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Ranking potential impacts of priority and emerging pollutants in urban wastewater through life cycle impact assessment

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ABSTRACT

Life cycle impact assessment (LCIA), a feature of the Life cycle assessment (LCA) methodology, is used in this work outside the LCA framework, as a means to quantify the potential environmental impacts on ecotoxicity and human toxicity of wastewater containing priority and emerging pollutants. In order to do this, so-called characterisation factors are obtained for 98 frequently detected pollutants, using two characterisation models, EDIP97 and USES-LCA. The applicability of this methodology is shown in a case study in which wastewater influent and effluent samples from a Spanish wastewater treatment plant located in the Mediterranean coast were analysed. Characterisation factors were applied to the average concentration of each pollutant, obtaining impact scores for different scenarios: discharging wastewater to aquatic recipient, and using it for crop irrigation. The results show that treated wastewater involves a substantially lower environmental impact when compared to the influent, and pharmaceuticals and personal care products (PPCPs) are very important contributors to toxicity in this wastewater. Ciprofloxacin, fluoxetine, and nicotine constitute the main PPCPs of concern in this case study, while 2,3,7,8-TCDD, Nickel, and hexachlorobenzene are the priority pollutants with highest contribution. Nevertheless, it must be stressed that the new characterisation factors are based on very limited data, especially with regard to toxicology, and therefore they must be seen as a first screening to be improved in the future when more and higher quality data is available.

1. Introduction

Water pollution is the most prominent environmental concern for European citizens (EC, 2005), and therefore a priority for environmental authorities. The main tool of the European water policy to reduce chemical pollution of surface water bodies is the water framework directive (WFD) (EU, 2000), setting out a strategy against pollution of water that involved establishing a list of substances presenting a significant risk to or via the aquatic environment (EU, 2001). These so-called priority substances, including heavy metals, biocides, polyaromatic hydrocarbons, and chlorinated solvents, among others, will soon be subject to water quality standards and emission controls currently under discussion in the European Commission (EC, 2006). Nevertheless, priority pollutants constitute only part of the large chemical pollution puzzle; there is a diverse group of unregulated pollutants, including pharmaceuticals and personal care products (PPCPs), raising an increasing concern on the risks they pose on humans and the environment (Daughton and Ternes, 1999). In the European Union (EU), there are thousands of substances used in prescription drugs such as antibiotics, beta-blockers, tranquilizers, lipid regulators, contraceptives, etc. Personal care products are also consumed in our daily life in a wide range of domestic products including soaps, fragrances, skin care products, and sunscreen agents, among others. For both pharmaceuticals and personal care products, wastewater is the main route of emission to the environment (Daughton and Ternes, 1999; Ternes et al., 2004). While priority pollutants are characterised by their chronic ecotoxicity or their persistence in the environment, PPCPs do not need to be persistent, since they are released on a continuous basis to aquatic ecosystems, where undetected or unnoticed effects may occur.

Quantitative risk assessment (RA) approaches, such as those included in the EU Technical Guidance Document (EC 2003) and in the new EU chemicals regulation REACH (EU, 2006) are considered as appropriate tools to determine the health and environmental risks associated with chemicals (Hoornstra et al., 2001). In addition, life cycle assessment (LCA) is increasingly gaining

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acceptance as a tool for a holistic environmental evaluation of chemicals and chemical processes (Domènech et al., 2002; Saling et al., 2002; Hellweg et al., 2004). As pointed out by several authors (Olsen et al., 2001; Udo de Haes et al., 2006), LCA and RA can not substitute each other, since these tools fulfil different purposes, but can rather play complementary roles and benefit from each other. LCA is currently the only environmental assessment tool standardized by means of ISO standards (ISO, 2006). According to ISO 14044, an LCA study is composed by four phases: (i) goal and scope definition, (ii) inventory analysis, (iii) life cycle impact assessment (LCIA), and (iv) interpretation. LCIA is defined by the ISO 14044 standard as the phase of LCA aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts for a product system throughout the life cycle of the product. These environmental impacts may include, for instance, global warming, stratospheric ozone depletion, acidification, eutrophication, and also toxicity, among others (Pennington et al., 2004). Within LCIA, characterisation factors constitute quantitative expressions of substance-specific potential impacts within each impact category, and are used as weighing factors to determine the contribution of a substance to a total impact score. These factors are the output of characterisation models, and they are made available to practitioners in literature, as well as in free and commercial databases and software tools. However, it is a typical problem for LCA practitioners to lack characterisation factors for relevant substances in toxicity-related impact categories (Larsen, 2004; Pennington, 2004), specially for non-regulated water pollutants, as they have not received attention until recently.

Few studies have attempted to include micropollutants in LCA of wastewater systems. Wenzel et al. (2008) carried out a complete LCA of different advanced wastewater treatment options, taking into account the potential toxicity of heavy metals, endocrine disruptors, PAHs, phtalates, and detergents. Nevertheless, these groups of pollutants were represented by only nine substances in total.

In this work we aim at exploring the suitability of LCIA to evaluate the potential toxicity of urban wastewater effluents containing priority and emerging pollutants, and at identifying the relative importance of individual pollutants in these effluents. We do not carry out a complete LCA (neither of wastewater treatment nor of the chemicals themselves), but a chemical analysis of 98 wastewater pollutants in a Spanish wastewater treatment plant (WWTP), combined with characterisation factors calculated with two widely used LCIA models for toxicity impacts, namely the EDIP97 method, and the multimedia fate and exposure model USES-LCA.

