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Occurrence of Selected Emerging Contaminants in Southern Europe WWTPs: Comparison of Simulations and Real Data

Daniel Sol [1], Andrea Menéndez-Manjón [1], Paula Arias-García [1], Amanda Laca [1], Adriana Laca [1,*], Amador Rancaño [2] and Mario Díaz [1]

[1] Department of Chemical and Environmental Engineering, University of Oviedo, C/Julián Clavería s/n, 33006 Oviedo, Spain
[2] ACCIONA Agua S.A., 28108 Alcobendas, Spain
* Correspondence: lacaadriana@uniovi.es; Tel.: +34-985-10-29-74

Abstract: Emerging contaminants (ECs) include a diverse group of compounds not commonly monitored in wastewaters, which have become a global concern due to their potential harmful effects on aquatic ecosystems and human health. In the present work, six ECs (ibuprofen, diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol) were monitored for nine months in influents and effluents taken from four wastewater treatment plants (WWTPs). Except for the case of ibuprofen, which was in all cases in lower concentrations than those usually found in previous works, results found in this work were within the ranges normally reported. Global removal efficiencies were calculated, in each case being very variable, even when the same EC and facility were considered. In addition, the SimpleTreat model was tested by comparing simulated and real ibuprofen, diclofenac and erythromycin data. The best agreement was obtained for ibuprofen which was the EC with the highest removal efficiencies.

Keywords: emerging contaminants; removal; wastewater; WWTP; SimpleTreat

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1. Introduction

The progressive population growth, closely related to industrial and technological development, has led to a considerable increase in the production of consumer goods [1]. Processes associated with the different stages of the life cycle of these products entail the emission of different pollutants into the environment. Among the numerous pollutants of anthropogenic origin, emerging contaminants (ECs) should be highlighted [2]. The United States Geological Survey (USGS) defined these contaminants as "any compound of engineered or normal root or any microorganism that is not usually observed in the surrounding, however it can possibly cause unfriendly environmental and human wellbeing impacts" [3].

The concentration of emerging pollutants in wastewater varies from ng·L^{-1} to µg·L^{-1} depending on the specific compound analysed [4,5]. Additionally, this group includes diverse contaminants with different origins, chemical characteristics and potential harmful effects [6,7]. Certainly, endocrine disrupting substances (e.g., hormones), drugs, hygiene and personal care products, nanoparticles, perfluorinated substances, fire retardants, fertilizers, pesticides, and oily contaminants, among others, are considered ECs [4,8,9]. It is very difficult to control the spread of ECs as they can be found in many everyday products. In addition, most of these compounds are toxic or chemical substances capable of mimicking the hormones of living organisms, which alters their proper development and behaviour [10]. Mostly, biologically active forms of emerging pollutants, with or without limited treatment, are intentionally or unintentionally dumped into marine ecosystems causing health hazards and directly affecting the aquatic environments [11].

One of the main obstacles to controlling EC dispersion is the absence of specific regulations and quality standards that establish limits for these pollutants [10–13]. Therefore, ECs

are not usually analysed in the environment, so their harmful potential is underestimated. Due to the lack of knowledge about these substances and their hazardousness, organizations such as the Environmental Protection Agency (EPA), the World Health Organization (WHO) and the European Commission are prioritizing the study of their effects on human health and on the environment with the final aim of reducing its presence in water [10,13].

One of the main routes of entry of these compounds in aquatic ecosystems is through wastewater. In most cases, their elimination in wastewater treatment plants (WWTPs) is not complete due to the use of conventional methods, which are ineffective or insufficient for EC removal, so an efficient and profitable additional water treatment would be required [14–17]. In general, the concentrations of ECs in the effluents of WWTPs are usually low, but their presence implies potential harmful effects on the environment and human health due to their structure and characteristics, such as their persistence and their ability to bioaccumulate even at low concentrations [18]. In addition, it should be noted that, even in the same facility, removal efficiencies in WWTPs are highly variable depending on the type of treatment, season, compound nature, etc. [15,17,19].

In the present work, a follow-up was conducted for nine months of influents and effluents of four WWTPs sited in the southwest of Spain to analyze the incidence of six selected ECs (ibuprofen, diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol). The occurrence and the effectiveness of EC removal of the different facilities were evaluated. In addition, the SimpleTreat 4.0 software was employed to compare simulated and real data with the aim to obtain results that could be extrapolated at European level.

2. Materials and Methods

2.1. Selected ECs

The following six emerging contaminants were analysed: ibuprofen, diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol. These compounds were chosen since they are representative of diverse groups of ECs widely reported in aquatic and land environments. Ibuprofen and diclofenac are non-steroidal anti-inflammatory drugs that, due to their high consumption, are included within the top ten high priority pharmaceuticals identified in a European assessment of pharmaceuticals and personal care products (PPCPs) [20–22]. Erythromycin is the most toxic antibiotic, which inhibits protein synthesis in bacteria [23–25]. Triclosan is a pharmaceutical drug (antiseptic) used in hospital and personal hygiene products [13,26]. Imidacloprid is a neuroactive insecticide [27,28] and 17α-ethinylestradiol is an estrogen derived from estradiol, used in the formulation of contraceptive pills [29].

2.2. Characteristics of Wastewater Treatment Plants (WWTPs)

Four WWTPs located in the southwest of Spain were studied. The flow diagram of each WWTP is shown in Figure 1.

WWTP 1 treats approximately 3000 m^3/day (11,375 population equivalent, PE) and it consists of: screening systems, a grit and grease removal system, an activated sludge treatment (6800 m^3) composed of three anaerobic chambers and two oxic biological reactors followed by a secondary settling, a tertiary treatment based on a coagulation/flocculation process, a lamellar settling, a filtration employing disc filters and, finally, UV disinfection equipment. The secondary sludge is removed from the secondary settler and driven towards the thickener, together with the sludge from the lamella decanter. After that, the mixed sludge is pumped up to two centrifuges for dehydration.

WWTP 2 treats around 2000 m^3/day (13,586 PE) and consists of two roughing channels equipped with automatic screens and automatic cleaning sieves, and a third channel equipped with a manual cleaning screen, two grit and grease removal systems, a primary decantation, a secondary treatment based on an activated sludge treatment (1191 m^3), followed by a secondary settling. The tertiary treatment is comprised a homogenization tank, a coagulation/flocculation chamber, a lamella settler, a sand filter (RSF) and a disinfection

UV system. The primary, biological sludge and homogenization-tank sludge are sent to the aerobic digester. Once digested, the mixed sludge is driven to the thickener and after that is dewatered in two centrifuges.

