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Review

Sources, factors, mechanisms and possible solutions to pollutants in marine ecosystems

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ABSTRACT

Algal toxins or red-tide toxins produced during algal blooms are naturally-derived toxic emerging contaminants (ECs) that may kill organisms, including humans, through contaminated fish or seafood. Other ECs produced either naturally or anthropogenically ultimately flow into marine waters. Pharmaceuticals are also an important pollution source, mostly due to overproduction and incorrect disposal. Ship breaking and recycle industries (SBRIs) can also release various pollutants and substantially deteriorate habitats and marine biodiversity. Overfishing is significantly increasing due to the global food crisis, caused by an increasing world population. Organic matter (OM) pollution and global warming (GW) are key factors that exacerbate these challenges (*e.g.* algal blooms), to which acidification in marine waters should be added as well. Sources, factors, mechanisms and possible remedial measures of these challenges to marine ecosystems are discussed, including their eventual impact on all forms of life including humans.

1. Introduction

Marine ecosystems are adversely affected because of increasing demand from human activities and the effect of global warming (GW), thereby facing a number of challenges (Mostofa et al., 2012). The key problems in marine ecosystems can be summarized as follows:

- Emerging contaminants (ECs) are discharged into water environments, including seawater, because of human activities (Teijon et al., 2010; De Laender et al., 2011; Richardson and Ternes, 2011; Vidal-Dorsch et al, 2012; Mostofa et al., 2013a);
- Production of algal toxins or red-tide toxins during algal blooms is increasing due to the effects of organic matter (OM) pollution and GW (Prince et al., 2008; Castle and Rodgers Jr., 2009; Yates and Rogers, 2011; Mostofa et al., 2013b);
- Marine surface waters are undergoing acidification (Doney et al., 2009; Beaufort et al., 2011; Cai et al., 2011; Xiao et al., 2011), which is known to cause changes in marine chemistry and production of algal toxins (Gao et al., 2012a, and references therein);
- Ship breaking and recycle industries (SBRIs) along with oil exploration and transportation can have catastrophic effects on biodiversity due to OM, metals and other pollutants (Reddy et al., 2007; Pasha et al., 2012; Neşer et al., 2012a; Abdullah et al., 2013);
- Overfishing depletes ecosystems and has led to a global decline in fish catches (Myers and Worm, 2003; Block et al., 2005; Rooker et al., 2008; Srinivasan et al., 2010).

Such problems are increasingly threatening the world's marine resources, and they are directly or indirectly linked with the world's growing population. It has been shown that >40% of the world's oceans is highly affected by human activities (Halpern et al., 2008). Coastal areas are understandably suffering from the biggest impact, and human activities have depleted >90% of formerly important species, destroyed >65% of seagrass and wetland habitats, degraded water quality, and accelerated species invasions in diverse and productive estuaries and coastal seas (Lotze et al., 2006). A recent review showed that 63% of assessed stocks are in need of rebuilding (Worm et al., 2009). At the same time, GW and related phenomena can accelerate the occurrence of algal blooms

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and acidification processes in marine ecosystems (Cooper et al., 2007; Albright, 2011; Anlauf et al., 2011; Mostofa et al., 2013b, 2013d). ECs are usually bioaccumulated into fish or other aquatic organisms and seafood, from which they can be transferred to humans and other organisms (Richardson and Ternes, 2011; van de Merwe et al., 2011).

Yet, marine ecosystems are also a key vital resource for fish and seafood, meeting the demand for fish proteins at relatively low prices (Meryl, 1996; FAO, 2008). More than half of the total animal proteins consumed in several small island states, as well as in Bangladesh, Cambodia, Equatorial Guinea, French Guiana, Gambia, Ghana, Indonesia and Sierra Leone comes from fish (FAO, 2008). Insufficient attention has been paid so far to the critical impacts of sequential declining in marine ecological communities (*e.g.* from ECs emissions, algal blooms, and overfishing), particularly by developing countries. Considering the importance of a sustainable use of marine resources and biodiversity, world communities should pay much more attention to the solution of current problems created by human activities on marine ecosystems.

This paper will provide an overview of important problems such as ECs, harmful algal blooms, acidification, ship breaking and recycle industries (SBRIs), and overfishing. The sources, factors, mechanisms and remedial measures of such challenges are discussed. As far as pharmaceuticals are concerned, the Chinese case of "100 tablets in a bottle" will be discussed as a major cause of ECs release into the environment, and as a suggestion for strategies aimed at the reduction of pharmaceutical pollution in other countries.

