measuring field parameters

Temperature

The temperature is measured with a mercury thermometer or with the pH and conductimeter thermometers. Care must be taken to allow the thermal balance between the thermometer and the water to be established.

The thermometer should be cleaned with distilled water after sampling is complete

Electrical conductivity (EC)

The electrical conductivity is directly proportional to the temperature, at the rate of a 2% increase for each °C increase. For this reason, the electrical conductivity must always be measured in relation to the temperature, even though a conductivity meter with a compensated temperature is available. The electrode is inserted into the water and, once stabilized, the electrical conductivity and the temperature are recorded at the same time. The electrode must then be cleaned with distilled water and stored to protect it from dust.

<u>рН</u>

It is important to measure the pH in the field, as it is likely to vary due to losses or gains in dissolved gases, such as carbon dioxide (CO_2) and oxygen (O_2). Groundwater is generally in equilibrium with CO_2 at a partial pressure above atmospheric. Thus, when exposed to atmospheric pressure, CO_2 escapes and can cause pH changes. pH also varies with temperature.

PH meters are subject to drift and require daily calibration, using two patterns within the range of measurements expected to be taken. Then, the electrode must be cleaned with distilled water and stored.

Redox potential (Eh)

Redox potential is a measure of a system's tendency to oxidize or reduce. The electrode is connected to the meter and, when the reading has stabilized (3 constant measurements, measured every 2 minutes).

Dissolved oxygen

Water in contact with air contains a large amount of oxygen, depending on atmospheric pressure and the temperature and salinity of the water. At 1 pressure atmosphere and 4 deC water temperature, the solubility of oxygen is 13.11 mg / L, while it is 8.42 mg / L at 24°C.

In groundwater the dissolved oxygen contents can vary between 0 and 100% saturation. Oxygen dissolved in water can be consumed by the oxidation of organic matter or by the oxidation of iron and manganese minerals.

To take the measurement, a volume of water sample is taken with the minimum possible aeration and the electrode is immersed.

<u>Alkalinity</u>

Alkalinity is defined as the ability to neutralize acids normally in meq / L or mg / L of calcium carbonate (CaCO3). The determination is made by titration of the sample using a strong acid.

3.5 Hydrogeochemical sampling

Majority sampling

Filter (0.22µm) the water before taking a sample for anions and cations, since the presence of colloidal and fine particles in suspension can modify the results of the analysis. A sample is taken in polyethylene containers of 25 mL for anions and 25 mL for cations. To maintain solubility conditions, 1 mL of 20% HNO3 must be added to the sample for cation analysis and in this way the pH is maintained below 2. The sample must be kept cold (4-5°C) and it is recommended to analyze it within 1 month.

Metal sampling

It is necessary (0.22μ m) water before taking a sample. A sample is taken in polyethylene containers of 50 mL capacity. To maintain the solubility conditions of metals in groundwater, 1 mL of 20% HNO3 must be added and in this way the pH is kept below 2. The sample must be kept cold (4-5°C) and recommends analyzing it within 1 month.

Sampling for Dissolved Organic Carbon (DOC)

Filter the sample at 0.45 μ m and it should be collected in a muffled glass bottle with a 25 mL capacity. Add 1 ml of 2N HCl until obtaining a pH value between 2 and 3. The water cannot be in contact with plastic (except when it is filtered). Between the plug (plastic) and the sample should be put clean parafilm without touching it with the hands. Avoid contact of air with the sample as much as possible. The sample must be kept cold (4-5°C).

4. Sample Identification, Transport and Storage

4.1 Labelling and sample identification

Label the bottles preferably before taking the sample. An adhesive label or indelible markers must be used, and indicate at least the following information:

- ✓ Sample reference.
- \checkmark Date and time of taking.
- ✓ Treatment (acidification, preservatives, etc.).

Covering the labels with clear tape is helpful to prevent moisture from altering the inscription.

Double numbering will never be carried out, as it can lead to serious later errors.

