PLAN BLEU NOTES
#40
APRIL 2021
Plan Bleu

CONTAMINANTS OF EMERGING CONCERN IN THE MEDITERRANEAN SEA

What are contaminants of emerging concern?

The term **"Contaminants of emerging concern"** describes a heterogeneous set of thousands of molecules and metabolites whose presence in the environment had not been detected in the past and whose study and monitoring are relatively recent, even though they may have been present in the environment for a long time. Contaminants of Emerging Concern (CoECs) are synthetic or naturally occurring **chemicals and microorganisms that are not commonly monitored** in the environment. They are not currently covered by existing water quality regulations, have not been studied before, and are thought to be **potential threats to ecosystems as well as human health** and safety. Contaminants of emerging concern include polycyclic aromatic hydrocarbons (PAHs), pesticides, metals, environmental oestrogens, microplastics and phthalates, nanoparticles, pharmaceuticals, personal care products, UV filters, flame retardants and disinfection by-products.

Drivers and sources of contaminants of emerging concern

The current prevalent lifestyles of people living in the Mediterranean countries are based on unsustainable linear (non-circular) resource consumption, with a high demand for consumer goods and other processed products and increasing use of pharmaceuticals due to an aging population and increased access to medical services. Many of these products contain molecules and metabolites that are not sufficiently treated at product end-of- life **and end up in the environment.** As a result of demographic growth and a rise in living standards in many parts of the Mediterranean basin, the **demand for these molecules and metabolites has soared in recent decades.**

Known sources of CoECs in the Mediterranean environment include runoff and seepage from landfills, agriculture, aquaculture, hospitals, industrial and domestic wastewater *(Fig 1)*. Many CoECs are incorporated into products ingested by humans and discharged into the environment via the wastewater flow. This represents their main pathway into the environment in developed countries. **Conventional wastewater treatment plants are not designed to remove these contaminants.** As a result, removal is limited even where tertiary treatment is in place.

The Mediterranean Sea is a highly exploited waterway with intense **cargo traffic and cruise tourism.** Under certain conditions, vessels are allowed to discharge wastewater and sewage sludge, as well as the operational residue of antifouling agents and hydrocarbons in the open sea, and can therefore be listed among the possible sources of contaminants. Some **industries** are also significant sources of CoECs which they release into the Mediterranean Sea. They include: oil and gas production and oil refineries (petroleum and by-products of the production processes), energy production (drilling fluids, nanoparticles, mercury), food industries (food additives, plasticizers), metallurgy including organic metals (metals), chemicals and plastic production (plastic additives, nanoparticles, etc.), leather and textile processing (microplastics, metals, flame retardants), the cement industry (metals, fuel residue), the pulp and paper industries (metals), and the pharmaceutical industry (non-steroidal anti-inflammatory drugs, antibiotics, beta-blockers, bactericidal and antifungal agents). These industrial pollutants are in addition to pollution stemming from **aquaculture and agriculture** (pesticides, fertilizers, pharmaceuticals), and **domestic liquid and solid waste** (pharmaceuticals, hormones, synthetic musk, personal care products, UV filters). Some of these pollutants originate far from the coastline but reach the sea via watercourses located within the Mediterranean basin or via the air.

Largely unknown concentrations

While data on pollutant concentrations ('traditional' and those of emerging concern) exist in some places, the Mediterranean is far from having complete comparable datasets on all relevant substances in all places, at regular coherent intervals. Environmental hotspots on the Mediterranean coast are **concentrated in areas of high anthropogenic pressure** and are primarily located in the Adriatic Sea and along the eastern Mediterranean Sea. CoECs have been reported in the ng/L range, but results are highly variable depending on the geographical location and the time of year. Bridging knowledge gaps is a costly and time-consuming endeavour: the costs can be disproportionate to the limited knowledge acquired.

