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

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25

26 **Abstract**

27

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

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50 **Keywords:** sample storage; solid phase extraction disk; certified reference material; sodium  
51 azide; organochlorine pesticides

52

## 53 1. Introduction

54 Organochlorine pesticides (OCPs) are a large group of structurally diverse organic  
55 compounds that belong to the group of persistent organic pollutants (POPs) (Kuranchie-  
56 Mensah et al., 2012), (Kim et al., 2007). Properties of these substances include high  
57 bioaccumulation, persistence in the environment and high toxicity to non-target organisms  
58 (Kim et al., 2008), (Zhang et al., 2005), (Pereira et al., 1996). Moreover, they are only slightly  
59 soluble in water and also show a high affinity for sediments (Kuranchie-Mensah et al., 2012),  
60 (Chee et al., 1996). Further biological or chemical degradation and sorption to organic matter  
61 are important factors (Domingues et al., 2009). The strong affinity of OCPs to organic matter  
62 leads to a large fraction bound to suspended particulate matter (SPM) or sediment (Font et al.,  
63 1993), (Andreu and Picó, 2004). SPM and sediment are therefore important reservoirs for  
64 OCPs, which contributes to the transport of these compounds in the aquatic environment  
65 (Yang et al., 2013). Generally, the half-lives of pesticides at low concentrations are, as one  
66 may expect, very much dependent on storage conditions of the collected water samples  
67 (Ferrer and Barceló, 1997). Due to the negative impact of the OCPs on the biological  
68 ecosystem the European Water Framework Directive (WFD, directive 2013/39/EU) demands  
69 an extensive monitoring of surface water (inland and other surface waters) and specifies  
70 annual average environmental quality standards (AA-EQS) for priority hazardous compounds.  
71 In the course of this decision, it was determined that the whole water sample including SPM  
72 has to be examined for the priority hazardous compounds such as OCPs (Directive  
73 2013/39/EU of the European Parliament and of the council of 12 August 2013 amending  
74 Directive 200/60/EC and 2008/105/EC a regards, 2013).

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

83 The method for appropriate collection and preservation of water samples is as important as  
84 sample preparation and the subsequent determination method (Moradi et al., 2015). In routine  
85 water analysis, it is common practice to collect and store water samples until determination of

86 target analytes begins. However, one needs to consider the stability of the analysed substances  
87 in water as well as on SPE disks (Chee et al., 1996), (Senseman et al., 1993). There are  
88 several processes, including hydrolysis, photolysis, biodegradation and oxidation that can lead  
89 to the loss of pesticides in water (Sabik and Jeannot, 2000). In order to ensure the stability of  
90 pesticides in water it is often necessary to add inhibitors (HgCl<sub>2</sub>, sodium azide, sodium  
91 bisulfate, ascorbic acid) to avoid biological degradation during the storage (Jeannot, 1994),  
92 (Maskarinec et al., 1990), (Gómez-Ariza et al., 1999), (Munch and Frebis, 1992).

93 Several studies have shown that the enrichment of organic contaminants on SPE disks and  
94 subsequent storage considerably enhances flexibility in the storage and transportation of water  
95 samples (Barceló et al., 1994), (Martinez and Barceló, 1996). However, only few studies  
96 focussed on the effect of storage conditions on compound stability. (Kuranchie-Mensah et al.,  
97 2012), (Gómez-Ariza et al., 1999), (Wegener et al., 1999). Studies that show results for the  
98 storage of certified reference materials (CRMs) spiked in water resembling storage of water  
99 samples containing SPM are still lacking although changes in the sample during storage can  
100 hardly be compensated by quality control measures. To prove the stability of CRMs in water  
101 during a storage period is not a regular method, and most of the studies used air-dry, freeze-  
102 dry and pasteurized sediments or CRM for stability tests, not aqueous samples (Kuranchie-  
103 Mensah et al., 2012), (Gómez-Ariza et al., 1999), (Wegener et al., 1999), (Lyytikäinen et al.,  
104 2003), (Yang et al., 2010), (Pham et al., 2016). , CRMs are not only important as surrogates  
105 of SPM but also play an important and essential role in achieving the traceability,  
106 comparability and reliability of analytical measurement results between laboratories and in  
107 different time periods. Furthermore, they are relevant in international standardizing activities  
108 and accreditation of laboratories (Guide, 2015), (Quevauviller, 1998), (Yarita et al., 2007),  
109 (Ulberth, 2006), (Kielbasa et al., 2016), (Ricci et al., 2016), (Ishikawa and Chiba, 2007).

110  
111 The influence of storage conditions on analytical measurements and the associated results is  
112 an important but hitherto often neglected part of the overall analytical process and is also  
113 emphasized in the EURACHEM / CITAC Guide CG 4 - Quantifying Uncertainty in  
114 Analytical Measurement (“Quantifying Uncertainty in Analytical Measurement,” 2012). The  
115 aim of the present work was therefore to provide for the first time comprehensive data for  
116 storage of OCPs as important class of compounds regulated as priority pollutants in the WFD  
117 in routine water monitoring. Basis of the assessment was a systematic study of storage  
118 conditions and stability tests for water samples containing OCPs and CRMs, including storage

119 of the water itself and SPE disks, both with and without sodium azide as chemical  
120 preservative and at various temperatures.

