# Risk assessment of organophosphate ester flame retardants in aquatic environments using EQS derivation with up-to-date REACH and research monitoring data

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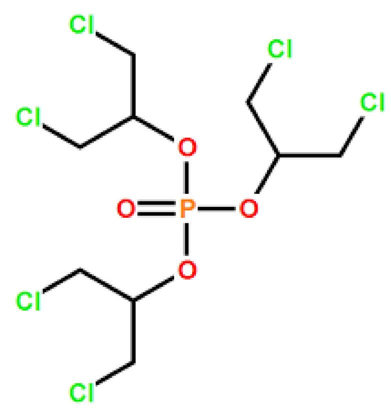
## INTRODUCTION

Organophosphate esters (OPEs), are a group of organophosphorus flame retardants (PFRs) and plasticizers in expanding use world-wide (annual global consumption of PFRs reached ~ 300 000 tons in 2011 and a 5% annual increase expected). Latest scientific works highlighted that some OPEs could exhibit similar properties to persistent organic pollutants (POPs), meaning they can be highly persistent, prone to long-range atmospheric transport, can bioaccumulate and may have adverse effects in the environment and humans.

Recent progress in the EU chemical policies together with the increasing research efforts on the monitoring of OPEs concentrations and on the study of their environmental partitioning and fate represent interesting opportunities to investigate if these chemicals could present a risk for environmental organisms and humans. First, the new data generated and disseminated through the REACH regulation framework and the up-to-date guidance to derive Environmental Quality Standards (EQS) under the Water Framework Directive (WFD), allow to assess safe concentrations, the so-called Quality Standards (QS), for **pelagic** and **benthic** species, **top predators** and **humans**. Second, the increase of the number and quality of field measurements of OPE concentrations in relevant environmental compartments (e.g. air, inland and marine surface waters, sediments and biota) provide current OPE environmental levels.

