One-year monitoring of legacy and emerging contaminants in a coastal setting (Cadiz Bay, Spain) using a combined approach: passive samplers and sentinel organisms

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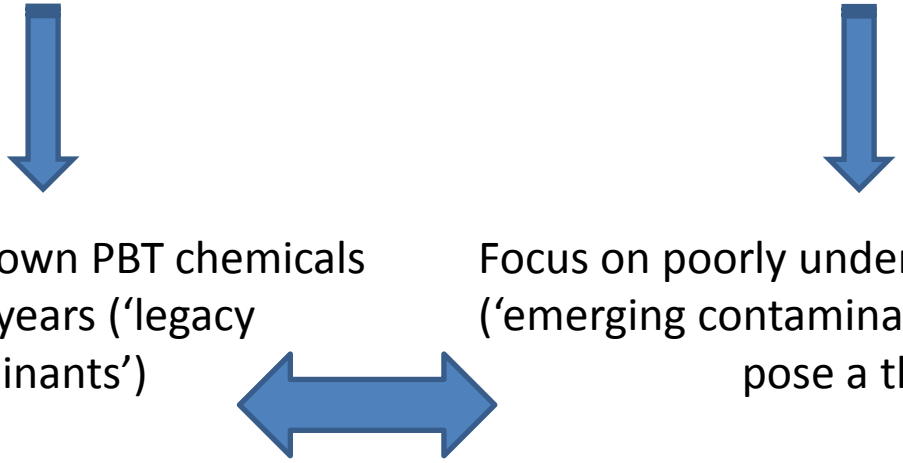
1. Introduction

Since the 1970s, monitoring of **persistent, bioaccumulative and toxic (PBT)** chemicals using analytical chemistry has provided important spatial and temporal trend data in three important contexts :

- Relating to human health protection from seafood contamination
- Addressing threats to marine top predators
- Providing essential evidence to better protect the biodiversity of commercial and non-commercial marine species



T.H. Hutchinson, B.P. Lyons, J.E. Thain and R.J. Law. Marine Pollution Bulletin 74 (2013) 517-525

2. Objectives

- To analyze a wide range of hydrophobic organic contaminants (log K_{ow} > 4, including legacy and emerging compounds) in water and biota from a highly urbanized coastal system (Bay of Cadiz, SW Spain).

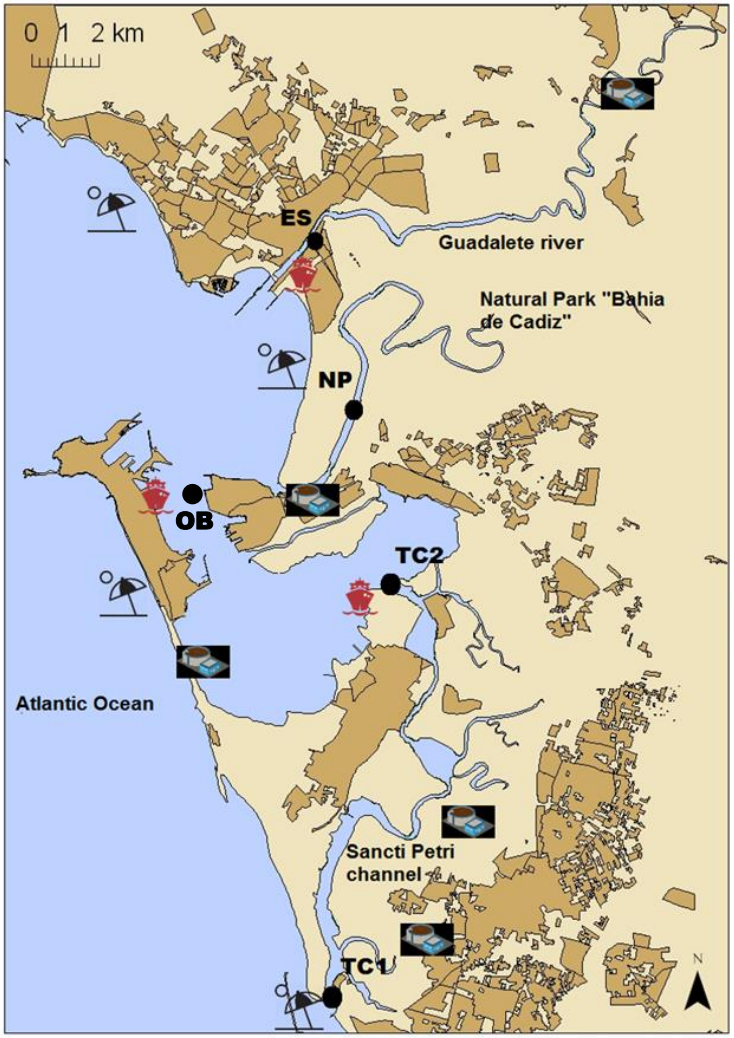
- To monitor their occurrence and distribution over a long time period (1 year) to determine seasonal changes in their inputs and concentrations by means of silicone-based passive samplers.

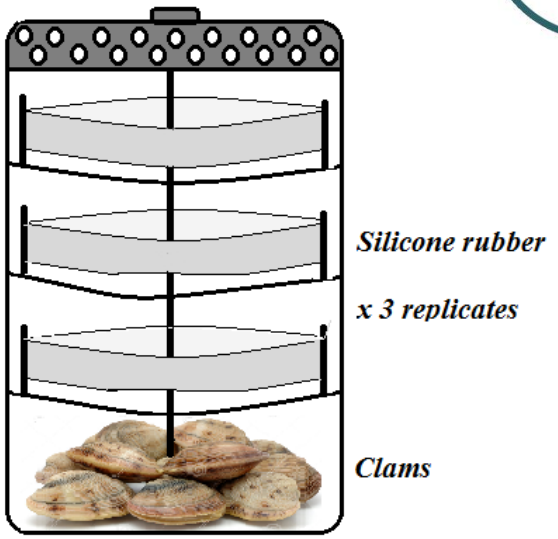
- To assess their bioaccumulation potential by parallel deployment of sentinel organisms (clams).

- To select those emerging compounds that are predominant in terms of concentration, frequency of detection and bioaccumulation potential and conduct further characterization of their environmental behavior and fate.

3. Methodology

3. Methodology





Silicone strips (100 x 2.5 cm) were prepared from Altesil™ (500 µm thickness). Performance reference compounds (PRCs) were added:

Fluoranthene d_{10} (FL-d_{10})
Chrysene d_{12} (CHR-d_{12})
Triphenylphosphate d_{15} (TPP-d_{15})
Triclosan d_3 (TCS-d_3)
Benzophenone d_{10} (BP- d_{10})

K. Booij, F. Smedes, and E.M. van Weerlee. Chemosphere 46 (2002) 1157-1161

3. Methodology

Passive samplers

Solid-liquid extraction

Every month in 2014

Clams (*R. philippinarum*)

PLE (ASE 200, Dionex)

GC-EI-MS/MS
(Scion, Bruker)

M.G. Pintado-Herrera, E. González-Mazo, and P. A. Lara-Martín. Journal of Chromatography A 1429 (2016) 107-118.

