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Original article

A novel method through solid phase extraction combined with gradient elution for concentration and separation of 66 (ultra) trace persistent toxic pollutants in Antarctic waters

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ABSTRACT

This study developed a method to perform the simultaneous concentration and selective separation of 66 (ultra) trace persistent toxic substances in Antarctic waters. The substances included 30 polychlorinated biphenyls, 17 organochlorine pesticides, 16 polycyclic aromatic hydrocarbons, 3 hexabromocyclododecanes. Solid phase extraction was performed using a C_{18} membrane and silica gel column. Gradient elution was conducted using organic solvents with different polarities; as a result, the efficiency of the C_{18} film is improved and the interferences from impurities and target compounds are eliminated. Extracts were subsequently analyzed through gas chromatography or liquid and gas chromatography coupled to tandem mass spectrometry. Method validation yielded the following values: recoveries of all target analytes in the Antarctic water ranged from 87.3% to 117.6% and reproducibility as percent relative standard deviation was lower than 5%. Quantification limits ranged from 0.004 μg L^{-1} to 0.030 μg L^{-1}. The established method improved the recoveries and reduced the limits of detection. Results indicated the method exhibited good performance in the simultaneous concentration and selective separation of 66 (ultra) trace organic pollutants; Therefore, the proposed sample pretreatment can potentially eliminate the effects of various classes of impurities to some extent.

1. Introduction

Polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and hexabromocyclodoecanes (HBCDs), which are listed as persistent toxic substances, exhibit properties similar to those of persistent organic pollutants (POPs). These pollutants are ubiquitous in nature and are found even in remote areas, such as in isolated areas in the polar region. The Antarctic is unique because it serves as an unparalleled natural laboratory for research on problems related to global pollution by persistent toxic substances (PTS) and an ideal site for baseline studies on the behaviors of PTS in the environment. The Antarctic region is mostly covered with snow, ice, and ocean. Although the concentrations of emerging pollutants in the Antarctic region are usually considerably low, these pollutants can be accumulated in sediments and organisms; thus, these pollutants can eventually endanger the ecosystem of the Antarctic region. Their transmission, source apportionment, and degradation can be analyzed when the mechanism of transmission and storage of these emerging pollutants in a multi-medium is fully understood. Therefore, analyzing the typical PTS in Antarctic water is necessary.

Over the past decades, researchers worldwide have developed analytical methods to analyze typical PTS in soil, sediment [1–4], and biological samples [5–8]. However, reports on these PTS in water are limited because of the low concentrations of these pollutants in bodies of water. Moreover, pollutants in the polar region have been rarely reported. Most of the published methods for water analysis have focused on specific families, such as pesticides [9–12], PAHs [13–15], or HBCDs [16,17]; only some of these studies could determine various compounds belonging to different families [12,18]. Furthermore, these studies have mostly

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focused only on one or two groups of contaminants. Nevertheless, studies have yet to analyze PCBs, OCPs, HBCDs, and PAHs simultaneously. The detection limits of these currently used methods also cannot satisfy the requirements to analyze Antarctic water samples. Sample preparation is of utmost importance in water analysis because these analytes belong to various chemical groups and are present at low concentrations in aquatic media.

To develop a simple and easy-to-use SPE- and gradient elusion-based sample preparation method of various groups of PTS (PCBs, OCPs, HBCDs, and PAHs) in water, we developed an environmentally friendly sample preparation technique that increases the overall sample throughput, eliminates the interference from impurities and target compounds and reduces cost. The factors influencing extraction efficiency to obtain optimum pretreatment conditions, for example sampling volume, extraction solvent, and variety and dosage of elution agent, are investigated.

2. Experimental

2.1. Chemicals and solutions

The following compounds were acquired from Wellington Laboratories and Cambridge Isotope Laboratories: a mixture standard of the 30 PCBs (8, 18, 28, 44, 52, 66, 77, 81, 87, 101, 105, 110, 114, 118, 123, 126, 128, 138, 153, 155, 169, 170, 180, 187, 189, 194, 195, 200, 205, and 206); a mixture standard of the 17 OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, Heptachlor, Aldrin, hextachlor exoxide, γ-chlorcan, α-endosulfan, α-chlorcan, *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, dieldrin, endrin, β-endosulfan, and endrinachyde); a mixture of the 16 PAHs [naphthalene (Nap), acenaphthylene (Ace), acenaphthene, fluorene, phenanthrene (Phe), anthracene, fluoranthene, pyrene, benz(*a*)anthracene, chrysene, benzo(*b*)-fluoranthene, benzo(*k*)-fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-cd)pyrene, diben-z(*a,h*)-anthracene, benzo(*g,h,i*)-perylene]; and a mixture of the 3 HBCDs. The substrate standard used in this study was polychlorinated biphenyl 209 (99%), and the isotope internal standards were Nap-d^8, Ace-d^{10}, Phe-d^{10}, Chr-d^{12}, Perylene-d^{12}, Terphenyl-d^{14}, and ^{13}C-γ-HBCD. All of the organic solvents (dichloromethane, *n*-hexane, methanol, and acetone) used in this study were of HPLC grade (Merck, Darmstadt, Germany). Water was purified using Milli-Qsystem (Molsheim, France). Silica, neutral alumina, and anhydrous sodium sulfate were purchased from Merck (Darmstadt, Germany). Neutral alumina and anhydrous sodium sulfate were activated for 8 h at 650 °C in a muffle furnace, cooled to room temperature, and then stored in a dryer. The silica gel was washed thrice with dichloromethane after the solvent was evaporated to dryness; a glass beaker filled with silica gel was stored in an oven at 170 °C.

