

The analytical problem of measuring total concentrations of organic pollutants in whole water

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The Water Framework Directive (WFD) (2000/60/EC) of the European Union provides protection from chemical pollutants through the Environmental Quality Standards (EQS) Directive (2008/105/EC), which sets EQSs for priority substances (PSs) and certain other pollutants, according to the requirements set out in Article 16(8) of the WFD. For organic PSs, these EQSs are expressed as total concentrations in the whole-water sample. Total concentrations can be obtained by direct analysis of the whole-water sample or by separate determinations on filterable and solid phases. Both solutions have their advantages and drawbacks, which we critically discuss in the present review.

Analysis of data in the literature and experience from standardization activities show that it is possible to find a simple extraction method for analyzing whole water without time-consuming separation steps. The solid-phase extraction disk is now subject to standardization efforts as the most promising technique to achieve this goal. We discuss limitations of this approach in the light of the consequences for chemical-status assessment.

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Abbreviations: CFC, Continuous-flow centrifugation; CRM, Certified reference material; EQS, Environmental quality standard; LLE, Liquid-liquid extraction; PAH, Polycyclic aromatic hydrocarbon; PBDE, Polybrominated diphenyl ether; PCB, Polychlorinated biphenyl; PCDD, Polychlorinated dibenzodioxin; PCDF, Polychlorinated dibenzofurans; PLE, Pressurized-liquid extraction; PT, Proficiency test; SBSE, Stir-bar sorptive extraction; SCCP, Short-chain chlorinated paraffin; SPE, Solid-phase extraction; SPM, Suspended particulate matter; TBT, Tributyltin; TOC, Total organic carbon; WFD, Water Framework Directive

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1. Introduction

Organic substances discharged into a water body are subjected to a partition between dissolved and suspended solid phases. Organisms are exposed to the contaminants present in both phases via bioconcentration from water and suspended solid ingestion. As a consequence, for ecosystem protection, it is important to analyze the total concentration of organic substances, which is defined as the concentration of substances in whole-water samples. This concept has also been recognized in the European monitoring programs for the chemical-status assessment of the water bodies. The implementation of monitoring plans requires the availability of reliable and cost-effective analytical

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methods for the determination of organic substances in whole-water samples.

1.1. Legislative framework

The concept of whole-water monitoring under the Water Framework Directive (WFD) (2000/60/EC) has been introduced by the Directive 2008/105/EC, which states, in the Annex 1, Part B, that the Environmental Quality Standards (EQSs) for organic priority substances (PSs) “are expressed as total concentrations in the whole water sample” [1].

In the WFD Common Implementation Strategy (CIS) Guidance on surface-water chemical monitoring [2], “whole water” is defined as a “*synonym for the original water sample and shall mean the water sample when solid matter and the liquid phase have not been separated*”; furthermore, in the same Guidance, it is stated that “*Total concentration of the analyte shall mean the total concentration of the analyte in the whole water sample, reflecting both dissolved and particle bound concentrations of the analyte*”. As reported in the Guidance, whole-water data may be generated by analysis of the whole-water sample, or by separate determinations on liquid and Suspended particulate matter (SPM) fractions. If it can be justified (e.g., by considerations of expected contaminant partitioning), it may be argued that there is no need to analyze a particular fraction. If a sampling strategy is selected involving only liquid or SPM fractions, then European Union (EU) Member States need to justify the choice (e.g., with measurements and calculations) [2].

1.2. The choice of the appropriate matrix for monitoring priority substances

The choice of the matrix to be monitored depends on various factors [e.g., physico-chemical characteristics (mainly the hydrophobicity) of the analyte, the amount of SPM and the granulometry, composition and organic matter content of the SPM]. General principles of pollutant partitioning can be found in the literature {e.g., [3] and references therein}.

The Expert Group on Analysis and Monitoring of Priority Substances (AMPS) [4] concluded that no specific requirements could be made regarding which matrix (whole water, liquid or particulate phase) should be analyzed, because variations in hydrological and environmental circumstances, which are reflected in the quantity and the quality of SPM, preclude rigid categorization and make it difficult to establish general rules for the choice of the appropriate matrix.

However, the first and simplest approach is to consider the hydrophobicity of the analyte, as recommended in the CIS Guidance on sediment and biota monitoring [5]. The proposed rule of thumb is that compounds with $\log K_{ow} > 5$ should preferably be measured in sediments, or in SPM, while compounds with a $\log K_{ow} < 3$ should preferably be measured in water. Of course, this proposed

rule of thumb is a simplification because it is well known that chemical substances with similar K_{ow} can show different behaviors in partitioning on solid phase and that different hydrological conditions of a water body can lead to different sources of SPM characterized by different surface and adsorption properties. Experimental evidence {e.g. [6,7]} indeed confirmed that simple equilibrium models of partitioning underestimate the contribution of the SPM-bound fraction with respect to the whole-water concentration. Furthermore, partitioning between SPM and the filterable phase may not be at equilibrium in field situations and shows considerable spatial and temporal variability due to changes in river discharges and quality and quantity of SPM [3].

Even if it is clear that it is impossible to establish a set of rules for the choice of the appropriate matrix, there are extreme cases (e.g., when the analyte has a $\log K_{ow} > 5$ and the SPM amount is > 50 mg/L or, on the other side, when the $\log K_{ow}$ is < 3 and SPM is < 5 mg/L) that can be easily managed analyzing, respectively, only the SPM or the dissolved fraction. In all other situations, it is necessary to find a reliable way to analyze the total concentration of organic substances in the whole water.

In 2008, more than 14 million data points from European laboratories in charge of WFD monitoring were collected in a database for assessing emerging priority pollutants. Data analysis showed that about 70% of the analyses for total concentration of organic substances were carried out without separation of liquid and SPM phases [8].

Not all the extraction and analytical methods ensure the same level of accuracy when they are applied to water samples with different levels of SPM [9]. This fact could imply a lack of comparability of monitoring data among Member States with the consequence that the chemical classification of the European water bodies could depend on the analytical method chosen.

In the present article, we review the approaches to analyzing organic compounds in whole water, as proposed and tested in the scientific literature and in European standardization activity.

2. Analytical approach

Total concentrations of organic substances in whole water may be generated by direct analysis of the whole-water sample or by separate determinations on filterable and solid phases. The main advantages and drawbacks of both general approaches are presented in Table 1.

2.1. Analytical methods with phase separation

Following this approach, the whole-water concentration for checking EQS compliance is obtained by summing the two concentrations obtained in two different analytical determinations characterized by their individual uncertainties.

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