



The effects of dredging and environmental conditions on concentrations of polycyclic aromatic hydrocarbons in the water column

Greta Vagge^a, Laura Cutroneo^a, Michela Castellano^a, Giuseppe Canepa^b, Rosa Maria Bertolotto^c, Marco Capello^{a,*}

^a DISTAV, University of Genoa, 26 Corso Europa, Genoa I-16132, Italy

^b Port System Authority of the Western Ligurian Sea, Port of Genoa, Palazzo San Giorgio, 2 Via della Mercanzia, Genoa I-16123, Italy

^c ARPAL, Ligurian Environmental Protection Agency, 8 Via Bombrini, Genoa I-16149, Italy

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ABSTRACT

Sediment dredging can cause damage to the marine environment due to mobilization of sediments and contaminants. The effects of dredging and boundary environmental conditions on the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in water were evaluated during dredging of the Oil Port of Genoa-Multedo (Italy). Results showed that turbidity and PAH concentrations increased in the water during dredging. However, the scenario was complex due to the high number of interacting physical-chemical factors influencing PAH concentrations and transport. Due to these, PAH distribution is different in water, where low-molecular-weight PAHs were predominant (maximum concentration $0.105 \mu\text{g L}^{-1}$), and in bottom sediments, where high-molecular-weight PAHs had the highest concentrations (from 299.3 to 1256.5 ng g^{-1}). Moreover, mainly during dredging the PAH concentrations in water were significantly higher inside than outside the port as a consequence of the lower dynamics within the port basin. Turbidity was the main parameter related to PAH concentrations.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a class of organic compounds present in all environments. PAHs are found in ambient air in the gas-phase and as sorbed to aerosols (Abdel-Shafy and Mansour, 2016; Hoffman et al., 2015; Hoffman et al., 2017), in fresh and sea waters (Kafilzadeh, 2015; Sower and Anderson, 2008), and in soils and bottom sediments (Abdollahi et al., 2013; Gan et al., 2009; Walker et al., 2013a, 2013b). Sixteen PAHs are indicated by the United States Environmental Protection Agency (USEPA) as “priority pollutants”, that is substances for which it is important to implement specific monitoring, especially with regard to their proven chronic toxicity and carcinogenicity (Abdel-Shafy and Mansour, 2016; Keshavarzifard et al., 2014; Man et al., 2013; Pashin and Bakhitova, 1979; Rengarajan et al., 2015). Based on the number of their benzene rings (C_6H_6), PAHs are divided into two major groups: low-molecular-weight (LMW), that have from two to three fused benzene rings, and high-molecular-weight (HMW), that have more than three benzene rings (Keshavarzifard et al., 2014). The release of PAHs into the environment is mainly due to both human activities and, but only to a much lesser extent, natural events (Keshavarzifard et al., 2014). They are introduced into the environment

by a great number of processes that can be categorized as either petrogenic or pyrogenic. Petrogenic PAHs are formed by diagenesis characterized by relatively low temperatures and production on a geological time scale (millions of years). They are derived from coal, crude oil and oil shale that contain high concentrations of these compounds (WHO/IPCS, 1998): the accidental spillage of crude oil is the main source of petrogenic PAHs in the water environment on a global scale (Eisler, 1987). Pyrogenic PAHs are the products of the incomplete combustion of organic substances during industrial production, food processing, and operation of machinery including automobiles, airplanes and ships, and also smoking of tobacco (Keshavarzifard et al., 2014; Pashin and Bakhitova, 1979; Yu, 2002). Using appropriate PAH diagnostic ratios, it is possible to determine the processes that generated these compounds (Budzinski et al., 1997; De Luca et al., 2004; Yunker et al., 2002). Therefore, PAH diagnostic ratios, combined with forensic analysis, allow to apportion the sources of PAH contaminated sediment (MacAskill et al., 2016; Walker et al., 2017) and to have useful information about source control for remediation decision making and environmental protection (Walker et al., 2017).

On the basis of physicochemical properties of PAHs, such as solubility, it is possible to find them in different forms in water (e.g. in the

* Corresponding author.

E-mail address: capello@dipteris.unige.it (M. Capello).

dissolved or colloidal phase) associated with suspended particulate matter in the surface sediments or in organisms (King et al., 2004). The PAH solubility in water is generally very low and tends to decrease with an increase in the number of the molecular rings (Nikolaou et al., 2009; Pane et al., 2005). Due to this characteristic, PAHs can cling to the surface of particulate matter, and this association with fast-sinking particles is considered the main transport mechanism of PAHs from the surface to the sea bottom, and, consequently, the main cause of their accumulation in bottom sediments (Kafilzadeh, 2015; Magi et al., 2002). Therefore, bottom sediments represent the main PAH stock and can be considered as a permanent source of these contaminants in the marine environment (Abdollahi et al., 2013).

Resuspension of bottom particles during dredging can produce an increase in the concentration of PAHs in the water column, causing their diffusion in the surrounding environment and restoring their bioavailability. The main processes involved in PAH diffusion during dredging are: a) the release of interstitial water from bottom sediments; b) the absorption of PAHs to resuspended material and their consequent transport from the dredging site to neighboring areas due to dynamics (Cutroneo et al., 2015); c) other physical and chemical processes that operate at the same time and control the release of PAHs from sediments and their concentration in the water column (e.g. PAHs sorption/desorption and biodegradation processes and erosion processes resulting in terrigenous run-off) (Keshavarzifard et al., 2014; Xia and Wang, 2008). Thus, the sediment characterization before the dredging and the monitoring of PAH dispersion during dredging activities are essential for the environmental protection (Casado-Martínez et al., 2006).

