QUALITY STANDARDS FOR ALKYL-ORGANOPHOSPHATE ESTER FLAME RETARDANTS TO PROTECT AQUATIC ECOSYSTEMS

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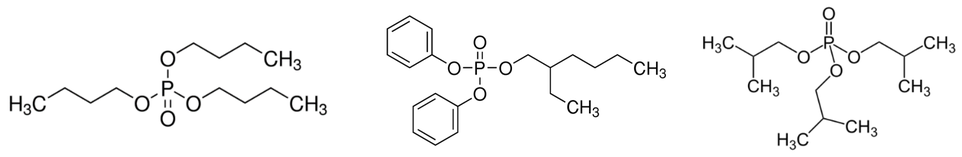
INTRODUCTION AND OBJECTIVES

Alkyl-organophosphate esters (OPEs) are a group of organophosphorus flame retardants (PFRs) in expanding use world-wide. The major drivers of growth for this market are stringent government regulations related to prohibition of polybrominated diphenyl ethers (PBDEs), growing awareness on fire safety and increasing market penetration of PFRs in various end-use industries including the manufacture of plastic products.

Latest scientific works highlighted that some OPEs could exhibit similar properties as Persistent Organic Pollutants [1]. However, while their environmental occurrence is more and more studied, little is known about the risk they could represent for living organisms. To address the issue, the CARE MED project (concentration. accumulation and potential risks of anthropogenic contaminants in coastal environments in the NW Mediterranean Sea) ambitions to investigate widely used OPEs (manufactured > 1000 T/y) coastal concentrations, their transfer in Mediterranean food webs and to derive quality standards in order to assess their potential risks to marine organisms and human health.

The specific objectives of this work are: (a) to estimate safe concentrations for pelagic and benthic species, top predators and humans consuming fishery products, or quality standards (QS), in marine water. sediment and biota of 3 widely used alkyl-OPEs (Fig.1): Tri-n-buthyl phosphate (TnBP). 2-Ethylhexyl diphenyl phosphate (EHDPP) and Tri-iso-buthyl phosphate (TiBP) according to the last version of the EC Technical Guidance to derive Environmental Quality Standards (TG EQS) [2] using up-to-date regulatory and research data (b) to assess their level of uncertainties in order to facilitate their use by risk managers and to highlight data gaps for consideration by policy makers and researchers.



TnBP
CAS number: 126-73-8

EHDPP
CAS number: 1241-94-7

TiBP
CAS number: 126-71-6

Fig. 1 Molecular structure and CAS number of the three studied alkyl-OPEs

APPROACH

QS derivation: As represented schematically in Fig.2, **r**elevant data on phys-chem properties, fate and behavior and toxicity were collected online from scientific published literature (mostly peer-reviewed) and disseminated data by regulatory bodies (mostly REACH registration data by ECHA). The reliability of data non previously validated by competent authorities has been assessed according to the Klimisch methodology [3]. In case of missing information, reliable QSARs predictions were used for non toxicological endpoints (e.g. BCF for TiBP) or for the uncertainty assessment of QS. In the CARE MED project, only saltwater bodies are considered and being not intended for the production of drinking water in the study area, this protection objective for humans haven't been taken into account for QS water derivation.