2. Materials and methods

2.1. Calculation of wastewater potential impact

The WWTP subject to the case study currently discharges the treated effluent to the sea. Nevertheless, the focus of this study is on testing a methodology to estimate the impact of wastewater in different scenarios. For this reason, not only the potential impact of current discharge in the marine environment is studied, but also the impact on freshwater ecosystems, terrestrial ecosystems, and human health, of discharging wastewater to a river or reusing it in agricultural fields.

Characterisation factors have been calculated with EDIP97 and USES-LCA for substances emitted to three initial compartments: freshwater, marine water and soil. The impact categories assessed are:

- Freshwater aquatic ecotoxicity potential (FAETP) of substances emitted to freshwater.
- Marine aquatic ecotoxicity potential (MAETP) of substances emitted to seawater. This impact category is only included in USES-LCA.
- Terrestrial ecotoxicity potential (TETP) of substances emitted to soil.
- Human toxicity potential (HTP) of substances emitted to soil. In EDIP97 the impact category is HTP via soil.

These impact categories all consider chronic toxicity and are intended to represent the environmental impact on aquatic ecosystems of discharging wastewater to a river (FAETP) and to the sea (MAETP), as well as the impact on terrestrial ecosystems and on humans of using wastewater for agricultural purposes (TETP and HTP, respectively). All remaining impact categories in both models are not taken into account in this study.

Eq. (1) shows how scores for each impact category are calculated in the characterisation step of LCIA:

$$\text{Impact potential} = \sum_{i=1}^{n} \text{Characterisation factor}_i \cdot \text{Emission}_i, \quad (1)$$

where 'Impact potential' corresponds to the score of either FAETP, MAETP, TETP, or HTP, and 'Emission' is the amount (in mass units) emitted to a given environmental compartment, in our case water or soil.

2.2. Target pollutants

Ninety-eight substances (Table 1) are subject to monthly analysis in wastewater samples from several Spanish WWTPs, in the framework of the TRAGUA research project (www.consolider-tragua.com). Concerning priority pollutants, 23 of the 33 substances or groups of substances included in annex X of the WFD were taken into account. As for emerging pollutants, the overall number of compounds analysed is 57. They are mainly represented by pharmaceuticals and some metabolites which are frequently found in wastewater, while personal care products include some synthetic fragrances (musks) an UV filter used in sunscreens, disinfectants, and a metabolite from the latter.

2.3. Characterisation models

It has not been necessary to calculate characterisation factors for all the target substances in Table 1, since for some of them, particularly metals and priority pollutants, they are already calculated and available in the EDIP97 and USES-LCA main reports. New characterisation factors were added for 90 chemicals in EDIP97, and 66 chemicals in USES-LCA.

2.3.1. EDIP97

The Danish method for Environmental Design of Industrial Products (EDIP97) is an approach for LCA of products (Wenzel et al., 1997; Hauschild and Wenzel, 1998), including its own LCIA method. Characterisation of toxic effects in EDIP97 is based on independent key properties of substances. These properties are used to model fate, exposure and effects, instead of using an integrated, quantitative model.

EDIP97 allows the user to calculate toxicity potentials for human toxicity and ecotoxicity, where human toxicity is divided in three impact categories: HTP via air, HTP via water, and HTP via soil. Ecotoxicity is in turn divided in four impact categories: acute FAETP, chronic FAETP, chronic TETP, and acute Sewage Treatment Plant Ecotoxicity Potential. Characterisation factors for human toxicity are calculated with Eq. (2):

Table 1
Target pollutants and analytical methods used

Compounds	Sample pre-treatment	Extraction method		Analytical method
		Technique	Solvent	
GROUP I *Pharmaceuticals*: acetaminophen, indomethacine, codeine, mefenamic acid, ketorolac, naproxen, ibuprofen, diclofenac, fenoprofen, ketoprofen, metronidazole, sulfamethoxazole, trimethoprim, ciprofloxacin, cefotaxime, ofloxacin, erythromycin, fenofibrate, bezafibrate, gemfibrozil, atenolol, propranolol, sotalol, metoprolol, fluoxetine, paroxetine, carbamazepine, diazepam, ranitidine, omeprazole, methylprednisolone, nicotine, furosemide, hydrochlorothiazide, salbutamol, terbutaline, caffeine, mepivacaine	Filtration (0.7-μm Glass-fiber filters) pH adjustment (pH 8)	Solid phase extraction (Oasis ® HLB, 200 mg, 6 cm^3)	MeOH	Liquid chromatography–QTRAP–Mass Spectrometry Column: C-18 (3 × 250 mm, 5-μm particle size)
Pharmaceuticals metabolites: carbamazepine 10,11-epoxide, paraxanthine, clofibric Acid, fenofibric acid, 4-methylaminoantipyrine (4-MAA), *N*-acetyl-4-aminoantipiryne (4-AAA), *N*-formyl-4-aminoantipiryne (4-FAA), 4-dimethylaminoantipiryne (4-DAA), 4-aminoantipiryne (4-AA), Antipyrine *Personal care products*: chlorophene *Priority pollutants*: atrazine, chlorpyriphos methyl, chlorfenvinphos, diuron, isoproturon, simazine				Interface polarity: ESI (+) and ESI (−) Mobile phase: ESI (+), water (formic acid 0.1%)/acetonitrile ESI (−), water (0.05% ammonium formate)/acetonitrile; Operation mode: MRM
GROUP II Personal Care Products: celestolide, phantolide, traseolide, galaxolide, tonalide, triclosan, benzophenone-3 *Personal care products metabolites*: 2, 7/2, 8-DCDD *Priority pollutants*: α-endosulfan, β-endosulfan, endosulfan sulphate, 2,3,7,8-TCDD *PAHs*: acenaphtylene , acenaphthene, fluorene, pyrene, chrysene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, anthracene, benzo[a]fluoranthene, fluoranthene, naphtalene, phenanthrene	No filtration pH adjustment (pH 3) NaCl Addition	Liquid–liquid extraction	Hexane	Gas chromatography–Mass Spectrometry/ Mass spectrometry Column: VF-5 ms (5% diphenyl 95% dimethylsiloxane) Operation mode: MS/MS
GROUP III Organic priority pollutants: 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, hexachloro 1,3-butadiene, hexachlorobenzene, pentachlorobenzene, α-hexachlorocyclohexane, β-hexachlorocyclohexane, γ-hexachlorocyclohexane (lindane), δ-hexachlorocyclohexane, alachlor, tetrabromodiphenyl ether, pentabromodiphenyl ether, heptabromodiphenyl-ether	No filtration pH adjustment (pH 3) NaCl addition	Liquid–liquid extraction	Hexane	Gas chromatography–High Resolution–Mass Spectrometry Column: ZB -5 ms Operation mode: high-resolution selected ion recording (HR/SIR)
GROUP IV Heavy metals: cadmium, lead, nickel, mercury	Filtration (0.7-μm Glass–fiber filters) 1:2 dilution with 3% HNO_3	None	None	Inductively Coupled Plasma Mass Spectrometry (ICP–MS) RF power: 1500 W Plasma gas flow: 15 L min^{-1} Nebulizer gas flow: 1 L min^{-1} Auxiliary gas flow: 0.9 L min^{-1} Sample uptake rate: 0.25 mL min^{-1}

