Elorri Igos

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Life Cycle Assessment of wastewater treatment solutions: How to consider pollutants removal benefits?

Betreuender:
Prof. Dr. Thomas Udelhoven
Department of Remote Sensing and Geoinformatics
University of Trier

Berichterstattende:
Dr. Andreas Krein
Department of Hydrology - University of Trier
Dr. Enrico Benetto
Department Environmental Research and Innovation – Luxembourg Institute of Science and Technology

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SUMMARY

The development of our society contributed to increased occurrence of emerging substances (pesticides, pharmaceuticals, personal care products, etc.) in wastewater. Because of their potential hazard on ecosystems and humans, Wastewater Treatment Plants (WWTPs) need to adapt to better remove these compounds. Technology or policy development should however comply with sustainable development, e.g. based on Life Cycle Assessment (LCA) metrics. Nevertheless, the reliability or consistency of LCA results can sometimes be debatable. The main objective of this work was to explore how LCA can better support the implementation of innovative wastewater treatment options, in particular including removal benefits. The method was applied to support solutions for pharmaceuticals elimination from wastewater, regarding: (i) UV technology design, (ii) choice of advanced technology and (iii) centralized or decentralized treatment policy.

The assessment approach followed by previous authors based on net impacts calculation seemed very promising to consider both environmental effects induced by treatment plant operation and environmental benefits obtained from pollutants removal. It was therefore applied to compare UV configuration types. LCA outcomes were consistent with degradation kinetics analysis. For the comparison of advanced technologies and policy scenarios, the common practice (net impacts based on EDIP method) was compared to other assessments, to better consider elimination benefits. First, USEtox consensus was applied for the avoided (eco)toxicity impacts, in combination with the recent method ReCiPe for generated impacts. Then, an eco-efficiency indicator (EFI) was developed to weigh the treatment efforts (generated impacts based on EDIP and ReCiPe methods) by the average removal efficiency (overcoming (eco)toxicity uncertainty issues). In total, the scenarios were compared with four types of assessment, showing the same trends: (i) ozonation and activated carbon perform better than UV irradiation, and (ii) no clear advantage distinguished between policy scenarios.

It cannot be however concluded that advanced treatment of pharmaceuticals is not necessary because other criteria should be considered (risk assessment, bacterial resistance, etc.) and large uncertainties were embedded in calculations. Indeed, a significant part of this work was dedicated to the discussion of uncertainty and limitations of the LCA outcomes. At the inventory level, it was difficult to model technology operation at development stage. For impact assessment, the newly developed characterization factors for pharmaceuticals (eco)toxicity showed large uncertainties, mainly due to the lack of data and quality for toxicity tests. The use of information made available under REACH framework to develop CFs for detergent ingredients tried to cope with this issue but the benefits were limited due to the mismatch of information between REACH and USEtox method. The highlighted uncertainties were treated with sensitivity analyses to understand their effects on LCA results.

This research work finally presents perspectives on the use of transparently generated data (technology inventory and (eco)toxicity factors) and further development of EFI indicator. Also, an accent is made on increasing the reliability of LCA outcomes, in particular through the implementation of advanced techniques for uncertainty management. To conclude, innovative technology/product development (e.g. based on circular economy approach) needs the involvement of all types of actors and the support from sustainability metrics.

1. INTRODUCTION

1.1. Technological challenges of wastewater treatment

Wastewater treatment appeared in cities in the 19th century to limit the pollutants discharge into the environment. The technologies are since then in constant evolution to adapt to the pollution load and to the legislative constraints. In 1991, the European legislation (Council directive, 1991) set removal objectives related to Chemical and Biochemical Oxygen Demand (COD and BOD), suspended solids, total phosphorous and total nitrogen.

However, the development of new products, technologies and consumption pathways contributed to increased occurrence of emerging substances in wastewater, including Pharmaceuticals and Personal Care Products (PPCPs), surfactants, additives, flame retardants, biocides and pesticides. Wastewater Treatment Plants (WWTPs) were not designed to eliminate these compounds that are not monitored due to the lack of specific regulations (Bolong et al, 2009). The concentration in the receiving water bodies was therefore observed significant for some substances, which raise several issues. First, studies found that these pollutants could be persistent in the environment (Petrović et al, 2003; Gomes and Lester, 2003). Then, they can damage ecosystems and human health. For example, some pesticides have negative effects on biodiversity (Geiger et al, 2010) and musk fragrance present carcinogenic potential (Maekawa et al, 1990). But one of the main adverse effects discussed in literature is that numerous substances are Endocrine Disrupters Compounds (EDCs). EDCs can interfere the hormonal system of mammals, causing cancerous tumours, reproduction or neuro- development anomalies, therefore representing an important threat for ecosystems and humans. Finally, the hazard of emerging substances is reinforced by their variety (e.g. EDC priority list includes 564 compounds (BKH, 2000) among which 147 are likely to be persistent), as well as their complexity for detection and analysis (Snyder, 2000). Huge efforts are therefore being deployed to better understand and monitor emerging substances.

Since the years 2000, many studies focused in particular on the emissions of pharmaceuticals and their metabolites into sewer system, after ingestion and excretion by humans. Kümmerer (2004), Heberer (2002) and Pailler et al (2009) observed significant concentrations through the water cycle (surface water, drinking water and sewage). Indeed, removal efficiencies of WWTPs were found negligible for some active ingredients, such as naproxen (Boyd et al, 2003), carbamazepine, metropolol (Vieno et al, 2007) or diclofenac (Bayerle et al, 2009). When released into the environment, pharmaceuticals residues can cause high damage on the ecosystems, due to their toxicity. Some contraceptive pills induced estrogenic effects on fish (e.g. desmasculinization) at extremely low concentrations; beta-blockers indicated chronic toxicity on cardiovascular and reproduction systems (Fent et al, 2006). Jolibois & Guerbert (2006) identified genotoxic effects of hospital wastewater. Also, pharmaceuticals cocktail could increase their hazard but this analysis is still challenging and needs further investigation (Vasquez et al, 2014).

It is therefore a technological challenge for WWTPs to adapt their processes in order to mitigate these effects and anticipate future regulations. There are several existing advanced treatments that could fulfil this function and that have been tested for pharmaceuticals

elimination. Hollender et al (2009) investigated the performances of an upgraded municipal WWTP, including post-ozonation and sand filtration, while Reungoat et al (2011) studied biofiltration with sand and granular activated carbon. Within the FP6 project NEPTUNE (New sustainable concepts and processes for optimization and upgrading municipal wastewater and sludge treatment), advanced post-treatments (ozonation, sand filtration, Powedered Activated Carbon (PAC) and ferrate) are compared (Siegrist et al, 2010). These research works showed promising results to improve removal efficiency of pharmaceuticals. In the European project PILLS (Pharmaceuticals Input and Elimination from Local Sources, http://www.pills-project.eu), funded by the EU INTERREG IVb program, a different wastewater management policy was proposed by implementing decentralized treatment of pharmaceuticals at source points. This strategy could avoid dilution effects, therefore increasing treatment efficiency, but also accidental pollution throughout the sewer system, especially due to overflows during heavy rain events. Pilot and full-scale plants equipped with advanced technologies were installed and tested at hospitals in Luxembourg, the Netherlands, Germany and Switzerland. The PILLS project aimed at characterizing hospital wastewater, in terms of composition, ecotoxicological potential and anti-biotic resistance bacteria spreading, at assessing the performances of advanced treatment processes and at raising awareness about the identified issues to scientific, politic, as well as broader public. Besides the technical aspects, innovative wastewater management strategies for pharmaceuticals removal should be sustainable regarding economic, environmental and societal aspects. In order to steer the choice of decision and policy makers for technology implementation, sustainability needed to be evaluated. In particular, the overall environmental impacts of the different wastewater treatment solutions were compared.

1.2. Environmental evaluation of wastewater treatment

1.2.1. Introduction to the Life Cycle Assessment methodology

Life Cycle Assessment (LCA) is a standardized methodology (ISO 14040/44, 2006) which evaluates the potential environmental impacts of a product or process along its overall lifecycle. With a first application in 1969 for the Coca-Cola Company to compare packaging materials, this evaluation tool aims firstly at supporting decision based on environmental criteria. Thanks to its comprehensive approach avoiding transfer of pollution from a lifecycle stage to another (e.g. improving the design of a product but requiring more energy during its use phase) and transfer of environmental effects (reducing climate change impacts while increasing toxic effects), LCA methodology became a reference to assess environmental impacts of systems from a holistic point of view. Its field of application is permanently expanding (ecodesign, process optimization, labelling, policy support, territorial strategy, etc.) and better framed, e.g. through the International Reference Life Cycle Data System (ILCD) handbook (European Commission, 2010) or the Product Environmental Footprint (PEF) Guide (European Commission, 2012).

ISO standards (2006) determine four methodological steps, presented in Figure 1.

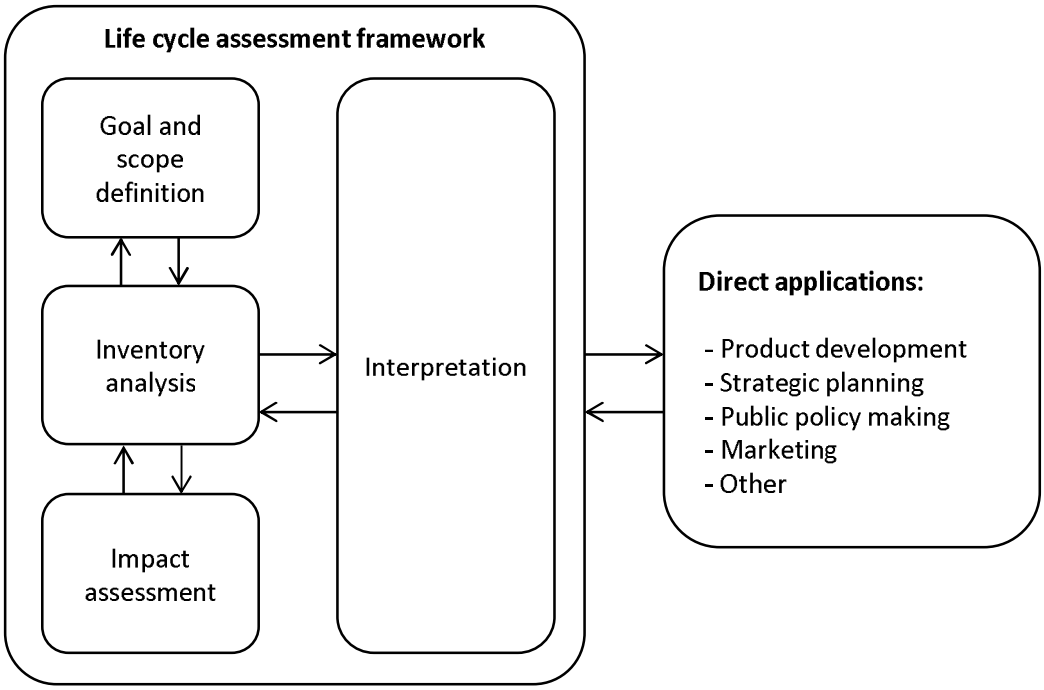

Figure 1: Stages of LCA, defined by ISO standards (2006)

First, the goal and scope of the study needs to be defined in order to identify the intended application, target audience, system boundaries and the functional unit. This latter is of particular importance because it determines the reference function (and flow) for which the systems are compared in order to have consistent results.

The second step, Life Cycle Inventory (LCI), consists in listing and quantifying all the inputs and outputs of the studied system. We can distinguish elementary flows, which represent direct exchanges with the environment (emissions of pollutants into air, water, soil or use of natural resources), and intermediary flows from the technosphere, which correspond to the consumption of transformed products (energy, chemicals, materials) or the generation of waste for treatment. Foreground data are usually collected on site and specific to the study, while background data, describing the lifecycle of intermediary flows (e.g. processes involved for the production of 1 kWh of electricity in Luxembourg), usually come from LCI databases (such as ecoinvent[1], GaBi[2] or ELCD[3]).

Once pollutants emissions and resources use are quantified for the functional unit, Life Cycle Impact Assessment (LCIA) phase aims at classifying the substances depending on their effects (e.g. greenhouse gases in climate change potential, nutrients in eutrophication potential) and at characterizing them according to the reference substance of the category (e.g. kg CO_2 eq for climate change, kg P eq for freshwater eutrophication). This problem-oriented evaluation refers to the so-called "midpoint" categories. However, it is possible to go further into the cause-effect chain and assess the potential damages on the three areas of protection, human health, ecosystems quality and resources depletion, called "endpoints". Finally, the practitioner can normalize and weight the impacts in order to obtain one single score,

[1] http://ecoinvent.org/
[2] http://www.gabi-software.com/databases/
[3] http://eplca.jrc.ec.europa.eu/ELCD3/index.xhtml

artificially expressed in "points", "eco-points" or monetary value. By increasing the level of results aggregation (from midpoints to endpoints to single score), the impacts assessment models become more uncertain (complexity of effects, data variability, objectivity) but the results can support decision making in an easier way (reducing potential trade-offs between categories).

The final LCA phase is results interpretation, which is supported by contribution and gravity analyses to identify the "hotspots" processes and elementary flows. Sensitivity and uncertainty analyses are also of importance to understand the effects of uncertainty in the LCA model on the results. The related outcomes can allow refining the assessment (goal and scope, LCI or LCIA) and therefore obtaining more accurate results through an iterative process.

1.2.2. Decision support for WWTP management

A significant number of LCA studies have focused on wastewater treatment since the 90s to support design and operation decisions (Corominas et al, 2013). Lifecycle of WWTPs includes construction, water and sludge treatment operation and dismantlement. LCA methodology has been applied to assess the environmental impacts of specific WWTPs or of control strategies, as well as to compare different WWTP configurations to improve environmental performances or to identify benchmarks (Corominas et al, 2013). During the last decade, advanced treatment technologies to better remove micropollutants have been evaluated to support their implementation based on environmental criteria. However, methodological constraints or uncertainties in LCA can represent a barrier to communication clear and reliable conclusions to decisions makers.

One of the main methodological issues related to the LCA of wastewater treatment concerns the choice of the functional unit. Most of the studies used the volume unit of treated wastewater as functional unit (Corominas et al, 2013). However, this is debatable since it does not consider influent quality or removal efficiency. Indeed, there is an environmental trade-off between improvement of discharged water quality (depending on influent composition and regulation constraints) and additional effort for process operation, which should be taken into account. In literature, some authors characterized the functional unit in terms of population equivalent derived from organic load (Tillman et al, 1998; Gallego et al, 2008), of phosphate removed (Rodriguez-Garcia et al, 2011) or specifying the specific input composition in COD and nutrients (Foley et al, 2010). While the two first approaches focus on one wastewater criteria (therefore ignoring other removal efficiencies); the last one can include more constituents but limits the comparability of results. This suggests the need for a more comprehensive and applicable approach encompassing the environmental impacts and the elimination benefits.

In Hoibye et al (2008), Wenzel et al (2008) and Larsen et al (2010), the chosen functional unit is 1 m^3 of treated wastewater; however, including both induced impacts from treatment operation (consumption of energy, chemicals, etc.) and prevented impacts for pollutants removal. The "zero" value therefore corresponds to the release of wastewater into the

environment without any treatment. Negative results mean the treatment plant has an overall benefit on the environment (avoided impacts higher than generated impacts) and vice-versa. This approach allows the comparison of different processes, even if the influent quality or the removed pollutants differ, as soon as they are characterized in the avoided impacts calculation. These three studies focused on the comparison of solutions to remove micropollutants. Hoibye et al (2008) compared sand filtration, ozone treatment, and Membrane Bioreactor (MBR), based on the EDIP method (Wenzel et al, 1997) for LCIA. Induced impacts (global warming, acidification and nutrient enrichment) and prevented ecotoxicity impacts are normalized in Person Equivalent Targeted (PET) to facilitate the comparison. Results showed sand filtration as the better technology. The authors however underlined the lack of data, both for the inventory (operation, removal efficiency) and for the impact assessment of hazardous substances. Wenzel et al (2008) performed a similar study, studying the environmental impacts of implementing sand filtration, ozonation or MBR in WWTP, leading to the same conclusions. In the deliverable 4.3 of NEPTUNE project, Larsen et al (2010) followed a similar approach (normalized EDIP results expressed as induced and avoided) for the comparative LCA of the post-treatments ozonation, sand filtration and PAC, but including larger panel of environmental indicators (acidification, global warming, nutrient enrichment, ozone depletion, photochemical ozone formation, human toxicity and ecotoxicity). A special focus is made on pharmaceuticals elimination. The authors concluded that ozonation combined with post sand filtration seems the most optimal solution. They also highlighted uncertainties related to pharmaceuticals characterization and found their avoided impacts minimal compared to nutrient and heavy metal removal.

