Chapter

Emerging Compounds in Mexico: Challenges for Their Identification and Elimination in Wastewater

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Abstract

In recent years, the presence of organic pollutants has received great attention due to their effects on public health and biota. Within this set of compounds, a new range of compounds that are characterized by their high persistence and low degradation have been identified, called Emerging Compounds. Emerging pollutants include a wide variety of products for daily use of different structures, domestic and industrial applications, such as: pesticides, industrial and personal hygiene products, hormones, and drugs, most of which are toxic, persistent and bioaccumulative. A characteristic of these types of pollutants is that current wastewater treatment plants are unable to remove them; they are designed to remove organic matter and nutrients in higher concentrations. In Mexico there is little information on the concentration levels of these compounds, due to the lack of public policies aimed at providing resources to institutions and researchers trained to carry out this type of study. On the other hand, the technological infrastructure of the wastewater treatment plants is insufficient for the country's demand. This situation represents one of the greatest challenges for the authorities responsible for the management of water resources, in the immediate time if it is intended to preserve said resource and therefore take care of the health of the population.

Keywords: emerging compounds, monitoring, wastewater, removal

1. Introduction

Currently one of the greatest challenges worldwide is the conservation of the quality of water resources. On a daily basis, a large amount of waste from different industrial, urban and livestock activities is discharged into water bodies, mainly through wastewater. According to UNESCO, 59% of total water consumption in developed countries is destined for industrial use, 30% for agricultural consumption and 11% for domestic activities [1]. It has been reported that more than 80% of hazardous waste in the world is produced in industrialized countries; it is also known that in developing countries 70% of the waste generated in industry is dumped to bodies of water without any type of previous treatment [1]. Specifically in Mexico, 54% of wastewater is not treated, which has become one of the biggest public health problems, since this type of water is reused for agricultural activities and in some cases for human consumption [2]. **Table 1** shows the percentage proportions of water uses according to their origin in Mexico.

In recent decades, the use of new chemical products has intensified in different anthropic activities, which has caused the degradation of water resources throughout the planet [3]. Within this set of compounds, a new range of compounds that are characterized by their high persistence and low degradation have been identified, called emerging compounds (EC). The term EC is used to refer to compounds of different origin and chemical nature, whose presence in the environment is not considered significant in terms of distribution and/or concentration, so they go unnoticed. What constitutes a high risk for the environment and the health of the population [4]. Emerging pollutants include a wide variety of products for daily use of different structures, domestic and industrial applications, such as: pesticides, industrial and personal hygiene products, hormones, and drugs, most of which are toxic, persistent and bioaccumulative. **Figure 1** briefly describes the classification of this type of compound by families.

It has been established that these compounds enter the environment through different sources, such as domestic and industrial wastewater [6], from waste, treatment plants [7], hospital effluents [8], agricultural and livestock activities [9] and septic tanks, among others [10], which are produced at different concentrations in surface waters, whose environmental quality criteria have not yet been specified [11].

One of the main problems of this type of pollutant is that the current wastewater treatment plants are unable to eliminate them. They are designed to remove organic matter and nutrients in higher concentrations (g L^{-1}). Therefore, emerging pollutants are present in surface water, groundwater and in purified water. In addition, the primary degradation of some of these compounds in wastewater treatment plants or in the environment itself, generate more persistent and more dangerous products, and synergistic effects may even occur if the compounds share the mechanisms of action [12].

This situation has been a matter of concern for the scientific community and for regulatory environmental entities, given the multiple impacts that they can cause on the environment and human health [11].

	Source			
	Superficial	**Groundwater**	**Total volume**	**Percentage of extraction**
Use	**(thousands of hm^3)**	**(thousands of hm^3)**	**(thousands of hm^3)**	**(%)**
Agricultural	42.0	23.2	65.2	76.7
Public supply	4.8	7.3	12.1	14.2
Industry	1.6	2.0	3.6	4.2
Electric power excluding hydroelectricity	3.7	0.5	4.2	4.9
Total	52.0	32.9	84.9	100

Table 1.
Water uses according to the source in Mexico [2].

