Evaluating Pollutants of Emerging Concern in Aquatic Media Through E-PRTR Regulation

A Case Study: Cordoba, Spain, 2009-2018

Rafael Marin Galvin
Control de Calidad
Empresa Municipal de Aguas de Córdoba, S.A. (EMACSA)
Cordoba, Spain
rmargal@emacsa.es

***Abstract*-The EU E-PRTR Regulation can be followed for the evaluation of the level of pollutants of emerging concern in treated wastewater. This regulation is of regional responsibility in the UE, and establishes for the Andalusian region of Spain the following pollution parameters as mandatory to be controlled periodically in treated wastewater in Waste Water Treatment Plants (WWTPs) with more than 100.000 equivalent inhabitants of treatment capacity: COD, Kjeldahl N, total P, Cl^-, F^- (conventional pollution); As, Cd, Cr, Cu, Hg, Ni, Zn and Pb, as heavy metals; PAHs (polycyclic aromatic hydrocarbons), adsorbed organic halides (AOXs), benzene and chloroform, as organic compounds. This paper shows results obtained in the application of the E-PRTR Regulation to the wastewater of Cordoba during 2009-2018. As shown, average of COD, Kjeldahl N an total P values, respectively, in urban and treated wastewater were 604 and 89 mg/L, 54.1 and 33.4 mg/L and 3.4 and 1.4 mg/L. With respect to heavy metals, the mean content in treated wastewater was 0.135 mg/L, starting from 0.226 mg/L in raw wastewater. The majority of these are Cu and Zn (0.043 mg/L and 0.107 mg/L, respectively, in raw wastewater). For pollutants of emerging concern, the mean content of PAHs was 13 ng/L in treated water vs 31 ng/L in raw wastewater. Moreover, concentration of AOXs in raw wastewater was of 20 ng/L while in treated wastewater decreased up to 16 ng/L. Also, benzene content in raw wastewater and treated wastewater decreased from 40 ng/L to 11 ng/L. Finally, the major organic compound was chloroform, with a level in raw wastewater of 5.6 μg/L that was reduced along the treatment up to 3.2 μg/L. The provided data indicated a low concentration of the compounds of emerging concern in the wastewater of Cordoba and its minimal impact on the receiving aquatic environment (the Guadalquivir river).**

Keywords-pollutants; emerging concern; E-PRTR Regulation; heavy metals; HAPs; AOXs; benzene; chloroform.

I. INTRODUCTION

Control of conventional and emerging pollutants that could be present in treated wastewater [1-3] in Spain, as well as the mandatory levels of compliance, are included in the Discharge Authorizations to environment, granted to the Waste Water Treatment Plant (WWTP) managers by the Basin Organizations (state or regional level) in compliance with the Hydraulic Public Domain Regulation (RD 509/1996). In this way, general limitations of 25 mg/L for BOD_5, 35 mg/L for suspended solids and 125 mg/L for COD, in addition to parametric values in N and P in sensitive aquatic media, are applicable for treated wastewater evacuated to aquatic environments [4-5].

On the other hand, the well-known EU E-PRTR Regulation applies a regional responsibility to Basin Organizations in each European country (according to the RD 508/2007 and Law 5/2013 in Spain), and it requires a yearly report of the emissions of several conventional and emerging pollutants present in treated wastewater discarded to aquatic media. However, the E-PRTR, whose data are of public knowledge, does not mark restrictions on the pollutants nor economic or other penalty charges. In this sense, in the Andalusian region, the following parameters were stablished as mandatory to be communicated periodically by the managers of the WWTPs (with treatment capacity larger than 100.000 equivalent inhabitants) to the regional administration (Junta de Andalucia):

- COD, Kjeldahl N, P-total, Cl^-, F^- as conventional pollutants;
- As, Cd, Cr, Cu, Hg, Ni, Zn and Pb, as heavy metals;
- PAHs (polycyclic aromatic hydrocarbons), adsorbed organic halides (AOXs), benzene and chloroform, as organic compounds.

It must be indicated that heavy metals and organic compounds are clearly emerging pollutants (or pollutants of emerging concern) and they can serve indirectly to evaluate the presence of these substances in aquatic media. For this reason, this paper presents the result of the mandatory monitoring carried out in the municipal sanitation of Cordoba in 2009-2018, considering the E-PRTR, as an insight to the contribution of this city's wastewater to the contamination of environment water (mainly the Guadalquivir river).

