FATE AND REMOVAL OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN SEWAGE SLUDGE

N. Pérez-Lemus[1,2]

[1]Departament of Analytical Chemistry. Faculty of Sciences. University of Valladolid. Campus Miguel Delibes. Paseo de Belén 9, 47008. Valladolid. nereida.perez@uva.es
[2]Institute of Sustainable Processes. Dr. Mergelina s/n. 47011. Valladolid

1. Introduction

Emerging pollutants (EPs) are compounds of diverse origin and chemical nature: pharmaceuticals (PhACs), flame retardants, pesticides, pefluorinated compounds, chlorinated paraffins, drugs of abuse, personal care products (PCPs), among others. Some of the pollutants (very few) are included as priority pollutants in European regulations, most of them are not regulated by any legislation, both European and Spanish, but they are considered potentially harmful to the environment and human beings as they can cause various deleterious effects on organisms, such as chronic toxicity, endocrine disruption, and bioaccumulation [1]. EPs enter the environment through some sources such as domestic and industrial wastewater [2], hospital effluents [3], waste from treatment plants, and agricultural and activities [4].

Many of these pollutants are not correctly and efficiently removed by the existing treatments in Wastewater Treatment Plants (WWTPs) as they are designed to remove solid materials and reduce bacteria, pathogens, and metal levels. However, they are not designed to remove EPs present at low concentrations (ng L^{-1} to µg L^{-1}), being a source of contamination [3]. An example is the sewage sludge generated, used in agricultural and forestry activities, especially due to its capacity to fertilise soils and economic impact [5], which leads to its diffusion into the environment.

One variety of EPs are pharmaceuticals and personal care products (PPCPs) used in everyday life and with both domestic and industrial applications. These compounds include a wide variety of chemicals such as therapeutic or veterinary medicines, containing from analgesics and antibiotics to lipid regulators. In addition, active ingredients in soaps, detergents, deodorants, fragrances, cosmetics used in cosmetic care, wellness, and personal health. The most frequently detected PPCPs include analgesics, antibiotics, antidepressants, steroids, disinfectants, fragrances, and cosmetics due to their daily use and consumption [6]. The general use of pharmaceuticals (PhACs) results in an incessant discharge into the environment, becoming retained in the environment or accumulating, affecting the ecosystem and humans through the food chain [7]. Sewage sludge is the matrix selected for this study of the presence of PPCPs due to its use a fertilizer in agriculture, minimising the use of chemical fertilizers.

The presence of PPCPs has been observed in sewage sludge from most WWTPs in different parts of the world. Among the PhACs present in this complex matrix are non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen, naproxen, or diclofenac, commonly used in the treatment of inflammation, pain and fever and analysed by authors such as Pérez-Lemus et al. (2020) [8]. PhACs also include anticonvulsants or antiepileptics such as carbamazepine [9] prevent or reduce the frequency and severity of seizures, antihypertensives such as propranolol [10], antipsychotics such as haloperidol [11], antidepressants such as amitriptyline [12]. There are also lipid regulators such as clofibric acid (CA) [8], used for the improvement and proper maintenance of healthy lifestyles, as well as the assessment and treatment, if appropriate, of other cardiovascular risk factors.

A particular case is that of cytostatic compounds such as vinblastine [13] or vincristine [13], designed and used to cause cell dysfunction because they can inhibit the disordered growth of cells, altering cell division and destroying rapidly multiplying cells. On the other hand, among PCPs, antibacterial agents such as triclocarban [10] and antifungicides such as ketoconazole [14] and miconazole [15] and UV filters such as benzophenone-1 [14] and benzophenone-2 [16], considered endocrine disruptors as they alter the body's endocrine system, can be detected [1].

2. Analytical methodology of sewage sludge samples

Sewage sludge is generated because of different stages of wastewater treatment. Sludge is characterised by the fact that it is a largely liquid waste (more than 95% water). Its composition is variable and depends on the pollution load of the initial wastewater and the technical characteristics of the wastewater treatments carried out. Sludge contains a wide variety of suspended or dissolved matter. Some of them have agronomic value (organic matter, nitrogen (N), phosphorus (P)) and others have polluting potential such as heavy metals, pathogens, and organic pollutants [17]. In general, sludge is treated at the WWTP itself to reduce its water and pathogen content and to ensure the stability of the organic matter. The most common biological treatments are anaerobic digestion (AD), aerobic stabilisation and composting.

