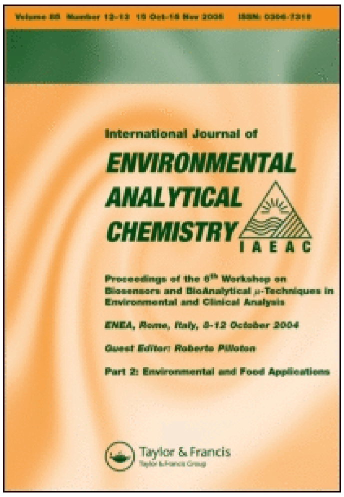

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Qixiang Wu[a]; William D. Marshall[a]
[a] Dept. of Food Science and Agricultural Chemistry, Québec, Canada

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APPROACHES TO THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) CONCENTRATIONS IN SOILS / SEDIMENTS BY DECHLORINATION TO BIPHENYL

QIXIANG WU and WILLIAM D MARSHALL*

*Dept. of Food Science and Agricultural Chemistry, Macdonald Campus of McGill, 21,
111 Lakeshore Road, Ste-Anne-de-Bellevue, Québec, Canada H9X3V9*

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A method for the dechlorination of PCB mixtures (Aroclor formulations) to biphenyl was extended to soils. The contaminated sample was mixed with magnesium flakes, potassium hexachloropalladiate (K_2PdCl_6), propan-2-ol and water then permitted to react for up to six hours. Biphenyl, recovered by extraction into hexane, was quantified by gas chromatography with flame ionization detection. The reaction was very efficient in propan-2-ol / water (~95%), surfactant emulsion or sand mixture and virtually complete in soil provided that excess magnesium (2 g) and the K_2PdCl_6 were added to the sample prior to the addition of water. Higher PCB loadings were readily determined in field contaminated soils either by direct determination within the matrix or by standard additions. However, analyte concentrations were appreciably over-estimated in Soxhlet or sonication extracts of a certified reference material that contained sub-ppm levels of analyte. The over-estimation is considered to result from the conversion in part of natural organic matter to biphenyl.

Keywords: PCB residues; soil/sediment; sand; dechlorination and biphenyl

INTRODUCTION

As a prelude to optimising remediation techniques/procedures for soils and sediments burdened with polychlorinated biphenyl compounds (PCBs), a rapid method to estimate the levels of the analytes in these matrices was required. Conventional procedures have employed a variety of approaches for extraction/mobilisation followed by quantitation of the analytes by high resolution gas chromatography (GC) frequently with electron capture or quadrupole mass spectrometric detection.[1–3] Successful approaches to the mobilisation stage of the

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* Corresponding author: Fax: +1-514-398-7977. E-mail: marshall@macdonald.mcgill.ca

analysis have included extractions with supercritical carbon dioxide[4], and sub-critical water[5] as well as the more conventional Soxhlet[6], sonication[6], solid-phase[5,7] or microwaver-assisted extraction[8]. Alternative approaches to the quantitation stage of the analysis have include immunoassay techniques[9,10] and conversion of the various PCB congeners to a common derivative prior to or during chromatography. Two approaches, complete perchlorination[11–13] to decachloriobiphenyl or complete hydrodechlorination[14–20] to biphenyl have been pursued. Earlier dechlorination methods were directed to the potentiometric determination of chloride ion liberated by sodium dispersion,[14] the action of $LiAlH_4$ in an inert atmosphere,[15,16] or the action of Pt/Pd catalysts at elevated temperature.[17,18] More recent procedures have employed facilely prepared iron/palladium[19] (Fe^0/Pd^0) or magnesium/palladium[20] (Mg^0/Pd^0) bimetallic mixtures that function efficiently at room temperature in mixed aqueous organic medium. Alternate procedures have involved the use of formate and Pd/C again in mixed medium.[21,22]

The generation of a single derivative to estimate the total PCB burden in natural matrices circumvents the influence of field weathering and variations in volatility that collectively cause appreciable alternations to the populations of specific PCB congeners with time. Subsequent quantitation of aged field residues based on the "standard" commercial PCB mixtures can become increasingly uncertain. These difficulties can be confounded by the presence of chlorinated pesticides or other chlorinated organics in the extracts that must be removed prior to quantitation.

