Monitoring of priority and emerging substances by means of a suite of passive samplers (DGTs, SR and POCIS) to comply with European Directives

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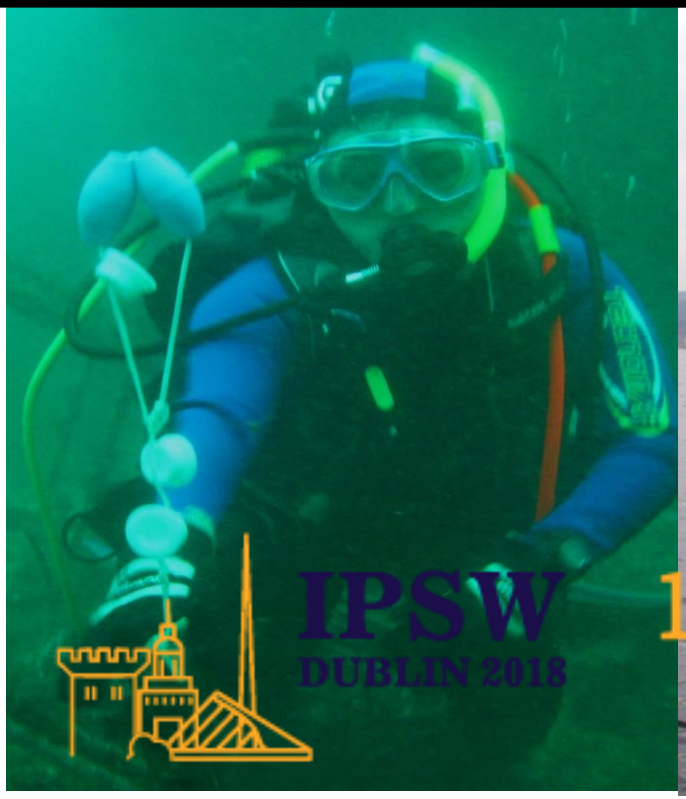
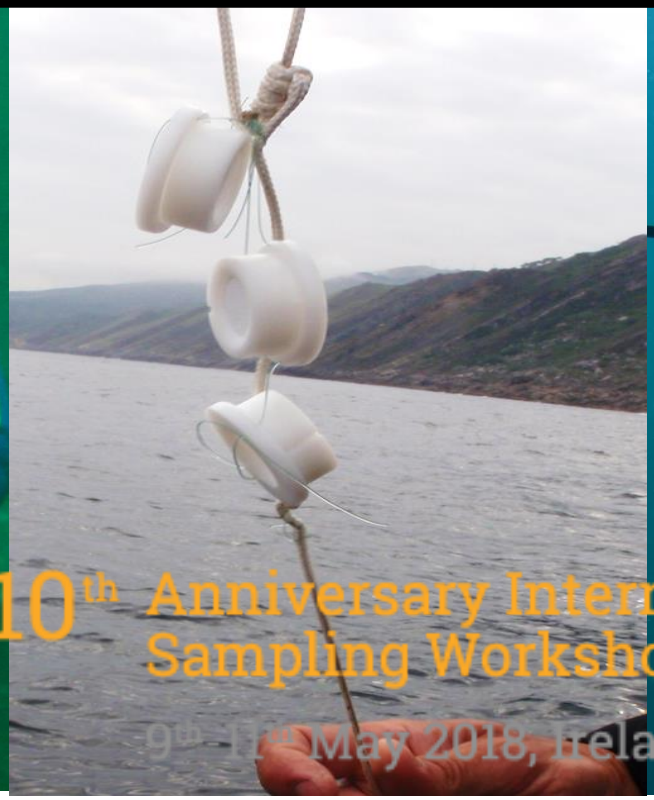
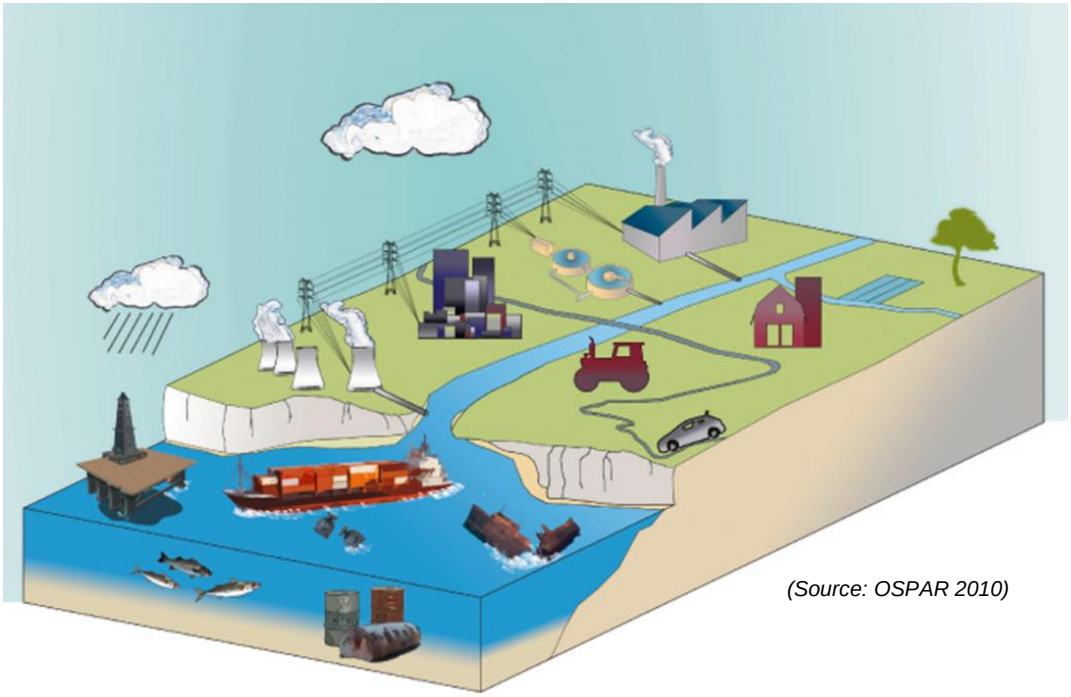




Introduction: Contaminants in transitional & coastal waters



(Source: OSPAR 2010)

- Protection of the marine environment

  - **Water Framework Directive (WFD; 2000/60/EC)**

  - **Marine Strategy Framework Directive (MSFD; 2008/56/EC)**

Introduction: The Water Framework Directive (WFD)

Aim: to achieve a 'Good Ecological and Chemical Status'

- List of priority substances & Environmental Quality Standards (EQS)
- Directive 2013/39/EU → 45 priority substances
  - Organic compounds & only four metals (Cd, Ni, Pb, Hg)
- The Watch List (2015/495/EU)→10 substances (or groups)
  - ❖May pose a risk but insufficient monitoring data
  - ❖High quality data needed → classify as priority substances

LACK OF READY-TO-USE TECHNIQUES

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

L 78/40 EN Official Journal of the European Union 24.3.2015

COMMISSION IMPLEMENTING DECISION (EU) 2015/495

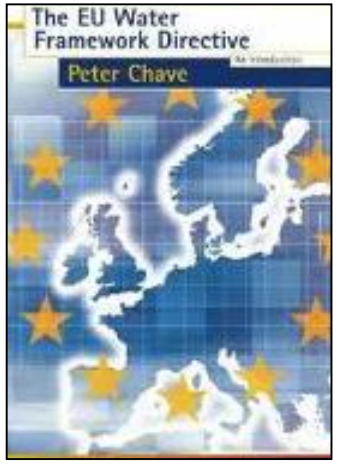
of 20 March 2015

establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council

(notified under document C(2015) 1756)

(Text with EEA relevance)

(2)	120-12-7	204-371-1	Anthracene	X



Objectives

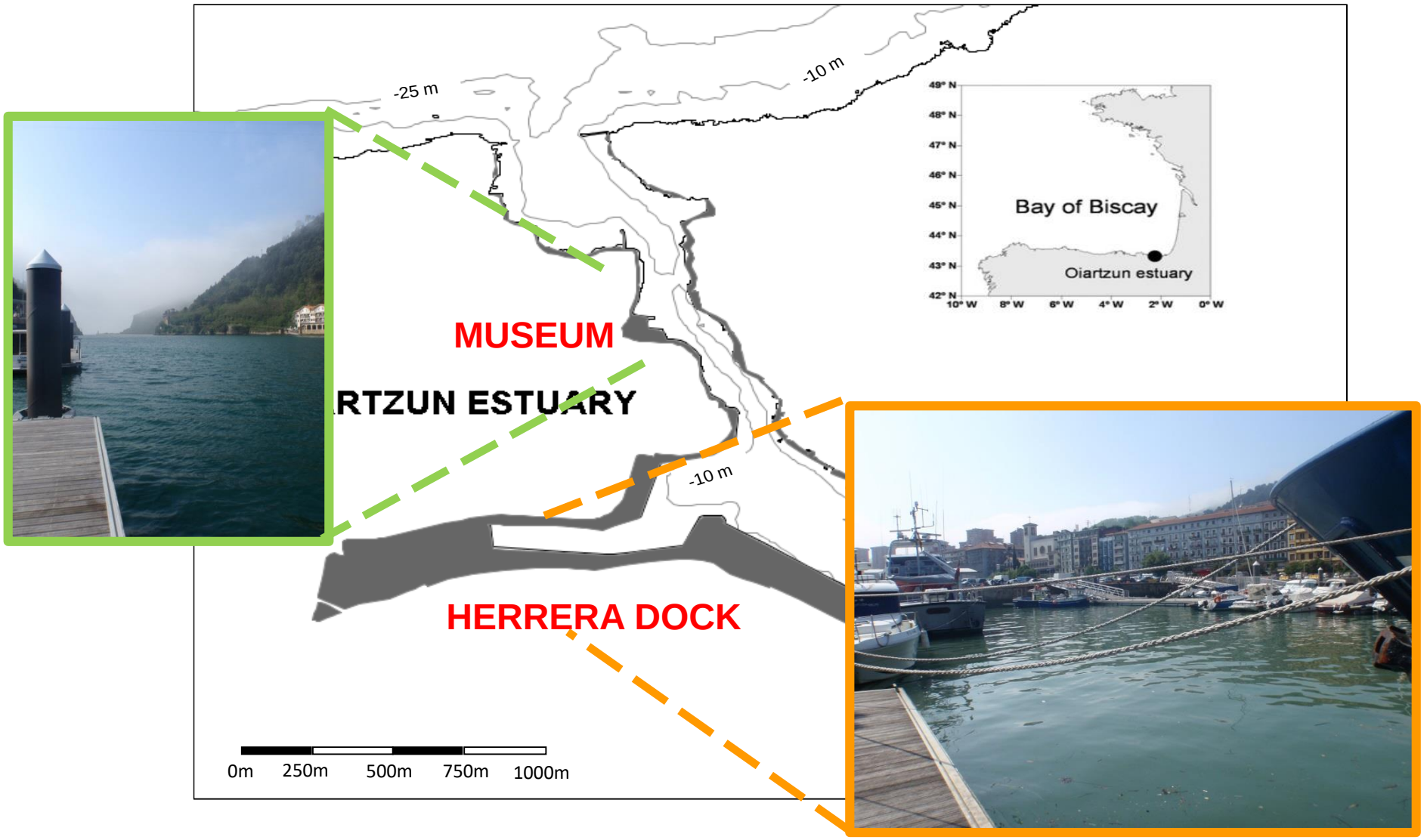
The **operational aims** of the present study were:

(i) to obtain a comprehensive overview of contaminants distribution within a highly-impacted estuary by means of a set of passive samplers

(ii) to investigate their potentiality to comply with the requirements of European Directives

Final Aim: to provide a step forward the inclusion of PS within monitoring networks of estuaries and coastal waters

Material & methods: Study area



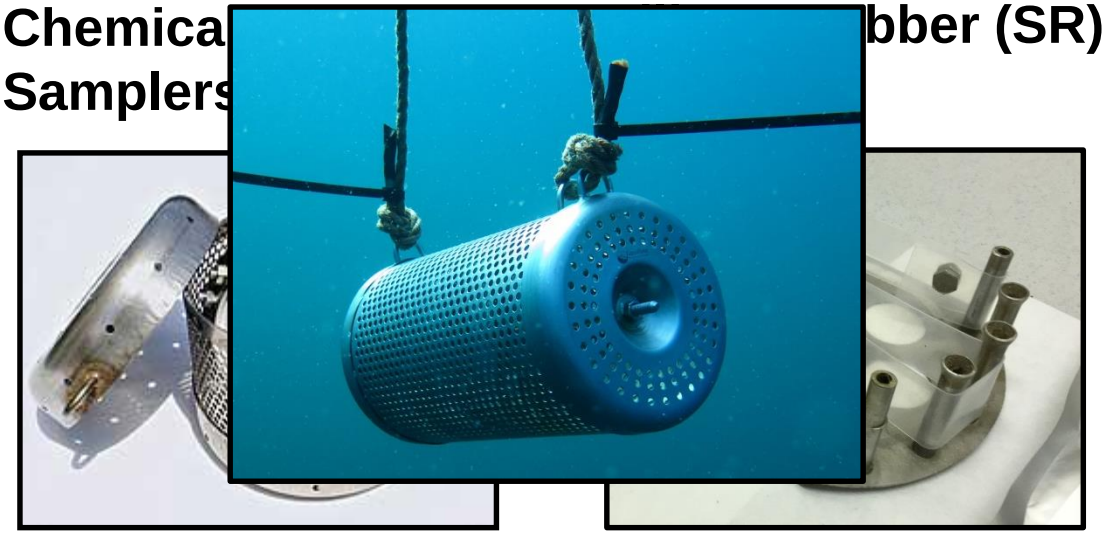
Material & methods: Passive samplers (I)

METALS

Diffusive Gradients in Thin-films (DGTs)

ORGANIC COMPOUNDS

Polar Organic Chemica… bber (SR) Samplers



hydrophilic

Hydrophobic

Hydrophobicity (log K_{ow})

Material & methods: Passive samplers (II)

- PS deployed at two stations and seasons (Sept 2016 & March 2017)
  - Triplicate SR & POCIS (40 d) & DGTs (triplicates every 13 days)
  - Physico-chemical parameters (pH, DO, Sal, Tª) & immersion time
- **SR** →spiking of 14 PRCs (log Ksw 3.23-7.59) & calculation of

$$\frac{N_t}{N_0} = e^{\left(\frac{-R_s t}{K_{sw} m_s}\right)}$$

- **SR & POCIS**→ Extraction with hexane (SR) & methanol (POCIS)

$$C_w = \frac{C_s}{K_{sw} m_s \left[1 - exp\left(\frac{-Rst}{K_{sw} m_s}\right)\right]}$$

- **DGTs**→ Extraction of accumulated metals (1M HNO_3, >24h)

$$M = \frac{C_e(VH_{NO3} + Vg_{el})}{fe} \qquad C_w = \frac{M\Delta g}{DtA}$$

Results & Discussion: PS

SR

- **PAHs**: **Naphthalene, anthracene, fluoranthene, benzo(b+j) fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene, indeno-(1,2,3-cd)pyrene, benzo(g,h,i)perylene**…. TOTAL: 18 PAHs + 17 Alkylated PAHs
- **PCBs**: PCB-18, PCB-28, PCB- 31, PCB-44….. TOTAL: 32
- **Musks:** Tonalide, Galaxolide
- **UV filters:** OCR, **2-ethilexyl-4-methoxycinnamate**, 4-MBC
- **OCP** (ng/sampler): **Aldrin, DDT, dieldrin, alachlor, atrazine, isodrin, hexachlorobenzene, pentachlorobenzene, heptachlor, heptachlor epoxide, hexachlorocyclohexane**….. TOTAL: 18

POCIS

- Alkylphenols, octylphenols (tOP, OP, OPE1), **4-n-nonylphenol**, nonylphenols (NPE1, NPE2), Bisphenol A
- **Steroids:** 17-α-estradiol (αE2), **Estrone (E1), 17-β-estradiol (E2)**, Mestranol (M1), **17-α-ethinylestradiol (EE2)**, Estradiol (E3)
- Acetilsalicilic acid, Ibuprofen, Gemfibrozil, Salbutamol, Ketoprofene