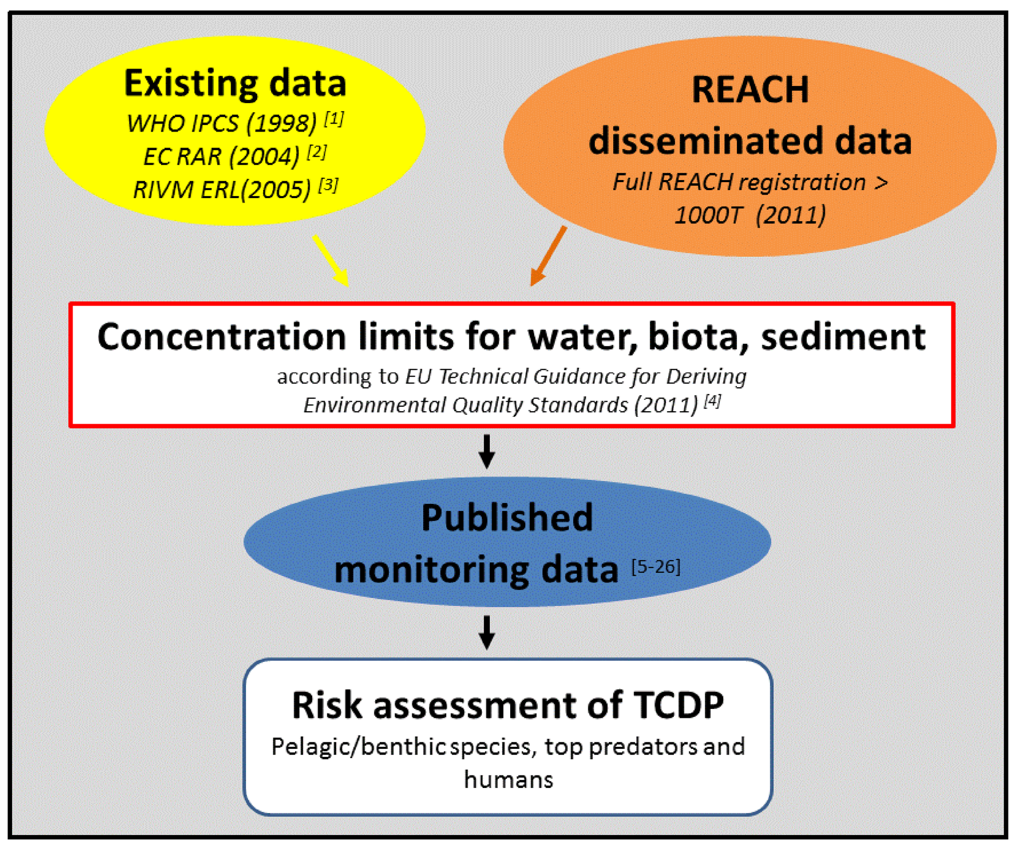
## OBJECTIVES

The objectives of this work are: (1) to estimate safe levels (in water, sediment and biota) of Tris [2-chloro-1-(chloromethyl ethyl)] phosphate (TDCP), one of the most widely used organochlorine OPEs, for humans consuming drinking water / fishery products, pelagic and benthic species and birds / mammals top predators; (2) to assess the suitability and availability of monitoring data in order to identify potential risks for target organisms and humans due to environmental exposure to TDCP.




TDCP
*CAS number: 13674-87-8*

## APPROACH




## RESULTS and DISCUSSION

### ESTIMATED (SAFE) THRESHOLD CONCENTRATIONS: Quality Standards (QS)

| | Protection Objective | Threshold levels | Rationale / Uncertainties |
|---|---|---|---|
| WATER | **PELAGIC** community freshwater | **1.1 µg L-1** | Driven by acute toxicity on the most sensitive species: fish |
| | **PELAGIC** community seawater | **0.1 µg L-1** | Driven by acute toxicity on the most sensitive species: fish |
| | **HUMAN** health *via* consumption of drinking water | **5.9 µg L-1** | Threshold level derived from repeated dose toxicity (DNEL) with an additional assessment factor for carcinogenicity |
| **BIOTA** (and WATER *via* concentration conversion) | **TOP PREDATORS** freshwater | **140 µg Kg-1 biota** | Mammals and birds reliable data available; Driven by mammals toxicity |
| | and corresponding value in water | **1.2 µg L-1** | Not assignable experimental BCF and default BMF |
| | **TOP PREDATORS** seawater | **140 µg Kg-1 biota** | Mammals and birds reliable data available; Driven by mammals toxicity |
| | and corresponding value in water | **1.2 µg L-1** | Not assignable experimental BCF and default BMF |
| | **HUMAN** health via consumption (fishery products) | **104 µg Kg-1 biota** | Threshold level derived from repeated dose toxicity (DNEL) with an additional assessment factor for carcinogenicity |
| | and corresponding value in freshwater and seawater | **0.9 µg L-1** | Not assignable experimental BCF and default BMF |
| SEDIMENT | **BENTHIC** community freshwater | **390 µg Kg-1dw** | Chronic toxicity data available on three species with different living and feeding conditions; Concentrations fluctuations in the *Chironomus riparius* test (most sensitive species) might led to over protective QS |
| | **BENTHIC** community seawater | **78 µg Kg-1dw** | Chronic toxicity data available on three species with different living and feeding conditions; Concentrations fluctuations in the *Chironomus riparius* test (most sensitive species) might led to over protective QS |

Existing data were available in three previous reports published by international, European and national authorities. New REACH data disseminated by ECHA allowed us to derive robust QS for:

**WATER***

**Freshwater: QS fw = 0.9 µg $L^{-1}$**
(humans consuming fishery products being the most sensitive group after water concentration conversion)

