

Screening for pharmaceuticals and other emerging pollutants in sediments of major European estuaries

Liza-Marie Beckers¹, Riccardo Massei¹, Lena Schinkel¹, Jens Prothmann¹, Martin Krauss¹, Werner Brack¹
¹Helmholtz Centre for Environmental Research (UFZ), Permoserstraße 15, 04318 Leipzig, Germany
 liza-marie.beckers@ufz.de

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ENVIRONMENTAL
RESEARCH - UFZ

Background

- Continuous production, distribution and discharge of organic pollutants such as **pharmaceuticals and pesticides**
- Biologically active substances
- Sediments important and often neglected **sinks** for organic pollutants

Aims

- Establishment of extraction, clean-up and screening method **suitable for non-target** screening
- Investigation of **extent** of sediment contamination with human pharmaceuticals and pesticides and assessment of **pollution patterns in European estuaries**

Step 1: Target selection

- **60** target pharmaceuticals selected according to the selection process (**Fig. 1**) from **28** therapeutic classes
- **55** target pesticides and **35** suspect pesticides selected in a similar process

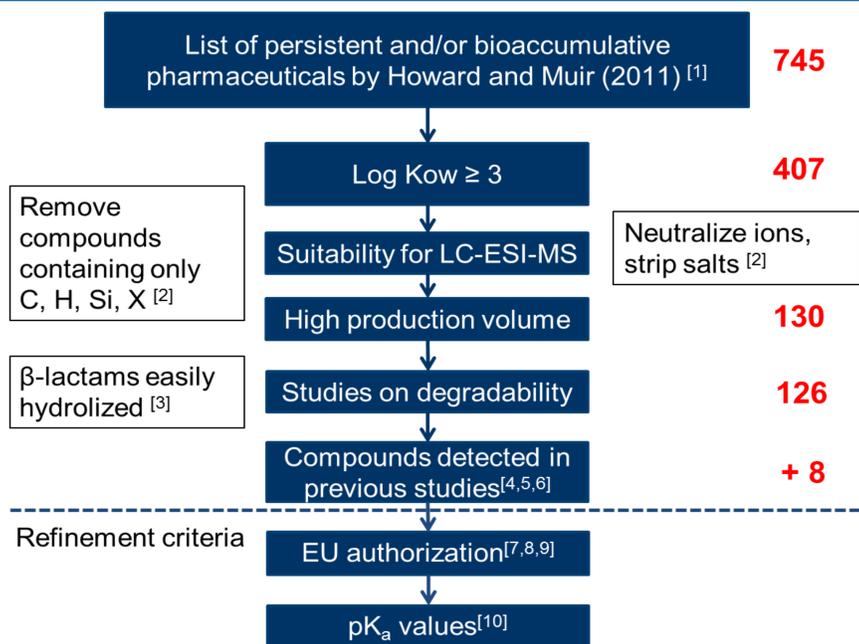


Fig. 1 : Criteria for target selection (red numbers indicating number of pharmaceuticals)