3. Methodology

Target compounds: legacy and emerging contaminants

PAHs
Naphthalene
Acenaphtene
Acenaphtylene
Anthracene
Fluorene
Phenanthrene
Pyrene
Chrysene
Benz[a]anthracene
Fluoranthene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Benzo[g,h,j]perylene
Indene[1,2,3-cd]pyrene

Organophosphorus flame retardants
TPP
TIBP
TNBP
TEHP
EHDPP
TTP

PCBs
PCB 52
PCB 101
PCB 138
PCB 180

Antimicrobials
Triclosan
Me-TCS

Nonylphenol
Chlorpyrifos
Irgarol

UV filters
2-OHBP
Benzophenone-3
Octocrylene
HMS
EHS
EHMC
4-MBC

Fragrances
Musk xylene
Musk ketone
Galaxolide
Tonalide
Celestolide
OTNE

3. Methodology

$$Cw = \frac{Np}{Kpw\ mp\ (1 - e^{-Rs\ t / Kpw\ mp})}$$

Np = measured mass of each analyte
mp = mass of the silicone strip
t = exposure time
Kpw = polymer-water partition coefficient (refs. 1 and 2)
Rs = sampling rate → PRC dissipation data and unweighted NLS model (refs. 3 and 4):

$$log\,Rs = log\,\beta - 0.08 \log K_{pw}$$

1. M.G. Pintado-Herrera, P.A. Lara-Martín, E. González-Mazo, and I.J. Allan. Environmental Toxicology & Chemistry 35 (2015) 2162-2172.

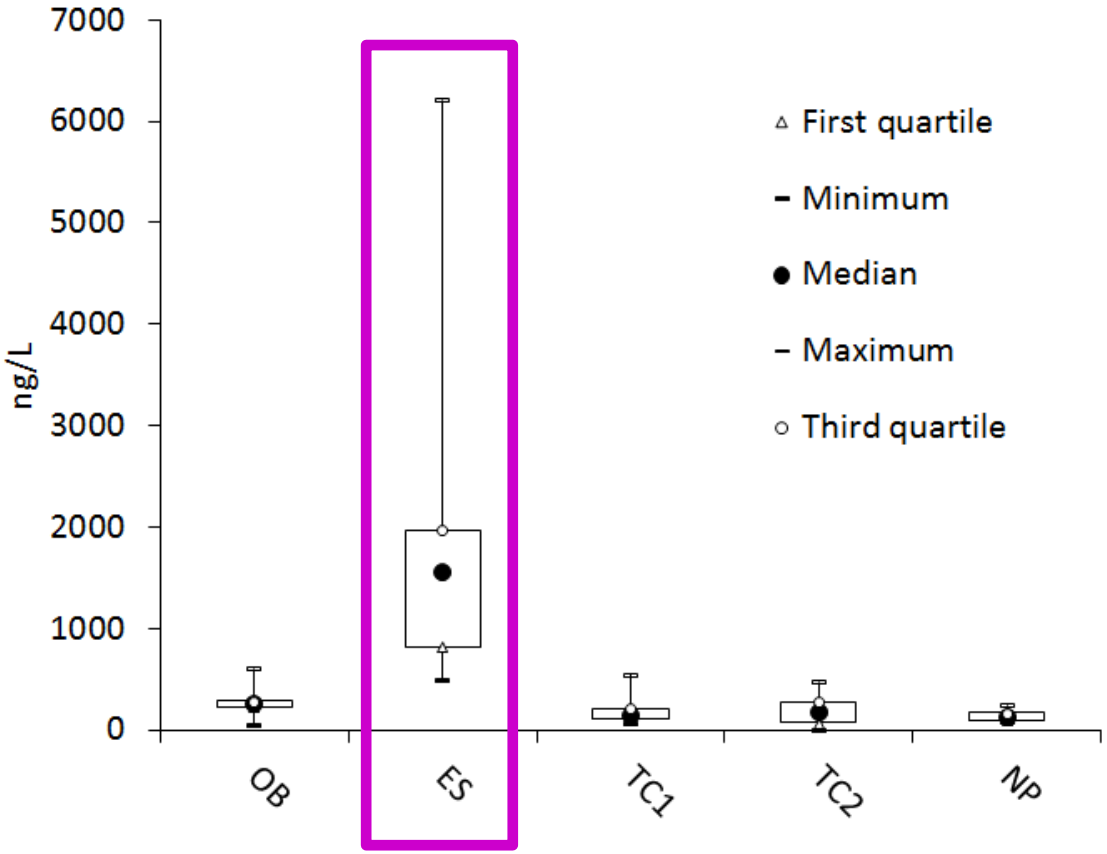
2. F. Smedes, R.W. Geertsma, T. van der Zande, and K. Booij. Environmental Science & Technology 43 (2009) 7047-7054.

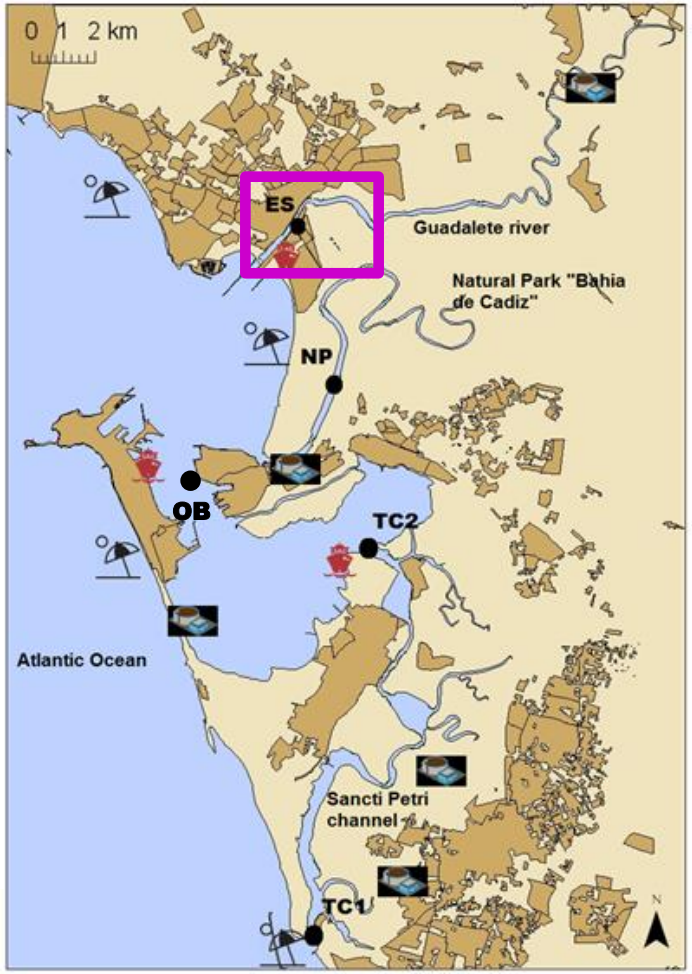
3. K. Booij and F. Smedes. Environmental Science & Technology 44 (2010) 6789-6794.