121

## 122 **2. Experimental**

123

### 124 *2.1 Standards, Reagents and Solvents*

125

126 In this study, the following 21 organochlorine pesticides were investigated: alachlor, aldrin,  
127 dieldrin, endrin, isodrin, 2,2-bis(o,p-chlorophenyl)-1,1,1-trichloroethane (*o,p'*-DDT), *p,p'*-  
128 dichlorodiphenyltrichloroethane (*p,p'*-DDT), *p,p'*-(dichlorodiphenyl)dichloroethane (*p,p'*-  
129 DDD), *p,p'*-(dichlorodiphenyl)-2,2-dichloroethylene (*p,p'*-DDE), hexachlorobenzene (HCB),  
130 hexachlorobutadiene (HCBd),  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH),  $\beta$ -hexachlorocyclohexane  
131 ( $\beta$ -HCH),  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH),  $\delta$ -hexachlorocyclohexane ( $\delta$ -HCH),  
132 pentachlorobenzene, 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB),  
133 1,3,5-trichlorobenzene (1,3,5-TCB),  $\alpha$ -endosulfan (I) and  $\beta$ -endosulfan (II). The analytical  
134 standards were purchased from Fluka, Dr. Ehrenstorfer, Riedel de Haen and Ultra Scientific.  
135 The internal standards used were hexachloro-1,3-butadiene- $^{13}\text{C}_4$ ,  $\alpha$ -endosulfan-D<sub>4</sub>, 4,4'-DDT-  
136  $^{13}\text{C}_{12}$ , alachlor-D<sub>13</sub>, hexachlorobenzene- $^{13}\text{C}_6$ , and 1,2,4-trichlorobenzene-D<sub>3</sub>. In addition  
137 fluoranthene-D<sub>10</sub> was used as volumetric standard. Isotope labelled substances were  
138 purchased from Dr. Ehrenstorfer and Cambridge Isotope Laboratories. The purity of all used  
139 analytical standards was at least 97%. The stock solutions were prepared by dissolving the  
140 pure analytical standard in ethyl acetate and stored at 4 °C.

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

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

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

157 For the concentration and analysis step nitrogen (Air Products) and helium gas (Air Liquid)  
158 were utilized with a purity of 5.0.

159

160

## 161 *2.2 Equipment and Analytical Procedure*

162

163 For sample extraction and storage a SPE disk of the type Bakerbond-Speedisk Extraction  
164 Disk C<sub>18</sub> (diameter: 50 mm, J.T. Baker) was used.

165 The drying process was performed with a SPE disk vacuum apparatus combined with SPE-  
166 disk holder (Macherey-Nagel). Furthermore, the vacuum system was connected to a high  
167 vacuum pump (LABOVAC-Tower Typ KCP 6/3Z SASKIA Hochvakuum und Labortechnik  
168 GmbH).

169 Determination of the analytes was carried out using an Agilent GC system (model 6890/MSD  
170 5973) equipped with a Gerstel autosampler (MultiPurpose Sampler MPS2). PTV injection  
171 was performed with a Gerstel CIS 4 inlet. The CIS 4 inlet was equipped with an empty,  
172 deactivated, single-baffled glass liner (Gerstel); a volume of 1  $\mu\text{L}$  was injected with the  
173 autosampler using a 10  $\mu\text{L}$  syringe; the CIS temperature was increased with 12  $^{\circ}\text{C}/\text{s}$  from  
174 60  $^{\circ}\text{C}$  (0 min) to 250  $^{\circ}\text{C}$  and held for 5 min; the PTV injection was operated in a splitless  
175 mode with a purge flow of 20.0 mL/min and a purge time of 2.00 min; helium was used as a  
176 carrier gas at a constant flow of 1.0 mL/min.

177 For the GC separation a Zebron ZB 5ms (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ) capillary column by  
178 Phenomenex was used, the oven temperature was increased with 10  $^{\circ}\text{C}/\text{min}$  from 65  $^{\circ}\text{C}$   
179 (0 min) to 300  $^{\circ}\text{C}$  and was held for 10 min (total run time: 33.50 min).

180 The analytes were ionized in electron impact ionization mode (70 eV) and detected in selected  
181 ion monitoring (SIM) mode. The compounds were identified by their retention times and  
182 maximum four characteristic mass-to-charge ratios (m/z ratio) of which one was used for  
183 quantification (as described in the Supplementary Material, Tab. S1 and S2). The  
184 temperatures for the transfer line and the ion source were set constantly to 280  $^{\circ}\text{C}$  and 250  $^{\circ}\text{C}$ ,  
185 respectively.

186

## 187 *2.3. Sample Preparation Procedure*

188

189 The procedures in this study represented several conditions for storage of samples for  
190 subsequent determination of OCPs, as summarized in Table 1.

191 1-L water samples with and without addition of 40 mg sodium azide were spiked with OCPs  
192 to a concentration level of 5 ng/L. The same spike procedure was also used for the enrichment  
193 of OCPs on SPE disks with a spike concentration level of 10 ng/L.

194 The preparation of water samples with CRM (I, II, III) was carried out with the same  
195 procedure. 1-L water samples with CRM (I, II, III) were spiked with up to 500 mg of each  
196 CRM in a concentration level between 0.032 µg/kg and 0.2 µg/kg with and without addition  
197 of 40 mg sodium azide. Recoveries were determined as the ratio of nominal and found  
198 concentration as determined with the previously established method (Günter et al., 2016).

199

200 The validated SPE method steps were carried out as described in our previous study (Günter  
201 et al., 2016) - and are visualized in Figure 1.

