Workshop PNRA - 5-6 dicembre 2023

Una visione del futuro

Verso una programmazione pluriennale del PNRA

Contaminanti emergenti in Antartide: l'impatto delle basi scientifiche

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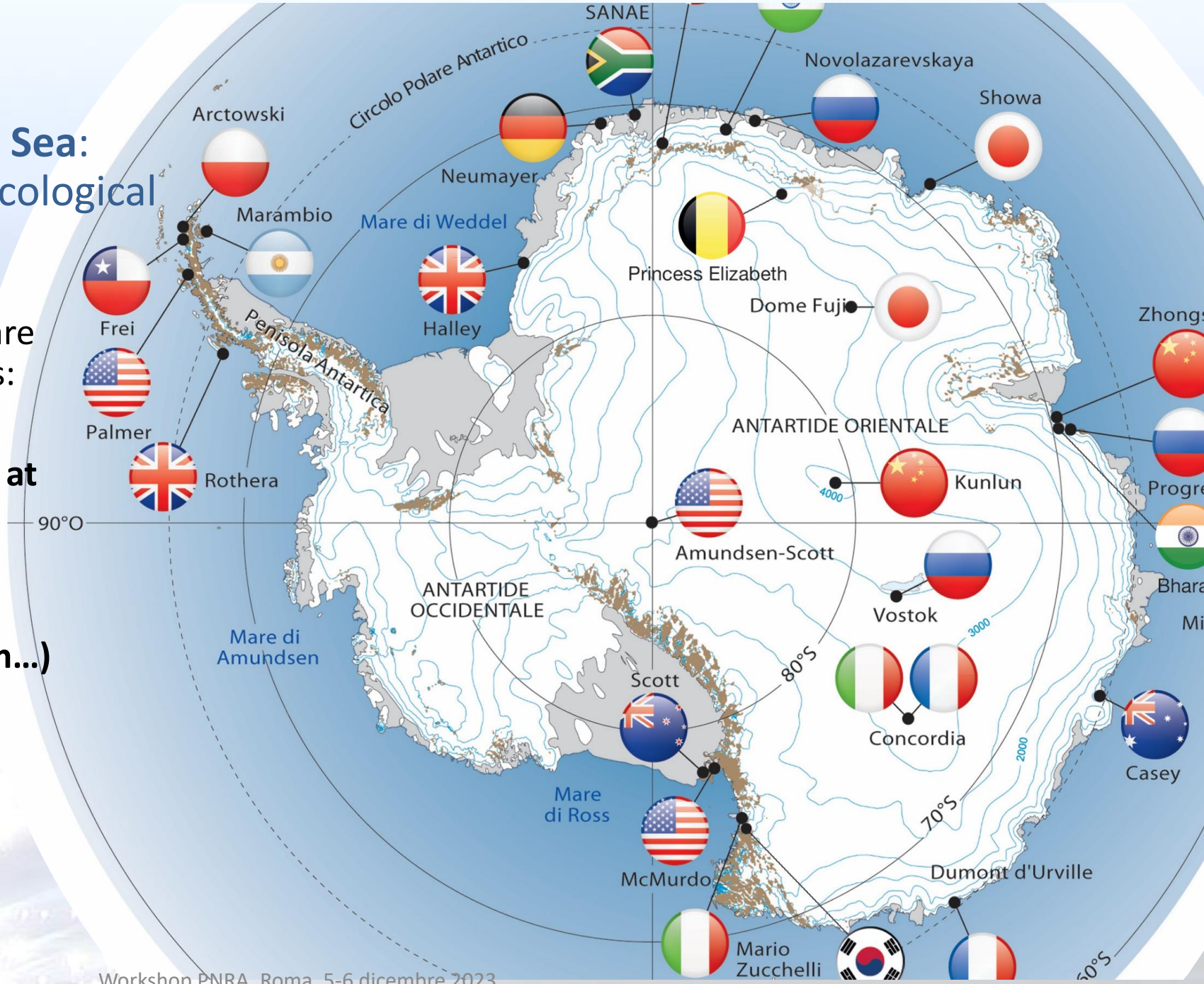
Project MATISSE

eMerging contAminanTs In roSs Sea: occurrence, sources and ecotoxicological risks *(PNRA18_00216 - B2)*

The research objectives of MATISSE are associated to the following three lines:

- **Providing a picture of the present levels of emerging contamination at BTN**
- **Identifying the contamination sources (wastewater treatment plants, research activities, tourism…)**
- **Evaluating the ecological and toxicological risk**




MarioZucchelliStation
74° 41' S - 164° 07' E
PROGRAMMA NAZIONALE DI RICERCHE IN ANTARTIDE
ITALIANTARTIDE

