# New Trends in the Sampling and Analysis of Atmospheric Persistent Organic Pollutants over the Open Ocean

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## Abstract

Persistent Organic Pollutants (POPs) are globally distributed and are of great concern due to their persistence, carcinogenicity and endocrine-disrupting effects. POPs include a wide range of xenobiotic chemicals, including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and brominated flame retardants (BFR). These chemicals have been detected in remote polar regions that lack historical usage and the atmosphere is considered to be the major pathway for their long-range transport. The collection of accurate atmospheric data for POPs is challenging for two reasons: firstly, there is a need to separate the prevailing background level of a POP from that arising from local sources; and secondly, accurately estimating low background levels with respect to contamination of samples and analytical sensitivity. The first difficulty can, in principle be resolved by sampling far from local sources, e.g. in the open ocean or Antarctica. The constraint is that remote sampling is more expensive and challenging to conduct. Reports on global background levels of POPs in the literature are therefore sparse - even though such data are of primary interest to gain a better understanding of their global fate and transport. This chapter reports several new developments in the collection and analysis of atmospheric POPs, including a cost-effective solution to air sampling over the open ocean. Sampling data are reported from the Indian Ocean - as acquired by Jocara Indian Ocean Quest, an expeditionary voyage that used a self-

fabricated air sampler to collect atmospheric samples onboard a sailing vessel. The ability to sample without running an engine greatly reduces sample contamination. Atmospheric samples were collected over polyurethane foam (PUF) plugs. An efficient microwave-assisted extraction (MAE) technique is described that can be used both for pre-cleaning PUF plugs and sample extraction. Details are also provided on quality control procedures - crucial for establishing statistically-significant estimates of background POP levels. This methodology outlined in this chapter represents a novel, cost-effective and accurate technique for measuring atmospheric POP concentrations.

## Introduction

Persistent Organic Pollutants (POPs) are globally pollutants that are readily detected in the environment, even in remote regions of the Earth with no historical usage [1-4]. POPs include a wide range of xenobiotic chemicals, such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticide (OCPs), e.g. hexachlorocyclohexane (HCHs), dichlorodiphenyltrichloroethane and related compounds (DDTs) and chlordanes. Such compounds are of great concern due to their persistence, carcinogenicity and endocrine-disrupting effects. The atmosphere is considered to be the mobile phase for the long-range transport of POPs towards polar regions, where cold condensation of these compounds to land and ocean occurs. Due to the high potential of POPs to undergo bioaccumulation in the food chain, the concern about POPs has extended to their ecotoxicological context as to which residues poses a toxic threat to humans and wildlife, in particular marine mammals [5-8]. Long-range transport of POPs has been described by various atmospheric dispersion models [9, 10]. However, field data on atmospheric POPs are sparse, in particular data collected over oceanic and polar regions - even though quantitative analysis of POPs in air samples in such regions is of primary interest. The collection of such data are challenging due to the need to separate prevailing background levels of POPs from those arising from local sources, and to accurately estimate low background levels with respect to potential sources of contamination incurred during sampling processing and analysis.

Even with the most sophisticated analytical techniques, high volumes of air need to be collected to trap sufficient amounts of the target compound on a solid adsorbent material

in order to ensure accurate and reliable quantification. A typical high-volume air sampling device consists of a high flow-rate pump (30-500 L/min), an upstream filter (glass-fiber filter) to trap particle-bound components followed by an adsorbent material to collect the gas-phase organic component that pass through the filter. Tenax® GC, Amberlite XAD2 and XAD4, Florisil and polyurethane foam (PUF) plugs have been used to trap organic components from the gas phase [11-14], whereas the latter has been most commonly used to trap POPs [1-4, 15, 16]. Atmospheric data of POPs over the open ocean have been previously acquired using air sampling devices onboard large research vessels [15-18]. However it is known that research vessels are a potential source of contamination to trace compound analysis including the analysis of POPs [19] due to the combustion of fossil fuels and wide range of activities onboard.

In this chapter we present the development of a self-fabricated and cost-effective high-volume air sampling system, and its application onboard a small sailing vessel to obtain atmospheric POPs data from the Indian Ocean. A novel approach for the efficient extraction of POPs collected on PUF plugs using microwave-assisted extraction (MAE) was developed. The risk of contamination and losses of trapped target compounds during transport and storage has been investigated over a period of several weeks. For quantification, a highly-sensitive gas-chromatographic technique coupled to a tandem mass spectrometer equipped with an ion trap (GC-IT-MSMS) has been validated for the accurate and precise analysis of POPs at low levels. The air sampling system has been used to obtain also the first atmospheric levels over the open ocean for PBDEs.

