



Stability of organochlorine pesticides during storage in water and loaded SPE disks containing sediment

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HIGHLIGHTS

- Stability study of 21 OCPs of the WFD in water and sediment samples.
- Comparison of different storage conditions of OCPs/CRMs spiked in water samples and pre-concentrated on SPE-disks.
- Addition of sodium azide in water samples as inhibitor during storage period.
- Recommendation to use SPE-disks for storage.

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ABSTRACT

With regard to the Water Framework Directive (WFD) and the required investigation of the whole water sample including suspended particulate matter (SPM), a storage stability study was conducted to determine the suitable storage time and conditions of 21 organochlorine pesticides (OCPs) spiked in water samples and pre-concentrated on solid-phase extraction disks (SPE disks). Furthermore, this work demonstrates the behaviour of three different certified sediment reference materials (CRMs) contaminated with OCPs in water samples as well as loaded on SPE disks under different temperature conditions and storage time periods. Extracts collected on SPE disks were stored for 3, 14 and 30 days at both 4 °C and –18 °C in darkness covered in (a) freezer bags and (b) aluminum foil. With few exceptions the results of these tests demonstrate stability of OCPs up to 30 days at –18 °C. The recoveries for most substances range between 84% and 133%. Furthermore, the stability of OCPs in water samples additionally spiked with CRM up to 500 mg and stored at a temperature of 4 °C in darkness up to 56 days was investigated. The addition of sodium azide enhanced the stability of some substances during storage, especially the endosulfans (I, II) but most substances were stable regardless of sodium azide addition over the entire storage period. An important conclusion of this study is that the storage of loaded SPE disks is an appropriate alternative to storing water samples.

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1. Introduction

Organochlorine pesticides (OCPs) are a large group of structurally diverse organic compounds that belong to the group of persistent organic pollutants (POPs) (Kuranichie-Mensah et al.,

2012), (Kim et al., 2007). Properties of these substances include high bioaccumulation, persistence in the environment and high toxicity to non-target organisms (Kim et al., 2008), (Zhang et al., 2005), (Pereira et al., 1996). Moreover, they are only slightly soluble in water and also show a high affinity for sediments (Kuranichie-Mensah et al., 2012), (Chee et al., 1996). Further biological or chemical degradation and sorption to organic matter are important factors (Domingues et al., 2009). The strong affinity of OCPs to organic matter leads to a large fraction bound to suspended particulate matter (SPM) or sediment (Font et al., 1993), (Andreu and Picó, 2004). SPM and sediment are therefore important reservoirs

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for OCPs, which contributes to the transport of these compounds in the aquatic environment (Yang et al., 2013). Generally, the half-lives of pesticides at low concentrations are, as one may expect, very much dependent on storage conditions of the collected water samples (Ferrer and Barcelo, 1997). Due to the negative impact of the OCPs on the biological ecosystem the European Water Framework Directive (WFD, directive 2013/39/EU) demands an extensive monitoring of surface water (inland and other surface waters) and specifies annual average environmental quality standards (AA-EQS) for priority hazardous compounds. In the course of this decision, it was determined that the whole water sample including SPM has to be examined for the priority hazardous compounds such as OCPs (Directive, 2013/39/EU of the European Parliament and of the council of 12 August 2013 amending Directive 200/60/EC and 2008/105/EC a regards, 2013).

Most commonly used methods for sample preparation prior to the measurement of OCPs in water involve liquid-liquid extraction (LLE), solid-phase extraction (SPE) and disk-based extraction using a solid-phase extraction disk (SPE disk) (Hennion, 1999), (Pichon, 2000), (Erger and Schmidt, 2014). Compared to LLE and SPE cartridges, SPE disks have several advantages, in particular the higher sampling flow without risk of channelling or clogging by SPM (Barceló et al., 1994). There are already numerous studies confirming good recoveries of pesticides in water and in soil/sediment using SPE disks (Barceló et al., 1994), (Viana et al., 1996), (Sabik et al., 2000), (Erger et al., 2012), (Erger et al., 2013), (Bao et al., 1996).

The method for appropriate collection and preservation of water samples is as important as sample preparation and the subsequent determination method (Moradi et al., 2015). In routine water analysis, it is common practice to collect and store water samples until determination of target analytes begins. However, one needs to consider the stability of the analysed substances in water as well as on SPE disks (Chee et al., 1996), (Senseman et al., 1993). There are several processes, including hydrolysis, photolysis, biodegradation and oxidation that can lead to the loss of pesticides in water (Sabik and Jeannot, 2000). In order to ensure the stability of pesticides in water it is often necessary to add inhibitors (HgCl₂, sodium azide, sodium bisulfate, ascorbic acid) to avoid biological degradation during the storage (Jeannot, 1994), (Maskarinec et al., 1990), (Gómez-Ariza et al., 1999), (Munch and Frebis, 1992).

