Applied Geochemistry 27 (2012) 146–150

Contents lists available at SciVerse ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

PCB contamination from sampling equipment and packaging

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ARTICLE INFO

Article history:
Received 25 January 2011
Accepted 22 September 2011
Available online 29 September 2011
Editorial handling by R. Fuge

ABSTRACT

Work reported in this paper suggests that there are cases of contamination of soil and water samples by polychlorinated biphenyls (PCB) from paper and plastic packaging. Soil samples, which have been stored in paper bags for more than 20 years, share a similar congener distribution as the bags. Analyses showed a predominance of light congeners. PCB-analyses of water also indicate that water samples could be contaminated by plastic packaging. All analytical results of solid material packaging, as well as soil stored in the packaging, show a high relative amount of light weight PCB congeners. The paper bags that were analysed are made of strong paper and very popular among geochemists because of their watertight quality. These paper bags were manufactured more than 20 years ago. The plastic packaging that was analysed was produced in 1997 and 2008. The analyses of plastic and paper show that the raw material that has been used in the production at different times contains a wide concentration range of PCB. Re-sealable plastic bags, which contained the highest levels of PCB of the plastic material, are used by researchers world-wide as sampling bags for soils and sediments. This paper raises an important issue that packaging may potentially contaminate the samples that they hold.

1. Introduction

Over the past 10 years the Geological Survey of Norway has conducted urban studies that often include polychlorinated biphenyls (PCB) as an investigative parameter. During the course of two of these studies, analytical results that were higher than expected, judging by results from earlier studies, arose suspicion concerning the packaging and storage material. The studies included water and soil samples. Unexpectedly high analytical results that displayed an unusual congener ratio led to the suspicion that PCBs in storage bags and sampling containers may have contaminated the samples. A few cases of packaging or general laboratory conditions contaminating sample materials with organic compounds have been reported previously; contamination by dibenzodioxins and – furans (PCDD/Fs) from screw caps (Fürst et al., 1989) or sample contamination by air in the laboratory (Alcock et al., 1994; Ferrario et al., 1997; Söderström et al., 2005).

In a previous soil sample study from remote areas of Norway, which was conducted in the 1980s, only inorganic parameters were determined, while PCB analysis was not carried out in the study. Analysis was, therefore, carried out in 2009 to determine background levels of PCBs in soil in Norway. The suite of dry soil sub-samples had been stored in paper bags of the Craft brand in a cool, dark storage area since the late 1980s. The subsequent analytical results for PCBs in the soil samples were surprisingly high for background samples from extremely remote areas in Norway, where no local sources are present, so addition of PCB to the soil should only have been in the form of atmospheric deposition. The PCB7 (the sum of the PCB congeners with IUPAC numbers #28, #52, #101, #118, #138, #153 and #180) levels ranged from 13 to 970 μg/kg (median 150 μg/kg, $N = 41$). The expected background levels of PCB in soil from that part of Norway were expected to be in the region of 0.18–0.78 μg/kg (Schlabach and Steinnes, 1999). In addition, the relative amount of the lightest congener in the PCB 7 suite, 2,4,4′-TriCB, #28 totalled 60–90% of PCB 7, which seemed unusually high comparing to similar studies (Fig. 1) (Schlabach and Steinnes, 1999; Eggen et al., 2010). These studies of background soil taken from the same area present a completely different congener distribution than the soil samples presented here. The significant difference in PCB levels, compared to other studies, and an unusual congener distribution is a strong indication that the soil samples had been contaminated during or after storage.