Corresponding author: R. Marin Galvin

II. MATERIALS AND METHODS

The data presented in this paper refers to treated wastewater in La Golondrina´s WWTP (EMACSA-Cordoba) along the 2009-2018 period and corresponding to both, raw and treated urban wastewater. The urban wastewater studied is that of the sanitation of the city of Cordoba (327,000 inhabitants) that includes 15% of industrial component. La Golondrina´s WWTP (maximum treatment capacity=148,000 m^3/d) is operated by aerobic activated sludge process being its average flow of treatment along 2009-2018 around 26 hm^3. Treated wastewater is after discarded to Guadalquivir river (Figure 1).

Fig. 1. Location of Cordoba and Guadalquivir river at Spain. Screenshot from Google Maps, Map data © 2015 Google.

The considered WWTP performs the following operations through its several components [4-5]: Lifting wastewater by means of 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 and reuse for agricultural practices of sludge produced.

For the study carried out, we have taken integrated samples of raw and treated wastewater, along periods of 24 h, with monthly frequency. All the applied techniques have been the usual in water analysis [5-6]. In this sense, organics compounds were analyzed by gass chromatography-mass spectrometry (GC-MS) while heavy metals, by induced coupling plasma-mass spectrometry (ICP-MS) and AOXs, finally, by combustion and coulometry. On the other hand, COD was obtained through sample digestion in sulphuric media by using the known method of potassium dichromate, Kjeldahl N corresponded to N obtained after digesting samples in acidic medium with potassium sulphate (Kjeldahl N method) and total P was obtained by means ICP-MS. Finally, chloride and fluoride were determined by means ionic chromatography.

III. RESULTS AND DISCUSSION

La Golondrina´s WWTP is authorized to discharge in Guadalquivir by the Watershed Agency (Guadalquivir Hydrographic Confederation or CHG) with the last renovation of this authorization given in 2014. The WWTP quite reach the purification criteria required, and during the period 2009-2018 it achieved mean annual average values of chemical oxygen demand (COD) of 89 mg/L, biochemical oxygen demand (BOD_5) of 12 mg/L, and suspended solids (S_{SUSP}) of 17 mg/L, being the initial levels of, respectively, 604 mg/L, 367 mg/L and 311 mg/L. The evolution of yearly flow of wastewater treated in the WWTP is shown in Figure 2. The 2011 and 2013 years were that of higher treated flow, and 2015 and 2017 that of lower treated flow.

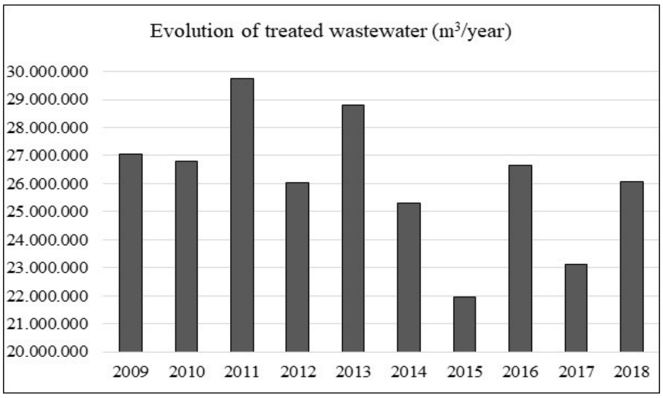

Fig. 2. Evolution per year of flow of wastewater in La Golondrina WWTP during 2009-2018.

A. Conventional Pollution

In this category we have included the following substances: COD, Kjeldahl N and total P [5-6]. In this way, the mean average COD values in urban and treated wastewater (as indicated above) were 604 and 89 mg/L, respectively, as well as 54.1 and 33.4 mg/L for N-Kjeldahl, and 3.4 and 1.4 mg/L for total P. On the other hand, the evolution for the above parameters in 2009-2018 is presented in Figure 3. Moreover, it must be taken into account that these parameters quantify different forms of organic matter present in raw and treated wastewater [4-6] and they are not equivalent. With relation to COD in raw wastewater the highest values were detected between 2009 and 2012, keeping since then reasonably stable; mean while, those of COD in treated water were always below 100 mg/L, except in 2009. In any case, the average COD removal rate in the plant was high, at 86%.

