

Occurrence of volatile organic compounds (VOCs) in Liverpool Bay, Irish Sea

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Abstract

Surface seawater samples were collected in the Irish Sea and Liverpool Bay area from the R.V. Prince Madog during the period of 25–31 of March 2006. VOCs were purged with nitrogen, pre-concentrated on a SPME fibre and analysed immediately on a GC–MS. Target compounds quantified were halogenated (0.2–1400 ng L⁻¹), BTEXs and mono-aromatics (1.5–2900 ng L⁻¹), aliphatic hydrocarbons and others (0.6–15,800 ng L⁻¹). Day and night sampling was performed at a single station and suggested that factors such as sunlight and tide affect the presence of many of these compounds. Sample variability was high due to the variable weather conditions at the station. Poor correlations were found between marine phytopigments and selected VOCs. Principal component analysis (PCA) analysis showed that chlorinated compounds such as 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride, predominantly from anthropogenic sources, originated from the River Mersey. Other brominated and iodinated compounds quantified were more likely to be from biogenic sources including novel marine compounds such as 2-chloropropane, 1-bromoethane and 1-chlorobutane.

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1. Introduction

Halogen-containing VOCs are potential greenhouse gases and ozone depletors and since their use and production has been regulated by the Montreal and Kyoto Protocol (Buchmann et al., 2003), their natural production has received more attention. Together, this group of small molecular weight compounds may have dramatic effects on the future global climate. Anthropogenic sources for many of these compounds have been identified and effort is being directed towards reducing their release to the environment. Anthropogenic sources of these compounds are well known and they can arise from several industrial processes and human activities (McCulloch et al., 1999). However, natural marine sources may be important too: oceans

may act as a sink or reservoir of these compounds (Chester, 1990) and the marine boundary layer is one of the most important places for gas exchange between water/atmosphere (Jones, 1980). Little is known about the mechanisms inducing the production of these compounds by macro and microalgae. There are many hypotheses regarding their production such as for removal of metabolic wastes (Gagosian and Lee, 1981), as chemical communicants (Gagosian and Lee, 1981), for chemical protection (Laternus, 1996), to rid the cell of harmful oxidants such as hydrogen peroxide (Manley, 2002), maybe as a form of oxidative stress relief (Mtolera et al., 1996), for anti-herbivore activity (Wolfe et al., 1997), anti-microbial properties (Fenical, 1981; Fenical, 1982; Neidleman and Geigert, 1987), to facilitate food gathering or as hormones (Gribble, 2000) and other reasons not yet clearly understood. It is proposed that the mechanisms of production are mediated by enzymes called haloperoxidases (van Pee and Unversucht, 2003). Biogenic halocarbons are broadly

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produced in the marine environment by macro and micro-algae, making the ocean a significant natural source of halocarbons and other VOCs (Chuck et al., 2005).

The incidence and distribution of halocarbons and other VOCs in marine water have been widely studied e.g. in South Asian and Western Pacific Oceans (Yokouchi et al., 1997), the Atlantic Ocean (Baker et al., 2000), the Northwest Atlantic and Pacific Oceans (Tokarczyk and Saltzman, 2001), the Arctic Ocean (Krysell, 1991), the North Sea (Huybrechts et al., 2005), estuaries (Christof et al., 2002), bays (Yamamoto et al., 2001) and different marine environments (Dewulf and VanLangenhove, 1997). The distribution and concentration of VOCs depended greatly on the location and, for biogenic sources, whether or not an algal bloom was present in ocean system or macroalgae in coastal zones. In relation to anthropogenic inputs, concentrations are dependent on the proximity of production to the sampling site.

VOCs are of special interest as they may photo-dissociate producing radicals that can participate in atmospheric reactions and able to deplete tropospheric and stratospheric ozone (Barrie et al., 1988). They also may participate in cloud condensation nuclei formation and reduce the oxidation capacity of the atmosphere (Liss et al., 1997). However, no studies of the incidence and distribution of these compounds in seawater have been reported

in the area of Liverpool Bay or Irish Sea. Liverpool Bay and especially the Mersey River are areas of intense human activity (Fox et al., 2001): the port and rivers have played a major role in the city development and many industries are next to the river and gas extraction activities occur offshore. This bay is influenced by several rivers including the Conwy, Dee, Ribble and Mersey. Tide plays an important role in water masses in this area with ranges up to 10 m. The aim of this research was to quantify the distribution of halocarbons and other selected volatile organic compounds which may have both natural and anthropogenic sources in the area of Liverpool Bay and Irish Sea.

2. Materials and methods

2.1. Seawater sampling and extraction procedure

Surface seawater samples were collected across Liverpool Bay and River Mersey between 25 and 31 March 2006 at eighteen stations (Fig. 1). Water samples were collected from the RV Prince Madog using a polished stainless steel container and transferred very slowly to avoid sample disturbance to a 4.85 L amber glass bottle; 4.5 L of water were added leaving a head-space of approximately 350 mL. The seawater was purged with extra pure nitrogen ($\sim 150 \text{ mL min}^{-1}$) for 1 h at ambient temperature with

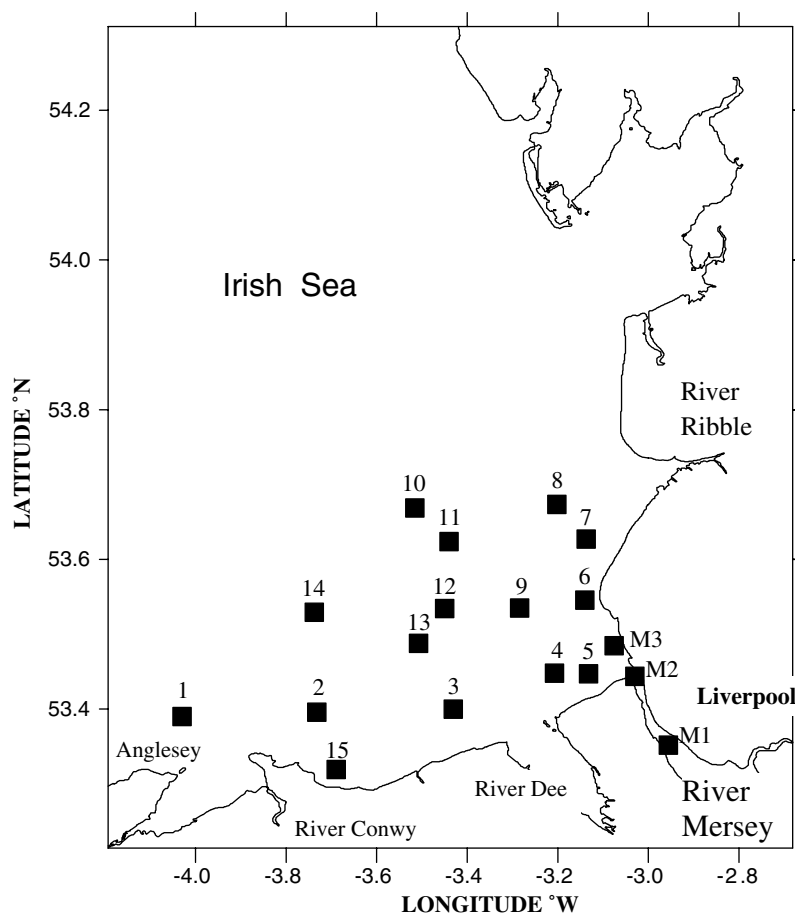


Fig. 1. Map of the sampling locations.

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