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Chlorination by-product concentration levels in seawater and fish of an industrialised bay (Gulf of Fos, France) exposed to multiple chlorinated effluents

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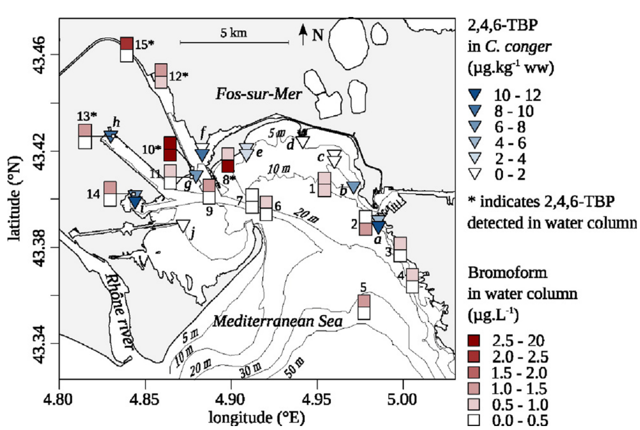
HIGHLIGHTS

- CTD profiles are a prerequisite to CBP analysis to avoid misleading interpretations.
- Different industrial activities lead to different discharge CBP patterns.
- Seasonal effect suggested an impact of temperature and other seawater parameters.
- A widespread contamination is observed, associated to an assessed environmental risk.
- Bioaccumulation levels of 2,4,6-TBP with a bioconcentration factor of 25 in conger eel.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorination is one of the most widely used techniques for biofouling control in large industrial units, leading to the formation of halogenated chlorination by-products (CBPs). This study was carried out to evaluate the distribution and the dispersion of these compounds within an industrialised bay hosting multiple chlorination discharges issued from various industrial processes. The water column was sampled at the surface and at 7 m depth (or bottom) in 24 stations for the analysis of CBPs, and muscle samples from 15 conger eel (*Conger conger*) were also investigated. Temperature and salinity profiles supported the identification of the chlorination releases, with potentially complex patterns. Chemical analyses showed that bromoform was the most abundant CBP, ranging from 0.5 to 2.2 μg L^{-1} away from outlets (up to 10 km distance), and up to 18.6 μg L^{-1} in a liquefied natural gas (LNG) regasification plume. However, CBP distributions were not homogeneous, halophenols being prominent in a power station outlet and dibromoacetonitrile in more remote stations. A seasonal effect was identified as fewer stations revealed CBPs in summer, probably due to the air and water temperatures increases favouring volatilisation and reactivity. A simple risk assessment of the 11 identified CBPs showed that 7 compounds concentrations were above the potential risk levels to the local marine environment. Finally, conger eel muscles

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presented relatively high levels of 2,4,6-tribromophenol, traducing a generalised impregnation of the Gulf of Fos to CBPs and a global bioconcentration factor of 25 was determined for this compound.

1. Introduction

Biofouling control is essential to industrial installations where large water volumes are used for cooling or heating purposes, and chlorination techniques are widely employed in order to maintain optimal operating conditions.

Chlorine is introduced either through the dissolution of chlorine gas or addition of a sodium hypochlorite solution, typically applying doses of 0.5–1.5 mg L^{-1} (expressed as Cl_2) (Allonier et al., 1999a, 1999b; Ma et al., 2011; Khalanski and Jenner, 2012). Bromine may also be directly produced by seawater electrolysis and in both cases form hypochlorous and hypobromous acid (HOCl and HOBr, respectively) species (Jenner et al., 1997; Taylor, 2006; Khalanski and Jenner, 2012). Once released in seawater, the products of this very quick reaction lead then to haloamines and various CBPs in presence of ammonia and organic matter (natural and anthropogenic). The nature and relative amounts of the CBPs in seawater may vary with the initial chlorine dose, pH, temperature, concentrations and composition of organic matter or inorganic species (Allonier et al., 1999a). The discharge of the chlorinated effluents is of main environmental concern, even if concentrations remain low, as the volumes released are generally very important. Along with residual free chlorine or bromine, the CBPs can constitute a threat to marine ecosystems (Taylor, 2006; Deng et al., 2010; Pignata et al., 2012; Khalanski and Jenner, 2012) and possibly to human health through atmospheric volatilisation and subsequent photolysis of brominated compounds into reactive oxidants (Quack and Wallace, 2003; Deng et al., 2010; Parinet et al., 2012).

In marine environments, much of the research on CBPs has focused on water desalination installations and thermal or nuclear power plants (Taylor, 2006; Agus and Sedlak, 2010; Khalanski and Jenner, 2012). These studies were concerned by cooling water releases, often sought for a limited number of compounds and more importantly by a single discharge point in open coast. Reactivity data of certain CBP classes, such as bromophenols (Sim et al., 2009), are particularly scarce, and rarely cover all the potential marine conditions of salinity, composition or temperature. In the same way, field impregnation data to CBPs are limited to a low number of compounds and species, and toxicological values based on few studies (Taylor, 2006; Khalanski and Jenner, 2012).

