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Aquatic Global Passive Sampling (AQUA-GAPS) Revisited – First Steps towards a Network of Networks for Organic Contaminants in the Aquatic Environment

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ABSTRACT

Organic contaminants, in particular persistent organic pollutants (POPs), adversely affect water quality and aquatic food webs across the globe. As of now, there is no globally consistent information available on concentrations of dissolved POPs in water bodies. The advance of passive sampling techniques has made it possible to establish a global monitoring program for these compounds in the waters of the world, which we call the Aquatic Global Passive Sampling (AQUA-GAPS) network. A recent expert meeting discussed the background, motivations, and strategic approaches of AQUA-GAPS, and its implementation as a network of networks for monitoring organic contaminants (e.g., POPs and others contaminants of concern). Initially, AQUA-GAPS will demonstrate its operating principle via two proof-of-concept studies focused

on the detection of legacy and emerging POPs in freshwater and coastal marine sites using both polyethylene and silicone passive samplers. AQUA-GAPS is set-up as a decentralized network, which is open to other participants from around the world to participate in deployments and to initiate new studies. In particular, participants are sought to initiate deployments and studies investigating the presence of legacy and emerging POPs in Africa, Central and South America.

■ INTRODUCTION

Recognizing the achievements of the Global Atmospheric Passive Sampling program (GAPS),[1,2] Lohmann and Muir (2010) called for the establishment of Aquatic Global Passive Sampling (AQUA-GAPS), aiming to understand better the geographical distributions and temporal trends of organic contaminants, such as persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), novel flame retardants and other contaminants of emerging concern.[3] AQUA-GAPS has the potential to facilitate the implementation of the Stockholm Convention (SC) on POPs, a global treaty under the United Nations Environmental Programme (UNEP) with the objective to protect human health and the environment from hazardous, long-lasting, bioaccumulative chemicals with long-range transport potential by restricting and ultimately eliminating their production, use, trade, and release.[4] Yet the scope of AQUA-GAPS goes beyond existing POPs by enabling studies into a wide range of organic contaminants.

So far, the SC, through its Global Monitoring Plan, measures POPs in air (active and passive samplers) for capturing their status of emissions and long-range transport, and in human samples (blood, milk) for assessing exposure status. Water monitoring was added to the Global Monitoring Plan for PFOS, which is far more water-soluble than legacy POPs; unlike other POPs, its emission and transport through water and not just air are thought to be significant.[5–7]

Reliance upon passive samplers has already been established via the GAPS program, as well as the Europe/Africa/Asian Monitoring NETworks (MONET), Latin American Passive Atmospheric Sampling (LAPAN), and UNEP/Global Environmental Facility (GEF) projects, all of which utilize passive air sampling devices at monitoring sites on all continents, mostly in remote regions, demonstrating the potential for global coverage.[7,8] While data from GAPS does address the atmospheric compartment and potentially plants and soils exchanging with air, it does not readily address prevailing concentrations or trends in aquatic environments. The aquatic environment represents a key compartment for many POPs, most notably for the HCH isomers and endosulfan [9] , and dissolved concentrations can be used to estimate human and wildlife exposure using bioaccumulation factors and food chain models.[10–12]

Passive samplers offer key benefits for global monitoring of aqueous contaminants, because of their high enrichment of their target analytes, and the ability to measure time-weighted average concentrations.[13–15] Most importantly, a key benefit consists of being able to expose the same sampler in all waters of the world, which cannot be achieved with any biological or other abiotic matrix. Passive samplers are also more cost-effective and relatively easier to handle for shipment and deployment than active sampling of large volumes of water.

The atmospheric GAPS program is based on monitoring sites at a defined height above ground that are relatively easy to access. The logistic requirements for AQUA-GAPS sites are inherently more challenging for on- and off-shore deployments and retrieval, requiring moorings and boat time, among other practical issues. The biggest hurdle for establishing a realistic AQUA-GAPS program is perhaps whether enough willing and capable participants from around the world can be secured to agree on and perform the logistics of field and laboratory work. GAPS samplers are often deployed at already established and protected atmospheric monitoring sites that are part of the World Meteorological Organization (WMO) network.[16] In parallel, AQUA-GAPS intends to deploy passive samplers at selected remote/background sites in water bodies around the globe. Similar to the GAPS program, though, AQUA-GAPS will also monitor selected urban/industrially impacted sites in an attempt to examine the impacts of anthropogenic activities on aquatic environments at a global scale.[17]

A meeting of 15 passive sampling and monitoring experts from 10 countries covering 5 continents was organized at Jinan University, Guangzhou, China, on 21–22 January, 2016, aiming to make progress towards the establishment of AQUA-GAPS. In particular, the group was tasked with addressing whether and how it will be feasible to make the assessment of global POP distributions through an analysis of global passive sampling devices in waters. The group then outlined the key steps for implementing them during the meeting. The aim of this feature article is to detail the framework, approach, and expectation of AQUA-GAPS, and solicit additional participation to cover extended sampling areas and initiate new global studies.