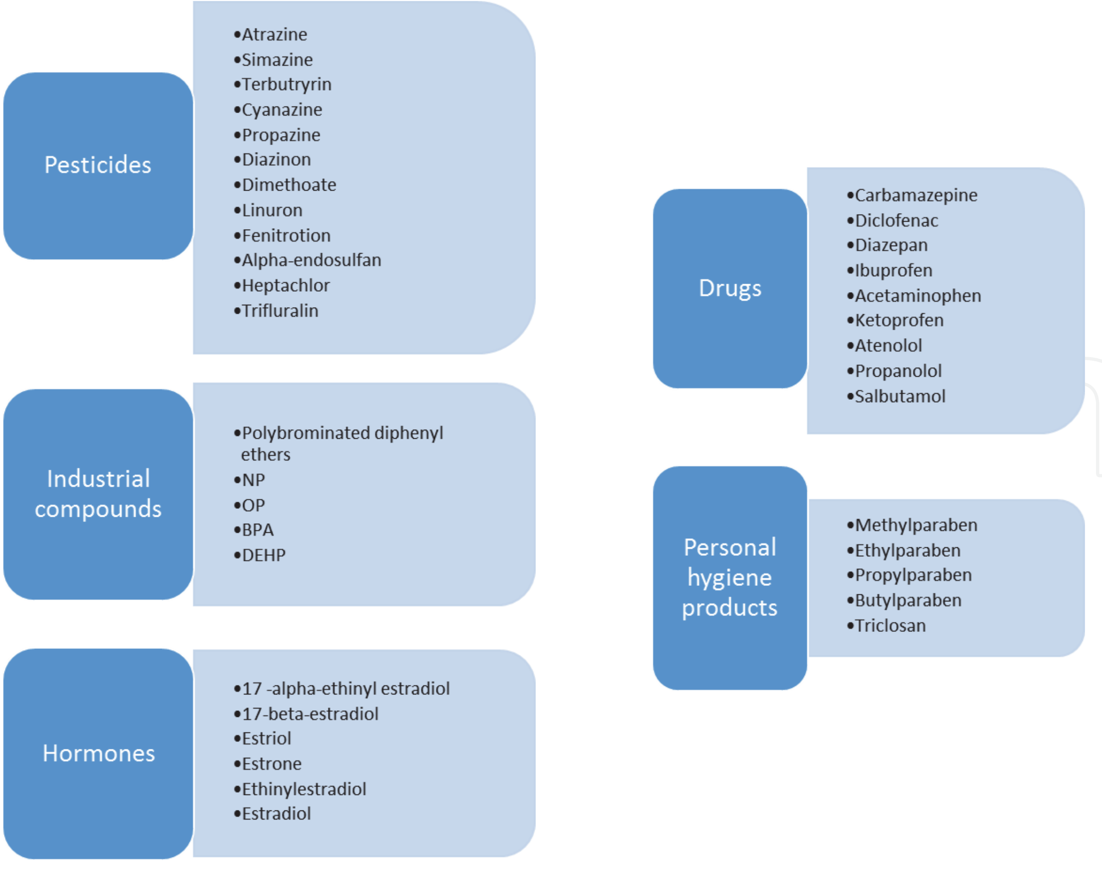

Figure 1.
Classification of emerging compounds by family. (Adapted from [5]).

Since 1989, the World Health Organization (WHO) has developed guidelines for the safe use of wastewater, and on this basis, each country has established its own regulatory framework. In this sense, Mexico has implemented a decentralized policy framework for managing water resources. In particular, the National Water Commission (CONAGUA, by its acronym in Spanish) was created, whose main function is the management of water resources, likewise is responsible for the formulation of public policies for water management. Water management legally incorporates Integrated Water Resources Management (IWRM), whose purpose is to promote stakeholder participation in coordinating the development and management of water, land and related resources [13]. Within the functions of the IWRM is the management of wastewater treatment and its reuse. However, the treatment and reuse of wastewater has not yet been adequately implemented within the sanitation services in terms of comprehensive water management, this is partly due to the fact that sanitation is not defined within the water legislation, in addition to institutional fragmentation, making it difficult to carry out such activity [14].

