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Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base



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ABSTRACT

Pharmaceutical and personal care products (PPCPs) are a major source of micropollutants to the aquatic environment. Despite intense research on the fate and effects of PPCPs in temperate climates, there is a paucity of data on their presence in polar environments. This study reports the presence of selected PPCPs in sewage effluents from two Antarctic research stations, the adjacent coastal seawater, sea ice, and biota. Sewage effluents contained bisphenol-A, ethinylestradiol, estrone, methyl triclosan, octylphenol, triclosan, and three UV-filters. The maximum sewage effluent concentrations of 4-methyl-benzylidene camphor, benzophenone-1, estrone, ethinylestradiol, and octylphenol exceeded concentrations previously reported. Coastal seawaters contained bisphenol-A, octylphenol, triclosan, three paraben preservatives, and four UV-filters. The sea ice contained a similar range and concentration of PPCPs as the seawater. Benzophenone-3 (preferential accumulation in clams), estradiol, ethinylestradiol, methyl paraben (preferential accumulation in fish, with concentrations correlating negatively with fillet size), octylphenol, and propyl paraben were detected in biota samples. PPCPs were detected in seawater and biota at distances up to 25 km from the research stations WWTP discharges. Sewage effluent discharges and disposal of raw human waste through sea ice cracks have been identified as sources of PPCPs to Antarctic coastal environments.

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1. Introduction

Pharmaceuticals and personal care products including soaps, lotions, toothpastes, sunscreens, fragrances, and moisturizers can contain a range of active ingredients that are collectively referred to as PPCPs (Brausch and Rand, 2011). The main inputs of PPCPs into the environment are industrial and household sewage (Daughton and Ternes, 1999; Ternes et al., 2004). PPCPs are increasingly being recognised as ubiquitous contaminants in freshwater and marine ecosystems (Klosterhaus et al., 2013; Luo et al., 2014).

Antarctica is acknowledged as one of the few remaining places on earth relatively untouched by humans. The majority of scientific research stations on the Antarctic continent are located adjacent to the coast, where their industrial and domestic sewage is usually released directly into the coastal seawater (Bruni et al.,

1997; Edwards et al., 1998). Under Annex III of the Protocol on Environmental Protection to the Antarctic Treaty (Article 5), liquid sewage needs to only be macerated before discharge into the ocean. Currently, the wastewaters from 37% of permanent research stations and 69% of summer stations lack any kind of sewage treatment (Groendahl et al., 2008). Furthermore, those Antarctic research stations with wastewater treatment plants (WWTPs) are often unable to cope with the high influx of wastewater during the summer season (Groendahl et al., 2008). Operational problems and malfunctions can occur from fluctuating water inflows, frozen pipes, or reduced microbial activity within the plant due to low temperatures (Groendahl et al., 2008). In addition, research parties stationed for long periods along the coast or on the sea ice to conduct their field work are allowed to dispose of raw human waste directly into the ocean via tidal cracks in the sea ice (Newman, 2012), a practise referred to as 'tide-cracking'. Ships are also allowed to release food waste and sewage into the ocean, but at a distance of at least 12 nautical miles from the coast or ice shelf (Barnes and Conlan, 2007).

Concerns have already been raised in the Arctic regarding the environmental risks of releasing contaminants via sewage

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discharges. These concerns have arisen due to the low biodiversity, low ambient temperatures, and consequently the more vulnerable ecosystems (Gunnarsdottir et al., 2013). To date, the majority of studies of organic contaminant pollution in the Antarctic have focused on organochlorine compounds (Risebrough, 1976), PAHs (Desideri et al., 1998), polychlorinated biphenyls (PCBs) (Risebrough, 1976; Weber and Goerke, 2003), polybrominated diphenyl ethers (PBDEs) (Dickhut et al., 2012; Hale et al., 2008), and organophosphorus flame retardants (Moeller et al., 2012). Long range transport (Desideri et al., 1998; Dickhut et al., 2012) as well as the research stations themselves (Hale et al., 2008) have been identified as the sources of these pollutants. To the best of our knowledge PPCPs and hormones have not previously been investigated as environmental pollutants in the Antarctic.

PPCPs such as sunscreens and moisturizers are high use products in Antarctica due to the dry atmosphere and high UV light conditions that require frequent application of sunscreen by those working outdoors. In addition large amounts of soaps, shampoos, detergents, and disinfection products are used to maintain an adequate level of hygiene to minimise the risk of disease amongst close quartered base occupants. As PPCPs are primarily designed for external use on the human body they are subjected to few if any metabolic alterations (Ternes et al., 2004), and are washed directly off the skin in an unaltered form during showering or recreational activities (Giokas et al., 2004). Removal rates for PPCPs in wastewater treatment plants are highly variable and depend on the type of treatment and the physicochemical properties of the target compounds. Reported removal rates for PPCPs from wastewater range from 12.5% to 100% (Luo et al., 2014). As a consequence large quantities of a wide variety of PPCPs may be present in wastewater entering the WWTPs of Antarctic research stations and the treated effluents subsequently released into the Antarctic aquatic environment.