202

### 203 3. Results and Discussion

204

#### 205 3.1 Stability of OCPs in Water Samples

206

207 The stability experiments of OCP spiked water samples were carried out for 4, 7, 12 and 15  
208 days. Table 2 shows the mean extraction recoveries of OCPs for storage of water samples  
209 without and with sodium azide at 4 °C after four and fifteen days in glass bottles. Detailed  
210 information about the results after seven and twelve measurement days can be found in the  
211 Supplementary Material, Table S7.

212

213 The recoveries of OCPs in water samples with sodium azide addition showed no substantial  
214 degradation of analytes during the two-week storage. Recoveries of OCPs after four days  
215 ranged between 75% and 129% and after fifteen days between 94% and 112%. After four and  
216 fifteen days of storage no statistically significant difference was observed between the  
217 recoveries of most OCPs ( $p > 0.05$ ). Detailed information about the statistically significant  
218 differences can be found in the Supplementary Material, Table S13. These values are similar  
219 to the recoveries obtained by Munch et al. (Munch and Frebis, 1992) for 14 OCPs and  
220 demonstrate an excellent stability of the investigated substances over a period of 14 days. In  
221 comparison, the results of the recoveries of the OCPs in water samples without sodium azide  
222 demonstrated a significant loss for some analytes after 15 days of storage. Especially the  
223 endosulfans (I) ( $56 \pm 14\%$ ) and (II) ( $47 \pm 9\%$ ) have a low stability as well as *p,p'*-DDE ( $46 \pm$   
224  $8\%$ ), hexachlorobenzene ( $54 \pm 8\%$ ), hexachlorobutadiene ( $64 \pm 10\%$ ),  $\alpha$  and  $\gamma$ -HCH ( $65 \pm$   
225  $13\%$ ,  $67 \pm 12\%$ ), pentachlorobenzene ( $58 \pm 10\%$ ) and the TCBs ( $63 \pm 9\%$ ,  $66 \pm 12\%$ ,  $63 \pm$   
226  $10\%$ ). These findings corroborate previous results by Chee et al. (Chee et al., 1996) on  
227 stability of a few OCPs in water ranging between 56% and 71% after a storage period of 14  
228 days at 4 °C without any use of inhibitors. These results demonstrate the importance of  
229 suppressing microbial degradation of OCPs by addition of sodium azide in the storage of  
230 water samples. This fact was also emphasized by Barceló et al. and Munch et al. (Barceló et  
231 al., 1994), (Munch and Frebis, 1992). Both used  $\text{HgCl}_2$  to inhibit biological degradation  
232 instead of sodium azide.

233

234

235 *3.2 Stability of OCPs in Contaminated Sediment (CRM) Suspended in Water*

236

237 The behaviour of three different CRMs (I, II, III) in water samples was investigated in this  
238 study in order to compare OCP stability in water samples with and without suspended  
239 particulate matter. Spiked water samples with both 100 mg and 500 mg of CRM (I, II, III)  
240 were stored for a period of 1, 3, 7, 14, 28, 42 and 56 days at 4 °C in the darkness. Each  
241 experiment was carried out in triplicates, both without (first batch) and with (second batch)  
242 addition of sodium azide. The three CRMs have some substances in common (Endrin, *p,p'*-  
243 DDT, *p,p'*-DDE, the endosulfans (I, II),  $\alpha$ -HCH and  $\beta$ -HCH). These substances show a  
244 different behaviour during storage (see Supplementary Material, Tables S8 to S9). This fact  
245 could be confirmed by statistically significant differences between substances present in all  
246 three CRMs ( $p < 0.05$ ), (for more information see Supplementary Material, Tables S14 to  
247 S17). The common substances of the three CRMs can be divided in several groups. Endrin,  
248 *p,p'*-DDT and *p,p'*-DDE show stability over the whole storage period independent of sodium  
249 azide use. Nevertheless, the statistical evaluation also indicates a different behaviour of the  
250 three CRMs, except for endrin. This fact is reflected in the different recoveries determined for  
251 CRM I, II and III (see Supplementary Material Tables S8 and S9). The stability of the next  
252 group of substances depended on the use of sodium azide ( $\alpha$ -HCH and  $\beta$ -HCH) and the last  
253 group of substances showed no stability during the storage although sodium azide was used.  
254 This group comprises the endosulfans (I, II) in all CRMs. The results demonstrate a  
255 significant biological degradation up to 90%, especially for  $\beta$ -endosulfan (II), (Figures 2 and  
256 3). The presented results could be evaluated by a multi-way ANOVA, see Supplementary  
257 Material, Tables S18 and S19.

258

### 259 3.3 Stability of OCPs Stored on SPE disks

260

#### 261 *Stability of OCPs in Sediment Free Samples, after being Loaded on SPE disks*

262

263 Results of the recovery showed a slow degradation of some OCPs when SPE disks were  
264 stored for 3 up to 30 days at 4 °C, while the SPE disks being wrapped in a freezer bag. It is  
265 noticeable that aldrin ( $69 \pm 7\%$ ), dieldrin ( $59 \pm 12\%$ ), isodrin ( $58 \pm 3\%$ ), endrin ( $68 \pm 30\%$ ) and  
266 *p,p'*-DDE ( $53 \pm 29\%$ ) are not stable when loaded on SPE disks wrapped in a freezer bag at  
267 4 °C after 30 days. All other substances are stable through the whole storage period under the  
268 same conditions. In comparison, storage at -18 °C results in stability of all OCPs during a  
269 period of 30 days (see Supplementary Material, Table S10). The only exception is isodrin,  
270 which shows a low recovery throughout the whole storage period at -18 °C ( $65 \pm 5\%$  at 3 days,  
271  $55 \pm 8\%$  at 14 days,  $70 \pm 2\%$  at 30 days). Furthermore, *p,p'*-DDD demonstrates lower recovery  
272 at -18°C ( $71 \pm 9\%$ ) in comparison to the storage at 4 °C ( $124 \pm 21\%$ ), see Figure -4.