■ THE MOTIVATIONS BEHIND AQUA-GAPS

To launch AQUA-GAPS successfully, it was the consensus of the workshop participants that prior experiences of GAPS must be learned and assimilated. The GAPS program has demonstrated that a global monitoring network using passive samplers is feasible and can be successfully implemented. GAPS was successful in establishing spatial distributions of targeted chemicals, while the identification of temporal trends requires longer time and continuing resource commitment. GAPS has been particularly impressive by making use of their samples for a wide range of contaminants, such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polybrominated diphenylethers (PBDEs), neutral and ionic perfluoroalkyl substances (PFASs).[2,18,19] GAPS has also demonstrated flexibility with their sampling matrix. Initially, GAPS relied on the use of polyurethane foam (PUF) disks, which were later modified to include sampling of compounds with higher volatility in accordance with the increase of list of POPs under the SC.[20,21] The key lesson here is that flexibility in the type of passive samplers may be required to respond to changing regulatory and scientific needs and interests (new compounds of emerging concern, novel samplers, etc.).

The success of GAPS and its relevance to the SC are a prime motivating factor for establishing AQUA-GAPS. Although the current priority sampling matrices under the SC are limited to air and human samples (and water in the case of PFOS), the workshop participants felt that AQUA-GAPS would have significant added value in yielding highly comparable concentration data that allow for better assessing and understanding of the role of water in the global fate of POPs, and in human and wildlife exposure to these chemicals. Both the data collection and the enhanced understanding of global distributions and trends in the aquatic environment would be beneficial for the SC, its Regional Organizational Groups and potentially to other international conventions such as the International Marine Organization's London Convention on prevention of marine pollution by dumping of wastes[22], and Convention on the Control of Harmful Anti-fouling Systems on Ships.[23] The data would also benefit regional and national legislative frameworks, such as the EU Water Framework Directive[24] and Marine Strategy Framework Directive[25], and the 18 Regional Sea Programs under UNEP[26], the United States Toxic Substances Control Act (recently updated and renamed the Frank R. Lautenberg Chemical Safety for the 21st Century Act) [27], the EU REACH legislation[28], and environmental protection and clean water legislation in many other countries.

The workshop proposed to have AQUA-GAPS focus on legacy and emerging POPs, as well as on other compounds of emerging concern both hydrophilic (e.g., pharmaceuticals and personal care products) and hydrophobic (novel flame retardants). Currently, the SC's main interest would be the development and deployment of passive samplers for perfluorinated compounds, such as PFOS and PFOA (which is currently under review for inclusion in the SC)[29] in waters around the globe. The SC has developed guidance for sample collection and determination of baseline levels of PFOS in water, caused by global dispersion/diffusion.[30] Yet the availability of high quality, consistent global concentration maps and trends on POPs and other contaminants will certainly support the SC and its regional programs.

■ A NETWORK OF NETWORKS

The GAPS program has been established around one central laboratory at Environment Canada, from which samplers are prepared, shipped, returned to, analyzed, and interpreted. This model is unlikely to be repeatable for AQUA-GAPS[1]. Instead, we propose to establish a '**network of networks**' open to anybody to participate in, but clustered around a central laboratory for sampler preparation and core analysis, the Research Center for Toxic Compounds in the Environment (RECETOX, Masaryk University, Czech Republic). Initially, the network consists of a group of scientists with experience in working with passive samplers. The proposed *modus operandi* of the AQUA-GAPS network consists of in-kind contributions of participating scientists to deploy passive samplers to the best of their abilities, and share ancillary data with respect to their sites. In return, the expectation is one of data sharing by the leading team and inclusion in the data discussion and interpretation. Possible authorship will depend on contributions to the interpretation and discussion of results. We foresee AQUA-GAPS to be a platform in which scientists offer mutual help in deploying samplers at specified locations (e.g., wastewater treatment plants, rivers, freshwater lakes, coastal seas, and oceans) and site characterization (e.g., urban, industrial, and remote). Examples of potential aquatic networks include:

An oceans network. This is logistically the most challenging, and would often require deployment time of several months up to 1 year, which is typical for open ocean mooring turnaround time.[31,32] In view of low concentrations, samplers would need to be designed to maximize the uptake of the target compounds to overcome detection limits for as many compounds as possible. Most likely target compounds are legacy POPs, non-polar current use pesticides, organophosphorus flame retardants, perfluorinated compounds, and other chemicals of interest that accumulate in samplers for hydrophobic POPs, such as hydrocarbons or natural halogenated compounds. The benefits of working with the oceanographic community's set of moorings is the general availability of ship-time and access to ancillary data.