Step 2: Analytical method - Scheme

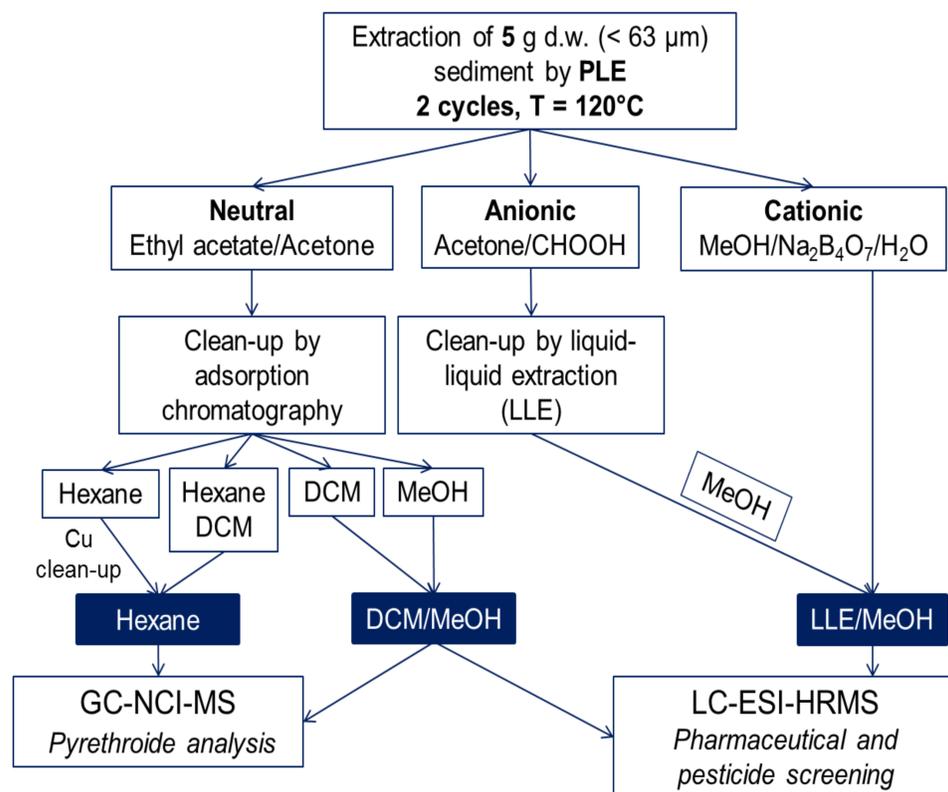


Fig.2: Scheme of analytical method. Copper clean-up and LLE to remove elemental sulfur. (PLE = pressurized liquid extraction; DCM = dichloromethane; MeOH = methanol)

Step 2: Analytical method - Performance

- Method validation and **matrix-matched calibration** with reference sediment
- Recovery **higher than 50%** for more than half of target compounds (**Fig. 3**)
 - Method unsuitable for macrolides and fluoroquinolones
- MDLs (depending on fraction and ESI mode): **0.2 ng/g to 348 ng/g**
- Generally **signal suppression** by matrix effects

Step 3: Target screening

- **11** out of 60 target pharmaceuticals detected (**Table 1**)
- High **matrix effects** hampered quantification in the Thames River
- **Antidepressants** and **antifungals** represented the most of all therapeutic classes
- Beta-blocker **propranolol** detected in each river and in similar concentrations

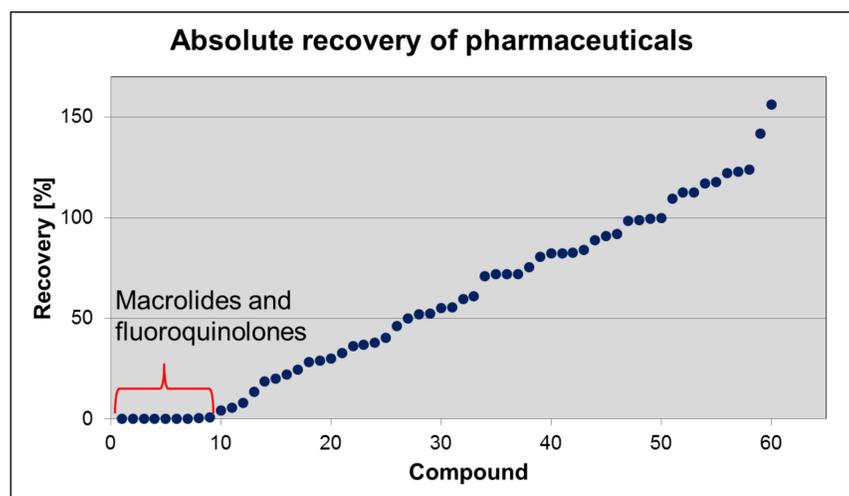


Fig.3: Absolute maximum recovery distribution of target pharmaceuticals

Conclusions

- Pharmaceuticals **ubiquitous** in river sediment, above all antidepressants, antifungals and propranolol
- **Method optimization/validation** for some compounds, improved quantification
- **Ongoing** analysis of further estuaries and screening for pesticides to assess **EU-wide and river basin specific** patterns

Table 1: Results target screening from Danube, Po and Thames River sediment (OC = organic carbon)

Compound	Therapeutic class	Danube (3 sites)		Po (4 sites)		Thames (6 sites)
		ng/g d.w.	mg/kg OC	ng/g d.w.	mg/kg OC	ng/g d.w.
Amiodarone	Antiarrhythmic agent	n.d.		n.d.		<3.3
Amitriptyline	Antidepressant	n.d.		0.8-3.6	0.1-0.5	n.d.
Citalopram	Antidepressant	<0.7		n.d.		<0.7
Efavirenz	Antiretroviral drug	n.d.		n.d.		<13.0
Fluoxetine	Antidepressant	n.d.		5.7-6.5	0.5-0.9	n.d.
Ketoconazole	Antifungal agent	n.d.		n.d.		<10.3
Miconazole	Antifungal agent	n.d.		1.9	0.2	<0.7
Propranolol	Beta-blocker	0.9-1.2	0.1-0.2	1.4-1.5	0.1-0.2	<0.8
Sertraline	Antidepressant	n.d.		<5.3		<5.3
Terbinafine	Antifungal agent	n.d.		6.9-7.4	0.6-1.0	n.d.
Tramadol	Narcotic analgesic	n.d.		0.4	0.04	n.d.

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