The water sample study, which is the second study presented here, investigated PCB in precipitation in Bergen, Norway. The precipitation samplers used in the study were cylinder-like constructions lined with plastic bags that stood continuously open for 3 weeks in order to collect precipitation in different parts of the

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doi:10.1016/j.apgeochem.2011.09.026

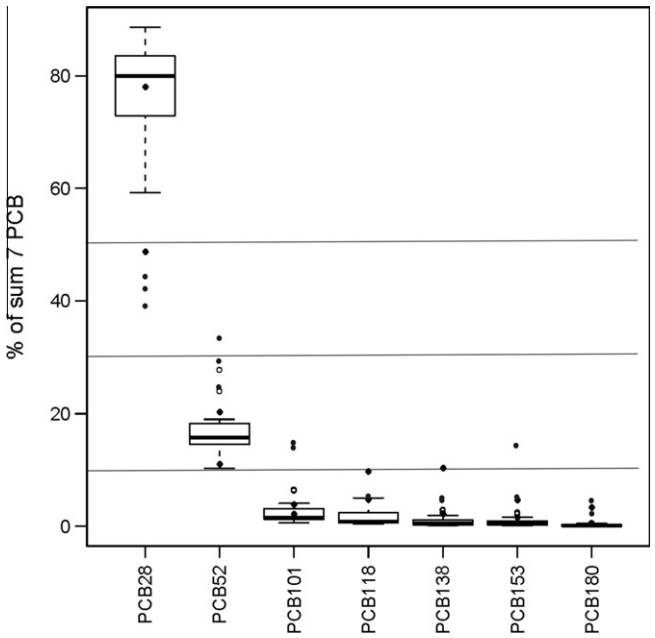

Fig. 1. Relative occurrence of PCB congeners in soil samples (boxplots) and paper bags, including replicate analyses (black dots). Circles represent outliers for the boxplots. Only samples with all congeners over the detection limit are presented ($N = 21$).

town. The aim of the study was to determine local variations in PCB levels in precipitation. Contamination was first suspected as some project blank samples within the study showed some unexpectedly high results that were in the region of 41–60 pg/L (Table 1B). These blank samples were not precipitation samples, but had been manufactured by storing double-distilled water (DDW) outside in the same kind of precipitation sampler for 2 weeks. The only difference between the collection of the precipitation samples and the manufacturing of the blank samples was that the samplers were covered during the making of the blank samples to avoid any atmospheric input. The manufactured, blank samples were designed to replicate the water collected from the precipitation samplers within the precipitation study. All samples were then transferred from the precipitation samplers into containers made out of white high-density polyethylene (HDPE). The elevated results of the blank samples were particularly notable as they at times exceeded concentrations detected in the original precipitation samples (Table 1A).

These anomalous analytical results from both the soil and precipitation study, which were unexpectedly high concentrations in both studies along with the congener distribution in the soil, prompted the need for further analysis of the packaging materials. The aim of this study was to investigate whether contamination from the packaging materials had indeed taken place. Results for PCB analysis of material such as Craft paper bags, plastic packaging and water where pieces of plastic bags and plastic containers had been soaked in DDW are presented in this paper.

2. Methods and analysis

Two types of paper bags were included in this study of packaging materials. Firstly, thick Craft paper bags that are used as sample bags in the field and were used in the above mentioned soil study (Fig. 2) and secondly, smaller, thinner paper bags used for storing dry material. In addition, 4 samples of different plastic materials were included in the analysis: (1) Low density polyethylene (LDPE) re-sealable bags, (2) LDPE plastic bags used in the precipitation sampler, (3) HDPE containers and (4) HDPE container lids (Fig. 3). The plastic packaging that was analysed was produced in 1997 and 2008. The paper bags and plastics were analysed in the same laboratory and were quantified for 7 PCB congeners (PCB IUPAC numbers 28, 52, 101, 118, 138, 153 and 180).