Regarding the Kjeldahl N behavior, the correlation between raw and treated wastewater is very remarkable, with an average reduction rate in the plant of 38%, the highest values having been detected in 2012 and 2018 in raw wastewater, and in 2009 and 2018 in treated wastewater. In addition, there seems to be an upward trend in the Kjeldahl N content from 2013 onwards, which can be explained both, by the decrease in treated flow (increase of concentration) and by the ascertainable increase in nitrogen compounds in household products. With respect to the total P, the average elimination in the plant was 60%, with higher values at the beginning of the study (2009-2010) and from 2015 onwards. In this sense, two periods are identified in the sequence obtained: since 2009 to 2013, with a tendency to decrease values; and from here until 2018 with a sustained increase in total P levels in both, raw and treated wastewater, whose explanation can be shared with that already given for the case of nitrogen.

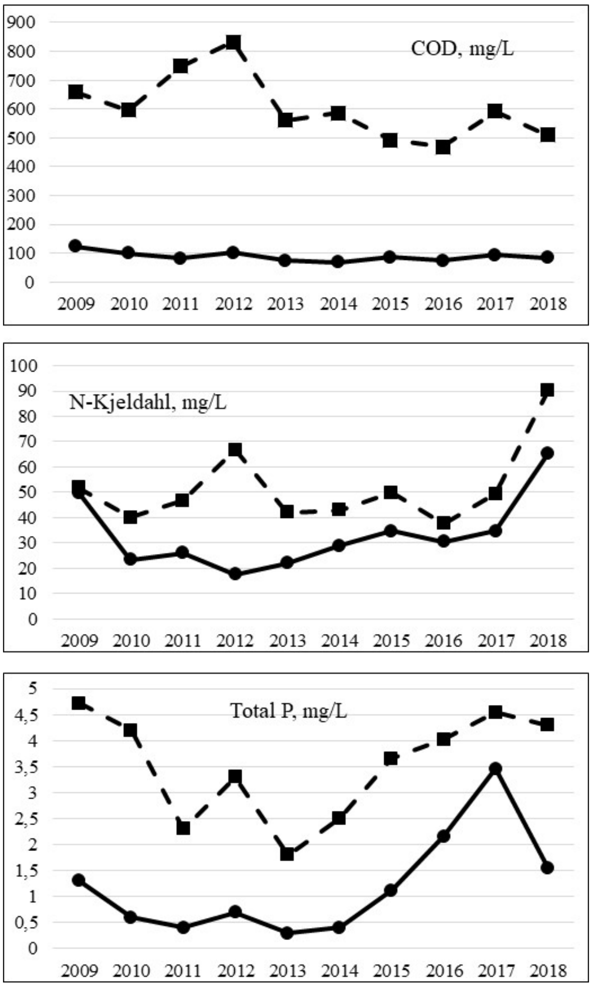

Fig. 3. Evolution per year of: COD (up); Kjeldahl N (middle); Total P (down). Raw wastewater (squares-striped line); treated wastewater (dots-continuous line).

The evolution of Cl^- and F^- in both, raw and treated wastewater is shown in Figure 4. It can be observed that the average Cl^- content is higher in treated wastewater than in raw wastewater (96.8 mg/L *vs.* 109.1 mg/L, respectively). This circumstance is due to the use in the WWTP of ferric chloride in the treatment process carried out to treat a specific industrial discharge of high polluting load, which must be treated before its incorporation into the flow of total urban wastewater. This effluent, treated via anaerobic, requires the use of ferric salts that promote enrichment in Cl^- of treated wastewater. On the other hand, the mean average F^- content of the raw and treated wastewater was practically the same (0.21 mg/L); in this way, this substance was weakly affected with biological treatment, as would be expected. It is also worth mentioning that the levels since 2011-2012 were significantly lower as result of the progressive cessation of activity of a glass industry in the city, and logically, with the non-existence of effluents rich in F^- to sanitation network.