EMERGING CONTAMINANTS

extremely low concentrations, from µg L^{-1} to sub-ng L^{-1}

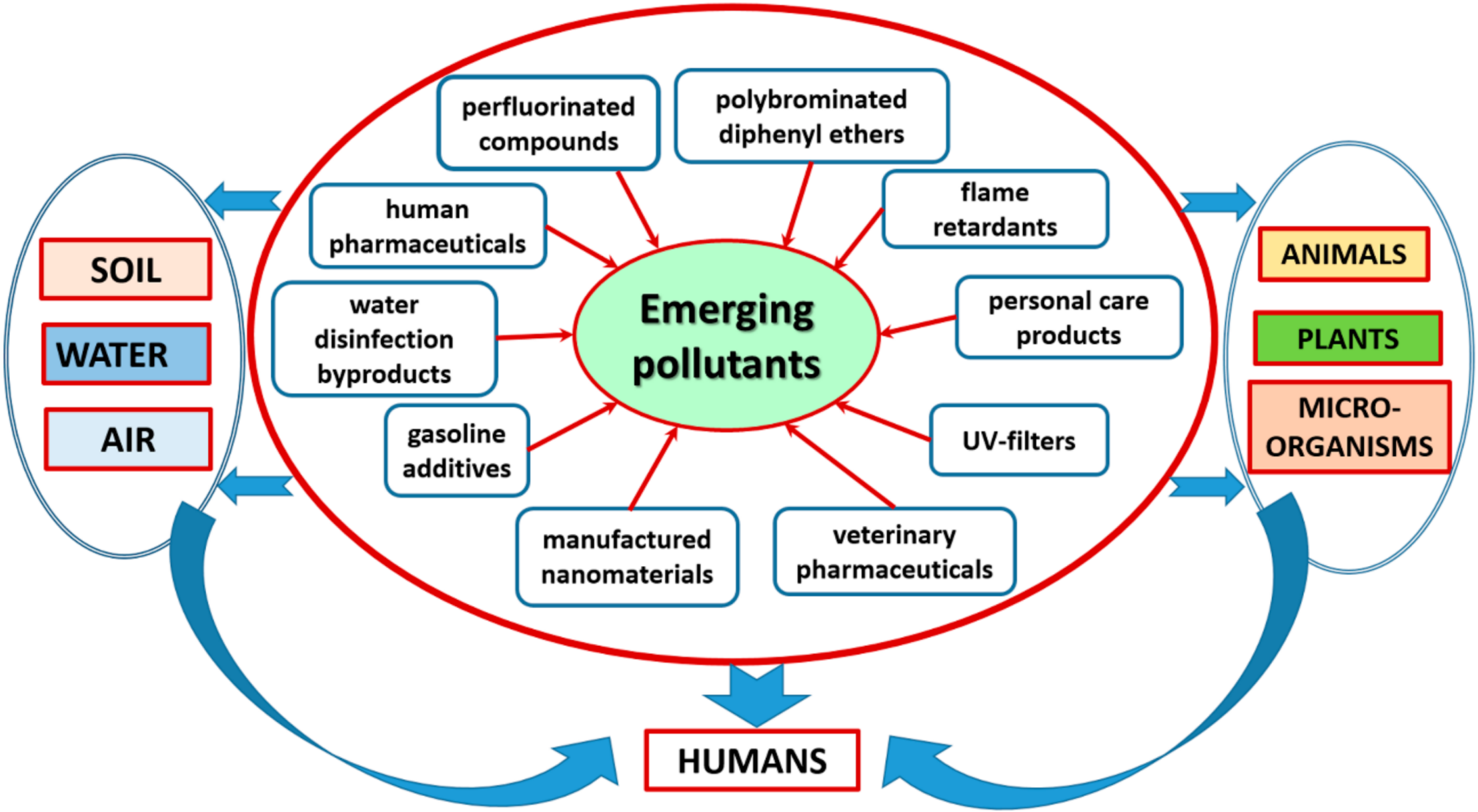
newly identified or previously unrecognized contaminants

less persistent but continuously discharged (semi-persistent)

mainly synthetic origin

potential water pollutants, even if largely unregulated

known or suspected negative ecological and/or human health effects



Vasilachi et al., Water **2021**, 13, 181. "Occurrence and Fate of Emerging Pollutants in Water Environment and Options for Their Removal"

Danovaro et al., **Sunscreens Cause Coral Bleaching by Promoting Viral Infections**, Environmental Health Perspectives, 116 (2008) 441-447

