



Review

Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy



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HIGHLIGHTS

- The occurrence of 298 EOCs in Italian surface water and groundwater has been reviewed.
- Data reveals a serious contamination by EOCs of a number of Italian water resources.
- Contamination of SW and GW in Southern Italy is poorly or not at all characterized.
- Pesticides, industrials and pharmaceuticals were detected in the highest concentrations.
- Future EOC studies should be prioritized based also on results of similar reviews.

ARTICLE INFO

Article history:

Received 11 December 2013

Received in revised form 6 February 2014

Accepted 11 February 2014

Available online 4 March 2014

Keywords:

Emerging organic contaminants

Surface-groundwater

Pesticides

Industrials

Pharmaceuticals

Estrogens

ABSTRACT

This paper provides the first review of the occurrence of 161 emerging organic compounds (EOCs) in Italian surface water and groundwater. The reported EOCs belong to the groups of industrials, pharmaceuticals, estrogens and illicit drugs. Occurrence of 137 pesticides was also reported. The reviewed research works have been published between 1997 and 2013. The majority of the studies have been carried out in Northern Italy (n. 30) and to a lower extent in Central Italy (n. 13). Only a limited number of research studies report EOC concentrations in water resources of Southern Italy. The EOCs that have been more frequently studied are in the following descending order, pesticides (16), pharmaceuticals (15), industrials (13), estrogens (7) and illicit drugs (2). Research activities investigating the EOC occurrence in surface water are more numerous than those in groundwater. This is consistent with the higher complexity involved in groundwater sampling and EOC detection. Among the reported EOCs, industrials and pesticides are those occurring in both surface water and groundwater with the highest concentrations (up to 15×10^6 and 4.78×10^5 ng L⁻¹, respectively). Concentrations of pharmaceuticals in surface water reach a maximum of 3.59×10^3 ng L⁻¹, whereas only the antimicrobial agent josamycin has been encountered in groundwater with a concentration higher than 100 ng L⁻¹. Both estrogens and illicit drugs appeared in surface water with concentrations lower than 50 ng L⁻¹. Groundwater concentrations for estrogens were measured to be below the detection limits, whereas illicit drugs have so far not been studied in groundwater. The present review reveals the serious contamination status of Italian surface water and groundwater especially by pesticides, industrials and to a lower extent by pharmaceuticals and the necessity to foster the research on EOC occurrence in Italian water resources, in particular in Southern Italy where a limited number of investigations currently exist.

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Contents

1. Introduction	281
2. Overview of geographical distribution in Italy of the research studies	281
3. Occurrence of EOCs in surface water and groundwater of Italy	283
3.1. Pesticides	283
3.1.1. Review of published research studies on pesticides	283
3.1.2. Occurrence	284

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3.2.	Industrials	285
3.2.1.	Review of published research studies on industrials	285
3.2.2.	Occurrence	286
3.3.	Pharmaceuticals	286
3.3.1.	Review of published research studies on pharmaceuticals	286
3.3.2.	Occurrence	288
3.4.	Estrogens	289
3.4.1.	Review of published research studies on estrogens	289
3.4.2.	Occurrence	289
3.5.	Illicit drugs	290
3.5.1.	Review of published research studies on illicit drugs	290
3.5.2.	Occurrence	290
4.	Relating EOC physico-chemical properties to their environmental occurrence	290
5.	Discussion	292
6.	Conclusions	293
	Acknowledgments	293
	References	293

