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Invited paper

Tracking human footprints in Antarctica through passive sampling of polycyclic aromatic hydrocarbons in inland lakes☆

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ABSTRACT

Freely dissolved polycyclic aromatic hydrocarbons (PAHs) were monitored in seven inland lakes of Antarctica by a polyethylene (PE)-based passive sampling technique, with the objective of tracking human footprints. The measured concentrations of PAHs were in the range of 14–360 ng L^{-1} with the highest values concentrated around the Russian Progress II Station, indicating the significance of human activities to the loading of PAHs in Antarctica. The concentrations of PAHs in the inland lakes were in the upper part of the PAHs levels in aquatic environments from remote and background regions across the globe. The composition profiles of PAHs indicated that PAHs in the inland lakes were derived mainly from local oil spills, which was corroborated by a large number of fuel spillage reports from ship and plane crash incidents in Antarctica during recent years. Clearly, local human activities, rather than long-range transport, are the dominant sources of PAH contamination to the inland lakes. Finally, the present study demonstrates the efficacy of PE-based passive samplers for investigating PAHs in the aquatic environment of Antarctica under complex field conditions.

1. Introduction

Antarctica is one of the most remote and pristine regions on Earth, and it is also a perfect place for exhilarating adventures. Besides scientific expeditions, the number of tourists visiting Antarctica, as registered by the International Association of Antarctica Tour Operators, rose from 16,000 in 2002 to 37,000 in 2014 (Gasparon et al., 2002; International Association of Antarctica Tour Operators, 2012). Increased human activities will inevitably introduce pollutants to this pristine environment, which was realized as early as in the 1960s (Murozumi et al., 1969). Although the Antarctic Treaty's Protocol on Environmental Protection enforced since 1998 prohibits the import of persistent organic pollutants (POPs) to Antarctica, a variety of POPs (such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs)) and POP-like compounds, e.g., polycyclic aromatic hydrocarbons (PAHs), have still been detected in snow (Fuoco et al., 2012), air (Dickhut et al., 2012; Ma et al., 2014), soil (Cabrerizo et al., 2013), vegetation types (Cabrerizo et al., 2012), seawater (Möeller et al., 2010), marine biota (Weber and Goerke, 2003), and sediment (Hale et al., 2008) in the polar region. In addition to local contamination from research stations, long-range transport (Cabrerizo et al., 2012; Dickhut et al., 2012; Rose et al., 2012), ocean currents (Cincinelli et al., 2005), and migratory biota (Roosens et al., 2007) are also considered as important input sources of POPs to Antarctica. Differentiating between local anthropogenic inputs and long-range transport of pollution is a key step for tracking human footprints in Antarctica, so that proper control measures can be implemented to minimize disturbances.

To date, elevated levels of contamination around scientific stations compared to those far away from them have been taken as clear evidence of the stations being local pollution sources (Martins

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et al., 2010). This is particularly relevant for PAHs and other chiefly particle-bound compounds, and the dominance of low molecular-mass POPs far away from the research stations was usually attributed to long-range atmospheric transport as the main contamination pathway (Cabrerizo et al., 2012). In addition, the presence of spheroidal carbonaceous particles, solely derived from incomplete combustion of fossil fuels at high temperatures (>1000 °C) (Swindles et al., 2015), in lake sediments in remote regions, provided a clear indication of long-range atmospheric transport of pollutants (such as PAHs) (Rose et al., 2003, 2012). Inland lakes, formed mostly by melting snow and ice during the retreat of the continental ice cap or deglaciation (Priscu and Foreman, 2009), are a large sink of contaminants associated with air deposition from both atmospheric transport and near-surface advection, and consequently provides an appropriate setting to evaluate anthropogenic impacts in Antarctica.

Because the concentration levels of POPs are expected to be low in inland lakes of Antarctica, the acquisition and analysis of the large water volumes needed for bulk water sampling make grab sampling protocols impractical. *In situ* passive sampling appears to be a viable alternative. Polyethylene (PE)-based passive sampler has been suggested as a preferred tool for monitoring POPs in aquatic environments at background and remote areas due to its low cost, large capacity, and high reproducibility (Lohmann and Muir, 2010).

The present study was conducted to map the occurrence of freely dissolved PAHs in selected inland lakes of Antarctica by employing the PE-based passive sampler. The objectives were (1) to validate the utility of PE-based passive sampler in the polar region and (2) to identify the potential sources of PAHs for evaluating the anthropogenic impacts in Antarctica. To maximize the utility of PE-based passive sampler, a calibration method using performance reference compounds (PRCs) (Huckins et al., 2002) was adopted. This approach shortens the sampling time, overcoming the time constraints for scientific expeditions to remote regions, but still maintains sufficient detection sensitivity.

