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Disinfection byproducts and related compounds in the coastal zone: a preliminary compilation

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Abstract Disinfection byproducts (DBPs) are formed whenever disinfectant ingredients contact organic matter. Due to widespread increase in production and use of disinfectants and antiseptics, the presence of their ingredients in coastal environments is increasing. However, very limited scientific literature is available in regard to the occurrence of DBPs and related compounds in the coastal zone and in particularly in seawater. In this context, the aim of this preliminary complilation is to outline the main up-to-date findings and raise awareness on their increasing occurrence in coastal environments. Sampling and analysis of marine samples in the USA, Spain, China, Taiwan, Malaisia, Korea, Kuwait and Hong-Kong revealed the presence of several categories of DBPs and related compounds in coastal environments, with the highest levels being detected in urban areas, probably related to the nearby wastewater treatment plants. The investigations considered in this preliminary compilation, report the detection of DBPs and related compounds as well as the formation of toxic brominated and iodinated DBPs in high levels due to chlorination of wastewater, especially after use of seawater for flushing in toilets. New DBP groups have also been detected, namely halogenated phenolic DBPs and halopyrroles.

Keywords: DBPs, synthetic antimicrobials, personal care products, seawater, coastal environment

1. Introduction

Disinfection byproducts (DBPs) are frequently detected in environmental samples, due to the widespread use of disinfectants and the release of untreated and treated wastewater into the environment (McCance et al., 2018, Ojemaye et al., 2019, Riviera-Utrilla et al., 2013, Salimi et al., 2019). Increase of global sales of disinfectant chemicals has been estimated to reach 3% annually by 2050 (Massey et al., 2013), resulting in further increase of their DBPs that end up in costal environments. Synthetic antimicrobials are also frequently used in personal sanitizing and cleaning products and personal care products (PCPs) such as soaps, antiseptics, bath foams and detergents namely parabens, triclosan (TCS) and triclocarban (TCC). Other ingredients include polyethoxy alcohols (AEOs), polyethylene glycols (PEGs), phthalates and chlorides (Chen et al., 2020, Eganhouse et al., 1983, Farzana et al., 2020, Hayman et al., 2021, Kueh et al., 2008, Lee et al., 2019, Moeris et al., 2020, Smith et al 2015, Traverso-Soto et al., 2014). The occurrence of these pollutants in the coastal zone can have adverse effects on biodiversity balance, degrade water quality and constitute a human health risk via human exposure. Research has already revealed the possible cancer risks and reproductive problems related to DBPs (Dodds et al., 1999, Hrudey et al., 2015, King et al., 1996, Richardson et al., 2007, Feng et al., 2017, Hong et al., 2017, Krasner et al., 2009, Le Roux et al., 2017, Sun et al., 2009, Zhu et al., 2016).

In several countries, the use of seawater for domestic and public toilet flushing has been adopted in order to reduce freshwater demand. However, wastewater deriving from seawater contains higher concentrations of bromide and iodide ions, which are oxidized during chlorine disinfection, forming brominated and iodinated species of DBPs that are toxic for the environment (Ding et al., 2013, Gong et al., 2014, Liu et al., 2014, Yang et al., 2013, Yang et al., 2015). Since wastewater treatment plants are located, in most cases, in coastal areas with beaches and ports, further than environmental concerns, risks are posed also for swimmers, via dermal contact, inhalation and swallowing during swimming. While numerous research papers have dealt with DBPs and related compounds formation in drinking water, very limited scientific literature is available in regard to their occurrence in the coastal zone and in particularly in seawater. In this context, the aim of this preliminary complilation is to outline the main up-to-date findings and raise awareness on the increasing occurrence of DBPs and related compounds in coastal environments.

2. DBPs and related compounds (synthetic antimicrobials, personal care products) in the coastal zone

2.1. AEOs & PEGs in USA and Spain

AEOs and PEGs concentrations detected in sewater were lower than 1 μg/L. Wastewater concentrations in the same area were 31.2 μg/L AEOs and 39.8 μg/L PEGs in the influent and respectively 0.16 μg/L and 1.6 μg/L in the effluent. (Lara-Martin et al., 2014). PEGs were present in both untreated and treated wastewater, probably because they are metabolites of AEOs, but they also frequently occur as constituents in a large number of personal care products (soaps, water foams, cleansing agents). Wastewater treatment as well as dilution in seawater seems to reduce their concentrations, however they are not completely eliminated from seawater, resulting in possible transformations as well as potential long-term environmental risks.