UN environment programme | Mediterranean Action Plan Barcelona Convention | Plan Bleu | agence de l'eau RHÔNE MÉDITERRANÉE CORSE

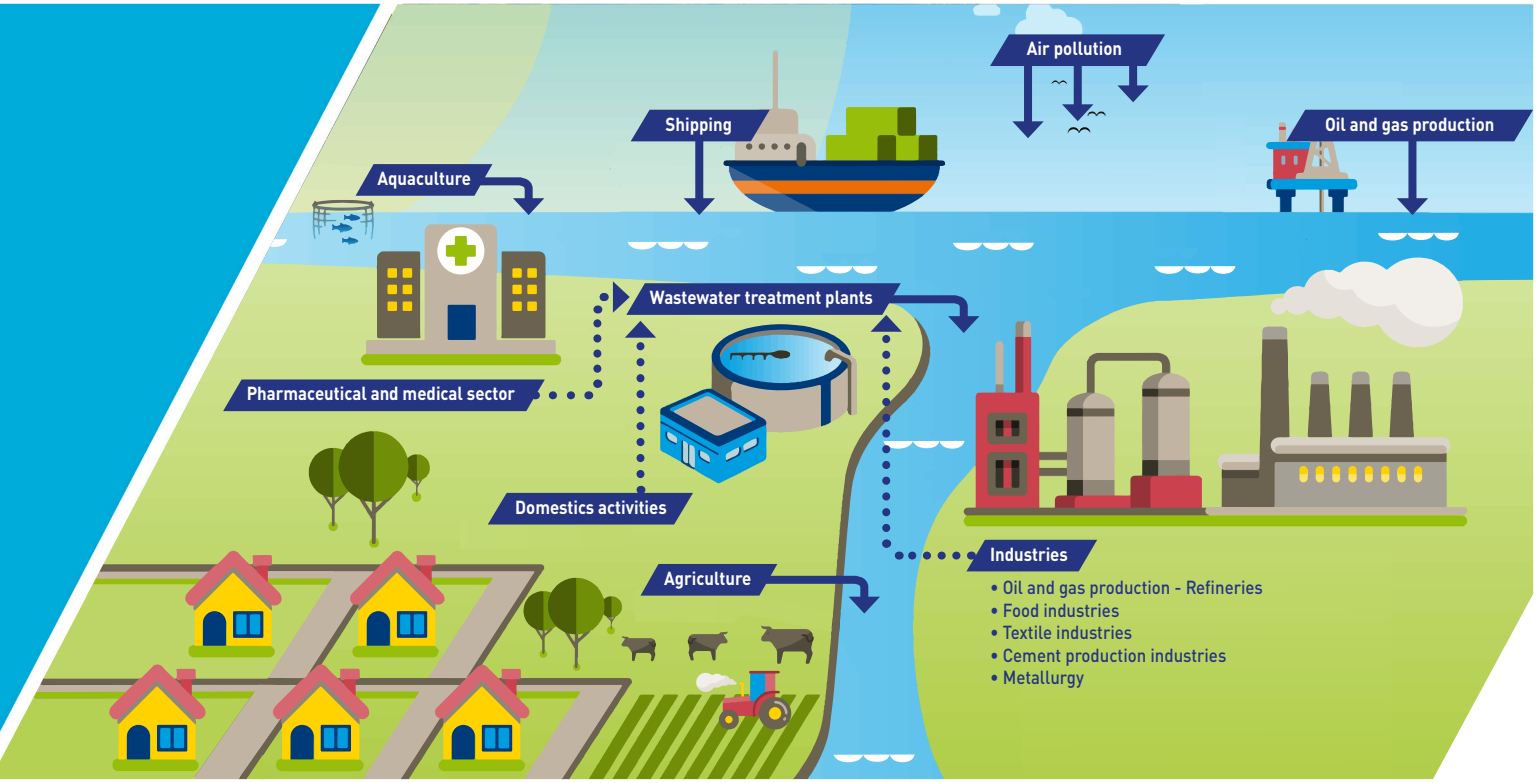

Fig. 1 - *Sources of emerging pollutants*

Impacts and the 'cocktail effect'

Although increasing, there is still limited **understanding** of the CoEC lifecycle in the ecosystem, their ecotoxicological significance, their cumulative and synergistic effect on each other and their impact on human health. Known impacts of CoECs are detailed in *Fig 2.* CoECs present in coastal waters can interact with each other and lead to a "cocktail effect". **The combinations of compounds can act synergistically** or antagonistically from an ecotoxicological point of view, in which the presence of a component increases or diminishes the effect of another component. The prevalent observation is that the cocktail effect increases the toxicity of molecules.