Additionally, conversion to a single derivative provides increased detectability so that flame ionization can suffice and the requirement for detection by electron capture and the attendant variations in congener-specific responses can be avoided. The current communication extends the dechlorination procedure to soils and sediments. The principle disadvantage of the derivatisation approach remains the loss of all congener-specific information.

EXPERIMENTAL

Chemicals, solvents and standard reference materials

Magnesium granules (12–50 mesh, 99.8% purity) and potassium hexachloropalladate (K_2PdCl_6) were purchased from Alfa Aesar, Ward Hill, MA. USA. Triton DF 16 and biphenyl were purchased from Sigma-Aldrich, Oakville, ON.

HPLC grade solvents, hexane and propan-2-ol and acid washed sea sand were purchased from Fisher Scientific, Ottawa, ON. Aroclor 1242 mixture was kindly donated by Monsanto Company, Sauget, IL USA. Aroclor standard 1242,1248,1254 and 1260 (1 mg ml^{-1} in hexane) was purchased from Supelco, Bellefont, PA. Standard reference material, SRM 1939a, was purchased from the National Institute of Standard and Technology, Gaithersburg, MD, USA. CRM 481 and CRM 536 were purchased from the European Commission via LGC Lt., Teddington, UK. All chemicals, solvent and materials were used as received.

Soil samples and pre-treatment

One agricultural soil and two field contaminated soil samples were collected from appropriate sites. The agricultural soil had been cultivated continuously for more than 70 years. The PCB-contaminated soil samples were collected from (*i.*) a manufacturing facility where intermittent contamination had occurred from broken hydraulic lines during 1960s and 70s and (*ii.*) a railway facility where contamination had accumulated for more than 17 years. After collection, all soils were air dried then passed through a 2 mm sieve (10 mesh) and mixed thoroughly. One third of each sample were further ground and passed through 50 mesh sieve, and then stored in refrigerator (-4°C) to await analysis. The soil samples varied in pH, texture, and organic matter (Table I).

TABLE I Properties of soil/sediment samples

Sample	*Certified PCB conc'n*	*pH (1:1 water soil)*	*Organic matter (%)*	*Particle mesh size*	*Note*
Soil 1		7.10	2.1	10~50	Agricultural soil that had been under active cultivation for > 70 y.
Soil 2		7.38	4.8	~50	Soil from a railway facility contaminated with Aroclors 1242, 1248, 1254 and 1260
Soil 3		7.75	3.6	~50	Soil from a manufacturing facility contaminated with Aroclors 1242, 1254, oil, grease and heavy metals
SRM1939a	27.2 ± 3.0			~325	Contaminated freshwater river sediment
CRM 481	472.5 ± 29		12	~170	Industrial soil
CRM 536	0.34 ± 0.04			~120	Freshwater harbor sediment

Aroclor standard solution

Aroclor 1242 stock solution (1% v/v) was prepared by diluting 1.0 ml pure Aroclor 1242 to 100 ml with hexane. Diluted working solutions of Aroclor 1242 (10 μg ml^{-1}) were prepared by further diluting 0.1 ml of 1% Aroclor 1242 solution with hexane or propan-2-ol. The 1% Aroclor aqueous emulsions were prepared by diluting 1 ml of Aroclor 1242 or 1248 or 1254 or 1260 stock solution plus 4.0 ml of Triton DF 16 to 100 ml with distilled water. Biphenyl standard solution was prepared by diluting biphenyl standard (50.0 mg) to 100 ml with hexane.

Soxhlet extraction

EPA method 3540 was followed. Briefly, an accurately weighed aliquot of soil, 10 g, was mixed with 10 g anhydrous sodium sulfate, added to an extraction thimble and extracted with 150 ml refluxing acetone – hexane (1 + 3, v/v) during 20 h. The extracts were subsequently concentrated to 40 ml under a gentle stream of nitrogen.

Sonication extraction

EPA method 3550 was followed. Briefly, a Polytron homogenizing unit (N.Y. 11590, Brinkmann Instruments, Mississauga, ON) was used with the output control knob set at 11 and the mode switch was on pulse. An aliquot of soil (20.0 g) was mixed with 33.3 ml of acetone – hexane (1 + 3, v/v) and sonicated for 3 min. The procedures were repeated three times and a total volume of 100 ml was filtered and combined. The extracts were concentrated to 40 ml with a gentle nitrogen stream.

