

# Emerging contaminants in Genoa harbour seawater: innovative monitoring approaches combining passive sampling and high-resolution mass spectrometry



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## INTRODUCTION



Emerging contaminants (ECs) are micropollutants that include molecules belonging to various categories such as pesticides, hormones, pharmaceuticals, additives, UV filters, endocrine disruptor, etc.



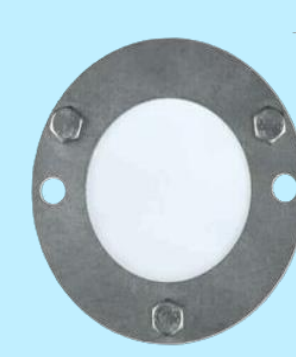
Their presence in the environment has raised the attention of the scientific community in the last two decades. ECs can include both "new contaminants" and chemical compounds that have long been present in the environment but have only recently become a source of concern.



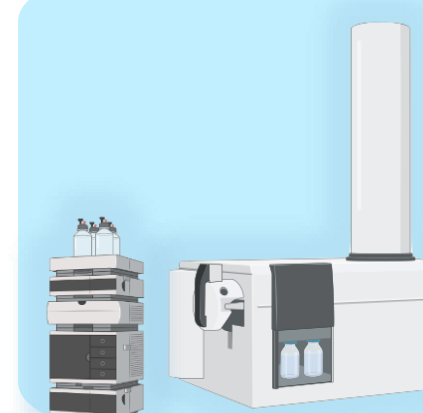
At present, ECs are not included in routine monitoring programs, but many of them have been introduced in some "watchlists", and they may be subjected to future regulation,



The analysis of these substances in seawater present a number of analytical challenges, including their low concentration (in the order of  $\text{ng L}^{-1}$ ) and the effect of the matrix itself, which can interfere with their determination.



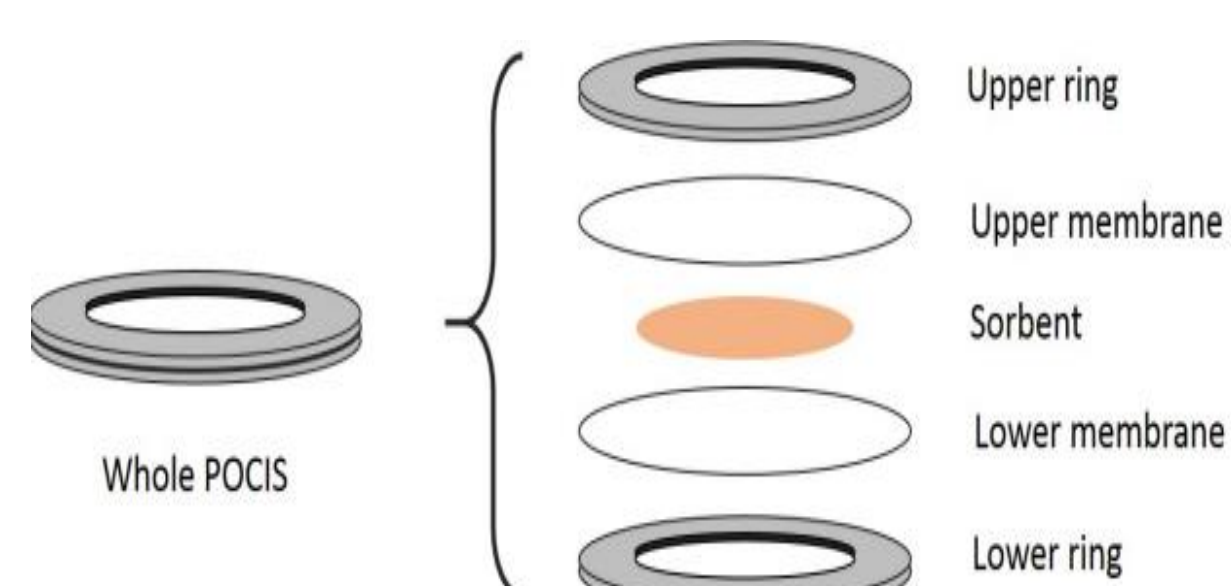
Passive sampling is a useful technique combining sampling and *in-situ* pre-concentration. Unlike spot sampling, time-integrative passive sampling allows the determination of time-weighted average (TWA) concentration of pollutants over extended sampling periods



LC-MS/MS is the analytical technique of choice; in this study, a high-resolution mass spectrometer (Q-TOF) was used, enabling both target and suspect screening analysis. 45 target analytes were chosen while, for suspect screening, a large database of substances potentially present in the sample was used to identify unknown chemicals

## RESULTS & DISCUSSION

### Polar Organic Chemical Integrative Samplers (POCIS)



After deployment, the sorbent is transferred into glass cartridges, washed with 5 mL of mQ water and eluted with 20 mL of methanol (MeOH) and 5 mL of a dichloromethane: isopropanol (DCM: IPA) 8:2 mixture. The extracts are dried by evaporation, reconstituted in 1 mL of methanol, and filtered before dilution and final analysis using LC-MS/MS, following a previously optimized protocol.

