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# Emerging pollutants and heavy metals into Spanish sanitation: a case study

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## Abstract

Emerging pollutants in urban waste water has increased significantly their levels over the last 15 years having both industrial origin and domestic one. Once these contaminants reach to an urban WWTP, in most cases operated by aerobic biological process, the treatment capacity of these effluents therein suffers greatly. Thus, we have studied the presence of several emerging pollutants and metals in urban waste water from Córdoba (Spain) along 2005-2015; moreover, it has also tested the practical ability of reducing the content of these substances in La Golondrina´s WWTP. The compounds studied were: pesticides, VOCs, THM´s, PAH´s, AOX´s and heavy metals. La Golondrina´s WWTP processed during 2.005-2.015 a mean flow of 25.6 $hm^3$/year: this plant is operated by activated sludge process. Results indicated that the wastewater influent presented 740 g/day of organics which were reduced to 387 g/day in the treated water, with reduction rates depending on compound and ranged from <5% and 83.8%. Almost, wastewater influent presented 92.4 kg/day of heavy metals which were reduced to 35.8 kg/day in the treated water: then, reduction rates depending on metal ranging from -16.7% and 68.9%. Finally, these results are not very different of those obtained in the rest of Spain.

**Keywords:** Wastewater, WWTP, activated sludge, emerging pollutants, heavy metals.

## Introduction

The presence of non-conventional pollutants in urban wastewater has made to pay attention to this issue in recent years (EU, 2009; Teijón et. al., 2010). This type of pollution, traditionally linked to industrial effluents, is increasing more and more associated with the use of household products such as cleaning, domestic hygiene, food, and finally several products used in home.

The chemical compounds present in industrial or domestic products are included into various types (Petrović et. al, 2003; Musolff et al., 2009): pesticides, synthetic organic compounds, solvents, plasticizers, cosmetics, pharmaceutical products, antibiotics, heavy metals and organic-metals, including drugs of abuse. In this sense, these pollutants present in urban wastewater can provoke two aspects which must be considered because of their importance: firstly, its environmental relevance as a sign of the growing dynamic undesirable from the point of view of environmental sustainability of the actual society (Reemtsma et. al., 2006; Mantecón Pascual, 2012; Marín Galvín, 2014; Simón Andreu et. al., 2015).

Secondly, considering that the great majority of urban WWTP operates by biological process (activated sludge or other), the purifying micro-organisms there existing may be strongly affected by different phenomena resulting from the chemical aggressiveness of these substances: this fact can seriously limit their effectiveness (Metcalf & Eddy, 2003; Novotny, 2003)).

As such, it now presents a study on the presence of a large number of emerging pollutants along 2005-2015 into the sanitation of Córdoba (Spain): we have studied raw wastewater influent to La Golondrina WWTP and treated wastewater there. All our data are not different enough than those found in the rest of Spain.

However local circumstances experienced by each specific sanitation may explain the differences detected in the content of the substances studied.

## Material and Methods

The urban wastewater studied is that of the sanitation of the city of Córdoba (330,000 inhabitants) made up 15% of industrial component. This effluent is treated in La Golondrina´s WWTP (EMACSA-Córdoba, Spain) which is operated by aerobic activated sludge process and which average flow of treatment along 2005-2015 was 25.6 $hm^3$. Treated wastewater is after discarded to Guadalquivir river (Fig. 1).

WWTP is integrated by the following systems:

-Lifting wastewater by means Archimedean screws.

-Thick and thin sieves.

-Removing of sand and oil-greases.

-Primary settling (not adding of chemical reactants).

-Biological treatment with atmospheric air dossing. The plant has also installed anaerobic selectors by removing of filamentous microorganisms (24% of total surface of biological treatment).

-Secondary settling.

-Discarding of treated wastewater to Guadalquivir river.

-Treatment of sludge produced.


