International Journal of Hygiene and Environmental Health xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Hygiene and Environmental Health

journal homepage: www.elsevier.com/locate/ijheh

Monitoring emerging contaminants in the drinking water of Milan and assessment of the human risk

Francesco Riva[a,*], Sara Castiglioni[a,*], Elena Fattore[a], Angela Manenti[b], Enrico Davoli[a], Ettore Zuccato[a]

[a] IRCCS–Istituto di Ricerche Farmacologiche "Mario Negri", Department of Environmental Health Science, Via La Masa 19, 20156, Milan, Italy
[b] Metropolitana Milanese S.p.A., Area Acquedotto, Via Giuseppe Meda 44, 20141, Milan, Italy

ARTICLE INFO

Keywords:
Drinking water
Emerging contaminants
Mass spectrometry
Human risk assessment
Hazard index

ABSTRACT

Emerging Contaminants (ECs) are ubiquitous in waters, arousing concern because of their potential risks for human health and the environment. This study investigated the presence of multiple classes of ECs in 21 wells over the drinking water network of Milan, in the most inhabited and industrialized area of Italy, and assessed the risks for consumers. Samples were analyzed using liquid chromatography coupled to mass spectrometry. Human risk assessment (HRA) was conducted by comparing the measured concentrations with drinking water thresholds from guidelines or calculated in this study; first considering the exposure to each single EC and then the entire mixture. Thirteen ECs were measured in the low ng/L range, and were generally detected in less than half of the wells. Pharmaceuticals, perfluorinated substances, personal care products, and anthropogenic markers were the most frequently detected. The results of the HRA excluded any risks for consumers in each scenario considered. This is one of the most comprehensive studies assessing the presence of a large number of ECs in the whole drinking water network of a city, and the risks for human health. Results improve the limited information on ECs sources and occurrence in drinking water and help establishing guidelines for regulatory purposes.

1. Introduction

The number of emerging contaminants (ECs) widespread in the aquatic compartment is growing continuously (Richardson and Kimura, 2016) arousing concern mainly because of potential risks for human health and the environment (Glassmeyer et al., 2017). Recent studies have identified a wide array of chemicals in surface and groundwater belonging to different classes, such as pharmaceuticals and hormones, illicit drugs, pesticides, personal care products, artificial sweeteners, perfluorinated compounds, disinfection byproducts, UV filters and other industrial chemicals which have been detected in the ng/L–μg/L range (Kasprzyk-Hordern et al., 2008; Lapworth et al., 2012; Petrovic et al., 2004; Richardson and Kimura, 2016; Zuccato and Castiglioni, 2009). The pathways through which these pollutants enter surface waters are well known and the main contributions are from effluents of wastewater treatment plants, where some residues are not removed, and from agricultural and industrial activities. Contacts and exchanges between the aquifers, rivers and sewage networks, and leaching from agricultural fields, can cause the contamination of shallow and deep groundwater (Buerge et al., 2009; Lapworth et al., 2012).

ECs may be a significant problem when surface and groundwater are used for drinking water production because the conventional drinking water treatments, like treatment with active carbon, flocculation, and disinfection, are not specifically designed to remove these micropollutants (Benotti et al., 2009; Simazaki et al., 2015; Stackelberg et al., 2004; Vulliet et al., 2011). Traces of ECs in drinking water were actually measured and reported in only a few studies (e.g. Leung et al., 2013; Rodil et al., 2012; Valcárcel et al., 2011; Zuccato et al., 2000), and the spatial and temporal variability of the majority of ECs in the environment is still poorly understood (Lapworth et al., 2012).

