IMEP-23: The eight EU-WFD priority PAHs in water in the presence of humic acid

Johannes van de Kreeke, Beatriz de la Calle, Andrea Held, Ofelia Bercaru, Marina Ricci, Penka Shegunova, Philip Taylor

Recently, the International Measurement Evaluation Programme (IMEP) organized an interlaboratory comparison on total concentrations of eight polycyclic aromatic hydrocarbons (PAHs) in natural inland waters. It was carried out in support to the European Union Water Framework Directive (EU-WFD) that lists these eight as priority substances.

As sample matrix, we used groundwater spiked with humic acid as a model for the colloidal substances that are present in natural inland waters. Humic substances can adsorb PAHs, but we found that some laboratories did not apply analytical procedures that sufficiently accounted for this. One of these laboratories was involved in establishing the reference values. We show how this impacted on the reliability of their measurements.

Many participants accepted our invitation to report their measurement uncertainties. We assessed their results against our reference values and uncertainties, and provided z and zeta scores. Although the overall measurement capability appears satisfactory, there is room for improvement of analytical procedures as regards the use of measurement standards.

Keywords: Dissolved organic matter (DOM); Humic substance; Interlaboratory comparison (ILC); Internal standard; International Measurement Evaluation Programme (IMEP); Polycyclic aromatic hydrocarbon (PAH); Reference value; Uncertainty; Water; Water Framework Directive (WFD)

Johannes van de Kreeke*, Beatriz de la Calle, Andrea Held, Ofelia Bercaru, Marina Ricci, Penka Shegunova, Philip Taylor
European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel, Belgium

*Corresponding author.
Address: BAM Federal Institute for Materials Research and Testing, 12200 Berlin, Germany.
Tel.: +49 30 81043706;
Fax: +49 30 81043717;
E-mail: johannes.kreeke@bam.de

1. Introduction

The Water Framework Directive (WFD) 2000/60/EC [1] is the legislative framework for protecting the quality of inland and coastal waters in the European Union (EU). It defines chemical substances for priority remediation in the daughter Decision 2455/2001/EC [2] and their maximum levels in Directive 2008/105/EC [3]. The priority group includes eight polycyclic aromatic hydrocarbon (PAH) congeners: naphthalene, anthracene, fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene. The WFD requires monitoring of whole water (i.e. water with suspended particulate and colloidal matter), which can pose an additional difficulty to analysis, particularly of hydrophobic compounds that strongly adsorb to particles [4,5].

In 2007/2008, an interlaboratory comparison (ILC) on total concentrations of the eight congeners in natural inland water was carried out in the frame of the WFD. With the aim of providing realistic, yet well-defined, sample material, groundwater was spiked with purified humic acid to mimic natural colloids. To identify potential complications better, reference values (in the sense of ISO 13528 [6]) were used for statistical evaluation instead of the more common consensus values. Participants were also invited to provide their uncertainty estimate. We report the set-up and the results of the study.

The International Measurement Evaluation Programme (IMEP) [7] has a tradition of organizing challenging ILCs, and using reference values and their uncertainties for evaluation. IMEP is a program of the Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre, a Directorate General of the European Commission. IRMM operates different water-quality monitoring activities in the frame of the WFD.

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2. Participation

Laboratories routinely involved in monitoring activities in the frame of the WFD were targeted as participants. Invitations for participation were channeled via IMEP regional coordinators, the European Co-operation for Accreditation, and the International Committee for Protection of the Danube River. A total of 59 laboratories from 27 countries took part, most of them from the EU, some from potential future accession states of the EU, and a few from other parts of the world. Analysis of participants showed that IMEP had reached a large proportion of experienced routine laboratories in Europe.

3. Test material

3.1. Sample set-up

The sample-material package comprised two bottles of filtered groundwater, a humic acid spiking solution and a PAH spiking solution. To enhance their stability, these constituents were kept separate until use. Laboratories prepared the sample material following a detailed reconstitution protocol. The reconstituted material comprised two water samples, each of 500 mL, spiked with 1 mL humic acid solution and 1 mL PAH spiking solution. Experience gathered in the SWIFT-WFD project (separate water and PAH constituents but no humic acid) had previously indicated the suitability of this approach [8,9].

3.2. Preparation of constituents

3.2.1. Water. Groundwater was pumped up in Belgium, filtered over a 0.45 μm membrane filter and filled into a 200 L polyethylene drum. To allow sedimentation, the drum was stored at 4°C for about one month. Then, the water was filtered through a 0.2 μm membrane filter and filled into 500 mL polypropylene bottles. These bottles were stored at 4°C until dispatch. The groundwater was checked for contamination by any of the eight target PAHs and shown to contain naphthalene below the quantification limit of 8 ng/L. The content of natural dissolved organic matter was ~1 mg/L.

3.2.2. Humic-acid solution. Three aliquots of 7.5 g humic acid each (Fluka, technical grade) were weighed into three beakers. The beakers were filled with 500 mL Milli-Q water each and placed in a sonication bath for 1 h at 40°C to enhance dissolution. Then, the content of the beakers was centrifuged and filtered through a 0.45 μm membrane filter. The filtrates were pooled. The humic acid concentration of the resulting solution was ~2 g/L. Amber glass bottles of 30 mL volume were each filled with 15 mL solution. These bottles were stored at 4°C until dispatch. The solution was free of measurable amounts of PAHs [10].

3.2.3. PAH solution. High-purity crystalline PAH substances provided by IRMM (Geel, Belgium) and Dr. Ehrenstorfer (Augsburg, Germany) were used for the PAH spiking solution. An aliquot of 10–30 mg of each congener was weighed and dissolved in ~25 mL of an acetonitrile/toluene mixture (in case of benzo[*ghi*]perylene) or acetonitrile only (the other congeners). Aliquots from these stock solutions were mixed and diluted. Amber glass ampoules of 10 mL volume were filled with the resulting solution. The ampoules were filled with argon and sealed. They were stored at 4°C until dispatch.

3.3. Homogeneity and stability

Homogeneity studies were carried out on the humic-acid and PAH-spiking solutions. The relative between-bottle standard deviation, s_{bb}, of the humic-acid samples was 3.3% (which is negligible, considering the excess humic acid present in the reconstituted sample) and 4.7% or less for each of the congeners in the PAH solution. This was shown to be sufficiently homogeneous for the purpose of this ILC according to the criteria laid down in ISO 13528 [6] and the IUPAC Harmonized Protocol [11].

The potential degradation of the PAH and humic-acid spiking solutions during the two months of the study was quantified with an isochronous stability study [12,13]. The stability standard deviation, s_{stab}, was 0.9% for the humic acid solution and 1.1% or less for each of the congeners in the PAH solution at 18°C. Participants were instructed to keep the materials below this temperature.

Further details on the sample materials are described elsewhere [14].

4. The role of humic acid

Hydrophobic organic pollutants (e.g., PAHs that are present in natural inland waters) are both adsorbed on particulate and colloidal organic matter (which is in fact a dimensional continuum) and dissolved in the water phase (although a distinction between the three phases remains operational in nature) [15]. A large part of the organic matter comprises humic substances, and purified commercially-available humic acid was chosen to mimic these substances.

The reconstituted sample material contained ~5 mg/L humic acid, which is within the range usually found in natural inland waters [16,17]. At this concentration, humic acid is present in excess. A higher content would not lead to a significant increase of adsorption of the eight congeners at their concentrations in this ILC, and a significant fraction of each of the congeners still remains in solution [6].

The sample-reconstitution protocol accounted for the adsorptive characteristics of humic acid and prescribed a