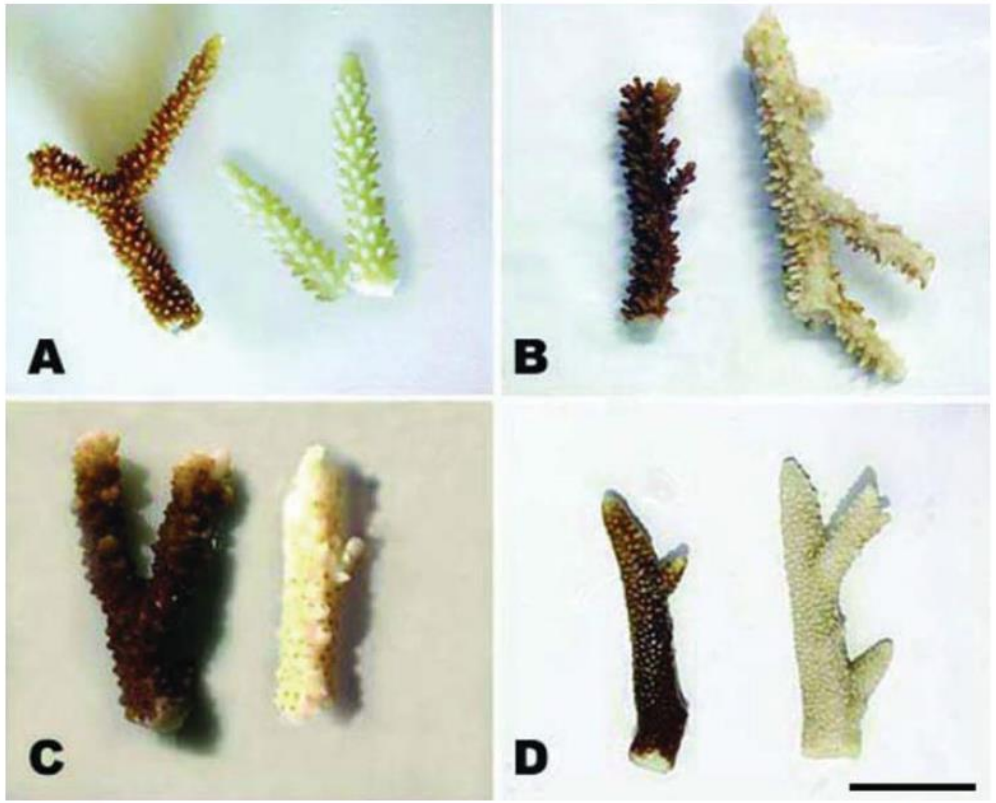
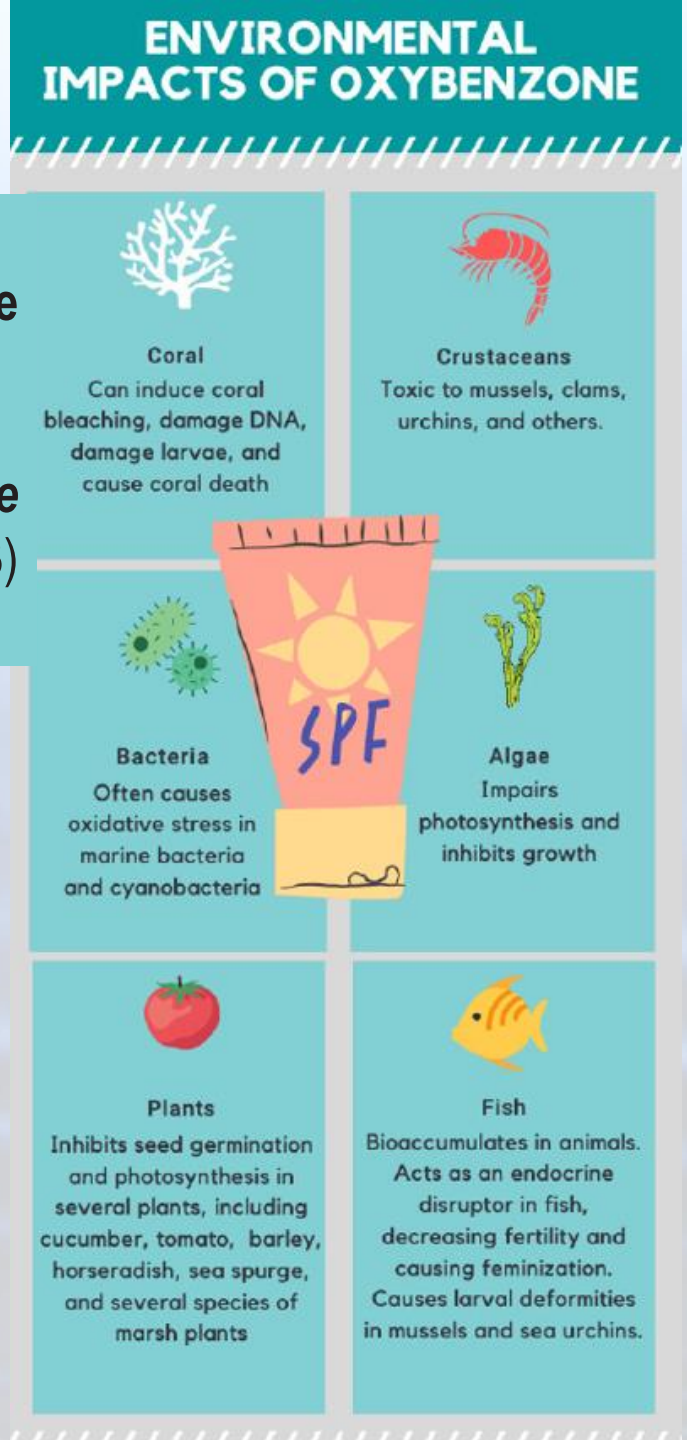


Figure 1. Impact of sunscreen addition on nubbins of *Acropora*. Untreated (brown) and treated (bleached) nubbins of (*A*) *Acropora cervicornis* (Caribbean Sea, Mexico); (*B*) *Acropora divaricata* (Celebes Sea, Indonesia); (*C*) *Acropora* sp. (Red Sea, Egypt); and (*D*) *Acropora intermedia* (Andaman Sea, Thailand). Images were taken within 62 hr of the start of sunscreen incubations. Scale bar = 2 cm.

Review 2023

Environmental impacts of the ultraviolet filter oxybenzone

Scheele et al., ***Science of the Total Environment***, 863 (2023) 160966



Analytical methods for EPs in water

- very low concentration
- possible matrix effects
- need of sensitive and selective analytical techniques (GC-MS, LC-MS…)
- need of **preconcentration** techniques *(i.e. Solid Phase Extraction - SPE)*

Critical issues

1. The analysis of trace contaminants often requires the collection of large volume of water and the subsequent sample preparation may cause troubles to the quantitative determination (*interferences, high blank levels, low reproducibility etc.)*

2. Spot (or grab) sampling can provide accurate and precise data but they represent just a “snapshot” of the contamination at the time of sample collection