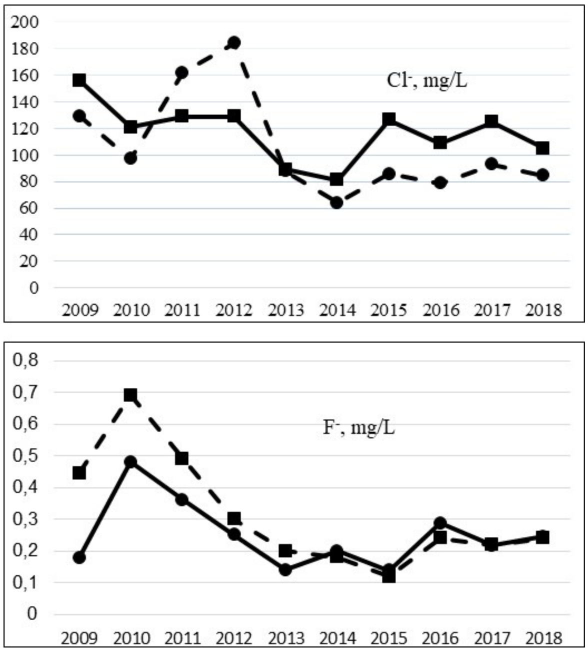

Fig. 4. Evolution per year of: Cl^- (up); F^- (down). Raw wastewater (squares-striped line); treated wastewater (dots-continuous line).

B. *Heavy Metals*

Table I shows the mean average values of the eight heavy metals investigated during our study, both in raw urban wastewater and in the treated one. Of all the heavy metals investigated, Zn and Cu were the majority: mean levels along our study were 0.107 mg/L and 0.071 mg/L for Zn, and 0.043 mg/L and 0.018 mg/L for Cu, raw and treated wastewater, respectively. On the other hand, the rest of metals did not exceed 0.010 mg/L in raw water (Ni) or in treated water, except Pb, with 0.011 mg/L in the final discharge to river (treated wastewater).

TABLE I. LEVELS OF HEAVY METALS (2008-2019)

Heavy metal	Raw wastewater (mg/L)	Treated wastewater (mg/L)
Arsenic (As)	0.005	0.004
Cadmium (Cd)	0.004	0.006
Chrome (Cr)	0.009	0.007
Copper (Cu)	0.043	0.018
Lead (Pb)	0.009	0.011
Mercury (Hg)	0.002	0.003
Níckel (Ni)	0.010	0.008
Zinc (Zn)	0.107	0.071

The origin of the presence of Cu and Zn in wastewater is clearly industrial since in Cordoba there are several industries of copper and brass processing; on the contrary, the rest of the metals have varied origins (Table II), both industrial, domestic and still diffuse [4-5, 7, 15-16]. The total content of heavy metals in urban wastewater was 0.226 mg/L while in treated wastewater it was reduced to 0.135 mg/L, reaching a reduction of 40%. It should also be noted that, in the cases of cadmium, mercury and lead, a slight increase in treated wastewater was detected compared to those of the initial content, which could be due to light and slow desorption phenomena from biological sludge to wastewater in the WWTP.

TABLE II. ORIGINS OF HEAVY METALS IN WASTEWATER.

Heavy metal	Uses and applications	Observations
Arsenic (As)	wood preservative, semiconductors and lasers, metallurgical industry, pigment and pyrotechnics, glass manufacturing, pesticides (very deprecated)	
Cadmium (Cd)	batteries, special surface treatments, pigments, PVC stabilizers, alloys, electronic components, welding	it appears as an impurity in phosphate fertilizers, detergents and refined petroleum products
Chrome (Cr)	manufacture of steels, dyes and paints, wood preservation, ammonia synthesis, manufacture of refractory and ceramic materials, and lasers, magnetic tapes, water analysis (COD)	
Copper (Cu)	water installations, electrical installations car industry, coins, ceramics, algicide, pig farms	
Lead (Pb)	batteries, car industry, jewelry, industrial paintings	
Mercury (Hg)	thermometers, lamps, catalysts, alloys, amalgams, explosives, medical applications, switches	it can be mobilized naturally from its deposits
Níckel (Ni)	alloys, surface treatments, pigments, batteries, jewelry, catalysts	
Zinc (Zn)	batteries, pipes, glass flux, pigments, alloys, welding, sulfuric acid manufacturing, gasoline additive, ammunition, paints, insecticides	