273 Figure -5 shows the recoveries of some investigated substances ( $\alpha$ -HCH,  $\beta$ -endosulfan (II)  
274 and *p,p'*- DDD) after 3, 14 and 30 days of storage at 4 °C and -18 °C when SPE disks were  
275 wrapped in aluminum foil. In comparison to wrapping the SPE disks in freezer bags, *p,p'*-  
276 DDD showed a higher stability at -18 °C ( $123 \pm 6\%$ ).

277

278 The data for SPE disks wrapped in aluminum foil demonstrate for aldrin ( $51 \pm 12\%$ ), isodrin  
279 ( $52 \pm 16\%$ ), and endrin ( $51 \pm 17\%$ ) nearly the same low recoveries at the storage at 4°C after  
280 30 days in comparison to the results of SPE disks wrapped in freezer bags. The recoveries for  
281 the same substances after storage at -18 C after 30 days were higher (aldrin  $65 \pm 5\%$ , isodrin  
282  $63 \pm 6\%$  and endrin  $73 \pm 17\%$ ). All other substances showed a constant stability when being  
283 stored up to 30 days at 4 °C and -18 °C. Only *o,p'*-DDT shows lower recoveries after 14  
284 ( $66\%$ ) and 30 ( $69\%$ ) days of storage at -18 °C in comparison to 4 °C (14 days:  $84\%$ ; 30  
285 days:  $107\%$ ). Detailed information of all other substances is given in the Supplementary  
286 Material, Table S11. In comparison to the findings by Chee et al. (Chee et al., 1996) this study  
287 could show better recovery results after 14 days of storage at 4 °C for some common OCPs in  
288 both studies like the group of HCHs, the endosulfans (I, II), dieldrin and few other substances.

289 In addition, Martinez and Barceló demonstrated in their work that for 3 months, storage at -20  
290 °C on Empore disks is always the best way for obtaining good recoveries, but storage for a  
291 maximum of 1-2 months at 4 °C is also feasible (Martinez and Barceló, 1996).

292 In summary, both methods of wrapping (freezer bag and aluminum foil) were suitable for SPE  
293 disk storage at 4 °C and -18 °C up to 30 days. With few exceptions such as *p,p'*-DDD and

294 three other substances, no statistically significant difference ( $p \geq 0.05$ ) was found between the  
295 results of the freezing bags and the aluminum foil, detailed information see Supplementary  
296 Material, Tables S20 to S23.

297

298 *Stability of OCPs in Sediment (CRM) Spiked Samples, after being Loaded on SPE disks*

299

300 The data of sediment loaded SPE disks wrapped in freezer bags, demonstrate a significant  
301 degradation of the substances after 30 days of storage at 4 °C, the recoveries ranged between  
302 64% and 80%. In comparison, the results of the storage at -18 °C show higher recoveries after  
303 30 days and ranged between 71% and 148%. The recoveries at 4 °C after 3 and 14 days were  
304 higher (97% - 122%) in comparison to the recoveries at -18 °C (58% - 84%), see Table 3.  
305 This is also shown in the statistically significant difference ( $p < 0.05$ ) between storage at 4 °C  
306 and at -18°C in both freezer bag and aluminum foil, Supplementary Material S24 and S25.  
307 These results demonstrate the need for storage of sediment loaded SPE disks wrapped in  
308 freezer bags at -18 °C if storage exceeds 14 days.

309 Nearly the same results were achieved when wrapping the SPE disks in aluminum foil, Table  
310 4. But in comparison with the result for freezer bag storage, there is no statistically significant  
311 difference between the recoveries of wrapped SPE disks in aluminum foil at 4 °C and at  
312 -18 °C ( $p \geq 0.05$ ), respectively after 30 days (see Supplementary Material Tables S26 and  
313 S27). Both wrapping methods demonstrate in this study stability of OCPs in sediment spiked  
314 samples for a storage period of 30 days at 4 °C and at -18 °C, respectively.

315

316 To compare the applied storage treatments in this study SPE disks were found to be a better  
317 storage medium than water. The obtained results demonstrate a better stability of OCPs  
318 loaded on SPE disks and stored under conditions shown above. Previous studies support these  
319 findings (Domingues et al., 2009), (Sabik et al., 2000), (Senseman et al., 1993), (Lyytikäinen  
320 et al., 2003), (Liška and Bíliková, 1998). Substances under investigation showed similar  
321 recovery results within 14 days of storage at 4 °C when being pre-concentrated on SPE disks  
322 from water samples with CRM rather than remaining in the water samples.

