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Estimates of Tiber River organophosphate pesticide loads to the Tyrrhenian Sea and ecological risk

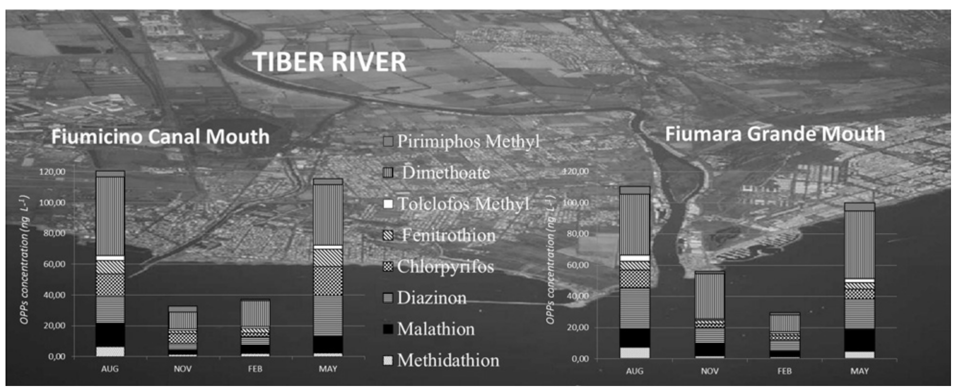
Paolo Montuori [a,*], Sara Aurino [a], Fatima Garzonio [a], Pasquale Sarnacchiaro [b], Salvatore Polichetti [a], Antonio Nardone [a], Maria Triassi [a]

[a] Department of Public Health, University "Federico II", Via Sergio Pansini nº 5, 80131 Naples, Italy
[b] Department of Economics, University Unitelma Sapienza, Viale Regina Elena nº 295, 00161 Rome, Italy

HIGHLIGHTS

- Spatial and temporal distribution of 8 organophosphate pesticides in Tiber River and Estuary were assessed.
- Concentrations were seasonally highly variable.
- All organophosphate pesticides concentrations complied with the Environmental Quality Standards.
- No organophosphate pesticides presented a Risk Quotient higher than unit when using mean values.

GRAPHICAL ABSTRACT



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ABSTRACT

The organophosphate pesticides pollution in the Tiber River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea) were estimated. Eight selected organophosphate pesticides (diazinon, dimethoate, malathion, chlorpyrifos, pirimiphos-methyl, fenitrothion, methidathion, tolclofos-methyl) were determined in the water dissolved phase, suspended particulate matter and sediment samples collected from 21 sites in different seasons. Total organophosphate pesticides concentrations ranged from 0.40 to 224.48 ng L^{-1} in water (as the sum of the water dissolved phase and suspended particulate matter) and from 1.42 to 68.46 ng g^{-1} in sediment samples. Contaminant discharges of organophosphate pesticides into the sea were calculated in about 545.36 kg $year^{-1}$ showing that this river should be consider as one of the main contribution sources of organophosphate pesticides to the Tyrrhenian Sea. In relation to the eco-toxicological assessment, the concentrations of most OPPs in the water and sediments from the Tiber River and its estuary were lower than guideline values.

1. Introduction

During the last decades organophosphate pesticides (OPPs) gained popularity worldwide compared to organochlorine pesticides.

* Corresponding author at: Department of Public Health, University of Naples "Federico II", Via Sergio Pansini nº 5, Naples 80131, Italy.
E-mail address: pmontuor@unina.it (P. Montuori).

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Organochlorine pesticides are persistent and damaging to the environment (Tankiewicz et al., 2011; Zheng et al., 2016; Yu et al., 2016), instead the OPPs break down more rapidly in the environment, have a milder impact and are safer and less persistent. It is estimated that OPPs are worth nearly 40% of the global market and that they are expected to maintain dominance for some time into the future. They are the most popular pesticides and their usage is still growing, mainly because of their low cost, reliability, wide spectrum of applications, multi-pest control capability and lack of pest resistance (Ma et al., 2009; Dujaković et al., 2010; Li et al., 2010; Sapbamrer and Hongsibsong, 2014).

The widespread application of the OPPs has been questioned as a potential risk to human health: they can influence body glucose homeostasis through several mechanisms including physiological stress, allergies and nausea, adverse physiologic effects, oxidative stress, inhibition of paraoxonase, nitrosative stress, pancreatitis, inhibition of cholinesterase, stimulation of the adrenal gland, and disturbance in the metabolism of liver tryptophan (Badrane et al., 2014). Other risks of organophosphate exposure include serious health consequences such as neurobehavioral and cognitive abnormalities, teratogenicity, endocrine modulation, immunotoxicity and compromised cognitive development especially for infants and children reproductive effects, spontaneous abortions, and fetal death. In fact the use of many organophosphate insecticides has been restricted by the Environmental Protection Agency (EPA) of the United States of America in order to prevent health risks (Wang et al., 2009; Epstein, 2014; Ophir et al., 2014; Yu et al., 2016).