## Experimental

### Sampling Conditions

The self-designed air sampler (see below) was installed on the sailing vessel *Jocara* (an 18 m long fiber glass boat) during an expedition over the Indian Ocean from August 2004 to August 2005. Samples were collected 4 m above sea level, into the prevailing wind and under sail to reduce potential contamination from combustion sources to an absolute minimum. In our studies, a single unit of stainless-steel dual-cartridges was loaded with pre-cleaned GF filter and PUF plugs prior sampling on the sailing vessel. This requires skillful handling to avoid to contamination to both the filter and plugs,

especially in rough sea conditions. After collection, PUF plugs were placed in tightly-closed tin containers sealed in polypropylene bags and then stored at -18 °C in air- and moisture-tight plastic containers. If storage capacity allows, dual-cartridges equal to the number of samples to be collected can be loaded with GF filters and PUF plugs in the laboratory under very clean conditions, e.g. under a purified $N_2$ atmosphere as described below. Individual dual-cartridges can be used for each sampling period. The cartridges can be sealed in polypropylene bags and stored individually in air- and moisture-tight plastic containers until sampling. After sampling, the used cartridge is sealed back in the propylene bag and stored inside the plastic container at -18 °C. As the material and fabrication of the cartridges are cost-effective, the use of individual cartridges for each sampling period has the advantage to further minimize the risk of contamination during the loading of cartridges such that crew members with little experience can conduct the sampling exercise.

## Design of High-Volume Air Sampling System

A 220 VAC high flow-rate air sampler H8400 TE (F&J Specialty Products, Inc.) fitted with a thermally protected motor has been proven to be reliable under rough sea conditions. It is recommended that users select an air pump with a thermal protection as previous experience with a similar 12VDC model (H8400B) without thermal protection of the motor led to a power decline of 15% within a few weeks of installation [4]. In a previous study conducted in Singapore the air sampler was equipped with a digital flow meter with an integrator to obtain the amount of air collected (Cole-Parmer, USA) [21]. However, its installation and use failed onboard the sailing vessel due to interference from the radio equipment. For this reason, the air sampler was calibrated in the laboratory with the digital flow meter prior the start of the sampling voyage and performance was subsequently monitored using a manual flow meter during sample collection. On larger vessels, such interferences may not exist due to the presence of superior-protected electronics, and larger distances between the flow meter and sources of interference.

For the development of the air sampling system, PUF has been selected as an adsorbent material for the following reasons (i) its open structure allows large volumes of air to be sampled [19], (ii) it has a good trapping efficiency for semi-volatile POPs [12, 20], (iii) it is easy to handle during sampling and sample processing and (iv) it is a low

cost material. The GF filter, used to separate particle-bound POPs in the gaseous phase and the PUF plugs are placed in the stainless-steel dual-cartridges (Fig. 1a). The cartridges have been made from commercial vacuum flask. The inner diameter of the flasks has to be of the correct diameter so that the PUF plugs fit tightly without squeezing or deformation of the plug. Drilled holes at the bottom and in the screw cap of the flask with a diameter of 40 mm and 10 mm respectively act as an air inlet and outlet. A 1mm stainless-steel mesh with a diameter equivalent to the flask is used as a support for the GF-filter at the inlet (Fig. 1a). The pre-cleaned PUF plugs are placed directly onto the filter. An internal polypropylene ring with 10 mm holes in its wall is glued over the outlet on the closure of the flask so that the upper PUF plug does not obstruct the outlet of the cartridge and allows free air flow. The outlets of the dual-cartridge are connected with brass plumber tubing. The dual-cartridge is connected to the air pump with a rigid plastic hose (i.d. 32 mm) containing an internal stainless-steel wire to stabilize the hose against vacuum forces (Fig. 1a). The dual-cartridges are then mounted at a height of 4 m above sea level (on the mast of the sailing vessel*)* with the air inlet facing downward to minimize the impact of sea spray (Fig. 1b).