**Figure 1. Location of Córdoba and Guadalquivir river at Spain.**

We have taken integrated samples over periods of 24 h with monthly frequency in both influent raw wastewater as treated wastewater. In this sense, organics were determined by gass chromatography (GC) and high pressure liquid chromatography (HPLC) while heavy metals by induced coupling plasma (ICP) and AOX ́s by combustion and coulometry. All the applied techniques have been the usual in water analysis.

## Results and Discussion

We have made the survey of the following emerging compounds: 19 pesticides (chlorinated, phosphoured, triazines and carbamates), four COV ́s (benzene, 1,2-dichlorethane, trichlorethylene and tetrachlorethylene), four THM ́s (chloroform, dichloromethane bro-mine, chlorinedibromo methane and bromoform), five PAH ́s (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indene(1,2,3-c,d)pyrene and benzo(a)pyre-ne) , and finally, total AOX ́s.

Figure 2 shows the behavior of total organic compounds between 2007 and 2015 (yearly main values) in both raw wastewater influent to WWTP and treated wastewater. Results as expressed in g/day, ie., as pollutant load (Mar ́n Galv ́n and Gonz ́lez Jim ́nez, MM, 2016).

According the results, organics in wastewater showed a weak downward trend from 2007 to 2015, although in 2014 the higher levels of the sequence were detected.

Moreover, a middle value of 740 g/d in raw wastewater influent was measured: this level was reduced after treatment up to 387 g/d.

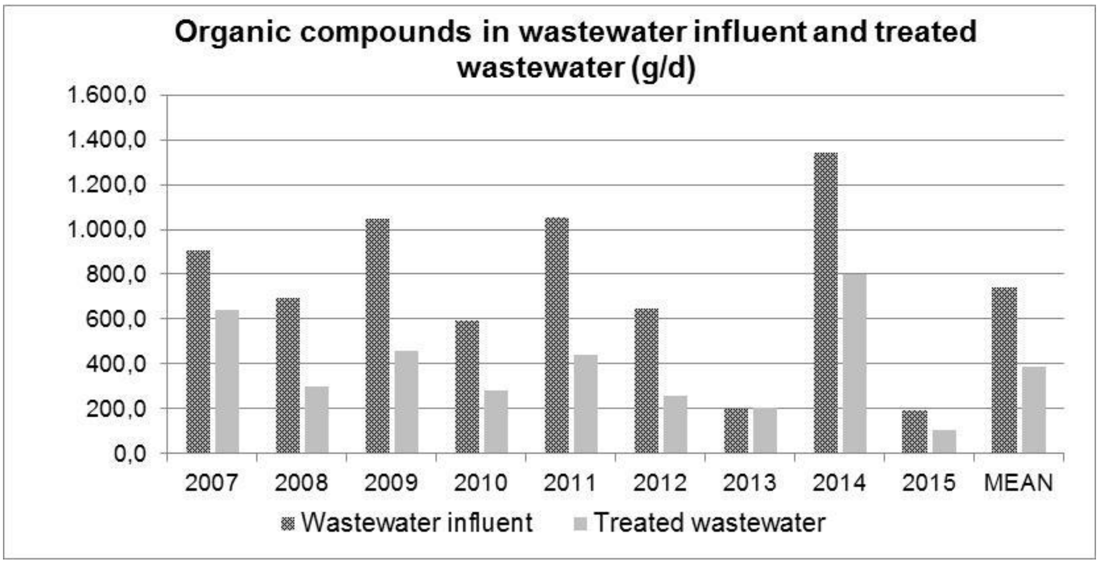


**Figure 2. Organics in wastewater and treated wastewater of La Golondrina ́s WWTP. Results expressed in g/d.**

On the other hand, Table 1 shows mean values of organics in raw wastewater wastewater treated and % reduction obtained in WWTP. Thus, the middle value of % reduction of total organics in the WWTP was only 20.1%.

