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ORGANIC MICROPOLLUTANTS IN THE DIFFERENT ENVIRONMENTAL COMPARTMENTS

Amado Enrique Navarro Frómeta
``Universidad Tecnológica de Izúcar de Matamoros``. Izúcar de Matamoros, Puebla, Mexico
https://orcid.org 0000-0002-4827-0670

Abstract: Organic micropollutants (OMCs), also called pollutants of emerging concern in certain circumstances, encompass a large group of chemical substances of natural or anthropogenic origin that, due to their molecular characteristics, present risks to human health. These include, among other chemicals, personal care products, food additives, flame retardants, and pharmaceuticals. In the light of the literature on the subject, the presence of OLS in the different environmental compartments is addressed: air, water and soil. Results of the determinations, by gas chromatography coupled to mass spectrometry, of the concentrations of a large group of MCOs in the atmospheric particulate matter of the city of Puebla, river water, irrigation water and groundwater from the Nexapa river basin, Puebla and in Colombian soils are presented. In these environmental matrices the concentrations were in the ppb to ppt range.
Keywords: Micropollutants, air, water, soil.

INTRODUCTION

The full and effective realization of the right to a healthy environment is threatened by contamination due to the presence of chemical substances, many of which have harmful effects on biota and affect the normal performance of ecosystems (Metcalfe et al., 2022). Already in 2019, the United Nations Environment Program indicated that the chemical industry had prospects of doubling by 2030, observing a rapid increase in production and consumption in emerging economies (UNEP 2019). The foregoing, considering only the contamination of water and the work environment, caused the loss of around 2.2 million lives in 2019, a possibly underestimated figure (Fuller et al., 2022). Globally there are more than 350,000 chemical substances and their mixtures registered for their production and use. It is evident that we have not yet advanced sufficiently in the evaluation of its risks to human health, which can even include damage to children from prenatal exposures, requiring alternative in vivo, in vitro and in silico methods to determine its effects in shorter times (Brooks, 2020).

One of the anthropic threats (not well known by the general public) for ecosystems comes from the emission to the different environmental compartments of the wide range of chemical substances that, due to technological development, the depletion or insufficiency of certain natural products and population growth, among other factors, are used by man in his daily activities (Krishnakumar et al., 2022). Its denomination is diverse: if its action on organisms is considered, endocrine disrupting compounds and carcinogenic substances are considered; based on their recent detection, attention and/or lack of regulation they are known as emerging pollutants or of emerging concern (CPE); Since they are found at a trace level in the environment, they are also called organic micropollutants, MCO, a denomination to which this work adheres. The metabolites resulting from their transformations must also be considered, sometimes more dangerous than the starting compounds (Daughton, 2005; Libralato et al., 2020; Reyes et al., 2021). Being anthropogenic contaminants, they are found in all spheres of our planet and even in food, accumulating and biomagnifying in food chains (Krishnakumar et al., 2022; Das et al., 2023; Li et al., 2023). Events that affect the human species such as climate change and the recent pandemic affect the increase in its presence, for example, antidepressant drugs and other EPCs (Castillo-Zacarías et al., 2021; Picó & Barceló, 2023). The most worrying thing is that we have not learned much about the impact of contamination by chemical substances on the environment and on living beings, including the human species and, although there is some progress in knowledge and legislation on the most dangerous substances (called priority pollutants), legislation in Latin America on the regulation of CPEs and MCOs is practically non-existent (Jacobo-Marín & Santacruz de León, 2021).

The objective of this work is to assess the information from the periodic literature on the presence of OCMs in the atmosphere, water and soil and to present the results of some experimental determinations of the same. This is intended to contribute to consolidating the social perception of these substances present in the environment.

OCMS AS CONTAMINANTS

Table 1 shows a general classification of the most relevant OLS (Navarro, 2019). Its structure in many cases favors its hydrophilicity and high solubility in water, which is why they can reach the cellular level when penetrating living organisms. As can be seen, its toxicology is very varied, including estrogenic and carcinogenic substances, among others, even reporting problems in fetal development due to maternal exposure to them (Hiranmai & Kamaraj, 2021; Sahoo et al., 2021; Cao et al., 2022).

Although they are not properly MCO, it is essential to mention microplastics, which are unquestionably CPE. In addition to their wide presence on the planet, as well as the dangers they entail for biota, including their transfer to the food chain with humans as the upper link, they can contribute to the transport of OCMs that can be absorbed into them (Bhatt et al., 2021; Gola et al., 2021; Jain et al., 2021; Martin et al., 2023; Picó & Barceló, 2023).