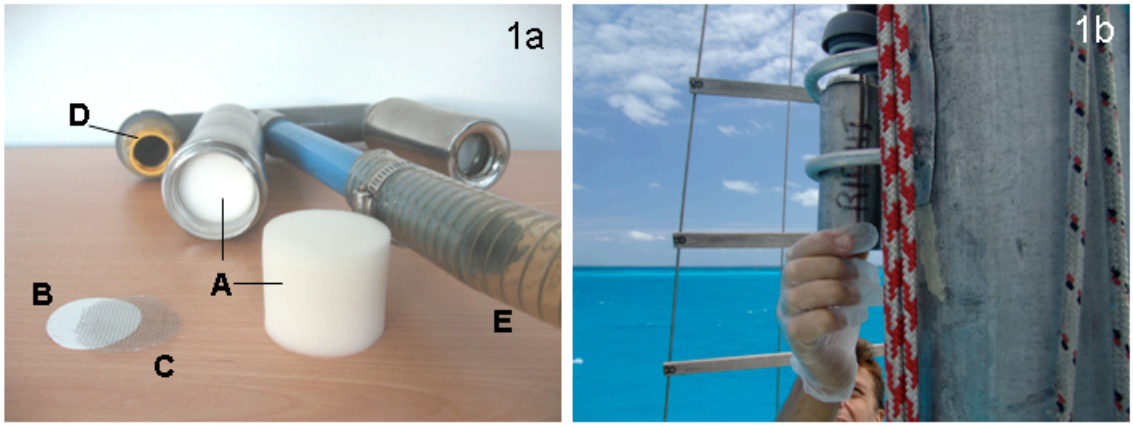


Fig. 1: a) Stainless steel cartridges with PUF plugs (A), glass fiber filters (B), stainless steel mesh (C), polypropylene ring (D) and hose (E). b) Sampling on the sailing vessel.

## Reagents and Materials

All solvents and sodium sulfate, used in the analysis of POPs were of pesticide grade. Mixed standard solutions for pesticides (Z-014C-R), PCBs (C-QME-01) and PBDEs (BDE-CSM) were obtained from AccuStandard (New Haven, USA). $^{13}C_{12}$ PCB congeners CB 28, 52, 101, 138, 153 and 180 were used as surrogate standards, and $^{13}C_{12}$ PCB congeners CB 32, 141 and 208 as internal standards, both purchased from Cambridge Isotope Laboratories (MA, USA). Sodium sulfate and silica gel (No. R10040B, Silicycle, Canada) were prepared at 450 ºC for > 10 hours prior to use. Tin containers used for the storage of PUF plugs and all glassware were soaked in laboratory detergent for 12 hours, rinsed with hot tap water, rinsed with copious amount of high-purified water and then dried at 220 ºC for > 12 hours. Prior to use, the glassware and tin containers were rinsed with acetone. Sample vials for GC-MSMS analysis were cleaned by rinsing with acetone, baking at 450 ºC for > 12 hours and then sealed in an acetone-rinsed glass bottle. Prior to use, the vials were rinsed with acetone and dried at 220 ºC.

## Filter and PUF Cleaning Procedure

GF/A filters (Whatman) were baked at 450 ºC for > 16 hours and stored in a glass jar. The glass jar was rinsed with acetone, baked at 450 ºC and rinsed with acetone prior to use. The glass jar containing the filter was stored in an air- and moisture-tight plastic container during the sampling program.

MAE was performed on a CEM Mars X microwave oven (CEM, Matthews, USA) equipped with pressure and temperature sensors. PUF plugs were purchased from Klaus Ziemer GmbH (Mannheim, Germany). The PUF plugs have a density of 0.03 g $cm^{-3}$ and a degradation temperature of 180 ºC. Each plug was soaked in 40 mL of hexane and squeezed using a stainless-steel house hold press (Fig. 2a) as a pre-cleaning procedure to remove any staining and major contaminants which may interfere with the GCMSMS analysis. A wet PUF plug was inserted into a Teflon-lined extraction vessel containing 40 mL hexane-acetone (2:3, v:v). The PUF plugs were extracted for 4 hours using an optimized extraction program as described below. After cooling, the solvent was squeezed out of the plug using the stainless-steel press. The extraction step was

repeated six times using fresh solvents for each step resulting in a total extraction time of 24 hours. After the last extraction step the PUF plugs were not exposed to the ambient laboratory air. Indoor levels of contaminants in laboratories and the passive adsorption effects of PUF to POPs may increase crucial blank values in the study of atmospheric POPs in remote regions. As an alternative to the use of high-maintenance clean rooms, a self-fabricated glove box was used, as shown in Fig. 2b. The box is filled with purified $N_2$ through a gas inlet prior the exposure of the PUF plugs to the interior of the box. All the following steps were conducted under an $N_2$ atmosphere. The solvent was squeezed out the PUF thoroughly and dried before transferring the PUF plugs into the pre-cleaned tin container. The tin containers were removed from the $N_2$ atmosphere, sealed in polypropylene bags and then stored in air-and moisture-tight plastic container (Fig. 2c).