Membrane: polyethersulfone (PES) Sorbent: HLB solid phase (200 mg)

### Real samples and sampling sites

In the framework of the Italian PNRR project "RETURN" (*multi-Risk sciEnce for resilient commUnities undeR a changiNg climate*), POCIS passive samplers were deployed in strategic sampling point of the Genoa port area, in particular at the mouth of the two small rivers Bisagno (BISA) and Polcevera (POLC).

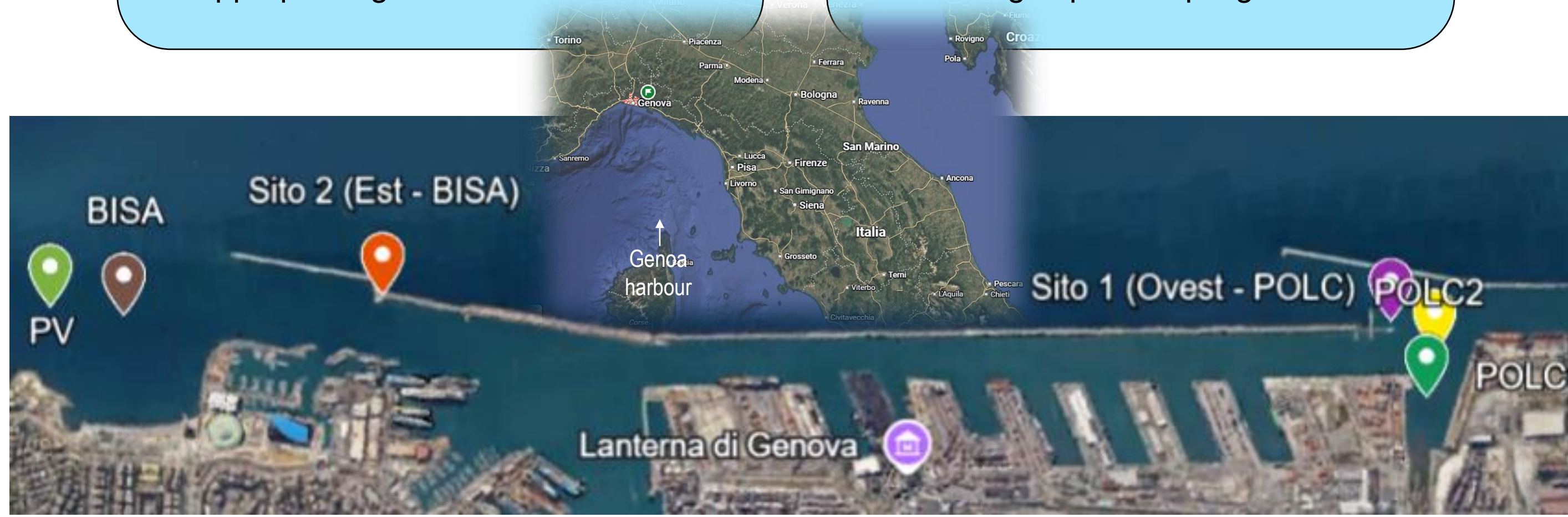
To obtain more comprehensive data, passive sampling was complemented by water spot sampling followed by Solid-Phase Extraction (SPE).