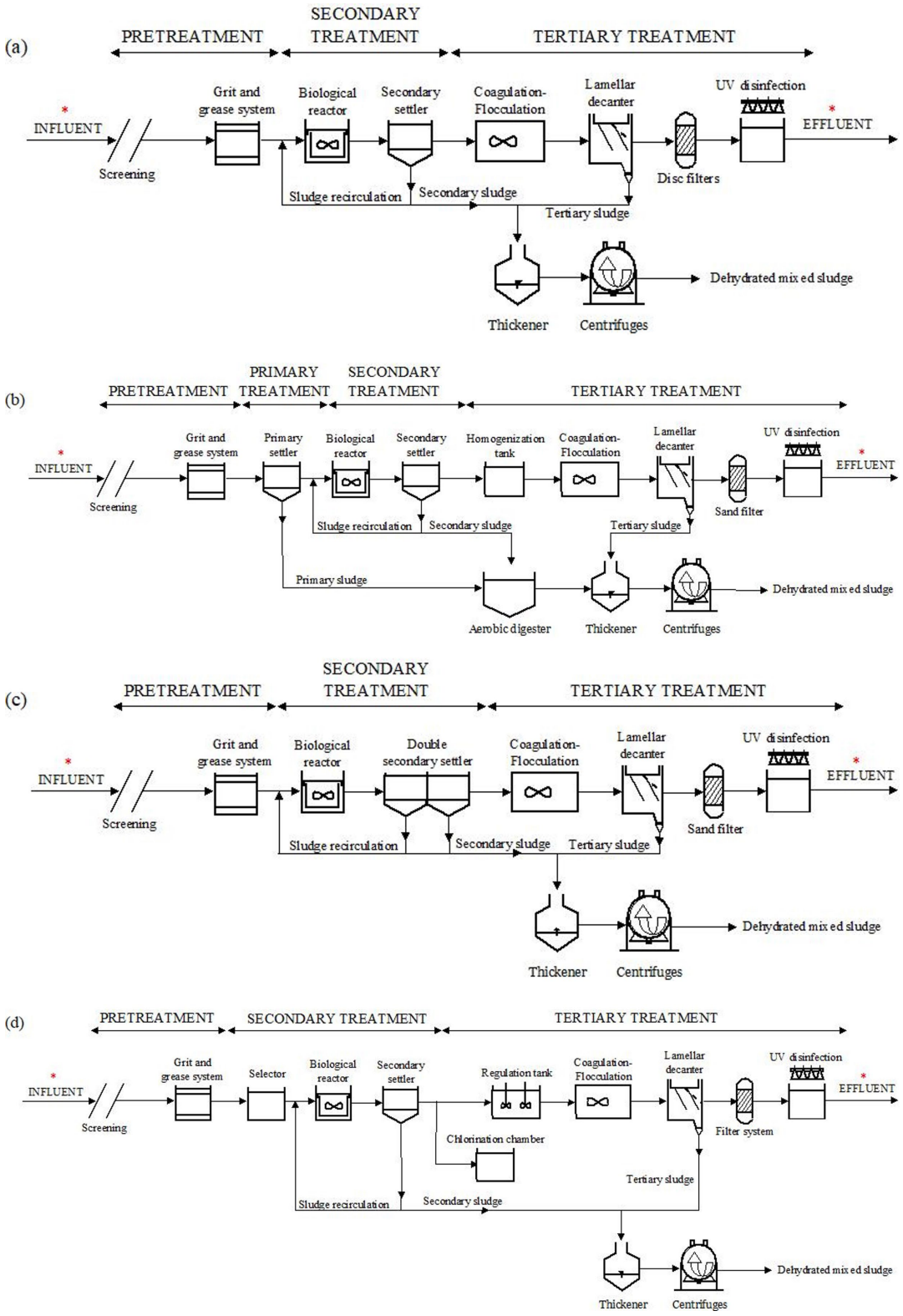


Figure 1. Scheme of the WWTPs studied in this work: (**a**) WWTP 1, (**b**) WWTP 2, (**c**) WWTP 3, (**d**) WWTP 4. Asterisks indicate the sampling points.

The wastewater that arrives at WWTP 3 (4800 m^3/day; 24,866 PE) is collected in channels with automatic and manual systems for wastewater screening. This facility has two grit and grease removal systems, a secondary treatment constituted by an anoxic chamber and two oxic biological reactors (19,000 m^3), followed by a double settler. Finally, a tertiary treatment consisting of coagulation/flocculation chambers, lamella settler equipment, a pair of sand filters and a UV disinfection channel. To treat the mixed sludge, a gravity thickener is employed and, subsequently, the sludge is driven to the centrifuges for dewatering.

The treatment carried out at the WWTP 4 (1500 m^3/day; 5423 PE) entails the following systems: two channels equipped with automatic grates and sieves for coarse roughing, two grit and grease removal systems, two biological treatment lines that have two carousel-type reactors (12,036 m^3) and a secondary settler. Finally, a tertiary treatment consisting of a chlorination chamber, a regulation tank, a coagulation/flocculation chamber followed by a lamella settler, a filter system and a UV disinfection system. Sludge collected from secondary and lamella settling is sent to a thickener, and after that, is centrifuged to obtain the dehydrated mixed sludge.

2.3. Sample Collection

Wastewater was sampled from the influent and effluent flows of the four WWTPs after the roughing processes. Grab samples were collected once a month for nine months, using a sample device consisting of a plastic bottle attached to a stick. After the collection, the samples were transferred to 2.5 L amber glass bottles and transported at 4 °C to the laboratory where 3% (v/v) of methanol (Sigma-Aldrich, San Luis, MO, USA) was added to them, avoiding the degradation of analytes until sample processing.

2.4. Analytical Method

Influent samples were centrifuged at 10,000 G for 30 min (Kubota 6500) and the supernatant was filtered under vacuum through 0.45 µm (Ahlstrom-Munksjö, Helsinki, Finland). The effluent samples were directly filtered. Once filtered, the pH of the samples was adjusted to 2 with H_2SO_4 (98%, Sigma-Aldrich, San Luis, MO, USA) and a solid-phase extraction (SPE) was carried out to concentrate the emerging pollutants using OASIS HLB cartridges (Waters, Milford, MA, USA) and a vacuum pump at 300 mbars as described below. First, acetone (2 × 5 mL), 5 mL of acetic acid and 5 mL of distilled water were successively flowed through the cartridge to prepare it. Then, 200 mL of sample was filtered through the cartridge and the retained compounds were desorbed employing firstly 6 mL of 40:60 acetone and buffer solution (0.1 M $NaHCO_3$ at pH 10 adjusted with 1 M NaOH), obtaining in this way the acidic fraction. After that, 6 mL of acetone was flowed through the cartridge, obtaining the acetonic fraction. The acidic fraction, after being adjusted again to pH 2, was subjected to three consecutive extractions employing each time 2 mL of ethyl acetate by centrifugation for 10 min at 3500 rpm (Sorvall ST-16R, Thermo Fisher, Waltham, MA, USA), and approximately 6 mL of supernatant was recovered. The acidic fraction (now in ethyl acetate) and the acetonic fraction were dried under a stream of nitrogen. The internal standards (2,4-dichlorophenoxyacetic acid for acidic fraction, 17β-estradiol d5 and Imidacloprid d4 for acetonic fraction) were added at this moment and the samples were again dried under a nitrogen stream. Next, the derivatization agents, 50 µL MTBSTFA + 1% TBDMCS (N-methyl-N-(tert-butyldimethylsilyl) trifluoroacetamide with 1% tert-butyldimethylchlorosilane) for acidic fraction and 50 µL BSTFA + 1% TCMS (N,O-Bis(trimethylsilyl)trifluoroacetamide with 1% Trimethylchlorosilane) for acetonic fraction, and the solvent (ethyl acetate for the acid fraction and pyridine for the acetone fraction) were added and the samples were placed in a water bath at 60 °C for 30 min. Once the samples and standards had been tempered, they are brought to a final volume of 1 mL with ethyl acetate. All reagents were supplied by Merck KGaA (Darmstadt, Germany).

The samples were analysed using the GC-MS technique, using a 7890A GC Gas Chromatograph coupled to a 5975C Inert XL MSD Mass Spectrometer (Agilent Technologies,

Santa Clara, CA, USA), fitted with a column DB5MS (Agilent Technologies, Santa Clara, CA, USA). Ultrapure helium was used as carrier gas at a constant flow of 1.3 mL/min. The oven temperature was held at 100 °C for 1 min, then programmed at 15 °C/min to 250 °C, and finally at 20 °C/min to 300 °C, with the final temperature being held for 10 min. 1 µL of sample was injected in the splitless mode. The transfer line and ion source were set at 280 °C and 230 °C, respectively. Calibration curves were obtained employing standards of each EC, and limits of quantification (LOQ) are shown in Table 1.

Table 1. LOQ for each compound.

	LOQ (ppb)
Ibuprofen	2
Diclofenac	3
Erythromycin	2
Triclosan	3
Imidacloprid	3
17α-ethinylestradiol	1

2.5. Kinetic Constants Estimation

SimpleTreat 4.0 is a basic tool used to predict exposure in environmental risk assessment and includes the most important processes such as sorption, volatilization, dissolution, and biodegradation [30]. The program requires several parameters to model the evolution of the six ECs analysed (ibuprofen, diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol). The physicochemical parameters employed for the modellization, i.e., type of compound, molecular weight, solubility, vapor pressure, octanol-water partition coefficient (K_{ow}), solubility, pKa and Henry coefficient, are available in Table S1. Some sorption parameters not found in the literature, such as K_{oc}, Kp_s and Kp_{as}, were estimated by the program [30]. In addition, physicochemical and biological parameters related to the specific wastewater treatment have been provided by the WWTPs and are shown in Tables S2–S5.

Firstly, the SimpleTreat 4.0 program was used to estimate the theoretical biodegradation constant (k) as a function of the experimental removal rate for each compound and sample. As samples were taken in different months, which implies different ambient temperatures, the kinetic constants were used to obtain Arrhenius parameters (only data with deviations lower than 10% from mean values were considered). Using these parameters, the theoretical k was obtained for each month, considering the daily temperature. This value was implemented in the SimpleTreat 4.0 program and predicted, and real ECs removal efficacies were compared.