**Table 1. Organics in wastewater and treated wastewater, and % reduction of organics in La Golondrina ́s WWTP (2007-2015). Results expressed in μg/L.**

| Compound | Influent | Treated | % Red. |
|---|---|---|---|
| Heptachlor | 0,005 | 0,005 | 0,0 |
| Aldrine | 0,004 | 0,005 | -25,0 |
| Heptachlor epoxide | 0,006 | 0,007 | -16,7 |
| Dieldrine | 0,022 | 0,013 | 40,9 |
| Methyl parathion | 0,244 | 0,232 | 4,9 |
| Malathion | 0,415 | 0,094 | 77,3 |
| Ethyl parathion | 0,303 | 0,049 | 83,8 |
| Ethion | 0,175 | 0,032 | 81,7 |
| Diazinon | 0,074 | 0,092 | -24,3 |
| Propazine | 0,183 | 0,095 | 48,1 |
| Atrazine | 0,308 | 0,139 | 54,9 |
| Simazine | 0,501 | 0,14 | 72,1 |
| Terbuthylazine | 1,134 | 0,287 | 74,7 |
| Prometrine | 0,811 | 0,134 | 83,5 |
| Ametrine | 0,383 | 0,118 | 69,2 |
| Terbuthryn | 0,151 | 0,145 | 4,0 |
| Diuron | 0,707 | 0,299 | 57,7 |
| Endosulfan I | 0,011 | 0,021 | -90,9 |
| Endosulfan II | 0,027 | 0,055 | -103,7 |
| Benzene | 0,555 | 0,262 | 52,8 |
| 1,2-dichlorethane | 0,29 | 0,262 | 9,7 |
| Trichlorethylene | 0,03 | 0,031 | -3,3 |
| Tetrachlorethylene | 0,55 | 0,626 | -13,8 |
| Chloroform | 7,397 | 3,976 | 46,2 |
| Dichloromethane bromine | 0,381 | 0,517 | -35,7 |

| Compound | Influent | Treated | % Red. |
|---|---|---|---|
| Chlorine dibromo methane | 0,35 | 0,042 | 88,0 |
| Bromoform | 0,045 | 0,043 | 4,4 |
| Benzo(b)fluoranthene | 0,008 | 0,007 | 12,5 |
| Benzo(k)fluoranthene | 0,004 | 0,005 | -20,1 |
| Benzo(g,h,i)perylene | 0,003 | 0,006 | -100,8 |
| Indene(1,2,3-c,d)pyrene | 0,009 | 0,011 | -20,2 |
| Benzo(a)pyrene | 0,012 | 0,005 | 56,1 |
| AOX ́s | 0,336 | 0,016 | 95,2 |

Nevertheless, as it can be seen in Table 1, each organic evoluted as different dynamics showing % reduction ranging between >80% for ethyl parathion, ethion, prometrine, chlorine dibromo methane and AOX ́s, and <5% (even with negative reduction) for several of the tested organics: aldrine, heptachlor, heptachlor epoxide, parathion methyl, diazinon, terbutryn, trichlorethylene, tetrachlorethylene, dichloromethane bromine, benzo(k)fluoranthene, benzo(g, h, i)perylene and indene(1,2,3,c-d)pyrene.

In this way, general mechanisms for reduction of pollutants in biological WWTP ́s are the following (Metcalf and Eddy, 2003):

-Assimilation of the compound by the microbial flora (metabolism) or adsorption within the microorganism: this is the predominant pathway for contamination biodegradable.

-Evaporation of the compound up to atmosphere along the process line, being this way experienced situation for compounds of high volatility.

-Total or partial destruction by chemically interacting with other compounds present in the wastewater (chemical antagonism phenomena).

-Chemical modification of the compound promoted by the aquatic environment and its subsequent transformation in a metabolite.

-Adsorption into suspended of settling matters of wastewater with the possibility of subsequent desorption or removal via decantation.

-Even finally, adsorption or fixing into the WWTP materials with possibility of subsequent desorption delayed both the wastewater itself and to the atmosphere.

Metabolic mechanism is always the desirable being led by the biodegradability of each compound. With relation of the other mechanisms, are minority but in some case can be outstanding.

Finally, compounds with potential negative activity over the WWTP microbial flora should promote important problems in the treatment of wastewater as a function of type and concentration of compound.

