EVALUATION OF EMERGING POLLUTANTS IN A MEXICAN RIVER

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ABSTRACT

The accelerated growth of the human population and its activities have produced an increased and unbalanced consumption and discharges of wastewater, causing increases in the release of contaminants, favoring the degradation of water quality and causing health, socio-economic and ecological problems. The basin of the Río Apatlaco, is an example of such problem since it is one of the most polluted river basins in central Mexico. The aim of this study was to evaluate water and sediment qualities in Río Apatlaco and its tributaries, with emphasis on emerging contaminants that are deposited in bottom sediments of the river. To assess the sediment quality on this river, 11 samples, were obtained along the river during two sampling events, including sites located upstream from metropolitan and industrial areas. Water and sediment samples were characterized and semi-volatile organic contaminants (SVOC) identified. It was found that quality of the Río Apatlaco water is acceptable in the highest part of the watershed, and this is reduced without improving further downstream. The results of analysis of water suggest that the pollution observed in the Río Apatlaco comes from anthropogenic activities. The contents of organic matter in sediments varied between medium, high and very high suggesting favorable conditions for the accumulation of hydrophobic pollutants [24]. A total of 596 SVOC were identified, and sediment samples collected downstream from the metropolitan area contained larger numbers of SVOC, that could be classified as hydrocarbons, carboxylic acids, benzene derivate, polycyclic hydrocarbons, pesticides, and residues pharmaceutical, cosmetic, and food products industries, that are abundant in the Río Apatlaco basin.

Keywords: Emerging contaminants, Semi-volatile Organic Compounds, Río Apatlaco, Sediment.

INTRODUCTION

Among pollutants that are discharged to water bodies, there are those regulated by environmental authorities around the world due to their known toxicities and persistence. However, most substances discharged to water bodies are still unregulated. These substances are known as emerging pollutants and these may produce negative effects on aquatic life and human health. Because of the limited information available on emerging pollutants in environmental systems, it is difficult to predict their transport and accumulation in aqueous systems [1]. Nevertheless, it has been found that several of these pollutants alter hormonal activity in humans and aquatic life and are suspected of contributing to the development of neurodevelopmental problems and behavioral, reproductive abnormalities, metabolic disorders and cancer [2], [3].

Negative effects of emerging pollutants are not necessarily related to their persistence, but rather to their continuous introduction in the environment, where they may be transformed and removed at even relatively high rates [4]. In addition, these contaminants may be found in all environments because they are essential materials for production systems such as pharmaceutical, cosmetics, steroids and hormone industries, fuel additives, raw materials and by products in the food and pesticide industries and uses.

The Río Apatlaco basin, located in the state of Morelos, Mexico, is not exempt from this problem as it receives municipal, agricultural and industrial discharges. The Strategic Plan for Recovery of the Río Apatlaco basin [5] indicates that this watershed is one of the most polluted in central Mexico.

The aim of this study was to evaluate water and sediment qualities in the Río Apatlaco, and to identify the presence of emerging pollutants in sediment samples from the river and its tributaries.

Study Area

The Río Apatlaco basin is located between the geographical coordinates 19°13´24´´ and 18°36´00´´N, 99°09´55´´ and 99°21´11´´W. It has an area of 765 km^2 and is drained by the Río Apatlaco, which has a length of 63 km. Along its course, the Río Apatlaco passes through metropolitan areas with a total population of 850,000 inhabitants [6]. In 2001, there existed over 2,000 wastewater discharges throughout the river basin [7].

The main land use in the Río Apatlaco basin is forest, mainly located in the upper part of the river basin, and occupies 32.5% of the area, followed by the cultivated areas that occupies 31% of the area of the river basin. Meanwhile, grasslands and urban areas occupy 18.5 and 17.9% of the basin, respectively (Fig. 1).