Antibiotics, antidepressants and non-steroidal anti-inflammatory drugs are known to induce cocktail effects. As an example, mixture effects were observed when five pharmaceuticals and personal care products were exposed to marine biofilms only at their individual no-observed-effect concentrations.

Prevention and remediation

Although depollution measures are improving in their capacity to effectively treat or eliminate certain CoECs, it is likely that **neither technology nor financial resources will ever be sufficient to treat 100%** of pollution. Therefore, pollution prevention and the application of **the precautionary principle must be a priority,** involving the following measures: to regulate and reduce the use of CoECs, phase-out known harmful substances, avoid the creation of new CoECs; impose and enforce mandatory environmental and health impact studies prior to placing new CoECs on the market; and develop emergency preparedness and responsiveness to accidental pollution, natural hazards and other emergencies.

For CoECs that cannot be prevented, **new remediation techniques** to effectively decontaminate wastewater and aquatic environments are needed. They include biomass-based technologies, including bio-adsorption using both terrestrial and marine bioresources and agro-industrial waste as well as derived activated carbons. Other techniques include phytoremediation, microbial remediation using bacteria, fungi and yeasts, and combinations of different techniques such as biodegradation/filtration, adsorption/biodegradation and adsorption/ozonation. However, treatment complexity and cost increase with treatment effectiveness, which is why pollution prevention should be given priority over remediation.

Monitoring and surveillance

In recent decades, great advances have been made in specific techniques to detect and analyse CoECs that are mobile and persistent in air, water, soil, and sediment *(Fig 3).* However, **an array of CoECs still remains undetected in the environment.**

In the EU, several biomonitoring programmes have been established to promote long-term CoEC monitoring. **The study of CoECs, their interactions with the environment and human health and their treatment is complex and costly and has not kept pace with the rate at which new substances are being "created".** To date, the European Chemicals Agency has registered more than 22,000 substances under the REACH regulation, whereas, worldwide, more than 142 million exist. The measures currently in place to monitor and manage these pollutants in the Mediterranean are discussed in the following section.

In the framework of the Barcelona Convention, the Integrated Monitoring and Assessment Programme (IMAP) targets chemicals under the **Ecological Objective on Pollution** (EO9), namely total Mercury (HgT), Cadmium (Cd) and Lead (Pb), as well as Petroleum derivates (PAHs) in biota and sediments. Moreover, **sub-indicators of contamination for PAHs and Emerging pollutants are recommended to be carried out on a country decision basis until a firm COP Meeting Decision will be taken.** To establish a minimum limit concentration of CoEC in the environment that pose a significant risk to ecosystems and/or human health, the 2013 amendment of the Environmental Quality Standards Directive (2008/105/EC) established a mechanism, the **EU Watch List.** This list is a dynamic structure which provides targeted and high-quality information on the concentrations of substances of possible concern in the aquatic environment in the EU. Emerging pollutants and other substances on this list have **insufficient monitoring data** for an EU-wide risk assessment.

Substances on the EU Watch List are limited to a maximum of 14 and would be monitored across the EU for up to four years. The list is frequently reviewed to keep monitoring costs at reasonable levels, and to identify substances of significant risk as quickly as possible. The 1st Watch List was reviewed in 2018 (Loos et al, 2018) and the painkiller diclofenac was removed from the list *(Fig 3).* Samples of substances are extracted from different sources, namely water, sediment and biota, using different methodologies. Costs can vary widely depending on the technique and matrix to be sampled. For biota, the current MED POL monitoring programme uses mussels as an indicator species.

