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Does the presence of caffeine in the marine environment represent an environmental risk? A regional and global study

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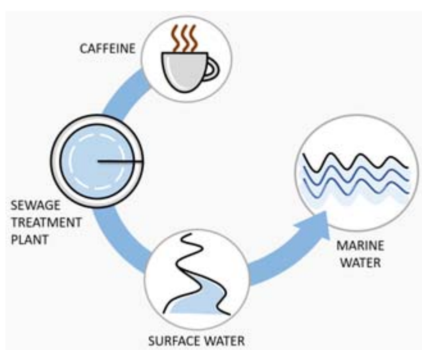
HIGHLIGHTS

- Caffeine was present, in 15 of the 23 samples analysed.
- The highest marine concentration of caffeine in Spain, and one of the highest in Europe, was detected in this study (857 ng L^{-1}).
- Six out of 22 seawater samples resulted in a Hazard Quotient (HQ) from chronic exposure higher than 1.
- Twenty-eight percent of all seawater and 69% of all estuary water samples where caffeine has ever been measured (Globally) exceeded an HQ of 1.

GRAPHICAL ABSTRACT



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ABSTRACT

Caffeine is an emerging contaminant considered to be an indicator of human contamination that has been widely detected in various aquatic systems, especially in continental waters. Nevertheless, the extent of its possible environmental impact is yet to be determined. This study determined the presence of caffeine, and evaluated the environmental hazard posed by this substance, in the "Rías Gallegas", a series of costal inlets in north-west Spain which are of great ecological value and in which fishing and bivalve farming, are a significant source of income. Caffeine was found to be present at concentrations higher than the limit of quantification (LOQ = 3.07 ng L^{-1}) in 15 of the 23 samples analysed, with the highest seawater concentration being 857 ng L^{-1} (the highest measured in seawater in Spain). Six out of 22 seawater samples resulted in a hazard quotient (HQ) from chronic exposure higher than 1 with the highest being 17.14, indicating a high probability of adverse effects in the aquatic environment. Environmental Exposure Distributions (EEDs) generated from a literature review of

Abbreviations: NW, North-west; LOQ, limit of quantification; HQ, hazard quotient; WWTP, wastewater treatment plant; US EPA, US Environmental Protection Agency; MEC, measured environmental concentration; PNEC, predicted no-effect concentration; NOEC, no-observed effect concentration; EC10, concentration required to cause a 10% toxic effect; EC25, concentration required to cause a 25% toxic effect; AF, assessment factor; EED, Environmental Exposure Distribution; SSD, species sensitivity distribution; EU, European Union; OECD, Organization for Economic Co-operation and Development.

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caffeine levels reported previously in four out of the five continents, showed that 28% of all seawater samples, and 69% of all estuary water samples where caffeine has ever been measured resulted in HQ > 1 for chronic exposure. Further studies into the potential adverse effects that may arise from exposure to caffeine in aquatic systems are still required. Indeed, the need to gain a more in-depth understanding of the long-term ecotoxicological effects of caffeine is essential to ensure the quality of our health and environment.

1. Introduction

The region of Galicia, which borders the Atlantic Ocean and Portugal, is found in north-western (NW) Spain. This region is a national and world leader in shellfish, especially mussel, production, although it is also known for its fishing industry. The latest production data available indicate that, in 2015, a total of 230,000 tonnes of fish and shellfish, which represents almost half the production for Spain as a whole, was captured off the coasts of Galicia (IGE, 2015), and that Spain is the third largest European producer of these marine products after Norway and Iceland (EC, 2015). The vast majority of shellfish production in Galicia is concentrated in the coastal inlets known as the "Rías Gallegas". This region in NW Spain leads European mussel production; 95% of all Spanish mussels are farmed in Galicia and Spain is the leading European mussel producer (approximately 300,000 metric tonnes per year) and the second leading producer worldwide (FAO, 2012; Polo et al., 2015). In addition, Spain is the leading European exporter of crustaceans and molluscs of the "non-prepared" and non-preserved type, with a value of 346 million Euros in 2015 (EC, 2015).

The Rías Gallegas are also of significant ecological importance given their wide-ranging diversity, including corals, molluscs, fish, anemones and algae, amongst others. Moreover, the Atlantic Islands (Ons, Cíes, Sálvora and Cortegada) National Park, which is found between the inlets of Arousa and Pontevedra, contains one of the most diverse ecosystems from the entire Spanish coastline (Bouzas et al., 2017; MAPAMA, n.d.,). The unique ecological value of these inlets, and their high production of fish and shellfish widely consumed worldwide, has led to increasing interest in the quality of their waters.