DGTs

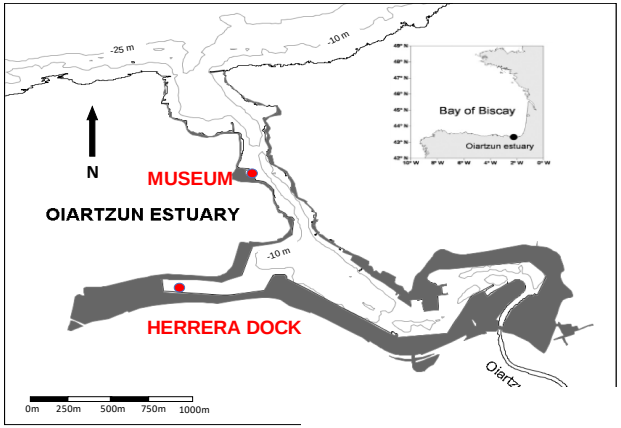
- **Cd, Ni, Pb**
- Cu, Zn, Cr

Water Quality Guidelines

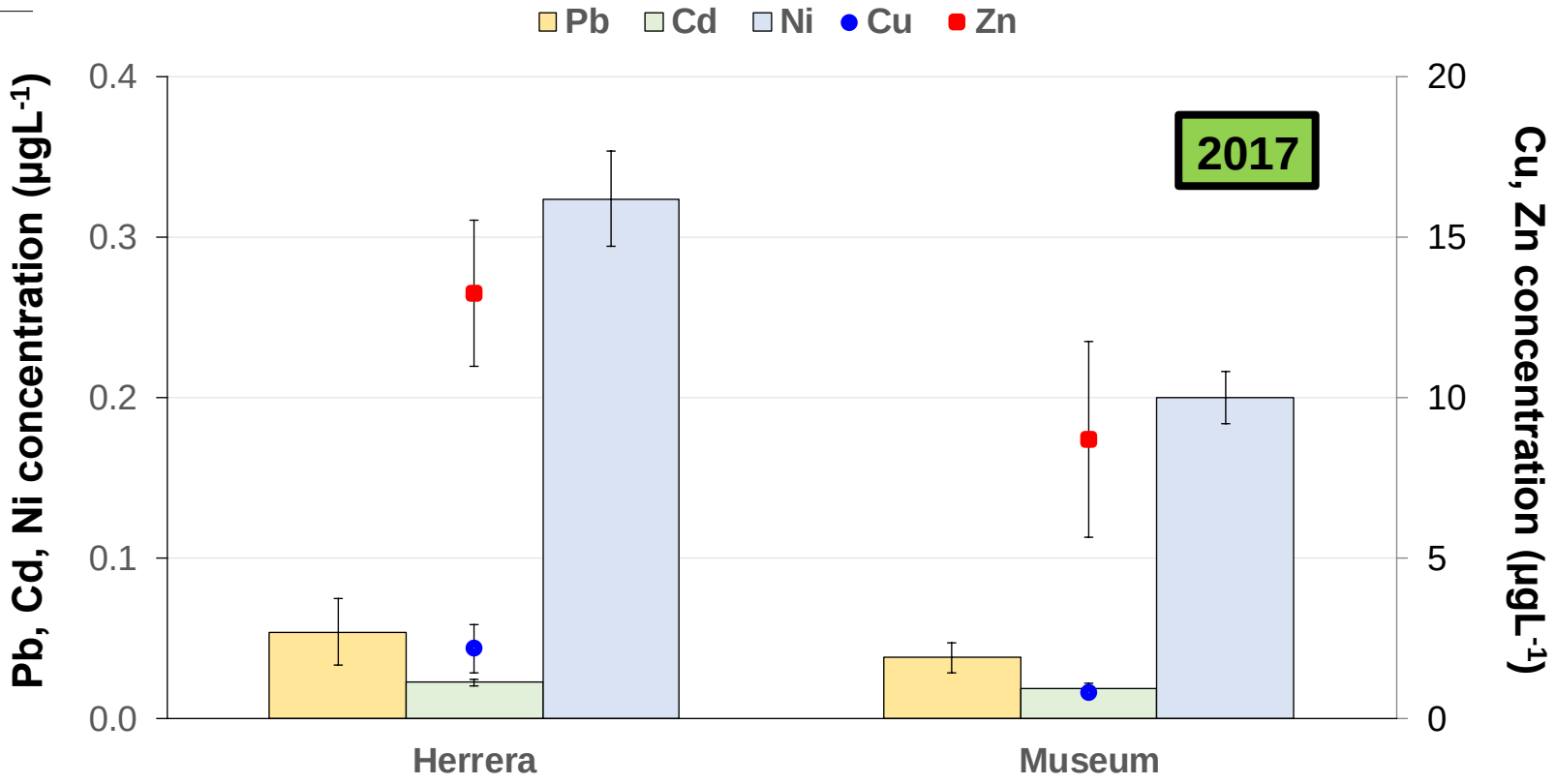
EQS- EC 2013/39/EU

'Watch list'- EC 2015/495/EU

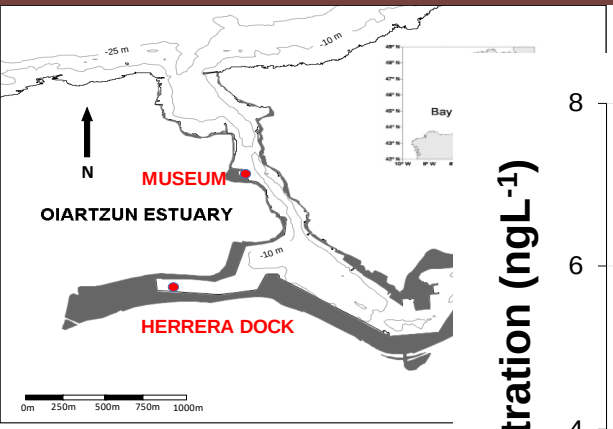
Results & Discussion: DGTs



- [Metal] inner station > [Metal] outer station
- More point sources at the inner station
- Longer water residence time (73 days)

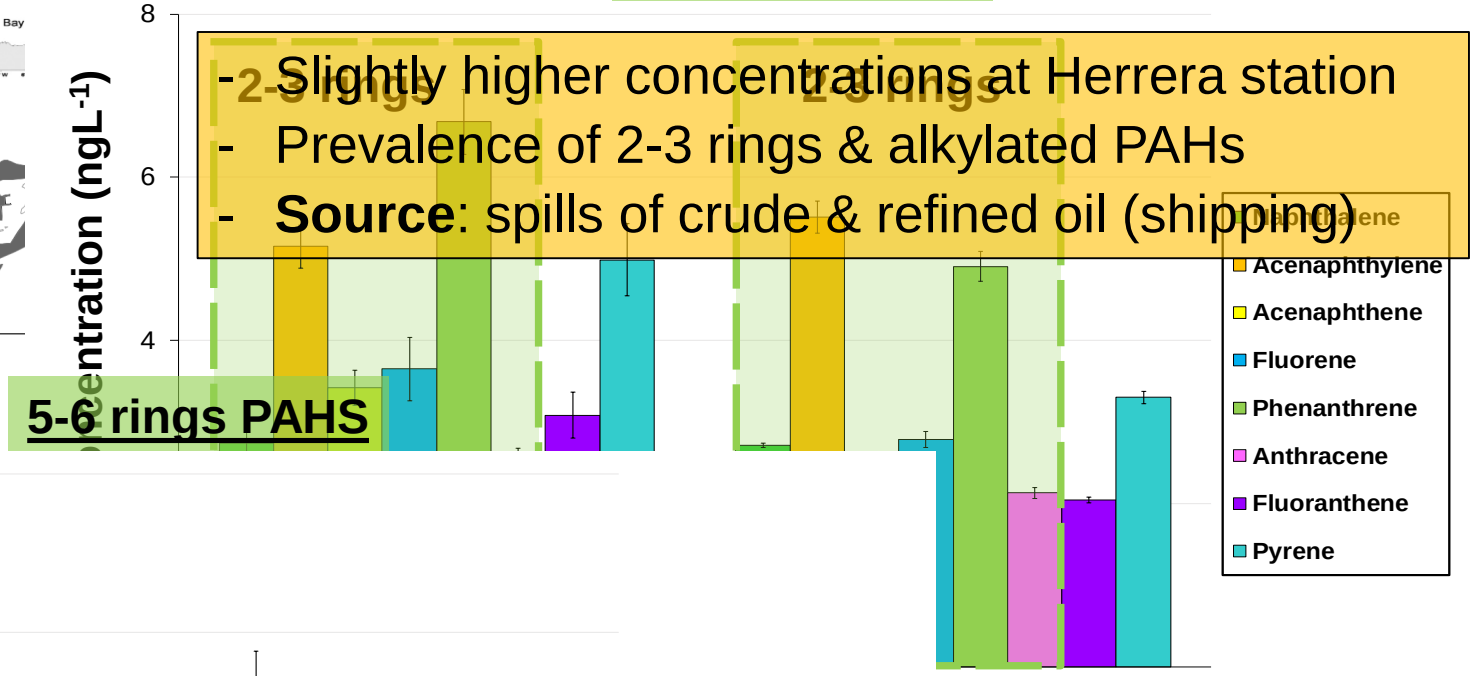


Results & Discussion: PAHs (SR)

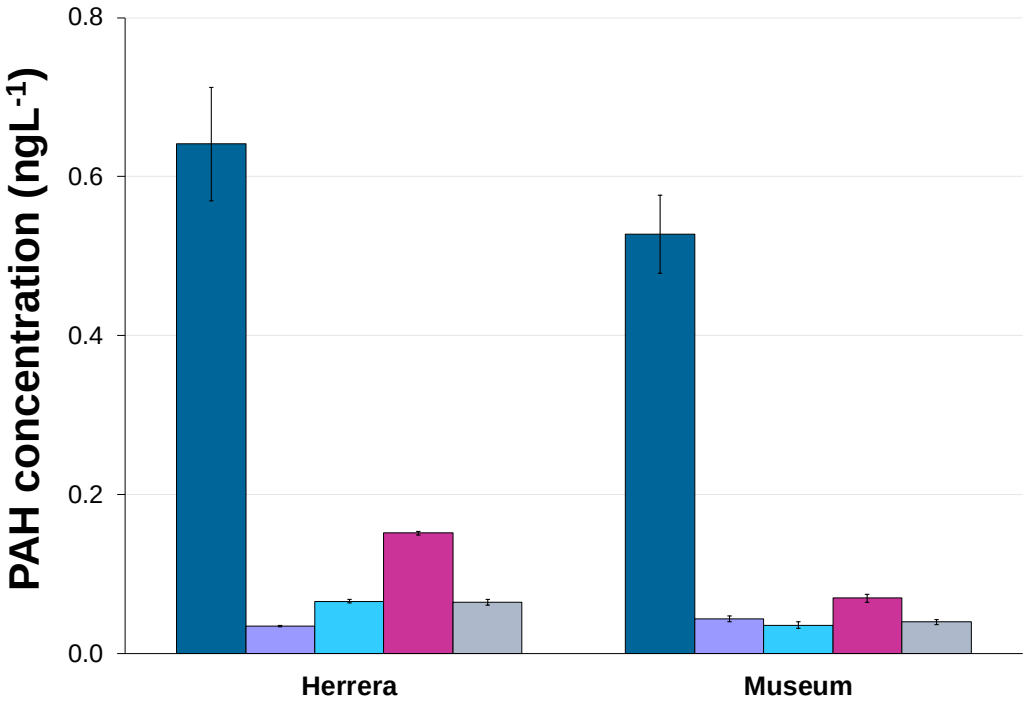


2-4 rings PAHS

- Slightly higher concentrations at Herrera station
- Prevalence of 2-3 rings & alkylated PAHs
- **Source**: spills of crude & refined oil (shipping)