**Seawater: QS sw = 0.1µg $L^{-1}$**
(pelagic species being the most sensitive group)

**BIOTA (freshwater and seawater)**

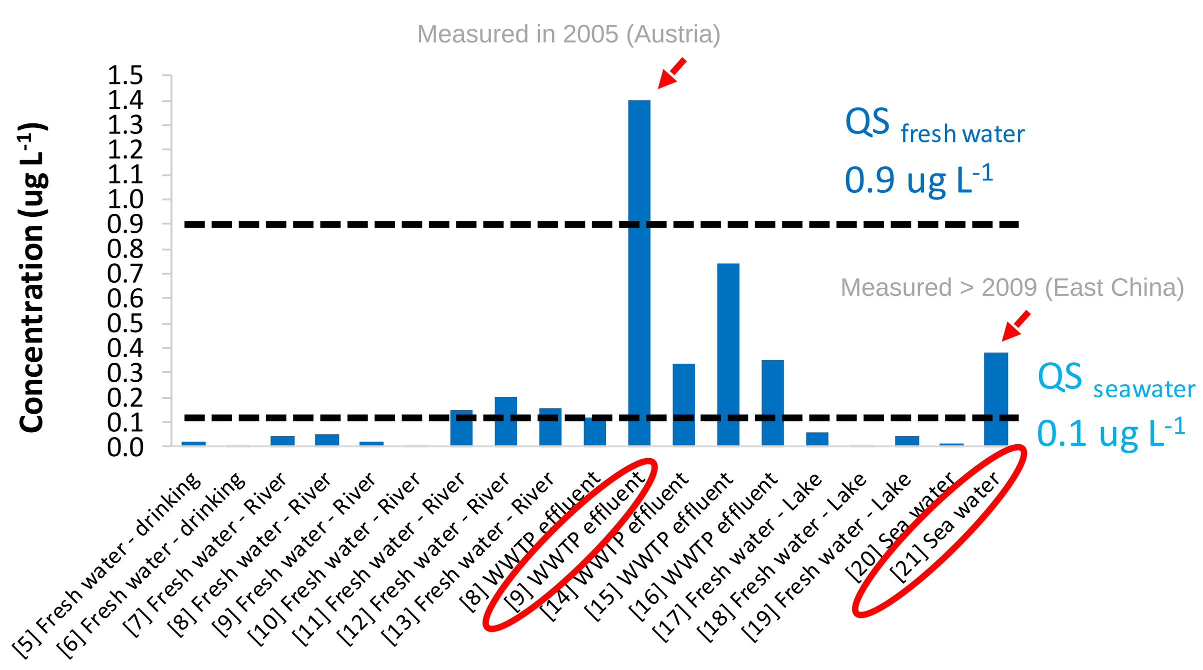
**$QS_{biota}$ = 104 µg $Kg^{-1}$**
(humans consuming fishery products being the most sensitive group)

**SEDIMENTS**

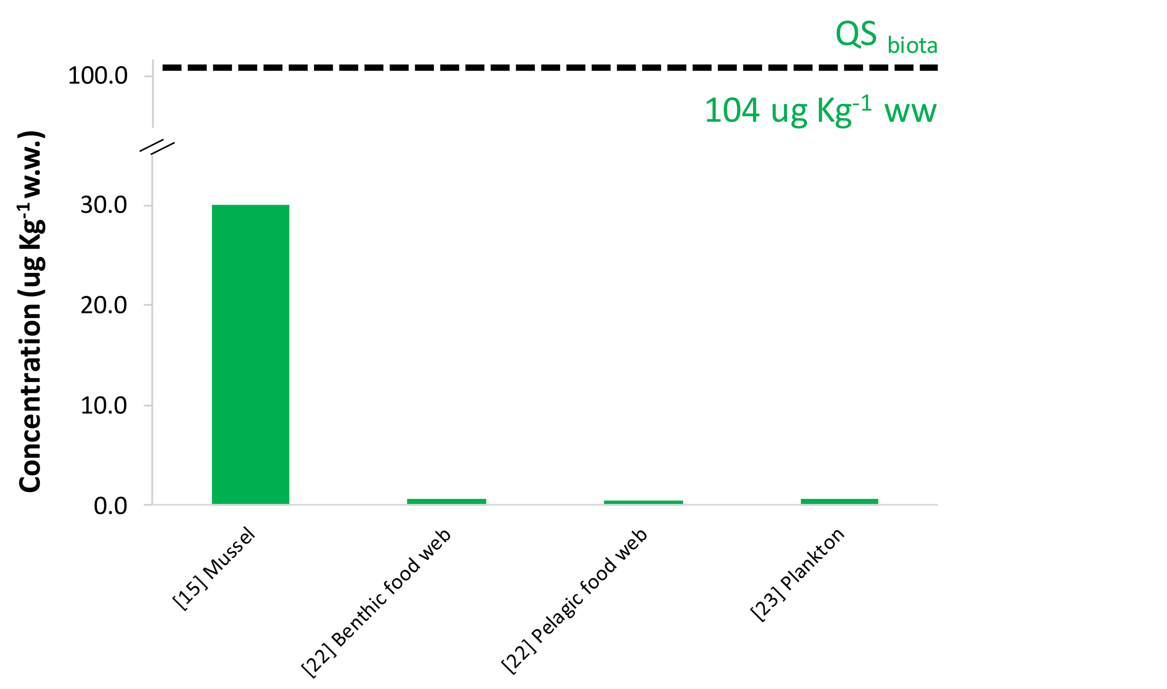
**Freshwater: $QS_{sed}$ fw = 390 µg $Kg^{-1}$dw**
**Seawater: $QS_{sed}$ sw = 78 µg $Kg^{-1}$dw**

* New chronic data on invertebrates were insufficient to reduce the uncertainty of the QS waters because they are not the most sensitive species.