3. Results and Discussion

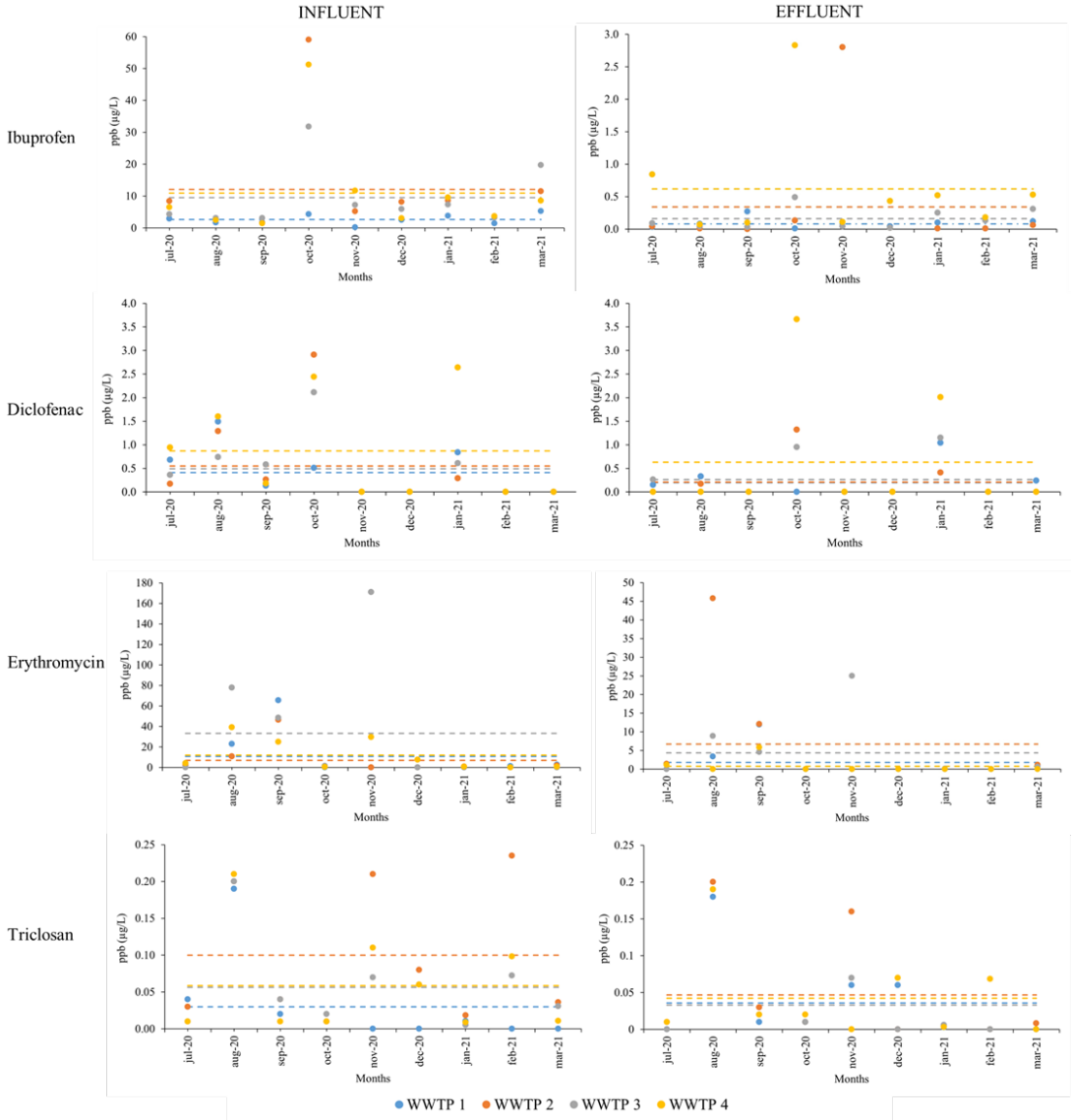
3.1. Occurrence and Removal Efficiencies

The occurrence and removal efficiency of six emerging contaminants (ibuprofen, diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol) were studied in four WWTPs. The results are shown in Figure 2 and Tables S6–S11. The removal efficiency was calculated in each case, except when the effluent concentration was higher than the influent concentration or the EC was "not detected".

3.1.1. Ibuprofen

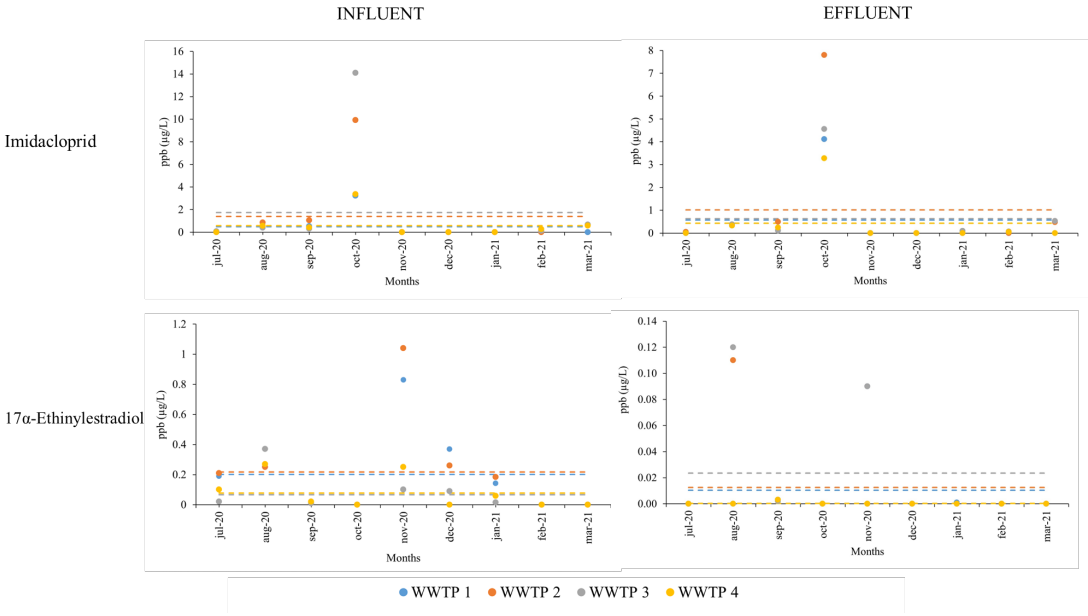
Ibuprofen is the third most prescribed drug worldwide and due to its high demand more than 30 kilotons are synthesized annually. The main route of emission is through the excretion of non-metabolized and metabolized drug in the urine of humans and animals after consumption. It has been detected in wastewater, sewage sludge, hospital wastewaters, surface waters and drinking water. Potential effects of this carcinogenic and endocrine disrupting drug have been described for microorganisms, algae, fish species, and even human health [31,32].

As can be observed in Figure 2a and Table S6, the concentration of ibuprofen in influent samples of the four WWTPs generally varies between 1 and 20 ppb with average values between 3 and 18 ppb. The highest values were observed in October (32–59 ppb in WWTP 2, WWTP 3 and WWTP 4). After wastewater treatment, the concentration of ibuprofen was notably reduced, with efficacies above 80%, in most cases (Figure 3a and Table S6). So, ibuprofen concentrations in the effluent usually ranged between "not detected" and 0.8 ppb. The only exceptions were in October and November with ibuprofen concentrations in the WWTP 2 and WWTP 4 effluents, respectively, of around 2.8 ppb. In the case of WWTP 2, this higher level was due to the poor elimination efficacy observed for ibuprofen in this month (46.2%). In general, in the literature, the ibuprofen concentrations in influents and effluents of urban WWTPs were within the ranges of 9–17,500 ppb and 1–3777 ppb, respectively. The ibuprofen concentrations observed in this work in the influents and effluents were lower than those usually obtained in previous works [5,33]. However, removal efficiencies reported for this micropollutant varied between 25% and 100% [30,34,35], in agreement with percentages obtained here.



(**a**)

Figure 2. *Cont.*



(**b**)

Figure 2. (**a**) Evolution of ibuprofen, diclofenac, erythromycin and triclosan from July 2020 to March 2021 in influent and effluent samples of the WWTPs studied. (**b**) Evolution of imidacloprid and 17α-ethinylestradiol in influent and effluent samples in the four WWTPs analysed, from July 2020 to March 2021. Dashed lines show the mean concentration for each WWTP.

3.1.2. Diclofenac

Diclofenac is one of the pharmaceutical wastes included in the watch list of the Commission Implementing Decision (EU) published by the European Commission in 2015. It is an oral tablet or topical gel non-steroidal anti-inflammatory drug (NSAID), and its global consumption is around 940 tons per year. A total of 65% is usually released through urine into wastewater [36,37].