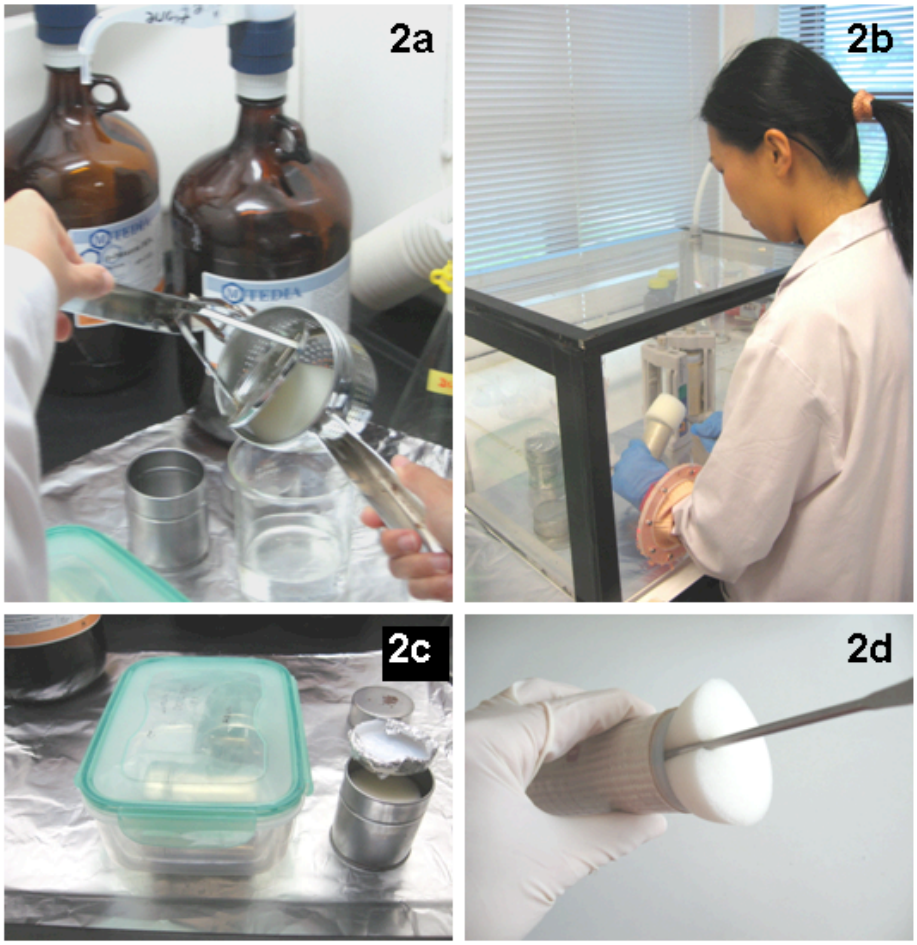


Fig. 2: Pre-cleaning step with stainless steel press (a), working under an $N_2$ atmosphere (b), storage of pre-cleaned PUF plugs (c) and loading plugs into extraction vessel (d).

## Sample Extraction

Spiked PUF plugs were used to test analyte recovery using either conventional Soxhlet extraction (SE) or MAE. Pre-cleaned PUF plugs were place in the SE apparatus or MAE extraction vessel, and spiked with 10 μL of OCPs (1000 μg $L^{-1}$), 10 μL of PCBs (500-2000 μg $L^{-1}$) and 10 μL of PBDEs (2000-20000 μg $L^{-1}$). Each plug was additionally spiked with the surrogate standard. Five hours after spiking, the plugs were extracted either for 12 hours using SE with hexane-acetone (1:1, v:v) or for 3 hours using MAE with hexane-acetone (2:3, v:v) using the program described below. For MAE, the solvent was changed after each one hour extraction step.