A coastal/estuarine network. Coastal and estuarine sites are easier to reach for deployments, and often coincide with major fishing grounds, which makes them relevant for human exposure and links to biomonitoring data. Deployment time can be shorter, in view of greater concentrations and challenges linked to biofouling of samplers during deployments in productive water bodies.

A lakes network. Lakes and reservoirs are of high relevancy for human and ecosystem exposure as they are regularly used for aquaculture and irrigation, and often serve as a source of drinking water. Remote lakes (e.g., Experimental Lakes Area in Canada) can serve to quantify background concentrations associated with minimal anthropogenic impacts.[30] For both estuarine and freshwater, sampler deployment at near-shore sites is straightforward, but carries a risk of sampler loss through theft, vandalism and loss from accidental ship strikes and fishing efforts.

A network of source waters (waste water treatment plant effluents and rivers). This network could be used to identify the compounds being introduced into lakes and oceans, before they become of concern. This network could act as an early warning system to identify chemicals of concern through their release to the aquatic environment from human activity and global spread. As concentrations of contaminants in such a network are likely to be much greater than in the other networks mentioned, this network would lend itself to target less persistent compounds, including breakdown products. Identification of major sources and establishment of reliable inventories are indispensable for the efficient and effective management of chemicals on the national, regional and global scale. The various AQUA-GAPS networks should each aim to collaborate and communicate with relevant stakeholders in local, national, or regional levels.

■ TECHNICAL FOUNDATION FOR AQUA-GAPS

Passive sampling in the water gives a direct measure of a chemicals' activity (or fugacity) in the water, as only freely dissolved contaminants diffuse into the passive sampler material.[33] Thus the freely dissolved concentration derived for passive sampler accumulated pollutants can be used to assess the gradient of chemical activities between different media (air, water, sediment, and biota), and these freely dissolved contaminant concentrations and chemical activities are more useful to assess net fluxes among environmental compartments and bioaccumulation in organisms. [34–38] Passive sampling derived dissolved pollutant concentrations are therefore fundamentally different from total concentrations reported for e.g., sediment or active water samples.

The novelty that AQUA-GAPS introduces is a coordinated effort at pollutant sampling with a chosen passive sampler for worldwide deployments towards the generation of globally comparative data sets. Passive sampling with a well-characterized polymer/sampler can help achieve a level of standardization on a global scale that cannot really be obtained with other environmental matrices (e.g. biota, sediments, etc.) due to their variable properties. Nowadays, silicone rubber and polyethylene are the two most widely used polymers for passive sampling of hydrophobic organic contaminants in water.[39] The increased use of these polymers is partly due to the availability of calibration data, i.e., polymer diffusion coefficients and polymer-water partition coefficients for a number of non-ionised hydrophobic chemicals [33,40–42] including chemicals of emerging concern.[43] These absorption-based passive samplers offer the opportunity to use performance reference compounds (PRCs) to assess contaminant exchange kinetics between water and the polymer in situ for every deployment location and exposure period.[44] In addition, these polymers facilitate the comparison of contaminant levels in different environmental compartments (i.e. air, biota, sediment or water). The critical review by Booij et al. demonstrated that absorption-based passive sampling is today the best available tool for chemical monitoring of non-ionised hydrophobic chemicals in the aquatic environment.[45] While a lack of robust quality assurance was identified as a weakness of passive sampling in water, recent results from the QUASIMEME Proficiency Testing schemes conducted using silicone rubber were very encouraging.[39] These results show that the analysis of passive samplers within the AQUA-GAPS network may not ultimately require analysis of all samplers by a single laboratory, so long as proficiency testing schemes are organized regularly to evaluate the performance of participating laboratories. At least initially, though, AQUA-GAPS studies will be organized around one central laboratory, RECETOX, for the above mentioned legacy and emerging pollutants from using SR and PE passive samplers prepared and analyzed there.