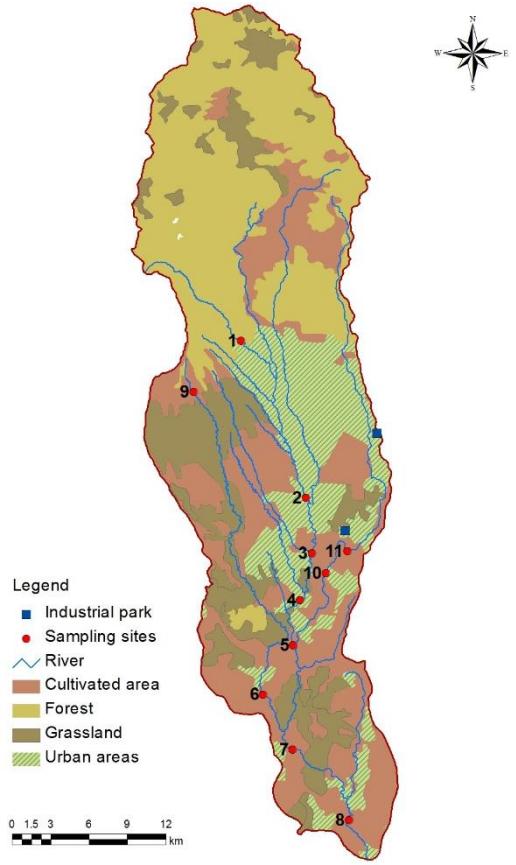

Fig. 1 Soil uses and sampling sites in the Río Apatlaco basin

Seventy five percent of industrial activities in the state of Morelos and part of an irrigation district are located in this river basin [8]. The irrigable area is 2,985 ha. Industrial activities in the basin are located in two industrial parks with 150 and 20 companies, respectively (Fig. 1), with different productive activities, such as pharmaceutical, chemical, food, cosmetics, and petrochemical [5].

METHODS

Samples were obtained at 11 sites, 7 located in the Río Apatlaco, and 4 in tributaries (Fig. 1). In the Río Apatlaco, one site (sampling site 1, Fig. 1) is located upstream from anthropogenic activities and urban areas (background site); three sites are downstream from urban areas (sampling sites 2, 3 and 4, Fig. 1); One site is located where the river converges with the tributary from industrial parks and urban areas (sampling site 5, Fig. 1). Finally, two sites are located downstream from the metropolitan area, in agricultural and grassland zones with low population density (sampling sites 6 and 7, Fig. 1).

In tributaries, one site is located upstream from anthropogenic activities and urban areas (sampling site 9, Fig. 1); two sites are downstream from urban and industrial areas (sampling sites 10 and 11, Fig. 1); and one sites are located downstream from the metropolitan area, in agricultural and grassland zones with low population density (sampling site 6, Fig. 1).

Two sampling events were conducted, the first during the rainy season (September 2012) and the second in the dry season (February 2013). Water samples were obtained during each sampling event, collecting the water samples in the center of the river watercourse.

At each site, water samples were obtained for analysis of total alkalinity, true color, biochemical oxygen demand at 5 days (BOD_5), fecal coliforms, nitrite nitrogen ($N\text{-}NO_2$), total nitrogen (N_T), phosphates phosphorus ($P\text{-}PO_4$), total phophorus (P_T), total hardness, aluminum (Al), manganese (Mn) and iron (Fe) (Table 1).

Table 1 Analytical methods for analysis of water samples

Parameter	Analytical method	Preservation method
Alkalinity	Tritation **[9]**	Stored over ice and in the dark
$N\text{-}NO_2$	Spectrophotometry **[10]**	
Color	Colorimetry **[11]**	
BOD_5	Microbiological incubation **[12]**	
Fecal coliforms	Microbiological incubation **[13]**	
N_T	Merck N 14537 **[14]**	
$P\text{-}PO_4$	Merck P 14848 **[14]**	
P_T	Merck P 14543 **[14]**	
Hardness	Visual method **[15]**	Ultrapure HNO_3 (Baker) pH<2, stored over ice and in the dark
Aluminium	Merck Al 14825 **[14]**	
Manganes	Merck Mn 14770 **[14]**	
Iron	Merck Fe 00796 **[14]**	

A Hydrolab DS5 probe was used for measurement of field parameters such as temperature, pH, turbidity, electrical conductivity, dissolved oxygen, salinity, chloride, ammonium nitrogen ($N\text{-}NH_4$) and nitrate

nitrogen (N-NO3), redox potential, and total dissolved solids.

Sampling results were analyzed with respect to the Mexican limits defined for the following water uses [16]: water supply, agricultural irrigation and protection of aquatic life. Besides, water of Río Apatlaco was classified according to concentrations of P_T and the limits set by OECD [17]

Sediment samples were obtained at each sampling site, in areas of low flow velocity [18], [19]. Sediment samples were stored in glass containers, previously cleaned with HPLC grade dichloromethane, and stored over ice and in the dark. Once in the laboratory pH, organic matter contents [20] and textures [21] were determined. Additionally, semi-volatile organic compounds (SVOC) were identified by gas chromatography (Varian CP-3800) followed by detection with mass spectrometer (Varian Saturn 2200) according to EPA method 8270C [22] in samples from the second sampling event.

Subsequently, using the Chemical Abstract Services databases (CAS), SVOC were classified according to their chemical group and their uses, [23].

RESULTS AND DISCUSSION

The results indicate that water of Río Apatlaco is not proper for use for water supply, agricultural irrigation or for protection of aquatic life. This is due to these water exceed the limits established in Mexicans regulations for fecal coliform and concentrations of manganese and aluminum [16] (Fig. 2 - 4). These results indicate that exist a negative effect of wastewater discharges on water quality.