#### 1° Campaign (2023-2024)

- A total of 11 seawater samples were collected of which:
- 3 with POCIS devices
  - 8 through spot sampling using appropriate glass bottles

#### 2° Campaign (2024-2025)

- A total of 10 seawater samples were collected of which:
- 4 with POCIS devices
  - 2 with simil-POCIS devices (ROCKs)
  - 4 through spot sampling

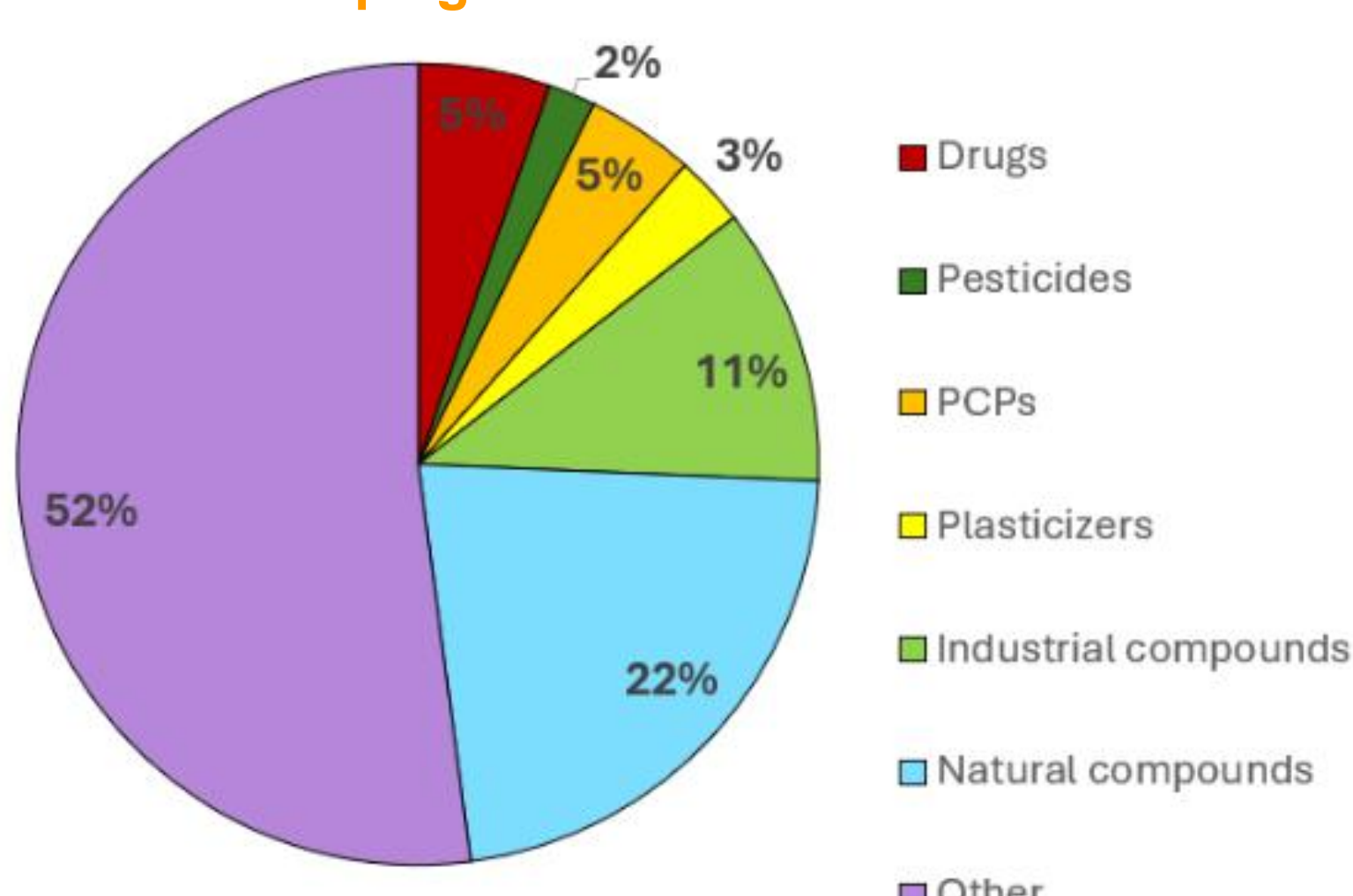


### Suspect screening

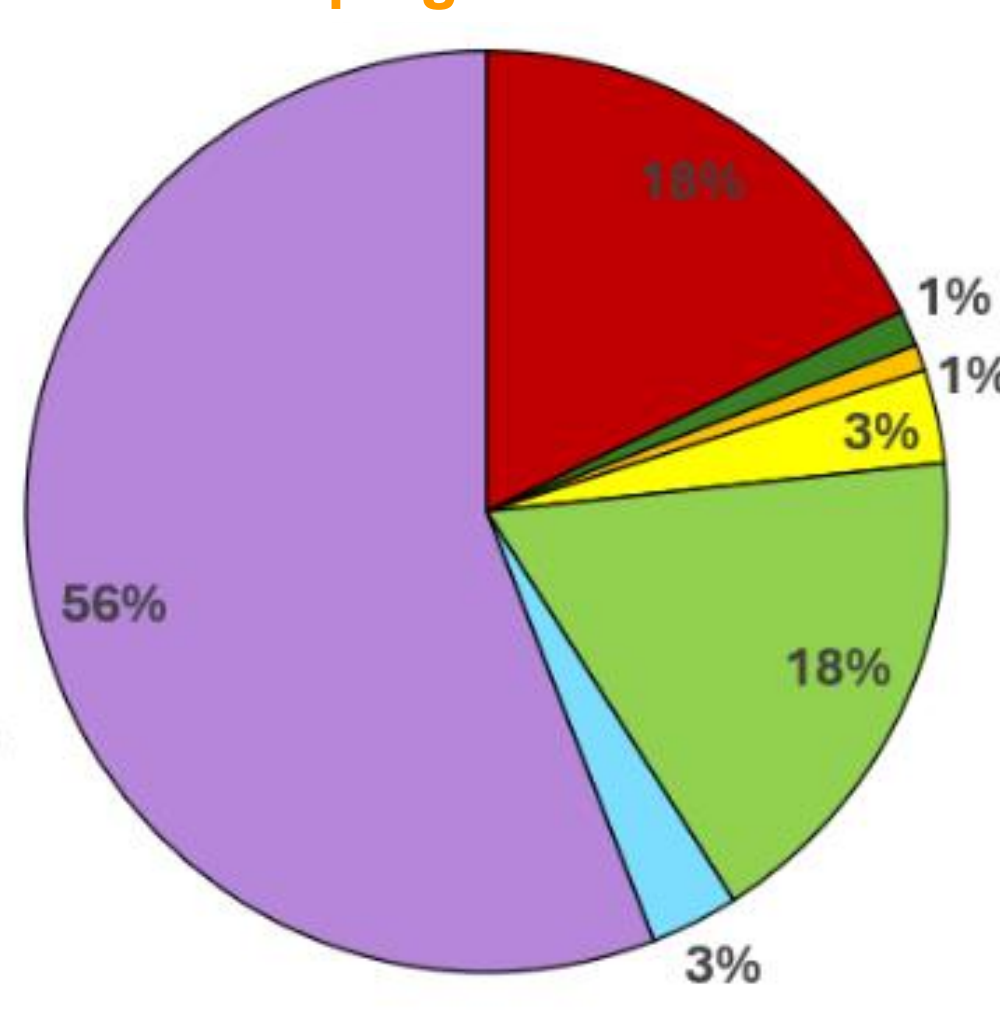
The Q-TOF spectrometer, operating in combination with the *Agilent QuantScreener SW* and its large database of substances, allowed the identification of a high number of unknown chemicals: 276 in the first campaign, and 196 in the second one.

In both campaigns, the predominant group was 'Other' (purple colour), reflecting the samples' heterogeneity and complexity; this group includes generic aromatic compounds, synthetic intermediates and degradation products which cannot be ascribed to specific classes such as drugs, pesticides, PCPs etc. Within the most frequently identified chemicals we found: acetaminophen (Paracetamol), benzotriazole (BTA) and bisphenol S (BPS).