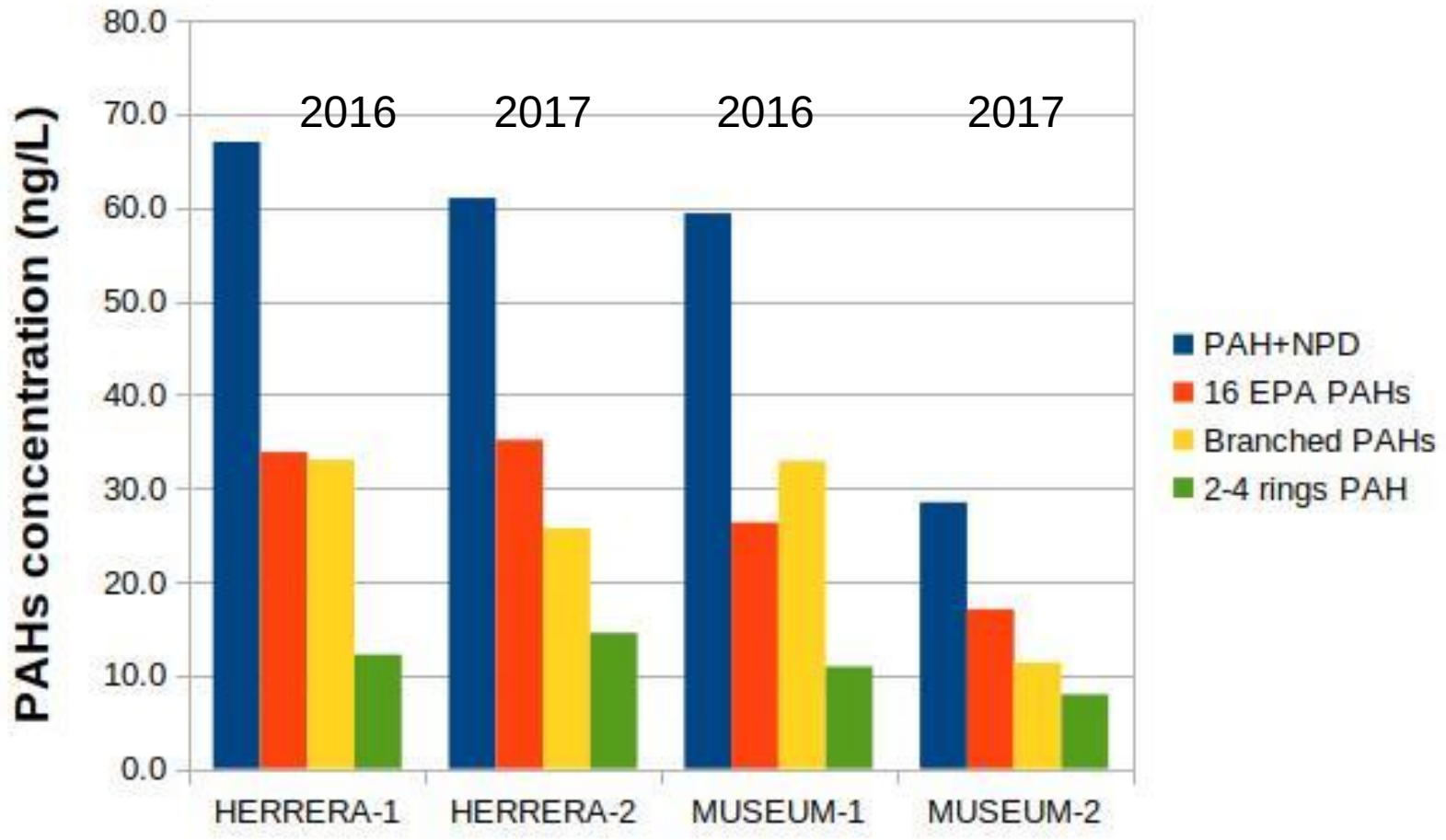


5-6 rings PAHS

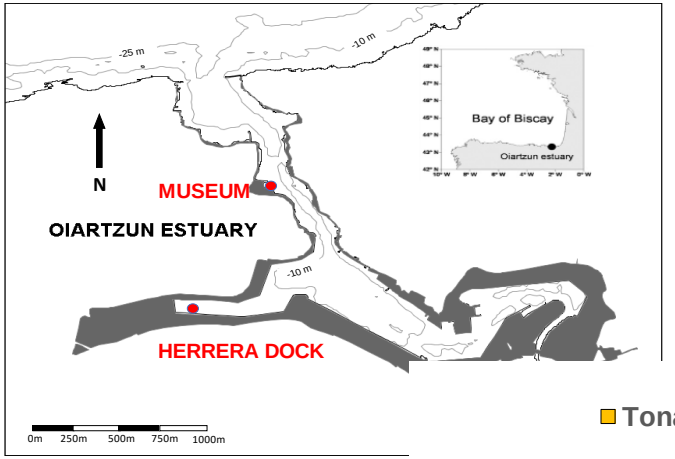


Results & Discussion: PAHs (SR)

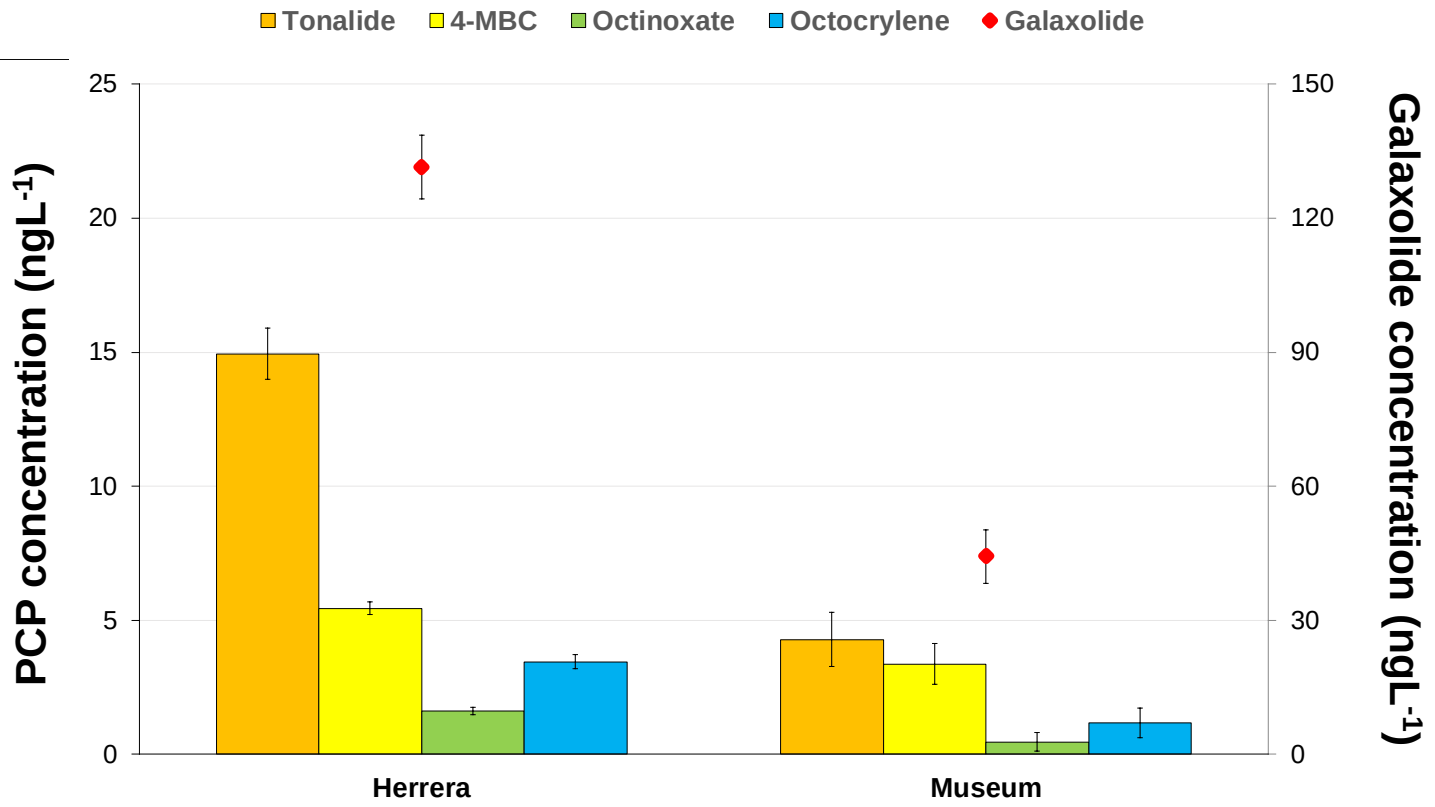
- Concentrations always remain higher in Herrera
- In the 2017 campaign concentrations are much lower in Museum.



Results & Discussion: PCPs (SR)

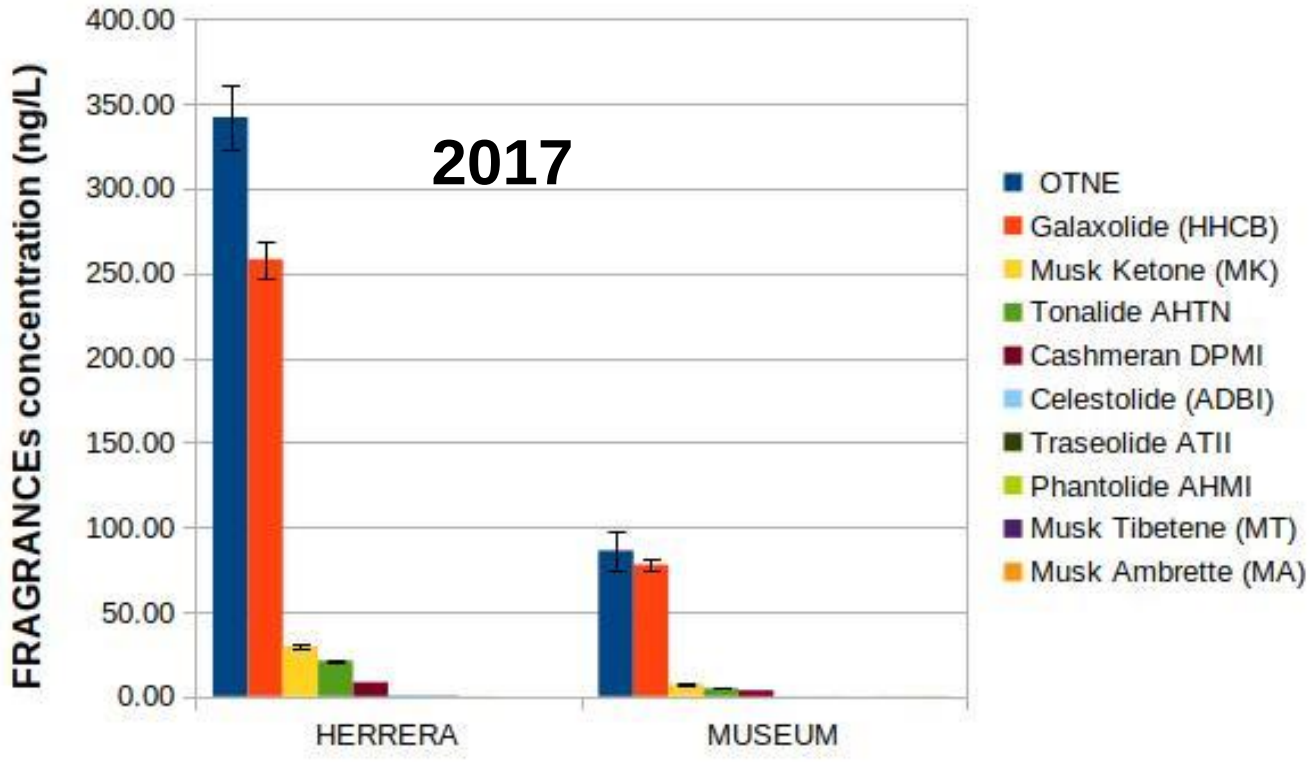


- **UV filters**: Slightly [higher] at Herrera station
  - Octinoxate (Watch List)
- **Musks:** higher concentrations in Herrera
  - Galaxolide (x3), Tonalide (x 3.5)