Apart from the functional unit formulation, the literature review on LCA of wastewater treatment done by Corominas et al (2013) highlighted also the lack of transparency and the variability of LCI data, the few numbers of studies comparing results from different LCIA methods (Ortiz et al, 2007; Renou et al, 2008; Hospido et al, 2012), the limited coverage of selected environmental impacts in some cases and the lack of sensitivity analysis and discussions regarding the study limitations in literature. All these points contribute to results uncertainty and could bias the conclusions of the LCA study. It is therefore essential to increase the transparency, consistency and reliability of inventory, impact assessment and results to better support decisions.

To conclude, LCA methodology has a huge potential to help stakeholders into the development of innovative wastewater treatment technologies and strategies. Moreover, it is flexible enough to adapt it to specific cases. Nevertheless, there is still room for improvement in each of the four stages defined by the ISO standards, in order to better support decisions towards more sustainable solutions. In particular, the characterization of (eco)toxicity impacts of the effluent, highly critical in literature and essential to assess the avoided impacts, should be further investigated.

1.2.3. (Eco)toxicity impacts characterization

Toxicity determines the harmfulness of a substance on humans (human toxicity) or ecosystems (ecotoxicity), provoked by single or short-term exposure (acute toxicity) or by

repeated or continuous exposure on an extended period (chronic toxicity). Ecotoxicity and human toxicity indicators are often pointed out as the most uncertain impact categories in LCA. For instance, Geisler et al (2005) calculated a dispersion factor (97.5th percentile divided by the median) of 50 for human toxicity results, 50 to 100 for freshwater ecotoxicity and 500 to 1000 for terrestrial ecotoxicity. In comparison, the dispersion factor for global warming, acidification, eutrophication or photo-oxidant creation ranged between 1.2 and 2.2.

Since 1990, numerous LCIA models characterize human toxicity and ecotoxicity potential (Figure 2). The most recent methods combined the best features of previous models, such as ReCiPe from CML 2001 and Eco-Indicator 1999 or STEPWISE 2006 from IMPACT 2002+ and EDIP 2003 (Pizzol et al, 2011). In 2008, based on the initiative of the United Nations Environment Program (UNEP) – Society for Environmental Toxicology and Chemistry (SETAC), a scientific consensus model called USEtox (Rosenbaum et al, 2008) was built, in collaboration with the developers of CalTOX (used in TRACI), IMPACT 2002, USES-LCA (used in ReCiPe and CML), BETR, EDIP, WATSON and EcoSense.

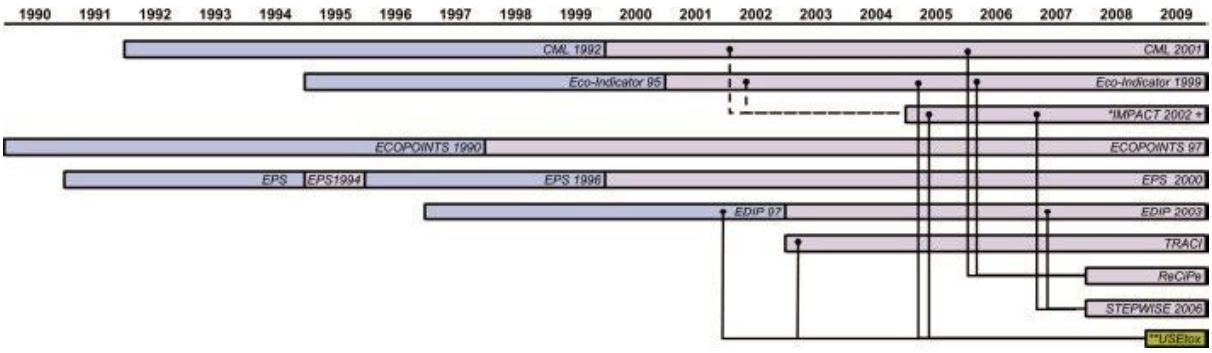

Figure 2: History of (eco)toxicity LCIA methods (Pizzol et al, 2011)

The (eco)toxicity cause-effect chain is quite complex. First, a fate model needs to predict the behaviour of the emitted substance in the environment (e.g. degradation, evaporation, deposition). Multimedia models have been more recently developed (e.g. in USEtox and USES-LCA) to better estimate the pollutant concentration in the environmental compartments (archetypes of soil, air and water). Then, exposure on species (for ecotoxicity) or humans (for human toxicity) needs to be determined. Human exposure is particularly challenging because it includes a multitude of pathways (e.g. ingestion of various types of food, air inhalation, water drinking). Finally, the damage on species and humans relies on toxicity tests, which can measure several types of effects (carcinogenic, respiratory disease, reproduction) on different exposure modes (acute, subacute, subchronic, chronic) with different indicators (No Observed Adverse Effect Level – NOAEL, Effect concentration which affects 50% of tested population – EC50). Besides the variety of toxicity indicators, the non-linearity of effects represents also a challenge for LCA methodology (Larsen & Hauschild, 2007).

In the field of wastewater treatment, ecotoxicity and human toxicity categories are very important since they characterize the environmental impacts linked to effluent release, together with aquatic eutrophication and acidification indicators. Moreover, the coverage of substances for (eco)toxicity is much larger than for these two categories. Also, aquatic acidification is not often included in LCIA methods.

Some LCA scholars have developed new Characterization Factors (CFs) for the priority or emerging substances that are not included in current methods (Hoibye et al, 2008; Wenzel et al, 2008; Muñoz et al, 2008; Larsen et al, 2010). These four studies used the EDIP 97 method, because of its easiness to use. Indeed, the model is based on few key properties of the assessed substance (e.g. Henry law constant, Predicted No Effect Concentration – PNEC) and rules of thumb. The CF represents the required dilution volume to observe no effect. In Hoibye et al (2008) and Wenzel et al (2008), the characterization of water ecotoxicity for three heavy metals, five endocrine disruptors and one detergent is not transparent (no detailed data and sources). The authors however underline the high results sensitivity to the inclusion of more hazardous substances and to the determination of PNEC value. Larsen et al (2010) calculated the aquatic ecotoxicity CFs for 22 pharmaceuticals and three metals based on databases and literature. They also showed the huge variation of results depending on the PNEC data used. In addition, they investigated the inclusion of pharmaceuticals in normalization factors (based on the total pollutants emissions per person equivalent), which resulted into negligible effects. The study of Muñoz et al (2008) has a larger scope: the authors included 98 substances (PPCPs, priority pollutants, PAH, heavy metals); they characterized not only freshwater ecotoxicity, but also marine and terrestrial ecotoxicity, as well as human toxicity; and compared EDIP97 method with USES-LCA model. This latter is based on multimedia model, therefore including more complex interactions for the fate modelling. The effect factor is calculated in a similar way than EDIP97, with PNEC value. The CF corresponds to the relative (eco)toxicity of a pollutant as compared to a reference substance (1,4-dichlorobenzene). Muñoz et al (2008) highlighted the issue of data quality and availability to develop new CFs, as well as the impossibility of considering synergistic or antagonistic effects.

To conclude, major efforts are still required to improve the characterization of (eco)toxicity in LCIA, in particular for substances not yet included in the methods. The development of multimedia models represents a great advancement to better represent pollutant fate in the environment, but the collection of input data to run the model needs to remain feasible (number and availability). The PNEC approach for the effect characterization seems quite fragile. As underlined by Larsen et al (2010), average based model such as USEtox can tackle this issue since several toxic endpoints are included in the assessment, making it less sensitive to new data from literature or database. The use of USEtox seems therefore promising to better represent the environmental performances of WWTPs. Also, most of the studies focused on freshwater ecotoxicity mitigation. The inclusion of other impacts, in particular human toxicity, should be pushed forward.

1.3. Objectives and methods

The main objective of this research work is to explore how LCA methodology can better support decisions for the implementation of innovative wastewater treatment solutions. Based on previous literature review, it seemed that the communication of net impacts represents an effective method to consider both environmental effects induced by treatment plant operation and environmental benefits obtained from pollutants removal. As a first step, this work

assessed the practical interest, feasibility and limitations of this method based on the PILLS case study, i.e. to support technological and policy choices to better remove pharmaceuticals from wastewater. Different decision levels were explored in this assessment to steer: (i) the design of a particular technology (ultraviolet – UV – irradiation), (ii) the choice between different advanced technologies (UV irradiation, ozonation and activated carbon adsorption) and (iii) the wastewater management policy regarding the potential decentralization of treatment.

The application of net impacts evaluation underlines however the difficulty of pollutants (eco)toxicity characterization because of methods uncertainties and the lack of covered substances in existing methods. To overcome this issue, two possibilities were investigated. The first one consisted in developing an eco-efficiency indicator representing the ratio of generated impacts (estimated through LCA) and the average removal efficiency (obtained from measurements). It can be more understandable and less confusing for stakeholders and the variation of treatment efficiency between pollutants is considered through statistical tests to compare scenarios in a consistent way.

The second solution is to refine the characterization of (eco)toxicity impacts, by using the scientific consensus USEtox. New CFs for pharmaceuticals were developed and compared to the ones based on EDIP method. Based on the acquired experience, the USEtox model was applied to detergents ingredients, by integrating information made available under the European REACH framework (Regulation (EC) 1907/2006). This interaction between LCA and REACH was investigated to better integrate official and up-to-date data into LCIA methods. This last study on dishwasher detergents was not focused on wastewater treatment but on the effects of effluent release and, in particular, of European legislation constraints applied to formulations. The development of new (eco)toxicity factors for both pharmaceuticals and detergents ingredients in a transparent way is an important asset to facilitate their potential reuse by the LCA community.

Finally, through the various assessments performed in this research work, sensitivity analyses on inventory data and impact assessment models were carried out to understand the effects of uncertainties on LCA results. As highlighted in section 1.2.2, this point is of most importance to ensure the validity of LCA results and not bias conclusions for decision makers.

1.3.1. Comparison of net impacts for pharmaceutical removal solutions

Within the PILLS project framework, the first part of this work assessed the environmental impacts of advanced treatment technologies for pharmaceuticals removal, to steer their design and their implementation in sewer systems. To do so, comparative LCA studies were performed at different levels.

In section 2, a focus on UV irradiation technology is made to understand the advantages and drawbacks of different types of treatment configuration (hydrogen peroxide dosage, lamp pressure, electricity input, wastewater flow rate). LCA methodology was here used as a support of the in-depth technical analysis focused on the degradation kinetics modelling. Both infrastructures and operational data were included in the LCI, to understand the effects of

these two components on the environmental profile of the treatment. Similarly to previous studies on pharmaceuticals removal from wastewater, EDIP method was applied to assess the net impacts (normalized person-equivalents). Fourteen new characterization factors were developed for pharmaceuticals substances. This first application, which was not focused on the environmental evaluation, applied the same LCA methodology framework from previous literature to compare the related results with technical outcomes for different UV technology configurations. This aimed at observing if similar trends were observed and at highlighting the added value and potential limits of LCA to support technology design.

The section 3 enlarges the scope of LCA by comparing different advanced treatment technologies and wastewater management strategies (centralized or decentralized treatment) to support policy makers. This second comparative LCA was therefore more complex with higher level of decision. The decentralized treatments installed by the PILLS partners allowed first comparing three technologies, UV radiation (UV), ozonation (O3) and activated carbon adsorption (AC), based on the treatment of 1 m^3 of hospital wastewater as functional unit. Data collection was quite challenging because of the treatment variability and data differences between partners. That is why extreme scenarios were considered for each technology (with minimum and maximum values). Then, the overall wastewater systems were compared, including: conventional centralized (CC), upgraded centralized with ozonation post-treatment (UC) and addition of decentralized treatment for hospital wastewater, equipped with ozonation (CC+D_O3), UV irradiation (CC+D_UV) or activated carbon adsorption (CC+D_AC). The functional unit was therefore the treatment of 1 m^3 of wastewater. Infrastructures were not included in this inventory based on previous conclusions.

As previously done for UV treatment analysis, normalized net impacts with EDIP method were evaluated. However, to increase the reliability of the assessment, the state-of-the-art methods ReCiPe (Goedkoop et al, 2009) and USEtox (for freshwater ecotoxicity and human toxicity) were also applied and combined into normalized net impacts to validate the results. ReCiPe method is more recent than EDIP and the related impact models are more complex and relevant. In particular, this is why the ILCD handbook (European Commission, 2011a) gave higher rates for this method than for EDIP (97 or 2003) and recommends following its characterization model for photochemical ozone formation and freshwater eutrophication. As stated in section 1.2, USEtox considers the latest developments, which are harmonized by the main developers of LCIA toxicity models. At the time of the study, it was the first time that CFs for pharmaceuticals were developed using USEtox.

Several sensitivity analyses were performed on data from operation stage. The objective was to observe the results variations due to different data (from partners or literature) for pharmaceuticals removal, treatment operating parameters and hospital wastewater volumes. Sensitivity analysis is a common technique which is recommended by ISO standards (2006). It becomes indispensable because of the large sources of uncertainties in LCA methodology and the potential barrier they represent to support decision makers. More recently, LCA scholars investigated the potential of global sensitivity analysis which consists in estimating the contribution of inputs uncertainties to output uncertainty, based on variance decomposition or sampling methods. However, due to the lack of uncertainty data and tools

(no functionalities in commonly used LCA software), only scenario analysis (comparison of results based on different set of data) was carried out for this study.

1.3.2. Development of eco-efficiency indicator

As stated before, the uncertainties of (eco)toxicity characterization suggest the need of a novel approach to consider removal benefits with a LCA study of wastewater treatment. Based on the same scenarios of PILLS comparison (comparison of UV, O3 and AC technologies; and of the policy scenarios CC, UC, CC+D_O3, CC+D_UV and CC+D_AC), an eco-efficiency indicator (EFI) was proposed in section 4. The idea is to keep the elimination efficiencies as percentages, avoiding the need to characterize the environmental effects of the studied substances.

A similar principle was already applied in Ferreira et al (2011). The authors assessed the environmental performances based on the Annual Performance Deficiency Index (ADPI), which reflects the COD removal efficiency with or without separate sewer system (ratio without unit). Then, they compared treatment alternatives based on the ratio of economic costs and ADPI reduction from the current scenario, therefore weighting the treatment costs by its efficiency. Also, in Igos et al (2013), a cost performance indicator was developed to compare the environmental performances of potable water production sites. The application is quite different but the approach is similar. In order to account for the treatment efficiency, the LCA results are divided by the water quality gain obtained from raw to potable water. The quality gain is based on quality parameters measurements (e.g. turbidity, suspended solids, *Escherichia coli*) which are normalized based on a French quality valuation system for water. In these two studies, the objective is the same than for the EFI indicator: develop a factor which weighs the water treatment efforts (expressed as generated environmental impacts or as costs) by the treatment quality (difference of water quality before and after treatment, without units). The section 4 therefore tests the EFI indicator, being the ratio between the generated LCA impacts and the average removal of pharmaceuticals, for the studied wastewater treatment solutions. As in Igos et al (2013), the variation of elimination efficiency between pharmaceuticals compounds is taken into account to perform statistical tests (*t*-tests), based on the null hypothesis (Berthouex and Brown, 2002).

1.3.3. Development of (eco)toxicity characterization factors

To assess the avoided impacts linked to pharmaceuticals removal, it was necessary to develop new CFs for 14 substances. Compared to previous studies, both freshwater ecotoxicity and human toxicity potentials were investigated. EDIP97 method was used as reference, but the focus was particularly on USEtox model because of its better representativeness and its recognition by scientific community (consensus recommended by ILCD handbook, 2011). This first development of CFs for pharmaceuticals compounds with USEtox could highlight the main interests and limitations of the methodology.