Diclofenac was observed in concentrations even lower than those obtained for ibuprofen, with similar profiles in the four WWTPs (Figure 2a and Table S7). In influent samples, diclofenac exhibited values that were in most cases below 1.5 ppb, with average concentrations of 0.41 ± 0.52 ppb, 0.55 ± 0.98 ppb, 0.49 ± 0.68 ppb and 0.87 ± 1.10 ppb for WWTP 1, WWTP 2, WWTP 3 and WWTP 4, respectively. The highest concentrations were measured in October in WWTP 2, WWTP 3 and WWTP 4, and in January in WWTP 4, with values between 2 and 3 ppb. After wastewater treatment, the concentration of diclofenac was notably reduced, with removal efficiencies usually above 50% (Figure 3b and Table S7) in most cases. These percentages are higher than those reported in the literature, typically below 40% [38]. In accordance with the literature data, poor removal efficiencies were obtained for WWTP 3 in July (28%) and WWTP 4 in January (24%). In effluents, most diclofenac concentrations were below 1 ppb, with slightly higher values observed in certain samples. Particularly, WWTP 4 in October and January exhibited concentrations between 2 and 4 ppb in both influent and effluent. The diclofenac concentrations found in this work are within the wide ranges reported for different WWTPs, including from "not detected" to 7100 ppb [5,39]. It is remarkable that, in a few cases, the concentrations of diclofenac detected in the effluent were higher than those found in the influent for the same date (October for WWTP 4 and January for WWTP 1, WWTP 2 and WWTP 3). This behaviour has been previously described and many studies reported the difficulty in removing this persistent analgesic from wastewaters [33]. In addition, it has to be considered that influent and effluent samples were taken almost simultaneously, and the water sample taken at the end of the treatment might correspond to a higher concentration with respect to the raw wastewater.

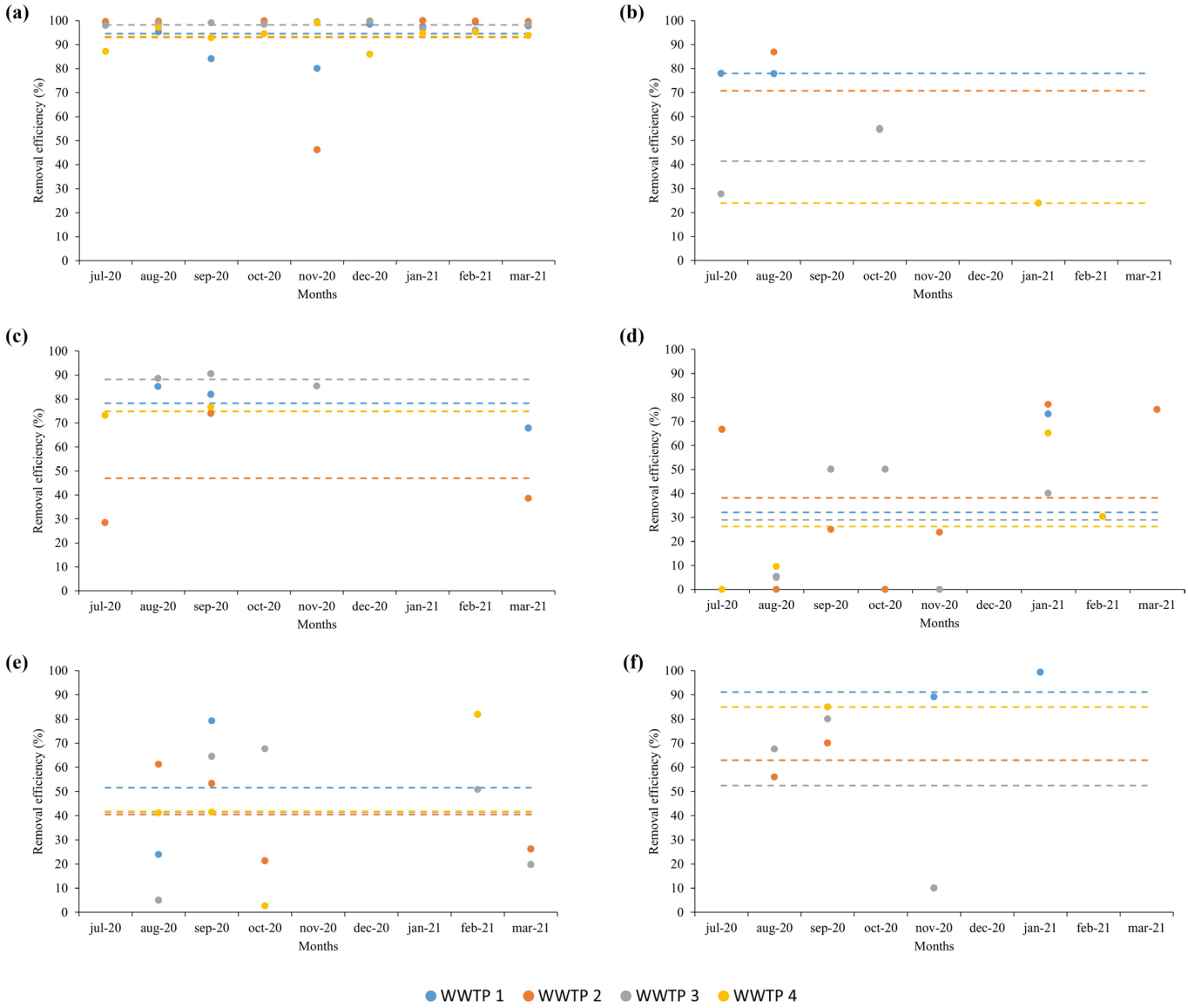


Figure 3. Removal efficiencies of the WWTPs studied obtained for: (**a**) ibuprofen, (**b**) diclofenac, (**c**) erythromycin, (**d**) triclosan, (**e**) imidacloprid and (**f**) 17α-ethinylestradiol from July 2020 to March 2021.

3.1.3. Erythromycin

Erythromycin is an antibiotic, also included in the watch list of the Commission Implementing Decision (EU) published by the European Commission in 2015. It has been found in different environments, such as rivers, surface water, wastewater, seawater, sediments, etc. Low concentrations of this compound can contribute to the proliferation of antibiotic resistant bacteria [40,41].

Regarding erythromycin (Figure 2a and Table S8), the influent samples showed higher concentrations in the warmest months (2–78 ppb, July–September) compared to the coldest months ("not detected"–8 ppb, October-March), with the exception of WWTP 3 and WWTP 4, which showed in November a peak in concentration of 171 ppb and 30 ppb, respectively. In general, in the effluent samples the concentrations of erythromycin were also higher during the warmest months ("not detected"–46 ppb) than in the coldest months, with concentrations at levels close to 0 ppb. Again, the only exception was a value of 25 ppb detected in November in WWTP 3. In the literature, a wide variation of erythromycin values can be found both in influent and effluent samples ("not detected"–14,700 ppb) [42],

having reported concentrations much higher than those obtained here. The concentration of erythromycin was reduced in the WWTPs studied with efficacies above 70%, except in WWTP 2 with 47% (Figure 3c and Table S8). WWTP 2 showed low efficacies of 29% and 39% in July and March, respectively, and, in addition, in August the concentration detected in the effluent was higher than that of the influent. In this work, removal efficiencies higher than those obtained by other authors were observed, typically below 59%, in conventional WWTPs [43].

3.1.4. Triclosan

Triclosan is an antimicrobial agent widely used in PPCPs. It has persistent characteristics and bioaccumulation properties that make it a major concern. In 2016, the US Food and Drugs Administration (FDA) regulated the use of this product in commercial products. Although it is a very stable chemical, it can be decomposed by light, ozone, chlorine and some microorganisms, into compounds harmful to living beings, such as chlorinated phenols and dibenzo-p-dioxins [44].

The emerging contaminant triclosan showed, in general terms, a similar behaviour in the influent and effluent samples of the four WWTPs, being in all cases in concentrations close to 0 ppb (Figure 2a and Table S9). Specifically, these values ranged between "not detected" and 0.24 ppb. These concentrations of triclosan were lower than those usually found in the literature (between 1 ppb and 33 ppm). It has been reported that triclosan is largely eliminated from wastewater by conventional treatments, with removal efficiencies between 85% and 98%. In this work, the removal efficiencies were very variable, even for the same WWTP, but always with values below those described in the literature [45,46] (Figure 3d and Table S9). The reason may be that the measured concentrations are very close to the quantification limit, which implies higher uncertainty associated with the values (Table 1).

3.1.5. Imidacloprid

Imidacloprid is a neonicotinoid insecticide that has been widely used as a pesticide, biocide and veterinary medicinal product. This compound presents a high toxicity, a long persistence, and is easily and flexibly applied. The most sensitive organisms to this EC are aquatic invertebrates [47].