PUF plugs used for air sample collection [4, 21, 22] were analyzed using the MAE procedure. Samples stored in the tin container and the outer air- and moisture-tight plastic container were defrosted after storage at -18 ºC. Tin containers were opened under the $N_2$ atmosphere and PUF plugs loaded into the extraction vessels. Each plug was spiked with surrogate standard 5 hours prior to extraction. 40 mL of hexane-acetone (2:3, v:v) was added to the plug and extracted using the same procedure as for spiked PUF plugs. The solvent extracts from each extraction step were collected under the $N_2$ atmosphere and combined. All extracts were slowly concentrated to approximately 2 mL at 15 ºC using a rotary evaporator.

## Clean-up Procedure of Sample Extracts

A clean-up column containing of 4 g of purified silica gel topped with a 2 cm layer of sodium sulfate was washed with 2x 15 ml hexane. Extracts were then transferred onto the column and eluted with 130 mL hexane and 15 ml dichloromethane. The extract was eluted in a one single fraction and concentrated to about 2 mL at 15 ºC using a rotary evaporator and then further to 200 μL using a gentle purified nitrogen gas stream. The extracts were kept in sealed vials at -20 ºC. Prior to analysis, the internal standard was added to the sample extracts.

## Analytical Instrumentation

Sample analysis was conducted using a Varian 4000 GC-MSMS equipped with an ion trap and an autosampler CP 8400. For the analysis of PCBs and OCPs a DB5 fused silica capillary column (60 m x 0.32 mm i.d., film thickness 0.25 μm) was used, and for PBDEs a CP-Sil8-fused silica capillary column (10 m x 0.53 mm i.d., film thickness 0.25 μm). Purified helium was used as a carrier gas at a flow rate of 1.5 mL $min^{-1}$. Manifold, injection, ion trap and transfer line temperature was set to 60, 260, 220 and 280 ºC. For the analysis of PCBs and OCPs the oven temperature was programmed from 70 to 140 ºC at a rate of 25 ºC $min^{-1}$, 140 to 179 ºC at a rate of 2 ºC $min^{-1}$, 179 to 210 ºC at a rate of 1 ºC $min^{-1}$ and 210 to 300 ºC at a rate of 5 ºC $min^{-1}$ and held for 10 mins. For the analysis of PBDEs the oven temperature was programmed from 80 (held for 1.5 mins) to 250 ºC at a rate of 12 ºC $min^{-1}$, 250 to 300 ºC at a rate of 25 $min^{-1}$, and held for 10 mins. The ion trap was operated in internal EI-MSMS mode. The development and parameters of the MSMS method are described below in the section '*Analytical Parameters and Performance'.*

## Quality Assurance (QA)

QA and control procedures are crucial to obtain accurate and precise data of POPs at low levels. The following QA procedures are recommended for the collection of atmospheric samples and analysis of POPs:

- Collection of at least duplicate samples to calculate relative percent differences (RPD, ISO ISO/IEC 17025) or standard deviation (SD, with n ≥ 3). The air sampler described above has been designed to collect duplicate samples using dual-cartridges. Due to the need for high volumes of air for each cartridge and the laborious sample processing required, the analysis of duplicate samples is acceptable to estimate analytical reproducibility .

- Estimating the breakthrough (BRT) of compounds through the PUF plugs. The two PUF plugs from each single cartridge are extracted and analyzed

individually. A correction factor for each sample is calculated according to an infinite Taylor Series.

$$S = 1 + \frac{1}{k} + \frac{1}{k^2} + \frac{1}{k^3} \ldots \frac{1}{k^n} \ldots \qquad (1)$$

where k is the multiplier factor that relates the concentration levels found in the first and second PUF plugs exposed to the sampled air flow. Equation 1 can be manipulated to obtain:

$$S = \frac{k}{k-1} \qquad (2)$$

- Collection and analysis of field and procedural blanks to estimate the limits of detections (LODs) for individual compounds. LODs are defined as average blank value (n≥5) plus 3 times the standard deviation. Data of field and procedural blanks are used in order to identify any contamination during storage/transport and sample processing, respectively. Procedural blanks are obtained by following the extraction, clean-up and analytical procedure without the PUF plug. The number of field blanks should constitute ≥20% of the total number of samples.

