Science of the Total Environment 463–464 (2013) 326–333

Contents lists available at ScienceDirect

Science of the Total Environment

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

Determination of polychlorinated biphenyls in soil and sediment by selective pressurized liquid extraction with immunochemical detection

Jeanette M. Van Emon [a,*], Jane C. Chuang [b,1], Alisa Bronshtein [c], Miriam Altstein [c,2]

[a] US Environmental Protection Agency, National Exposure Research Laboratory, P.O. Box 93478, Las Vegas, NV 89193-3478, USA
[b] Battelle, 505 King Avenue, Columbus, OH 43201-2693, USA
[c] Institute of Plant Protection, ARO, Agricultural Research Organization, The Volcani Center, P.O. Box 6, Bet Dagan 50250, Israel

HIGHLIGHTS

- A selective pressurized liquid extraction (SPLE) method was developed for analyzing PCBs.
- Aroclor and Coplanar PCB ELISAs were applied to the SPLE extracts.
- Soil and sediment samples from five different sites were analyzed using the SPLE–ELISA.
- SPLE–ELISA compared favorably with a conventional PCB multi-step analysis.
- SPLE–ELISA is useful for quantitative or qualitative analysis of PCBs.

ARTICLE INFO

Article history:
Received 28 February 2013
Received in revised form 8 May 2013
Accepted 9 May 2013
Available online 2 July 2013

Editor: D. Barcelo

Keywords:
Selective pressurized liquid extraction
ELISA
PCBs
Aroclors

ABSTRACT

A selective pressurized liquid extraction (SPLE) method was developed for a streamlined sample preparation/cleanup to determine Aroclors and coplanar polychlorinated biphenyls (PCBs) in soil and sediment. The SPLE was coupled with an enzyme-linked immunosorbent assay (ELISA) for an effective analytical approach for environmental monitoring. Sediment or soil samples were extracted with alumina, 10% $AgNO_3$ in silica, and sulfuric acid impregnated silica with dichloromethane at 100 °C and 2000 psi. The SPLE offered simultaneous extraction and cleanup of the PCBs and Aroclors, eliminating the need for a post-extraction cleanup prior to ELISA. Two different ELISA methods: (1) an Aroclor ELISA and (2) a coplanar PCB ELISA were evaluated. The Aroclor ELISA utilized a polyclonal antibody (Ab) with Aroclor 1254 as the calibrant and the coplanar PCB ELISA kit used a rabbit coplanar PCB Ab with PCB-126 as the calibrant. Recoveries of Aroclor 1254 in two reference soil samples were 92 ± 2% and 106 ± 5% by off-line coupling of SPLE with ELISA. The average recovery of Aroclor 1254 in spiked soil and sediment samples was 92 ± 17%. Quantitative recoveries of coplanar PCBs (107–117%) in spiked samples were obtained with the combined SPLE–ELISA. The estimated method detection limit was 10 ng $g^{-1}$for Aroclor 1254 and 125 pg g^{-1} for PCB-126. Estimated sample throughput for the SPLE–ELISA was about twice that of the stepwise extraction/cleanup needed for gas chromatography (GC) or GC/mass spectrometry (MS) detection. ELISA-derived uncorrected and corrected Aroclor 1254 levels correlated well ($r = 0.9973$ and 0.9996) with the total Aroclor concentrations as measured by GC for samples from five different contaminated sites. ELISA-derived PCB-126 concentrations were higher than the sums of the 12 coplanar PCBs generated by GC/MS with a positive correlation ($r = 0.9441$). Results indicate that the SPLE–ELISA approach can be used for quantitative or qualitative analysis of PCBs in soil and sediments. To our knowledge, this is the first report of an SPLE–ELISA approach not requiring a post-extraction cleanup step for detecting Aroclors and coplanar PCBs in soil and sediment.