The profile of imidacloprid concentrations in the influent and effluent samples are remarkably similar for the four WWTPs (Figure 2b and Table S10). Low concentrations, ranging between "not detected" and 1 ppb in influent and below 0.6 ppb in effluent, were detected. Oddly, higher concentrations were found in October in all the WWTPs, varying between 3 and 14 ppb in influent and effluent samples. In general, imidacloprid concentrations in the literature range between 20 and 387 ppb, and its removal during wastewater treatment was quite low (<20–30%) [48]. In the present work, imidacloprid showed concentrations much lower, which is in agreement with the amount of this EC detected in the effluents of 16 Spanish WWTPs sampled in 2019 (<0.4 ppb) [49]. The reduction in the concentrations of imidacloprid in European wastewaters and water courses is expectable due to its use as a plant protection product is no longer authorized in the EU (Regulation EU 2020/1643), and since 2020 no emission is expected from this use. Regarding the removal efficiencies here again the results were very variable (Figure 3e and Table S10) since the concentrations used to calculate them were very close to the detection limit.

3.1.6. 17α-ethinylestradiol

In 2013, Directive 2013/39/EU extended the list of Priority Pollutants, including the 17α-ethinylestradiol. WWTPs are considered the main source of emission of this EC into the aquatic environment. In 2018, this emerging contaminant was included in the watch list of the Commission Implementing Decision 2018/840/EU as a substance to be monitored in water in the field [50,51].

The concentration of 17α-ethinylestradiol in the four facilities was between "not detected" and 0.37 ppb, with the exception of samples taken in November from WWTP 2 and WWTP 3 that exhibited concentrations around 1 ppb (Figure 2b and Table S11). In the effluent samples, the concentration varied between "not detected" and 0.12 ppb in all cases. These results were quite low but in agreement with other concentrations published, usually below 78 ppb. The reported removal efficiencies of this hormone were between 47.5–83.6% [29,52]. In concordance with these data, the removal efficiencies obtained here were usually above 56% (Figure 3f and Table S11).

3.2. Simulation of Emerging Contaminants Removal

SimpleTreat is the recommended sewage treatment plant model in Europe for environmental risk assessment of industrial chemicals (REACH), chemicals covered under the Biocidal Products Regulation (BPR) and active pharmaceutical ingredients regulated by the European Medicines Agency (EMA) [30]. Using a software that implements this model (SimpleTreat 4.0), a first-order biodegradation constant (k_i) was determined as a function of the percentage of removal obtained for each compound analysed in each WWTP each month. Samples where an EC was "not detected" in the effluent have not been considered for the estimation, as considering 100% efficacies could lead to a large error. So, using data shown in Tables S1–S11, k_i values were obtained (Tables S12 and S13). It should be borne in mind that the software does not allows the consideration of all the treatment processes employed in the WWTPs. For example, most parts of tertiary treatments cannot be considered, and it is evident that these can contribute to reduce the concentrations of ECs [53–55]. So, the kinetic constants calculated could be overestimated to a certain extent. Another factor to be considered is the existence of errors due to the estimation of sorption parameters by the program, leading to a deviation in the accuracy of the model results [56,57].

In the case of ibuprofen, the majority of the apparent degradation constants for WWTP 1, WWTP 3 and WWTP 4 were between 0.4 and 3 h^{-1}, values in general higher than those obtained in WWTPs which did not include tertiary treatments (0.06–0.7 h^{-1}) [5], whereas the simulation of ibuprofen in SimpleTreat usually employs a default value of 1 h^{-1} [55,58]. Specifically, Alvarino et al. [59] indicated a degradation rate for ibuprofen of 0.3 h^{-1} in an UASB reactor coupled to a hybrid aerobic membrane bioreactor for municipal wastewater treatment. Furthermore, values above 30 h^{-1} were obtained in WWTP 2, which was the only facility that includes primary settling. Ibuprofen is a fairly easily biodegradable compound and can be removed by sorption on several materials [60], so this settling step contributed to ibuprofen removal by being adsorbed on primary sludge or even biodegradation.

For diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol, kinetic constants were quite similar, most of them being within the range 0.02 to 0.3 h^{-1}. These values were lower than those obtained in this work for ibuprofen. This is in agreement with other authors who reported slow biodegradations for these compounds, being 0.75, 0.03 and 0.08 h^{-1} for diclofenac, erythromycin and 17α-ethinylestradiol, respectively, in an UASB reactor employed at pilot scale to treat municipal wastewater [59], 0.002–0.005 h^{-1} for imidacloprid degraded by pure bacterial isolates in the laboratory [61] and 0.1–0.2 h^{-1} for triclosan when bioaugmentation treatment for wastewater was applied [62]. Furthermore, it should be noted that default values employed in previous works to simulate the evolution of these contaminants by means of the SimpleTreat model were, in all cases, 0.3 h^{-1} for diclofenac, erythromycin and 17α-ethinylestradiol, and 0.1 h^{-1} for triclosan [55,58]. However, no data for imidacloprid has been reported until now, since, to the best of our knowledge, this is the first time that the SimpleTreat software has been used to model the behaviour of this EC in WWTPs. It is noteworthy that few constants could be estimated in the cases of diclofenac, erythromycin, triclosan and 17α-ethinylestradiol because effluent concentrations were below the LOQ or even slightly higher than the influent concentrations. This behaviour has already been described in previous works for several ECs [5] and

indicates that conventional wastewater treatment processes are not effective enough to remove these complex compounds. In addition, some products of human metabolism may act as a reservoir from which a later yield of the parent EC can occur [63]. Additionally, measured concentrations were very low, near to the LOQ, which implies higher uncertainty of the values quantified.

As wastewater samples were taken on different dates with different ambient temperatures, the calculated constants correspond to different temperatures. It would be expected that ki values were higher for higher temperatures, following the Arrhenius expression $k_i = Ae^{-E_a/RT}$. Nevertheless, a lack of tendency with temperature was observed for triclosan, imidacloprid and 17α-ethinylestradiol kinetic constants. This can be explained because the concentrations measured, in particular in the effluent, were very low, near LOQ, which means a larger uncertainty in the data and, therefore, in the calculated kinetic constants. So only the kinetic constants obtained for ibuprofen, diclofenac and erythromycin were used to estimate the parameters A and E_a (apparent activation energy) of a type of Arrhenius equation. The next line equations were obtained, $\ln k_{ib} = 11.292 - 3281.3\frac{1}{T}$, $\ln k_{di} = 31.767 - 9971.3\frac{1}{T}$ and $\ln k_{er} = 6.7050 - 2526.2\frac{1}{T}$ for ibuprofen, diclofenac, and erythromycin (k in h^{-1} and T in K), and the apparent activation energies were 27.3, 82.9 and 21.0 kJ/mol, respectively. These values were similar to those reported for the apparent activation energies in the biodegradation of other ECs, i.e., caffeine, paracetamol, naproxen and ibuprofen (21–86 kJ/mol) [5]. Using the obtained equations, new kinetic constants were calculated for these ECs for each sampling temperature. In Tables S14–S16 these kinetic constants (h^{-1}) for each month are shown. These values have been used in SimpleTreat 4.0 to obtain the theoretical percentage of removal for ibuprofen, diclofenac and erythromycin for each month and WWTP. In Figure 4, the theoretical percentages are represented versus those obtained experimentally. Considering a 10% error interval (dashed green lines), it can be seen that the majority of the points fall within this interval for ibuprofen in WWTPs 1, 3 and 4, indicating that the simulation of ibuprofen is acceptable for these cases (Figure 4a). These plants have in common that they do not have primary treatment, whereas WWTP 2 does. It seems that the presence of this settling step makes the software predict lower removal efficacies than those obtained from the real data.

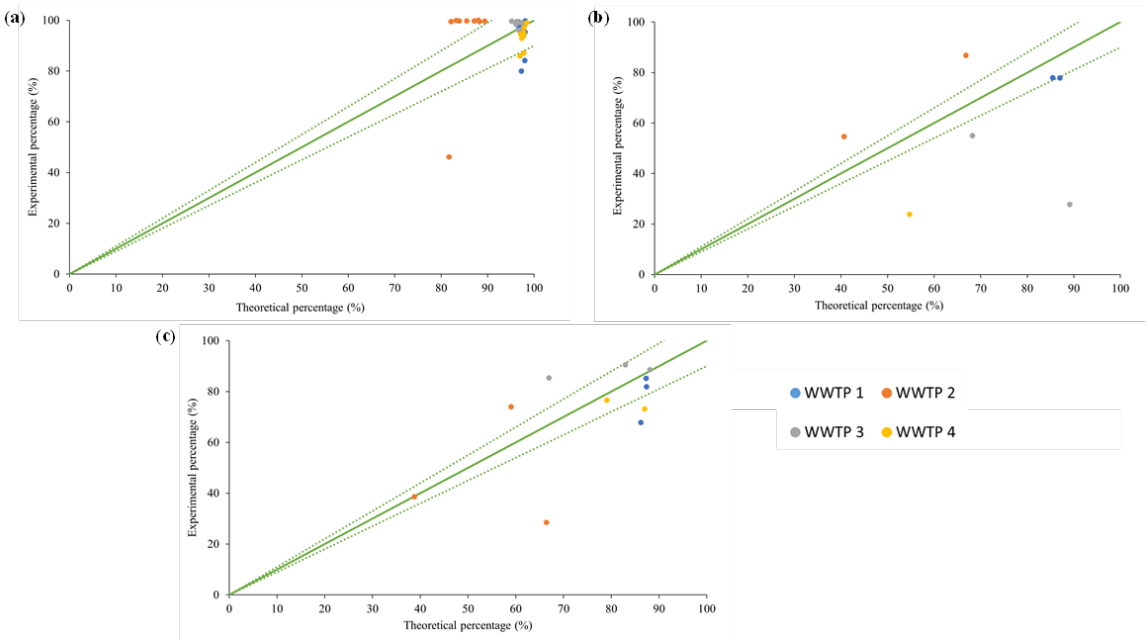


Figure 4. Representation of the experimental percentage (%) obtained by simulation in SimpleTreat 4.0 and theoretical percentage (%) of the WWTPs studied for (**a**) ibuprofen, (**b**) diclofenac and (**c**) erythromycin. The green dashed lines indicate a 10% error.