Extract clean-up

During Soxhlet or sonication extractions appreciable quantities of organic matter were co-extracted. Concentrated sulphuric acid was added (at 1 +10, v/v) to the extract. After 30 min reaction, the decomposition products and excess acid were removed by washing the extract with copious quantities of distilled water.

Biphenyl formation and determination

Magnesium flakes (2 g, 10–50 mesh), potassium hexachloropalladate (K_2PdCl_6), 10 mg, propan-2-ol, 2 ml, and test substrate were combined in a 50 ml flask. Distilled water, 2 ml, was added to initiate the reaction and the mixture was stirred for 1 min. The stirring procedure was repeated every 30 min. After 0.5–6 h of reaction, the mixture was extracted with 2 ml hexane (by vortex stirring for 1 min). After separation of the layers, one ml of the organic phase was withdrawn for biphenyl quantification. For sand or soil/sediment matrices, 1 g of sample was added to the reaction vial after the Mg particles (2 g) and 10 mg of K_2PdCl_6 (10 mg). The reaction procedure, as described above, was followed.

Quantification of biphenyl was carried out using a Hewlett-Packard model 5890 gas chromatography (GC) equipped with flame ionization detection (FID) and a model 5971 autoinjector. The 30m (0.53 mm i.d.) DB-5 column was held at 50°C for 1 min then ramped to 270°C at 10°C min^{-1} and held for 5 min. Analyte identity/purity was corroborated with a Hewlett-Packard model 5890 GC equipped with splitless injection and a model 5971 mass-selective detector. An HP-1 column (30 m x 0.25 mm I.D.) was used and the MSD was operated in an electron impact (EI) mode. Samples were resolved with a temperature program that started at 50°C for 2 min followed ramping to 280°C at 10°C /min and held for 5 min.

RESULTS AND DISCUSSION

Conversion of PCB compounds to biphenyl

Biphenyl formation from PCB mixtures can be efficient (greater than 98%)[20] under mild condition in the presence of excess Mg particles and potassium hexachloropalladiate. As summarized in Table II, conversion factors can be calculated based on the mean molecular weight for each commercial formulation.

TABLE II Conversion coefficients[a] for Aroclor formulations

Aroclor Mixture	*Slope linear regression*	*Average M.W. for mixture*		*Conversion coefficient ($mass_{12XX}$ to $mass_{C12H10}$)*		*$slope_{12xx}$/ $slope_{biphenyl}$*
1242	1289.3	258.2[b],	257.5[c]	0.5972,	0.5988	0.566
1248	1142.1	289.4[b]	291.9[c]	0.5328,	0.5283	0.501
1254	984.8	329.7[b]	326.4[c]	0.4677,	0.4724	0.432
1260	914.7	368.0[b]	366.0[c]	0.4190,	04213	0.401
biphenyl	2279.6	154.2		1.0		

a. Ratio was calculated by dividing the MW for biphenyl by the mean MW for the Aroclor formulation.

b. Data were adapted from [23].

c. Data were taken from [8].

The biphenyl conversions of Aroclors 1242, 1248, 1254 and 1260 in propan-2-ol / water solution are summarized by the linear regressions of Figure 1 and for comparison, the FID response to biphenyl standard is also presented. As indicated in Figure 1, there was good agreement between the measured amount of biphenyl generated from the Aroclor standard mixtures and the predicted amount for quantitative conversion when the dechlorination was conducted in propan-2-ol/water solution. Within experimental error, the ratio of the slope of the regression equation for each Aroclor formulation relative to the regression line for biphenyl standard (Table II) was similar to the corresponding ratio of their molecular weights (and accounted for approximately 95% conversion). Thus, over the limited range of concentrations (0.5–20 μg ml^{-1}) each formulation was converted efficiently but not quantitatively to biphenyl.