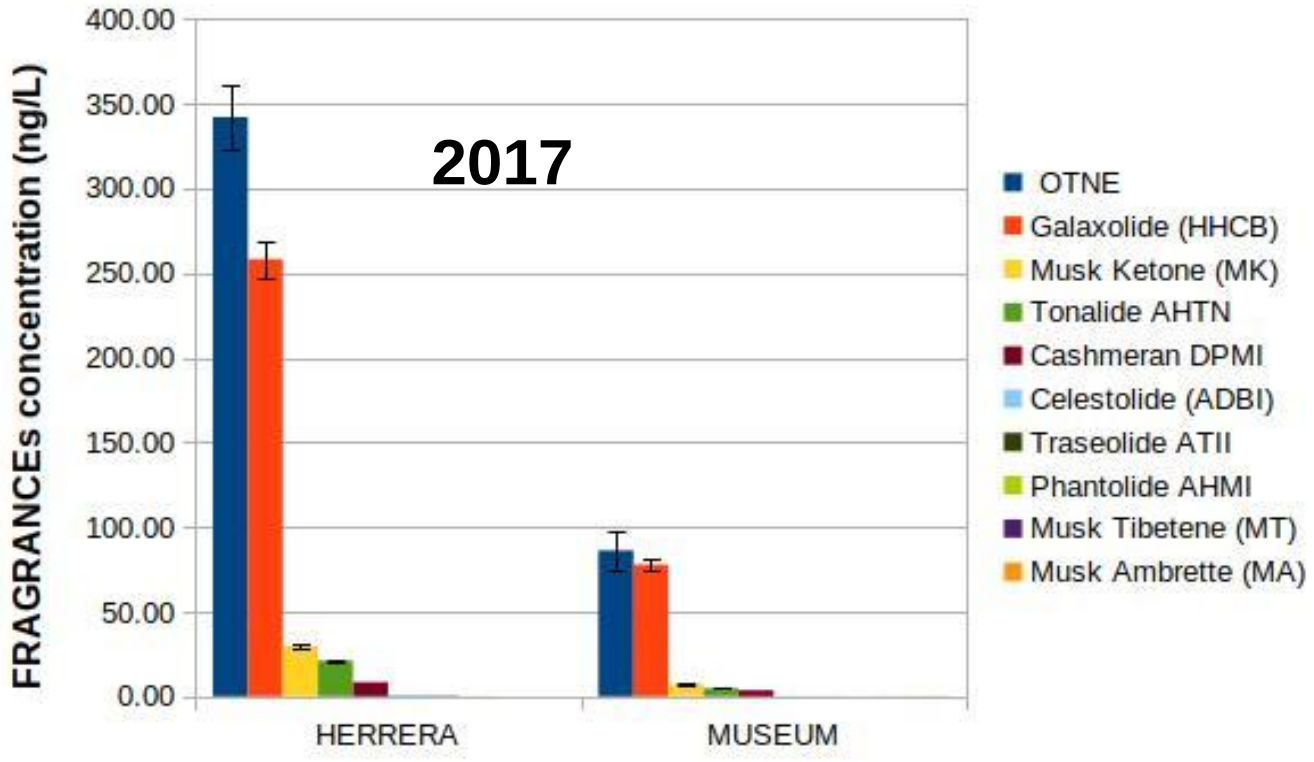
Results & Discussion: PCPs (SR)

Calibration data for sampling with silicone rubber for many more emerging substances were published in 2016 (Pintado-Herrera et al. - Environ Toxicol Chem 35, 2016).



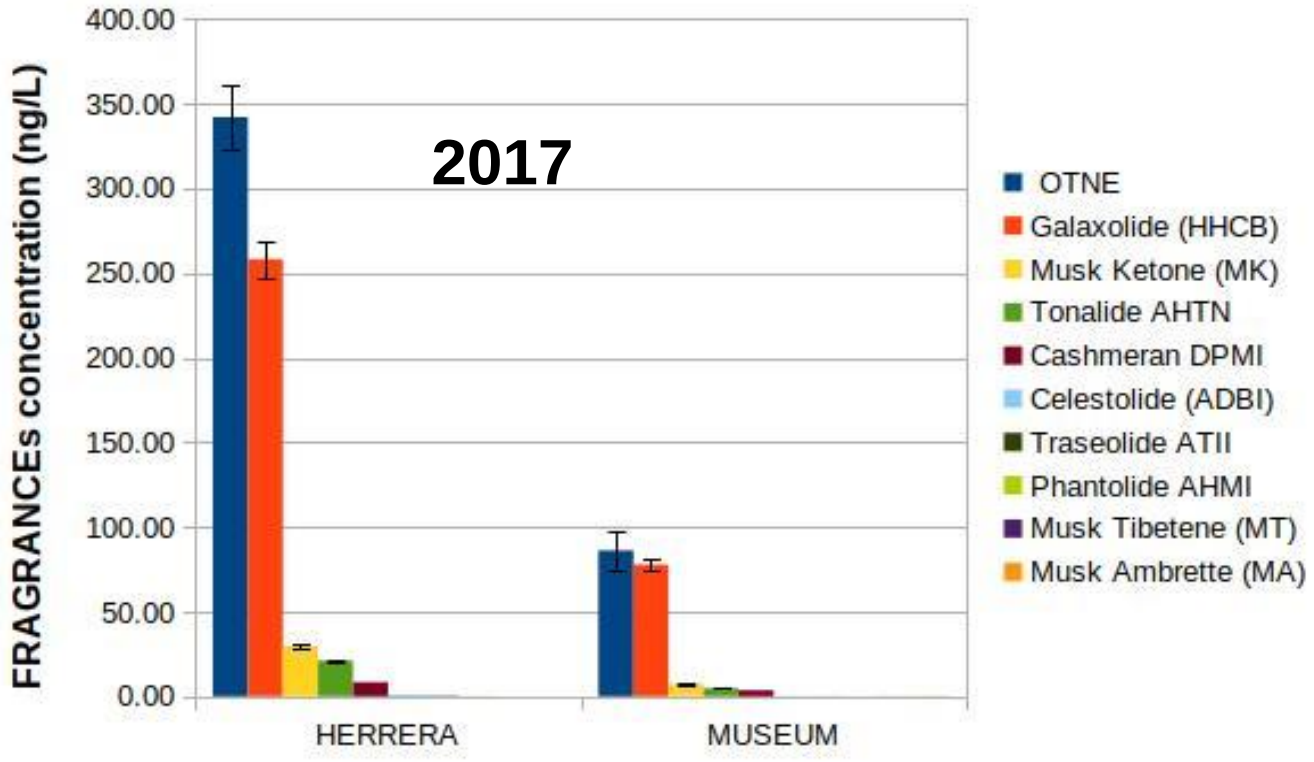
Results & Discussion: PCPs (SR)

This allowed us to increase the number of target compounds in 2017.



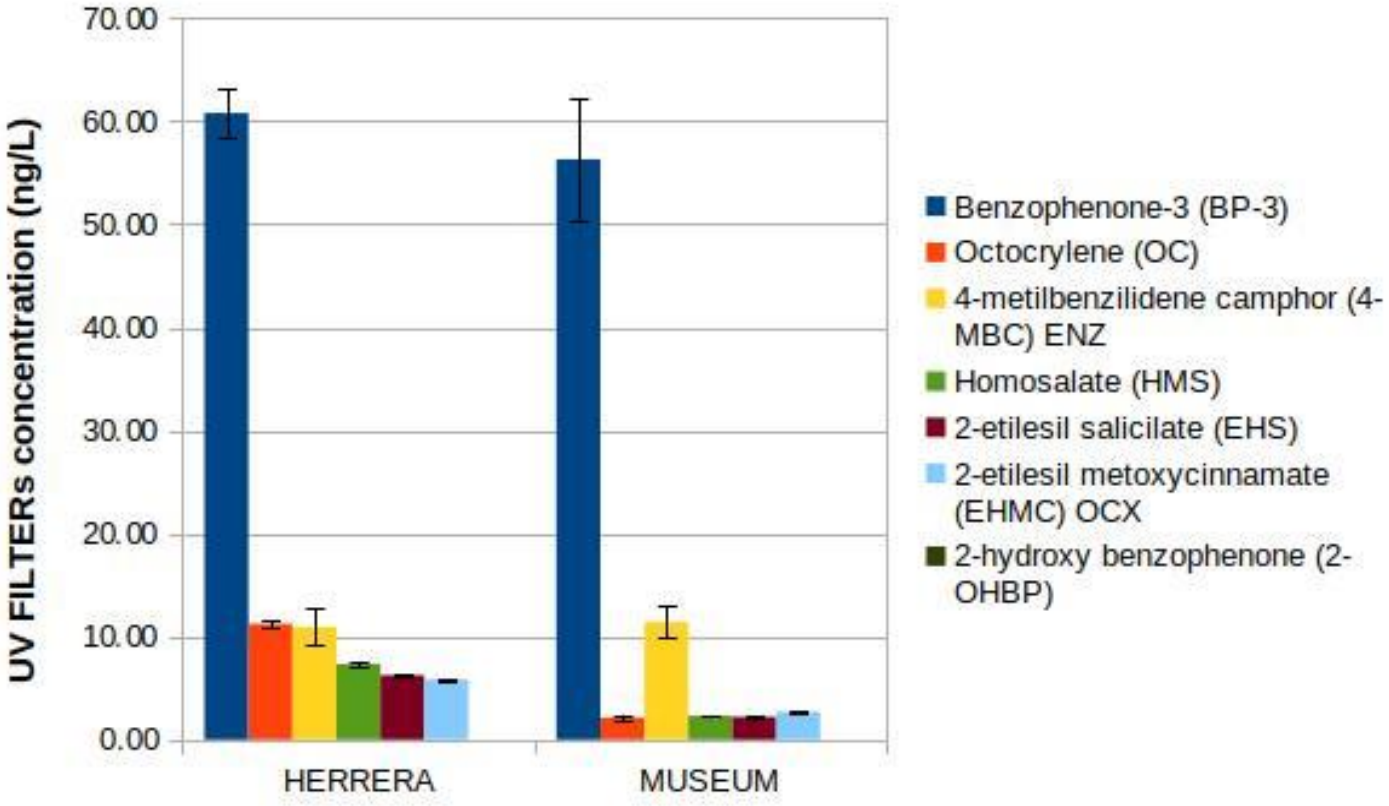
Results & Discussion: PCPs (SR)