C. *Organic Compounds*

In this category we have included the following substances or group of substances: PAHs, AOXs, benzene and chloroform [7-11, 13-15, 17]. The total of the five PAHs investigated (benzo(a)pyrene, benzo(b) and (k)fluorantene, benzo(g,h,i,) perylene and indene(1,2,3-c, d)pyrene) was of 31 ng/L in raw wastewater decreasing to 13 ng/L in treated wastewater (58% reduction). The emission of PAHs to wastewater is related to use of fossil fuels (fuel or diesel in boilers) and cars (gasoline). In the sequence studied, the years 2010, 2015, 2016 and 2018 presented the maximum values of those measured, with concentrations between 50 and 100 ng/L (Figure 5) which did not really affected the concentration of PAHs in treated wastewater. As for AOXs, the so-called adsorbed organic halides are organic substances that contain one or more atoms of a halogen element (generally Cl, although there are also compounds formed with Br and I). They can be simple and volatile substances (trichlorethylene, for example) or complex organic molecules such as dioxins and furans, which can have a wide variety of physical properties. Dioxins and furans are toxic substances at very low levels, being solid and crystalline compounds, very little soluble in water, but easily soluble in organic solvents, fats and oils. The emission of dioxins and furans to the environment comes from incineration and combustion processes (garbage and other solid waste, medicines, biological remains and other dangerous elements). They also can be byproducts of metallurgical processes (high temperature steel production, recovery of metals in blast furnaces, combustion of coal, wood, used petroleum products and tires), chlorine production and organic chlorinated derivatives for different purposes (insecticides, herbicides, catalysts and intermediate products for the synthesis of other substances) and, finally, from paper production. Finally, other minor sources of emission are the processes of disinfection with chlorine of drinking water, disinfection of swimming pool water, and those of process water in industrial laundries.

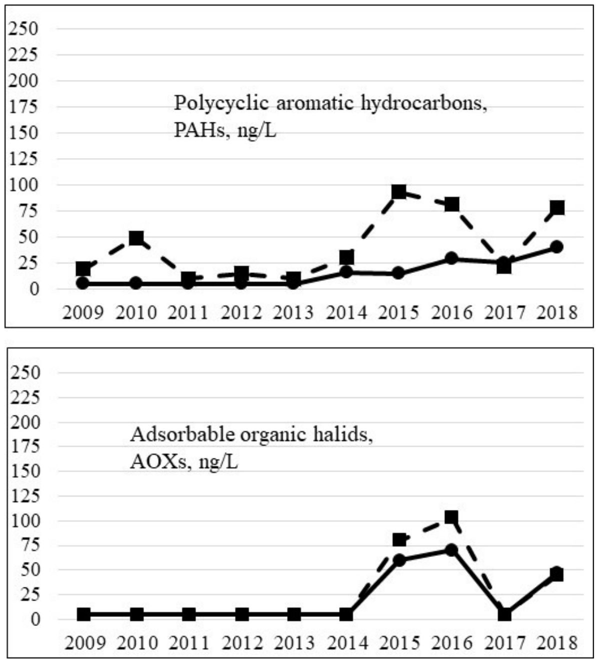

Fig. 5. Evolution per year of: PAHs (up); AOXs (µg/L) (down). Raw wastewater (squares-striped line); treated wastewater (dots-continuous line).

The average concentration of AOXs was reduced by 20% in the treatment, from 20 ng/L to 16 ng/L. These compounds emanates specially from a paper industry located in Cordoba, in addition to the tap water itself and the discharges to the sanitation of public and private pool waters (very notable activity in the city due to its hot weather). Figure 5 shows the evolution of AOXs in raw wastewater and treated one throughout the study: the years 2015 and 2016 exhibited the maximum detected near 100 ng/L in raw wastewater, and somewhat lower in the treated one. Benzene is employed in the manufacture of other chemicals used for the manufacture of plastics, resins, nylon and synthetic fibers, as well in the manufacture of different types of rubber, lubricants, dyes, detergents, medicines and pesticides. Benzene is usually the main compound of all the benzene compounds present in wastewaters (between they, naphthalene, phenanthrene, xylene) [13, 17]. Likewise, fires in general and forest fires in particular represent the main natural sources of benzene emissions, although it is also a natural constituent of crude oil, gasoline and cigarette smoke. It is, therefore, a clear exponent of the diffuse contamination of our environment (also in Cordoba). The evolution of benzene in wastewater and treated wastewater during 2009-2018 is shown in Figure 6. This compound evolved from 40 ng/L in raw wastewater to 11 ng/L in treated wastewater (a 72% reduction). To highlight, in the year 2013 with a maximum of 290 ng/L in raw wastewater no increase was detected in treated wastewater (39 ng/L was the mean value in that year).

