TNA PROJECT REPORT

1. Project Information

Proposal reference number	JN_CALL_2_10
Project Acronym (ID)	MOCo SEa Pass
Title of the project	Monitoring of Organic Contaminant in the water of the Southern Europe with Passive Sampling
Host Research Infrastructure	Port Operational Marine Observing System - st. Balchik (POMOS) Meteoceanographic site S1-GB (S1-GB)
Starting date - End date	7/12/2017 – 29/11/2018
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2. Project objectives

Organic contaminants, in particular persistent organic pollutants (POPs), adversely affect water quality and aquatic food webs across the globe. To date, 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. ***The main objective/ goal of the proposed project was the use of state of the art passive sampling devices for monitoring and study the process (air sea exchange) govern the fate of POPs in marine boundary layer***. This technique will contribute to reach the aims of AQUA-GAPS including the investigation of the global distribution of POPs without discrepancies caused by individual or local approaches. Through the current project, this objective was implemented in the water of Southern Europe including the following:

1. Evaluation of the present state of POPs pollution in the water of the Southern European coastal areas

The activity described in this report has received funding
from European Commission's H2020 Framework Programme
under JERICO-NEXT project, grant agreement No. 654410.

2. Investigation of different sites with different sources of anthropogenic inputs and different environmental characteristics (e.g. depth, salinity, currents etc).
3. Study of the air-sea exchange of organic contaminants.

3. Main achievements and difficulties encountered

Through the current project, selected urban/industrially impacted sites were monitored in an attempt to examine the impacts of anthropogenic activities on aquatic environments and to combine these results with AQUA-GAPS for a global scale estimation. The present project was aimed at developing new monitoring technologies to detect POPs in marine water and to evaluate the air-sea exchange of organic contaminants. Thus, it was achieved, for the first time, the simultaneous deployment of two passive samplers (air- and sea-samplers) resulting in (1) the evaluation of the present state of POPs pollution in the water and in the air of the Southern European coast and (2) the simultaneous monitoring of air-sea exchange of organic contaminants.

The selected sites for deployment were in the Western part of Black Sea (43.4042°N, 28.1653°E) and in the Northern Adriatic Sea (44.7384°N, 12.4526°E). Deployment sites included the Port Operational Marine Observing System (POMOS) (st.Balchik) in Black Sea and the Meteoceanographic site (S1-GB) in Mediterranean Sea. No technical difficulties were encountered. Both infrastructures' personnel was very helpful and cooperative.

4. Dissemination of the results

As soon as samples will be analysed and data will be interpreted, the results from the work, which was carried out under the TNA in JERICO NEXT, will be disseminated through scientific conferences and scientific articles in peer-reviewed journals.

Meta-data of ratios/ comparisons of the organic contaminants will be given immediately after analysis to JERICO NEXT. Most of the original data will be closed for one year for usage by our team. Then the original data will be available through publications in peer-reviewed journals. If there will be no publications after the first year, then the original data will be provided to JERICO NEXT for on-line publication.

5. Technical and Scientific preliminary Outcomes

Sites Description and Selection

Considering the advantages of passive sampling techniques, two observing systems have been selected for the monitoring of organic contaminants in the Southern European coastal area (Figure 1). The Mediterranean Sea and Black Sea are unique marine environments subject to important anthropogenic pressures due to atmospheric and riverine inputs of organic contaminants. It is therefore of paramount importance 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.

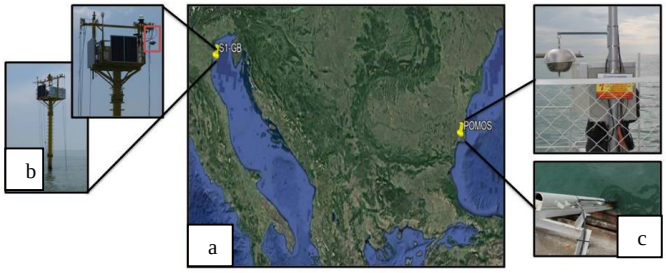

Figure 1. (a) The different observing systems selected for the monitoring of POPs in the Southern European coastal area; **(b)** Meteoceanographic site (S1-GB) in the Mediterranean Sea; and **(c)** Deployment aquatic and air passive samplers in the Western part of the Black Sea.