Based on these conclusions, section 5 tries to overcome the barrier related to data source and data quality. By using toxicity endpoint values published under the European REACH

regulation, the work aimed at developing new CFs in a more consistent and reliable way for dishwasher detergents ingredients. This case study was chosen to observe the effects on wastewater environmental profile generated by phosphate ban and eco-labelling in detergent formulations. In literature, only Van Hoof et al (2011) developed USEtox factors for detergents, but applied for laundry products and focused on freshwater ecotoxicity. The work performed was therefore quite novel, and the detailed and transparent materials used makes it easily reusable for the future.

The link between LCA and REACH was already studied in Askham (2012). The author highlighted in particular the benefits of data availability from REACH on the robustness of LCA toxicity assessment. However, the paper stays quite theoretical. The characterization of (eco)toxicity in this research work aimed at presenting the most consistent data to be considered in USEtox model, from the physic-chemical properties of the substances (Human & Environmental Risk Assessment – HERA – reports on ingredients of European household cleaning products) and the toxicity data (European Chemicals Agency portal[4], collecting REACH information). The results were compared to previous studies to check their validity. Finally, sensitivity analysis was performed on the model parameters to assess the results robustness.

[4] http://echa.europa.eu/

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Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater using advanced UV irradiation technology: A comparative assessment

C. Köhler*, S. Venditti, E. Igos, K. Klepiszewski, E. Benetto, A. Cornelissen

Public Research Centre Henri Tudor/Resource Centre for Environmental Technologies, 66 rue de Luxembourg, BP 144, L-4002 Esch-sur-Alzette, Luxembourg

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ABSTRACT

UV irradiation technology as a membrane bioreactor (MBR) post-treatment was investigated and assessed. Both UV low pressure (LP) and medium pressure (MP) lamps were examined. The technology was installed in a pilot plant treating hospital wastewater to provide the study with adequate field data.

The effect of the UV irradiation was enhanced with varying dosages of H_2O_2 to establish an advanced oxidation process (AOP). The efficiency of the pharmaceutical removal process was assessed by examining 14 micropollutants (antibiotics, analgesics, anticonvulsants, beta-blockers, cytostatics and X-ray contrast media) which are typically released by hospitals and detected with liquid chromatography coupled tandem mass spectrometry (LC–MS/MS).

While the MBR treatment generally showed only a low degradation capacity for persistent pharmaceuticals, much better degradation was obtained by applying UV irradiation and H_2O_2 as AOP. The "conventional" cost-benefit analysis of the different technology options taking into account both electrical energy consumption and pharmaceutical removal efficiency, revealed clearly better performance of low pressure UV lamps as AOP. However, a holistic comparison between the different scenarios was carried out by evaluating their environmental impacts using the life cycle assessment (LCA) methodology. Decisive advantages were highlighted to include this approach in the decision making process.

1. Introduction

Pharmaceuticals and their metabolites are excreted by humans through faeces and urine. Hospitals are considered as point sources within the urban wastewater system [1,2] and they significantly influence the load of certain pharmaceuticals being transported to municipal wastewater treatment plants (WWTPs). Since standard treatment plants (STP) are not designed to remove pharmaceutical residues from wastewater, elevated concentrations of these contaminants have been detected in receiving waters downstream WWTPs [3]. Recent studies have revealed that pharmaceuticals persist in the water cycle [1,4,5].

In-house studies found elevated levels of relevant trace-pollutants at both the inlets and outlets of two investigated STPs [6]. The observed removal rate for Carbamazepine and Diclofenac was almost negligible. This resulted in a chronic ambient concentration of around 400 ng L^{-1} of both pharmaceuticals in the receiving river. With respect to the environmental impact of pharmaceutical residues, they generally show low acute toxicity to aquatic organisms but a number of pharmaceuticals are of concern to ecosystem health due to chronic effects [7–9].

This study focuses on the treatment of wastewater with high levels of pharmaceuticals from point sources. A pilot membrane bioreactor (MBR) was installed at a hospital containing around 360 beds. The MBR was continuously operated with a permeate flow of 2 m^3 d^{-1}. It served as pre-treatment to obtain a suitable wastewater quality for the subsequent advanced treatment using ultraviolet (UV) irradiation. So far, only a few and incoherent data can be found about UV irradiation as an advanced treatment technology. Also, current research is focussing at MBR permeate treatment with ozone, since satisfying results were obtained [10]. However, with regards to operation and maintenance UV technology is considered to have decisive advantages.

The removal efficiency of different MBR and UV treatment process setups were evaluated for pharmaceuticals which are part of the medication groups of analgesics, antibiotics, anticonvulsants, beta-blockers, cytostatics and X-ray contrast media. Additionally, the effects of a low and a medium pressure UV lamp on the removal of the pharmaceutical substances were examined. The former was used with a fixed power of 0.25 kW while the

* Corresponding author.
E-mail address: christian.koehler@tudor.lu (C. Köhler).

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latter was investigated with an adjustable power between 2 kW and 10 kW. Furthermore, the effect on the pharmaceutical degradation by UV irradiation in combination with hydrogen peroxide (H_2O_2) as advanced oxidation process was also determined. The pharmaceutical degradation kinetic of each operational/experimental UV setup was modelled and compared. The main objective of the investigation was to assess the feasibility of eliminating pharmaceuticals from hospital wastewater in a cost-effective and environmentally sound way and to obtain field data that could serve as important design information for these technologies. To this end, LCA was applied as one of today's most consensual methodologies for environmental assessment of products and processes. In this context, for each treatment scenario, the environmental impact generated by the infrastructure and the resources used, such as electrical energy and H_2O_2, was directly compared to the reduced environmental impact caused by the treatment efficiency in terms of macro- and micropollutants. It is worth pointing out that the pilot study could directly feed the LCA with first-hand data. This makes the present work particularly coherent and closes the gap in previous investigations [11,12].

2. Experimental

The efficiency of the MBR has been determined by a seven and a five-day measurement campaign in which typical wastewater compounds and pharmaceuticals were analysed, both observing the influent and the effluent of the MBR treatment. Subsequently, several batch experiments were conducted to evaluate the UV treatment.

2.1. MBR treatment

The pilot plant (MBR and UV treatment) is housed in a container and is located at the hospital Centre Hospitalier Emil Mayrisch (CHEM) in Esch-sur-Alzette, Luxembourg. The MBR treats in continuous operation about 1% of the diurnal hospital sewage. Technical details are given by Venditti et al. [13]. Before pharmaceutical measurement, the MBR treatment efficiency was assessed using the removal of suspended solids, organic carbon, nitrogen and phosphorus. Two-hour composite samples, with a 3 min sampling frequency, were taken from the influent and effluent of the MBR and stored in glass vessels at 4 °C. The maximum storage time did not exceed 72 h before the samples were analysed in the laboratory. Five days composite samples were prepared, from the 2 h composites for pharmaceutical analysis, to eliminate weekly fluctuations.

2.2. UV treatment

Two different UV lamps (IBL Umwelt- und Biotechnik GmbH, Heidelberg, Germany) were applied in the framework of this study. A medium pressure (MP) lamp with an adjustable power of 2–10 kW and a low pressure (LP) UV lamp with a fixed power of 0.25 kW (see Table 1). Besides the composition of the noble gases, their filling pressure influences the UV spectrum significantly. Consequently, the LP lamp offers two energy emission peaks at UV light wavelengths of 254 nm and 185 nm while the MP lamp has a polychromatic emission along the UV spectrum. Furthermore, the latter offers (besides direct photolysis) photochemical oxidation process, i.e. in situ production of hydrogen and hydroxyl radicals that are formed within the vacuum UV (VUV) spectrum (100–200 nm) [14].

For each test with the low and medium pressure UV reactor 1 m^3 of MBR permeate collected in a buffer tank served as influent. Tests have always been conducted by operating just one UV lamp. Before the water enters the reactor, H_2O_2 can be added to provide (besides the photochemical oxidation process) advanced oxidation processes. The hereby formed hydroxyl (OH) radicals are considered to react non-selectively in oxidizing organic material and therefore enhance the elimination of pharmaceuticals. The resulting photochemical oxidation is much faster than direct photolysis, i.e. when no H_2O_2 reactant is used [14,15].

In the comprehensive monitoring program several UV operation modes have been investigated. The operation modes were based on four different process conditions assumed to have significant effects on the degradation efficiency of pharmaceuticals and on the operation expenses:

i) electrical energy needed to reduce the content of pharmaceuticals to a specific concentration level
ii) power variation of the MP UV lamp
iii) difference between the MP and LP UV lamp
iv) dosage of H_2O_2

The variation of the MP UV lamp power (ii) was chosen to investigate potential effects of changes in the UV spectrum when a different lamp power is applied. For each of the observed scenarios one cubic meter of pre-treated hospital sewage (permeate) was recirculated in the UV reactor until a total electrical energy input of 10 kWh was obtained. Samples were taken at specific intervals as a function of the electrical energy input (e.g. at 0, 1, 2, 4, 8, and 10 kWh m^{-3}). The interval depended on the applied lamp power and contact time, which was not longer than 91 s (5 h operation) for the MP lamp and 1013 s (40 h operation) for the LP lamp. This sampling scheme has been used to show the degradation kinetics of the pharmaceuticals and the interaction with electrical energy input. The aim was to achieve a reasonable comparison of the different operational setups and to produce valuable results for possible full scale applications.

2.3. Analysis

Grab samples of 500 ml were directly taken from the 1 m^3 buffer tank prior to the UV treatment of the wastewater (MBR permeate) and throughout the experiments depending on the different UV treatment scenarios described before.

Pharmaceuticals were chosen considering those known to be excreted in the highest amount in the hospital and with the highest eco-toxicity: antibiotics (Acetyl-Sulfamethoxazole CAS-Reg. 21312-10-7, Ciprofloxacin CAS-Reg. 85721-33-1, Clarithromycin CAS-Reg. 81103-11-9, Erythromycin CAS-Reg. 114-07-8 and Sulfamethoxazole CAS-Reg. 723-46-6), analgesics (Diclofenac CAS-Reg. 15307-86-5, Lidocaine CAS-Reg. 137-58-6 and Naproxen CAS-Reg. 22204-53-1), anticonvulsant (Carbamazepine CAS-Reg. 298-46-4), betablocker (Atenolol CAS-Reg. 29122-68-7), cytostatics (Cyclophosphamide CAS-Reg. 50-18-0 and Ifosfamide CAS-Reg. 3778-73-2), X-ray contrast media (Iodixanol CAS-Reg. 92339-11-2 and Iohexol CAS-Reg. 66108-95-0).The analyses of the pharmaceuticals were performed in two steps: enrichment by solid phase extraction (SPE) and analysis of the SPE extracts by LC–MS/MS. The analytical method found in the literature [16] was adapted to the specific compounds: acid (pH 3) for ciprofloxacin and X-ray media with OASIS reversed-phase sorbent Hydrophilic Lipophilic Balanced (HLB) and resin-based sorbent ENV+ cartridges respectively; neutral (pH 7) with OASIS HLB cartridges for all the other compounds.

2.4. Life cycle assessment

The chosen functional unit (FU) is the treatment of 1 m^3 of MBR permeates in order to compare the different treatment scenarios. Accordingly, data concerning the operation and infrastructure of the treatment processes were collected from the experiments

Table 1
UV treatment design data (IBL Umwelt- und Biotechnik GmbH, Heidelberg, Germany).

	UV low pressure lamp	UV medium pressure lamp
Name	uviblox® WPT 250	uviblox® WPT 10
Nominal power	0.25 kW	10 kW
Effective radiated power	UVC (185 nm, 254 nm): 110 W	UVC (200–280 nm): 1500 W UVB (280–315 nm): 800 W UVA (315–400 nm): 700 W

Table 2
Foreground process data relative to the operation and infrastructure of treatment processes.

	Unit	Ecoinvent process	Scenario A	Scenario B	Scenario C	Scenario D
For 1 m^3 of treated water						
Electricity	kWh	Electricity, low voltage, at grid[a]	3	3	1	1
Hydrogen Peroxide	kg	Hydrogen peroxide, 50% in H_2O, at plant[b]	0.83	1.11	1.11	1.11
UV lamp	Unit*	–	0.00010	0.00010	0.00007	0.00045
UV lamp type	–	–	MP	MP	MP	LP
UV power	kW	–	10	10	5	0.25
For 1 UV lamp						
UV lamp life time	h		3000	3000	3000	8800
Steel	kg	Steel product manufacturing, average metal working[b]	56.8	56.8	56.8	61.5
Synthetic silica glass	kg	Glass tube, borosilicate, at plant[c]	2.57	2.57	2.57	2.71
Copper	kg	Copper, at regional storage[b]	0.095	0.095	0.095	0.095
Molybdenum	kg	Molybdenum, at regional storage[b]	0.0017	0.0017	0.0017	0.0017
Ceramic	kg	Ceramic tiles, at regional storage[d]	0.12	0.12	0.12	0.12
Argon	kg	Argon, liquid, at plant[b]	0.0063	0.0063	0.0063	0.0015
Mercury	kg	Mercury, liquid, at plant[e]	0.0001	0.0001	0.0001	0.0001

Notes represent the region from which the lifecycle of the process was studied: [a]Luxembourg, [b]European average, [c]Germany, [d]Switzerland, [g]global average.
*Quotient of infrastructure unit calculated based on the operation time to treat 1 m^3 and the lamp lifetime.

(Table 2). Then, a life cycle inventory (LCI) was constructed, using Ecoinvent datasets relative to the lifecycle of the energy and raw materials consumed by the treatment processes [17].

For the production of a UV lamp, data on silica glass, molybdenum, argon, mercury, and the copper cable and ceramic socket were requested from the supplier.

The structure composition (steel and silica glass) was derived from the lamp's dimensions. No data were found for the quantity of argon used for filling the bulb. Therefore, the amount needed was estimated from the dimensions of the UV lamp and the gas pressure (1 bar minimum for the low pressure UV lamp and 10 bar for the medium pressure lamp). 0.1 g of mercury filling was also taken into account for both lamp types.

The result from the LCI is an inventory of pollutant emissions and resource consumptions relative to the whole lifecycle of the treatment processes. In order to facilitate the comparison of UV scenarios, potential environmental impacts are calculated from the LCI results by means of the EDIP2003 method [18,19]. Impact results for a broad range of categories (climate change, acidification, ecotoxicity, etc.) are evaluated, further normalized to person-equivalents PE (considering the background load on the environment from an average person in a reference year [20]) and finally aggregated into a single score (without weighting). This method allows evaluating the avoided impact due to pharmaceuticals removal and the generated impact relative to the infrastructure and operation of the treatment in the same normalized units, therefore leading to a net single score which is easy to understand and interpret.

The avoided impacts due to pharmaceuticals removal (Table 3) are evaluated by multiplying the inventory data to fate and effect factors calculated using a simplified multimedia fate and effect model.

As the Henry's law constants [21] of the pharmaceutical considered are very low, they are assumed to remain in water. The fate factor corresponds to a change in concentration because of distribution and biodegradation. In the case of pharmaceuticals, distribution does not apply since the log of the partitioning coefficient of octanol–water is lower than 3 [18]. A biodegradation factor of 0.5 applies only to Naproxen and was determined according to regression models from EPI Suite [21]. The effect factor for ecotoxicity is defined as the inverse of the predicted no-effect concentration (PNEC) (the higher is the PNEC, the lower is the impact) [19]. The PNEC for acute toxicity is based on the lowest median effective concentration (EC50) among the ones collected from the literature and from the ECOSAR [21] model. The PNEC for chronic toxicity can be extrapolated from the lowest EC50, the lowest no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC) or from the lowest chronic value provided by QSAR [21] or the database WikiPharma [22]. Depending on the data quality the EC50 is divided by a safety factor (10–100 for acute and 10–1000 for chronic toxicity). Among all the toxicity effect factors calculated, the highest one is retained and used for calculating the impact of each pharmaceutical.

Human toxicity was assumed to occur mainly via fish and shellfish. In the effect factor, the average daily intake of fish and shellfish is considered for the exposure and then PNECs are derived from human Toxic Dose Low (TDLo), animal Lethal Dose Low (LDLo) and

Table 3
Removal rates (%) derived from analytical data of the four scenarios Scenario A: 3.33 $m^3\ h^{-1}$ and 0.83 $gH_2O_2\ L^{-1}$; Scenario B: 3.33 $m^3\ h^{-1}$ and 1.11 $gH_2O_2\ L^{-1}$; Scenario C: 5.00 $m^3\ h^{-1}$ and 1.11 $gH_2O_2\ L^{-1}$; Scenario D: 0.25 $m^3\ h^{-1}$ and 1.11 $gH_2O_2\ L^{-1}$.