On the other hand, in Table 2 we compare the situation for several organics in Spain (Marín Galván et. al., 2.009) *vs* La Golondrina WWTP. Although results are very similar, spanish wastewater shows different pesticides than Córdoba WWTP wastewater (i.e., heptaclor the first ones, and atrazines and diuron the second one). Moreover, the main organic detected in both cases was chloroform.

**Table 2. Comparison between organics in wastewater and treated wastewater, in La Golondrina´s WWTP and the rest of Spain (middle values). Results expressed in µg/L.**

| **Compound (µg/L)** | **Spanish Influent** | **La Golondrina Influent** | **Spanish Treated** | **La Golondrina Treated** |
|---|---|---|---|---|
| *Heptachlor* | 1,868 | 0,005 | 0,006 | 0,005 |
| *Aldrin* | 0,001 | 0,004 | 0,005 | 0,005 |
| *Dieldrin* | 0,002 | 0,022 | <0,001 | 0,013 |
| *Atrazine* | 0,026 | 0,308 | 0,037 | 0,139 |
| *Simazine* | 0,022 | 0,501 | 0,318 | 0,140 |
| *Diuron* | 0,028 | 0,707 | 0,119 | 0,299 |
| *Endosulfan I* | 0,061 | 0,011 | 0,100 | 0,021 |
| *Endosulfan II* | 0,017 | 0,027 | 0,022 | 0,055 |
| *Benzene* | 0,082 | 0,555 | 0,004 | 0,262 |
| *1,2-dichlorethane* | 0,778 | 0,290 | 3,708 | 0,262 |
| *Tetrachlorethylene* | 0,720 | 0,550 | 0,044 | 0,626 |
| *Chloroform* | 1,904 | 7,397 | 0,637 | 3,976 |
| *Benzo(b)fluoranthene* | 0,010 | 0,008 | 0,004 | 0,007 |
| *Benzo(k)fluoranthene* | 0,013 | 0,004 | 0,005 | 0,005 |
| *Benzo(g,h,i)perylene* | 0,010 | 0,003 | 0,002 | 0,006 |
| *Indene(1,2,3-c,d)pyrene* | 0,010 | 0,009 | 0,015 | 0,011 |

| Compound (µg/L) | Spanish Influent | La Golondrina Influent | Spanish Treated | La Golondrina Treated |
|---|---|---|---|---|
| *Benzo(a)pyrene* | 0,006 | 0,012 | 0,005 | 0,005 |
| *AOX ́s* | 0,420 | 0,336 | 0,016 | 0,016 |

Regarding now by the evolution of heavy metals in the wastewater during the period 2005-2015, Figure 2 presents this question (results are expressed in kg/d, ie., as pollutant load). A marked downward trend is checked from 2005 to 2013 where we detected the lower values, although a slight increase is observed since then until today.