The paper analysis was conducted by cutting the paper bags into small pieces. About 1 g of paper was extracted with 4×10 mL dichloromethane (DCM) in an ultrasound bath (4×15 min). The sample was filtered through a separation packed column (30×10 mm ID, Water cartridges plus florisil WAT 020525). The sample volume was reduced to 3000 μL and was injected into a Bio Beads column (1000 mm length/10 mm ID), 1500 μL at a time (S-X3-200-400 mesh, US EPA 3640 method). The flow was adjusted to 0.7 mL/min DCM. After the sampling of the PCB-fraction, the extract was concentrated with toluene in a Zymark evaporator to 500 μL toluene. Finally, the extracts were analysed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

The plastic analysis was conducted by extracting 1.5 g of plastic in a Soxhlet for 24 h with toluene. Twelve 13C-labeled PCB congeners were added to each sample as an internal standard prior to the extraction. The extract was dried and *n*-hexane was added. The extracts were then cleaned on an Al oxide column (Alumina PCBA-BAS-011, size 7 3/4") and a silica column (PCB ABN STD, size 7 3/4"). The plastics analysis included an additional extra clean-up step by eluting half of the extract on an Al oxide column with dichloromethane. Only half of the extract was used in order to retain the other half in case of complications. The plastic extract was washed three times to separate precipitated plastic from the extract. The samples were then analysed using HRGC/HRMS. The recovery standard: PCB WP-LCS Lot WPL 0S0407 WHO 13 C (PCB #77, #118, #169) was used to monitor extraction efficiency. The average recovery for #77 was 70% (spread 25–124%), #118 65% (23–116)

Table 1
Concentrations of $\sum PCB_7$ and the individual congeners in 3 steps of studying PCBs in precipitation and packaging. Step A: 14 original precipitation samples from the Bergen area. Step B: Blank, duplicate test of DDW in precipitation sampler lining bag. Step C: Two samples of DDW only, one sample of DDW in laboratory glass with pieces of plastic bag, and one sample with DDW in laboratory glass including pieces of PE-can and screw cap material (Controls A–B, respectively). The "Lab blank" is internal test water from the laboratory. All results in pg/L $\sum PCB_7$.

	pg/L	∑PCB7	PCB #28	PCB #52	PCB #101	PCB #118	PCB #138	PCB #153	PCB #180
A	Precipitation range	*23–1079*	2.0–8.3	3.2–153	2.8–290	3.8–224	2.5–204	5.0–166	0.3–36
	Precipitation median	*48*	4.3	6.1	7.1	8.0	6.0	9.6	2.2
B	DDW 1 from precipitation sampler	*40.9*	4.51	5.11	9.84	4.83	6.06	8.22	2.35
	DDW 2 from precipitation sampler	*59.3*	3.98	5.25	11	8.88	10.2	16	3.98
C	DDW 3	*78.6*	7.21	12.5	19.7	12	7.45	16	3.73
	DDW 4	*49.7*	4.27	5.16	13.6	5.27	5.91	11.7	3.85
	Plastic bag in DDW	*243*	19.5	18.6	42.2	33.8	43.4	66.9	18.7
	Plastic container in DDW	*583*	70.8	75.1	109	86.3	78.9	143	19.9
	Lab blank	*<0.08*	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01

Fig. 2. Examples of the thicker Craft paper bags.

Fig. 3. Example of HDPE container used in study.

and for #169 55% (24–96). All components were compensated for the recovery of the standards.

Replicate sample analyses of paper and plastics were also conducted at a later date. For these, isotope labelled internal standards for PCB #77, #118 and #167 were used to monitor extraction efficiency. The average recovery for #77 was 83% (spread 70–94%), #118 80% (67–92) and for #167 87% (71–102) for paper and for plastic the average recovery for #77 was 64% (spread 41–96%), #118 60% (38–92) and for #167 94% (38–158).

Unfortunately, the analysis for the paper bags and plastic material were performed at a different laboratory from the water and precipitation sample analysis. This is the reason for the differences in analytical methods.

To investigate whether the plastic influences the levels of PCB in the water samples during storage, two water samples were manufactured. In addition, two samples which consisted of only DDW stored in laboratory glass bottles were analysed.