For the determination of OLS, various analytical techniques and bioassays are used, an aspect that is not discussed in this work, being the chromatographic methods coupled with mass spectrometry the most widespread. Most of the methods concern the determination of OLS in aqueous matrices. As in any other chemical analysis, the correct preparation of the sample is decisive (di Paolo et al., 2016; Pena-Pereira et al., 2021; Hajeb et al., 2022; Chen L. et al., 2023).

Regarding the technologies for their removal, they have been more widely discussed and described for the aqueous medium, since it is the fundamental means of disposal of OCMs. It has also been reported that traditional wastewater treatment methods are not very effective for its removal, with advanced treatments, still relatively expensive, and nature-based systems such as phytoremediation techniques and treatment wetlands being more effective (Zhang, 2019; Lee et al., 2021; Shahid et al., 2021; Ilyas, 2021; Shi et al., 2023).

OCMS IN THE ATMOSPHERE

OCMs and other CPEs, such as antibiotic-resistant bacteria and genes, enter the atmosphere through volatilization, aerosol and bioaerosol formation, or diffusive exchange processes from their emission from various sources. Once in the atmosphere, they can be transported even long distances from emission sources. Its presence is more worrying in urban environments and due to the exchange between interiors and exteriors and its concentration in rooms and workplaces can be higher than in the exterior, for which reason inhalation is the most important route of exposure (Chen et al., 2022; Gwenzi, 2022; Simões et al., 2022). For its study, active or passive sampling techniques are used for both air and atmospheric particulate matter (PM). This way, OLS belonging to practically all the types shown in Table 1 and volatile organic compounds (VOCs), of different types, have been detected and quantified in concentrations ranging from tenths of pg m-3 to hundreds of ng m-3 (Barroso et al., 2019; Hsiao et al., 2019;

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Family	Example	Use/application	Toxicological effects
Drugs	ethinyl estradiol	oral contraceptive	fish feminization
personal care products (PCPs)	galaxolide	colonies and detergents	inhibitor of multixenobiotic resistance transporters
perfluorinated compounds	perfluorooctanoic acid	non-stick pans with Teflon	cellular toxicity and possible human carcinogen
surfactants	octylphenol	industrial detergents	fish feminization
polymer additives	bisphenol A	plastic production	fish feminization
polar pesticides	terbutylazine	herbicide	classified as possible carcinogen (group 2B)
drugs of abuse	amphetamine	medical applications	hepatotoxic in fish
flame retardants	polybrominated diphenyl ether	plastics and foams	impact on the development, growth and reproduction of crustaceans
nanoparticles	Fullerenes	nanomaterials	possible cell damage due to oxidation

Table 1. Classification of the most widely distributed OLS (Navarro, 2019).

	Average	Median	Minimum	Maximum	Standard deviation	Standard error of the mean
DCB	0.179	0.182	0.024	0.708	0.152	0.026
TCB	0.371	0.313	0.020	1.405	0.329	0.056
DM3Oc	0.081	0.033	0.001	0.666	0.133	0.024
DMAcPhen	0.143	0.101	0.014	0.632	0.138	0.024
BzPhen	0.831	0.725	0.338	1.906	0.355	0.061
MDHJ	0.681	0.573	0.301	2.094	0.426	0.073
Gal	0.256	0.235	0.124	0.704	0.110	0.019
Ton	0.140	0.127	0.079	0.296	0.057	0.010
OctBenz	0.219	0.200	0.031	0.509	0.108	0.019
DOctSeb	0.278	0.138	0.019	1.062	0.296	0.050

Table 2. Some MCO present in the atmosphere of the city of Puebla (ng m-3).

Note: DCB – dichlorobenzenes, TCB – 1,2,4-trichlorobenzene, DM3Oc – 2,3-dimethyl-3-octanol, DMAcPhen – 2',4'-acetophenone, BzPhen – benzophenone, MDHJ – Methyldihydrojasmonate; Gal-Galaxolide; Ton – Tonalide; OctBenz – octylbenzoate, DoctSeb – dioctyl sebasate.

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Enyoh et al., 2020; Robichaud 2020; Kim et al., 202 1).

During the years 2009 and 2010, samples of PM smaller than 10 μm were analyzed, coming from 3 stations of the Environmental Monitoring Network of the City of Puebla. Table 2 shows the descriptive statistics of some of the OLS identified and determined. As can be seen, VOCs, plasticizers and, as expected, the musk-type fragrances with a broad spectrum of use MDHJ, Gal and Ton were detected and quantified. Some alkylamides possibly from biomass burning were detected but not quantified. Temporal patterns of some of the substances studied did not show consistency with seasonal temperature, suggesting that other factors influence pollutant concentrations beyond volatilization (Navarro, 2013).