Most of the compounds in the Fourth Contaminant Candidate List (CCL4) (U.S. EPA, 2016) are pesticides or industrial chemicals which are currently not subject to national primary drinking water regulations, but are known to occur in public water systems, with potential human health effects associated with chronic exposure. Most ECs are currently not included in the legislation for drinking water, e.g., the Guideline for Drinking-water Quality (WHO, 2011) and the Drinking Water Directive – Council Directive 98/83/EC – (EC, 1998), mostly because there is not enough information on toxicity, impact, behavior and monitoring data to establish threshold values. Few agencies have dealt with this or proposed methods for establishing provisional safety levels, also known as Drinking Water Guideline Levels (DWGLs), based

* Corresponding authors at: Department of Environmental Health Sciences, IRCCS–Istituto di Ricerche Farmacologiche "Mario Negri&rdquo Via La Masa 19, 20156, Milan, Italy.
E-mail addresses: francesco.riva@marionegri.it (F. Riva), sara.castiglioni@marionegri.it (S. Castiglioni).

https://doi.org/10.1016/j.ijheh.2018.01.008
Received 8 September 2017; Received in revised form 9 January 2018; Accepted 12 January 2018
1438-4639/

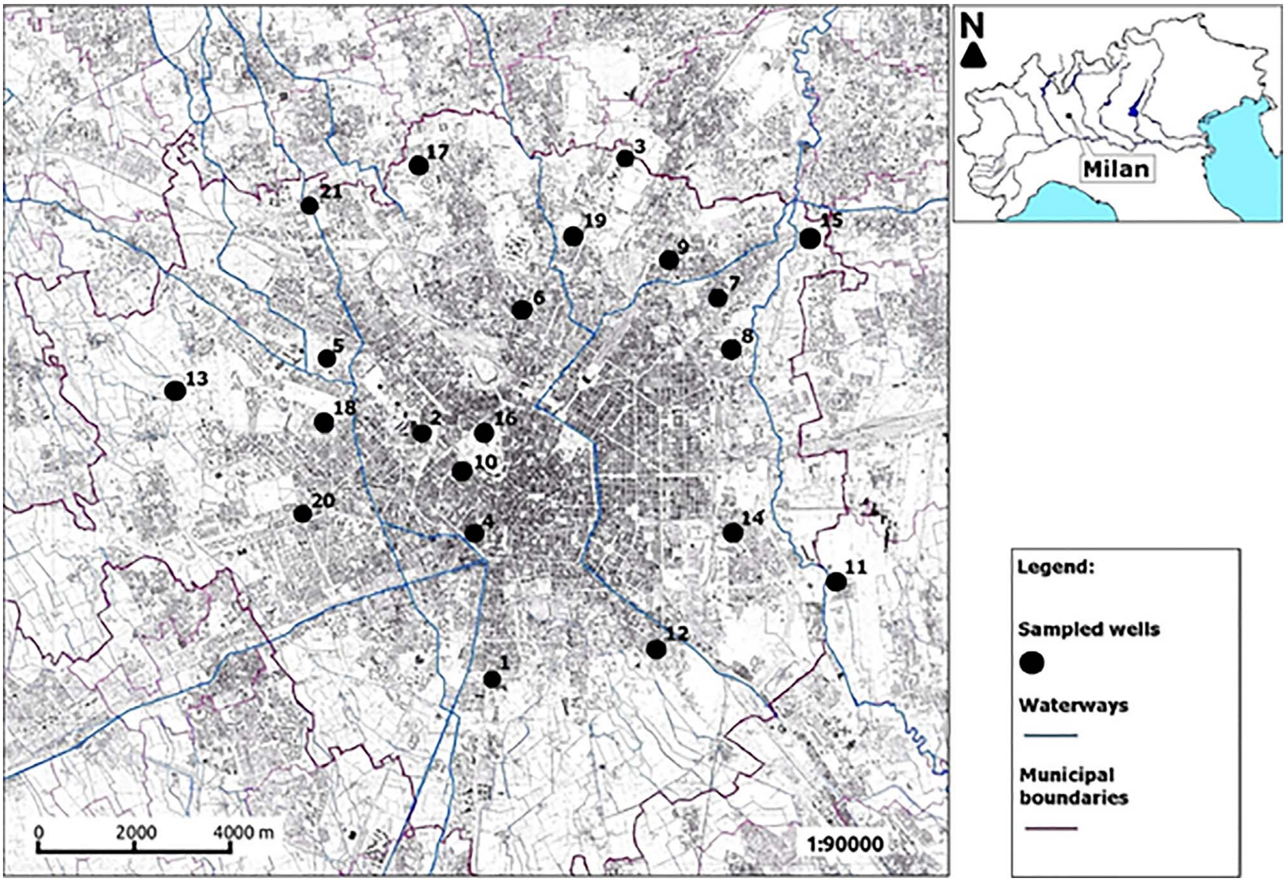

Fig. 1. Location of the 21 wells investigated in the city of Milan.

on chronic mammalian toxicity data or following the Threshold of Toxicological Concern concept (AwwaRF, 2008; Environment Protection and Heritage Council, Natural Resource Management Ministerial Council, 2008; IL-EPA, 2008; WHO, 2011).

In previous studies from our group, the occurrence, sources, and fate of several classes of ECs (i.e. over 80 ECs among pharmaceuticals, personal care products, disinfectants, illicit drugs, perfluorinated substances, alkylphenols, plasticizers and anthropogenic markers) were studied in the most urbanized and industrialized area in Italy, the river Lambro basin (Castiglioni et al., 2018, 2005; Palmiotto et al., 2018) and in the subsoil of the city of Milan. Under the city the groundwater is divided into three aquifers, separated by low permeability layers. The first aquifers reach 40 m and the second extends from 40 to 100 m. The water tables of these two levels are often connected. The third aquifer, separated by silts and clays, contains the deepest water tables and is located between 100 and 200 m of depth. The water for human consumption is taken from the last two aquifers.