2. Emerging contaminants (ECs)

Emerging contaminants (ECs), a diverse group of both organic and inorganic compounds, occur in very small amount (usually at concentration levels of nanograms to micrograms per liter), are persistent, have potential health effects on organisms including humans, fish and wildlife, and may have other adverse ecological effects (Mostofa et al., 2013a). ECs include: pharmaceuticals; personal care products (PCPs); endocrine-disrupting compounds (EDCs); steroids and hormones; drinking water disinfection byproducts (DBPs); perfluorinated compounds (PFCs); brominated flame retardants including polybrominated diphenyl ethers; sunscreens/UV filters; surfactants; fragrances; antiseptics; pesticides and herbicides; organotins; plasticizers; heavy metals including As, Sb, Pb and Hg; algal toxins or red-tide toxins (De Laender et al., 2011; Richardson and Ternes, 2011; Vidal-Dorsch et al, 2012; Mostofa et al., 2013a).

Most ECs in the aquatic environment originate from three major sources (Hirsch et al, 1999; Fent et al., 2006; Mostofa et al., 2013a): (*i*) anthropic emissions including atmospheric deposition, effluents of municipal, industrial and agricultural activities, aquaculture, livestock and compounds excreted from the human body (*e.g.* pharmaceuticals and their metabolites); (*ii*) natural production, including most notably algal (or phytoplankton) blooms in surface water; and (*iii*) photochemical and/or microbial origin, following alteration of primarily emitted organic substances by photoinduced and/or microbial processes during transport from rivers to lakes, oceans or other water sources (secondary pollution).

2.1. Sources of pharmaceuticals

Point sources of pharmaceuticals and other drugs are (Jones et al., 2001; Fent et al., 2006; Corcoran et al., 2010; Richardson and Ternes, 2011; Mostofa et al., 2013a, 2012):

- Discharge of expired and unused pharmaceuticals or drugs from household. The Chinese case of '100 tablets in a bottle' will be discussed later as a showcase example;
- Disposal of unused pharmaceuticals from hospitals;
- Wastewater and solid wastes discharged from pharmaceutical industries;
- Hormones and antibiotics used in aquaculture and livestock;
- Compounds excreted from the human body in the form of non-metabolized parent molecules or as metabolites, after drug ingestion and subsequent excretion. Note that in some cases there is an excretion of 50–80% of the parent compound (Hirsch et al, 1999).

All of the above issues are strongly affected and exacerbated by the increase in world's population.

2.2. Factors affecting the pharmaceutical pollution

Incorrect drug disposal is particularly important as a cause of pollution by pharmaceuticals (Hirsch et al, 1999; Jones et al., 2001; EMEA, 2006; Fent et al., 2006; Islam et al., 2010). It is in this context that a popular initiative by Chinese pharmaceutical manufacturers (the so-called '100 tablets in a bottle') comes into play as a case study of what should be avoided. The manufacture and commercialization of widely sold drugs in relatively big tablet stocks, with relatively low cost per single tablet, was initially welcome as a way to decrease expenditure for medicines. Following commercial success, at least 88 pharmaceuticals have been sold in China in the '100 tablets in a bottle' format, with a wide variety of active principles (see Table 1; Mostofa et al., 2012).

The main environmental drawback of this initiative is that only a fraction of the tablets is actually used before the expiration period, while the remaining ones are often discharged into household wastes or (even worse) wastewater. In the cases of paracetamol (anti-inflammatory and antipyretic) and prednisone acetate (used for allergic or autoimmune inflammatory diseases), the structures of which are reported in Fig. 1, it has been estimated that the ratio of consumed *vs*. disposed-of tablets would be around 10–20% *vs*. 80–90% (Mostofa et al., 2012).

It should be highlighted that incorrect drug disposal is a worldwide problem (EMEA, 2006; Roig, 2008). In Europe, the disposal of waste pharmaceuticals is bound by strict control in the cases of manufacturers, wholesalers, retailers and hospitals (EU, 1994). However, the general public is under no obligation to do such action (Daughton and Ternes, 1999). Therefore, most people will either flush unused pharmaceuticals down the drain, or dispose of them in household wastes. The latter will ultimately enter waste landfill sites or, to a lesser degree, be incinerated (Jones et al., 2001). Similar situations are observed in Japan and North America, whereas specific legislative requirements are introduced to ensure that any pharmaceutical reaching the market is assessed for its likely environmental fate and biological effects (EMEA, 2006). There is more limited regulation concerning the environmental impact of pharmaceuticals, and of effluents released from pharmaceutical industries in China, India, Bangladesh, and other developing countries (EMEA, 2006; Islam et al., 2010).

The combination of over-production and excessive disposal of pharmaceuticals can cause environmental pollution *via* several pathways. First of all, unused pharmaceuticals can mix up with natural waters, either through leaching of household wastes by rainwater or upon direct input of household wastes into natural waters (Mostofa et al., 2012; Jones et al., 2001; Fent et al., 2006). Second, residues of pharmaceuticals are present in manufacturers' wastewaters resulting from production processes (Holm et al., 1995; Mostofa et al., 2012). The released compounds are