The manufactured water samples were produced by filling a 2.5 L laboratory glass bottle with DDW and adding cut up pieces of one LDPE plastic bag that were used to line the precipitation samplers. The second sample was manufactured in the same way, except it involved the addition of 2×2 cm pieces of the 10 L HDPE container and screw cap that were used for sample transportation. The plastic pieces remained in the DDW for 2 weeks before analysis. All DDW was acquired from the laboratory in the Geological Survey of Norway and not from the analytical laboratory.

The water samples were quantified for 32 PCB congeners (PCB IUPAC numbers 18, 28, 31, 33, 37, 47, 52, 66, 74, 99, 101, 105, 114, 118, 122, 123, 128, 138, 141, 149, 153, 156, 157, 167, 170, 180, 183, 187, 189, 194, 206 and 209). In order to allow comparison with the paper and plastics, the results for 7 seven of them have been included here. Isotope-labelled internal standards were added to the water samples, which were subsequently extracted with cyclohexane under continuous stirring in a graduated flask for 4 h. The cyclohexane phase was concentrated to 1 mL and treated with concentrated H_2SO_4. The organic phase was then dried using Na_2SO_4 and transferred to a glass column packed with Na_2SO_4 and SiO_2. A hexane/diethylether mixture was used to elute the extract before another concentration step. A recovery standard was added to the final extract, which was analysed by GC–MS. The laboratory inserted a laboratory blank (Table 1) for quality assurance.

3. Results and discussion

The results for the first analyses of paper bags and plastics are presented in Table 2. The larger size Craft paper bags (Paper 1) display the highest levels of PCB, while the smaller size paper bags, which are somewhat thinner (Paper 2), show lower levels of PCB. The Craft paper bags have been previously analysed and tested for inorganic components, the results showing very low levels of metals that pose no contamination risk of inorganic components (unpublished results, Geological Survey of Norway). The plastic packaging all contain PCB to varying degrees, the re-sealable bags had the highest PCB content. The HDPE container, which was similar to but not exactly the same as containers used in the original precipitation study, as well as the plastic bag, showed lower concentrations than the re-sealable bags.

All analyses of solid packaging (Table 2) show a similar congener pattern where the lightest congeners have the highest occurrence. The paper bags (black dots in Fig. 1), which are very popular in geochemical studies because of their watertight quality, have a high relative occurrence of the light congeners, with almost exactly the same PCB congener profile as the sediment samples that were analysed (boxplots in Fig. 1). The paper bags are made of strong paper that has been coated with a water-resistant coating. Whether the PCB lies in the coating matter or the material that glues the bags together is uncertain. The mixture that is the source of PCB in the bags is mainly composed of light PCB congeners, which are more volatile than heavy congeners. These volatile, light congeners have probably been more prone to escaping from the packaging materials, thus altering the congener distribution in the sediment samples.

In order to further investigate the high levels of PCBs in paper and plastic, 3 replicate analyses of the larger size paper bags (Paper

Table 2
PCB concentrations of packaging material. All results in ng/kg $\sum PCB_7$.

ng/kg	∑PCB7	PCB #28	PCB #52	PCB #101	PCB #118	PCB #138	PCB #153	PCB #180
Thick paper bag (paper 1)	*91000*	71000	10000	1900	4300	1900	1400	410
Thin paper bag (paper 2)	*3900*	1900	790	150	380	400	180	130
Ziplock bag	*4300*	2400	900	480	140	140	200	<100
Plastic bag	*2500*	1300	460	320	110	110	160	<100
HDPE container	*870*	510	230	130	<100	<100	<100	<100
HDPE container lid	*400*	290	110	<100	<100	<100	<100	<100

Table 3
PCB concentrations of 3 replicate analysis of paper 1 and HDPE container plastic.