The associated matrix is indeed complex, it is not uniform in its composition and the sludge contains certain substances that could interfere with the determination of the compounds of interest. The interferences can affect the whole analytical process from sample preparation to instrumental detection. Therefore, it is necessary to remove them from the samples by clean-up procedures [18].

2.1. Collection and pre-treatment of sludge samples

Sludge samples were collected at the WWTP of Valladolid (Spain). This WWTP serves a population of 344,600 inhabitants. The wastewater treatment consists of a primary purification stage (primary sludge) followed by a biological treatment consisting of a conventional activated sludge process (secondary sludge). The sludge mixture generated is treated in a thickening stage which reduces the sludge volume by concentration or partial removal of water. Samples collected randomly and combined to provide a final sample from the WWTP are frozen and freeze-dried to remove the water content of the environmental samples and then stored at -20°C until analysis. Sample preparation usually includes an extraction process followed by a clean-up step [18]. The analytical methodology used for sludge analysis is described in detail in a study by Pérez-Lemus el at. [8]. The sample pre-treatment includes a microwave-assisted extraction (MAE) and an in-situ clean-up stage with a cleaning agent such as active alumina (100ºC). A filtration step is carried out prior to sample analysis based on gas chromatography-mass spectrometry (GC-MS).

2.2. Analysis by GC-MS

Ten PPCPs found in this type of environmental matrices were selected. Their choice was based on their physico-chemical properties (solubility, vapour pressure, lipophilicity, among others), their high use in daily life, their recognised toxicity, and their presence in aquatic environments. The PPCPs of interest belong to diverse categories (analgesics, non-steroidal anti-inflammatory drugs, preservatives, fungicides, lipid regulators, antiseptics, and endocrine disruptors). Three PPCPs are non-steroidal anti-inflammatory drugs (naproxen, ibuprofen, diclofenac), three preservatives (methylparaben, ethylparaben and propylparaben), two endocrine disruptors (triclosan and bisphenol A), one lipid regulator (clofibric acid), and one antiseptic (salicylic acid). All of them are analysed by a fully automated method consisted of a direct immersion solid-phase microextraction followed by on-fiber derivatization coupled to gas chromatography-mass spectrometry (DI-SPME-On-Fiber derivatization-GC-MS) [8].

3. Concentrations of pharmaceuticals and personal care products in sludge samples

The analytical method was successfully applied to different types of sludge (thermally treated mixed sludge and digested mixed sludge) originating from two indoor pilot scale reactors located at the University of Valladolid (Spain). The experimental devices to treat the sludge consisted of a thermal hydrolysis (HT) treatment plant, processing the thickened mixed sludge (described in section 2.1) at 180°C for 30 minutes and a continuous anaerobic digester, operating under mesophilic conditions.

HT is a pre-treatment that overcomes the main limitation of AD which is the hydrolysis stage. This process can reduce the volume of sludge and the cost associated with its handling, increase its organic load, and improve the dewaterability and degradability of the treated sludge [19]. On the other hand, AD is the process in which microorganisms decompose organic matter in the absence of oxygen, generating value-added products such as biogas (60-70%) and biomass that can be used as fertiliser [20].

