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Electrical conductivity and emerging contaminant as markers of surface freshwater contamination by wastewater

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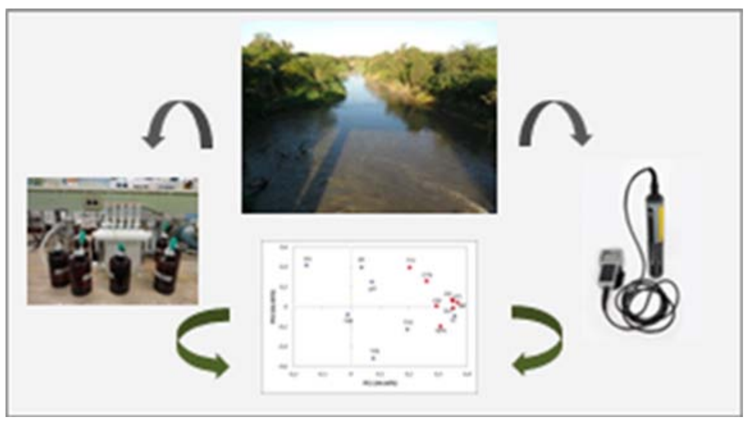
HIGHLIGHTS

- Emerging contaminants as markers of wastewater contamination
- Linear correlation between electrical conductivity and pharmaceutical products
- Principal component analysis as a tool for the identification of polluted sites
- Unambiguous anthropogenic pollution markers

GRAPHICAL ABSTRACT



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ABSTRACT

The use of chemical markers of undoubted anthropogenic sources for surface freshwater contamination by wastewaters was evaluated employing correlations observed between measured physico-chemical parameters as the electrical conductivity and the concentration of different emerging organic compounds. During the period from April/2011 to April/2012 spatial–temporal variations and contamination patterns of two rivers (Piraí and Jundiaí rivers), São Paulo state, Brazil were evaluated. Seven physico-chemical parameters and concentrations of different classes of emerging contaminants were determined in samples collected in seven field campaigns. The high linear correlation coefficients obtained for the compounds diclofenac ($r = 0.9085$), propanolol ($r = 0.8994$), ibuprofen ($r = 0.8720$) and atenolol ($r = 0.7811$) with electrical conductivity, also corroborated by principal component analysis (PCA), point to the potential use of these compounds as markers of investigated surface water contamination by wastewaters. Due to specific inputs, these environmental markers showed very good effectiveness for the identification and differentiation of water body contamination by discharges of treated and untreated urban sewage.

1. Introduction

The contamination of aquatic ecosystems with discharges of treated and/or non-treated wastewaters is a historical challenge to civilization (Schwarzenbach et al., 2010). The changes in the environmental context

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caused by the strong development in the economic activities and urban growth have been assigned as one of the main effects on the acceleration of the water resource degradation. Regions with high industrialization and strong demand for water for multiple use often present water quality and availability problems.

Usually, wastewater treatment plants (WWTP) are designed aiming at the removal of solids, dissolved organic matter and nutrients, whereas specific classes of chemical compounds are not always targeted in the treatment systems. Among these compounds there are the emerging contaminants, which include those of different classes such as pharmaceuticals, steroids, hormones, personal care products, flame retardants, drugs of abuse, and others (Daughton and Ternes, 1999; Kolpin et al., 2002). These compounds have been of great environmental concern which has encouraged the development of an increasing number of studies and publications which have appeared in the current literature.

Many of these substances, obeying their degradation characteristics, have presented a regular and constant consumption pattern giving them behavior of pseudo-persistence in the environment (Daughton, 2002). These contaminants have been detected in a wide variety of matrices that include environmental matrices as surface water and groundwater (Grujic et al., 2009 and Yoon et al., 2010) wastewater (Lacey et al., 2008 and Yu et al., 2011) soils and sediments (Tadeo et al., 2012; Xu et al., 2008) and biological materials (Fick et al., 2010; Gelsleichter and Szabo, 2013; Subedi et al., 2012). The concentration values detected in these matrices are currently measured using the LC–MS/MS technique that allows the use of these compounds as chemical markers of effluent discharge from domestic waste.

Among a wide range of compounds, caffeine has been one of the most studied compounds and most frequently indicated as a good chemical marker of anthropogenic contamination of surface waters by wastewaters, mainly due to its correlation of average per capita consumptions (Buerge et al., 2003; Buerge et al., 2006), microbiological markers (Kurissery et al., 2012; Peeler et al., 2006), and nitrate (Seiler et al., 1999). Currently, other emerging contaminants as human pharmaceuticals have been studied as potential indicators of contamination by the discharge of domestic sewage (Clara et al., 2004; Gasser et al., 2010; Gasser et al., 2011; Vystavna et al., 2012; Young et al., 2008).