2.2. Instrumentation

The following instruments were used: a gas chromatograph equipped with an electron capture detector (GC–ECD) and an auto injector (Shimadzu, model 2010); a gas chromatograph coupled with a mass spectrometer (GC–MS) and an auto injector (Agilent, model 6890 and MSD 5975B); a liquid chromatograph coupled with a triple-stage quadrupole mass spectrometer TSQ Quantum, equipped with an electrospray ionization source (Thermo scientific) (LC–MS/MS); DB-5 capillary column (30 m × 0.25 mm, 0.25 μm; Agilent); BDS HYPERSIL C_{18} column (100 mm × 2.1 mm, mm, 2.4 μm, Thermo Scientific); Glass fiber membrane (50 mm, 0.45 μm, Whatman); C_{18} membrane (47 mm, 3 M Co, USA); organic microporous membrane (0.22 μm, Xinya, Shanghai); solid-phase extraction device (Hengao, Tianjin); semi-automatic solid-phase extraction device (Supelco, USA); and glass column (10 mm × 300 mm).

2.3. Sample collection

The Fildes Peninsula is located southwest of King George Island and receives a marine climate. Fildes Peninsula, where eight scientific stations are found, is rich in biological resources and is the site of intensive scientific investigations in the Antarctic. Sea water, lake water, and snow water samples were collected from 10 (A1–A5 and G1–G5, Fig. 1), 8 (SW1–SW8, Fig. 1), and 4 (LW1–LW4, Fig. 1) sampling sites, respectively. All of these samples were collected from January 2013 to February 2014; from each site, approximately 8 L of water sample was collected in dark glass containers with Teflon cover. Snow samples were collected using stainless steel shovel and aluminum barrel, washed several times with deionized water, and soaked for 24 h with methanol.

2.4. Procedures

2.4.1. Sample pretreatment

The water sample (8 L) was measured using a volumetric cylinder, spiked with methanol (5 mL L^{-1}), and was shaken well. Each sample was spiked with four different isotopically-labelled internal standards: 50 μL of PCBs and OCPs at 500 ng mL^{-1} (PCB 209); 50 μL of PAHs at 500 ng mL^{-1} (Nap-d^8, Ace-d^{10}, Phe-d^{10}, Chr-d^{12}, Perylene-d^{12}, and Terphenyl-d^{14}); 20 μL of HBCDs at 600 ng mL^{-1} (^{13}C-γ-HBCD). The calibrated samples were spiked with internal standards and with calibration standards at appropriate concentrations (matrix-matched surrogate standards).

2.4.2. Membrane pretreatment and targets concentration

C_{18} films were primed with 5 mL dichloromethane-*n*-hexane (v/v, 1:1), 5 mL methanol, and 5 mL reverse osmosis water. This procedure was performed two times. Most water was effluented

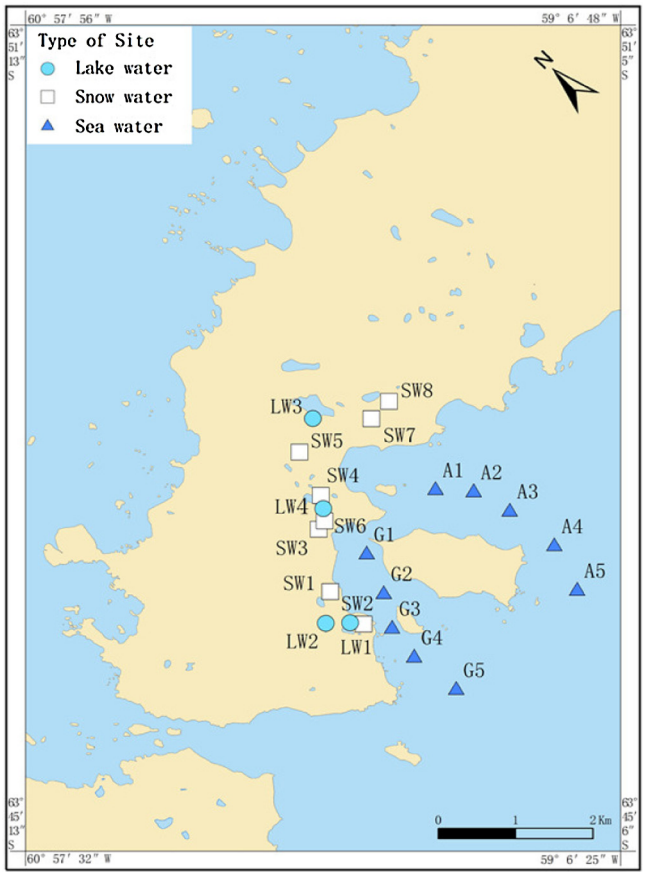

Fig. 1. Sampling sites of Fildes Penisula.