# EFFICIENCY OF DIFFERENT WASTEWATER SECONDARY TREATMENTS IN THE REMOVAL OF 16 PHARMACEUTICAL ACTIVE COMPOUNDS

D. Camacho-Muñoz, J. Martín, J.L. Santos, I. Aparicio, E. Alonso

Department of Analytical Chemistry, University of Seville, C/ Virgen de África 7, E-41011 SEVILLE (Spain), e-mail: ealonso@us.es

## Abstract

Surface waters are being increasingly contaminated worldwide with pharmaceutical active compounds (PhACs) due to their high consumption and persistence alongside wastewater treatments. To treat wastewater from small communities, wastewater treatments with low operational and maintenance costs are commonly used. Three of the wastewater treatments generally employed to treat wastewater from small communities (oxidation ditch, lagooning and constructed wetlands) were evaluated to determine their effectiveness in removing PhACs. Five anti-inflammatory drugs (diclofenac, ibuprofen, ketoprofen, naproxen and salicylic acid), a psychostimulant (caffeine), two antibiotics (sulfamethoxazole, trimethoprim), two lipid regulators (clofibric acid and gemfibrozil), an antiepileptic drug (carbamazepine), a β-blocker (propranolol) and four hormones (17α-ethinylestradiol, 17β-estradiol, estriol and estrone) were monitored. Analytical method was based on solid-phase extraction and determination by high performance liquid chromatography with diode array and fluorescence detectors online. The anti-inflammatory drugs salicylic acid (30.0 μg $L^{-1}$) and ibuprofen (15.5 μg $L^{-1}$) were the ones with the highest mean concentration levels in influent wastewater. In general, the compounds more efficiently removed were the anti-inflammatory drugs naproxen, salicylic acid and the antibiotic sulfamethoxazole with removal rates up to 74.8%. No significant differences, due to the different wastewater treatment evaluated, was observed for such compounds. However, carbamazepine was better removed by oxidation ditch (52.4%) than by lagooning (11.4%) or constructed wetlands (30.1%). These results show the necessity to implement tertiary treatments to reduce the presence of PhACs in effluent wastewater to improve water quality before its discharge to the aquatic media.

Keywords: Pharmaceutical compound; removal rate; oxidation ditch; lagooning; constructed wetlands.

## Introduction

Wastewater discharges from urban wastewater treatment plants (WWTPs) are considered the main way of entering pharmaceuticals into the environment. Several studies have shown that PhACs are not completely removed in wastewater treatments and a wide variability of removal efficiencies has been reported depending on the pharmaceutical compound (Santos *et al.*, 2005; Nakada *et al.*, 2006).

Small communities commonly employ wastewater treatments with low energetic consume and easy to maintain and to operate which are suitable to their low economic resources. Oxidation ditch, lagooning and constructed wetlands are the secondary treatments most commonly used to treat wastewater from small communities.

The aim of this work was to evaluate the efficiencies of removal pharmaceutical compounds of secondary wastewater treatments based on oxidation ditch, constructed wetlands and lagooning. To achieve this aim sixteen pharmaceutical compounds were monitored in influent and effluent wastewater from an experimental WWTP in which the three secondary treatments are available in different treatment lines.

## Methods

Twenty-four hour composite samples of influent and effluent wastewater were taken with an automatic device. Three samples of each wastewater treatment line were collected in May 2008, September 2008 and January 2009. Samples were kept at 4°C until analysis when necessary.

Analysis of pharmaceutically active compounds was carried out according to the method reported by Camacho-Muñoz et al. (2009) based on sample treatment by solid-phase extraction and determination by high performance liquid chromatography (HPLC) with diode array and fluorescence detectors. Chromatographic analysis was performed on an Agilent Technologies HPLC 1200 Series instrument (Agilent, USA). Separation was carried out using a Zorbax Eclipse XDB-C18 (150 mm x 4.6 mm, particle size 5 μm) cartridge column (Agilent, USA). Analytes were separated by gradient elution with acetonitrile and a 25 mM potassium dihydrogen phosphate solution at a flow-rate of 1.2 mL/min.

## Results and Discussion

The pharmaceutical compounds at the highest mean concentration levels in influent wastewater were the anti-inflammatory drugs salicylic acid (30.0 μg $L^{-1}$) and ibuprofen (15.5 μg $L^{-1}$) (Table 1).

*Table 1. Concentration levels of the PhACs monitored in influent and effluent wastewater*