2. Challenges in the management of water resources in Mexico

Until now, all strategies and policies for the administration of water resources in Mexico have been ineffective, mainly because of the economic and political interests of some groups in society, which has not allowed the application of the principles established in IWRM, considering the participation of interest groups. This situation has not allowed the investment of resources to address the environmental problem generated by the presence of EC in water bodies. Currently only a few very specific studies have been carried out in a few states of the republic which indicates that there are many pending tasks on the part of the entities responsible for the management of water resources, in terms of the diagnosis of water quality and the development of advanced technologies to face such problem.

2.1 Identification of emerging compounds

Some examples of these contaminants are drugs, products for personal use and care, surfactants, fire retardants, steroids, hormones and derivatives of disinfection processes. These products correspond in most of the cases to contaminants that may be candidates for regulation; however, extensive research is required on its potential health effects [15, 16]. In some cases it is assumed that several of the EC have been discharged into the environment for periods prolonged but not detected due to the little information and a lack of analytical methods to detect low concentrations in different matrices [16].

The identification of this family of compounds in all types of waters has become a challenge for the scientific community, which requires highly sensitive analytical techniques for detection at nanograms per liter (ngL^{-1}) scales. Therefore, the development of rapid and sensitive analytical methods for EC monitoring is important [17].

The analytical techniques most used today are gas and liquid chromatography, both coupled to mass spectrometry. Coupling to mass spectrometry for the identification of EC in environmental matrices has shown significant results, mainly due to its high sensitivity, specificity and selectivity [17].

The detection of this type of compounds in environmental matrices requires efficient sample treatment procedures to concentrate analytes of interest and eliminate interferences [17].

Sample preparation techniques include solid phase extraction, solid phase microextraction, liquid-liquid extraction, microwave assisted extraction, liquid phase microextraction techniques, stir bar sorption extraction, and pressurized liquid extraction, among others [18].

However, access to these techniques requires large investments of money and highly specialized personnel for the development and validation of adequate methodologies. This situation has not made it possible to carry out diagnoses of the real situation of the presence of these compounds and in the main water bodies of the republic, since the states do not have the necessary resources.

In Mexico, there are few studies that have determined the concentration levels of this type of compounds in wastewater, groundwater, and surface water, almost all made in the center of the country (Guanajuato, Hidalgo, Jalisco, Morelos states, and Mexico city). Among the reported compounds are estradiol, ethinylestradiol, 4-nonylphenol, bisphenol A, 4-tert-octylphenol, naproxen, acetaminophen, diclofenac, bezafibrate, atenolol and carbamazepine, among others. This situation is worrying if we consider the great industrial and agricultural activity that takes place in a large part of the republic (**Table 2**).

2.2 Removal of EC from wastewater

The pollution of water bodies is a technical, social, and environmental challenge, attributable to continuous population increase and limited waste elimination strategies coupled with poor public management of water contaminants [24, 25]. The treatment of wastewater has been carried out for a long time, with the intention of reducing adverse effects on the environment and human health.

Although wastewater treatment plants are designed to remove solid materials, dissolved organic matter, nutrients and reduce the levels of metals, bacteria, and other pathogens. Most are not designed to efficiently remove organic pollutants,

Site		Compound	Concentration (ng/L)	Reference
Hidalgo state	**Residual water**	4-nitrophenol	16.7	[19]
		Bisphenol A	2.5	
		Estradiol	0.022	
Xochimilco channel	**Farming and livestock**	Bisphenol A	15200-22370	[20]
		Estradiol	980-1680	
Morelos state	**Surface water**	4-nitrophenol	85.5	[21]
		Bisphenol A	88.8	
		Estradiol	103.6	
		ethinylestradiol	91.5	
Morelos state	**Surface water**	Acetaminophen	2400-4460	[22]
		Diclofenac	1100-1276	
		Ibuprofen	502-1106	
		Indomethacin	112-164	
		Naproxen	3000-4820	
		Salicylic acid	200-664	
		Sulfamethoxazole	76-222	
		Atenolol	12-16	
		Carbamazepine	52-276	
Guanajuato state	**WWTP (influent, dry season)**	Atenolol	277	[23]
		Atorvastatin	18.7	
		Enalapril	149	
		Cotinine	1580	
		Metformin	94,600	
		Ranitidine	2720	
		Ibuprofen	1800	
		Naproxen	12,800	
		Triclosan	926	
		Paracetamol	66,000	
		Caffeine	31,100	
		Carbamazepine	167	
		Sulfamethoxazole	1100	
		Valsartan	1620	
		Androstenedione	390	
		Androsterone	750	
		Mestranol	741	
		Estrone	39.9	
		17 b estradiol	20	