Once in the environment, many PPCPs degrade relatively quickly due to photo-degradation, hydrolysis, and microbial degradation processes (Caliman and Gavrilescu, 2009). However daily use combined with the wide range of consumer products in which they are present results in their continual release into the environment, which confers them a degree of pseudo-persistence (Daughton and Ternes, 1999; Munoz et al., 2008) and promotes them as chemicals of environmental concern. In addition the prevailing polar climatic conditions, in particular the cold temperatures, extended periods of darkness, and the presence of sea ice covering coastal sea waters for a large part of the year, may reduce the degradation and therefore extend the persistence of micropollutants including PPCPs in Antarctic coastal environments.

Two field studies were conducted to investigate the presence of PPCPs in Antarctica. A pilot study was conducted in October during the summer research season of 2009/2010 to determine if PPCPs were present in the sewage effluents of Scott Base (New Zealand) and McMurdo Station (USA) and the receiving coastal environment, and to collect marine biota for subsequent analysis. A larger study was conducted over November/December during the summer research season of 2012/2013 to investigate the distribution of PPCPs over a wider area of coastal water around the research stations.

The specific objectives of this study were to: identify and quantify PPCPs in the effluents from the WWTPs at Scott Base and McMurdo Station on Ross Island; determine the concentration and distribution of PPCPs in the seawaters of Erebus Bay which receive these WWTP discharges and to determine if PPCPs accumulate in aquatic biota living in Erebus Bay. A preliminary assessment of the potential risk detected PPCPs may pose to Antarctica's unique marine ecosystem was carried out.

2. Materials and methods

2.1. Study area

Ross Island is a volcanic island situated in the McMurdo Sound region of the Ross Sea. To the south the island is bordered by permanent ice from the Ross Ice Shelf (Fig. S1, Supporting Information). The remainder of the island is surrounded by annual sea ice which begins to break up and disperse between December and February (Falconer and Pyne, 2004). The two research stations Scott Base (New Zealand) and McMurdo Station (USA) are located on Hut Point Peninsula in the southwest of Ross Island along Erebus Bay (Fig. S1, Supporting Information). Scott Base and McMurdo Station can house up to 86 and 1200 personnel respectively over summer, with a reduced population over winter (Hale et al., 2008). The sewage treatment plants of Scott Base (aerated fixed thin-film beds) and McMurdo (extended aeration system using aerobic digestion) produce approximately 17,000 L and 416,000 L of effluent per day respectively over the summer season (October–February) (ANZ, 2011; Law et al., 2006). Scott Base began to use ozone disinfection during the 09/10 season. Further details of the sewage treatment systems, the outflow volume and temperature over one research season, the population changes of Scott Base, and the regions' prevailing ocean currents are provided in the SI.

2.2. Sample collection

Detailed sample collection protocols for each season are provided in the Supporting Information (SI).

A number of precautionary measures were taken to avoid contamination of samples while working under challenging environmental field conditions. All equipment and sampling bottles were wiped with methanol before sampling to remove any contaminants from the surface. The internal surfaces of sample bottles were thoroughly rinsed with methanol and ACN. A zinc-based sunscreen was required to be worn by all field personal for protection against UV light during sampling activities. Therefore during field sampling activities all equipment was handled only while wearing disposable nitrile gloves.

Samples of WWTP effluent were collected into pre-cleaned amber glass bottles, capped firmly, and transported to the laboratory at Scott Base, where they were immediately acidified to pH 2 using sulphuric acid. Seawater grab samples were collected into pre-cleaned amber 4 L Winchester bottles via bore holes in the sea ice drilled using either a Kovac or Jiffy drill. A 4 L field blank sample (Milli-Q) was included within each individual sampling trip to account for any cross-contamination of samples during their collection and subsequent handling. The bottles were stored in polystyrene padded boxes during transport back to Scott Base, where they were immediately acidified to pH 2 using sulphuric acid.

2.2.1. 2009/2010 research season

Sewage effluent samples were obtained from McMurdo and Scott Base at the beginning of the summer research season, between the 23rd and 31st of October 2009. Seawater grab samples were obtained from four locations; the coast off Scott Base, Winter Quarters Bay, Cape Armitage located in between the two research stations, and a reference site at Cape Evans (Fig. S1).

Clams (*Laternula elliptica*) were collected from Winter Quarters Bay by the McMurdo SCUBA team. Sea urchins (*Sterichinus neumayeri*) were collected from Cape Armitage using a remote controlled mini-submarine. Fish (*Trematomus bernachii*) were collected from Cape Evans by ice fishing.

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