ng/kg	∑PCB7	PCB #28	PCB #52	PCB #101	PCB #118	PCB #138	PCB #153	PCB #180
1 (Paper 1)	*2500*	970	720	380	140	130	160	<100
2 (Paper 1)	*930*	420	240	140	<100	<100	130	<100
3 (Paper 1)	*2200*	920	720	300	110	<100	120	<100
1 HDPE container	*61000*	11000	6000	21000	4100	7200	11000	690
2 HDPE container	*39000*	4300	3200	14000	3100	6000	7900	300
3 HDPE container	*51000*	7500	6300	23000	2800	3900	7200	230

1) and HDPE container plastics were conducted at a later date (Table 3). The analyses were conducted to give a demonstration of the validity of the results. The replicate analyses were performed in the same laboratory as the first analyses, using the same methodology. The replicate analyses showed a better recovery when looking at the internal standards. The analyses were not, however, conducted on paper bags or plastic containers from the same production batch as the first analysis as these were not available. The results show some differences in concentrations from the first results (Table 2). The concentrations of the replicate analyses of the paper show much lower values than the first analysis, while the container of which the replicate analysis was made, showed much higher concentrations of PCBs than the first container. This is to be expected as the plastic containers are produced from recycled plastic where the recycled materials are not of consistent quality and chemical content. The differences in PCB concentration of the paper bags can be explained by changes in production methods of the paper bags, as well as different storage times of the bags that were analysed. The replicate analyses, however, show fairly consistent concentrations and congener distribution (Table 3).

Table 1C presents the results of water samples, where pieces of plastic were soaked in water, as well as the results for DDW only. The results show that the DDW-only samples also showed detectable levels of PCB compared to the laboratory blank. This suggests that some unknown source of PCB exists within the water distillation system. The laboratory where the DDW was acquired, which is not the laboratory where the samples were analysed, is only used for inorganic component analyses; therefore, potential contamination sources of organic compounds have never been investigated. Even though the DDW-only samples used in the study were contaminated with PCB at some point in the distillation process, the higher levels of PCBs in the leaching water suggests that the plastic must be an additional source. This can be seen in the higher PCB levels in the leaching water samples (243–583 pg/L) than in the DDW-only samples (50–79 pg/L). High PCB-levels in plastic are shown here, and it is suggested that some of that PCB has leached into the original precipitation and blank water samples originally analysed. It must be noted that the HDPE containers that were used in the leaching experiment and the one where the plastic itself was analysed were not of the same containers. Therefore, the results of the leaching experiment and the analytical results of the plastic mass for the HDPE container cannot be directly related to each other.

The study of PCB levels in different plastics was not within the scope of this preliminary study, but there are likely to be different levels of PCB in various plastic containers and bags due to the fact that the production of plastic articles uses a spectrum of recycled plastic material. Whether samples and material have been contaminated by laboratory air has not been addressed in this study either. The results of the replicate analyses from one production batch of materials emphasises that a more extensive study should be done on different types of packaging including products from different producers and production countries to fully understand the extent of packaging containing PCBs. The presence of other organic pollutants as a result of similar processes is also a matter for further study.

4. Conclusions

Plastic and paper packaging that were analysed in the study contain PCB and these materials have probably contaminated sample material that was stored in them. The light congeners are present in relatively large concentrations in the sample material. Analyses suggest a contamination path from both plastic into water and from paper into soil.

The results from the small study on sampling bags and packaging done here, suggests the possibility of contaminating samples through the wrong choice of storage and sampling containers. Packaging must be thoroughly controlled by chemical analysis before use for storage or using stored samples for the analyses of organic compounds. Samples stored in Craft paper bags should, therefore, only be analysed for inorganic components. It is a real possibility that the use of recycled material in the production of packaging articles carries organic compounds that were prohibited for use decades ago. These compounds may leak into water or soil stored in the packaging.

The continued presence of PCBs in plastic materials, 30 years after production and use of PCBs in most countries was prohibited, might be a side effect of the recycling process of plastic materials.

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