Table 2.
Emergent compounds concentrations detected in surface and wastewater in different states of the Mexican Republic.

since the presence of different ECs has been detected in the wastewater and in sludge at high concentrations of up to thousands of μg/L or μg/kg [26].

In this context, contamination of water with EC represents a technical problem for its treatment and purification, since conventional treatments: aerobic biological, anaerobic, coagulation-flocculation, inverse osmosis filtration and disinfection with chlorine are not enough to completely eliminate or degrade this type of compounds [27, 28].

For this reason, the latest technological developments have focused on advanced oxidation processes (AOP), which focus on the generation of hydroxyl radicals (° OH), which have a greater oxidation potential than ozone or chlorine. The interactions with the compounds of interest are controlled mainly by diffusion and eventually result in the fragmentation of organic compounds and mineralization to CO2 [29].

In order to provide these radicals, several processes have been implemented that are based on the application of electrical energy (electrochemical oxidation), radiation (UV), ultrasound (US), chemical additives (O_3, H_2O_2) photo-fenton (Fe^{2+}/UV/H_2O_2) or a combination of these methods (**Table 3**). A consequence of the high reactivity of the oxidizing agent (° OH) is its low selectivity; which is a desirable feature in the case of wastewater pollutant removal.

Homogeneous processes	
(a) No external energy input	
	* Ozonolysis in alkaline medium ($O_3/^{-}OH$)
	* Ozonolysis with hydrogen peroxide (O_3/H_2O_2) and ($O_3/H_2O_2/^{-}OH$)
	* Hydrogen peroxide and catalyst
(b) With external energy input	
(b1) Energy from UV radiation	
	* Ozonolysis and UV radiation (O_3/UV)
	* Hydrogen peroxide and UV radiation (H_2O_2/UV)
	* Ozone, hydrogen peroxide and UV radiation (O_3/H_2O_2/UV)
	* Photo-fenton (Fe^{2+}/H_2O_2/UV)
(b2) Energy from ultrasound (US)	
	* Ozonolysis and US (O_3/US)
	* Hydrogen peroxide and US (H_2O_2/US)
(b3) Electrochemistry	
	* Electrochemical oxidation
	* Anodic oxidation
	* Electro-fenton
Heterogeneous processes	
	* Catalytic ozonolysis (O_3/TiO_2)
	* Photocatalytic ozonolysis (O_3/TiO_2/UV)
	* Heterogeneous photocatalysis (H_2O_2/TiO_2/UV)

Table 3.
Summary of the main AOPs used for the degradation of organic compounds.

On the other hand, these are processes that use expensive reagents such as hydrogen peroxide or ozone, so its use should be restricted to situations in which other processes cheaper, such as biological, are not possible. Their full potential is exploited when they are achieved integrate with other treatments, such as adsorption or biological treatments, in order to achieve the maximum oxidant economy.

Faced with this panorama, the challenge for Mexico is great if we consider that in the country there are 2540 wastewater treatment plants, of which 3.2% apply primary treatment, 96% secondary treatment and only 0.12% apply tertiary treatment (**Table 4**).

In recent years, various government agencies responsible for carrying out research in the management processes and development of water remediation strategies have led to some studies aimed at the application of advanced technologies for the removal and/or degradation of organic compounds in wastewater.