On the opposite, the simulations carried out for diclofenac (Figure 4b) and erythromycin (Figure 4c) led to worse results. Approximately half the erythromycin estimated removal efficacies are within the 10% error interval, whereas only one third of diclofenac predicted efficacies could be considered as acceptable under this criterion. Lautz et al. [55] suggested that, when using SimpleTreat software, the most influentual parameters are biodegradation and the hydraulic retention time and, in addition, model performance is highly dependent on the nature and quality of the data, i.e., the degree of uncertainty.

Table S1 shows the chemical character of the compounds analysed, i.e., acidic (ibuprofen and diclofenac), basic (erythromycin, imidacloprid and 17α-ethinylestradiol) and neutral (triclosan). Although an exhaustive analysis has not been conducted in this sense, the results seem to indicate more reliable simulations for those acidic compounds. Nevertheless, it is remarkable that Lautz et al. [55], who evaluated the SimpleTreat performance to predict the removal of 43 pharmaceuticals from wastewater, indicated that there were no significant differences depending on the nature of the compound (acidic, base or neutral).

4. Conclusions

After having evaluated the incidence of six selected ECs (ibuprofen, diclofenac, erythromycin, triclosan, imidacloprid and 17α-ethinylestradiol) for nine months in four WWTPs sited in the southwest of Spain, the most remarkable fact is the low concentrations (at ppb level) and the high variability found, regarding not only the occurrence, but also the removal efficiencies. In general, these fluctuations were in accordance with the literature data, which show wide ranges of concentrations and elimination percentages for the ECs studied.

By using the SimpleTreat 4.0 software, apparent first kinetic constants were obtained for each sample and an Arrhenius-type equation was employed to determine the relation between the constants and the temperature in the cases of ibuprofen, diclofenac and erythromycin (it was not possible for the rest of the ECs due to the high dispersion of data). These equations were employed to obtain new kinetic constants, which were used to predict the removal efficacies for each case. The agreement between theoretical and experimental efficacies was not very good for diclofenac and erythromycin. However, the software could reasonably predict, with an error lower than 10%, the behaviour of ibuprofen in three of the four WWTPs studies. This could be due to the fact that the presence of a primary clarifier made the software underestimate the removal efficacy in the WWTP 2.

The present work seems to indicate that SimpleTreat is suitable to predict the behaviour of emerging pollutants with a high degree of biodegradability, such as ibuprofen, in simple-configuration WWTPs. Nevertheless, in order to transform this software into a model for general application, even for ECs present in very low concentrations, it should be updated to better reflect the real processes that takes place in WWTPs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10122491/s1, Table S1: Physicochemical characteristics of selected emerging compounds analysed in the present work; Table S2: Physicochemical and biological parameters provided by WWTP 1. BOD, biological oxygen demand; TTS, total suspended solids (INF: influent water after screening; TER: influent tertiary treatment); MLSS, mixed liquor suspended solids suspended within the mixed liquor; Table S3: Physicochemical and biological parameters provided by WWTP 2. BOD, biological oxygen demand; TTS, total suspended solids (INF: influent water after screening; TER: influent tertiary treatment); MLSS, mixed liquor suspended solids suspended within the mixed liquor; Table S4: Physicochemical and biological parameters provided by WWTP 3. BOD, biological oxygen demand; TTS, total suspended solids (INF: influent water after screening; TER: influent tertiary treatment); MLSS, mixed liquor suspended solids suspended within the mixed liquor; Table S5: Physicochemical and biological parameters provided by WWTP 4. BOD, biological oxygen demand; TTS, total suspended solids (INF: influent water after screening; TER: influent tertiary treatment); MLSS, mixed liquor suspended solids suspended within the mixed liquor; Table S6: Ibuprofen concentrations (μg/L) and removal efficiencies (%) in influent and effluent in the four WWTPs analysed; n.d. is not detected; Table S7: Diclofenac concentrations (μg/L) and removal

efficiencies (%) in influent and effluent in the four WWTPs analysed; n.d. is not detected; Table S8: Erythromycin concentrations (μg/L) and removal efficiencies (%) in influent and effluent in the four WWTPs analysed; n.d. is not detected; Table S9: Triclosan concentrations (μg/L) and removal efficiencies (%) in influent and effluent in the four WWTPs analysed; n.d. is not detected; Table S10: Imidacloprid concentrations (μg/L) and removal efficiencies (%) in influent and effluent in the four WWTPs analysed; n.d. is not detected; Table S11: 17α-ethinylestradiol concentrations (μg/L) and removal efficiencies (%) in influent and effluent in the four WWTPs analysed; n.d. is not detected; Table S12: Biodegradation constant (ki) for ibuprofen, diclofenac and erythromycin in the four WWTPs analysed; Table S13: Biodegradation constant (ki) for triclosan, imidacloprid and 17α-ethinylestradiol in the four WWTPs analysed; Table S14: Biodegradation constant (kib) obtained using the Arrhenius equation for ibuprofen in the four WWTPs analysed; Table S15: Biodegradation constant (kdi) obtained using the Arrhenius equation for diclofenac in the four WWTPs analysed; Table S16: Biodegradation constant (ker) obtained using the Arrhenius equation for erythromycin in the four WWTPs analysed.

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Abbreviations

BPR	Biocidal products regulation
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
EC	Emerging contaminant
EMA	European Medicines Agency
EPA	Environmental Protection Agency
FDA	US Food and Drugs Administration
GC-MS	Gas chromatography–mass spectrometry
k	Biodegradation rate
K_{oc}	Organic carbon partition coefficient
K_{ow}	N-octanol-water partition coefficient
Kp_{as}	Activated sludge solids-water equilibrium partition constant
Kp_{s}	Sewage solids–water equilibrium partition constant
LOQ	Limit of quantification
MTBSTFA	N-Methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide
NSAID	Non-steroidal anti-inflammatory drugs
PE	Population equivalent
PPCP	Pharmaceutical and personal care product
RSF	Rapid sand filter
SPE	Solid-phase extraction
TBDMCS	tert-butyldimethylchlorosilane
TCMS	Trimethylchlorosilane
USGS	United States Geological Survey