4. T.P. Rusina, F. Smedes, M. Koblizkova, and J. Klanova. Environmental Science & Technology 44 (2010) 362-367.

4. Results and discussion

Passive samplers





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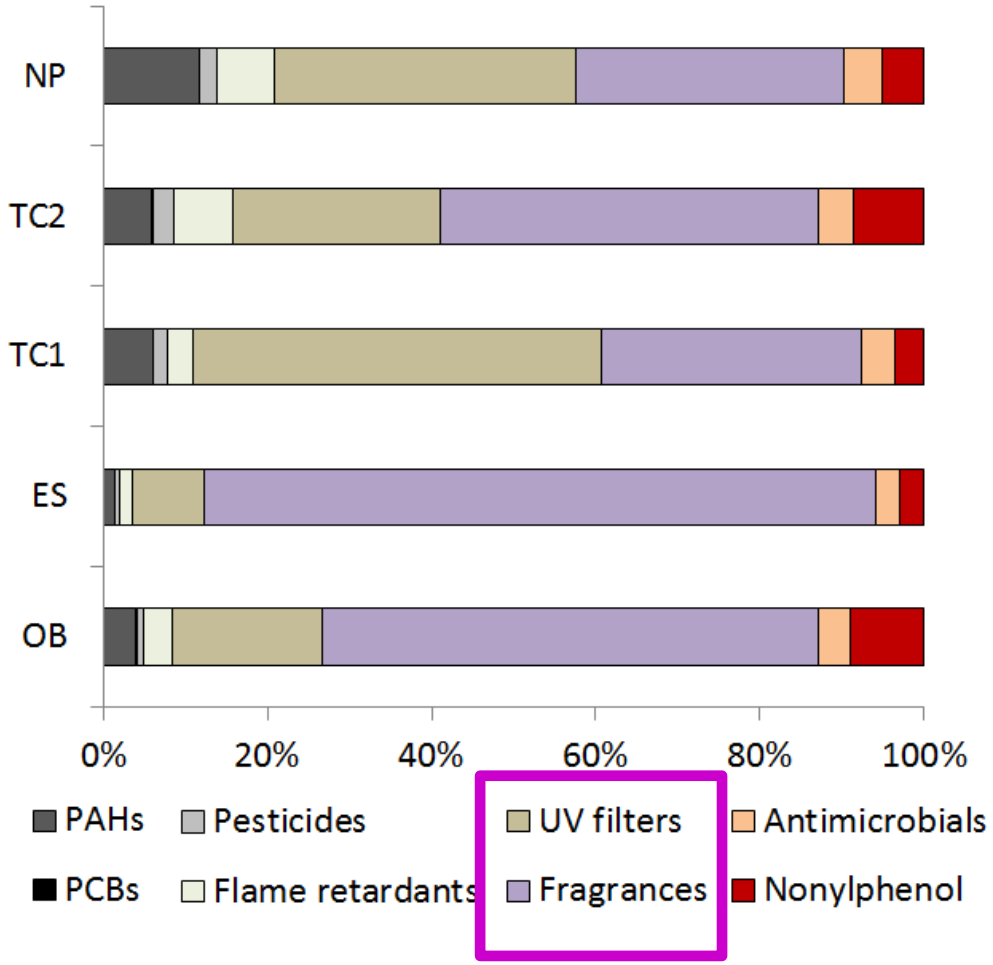
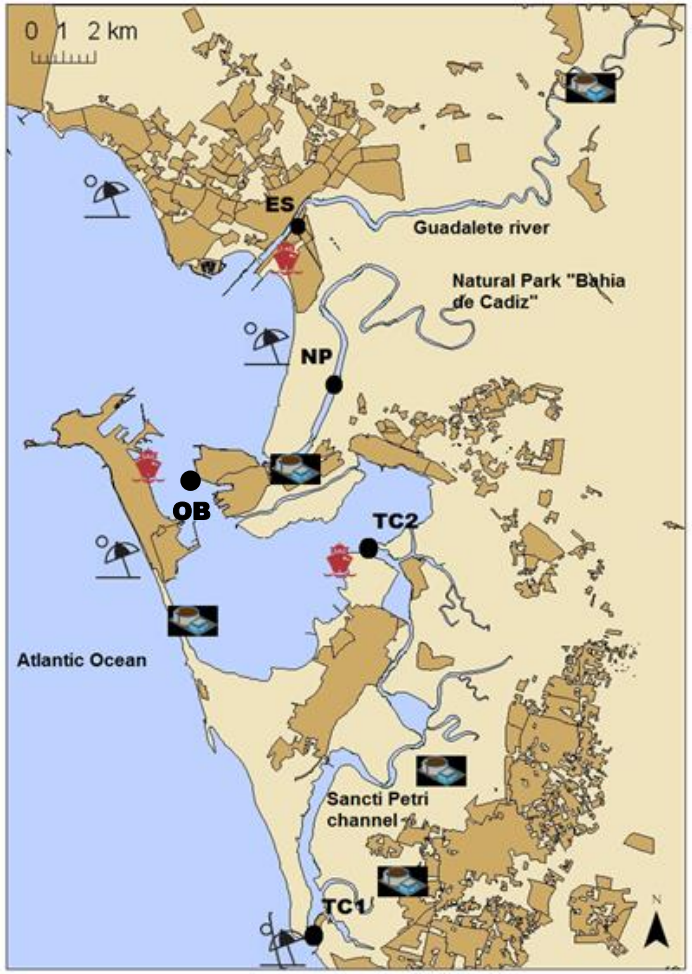
Passive samplers





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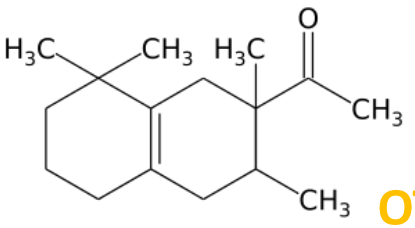
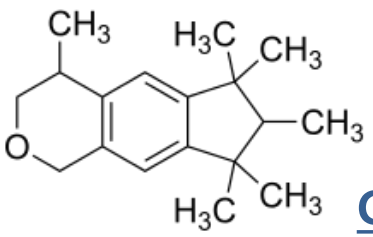
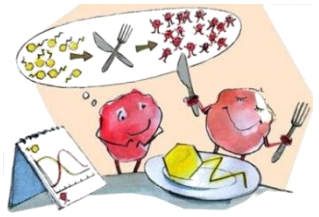