Compound	Scenario A	Scenario B	Scenario C	Scenario D
Atenolol	88.3	89.4	35.0	89.1
Carbamazepine	96.4	93.9	47.4	94.4
Ciprofloxacin	96.2	95.1	52.7	93.1
Clarythromycin	85.6	83.4	47.2	84.8
Cyclophosphamide	77.0	71.2	31.4	70.2
Diclofenac	99.5	99.4	57.7	97.5
Erythromycin	0.0	0.0	0.0	0.0
Ifosfamide	0.0	0.0	0.0	0.0
Iodixanol	49.1	87.9	36.2	83.7
Iohexol	0.0	92.4	46.9	0.0
Lidocaine	91.4	81.9	38.9	86.5
Naproxen	6.3	85.5	0.0	0.0
Sulfamethoxazole	90.5	89.9	32.3	82.4

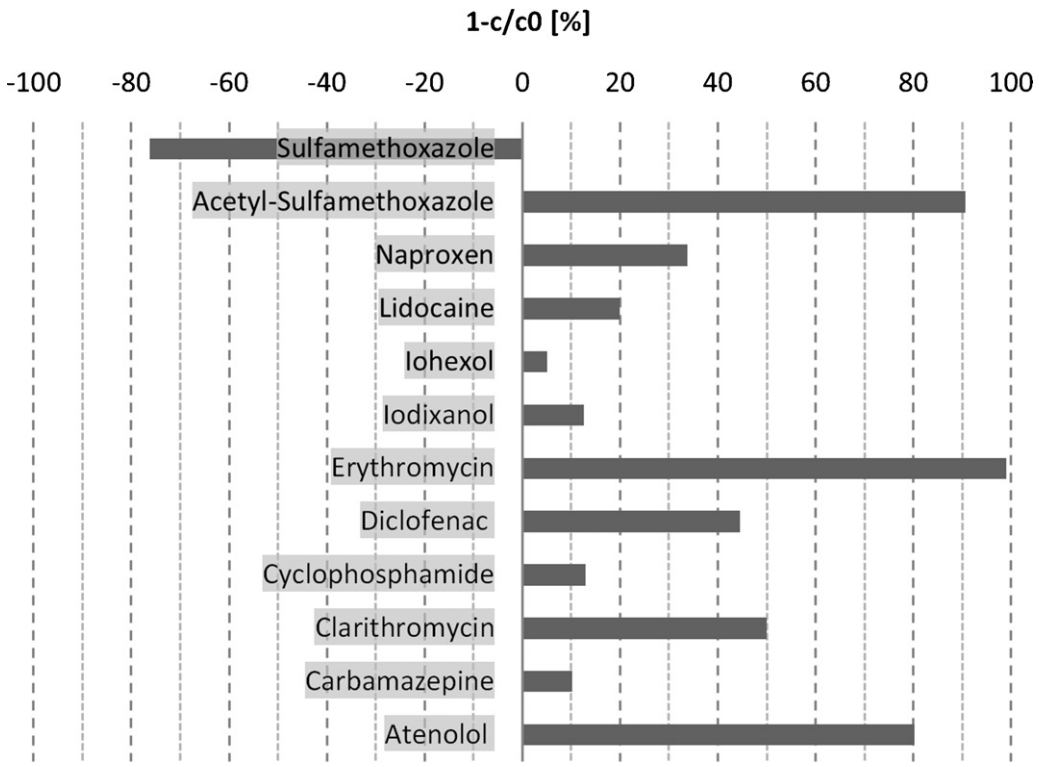

Fig. 1. Elimination rates ($1 - c/c_0$) of selected pharmaceuticals during MBR treatment (average values from 5 days composite samples).

half Lethal Dose low (LD50) [23] and obtained from the ChemID database [23].

3. Results and discussion

3.1. Efficiency of the biological treatment

The evaluation of the MBR performance revealed a very efficient degradation of organic matter (expressed as chemical oxygen demand COD) of about 93%, corresponding to an average effluent concentration of 27 mgCOD L^{-1}. The latter is considerable lower than STPs. With respect to nitrogen elimination, a removal rate of 70% was found. 56% of the total nitrogen effluent concentration (18 mgTN L^{-1}) accounted therefore for nitrate. A more in-depth study about the MBR efficiency has been published in Venditti et al. [13].

In the following text, the terms "removal", "elimination" and "degradation" of pharmaceuticals are used to describe the difference between the concentration of the parent compound in the influent and in the effluent of the treatment step. Any metabolites or transformation products that may occur during the treatment process are not considered within this study. During MBR treatment a wide removal range of the investigated pharmaceuticals could be observed (Fig. 1).

Several compounds, including X-ray media, showed low elimination efficiencies with the lowest value for Iohexol (5%) and Carbamazepine (10%) with an average influent concentration of 763.31 μg L^{-1} and 2.32 μg L^{-1} respectively. Taking into account the individual character (with respect to sludge and measurement inaccuracy) of previous investigations, the latter value is in agreement with the results of Joss et al. [24]. The enrichment of the antibiotic Sulfamethoxazole in the effluent which results in a negative elimination rate (−76%), can be explained considering that Sulfamethoxazole is excreted in an acetylated form which reverts to its mother compound during the biological treatment as observed elsewhere [25]. Ifosfamide was at a concentration below the limit of quantification (LOQ) in the hospital wastewater while Ciprofloxacin was not eliminated at all during the biological treatment.

3.2. Evaluation of UV scenarios based on the kinetic degradation model

The first investigations with the UV technique showed that a large amount of electrical energy is required if UV irradiation is applied in the absence of H_2O_2 as chemical oxidant. Without hydrogen peroxide dosage an overall elimination of about 86% of all investigated pharmaceuticals was found after an electrical energy input of 10 kWh m^{-3} wastewater treated with the medium pressure lamp (10 kW). With respect to the low pressure lamp (0.25 kW), an overall elimination of 65% was found after an electrical energy input of 6 kWh m^{-3}. Due to these extremely large values, further tests were always conducted in combination with H_2O_2 to boost the elimination process.

Good pharmaceutical elimination was found for a H_2O_2 dosage between 0.56 g L^{-1} and 1.11 g L^{-1}. An average elimination of Sulfamethoxazole, Clarithromycin and Lidocaine was found over 94% at the same MP power (5 kW) when adding 0.56 gH_2O_2 L^{-1}. Below this range, the removal efficiency decreased dramatically by 30%. A reasonable dosage of 1 gH_2O_2 L^{-1} in combination with MP UV technology has already been reported by Börgers et al. [26] for hospital wastewater. No significant difference could be discovered between a dosage of 0.56 g L^{-1} and 1.11 g L^{-1} as long as the electrical energy input was below 2 kWh m^{-3}. With increasing UV contact time (corresponding to a higher electrical energy input) the pharmaceutical elimination increases with higher hydrogen peroxide dosages, e.g. 47% of Carbamazepine was removed during the treatment with the 10 kW MP lamp using 2 kWh m^{-3} electrical energy input with 0.83 gH_2O_2 L^{-1} added, in comparison to 67% removed when 1.11 gH_2O_2 L^{-1} was applied.

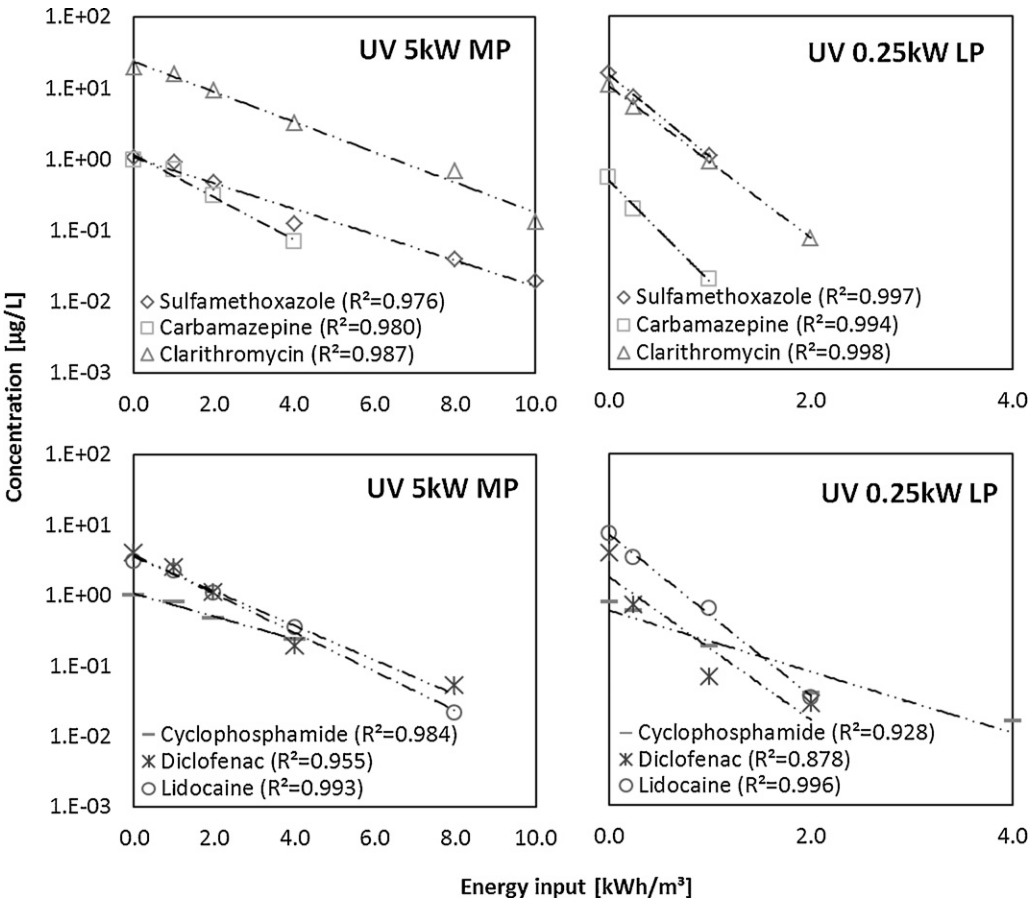

Fig. 2. Degradation kinetics of selected pharmaceuticals while UV treatment in combination with1.11 $gH_2O_2\ L^{-1}$ dosage.

To evaluate the efficiency of the medium pressure UV lamp, the influence of different lamp power levels (i.e. 2 kW, 5 kW and 10 kW) using a dosage of 1.11 $gH_2O_2\ L^{-1}$ were examined. Regarding the overall pharmaceutical elimination, best results were obtained when the medium pressure UV lamp was adjusted to 5 kW power.

However, the most interesting results were obtained with the LP UV lamp. The pharmaceutical degradation kinetics of both lamps, medium pressure (5 kW) and low pressure (0.25 kW) are shown in Fig. 2. It can be clearly observed that considerable less electrical energy is needed for the treatment with the LP UV lamp, e.g. with a specific electrical energy demand of 2 kWh m^{-3} the antibiotic substance clarithromycin is degraded from 20.14 $\mu g\ L^{-1}$ to 9.26 $\mu g\ L^{-1}$ (54% removal) while operating the MP UV lamp. In contrast, the elimination of clarithromycin from an MBR permeate concentration of 10.52–0.07 $\mu g\ L^{-1}$ (99% removal) was obtained applying the same electrical energy amount but using the low pressure UV lamp. Similar results were obtained for all other investigated pharmaceuticals.

These findings confirm the results from IJpelaar et al. [27]. The authors reported higher energy efficiencies for LP UV lamps in comparison to MP lamps. IJpelaar et al. [27] described a general 30–50% lower energy demand for LP UV lamps during the treatment of 23 different pharmaceuticals and pesticides. The specific electrical energy demand of the LP lamp is a promising result; compared to competitive oxidation treatments, e.g. ozonation. Haberkern et al. [28] estimates a specific energy need of $\leq$0.8 kWh m^{-3} for an oxidation process with ozone. Yet, ozonation demands more maintenance and operating efforts compared to UV treatment. Considering a full-scale realisation of the decentralised treatment of hospital wastewater by UV technology, a total specific energy need of 2.5 kWh m^{-3} is estimated as a sum of 1.4 kWh m^{-3} for the MBR treatment [29] and 1.1 kWh m^{-3} for LP UV treatment as AOP (according to the outcome of this study). As a comparison, Haberkern et al. [28] reported a mean specific energy demand of around 0.8 kWh m^{-3} for STPs with a capacity $\leq$1000 population equivalents.

It was further shown that 254 nm is an excellent wavelength for H_2O_2 irradiation, because it is the best compromise between low background absorbance of the investigated water and high H_2O_2 absorbance resulting in an efficient OH-radical formation. The LP lamp is operating much more efficiently since around 90% of its UVC irradiation is emitted at 254 nm where the MP lamps has just for 5–10% of the total emission [27]. The good removal results with the LP UV treatment in AOP operation lead to the assumption that the pharmaceutical degradation process is more affected by chemical oxidation processes, i.e. the dosing of H_2O_2 and the subsequent oxidation through OH radicals than to direct photolysis.

The individual pharmaceutical degradation kinetic follows a pseudo-first order approximation along the UV contact time, i.e. the applied power to treat 1 m^3 of water. To model the overall elimination rate of each UV setup the exponential distribution of each pharmaceutical has been determined by curve fitting where the regression coefficient (square of the Pearson Product-Moment Correlation Coefficient) resulted from each scenario was in a range between 0.72 and 0.97. Subsequently, the median (i.e. the global) degradation curve to supply the theoretical energy demand was calculated (see Fig. 3).

According to the modelled global degradation kinetics, the results of the UV test scenarios could easily be compared. The first diagram clearly shows that the energy need for the UV LP lamp is

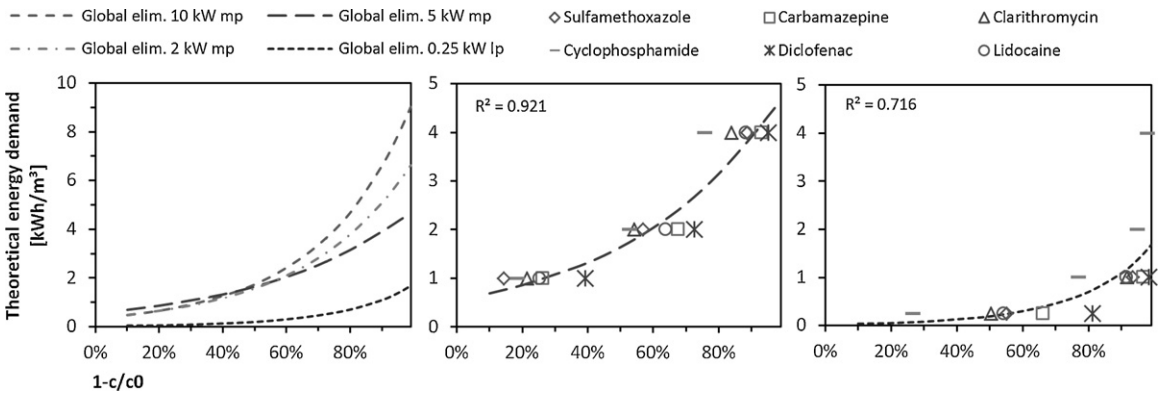

Fig. 3. Modelled overall pharmaceutical degradation kinetics of different UV operation scenarios (left: comparison of different UV lamp and power tests in combination with a H_2O_2 dosage of 1.11 g L^{-1}; middle: overall degradation model of 5 kW MP lamp with 1.11 gH_2O_2 L^{-1} dosage in comparison to measured values; righ: overall degradation model of 0.25 kW LP lamp with 1.11 gH_2O_2 L^{-1} dosage in comparison to measured values).

much lower than for the UV MP lamp while gaining the same treatment effect. For both scenarios 5 kW UV MP lamp and 0.25 kW UV LP lamp the modelled overall degradation kinetic of the pharmaceuticals is compared to the laboratory measurements in Fig. 3. A satisfying degradation prediction can be found for both scenarios.