- **Fragrances**: Higher at Herrera station
  OTNE (Tetramethyl acetyloctahydronaphtalene) and HHCB, (Galaxolide) predominant



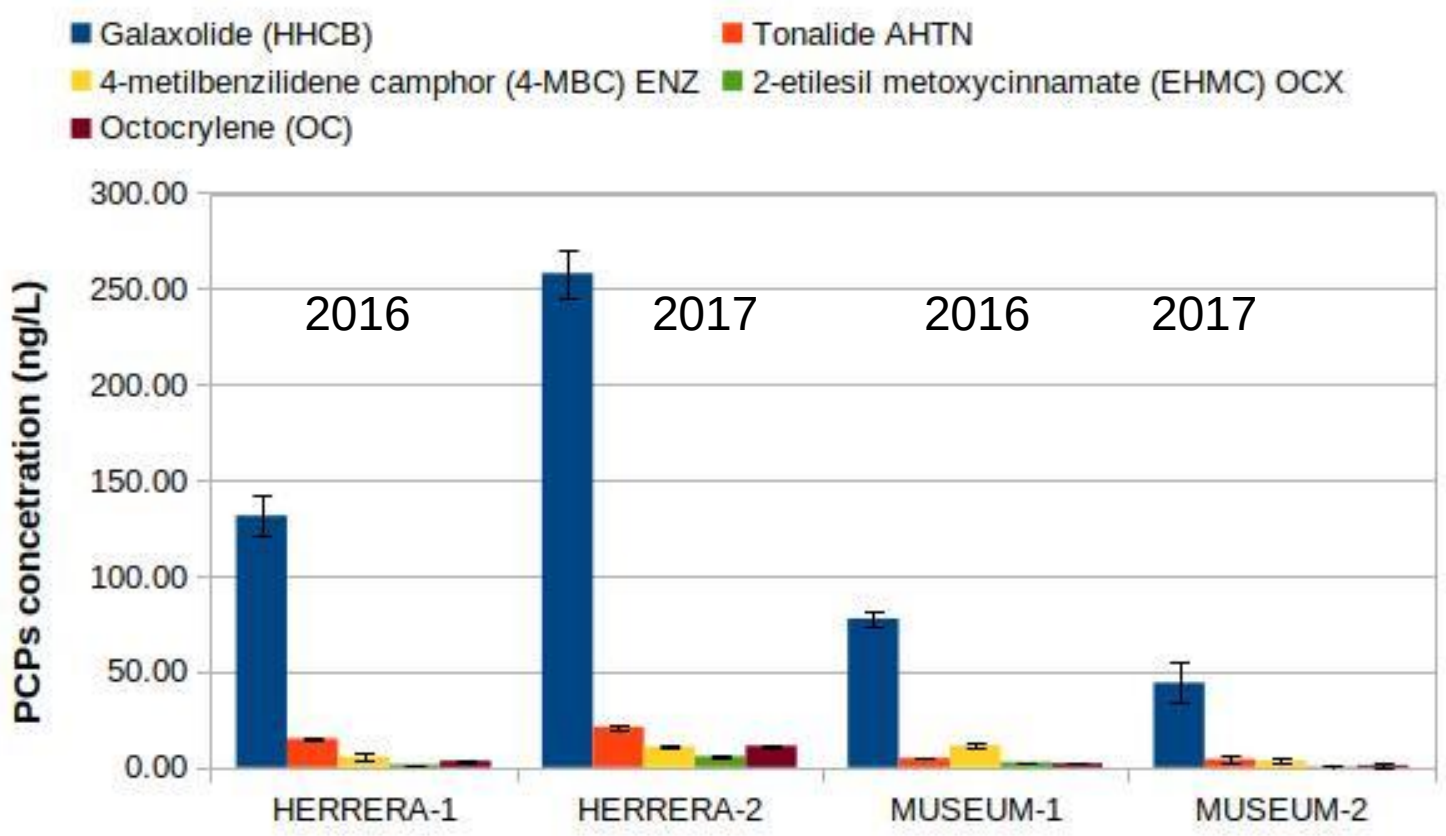
Results & Discussion: PCPs (SR)

- **UV filters (2017):** BP-3 and 4-MBC are present at the same levels at both sampling points.
- The other substances are higher in Herrera.



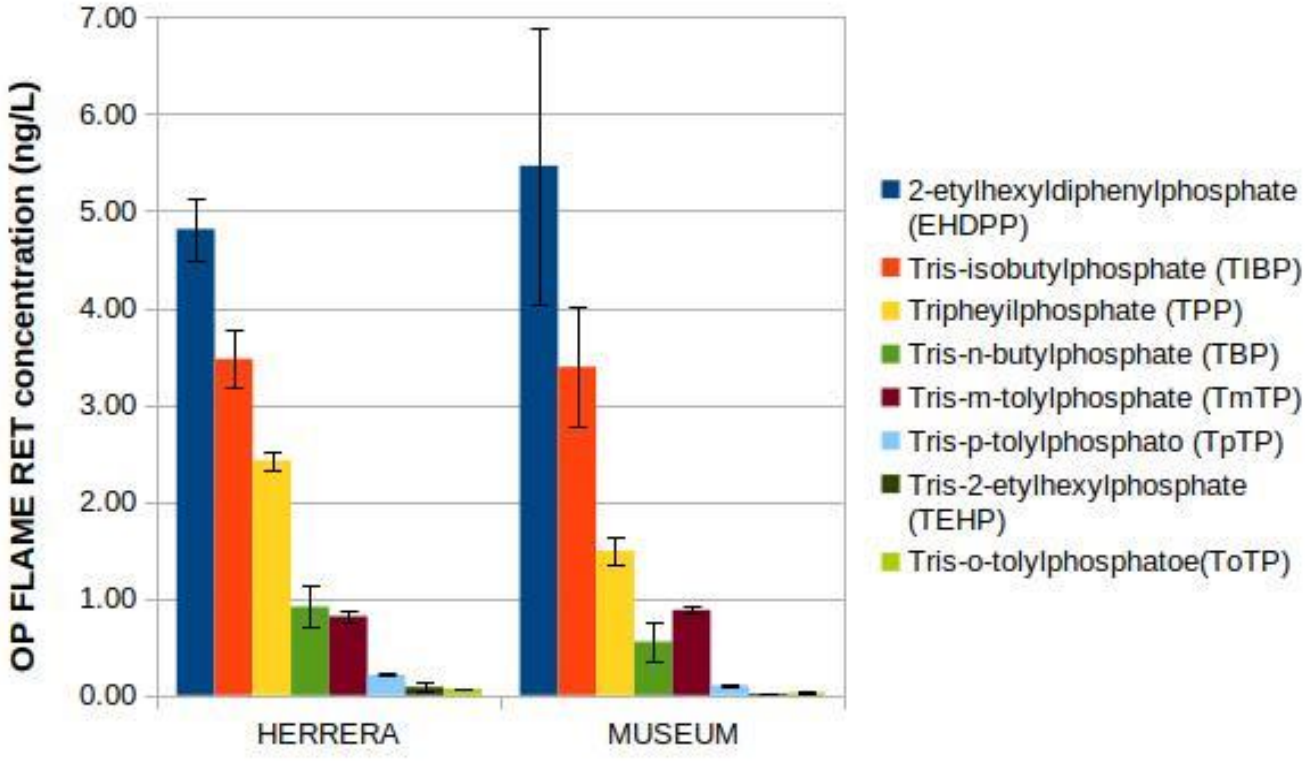
Results & Discussion: PCPs (SR)

- **Personal Care Products :** Galaxolide is prevalent in all samples and is always higher in Herrera