OTNE



Galaxolide



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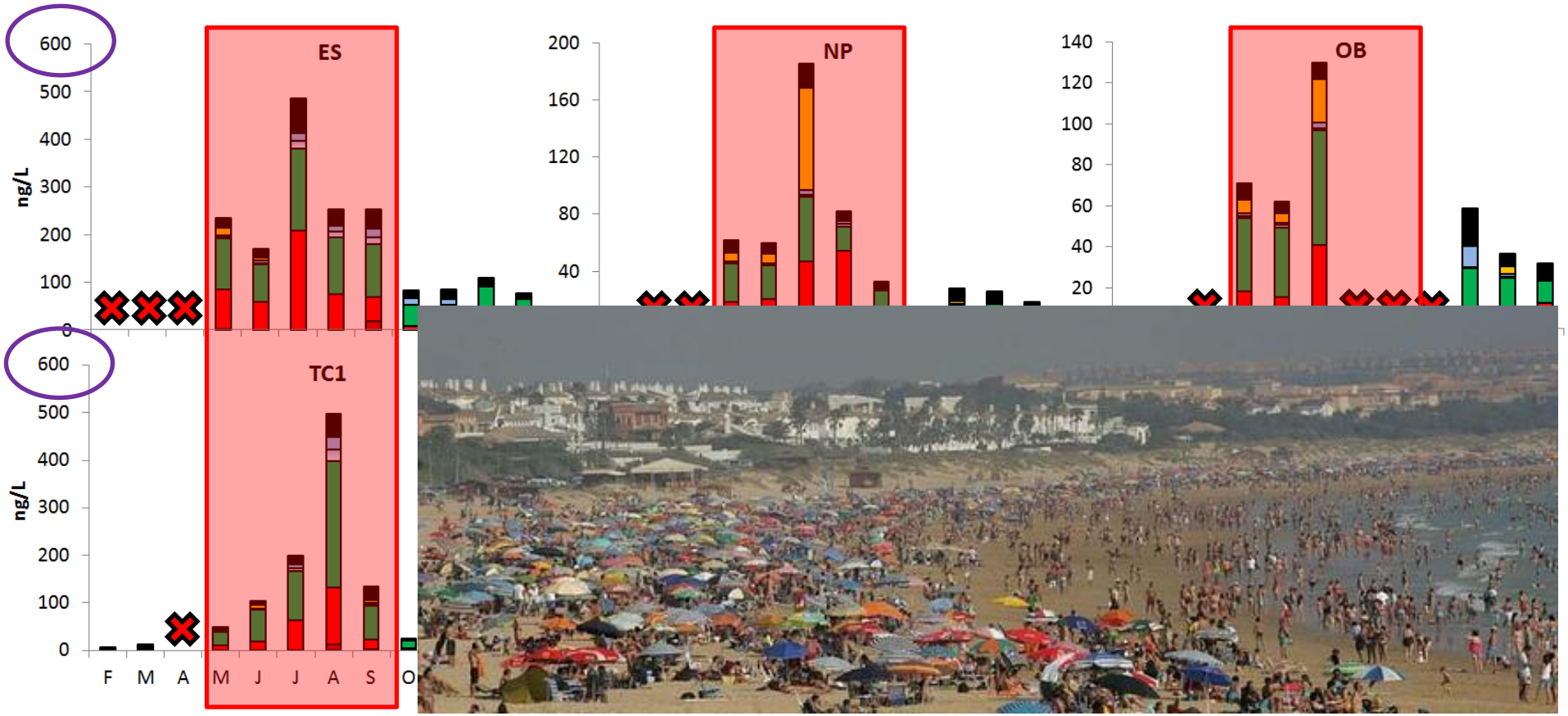
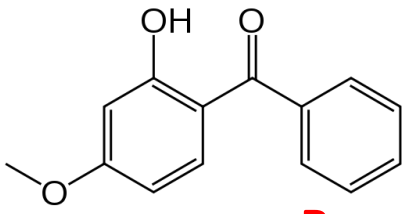
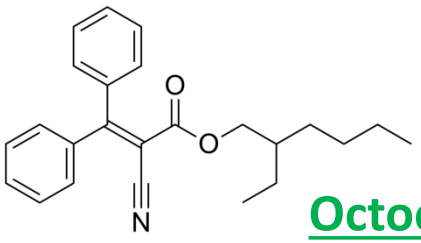