The case of the capital dredging of the Oil Port of Genoa-Multedo (hereafter Oil Port) (Italy; Fig. 1) has allowed us to study the characteristics of PAH dispersion during dredging. The Oil Port is an oil terminal for the loading, landing and movement of petroleum and petrochemical products such as both crude oil and finished products

(petrol, diesel, fuel oil, and finished and basic petrochemical products). Besides the activities linked to the oil industry, the urbanization of the area and the input of different torrents play important roles in the transport of contaminants and different PAHs to the sea. In fact, the area is subjected to the inputs of waste waters derived from two waste treatment plants and the leachate of the municipal waste landfill of the City of Genoa (500,000 m² surface, opened in 1968 and closed in 2014). The Oil Port was subjected to a capital dredging between July 2009 and May 2010 with the removal of 40,000 m³ of sediment. The objective was to obtain a depth of 14.5 m in the Port entrance channel and from 11 m to 14.5 m in surrounding pier areas (Fig. 1). Sediments were characterized in October 2008 before the dredging highlighting exceeding of the limits provided by the Italian Legislative Decree 152/06 for polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), benzo[a]pyrene, benzo[g,h,i]perylene, total chromium, nickel, zinc and heavy hydrocarbons (C > 12). Therefore, depending on their contaminant concentrations, the dredged sediments were used for filling a hazardous waste containment cell in the reclamation area of Bettolo Quay inside the Port of Genoa (Capello et al., 2010; Cutroneo et al., 2014). Environmental monitoring of the dredging activities was carried out between June 2009 (with the determination of the pre-dredging condition) and November 2010 (with post-dredging monitoring).

The aim of this study was to evaluate the influence of dredging on the PAH concentrations in the water column improving a previous study carried out by Cutroneo et al. (2015) and considering the number of dredges active during the monitoring campaigns, and environmental conditions, such as wind, rain, temperature and salinity of the water column, as external forcing.

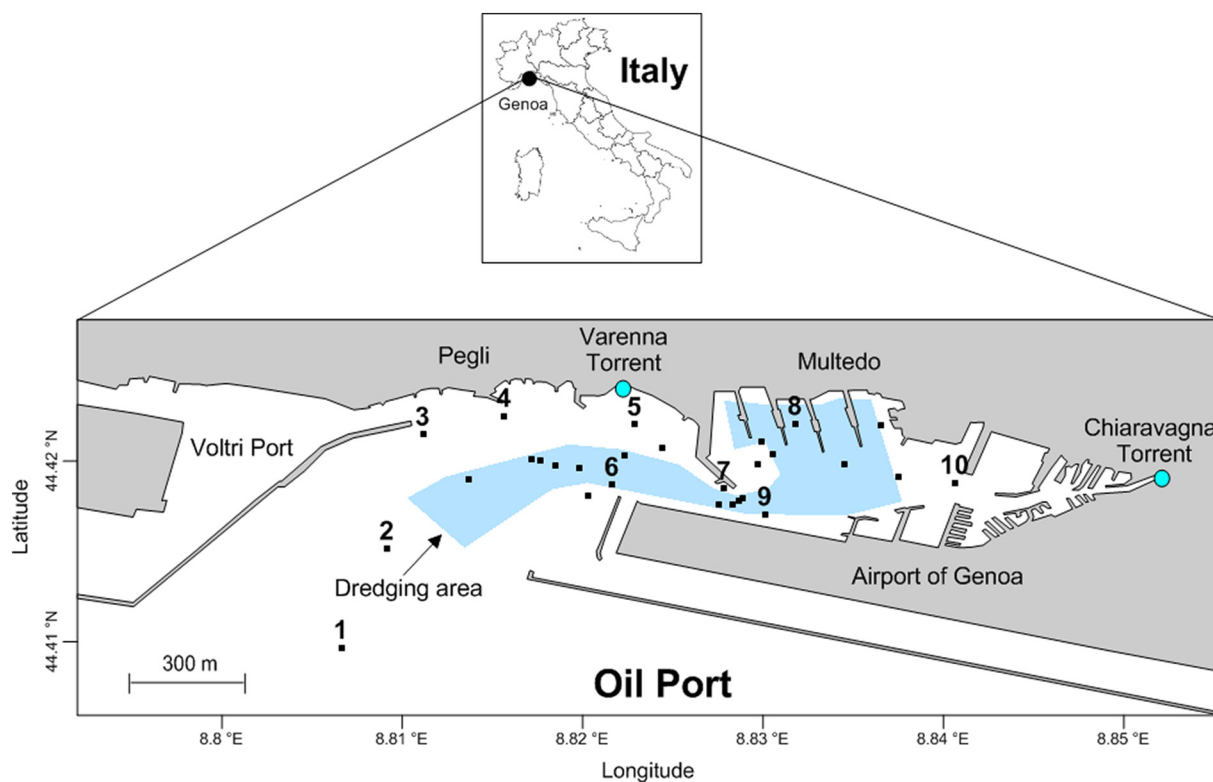


Fig. 1. Map of the Oil Port of Genoa-Multedo. The black dots indicate the fixed (numbered 1–10) and the mobile monitoring stations; the light blue dots show the mouths of the Varenna and Chiaravagna Torrents; the light blue area represents the dredging area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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