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1. Introduction

Polychlorinated biphenyls (PCBs) are synthetic organic compounds with 209 distinct congeners. PCBs are commonly used in capacitors and other electrical equipment because of their stability, insulating properties, and low burning capacity. PCBs were originally produced as specific mixtures of congeners known as Aroclors. The International Agency for Research on Cancer (IARC) classified PCBs as probable human carcinogens (2A group) (IARC., International Agency for

* Corresponding author. Tel.: +1 702 798 2154; fax: +1 702 798 2243.
E-mail addresses: vanemon.jeanette@epa.gov (J.M. Van Emon), ccjane20@hotmail.com (J.C. Chuang), alisa@volcani.agri.gov.il (A. Bronshtein), vinnie2@agri.gov.il (M. Altstein).
[1] Tel.:+1 614 424 5222; fax: +1 614 458 5222.
[2] Tel.:+972 3 968 3710; fax: +972 3 968 3835.

0048-9697/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.scitotenv.2013.05.020

Research on Cancer, 1987). Concern over the harmful ecological and human effects and the persistence of PCBs in the environment led the United States Congress to ban their domestic production in 1977. PCBs are still detected in various micro-environments (e.g., air, soil, dust, sediment, food, tissue) either as Aroclors or as individual congeners (ATSDR, Agency for Toxic Substances, Diseases Control Registry, 2000; Deng et al., 2002; Wilson et al., 2003; Kim et al., 2004; Sapozhnikova et al., 2004; Martinez et al., 2010). Human exposure to PCBs is through inhalation of contaminated air (outdoor or indoor), ingestion of contaminated food or non-food items, and dermal contact of contaminated surfaces. The primary route of exposure to PCBs is through consumption of contaminated lipid-enriched foods (e.g., fish and cooking oils) as PCBs can accumulate in these and other foodstuffs (ATSDR, Agency for Toxic Substances, Diseases Control Registry, 2000). PCB exposure has been associated with a variety of adverse health effects in humans, including hepatotoxicity, reproductive toxicity, reduced birth rate and neurodevelopmental disruption (ATSDR, Agency for Toxic Substances, Diseases Control Registry, 2000; Aoki, 2001; Schantz et al., 2003). They can affect the immune, reproductive, nervous, and endocrine systems, and have been linked to low intelligence quotients in children.

The analysis of PCBs in environmental samples is generally a multi-step process. Conventional methods including gas chromatography (GC) with electron capture detection (ECD) and/or mass spectrometry (MS) typically require a thorough sample cleanup (Muir and Sverko, 2006; US EPA, 2007, 2010). These methods are generally reliable and sensitive, however, they are time consuming, require tedious laboratory preparation steps and expensive equipment with highly trained personnel. The high costs for monitoring PCBs and related compounds are often a concern for regulatory agencies. Effective and low cost screening methods are needed for large-scale environmental monitoring and human exposure assessment programs. Sample extraction and cleanup are rate limiting factors for the overall throughput in PCB analysis of environmental and biological samples. Pressurized liquid extraction (PLE) is an automated, fast and efficient sample extraction technique that utilizes elevated temperatures and high pressures to achieve effective extraction of organic pollutants from solid matrices (Richter et al., 1996). PLE uses less solvent, and requires less time compared to the Soxhlet extraction employed in several methods for extracting solid samples (US EPA, 1994, 1996a). PLE techniques have been reported for the effective extraction of persistent organic pollutants including PCBs, dioxins, and furans from complex sample media (e.g., sediment, soil, tissue, oil), but required post-extraction cleanup of the extracts (Misita et al., 2003; Wilson et al., 2003; Robinson et al., 2004). Multi-step cleanup procedures such as acid wash, open-bed column chromatography, or gel permeation chromatography are required prior to GC or GC/MS. A streamlined sample preparation/cleanup strategy, of selective pressurized liquid extraction (SPLE) utilizing various adsorbents as an in-situ cleanup tool, was recently reported to retain fat and other co-extracted interferences during extraction of lipophilic contaminants including PCBs, polybrominated diphenylethers, dioxins, and furans from oil, feed, food, soil sediment, and tissue (Nording et al., 2005, 2006; Bjorklund et al., 2006; Haglund et al., 2007; Chuang et al., 2009; Zhang et al., 2011). SPLE incorporates cleanup adsorbents with the sample in an extraction cell for simultaneous extraction and cleanup of target analytes in complex matrices minimizing or completely eliminating the tedious cleanup steps prior to detection by either instrumental or immunochemical methods.