UV	Ultraviolet
WHO	World Health Organization
WWTP	Wastewater treatment plant

References

1. Ahammad, N.A.; Ahmad, M.A.; Hameed, B.H.; Din, A.T.M.D. A mini review of recent progress in the removal of emerging contaminants from pharmaceutical waste using various adsorbents. *Environ. Sci. Pollut. Res.* **2022**. [CrossRef] [PubMed]
2. Rout, P.R.; Zhang, T.C.; Bhunia, P.; Surampalli, R.Y. Treatment technologies for emerging contaminants in wastewater treatment plants: A review. *Sci. Total Environ.* **2021**, *753*, 141990. [CrossRef] [PubMed]
3. USGS. Contaminants of Emerging Concern in the Environment. Environmental Health—Toxic Substances Hydrology Program. U.S. Geological Survey. 2017. Available online: https://toxics.usgs.gov/investigations/cec/index.php (accessed on 15 September 2022).
4. Olasupo, A.; Suah, F.B.M. Recent advances in the removal of pharmaceuticals and endocrine-disrupting compounds in the aquatic system: A case of polymer inclusion membranes. *J. Hazard. Mater.* **2021**, *406*, 124317. [CrossRef] [PubMed]
5. Fernández, M.; Fernández, M.; Laca, A.; Laca, A.; Díaz, M. Seasonal occurrence and removal of pharmaceutical products in municipal wastewaters. *J. Environ. Chem. Eng.* **2014**, *2*, 495–502. [CrossRef]
6. Gogoi, A.; Mazumder, P.; Tyagi, V.K.; Chaminda, G.G.T.; An, A.K.; Kumar, M. Occurrence and fate of emerging contaminants in water environment: A review. *Groundw. Sustain. Dev.* **2018**, *6*, 169–180. [CrossRef]
7. Bhagat, C.; Kumar, M.; Tyagi, V.K.; Mohapatra, P.K. Proclivities for prevalence and treatment of antibiotics in the ambient water: A review. *npj Clean Water* **2020**, *3*, 42. [CrossRef]
8. Tran, N.H.; Reinhard, M.; Gin, K.Y.H. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. *Water Res.* **2018**, *133*, 182–207. [CrossRef]
9. McCance, W.; Jones, O.A.H.; Edwards, M.; Surapaneni, A.; Chadalavada, S.; Currell, M. Contaminants of Emerging Concern as novel groundwater tracers for delineating wastewater impacts in urban and peri-urban areas. *Water Res.* **2018**, *146*, 118–133. [CrossRef]
10. Ahmad, A.; Kurniawan, S.B.; Abdullah, S.R.S.; Othman, A.R.; Hasan, H.A. Contaminants of emerging concern (CECs) in aquaculture effluent: Insight into breeding and rearing activities, alarming impacts, regulations, performance of wastewater treatment unit and future approaches. *Chemosphere* **2022**, *290*, 133319. [CrossRef]
11. Wilkinson, J.; Hooda, P.S.; Barker, J.; Barton, S.; Swinden, J. Occurrence, fate and transformation of emerging contaminants in water: An overarching review of the field. *Environ. Pollut.* **2017**, *231*, 954–970. [CrossRef]
12. Vale, F.; Sousa, C.A.; Sousa, H.; Santos, L.; Simões, M. Parabens as emerging contaminants: Environmental persistence, current practices and treatment processes. *J. Clean. Prod.* **2022**, *347*, 131244. [CrossRef]
13. Surana, D.; Gupta, J.; Sharma, S.; Kumar, S.; Ghosh, P. A review on advances in removal of endocrine disrupting compounds from aquatic matrices: Future perspectives on utilization of agri-waste based adsorbents. *Sci. Total Environ.* **2022**, *826*, 154129. [CrossRef] [PubMed]
14. Rizzo, L.; Malato, S.; Antakyali, D.; Beretsou, V.G.; Đolić, M.B.; Gernjak, W.; Heath, E.; Ivancev-Tumbas, I.; Karaolia, P.; Ribeiro, A.R.L.; et al. Consolidated vs. new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater (Review). *Sci. Total Environ.* **2019**, *655*, 986–1008. [CrossRef] [PubMed]
15. Lozano, I.; Pérez-Guzmán, J.; Mora, A.; Mahlknecht, J.; Aguilar, C.L.; Cervantes-Avilés, P. Pharmaceuticals and personal care products in water streams: Occurrence, detection, and removal by electrochemical advanced oxidation processes. *Sci. Total Environ.* **2022**, *827*, 154348. [CrossRef]
16. Chen, Y.; Lin, M.; Zhuang, D. Wastewater treatment and emerging contaminants: Bibliometric analysis. *Chemosphere* **2022**, *297*, 133932. [CrossRef]
17. Kumar, M.; Ngasepam, J.; Dhangar, K.; Mahlknecht, J.; Manna, S. Critical review on negative emerging contaminant removal efficiency of wastewater treatment systems: Concept, consistency and consequences. *Bioresour. Technol.* **2022**, *352*, 127054. [CrossRef] [PubMed]
18. Yang, Y.; Ok, Y.S.; Kim, K.H.; Kwon, E.E.; Tsang, Y.F. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. *Sci. Total Environ.* **2017**, *596–597*, 303–320. [CrossRef]
19. Mainardis, M.; Cecconet, D.; Moretti, A.; Callegari, A.; Goi, D.; Freguia, S.; Capodaglio, A.G. Wastewater fertigation in agriculture: Issues and opportunities for improved water management and circular economy. *Environ. Pollut.* **2022**, *296*, 118755. [CrossRef]
20. Sousa, J.C.G.; Ribeiro, A.R.; Barbosa, M.O.; Pereira, M.F.R.; Silva, A.M.T. A review on environmental monitoring of water organic pollutants identified by EU guidelines. *J. Hazard. Mater.* **2018**, *344*, 146–162. [CrossRef]
21. Rastogi, A.; Tiwari, M.K.; Ghangrekar, M.M. A review on environmental occurrence, toxicity and microbial degradation of Non-Steroidal Anti-Inflammatory Drugs (NSAIDs). *J. Environ. Manag.* **2021**, *300*, 113694. [CrossRef]
22. Maculewicz, J.; Kowalska, D.; Świacka, K.; Toński, M.; Stepnowski, P.; Bialk-Bielińska, A.; Dołżonek, J. Transformation products of pharmaceuticals in the environment: Their fate, (eco)toxicity and bioaccumulation potential. *Sci. Total Environ.* **2022**, *802*, 149916. [CrossRef] [PubMed]
23. Dos Santos, C.R.; Arcanjo, G.S.; Santos, L.V.S.; Koch, K.; Amaral, M.C.S. Aquatic concentration and risk assessment of pharmaceutically active compounds in the environment. *Environ. Pollut.* **2021**, *290*, 118049. [CrossRef]