OCMS IN THE AQUATIC ENVIRONMENT

Since freshwater bodies are the destination of many treated and untreated wastewater discharges, most of the studies on the presence of MCOs have been aimed at determining their concentrations in surface streams, lakes and reservoirs, estuaries and, of course, drinking water supply sources. Given the possible migration routes due to point or diffuse contamination and their presence in the biota through trophic chains, their fate and bioaccumulation have also been of interest in many studies, a relevant aspect if we consider the consumption of aquatic species by humans (Alagan et al., 2023; Chen X. et al., 2023; Guo et al., 2023). It must be considered that water contamination by MCOs is not a static phenomenon and the lists and priorities regarding the MCOs to study are affected by some important variables: climate change; demographic changes, substitution of some chemicals with less problematic ones, new evidence on the toxicology and effects of OCMs, and technological development with the emergence of new applications of chemicals (Bunke et al., 2019, Yankui et al., 2019; Deere et al., 2021; Hatje et al., 2022).

In studies carried out in the upper part of the course of the Nexapa River in Puebla, Mexico, 398 OCM were identified in the samples obtained in campaigns carried out in the years 1999 to 2013 (Figure 1). Of these, most are used in daily life as personal care products, cleaning products, food components, pharmaceuticals and pesticides. Of these, a group of 16 individual compounds and 3 families of compounds were quantified, observing the increase in concentration in dry season, at the point of transfer of 4 m3 per second of heavily contaminated water from the Atoyac River and after the most important populations as shown in figure 1B (Navarro et al., 2014). As can be seen in figure 1A, as a result of a principal component analysis carried out with the OLS concentrations, four groups of samples are distinguished, made up of the SD and LF samples in dry conditions, those from those points in rain, and the samples from the rest of the points differentiated into dry and rain. The LM samples are closest to the vertex of the minimum values of the three axes. This way, the PCA summarizes the main spatiotemporal trends of OLS concentrations observed in this study.

OLS have been used as chemical markers to study the impact of wastewater on freshwater (Lim et al., 2017). Similarly, they can be used to assess the anthropogenic impact on coastal marine ecosystems, as shown in Figure 2, for the determination of alkylphenols (AF) and coprostanol (POP) in waters and sediments of Cispatá Bay. As can be seen, the concentrations of POPs in the sediments reflect the dragging of these by the Sinú River, while the AF reflect the incipient impact of human settlements located on the coastline (Navarro et al., 2016).

In the irrigation waters in the Atlixco-

Izúcar valley, Puebla, part of which is derived from the Nexapa river, numerous OCMs were also detected (Navarro et al., 2017). Figure 3 shows the concentrations of these, compared with those present in irrigation water with similar characteristics from a region of Spain (Calderón-Preciado et al; 2011a). As it can be seen, the concentrations detected in Mexico are much higher than those determined in Spain. Unquestionably, this represents a greater risk of these contaminants passing through the food chain and reaching humans.

The impact of MCOs also reaches groundwater (Pradhan et al., 2023). In wells for irrigation in the Izúcar region, some MCO were detected (CAF, GAL, TON, Sunscreen, MDHJ, AF and monoethoxylated alkylphenols in concentrations up to 13 μg L^{-1} (Navarro et al., 2019).

OCMS IN SOILS

The main source of OCMs in agricultural soils is wastewater irrigation (Lyu et al., 2022; Minhas et al., 2022). Once present, both aerobic and anaerobic degradation processes occur, with greater speed than the former. Regardless of the degradation by microorganisms and other components of the soil biota, MCOs are absorbed by different routes by crops. Different factors influence this, such as plant species, the type of contaminants, microorganisms present in the soil, and environmental factors such as temperature and soil erosion. This shows the importance of controlling the levels of these contaminants in the soil to assess the risks due to it (Pullagurala et al., 2018; Biel-Maeso et al., 2019; García Valverde et al., 2021; Murrel et al., 2021).

The determination of some MCO in Colombian agricultural soils irrigated with water from the Sinú river, shows that the sum of the concentrations of 5 MCO turned out to be 27.7 g ha-1 (Navarro et al., 2017), much higher than the sum of these same compounds in a soil from a region of Spain (Calderón Preciado et al., 2011b).

CONCLUSIONS

MCOs are ubiquitous pollutants in different environmental compartments, generally having, as the main source, the disposal of personal care products, drugs, surfactants and other substances in domestic and municipal wastewater. In Latin America, more studies are needed to determine their levels in the different environmental matrices and legislation to begin regulating their levels in them and mitigate the risks due to the exposure of the population to these pollutants.

