



Marine pollution in the Libyan coastal area: Environmental and risk assessment

Maria Bonsignore^a, Daniela Salvagio Manta^a, Ehab A. Al-Tayeb Sharif^a, Fabio D'Agostino^a, Anna Traina^a, Enza Maria Quinci^a, Luigi Giaramita^a, Calogera Monastero^a, Mohamed Benothman^b, Mario Sprovieri^{a,*}

^a Institute for Coastal and Marine Environment (IAMC – CNR), Via del Mare, 3, 91021 Capo Granitola, Campobello di Mazara, TP, Italy

^b Faculty of Veterinary Medicine, Tripoli University-Libya, Tripoli, Libya

ARTICLE INFO

Keywords:

Heavy metals
Polycyclic aromatic hydrocarbons
Bioaccumulation
Health risk assessment
Libya coast

ABSTRACT

A comprehensive assessment of the potential adverse effects on environment and human health generated by the inputs of chemicals from the most important Libyan petrochemical plant is presented. Ecotoxicological risk associated with the presence of As, Hg, Ni, Zn and PAHs in marine sediments is low or moderate, with a probability of toxicity for ecosystem < 9% and < 20% for heavy metals and PAHs respectively. However, surface sediments result strongly enriched in Hg and As of anthropogenic origin. Investigation of metals in fish allowed to assess potential risks for human populations via fish intake. Target hazard quotients values indicate potential risk associated to toxic metals exposure by fish consumption and lifetime cancer risk (TR) values highlight a potential carcinogen risk associated to As intake. Noteworthy, the presented results provide an unprecedented environmental dataset in an area where the availability of field data is very scant, for a better understanding of anthropogenic impacts at Mediterranean scale.

1. Introduction

Coastal environments are considered as places of high ecological risk due to the complex biogeochemical processes and the intensive human activities, which dramatically increase the occurrence of organic and inorganic pollutants in the environment (Li et al., 2014). Heavy metals are among the most common pollutants and their occurrence in aquatic system indicates either natural origin (weathering and erosion) or anthropogenic sources (mining, industrial processing, waste disposal and agricultural activities) (Keshavarzi et al., 2015). Because of adsorption, hydrolysis and co-precipitation, only a small proportion of heavy metal ions remain dissolved in water, while a large amount deposit in the sediments (Gaur et al., 2005), which act as sink of these elements, representing a source of exposure for the involved food chains. Heavy metals accumulated in fatty tissues of organisms can affect the digestive, cardiovascular, and central nervous systems. Furthermore, some metals, such as As, could cause mutagenic, teratogenic, and carcinogenic effects in living organisms (Wong, 1988). Carcinogenicity, immunotoxicity, genotoxicity and reproductive toxicity is also associated with exposure to polycyclic aromatic hydrocarbons (PAHs) (Keshavarzi et al., 2015), a group of compounds of petrogenic and pyrogenic origins (high temperature combustion of fossil fuels and

biomass, volcanic eruptions, forest fires, oil spills, petrol and diesel leaks, domestic and industrial wastes and biological production) (Kucuksezgin et al., 2012; Xu et al., 2007) that can be widely dispersed into the environment via atmospheric transport or through stream pathways (Liu et al., 2009). Because of their hydrophobicity, PAHs show high persistence in the marine sediments which represent the main sources of exposure for the aquatic food chains, where PAHs accumulate and biomagnificate (Bastami et al., 2013). Consumption of fish represents the main pathway of exposure of these contaminants for humans causing chronic or acute diseases (Jørgensen and Pedersen, 1994, Förstner and Wittman, 1981).