Furthermore, the TOC has been analysed during all tests. With respect to the investigations of the MP lamp a TOC elimination between 5% and 32% was reached when 4 kWh m^{-3} of electrical energy were used. No TOC elimination suggests that a full mineralisation of pharmaceuticals is not taken place rather cleavage of organic compounds into smaller molecules. At full-scale, sand filtration as post advanced treatment could therefore serve as suitable barrier for possible harmful transformation products as proposed in Hollender et al. [10].

3.3. Evaluation of UV scenarios based on LCA methodology

The presented holistic results and discussion give a more complete picture for the evaluation of the UV technology. In a LCA not only pharmaceutical removal and energy consumption are considered but infrastructure and natural resources used as well. The benefit to the environment due to the use of this technology is here evaluated by considering the net impact from the difference between the generated and avoided impacts.

At first glance, the positive net impact in Fig. 4 may address the conclusion that UV technology is generally not a suitable choice from an environmental prospective. Yet, the net impact of all scenarios is considered overestimated due to the relative small selection of pharmaceuticals (only 14) taken into account in this study. Additionally, the broad range of organic micropollutants besides pharmaceuticals (e.g. pesticides, plasticisers and hormones) present at centralised WWTPs and their potential removal by UV AOP would decrease the net impact of these technologies even further. A similar phenomenon was found in Høibye et al. [11] and Wenzel et al. [12]. These authors report a significant influence from heavy metals on the LCA results since they are from an ecotoxicological perspective highly relevant. However, in a full-scale application and with an installation of a sand filtration unit there would be a strongly decrease in the net impact of the UV AOP technology.

The comparison between scenarios A and B shows that the use of H_2O_2 has a significant influence on the generated environmental impact due to its production process. The pharmaceutical removal with 0.83 gH_2O_2 L^{-1} and 1.11 gH_2O_2 L^{-1} is almost similar for all pharmaceuticals except for Naproxen and X-ray contrast media Iohexol and Iodixanol. For the last two compounds, no ecotoxicological information could be found in the literature. Consequently, the PNEC was estimated by the ECOSAR model with a chronic toxicity effect at 39 μg L^{-1} for Iohexol and 106 μg L^{-1} for Iodixanol.

Electricity consumption is the main contributor to the generated impacts (it accounts for around two thirds of the total). The contribution of the infrastructures is minor (0.6%) because of the long lifetime of a UV lamp.

In scenarios C and D, the operational conditions (applied electrical energy and H_2O_2 dosage) are identical but the flow rates (volume of treated water per time) are different. Therefore, the generated impacts from the MP and the LP UV lamp operation can be directly compared. The high power of the MP UV devices allows the processing of much higher volumes compared to LP UV lamps, even if the removal efficiency of the former is significant lower as

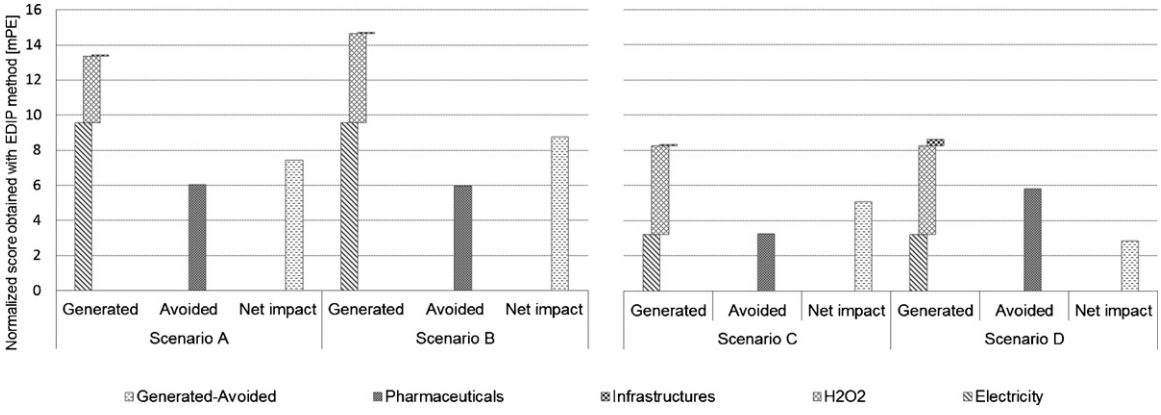

Fig. 4. LCA results for scenario A, B, C and D.

previously stated. This is the rationale of the higher contribution of the LP UV lamp infrastructure which increases by a factor of 7 resulting in 4.1% of the total generated impact. With respect to the infrastructure (i.e. the whole UV reactor) impact, stainless steel material, mercury and silica glass contribute to the total at ratios of 81%, 5% and 4% respectively. In contrast, the higher removal efficiency of the LP UV lamps (e.g. Diclofenac elimination increases by 40%) results in a higher avoided environmental impact (about 80%) compared to MP UV technology. Accordingly, the net impact of Scenario D is 45% lower than the single score of Scenario C (2.8 mPE and 5.1 mPE respectively).

Despite the LCA analysis indicating scenario D (LP UV lamp with 1.11 $gH_2O_2\,L^{-1}$ dosage) as the favourite treatment option, the lower investment and maintenance costs due to the high power of the MP lamp (max. 10 kW) makes Scenario C still attractive. It is therefore worth to point out the need for a case-by-case assessment containing economic aspects.

4. Conclusion

The MBR technology was shown to be an adequate pre-treatment (in terms of the low organic carbon content and the elimination of particulates) before an energy intensive advanced technique is applied. UV AOP technology demonstrated to be suitable to eliminate most persistent pharmaceuticals.

The cost-benefit-analysis for the UV technology has revealed 70% higher energy efficiency when using the LP UV lamp compared to the MP UV lamp. The best results for both configurations were gained as AOP operation when dosing 1.11 $g\,L^{-1}$ H_2O_2.

Subsequently, life cycle assessment was applied as a more complete and consensual methodology for a decision making process. Here, AOP with medium pressure UV lamp has shown some potential under case-specific conditions. For simplicity's sake, its disadvantage compared to the low pressure UV device can be expressed by a factor of 4 regarding the "conventional" cost-benefit analysis and this factor decreases to 2 if the environmental aspects are taken into account.

The strength of the LCA methodology to compare and to optimise treatment technologies from an environmental perspective was demonstrated with in-house field data. Also some weakness (calculated positive net impact, etc.) in interpretation of this holistic approach could be explained considering limited data records. This can particularly be the case if third party information is used as it is often practice.

Integrated results reported in the present study can provide important in-sights into the usefulness of UV irradiation technology when applied to the treatment of micropollutants. The assessment approach used in this work can be adapted for specific case studies and extended to a full scale plant including economic aspects. Moreover, for future investigations it is recommended to consider the impact of further relevant tracepollutants such as heavy metals and transformation products from a more comprehensive perspective beyond this technology.

Acknowledgements

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Is it better to remove pharmaceuticals in decentralized or conventional wastewater treatment plants? A life cycle assessment comparison

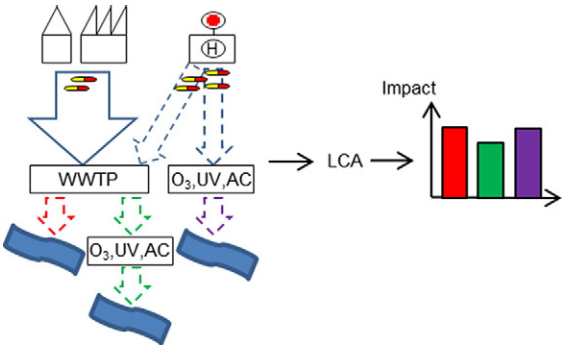
Elorri Igos, Enrico Benetto *, Silvia Venditti, Christian Kohler, Alex Cornelissen, Ruth Moeller, Arno Biwer

Public Research Centre Henri Tudor (CRPHT)/Resource Centre for Environmental Technologies (CRTE) — 66, rue de Luxembourg — P.B. 144, L-4002, Esch-sur-Alzette, Luxembourg

HIGHLIGHTS

- Three post-treatments are investigated in centralized and decentralized WWTPs.
- Generated and avoided environmental impacts evaluated using LCA.
- Pharmaceuticals were found to have a comparatively minor contribution.
- Additional post-treatment does not provide significant environmental improvement.
- Uncertainties on toxicity assessment and limitations of LCA invoke caution.

GRAPHICAL ABSTRACT



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ABSTRACT

After ingestion, pharmaceuticals are excreted unchanged or metabolized. They subsequently arrive in conventional wastewater treatment plants and are then released into the environment, often without undergoing any degradation. Conventional treatment plants can be upgraded with post treatment, alternatively the removal of pharmaceuticals could be achieved directly at point sources. In the European project PILLS, several solutions for decentralized treatment of pharmaceuticals at hospitals were investigated at both pilot plant and full scale, and were then compared to conventional and upgraded centralized treatment plants using Life Cycle Assessment (LCA). Within the scope of the study, pharmaceuticals were found to have a comparatively minor environmental impact. As a consequence, an additional post treatment does not provide significant benefits. In the comparison of post treatment technologies, ozonation and activated carbon performed better than UV. These results suffer however from high uncertainties due to the assessment models of the toxicity of pharmaceuticals in LCA. Our results should therefore be interpreted with caution. LCA is a holistic approach and does not cover effects or issues on a local level, which may be highly relevant. We should therefore apply the precautionary ALARA principle (As Low As Reasonably Achievable) and not conclude that the effect of pharmaceuticals is negligible in the environment.

1. Introduction

Nowadays, our medical care system provides a large amount of pharmaceuticals to the population. After ingestion, the human body releases a certain amount of unchanged as well as metabolized pharmaceuticals via excretion of urine or feces to the public sewer system. However, existing Waste Water Treatment Plants (WWTPs) are not designed to remove this pollution and most of the pharmaceuticals or their metabolites are released to the environment without undergoing any degradation (Ternes and Joss, 2006; Vieno et al., 2007). To alleviate this problem, conventional treatment plants could be upgraded with technologies specifically developed to remove these compounds. Another solution could involve the treatment of pharmaceuticals on highly concentrated

* Corresponding author.
E-mail address: enrico.benetto@tudor.lu (E. Benetto).

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wastewater at point sources (in particular hospitals). This would have the additional positive effect of reducing pollutant emissions from combined sewer overflows during heavy rain events. The European Interreg IVB project PILLS investigated this decentralized treatment approach, through the testing of several technological solutions which removed pharmaceuticals at hospitals, both at pilot and full scale. Strengths and weaknesses of centralized and decentralized solutions were identified based on environmental, economic, technical and sanitary criteria. The release of pharmaceuticals to the environment leads to a number of negative effects such as anomalies in the reproduction system of fish due to hormones (Fent et al., 2006; Jolibois and Guerbet, 2006), which are already evaluated and discussed in Environmental Risk Assessment (ERA) studies (Escher et al., 2011; Gros et al., 2010; Kratz, 2008). Specific treatment processes and technological solutions allow avoiding these effects, but generate additional environmental impacts, because of the consumption of reagents and energy. Indeed, the appraisal of the environmental performances of treatment solutions is not trivial. Life Cycle Assessment (LCA) is a recognized methodology to evaluate the potential environmental impacts of a product or a process throughout its lifecycle, from cradle to grave. The methodology has been standardized by ISO 14040-44 (ISO-International Organisation For Standardisation, 2006). A few LCA studies (Hospido et al., 2010; Larsen et al., 2010; Muñoz et al., 2008) have assessed the generated and avoided impacts involved in pharmaceutical treatment. In the FP6 project NEPTUNE (Larsen et al., 2010) post-treatment of municipal wastewater to remove selected micropollutants and pathogens, as well as advanced nutrient removal control methods and sludge inertisation processes were assessed. The existing treatment technology (i.e. the reference scenario) considered is a municipal wastewater treatment plant with primary and secondary treatment only, without any post-treatment. The reference scenario for sludge treatment was incineration. Depending on the characterisation approach it was found that the effect of pharmaceuticals can vary within three orders of magnitude (Larsen et al., 2010). The contribution of the pharmaceutical removal to the avoided impacts was found to be minimal when compared to nutrient and heavy metal removal. The negligible impact of pharmaceuticals was also observed in the NEPTUNE project during the evaluation of the total ecotoxicity impact of Europe in 2004 for the calculation of normalization factors. Hospido et al. (2010) evaluated agricultural applications of sewage sludge, and quantified the potential impacts of emerging pollutants, including pharmaceuticals. Again, the contribution of pharmaceuticals was found to be minimal. In contrast, Muñoz et al. (2008) compared five wastewater treatment scenarios, focused on the improvement of water reuse, including the assessment of pharmaceuticals. In this particular study, the contribution of pharmaceuticals (in particular the antibiotic Ciprofloxacin) was found to be predominant. These studies show quite divergent conclusions. In the PILLS project, the comparison of treatment scenarios with respect to environmental impacts was based on LCA of which the results and conclusions are presented in this paper. Particular attention is given to the discussion of the limitations of the LCA study with respect to the initial decision making context, i.e. the choice between centralized and decentralized treatment plants. The scenarios are assessed on the basis of the net impacts calculated from the generated (due to electricity and chemical consumptions, transports or direct emissions of the plant) and the avoided (assessing the benefit of pollutant elimination) impacts. Fig. 1 illustrates the methodology used in this study along with the different LCA steps, which are detailed in Section 2. The comparison of scenarios focuses first on the full scale policy, i.e. the relevance of implementing a decentralized WWTP at the hospital. The choice of post treatment to improve the elimination rates of pharmaceuticals is considered in a second step.

2. Materials and methods

2.1. Goal and scope definition

A centralized WWTP receiving all the wastewater produced in a given catchment normally includes a conventional treatment chain (scenario CC) or, at present in rare cases, may have been upgraded with an ozonation step (scenario UC). In a decentralized plant (at a hospital) biological treatment using a Membrane Biological Reactor (MBR) is followed by three options for post treatment: ozonation (O3), activated carbon adsorption (AC) or ultraviolet radiation (UV). The decentralized plant treats only the wastewater output from the hospital, and the remaining wastewater produced in the catchment is still treated at the conventional centralized plant. The

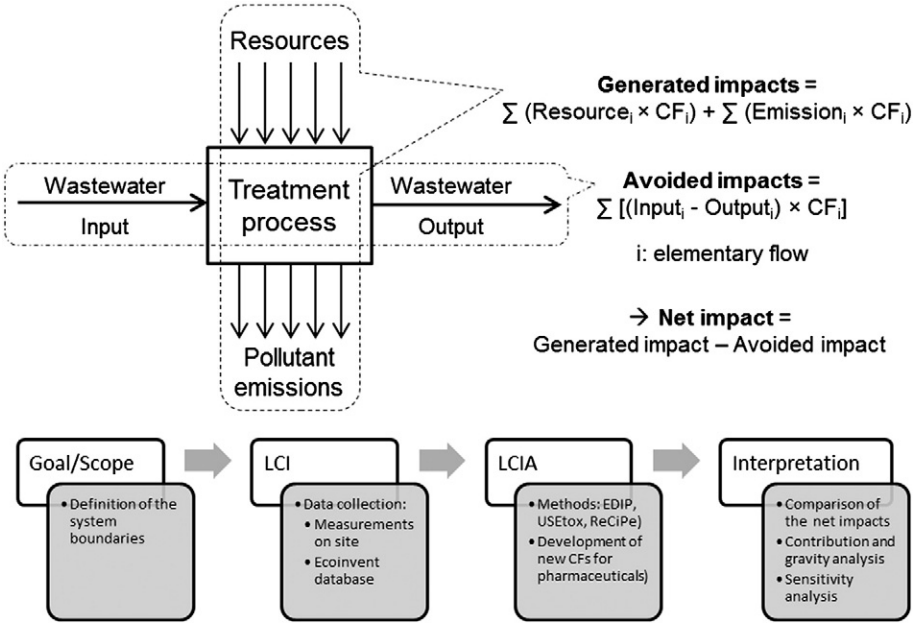

Fig. 1. Methodology used to assess the potential environmental impacts of a process, based on the LCA phases as defined in the ISO 14040-44 standards. The generated impacts are due to the consumption of natural resources and to the pollutant emissions. The avoided impacts correspond to the amount of pollutants removed by the treatment process. The amount of each elementary flow i is multiplied by a Characterisation Factor (CF_i) representing its impact per unit of mass. The four steps defined by the ISO 14040-44 standards are briefly detailed: Goal and scope definition, Life Cycle Inventory (LCI), Life Cycle Impact Assessment (LCIA) and results interpretation.