Very few studies have been conducted into the presence of emerging contaminants in NW Spain, with those published mainly concerning the continental waters. In these studies, drugs of both human (Carballa et al., 2005; Esteban et al., 2012; Rodil et al., 2012), and veterinary origin (Iglesias et al., 2013), personal care products (Carballa et al., 2005; Rodil et al., 2012), and other contaminants such as flame-retardants, insect repellents and UV filters (Rodil et al., 2012) have all been detected. The presence of caffeine in this region has not been studied to date.

Caffeine, and its metabolite paraxanthine (1,7-dimethylxanthine), are emerging contaminants linked to human activities. Indeed, various studies have shown that caffeine is a good indicator of anthropogenic contamination in several types of matrices, such as river water, reservoir, or estuary water(Buerge et al., 2003a; Ferreira et al., 2005; Peeler et al., 2006). The presence of caffeine in continental waters has been much more widely studied. Internationally, concentrations of up to 1,100,000 and 753,500 ng L^{-1} have been detected in surface water (not including wastewater, treatment or drinking water plant in- and outflows or subterranean waters) in Costa Rica (Spongberg et al., 2011b) and Brazil (Spongberg et al., 2011b), respectively, whereas the highest levels detected in these types of waters in Europe were found in Romania (17,400 ng L^{-1}) (Gheorghe et al., 2016) and Spain (13,200 ng L^{-1}) (Valcárcel et al., 2011).A few studies have investigated the presence of this substance in drinking water, with maximum concentrations of 5000 (Ayman and Işık, 2015) and 500 ng L^{-1} being reported in Turkey and Spain, respectively (Mendoza et al., 2016). Additionally, caffeine has also been detected at concentrations of up to 182 ng L^{-1} in rain water (Loos et al., 2007). The presence of caffeine has also been reported in coastal and estuarine systems. Caffeine has been reported in estuary water in concentrations as high as 5.86 μg L^{-1} in Jamaica Bay (NY, USA) (Benotti and Brownawell, 2007).The highest measured concentration of caffeine in seawater (11 μg L^{-1}), was measured in the Darwin Harbour (Northern Australia) (French et al., 2015a, 2015b). A small number of studies have reported caffeine in the coastal waters of Spain and Portugal (Buerge et al., 2003a; Neng and Nogueira, 2012; Nodler et al., 2014; Silva et al., 2014) however, no information is available for the economically and environmentally important coasts of Atlantic Spain.

So far, the use of site-specific maximum measured concentrations (such as those listed above) has been the most common approaches for the assessment of the risk posed by emerging contaminants. Limited data availability, as well as large inconsistencies in the way that these data is presented in the literature have limited our ability to fully characterize the distribution of caffeine concentrations, and thus, determine how likely it would really be to encounter those high values.

In this context, the aims of this study were: 1) to characterize the presence of caffeine in the Rías Gallegas area of northern Spain; 2) to assess the hazard/risk posed by these two compound to the marine environment, both in the Rias Gallegas area and international, and 3) compare the results of traditional Tier-1 deterministic hazard assessment methodologies to those obtained from the application of probabilistic techniques.

2. Materials and methods

2.1. Study site

Seawater samples were collected in the region of Galicia, in NW Spain, which borders the Atlantic ocean along a coastline of some 1660 km (Polo et al., 2015). The estuarine inlets known as the "Rías Gallegas" are found along this coast and further sub-divided into the "Rías Altas", on the northern coast, and the "Rías Bajas" to the west. Rias are occasionally considered as a type of estuary, however, due to their geomorphology and geological origin (they are incised valleys, more similar to fjords), it is generally considered that typical estuarine process are of limited influence in this systems (Evans and Prego, 2003). In this way, the water bodies enclosed within the ria can be considered more as coastal waters than as estuaries. In this way, the samples collected in this study have been classified as coastal and compared to other coastal water samples.

The selected sampling points for this study were located along the coastline of the three "Rías Bajas", namely Arousa (the largest), Muros and Noia, and Pontevedra (Fig. 1), which have a combined population of 368,000 (IGE, 2015) and are served by 16 wastewater treatment plants (Aguas de Galicia, 2017).

2.2. Sample collection

Fig. 1 shows the geographic location of the selected sampling sites. A total of 22 grab seawater samples and a single sample from a WWTP outflow were collected during the second and third week of July 2015. At least one of the following characteristics was taken into consideration when selecting the sampling points: distance from, and ease of access to, the discharge zone for a wastewater treatment plant, and distance from municipalities with the highest population. In the case of the Noia sampling point (Muros and Noia), the sample was taken from the treatment plant outflow (before dilution in seawater) as it proved