

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

E. Magi¹, Marina Di Carro¹, Laura Cutroneo², Marco Capello², Laura Gaggero², Daniel Bona¹, Barbara Benedetti¹

¹Department of Chemistry and Industrial Chemistry (DCCI), University of Genoa, Genoa, 16146, Italy

²Department of Earth, Environmental and Life Sciences (DISTAV), University of Genoa, Genoa, 16146, Italy

Keywords: Emerging contaminants, coastal discharges, micro-chemical contaminants, innovative monitoring.

Presenting author email: emanuele.magi@unige.it

Emerging contaminants (ECs) are substances for which limited information is available regarding their distribution and their environmental effects; they are a wide group of substances whose presence in the environment has raised the attention of the scientific community in the last two decades. ECs may be both “new contaminants” and also chemical species which have been in the environment for a while but for which concerns have been raised much more recently. 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 [1].

Monitoring these compounds in marine waters, particularly in port areas, is crucial for assessing their environmental impact. ECs detection can be challenging due to their typically low concentrations; nevertheless, classical approaches are usually reported in the literature both in sampling (spot-sampling) and sample treatment, (i.e. as solid phase extraction) [2].

Unlike spot sampling, time-integrative passive sampling allows the determination of time-weighted average (TWA) concentration of pollutants over extended sampling periods; it also enables the in situ preconcentration of trace compounds and the detection of contaminants deriving from episodic events, not always possible by spot sampling. By using passive sampling, regular monitoring of the chemicals can be used to track spatial and temporal trends in waters (Alvarez et al., 2014).

In the framework of the Italian PNRR project “RETURN” (*MUR code: PE00000005*), passive samplers POCIS (*Polar Organic Chemical Integrative Samplers*) were deployed in the Genoa port area. These devices integrate contaminant presence over extended periods, allowing for the estimation of TWA concentrations. To obtain more comprehensive data, passive sampling was complemented by water spot sampling followed by Solid-Phase Extraction (SPE).

Two main sampling campaigns, covering a period of two years (May 2023-April 2025). During the 1st campaign (2023-2024) a total of 11 seawater samples were collected in the port of Genoa, selecting strategic sampling points located near the discharge outlets of wastewater treatment plants (WWTPs). Among these, 3 samples were collected using passive sampling with POCIS devices, while the remaining 8 were obtained through spot sampling, using appropriate glass bottles. The study areas were located in the Polcevera, Puntavagno, and Bisagno zones. During the 2nd campaign (2024-2025), a total of 10 samples were collected from the same locations. Specifically, 4 samples were obtained using POCIS passive sampling, 2 using ROCKS passive sampling, and 4 through spot sampling followed by SPE. ROCKS (*Resistant Organic Chemical Kinetic Samplers*) are novel passive samplers developed in our laboratories to overcome certain limitations of POCIS, particularly membrane fragility and low sampling rates for more hydrophobic contaminants.

During the sampling campaigns, about forty ECs were investigated, including drugs, additives, tracers, pesticides, and UV filters. The analytical determination was performed by liquid chromatography (HPLC) coupled to a high-resolution tandem mass spectrometer (Q-TOF); this instrument can be used for both target and suspect screening analysis; in the first case, the analytes to be measured are chosen in advance while, in the second case, a large database of substances potentially present in the sample is used to identify unknown chemicals. Q-TOF is an extremely effective technique for studying emerging contaminants in different matrices.

The results obtained by target analysis on port seawater sampled by POCIS and spot sampling, are summarized in figure 1 and 2, for both the sampling campaigns; for brevity, detected ECs have been gathered in 5 classes, highlighted in different colours. Up to 21 ECs were detected in POCIS extracts, much more than in spot samples. Regarding suspect screening analysis, besides the ECs measured by target analysis, further unknown

compounds were detected: 44 ECs in the POCIS extracts of the 1st campaign and 41 ECs in the POCIS extracts of the 2nd campaign. Also in this case, the spot sampling was less effective; in fact, it allowed the identifications of 15 unknown chemicals. Most frequently identified ECs were pharmaceuticals, in particular beta-blockers.

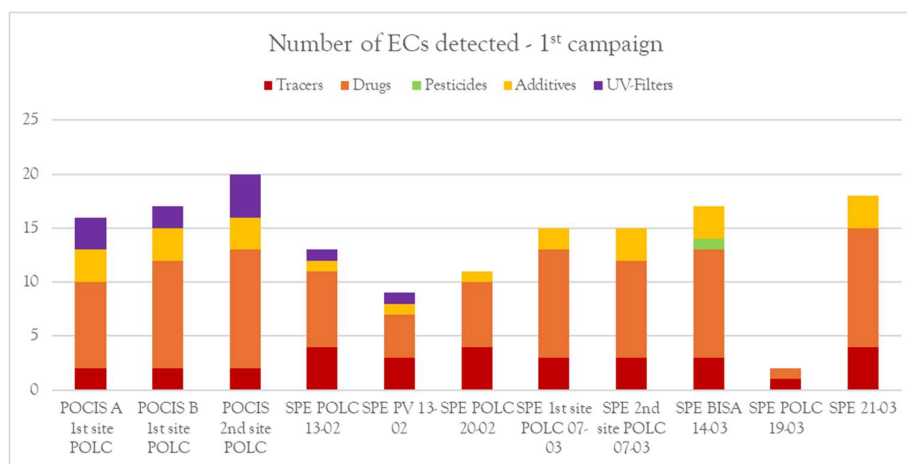


Figure 1 Number of ECs detected for each sample in the first campaign

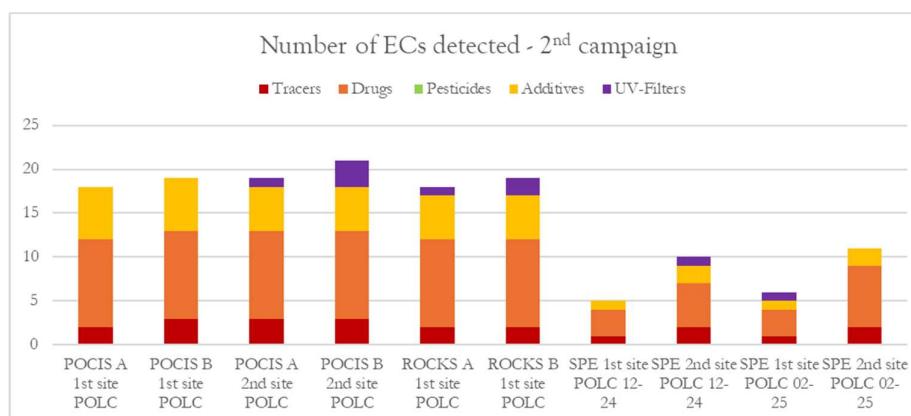


Figure 2 Number of ECs detected for each sample in the second campaign

The study is still running, particularly focusing on suspect screening analysis; new evidence together with more detailed quantitative data will be presented during the meeting.

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. Białk-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.