$$HTP_{i,b,c,r} = f_{i,b,c} \cdot I_{c,r} \cdot T_{i,c,r} \cdot BIO_i \cdot Effect_i \quad (2)$$

where $HTP_{i,b,c,r}$ is the human toxicity potential via compartment c and exposure route r of substance i emitted to compartment b ($m^3\ g^{-1}$), $f_{i,b,c}$ is the distribution factor indicating how much of the substance i emitted to compartment b reaches compartment c (dimensionless), $I_{c,r}$ is the intake factor expressing the average human ingestion of the polluted compartment c via exposure route r (e.g. kg milk kg body weight^{-1} d^{-1}), $T_{i,c,r}$ is the factor expressing the transport efficiency of substance i from the environmental compartment c to humans via exposure route r (e.g. kg soil kg $milk^{-1}$), BIO_i is a substance-specific factor, the magnitude of which expresses the biodegradability of the substance i (dimensionless), and $Effect_i$ is the toxicity factor of substance I ($m^3\ g^{-1}$).

Characterisation factors for ecotoxicity are obtained with a similar expression (Eq. (3)):

$$ETP_{i,b,c} = f_{i,b,c} \cdot BIO_i \cdot Effect_{i,c} \quad (3)$$

where $ETP_{i,b,c}$ is the ecotoxicity potential in compartment c of substance i emitted to compartment b ($m^3\ g^{-1}$), and $Effect_{i,c}$ is the ecotoxicity factor of substance i in compartment c ($m^3\ g^{-1}$).

Fate analysis in EDIP97 is made operational by means of the parameters $f_{i,b,c}$ and BIO_i, which are assigned discrete values between 0 and 1 based on simple rules of thumb. $f_{i,b,c}$ is a function of Henry's law constant and atmospheric half-life, while BIO_i is determined from biodegradability studies. Exposure in humans is modelled by means of the parameters $T_{i,c,r}$ and I_c. The former indicates the partitioning between environmental compartment concentration and concentration in the exposure medium, while I_c expresses the average amount of polluted medium ingested. EDIP97 considers five exposure routes, by ingestion of: soil, fish, plants, meat, and milk. The effect factors are expressed as the reciprocal of a reference dose/concentration. These effect factors can be obtained from policy targets such as acceptable daily intake (ADI) values, or from animal testing after applying assessment factors. For ecotoxicity, the reference concentration is the quality criteria for water, e.g., as defined in EC (2006) or the predicted

no-effect concentration (PNEC) based on ecotoxicological data with single species and assessment factors.

2.3.2. USES-LCA

Huijbregts et al. (2000) developed the multimedia fate, exposure and effects model USES-LCA, based on the uniform system for the evaluation of substances (RIVM et al., 1998) to calculate characterisation factors related to human toxicity and ecotoxicity, where ecotoxicity is separated in five impact categories: FAETP, Freshwater Sediment Ecotoxicity Potential, MAETP, and TETP. As opposed to EDIP97, impacts in USES-LCA are not expressed as dilution volumes, but as equivalents of a reference substance, namely 1,4-dichlorobenzene (DCB). Characterisation factors for human toxicity are calculated with Eq. (4):

$$\mathrm{HTP}_{i,b} = \frac{\sum_r \sum_s \mathrm{PDI}_{i,b,r,s} \cdot \mathrm{Effect}_i \cdot W_s}{\sum_r \sum_s \mathrm{PDI}_{\mathrm{DCB,air},r,s} \cdot \mathrm{Effect}_{\mathrm{DCB},r,s} \cdot W_s} \quad (4)$$

where $\mathrm{HTP}_{i,b}$ is the human toxicity potential for substance i emitted to environmental compartment b (kg-DCB-eq. kg^{-1}), $\mathrm{PDI}_{i,b,r,s}$ is the predicted daily intake via exposure route r at geographical scale s, of substance i emitted to environmental compartment b (kg kg-body-weight^{-1} d^{-1}), Effect_i is the effect factor for substance i (kg-body-weight d kg^{-1}), and W_s is a weighting factor for geographical scale s, calculated as a function of the total population exposed in that scale (dimensionless).