Type of treatment	Process	Number of plants	Treated flow (m^3/s)
Primary	Primary	13	0.035
	Advanced primary	10	4.431
	Imhoff tank	58	0.326
Secondary	Aerobic	20	1.849
	Anaerobe	100	0.625
	Biodiscs	30	0.872
	Biological	30	0.737
	Dual	24	27.402
	Biological filters	39	5.13
	Septic tank	100	0.142
	Septic tank + biological filter	40	0.044
	Septic tank + wetland	115	0.207
	Wetlands	74	1.249
	Aerated lagoons	29	7.024
	Stabilization lagoons	774	13.739
	Activated sludge	725	70.239
	UAR + biological filter	62	0.577
	UAR + wetland	34	0.331
	Upflow Anaerobic Reactor (UAR)	133	1.175
	Enzymatic reactor	44	0.097
	Sedimentation + wetland	21	0.04
	Imhoff tank + biological filter	26	0.181
	Imhoff tank + wetland	6	0.017
	Oxidation trenches	13	0.985
Tertiary	Tertiary	3	0.044
Not specified	Others	17	0.203
	Total	**2540**	**137.701**

Table 4.
Main municipal wastewater treatment processes (source CONAGUA [2]).

For example, since 2014 the Mexican Institute of Water Technology (IMTA, for its acronym in Spanish), has been developing different technologies for the removal of EC. Within these developments, they used biofiltration systems for biodegradation of two drugs, metformin and ciprofloxacin. Obtaining biodegradation efficiencies of 83 and 71% respectively, during 103 days of operation [30]. Likewise, in another study carried out in two wastewater treatment plants located in the states of Guanajuato and Mexico, they used a system integrated by oxidation ditches and UV light lamps, obtaining EC elimination efficiencies between 20% and 22% % (Guanajuato). Likewise, while in the other treatment that consisted of anaerobic / anoxic/aerobic tanks together with two disinfection processes; chlorine dioxide and ultraviolet lamps, the removal of EC was significant (up to 80%) (Mexico) [23].

Also used a submerged membrane bioreactor for the degradation of compounds estrone, estradiol and 17α-ethinylestradiol, obtaining removals close to 96% for all compounds [31]. Meanwhile Flores and Mijaylova 2017, evaluated the removal of three pharmaceutical micropollutants (fluoxetine, mefenamic acid and metoprolol) from municipal wastewater, by using four aerated submerged attached growth bioreactors, with removal efficiencies of 95, 82 and 73% for fluoxetine, mefenamic acid and metoprolol, respectively [32]. In another study conducted by García-Espinosa et al. 2018, obtained degradation percentages of Carbamazepine in wastewater of 88.7%, using an electrochemical oxidation process [33].

3. Conclusions

The main challenge facing Mexico for the comprehensive management of water resources, to do with current legislation has some structural deficiencies, for example, the sanitation process is not defined within the water legislation, as well as to institutional fragmentation. On the other hand, it must be considered that decision-making is strongly influenced by political interests and social pressure, which makes it difficult to align common goals in public health and environmental protection between local authorities and different sectors of society. It is also important to note that many official guidelines for water management are generally prepared by new presidential administrations every six years, which prevents the continuity of plans and programs, which causes waste of economic resources, which accelerates the deterioration of water and sanitation services.

As can be seen in scientific reports and publications, in Mexico there is little information on the real level of concentration levels of emerging compounds, which is worrisome considering that there are currently no laws that regulate said compounds in bodies of Water. Some of the studies carried out reveal alarming concentrations of some compounds. The foregoing suggests the implementation of intensive programs in the areas with the highest population, and regions with high industrial and agricultural activity; however, access to this type of methodologies requires highly qualified personnel, as well as high investments in the acquisition of supplies and equipment.

Finally, the number of waste treatment plants is insufficient; in addition, the vast majority are concentrated in primary and secondary treatments, and only 0.12% apply tertiary treatments. Although some advanced methods have been implemented for the removal of organic compounds, some of them with high efficiencies, which is encouraging, however these technologies continue to be expensive, which suggests the participation of government and private companies to support projects, that yields mutual benefits for both parties; that is to say, environmental, social and economic.

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Conflict of interest

The authors declare no conflict of interest.

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