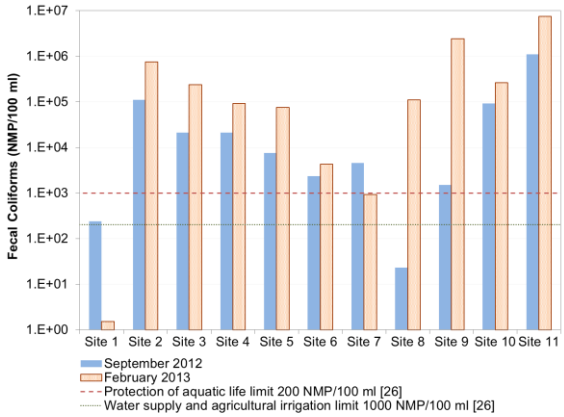

Fig. 2 Fecal coliforms in water of Río Apatlaco and tributaries

Concentrations of P_T were higher in urban areas, suggesting a larger contribution of phosphorus by municipal discharges (Fig. 5). According to these data, the water of the river was classified as hypereutrophic except in sampling site 1.

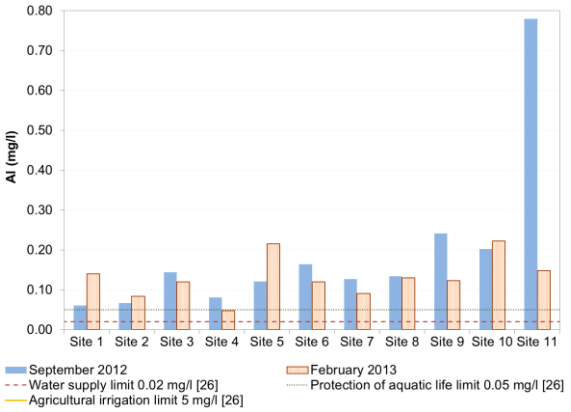

Fig. 3 Aluminum concentrations in water of Río Apatlaco and tributaries

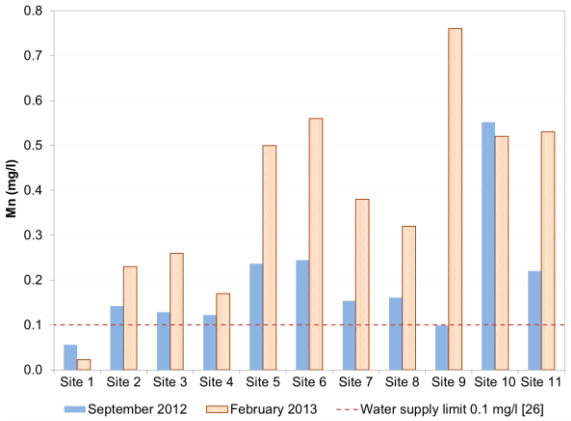

Fig. 4 Manganese concentrations in water of Río Apatlaco and tributaries

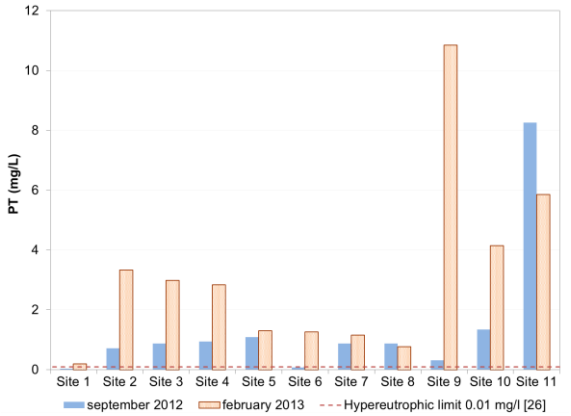

Fig. 5 Total phosphorus in water of Río Apatlaco and tributaries

Sediment samples had neutral pH (between 6 and 8) and silty sand textures with organic matter contents varying between 3.5 and 19%, suggesting favorable conditions for the accumulation of hydrophobic pollutants [24].

A total of 596 SVOC were identified in the Río Apatlaco sediment samples, 51% of which are of

synthetic origin, 30% are natural, and 19% may be from both natural and synthetic origins. It was observed that sediment samples obtained downstream from urban and industrial areas had more SVOC (between 117 and 208 SVOC per sample).

Additionally, sites with larger presence of substances from the manufacture and use of detergents are located in urban areas. This allows us to assume that these pollutants come mainly from municipal discharges. Furthermore, the presence of SVOC related to the use of pesticides is found in agricultural areas.

Generally, sampling sites that have lower amounts of SVOC are those located upstream and downstream far away from urban areas. However, in sampling site 8 located furthest downstream in Río Apatlaco, 89 different SVOC were identified. This may be due to the activities of farming and milling of sugar cane in the area of influence of this site.