Characterisation factors for ecotoxicity are obtained with Eq. (5):

$$\mathrm{ETP}_{i,b,c} = \frac{\mathrm{PEC}_{i,b,c} \cdot \mathrm{Effect}_{i,c}}{\mathrm{PEC}_{\mathrm{DCB},c} \cdot \mathrm{Effect}_{\mathrm{DCB},c}} \quad (5)$$

where $\mathrm{ETP}_{i,b,c}$ is the characterisation factor for substance i emitted to environmental compartment b in final compartment c, like freshwater, sediments, etc. (kg-DCB-eq. kg^{-1}), $\mathrm{PEC}_{i,b,c}$ is the predicted environmental concentration of substance i initially emitted to compartment b in final compartment c (kg m^{-3}), and $\mathrm{Effect}_{i,c}$ is the effect factor for substance i in final compartment c (m^3 kg^{-1}).

The fate part of USES-LCA calculates steady-state concentrations on two spatial scales (continental and global) as well as three climatic zones (arctic, temperate and tropic). The continental scale is embedded in the temperate climate zone and comprises six compartments: air, freshwater, sea water, agricultural soil and industrial soil, while the global scale comprises all three climates and only includes the compartments air, sea water and soil. Exposure to humans includes eight possible routes: ingestion of soil particles, inhalation, ingestion of dairy products, ingestion of fish, ingestion of meat, drinking water and ingestion of vegetables, i.e. leaf crops and root crops. Finally, effects assessment is carried out in a similar way as in EDIP97, by means of PNEC in ecotoxicity, and ADI values in human toxicity.

2.4. Substance-specific data used in the models

Calculating characterisation factors for 98 substances required a large amount of substance-specific data, which is detailed in the Appendix. Physico-chemical properties and degradation rates were obtained from the estimation program interface suite (EPI Suite) by the USEPA's Office of Pollution prevention toxics and syracuse research corporation (USEPA, 2008). Concerning ecotoxicity of substances, several data sources were used: environmental quality standards in EC (2006) were used as PNEC values for priority pollutants, whereas for PPCPs PNECs were derived from literature (see Appendix), the USEPA Ecotox database (USEPA, 2007a), and the ECOSAR software (USEPA, 2001). As for human toxicity, ADI values were obtained from literature (see Appendix) and from the USEPA IRIS database (USEPA 2007b), while other experimental data on oral exposure in humans or mammals were obtained from the ChemIDplus Advanced database (U.S. National Library of Medicine, 2007).

2.5. Experimental work

2.5.1. Wastewater sampling

Wastewater samples were collected from the municipal WWTP of El Ejido (Almería, southern Spain). This plant treats urban wastewater with important contributions from greenhouses, plastic industry also related to greenhouses, and from a local hospital. Input wastewater undergoes a physical pre-treatment to remove coarse solids and greases, primary settling of particulates, and secondary treatment with activated sludge, after which the water is discharged to the sea.

A wastewater influent and effluent sample was collected each month, from January to November 2007. Samples were obtained by collecting wastewater every hour during a 24 h-period, and collecting a final sample from the mixed volume. Glass bottles were used to collect and store the samples, except those intended for heavy metals analysis, which required using PTFE bottles in order to avoid chemical interaction of metal ions with glass.

2.5.2. Chemicals and reagents

All the chemicals to be analysed (Table 1) were purchased at analytical grade (purity > 90%) from several companies; group I and II compounds were supplied by Sigma–Aldrich (Steinheim, Germany), BASF (Burgbernheim, Germany), Dr. Ehrenstorfer-Schäfers (Augsburg, Germany), Merck (Mollet del Vallès, Spain), and LGC Promochem (Barcelona, Spain). However, Codeine and Diazepam were obtained by dissolving a Codeisan tablet from Lab. Belmac (Madrid, Spain) and a Valium tablet from Lab. Andreu (Barcelona, Spain), respectively. Compounds classified in Table 1 as group III were purchased from Fluka (Buchs, Switzerland) and Riedel-de-Haën (Seelze, Germany).

Methanol and acetonitrile were supplied by Merck (Darmstadt, Germany), and sodium sulphate anhydrous from Panreac (Barcelona, Spain) and J.T. Baker (Deventer, Holland). Water was generated from a Direct-Q5 Ultrapure Water System from Millipore (Bedford, MA). Formic acid and ammonium formate were obtained from Fluka (Buchs, Germany), and Oasis HLB (divinylbenzene/*N*-vinylpyrrolidone copolymer, 200 mg/6 cm^3) were purchased from Waters (Milford, USA). Hexane, sodium chloride, sodium sulphite and sulphuric acid were purchased from Panreac (Barcelona, Spain).

Individual stock standard solutions of the organic compounds were prepared in methanol at a concentration between 1 and 2 mg mL^{-1} and stored at −20 °C. Working solutions at different concentrations were prepared for group I compounds by appropriate dilution of the stock solutions in MeOH/water, 10:90 (v/v), whereas for groups II and III *n*-hexane was used as solvent. As for heavy metals (group IV in Table 1) the Standard stock solutions for ICP analyses were obtained from Agilent Technologies (Multielement Calibration Standard-2A (10 mg l^{-1}), 100 ml, 50% HNO_3). Standard solutions for ICP (Merck) were prepared by appropriate dilutions with ultra-pure water, purified with a Milli-Q system (Waters, Milford, MA, USA) with 3% ultra-pure grade 65% HNO_3 (Merck Suprapur).

2.5.3. Sample preparation

For analysis of pollutants included in group I (see Table 1), samples were filtered with glass fiber filters from Millipore (Milford, USA) and concentrated by means of solid phase extraction and

an automated sample processor ASPEC XL fitted with an 817 switching valve and an external 306 LC pump from Gilson (Villiers-le-Bel, France). For further details see Martinez-Bueno et al. (2007).