- Spiked PUF plugs are stored and transported during the cruise together with PUF plugs used for sampling so as to estimate any losses of analytes during storage and transport.

- Each PUF plug is spiked with $^{13}C_{12}$–labeled PCB congeners (surrogate standard) prior to extraction to monitor the efficacy of sample processing .

- Control standards were analyzed for every 6-8 samples to check for any instrument drift during analysis.

- Three quality assurance criteria were used to ensure correct analyte identification: (a) signal-to-noise ratio greater than three; (b) GC retention times matched (± 0.1 min) those of standard compounds; and (c) the threshold match calculated by the GC-MSMS software library and sample spectrum was greater

than 600. The lower value of 600 for positive identification was derived from a comparison of the threshold match for both standard solution and samples at low levels.

# Analytical Procedure

## Optimization of MSMS Parameters

There are significant advantages in using an ion trap system approach to quadrupole GCMS. The use of a single ion trap does the work of three quadrupoles, each with its own vacuum system. The three common steps for both approaches are: (a) formation of ions and separation of a target ion; (b) energetic collisions to fragment target ion (collision induced dissociation, CID); and (c) CID product separated from unreacted ions. All three steps occur in the ion trap leading to lower cost and space requirements of the system. The most important advantage relates to the sensitivity of the parent ion which is lower in a quadrupole system due to transmission losses.

To obtain the lowest possible LOD, parameters affecting the sensitivity were optimized for large volume injection and for the MSMS acquisition method (see Table 1).
Large volume injection was used to increase the signal-to-noise ratio. A 4-μL portion of sample was injected into the GC-MSMS in splitless mode. After taking the sample portion, the autosampler is programmed to take an air plug of 5 μl. The autosampler program delays the actual injection for 15 seconds after the injection needle drives into the injector. During this delay the stainless-steel needle is heated up to induce a faster evaporation of the sample portion within the injector. The pre-heated needle permits maximum vaporization of the sample without any peak distortion. The sampling time was adjusted to one minute to allow for quantitative transfer of the sample to the column. An increase in analytical sensitivity by a factor of 1.5 to 2 has been observed using the hot-needle-injection (HNI) technique.

The GC total run time of 83 mins yields peak widths in the range of 8 to 12 sec. Even so narrower peaks are often desirable, wider peaks allow acquisition of more data points

across the peak that improves quantitative analysis of MS segments containing up to 5 MS/MS of parent ions.

Table 1: MSMS conditions for PCBs, OCPs and PBDEs.

| Compound | Precursor Ion [m/z] | Excitation Storage Level [m/z] | Exciatation Amplitude [V] | Quantification Ion [m/z] |
|---|---|---|---|---|
| α-HCH | 219 | 120 | 1.10 | 183 |
| γ-HCH | 219 | 75 | 0.70 | 183 |
| p,p-DDE | 318 | 104 | 0.80 | 246 |
| p,p-DDD | 281 | 124 | 1.20 | 200 |
| p,p-DDT | 272 | 171 | 1.00 | 200 |
| CB 18 | 256 | 75 | 2.90 | 186 |
| CB 44 | 292 | 75 | 1.10 | 257 |
| CB 49 | 292 | 75 | 1.50 | 257 |
| CB 52 | 292 | 75 | 1.50 | 257 |
| CB 70 | 292 | 128 | 3.60 | 222 |
| CB 74 | 292 | 75 | 3.60 | 222 |
| CB 87 | 326 | 90 | 1.90 | 291 |
| CB 95 | 326 | 90 | 1.60 | 291 |
| CB 101 | 326 | 90 | 2.20 | 291 |
| CB 110/82 | 326 | 90 | 1.50 | 291 |
| BDE 28 | 246 | 108 | 1.50 | 167 |
| BDE 47 | 326 | 144 | 2.60 | 219 |
| BDE 99 | 566 | 249 | 1.00 | 297 |
| BDE 100 | 566 | 249 | 1.00 | 297 |