4.2 Chain of custody

Following appropriate chain of custody, tracking and security procedures is basic to keep up the integrity and lawful legitimacy of your samples. Samples and shipper safety efforts guarantee that the samples were not altered before analysis.

Chain of custody records document a sample from collection, through handling, storage and shipment, to final analysis. Such records and documentation include: labeling to prevent sample mixup; container and shipper seals to prevent unauthorized tampering; and documenting who has custody of the samples.

A chain of custody record must be completed for each sampling field. A set of samples, or a sample shipper changes possession, the person relinquishing and the person receiving the samples or shipper must sign, date and record the time on the chain of custody record.

4.3 Transport and storage

The samples will be sent to the laboratory as quickly as possible. Delivery to the laboratory will be made, as general rule, within 24 hours to take; however, this period may vary depending on storage conditions water and type of determinations what will be done. The shipment will attach a list of samples, a completed record with the data: identification of the point, date, determinations to be made on each sample, as well as other laboratory requirements, for example, conductivity measured in the field.

Likewise, the laboratory will be asked to verify the reception and status of the samples regarding: integrity of the containers, labeling in good condition, storage conditions, etc.

The transport of the samples must be carried out in hermetically sealed containers from light and preventing the sample from heating up.

Preservatives (sulfuric, nitric acid, sodium thiosulfate, etc.). They will be of RA quality (reagent for analysis).

The stabilization of the components of the water samples by adding chemical preservatives must be carried out with great care, the preservatives must not interfere with the analytical determination, in case of doubt a test must be carried out to check the compatibility. During the analysis, the possible dilutions introduced when adding preservatives should be taken into account when calculating the results.

5 SAFETY AND HEALTH.

As a general rule, the use of disposable latex gloves is recommended for sampling, to prevent contamination of containers and equipment, as well as to avoid accidental burns when handling acids.

In sampling locations where dust may be generated that may pose a risk of respiratory or skin contact, precautions will be taken during sampling, using masks and special clothing (long sleeves, glasses, suitable footwear).

All waste produced during the sampling tasks (cardboard, paper, plastics, etc.) will be collected in bags and then deposited in the appropriate waste containers.

6 **RESPONSIBILITIES.**

The technician who performs the sampling will be duly trained, qualified and trained in the theory and practice of specific sampling, thus being responsible for applying the content of this protocol. It must be taken into account that specific circumstances, unforeseeable in each case, may require the technician to decide to modify, with professional criteria, some of the steps. These deviations must be communicated to the project manager and documented in writing in the field record.



URBANWAT Tools and criteria for URBAN groundwater management

SOP for virus concentration from groundwater, surface and runoff water.

Deliverable No.	D2.1
Version	2
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Author(s)	Marta Russiñol, Silvia Bofill



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SOP for virus concentration from groundwater, surface and runoff water.

The aim of the protocol is to concentrate viruses present in 50-100L of water with a Large Volume Concentration (LVC) Kit (Innovaprep), using a **Rexeed-25A** single-use filter, and a Centrifugal-ultrafiltration (CeUF) filter, such as the **Centricon® Plus-70** device, into a final volume of 200-500ul.

Equipment & reagents:





Figure 1: Large Volume concentration Kit components







Figure 2: Centricon[®] Plus-70 components

Rexeed-25S Filter Setup:



1. Place the Filter cell (A) vertically in the holder with the BLUE header facing upward.

2. Remove the cap and attach the Feed tube (D) to the BLUE header of the filter cell.

3. Put a waste container to collect the priming volume and remove the cap of the RED bottom.

4. Collect and discard the residual liquid that pours from the Filter Cell.

5. Attach the Drain tube with clamp (E) to the RED bottom of the Filter Cell.

6. Attach the Permeate tube with clamp (F) to the top side port, near the BLUE header.

7. Attach Feed Tube (D) to the feed line tube connected to the peristaltic pump and face permeate tube (F) and the drain tube (E) to the waste container.



