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Phosphorus content in a deep river sediment core as a tracer of long-term (1962–2011) anthropogenic impacts: A lesson from the Milan metropolitan area

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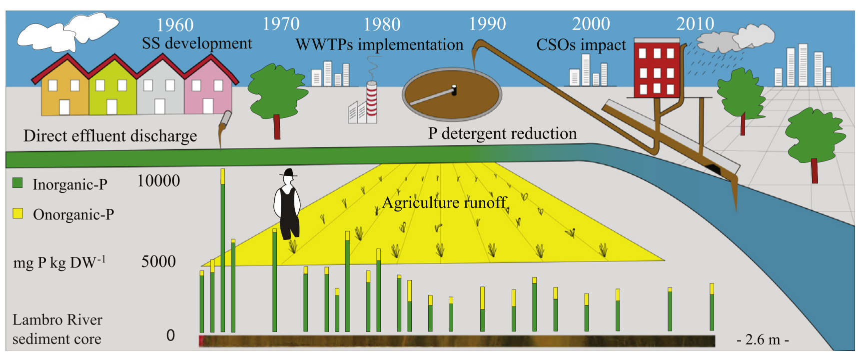
HIGHLIGHTS

- Phosphorus fractions were detected in a sediment core (2.6 m) of the Lambro River.
- Phosphorus content was related to anthropogenic impacts in the period 1962–2011.
- Management of phosphorus resulted more incisive between the 1980s and the 1990s.
- Recent management efforts were less performing due to the impact of surface runoff.
- Lambro River still covers high portions of nutrient loads to Po River and Adriatic Sea.

GRAPHICAL ABSTRACT



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ABSTRACT

Reconstructions of past fluvial contamination through the analysis of deep sediment cores are rarely reported in literature. We examined the phosphorus fractions in a deep (2.6 m) sediment core of the Lambro River downstream of the highly anthropized Milan metropolitan area and upstream of the Po river the main Italian watercourse. The core covered the period 1962–2011. Total phosphorus concentrations resulted typical of a strongly impacted environment (4788 mg P kg DW^{-1} on average) with the highest concentrations related to the 1960s (7639 mg P kg DW^{-1}) reflecting the period of maximum demographic growth. Afterwards, phosphorus concentrations decreased thanks to the infrastructural and legislative initiatives carried out in the 1980s and the 1990s to reduce the impact of urban point sources. Subsequently, total phosphorus concentrations stabilized on values around 3000 mg P kg DW^{-1} and did not diminish further, even after the second phase of infrastructural interventions carried out in the second half of the 2000s. This was related to the increasing relative impact of the combined sewer overflows in the sewage system and to the strong phosphorus enrichment of the basin. Most of the phosphorus was in inorganic forms (86% of the total) that have been identified as the final target of the domestic effluent inputs. The contribution of organic phosphorus was lower but constant over the period 1962–2011. It likely originated from the agricultural areas located south of the city of Milan. In conclusion, this study underlines how past interventions have been effective in reducing urban point sources but it also highlights

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the current difficulties related to the growing importance of other sources influenced by the surface runoff (i.e., combined sewer overflows and agriculture). The study also emphasizes a general phosphorus enrichment of the Lambro River basin and its impact on the Po River and the Adriatic Sea.

1. Introduction

Phosphorus is an essential element for life, generally limiting the production of both terrestrial and aquatic ecosystems (Vollenweider, 1968; Güsewell, 2004; Elser, 2012; Garnier et al., 2015). Phosphorus concentrations in waterbodies scarcely influenced by human activities are normally low and approach the pristine/natural conditions (Salerno et al., 2014). These basal levels were established under the soil and landscape stabilization occurred after the last glaciation (Filippelli and Souch, 1999). Phosphorus concentrations then increased with the growing of anthropogenic pressure (Smith and Schindler, 2009; Battarbee and Bennion, 2011; Beusen et al., 2016; Bouwman et al., 2017; Khasawneh, 1980; Elser and Bennett, 2011). At present days about half of the water bodies in the world is estimated to be in pristine conditions (Compton et al., 2000), while the others show some degree of phosphorus enrichment.

High phosphorus concentrations in inland waters are cause of eutrophication (OECD, 1982; Mainstone and Parr, 2002; Smith, 2003; Liu et al., 2016) which represents the primary worldwide water quality issue (Smith and Schindler, 2009; Lürling et al., 2016). Eutrophication is triggered by excessive algal growth and cause profound ecosystem changes, with loss of ecosystem services (Moss, 2012) and various economic damages (Dodds et al., 2009; Elser and Bennett, 2011; Roy et al., 2014; Chen and Graedel, 2016). Besides the direct impact of human activities, the phosphorus cycle is also currently affected by climate change and particularly by the intensification of extreme hydrological events and by global warming, enhancing the phosphorus release from soils and sediments and in turn exacerbating the detrimental effects of eutrophication (Copetti et al., 2013; Smith and Schindler, 2009).