#### 1° Campaign 2023-24

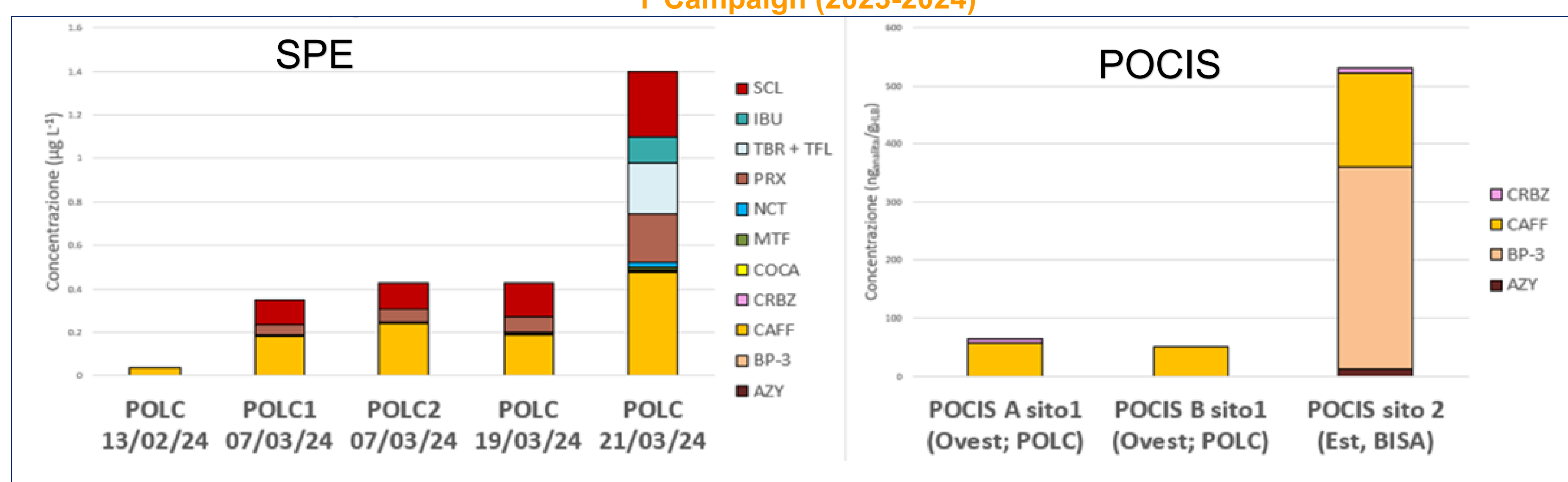


#### 2° Campaign 2024-25



### Target analysis of real samples

1° Campaign (2023-2024)



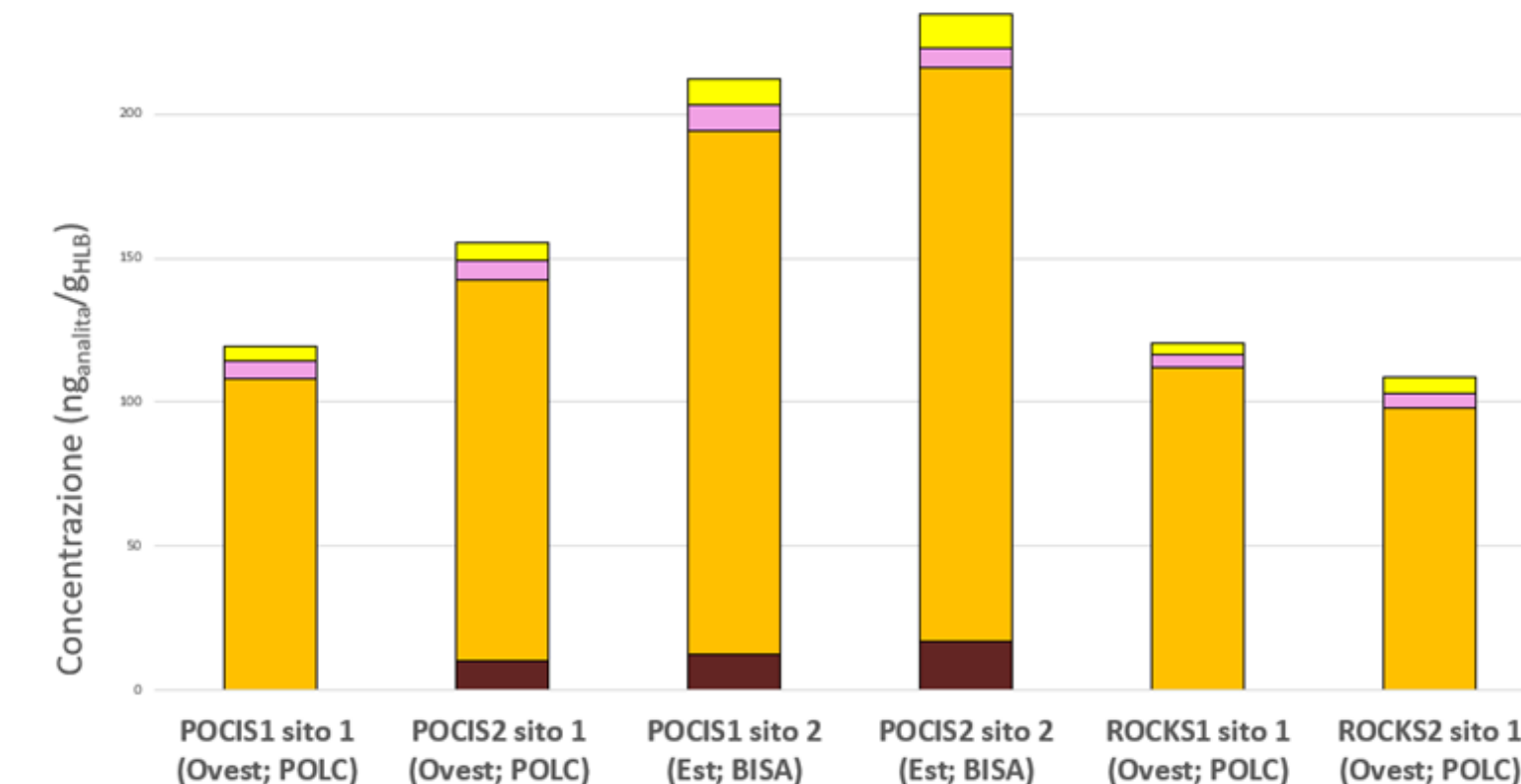
- Among the SPE samples, the compounds detected at the highest concentrations and present in almost all samples were sucralose, caffeine, and its main metabolite paraxanthine. Their detection and quantification highlights the significant anthropogenic impact on the marine environment. The highest number of analytes were measured in the sample SPE POLC 21/03/24
- In the POCIS samples, four analytes were quantified: azithromycin, benzophenone-3, caffeine, carbamazepine; the highest concentrations were observed for caffeine and benzophenone-3 (UV-filter)
- A clear difference was observed between sites, with sito 2 showing a higher number of detected analytes and generally higher concentrations. This result highlights the different inputs reaching the two areas, Polcevera (POLC) and Bisagno (BISA), with POLC characterized by higher civil and industrial activities