Pollutants in group II and III were extracted by means of liquid–liquid extraction. In group II, 500 mL of each sample were extracted in two steps with 100 mL and 50 mL of *n*-hexane in the first and second steps, respectively. A teaspoon of NaCl was added to facilitate the extraction, and next the immiscible phases were shaken for 3 min in the first step and 2 min in the second step. The organic phase was collected and passed through sodium sulphate anhydrous to remove water traces, and next evaporated in a Büchi Syncore Polyvap System (Flawil, Switzerland) until only 3 mL were left; this extract volume is then ready for analysis. In group III, aliquots of 200 mL were extracted with 25 mL of *n*-hexane and 250 mg of NaCl, in a three-step procedure, shaking the mixture for three min each step. Water traces were removed from the organic phase by means of sodium sulphite anhydride. The extract was then evaporated using a Büchi Rotavapor R200 (Flawil, Switzerland). The residue was finally redissolved with two mL of *n*-hexane.

Samples for heavy metal analysis (group IV) were filtered and diluted 1:2 with mQ water containing 3% HNO_3. 100 μL of Au solution (5 mg L^{-1}) were added to each solution in order to avoid memory effects in mercury measurements, and blanks of water and nitric acid were checked to control the presence of metals.

2.5.4. Analysis

Pollutants classified in group I were analysed with HPLC (series 1100, Agilent Technologies, Palo Alto, USA) and a 3200 QTRAP MS/MS system (Applied Biosystems, Concord, Canada). For further details see Table 1 and Martinez-Bueno et al. (2007).

Analysis of group II pollutants were carried out using a Varian 4000 GC–MS/MS system (Varian, Walnut Creek, CA, USA) equipped with a CP-8400 autosampler. The system worked under internal configuration, using electron ionization. Analytes were separated in a Varian FactorFour VF-5ms capillary column, 30 m × 0.25 mm i.d., 0.25 μm film thickness. Sample injections were performed in a 1079 PTV injector, through an empty liner, filled with 0.5 cm Carbofrit (Restek, Bellefonte, USA).

Gas Chromatography–High Resolution Mass Spectrometry was used to analyse volatile priority pollutants (classified as group III in Table 1) were run on a HP 6890 Series gas chromatograph (Hewlatt-Packard, Palo Alto, USA) interfaced to a double focusing magnetic sector mass analyzer Micromass AutoSpec NT (Manchester, UK), operating in high resolution selected ion recording mode. Analytes were separated in a ZB-5MS capillary column (Phenomenex, Torrance, USA), 30 m × 0.25 mm I.D., 0.25 μm film thickness. A split/splitless injector was used in pulse splitless mode.

Heavy metals analysis was carried out by means of inductively coupled plasma mass spectrometry (ICP-MS), with an Agilent Technologies 7500 Series (Palo Alto, USA). It was equipped with Agilent 7500 ICP-MS ChemStation software, a Babington-type nebulizer, a peltier cooled (2 °C) quartz Scott-type double pass spray chamber and an Agilent I-AS integrated autosampler.

3. Results and discussion

3.1. LCIA results

Figs. 1 and 2 summarize the results of applying the LCIA models EDIP97 and USES-LCA, respectively, to the concentration of chemicals in the WWTP influent and effluent (see Appendix), considering the impact categories presented in Section 2.1. These graphics show, for each impact category, the total score obtained per L wastewater, and the main contributing substances.

Figs. 1 and 2 show that the overall potential environmental impact of the effluent is significantly reduced with regard to the input wastewater. A clear improvement in wastewater quality is observed in the four impact categories. This improvement is highest in HTP according to the EDIP97 model (85% reduction), and lowest in terrestrial ecotoxicity when assessed with both models (42% reduction).

Concerning the contribution of individual pollutants to each impact category, 16 predominating substances can be identified in Figs. 1 and 2; each of these 16 substances contributes to at least 1% of the total influent or effluent scores. When wastewater is released to fresh water ecosystems (Figs. 1a and 2a) the impact is mainly caused by fluoxetine, triclosan, and ciprofloxacin, according to both models. If these wastewaters are instead discharged to the sea, the most critical substance is nickel according to USES-LCA (Fig. 2b), while the EDIP97 model does not to include this impact category. Another scenario considers using wastewater for irrigation and thus releasing it to soil: the impact on terrestrial ecosystems (TETP) is in this case mostly due to ciprofloxacin according to both models (Figs. 1b and 2c). Finally, the impact on human health of using wastewater for crop irrigation (Fig. 1c) is mostly due to nicotine and gemfibrozil in EDIP97, while USES-LCA (Fig. 2d) attributes the impact to nicotine and hexachlorobenzene in the influent, and to 2,3,7,8-TCDD and hexachlorobenzene in the effluent.

3.2. Discussion

According to these results, the potential environmental impact of wastewater is reduced significantly. Nevertheless, we can not conclude that the overall impact is reduced, since we did not study the fate of these substances, including such processes as biodegradation, volatilisation, or adsorption to sludge. If these compounds are merely transferred to sludge, and the latter is in turn applied to agricultural soil, then probably no toxicity reduction at all is achieved. However, the characterisation factors obtained in this work could be used in a more complete study dealing with the whole wastewater treatment system.

With regard to the substances identified in the case study, more than half of them are PPCPs, more precisely 10 out of 16 substances, and they are responsible for a great share of the total impact. Thus, these models attribute more environmental impact to these urban wastewaters on the basis of their PPCP content rather than to the priority pollutants they contain. It is also remarkable the fact that from around 80 substances found in the samples, just a few of them are actually significant in each impact category. This relative importance of some substances above others is the result of two main variables, as seen in Eq. (1), namely the amount of pollutant released to the environment, and the magnitude of the characterisation factor for each impact category. For all these 16 substances, impact contributions are caused by both a relatively high concentration in wastewater and a high characterisation factor, with the exception of 2,3,7,8-TCDD, the impacts of which are caused, to a great extent, by the magnitude of its characterisation factors.