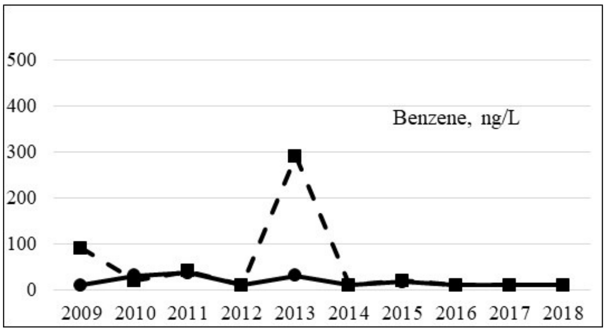

Fig. 6. Evolution per year of benzene. Raw wastewater (squares-striped line); treated wastewater (dots-continuous line).

Finally, the majority organic compound of those investigated was chloroform. This compound is used primarily as a solvent for organic compounds and as a component of some fire extinguishers, although it is also involved in the manufacture of dyes, being almost a generic fumigant and insecticide. However, its main source for sanitation in urban wastewater is tap water: this one yet contains chloroform as a disinfection byproduct [13-15, 17]. Figure 7 shows the evolution of chloroform content in raw and treated wastewater during our study: two periods of higher levels are years 2009 to 2011 and 2013-2014, with values higher than 5 μg/L, while in the rest of the years investigated the levels were below 2 μg/L in raw wastewater. Otherwise, the highest values in treated wastewater corresponded to 2011, 2013 and 2014 with close levels and even slightly higher than 5 μg/L. Computing the average concentrations during the period studied, the level in the treated effluent was 3.2 μg/L compared to the initial in urban wastewater of 5.6 μg/L (42% reduction in plant). As reference, the city's drinking water contains chloroform in the order of 10 μg/L, justifying clearly the origin of this substance in the wastewater.

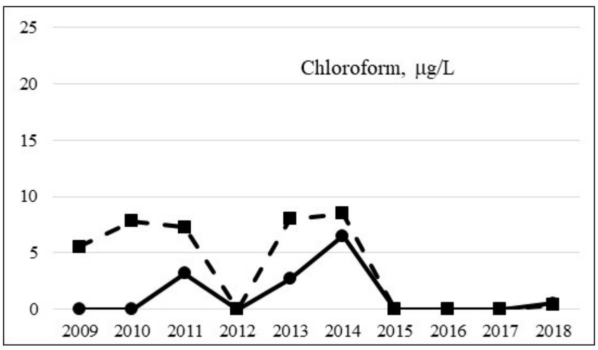

Fig. 7. Evolution per year of chloroform. Raw wastewater (squares-striped line); treated wastewater (dots-continuous line).

IV. CONCLUSIONS

The well-known EU E-PRTR Regulation shows a regional responsibility to Basin Organizations in each European country requiring a report of the content of several pollutants present in treated wastewater discarded to aquatic media. In this study, covering the time span of 2009 to 2018, analysis in the wastewater of Cordoba, Spain shows that the average COD values in urban and treated wastewater were 604 and 89 mg/L, respectively, for Kjeldahl N was 54.1 and 33.4 mg/L respectively, and for total P was 3.4 and 1.4 mg/L respectively. Their origin is both domestic and industrial. In relation to heavy metals, their average content in treated wastewater was 0.135 mg/L, 0.226 mg/L in raw wastewater, mostly of Cu and Zn. Their presence is mostly due to copper and brass processing industries located in the city. Regarding contaminants of emerging concern, the average content of PAHs in treated wastewater was 13 ng/L with a 58% reduction from the content found in raw water. It is estimated that its majority origin is the use of fossil fuels in industries, homes and urban traffic. In relation to AOXs, the concentration in raw wastewater, 20 ng/L, was decreased by 20% along the treatment. Its major source seems to be a paper industry located in the city. The benzene content in wastewater and treated wastewater was 40 ng/L and 11 ng/L respectively (reduction of 72%). Finally, the major organic compound was chloroform, with a level in raw wastewater of 5.6 μg/L, which was reduced to 3.2 μg /L after treatment. The chloroform contained in tap water and pool renewal water was essentially the origin of the levels detected. The data verify the low concentrations of compounds of emerging concern in the wastewater of Cordoba and their minimal impact on the aquatic environment.