Within the framework of AQUAGAPs and JERICOnext TNA programs, passive samplers were deployed at 1.5m below the sea surface at the Port Operational Marine Observing System (POMOS) (st.Balchik) in the Black Sea and at the Meteoceanographic site (S1-GB) in the Mediterranean Sea (Figure 1b,c). Those two observing systems are of great interest for the detection of organic pollutants as they receive chemical contaminants from a variety of sources. The S1-GB is located offshore the Po river delta, in a key monitoring point for studying the interactions between the Northern Adriatic and the Po River. The POMOS is near the major Bulgarian ports, channels and bays, thus, the combination of the industrialised nature of the area surrounding the ports, the extent of marine traffic and population density.

Sampler Deployment and Retrieval

The passive sampler (PS) holders were attached to the sampler frame (Figure 2a). Twelve silicone rubber (SR) and twelve low density polyethylene (LDPE) sheets were secured to each holder. SR and LDPE were deployed in parallel (Figure 2b). At the same time, passive air sampler (PAS) were deployed to the observing systems using polyurethane foam (PUF) disks (Figure 2c). The preparation of the sheets and PUF was carried out at the Research Centre for Toxic Compounds in the Environment (RECETOX, Masaryk University, Czech Republic).

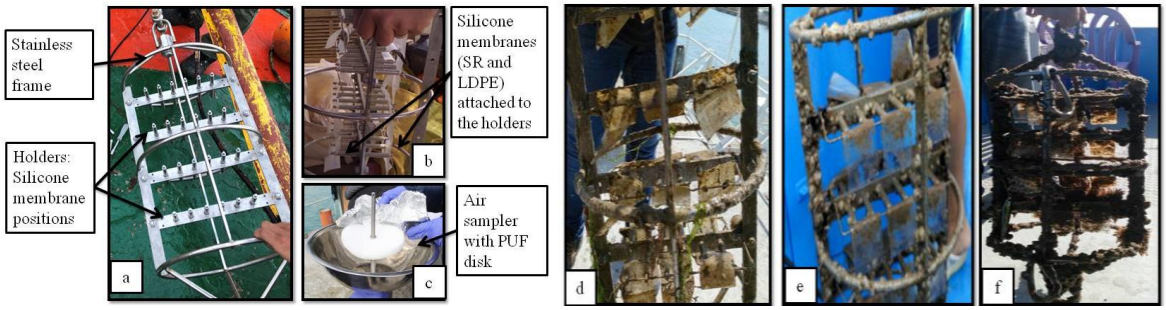

Figure 2. Passive sampling device assembly showing **(a)** the skeletal structure consisting of the stainless steel frame and holders; **(b)** the attached silicone rubber (SR) and LDPE membranes; **(c)** the air sampler with the PUF disk; **(d)** The mesh covered passive sampling devices recovered from POMOS; and **(e-f)** S1-GB experienced different degrees of biofouling.

The steel devices together with SR and LDPE sheets were deployed once at POMOS (9th March, 2018) and twice at S1-GB (17th March, 2018 and 19th July 2018). At the same deployment period, PAS were deployed at each site for the simultaneous monitoring of air-sea exchange of organic contaminants. At the end of the exposure period (Table 1), both samplers, PAS and aquatic PS, were retrieved and the sheets and PUF disks were kept in the freezer until shipment to the central laboratory, RECETOX, for analysis.

Table 1: Samplings of air and aquatic passive samplers at the POMOS and S1-GB.

Country		Installation	Start time - End time	Sampling time
Italy	Remote access 1	S1-GB	17/5/2018-19/7/2018	2 months and 2 days
	Remote access 2	S1-GB	19/7/2018-25/10/2018	3 months and 6 days
Bulgaria	Remote access 1	POMOS	09/3/2018-14/5/2018	2 months and 6 days

All analyses will be performed in the same lab at the RECETOX using identical methods. PUFs and SRs will be extracted with DCM and methanol, respectively, in an automatic extractorF2d. Prior to extraction, SRs will be brushed to remove biofouling from the surface and surrogate recovery standards will be added on SRs and on PAS PUFs. Volume will be reduced and extracts will be split into two portions, for PAH analysis (10 %) and analysis of PCBs, OCPs and PBDEs (90 %) (Lammel et al., 2015). Samples will be analysed using a GC-MS (Gas Chromatograph coupled with a Mass Spectrometer) Agilent 7890 coupled to Agilent 7000B. Air–sea exchange will be studied by determining the vertical concentration gradients (Tsapakis eta l., 2006; Lammel et al. 2016). Surface seawater temperature (SST) will be retrieved from satellite data using AVHRR (Advanced Very High Resolution Radiometer).

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