Concerning the level of agreement between the two characterisation models used, both of them lead to a similar picture: impact is reduced after treatment in the three common impact categories, although the magnitude of this reduction only matches in terrestrial ecotoxicity. The substances identified as causing the greatest share of the environmental impacts are mostly the same in both models, although the extent of the contribution for each substance can be different. The latter is illustrated by 2,3,7,8-TCDD in the effluent's HTP: according to USES-LCA results, this substance is responsible of 65% of the total score, while according to USES-LCA it only represents 1.5% of the total score. It is important to bear in mind that scores obtained with different models can not be compared, since they use different units (a dilution volume in EDIP97, and a reference

substance in USES-LCA); what is important instead is the relative scores within each model, and to interpret the changes. These scores, thus are only useful from a comparative point of view; they don't indicate if the treated effluent has sufficient quality to be discharged to a river, or to agricultural soil. In other words, this method is not a RA, it indicates to what extent treating the wastewater involves a subsequently lower potential impact in the environment and which chemicals have a dominant contribution to the overall potential impact. An RA would estimate the "actual" impact in a given specific location, while the method presented here determines the "potential" impact, without specifying it in space and time.

Concerning the limitations of this approach, we can highlight three issues: data quality and availability, exclusion of relevant substances, and the impossibility of taking into account synergistic/antagonistic effects. The first limitation refers to the difficulty in finding the necessary substance-specific data, specially concerning toxicology of PPCPs. In this work, structure–activity relationship models had to be used to determine many parameters, and experimental toxicological data for some substances is scarce or non-existent. Many substances had to be assigned PNEC values on the basis of ECOSAR toxicological estimations. Another problem with ecotoxicological data is that different endpoints are used (growth, death, behaviour, etc.), making difficult to fairly compare ecotoxicity of substances. Another example of data gaps and data uncertainty can be illustrated by means of nicotine and gemfibrozil, two of the most relevant substances in human toxicity; their reference dose for humans has been based on oral LD50 values for mouse/rat and an assessment factor of 10^5. Ciprofloxacin, on the other hand, is an example of a substance for which ecotoxicological data was rather complete (experimental NOECs were available in the USEPA Ecotox database for algae, crustaceans, and fish) and has been found to be the main contributor to terrestrial ecotoxicity. These examples show the heterogeneity, and many times the lack of data encountered while carrying out this research. This means that the characterisation factors for many of these substances, and therefore their environmental impact, as modelled in this study, must be seen as a first screening using the data and methods currently available. These characterisation factors should be updated in the future when more and higher quality data for emerging pollutants is accessible.

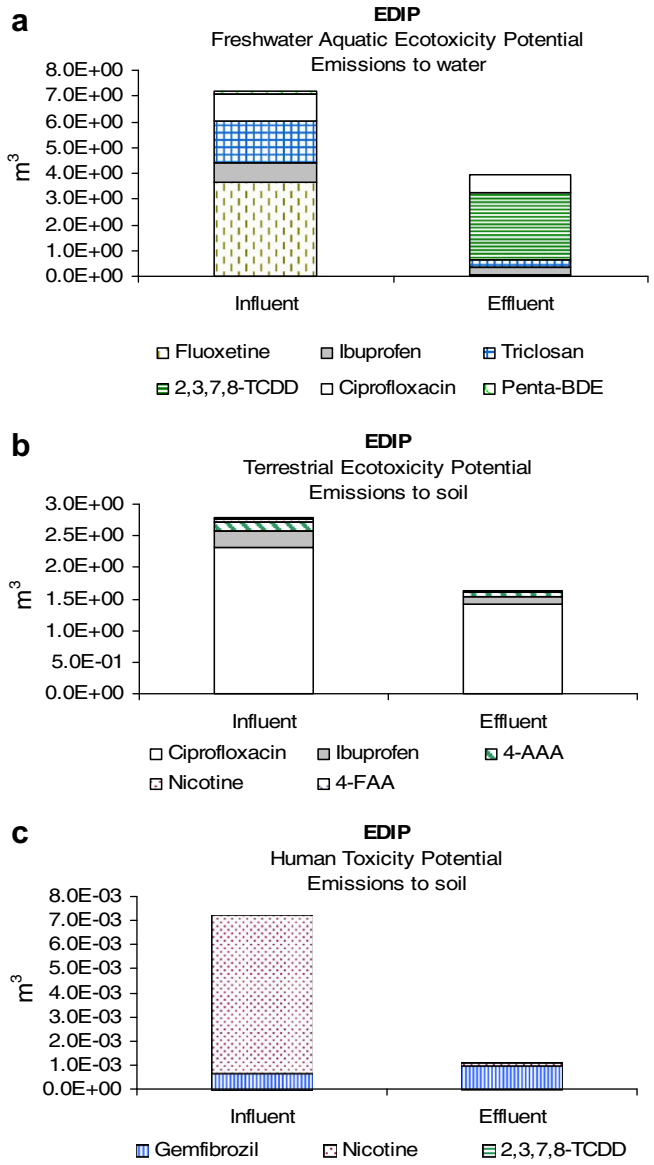

Fig. 1. Eco- and human-toxicity scores obtained for El Ejido WWTP influent and effluent, per L wastewater, with the EDIP model.