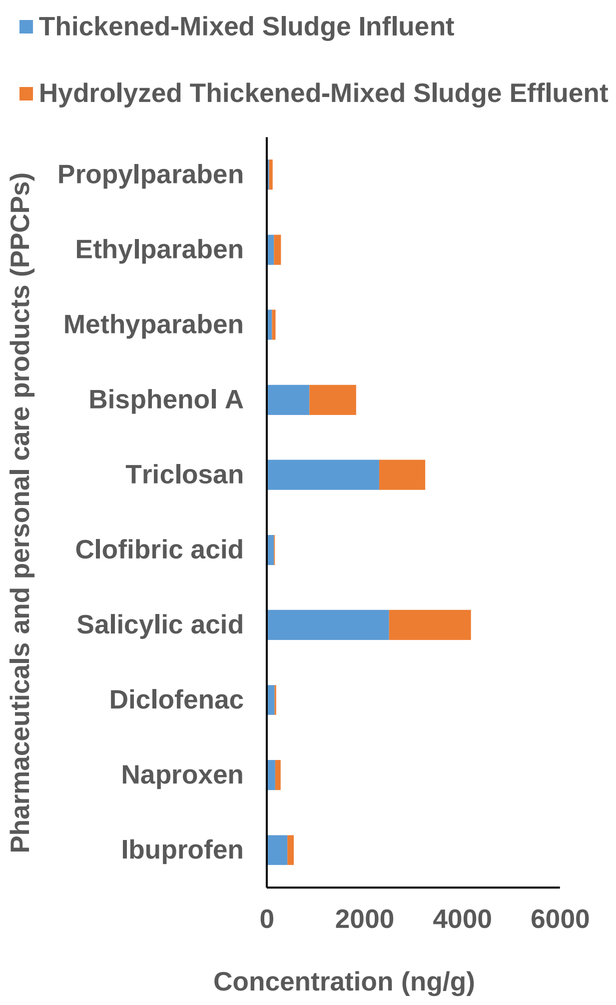

Fig.1. Concentrations of PPCPs for thermally mixed sludge

The results showed a degradation of most of the compounds of interest during HT (fig. 1). Clofibric acid (90%), diclofenac (77%), ibuprofen (71%) and triclosan (59%) showed the highest percentage of degradation. However, two of the contaminants such as propylparaben (30%) and Bisphenol A (9%) showed a small increase in concentration. In the case of AD, a decrease in the concentration of some PPCPs of interest was also observed such as salicylic acid (99%), triclosan (48%), bisphenol A (32%), and diclofenac (22%). As in the case of HT, some contaminants slightly increased in concentration such as clofibric acid (19%), naproxen (12%) and propylparaben (9%) after AD (figure 2). One explanation for these increased concentration actions may be a relation to adsorption phenomena of the pollutants on the solid residue during sludge treatment.

