Chemical-monitoring on-site exercises to harmonize analytical methods for priority substances in the European Union

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In support of the implementation of the Water Framework Directive (WFD, 2000/60/EC), three intercomparison exercises were carried out on European rivers (Po, Danube and Meuse) in order to assess the current state of monitoring methodologies. Laboratories from European Union (EU) Member States (MSs) were invited to gather at the selected EU river and sample together, each laboratory with its own method. Participants simultaneously sampled the river water and analyzed according to their protocols.

A selection of priority substances (PSs) [i.e. polybromodiphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs) and alkyl phenols (APs)] included in Directive 2008/105/EC were analyzed in standard solutions, extracts from river waters and river-water samples in order to investigate variabilities in different steps of the analytical process.

Concentrations measured in river samples using WFD-monitoring protocols showed that even some of the most challenging WFD PSs (e.g., PAHs, PBDEs and APs) can be measured at WFD-relevant concentrations with methods currently applied in MSs, but variability is still too great and not all laboratories meet required limits of quantification.

Hindrance to the implementation of the monitoring requirements is therefore not the technical feasibility of analysis at these concentration levels, but rather communication, knowledge exchange and harmonization among the laboratories involved.
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Abbreviations: AP, Alkyl phenol; EQS Directive, Environmental Quality Standard Directive (2008/105/EC); EQS, Environmental Quality Standard; LLE, Liquid-liquid extraction; LOQ, Limit of quantification; PAH, Polycyclic Aromatic Hydrocarbon; PBDE, Polybromodiphenyl ether; RSD, Relative standard deviation; SBSE, Stir-bar sorptive extraction; SD, Standard Deviation; SPE, Solid-phase extraction; WFD, Water Framework Directive (2000/60/EC)

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1. The Water Framework Directive and the chemical monitoring exercises

The Water Framework Directive (WFD, 2000/60/EC) sets out environmental objectives to achieve ''good chemical and ecological water status'' for all European waters by 2015, and establishes a clear framework to enable these objectives to be attained, in particular through characterization of European river basins, development of river-basin-management plans, analysis and mitigation of the main

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pressures and impacts, and the establishment of monitoring programs for priority pollutants.

The comparability of monitoring data is of major importance for the implementation of the monitoring requirements under the WFD. European Union (EU) Member States (MSs) need to ensure that all monitoring results meet the required data-quality levels. Minimum performance criteria of analytical methods have been identified by the Commission Directive 2009/90/EC, laying down technical specifications for chemical analysis and monitoring of the state of water. According to this Directive, MSs shall ensure that the minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50% or below (k = 2) estimated at the level of relevant environmental quality standards (EQSs) and a limit of quantification (LOQ) equal or below a value of 30% of the relevant EQS.

In support of the implementation of the WFD, the Institute for Environment and Sustainability (IES) of the EC Joint Research Centre (JRC, Ispra, Italy), in cooperation with the Italian Water Research Institute (IRSA-CNR), organized three collaborative intercomparison exercises, carried out on European rivers (Po, Danube and Meuse). In order to assess the current state of monitoring methodologies, in these exercises, laboratories from EU MSs, national reference laboratories or laboratories chosen among those in charge of WFD monitoring, were invited to meet at a selected EU river and analyze independently the river water. Participants simultaneously sampled river water and analyzed it according to their protocols for a selection of organic priority substances (PSs) included in the Environmental Quality Standard Directive (EQS Directive, 2008/105/EC).

The exercises were planned as collaborative field trials with a scientific perspective, thus not related to proficiency tests and their requirements. Participants had to report data as planned in the WFD-reporting procedure.

Due to the nature of the trials and the number of reported data, a statistical evaluation according to international guidelines and standards [1] was not aimed at. The scope of the exercises was to obtain a realistic picture of the analytical method performance for WFD monitoring of a selected set of compounds and to stimulate harmonization among the MSs. The workshop character of the meeting and the on-site discussion about sampling and analysis of PSs were therefore an integral and important aspect of the exercises.

The present article aims to present the main results obtained in the three campaigns and to highlight gaps in the methods employed for WFD monitoring.

2. Experimental set-up

The approach involved organization of three field campaigns in 2006, 2008 and 2010, respectively, for joint sampling of river water and comparison of the resulting data. The experimental set-up for the campaigns focused on a collaborative approach under realistic field conditions. Each campaign was preceded by a preparatory workshop that aimed at information exchange and briefing of the participants.

The setting of the exercises on European rivers, the use of the three different sample types and the target compounds were the same in order to allow comparability of the results.

The sampling locations were selected for easy access to the water surface with common sampling tools. Logistics included the availability of on-site laboratory facilities for sample preparation and packaging, and the possibility to ship cooled samples via express courier service.

Laboratories participating in the exercises analyzed three types of samples in order to assess the performance of different steps in their analytical methodologies:

- **Standard solutions**

Laboratories received standard solutions of target compounds sealed in brown borosilicate glass ampoules. Standard solutions with certified concentrations for the PBDE congeners and PAHs were purchased and shipped to the participants of the exercise. For the APs, standard solutions were prepared by the organizing team or purchased with certified concentrations. Analysis of these solutions by the participants should provide information on the instrumental analysis variability, but excluding variations deriving from sampling and sample-preparation procedures.

- **Sample extracts**

A homogenized extract from a sample from natural river water should show the result variability when analyzing samples containing natural environmental matrix. Samples for PAHs and PBDEs were prepared by filtering 300 L of river water, collected in a pre-campaign on the selected river, on a heat-purified glass-fiber-wound filter cartridge (5 cm diameter, 15 cm long) with a nominal retention rate of 1 μm (General Filtration, Concord, Canada). The filter was Soxhlet extracted with acetone/n-hexane 1:1. The extract was dried over Na_2SO_4, then homogenized and the solvent changed to toluene. The aliquots for each participant were filled into flame-sealed borosilicate brown glass ampoules. For APs, 15 L of river water (River Seveso, Northern Italy) were extracted by SPE using 15 C18. The eluates were merged and evaporated to 15 mL. Each laboratory obtained 1 mL of this extract, corresponding to 1-L of river water

- **River water**

Samples from the river-water body were taken by each participant. The participants, specified by the individual

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