The Marine Strategy Framework Directive (MSFD) (2008/56/EC) is a legal instrument, similar to others existing worldwide (Oceans Act in the USA, Australia or Canada; EC Water Framework Directive, National Water Act in South Africa, European Regional Sea Conventions and others), that has been adopted in the European Seas in order to protect more effectively the marine environment. The MSFD requires that all EU Member States (MSs) take measures to maintain or achieve the Good Environmental Status (GES) in their seas by 2020. Basically, it should be possible, as mere assumption at the present level of knowledge on the functioning of the marine ecosystem, to determine how to keep the pressure of human activities within levels compatible with the

* Corresponding author.

E-mail address: mario.sprovieri@iamc.cnr.it (M. Sprovieri).

preservation or restoration of GES which integrates physical, chemical and biological aspects, together with the services provided by ecosystems.

The holistic view of the MSFD is clearly reflected in the descriptors that, despite their qualitative or semi-qualitative character, address key requisites of a healthy ecosystem such as diversity, food web robustness, sustainable inputs of xenobiotic substances and biological immigration or physical perturbations.

The MSFD covers the coastal waters up to 1 nautical mile, except for chemical information where 12-miles territorial waters are also included. Nonetheless, the geopolitical complexity of the Mediterranean area reduces an appropriate knowledge of the anthropogenic impact in the southern part of the basin, where MSFD does not represent a mandatory regulation and also where chemical and physical investigations are extremely limited. A specific survey on the available literature (based on a specific research on the ISI web on knowledge database) highlighted that investigation on the distribution of pollutants in seawater and sediment from the southern coast of the Mediterranean (from Morocco to Libya) are limited to 17 papers and restricted to 5 if combined information from pollutants in sediments and biota are considered. The present work contributes to filling this lack of knowledge, providing a new dataset of contaminants in surface sediments and fish from Libyan coastal marine area, between the Abu-Kamash and the Tunisian border. The Libyan coast and its lagoons play an important role in terms of biodiversity and productivity of Mediterranean marine ecosystem, mainly thank to the presence of *Posidonia oceanica* used by different fauna species for shelter and nursery grounds during breeding and other stages of their life cycle. Since 70s years, Abu-Kamash has hosted the General Company of Chemical Industries (GCCCI), the most important national chemical plant, which poses significant environmental threats and health concerns for local population (Banana et al., 2016). The purpose of the work is to investigate the effects of this industrial activity on the surrounding marine environment where artisanal fisheries, aquaculture activities and ecosystem have to be preserved (Banana et al., 2016). The main objectives can be therefore synthesized in the following points: 1) to determine the potential risk for the ecosystem associated with the PAHs and metals content in the sediments in proximity of the GCCCI Libyan chemical plant; 2) to explore the bioaccumulation of metals in the muscle of some commercially available fish species collected from deep and shallower waters; 3) to assess the potential human health risks associate with consumption of fish from the study area. Notably, this work represents a pilot tentative to integrate chemical and biological information in a MSFD conceptual framework from the southern coast of the Mediterranean Sea.

2. Materials and methods

2.1. Study area

The city of Abu-Kammash is located on the Mediterranean Sea, in the western coast of Zawya, Libya (Fig. 1). Since 1970s, this area has hosted the General Company of Chemical Industries (GCCCI), which consist of 3 sub-units producing annually 104,000 tons ethylene dichloride, 60,000 tons poly-vinyl-chloride (PVC), 50,000 tons caustic soda and 45,000 tons chlorine, respectively (www.gcci.ly). The wastewaters generated from GCCCI are received in the Farwa Island, an elongated sand bar extending from east to west for 11 km, isolated from the mainland by a lagoon (Farwa lagoon) and connected to the sea on the west with an opening of 10 m wide. This area is well known for its high fishery productivity, but also for its vulnerability to pollution and other man-made threats to the coastal marine environment (IUCN, 2011; Laurent et al., 1999; Haddoud and Zgouzi, 1998; Haddoud and Rawag, 2003; Etayeb and Essghaier, 2007).