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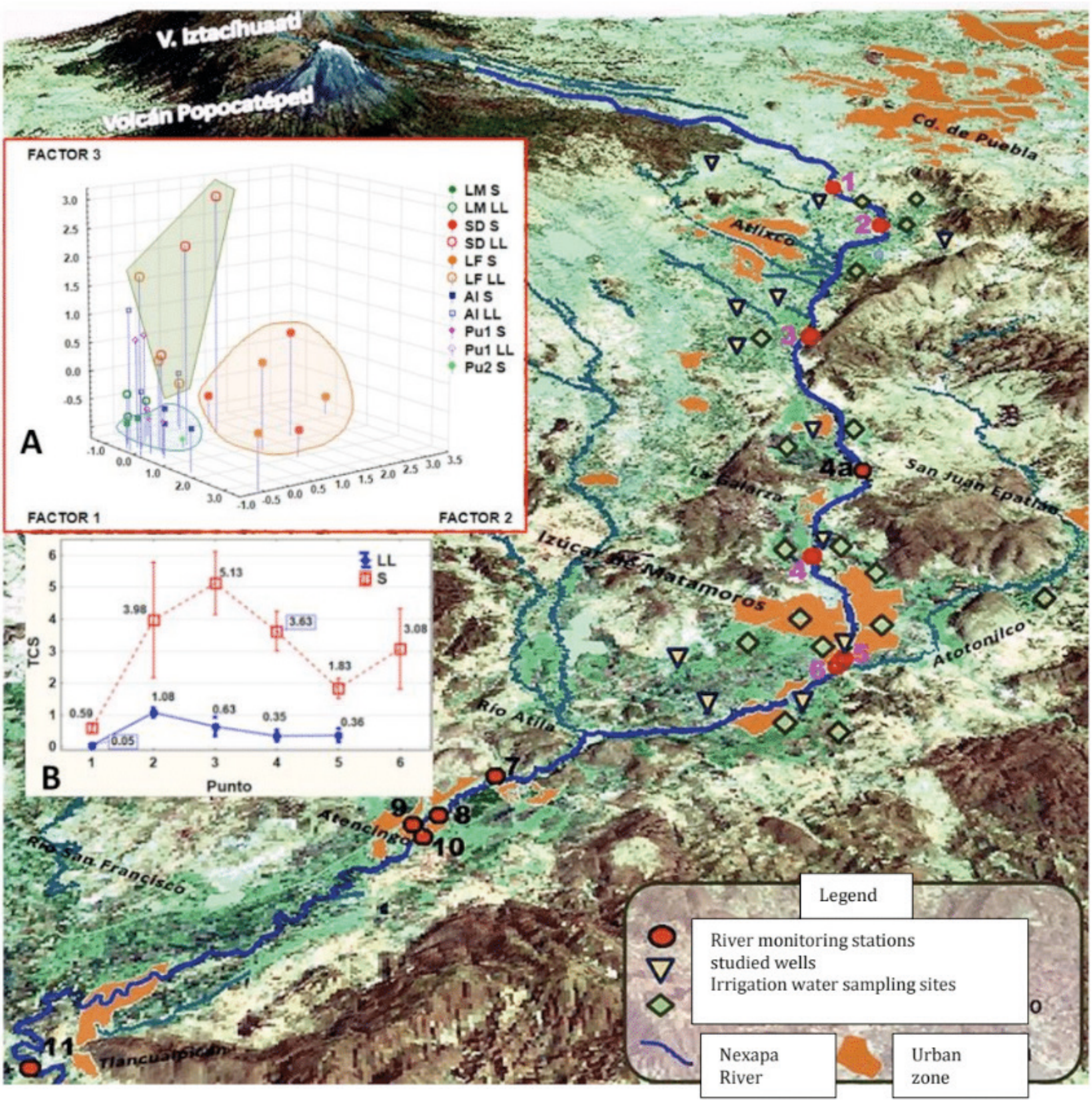

Figure 1. Main trends of MCO concentrations in the Nexapa River. A – PCA results; B – Concentration of triclosan at the sampling points. Location of sampling points: 1 – LM (Los Molinos); 2 – SD (Santo Domingo Atoyatempan), after the transfer of water from the Atoyac; 3 – LF (Las Fajanas, after the city of Atlixco); 4 – Al (Alchichica); 5 – Pu1 (Puctla before discharge from the treatment plant); 6 – Pu2 (Puctla after discharge from the plant).