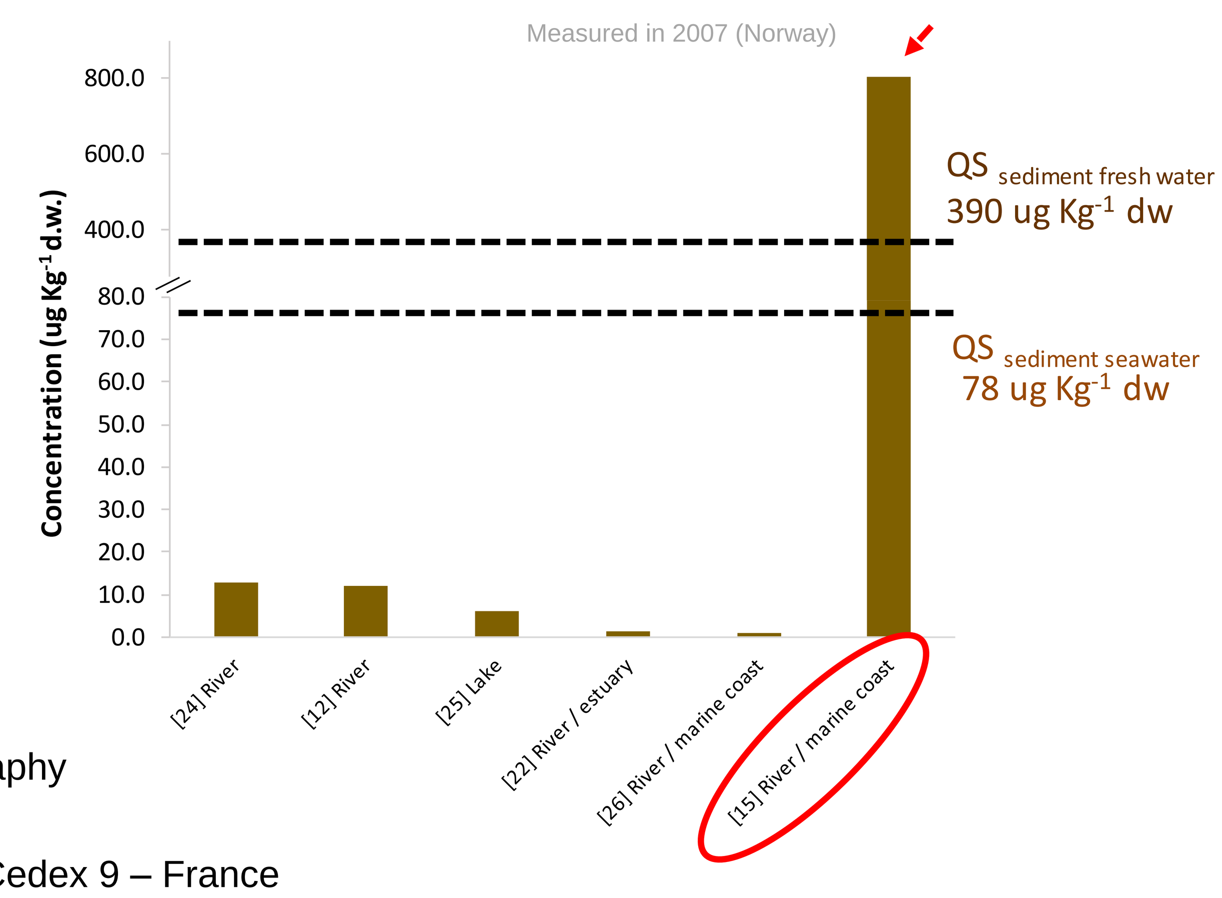
### RISK ASSESSMENT of TDCP in WATER




### RISK ASSESSMENT of TDCP in BIOTA




### RISK ASSESSMENT of TDCP in SEDIMENTS




**Monitoring data** (environmental concentrations of TDCP in water, sediment and biota) were extracted from available scientific literature (mostly peer-reviewed) published over the last ten years. Results revealed that most measurements have been carried out in inland surface waters (in particular rivers) with a general lack of data in marine waters. Few studies have been performed in sediments (and mostly from rivers and lakes) and very few data exists for biota. Many different sampling, analytical approaches and techniques were employed to quantify TDCP concentrations in selected matrixes. A particular issue was found with the analysis of TDCP (and others OPEs) in biota. Different parts of the organisms were analyzed (e.g. leaver, muscle, eggs, whole organism) and concentrations were expressed in different units (e.g. normalized by lipids, as dry weigh, as wet weight) difficult to compare and not always useful for the scope of the present work.

## CONCLUSIONS and RECOMMENDATIONS

- ✓ Disseminated data of REACH registered dossiers from ECHA website haven't been reviewed by the authorities and often the information provided is too scarce to allow an in-depth review of their reliability.
- ✓ Chronic data on fish (currently missing) would allow to reduce the uncertainties of the QS for waters.
- ✓ Although the reported TDCP environmental concentrations were generally below the estimated QS, these safe levels were overpassed in some environments indicating a potential risk. In addition, existing and new data on degradation don't allow to disregard the potential high persistency of TDCP, which could result in the increase of its environmental concentrations and stocks in the near future. So more efforts on the monitoring side (in particular in marine environments) and on the accurate determination of TDCP degradation rates under environmental conditions are recommended.
- ✓ QS should be derived for other OPEs widely used.
- ✓ An effort should be performed to generate reliable and comparable data on biotic matrixes.