■ STRATEGIES FOR FIELD SAMPLING AND DATA ASSIMILATION

The unique feature of AQUA-GAPS is that studies can be initiated by anybody with an interest in answering a global question linked to contaminants in water. The lead team initiating an AQUA-GAPS sampling campaign needs to have sufficient resources to organize sampler preparation, distribution/retrieval, analysis, and interpretation. AQUA-GAPS is intended to be flexible on which sampler to use, how to deploy it, for how long, and where. This will all be decided by the leading team, who will ask others to participate in-kind by deploying in their water body (Figure 1). It may be cost efficient to deploy different types of samplers targeting a wide range of compounds simultaneously (e.g., nonpolar, hydrophilic neutral, positively and negatively charged, etc.).[46] Passive samplers are relatively inexpensive, and have the potential to be archived. [47]

Similar to the GAPS deployments, AQUA-GAPS' challenge will be on how to identify sites in aquatic environments suitable for evaluating spatial and temporal changes in contaminant levels, that would therefore help assess the effectiveness of the control measures implemented under the SC and/or regional efforts. AQUA-GAPS networks will benefit greatly by selecting sites overlapping with other continuous sampling efforts and programs, such as existing GAPS stations. Many GAPS samplers were strategically placed at WMO sites, such that GAPS had site-specific meteorological data available. It will be important to work with sites and groups that are capable of conducting repeatable, long-term deployments.

Beyond GAPS sites, other examples for AQUA-GAPS include lakes, ocean and coastal sea monitoring initiatives using regularly serviced buoys and moorings, which can provide ancillary data (temperature profiles, salinity, and current data), and potentially ships of opportunity. There are also on-going contaminant sampling initiatives or networks (Canada's National Water Quality Monitoring Program [48], The Great Barrier Reef Marine Monitoring Program [49], etc.) which can contribute to AQUA-GAPS for mutual benefits. AQUA-GAPS will of course be open to other programs as it evolves.

Across the globe various types of passive samplers have been successfully used for the detection of a range of organic contaminants in waters, resulting in a global ISO standard protocol.[50] Semi-Permeable Membrane Devices (SPMDs) were arguably the first passive samplers that were used on a wide geographical scale in water sampling.[51] Over time, other sampler types, often single-phase polymers, have become more commonplace. Notable examples include the use of silicone rubber (SR) in an OSPAR-lead initiative across Europe and Australia [52], The Great Barrier Reef Marine Monitoring Sampling Campaign [53], and several years of polyethylene (PE) deployments across the Great Lakes [54,55] and in the Canadian Arctic.[56]

■ PROOF OF CONCEPT STUDIES: FRESHWATER AND COASTAL AQUA-GAPS

Initially, it will be necessary to establish a proof of concept for AQUA-GAPS to show that this network of networks can actually achieve meaningful results and global coverage. At the proof of concept stage, we aim to demonstrate that it is feasible to ship and deploy passive samplers to participating volunteers around the globe, have them deployed, returned for analysis, and yield meaningful results. At this stage, two proof-of-concept studies are being planned and performed

(Figure 1). In both cases, both polyethylene (PE) and silicone rubber (SR) samplers will be co-deployed, such that spare samplers are available for archiving. While actual sampler designs differ between the proof-of-concept studies (Figure 2), both are designed to be easily deployed, provide basic shelter and house several PE and SR sheets simultaneously. Initially, the analytical target compounds include polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and various hydrophobic novel flame retardants (NFRs). The first proof-of-concept study will focus on legacy and emerging POPs in lakes (Figure 3); the second study will focus on global passive sampling deployments at coastal sites. The two proof-of-concept studies illustrate the flexibility within the AQUA-GAPS network. The first freshwater study shares the responsibilities of logistics, analysis and interpretation among three research groups, while the coastal study will be performed by two academic/research laboratories (Figure 1).