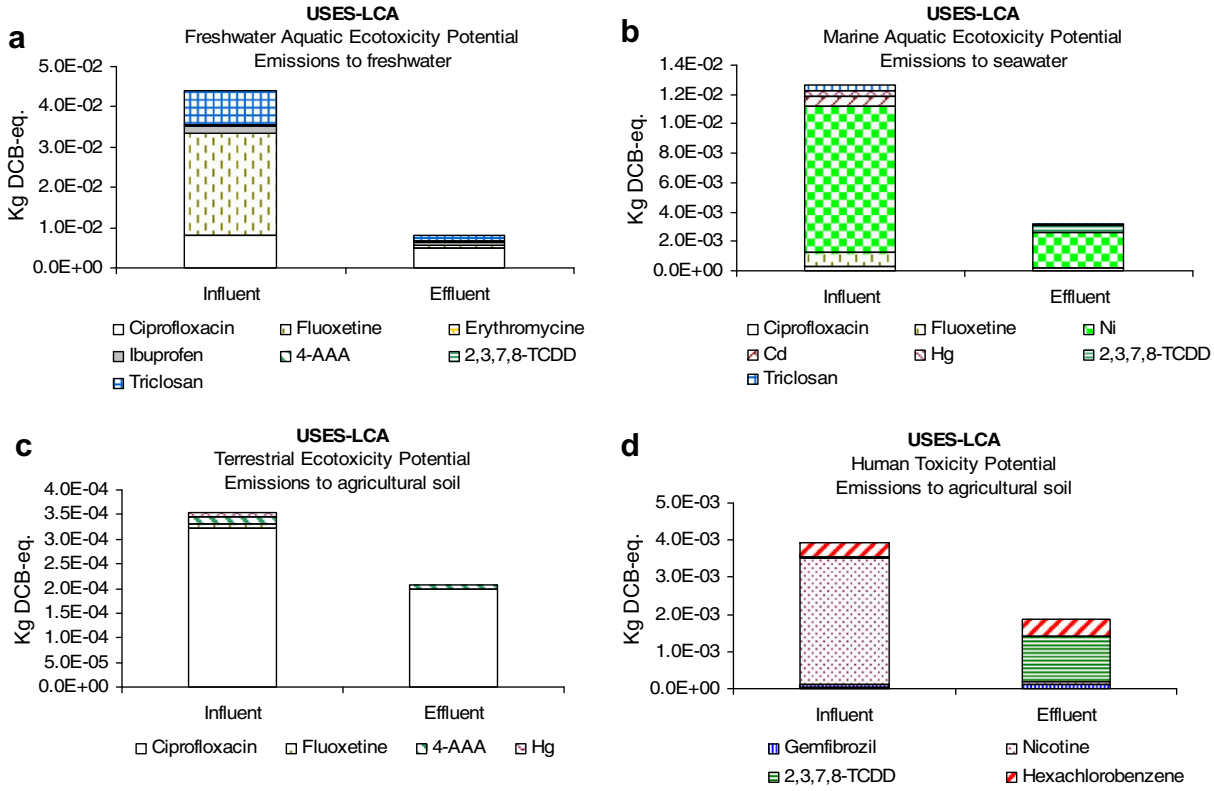

Fig. 2. Eco- and human-toxicity scores obtained for El Ejido WWTP influent and effluent, per L wastewater, with the USES-LCA model.

The second limitation refers to leaving out of the assessment one or more critical substances. An example for wastewater would be excluding from the assessment important metabolites. It might be the case that a parent compound is degraded during the treatment, but a more toxic metabolite appears. If this metabolite is neither analysed in the samples nor assigned a characterisation factor, its impact will be zero with this approach. In our case study, the painkiller dipyrone constitutes an example. After oral intake, this pharmaceutical is spontaneously hydrolyzed into several metabolites, among which we find 4-AAA and 4-FAA, which we have identified as relevant contributors to terrestrial ecotoxicity.

Another limitation for this approach is that, since potential toxicity of a mixture of substances is modelled as the sum of individual contributions, synergistic and antagonistic effects are not taken into account. Up to date, to our knowledge no LCIA method dealing with toxicity has tackled this issue.

4. Conclusions and outlook

Toxicity-related characterisation factors for 98 priority and emerging pollutants present in wastewater have been calculated, using two characterisation models: EDIP97 and USES-LCA. These characterisation factors were applied to calculate the reduction in potential impact of wastewaters treated in a Spanish urban sewage treatment plant and to identify those pollutants with a relatively high contribution to the overall impact. The application of characterisation to the influent and effluent leads to a substantial impact reduction in ecotoxicity and human toxicity after treatment (between 42% and 85% depending on the impact category). This impact reduction is observed either if wastewater is discharged to an aquatic recipient, or used for agricultural purposes.

Toxicity of both influent and effluent is mainly caused, according to these models, to pharmaceuticals and personal care products (PPCPs) rather than to priority pollutants, with the exception of ecotoxicity in marine water. Out of around 80 substances found in the wastewater samples, only 16 have a significant contribution, being 10 of these substances PPCPs. When quantifying the percentage of impact reduction in the treated effluent, the models only agree in terrestrial ecotoxicity, but the substances identified as causing the impact are basically the same, although the extent of each substance's contribution can be different.

This case study has shown how LCA characterisation factors, can be used to estimate the potential environmental impacts of wastewater pollutants in different compartments and scenarios, as well as to prioritise the pollutants causing the greatest share of these impacts. The next step should be to use this methodology in a complete LCA study assessing the fate of pollutants not only in wastewater, but also in excess sludge and sludge treatment, in order to evaluate whether or not potential impacts on ecosystems and human health are actually reduced.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.09.029.

References

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107, 907–938.

Domènech, X., Ayllón, J.A., Peral, J., Rieradevall, J., 2002. How green is a chemical reaction? Application of LCA to green chemistry. Environ. Sci. Technol. 36, 5517–5520.