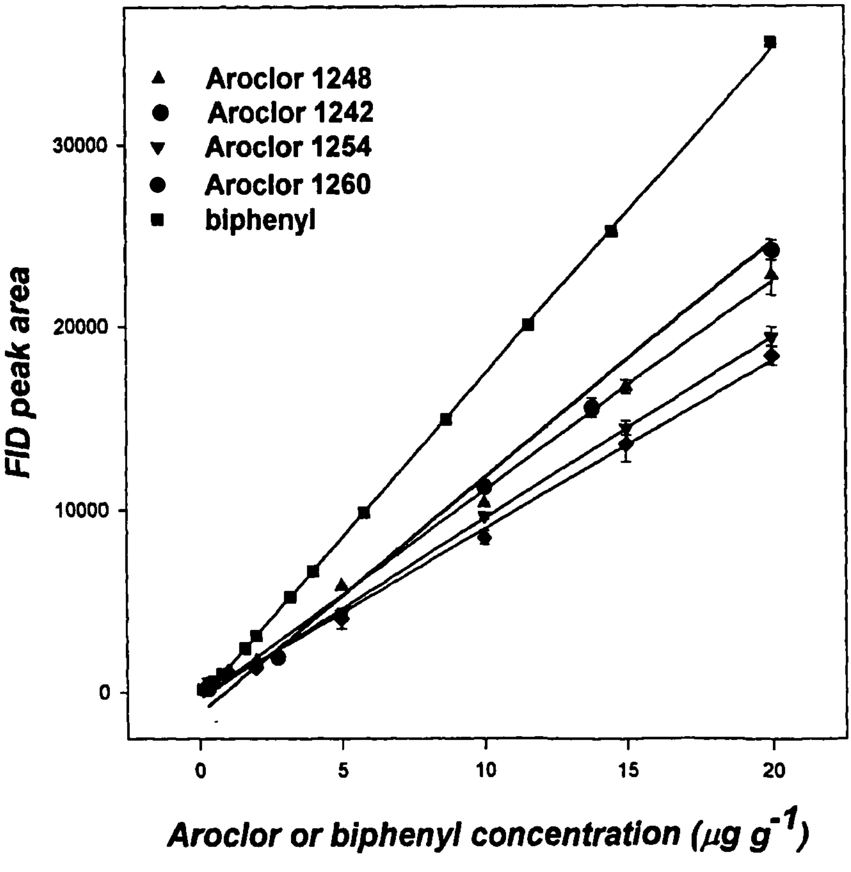

FIGURE 1 Linear regressions of flame ionization peak area as a function of concentration (0.3–22 μg g^{-1}) of biphenyl (■), Aroclor 1242 (•), Aroclor 1248 (▲), Aroclor 1254 (▼) or Aroclor 1260 (♦)

To identify the parameters that influenced the efficiency of conversion of Aroclor mixtures, various matrices were also studied. Figure 2 summarizes the biphenyl conversion within: (*i.*) a four percent (v/v) non ionic surfactant (Triton DF 16) emulsion, (*ii.*) a sand mixture, and (*iii.*) the propan-2-ol/water solution. Reaction products were extracted with 2 ml hexane after 2h reaction. There were no substantial differences in the contents of biphenyl generated from Aroclor 1242 that had been added, at 0.3–27 $\mu g\ g^{-1}$, to the different matrices. From the results of biphenyl formation from 1242, 1248, 1254 and 1260 in different media, several conversion models were established. As summarized in Table III, all models were significant and could be used to estimate the concentration of PCBs in the different matrices. The Student T-test did not identify any statistically significant differences among models for different media.