■ BEYOND ROUTINE MONITORING

Beyond its focus on sampling of contaminants in water, AQUA-GAPS could be well positioned to address additional research questions, such as air–water exchange and/or sediment porewater–overlying water gradients by including additional samplers in adjacent media. As mentioned above, expected or measured equilibrium polymer concentrations are directly proportional to the activity of the chemical in the medium being sampled, and can help compare contaminant levels and gradients in/between various environmental media.[57] This holds true whether equilibrium between the contaminant concentration in the medium being sampled and the polymer is reached (e.g. during sediment or biota exposures) or not (e.g. when sampling air or water).[58,59] Having passive samplers measure freely dissolved concentrations in close proximity to biomonitoring locations can help understand bioaccumulation potential and chemical concentration gradients. Passive samplers can also be used for non-target screening to detect the presence of other chemicals, derived from industrial, natural or transformation products. Linking to regional efforts, particularly biomonitoring programs (e.g., Mussel Watch[60]), AMAP[61] or GAPS[1] seems particularly useful to enable a comparison of POP concentrations across media. Results from passive sampling will represent time-weighted-average concentrations in water and thus support model development and validation, while biological monitoring has a longer history including archived samples and is often better suited for assessing human exposure (particularly in the case of edible fishes, shellfish, and other aquatic biota).

GAPS has derived part of its strength by having a centralized laboratory (i.e., Environment Canada) initiating deployments and analyzing all samples within a particular study, in order to enhance data comparability. As noted, AQUA-GAPS will operate slightly differently, though RECETOX will perform the sampler preparation and analysis for the routine suite of hydrophobic compounds (PAHs, PCBs, OCPs, PBDEs and NFRs). Yet AQUA-GAPS will have different research groups leading deployments, and potentially extra analyses for a specific project. The leading group will provide passive samplers that are suitable for the specific compounds of interest to all participating scientists; the samplers will be returned to the same lead group and analyzed in a single laboratory. Additional samplers can be shared with the local deploying groups, as a secondary aim of enhancing QA/QC, to enable cross-validation of results, and the assessment of inter-laboratory variability. This can also lead to capacity-building (see below). An AQUA-GAPS deployment can be shared/initiated by 2 or more groups, such that different samplers can be exposed during the same deployment. The leading group needs not perform all tasks themselves; it could finance another team to produce samplers and deployment cages, organize the distribution, perform the analysis, and calculate the dissolved concentrations, etc.

For AQUA-GAPS to become successful and global, it should lead to global capacity building linked to passive sampling. There are several regions where little to no information exists on organic contaminants in water, in particular from Africa, South Asia, Central and South America. Additionally, non-traditional deployment opportunities can also be leveraged, including ferrybox samplers, towing samplers and ships of opportunity (expedition vessels; regular cargo or ferry routes) to target remote locations.[62,63] The network will become more useful in addressing scientific questions only if more support of AQUA-GAPS deployments is secured. It would be ideal if the Stockholm Convention could support the capacity building with their own efforts, via the Global Environment Facility, or other funding systems. For the GEF passive sampling of PFOS and PFOA could be of interest, as these are compounds for which water is a matrix of concern.

■ GOING FORWARD

The organization of sampler deployments, and the deployments themselves are among the biggest cost for AQUA-GAPS. Hence the more samplers can be deployed at the same time, the better. Spare samplers should be archived to enable retrospective analysis. Expansion to include passive samplers designed for other contaminants (e.g., polar and nonpolar chemicals of emerging concern) would enhance the utility of the program. Samplers, and/or extracts, could be analyzed for possible temporal trends later. Spare samplers will be stored in a specimen bank operated by RECETOX. To enable quality control over time, specific samplers for QA/QC purposes will also be made available. Scientists interested in new studies, retrospective analysis of extracts or samplers can request this by contacting the AQUA-GAPS co-chairs (email: aqua-gaps@passivesampling.net).

A welcome side-effect of AQUA-GAPS is the opportunity to increase awareness of the benefits and uncertainties of passive sampling of aqueous organic contaminants on the global scale. This might help regulatory agencies, academics, and industries still unfamiliar or hesitant to use passive sampling techniques for their own monitoring programs and other purposes. The roster of AQUA-GAPS thus also becomes a network of experts who can serve as points of contact within their regions. News and results from AQUA-GAPS will be shared via its own website (www.aqua-gaps.passivesampling.net), publications, and presentations.

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FIGURE CAPTIONS

Figure 1. **General approach of an AQUA-GAPS campaign for dissolved organic pollutants, with the proof-of-concept campaigns for a freshwater and a coastal water deployments.** (OMoE-CC – Ontario Ministry of the Environment and Climate Change; RECETOX – Research Center for Toxic Compounds in the Environment, Masaryk University; Jinan U – Jinan University; PCBs – polychlorinated biphenyls; OCPs – organochlorine pesticides; PAHs – polycyclic aromatic hydrocarbons; PBDEs – polybrominated diphenylethers; NFRs – novel flame retardants; PE – polyethylene; SR – silicone rubber).