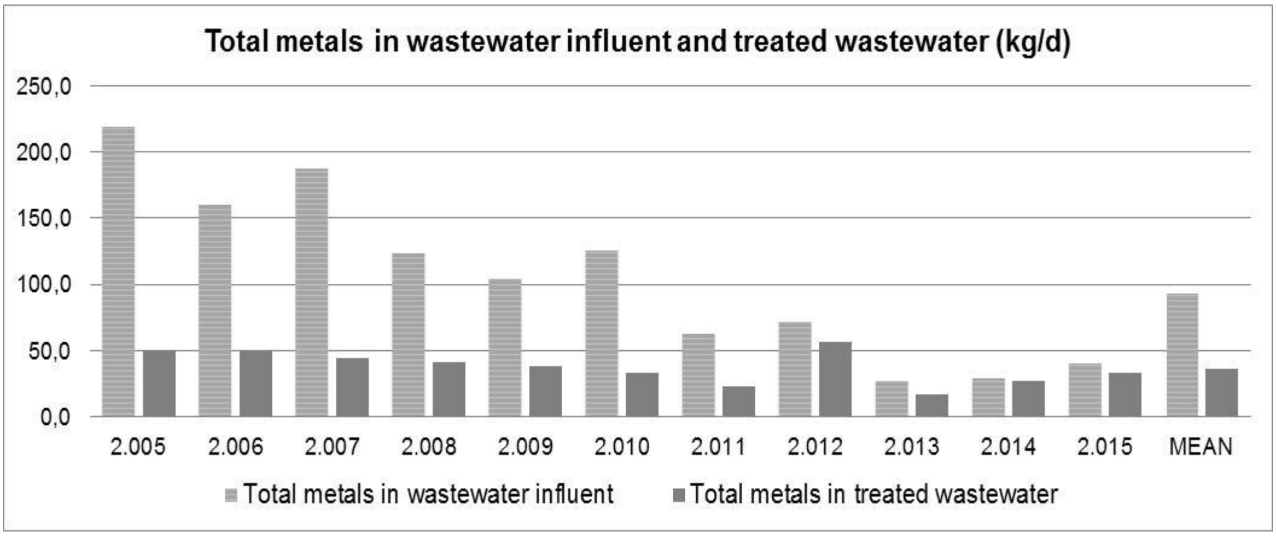


**Figure 2. Heavy metals in wastewater and treated wastewater of La Golondrina ́s WWTP. Results expressed in kg/d.**

In relation to metals, a middle value of 92.4 kg/d of total heavy metals in influent was measured which was reduced after treatment up to 35.8 kg/d. Thus, the middle value of % reduction of total metals in the WWTP was 61.2%; almost, it can be seen in Table 3 all the results of heavy metals in raw wastewater, treated water and their % reduction in WWTP.

In this way, each metal evolves as different dynamics showing % reduction ranging bet-ween 68.9% for iron and -16.7% for mercury: this fact can be relevant taking into account the special toxicity associated to this metal.

At the same time, we can read in Table 3 that levels obtained in the La Golondrina WWTP are generally very similar to tested in the rest of Spain (Mar ń Galv ń et. al., 2009) with the exception of Cu, Zn and Cr (raw wastewater) and Cu, Zn and Hg (treated wastewater).

**Table 3. Comparison between hevay metals in wastewater and treated wastewater, in La Golondrina´s WWTP and the rest of Spain (middle values). Results expressed in µg/L.**

| Metal (mg/L) | Spanish Influent | La Golondrina Influent | Spanish Treated | La Golondrina Treated |
|---|---|---|---|---|
| *Arsenic* | 0,001 | 0,006 | 0,002 | 0,002 |
| *Lead* | 0,024 | 0,025 | 0,002 | 0,009 |
| *Copper* | 0,159 | 0,112 | 0,027 | 0,046 |
| *Zinc* | 0,465 | 0,145 | 0,107 | 0,065 |
| *Nickel* | 0,023 | 0,013 | 0,020 | 0,008 |
| *Cadmium* | 0,001 | 0,011 | <0,001 | 0,006 |
| *Mercury* | 0,001 | 0,006 | <0,001 | 0,007 |
| *Chromium* | 0,033 | 0,008 | 0,008 | 0,004 |

## Conclusions

Amount of several organics in the Córdoba´s sanitation (2.007-2.015 period) ranged from 740 g/d in influent wastewater to La Golondrina WWTP and 387 g/d in the treated effluent. We there detected chloroform as the main organic followed of benzene and some triazines.

Dynamics in reduction of organics in the WWTP widely vary between >80% for ethyl parathion, ethion, prometrine, chlorine dibromo methane and AOX´s, and <5% (even negative %) for several organics (i.e., aldrine, heptachlor, heptachlor epoxide, trichlorethylene, tetrachlorethylene..).

With respect to heavy metals in the sanitation, influent wastewater to La Golondrina WWTP showed 92.4 g/d in total heavy metals which were reduced to 35.8 g/d in treated wastewater. Also in this case the % reduction varied very much: from 68.9 % (iron) to -16.7 % (mercury).

Finally, these results are not very different of those obtained in the rest of Spain.

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