Industrialised embayments are found worldwide and the adjacent coasts and bays generally suffer from numerous aqueous discharges in a narrow area, inducing a particular stress on the local marine ecosystems and possibly more distant ones. The Gulf of Fos represents a semi-enclosed bay favouring water confinement in some of its more restricted inlets and docks and receives the plume of the second greatest Mediterranean river among other freshwater inputs, namely Rhône river (Ulses et al., 2005). It hosts the largest port of trade in France and in the Mediterranean Sea along with a major industrial zone mainly centred on steel and petrochemical industries but also waste incineration, cement works and other. Many of them use chlorination for biofouling control, principally for water cooling and LNG regasification purposes. The large volumes of chlorinated waters discharged in this coastal semi-enclosed system (several millions m^3 day^{-1}) can lead to a chronic exposure of the environment to CBPs, as well as a possibly significant atmospheric emission by the volatilisation of the semi-volatile CBPs from the seawater surface.

A better knowledge of the behaviour of CBPs in industrialised embayments is a prerequisite to evaluate their potential impact on the marine ecosystems and their transfer to the atmosphere. It is also essential for modelling and considering solutions with the industrial and local stakeholders. The present study aims to determine CBPs in the Gulf of Fos, taken as a whole with its multiple industrial releases, at a geographical scale which has not been documented in the literature. The measurements include outlet characterisation and distant seawater stations as well as fish bioconcentration. Water sampling was coupled to CTD measurements to identify the outflows and realised in winter and summer seasons to evaluate the influence of these parameters on CBP concentrations, while fish samples were conger eel muscles reflecting several months exposure.

2. Materials and methods

2.1. Study area

The Gulf of Fos is located in the North of the Gulf of Lion (Western Mediterranean), approximately 50 km west from Marseilles. It's flanked by the Berre lagoon to its east and the Rhône river delta to the west (Fig. 1).

The gulf has an average depth of about 20 m. It is characterised by several fresh-water inputs, the largest being the Rhône river (500 to 3500 $m^3 \cdot s^{-1}$) and a smaller being via the Berre lagoon brackish waters (100 to 200 $m^3 \cdot s^{-1}$). Additional fresh-water inputs from irrigation or navigation canals can also have some local incidence, mainly in the Dock 1 and the South Dock (estimated between 10 to 100 $m^3 \cdot s^{-1}$). Several sampling stations have been placed in these fresh water inputs (Fig. 1) to control potential CBP transport from non-local sources to the Gulf of Fos, even though THM were never detected for years in the last station before the Rhône river mouth (Arles, France), neither dissolved, associated to particulate or sediment materials (Eaufrance database, 2015). Tides are very limited in this part of the Mediterranean. The average tidal range is approximately 0.4 m, but it may still rule important water transports such as the exchanges between the Berre lagoon and the Gulf of Fos. Meteorological conditions are dominated by frequent and relatively strong north winds (around 40% per year) that can induce local upwelling phenomena within the gulf and, south-east winds (10 to 20% per year).

The Gulf of Fos undergoes a great anthropic pressure related to the major industrial activities in the area and to a lesser extent to agriculture and urbanisation. The industrial zone of Fos is the largest in Southern Europe. It includes two large liquefied natural gas (LNG) terminals (Fos-Cavaou by sampling station 8 and Fos-Tonkin by station 12) with maximum hourly regasification seawater flows of 30,000 $m^3 \cdot h^{-1}$ (electrochlorination) and 15,000 $m^3 \cdot h^{-1}$ (hypochlorite dosing), respectively. There is also four power plants with very irregular operating levels according to seasonal and economical fluctuations with maximum cooling water flows up to 45,000 $m^3 \cdot h^{-1}$, which is more than the estimated flow of the canal leading from Rhône river to Dock 1 in its northern end (Ulses et al., 2005). They are located by stations 4, 17, 10 and 100 m off station 21. The plant by station 4 does not use chlorination, but the plants by stations 10 and 21 which outlets are directed in Dock 1 employ electrochlorination. In addition, steel industry (main outlet by station 21) and oil refineries (outlets by station 17 and within South Dock) may also chlorinate sea water in volumes exceeding 10 000 $m^3 \cdot h^{-1}$ (Fig. 1).

2.2. Water sampling

Two sampling campaigns were realised, during winter (17 and 18 February 2014, 15 stations) and summer (23 and 24 June 2014, 21 stations). The sampling stations were located within the whole Gulf of Fos and by the major industrial outlets (Fig. 1), in order to evaluate sources