3. To increase the sampling frequency is expensive and not always possible

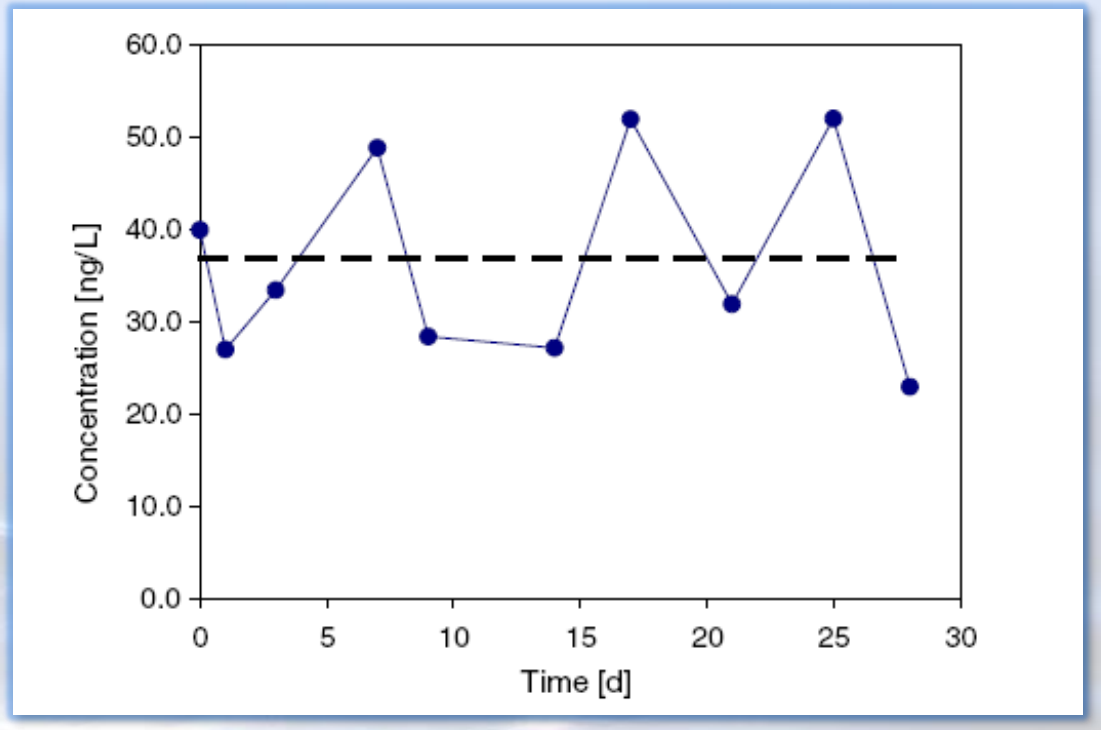
Passive Sampling

Sampling technique based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device

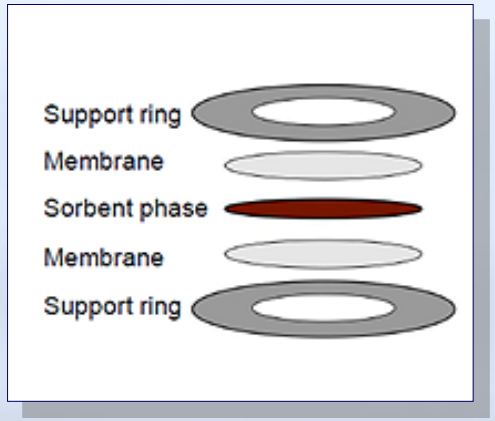
The "driving force" is the different chemical potential of the analyte in the two media

- Enables sampling, selective extraction and *in-situ* preconcentration at the same time
- Allows sequestration of pollutants from episodic events
- Does not affect the speciation, sampling only the dissolved phase
- Does not require energy and simplifies the sample preparation procedure
- Provides Time-weighted average (TWA) concentrations

TWA concentrations of pollutants: *passive vs. spot sampling*

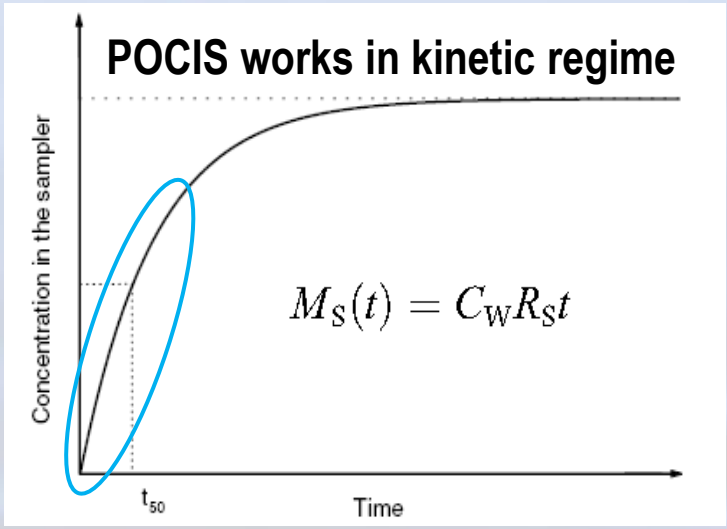


Polar organic chemical integrative sampler (POCIS)*



- Two microporous membranes of polyethersulfone (PES, *porosity 0.1 μm*) which enclose the sorbent

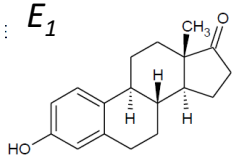
- Most common sorbents:
  - Oasis HLB (Hydrophilic modified styrene polymer)
  - Trifasic (Isolute ENV / Ambersorb 1500 / SX-3Biobeads)



** Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E., Environ. Toxicol. Chem., 2004, 23, 1640-1648.*

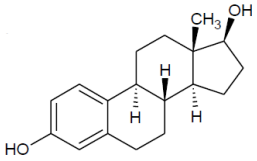
Estrogens

E_1



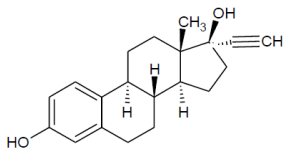
Log Kow: 3,13

E_2



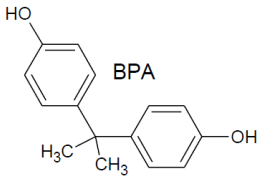
Log Kow: 4,01

EE_2



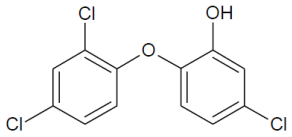
Log Kow: 3,67

BPA



Log Kow: 3,32

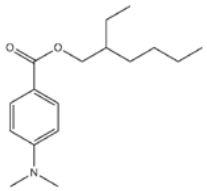
Triclosan



Log Kow: 4,76

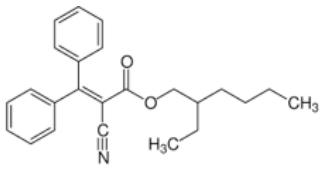
UV Filters

OD-PABA



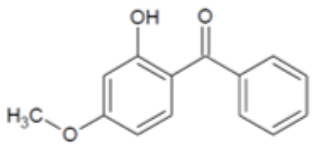
Log Kow: 5,8

OC



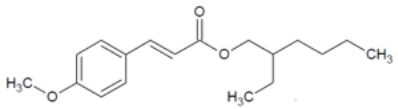
Log Kow: 7,1

BP-3



Log Kow: 3,79

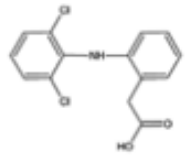
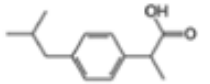
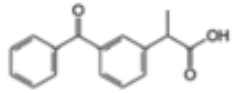
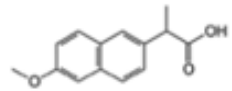
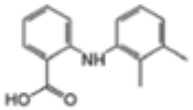
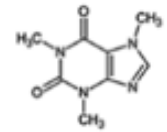
EHMC



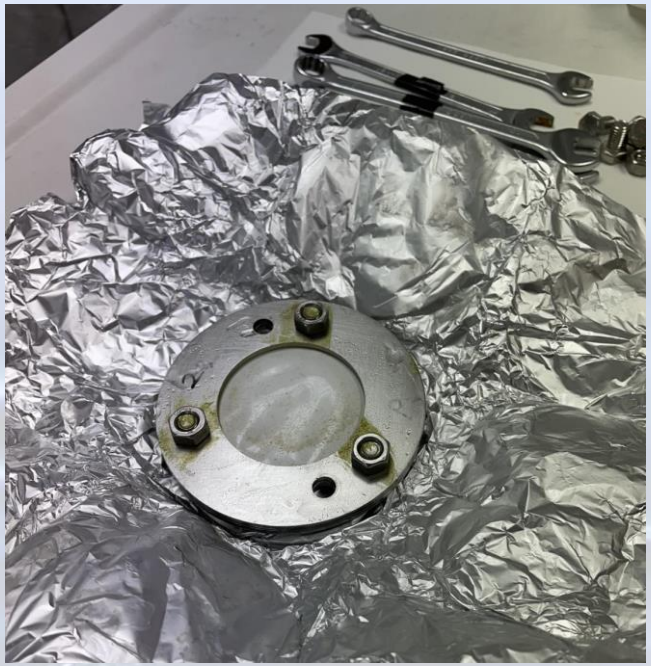
Log Kow: 5,3

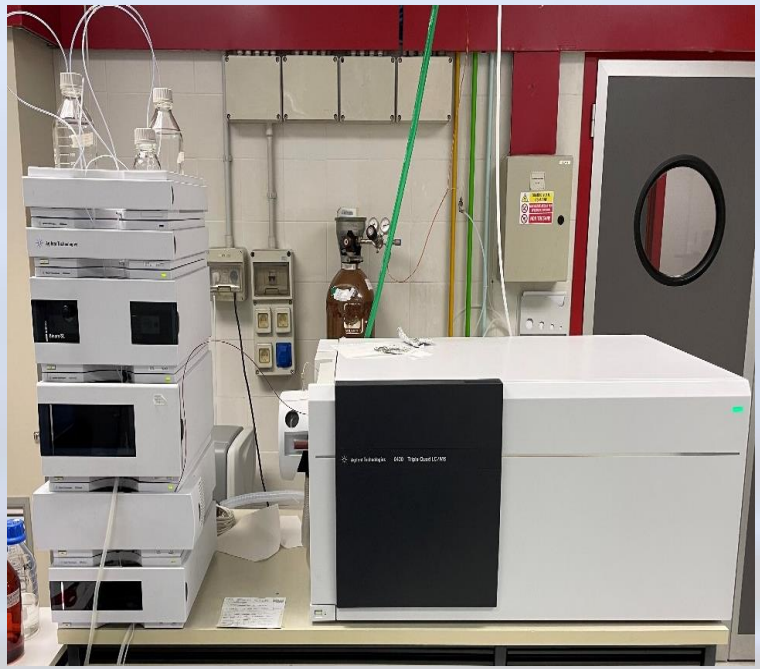
Journal of MASS SPECTROMETRY

Table 1. Structure of the selected emerging pollutants and their acid dissociation constant

Group	Compound	Structure
Arylalkanoic acids	Diclofenac 2-[(2,6-dichlorophenyl) amino]benzene acetic acid	
Arylpropionic acids (profens)	Ibuprofen 2-(p-isobutylphenyl)propionic acid	
	Ketoprofen (RS)2-(3-benzoylphenyl)-propionic acid	
	Naproxen 2-(6-methoxynaphthalen-2-yl)propanoic acid	
Non-steroidal anti-inflammatory drugs (NSAID)		
	Caffeine	
Polyfluoroalkyl substances (PFAS)	PFOA	
	PFOS	

POCIS processing and analysis





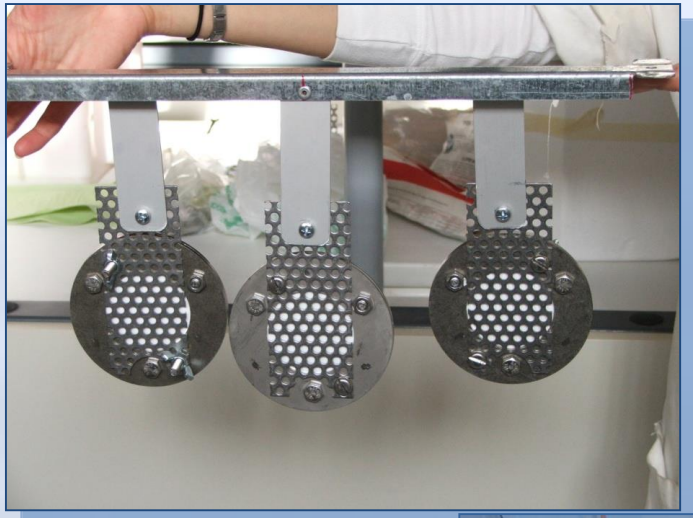
HPLC-ESI-MS/MS

High performance liquid chromatography - electrospray ionization – tandem mass spectrometry