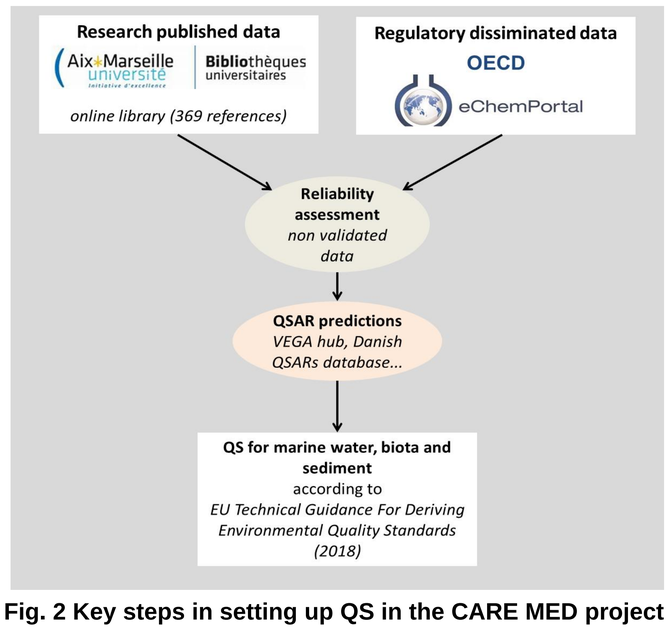


Fig. 2 Key steps in setting up QS in the CARE MED project

Reliability of QS: As part of the project, the uncertainties associated with the derivation of the QS were translated in terms of a reliability index represented by a "star code" assessed according to the general methodology described in Fig.3. However, the final score can be modulated according to other factors and remained subject to expert judgment.

Reliability	Available dataset	Assessment factor	Other factor of uncertainty
High ***	Extended	Minimal	None
Medium **	Fair	Medium	Medium
Low *	Minimal	Maximal	High

Fig. 3 Main criteria to assess the reliability of the derived QS

RESULTS

	TnBP	EHDPP	TiBP
Saltwater	Driven by the protection of pelagic species	Driven by the protection of pelagic species	Driven by the protection of pelagic species
MAC-QS (µg.L^{-1})	**6.6 ****	**0.2 ****	**110 ****
AA-QS (µg.L^{-1})	**6.6 ****	**0.2 ****	**1.1 ***
Saltwater biota	Driven by the protection of humans from secondary poisoning	Driven by the protection of predators from secondary poisoning	Driven by the protection of predators from secondary poisoning
QSbiota. sec pois (µg.kg^{-1}biota)	**3652 ****	**811 ****	**18888 ****
Saltwater sediment	Driven by the toxicity on pelagic organisms (EqP)	Driven by the toxicity on pelagic organisms (EqP)	Driven by the toxicity on pelagic organisms (EqP)
QSsediment (µg.kg^{-1}sed ww)	**252 ***	**41 ***	**28 ***
(µg.kg^{-1}sed dw)	**656 ***	**106 ***	**73 ***

Fig. 4 Quality Standards as marine threshold concentrations for three alkyl-OPEs

QS water: Maximum Acceptable Concentration (MAC-QS) and Annual Average concentration (AA-QS) are driven by the protection of pelagic species. In the absence of toxicological data on marine organisms (except on bacteria for TnBP), data on freshwater organisms were used to derive QS in saltwater in accordance with TG EQS recommendation. AA-QS values for TnBP are similar or equivalent to previously derived standards by RIVM [4] and INERIS [5], respectively.

QS biota: are driven by the protection of predators for EHDPP and TiBP and by the protection of humans for TnBP. QS biota values are highly variable between the three OPEs with the lowest value for EHDPP**.** The updated methodology for the derivation of QS biota for top predators being not applicable due to the lack of relevant data, the standard approach described in the previous version of the TG EQS [6] was used instead.

QS sediment: were derived based on the Equilibrium Partitioning approach since no toxicity data on sediment organisms where available for none of the three OPEs.

Reliability of QSs: All derived QS have a medium reliability except the AA-QS for TiBP and the QS sediment that have all a low reliability.

CONCLUSIONS and PERSPECTIVES

- ✓ Dissemination activities by the regulatory authorities is a major source of data for the derivation of QS and contribute greatly to improve their reliability.
- ✓ Main data gaps on toxicity are identified for marine pelagic organisms, birds and benthic organisms for the derivation of QS for saltwater, biota and sediment, respectively.
- ✓ Bioconcentration and biomagnification data in relevant food chains for secondary poisoning consideration are also missing jeopardizing the use of the methodology described in the updated TG EQS.
- ✓ In the framework of the CARE MED project, BCF and BMF/TMF values for a representative coastal Mediterranean trophic chain will be estimated allowing the improvement of the established QS.
- ✓ The comparison of the QS with the environmental concentrations measured in water, fish and sediment will allow to assess if the 3 alkyl-OPEs present a risk for the marine organisms living in the Golf of Lion (NW Mediterranean Sea) and humans consuming fishery products from this area.
- ✓ Finally, more QS will be derived for substances used in plastic products, including chlorinated OPEs and phthalates, some having validated or potential endocrine disrupting properties.

References

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