2.2 Phtalate esters and methyl-paraben in seawater in Southern China

The average concentration of phthalate esters in seawater in Southern China Gulf was 3.27 μg/L, i.e. lower than global marine water quality criteria – MWQC. On the contrary, the average concentration of benzyl-butyl-phthale in seawater was 1.18 μg/L, a value exceeding European MWQC therefore indicating the need for preventive measures in regard to this type of marine pollution (Farzana et al., 2020).

Methylparaben was the main paraben species detected in seawater, with average concentration 4.87 ng/L (Chen et al., 2007). According to NICNAS 2016 (National Industrial Chemicals and Assessment Scheme in Australia, the maximum environmentally acceptable concentration for methylparaben is 20 μg/L. Several marine areas in Southern China are important for biota conservation. Important marine envrironments such as coral reefs and Posidonia forests are considered Marine Protection Areas and are protected by the law. Areas where endangered species or protected species live, such as the Chinese dolphin (*Sousa chinensis*), corals and green turtles (*Celonia mydas*), are considered sensitive areas. Therefore it is important to minimize the environmental risks posed from synthetic pollutants.

2.3 PCPs and chlorinated analogues in Taiwan and Malaysia

PCPs and their chlorinated analogues were analyzed in in a surface water stream receiving treated wastewater as well as in receiving seawater. The results are comparatively presented in Table 1. Their concentrations in stream water samples were significantly higher than those in the seawater samples, probably due to dilution. All compounds were present both in stream water and in seawater, except for Cl-methyl-paraben, which was detected only in stream water. The highest levels of all compounds, except for Cl-methyl-paraben and triclosan, occurred in the sampling point located nearest to the urban area with a hospital (Chen et al., 2020).

2.4 Parabens and antimicrobials in the coastal zone of Korea

The concentrations of parabens, TCS and TCC in sediment samples from the coastal zone of Korea are presented in Table 2 (Lee et al., 2019).

Table 1. Range of average concentrations of PCPs and chlorinated analogues in surface water and seawater (nd: not detected) (Chen et al., 2020).

Compound	C(ng/L) in water stream	C (ng/L) in receiving seawater
Butylparaben	nd-71,1	nd
Ethylparaben	503-1810	115-228
Methylparaben	1810-9400	225-1030
Propylparaben	369-4810	25-314
Triclosan	1010-2560	nd
2Cl-Methylparaben	nd-13400	645-2180
2Cl-Propylparaben	299-1430	13.5-77.8
Cl-Propylparaben	nd-2480	nd-2.20

Methyl-paraben was detected in all sediment samples, a fact revealing the range of sediment pollution in the coastal zone. The percentages of detection of ethyl-paraben, propyl-paraben and butyl-paraben were 36%, 34% and 26% respectively. Similar concentrations of methyl-paraben were measured in marine sediments in Florida, USA (Xue et al., 2016), Tokyo, Japan (Liao et al., 2013) and in Chinese river sediments (Peng et al., 2017, Liu et al., 2015). TCC concentrations were higher and TCS lower than those measured in Spain (Gorga et al., 2015) USA, (Katz et al., 2013), Italy (Casatta et al., 2015) and China (Peng et al., 2017). These comparisons indicate that the degree of pollution and the profiles of occurrence of antimicrobials and parabens in the sediments reflect the local use and consumption of these particular pollutants.

2.5 DBPs and related compounds in Kuwait seawater

Smith et al. (2015) conducted measurements of DBPs and related compounds in seawater from Kuwait after phenomena of fish deaths associated with a release of non-treated wastewater. The results are presented in Table 3. The levels of phthalates and terpineol were particularly high, while marine pollution from methyl and propyl- parabens, chloroxylenol, dimethylphenol, biphenyl ether as well as bromoform was considerable. These results indicate the need for safeguarding coastal water quality from increased levels of DBPs and related pollutants contained in wastewater that eventually enter the sea.

Table 2: Concentrations of parabens and antimicrobials (ng/L) detected in coastal sediments in Korea (nd: not detected)(Lee et al., 2019).

Compound	min	max	average
Methylparaben	0,13	11,2	2,3
Ethylparaben	nd	0,08	0,02
Propylparaben	nd	0,1	0,01
Butylparaben	nd	0,07	0,02
Benzylparaben	nd	0,06	0,01
Heptylparaben	nd	0,02	0,01
Triclosan	nd	41	2,78
Triclocarban	nd	47	3,25

Table 3. DBPs and related compounds concentrations in seawater receiving wastewater (nd: not detected) (Al Gazali, Kuwait) (Smith et al., 2015).