323

324

#### 325 4. Conclusions

326  
327 The results of this study revealed the relevance of storage conditions of 21 priority pollutant  
328 OCPs in water and CRMs. The study has shown that storage of loaded SPE disks seems to be  
329 a better alternative to storing water samples. This was demonstrated for synthetic water  
330 samples both without SPM and containing sediment (CRM) up to 500 mg. Considering the  
331 fact that all these OCPs are categorized as persistent organic pollutants, the limited stability in  
332 non-conserved water samples even at rather low temperatures is surprising. The use of sodium  
333 azide for preservation of water samples without or with CRM showed a significant influence  
334 on the stability for some OCPs, especially the HCHs ( $\alpha$ ,  $\beta$ ). Therefore, sodium azide is  
335 recommended for storing of water samples containing OCPs.

336 SPE disks containing pre-concentrated pesticide samples without additional CRM were  
337 wrapped in freezer bags and aluminum foil and stored for 30 days at 4 °C or at -18 °C. With  
338 few exceptions, both wrapping methods showed high recoveries. The same results were  
339 achieved when loaded SPE disks containing pre-concentrated pesticides bound to CRM were  
340 wrapped in both freezer bags and aluminum foil stored for 30 days at 4 °C or at -18 °C.

341 A further aspect is the storage space. A great advantage of using SPE disks for stabilizing  
342 OCPs after sampling is the reduction of storage space in comparison to 1-L bottles filled with  
343 water (Gómez-Ariza et al., 1999). Furthermore, the necessary equipment to analyze water  
344 samples is often not as suitable and complete as it should be; thus, laboratories have the need  
345 to send these samples to other reference laboratories for analysis, increasing costs of  
346 transportation and processing time (Senseman et al., 1993). The possibility to extract samples  
347 on-site implies simple and safe transportation of SPE disks to the laboratory for final analysis.  
348 Despite its importance, sample storage typically receives less attention in laboratories. This  
349 study has shown the advantages of SPE disk storage over the storage of water samples in  
350 glass bottles. Therefore, the recommendation of this study is the use of SPE disks for storage  
351 of substances like OCPs in samples with and without CRM.

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481 **Figure Captions:**

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483 Fig. 1 Steps of the sample preparation procedure in dependency of the storage treatment  
484 described with A) and B) as defined in Table 1

485

486 Fig. 2 Recovery (%) and SD (%) of  $\beta$ -endosulfan (II) in 1 L water containing 500 mg CRM (I,  
487 II, III) without addition of sodium azide; stored at 4 °C; n = 3

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489 Fig. 3 Recovery (%) and SD (%) of  $\beta$ -endosulfan (II) in 1 L water containing 500 mg CRM (I,  
490 II, III) with addition of sodium azide; stored at 4 °C; n = 3

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492 Fig. 4 Recoveries (%) of  $\alpha$ -HCH,  $\beta$ -endosulfan (II) and  $p,p'$ -DDD after 3, 14 and 30 days of  
493 storage at 4 °C and -18 °C; SPE disks wrapped in freezer bag; n = 3; (SD available in  
494 Supplementary Material, Table S9)

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496 Fig. 5 Recoveries (%) of  $\alpha$ -HCH,  $\beta$ -endosulfan (II) and  $p,p'$ -DDD after 3, 14 and 30 days of  
497 storage at 4 °C and -18 °C; SPE disks wrapped in aluminum foil; n = 3; (SD available in  
498 Supplementary Material, Table S9)

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503 **Table 1:** Different storage conditions of OCPs in spiked water samples and on SPE disks used in this study

	Treatment	Conditions					Total number of samples
		Temperature in °C	Storage period (days)	Addition of sodium azide (40 mg/L) [+ / -]	Number of samples per storage condition n	Wrapping method	
(A)	spiked water samples using an OCP-mix*	+ 4	1, 4, 7, 12, 15	+ / -	6	-	60
	spiked water samples with sediment** (1) with 100 mg/L (2) with 500 mg/L	+ 4	1, 3, 7, 14, 28, 42, 56	+ / -	3	-	252
(B)	OCPs loaded on SPE disks without sediment	+ 4 - 18	3, 14, 30	-	3	(a) freezer bag (b) aluminum foil	36
	OCPs loaded on SPE disks with 500 mg/L sediment***	+ 4 - 18	3, 14, 30	-	3	(a) freezer bag (b) aluminum foil	36

504 \*OCP-mix included 21 OCPs

505 \*\*Sediment (CRM): (I) Pesticides Clay 1; (II) Pesticides-Loam 1; (III) Pesticides-Sandy Loam 4

506 \*\*\*Sediment (CRM): (I) Pesticides Clay 1

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509 **Table 2:** Recovery (%) and SD of OCPs in water samples under different storage conditions; spike level 5 ng/L;  
 510 n = 6

Compound name	Recovery (%) and SD (%)			
	A1	A2	B1	B2
<b>storage at 4°C for x days:</b>				
Alachlor	113±18	91±22	101±12	100±7
Aldrin	88±12	68±16	84±3	106±6
Dieldrin	97±13	67±7	100±3	107±4
Endrin	118±18	108±25	113±5	96±8
Isodrin	83±8	61±10	103±14	99±4
<i>o,p'</i> -DDT	107±23	79±22	96±9	101±9
<i>p,p'</i> -DDT	105±30	86±29	78±9	107±10
<i>p,p'</i> -DDD	111±25	103±22	98±8	101±9
<i>p,p'</i> -DDE	65±17	46±8	90±5	103±14
α-Endosulfan (I)	92±7	56±14	75±3	112±5
β-Endosulfan (II)	91±17	47±9	106±24	97±15
Hexachlorobenzene	66±12	54±8	81±16	106±6
Hexachlorobutadiene	72±17	64±10	106±2	97±10
α-HCH	88±8	65±13	78±15	105±12
β-HCH	113±9	82±14	88±8	104±5
δ-HCH	125±22	94±20	87±6	106±5
γ-HCH	92±5	67±12	78±11	107±7
Pentachlorobenzene	77±6	58±10	99±20	100±13
1,2,3-TCB	77±9	63±9	107±20	96±15
1,2,4-TCB	76±11	66±12	92±8	103±18
1,3,5-TCB	67±10	63±10	129±2	94±25