Field activity at Terra Nova Bay

WWTP effluent of M.Zucchelli Station
(expedition 2021-22)

WWTP spot sampling	WWTP passive sampling
07-nov (SPE-1)	7-21 nov
14-nov (SPE-2)	
21-nov (SPE-3)	
28-nov (SPE-4)	21 nov- 5 dic
05-dic (SPE-5)	
12-dic (SPE-6)	5 dic - 19 dic
19-dic (SPE-7)	
26-dic (SPE-8)	19 dic - 2 gen
02-gen (SPE-9)	
09-gen (SPE-10)	2 gen - 16 gen
16-gen (SPE-11)	
23-gen (SPE-12)	16 gen - 30 gen
30-gen (SPE-13)	



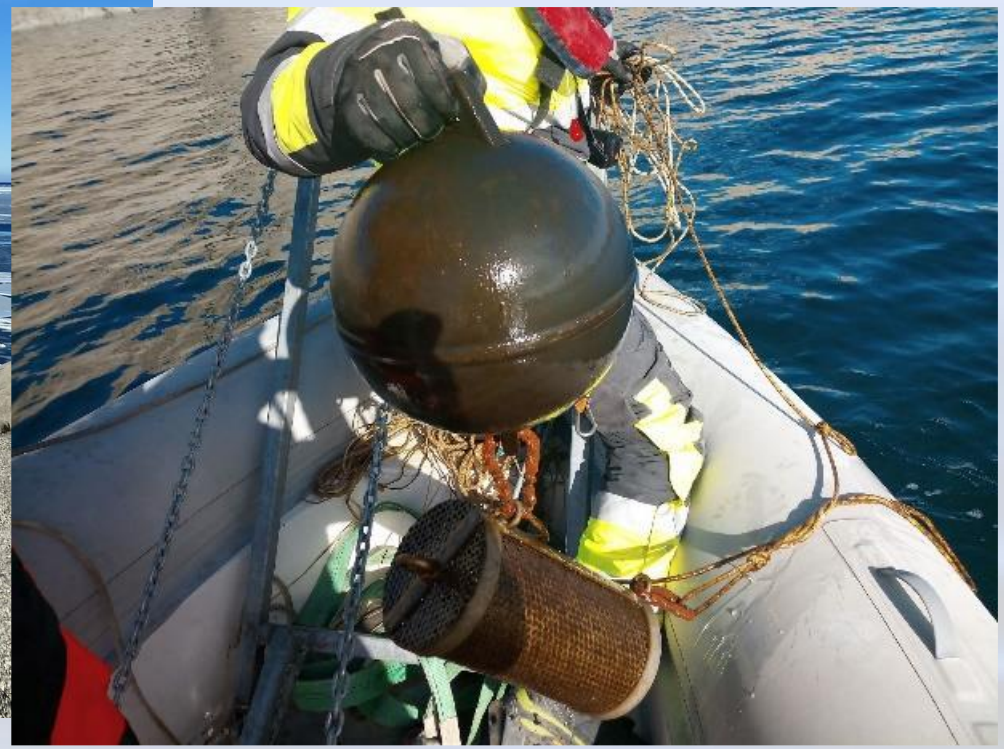

Road Bay
WWTP discharge
Sampling site

Field activity at Terra Nova Bay

Seawater sampling in Road Bay
(expedition 2021-22)

Road Bay Spot sampling	Road Bay Passive sampling
04-nov	4 nov - 25 nov
13-nov	
25-nv	
15-gen	15 gen - 2 feb
24-gen	
02-feb	

Road Bay



Results WWTP - Spot sampling

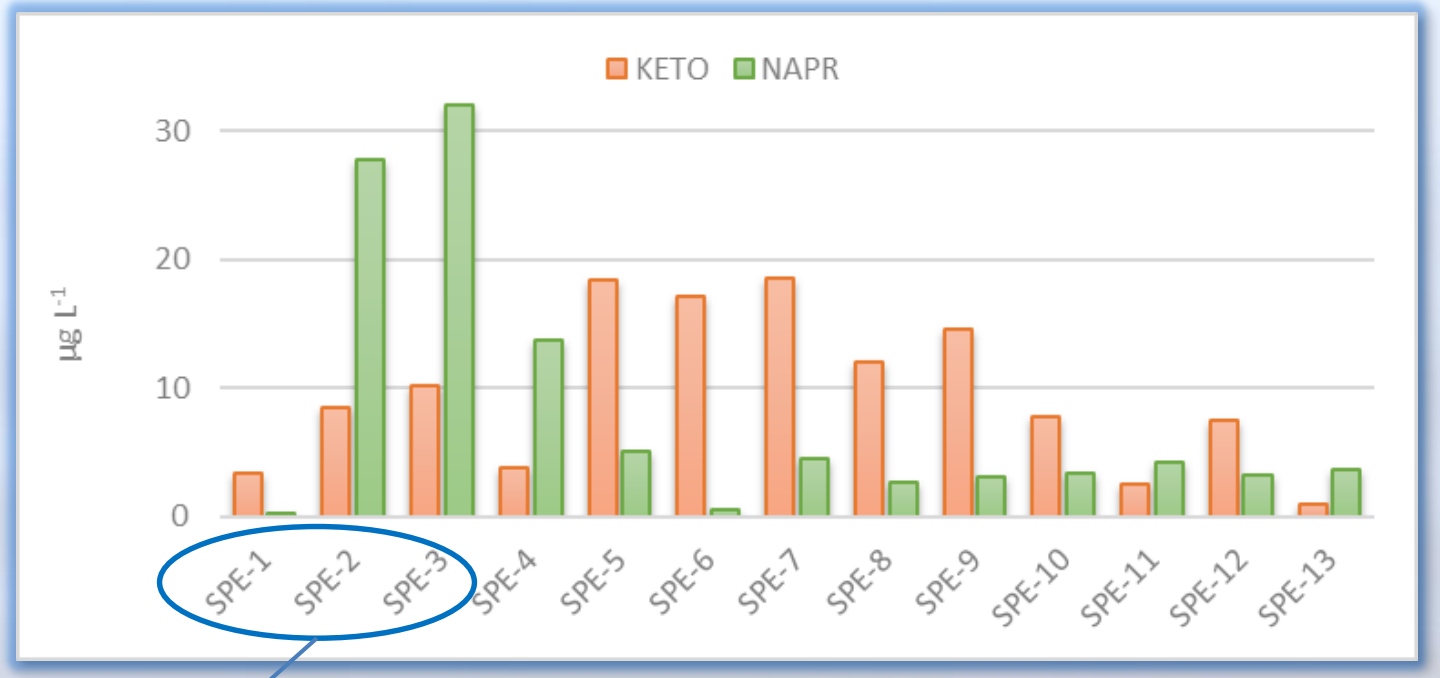
14 ECs measured during the 37th campaign (25 ECs detected during the two campaigns)