Figure 2. Passive sampling holders to be deployed during AQUA-GAPS proof-of-concept studies in freshwater (left) and coastal water (right) equipped with both polyethylene and silicone rubber samplers.

Figure 3. Projected sites for freshwater and coastal water AQUA-GAPS proof-of-concept deployments.

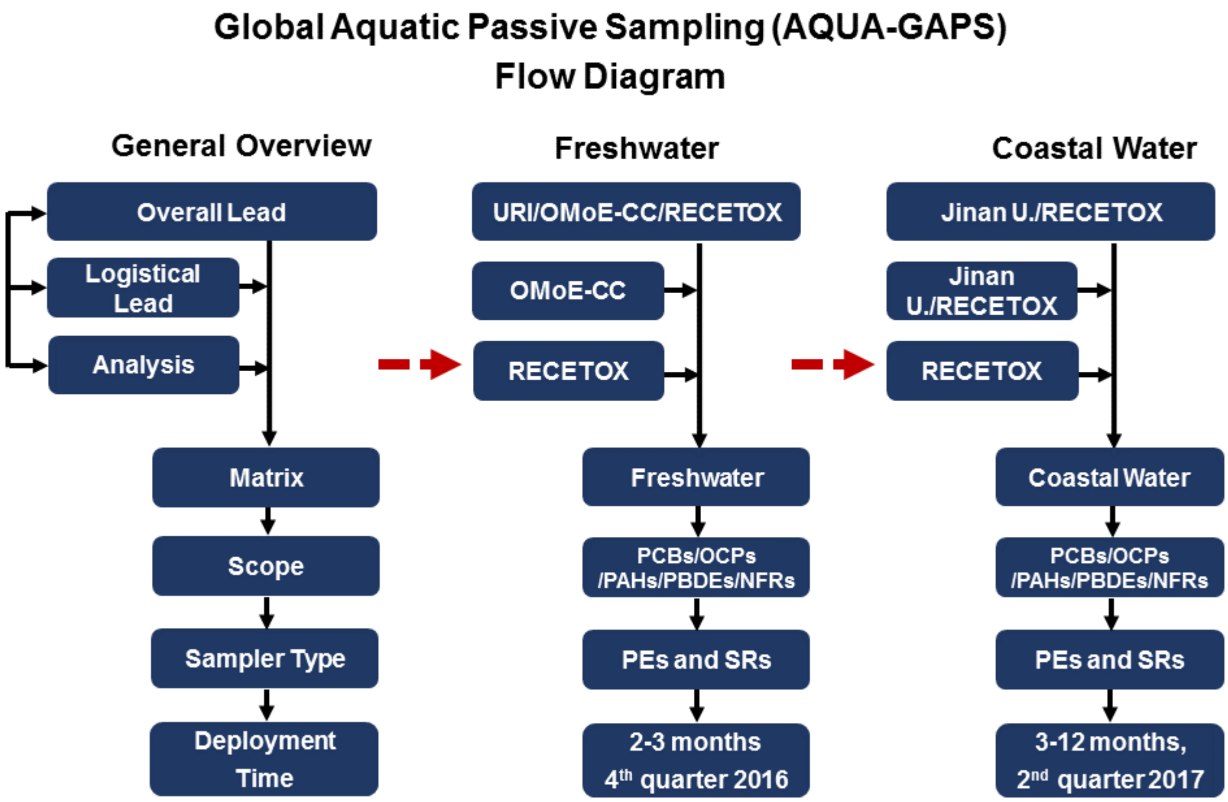
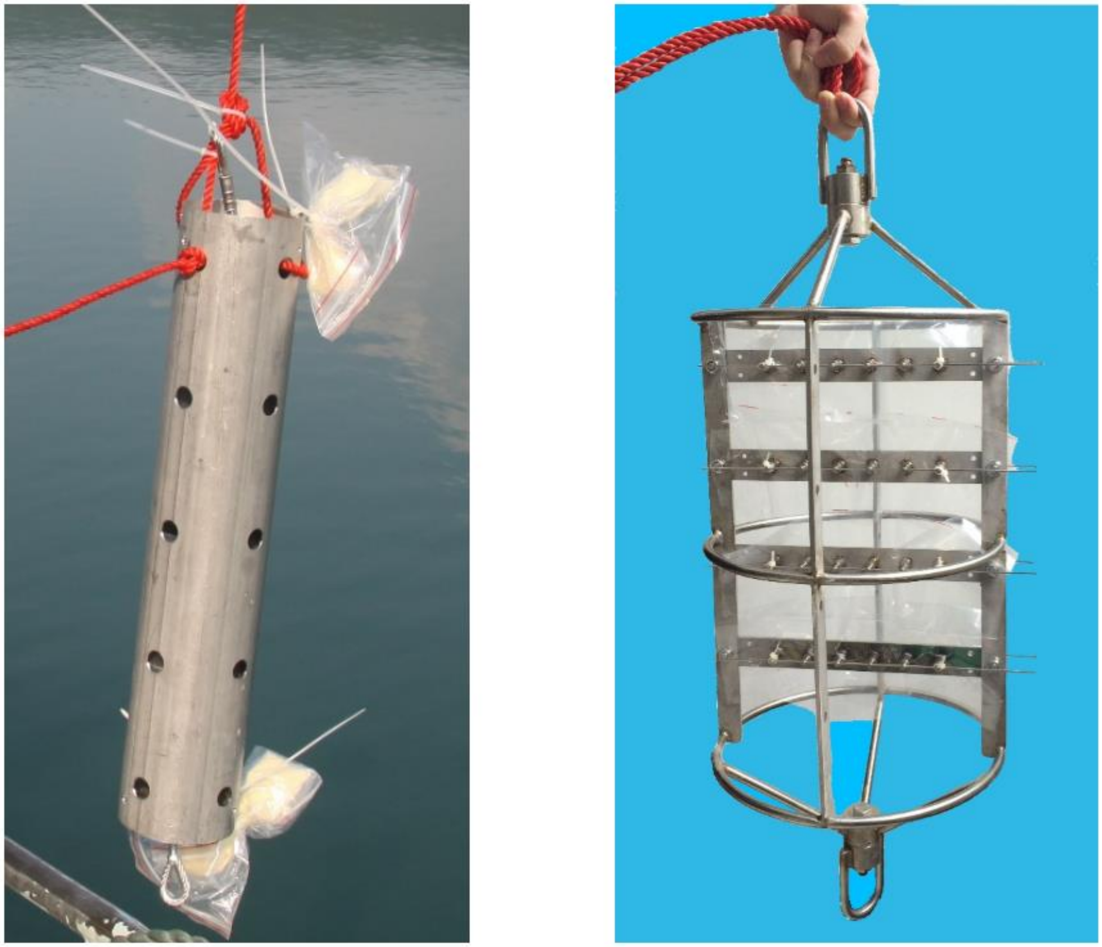