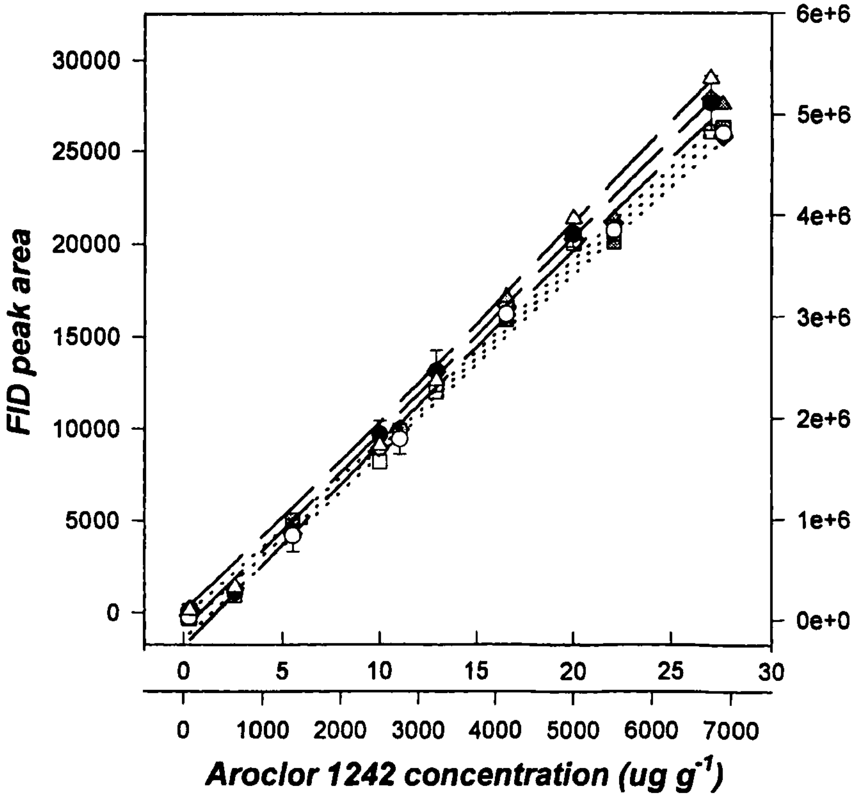

FIGURE 2 Means (-•-, ···o···) plus 95% confidence interval for biphenyl recovered from sand (◊, ♦), surfactant emulsion (□, ■) or propan-2-ol/water solution(Δ, ▲) for Aroclor 1242 formulation added to each matrix at 0.3–27 (grey symbols) or 69–6900 $\mu g\ g^{-1}$ (black symbols) respectively

TABLE III Linear regression models for the conversion of Aroclor formulations to biphenyl in various matrices

Aroclor	*Matrix*	*Regression Model*[a]	*Range (ppm)*	*Coefficient of Determination* (R^2)[b]
1242	propan-2-ol / water (3h reaction)	Y=1141[PCB] – 778	0.1~45	0.993
	surfactant emulsion	Y = 1106[PCB]-1136	0.1~45	0.997
	sand mixture	Y = 1059[PCB]-879	0.1~45	0.997
	soil matrix (6h reaction)	Y = 1230[PCB]-564	0.1~140	0.993
	Mean	Y = 1060[PCB]-816	0.1~15	0.993
1248	propan-2-ol / water (3h reaction)	Y = 1142[PCB]-337	0.1~20	0.996
	soil matrix (6h reaction)	Y = 1060[PCB]+38	0.1~20	0.996
1254	propan-2-ol / water (3h reaction)	Y = 985[PCB]-298	0.1~20	0.998
	soil matrix (6h reaction)	Y = 874[PCB]+210	0.1~20	0.995
1260	propan-2-ol water	Y = 824[PCB]-9	0.1~40	0.997
	soil matrix (2h reaction)	Y = 184[PCB]+420	0.1~40	0.984
	soil matrix (6h reaction)	Y = 770[PCB]-845	0.1~40	0.996

a. Y = flame ionization response.
b. significant at 99% level of confidence ($p < 0.0001$).

To monitor the conversion efficiency at higher concentrations, Aroclor 1242 and a 25 ml volume of hexane extractant were used. The reactions were performed with the same conditions as before [2 g Mg, 0.1 g K_2PdCl_6, 4 ml of 1 + 1 (v/v) propan-2-ol: water]. The results are summarized in Figure 2. Again, the efficiencies of conversion for Aroclor 1242 added at 69–6900 μg ml^{-1} to each of the three matrices were within the 95% confidence interval of the means. Again, there were no significant differences among models for different media (Table III). Neither the presence of the surfactant nor sand had any discernable effect on the conversion of PCB compounds to biphenyl at either higher or moderate concentrations.

Biphenyl conversion within soil matrices

To test the efficiency of the dechlorination of PCBs compounds within soil matrices, a spike of a cultivated soil (soil No.1) was used. Figure 3 summarizes the recoveries of biphenyl from Aroclor 1242 and 1260 standard spiked into to the soil. For comparison, data obtained in propan-2-ol/water mixture are also presented. Surprisingly, the biphenyl concentrations generated within the soil were modestly greater (2.4–6.7%) than if the same quantity was added to the propan-2-ol/water mixture. However this increase, although consistent, remained within the 95% confidence interval associated with the linear regression model.