511 A1 = water without sodium azide at 4 °C after 4 days  
 512 A2 = water without sodium azide at 4 °C after 15 days  
 513 B1 = water with sodium azide at 4 °C after 4 days  
 514 B2 = water with sodium azide at 4 °C after 15 days  
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 516

517 **Table 3:** Recovery (%) and SD (%) of OCPs from 500 mg contaminated sediment [(I) Pesticides Clay 1] loaded  
 518 on SPE disk; wrapped in freezer bags; stored at 4 °C and -18 °C for 3 to 30 days; n = 3

Compound name	Recovery (%) and SD (%)					
	4 °C			-18 °C		
	3 days	14 days	30 days	3 days	14 days	30 days
<i>freezer bag</i>						
$\alpha$ -HCH	122±2	122±7	73±8	98±34	69±17	92±11
$\beta$ -HCH	107±5	116±2	80±4	90±25	84±8	96±5
$\gamma$ -HCH	114±1	111±6	72±8	89±30	70±12	87±8
$\delta$ -HCH	121±3	111±4	67±10	104±33	70±12	83±10
Aldrin	84±3	99±3	64±15	69±30	58±7	71±15
$\alpha$ -Endosulfan (I)	95±1	110±9	79±1	87±38	74±16	101±10
<i>p,p'</i> -DDE	89±4	99±2	68±7	76±25	69±12	80±6
Dieldrin	92±3	101±0	70±8	76±29	68±10	80±8
Endrin	49±15	99±3	66±12	63±6	68±18	78±10
$\beta$ -Endosulfan (II)	89±3	97±4	66±9	72±26	76±9	79±14
<i>p,p'</i> -DDD	113±4	103±6	74±5	81±24	72±9	126±6
<i>p,p'</i> -DDT	143±1	115±6	74±5	90±21	78±12	148±4

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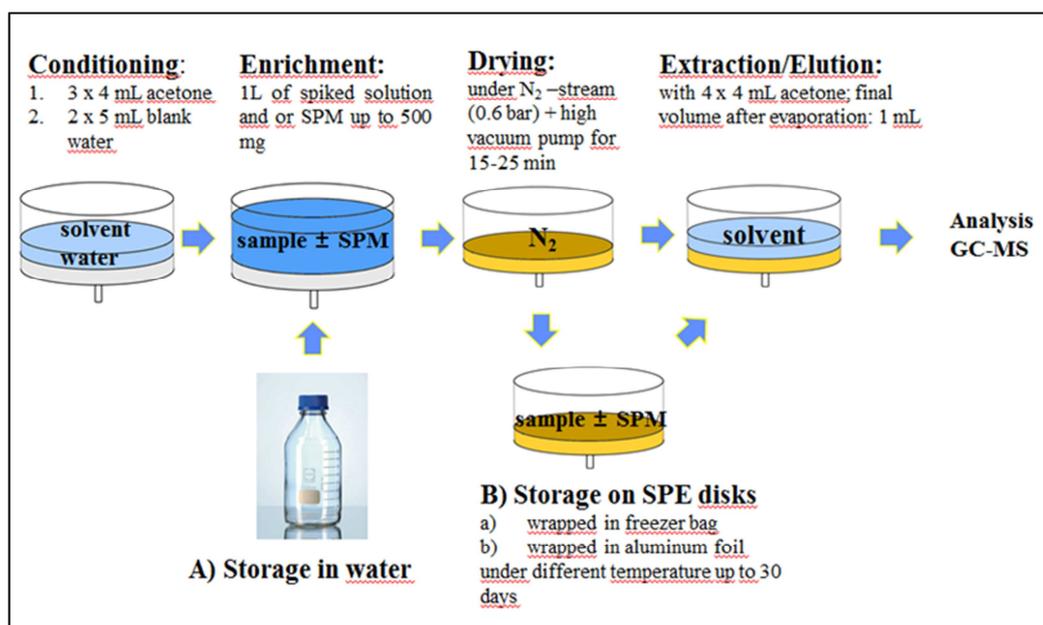
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521 **Table 4:** Recovery (%) and SD of OCPs from 500 mg contaminated sediment [(I) Pesticides Clay 1] loaded on  
 522 SPE disk; wrapped in aluminum foil; stored at 4 °C and -18 °C for 3 to 30 days; n = 3