Several studies have shown that the enrichment of organic contaminants on SPE disks and subsequent storage considerably enhances flexibility in the storage and transportation of water samples (Barceló et al., 1994), (Martinez and Barceló, 1996). However, only few studies focussed on the effect of storage conditions on compound stability. (Kuranchie-Mensah et al., 2012), (Gómez-Ariza et al., 1999), (Wegener et al., 1999). Studies that show results for the storage of certified reference materials (CRMs) spiked in water resembling storage of water samples containing SPM are still lacking although changes in the sample during storage can hardly be compensated by quality control measures. To prove the stability of CRMs in water during a storage period is not a regular method, and most of the studies used air-dry, freeze-dry and pasteurized sediments or CRM for stability tests, not aqueous samples (Kuranchie-Mensah et al., 2012), (Gómez-Ariza et al., 1999), (Wegener et al., 1999), (Lyytikäinen et al., 2003), (Yang et al., 2010), (Pham et al., 2016). CRMs are not only important as surrogates of SPM but also play an important and essential role in achieving the traceability, comparability and reliability of analytical measurement results between laboratories and in different time periods. Furthermore, they are relevant in international standardizing activities and accreditation of laboratories (Guide, 2015), (Quevauviller, 1998), (Yarita et al., 2007), (Ulberth, 2006), (Kieflasa

et al., 2016), (Ricci et al., 2016), (Ishikawa and Chiba, 2007).

The influence of storage conditions on analytical measurements and the associated results is an important but hitherto often neglected part of the overall analytical process and is also emphasized in the EURACHEM/CITAC Guide CG 4 - Quantifying Uncertainty in Analytical Measurement (Quantifying Uncertainty in Analytical Measurement, 2012). The aim of the present work was therefore to provide for the first time comprehensive data for storage of OCPs as important class of compounds regulated as priority pollutants in the WFD in routine water monitoring. Basis of the assessment was a systematic study of storage conditions and stability tests for water samples containing OCPs and CRMs, including storage of the water itself and SPE disks, both with and without sodium azide as chemical preservative and at various temperatures.

2. Experimental

2.1. Standards, reagents and solvents

In this study, the following 21 organochlorine pesticides were investigated: alachlor, aldrin, dieldrin, endrin, isodrin, 2,2-bis(*o,p*-chlorophenyl)-1,1,1-trichloroethane (*o,p'*-DDT), *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT), *p,p'*-(dichlorodiphenyl) dichloroethane (*p,p'*-DDD), *p,p'*-(dichlorodiphenyl)-2,2-dichloroethylene (*p,p'*-DDE), hexachlorobenzene (HCB), hexachlorobutadiene (HCBd), α -hexachlorocyclohexane (α -HCH), β -hexachlorocyclohexane (β -HCH), γ -hexachlorocyclohexane (γ -HCH), δ -hexachlorocyclohexane (δ -HCH), pentachlorobenzene, 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,3,5-trichlorobenzene (1,3,5-TCB), α -endosulfan (I) and β -endosulfan (II). The analytical standards were purchased from Fluka, Dr. Ehrenstorfer, Riedel de Hën and Ultra Scientific. The internal standards used were hexachloro-1,3-butadiene-¹³C₄, α -endosulfan-D₄, 4,4'-DDT-¹³C₁₂, alachlor-D₁₃, hexachlorobenzene-¹³C₆, and 1,2,4-trichlorobenzene-D₃. In addition fluoranthene-D₁₀ was used as volumetric standard. Isotope labelled substances were purchased from Dr. Ehrenstorfer and Cambridge Isotope Laboratories. The purity of all used analytical standards was at least 97%. The stock solutions were prepared by dissolving the pure analytical standard in ethyl acetate and stored at 4 °C.

The stock solutions were used for the preparation of diluted standard solutions and for spiking water samples using acetone as solvent. All solutions were stored at 4 °C in darkness (details can be found in the Supplementary Material, Tables S1–S5).

For the tests with sediments, three different certified sediments (certified reference material = CRM) were used: (I) Pesticides-Clay Loam 1 (Sigma Aldrich RTC, CRM847-50G, Lot-No002405). This sediment contains 12 of the 21 OCPs included in this study with concentrations between 65 µg/kg and 380 µg/kg (II) Pesticides-Loam 1 (Sigma Aldrich RTC, CRM818-50G, Lot-No LRAA4271). This sediment contains 9 of the 21 OCPs. The concentration range of the substances varies between 94 µg/kg and 380 µg/kg (III) Pesticides-Sandy Loam 4 (Sigma Aldrich RTC, CTM824-50G, Lot-No BL824). This sediment contains 9 of the 21 OCPs, in concentrations between 340 µg/kg and 400 µg/kg (details, see Supplementary Material, Table S6).

For biological inhibition sodium azide (Merck Schuchardt OHG) with a purity of $\geq 99\%$ was used. Tap water filtered over activated carbon was used as blank water. It was also used for rinsing the sample bottles after the extraction step. Water from the river Ruhr was used for the stability tests.

For the concentration and analysis step nitrogen (Air Products)

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