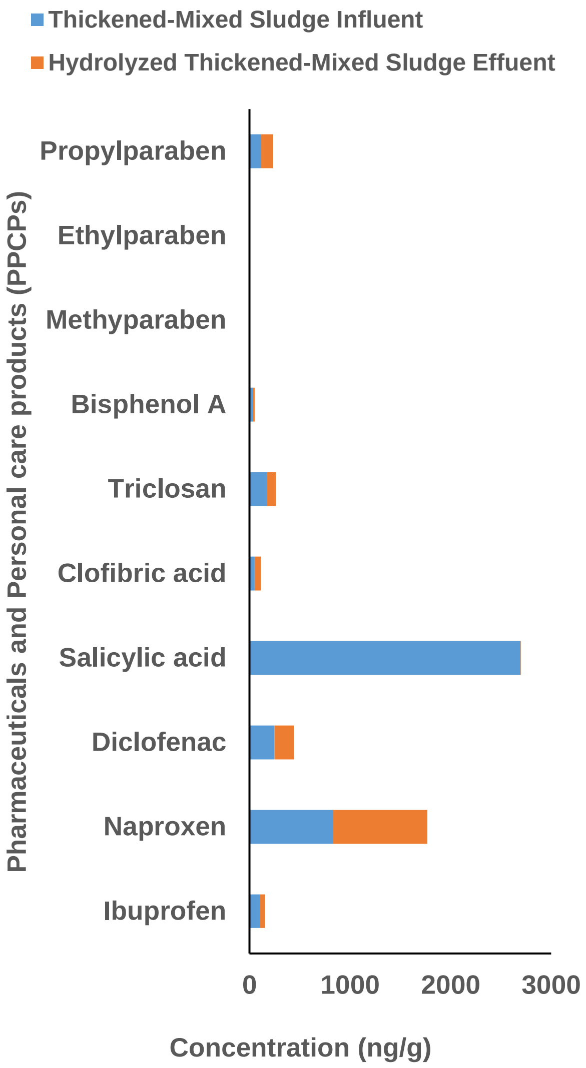

Fig.2. Concentrations of PPCPs for digested mixed sludge

The observed concentrations of the PPCPs of interest in the thickened mixed sludge were found to range between <LOQ-8,330 ng g^{-1}. Naproxen (8,330 ng g^{-1}), salicylic acid (2,695 ng g^{-1}) and triclosan (2,300 ng g^{-1}) having the highest concentrations. In contrast, thermally pre-treated mixed sludge and digested mixed sludge showed a range of concentrations between 15-1670 ng g^{-1} and <LOQ-9350 ng g^{-1}, respectively. Salicylic acid (1,675 ng g^{-1}), bisphenol A (957 ng g^{-1}) and triclosan (945 ng g^{-1}) showed the highest concentrations for thermally pre-treated mixed sludge. In contrast, naproxen had a concentration of 9350 ng g^{-1} for digested mixed sludge.

4. Conclusions

An analytical methodology developed was successfully used for various types of sludge (thickened mixed sludge, thermally pre-treated mixed sludge and digested mixed sludge). It was based on a sample pre-treatment with extraction process as MAE with a clean-up step using an adsorbent as active alumina (100ºC), and a filtration step prior to sample analysis. The instrumental analysis consisted of a fully automated method based on DI-SPME-On-Fiber derivatization-GC-MS. The results showed a significant degradation in PPCPs of interest such as clofibric acid (90%), diclofenac (77%), ibuprofen (71%) and triclosan (59%) for thermally treated mixed sludge. For the digested sludge, a large degradation was observed for salicylic acid (99%), triclosan (48%). However, an increase in concentration was observed for some pollutants of interest such as propylparaben and BPA after TH. Clofibric acid, naproxen and propylparaben after AD. Salicylic acid (1,675 ng g^{-1}), showed the highest concentration for thermally pre-treated mixed sludge. In contrast, naproxen (935 ng g^{-1}) exhibited the highest concentration after AD.

Acknowledgements

The author is grateful for funding from the Spanish Government (MINECO-CTM2015-70722-R), the Regional Government of Castilla y León and the EU-FEDER (CLU 2017-09, UIC 071) and Red Novedar.

5. References

[1] A. Gogoi, P. Mazumder, V.K. Tyagi, G.G. Tushara Chaminda, A.K. An, M. Kumar, Occurrence and fate of emerging contaminants in water environment: A review, Groundw. Sustain. Dev. 6 (2018) 169–180. https://doi.org/10.1016/j.gsd.2017.12.009.

[2] C.G. Daughton, Non-regulated water contaminants: Emerging research, Environ. Impact Assess. Rev. 24 (2004) 711–732. https://doi.org/10.1016/j.eiar.2004.06.003.

[3] K. Kümmerer, Antibiotics in the aquatic environment - A review - Part I, Chemosphere. 75 (2009) 417–434. https://doi.org/10.1016/j.chemosphere.2008.11.086.

[4] A.M. Gorito, A.R. Ribeiro, C.M.R. Almeida, A.M.T. Silva, A review on the application of constructed wetlands for the removal of priority substances and contaminants of emerging concern listed in recently launched EU legislation, Environ. Pollut. 227 (2017) 428–443. https://doi.org/10.1016/j.envpol.2017.04.060.

[5] G. Llorens-Blanch, M. Badia-Fabregat, D. Lucas, S. Rodriguez-Mozaz, D. Barceló, T. Pennanen, G. Caminal, P. Blánquez, Degradation of pharmaceuticals from membrane biological

reactor sludge with Trametes versicolor, Environ. Sci. Process. Impacts. 17 (2015) 429–440. https://doi.org/10.1039/c4em00579a.

[6] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: Agents of subtle change?, Environ. Health Perspect. 107 (1999) 907–938. https://doi.org/10.1289/ehp.99107s6907.

[7] A.J. Ebele, M. Abou-Elwafa Abdallah, S. Harrad, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment, Emerg. Contam. 3 (2017) 1–16. https://doi.org/10.1016/j.emcon.2016.12.004.

[8] N. Pérez-Lemus, R. López-Serna, S.I. Pérez-Elvira, E. Barrado, Sample pre-treatment and analytical methodology for the simultaneous determination of pharmaceuticals and personal care products in sewage sludge, Chemosphere. 258 (2020) 127273. https://doi.org/10.1016/j.chemosphere.2020.127273.