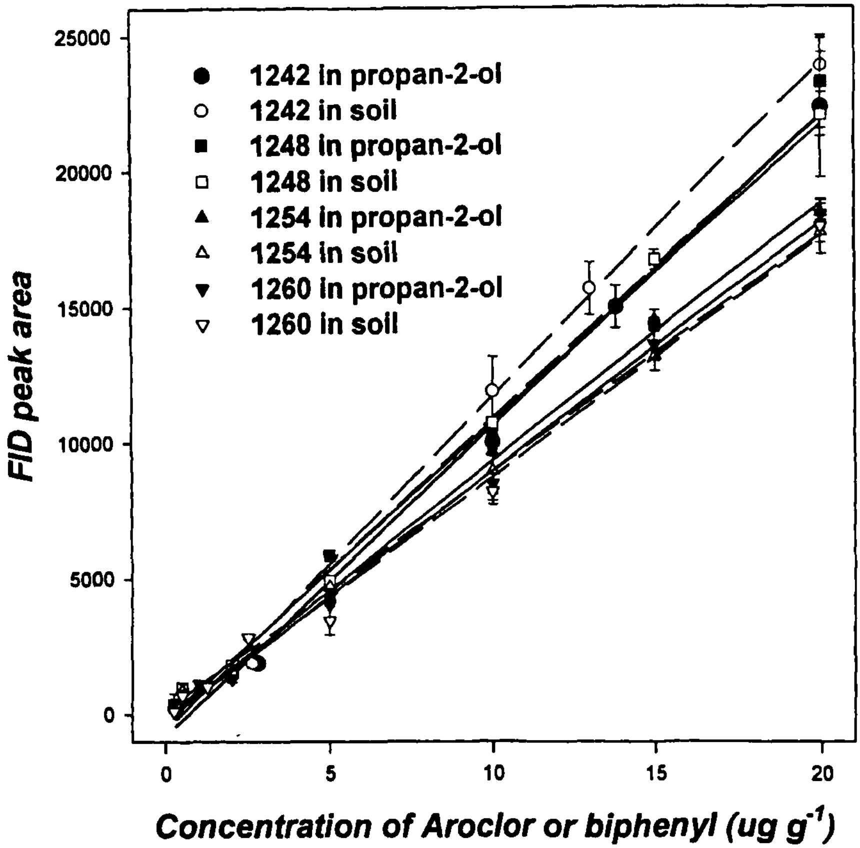

FIGURE 3 Variations in recoveries of biphenyl from Aroclor 1242 (•, ○), Aroclor 1248 (■, □), Aroclor 1254 (▲, △) or Aroclor 1260 (▼, ▽) added to soil (filled symbols) or propan-2-ol/water (hollow symbols) at 0.3–22 μg g^{-1}

As indicated in Table III, soils that had been spiked with Aroclor 1242 or 1248 or 1254 or 1260 standard, resulted in recoveries of biphenyl that were in good agreement with predicted values. It was observed that the Aroclor 1260 conversion model provided the closest agreement for the estimation of PCBs concentration for contaminated soil samples, especially good for certified reference materials. As a result, all estimations of PCB concentration with soil samples were calculated based on the Aroclor 1260 model.

The method limit of detection in terms of direct PCB conversion to biphenyl within the soil was approximately 150 ug/kg using the model of three times baseline noise divided by the slope. The capacity to convert PCB mixtures to biphenyl within the soil was increased when the quantity of added magnesium was increased. One gram of Mg was insufficient for quantitative conversion within the soil if the PCB concentration was in excess of 5 mg/kg. This was true especially for more highly chlorinated substrates such as Aroclor 1260. All subsequent experiments were conducted with 2 g Mg added to the sample matrix. The quantity of K_2PdCl_6 used for the reaction mixture has less of an effect on the conversion efficiency of the PCBs. In preliminary studies, the yield of biphenyl from Aroclor 1242 was similar for increasing amounts of K_2PdCl_6 (10–40 mg) added to 2 g Mg in the presence of various quantities of 1242 substrate. Subsequent experiments were carried out with 10 mg K_2PdCl_6.