8. Ensure that clamps are open on both the Permeate (F) and the Drain tube (E).

9. Connect the pump and the stirrer to a battery.

Filtering the sample

- 1. Water samples should be firstly pumped to a 50L bucket for preconditioning before filtered.
- 2. Add thiosulphate (45mg/L of water).
- 3. Let the water to stand for 10 minutes to neutralize the chlorine.
- 4. Take a MS2 lyophilized tube, add some of the water from the bucket, mix well and put the full content of the tube into the water container again.
- 5. Start the feed pump.





- 6. When a steady stream of water comes out of the bottom **Drain Tube**, close the clamp or remove the tube and attach the cap.
- 7. The filtered liquid will continue to flow out of the **Permeate tube** until you have processed the entire sample. Safety Precaution: Do not exceed 10 psi.
- 8. When liquid stops, allow the pump to continue running for 5 seconds and turn off pump.
- 9. Allow Filter cell to rest for 10 seconds before continuing to the next step.

Collecting the Rexeed 25A eluate

- 1. Keep the Filter cell vertical with the Feed tube on top, grasp the Feed tube fitting firmly and slowly disconnect it from the Filter cell (pressure will vent as you remove the fitting).
- 2. Pinch the **Permeate tube** clamp closed.
- 3. Screw the LVC Can Interface (C) tightly into the BLUE top of the Filter Cell.
- 4. Remove the **Drain tube** (E) and place the filter cell down near a 100ml plastic container to catch the concentrated sample.
- 5. To Elute, firmly press the Elution Fluid Can (B) down into the LVC Interface. Apply constant firm pressure until all foam and all the CO2 has been expelled out. Sample eluate will have between 30-50ml.
- 6. Clean the work area with the following reagents: first soap solution, second HCl 0.1 N, third distilled water.
- 7. Keep the container at 4°C until secondary concentration step.

Centricon Filter Set-up

- 1. Use one Centricon[®] unit per 70ml sample plus one for negative control.
- 2. Add one cap to a filter cup attached to a collection cup.
- 3. Pre-rinsing: Centricon[®] Plus-70 membranes contain trace amounts of glycerine, used as a humectant. To remove glycerine, fill the filer part with 70 mL of Milli-Q[®] water and spin up to 3,000g for 15min and attach the filter and the collection cup again.

ATTENTION: Do not allow the membrane in the filter device to dry out once wet. If the device is not being used immediately after pre-rinsing, leave fluid on the membrane until the device is used.

Ultrafiltration with Centricon® Plus-70 device

- Add the **Rexeed 25A eluate** to the filter cup and seal with the cap (maximum volume 70ml). (See Figure 2)
- 2. Spin up to 3000xg for 30 min. In case there some sample unfiltered sample remain in the filter cup, discharge it with a (micro)pipette.





CAUTION: Always counterbalance centrifuge with a second bucket containing a second Centricon[®] Plus-70 device and an equal volume of sample or water. If the amount of concentrate remaining in the sample filter cup is above the top of the filter cores, decant to a suitable container before proceeding.

3. Turn the *concentrate cup* upside down and place on top of the *sample filter cup*. Carefully invert device, place in centrifuge. Spin at 1000g for 3min.



Figure 3: Shcematic procedure to proceed with the recovery of the concentrate

Remove the *concentrate cup* containing the concentrated sample from the *sample filter cup*. Keep the *filter cup* inverted during this process. Remove the sample with a pipette and store sample (approximately 200µl) in a 1,5ml plastic tube at -80°C.



Figure 4: Collection cup with filtered sample

Negative process control:

A negative process control should be included in every batch of concentrated samples. Use 10L of tap water containing 100 ml of a solution of 10% sodium thiosulphate to eliminate residual free chlorine.

Internal control process (suggested):

Add 1ml of the MS2 phage suspension as a process control to each water sample.



URBANWAT Tools and criteria for URBAN groundwater management

Development of the experimental setup

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Author(s)	Linda Liquot, Maria Rios

Soil samples from 3 piezometers located in Barcelona (piezometers I, J and H in Figure 1) are used in the experiments. Piezometer H (PZH) is placed in the Poblenou neighbourhood, near the coast, and piezometers I and J (PZI and PZJ) are situated near the Glories square and further from the coast than piezometer H.