Categories	Sources	Human health Impact	Environmental Impact
Polycyclic aromatic hydrocarbons (PAHs)	Found in asphalt used in road construction, medicines, dyes, plastics, and pesticides. They can also be found in substances such as crude oil, coal, coal tar pitch, creosote, and roofing tar.	• Carcinogenic and potential neurotoxin.	• Have moderate to high acute toxicity to aquatic life and birds. • In high concentrations in soil, can have ad- verse effects on terrestrial invertebrates including on reproduction, development, and immunity, and may cause tumours.
Pesticides	Agricultural run-off and urban green spaces and parks (include herbicides and insecticides).	• Short-term impacts such as hea- daches and nausea. • Chronic impacts such as cancer, reproductive harm, and endocrine disruption.	• Can contaminate soil, water, turf, and other vegetation. • Can cause mortality in insects and weeds. • Toxic to other organisms including birds, fish, beneficial insects, and non-target plants.
Environmental oestrogens	Synthetic chemicals found in food, animals and plant products and some household items.	• Have been linked to breast cancer in women and prostate cancer in men. • Oestrogen has a wide range of effects on the body and brain, including on emotional processing via neuropsychological factors.	• Impact fish physiology and can affect reproductive development in both domestic and wild animals. • Can mitigate the effects of other environmental stresses on the plant.
Phthalates	Industrial chemicals used to soften PVC plastic and as solvents in cosmetics and other consumer products.	• Damage to the liver, kidneys, and lungs. • Damage the reproductive system, and can cause infertility and reproductive problems in men.	• Toxicity impacts in animals including damage to liver, kidney, lungs and reproductive systems.
Pharmaceuticals	Introduced through sewage from households with patients using drugs.	• Development of antibiotic-resistant strains of bacteria that can lead to a serious threat to human health.	• Development of antibiotic-resistant strains of bacteria that can critically disturb natural bacterial ecosystems in the environment. • Under certain conditions direct impact on fish reproduction.
Personal Care Products	Health, beauty and cleaning products.		• Negative impact on aquatic ecosystems, especially related to endocrine disruption and reproductive disorders. • Create a layer on the water surface that hinders gaseous exchanges between the air and the sea.
UV filters	Found in sunscreen and other topical products.	• Certain chemical filters are potential endocrine disruptors.	• Endocrine-disrupting potential impacting animals. • Create a layer on the water surface that hinders gaseous exchanges between the air and the sea.
Flame retardants	Used as coatings.	• Have carcinogenic properties. • Brominated and chlorinated flame retardants can increase fire toxicity including fire growth rate and smoke toxicity.	• Toxic effects on marine fauna.
Disinfection by-products	From household and domestic, hospital and industry waste.		• There is evidence of carcinogenic and mutagenic properties of these by-products in small animals.

Fig. 2 - *Sources, health and environmental impacts of emerging pollutants*

Pharmaceutical consumption is likely to increase in the coming years, particularly in countries with high demographic growth and those with an aging human population and increasing livestock production. Three macrolide antibiotics (azithromycin, clarithromycin and erythromycin) that are widely used in human and veterinary medicine are of particular concern and are present in soil and water including in marine ecosystems. In the environment, antibiotics can impact natural microbial communities, which play key roles in ecological processes, such as the soil and water quality preservation (biogeochemical cycling, organic contaminant degradation, biomass production). Antibiotics can inhibit or kill these microbial communities with the consequent altering or disappearance of their ecological functions and the linked ecosystem services. Antibiotic concentrations in natural environments are generally highest in areas with high anthropogenic pressure. Given the dense population, the Mediterranean coastal zone is therefore potentially subject to high concentrations that can have - largely unknown - synergistic effects with other contaminants. Turkey is reported to have the highest consumption of antibiotics in the Mediterranean region, with 38.18 DDD/1000 inhabitants/day, respectively. The consumption of antibiotics in southern European countries is up to four times higher than in northern European countries, with Greece, Spain, and France among the highest per capita consumption of antibiotics (>23DDD/1000 inhabitants/day) (ECDC, 2019). In addition, the chronic presence of subtherapeutic quantities in natural environments, raises concerns about the development of antibiotic resistance in bacteria. The emergence of antibiotic-resistant bacteria poses a high risk to human and veterinary health, making it harder or even potentially impossible to cure certain infectious diseases in the future, and leading to longer hospital stays, higher medical costs and increased mortality. Medical research aimed at developing new antibiotics is currently not keeping pace with the rate at which bacteria develop antibiotic resistance.*