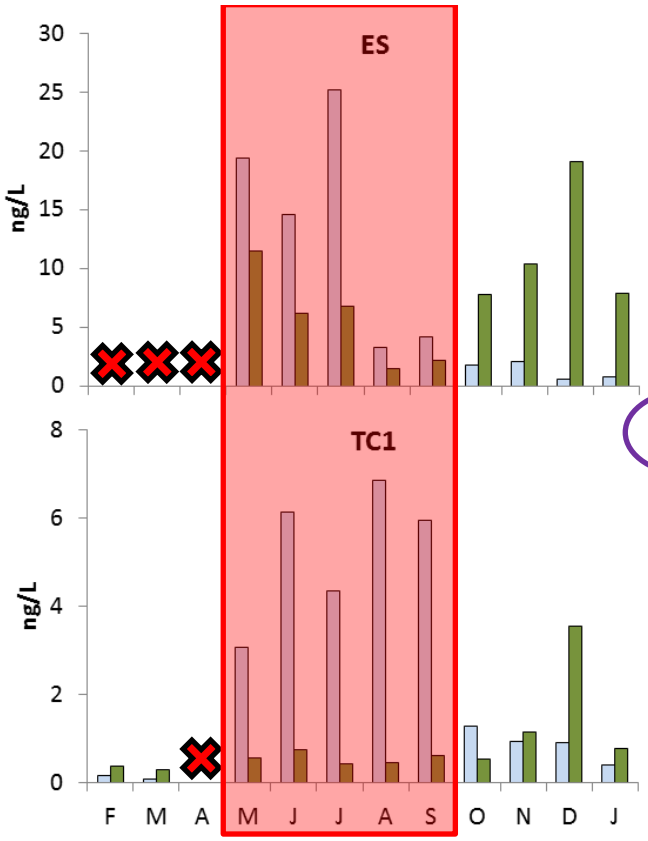


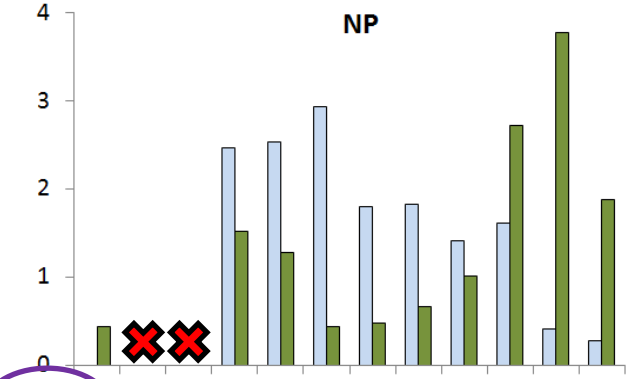
Benzophenone 3

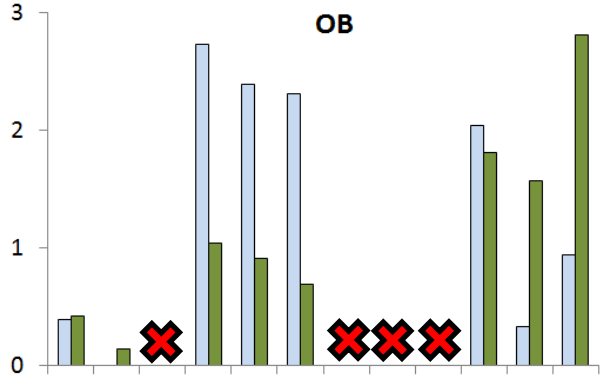


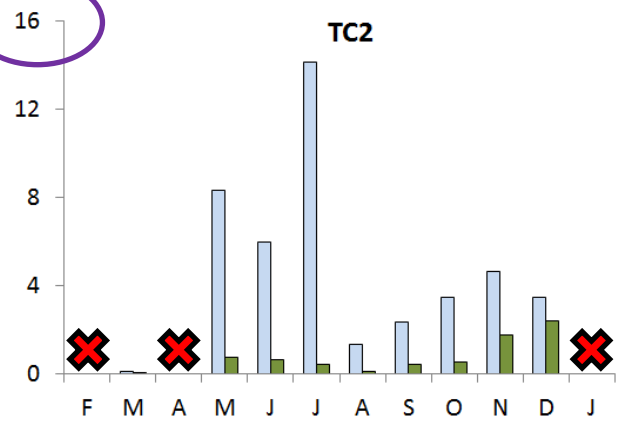
Octocrylene

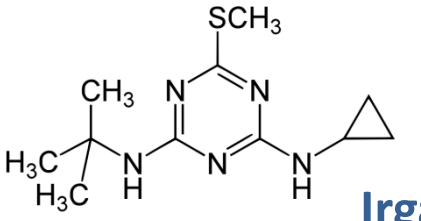
4. Results and discussion



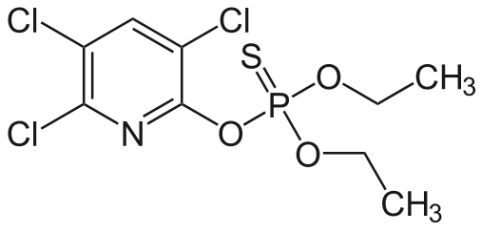








Irgarol

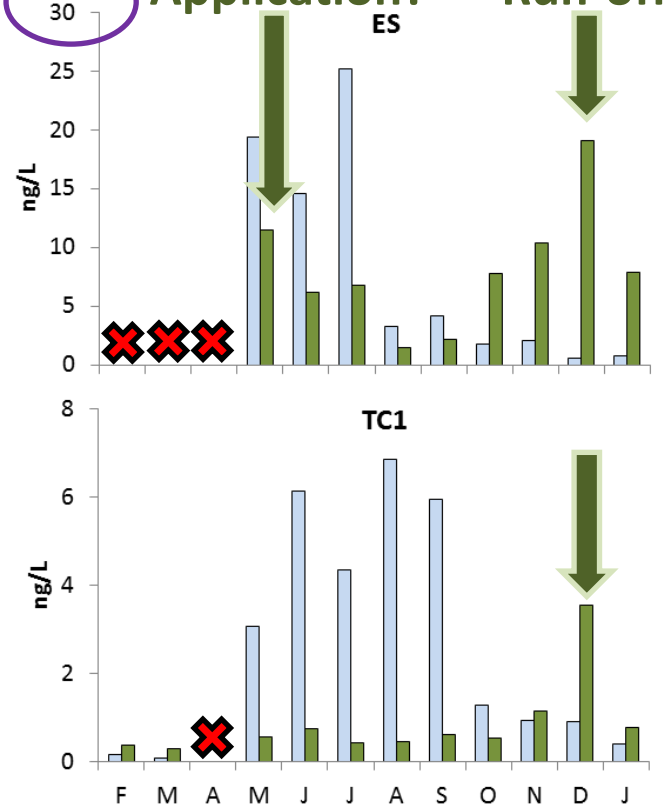


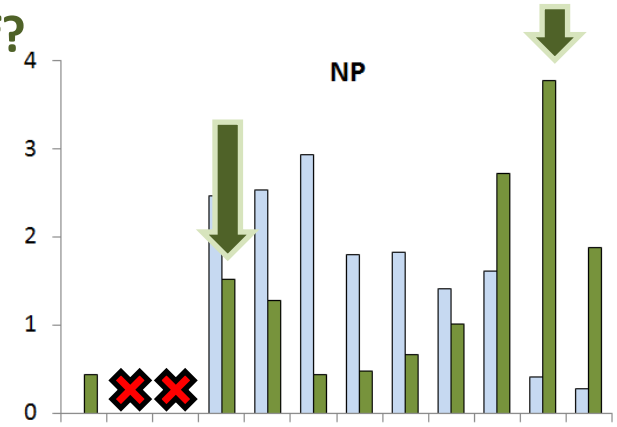
Chlorpyrifos

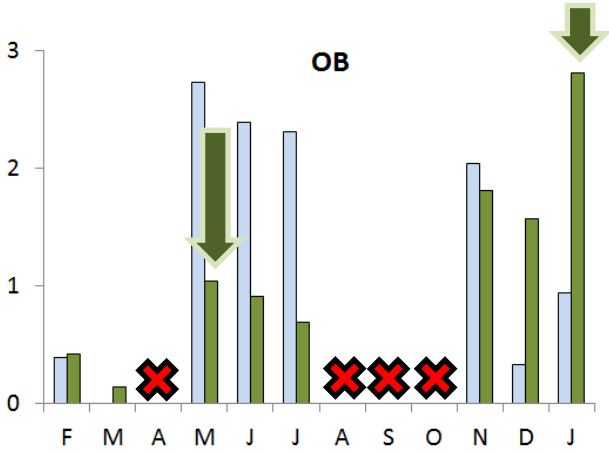
4. Results and discussion

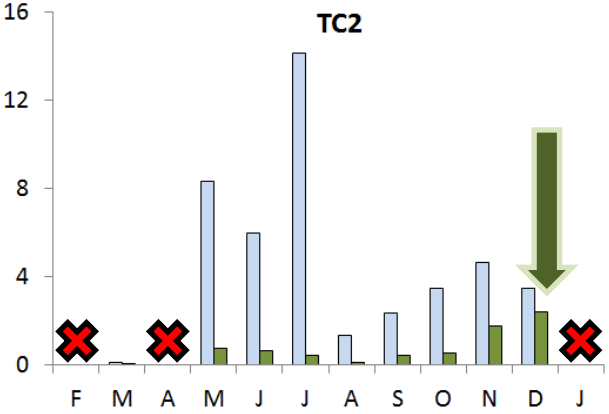
Application?

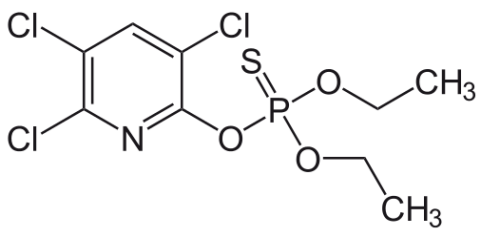
Run-off?