More recently artificial low-calorie sweeteners have been pointed as good markers of wastewater contamination (Harwood, 2014; Robertson et al., 2013). The presence of these substances in the environment is associated with sewage discharges, due the poor alteration by the human metabolism, after their ingestion and persistence in the environment. Buerge et al. (2009) verified the presence of four sweeteners in different matrices, such as wastewaters, surface waters, groundwater and drinking waters, in the Switzerland regions. This study demonstrated the potential use of the acesulfame-K as a marker. Similar results concerning acesulfame-K and sucralose were reported by Scheurer et al. (2009) in Germany.

As markers of pollution, pharmaceuticals and other emerging contaminants are more effective than microbiological markers as the chemical analyses are time consuming and do not discriminate between human and animal sources of contamination. An ideal marker should promote the identification of the kind of contamination source and the degree of pollution. In this context, the electrical conductivity has been investigated as a marker of pollution by wastewater discharges (Chalupová et al., 2012; Stewart, 2001; Thompson et al., 2012). The electrical conductivity measurement by itself is useful in providing a screening of the pollution level but, when in association with emerging contaminant concentrations, can provide unambiguous information about anthropogenic sources of contaminant discharges.

In the present study the occurrences and concentrations of 11 emerging contaminants, including caffeine, were studied aiming at the evaluation of the potential of these compounds as chemical markers of surface water contamination by wastewaters. To investigate this hypothesis, these compounds were analyzed in surface waters during a period of one year of sampling totaling 7 campaigns in the abovementioned rivers. Concentration values of these chemical compounds and physico-chemical characteristics were also evaluated by principal component analysis seeking correlations between measured emerging contaminant concentrations and their occurrence and classical pollution indicators like electrical conductivity.

2. Experimental

2.1. Sampling area

Located within the metropolitan region of São Paulo and Campinas city, the Jundiaí River Basin, with its 1.114 km^2, is characterized by water scarcity as a result of high urban density and intense industrial activities in the region. This watershed is also impacted by the discharge, into the water bodies, of treated and untreated domestic and industrial wastewaters generated by about 1 million of inhabitants. Description of the sampling site locations is presented in Table 1. Samplings were carried out during the months of April/2011 to April/2012, every two months (7 different dates). For the analysis of emerging contaminants, a total of 42 samples were collected from two sites along the Piraí River (Sites S1 and S2) and four sampling sites along the Jundiaí River (Sites S3–S6). These sampling sites are illustrated in Fig. 1.

Sites S1 and S2 are considered low pollution degree areas belonging to a relatively clean water body used as a water source for public supply. From Site S3 up to Site S6, the pollution level increases from a relative medium pollution level in Site S3 that evolves into Sites S4 and S5, until a high degradation level at Site S6. The last three sites are in regions of high degree of pollution and intensive industrial activity. The river mouth region, located in the city of Salto (São Paulo state), represents the zone with the worst water quality of all the extension of the Jundiaí River.

The pollution degree of rivers in the São Paulo state is evaluated on the basis of periodic monitoring of several physical, chemical and microbiological parameters in different sampling sites. Results are published by the Environmental Company of the São Paulo state (CETESB) in annual reports including water quality indices for the different aquatic ecosystems (São Paulo, 2013). Nationally, the National Council of Environment (CONAMA) makes a similar work and in both evaluations, the Jundiaí River is classified in the worst possible pollution level.

2.2. Determination of physico-chemical parameters

The physico-chemical parameters were monitored using a multiparameter probe model YSI 6820 V2-2 (Yellow Springs, Ohio, USA). Electrical conductivity (EC), dissolved oxygen (DO), turbidity (TRB), pH, temperature (TPR) and redox potential (RP) were also determined in this study as potential chemical markers, all being determined as in situ parameters during the monitoring period. Total organic carbon (TOC) was performed by a Shimadzu TOC-L CPH/CPN analyzer (Tokyo, Japan).

Table 1
Description of the sampling sites and their geographical location coordinates.

Sampling site	Description	Location	Latitude (S)	Longitude (O)
S1	Piraí River	Near the river source, Itupeva	23.26201°	−47.05790°
S2	Piraí River	Near the river mouth, Indaiatuba	23.18542°	−47.23906°
S3	Jundiaí River	Campo Limpo Paulista	23.20717°	−46.78303°
S4	Jundiaí River	Downstream WWTP, Jundiaí	23.14015°	−47.03800°
S5	Jundiaí River	Industrial district, Indaiatuba	23.13860°	−47.21755°
S6	Jundiaí River	River Mouth, Salto	23.21055°	−47.29176°