24. De Ilurdoz, M.S.; Sadhwani, J.J.; Reboso, J.V. Antibiotic removal processes from water & wastewater for the protection of the aquatic environment—A review. *J. Water Process Eng.* **2022**, *45*, 102474. [CrossRef]
25. Hu, Y.; Zhu, Q.; Wang, Y.; Liao, C.; Jiang, G. A short review of human exposure to antibiotics based on urinary biomonitoring. *Sci. Total Environ.* **2022**, *830*, 154775. [CrossRef]
26. Dar, O.I.; Aslam, R.; Pan, D.; Sharma, S.; Andotra, M.; Kaur, A.; Jia, A.Q.; Faggio, C. Source, bioaccumulation, degradability and toxicity of triclosan in aquatic environments: A review. *Environ. Technol. Innov.* **2022**, *25*, 102122. [CrossRef]
27. Rezende-Teixeira, P.; Dusi, R.G.; Jimenez, P.C.; Espindola, L.S.; Costa-Lotufo, L.V. What can we learn from commercial insecticides? Efficacy, toxicity, environmental impacts, and future developments. *Environ. Pollut.* **2022**, *300*, 118983. [CrossRef]
28. Zhang, D.; Lu, S. Human exposure to neonicotinoids and the associated health risks: A review. *Environ. Int.* **2022**, *163*, 107201. [CrossRef]
29. Wan, Y.P.; Chai, B.W.; Wei, Q.; Hayat, W.; Dang, Z.; Liu, Z.H. 17α-ethynylestradiol and its two main conjugates in seven municipal wastewater treatment plants: Analytical method, their occurrence, removal and risk evaluation. *Sci. Total Environ.* **2022**, *812*, 152489. [CrossRef]
30. Strujis, J. *Application of SimpleTreat 4.0 in European Substance Regulations, Texte 13/2015*; German Environment Agency (Umweltbundesamt, UBA): Dessau-Roßlau, Germany, 2015; Available online: https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_13_2015_application_of_simple_treat_4.0.pdf (accessed on 1 October 2022).
31. Chopra, S.; Kumar, D. Ibuprofen as an emerging organic contaminant in environment, distribution and remediation. *Heliyon* **2020**, *6*, e04087. [CrossRef]
32. Brillas, E. A critical review on ibuprofen removal from synthetic waters, natural waters, and real wastewaters by advanced oxidation processes. *Chemosphere* **2022**, *286*, 131849. [CrossRef]
33. Adeleye, A.S.; Xue, J.; Zhao, Y.; Taylor, A.A.; Zenobio, J.E.; Sun, Y.; Han, Z.; Salawu, O.A.; Zhu, Y. Abundance, fate, and effects of pharmaceuticals and personal care products in aquatic environments. *J. Hazard. Mater.* **2022**, *424*, 127284. [CrossRef] [PubMed]
34. Archer, E.; Petrie, B.; Kasprzyk-Hordern, B.; Wolfaardt, G.M. The Fate of Pharmaceuticals and Personal Care Products (PPCPs), Endocrine Disrupting Contaminants (EDCs), Metabolites and Illicit Drugs in a WWTW and Environmental Waters. *Chemosphere* **2017**, *174*, 437–446. [CrossRef] [PubMed]
35. Kermia, A.E.B.; Fouial-Djebbar, D.; Trari, M. Occurrence, Fate and Removal Efficiencies of Pharmaceuticals in Wastewater Treatment Plants (WWTPs) Discharging in the Coastal Environment of Algiers. *C. R. Chim.* **2016**, *19*, 963–970. [CrossRef]
36. Elshikh, M.S.; Hussein, D.S.; Al-khattaf, F.S.; El-Naggar, R.A.R.; Almaary, K.S. Diclofenac removal from the wastewater using activated sludge and analysis of multidrug resistant bacteria from the sludge. *Environ. Res.* **2022**, *208*, 112723. [CrossRef] [PubMed]
37. Alessandretti, I.; Rigueto, C.V.T.; Nazari, M.T.; Rosseto, M.; Dettmer, A. Removal of diclofenac from wastewater: A comprehensive review of detection, characteristics and tertiary treatment techniques. *J. Environ. Chem. Eng.* **2021**, *9*, 106743. [CrossRef]
38. Kasonga, T.K.; Coetzee, M.A.A.; Kamika, I.; Ngole-Jeme, V.M.; Momba, M.N.B. Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and surface water: A review. *J. Environ. Manag.* **2021**, *277*, 11485. [CrossRef]
39. Shamsudin, M.S.; Azha, S.F.; Ismail, S. A review of diclofenac occurrences, toxicology, and potential adsorption of clay-based materials with surfactant modifier. *J. Environ. Chem. Eng.* **2022**, *10*, 107541. [CrossRef]
40. Shang, Q.; Chi, W.; Zhang, P.; Ling, Y.; Liu, X.; Cui, G.; Liu, W.; Shi, X.; Tang, B. Optimization of Bi_2O_3/TS-1 preparation and photocatalytic reaction conditions for low concentration Erythromycin wastewater treatment based on artificial neural network. *Process Saf. Environ. Prot.* **2022**, *157*, 297–305. [CrossRef]
41. Da Silva Rodrigues, D.A.; da Cunha, C.C.R.F.; do Espirito Santo, D.R.; de Barros, A.L.C.; Pereira, A.R.; de Queiroz Silva, S.; da Fonseca Santiago, A.; de Cássia Franco Afonso, R.J. Removal of cephalexin and erythromycin antibiotics, and their resistance genes, by microalgae-bacteria consortium from wastewater treatment plant secondary effluents. *Environ. Sci. Pollut. Res.* **2021**, *28*, 67822–67832. [CrossRef]
42. Omuferen, L.O.; Maseko, B.; Olowoyo, J.O. Occurrence of antibiotics in wastewater from hospital and convectional wastewater treatment plants and their impact on the effluent receiving rivers: Current knowledge between 2010 and 2019. *Environ. Monit. Assess.* **2022**, *194*, 306. [CrossRef]
43. Aziz, A.; Sengar, A.; Basheer, F.; Farooqi, I.H.; Isa, M.H. Anaerobic digestion in the elimination of antibiotics and antibiotic-resistant genes from the environment—A comprehensive review. *J. Environ. Chem. Eng.* **2022**, *10*, 106423. [CrossRef]
44. Nandikes, G.; Pathak, P.; Razak, A.S.; Narayanamurthy, V.; Singh, L. Occurrence, environmental risks and biological remediation mechanisms of Triclosan in wastewaters: Challenges and perspectives. *J. Water Process Eng.* **2022**, *49*, 103078. [CrossRef]
45. Abbott, T.; Kor-Bicakci, G.; Islam, M.S.; Eskicioglu, C. A Review on the Fate of Legacy and Alternative Antimicrobials and Their Metabolites during Wastewater and Sludge Treatment. *Int. J. Mol. Sci.* **2020**, *21*, 9241. [CrossRef] [PubMed]
46. Montes-Grajales, D.; Fennix-Agudelo, M.; Miranda-Castro, W. Occurrence of personal care products as emerging chemicals of concern in water resources: A review. *Sci. Total Environ.* **2017**, *595*, 601–614. [CrossRef] [PubMed]
47. Mundhe, S.; Birajdar, S.; Chavan, S.; Pawar, N. Imidacloprid poisoning: An emerging cause of potentially fatal poisoning. *Indian J. Crit. Care Med.* **2017**, *21*, 786–788. [CrossRef] [PubMed]
48. Webb, D.T.; Zhi, H.; Kolpin, D.W.; Klaper, R.D.; Iwanowicz, L.R.; LeFevre, G.H. Emerging investigator series: Municipal wastewater as a year-round point source of neonicotinoid insecticides that persist in an effluent-dominated stream. *Environ. Sci. Process. Impacts* **2021**, *23*, 678–688. [CrossRef]

49. De la Casa-Resino, I.; Villegas, J.M.; Puig, A.; Haro, A.; Bartolomé, A.; Herrera, E.M.; Flores, C.; Caixach, J.; Carapeto, R. *Residues of Imidacloprid in Surface Water Treatment Plants and Watercourses in Spain: Are Veterinary Medicinal Products (VMPs) a Significant Source of Emission?* Spanish Agency of Medicines and Medical Devices (AEMPS): Madrid, Spain, 2022. Available online: https://www.aemps.gob.es/publicaciones/publica/docs/Imidacloprid.pdf (accessed on 1 October 2022).
50. Wang, L.; Jiang, X.; Li, A. Ammonia oxidation intermediates-induced abiotic transformation of 17α-ethinylestradiol in nitrification process of wastewater biological treatment. *J. Environ. Chem. Eng.* **2022**, *10*, 108171. [CrossRef]
51. Klaic, M.; Jirsa, F. 17α-Ethinylestradiol (EE2): Concentrations in the environment and methods for wastewater treatment—An update. *RSC Adv.* **2022**, *12*, 12794–12805. [CrossRef]
52. Tang, Z.; Liu, Z.H.; Wang, H.; Dang, Z.; Liu, Y. Occurrence and removal of 17α-ethynylestradiol (EE2) in municipal wastewater treatment plants: Current status and challenges. *Chemosphere* **2021**, *271*, 129551. [CrossRef]
53. Ahmed, M.B.; Zhou, J.L.; Ngo, H.H.; Guo, W.; Thomaidis, N.S.; Xu, J. Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. *J. Hazard. Mater.* **2017**, *323*, 274–298. [CrossRef]
54. Rivera-Utrilla, J.; Sánchez-Polo, M.; Ferro-García, M.A.; Prados-Joya, G.; Ocampo-Pérez, R. Pharmaceuticals as emerging contaminants and their removal from water. A review. *Chemosphere* **2013**, *93*, 1268–1287. [CrossRef] [PubMed]
55. Lautz, L.S.; Strujis, J.; Nolte, T.M.; Breure, A.M.; van der Grinten, E.; van de Meent, D.; van Zelm, R. Evaluation of SimpleTreat 4.0: Simulations of pharmaceutical removal in wastewater treatment plant facilities. *Chemosphere* **2017**, *168*, 870–876. [CrossRef] [PubMed]
56. Li, W.L.; Zhang, Z.F.; Kilgallon, J.; Sparham, C.; Li, Y.F.; Yuan, Y.X. Fate of household and personal care chemicals in typical urban wastewater treatment plants indicate different seasonal patterns and removal mechanisms. *Environ. Pollut.* **2022**, *294*, 118618. [CrossRef] [PubMed]
57. Schulte, R.A.A.; Link, A.; Siegert, M.W.; Finkbeiner, M. Modeling the use and end-of-life phase of pharmaceuticals in support of a life cycle inventory analysis—Case study on different antibiotics in Germany. *Sustain. Chem. Pharm.* **2022**, *25*, 100589. [CrossRef]
58. Comber, S.; Gardner, M.; Sörme, P.; Ellor, B. The removal of pharmaceuticals during wastewater treatment: Can it be predicted accurately? *Sci. Total Environ.* **2019**, *676*, 222–230. [CrossRef]
59. Alvarino, T.; Suárez, S.; Garrido, M.; Lema, J.M.; Omil, F. A UASB reactor coupled to a hybrid aerobic MBR as innovative plant configuration to enhance the removal of organic micropollutants. *Chemosphere* **2016**, *144*, 452–458. [CrossRef]
60. Show, S.; Chakraborty, P.; Karmakar, B.; Halder, G. Sorptive and microbial riddance of micro-pollutant ibuprofen from contaminated water: A state of the art review. *Sci. Total Environ.* **2021**, *786*, 147327. [CrossRef]
61. Gautam, P.; Dubey, S.K. Biodegradation of imidacloprid: Molecular and kinetic analysis. *Bioresour. Technol.* **2022**, *350*, 126915. [CrossRef]
62. Balakrishnan, P.; Mohan, S. Treatment of triclosan through enhanced microbial biodegradation. *J. Hazard. Mater.* **2021**, *420*, 126430. [CrossRef]
63. Kosma, C.; Lambropoulou, D.; Albanis, T. Occurrence and removal of PPCPs in municipal and hospital wastewaters in Greece. *J. Hazard. Mater.* **2010**, *179*, 804–817. [CrossRef]