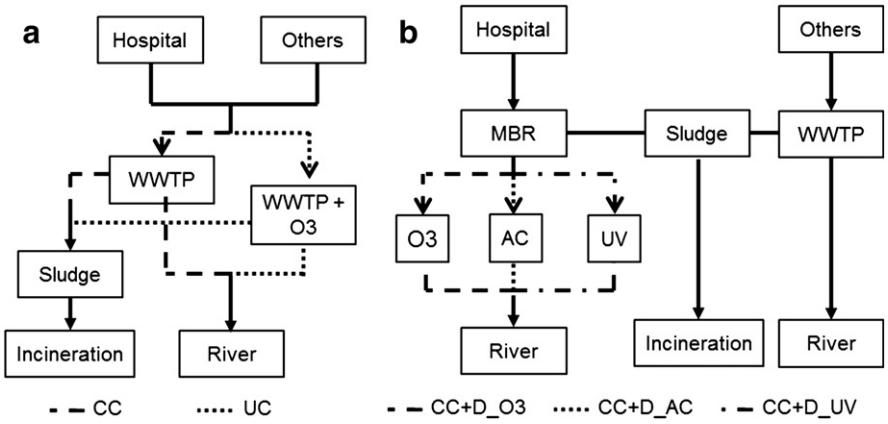

Fig. 2. Flow diagrams for a) centralized scenarios (CC or UC) and b) decentralized scenarios (CC + D_O3, CC + D_AC or CC + D_UV). In a), the wastewater treatment plant (WWTP) can include (scenario UC) or not (scenario CC) a post-treatment (ozonation). In b), a decentralized treatment is carried out at the hospital, including a MBR (Membrane Biological Reactor) and an advanced treatment (ozonation, activated carbon adsorption or UV radiation). The format of the dash lines corresponds to the different scenarios.

corresponding scenarios are therefore CC + D_O3, CC + D_AC and CC + D_UV (D for decentralized).

The primary function of all wastewater treatment scenarios is to achieve a given quality standard with individual pollutant thresholds, in the treated wastewater effluent. The scenarios are compared according to a common functional unit, i.e. the treatment of 1 m^3 of wastewater. For the same composition of wastewater, the volume ratio between the effluent from the hospital and from other sources is defined, as well as the virtual composition of wastewater without considering the hospital emissions, regarding the scenarios CC + D_O3, CC + D_AC and CC + D_UV (see Fig. 2). Based on the average bed occupancy rate in the hospital, on long-term flow measurements and on the wastewater volume treated by the local WWTP during dry weather, in Luxembourg, the percentage of wastewater flow from the hospital has been estimated to be 0.86% (v/v). This value has been analyzed further in a sensitivity analysis, detailed later.

When comparing the post treatments used in the decentralized plant (scenarios D_O3, D_AC and D_UV), the functional unit is the treatment of 1 m^3 of hospital wastewater, so the wastewater from households is no longer included. Sludge management is considered in all scenarios, since it represents a key issue for WWTPs. In this study, sludge incineration (in agreement with the reference scenario in the Neptune project) has been assumed. Only the operational phase of the scenarios is considered and the construction and demolition phases are not included and neither is infrastructure (tanks, pumps, etc.). Previous studies reported a minor influence of infrastructures in a WWTP lifecycle (Doka, 2007; Lassaux et al., 2007). However, the construction of a new sewer building is certainly not negligible with a contribution of up to 8% of the overall impact. Here, it has been assumed that the effects of (additional) infrastructure are comparatively small. This is especially true when comparing advanced technologies. This issue is discussed further in this paper.

These scenarios have been modeled using the LCA software Umberto 5.6® (Umberto, 2012).

2.2. Life Cycle Inventory (LCI)

2.2.1. Operational data

For the decentralized treatment scenarios, foreground inventory data were collected at pilot and full scale plants of the PILLS partners, i.e. CRP Henri Tudor (LU), the Emschergenossenschaft (DE), Waterschap Groot Salland (NL) and EAWAG (CH), treating wastewater from their respective local hospital with different advanced technologies (Table 1). It was found that electricity consumption of the MBR can vary by a factor 2 depending on the level of optimization. During ozonation, electricity consumption for the on-site ozone generation from air varies significantly with respect to the plant. Therefore minimum and maximum values were considered in the inventory. The same applies for the

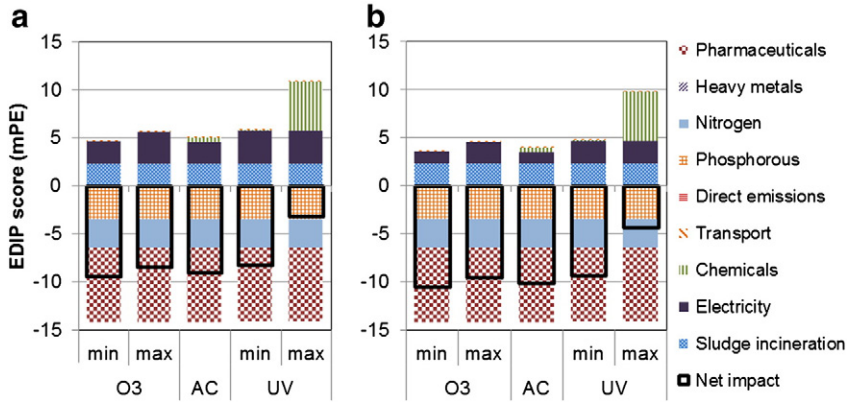

Fig. 3. Normalized EDIP results for decentralized treatment considering standard (a) and optimized (b) electricity consumption in the MBR. The generated impacts (from sludge incineration, electricity, chemicals, transport and direct emissions) and the avoided impacts (thanks to the removal of phosphorous, nitrogen, heavy metals and pharmaceuticals) are assessed for the decentralized treatment alternatives using the EDIP method. The difference between generated and the avoided impact sum leads to the net impact, represented by a thick black line. The score is expressed in mPE (milli Person Equivalent).

Table 1
Main operational data considered in the treatment scenarios.

Scenario	CC	UC (ozonation)	D_MBR	D_O3	D_AC	D_UV
Electricity (kWh/m^3)	0.34	0.06	0.9–1.8	0.1–0.9	Negligible	1
Chemicals (g/m^3)	Coagulant, flocculant and auxiliary for sludge treatment	O_2: 50	NaClO: 4.5	O_3: 5	GAC: 58.6	H_2O_2: 5–1100
Transport (km)	Chemicals: 20 to 600	O_2: 100	Sludge: 20	–	–	–
Sludge (gDM/m^3)	250	–	80	–	–	–

consumption of hydrogen peroxide during UV treatment. Annual consumption of granulated activated carbon (GAC) is based on the number of regeneration cycles and the relative mass loss per regeneration (for more details refer to SI 1). For the scenario CC, foreground inventory data were calculated using the Ecoinvent tool considering a given input composition (Doka, 2007). This calculation is based on average data from conventional WWTPs in Switzerland. For the scenario UC, specific data for the ozonation unit was available for two existing plants located in Bad Sassendorf (DE) and Regensdorf (Abegglen et al., 2009) (CH). The German data was used by default and then compared to the Swiss plant in a sensitivity analysis. In both of these plants ozone is generated from liquid oxygen. Background data (e.g. regarding the production of electricity, reactants, ..) for all the scenarios was extracted from the Ecoinvent 2.2 database (Ecoinvent, 2012).

2.2.2. Removal of pollutants

As the volume ratio for wastewater was calculated based on Luxembourgish conditions, the influent wastewater compositions of the local WWTP and pilot plant were also used (see SI 2). Organic matter, such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Dissolved Organic Carbon (DOC) is not characterized in Life Cycle Impact Assessment (LCIA) methods and its removal is therefore not included in the inventory. Total phosphorous and total nitrogen are relevant for the assessment since they are regulated with limit values by European legislation (Council Directive, 1991) and their measurement encompasses related compounds (phosphate, nitrate, nitrite, etc.). Concerning heavy metals and nutrients eliminated in the decentralized scenario, we only consider the removal during the MBR step. Concentrations after advanced treatment were not measured. It was assumed that no significant supplementary removal took place.

Ten pharmaceuticals were focused upon, because of their substantial concentration in the influent wastewater and their significant removal in the advanced treatment. Sufamethoxazole is the mother compound of N4-acetyl-sulfamethoxazole and is reformed during the biological treatment (Clara et al., 2005; Göbel et al., 2005). Consequently, a negative removal was found in the pilot plant MBR (Table 2). However, this phenomenon was not found at full scale. It is assumed that biological processes within the sewer system were responsible for the relatively low N4-acetyl-sulfamethoxazole concentration in the effluent of the WWTP. The consideration of the sewer system as bioreactor has been investigated and discussed by other authors (Ahnert et al., 2005; Hvitved-Jacobsen et al., 2002).

Table 2
Removal rates of pharmaceuticals according to each treatment.

Pharmaceuticals	CC	UC	D_MBR	D_O3	D_UV	D_AC
Atenolol	48%	98%	80%	97%	88%	71%
Carbamazepine	−33%	99%	10%	99%	96%	96%
Ciprofloxacin	65%	91%	0%	91%	96%	99%
Clarithromycin	−20%	97%	50%	97%	86%	76%
Cyclophosphamide	−1%	58%	13%	58%	77%	94%
Diclofenac	7%	99%	44%	99%	99%	97%
Lidocaine	−21%	100%	20%	100%	91%	93%
Paracetamol	98%	100%	99%	83%	48%	64%
Sulfamethoxazole	53%	94%	−76%	88%	91%	93%
Trimethoprim	9%	97%	31%	97%	38%	96%

The concentration of four of the pharmaceuticals appears to have increased after CC treatment. This is presumably due to experimental errors and uncertainties and in accordance with previous literature, the removal was assumed to be equal to zero (Clara et al., 2004; Giger et al., 2003; Joss et al., 2005).

Sewer overflows due to heavy rain events were not measured during the PILLS project and depend on the quality of the infrastructures and of the local meteorological conditions. Based on the experience of the project partners, sewer overflow was estimated at 5% of the water volume in the sewer system. The effluent leaving the sewer system because of an overflow event is not treated in a centralized WWTP and the resulting pollution has been added to this scenario. In the decentralized treatment approach, the pharmaceutical contribution from the hospital would have already been removed.

2.3. Life Cycle Impact Assessment (LCIA)

2.3.1. EDIP97 and EDIP2003

First, the EDIP2003 methodology, used in Neptune, was tested. Fourteen endpoint impact categories (eutrophication, climate change, ecotoxicity, etc.) were evaluated with respect to a reference unit (e.g. kg P eq, kg CO2 eq, etc.) and further normalized in order to obtain a single score impact (Potting and Hauschild, 2005). The single score is expressed in Person-Equivalent (PE). The normalization factor for each category is calculated as the ratio between the population of a reference area and period (Europe, 2004 in the specific case) and the total category impact generated (Laurent et al., 2011). Pharmaceuticals were not added to the overall inventory used to derive normalization factors since results from Neptune showed that their contribution is negligible. The avoided impact of pharmaceuticals, regarding freshwater ecotoxicity (chronic and acute effect) and human toxicity via surface water, is specifically assessed using EDIP97 (Hauschild and Wenzel, 1998). According to the EDIP model, if the pharmaceutical is volatile (Henry's law constant higher than 10^{-3} atm.m^3/mol), fate factors in water and in soil have to be calculated. Given the very low Henry's law constant of the considered pharmaceuticals (up to 10^{-10} atm.m^3/mol), no fate factor to soil has been considered. Toxicity is defined as the inverse of the PNEC (Predicted No Effect Concentration). The resulting LCIA characterisation factor (CF) represents the volume required to dilute the mass of pollutant down to a level of no observed effect (expressed in m^3/kg). The rough assessment based on PNEC is further refined by considering the persistence in the environment (depending on its biodegradability), the bioaccumulation and the quality of data. Concerning the persistence in the environment, only paracetamol is assumed to be biodegradable and therefore the CF is divided by 2. An Assessment Factor (AF) is applied to account for data quality. For acute ecotoxicity, PNEC is derived from the lowest EC_{50} (median Effect Concentration), corresponding to the most sensitive species. This endpoint value is multiplied by AF = 10 if it comes from measurements on three trophic levels or by AF = 100 in the case of less representative species or predicted value from Structure Activity Relation (SAR). For chronic ecotoxicity, PNEC is calculated from literature data: NOEC (No Observed Effect Concentration, AF = 10 or 100 depending on the representativeness), LOEC (Lowest Observed Effect Concentration, AF = 20 or 200) or EC_{50} (AF = 100 or 1000). Predicted values can also be used: the geometric mean of NOEC and LOEC (design as chronic value ChV, AF = 100) or the EC_{50} (AF = 1000). For human toxicity, whenever the log[Kow]

(partitioning coefficient octanol-water) is above 3, a bioaccumulation factor for the human body which is equal to 10^(log[Kow]-1) is applied. This is the case for clarithromycin and diclofenac. Given the assumption that human toxicity is mainly due to fish and shellfish ingestion, the average daily intake as set in EDIP97 is used. Finally, the PNEC is calculated using the human Toxic Dose Low (TDLo, AF = 100), the animal Lethal Dose Low (LDLo, AF = 50000) and the Lethal Dose causing death of 50% of group animals (LD50, AF = 100000).

From a conservative perspective, the highest CF obtained is retained for each pharmaceutical. This approach suffers however from several shortcomings. First, the use of AF can lead to overestimation. The high variability of toxicity values results in a broad range of possible CFs (six orders of magnitude can be observed between the lowest and the highest values): sensitivity analysis is therefore mandatory. Since AF is applied dependent on the quality of (eco)toxicity data, CFs derived on basis of the lowest AF are considered to be more reliable and realistic. For example, the AF is divided by 10 if the endpoint toxicity has been measured, and not derived from a predicting model. CFs of ecotoxity derived following this approach by Larsen et al. (2010) and Muñoz et al. (2008) are also studied in a sensitivity analysis in Section 3.1.

In order to check the consistency of the conclusions, an alternative LCIA approach has been developed by combining two state-of-art methods, ReCiPe and USEtox.

2.3.2. ReCiPe and USEtox

The USEtox model is based on scientific consensus on the toxicity assessment of pollutants, namely freshwater ecotoxicity and human toxicity with both carcinogenic and non-carcinogenic effects (Rosenbaum et al., 2008). The impact characterisation includes three steps: fate of the pollutant, exposure and effect. Fate is evaluated using a multimedia model, i.e. a matrix describing the mass of the substance in each environment compartment (water, soil, air), depending on its physical–chemical properties (molecular weight, Henry's law constant, vapor pressure, solubility, partitioning coefficient, degradation rate and bioaccumulation factor). The exposure factor is the fraction of a chemical in a model compartment, extrapolated from the K_{ow} constant. For human exposure, seven pathways are modeled: air inhalation, drinking water, exposed produce (above-ground leaf crops, including fruit and cereals), unexposed produce (below-ground root crops), meat, dairy products and fish. The freshwater ecotoxicity effect factor is equal to 0.5 divided by the corresponding HC50 (the Hazardous Concentration at which 50% of the species are exposed above their EC50). HC50 is the geometric mean of single species EC50s. Chronic values have priority and at least three trophic levels must be represented. If only acute values are available, a correction factor of 2 is applied. Literature EC50 values were available and used to calculate the effect factor of all pharmaceuticals except for cyclophosphamide, for which predicted EC50s were used. For human toxicity effects, ED50 (Effective Dose for human that causes a disease probability of 50%) is used instead of HC50. Surrogates for ED50 are based on NOAEL (No Observed Adverse Effect Level) or LOEAL (Lowest Observe Adverse Effect Level) using an extrapolation factor (9 from NOAEL to ED50 and 4 from LOAEL to NOAEL). In the case of pharmaceuticals, TDLo has been used as a surrogate for LOEAL, adding an extrapolation factor for differences in exposure duration whenever necessary (2 for subchronic to chronic, 5 for subacute to chronic). However, if available, animal tests with the corresponding allometric scaling factor are preferred since animal toxicity studies are likely to be more comprehensive than human studies on certain endpoints (usually pharmacodynamic or side-effects). Among the selected pharmaceuticals, carcinogenic properties have been found for cyclophosphamide (CPDB, 2012) and have been taken into account in the assessment.