**References**
**[1]** WHO IPCS. 1998. Flame Retardants: Tris(Chloropropyl) Phosphate and Tris(2-Chloroethyl) Phosphate. Environmental Health Criteria, Vol. 209. Geneva, Switzerland: World Health Organization; **[2]** European Commission JRC. 2004. TDCP. European Risk Assessment Report, Vol. 426. Ispra, Italy: European Chemicals Bureau, Institute for Health and Consumer Protection; **[3]** RIVM report 601501024/2005. Environmental Risk Limits for several phosphate esters, with possible application as flame retardant.; **[4]** European Commission - Guidance Document No. 27.Technical Report - 2011 – 055. Guidance For Deriving Environmental Quality Standards of Common Implementation Strategy for the WFD.; **[5]** Khan et al., Sci.Total Environ. 2016, 565 , 346–359.; **[6]** Li et al., Water Res. 2014, 53-61.; **[7]** Wang et al., Environ. Pollut. 2015, 198, 172-178.; **[8]** Andresen et al., Sci. Total Environ. 2004, 332 155–166.; **[9]** Martínez-Carballo et al., Sci. Total Environ. 2007, 388, 290-299.; **[10]** Van der Veen & de Boer. Chemosphere 2012, 88, 1119-1153., **[11]** Cristale et al., Environ. Pollut. 2013, 172, 163-169.; **[12]** Cristale et al., Environ. Int. 2013, 59, 232-243., **[13]** Wolschke et al., Environ. Pollut., 2015, 206, 488-493.; **[14]** Marklund et al., Environ. Sci. Technol. 2005, 39, 7423-7429.; **[15]** Green et al., NIVA Report 5569, 2008.; **[16]** Cristale et al., Environ. Res. 2016, 144, 11–18.; **[17]** Bacaloni et al., Environ. Sci. Technol. 2008, 42, 1898–1903.; **[18]** Venier et al., Environ. Sci. Technol. 2014, 48, 9563–9572.; **[19]** Huan et al., Chin. J. Anal .Chem. 2012, 40, 1693–1697.; **[20]** Andersen et al., Environ. Toxicol. Chem. 2007, 1081–1089.; **[21]** Hu et al., Mar. Pollut. Bull. 2014, 569–574.; **[22]** Brandsma et al., Sci. Total Environ. 2015, 505, 22–31.; **[23]** Greaves et al., Environ. Res. 2016, 150, 255–263.; **[24]** Stachel et al., J.Environ. Sci. Health A, 2005, 40, 265-287.; **[25]** Cao et al., Environ. Toxicol. Chem. 2012, 31, 1478–1484., **[26]** Chung & Ding. Anal. Bioanal. Chem. 2009, 95, 2325-2334

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