Marine Pollution Bulletin 93 (2015) 266–269

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Persistent organic pollutants and polycyclic aromatic hydrocarbons in mosses after fire at the Brazilian Antarctic Station

Fernanda Imperatrice Colabuono [a,*], Satie Taniguchi [a], Caio Vinícius Zecchin Cipro [a,b], Josilene da Silva [a], Márcia Caruso Bícego [a], Rosalinda Carmela Montone [a]

[a] Laboratório de Química Orgânica Marinha, Instituto Oceanográfico, Universidade de São Paulo, São Paulo, Brazil
[b] Littoral Environnement et Sociétés (LIENSs), UMR 7266, CNRS-Université de La Rochelle, 2 rue Olympe de Gouges, 17042 La Rochelle Cedex 01, France

ARTICLE INFO

Article history:
Available online 7 February 2015

Keywords:
Antarctic vegetation
PCBs
HCB
PBDEs
PAHs
Fire emissions

ABSTRACT

A fire at the Brazilian Antarctic Station on February 25th, 2012 led to the burning of material that produced organic pollutants. To evaluate the impact in the surrounding area, polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) were analyzed in moss samples collected in the vicinities of the station before and after the incident and compared to findings from previous studies in the same region. PCBs were on the same magnitude as that reported in previous studies, which could be associated to the global dispersion of these compounds and may not be related to the local fire. In contrast, concentrations of HCB and PAHs were higher than those reported in previous studies. No PBDEs were found above the method detection limit. Organic contaminant concentrations in mosses decreased a few months after the fire, which is an important characteristic when considering the use of mosses for monitoring recent exposure.

Located on King George Island (South Shetland Archipelago) in Admiralty Bay (62°10′S; 58°24′W), the Brazilian Antarctic Station was established in 1984 as a research station and is occupied throughout the year by both scientific and military personnel. On February 25th, 2012, a large fire occurred at the station, destroying 70% of the facilities (Guerra et al., 2013), including the research laboratories, materials, equipment, personal belongings and the energy generators (four powered by Arctic diesel and one by ethanol).

The combustion process can send semi-volatile organic pollutants into the environment. Polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) are common contaminants produced by a wide variety of combustion sources, such as plastics, wood, fuel and other chemicals (Lohmann et al., 2000; Breivik et al., 2004; Barber et al., 2005). These pollutants are released into the atmosphere, dispersed and deposited in the environment (Meharg et al., 1998). Vegetation and soil are generally the first receptors of atmospheric pollutants (Simonich and Hites 1994, 1995).

Mosses constitute one of the principal components of terrestrial flora in the Antarctic ecosystem, whose nutrient supply depends largely on atmospheric deposition (Borghini et al., 2005). Since mosses have no root system or cuticle, they absorb/adsorb nutrients and contaminants directly from the environment; they are also relatively easy to collect (Harmens et al., 2011). Thus, mosses can play a very important role as biomonitors and long-term integrators of persistent contaminant depositions and have been used extensively in environmental pollution studies throughout the world (Yogui and Sericano, 2008; Cipro et al., 2011; Ciesielczuk et al., 2012).

PAHs, hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were analyzed in moss samples collected in the vicinities of Brazilian Antarctic Station before and after the incident to evaluate the impact in the surrounding area. The concentrations of other chlorinated compounds were also evaluated, such as DDT and HCHs, which, although not closely related with fire, are important pollutants in polar regions. The data were compared with findings described in previous contamination studies in the same region.

Moss samples were collected from areas adjacent to the Brazilian Antarctic Station (Fig. 1), in Admiralty Bay, on King George Island during the austral summer. Two sampling campaigns were performed: the first was in March 2012, less than one month after the fire, and the second was in December 2012, about eight months after the fire. In March 2012, seven samples of *Sanionia uncinata* were collected from six different sites (Sites 1–6) and one sample of *Warnstorfia sarmentosa* was collected from Site 1. In December

* Corresponding author.
E-mail address: ficolabuono@gmail.com (F.I. Colabuono).

http://dx.doi.org/10.1016/j.marpolbul.2015.01.018
0025-326X/

2012, two samples of *S. uncinata* were collected (Sites 3 and 7). Due to the removal of debris and modifications to the environment around the Brazilian Antarctic Station, sampling could not be performed at exactly the same sites during the second campaign. Samples of *Brachitecyum* sp. ($n = 1$), *Syntrichia princeps* ($n = 2$) and *S. uncinata* ($n = 7$) collected in December 2004/January 2005 (Sites 5, 7–9, 11–12) in a previous campaign were analyzed for the determination of the concentrations of organic contaminants prior to the fire. All vegetation was collected manually, stored in aluminum containers and kept frozen at −20 °C until analysis.

The analytical procedure followed that described by MacLeod et al. (1985) with minor modifications. Briefly, 3 g of dry sample was extracted in a Soxhlet apparatus for 8 h using 80 ml of n-hexane and methylene chloride (1:1, v/v). Before extraction, the surrogates d_8-naphthalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-chrysene and d_{12}-perylene (for PAHs), 2,2′,4,5′,6-pentachlorobiphenyl and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (for PCBs, OCPs and PBDEs) were added to all samples, blanks and reference material. The extracts were cleaned using column chromatography with 8 g of silica and 16 g of alumina (both 5% water deactivated) and eluted with 80 ml of n-hexane and methylene chloride (1:1, v/v). The internal standards 2,4,5,6-tetrachlorometaxylene (TCMX) and d_{10}-fluorene and d_{12}-benzo[b]fluoranthene were added before the gas chromatographic analysis. A procedural blank was included in each analytical batch.