2.2. Sampling

2.2.1. Sediments

During April and August 2014, a total of 14 surface sediment samples (depth of 2 cm) were manually collected by scuba diving, in the Farwa coastal-marine area. Sampling stations were selected along the coast, to the east and west of the GCCCI plant, in shallow water (S5–S9) and in deeper water, offshore the Farwa Island (S1, S2, S3) (Table 1; Fig. 1). After the collection, the samples were immediately stored at $T = -20\text{ }^{\circ}\text{C}$, until grain size and chemical evaluation. All the analyses were performed at the biogeochemical laboratories of the Institute for Coastal and Marine Environment (IAMC-CNR) of Capo Granitola.

2.2.2. Fish

In the same period, a total of 133 fish specimens, including benthic, demersal and pelagic species, were collected from deep and shallow waters (Fig. 1; Table 1). Specifically, 41 pelagic specimens (*Sardinella* spp. and *Boops boops*) were caught during the night by means of a Lampara fishing unit equipped with a purse seine net, while 92 benthic and demersal specimens (*Pagellus* and *Mullus* spp.) were collected from mid and bottom-water using gillnet or fish line (Fig. 1; Table 1). Immediately after the sampling each specimen was measured to record the total length (TL) and then stored at $T = -20\text{ }^{\circ}\text{C}$ until chemical analyses. Heavy metals determinations were carried out performed at the biogeochemical laboratories of the IAMC-CNR of Capo Granitola.

2.3. Analytical methods

2.3.1. Grain size analyses

About 3.5 g of wet sediment were treated with a solution of hydrogen peroxide H_2O_2 and MilliQ (2:8 v/v) for 48 h at room temperature in order to remove organic material and cemented salts (Romano, 2001). Finally, the samples were washed several times with distilled water in ultrasonic bath (for ~4–5 min at a time) to remove hardened salt (mainly sodium chloride) and analyzed for particle size determination by Horiba Partica LA-950V2 laser granulometer.

2.3.2. Polycyclic aromatic hydrocarbon (PAHs) analyses

Measurement of PAHs congeners (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene) concentrations in the sediment samples was carried out by gas chromatography coupled with mass spectrometry detection (Thermo-Fischer- GC/MS), after extraction by accelerated solvent extractor (Dionex ASE 200). About 3 g of dry and homogenized sample were mixed with ~5 g of inert dispersal phase Extrelut NT and loaded into 33 ml reactor cell containing ~2 g of Na_2SO_4 anhydrous. A mixture ($V = 30\text{ ml}$) of hexane and acetone (80:20 v/v) was used to extract PAHs from the sediment and activated copper (200 mg) was added in order to remove elemental sulfur (EPA Method 3545A (SW-846), 1998). The cells were heated to $100\text{ }^{\circ}\text{C}$ until the pressure reached 1500 psi. The obtained extract was reduced up to ~2 ml volume by rotavapor and purified using SPE SIL 6 ml/1000 mg cartridge (EPA method 3630C, 1996). PAHs were recovered using 5 ml of hexane, the eluted was dried by multivapor, re-dissolved with 1 ml of hexane with a spike of 200 ng/ml of PAH-mix9 (deuterated internal standard) and finally analyzed by GC/MS. The injection volume was 2 μl in splitless mode. A capillary column DB5-MS (30 m \times 0.25 mm \times 0.5 μm) was used. The oven temperature program was the following: $T = 60\text{ }^{\circ}\text{C}$ for 4 min, $T = 270\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$ (hold for 5 min), $T = 340\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C}/\text{min}$ (hold for 5 min). The operative conditions were: inlet $T = 250\text{ }^{\circ}\text{C}$ and carrier gas (He) flow = 1.2 ml/min. The mass spectrometer was operated in selective ion monitoring (SIM) mode, following the EPA method 8270D, 2014. The accuracy of the method was checked using the SRN NIST1941b-Organics in marine

Download English Version:

<https://daneshyari.com/en/article/8871715>

Download Persian Version:

<https://daneshyari.com/article/8871715>

[Daneshyari.com](https://daneshyari.com)