Figure 1. General approach of an AQUA-GAPS campaign for dissolved organic pollutants, followed by details about the first two proof-of-concept campaigns for a freshwater and a coastal water deployments. (OMoE-CC – Ontario Ministry of the Environment and Climate Change; RECETOX – Research Center for Toxic Compounds in the Environment, Masaryk University; Jinan U – Jinan University; PCBs – polychlorinated biphenyls; OCPs – organochlorine pesticides; PAHs – polycyclic aromatic hydrocarbons; PBDEs – polybrominated diphenylethers; NFRs – novel flame retardants; PE – polyethylene; SR – silicone rubber).



Freshwater Passive Sampler   Coastal Water Passive Sampler

Figure 2. **Passive sampling holders to be deployed during AQUA-GAPS proof-of-concept studies in freshwater (left) and coastal water (right) equipped with both polyethylene and silicone rubber samplers.**

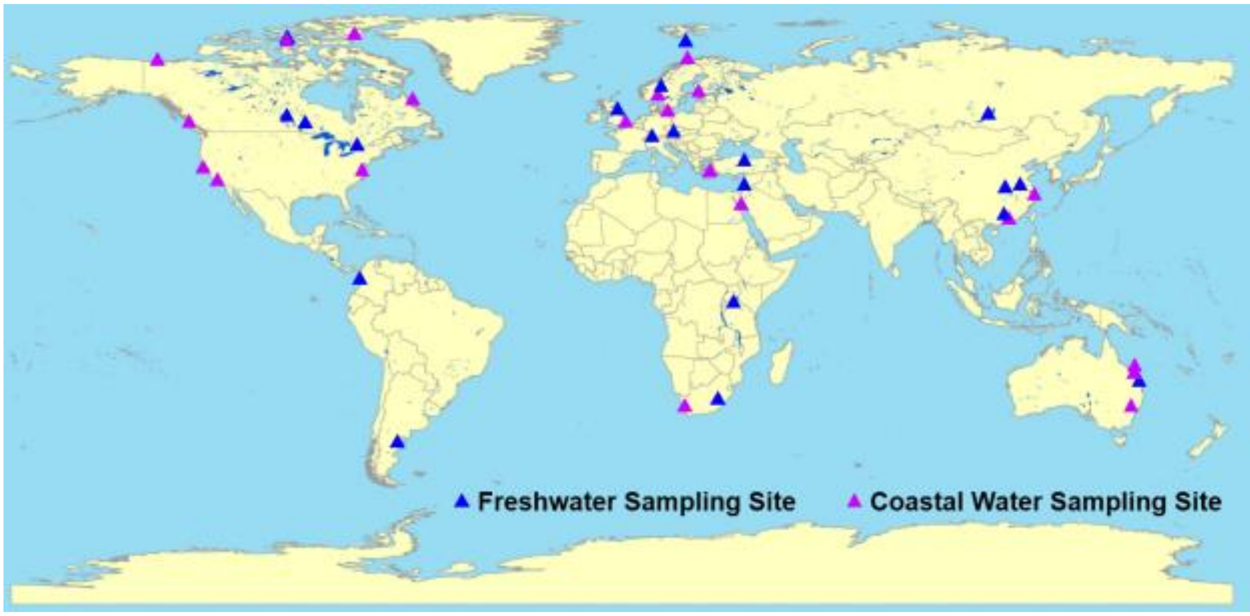


Figure 3. Projected sites for a freshwater and coastal water AQUA-GAPS proof-of-concept deployments. The map was created using ArcGIS 10.2.

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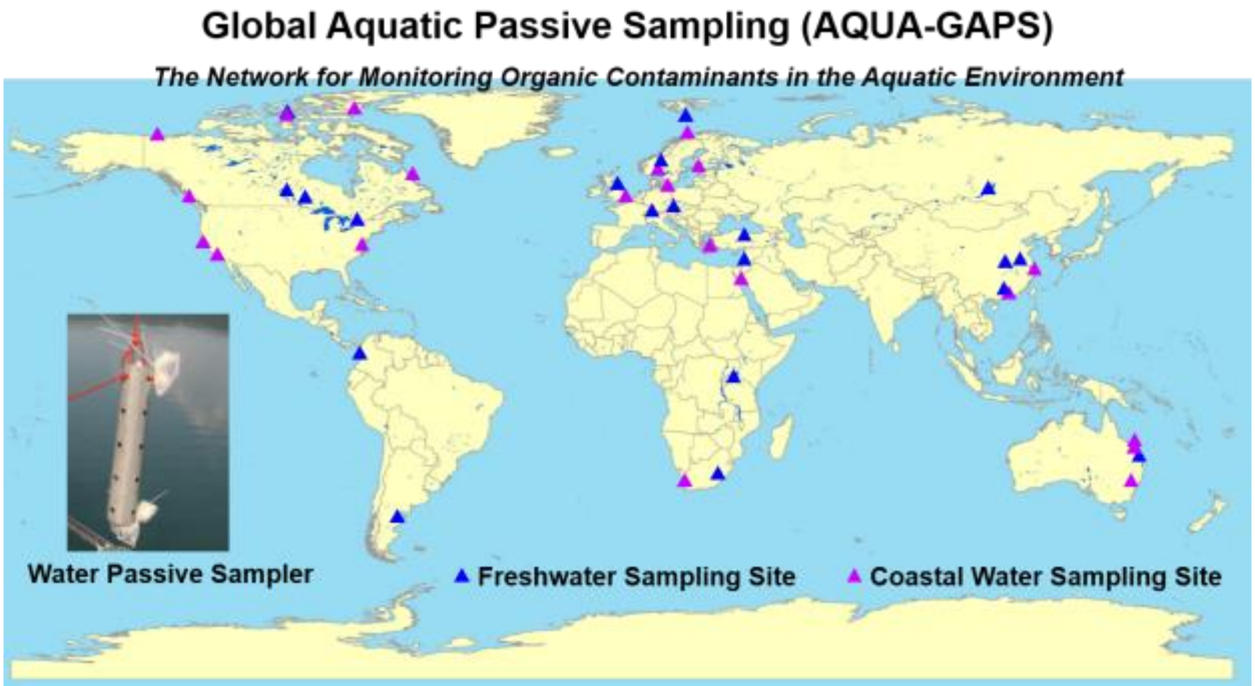
Global Aquatic Passive Sampling (AQUA-GAPS)
The Network for Monitoring Organic Contaminants in the Aquatic Environment
Water Passive Sampler
Freshwater Sampling Site
Coastal Water Sampling Site