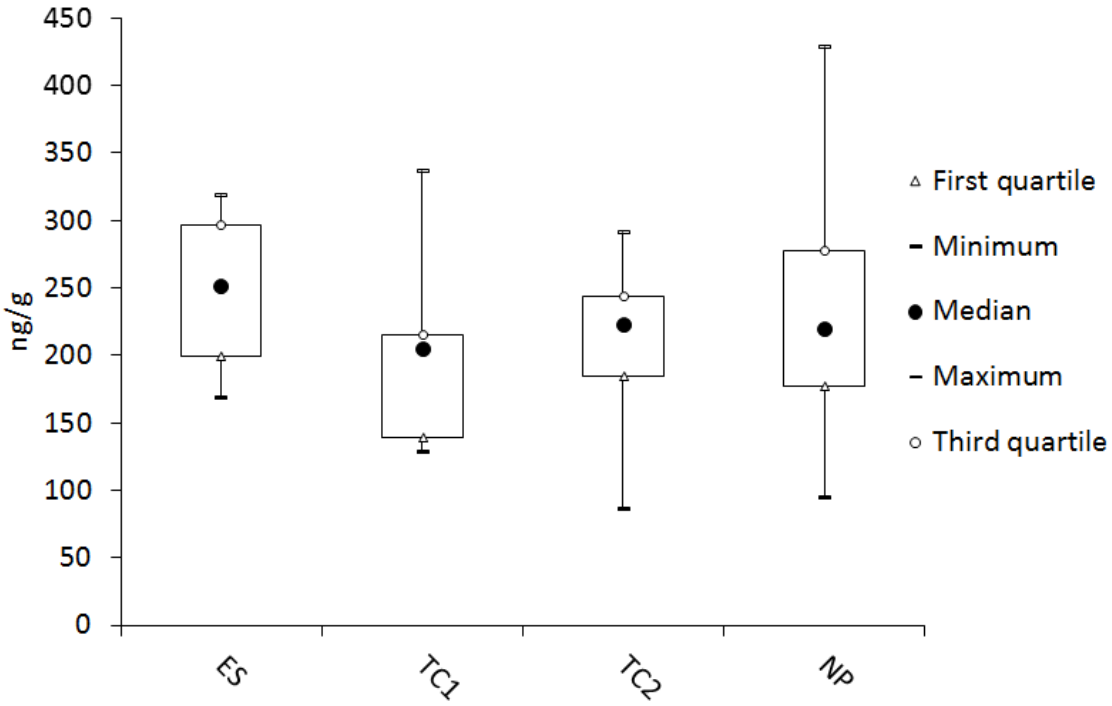


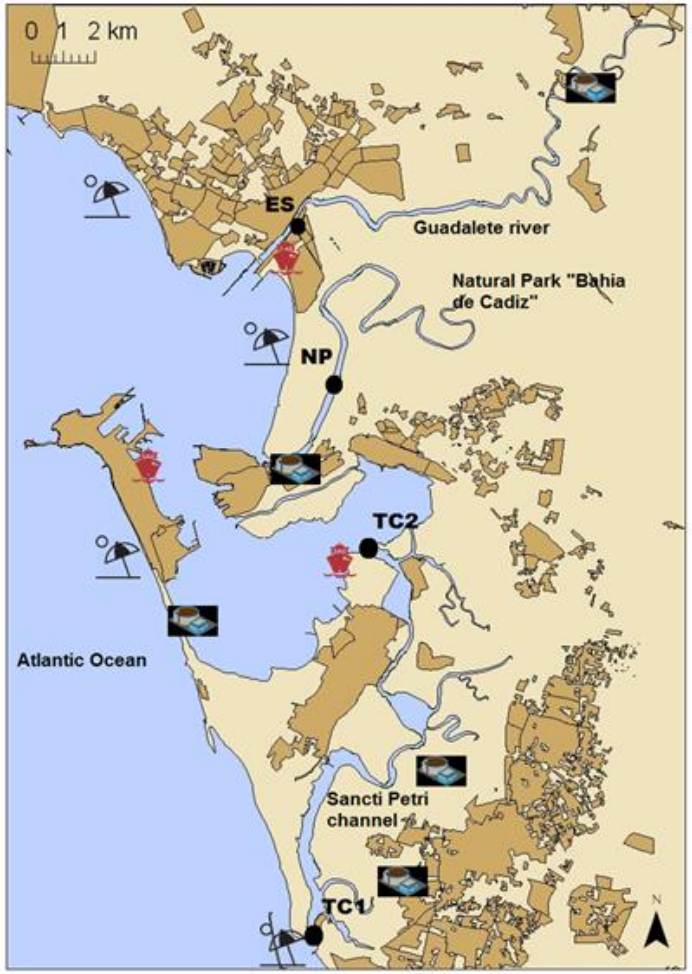


Chlorpyrifos

4. Results and discussion

Sentinel organisms





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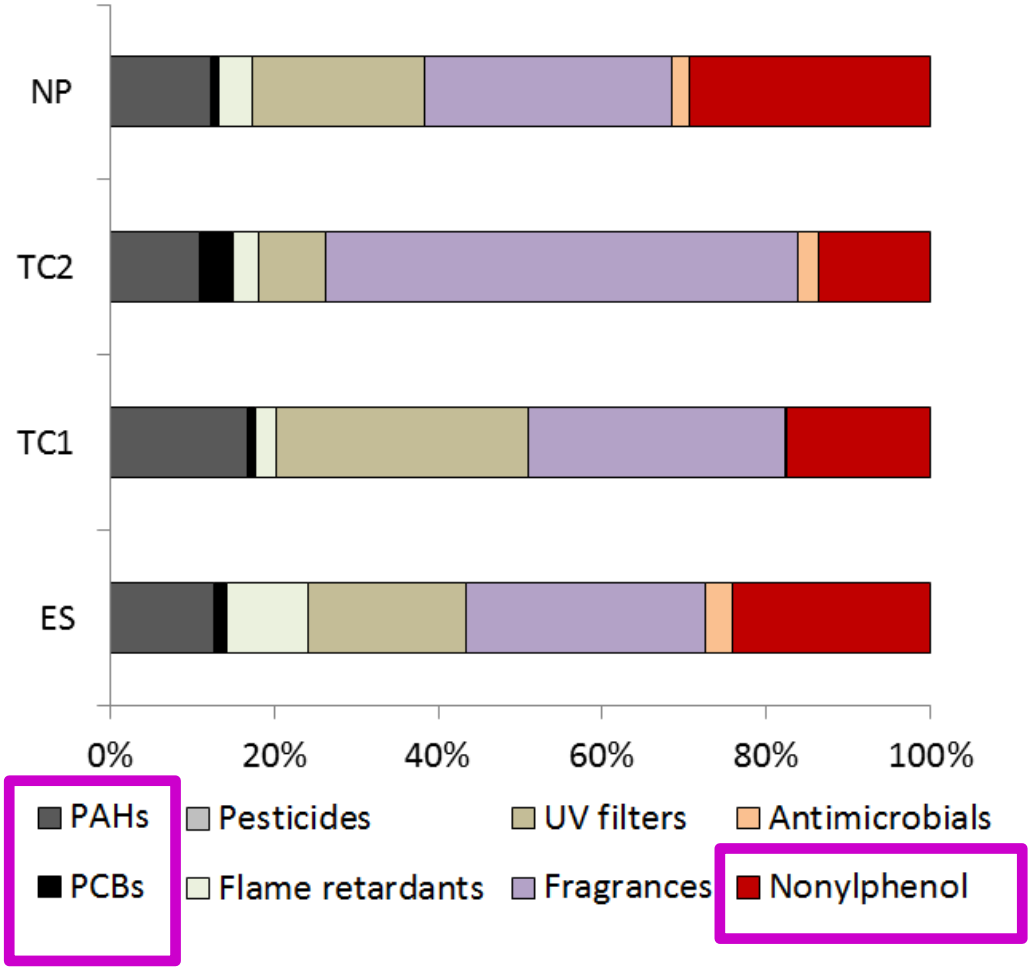
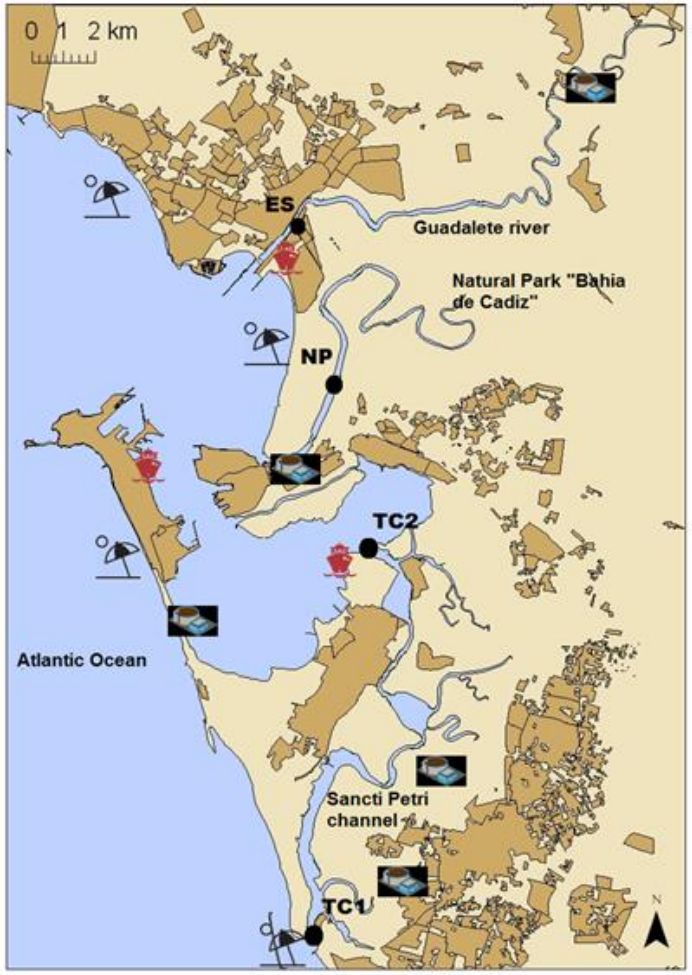
Sentinel organisms