In order to account for the impact categories other than toxicity, the ReCiPe method (Goedkoop et al., 2009) was combined with USEtox. Except for freshwater ecotoxicity and human toxicity, which are calculated by USEtox, ReCiPe covers all the other environmental effects, both generated impacts of the treatment scenarios and avoided impacts of nutrient and heavy metal removal. For a proper combination of the results from the two methods into a single score, normalization is needed and the same rationale that is used for EDIP was utilized. The reference year used by ReCiPe, i.e. Europe in 2000 (Sleeswijk et al., 2008) has been retained and normalization factors for USEtox were recalculated (for details refer to SI 3).

3. Results

3.1. EDIP97 and EDIP2003

In Fig. 3, alternative post treatments in decentralized plants are compared considering standard and optimized electricity consumption in the MBR. The removal of pharmaceuticals is the main contributor to the avoided impacts (54%) and is quite uniform among all post-treatments. Sludge incineration becomes significant only when the electricity consumption of the MBR is optimized. Even considering the lowest consumption of hydrogen peroxide, UV technology shows the highest net impact. Depending on the electricity consumption of ozonation, scenario D_O3 may be ranked better or worse than scenario D_AC. However, the difference between the two (circa 6%) is insufficient to state a clear preference.

In Fig. 4, policy scenarios are compared, including the best (optimized MBR and ozonation) and the worst (non-optimized MBR with UV) performing decentralized treatment alternatives. A significantly high avoided impact is observed, due to 90% total phosphorous removal. The removal rate of nutrients in the centralized WWTP is much higher than in the MBR. Similar results were found in the Neptune project. Contrary to Neptune, the avoided impacts of heavy metals elimination are negligible. This could be explained by the low concentration of heavy metals in the Luxembourgish wastewater keeping in mind that around 50% of the Luxembourgish WWTP catchment consists of a separated sewer system. Therefore, heavy metal input from surface run off during rain events is collected separately. Furthermore, the industrial impact on the wastewater quality may be lower than in the catchment of the WWTP considered in Neptune. Sixty percent of the generated impact is caused by direct emissions from the sludge digester. Based on the results in Fig. 4, the best policy decision might be to upgrade the centralized plant (scenario UC). The implementation of a decentralized plant would increase the net impact due to the higher generated impacts and lower phosphorous removal. The difference between the two scenarios is however minimal (<3%) and no clear conclusion can be drawn within the scope of the study.

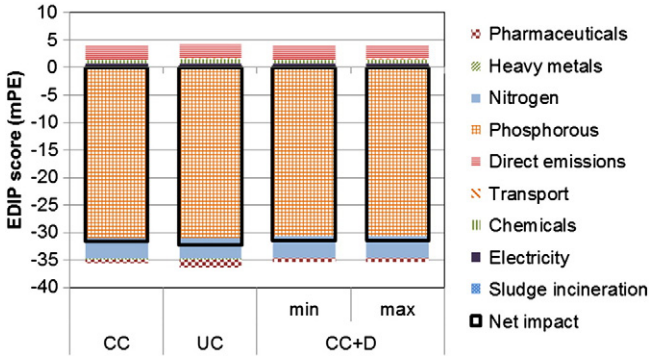

Fig. 4. Normalized EDIP results for policy scenarios. Generated, avoided and net impacts are evaluated using the EDIP method for the policy scenarios: CC (conventional centralized), UC (upgraded centralized) and CC + D (conventional plus a decentralized treatment at the hospital). The impact is expressed in mPE (milli Person Equivalent).

The CFs for ecotoxicity of pharmaceuticals were recalculated for each type of endpoint value: NOEC, LOEC, EC50 from Wikipharma (2012) literature but also ChV and EC50 from the ECOSAR model (USEPA, 2012). These five sets of values were used to reevaluate the environmental impact of the scenarios and compare them with the first results described above where the highest CF has been chosen for each pharmaceutical. Another point of comparison was added by choosing the CF with the lowest AF for each pharmaceutical in a less conservative approach. The most sensitive pharmaceuticals to the endpoint choice are atenolol, carbamazepine, ciprofloxacin, clarithromycin and paracetamol, for which high variability of the CF is observed or a large fraction is removed by the treatment. When comparing the net impact of alternative scenarios, the preference for scenario UC does not always hold depending on the endpoint chosen (see SI 4). By applying NOEC from literature and EC50 or chronic value from ECOSAR, the scenario UC has a slightly higher net impact than scenario CC (between 0.2 and 0.8%). In all other cases, UC is still the best solution but the differences are small (0.2% with the lowest AFs). The high variability in PNECs depending on the source data has already been discussed (Larsen and Hauschild, 2007) and it is apparent when comparing the CFs for pharmaceuticals used in Neptune (Larsen et al., 2010) and in Muñoz et al. (2008).

3.2. ReCiPe and USEtox

Fig. 5 compares the decentralized treatment alternatives. Phosphorous has still the larger contribution to avoided impacts and the contribution of pharmaceuticals is negligible. The results confirm the trend shown by EDIP. The low environmental impact of pharmaceuticals using ReCiPe + USEtox is mainly due to the normalization of ecotoxicity results. USEtox characterizes toxic emissions to soil whereas these are not included in EDIP. As these emissions largely dominate the USEtox result, it is apparent that the total ecotoxicity impact of Europe 2000 is much higher than in EDIP, and so is the normalization factor representing the impact per person equivalent. As a result, the normalized impact using ReCiPe + USEtox is much lower than in the case of EDIP.

In the comparison of policy scenarios (Fig. 6), despite the fact that the avoided impact of pharmaceuticals in scenario UC is higher than in the other scenarios, the magnitude relative to the other substances is so low that it does not affect the net impact. As a result, scenario UC shows the highest net impact. The current situation (scenario CC) appears to be the best solution but, again, the difference between the scenarios is too small to state any definitive preference.

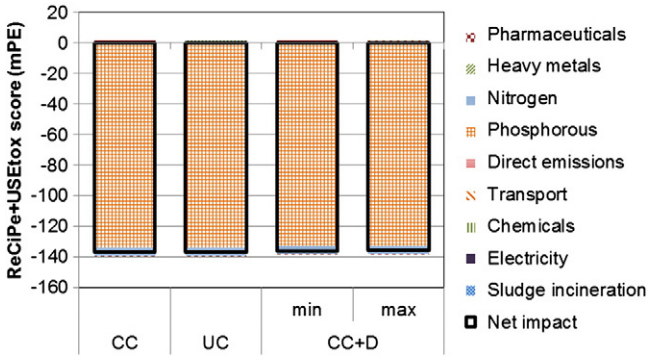

Fig. 6. Normalized ReCiPe + USEtox results for policy scenarios. Generated, avoided and net impacts are evaluated with the combination of ReCiPe and USEtox for the policy scenarios: CC (conventional centralized), UC (upgraded centralized) and CC + D (conventional plus a decentralized treatment at the hospital). The impact is expressed in mPE (milli Person Equivalent).

3.3. Sensitivity analysis

3.3.1. Pharmaceutical removal

Several sets of data were available for each treatment step from the PILLS project partners (McArdell et al., 2011; Mulder et al., 2012) or from other literature studies (Abegglen et al., 2009; Miège et al., 2009): three sets for scenario CC, three for the MBR operation, three for ozonation, two for UV and one for activated carbon. The scenario UC is almost unaffected by variability as only one unit operation, ozonation, participates to pharmaceutical removal and the operational data from the partners involved are quite similar. In contrast, the biological treatment in CC is affected by significant variability. The impact on the overall results, however, is small (see SI3). The maximal variation of net impact as compared to the previous results is lower than 0.5% using EDIP and 0.001% using ReCiPe + USEtox, as the impact of pharmaceuticals is very low.

3.3.2. Operational data of scenario UC

The two sources of operational data are in Germany (Bad Sassendorf) and in Switzerland (Regensdorf). The Swiss plant shows a lower electricity and oxygen consumption and this is reflected in the impact results (−3.3% with EDIP and −6.1% with ReCiPe + USEtox). The ranking of policy scenarios does not change (see SI 5). Hypothetical marginal values have been tested in order to identify the breakthrough points, i.e. where the ranking of scenarios changes. Using the EDIP method, higher values of operational data would worsen the performance of the UC scenario, whereas using ReCiPe + USEtox lower values would be the opposite. Oxygen consumption was

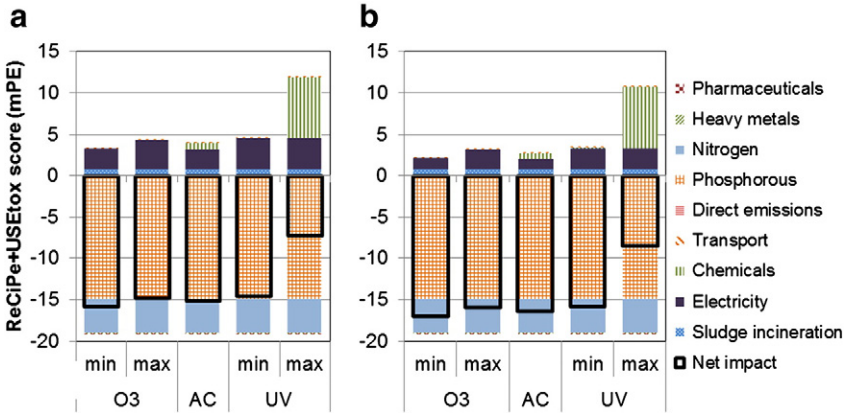

Fig. 5. Normalized ReCiPe + USEtox results for decentralized treatment considering standard (a) and optimized (b) electricity consumption in the MBR. Generated, avoided and net impacts are evaluated for the decentralized treatment alternatives with the combination of ReCiPe and USEtox. The score is expressed in mPE (milli Person Equivalent).

varied together with electricity consumption and transport use, which are correlated parameters. The breakthrough values obtained are lower or higher of one order of magnitude as compared to measured data and seem to be unrealistic (more detailed discussion is provided in SI 5).

3.3.3. Wastewater volume ratio between hospitals and other sources

Standard results were calculated for Luxembourg's conditions (0.86% of hospital wastewater, assuming 6.1 beds per 1000 inhabitants). For the Limoges area (France), a ratio of 14.1 beds per 1000 inhabitants would apply, leading to 2% of the wastewater volume coming from the hospital. Whereas for the Swiss conditions the number of beds per 1000 inhabitants is between 5 and 50, leading to a volume percentage from the hospital of between 0.7% and 7%. When calculating the virtual composition of wastewater without the hospital effluent, a few pharmaceutical concentrations become negative starting from 20 beds per 1000 inhabitants; because of an excessive amount of pharmaceuticals coming from the hospital (see SI 6). As a result, only five alternative ratios were considered in the sensitivity analysis: 5, 10 and 15 beds per 1000 inhabitants for Switzerland, 6.1 for Luxembourg and 14.1 for France. In the sensitivity analysis, the ranking of scenarios does not change. It is observed that the higher the wastewater volume percentage from the hospital, the higher the net impact of the decentralized scenarios. The reason is the significant increase of generated impacts compared to the negligible benefit in terms of avoided pharmaceutical impact.

4. Discussion

Based on the LCIA results, the negligible impact of pharmaceuticals does not favor an additional post-treatment, neither in a centralized nor in a decentralized WWTP. The post-treatments generate significant additional impacts (related to energy and chemical consumption), for a relatively poor gain. If a decentralized treatment is implemented at a hospital, LCA gives a preference to ozonation or activated carbon treatment as compared to UV.

This assessment, however, suffers from limitations and uncertainties. With regards to the LCI, a high variability on operational data, especially on the consumption of electricity and chemicals, was observed. As a result, the ranking of the technologies and in some cases also the scenarios, could change depending on the specific geographical context of the application. Sewer system adaptations have not been included and their construction would increase the impact of the decentralized scenarios. However, even with an increase of 10% on the generated impacts (a contribution of 8% was reported by Lassaux et al., 2007), the conclusions do not change. Finally, considering heavy metal and nutrient removal during post-treatment could decrease the net impacts of the decentralized scenarios and affect the final results.

With regards to the assessment of toxicity of pharmaceuticals in LCIA, several levels of uncertainty are observed. A first level of uncertainty is in the toxicity tests. The measured toxicity value is usually related to a high substance concentration during the tests. Long-term low-level exposure acting on the physiological control systems (central nervous system, hormones, reproductive system, immune system and genes) is often addressed only to a limited extent. Certain effects, especially relevant for pharmaceuticals, are barely reflected. For instance, the resistance of bacteria to antibiotics like ciprofloxacin and clarithromycin as well as endocrine disrupting effects of hormonally active medication is not considered. A second level of uncertainty is related to the lack of suitable data. LCA deals with chronic exposure, but often only acute endpoints are available for assessment. The question on whether an extrapolation from acute to chronic scenario should be done at all is fully justified. Beside chronic assessment, EDIP also defines an acute impact on freshwater ecotoxicity. The relevance of this category is debatable: an acute effect would be expected in case of an accidental release of high amounts of a substance. However, the observed substance concentration in the environmental media should be reflected by EDIP which is not the case, instead EDIP considers the same value for acute and chronic assessment. In the databases used (Wikipharma database, 2012 or ChemID plus Advance database, 2012), some referenced studies cannot be found and test information (for example the time exposure) is missing. The relevance of these values is therefore questionable since the endpoint is based only on the most sensitive species and lowest endpoint.

When applying the LCIA models, there are some other issues which give reasons for debate. The first issue is the choice of the right test: should we select on relevant species, animal or human tests or on the most accurate endpoint? The USEtox approach is based on ecotoxicological and human effect factors using EC50 and ED50 values. This data is not easily available however and neither is data from which they could be extrapolated (NOAEL or LOAEL for ED50). For human toxicity, the acute toxicity data from animal tests, expressed as LD50, is easily available but its use in LCIA implicates extrapolation to a chronic scenario, which is not recommended from a toxicological point of view and therefore generates a high degree of uncertainty. The balance of uncertainty and conservatism is therefore a challenge. Furthermore, the use of the assessment factors needs some discussion. In USEtox, an allometric factor is applied to extrapolate an animal toxicity value to a human one. But this factor does not account for differences between species (e.g. in metabolism). In certain regulatory frameworks like the REACH Regulation (EC) 1907/2006, other safety factors are applied to take into account interspecies and intraspecies differences. The use of the geometric mean of EC50s generally seems less conservative than the PNEC approach. However, the latter strongly depends on the availability of data. The use of very high assessment factors has the potential to completely change the final LCA results.

The previous LCA studies which included pharmaceuticals compounds have made similar observations (Hospido et al., 2010; Larsen et al., 2010; Muñoz et al., 2008). Modeling toxicity within LCA methodology is recognized to be quite uncertain (e.g. Geisler et al., 2005 and Larsen and Hauschild, 2007) mainly because of the lack of reliable toxicity data. An international research effort is on-going (e.g. at the level of the UNEP-SETAC initiative, within the USETox project, ..) to improve the assessment of this impact category.

Because of the above limitations, it cannot be concluded that the effect of pharmaceuticals is negligible in the environment although the application of current LCIA methods does indicate this.

Indeed, LCA addresses only part of the problem of pharmaceutical treatment. It should be an accepted practice that if genotoxic compounds (e.g. cyclophosphamide) are present at all, they should only be there in concentrations that are as low as reasonably achievable. Furthermore, effects like bacterial resistance and endocrine disruption are not or not fully considered in current toxicity assessments. Also, by definition, the LCA approach is holistic and LCIA methods consider global average conditions (at best at continental level) and therefore do not properly cover effects or issues on a local level. Spatial differentiated LCIA methods could provide a more precise assessment, by considering spatially defined CFs, taking into account local specificities (e.g. more or less sensitive areas). These methods, which are still under definition, could not replace, detailed risk assessment, which remain the most reliable assessment approach at local level. Another critical point is that terrestrial ecotoxicity of pharmaceuticals is not included in the present study. Despite their low Henry's constant, there is evidence of accumulation in wastewater irrigated soils of a few among the studied pharmaceuticals, namely carbamazepine, diclofenac and trimethoprim (Chfetz et al., 2008; Gibson et al., 2010; Kinney et al., 2009). In ReCiPe no CF for terrestrial ecotoxicity of pharmaceuticals is provided and USETox has not included this impact category so far. In EDIP, terrestrial ecotoxicity is potentially included but the fate modeling, determining the transfer of the pollutant from the water to the soil compartment,

relies only on Henry's law constant. Because of the low constants of the above mentioned pharmaceuticals, terrestrial ecotoxicity was not assessed. For the sake of consistency, we decided not to arbitrarily modify the EDIP method only for a few pharmaceuticals. Furthermore, the terrestrial ecotoxicity assessment requires the adsorption coefficient K_d of the pharmaceuticals, which can vary from <0.1 to 500 L/kg (Ternes et al., 2004), introducing additional uncertainty in the LCIA results. Another important missing point is the formation of metabolites and transformation products caused by post-treatment (ozonation or UV radiation), since they are potentially more toxic than the parent substance. In order to properly address the question of decentralized and centralized treatment of pharmaceutical, a multicriteria approach, involving additional criteria other than LCA, is therefore strongly suggested. To this aim, a specific geographical scope, targeting specific environmental media, is mandatory to obtain meaningful and comprehensive results for decision making support.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.08.096.