Considering the averaged concentrations for the whole period (*12 weeks for 37th*):

- most abundant: CAFF, KETO and NAPR (11-8 µg L^{-1})
- intermediate: OC, BP-3, IBU, DCF and PRX/TFL (1.5-0.8 µg L^{-1})
- lower concentrations: EHMC and TCS (0.3-0.09 µg L^{-1})
- detection/quantitation limit: E1, PFOA and PFOS

NSAIDs

Non-steroidal anti-inflammatory drugs



First POCIS deployement
7-21 nov 2021

Passive sampling: detected analytes

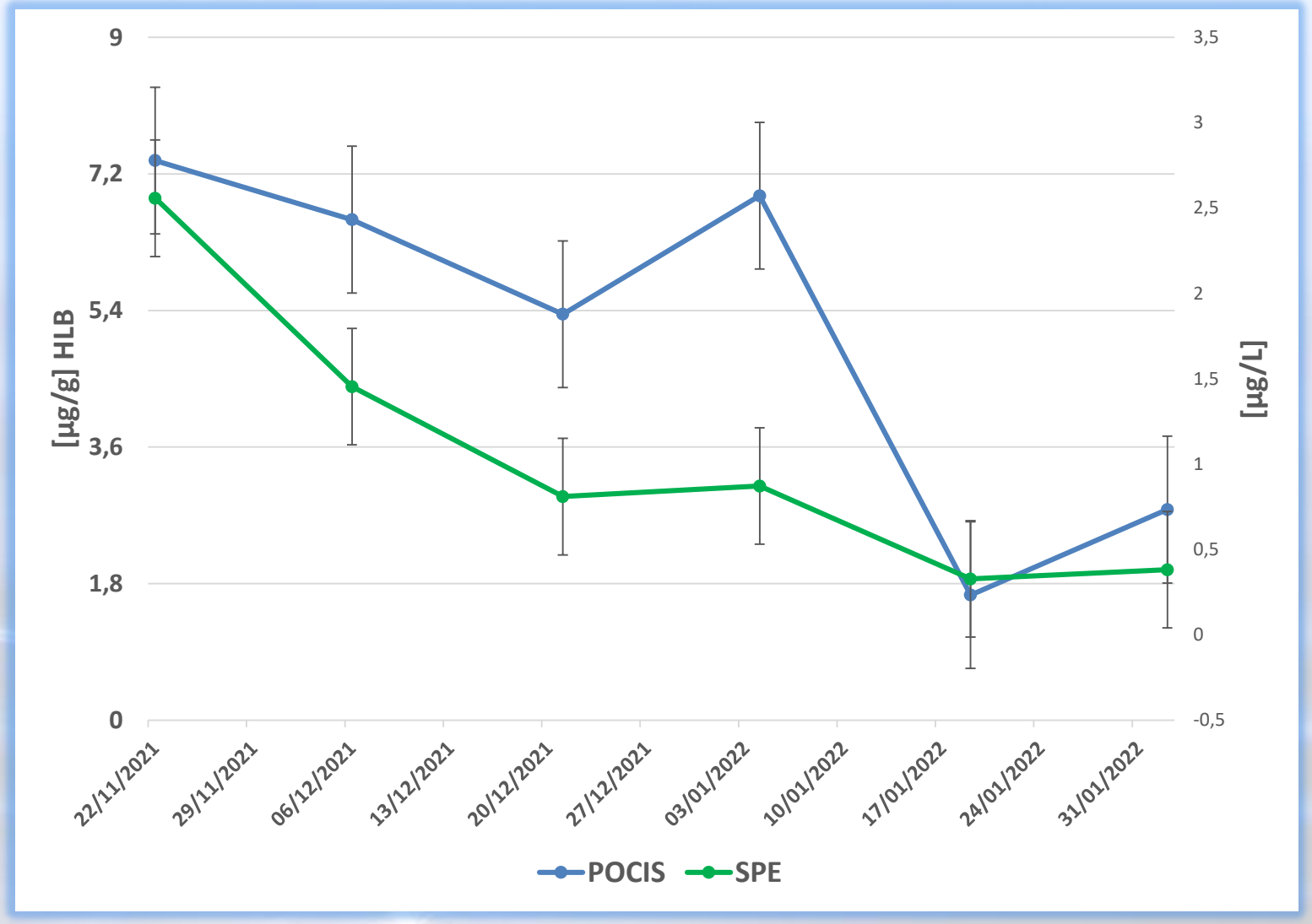
Both the HLB sorbent and PES membranes have been eluted (relevant for UV filters and TCS).