The environmental risk was assessed in the catchment area of the Lambro river and in the untreated groundwater of the city of Milan using, respectively, the concentrations of ECs in surface and ground waters (Castiglioni et al., 2018, 2005; Palmiotto et al., 2018).

These studies revealed a complex pollution picture of the waterways, and the contamination of the upper layers of the groundwater was highest in correspondence of the main rivers flowing through the city (Lambro in the west, and Seveso and Olona in the north-east) suggesting a possible contribution of surface waters to the contamination. This was potentially worrying because the deeper layers of groundwater are the main source of drinking water in Milan.

The main purposes of this study were 1) to quantify multiple classes of ECs selected during previous investigations in drinking water samples collected after the drinking water treatments in the entire drinking water network of Milan; 2) to evaluate the risk associated with exposure to these substances in the waterways by making a Human Risk Assessment (HRA) for consumers.

2. Experimental

2.1. Sampling and analysis

Drinking water was sampled in collaboration with the company that manages the integrated water service in Milan (Metropolitana Milanese S.p.A.). The technical staff collected groundwater after the drinking water treatments, which mainly consisted of active carbon filters or reverse osmosis, aeration towers, and disinfection. Samples (2 L) were taken from 21 wells among the 29 spread throughout the city (Fig. 1), and stored in polypropylene bottles at −20 °C until analysis. Over 80 anthropogenic pollutants were measured from different classes of pharmaceuticals, personal care products, disinfectants, illicit drugs, perfluorinated substances, alkylphenols, plasticizers and anthropogenic markers (Table 1).

In view of the heterogeneity of the substances, different analytical methods, were used as described elsewhere. Illicit drugs and pharmaceuticals were analyzed updating already published methods (Castiglioni et al., 2005, 2006). A novel method was developed for perfluorinated compounds (Castiglioni et al., 2015) and personal care products (Palmiotto et al., 2018), and specific analytical methods were developed adapting already published methods for anthropogenic markers (Senta et al., 2015) and alkylphenols (Maggioni et al., 2013). Briefly, 500 mL of samples were filtered on glass microfiber filters GF/A 1.6 μm (Whatman, Kent, UK) and on mixed cellulose ester microfiber filters ME25 0.45 μm (Whatman, Kent, UK) and were solid-phase extracted by Oasis MCX and HLB 60 mg cartridges (Waters Corp., Milford,