Environmental Pollution 229 (2017) 241–254

Contents lists available at ScienceDirect

Environmental Pollution

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

Occurrence of pharmaceutical, recreational and psychotropic drug residues in surface water on the northern Antarctic Peninsula region☆

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ARTICLE INFO

Article history:
Received 16 January 2017
Received in revised form
15 May 2017
Accepted 22 May 2017
Available online 7 June 2017

Keywords:
Antarctica
Pharmaceuticals
Recreational drugs
Caffeine
Risk assessment

ABSTRACT

Human presence in the Antarctic is increasing due to research activities and the rise in tourism. These activities contribute a number of potentially hazardous substances. The aim of this study is to conduct the first characterisation of the pharmaceuticals and recreational drugs present in the northern Antarctic Peninsula region, and to assess the potential environmental risk they pose to the environment. The study consisted of a single sampling of ten water samples from different sources, including streams, ponds, glacier drains, and a wastewater discharge into the sea. Twenty-five selected pharmaceuticals and 21 recreational drugs were analysed. The highest concentrations were found for the analgesics acetaminophen (48.74 μg L^{-1}), diclofenac (15.09 μg L^{-1}) and ibuprofen (10.05 μg L^{-1}), and for the stimulant caffeine (71.33 μg L^{-1}). All these substances were detected in waters that were discharged directly into the ocean without any prior purification processes. The hazard quotient (HQ) values for ibuprofen, diclofenac and acetaminophen were far in excess of 10 at several sampling points. The concentrations of each substance measured and used as measured environmental concentration values for the HQ calculations are based on a one-time sampling. The Toxic Unit values indicate that analgesics and anti-inflammatories are the therapeutic group responsible for the highest toxic burden.

This study is the first to analyse a wide range of substances and to determine the presence of pharmaceuticals and psychotropic drugs in the Antarctic Peninsula region. We believe it can serve as a starting point to focus attention on the need for continued environmental monitoring of these substances in the water cycle, especially in protected regions such as the Antarctic. This will determine whether pharmaceuticals and recreational drugs are hazardous to the environment and, if so, can be used as the basis for risk-assessment studies to prioritise the exposure to risk.

☆ This paper has been recommended for acceptance by Klaus Kummerer.

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http://dx.doi.org/10.1016/j.envpol.2017.05.060
0269-7491/

1. Introduction

Antarctica is generally perceived as a distant territory isolated from human influence. Due to its remoteness and its extremely cold climate, it is the only continent with no permanent human population.

The Antarctic has been at least partially covered by ice for approximately 34 million years, when South America and Australia separated and the Antarctic Circumpolar Current became established, and the cooling and isolation of the Antarctic continent began (e.g. Barker, 2001). Clear symptoms of a range of anthropogenic impacts have been observed for several decades, including changes in the surface (e.g. O'Neill et al., 2012), direct pollution from hydrocarbons (Aislabie et al., 2004) and urban effluent (Connor, 2008), among others; and indirect pollution carried through the atmosphere from remote areas (e.g.Vinit et al., 2004). In our opinion, the form of anthropogenic pollution with the greatest impact on the Antarctic continent is global warming, a type of thermal contamination that affects both the biota and inorganic equilibria.

The northern Antarctic Peninsula region is an ideal zone to study environmental changes, particularly those related to global warming (Vaughan et al., 2003) and the introduction of synthetic chemical products, as the climate conditions allow snow and ice to melt in the summer and conform a particular water cycle (Moreno et al., 2012). The waters of the Antarctic Peninsula region are located far from inhabited or industrial areas and are therefore generally assumed to be in pristine condition and suitable for use as a baseline for a natural composition with no human influence (Bargagli, 2008).

The Antarctic Treaty (AT) of 1959 and the Protocol on Environmental Protection to the AT (Madrid Protocol) signed in 1991 aim to prevent environmental deterioration. There are currently 53 signatory countries to the Treaty and 38 to the Protocol. The AT established the Antarctic as a place for peace and science, and specified a series of limitations to the activities permitted within its territory. However, these constraints have not prevented the measurable influence of humans. Human presence in the Antarctic derives primarily from two types of activities, namely research and tourism, both of which have a similar type of impact and generate residues of an industrial and urban nature, particularly organic matter and nutrients.