To know if the identified SVOC in the Río Apatlaco and tributaries are regulated by international environmental standards, the SVOC were compared to the list of substances and regulations compiled by Friday [25]. It was found that only 2% of the 596 identified SVOC are regulated. Therefore, most of these substances may be identified as emerging pollutants. However, for inventorying the identified SVOC, it is recommended to quantify these substances in the river sediment, and collect and obtain information on the harmful effects these would have on aquatic life in the river.

The chemical classification of the SVOC according to CAS [23], over 20% of the identified SVOC are aliphatic hydrocarbons, 13% are benzene derivate, 8% belong to the polyaromatic hydrocarbons (PAH), and 3% are phenols (Fig. 6).

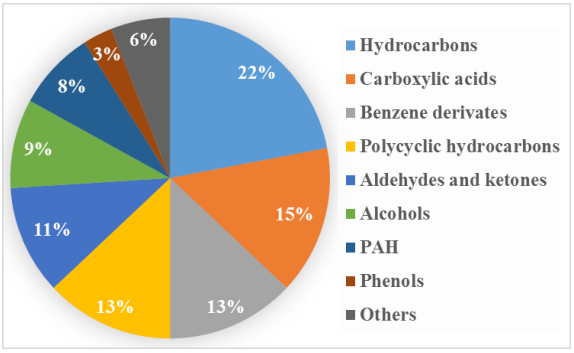

Fig. 6 Chemical classification of the identified SVOC

Furthermore, the uses of identified SVOC were classified, finding that only 70% of the compounds could be classified, because there is not information available about the uses of the remaining 30% in the CAS database [23] and in the consulted literature.

Of this 70%, 24 compounds are originated from the pharmaceutical industry, 22% from the production of cosmetics, 12% are pesticides, and 12% are originated from the food industry (Fig. 7).

In sampling sites located downstream from the urban areas, the larger diversity of SVOC from the manufacture and use of pharmaceuticals was recorded, which is an indication that municipal discharges are those with the main contribution of these substances. Moreover, for river sediments downstream from municipal areas and industrial parks, a large number of substances from the pharmaceutical and food industries, as well as pesticides, was observed.

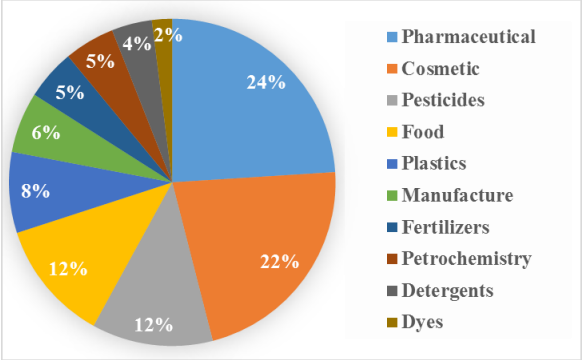

Fig. 7 Classification according to uses of identified SVOC

CONCLUSIONS

Water in Río Apatlaco, central Mexico, is contaminated; exceeding the Mexican limits for several parameters for water supply and for protection of aquatic life.

Only near the spring that feeds the river in the upstream basin is suitable for use in agricultural irrigation. However, other parts of the river present concentrations of fecal coliforms, turbidity, aluminum and manganese, which exceed the established limits.

Thus, the quality of the river water is acceptable in the highest part of the watershed, but on reaching the urban area, the quality is reduced without improving further downstream. In addition, results for the Río Apatlaco tributaries did not indicate better water quality than in the main river.

The results suggest that the pollution observed in the Río Apatlaco comes from anthropogenic activities, so it is necessary to regulate and treat municipal and industrial discharges that are currently discharged to the river without treatment.

The amount of SVOC identified in sediment of the river and its tributaries was high throughout the river except in the uppermost part of the basin, being higher in urban areas, and decreasing with increased distance downstream. However, in the site located furthest downstream in Río Apatlaco, 89 different SVOC were identified, probably due to the activities

of farming and milling of sugar cane in the area of influence.

The chemical classification of the 596 identified SVOC indicates that 63% are aliphatic hydrocarbons, carboxylic acids, benzene derivatives and polycyclic hydrocarbons, 8% are PAHs and 3% are phenols.

The classification of SVOC according to its use, points out that products from the pharmaceutical, cosmetic and food industries, as well as derivate from use of pesticides, represent 70% of SVOC detected in the sediment of Río Apatlaco. Larger numbers of these pollutants were detected in sediments within urban areas and in the junction between the main river and its tributaries carrying water from the industrial parks.

Currently, there are established limits only for 2% of the 596 identified SVOC. For future ecotoxicological investigations in the study area, it is recommended to measure at least these SVOC, and also consider the determination of toxic metals.

ACKNOWLEDGEMENTS

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