Identification and quantification of organochlorine pesticides were performed with a gas chromatograph (6890 N Agilent Technologies) coupled to an electron capture detector (GC-ECD) using a 30 m × 0.25 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (film thickness: 0.5 μm). Automatic splitless injections of 2 μl were applied and the total purge rate was adjusted to 50 ml min^{-1}. Hydrogen was used as the carrier gas (constant pressure of 40 kPa at 100 °C), while nitrogen was the make up gas at a rate of 60 ml min^{-1}. Parental PAHs and their alkyl substituted compounds, PCBs and PBDEs were quantitatively analyzed using a gas chromatograph (5973 N Agilent Technologies) coupled to a mass spectrometer (GC/MS) in selected ion mode (SIM 70 eV), using the same column employed for GC-ECD. The volume injected was 1 μL in automatic splitless mode. Helium was used as the carrier gas (constant flow of 1.1 ml min^{-1}).

For quality assurance/quality control (QA/QC), the analytical method was validated using a standard reference (SRM 1945) purchased from the National Institute of Standards and Technology (NIST, USA). SRM 1945 was analyzed in duplicate and the average recovery of analytes was within the range accepted by the NS&T (Wade and Cantillo, 1994). The recovery of analytes in spiked blanks and matrices produced satisfactory results (67–115%). Analytes in laboratory blanks were subtracted from the samples. The quantification of analytes was performed using a nine-level analytical curve and followed the internal standard procedure. Method quantification limits (QL) ranged (in ng g^{-1} dry weight) from < 0.19 to 0.47 for OCPs, < 0.30 to 1.09 for PCBs, < 0.76 to 1.06 for PBDEs and < 1.14 to 10.3 for PAHs. When summing compound classes, concentrations below the QL were set to zero.

Table 1 shows the mean concentrations of organic pollutants from mosses sampled from areas surrounding the Brazilian Antarctic Station, in Admiralty Bay, and data from previous studies in the same region. Individual concentrations are presented as supplementary data.

PCBs are usually the dominant contaminant in moss samples from Antarctica (Bacci et al., 1986; Borghini et al., 2005; Cipro et al., 2011; Wu et al., 2014). Mosses sampled after the fire (March/2012) showed a different pattern: low concentrations of PCBs and a predominance of HCB (see discussion below). Tri-, tetra- and penta-CBs were prevalent in moss samples and hexa-CBs were also detected (supplementary data: Table S1).

HCB concentrations increased of one order of magnitude soon after the fire at the Brazilian Antarctic Station, but the levels were restored about eight months later and were similar to those reported by Cipro et al. (2011) from previous years (Table 1; supplementary data: Table S2). Studies from other locations in Antarctica also report that HCB concentrations are generally low in mosses. For example, Bacci et al. (1986) and Cabrerizo et al. (2012) found HCB concentrations of 0.49 ng g^{-1} (dw) and 0.02 to 0.12 ng g^{-1} (dw), respectively, in mosses from the Antarctic Peninsula, while Borghini et al. (2005) found HCB levels from 0.82 to 1.95 ng g^{-1} (dw) on Victoria Land in the Ross Sea. Although HCB

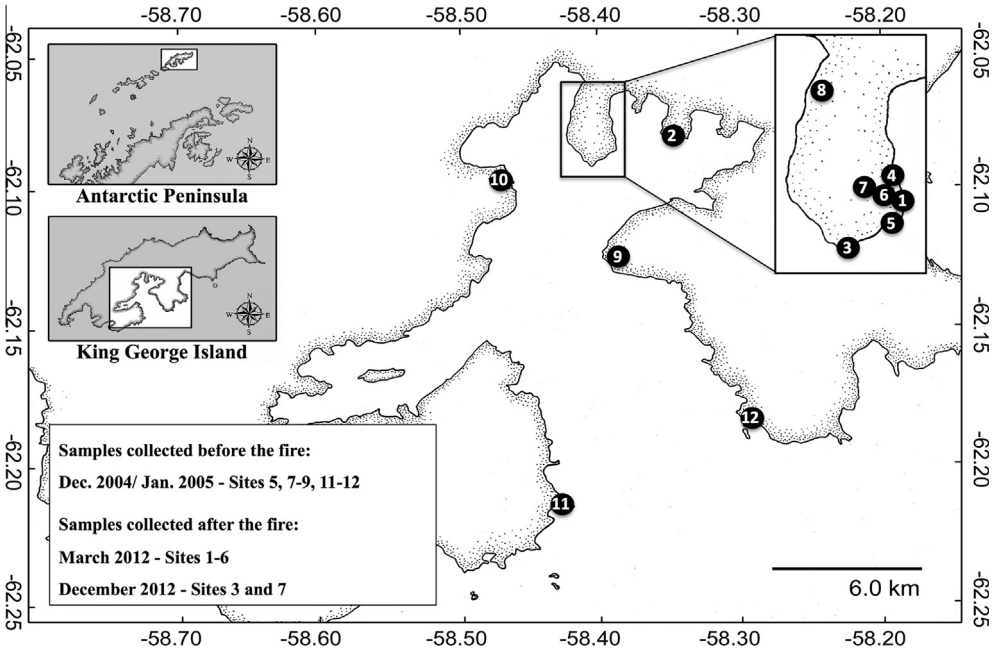

Fig. 1. Sampling site on King George Island in Admiralty Bay, Antarctica (Site 1: Brazilian Antarctic Station).