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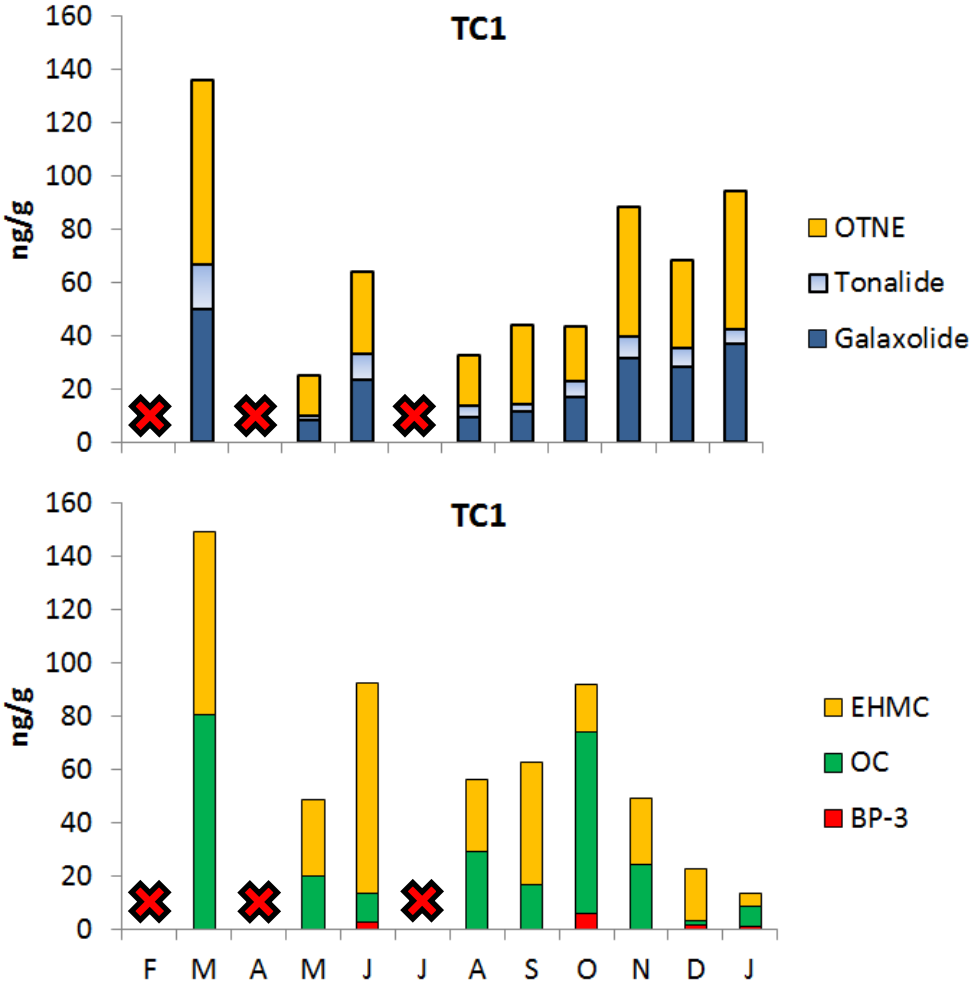
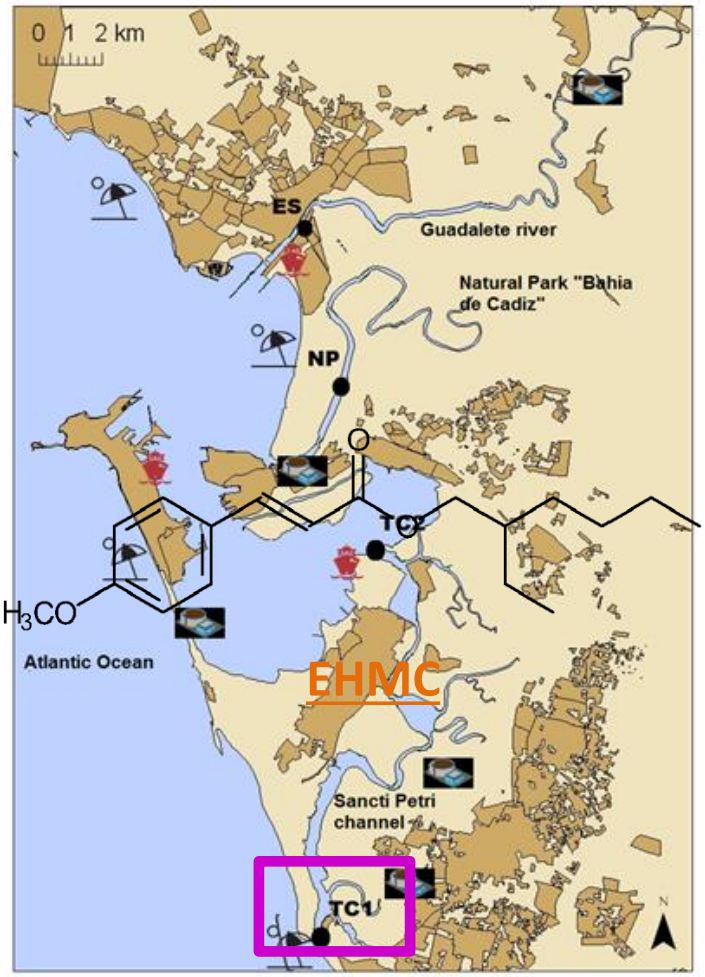
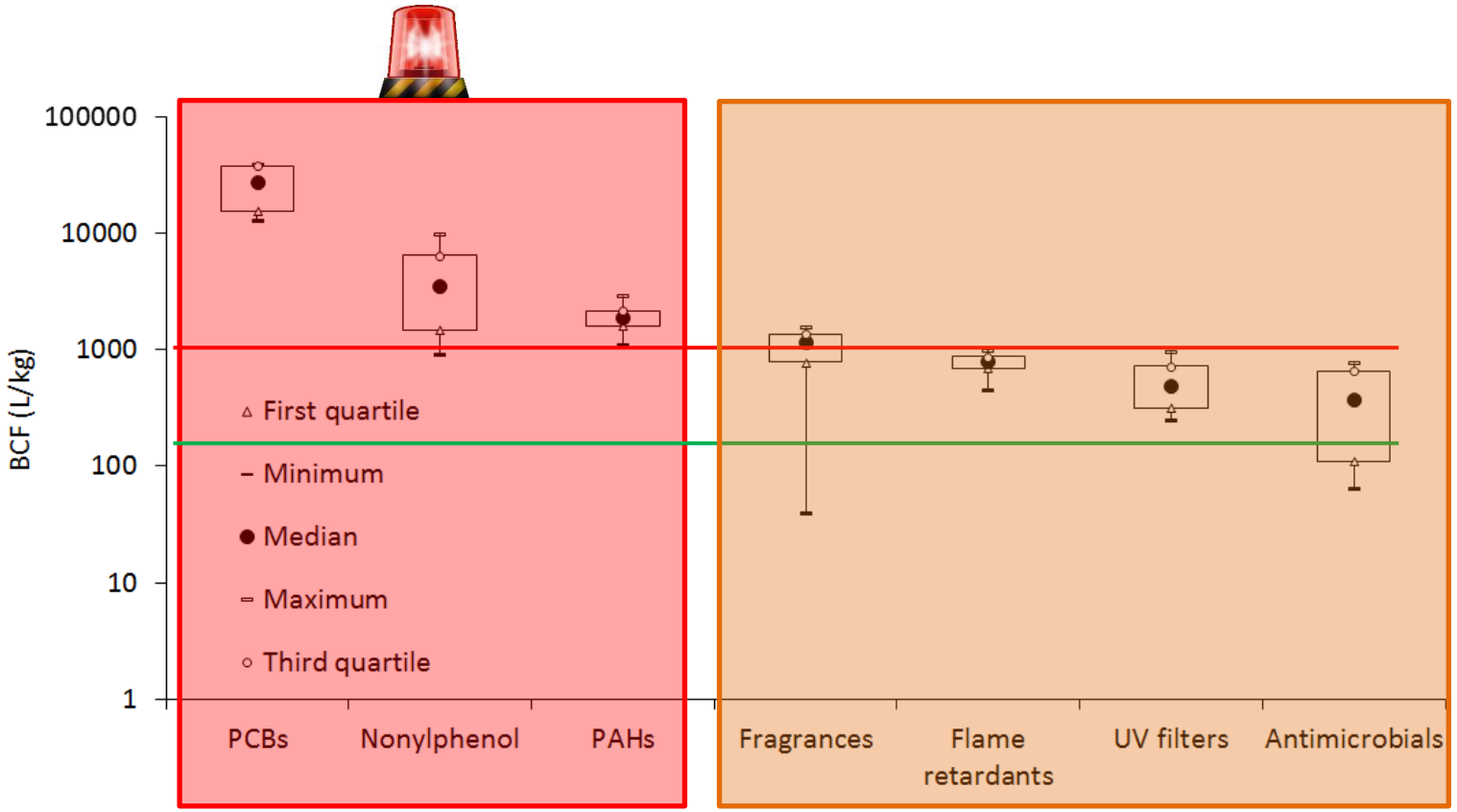