**DDD - Defined Daily Dose*

Catégories	Environmental Mixtures	
Organohalogenated compounds	Perfluorooctane sulfonate (PFOS)	● ●
	Perfluorooctanoic acid (PFOA)	● ●
	Perperfluorobutanoicacid (PFBA)	● ●
	Perfluorobutanesulfonate (PFBS)	● ●
	Tetrabromobisphenol A (TBBP-A)	● ●
	Dicofol (pesticide)	● ●
	Hexabromocyclododecanes (HCDs)	● ●
	Endosulfan (pesticide)	● ●
	Hexachlorocyclohexane isomers (HCHs)	● ●
	Methoxychlor (pesticide)	● ●
	Pentachlorophenol (PCP) (pesticide)	● ●
	Trifluralin (pesticide)	● ●
Organic nitrogen compounds	4-(dimethylbutylamino) dyphenilamine (6PPD)	● ●
Organic ester	Neodecanoic acid, ethenyl ester	● ● ●
Environmental phenols	Nonylphenol/Ethoxylates (NPs/NPEs)	● ●
	Octylphenol/Ethoxylates (OPs/OPEs)	● ●
	2, 4, 6-tri-tert-butylphenol	● ●
Pharmaceuticals	Clotrimazole	●
	Triclosan (phenol) and by-products	● ●
	Non-steroidal anti-inflammatory drugs	● ●
	Other antibiotics, bactericides, etc.	● ● ●
Hormones	Estrone (E1)	●
	17βEstradiol (E2)	●
	17αEthylinestradiol (EE1)	●
Phtalate esters	Dibutylphthalate (DBP)	●
	Diethylhexylphthalate (DEHP)	●
Synthetic musks	Musk xylene	
	Tonalide (AHTN)	● ● ●
	Galaxolide (HHCB)	● ● ●
Plastic additives (BVUSs)	Benzotriazoles (e.g., UV-P, UV-320, UV-326, UV-327, UV-328)	● ●
Metals/Elements	Arsenic	● ●
	Baryum	● ●
	Iron	● ●
	Manganese	● ●
	Molybdenum	● ●
	Nickel	● ● ●
	Vanadium	● ● ●
Organometallic compounds	Organic mercury (fish) (e.g., methylmercury)	(fish) ●

Primary matrices where pollutants are found:
● Biota ● Sediments ● Seawater

Fig. 3 - *Contaminants of Emerging Concern and detection in the environment*

Sources: USEPA; OSPAR, 2013; HELCOM, 2010; Richarson and Kimura, 2016; Tanabe et al., 2012; Dodder et al., 2014; MED POL, 2009; JRC, 2015; EU-WFD Watch List, 2015; Nakata et al., 2012; Picot et al., 2014; WHO

Conventions, Directives, Standards and Processes related to the monitoring and measurement of contaminants of emerging concern in the Mediterranean

Numerous conventions and protocols have been drafted and adopted over the years to outline CoEC monitoring and measuring in Europe and the Mediterranean. The following list provides these measures in sequential order:

- MAP/Barcelona convention (1976) prioritizing emerging pollutants in the Mediterranean region. This measure is relevant to the 22 Contracting Parties.
- EU water framework directive (2000), the aim is to achieve good ecological and chemical status of surface water. This directive is relevant to all EU member states.
- EU Environmental Quality Standards (EQS), defining maximum concentrations of a pollutant or group of pollutants in water, sediment or biota in order to protect human health and the environment. This measure is relevant to all EU member states.
- Stockholm Convention (2001) on Persistent Organic Pollutants (POPs), with the aim to eliminate or restrict the production and use of POPs. There are 184 parties to the Convention, including 183 states and the EU. In the Mediterranean area, only Israel and Italy have not yet ratified the Convention.
- EU Marine Strategy Framework Directive (2008), the aim is to achieve good environmental status of the European marine waters, with two descriptors linked to contaminants. This directive is relevant to all EU member states.
- The Ecosystem Approach (EcAP), adopted by the Contracting Parties to the Barcelona Convention (2008). With the aim of achieving good environmental status of the Mediterranean Sea, it includes an ecological objective on pollution.
- Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. This measure is relevant to all EU member states.