Figure 1: Map of Barcelona showing the location of the soil samples (piezometers I, J and H) and the conductivity of the groundwater (coloured points).

Soil samples were taken from two different depths: 2 surface samples 0-1.5 m depth and 2 deep samples 20-25 m depth (Table 1).

The two surface samples, taken from piezometers I and J, have an anthropogenic origin and similar lithology. However, the two deep samples, taken from piezometers J and H, have different lithology; the deep sample from piezometer J is more clayey and the deep sample from piezometer H is sandy.

Table 1. Summary of soil samples. Location, depth and lithology of the soil samples used in the experiments.

	PZH	PZI	PZJ
SURFACE sample		Х	Х
(0-1.5 m)		(anthropic)	(anthropic)
DEEP sample	Х		Х
(20-25 m)	(sandy)		(clayey)

Surface samples, which theoretically are more polluted and less permeable, are proposed to be used only in the desorption experiments (batch experiments) to evaluate the amount and type of contaminants retained in the shallowest soil. However, deep samples, which

theoretically are less polluted and more permeable, are planned to be used in the sorption, desorption and the percolation column experiments.

Due to the current COVID situation, there has been a delay related to the soil availability which, consequently, has postponed the suitable soil characterization. Surface soil samples are planned to be characterized by DRX analysis, and for deep soil samples a detailed characterization is proposed: DRX analysis, fluorescence analysis, BET (reactive surface are), ICP-AES analysis, and determination of the total C, total N, organic matter, pH, and carbonate/bicarbonate composition. All these analyses are in progress.

The particle size distribution of the deep soil samples has been performed (Figure 2). From the figure it is deduced that soil sample PZH is more uniform that soil sample PZJ, showing the higher amount of particles with a diameter between 0.2 and 0.5 mm. The grain diameter of the soil samples selected to perform the percolation column experiments is between 2 and 0.063 mm. The finest portion of the soil samples has been discarded to avoid clogging mechanism in the column experiments.



Figure 2: Particle-size distribution of soil samples PZH and PZJ.

Soil samples PZH and PZJ were grinded to be used in the sorption and desorption experiments.

The chemical composition of the groundwater located close to the deep soil samples is shown in Table 2. The conductivity of the groundwater close to piezometer H (wPZH) is one order of magnitude higher than the conductivity of the groundwater close to piezometer J (wPZJ) probably due to the marine intrusion. Synthetic waters reproducing the resident groundwater located in Barcelona (Table 2) are planned to be prepared. They will be used as input solution in the percolation column experiments. Each type of water will be injected in the column filled with the corresponding soil sample. The high-conductivity synthetic water

(wPZH) will be injected in columns filled with PZH soil sample and the low-conductivity synthetic water (wPZJ) will be injected in columns filled with PZJ soil sample.

Groundwater label	<u>wPZH</u>	<u>wPZJ</u>	<u>UNITS</u>
Conductivity (25ºC)	1651	723	μS/cm
Alkalinity	366.3	154.3	mg/L
Bicarbonate	446.9	188.3	mg/L
Calcium	163.6	70.1	mg/L
Chloride	215.8	106.1	mg/L
pH a 20⁰C	7.6	7.9	
Magnesium	43.8	15.4	mg/L
Nitrates	14.5	8.0	mg/L
Nitrite	0.1		mg/L
Total Nitrogen (TKN)	4.9	4.9	mg/L
organic and ammoniacal Nitrogen	5.58		mg/L
Potassium	11.01	11.61	mg/L
Sodium	173.6	62.3	mg/L
Sulphates	304.9	74.4	mg/L

 Table 2. Chemical composition of the groundwater close to piezometers PZJ and PZH.

Emergent contaminants will be added to these synthetic waters based on the chemical analysis performed on water samples from the same location. Then, two types of experiments are planned to be performed: batch and percolation column experiments using the soils extracted from PZJ and PZH and synthetic waters based on the chemical composition presented in Table 2.