Compound name	Recovery (%) and SD (%)					
	4 °C			-18 °C		
	3 days	14 days	30 days	3 days	14 days	30 days
<i>aluminum foil</i>						
$\alpha$ -HCH	119±2	119±18	91±9	108±9	84±22	75±11
$\beta$ -HCH	104±4	106±16	82±9	100±19	72±35	80±8
$\gamma$ -HCH	110±2	120±3	85±11	103±9	76±12	72±7
$\delta$ -HCH	156±5	89±20	83±16	127±6	76±15	71±14
Aldrin	88±2	108±4	74±12	87±5	70±4	57±10
$\alpha$ -Endosulfan (I)	111±15	137±9	88±14	117±32	98±4	83±14
<i>p,p'</i> -DDE	88±4	107±2	69±14	89±9	84±10	64±9
Dieldrin	93±3	104±3	78±14	86±9	80±7	69±5
Endrin	28±17	110±2	75±13	45±12	85±4	70±8
$\beta$ -Endosulfan (II)	91±2	101±6	80±15	82±12	80±8	76±13
<i>p,p'</i> -DDD	90±2	116±0	83±13	100±1	89±8	80±9
<i>p,p'</i> -DDT	86±12	112±23	87±16	105±3	102±9	79±7

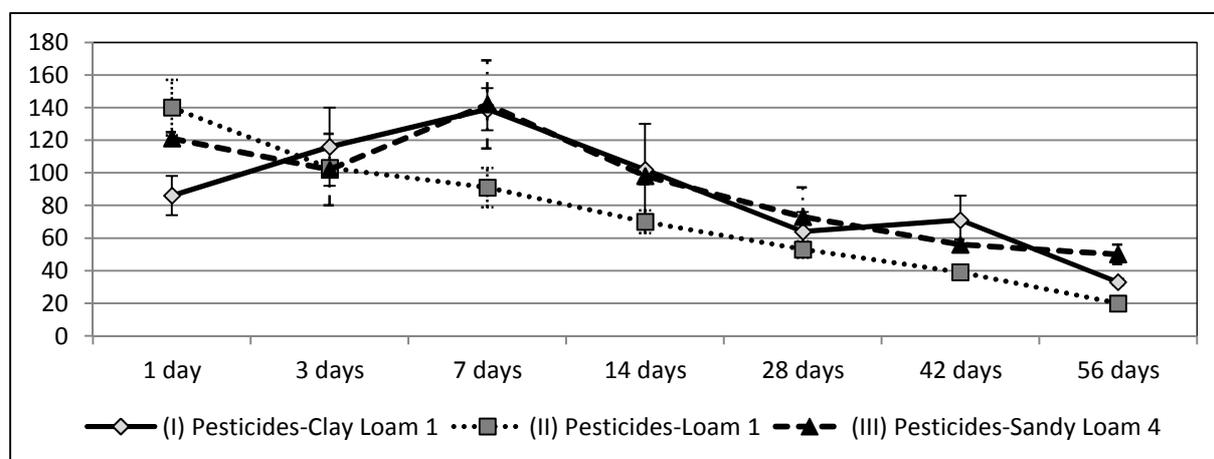
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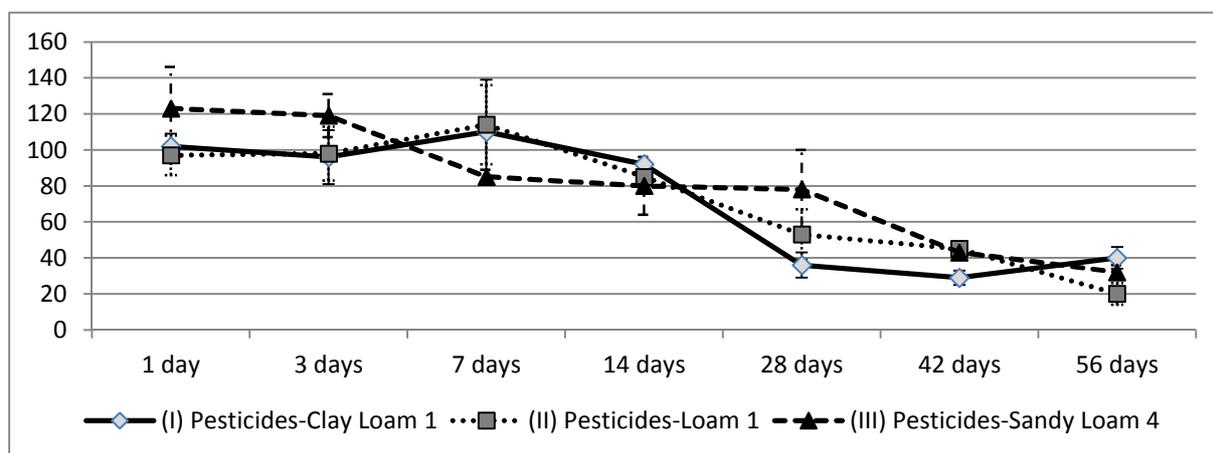
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**Fig. 1:** Steps of the sample preparation procedure in dependency of the storage treatment described with A) and B) as defined in Table 1