Immunochemical methods such as the enzyme linked immunosorbent assay (ELISA) typically provide advantages (e.g., lower cost, higher sample throughput) over GC methods for certain monitoring applications (Van Emon and Lopez-Avila, 1992, Van Emon, 2001, Van Emon et al., 2008a, 2008b). Immunochemical methods can easily be introduced into a chemical analysis laboratory and integrated with instrumental methods particularly for a tiered analytical approach (Van Emon et al., 2007). The U.S. EPA Office of Solid Waste has approved enzyme immunoassay methods for screening PCBs in soils and non-aqueous waste liquids (US EPA, 1996b) and for dioxins/furans in soils (US EPA, 2002). The use of various ELISA methods for the determination of PCBs in water, soil, and sediment has been reported (Franek et al., 1997, 2001; Johnson and Van Emon, 1996; Johnson et al., 2001; Lawruk et al., 1996; Chuang et al., 1998; Altstein et al., 2010; Bronshtein et al., 2012). In a previous study, sample matrix interferences were observed in a PCB ELISA that did not employ a post-extraction cleanup step. A more selective extraction procedure, supercritical fluid extraction (SFE) had to be developed to minimize the matrix interference (Johnson et al., 2001). However, SFE may not be suitable for the routine preparation of soil and sediment samples as it is not an exhaustive extraction procedure and is dependent on the physiochemical properties of the sample for efficient extraction. Samples from heterogeneous environmental sites may differ significantly and require extensive SFE method optimization per sample set. Post-extraction cleanup procedures are often required to minimize matrix interference by ELISA for the determination of lipophilic compounds such as PCBs, dioxins, furans, and polybrominated diphenylethers when more exhaustive extraction methods (e.g., Soxhlet extraction, PLE) are employed (Nichkova et al., 2004; Muir and Sverko, 2006 Shelver et al., 2008; Van Emon et al., 2008b). The addition of a cleanup step often reduces the advantages of low cost and high throughput of ELISA detection. These advantages can be maintained with the coupling of an effective single-step sample extraction/cleanup procedure such as SPLE with ELISA methods.

Described here is the development and evaluation of SPLE–ELISA methods for Aroclors and coplanar PCBS using contaminated soil and sediment samples with comparison to GC or GC/MS procedures. Contaminated sediment and soil samples from a field study conducted under an EPA Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) program (US EPA, 2004; Dindal et al., 2007) were analyzed using the optimal SPLE followed by an ELISA with specificity for either Aroclors or coplanar PCBs. The SPLE–ELISA results were compared with those obtained by conventional methods (stepwise extraction, cleanup and GC or GC/MS). The performance of the SPLE–ELISA technique was evaluated in terms of false positive and false negative rates, recovery, detection limit, method precision, sample throughput and appropriateness for environmental monitoring.

2. Experimental section

2.1. Samples

Two Aroclor standard reference soils (Environmental Resource Associates, Arvada, CO) and soil and sediment samples from a field study conducted under an EPA SITE MMT program (Dindal et al., 2007; US EPA, 2004) were used in the recovery experiments. Sediment and soil samples ($N = 32$) collected from five SITE MMT sampling sites were prepared by the SPLE–ELISA method for Aroclor 1254 and a subset of samples ($N = 10$) was used for coplanar PCB analysis.

2.2. Chemicals

Primary rabbit polyclonal (AC 3) anti-PCB antibodies (Abs) and a PCB coating antigen (Co-Ag 560-52 made by conjugating a PCB hapten to conalbumin) were previously prepared and described (Johnson and Van Emon, 1996). Goat anti-rabbit conjugated to horseradish peroxidase (HRP), mixed Aroclor standard solutions, alumina, phosphate buffered saline (PBS), PBS containing 0.1% (v/v) Tween-20 (PBST), and silver nitrate ($AgNO_3$) were obtained from Sigma (St. Louis, MO). Coplanar PCB standards were obtained from Cambridge Isotope Laboratories (Andover, MA). One-step, Ultra 3,3′,5,5′-tetramethylbenzidine (TMB) ELISA substrate was purchased from Pierce (Rockford, IL). Coplanar PCB ELISA testing kits were purchased from Abraxis (Warminster, PA). Dichloromethane (DCM), ethyl ether (EE), hexane, methanol, toluene,