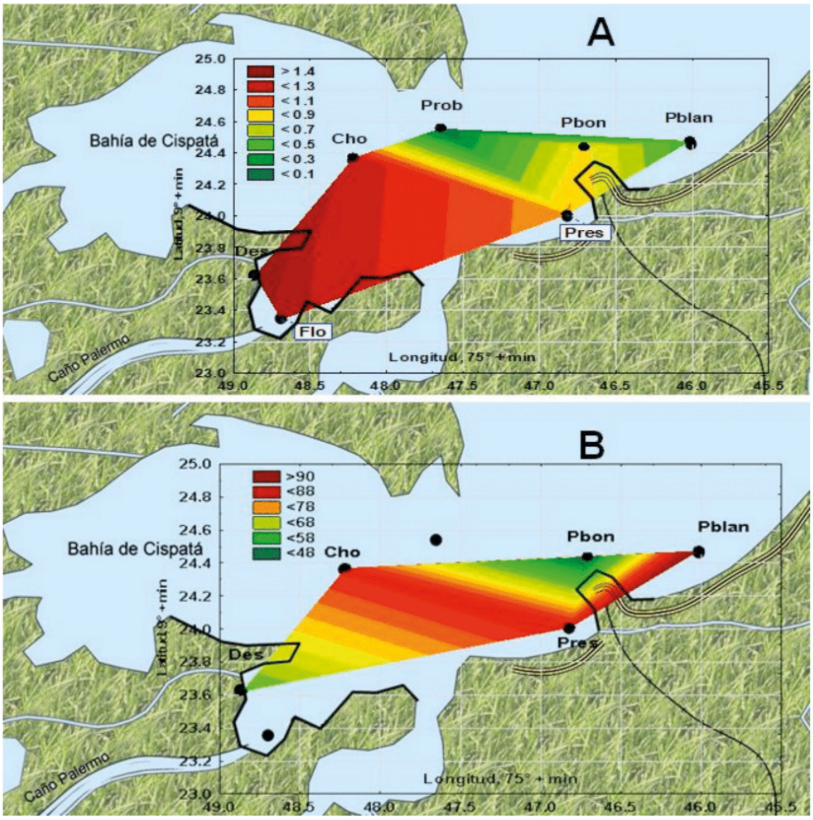

Figure 2. POP and AF concentrations in samples from Cispatá Bay (source Navarro et al., 2016).

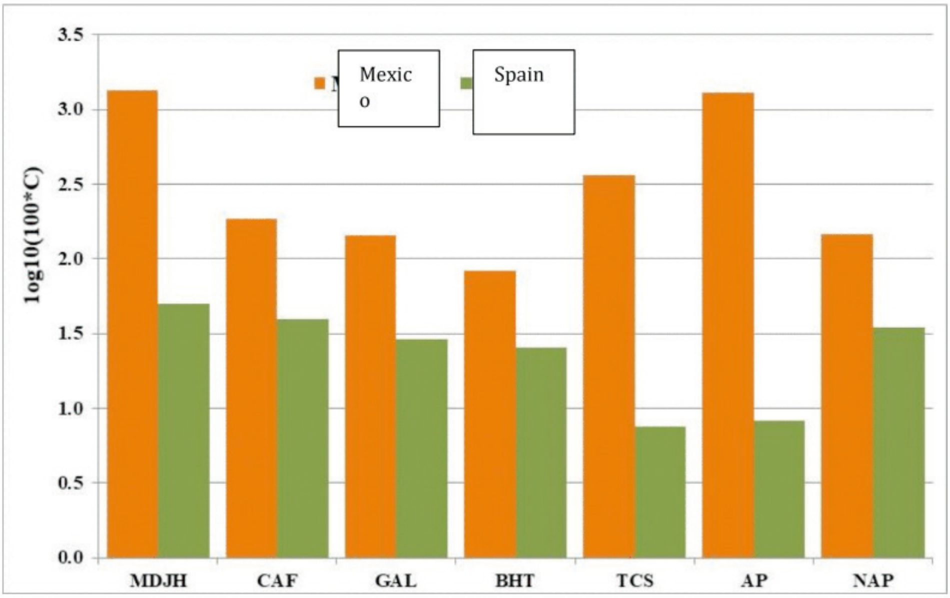

Figure 3. OLS concentrations in irrigation waters from Mexico and Spain (adapted from Navarro-Frómeta et al., 2017); MDHJ – methyl-dihydrojasmonate, CAF – caffeine, BHT – butylated hydroxytoluene, TCS – triclosan, AP – alkylphenols- NAP - naproxen