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Chemosphere 61 (2005) 827–833

CHEMOSPHERE

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Steroid estrogens in ocean sediments

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Received 24 January 2005; received in revised form 24 March 2005; accepted 7 April 2005
Available online 20 June 2005

Abstract

This paper gives results from a study measuring the abundance of steroid hormones in ocean sediments in the proximity of a deep ocean sewage outfall. The outfall is discharge point for an enhanced primary sewage treatment plant and sediment samples were taken adjacent and 7 km from the outfall. All samples contained steroid estrogens at nanogram per gram levels with higher concentrations at the 7 km sampling site. The concentration of estrone ranged from (0.16–1.17 ng/g), 17β-estradiol (0.22–2.48 ng/g) and the synthetic 17α-ethinylestradiol (<0.05–0.5 ng/g). The values detected correspond with estimates based on the proportion of estrogens sorbed to particles in the effluent and the expected proportion of particles originating from sewage in the ocean sediments. The results suggest that estrogens associated with the particulate fraction aggregate on contact with high ionic strength seawater and settle to the seafloor after discharge through deep ocean outfalls.

Keywords: Estrone; Estradiol; Ethinylestradiol; Outfall; Wastewater; Sewage

1. Introduction

Understanding the fate of estrogens in the environment is key to understanding the potential for human released estrogens to induce abnormal reproduction in aquatic environments (Purdom et al., 1994; Desbrow et al., 1998; Routledge et al., 1998). Estrogens have been detected in rivers (Alder et al., 2001; Kuch and Ballschmitter, 2001; Snyder et al., 2001), lakes (Matsui et al., 2000; Shen et al., 2001; Snyder et al., 2004) and marine samples (Atkinson et al., 2003; Tashiro et al., 2003). The primary sources are considered to be from sewage treatment plants and agricultural runoff or discharge (Tashiro et al., 2003; Kolodziej et al., 2004). There is now increasing evidence that estrogens such as estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) are sorbing to riverbed (de Alda et al., 2002; Holthaus et al., 2002; Williams et al., 2003; Peck et al., 2004), lake (Mibu et al., 2004) and estuarine (Thomas et al., 2001, 2004) sediments where degradation, especially for EE2 under anaerobic conditions, is slow (Jürgens et al., 2002; Ying and Kookana, 2003; Ying et al., 2003). The release and fate of estrogens into the marine environment is little studied but of considerable interest, as estrogens appear to be relatively stable and show limited degradation even under aerobic conditions (Ying et al., 2003). Their effect on sensitive environments such as

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0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.04.053

coral reefs is of particular concern (Atkinson et al., 2003). When estrone concentrations are greater than 300 pg/l, there is the potential of net uptake and potential accumulation in the reef benthos (Atkinson et al., 2003). Estrogens in the coastal marine environment may affect reproductive biology through embryonic development (Hathaway and Black, 1969), altered enzymatic activities (Ghosh and Ray, 1993a,b) or cellular damage or apoptosis (Wiens et al., 1999; Viarengo et al., 2000). Much more information is required to characterise the presence of human-derived estrogens in marine environments and to determine their potential effects on the marine ecosystem. This paper reports on preliminary measurements of estrogens in ocean sediments.

2. Materials and methods

2.1. Ocean sediment sampling

Ocean sediment samples were collected near the discharge point from a large coastal enhanced primary sewage treatment plant (STP) at Malabar, Sydney. The STP is located in eastern Sydney and services domestic sewage (75%) and industrial wastewater (25%). It provides enhanced primary treatment (i.e. with $FeCl_3$ addition) for an average flow of 480 Ml/day with ultimate disposal by deep ocean discharge (3.6 km offshore, average 80 m deep). A motor vessel (MV) oceanographer was used as a stable platform, from which a "Smith McIntyre" grab (capacity approximately 5 l) was deployed to collect sediment samples. Samples were collected from 2 locations (2 samples per location), adjacent to the Malabar deep ocean outfall and approximately 7 km south of the outfall (Fig. 1). The vessel was manoeuvred to hold its position until the grab had reached the seafloor and a sediment sample was taken. In order to ensure samples are as representative as possible, the angle and speed at which the grab was lowered to the seafloor, was controlled and maintained for all the subsites. The grab was lowered to approximately 3 m above the seafloor and then released to collect the sample. In setting the angle and speed at which the grab is lowered, consideration was given to two things: maximising the volume of the sediment sample retrieved; and minimising the bow wave generated from the grab moving through the water column. This method of controlling the grab fall rate has been shown elsewhere to reduce the loss of the fine surface material (Blomquist, 1992). The samples were transferred to 0.5 l glass bottles and stored at −20 °C prior to analysis.

2.2. Standard preparation

Estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2), and deuterated E1-2,4,16,16-*d*4 (d4-E1) were obtained from Sigma Aldrich (Sydney, Australia). The d4-E1 was used as internal standard. Stock solutions of individual non-deuterated standards and deuterated internal standard were prepared by dissolving known amounts of in methanol to obtain concentration of 0.10 mg/ml. Working standard solutions were obtained by further diluting stock solutions with water to obtain final concentrations of 0.5 pg/μl to 500 pg/μl. The stock solution of internal standard was further diluted with water to obtain a final concentration of 100 pg/μl. Methanol and acetonitrile HPLC grade were obtained from Ajax Finechem (Sydney, Australia). Other solvents were of analytical grade, and they were used as supplied Ajax

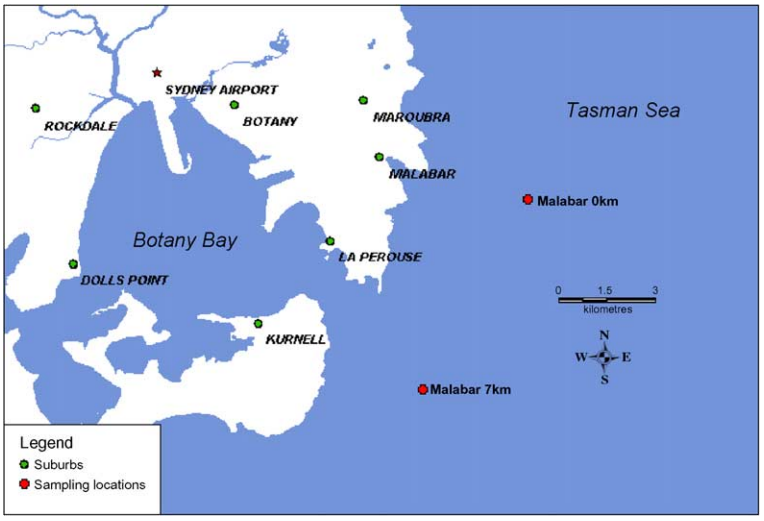

Fig. 1. Sediment sample collection locations.