For best sensitivity and selectivity, resonant non-modulated CID was performed on the parent ions. The multiplier offset was +300 V and the filament emission current was set to 80 μA. For ionization mode, the following parameters were established: electron impact at 70 eV, target total ion counts (TIC) at 2000, maximum ionization time 25,000 μs, pre-scan ionization time 1500 μs, background mass 45 m/z, RF dump value 650 m/z and ejection amplitude 20 volts. The first step in the MSMS optimization procedure was the selection of an appropriate precursor ion for each PCB congener. Standard solutions of OCPs, PCBs and PBDEs were injected into the GC–IT-MSMS operating in full scan mode. The most abundant ion, from each congener's full scan spectrum, was selected

as the precursor ion for the sequential application of MSMS. After the application of the second ionization step (CID) to parent ions, the MSMS spectrum was obtained for each compound. Two product ions were then selected, on the basis of highest abundance, as the characteristic ions for each compound. CID voltage, to control dissociation of parent ions, for each compound was determined using the automated method development (AMD) option built into the Varian GC-IT-MSMS software. The optimization includes the incremental increase of the amplitude and the best value is the one which gives the highest yield of the daughter ions and little of the precursor ion. Optimization of CID parameters was performed for all compounds and the optimum values established are reported in Table 1.

## Microwave-Assisted Extraction (MAE) Procedure

A hexane-acetone ratio of 2:3 (v:v) was selected as the best solvent mixture, with a volume set to 40 mL. The used PUF plugs were found to decompose at ≥ 180 ºC and an initial extraction temperature of 100 ºC led to a weight loss of PUF plugs of 9.2 ± 2% after six extraction steps of 4 hours. The weight loss was minimized to 2.0 ± 0.3 % after decreasing the temperature to 85 ºC. A weight loss of 2% is comparable to that encountered upon soaking PUF in hexane [14] and acetone [28], and indicates that elevated pressures during MAE do not contribute significantly to weight loss. It is important that PUF plugs (Diameter 50 mm) are soaked in hexane prior transfer into the extraction vessels (I.D. 35 mm). The hexane is squeezed out of the PUF plug using a household press so the plug remains wet. The plug is rolled without squeezing and transferred carefully into the extraction vessel as shown in Fig. 2d. PUF plugs with a larger diameter than 50 mm are not recommended as they may be squeezed in the extraction vessel leading to deformation of the plug. Teflon-lined extraction vessels with larger inner diameter are currently not available from CEM.

Microwave power was set to 600 W, at which the temperature and pressure remained constant for 4 hours by using 8 of the maximum 14 extraction vessel slots available. The optimized microwave program for sample extraction step was as follows: 7 mins to 85 ºC, hold at 85 ºC for 60 mins. Cleaning of the PUF plugs was achieved by holding the temperature at 85 ºC for 240 mins.

The extraction efficiency for an extraction time of 1 hour was between 55.7 to 72.0% for PCBs and OCPs, whereas after a second extraction step of 1 hour further an 11.3 to 37.8% was recovered. A third extraction step resulted in further recoveries between 2.7 and 11.9%. Overall, the recoveries of PCBs and OCPs were in a range of 70 to 120% and 72 to 111% for SE and MAE respectively. Recoveries of PBDEs were in the range of 68 to 91% using the above MAE procedure. All recoveries can be regarded as being in the 'good' range.

## Sampling Procedure and Performance

### Oceanic Air Samples: Blanks, Reproducibility and Stability during Storage

Low blank values are crucial for the accurate quantification of atmospheric POPs, in particular over oceanic regions. In earlier studies conducted in the 1970's and 1980's the awareness of potential contamination of atmospheric samples was low. Tanabe and Tatsukawa [15] reported a LOD value for ΣPCBs with 500 pg $m^{-3}$ during cruises conducted between 1975 and 1979 on research and commercial vessels, which is higher by a magnitude of two compared to more recent studies (Table 2). Bidleman and Leonard [16] found that atmospheric samples collected from the Arabian Sea and Atlantic Ocean were 2-3 times higher in PCB levels compared to land-based measurements. They concluded that the samples could have been affected by ship-based sources and excluded the data from their report. From more recent data collected over the Atlantic Ocean [17] it can be derived that the LOD for the sum of seven PCB congeners was at least 5.6 pg $m^{-3}$, which is in the same range as the LOD of the sum of 38 congeners in our study (5.5 pg $m^{-3}$) over the Indian Ocean [4]. The LOD of individual congeners ranged between 0.002 to 0.1 pg $m^{-3}$. LOD values for DDT compounds (p,p-DDT, p,p-DDD and p,p-DDE) were between 0.17 to 0.19 pg $m^{-3}$ (ΣDDTs = 0.48 pg $m^{-3}$), which are lower by a factor of 2 to 3 compared to those found in the blanks