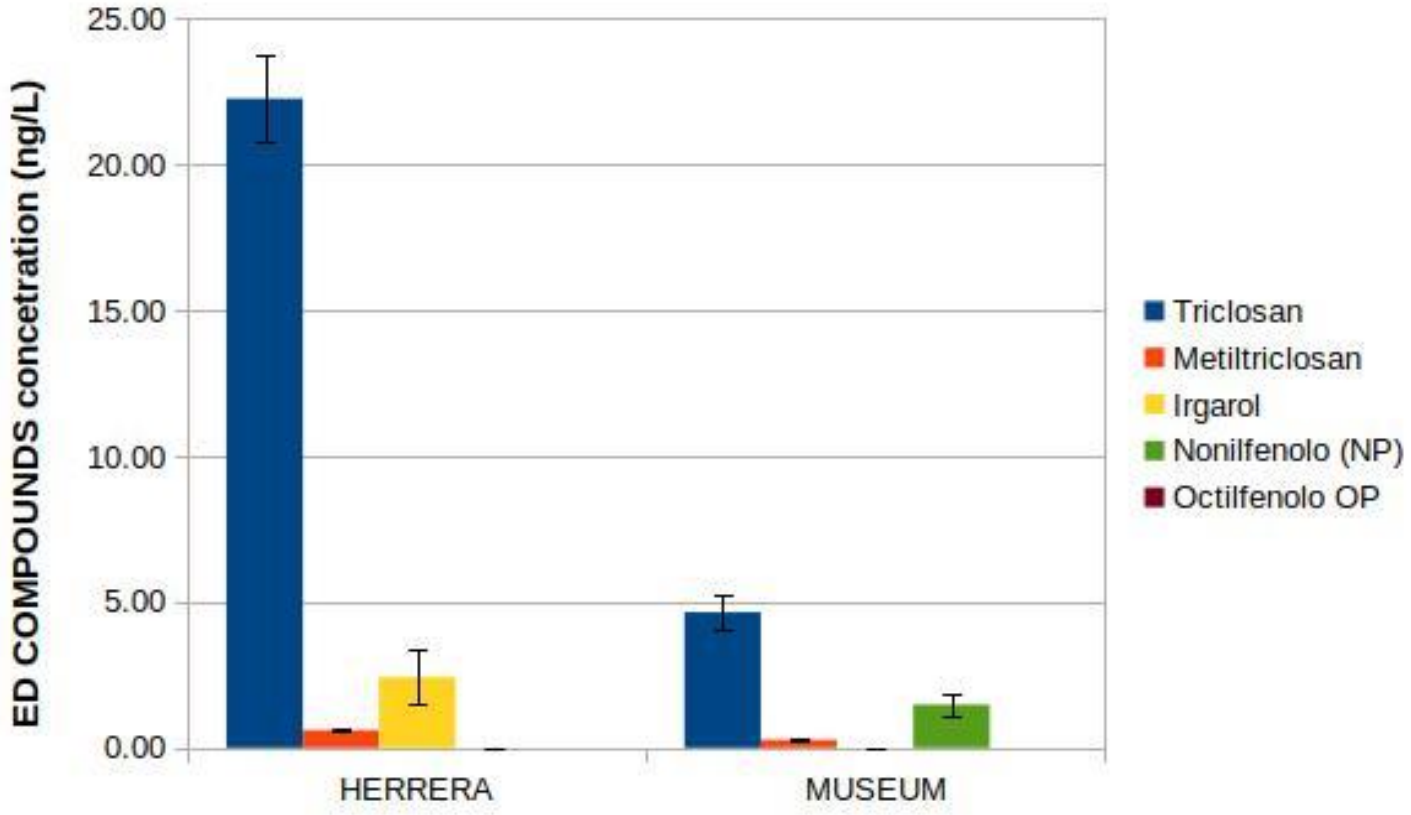
Results & Discussion: PCPs (SR)

- **Organophosphate flame retardant**:
- The measured concentrations are similar at the two sampling site.
- The experimental error is rather high

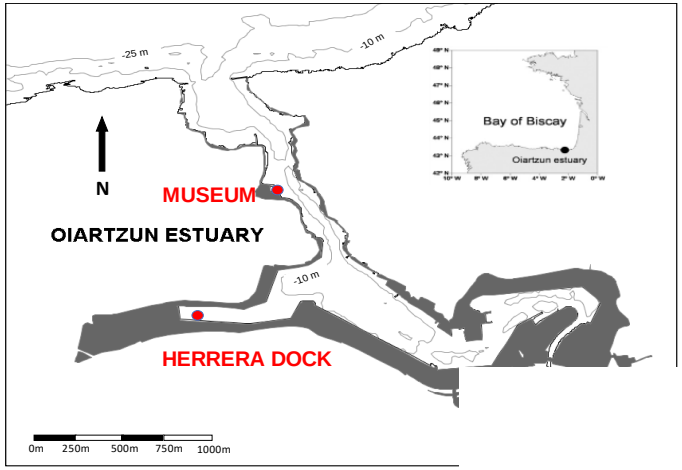


Results & Discussion: PCPs (SR)

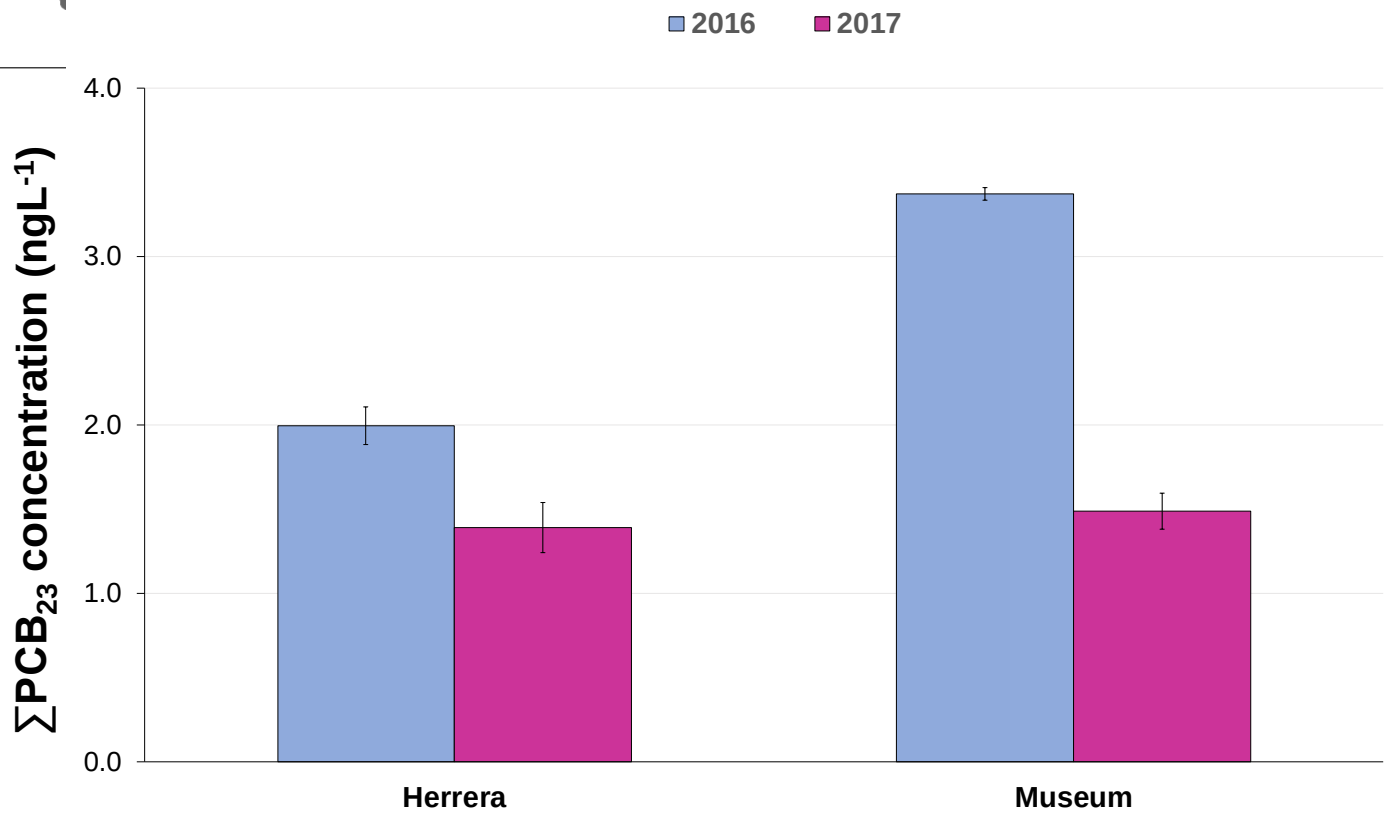
- **Endocrine disruptor (2017) :**
- **Triclosan and methyltriclosan are higher in Herrera**
- **Irgarol is present only in Herrera**
- **Nonylphenol is present only at Museum**



Results & Discussion: PCBs (SR)



- Individual PCBs in very low concentrations (pgL^{-1})
- **2017:** similar PCB patterns at both stations
  - CBs: 44, 153, 149, 95 & 101
- **2016:** Same dominant PCBs than in 2017
  - Present at higher concentrations (M>>H)
  - Presence of other congeners (especially in M)



Results & Discussion: Overall assessment

Location	No. Congeners	Mean ± SD (ngL^{-1})	Reference
Norway, inner Oslofjord	∑16 PAHs	**6.0 ± 3.3**	Schaaning et al. (2011)
Ireland, Galway & Dublin Bay	∑16 PAHs	**42 ± 36**	O'Hara (2009)
Belgium, coastal harbors	∑15 PAHs	**27 ± 18**	Monteyne et al. (2013)
Ireland, Galway Bay	∑7 PCBs	**0.021**	O'Hara (2009)
Ireland, Dublin Bay	∑7 PCBs	**0.15**	O'Hara (2009)
Australia, Sydney harbor	∑12 PCBs	**0.028 ± 0.005**	Roach et al. (2009)
Australia, Sydney harbor	∑12 PCBs	**0.23 ± 0.21**	Roach et al. (2009)
Belgium, coastal harbors	∑14 PCBs	**0.65 ± 0.60**	Monteyne et al. (2013)
Australia, estuarine lagoon	Ni, Pb, Zn	**Ni (0.12-0.26), Pb (0.02-0.16), Zn (3.3-38.4)**	Warnken et al. (2004)
Mediterranean, marine sites	Cd, Ni, Pb	**Cd (0.01-0.02), Ni (0.2-1.4), Pb (0.04-0.08)**	Lafabrie et al. (2007)
Spain, Oiartzun estuary	Cd,Cu,Pb,Zn	**Cd (0.07-0.3), Cu (0.4-1.3), Pb (0.02-0.08), Zn (7-13)**	Montero et al. (2013)