References

- European Centre for Disease Prevention and Control. Antimicrobial consumption in the EU/EEA, annual epidemiological report for 2018. Stockholm: ECDC; 2019.
- Robert Loos, Dimitar Marinov, Isabella Sanseverino, Dorota Napierska and Teresa Lettieri, Review of the 1st Watch List under the Water Framework Directive and recommendations for the 2nd Watch List, EUR 29173 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-81839-4, doi: 10.2760/614367 ,JRC111198.
- Brumovský, M., et al., Contaminants of emerging concern in the open sea waters of the Western Mediterranean, Environmental Pollution (2017), doi: 10.1016/j.envpol.2017.07.082.
- Barbosa, M.O., Moreira, N.F.F., Ribeiro, A.R., Pereira, M.F.R. & Silva, A.M.T. (2016). Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. Water Research, 94: 257–279. doi: 10.1016/j.watres.2016.02.047.
- Backhaus, T., Scholze, M., Grimme, L.H. The single substance and mixture toxicity of quinolones to the bioluminescent bacterium Vibrio fischeri, Aquatic Toxicology, Volume 49, Issues 1–2, 2000, Pages 49-61, ISSN 0166-445X.
- Backhaus, T., Porsbring, T., Arrhenius, Å., Brosche, S., Johansson, P. and Blanck, H. (2011), Single-substance and mixture toxicity of five pharmaceuticals and personal care products to marine periphyton communities. Environ- mental Toxicology and Chemistry, 30: 2030-2040. doi: 10.1002/etc.586.
- Dulio, V., van Bavel, B., Brorström-Lundén, E. et al. Emerging pollutants in the EU: 10 years of NORMAN in support of environmental policies and regulations. Environ Sci Eur 30, 5 (2018). doi: 10.1186/s12302-018-0135-3.
- Gadelha, J.R., Rocha, A.C., Camacho, C., Eljarrat, E., Peris, A., Aminot, Y., Readman, J.W., Boti, V., Nannou, C., Kapsi, M., Albanis, T., Rocha, F., Machado, A., Bordalo, a., Valente, L.M.P., Nunes, M.L., Marques, A and Almeida, C.M.R. 2019. Persistent and emerging pollutants assessment on aquaculture oysters (Crassostrea gigas) from NW Portuguese coast (Ria De Aveiro). Science of The Total Environment. Volume 666, Pages 731-742, ISSN 0048- 9697. doi: 10.1016/j.scitotenv.2019.02.280.
- Nodler, K., Voutsa, D., Licha, T., 2014. Polar organic micropollutants in the coastal environment of different marine systems. Mar. Pollut. Bull. 85, 50e59. doi: 10.1016/j.marpolbul.2014.06.024.
- WHO, 2018. WHO report on surveillance of antibiotic consumption: 2016-2018 early implementation. Geneva: World Health Organization; 2018. Licence: CC BY-NC-SA 3.0 IGO.

Head of publication: François Guerquin, (Plan Bleu Director)
Authors: Severine Larroze (Aquabiotech), Manya Russo (Aquabiotech), Juliana R. Gadelha (Aquabiotech), Lina Tode (Plan Bleu Deputy Director)
Reviewers: Yves Henocque (Plan Bleu Vice-President), Pierre Boissery (Agence de l'eau Rhône Méditerranée Corse)
Design and production: Manlio Malenchini (Aquabiotech), Pauline Simon (Plan Bleu Communication Officer), Zen Studio (Marseille)
Legal deposit: ISSN 2606 61 06