### 2° Campaign (2024-2025)

#### SPE

Analytes	Concentration ( $\mu\text{g L}^{-1}$ ) $\pm$ standard deviation			
	SPE sito 1 (Ovest, POLC) 23/12/24	SPE sito 2 (Est, BISA) 23/12/24	SPE sito 1 (Ovest, POLC) 04/02/25	SPE sito 2 (Est, BISA) 04/02/25
AZY	<LOQ	<LOQ	<LOQ	<LOQ
CAFF	0.051 $\pm$ 0.006	0.08 $\pm$ 0.01	0.026 $\pm$ 0.003	0.020 $\pm$ 0.002
MITPL	<LOQ	ND	ND	<LOQ
OD-PABA	ND	ND	<LOQ	<LOQ

#### POCIS



- In the second campaign, fewer analytes were detected by spot sampling; as reported in the table above, only caffeine was quantified in these samples, with an average concentration of 0.044  $\mu\text{g/L}$
- In the POCIS samples, four analytes were quantified: azithromycin, cocaine, caffeine, carbamazepine. As in the previous campaign, the highest concentration were observed for caffeine
- Although a direct comparisons between concentration data obtained by spot sampling ( $\mu\text{g/L}$ ) and those by POCIS (ng/g HLB sorbent phase), it appears evident that the POCIS devices have a considerable accumulation capacity, increasing the preconcentration factor and thus enabling the quantification of four analytes instead of one

## CONCLUSIONS

- Passive sampling using POCIS samplers presents several advantages respect to spot sampling followed by SPE; in particular, the POCIS accumulation capacity results in greater sensitivity for the studied analytes
- The use of the high-resolution LC-Q-TOF instrument is a suitable technique for the determination of emerging contaminants in water, both for targeted quantitative analysis and for the exploratory screening of unselected contaminants. The high number of unknown chemicals identified using the "suspect-screening" approach demonstrates the potential of high-resolution mass spectrometry for monitoring the chemical impacts on the environment
- Future studies will focus on the assessment of temporal variations in ECs contamination; the results will provide valuable insights into emerging pollution trends in the marine areas of Genoa harbour, to better understand the distribution and potential sources of these micropollutants

## References

- [1] S. Sauvé, M. Desrosiers, A review of what is an emerging contaminant, *Chem. Cent. J.*, 2014, 8, 15.
- [2] M. Paszkiewicz, K. Godlewska, H. Lis, M. Caban, A. Biak-Bielińska, P. Stepnowski, *Advances in Suspect Screening and Non-Target Analysis of Polar Emerging Contaminants in the Environmental Monitoring. Trends in Analytical Chemistry*, 154 (2022), 116671.
- [3] H. MacKeown, B. Benedetti, M. Di Carro, E. Magi, *The study of polar emerging contaminants in seawater by passive sampling: A review*, *Chemosphere*, 2022, 299, 134448
- [4] E. Magi, M. Di Carro, *Marine environment pollution: The contribution of mass spectrometry to the study of seawater*, *Mass Spectrom. Rev.*, 2018, 37, 492-512.