Sentinel organisms



4. Results and discussion

$$BCF = \frac{\text{Concentration in organisms}}{\text{Concentration in water (derived from passive samplers)}}$$



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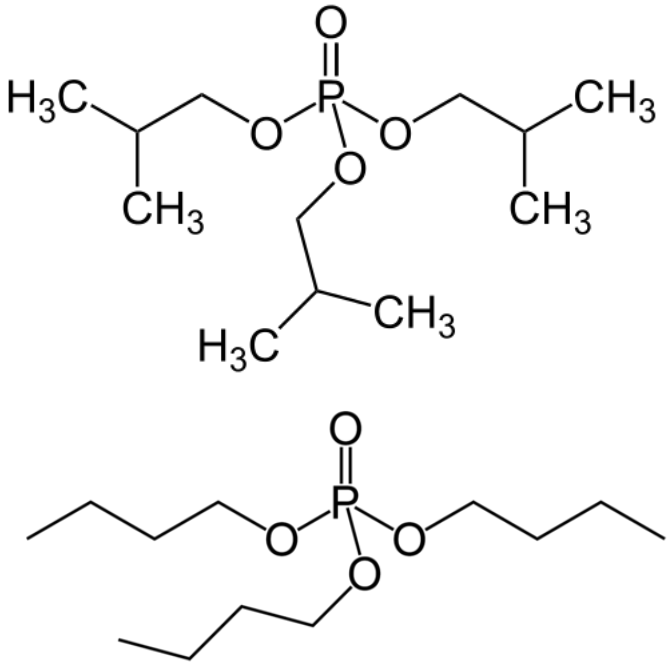
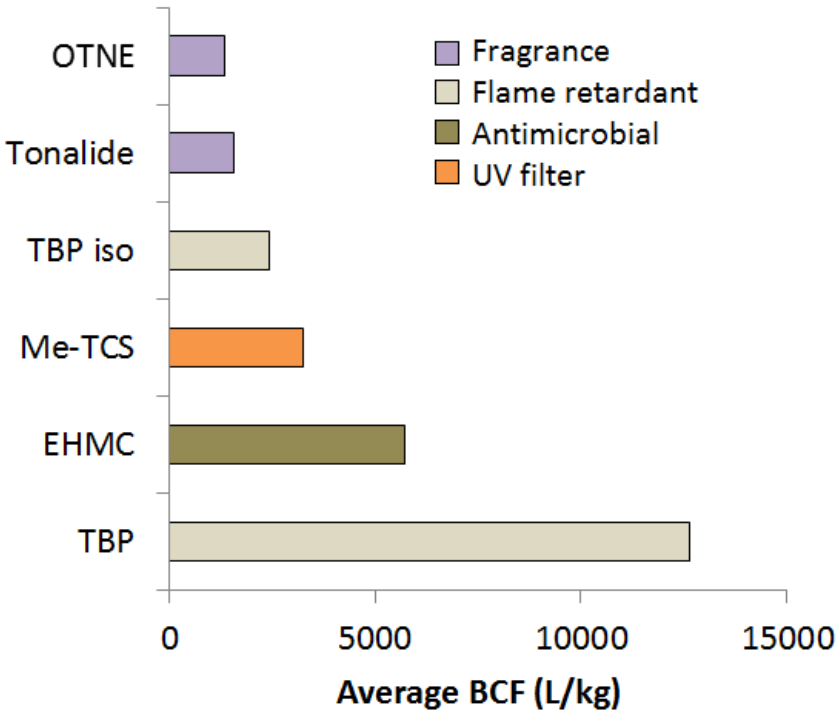


Tributylphosphate (TBP) and
tri-isobutylphosphate (TBP iso)



5. Conclusions

- Hydrophobic legacy and emerging contaminants were detected in water and biota samples from Bay of Cadiz at ng/L and ng/g levels, respectively. Fragrances and UV filters were predominant in both types of samples.

- Contaminants showed highest aqueous concentrations in a sewage-impacted estuary in the north, with values decreasing during summer (except for UV filters). Bioconcentration factors in clams for legacy compounds (e.g., PAHs, PCBs and nonylphenol) were clearly beyond 1000.

- We have selected the following predominant hydrophobic emerging contaminants for further studies: organophosphate flame retardants (EDHP, TPP, TBP), UV filters (octocrylene, benzophenone 3, EHMC), fragrances (OTNE), and antimicrobials (triclosan and methyl triclosan).

6. Work in progress

Lab characterization of environmental processes for selected target compounds:

- Sorption/desorption tests

- Aerobic/anaerobic degradation assays

- Bioaccumulation/toxicity experiments → omics

Thanks for your attention

Questions?

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TECHNICAL DETAILS:

- Log β ranged between 1.1 L/kg and 1.5 L/kg

- Rs values ranged between 6.4 and 18.5 L/d during the warm months and between 3.55 and 8.54 L/d during the cold months

- PRC mass percentage retained in the silicone rubber after 1 month ranged between 10% for more polar compounds (i.e., TCS-d3 and BP-d10) and more than 65% for fluoranthene-d10, TPP-d15, and chrysene-d12.

- The equilibrium time for PRCs was between 8 days for BP-d10 and 167 days for the most hydrophobic chemicals.

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