1. Introduction

The rapid population growth and the increment of agricultural and industrial activities result in an increased water demand and wastewater production. Consequently, water resources are increasingly exposed to contamination by many sources such as leakage from sewer networks and septic tanks, application of fertilizers on agricultural fields, intentional or inadvertent waste disposals, discharges of wastewater effluents, and urban and rural storm water run-off (Slack et al., 2005; Osenbrück et al., 2007; Barnes et al., 2008). In recent years, a large number of microorganic contaminants have been encountered worldwide in surface and ground water (Swartz et al., 2006; Godfrey et al., 2007; Barnes et al., 2008; Kasprzyk Hordern et al., 2008; Peng et al., 2008; Strauch et al., 2008; Loos et al., 2009, 2010; Reinstorf et al., 2009; Teijon et al., 2010; Valcárcel et al., 2011; Cabeza et al., 2012; Meffe et al., 2013). The presence of these xenobiotic substances raises concern especially when water is used for drinking water production. Among the microorganic contaminants, there are those referred as “emerging organic contaminants” (EOCs). EOCs are defined as natural or synthetically occurring substances that are not commonly monitored in the environment but that can induce known or suspected undesirable effects on humans and ecosystems (Stuart et al., 2012). EOCs are not necessarily newly developed compounds; they may have been present in the environment for long time but their presence and implication for the environment's integrity are only recently recognized (Daughton, 2004). The advances in analytical techniques result in the detection of EOCs at very low concentration in water samples (Richardson and Ternes, 2011). EOCs include different chemical classes of pollutants such as disinfectants, industrials, pharmaceuticals, detergents, personal care products, and “life-style compounds” and the list of EOCs is expected to expand with the development of new analytical methods for their detection. In the European context, surface water and groundwater quality standards are regulated under the Water Framework Directive (EC, 2000), the Groundwater Daughter Directive (EC, 2006) and the Directive 2008/105/EC (EC, 2008). These directives require monitoring of “priority” organic contaminants in the aquatic environment such as certain pesticides and their degradation products, chlorinate solvents, polycyclic aromatic hydrocarbons, disinfection by products, volatile organic compounds and biocides (Lapworth et al., 2012). However due to the lack of information on toxicity and environmental impacts, a large number of contaminants, especially organic compounds, are not included in the list of chemicals to be monitored. The number of compounds that are currently regulated by the legislation is therefore likely to grow. Although EOC concentrations encountered in the environment are quite low, ranging between ng L^{-1} and $\mu\text{g L}^{-1}$, a continuous exposure of the aquatic communities may result in potentially harmful effects. This is especially true for pharmaceutical compounds that are specifically designed to regulate

endocrine and immune systems and that have therefore potential consequences as endocrine disruptors (Daughton and Ternes, 1999). An additional concern is related to the effects that mixtures of EOCs can have on the aquatic biota (Daughton and Ternes, 1999).

In recent years, there have been a number of reviews dealing with the occurrence at national, European and worldwide scale of a vast array of EOCs in fresh water resources. These studies investigated the presence of EOCs in surface water (Murray et al., 2010; Pal et al., 2013) and in groundwater (Jurado et al., 2012; Lapworth et al., 2012; Stuart et al., 2012). None of these reviews report concentrations of EOCs in Italian water resources. To the best of our knowledge, the only existing work on the occurrence of EOCs in Italian environment has been provided by Zuccato et al. (2006). In their paper, Zuccato et al. (2006) presented a reconnaissance study of some pharmaceuticals in surface water, drinking water and effluents of wastewater treatment plants (WWTPs). Therefore, the present paper intends to furnish a comprehensive overview of the occurrence of a number of EOCs (including pesticides) in Italian surface water and groundwater which is not available in the literature. We aim at identifying those contaminants that represent a major concern for Italian water resources. Furthermore, we wish to recognize the areas which have so far not being the subject of investigation and where therefore more studies are particularly needed. The EOCs reviewed in this work belong to the classes of pharmaceuticals, estrogens, industrials and illicit drugs. Pesticide concentrations have also been addressed in this review. In the following, we will refer to EOCs including the class of pesticides.

2. Overview of geographical distribution in Italy of the research studies

This study reviews 47 articles that have been published between 1997 and 2013 and reported concentrations of 298 EOCs (including pesticides) in Italian surface water and groundwater (Table A1). Fig. 1a–e shows the distribution and number of studies concerning EOCs in both surface water and groundwater considered in this paper. Compared to other European countries (England, Germany, Spain), the studies of the occurrence of EOCs in Italian aquatic environment are rather scarce. This holds true especially for studies in groundwater. The majority of the research activities have been carried out in Northern Italy (Fig. 1a–e). The most frequently investigated river is the Po River, the longest surface water course of Italy (652 km) with an average flow rate at its mouth of $1540 \text{ m}^3 \text{ s}^{-1}$. The Po River has a wide watershed ($71,000 \text{ km}^2$) where most of the agricultural and industrial activities of the country are located. However, only industrial contaminants have been investigated in Po River tributaries covering a vast area of its watershed (Fig. 1b). Tiber River, the main river of Central Italy, has been often investigated to determine the occurrence of all the EOC

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