[9] W. Peysson, E. Vulliet, Determination of 136 pharmaceuticals and hormones in sewage sludge using quick, easy, cheap, effective, rugged and safe extraction followed by analysis with liquid chromatography-time-of-flight-mass spectrometry, J. Chromatogr. A. 1290 (2013) 46–61. https://doi.org/10.1016/j.chroma.2013.03.057.

[10] B. Subedi, K. Balakrishna, D.I. Joshua, K. Kannan, Mass loading and removal of pharmaceuticals and personal care products including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in southern India, Chemosphere. 167 (2017) 429–437. https://doi.org/10.1016/j.chemosphere.2016.10.026.

[11] M.B.R. Cerqueira, K.L. Soares, S.S. Caldas, E.G. Primel, Sample as solid support in MSPD: A new possibility for determination of pharmaceuticals, personal care and degradation products in sewage sludge, Chemosphere. 211 (2018) 875–883. https://doi.org/10.1016/j.chemosphere.2018.07.165.

[12] B. Albero, C. Sánchez-Brunete, E. Miguel, R. Aznar, J.L. Tadeo, Determination of selected pharmaceutical compounds in biosolids by supported liquid extraction and gas chromatography-tandem mass spectrometry, J. Chromatogr. A. 1336 (2014) 52–58. https://doi.org/10.1016/j.chroma.2014.02.020.

[13] S. Santana-Viera, J. Tuček, M.E. Torres-Padrón, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, R. Halko, Cytostatic compounds in sludge and sediment: extraction and determination by a combination of microwave-assisted extraction and UHPLC–MS/MS, Anal. Bioanal. Chem. 412 (2020) 3639–3651. https://doi.org/10.1007/s00216-020-02600-0.

[14] A. Luque-Muñoz, J.L. Vílchez, A. Zafra-Gómez, Multiclass method for the determination of pharmaceuticals and personal care products in compost from sewage sludge using ultrasound and salt-assisted liquid–liquid extraction followed by ultrahigh performance liquid chromatography-tandem mass spectrometr, J. Chromatogr. A. 1507 (2017) 72–83. https://doi.org/10.1016/j.chroma.2017.05.051.

[15] Q. Sun, M. Li, C. Ma, X. Chen, X. Xie, C.P. Yu, Seasonal and spatial variations of PPCP occurrence, removal and mass loading in three wastewater treatment plants located in different urbanization areas in Xiamen, China, Environ. Pollut. 208 (2016) 371–381. https://doi.org/10.1016/j.envpol.2015.10.003.

[16] C. Abril, J.L. Santos, J. Martín, I. Aparicio, E. Alonso, Occurrence, fate and environmental risk of anionic surfactants, bisphenol A, perfluorinated compounds and personal care products in sludge stabilization treatments, Sci. Total Environ. 711 (2020). https://doi.org/10.1016/j.scitotenv.2019.135048.

[17] I. Díaz, A. Díaz-Curbelo, N. Pérez-Lemus, F. Fdz-Polanco, S.I. Pérez-Elvira, Traceability of organic contaminants in the sludge line of wastewater treatment plants: A comparison study among schemes incorporating thermal hydrolysis treatment and the conventional anaerobic digestion, Bioresour. Technol. 305 (2020) 123028. https://doi.org/10.1016/j.biortech.2020.123028.

[18] N. Pérez-Lemus, R. López-Serna, S.I. Pérez-Elvira, E. Barrado, Analytical methodologies for the determination of pharmaceuticals and personal care products (PPCPs) in sewage sludge: A critical review, Anal. Chim. Acta. 1083 (2019) 19–40. https://doi.org/10.1016/j.aca.2019.06.044.

[19] W.P.F. Barber, Thermal hydrolysis for sewage treatment: A critical review, Water Res. 104 (2016) 53–71. https://doi.org/10.1016/j.watres.2016.07.069.

[20] S. Jain, S. Jain, I.T. Wolf, J. Lee, Y.W. Tong, A comprehensive review on operating parameters and different pretreatment methodologies for anaerobic digestion of municipal solid waste, Renew. Sustain. Energy Rev. 52 (2015) 142–154. https://doi.org/10.1016/j.rser.2015.07.091.