| Pharmaceutical compound | Influent wastewater | | Effluent wastewater | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Oxidation ditch effluent | | Lagooning effluent | | Constructed wetlands effluent | |
| | Range (μg $L^{-1}$) | Mean (μg $L^{-1}$) | Range (μg $L^{-1}$) | Mean (μg $L^{-1}$) | Range (μg $L^{-1}$) | Mean (μg $L^{-1}$) | Range (μg $L^{-1}$) | Mean (μg $L^{-1}$) |
| Diclofenac | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD–0.50 | 0.17 |
| Ibuprofen | <LOD–24.9 | 15.5 | <LOD–4.63 | 2.77 | <LOD–4.71 | 2.75 | 0.86–6.04 | 3.87 |
| Ketoprofen | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Naproxen | 3.41–8.21 | 6.35 | <LOD–1.95 | 0.99 | <LOD–2.19 | 1.01 | <LOD–0.79 | 0.36 |
| Salicylic acid | 8.82–54.9 | 30.0 | <LOD–3.25 | 1.26 | 0.11–0.93 | 0.42 | 0.08–2.19 | 0.80 |
| Sulfamethoxazole | <LOD–3.79 | 1.26 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Trimethoprim | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Carbamazepine | <LOD–18.5 | 6.62 | <LOD–8.56 | 3.08 | 0.10–12.2 | 4.58 | 0.29–13.3 | 4.70 |
| Propranolol | <LOD–0.62 | 0.21 | <LOD–0.27 | 0.14 | <LOD–0.85 | 0.44 | 0.21–1.36 | 0.75 |
| Caffeine | <LOD–3.92 | 1.80 | 0.45–3.51 | 1.82 | <LOD–1.79 | 0.84 | <LOD–0.83 | 0.52 |
| 17α-Ethinylestradiol | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| 17β-Estradiol | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Estriol | <LOD | <LOD | <LOD–0.44 | 0.15 | <LOD | <LOD | <LOD–0.53 | 0.18 |
| Estrone | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Clofibric acid | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Gemfibrozil | 3.44–5.81 | 4.32 | 2.67–10.6 | 5.50 | 5.29–13.3 | 8.63 | 2.34–11.1 | 5.75 |

In general, the compounds more efficiently removed were the anti-inflammatory drugs naproxen, salicylic acid and the antibiotic sulfamethoxazole with removal rates up to 74.8% (Fig 1). Ibuprofen was moderately removed with removal rates up to 57.3%. For all the mentioned compounds not significant differences were observed between wastewater treatments. However, carbamazepine and propranolol were better removed in oxidation ditch than in lagooning or constructed wetlands whereas removal of caffeine was improved in lagooning or constructed wetlands.

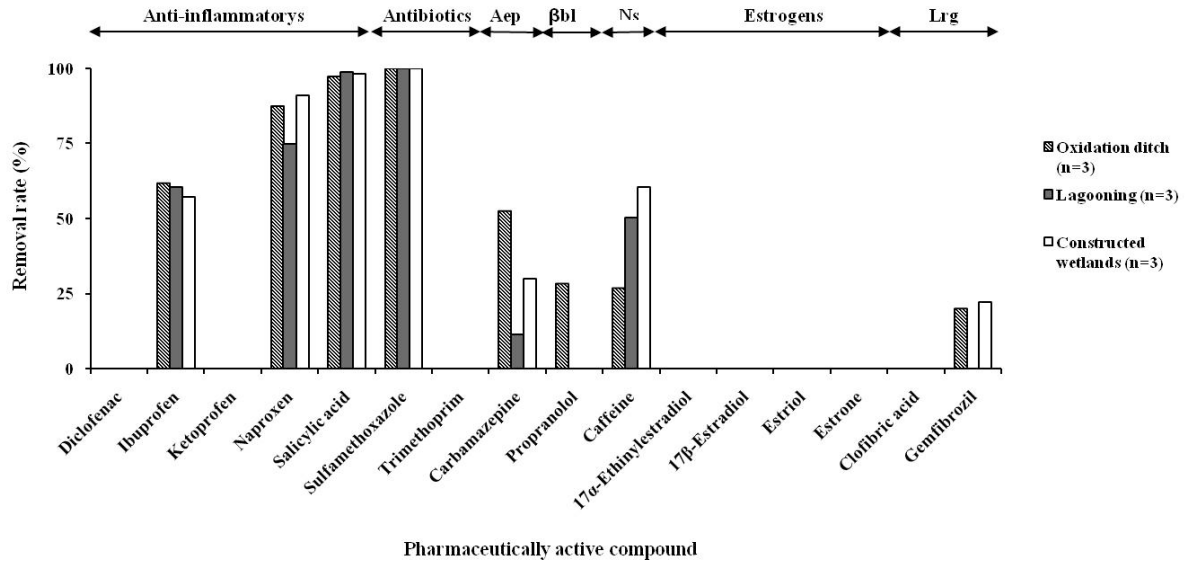


*Figure 1.Mean removal rates of PhACs achieved in oxidation ditch, lagooning and constructed wetlands treatments. Aep: antiepiletic drug; βbl: β-blocker; Ns: nervous stimulant.*

## Conclusions

PhACs were detected, at high or low concentration levels, in all the types of effluent wastewater evaluated. Their presence in effluent wastewater shows that secondary treatments evaluated are not efficient enough to remove these pollutants from the aqueous phase and that tertiary treatments are needed to improve water quality before its discharge to the aquatic media.

## References

Camacho-Muñoz, D., Martín, J., Santos, J.L., Aparicio, I. and Alonso, E. (2009). An affordable method for the simultaneous determination of the most studied pharmaceutical compounds as wastewater and surface water pollutants. J. Sep. Sci., 32, 3064–3073.

Nakada, N., Tanishima, T., Shinohara, H., Kiri, K. and Takada, H. (2006). Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res., 40, 3297–3303.

Santos, J.L., Aparicio, I., Alonso, E. and Callejón, M. (2005). Simultaneous determination of pharmaceutically active compounds in wastewater samples by solid phase extraction and high-performance liquid chromatography with diode array and fluorescence detectors. Anal. Chim. Acta, 550, 116–122.

## Acknowledgements

The authors wish to thank the financial support received from the Agencia Andaluza del Agua, Consejería de Medio Ambiente, Junta de Andalucía, Spain and from the Ministerio de Ciencia e Innovación, Spain (Project No. CGL2007-62281).