Domestic effluents are one of the main sources of phosphorus. In Europe, these sources increased in the last two centuries due to the growing urbanization. Initially wastewaters were directly discharged to surface waters. In most major European cities, for instance, the construction of large sewer systems started only in mid-19th century, to meet sanitary problems (Lestel and Carré, 2017). Attention on the release of nutrients on surface waters was placed only later, since the sixties, when the role of the nutrients loads on the eutrophication of inland and coastal waters was clarified (OECD, 1982; Sharpley and Wang, 2014). In Italy, major efforts have been carried out between the second half of the seventies and the nineties, when many sewer systems (SSs) were constructed and progressively connected to waste water treatment plants (WWTPs) throughout the country. The main limitation of this enormous infrastructural effort was the lack of separation of the urban runoff waters from the domestic effluents (Gasperi et al., 2010) that were both collected in combined sewer systems (CSSs). To prevent damages on the WWTPs these systems were endowed by combined sewer overflows (CSOs) that during high precipitation events discharge their effluents directly to surface waters, thus limiting the efficiency of the overall wastewater treatment system (Viviano et al., 2014). At the legislative level, on the other hand, in the second half of the eighties, specific and advanced laws to reduce the phosphorus content in detergent products were promulgated. Maximum allowable percentage of phosphorus was set at 4.5% and subsequently reduced to 1% (Ministerial Decree 413, September 13, 1988) in 1985 and 1989 respectively.

Agriculture is another important source of phosphorus and compared to domestic effluents, it is more difficult to manage due to its diffusive nature (Leinweber et al., 2002). In agricultural soils, phosphorus is mainly concentrated in the first 30 cm depth (Owens et al., 2008). The transfer of phosphorus from soils to aquatic environments depends on a number of physical, chemical and biological features and it is modulated by hydrological factors in turn influenced by physiographic features (e.g., soil texture, vegetation cover, ground slope) and by the amount and intensity of precipitation (Verheyen et al., 2015).

Through the particle settling phosphorus compounds can reach the bed sediments of the water bodies, where they undergo different physical (e.g., diffusion, adsorption), chemical (e.g., coagulation), and biological (e.g., uptake) processes of transformation (Golterman, 2004; Spears et al., 2007; Condron and Newman, 2011), together referred as diagenesis (Turner et al., 2004).

Sediments can maintain a memory of the past contamination. Accordingly the study of deep (e.g., >1m) sediment cores can allow reconstructing the history of contamination and pressure acting on the water body. This approach has been extensively adopted for the study of lakes using different paleolimnological techniques and proxies (Battarbee, 1978; Moss, 1980; Battarbee and Bennion, 2011). In these environments the continuous sedimentation and the high stability of sediments allow to reconstruct past impacts on time scales of the order of centuries (e.g., Battarbee and Bennion, 2011). The higher dynamic of river sediments, instead, often limits the studies to the upper layers (e.g., Viganò et al., 2003; Farkas et al., 2007) with the investigations on the phosphorus content generally oriented to the definition of the bioavailable portion (House and Denison, 2002a; Owens and Walling, 2002; Selig and Schlungbaum, 2002; Banaszuk and Wysocka-Czubaszek, 2005; Sun et al., 2009; Yang et al., 2010). The study of deeper profiles can be performed only when the presence of dams or other barriers slows down the river current velocity and allows a long-term sediment deposition. However, these suitable conditions are infrequent in rivers and consequently analytical records of deep river sediment cores are very rare in the scientific literature. When available these studies cover a period of some decades and generally focus on trace elements (e.g., Meybeck et al., 2007; Le Cloarec et al., 2011) or organic pollutants (e.g., Viganò et al., 2016) whereas no study reporting the phosphorus concentrations in a deep riverine sediment core seems to be currently available.

The objective of this study is to describe the trend of the phosphorus content in a deep sediment core (2.6 m) collected from a deposition area of the highly polluted Lambro River located in Northern Italy downstream of the Milan metropolitan area, one of the most anthropized regions in Europe and upstream of the Po River the main watercourse in Italy. The results have been related to the changes in anthropogenic pressures, to the mitigation policies carried out in the last decades and interpreted on the basis of possible changes in the hydrological river regime.

2. Material and methods

2.1. Study site

The Lambro River basin is characterized by a geological substrate of carbonate origin (Doglioni and Flores, 1997; De Caro et al., 2016) and by a rather complex hydrological network, which drains one of the most anthropized areas in Italy (Viganò et al., 2016). The basin of the Lambro River is part of the Po River basin of which it covers about 6% of the total area (Pettine et al., 1996). The sediment sampling point used in this study (Fig. 1) was located near the municipality of San Zenone al Lambro, about 25 km upstream of the junction of the Lambro River with the Po River and about 20 km downstream of the center of Milan.