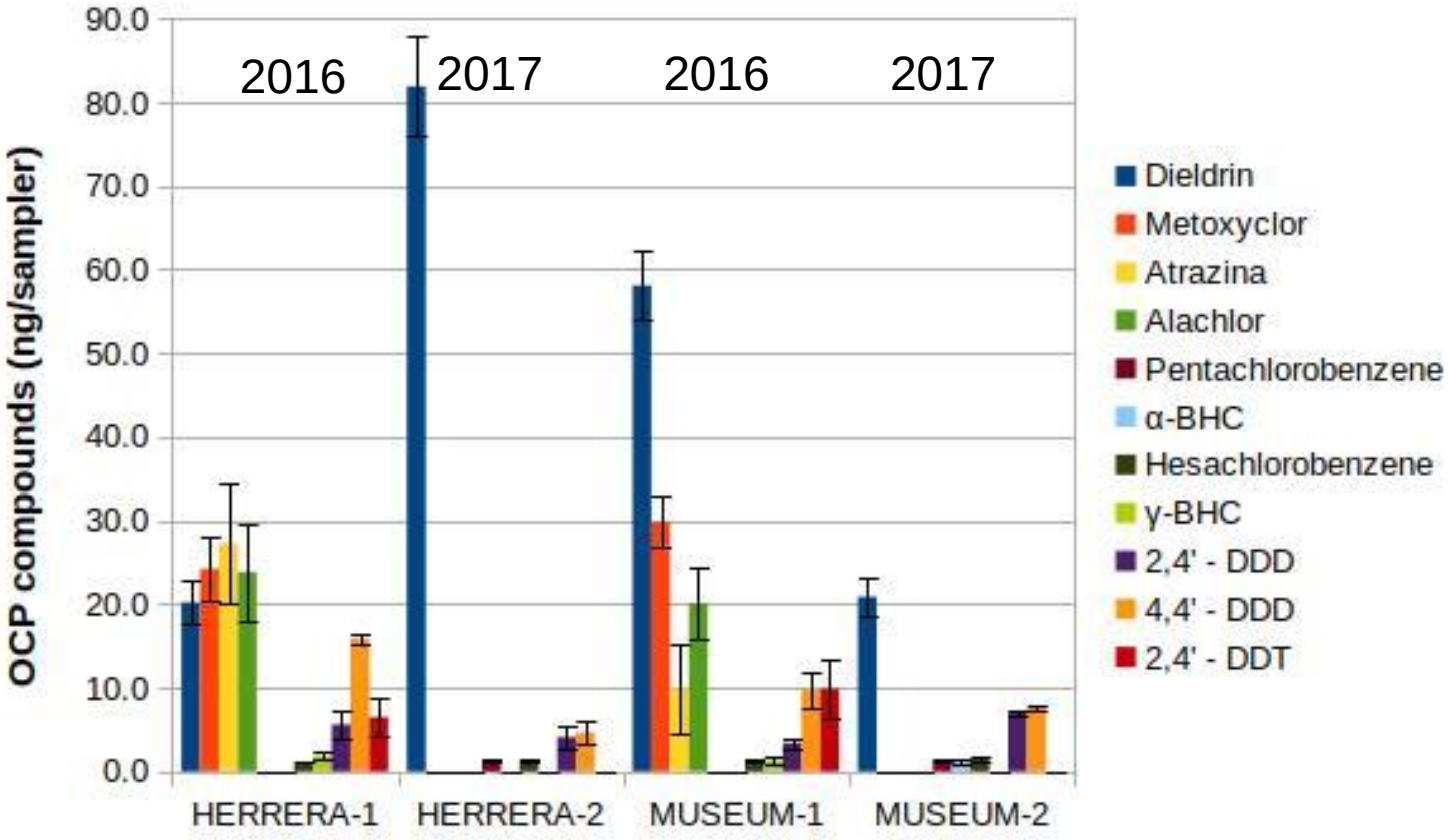
Current study

24-31 ngL^{-1}

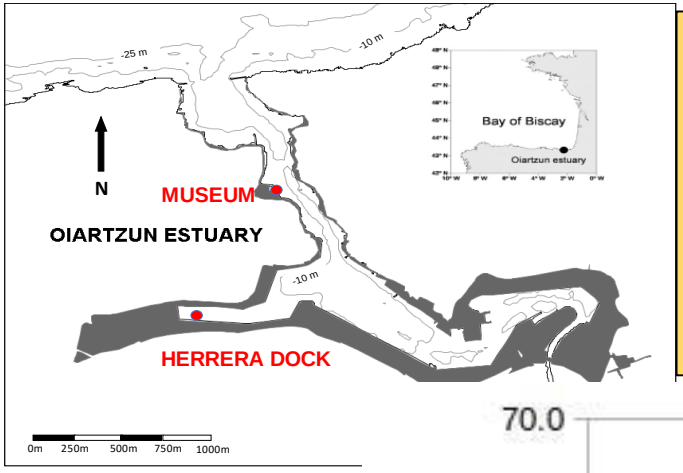
0.9-2 ngL^{-1}

Modified from Monteyne et al. (2013)

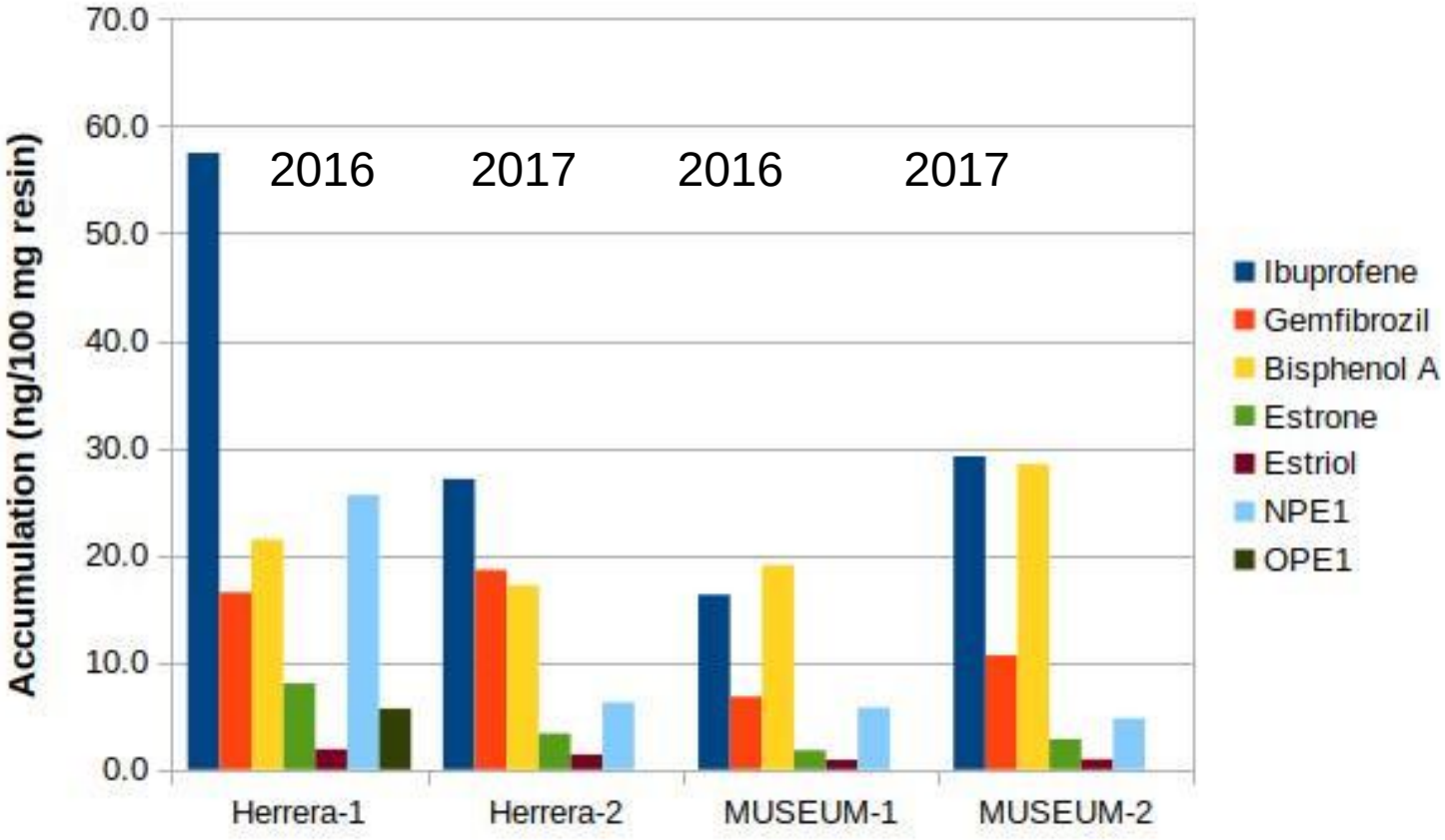
- **Pesticides :** no concentrations. Accumulation results are presented
- Dieldrin is present in all samples
- Metoxychlor,Atrazine and Alachlor was been accumulated only in 2016



Results & Discussion: POCIS



- Accumulation results are presented as ng for 100 mg of resin.
- Several substances were identified
- Ibuprofen was higher in Herrera at 2016



Conclusions

- PS within regulatory monitoring:
  - Measurement of very low concentrations (ppt-level) of a large range of pollutants
  - More representative than monthly-to-quarterly spot sampling
  - Cost-effective: costs vs spatial/temporal information
  - Drawbacks: (i) lack of equilibrium constants for some compounds (ed . Pesticides) (ii) not comparable with EQS

Thank you very much for your attention!

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