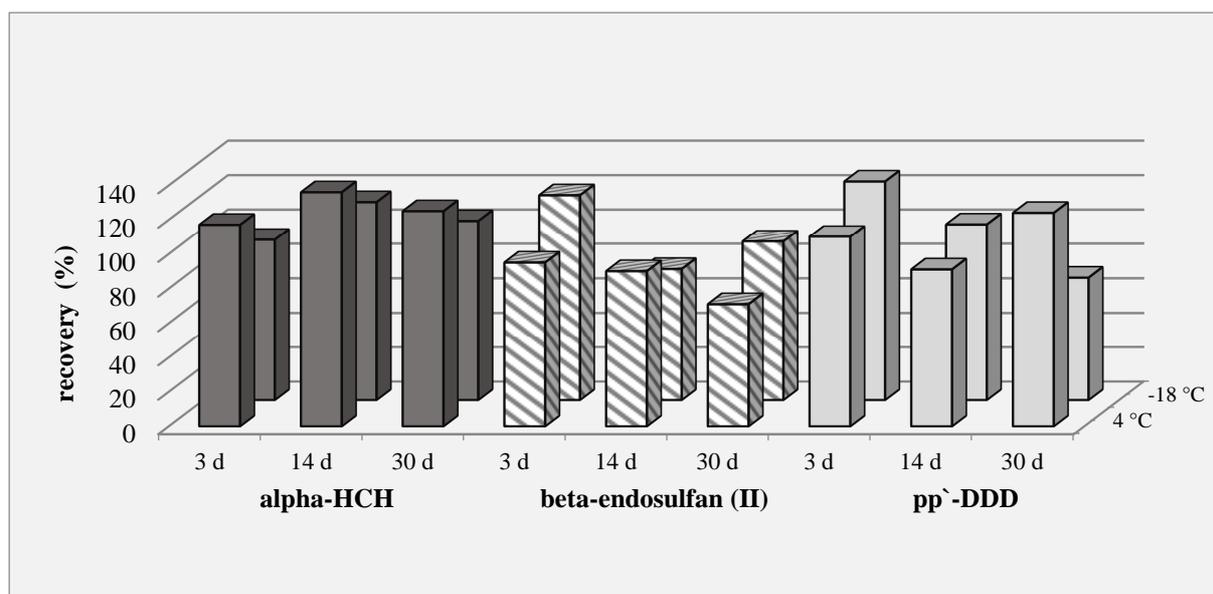
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**Fig. 2:** Recovery (%) and SD of  $\beta$ -endosulfan (II) in 1 L water containing 500 mg CRM (I,II,III) without addition of sodium azide; stored at 4 °C; n = 3



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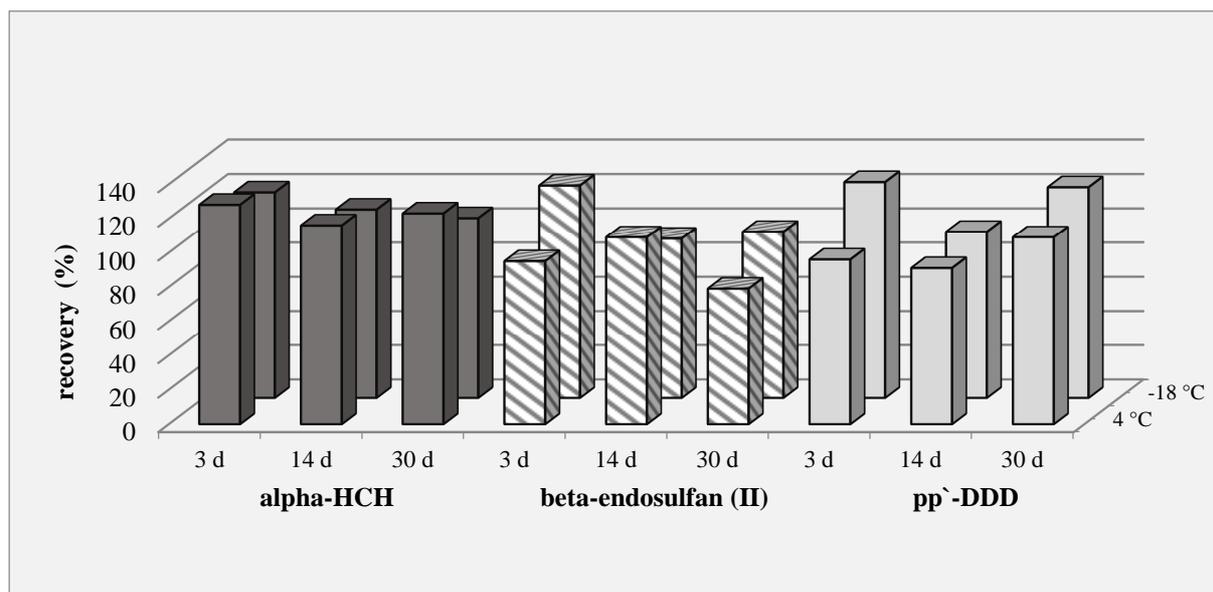
**Fig. 3:** Recovery (%) and SD of  $\beta$ -endosulfan (II) in 1 L water containing 500 mg CRM (I, II, III) with addition of sodium azide; stored at 4 °C; n = 3



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 550 **Fig 4:** Recoveries (%) of  $\alpha$ -HCH,  $\beta$ -endosulfan (II) and  $p,p'$ -DDD after 3, 14 and 30 days of storage at 4 °C and  
 551 -18 °C; SPE disks wrapped in freezer bags; n = 3 (SD available in Supplementary Material, Table S10)  
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 556 **Fig. 5:** Recoveries (%) of  $\alpha$ -HCH,  $\beta$ -endosulfan (II) and  $p,p'$ -DDD after 3, 14 and 30 days of storage at 4 °C and  
 557 -18 °C; SPE disks wrapped in aluminum foil; n = 3 (SD available in Supplementary Material, Table S11)  
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## Highlights

- stability study of 21 OCPs of the WFD in water and sediment samples
- compare different storage conditions of OCPs/CRMs (contaminated with OCPs) 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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