POCIS allowed the **detection of the same 14 ECs** measured by spot sampling during the whole 37th campaign

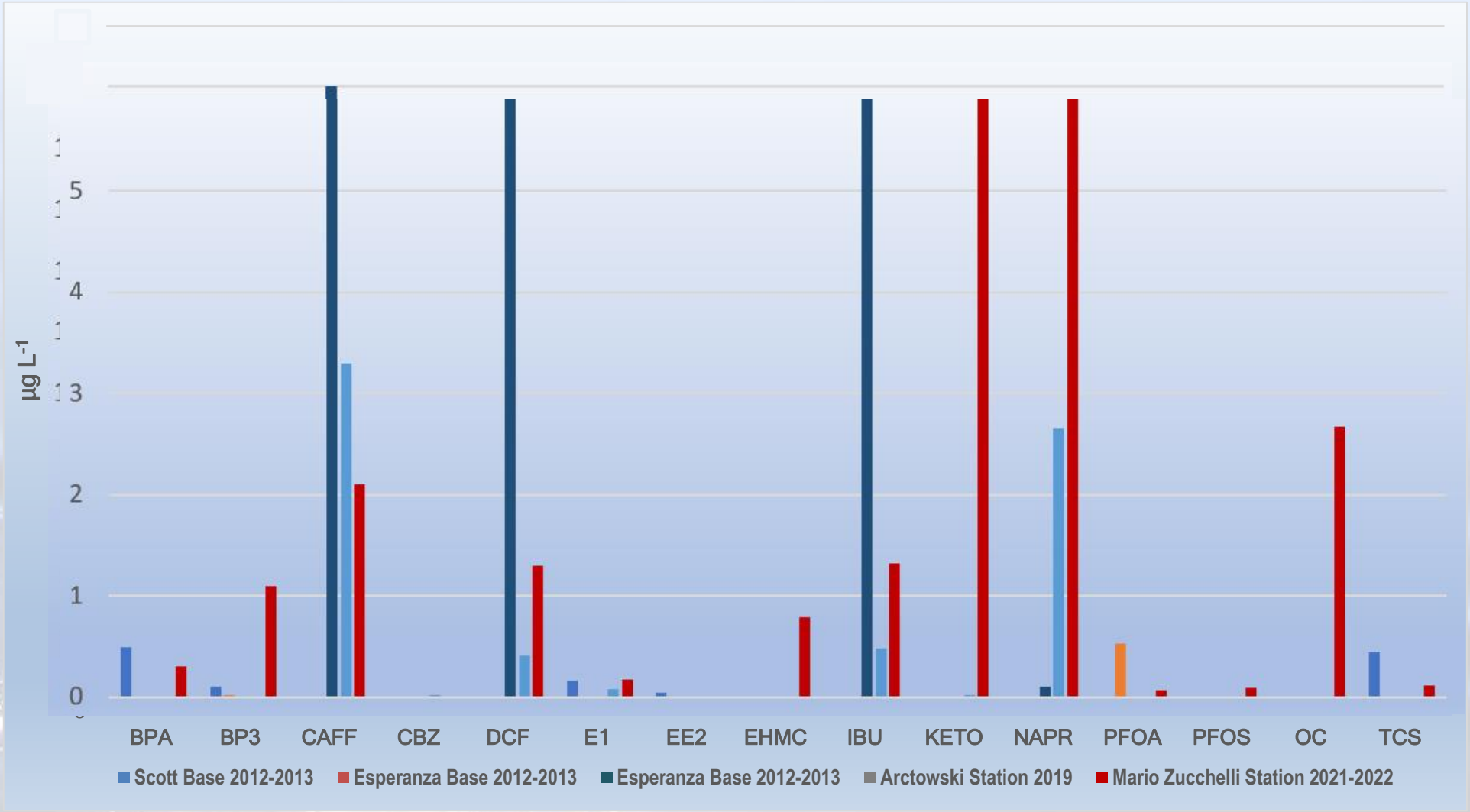
Good reproducibility between duplicate POCIS (except for the more polar CAFF and PRX-TFL)

- **<10%** for more than half the POCIS compound concentrations
- **<30%** for nearly all compounds (including BPA, E1, BP-3, TCS)

Ibuprofen


9
7,2
5,4
3,6
1,8
0
[µg/g] HLB
3,5
3
2,5
2
1,5
1
0,5
0
-0,5
[µg/L]
22/11/2021
29/11/2021
06/12/2021
13/12/2021
20/12/2021
27/12/2021
03/01/2022
10/01/2022
17/01/2022
24/01/2022
31/01/2022
POCIS
SPE

Comparison with spot sampling of other WWTP effluent in Antarctica



Seawater

2021-2022

- **Traces of 9 ECs** detected at least once in either the spot or the passive samplers:
- OC, BP-3, EHMC
- PFOA, PFOS
- NAP, DCF, IBU
- GEM*

2022-2023

- **Traces of 19 ECs** detected at least once in either the spot or the passive samplers:
- OC, BP-3,
- PFOA, PFOS
- NAP, DCF, IBU, KET
- GEM*, ATN, SLBT, TBTL
- CAFF, PRX+TFL, TRN, TBR
- TCS, BPA
- ACS

Jang Bogo Station

Terra Nova Bay

Cooperation with KOPRI

Concluding remarks

- Emerging contaminants have been detected during the 37th and 38th Expedition of PNRA in Terra Nova Bay, in the WWTP effluent of M. Zucchelli Station
- Both classical (spot) and innovative (passive) sampling allowed the determination of 25 compounds
- POCIS passive samplers provided results in substantial agreement with spot sampling, simplifying the whole analytical procedure and reducing the number of analysis thanks to the integrative sampling
- Seawater in Road Bay showed traces of most of the studied Ecs
- The risk on the local marine ecology, in particular from OC and BP-3, is under study.

Acknowledgments

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