It is estimated that the total number of researchers and logistic personnel present at any time on the Antarctic continent ranges between 1000 and 4500 people (Vöneky and Addison-Agyei, 2011). This population is mainly centred on the coastal areas and in regions with no ice cover, particularly on the Antarctic Peninsula region. Tourist visits show a greater variability and are on the rise. In 2010 there were over 30,000 visitors (Hall, 2010), and during the 2013–2014 season this figure rose to 37,405 (Vila et al., 2016). The tourist season is highly variable, and ranges from 107 days in 1995/96 to 175 days in 2008/09 (Bender et al., 2016), coinciding with summer in the southern hemisphere. This is the most sensitive period for terrestrial biota (Gröndahl et al., 2009), when biological activity and the thaw activate the hydrological processes and the drainage of continental waters towards the sea, particularly in some areas of the northern Antarctic Peninsula region.

Although it was previously assumed that the main impact of tourism was on the sea, this view is now changing. A drastic increase has been observed in the overall number of passengers disembarking since the 1989-90 season, with sites such as Neko Harbour and Goudier Island receiving as many as 16,000 visitors in the 2012–2013 season (Bender et al., 2016). Both tourists and scientists are sources of pollution through their excreta (faeces, urine, sweat, skin peeling), not only of the organic matter typical of natural biological activity, but also of microorganisms alien to the Antarctic environment, and particularly synthetic chemical products (pharmaceuticals, recreational drugs, personal care products, equipment such as tents, clothing and others) and their metabolites, which are generally eliminated through the urine.

Numerous studies have described the presence of these synthetic substances throughout the world. Pharmaceuticals, recreational and stimulant drugs, personal care products, plastics and flame retardants, among others, are the main chemicals studied. However, the presence of these substances in the Antarctic area has been very scarcely documented. This study is part of a broader research into synthetic substances in the Antarctic. The article by Esteban et al. (2016) warned of the presence in freshwater of substances that were considered endocrine disrupters. High concentrations were found of the organophosphate flame retardant and alkylphenol group, and significant concentrations of the metal aluminium, a possible hormonal modifier.

There is no record of the type of pharmaceuticals consumed on the research stations, nor of the entry of these substances through tourists. Studies on the presence of these synthetic products on the Antarctic continent therefore contribute new information on their distribution in an area with minimum anthropogenic influence, and on the possible risks at the ecosystem level.

Annex III to the Madrid Protocol (Article 1.2) requires the application of responsible waste management principles and the development of waste management plans. It offers recommendations for minimizing the impact of scientific research on the Antarctic environment and interference with natural resources. However, some authors (Emnet et al., 2015) have called attention to the numerous direct effluents into the sea from Antarctic scientific stations. In 2008 (Gröndahl et al., 2009) warned: *Stations with existing treatment systems have reported operational problems and malfunctions*. This work concludes that 37% of the permanent bases (28 nations with 71 stations in Antarctica) and 69% of the summer bases discharge directly with no purification, and in an unspecified number the purification process is inefficient: *Many stations are not efficient enough to reduce the release of microorganisms*. The studies have focused predominantly on microbiological contamination rather than on emerging contaminants, which are always associated with urban effluents. However, it can be assumed that these types of substances are not eliminated either.

The presence of emerging contaminants in the environment is expected to rise due to the increase in visitors to the Antarctic continent. Numerous studies (Gómez-Oliván et al., 2014; Cleuvers, 2003; Parolini et al., 2015; Fatta-Kassinos et al., 2011; Atkinson et al., 2009) highlight the ecotoxicological effects of pharmaceuticals and recreational substances on aquatic and terrestrial organisms and wildlife. These substances are designed to cause specific effects even at low concentrations. Aquatic organisms are particularly vulnerable (Kostich and Lazorchak, 2008), as they are exposed via wastewater residues throughout their whole life cycle. Substances such as diclofenac have been added to the Watch List (Commission Implementing Decision (EU) 2015/495) for possible future inclusion as priority substances (Directive 2013/39/EU), as the available information indicates they may pose a significant risk to or through the aquatic environment. Other substances such as acetaminophen, ibuprofen and antibiotics have also been reported to have toxic effects on the environment (Santos et al., 2010).

Acute ecotoxicity values have been reported for a number of pharmaceutical products, although these data alone are not sufficient to specifically address the issue of environmental effects or risk assessment (Fent, 2003). The same author warned that long-term exposure to low doses of these chemicals can cause adverse effects in environmental ecosystems, and also highlighted gaps in current knowledge and future research (Fent et al., 2006). Further