The conversion of PCBs to biphenyl within soil, was also time dependent. There were substantial differences between the recoveries after 2h and 6h of reaction in the soil matrix. Although the calibration plots generated with 1260 substrate for both reaction times provided good fits with linear models, (coefficients of determination, $r^2 = 0.996$, 0.983), 2h of reaction was insufficient to quantitatively dechlorinate the substrates within the soil. By contrast, there was a good agreement with the theoretical biphenyl content of Aroclor 1260 for the longer reaction time. As measured by GC-FID (and peak purity corroborated by GC-MS), the conversion of PCBs to biphenyl within soil matrices was greater than 98% over the substrate concentration range of 1–52 µg/g.

The soil particle size influenced the dechlorination rate for PCBs. For samples of soil No.1 that had been spiked with Aroclor 1242 at 5 mg/kg, no differences in recoveries were observed from substrate that had been sieved to pass a 50-mesh screen vs. material that had been sieved to pass a 10-mesh screen. Analogous results were obtained for soils 2 and 3; the samples with a smaller particle size required a longer reaction time. In this study, 2h of reaction were suitable for soils sieved to 10-mesh, 4h for the samples of 50-mesh and 6h for the samples of greater than 125-mesh.

Certified Reference Materials

The contaminated soils in this study were characterized by a relatively low content of organic matter that might have affected the recovery of biphenyl from PCBs. Other soil properties were anticipated to have less of an effect on the conversion. Table IV summarizes the results obtained for soil/sediment matrices. Acceptable agreements were obtained between the PCBs concentration obtained by dechlorination to biphenyl and the certified PCB content for two of the three reference materials. The PCB content of the third reference material (certified 0.34 μg g^{-1}) was appreciably overestimated by the biphenyl conversion procedure. Acceptable agreements were also observed between the estimated PCB concentrations for additions of standard back to contaminated soils and estimates based on direct conversion within the soil matrix.

TABLE IV PCB concentrations (μg/g ± one standard deviation) in soil/sediment as determined with different procedures

Method	*Soil 1*	*Soil 2*	*Soil 3*	*SRM1939a*	*CRM 481*	*CRM 536*
Direct conversion within soil matrix	N.D.[a]	20.8 ± 1.2[b]	19.3 ± 0.9	32.7 ± 3.5	437.4 ± 14.2	1.8 ± 0.2
Standard addition to the soil	N.D.	22.5 ± 1.4	21.3 ± 1.8	---	---	---
Conversion on the Soxhlet extract	N.D.	30.3 ± 6.6	36.2 ± 2.0	35.4 ± 1.8	478 ± 46.5	2.2 ± 0.2
Conversion on the sonication extract	N.D.	24.9 ± 1.1	28.1 ± 1.0	---	---	---

a. N.D. none detected – less than 0.1 mg kg^{-1}.
b. One standard devation based on 3 replicate determinations.

To corroborate the hypothesis that organic matter could provide a source of biphenyl in soil samples, Soxhlet and sonication extractions were conducted with the three soils and the reference materials. For identical derivatization procedures performed directly on the three soils in the absence or presence of added PCB substrate, no contribution from the organic matter was observed. By contrast, both the sonication and the Soxhlet extracts from the soils 2 and 3 as well as the reference materials did reveal a contribution to the apparent biphenyl recovery from the background. These results indicated that soil samples, even with relatively low content of organic matter, can be converted in part to biphenyl under the mild reaction conditions. The biphenyl that results from soil organic compounds could cause an overestimation of PCB concentration in soil under the conversion conditions (CRM 536 in Table IV). Attempts were made to overcome the contribution from this source. Clean-up with concentrated $H_2SO_4$was ineffective however. The use of this approach can result in increased variability of recoveries. (European Commission, bcr information, CRM 481 manual).

In summary, the direct derivatization within the sample matrix can be used to estimate the PCB concentration for soil/sediments and contaminated solutions. The concentrations of PCBs in two of the three reference materials (up to 473 mg kg^{-1}) were determined successfully. The principle advantages of this procedure include convenience and simplicity but the principle disadvantage is that organic matter can also contribute to the apparent analyte recovery and must be accounted for in accurate estimates. The method of standard additions can provide reliable estimates. The Aroclor 1260 model can be used to estimate the PCB concentration in contaminated soil/sediments samples.

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