As confirmed by numerous studies, the aquatic environment appears to be one of the primary locations for OPPs (Wang et al., 2009; González-Curbelo et al., 2013; Sangchan et al., 2014; Masiá et al., 2015). They are carried from terrestrial sources through various pathways, such as atmospheric and river transports. The input pathways of OPPs into aquatic environment include discharge of agricultural sewage, runoff from non-point sources, and direct dumping of wastes (Vryzas et al., 2009; Tankiewicz et al., 2010; Thomatou et al., 2013; Poulier et al., 2014; Mamta et al., 2015). OPPs represent nowadays the group of compound posing the highest risk for the ecosystem. They are source of contaminants to aquatic biota, because a large portion of the pesticides used in watersheds is rushed into river system and carried into the estuaries. Thus, the assessment of OPPs in aquatic environments is of primary importance as these areas could receive considerable amounts of pollutant inputs from land-based sources through coastal discharges, which could potentially threaten the biological resources (De Lorenzo et al., 2001; Poulier et al., 2014; Dzul-Caamal et al., 2014; Kuzmanović et al., 2015). Nevertheless, few studies evaluated the pollution from organophosphate pesticides in surface waters compared to organochlorine pesticides (Zulin et al., 2002; Fadaei et al., 2012; Assoumani et al., 2013).

Indeed, we chose the Tiber River, the second biggest river in Italy, and its estuary as a case for total OPP pollution and risk evaluation. The Tiber River is the most polluted river among the twenty longest river in Italy (Legambiente, 2006). The Tiber Valley, with a catchment area of 17,375 km^2, is one of the most fertile in Italy thanks to the high quality of the soil and Mediterranean climate. A large portion of the Tiber Valley is devoted to agricultural use which might result in water quality deterioration because of the input of pesticides and fertilizers. In an attempt to estimate the risk organisms and humans could face when exposed to pesticides, the ecological risk assessment of this river is carried out.

Ecological risk assessment is a technique applied to evaluate the undesirable impacts caused by the environmental pollutants in an ecological system; in particular, the Risk Quotient (RQ) is one general assessment approach to characterize ecological risk from OPPs in waters. RQ of selected pesticides is calculated using the ratio of the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC) (Palma et al., 2014).

This study is part of a large project aimed at contributing to the knowledge of the pollution affecting the Tiber River and its environmental impact on the Tyrrhenian Sea. The purpose of this project is to assess the pollution due to effluents from local industries, agriculture and the urban impact by identifying several groups of organic and inorganic chemical and some indicators of microbial pollution in water and sediments. This paper reports the data on the distribution pattern and potential impact of OPPs in Tiber River system and its estuary and assesses the ecological risk to human health risk.

2. Materials and methods

2.1. Study area

The Tiber River rises in the Apennine Mountains (Central Italy) and, with a length of 409 km, passes through the city of Rome before flowing into the Tyrrhenian Sea by two mouths, Fiumara Grande and Fiumicino Canal, with an annual mean flow rate of 230 $m^3\ s^{-1}$. Rome, a city rich in history with 2,863,322 inhabitants, has an ancient agricultural tradition that is still the main resource for the socio-economic development. Indeed, with 37,000 ha of Utilized Agricultural Surface (SAU), Rome is the largest agricultural district in Europe (Minissi and Lombi, 1997; ISTAT, 2014). The climate of the area is characterized by Mediterranean climate with warm and dry summers (from July to August) and relatively wet and mild winters. The rainy season is from autumn to spring. The hydrology of the basin is highly influenced by the intense rainfall at the upstream part that causes frequent floods in the downstream areas (Fiseha et al., 2014).

2.2. Pesticides investigated

The last Italian agriculture census (Italian Statistical Institute, 2010, ISTAT) reports that the main crops in the Tiber River basin are fruit and vegetables (such as cereals and potatoes), vineyards, olive and tobacco. The intensive agricultural activities might result in water quality deterioration due to the usage of pesticides and fertilizers. In particular, the most widely used pesticides in the Tiber flatland are organophosphate pesticides, such as chlorpyrifos and dimethoate, with 62.50 and 72.27 t annual sold (database of the National Agricultural Information System, 2012, SIAN), which are consistent with the main crops of the area. With the exception of chlorpyrifos and dimethoate, in this study the others OPPs investigated (diazinon, malathion, pirimiphos-methyl, fenitrothion, methidathion and tolclofos-methyl) were selected according to the last Italian agriculture census by ISTAT (2010) and the current EU regulations, such as the Water Framework Directive (WFD) (EC, 2000). Also, the current literature was considered to select the pesticides to be monitored (Bonansea et al., 2013; Kanzari et al., 2014; Cruzeiro et al., 2015; Ccanccapa et al., 2016; Zheng et al., 2016). Therefore, the distribution pattern and potential impact of the following OPPs in Tiber River system and its estuary were investigated: diazinon, dimethoate, malathion, chlorpyrifos, pirimiphos-methyl, fenitrothion, methidathion and tolclofos-methyl.

2.3. Sampling

Considering the seasonal variations of the Tiber flow and in the attempt to asses temporal trends of pollutants, four intensive sampling campaigns have been conducted in the summer, autumn, winter and spring of 2014–2015. In each campaign three locations were sampled (before and after the fork in the river) in order to have a proper idea of the evolution of the contamination downriver (Fig. 1). In addition, nine points in the continental shelf around the Tiber artificial mouth (Fiumicino canal) and other nine points in the continental shelf around the Tiber natural mouth (Fiumara Grande)were sampled in each campaign to assess the environmental impact of the Tiber River on the Tyrrhenian Sea (Fig. 1). Three points were sampled 500 m from the