EC, 2003. Technical Guidance Document on Risk Assessment. European Commission and European Chemicals Bureau, Joint Research Centre, Ispra, Italy.

EC, 2005. The Attitudes of European Citizens Towards Environment. Special Eurobarometer 217/Wave 62.1 – TNS Opinion & Social.

EC, 2006. Proposal for a Directive of the European Parliament and of the Council on Environmental Quality Standards in the Field of Water Policy and Amending Directive 2000/60/EC. COM(2006) 397 final. Brussels, 17.7.2006.

EU, 2000. Directive of the European Parliament and of the Council 2000/60/EC Establishing a Framework for Community Action in the Field of Water Policy, Official Journal, 2000, C513, 23.10.2000.

EU, 2001. Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 Establishing the List of Priority Substances in the Field of Water Policy and Amending Directive 2000/60/EC. Official Journal L 331, 15.12.2001, pp. 0001–0005.

EU, 2006. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Establishing a European Chemicals Agency, Amending Directive 1999/45/EC and Repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. Off. J. Eur. Union L 396/1, 30.12.2006.

Hauschild, M., Wenzel, H., 1998. Environmental assessment of products. Scientific Background, vol. 2. Chapman and Hall.

Hellweg, S., Fischer, U., Scheringer, M., Hungerbühler, K., 2004. Environmental assessment of chemicals: methods and application to a case study of organic solvents. Green Chem. 6, 418–427.

Hoornstra, E., Northolt, M.D., Notermans, S., Barendsz, A.W., 2001. The use of quantitative risk assessment in HACCP. Food Control 12, 229–234.

Huijbregts, M.A.J., Thissen, U., Guinée, J.B., Jager, T., Kalf, D., van de Meent, D., Ragas, A.M.J., Wegener-Sleeswijk, A., Reijnders, L., 2000. Priority assessment of toxic substances in life cycle assessment. Part I: calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES–LCA. Chemosphere 41, 541–573.

ISO, 2006. ISO 14044: Environmental Management – Life Cycle Assessment – Requirements and Guidelines. Geneva, Switzerland.

Larsen, H.F., 2004. Assessment of Chemical Emissions in Life Cycle Impact Assessment – Focus on Low Substance Data Availability and Ecotoxicity Effect Indicators. Ph.D. Thesis, October, 2004. Department of Manufacturing, Engineering and Management, Technical University of Denmark.

Martinez-Bueno, M.J., Agüera, A., Gómez, M.J., Hernando, M.D., Garcia-Reyes, J.F., Fernandez-Alba, A.R., 2007. Application of liquid chromatography/quadrupole-linear ion trap mass spectrometry and time-of-flight mass spectrometry to the determination of pharmaceuticals and related contaminants in wastewater. Anal. Chem. 79, 9372–9384.

Olsen, S.I., Christensen, F.M., Hauschild, M., Pedersen, F., Larsen, H.F., Tørsløv, J., 2001. Life cycle impact assessment and risk assessment – a methodological comparison. Environ. Impact Asses. 21, 385–404.

Pennington, D., 2004. OMNIITOX: increasing the acceptance and practicality of toxicological effects assessment in LCA. A 5th European Research Framework Programme Project. Int. J. Life Cycle Ass. 9, 281.

Pennington, D.W., Potting, J., Finnveden, G., Lindeijer, E., Jolliet, O., Rydberg, T., Rebitzer, G., 2004. Life cycle assessment Part 2: current impact assessment practice. Environ. Int. 30, 721–739.

RIVM, VROM, VWS, 1998. Uniform System for the Evaluation of Substances 2.0 (USES 2.0). RIVM report no. 679102044. National Institute of Public Health and the Environment (RIVM), Ministry of Housing, Spatial Planning and the Environment (VROM), Ministry of Health, Welfare and Sport (VWS), The Hague.

Saling, P., Kicherer, A., Dittrich-Krämer, B., Wittlinger, R., Zombik, W., Schmidt, I., Schrott, W., Schmidt, S., 2002. Eco-efficiency by BASF: the method. Int. J.Life Cycle Ass. 7, 203–218.

Ternes, T.A., Joss, A., Siegrist, H., 2004. Scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environ. Sci. Technol 38, 392A–399A.

Udo de Haes, E.A., Wegener Sleeswijk, A., Heijungs, R., 2006. Similarities, differences and synergisms between HERA and LCA – an analysis at three levels. Hum. Ecol. Risk Assess. 12, 431–449.

U.S. National Library of Medicine. ChemIDplus Advanced. <http://chem.sis.nlm.nih.gov/ChemIDplus/> (accessed March to November 2007).

USEPA, 2001. ECOSAR (Ecological Structure Activity Relationships) v. 099g <www.epa.gov/oppt/newchems/tools/21ecosar.htm>.

USEPA. 2007a. Ecotox Release 4.0. <http://cfpub.epa.gov/ecotox/> (accessed March to November 2007).

USEPA, 2007b. Integrated Risk Information System <http://www.epa.gov/IRIS/> (accessed March to November 2007).

USEPA, 2008. Estimation Program Interface (EPI) Suite <http://www.epa.gov/oppt/exposure/pubs/episuite.htm>.

Wenzel, H., Hauschild, M., Alting, L., 1997. Environmental assessment of products. Methodology Tools and Case Studies in Product Development, vol. 1. Chapman and Hall.

Wenzel, H., Larsen, H.F., Clauson-Kaas, J., Høibye, L., Jacobsen, B.N., 2008. Weighing environmental advantages and disadvantages of advanced wastewater treatment of micro-pollutants using environmental life cycle assessment. Water Sci. Tech. 57 (1), 27–32.