2. Materials and methods

2.1. Site description

Larsemann Hills (69.30 ^{o}S, 76.3 ^{o}E) consisting of two major peninsulas (Stornes and Broknes) located in East Antarctica is often considered as an ice-free “oasis” area, because there are more than 150 freshwater lakes in the areas which are ice-free or partially ice-free in summer, i.e., from late December to early March (Pickard, 1986). In summer, strong easterly katabatic winds with an average velocity of 7 m s^{-1} blow almost every sunny day in early morning and late evening and allow the lakes to well mix (Ma et al., 2010). Five research stations, including the Romanian Law Base Station (1987), Russian Progress I (1988) and II (1989) Stations, Chinese Zhongshan Station (1989) on Mirror Peninsula, eastern Broknes (one of the two major peninsulas of Larsemann Hills), and Indian Bharati Station (2012) on an unnamed promontory between Stornes and Broknes, were built one after another, and currently three stations are operated all year around and one seasonally. The rapid infrastructure development and intensive scientific expeditions in this area may have substantially influenced the surrounding environment.

2.2. Passive sampler preparation

Low density polyethylene (LDPE) sheets of 25-μm thickness were purchased from TRM Manufacturing (Corona, CA). Strips of 25-μm LDPE (2.30 ± 0.01 g) were pre-cleaned by soaking twice in hexane for 24 h each. The pre-cleaned LDPE strips were kept in purified water for 24 h. To prepare preloaded LDPE sheets, seven cleaned LDPE strips for each passive sampler were placed in a mixed solution of methanol and water (50:50 in volume, 500 ml) containing six PRCs with anthracene-d_{10} at 34 μg L^{-1} and benzo[*a*]anthracene-d_{12}, PCB-29, PCB-61, *p*,*p*′-DDT-d_8, and *p*,*p*′-DDE-d_8 at 17 μg L^{-1} each for 30 d. All PRC-loaded strips were rinsed with purified water, wrapped in aluminum foil and stored at −20 °C until field deployment. Seven pre-loaded LDPE strips were processed to determine the initial concentrations of PRCs, and a field control prepared from the same batch of samplers was used to assess any possible external contamination during sampler preparation, transport, and retrieval. The passive sampler (Fig. S1 of the Supplementary data, “S” indicates tables and figures in the Supplementary data afterwards) consists of two copper end caps, a sandwich sieve plate (two 20-mesh stainless steel sieve plates and a piece of qualitative filter paper), two polyethylene seal rings, one copper bracket, and LDPE strips from outside to inside. The use of the sandwich sieve plate and copper box was designed to protect the LDPE from sunlight and coarse particles. Detailed procedures for preparing the passive sampler's components, such as copper box, end cop, stainless steel sieve plate and screen, and bracket, were described in the Supplementary data.

2.3. Sampler deployment

The samplers were deployed in seven inland lakes along a 2000-m Russia–China runway Road connecting a Russian airport with four research stations, i.e., the Chinese Zhongshan Station, the Russian Progress I and II Stations, and the Romanian Law Base Station on Mirror Peninsula, eastern Broknes along the southern shore of Prydz Bay in East Antarctica (Fig. 1). Snowmelt and rain from strong easterly katabatic winds converge into the seven inland lakes with water depths of 2–5 m. The salinity was below 1‰, the average pH value was 7 ± 1 and water temperature was 0–6 °C (Gasparon and Burgess, 2000; Gasparon et al., 2002). The surroundings of the lakes appeared similar, i.e., large numbers of rocks, soil and snow were around the lakes. The average air temperature and wind velocity were −3.7 °C (−10.9 to 1.8 °C) and 7.5 m s^{-1}, respectively, during the sampling period (calculated by daily data collected at 00:00, 06:00, 12:00, and 18:00 by an automatic weather recorder at the Zhongshan Station) (Polar Research Institue of China, 2013).

Three parallel passive samplers were deployed about 10 m away from each other in each inland lake, at a water depth of 1–2 m for 25 d from February 6 to March 4, 2013 (Table S1). Each sampler was attached to a rope and anchored to some rocks, and suspended in water with a buoy. Due to lake surface water freezing, only nine of the 21 deployed samplers were successfully recovered and the sampler surfaces were intact. Upon collection, LDPE strips were taken out of the passive samplers, wrapped in cleaned aluminum foil, and cooled during transport to the laboratory, where they were frozen at 0 °C with ice chests until extraction.

2.4. Extraction of polyethylene strips

The LDPE strips were rinsed with purified water and extracted twice by soaking in hexane (100 mL, 24 h). Recovery surrogate standards, i.e., naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, 2,4,5,6-tetrachloro-m-xylene, PCB-67, PCB-191, and PCB-209 were added to each sample before extraction. Two extracts were combined and concentrated to 10 mL with a Zymark Turbo Vap II at 30 °C. After dehydration with sodium sulfate, the extract was reduced to 0.5 mL in the Zymark Turbo Vap II and purified on a glass column (8 mm inner diameter) consisting of neutral alumina (0.8 g), neutral silica gel (0.8 g), and sodium sulfate