REFERENCES

[1] D. Barcelo, M J. Lopez, “Contaminacion y calidad química del agua: el problema de los contaminantes emergentes”, Panel Científico-Técnico de seguimiento de la política de aguas, Instituto de Investigaciones Químicas y Ambientales-CSIC, Barcelona, 2007 (in Spanish)

[2] R. Lopez, R. R. Irusta, “Tendencias en el tratamiento de contaminantes emergentes”, Foro Regional de Sostenibilidad e I+D+i (Junta de Castilla y Leon), 2010 (in Spanish)

[3] M. J. Gil, A. M. Soto, J. I. Usma, O. D. Gutierrez, “Contaminantes emergentes en aguas, efectos y posibles efectos”, Produccion+Limpia, Vol. 7, No. 2, pp. 52-73, 2012 (in Spanish)

[4] Metcalf and Eddy, Wastewater engineering: treatment and reuse, 4th ed., Mc Graw Hill, Boston, 2003

[5] R. Marín Galvin. Fisicoquimica y microbiologia de los medios acuáticos. Tratamiento y control de calidad de aguas, 2ª ed. Ed. Diaz de Santos, Madrid, 2018 (in Spanish)

[6] American Water Works Association, Standard Methods for the examination of water and wastewater, Water Environment Federation, 23rd ed., New York, 2017

[7] R. Marin Galvin, “El estado de las aguas continentales espanolas y la contribucion de las EDAR en su consecucion”, VIRTUALPRO, No. 208, pp. 1-30, 2019

[8] M. Petrovic, S. Gonzalez, D. Barcelo, “Analysis and removal of emerging contaminants in wastewater and drinking water”, Trends in Analytical Chemistry, Vol. 22, No. 10, pp. 685-696, 2003

[9] T. Reemtsma, S. Weiss, J. Mueller, M. Petrovic, S. Gonzalez, D. Barcelo, F. Ventura, T. P. Knepper, “Polar pollutants entry into the water cycle by municipal wastewater: a European perspective”, Environmental Science and Technololgy, Vol. 40, No. 17, pp. 5451-5458, 2006

[10] A. Musolff, S. Leschik, M. Moder, G. Strauch, F. Reinstorf, M. Schirmer, "Temporal and spatial patterns of micropollutants in urban receiving waters", Environmental Pollution, Vol. 157, No. 11, pp. 3069–3077, 2009

[11] G. Teijon, L. Candela, K. Tamoh, A. Molina-Diaz, A. R. Fernandez-Alba, "Occurrence of emerging contaminants, priority substances (2008/105/CE) and hevay metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain)", Science of The Total Environment, Vol. 408, No. 17, pp. 3584-3595, 2010

[12] P. J. Simon Andreu, C. Lardin Mifsut, R. Gonzalez Herrero, A.V. Sanchez Beltran, J. A. Vicente Gonzalez, "Estudio de la presencia de contaminantes emergentes en las distintas etapas de las depuradoras", RETEMA, Vol. 186, pp. 84-91, 2015 (in Spanish)

[13] S. Sauve, M. Desrosiers, "A review of what is an emerging contaminant", Chemistry Central Journal, Vol. 8, No. 15, pp. 1-7, 2014

[14] C. C. Montagner, C. Vidal, R. D. Acayaba, "Contaminantes emergentes em matrizes aquáticas do Brasil: cenário atual e aspectos analiticos, ecotoxicologicos e regulatorios", Quimica Nova, Vol. 40, No. 9, pp. 1094-1110, 2017 (in Spanish)

[15] R. Marin Galvin, "Emerging pollutants and heavy metals into Spanish sanitation: a case study", SCIREA Journal of Enivronment, Vol. 2, No. 1, pp. 1-11, 2017

[16] K. Khaskhoussy, B. Kahlaoui, B. Messoudi Nefzi, O. Jozdan, A. Dakhell, M. Hachicha, "Effect of treated wastewater irrigation on heavy metals distribution in a tunisian soil", Engineering, Technology & Applied Science Research, Vol. 5, No. 3, pp. 805-810, 2015

[17] M. Narasimha Vara Prasad, M. Vithanage, A. Kapley, Pharmaceuticals and personal care products: waste management and treatment technology, Butterworth-Heinemann, 2019