Compound	Concentration in seawater (ng/L)
Bromoform	10.0-20.0
Dimethyl-phenol	20.0-80.0
Chloroxylenol	nd-300.0
Fluoranthene	nd-10.0
Triclosan	nd-20.0
Methylparaben	nd-200.0
Propylparaben	nd-160.0
Terpineol	4,800-12,000
Biphenylether	nd-30
Phthalates	1,500-4,000

2.6 DBPs in Hong-Kong coastal zone

Recent research in the coastal zone of Hong-Kong (Feng et al., 2019) has focused on the identification of new categories of DBPs that are formed during chlorination of seawater-based wastewater. This kind of wastewater is produced from the use of seawater for toilet flushing, in an effort to reduce freshwater demand. However, the different properties of seawater compared to freshwater, can enhance the formation of different categories of DBPs. Further than trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs), new categories include trihalophenoles (THPs) and halocarbazoles (HCZs), while the speciation of the compounds detected shifts to more brominated analogues and iodinated DBPs are also formed (Yang et al., 2013, Zhao et al., 2014, Xu et al., 2017).

Recent literature has reported that iodinated DBPs exhibited significantly higher developmental toxicity and growth inhibition compared to their brominated and chlorinated counterparts, and that halogenated phenolic DBPs exhibited significantly higher toxicity and growth inhibition than haolgenated aliphatic DBPs (Yang et al., 2013, Liu et al., 2014). A new category of DBPs includes iodinated -trihydroxybenzosulfidic acids which belong to "iodinated phenolic DBPs", with higher toxicity and environmental persistence being of particular interest. Accoring to the results of analysis performed by Feng et al. (2019), iodinated DBPs were not detected in the chlorinated wastewater effluents after use of seawater in toilets, and this was attributed to the fact that they could be formed at a very early stage and fully decompose thereafter, due to the reaction both with chlorine and chloramines. Halocarbazoles levels were also not detectable during this research. However trichlorophenol and tribromophenol were detected at levels up to 1000 ng/L in chlorinated saline wasetwater effluent samples.

Yang et al. (2014) investigated another new category of DBPs, halopyrroles, and the factors that can affect their formation: chlorine dose, contact time, temperature and pH. Their research outlined that relatively low chlorine doses, 6 and 10 mg/L enhanced halopyrrole formation. Increase of chlorine dose from 10 mg/L to 20 mg/L, resulted in decrease of the levels of tetrabromopyrrole, tribromochloropyrrole, 2,3,4-tribromopyrrole and 2,3,5-tribromopyrrole by 92.2%, 88.9%, 79.9% and 97.3% respectively. The authors attributed this fact to decomposition of the pyrrolic ring due to chlorine. The concentrations of tetrabromopyrrole measured in chlorinated saline wastewater after chlorine dosages 6, 10, 15 and 20 mg/L were 0.74, 0.69, 0.14 και 0.08 mg/L respectively (Yang et al., 2014).

The precursors of halopyrroles were also investigatesd by Yang et al. (2014). Tetrapyrroles, with molecules containing four pyrrolic rings, were considered to be the major precursors. Tetrapyrroles are compounds of particular importance for the ecosystems, as they contain chlorophylls, aimins and porfyrins, essential metabolites for almost all living organisms, which for the same reason are present in effluent wastewater samples. Therefore, the basic hypothesis for the formation of halopyrroles is that, in presence of bromine and iodine, chlorine reacts with such pyrrole containing compounds, creating halopyrroles.

As tetrabromopyrrole (Figure 1) was the dominant species of this category, its developmental toxicity was assessed. The species *P. dumerilii* was used. The results have shown that tetrabromopyrrole exhibited the maximum developmental toxicity as it was 460 and 8805 times more toxic than bromoform and bromoacetic acid. Taking into account that the concentrations of tetrabromopyrrole in the chlorinated saline water samples ranged at levels 1/10 to 1/20 of those of bromoform and bromoacetic acid respectively, the risk posed by tetrabromopyrrole for the marine environment is 10 to 100 times higher than that of bromoform and bromoacetic acid (Yang et al., 2014). These results highlight the importance of new categories of DBPs due to saline water utilization and chlorination in the coastal zone and the need for further investigation of compounds and mechanisms involved.

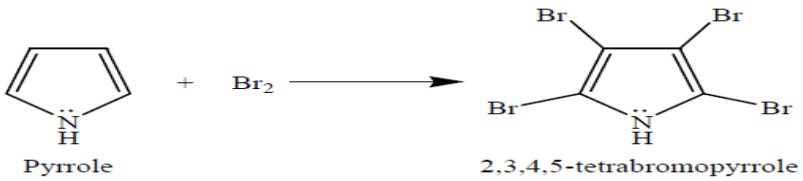

Figure 1. Formation of 2,3,4,5-tetrabromopyrrole (Sky of Chemistry, 2020)

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