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Is it better to remove pharmaceuticals in decentralized or conventional wastewater treatment plants? A life cycle assessment comparison

Supporting information

Elorri Igos, Enrico Benetto*, Silvia Venditti, Christian Koehler, Alex Cornelissen, Ruth Moeller, Arno Biwer

Public Research Centre Henri Tudor (CRPHT)/Resource Centre for Environmental Technologies (CRTE) - 66, rue de Luxembourg – P.B. 144, L-4002, Esch-sur-Alzette, Luxembourg

* Corresponding author: enrico.benetto@tudor.lu

SI 1: Calculation of Granular Activated Carbon (GAC) consumption

Granular Activated Carbon (GAC) is a filter media which can be regenerated indefinitely. Activated carbon production and regeneration has been modeled by Meier (1997).

To express the regenerated mass per m^3 of wastewater, the volume of treated water by one GAC filter during its lifetime should be known. From the Dutch partner of the project, a GAC filter of 10 m^3 can treat 64800 m^3 of water (lifetime of 270 days and water flow of 240 m^3/day). Taking into account the GAC density, the regenerated mass is 58.6 g/m^3.

When a GAC filter should be regenerated, 10% of carbon is lost during the reactivation and should be replaced by fresh activated carbon. The volume of a GAC filter will be replaced after 10 cycles of regeneration, i.e. there are two productions of GAC filters for 10 regenerations. An additional consumption of 20% of 58.6 g/m^3 should therefore be added to the 58.6 g/m^3 of GAC regeneration.

Reference

Meier MA. Eco-Efficiency Evaluation of Waste Gas Purification Systems in the Chemical Industry. Swiss Federal Institute of Technology Zurich, Switzerland; 1997.

SI 2: Input concentrations of pollutants in wastewater

The concentration of the pollutants was measured in the influent of the Schifflange WWTP (Luxembourg) to model the scenarios CC and UC. Measurements at the Luxembourgish pilot plant, installed at the local hospital CHEM (Centre Hospitalier Emile Mayrisch) were used for the decentralized scenarios (D_O3, D_AC and D_UV). The virtual composition of wastewater without hospital effluent is calculated from the volume ratio between hospital wastewater and other sources. This composition will be used to model the scenarios CC+D_O3, CC+D_AC and CC+D_UV.

Table 1: Input composition of wastewater

Parameter	Centralized WWTP (CC and UC)	Pilot plant (D_O3, D_AC and D_UV)	WWTP without hospital release (CC+D_O3, CC+D_AC and CC+D_UV)
Organic matter		**g/m3**	
BOD5	175	190	175
COD	1030	358	1036
DOC	27.5	58.6	27.2
Nutrients		**g/m3**	
Total Nitrogen	62.5	59.2	62.6
Total phosphorous	11.5	6.4	11.5
Pharmaceuticals		**mg/m3**	
Atenolol	1.6	0.735	1.6
Carbamazepine	0.6	2.31	0.6
Ciprofloxacin	1.0	42.9	0.7
Clarithromycin	1.3	12.7	1.2
Cyclophosphamide	0.01	0.432	0.01
Diclofenac	2.1	9.82	2.0
Lidocaine	0.2	5.76	0.2
Paracetamol	252	29.8	254
Sulfamethoxazole	0.6	6.35	0.6
Trimethoprim	8.7	10.9	8.7
Heavy metals		**mg/m3**	
Aluminum	14	22	14
Antimony	1	1	1
Arsenic	1	0.5	1
Barium	15	20	15
Beryllium	1	0.5	0.5
Bore	208	48	209
Cadmium	0.1	0.1	0.1
Calcium	99120	93080	99170
Chromium	1	1	1
Cobalt	0.8	0.2	0.8

Copper	10.6	16	11
Iron	160	139	160
Lead	0.9	1.4	0.9
Manganese	96	25	96
Magnesium	10156	9170	10165
Molybdenum	12.6	26	13
Nickel	4	3	4
Potassium	24000	26700	23900
Selenium	1	3	1
Sodium	99500	409000	96800
Strontium	627	223	630
Thallium	0.5	0.5	0.5
Zinc	75	124	74

SI 3: Calculation of normalization factors for USEtox using ReCiPe reference

Normalizations factors for ReCiPe have been calculated for Europe in 2000 (Sleeswijk, 2008). All the emissions have been inventoried for this reference, as well as the population census. The normalization factor for an impact category corresponds to the population divided by the impact associated to this reference inventory.

For a consistent assessment, the same inventory was used to calculate the normalization factors of the USEtox method. The 465 millions of persons were divided by the impact associated to the three impact categories (ecotoxicity, carcinogenic effects on human toxicity and non-carcinogenic effects on human toxicity). The resulting normalization factors are:

- Ecotoxicity: 1.04 10^{-4} PE/CTU
- Human toxicity (carcinogenic effect): 9004 PE/CTU
- Human toxicity (non-carcinogenic effect): 182 PE/CTU

With PE: Person Equivalent, and CTU: Comparative Toxic Unit.

SI 4: Sensitivity analysis on ecotoxicity characterization factors of pharmaceuticals using EDIP

Lowest assessment factor for acute effect (yellow) and chronic effect (green).

Table 2: Assessment factor applied to PNEC according to the endpoint used

Assessment factor for ecotoxicity	Wiki EC50		Wiki NOEC	Wiki LOEC	ECOSAR EC50		ECOSAR ChV
	Chronic	Acute			Chronic	Acute	
Atenolol	1000	100	100	200	1000	100	100
Carbamazepine	100	10	10	20	1000	100	100
Ciprofloxacin	1000	100	10	200	1000	100	100
Clarithromycin	1000	100	100	200	1000	100	100
Cyclophosphamide				200	1000	100	100
Diclofenac	100	10	10	20	1000	100	100
Lidocaine	1000	100			1000	100	100
Paracetamol	100	10		20	1000	100	100
Sulfamethoxazole	100	10	10	200	1000	100	100
Trimethoprim	100	10	100	20	1000	100	100

Highest CF (red), CF with the lowest AF (yellow) and both (orange).

Table 3: Characterisation factors for ecotoxicity according to the endpoint used

Characterization factor for ecotoxicity (mPE/kg)	Wiki EC50	Wiki NOEC	Wiki LOEC	ECOSAR EC50	ECOSAR ChV
Atenolol	2	28	18	220	651
Carbamazepine	11	113	546.004	3.003	1.420
Ciprofloxacin	84.600	30.000	30.183	48	48
Clarithromycin	211.500	80.187	76.365	207	483
Cyclophosphamide	4	4	4	2	11
Diclofenac	1.819	6.105	6.105	26	282
Lidocaine	12	12	12	677	1.141
Paracetamol	22	101	101	285	2.879
Sulfamethoxazole	1.565	1.019	1.101	372	460
Trimethoprim	3	6	18.838	127	400

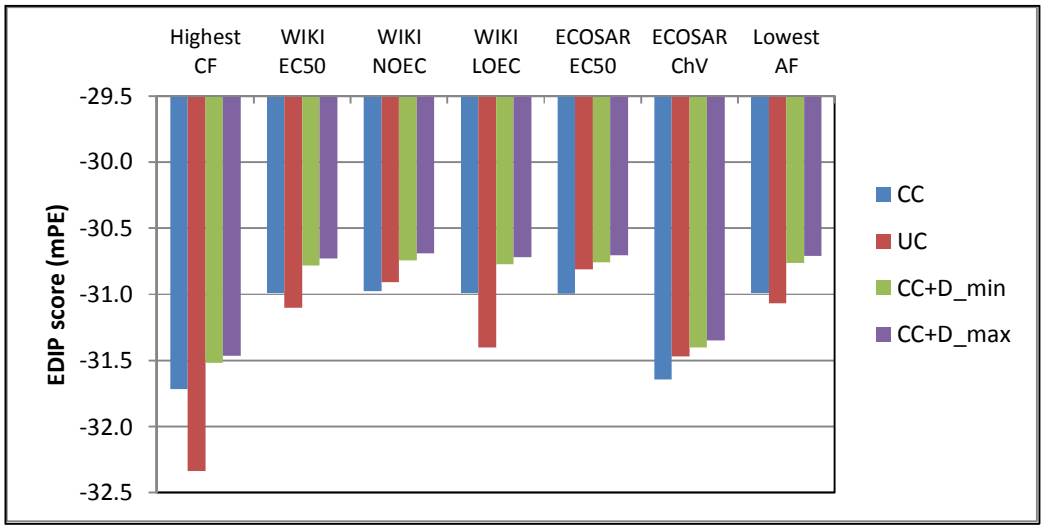

Figure 1: Comparison of the net impact of the scenarios according to the characterization factor used for pharmaceuticals ecotoxicity

CFs for chronic freshwater ecotoxicity were compared to the ones calculated within Neptune project (Larsen et al., 2010) (6 common pharmaceuticals) and by Muñoz (2008) (7 common substances). In Neptune, the references used to estimate the PNEC are not given per substance, instead are listed together at the end of the final report. As a result, a finer comparison was not possible.

For carbamazepine and sulfamethoxazole, the CF from Neptune is the closest to the one calculated with the lowest assessment factor (NOEC endpoint). For Diclofenac, NOEC from Ferrari (2004) is used despite a lower NOEC is available (Hoeger, 2005) and was used in this study. For the other substances, the PNEC values used by Neptune are issued from publications not listed in Wikipharma. The PNEC of atenolol not found in the list of references given in the final report.

Muñoz obtained a similar CF for carbamazepine than Larsen or the lowest assessment factor calculated in this study. For ciprofloxacin he refers to the ECOTOX of the USEPA, which has data in common with the Wikipharma database, used in this study. For the other substances, Muñoz has chosen other references (listed as well in Wikipharma) than the one considered in this study. These references give higher endpoint values and thus, do not represent the most sensitive species. With higher PNECs, Muñoz obtained lower CFs for these substances.

		CF (m3/kg)	**PNEC (mg/L)**	**Endpoint**	**Source**
Atenolol	Highest CF	2.08E+06	4.8E-04	ChV	ECOSAR
	Lowest AF	1.00E+05	0.01	NOEC	Winter (2008)
	NEPTUNE	2.99E+03	0.33		Not found

	Muñoz	1.60E+03	0.31	EC50	Cleuvers (2005)
Carbamazepine	Highest CF	2.00E+09	5.0E-07	LOEC	De Lange (2006)
	Lowest AF	4.00E+05	2.5E-03	NOEC	Ferrari (2003)
	NEPTUNE	4.00E+05	2.5E-03	NOEC	Ferrari (2003)
	Muñoz	4.00E+05	2.5E-03	NOEC	Ferrari (2003)
Ciprofloxacin	Highest CF	2.00E+08	5.0E-06	EC50	Isidori (2005)
	Lowest AF	1.67E+02	6	NOEC	Harada (2008)
	Muñoz	8.33E+08	1.2E-06	NOEL	Ecotox database
Clarithromycin	Highest CF	5.00E+08	2.0E-06	EC50	Isidori (2005)
	Lowest AF	1.92E+07	5.2E-05	NOEC	Harada (2008)
	NEPTUNE	3.23E+06	3.1E-04	EC50	Yamashita (2006)
Cyclophosphamide	Highest CF	1.11E+04	0.09	LOEC	Canty (2009)
	Lowest AF	3.72E+03	0.269	ChV	ECOSAR
Diclofenac	Highest CF	2.00E+07	5.0E-05	NOEC	Hoeger (2005)
	Lowest AF	2.00E+07	5.0E-05	NOEC	Hoeger (2005)
	NEPTUNE	1.00E+04	0.1	NOEC	Ferrari (2004)
	Muñoz	3.51E+04	0.028	NOEC	Ferrari 2003
Lidocaine	Highest CF	3.33E+06	3.0E-04	ChV	ECOSAR
	Lowest AF	3.33E+06	3.0E-04	ChV	ECOSAR
Paracetamol	Highest CF	1.00E+07	5.0E-05	CHV	ECOSAR
	Lowest AF	3.33E+05	3.3E+05	LOEC	Parolini (2009)
	Muñoz	5.38E+01	9.3E-03	EC50	Stuer-Lauridsen (2000)
Sulfamethoxazole	Highest CF	3.73E+06	2.7E-04	EC50	Ferrari (2004)
	Lowest AF	1.69E+06	5.9E-04	NOEC	Ferrari (2004)
	NEPTUNE	1.69E+06	5.9E-04	NOEC	Ferrari (2004)
	Muñoz	4.76E+05	2.1E-03	EC50	Isidori (2005)
Trimethoprim	Highest CF	6.90E+07	1.5E-05	LOEC	Binelli (2009)
	Lowest AF	6.90E+07	1.5E-05	LOEC	Binelli (2009)
	NEPTUNE	1.25E+03	0.80	EC50	Yamashita (2006)
	Muñoz	3.92E+03	0.26	NOEC	Eguchi (2004)

Reference

Larsen HF, Hansen PA, Boyer-Souchet F. NEPTUNE: Deliverable 4.3 – Decision support guideline based on LCA and costs/efficiency assessment. FP6 project; 2010

Muñoz I, Gómez M-J, Molina-Díaz A, Huijbregts M-A-J, Fernández-Alba A-R, García-Calvo E. Ranking potential impacts of priority and emerging pollutants in urban wastewater through life cycle impact assessment. Chemosphere 2008;74:37–44.

SI 5: Sensitivity analysis on removal rates of pharmaceuticals

Several removal rates were collected from the different partners for the decentralized unit processes. For the biological treatment of a centralized plant, measurements from the Luxembourgish partners in Schifflange WWTP could be compared to the literature (Miège[1] and Abegglen[2]). In Abegglen, the removal rates of an upgraded plant with ozonation are evaluated for the different steps of the treatment chain. The removal rates for the ozonation unit could be separated from the ones during biological treatment.

Table 4: Removal rates of pharmaceuticals for scenarios CC and UC

Removal of pharmaceuticals (%)	Biological treatment CC			Ozonation UC		
Data source	LU	Miège	Abegglen	LU	NL	Abegglen
Atenolol	48	-413	42	97	91	82
Carbamazepine	-33	4	-5	99	98	100
Ciprofloxacin	65	79		91	99	
Clarythromycin	-20	45	49	97		97
Cyclofosfamid	-1			58	82	
Diclofenac	7	55	16	99	99	100
Lidocaine	-21			100	98	
Paracetamol	98	100	99		83	
Sulfamethoxazole	53	61	32	99	98	96
Trimethoprim	9	77	16		97	96

Table 5: Removal rates of pharmaceuticals for decentralized treatment

Removal of pharmaceuticals (%)	D_MBR			D_O3			D_UV		D_AC
Data source	NL	LU	CH	NL	LU	CH	NL	LU	NL
Atenolol	81	80	99		97	23	20	88	71
Carbamazepine	0	10	0	98	99	99	28	96	96
Ciprofloxacin	70	0	51	99	91	100	77	96	99
Clarythromycin	0	50	50		97	100		86	76
Cyclofosfamid	48	13	20	82	58	33	4	77	94
Diclofenac	31	44	0	99	99	100	99	99	97
Lidocaine	79	20	56	98	100	98	35	91	93
Paracetamol		99	99	83			48		64
Sulfamethoxazole	72	0	7	98	99	96	55	91	93
Trimethoprim	75	31	96	97			38		96

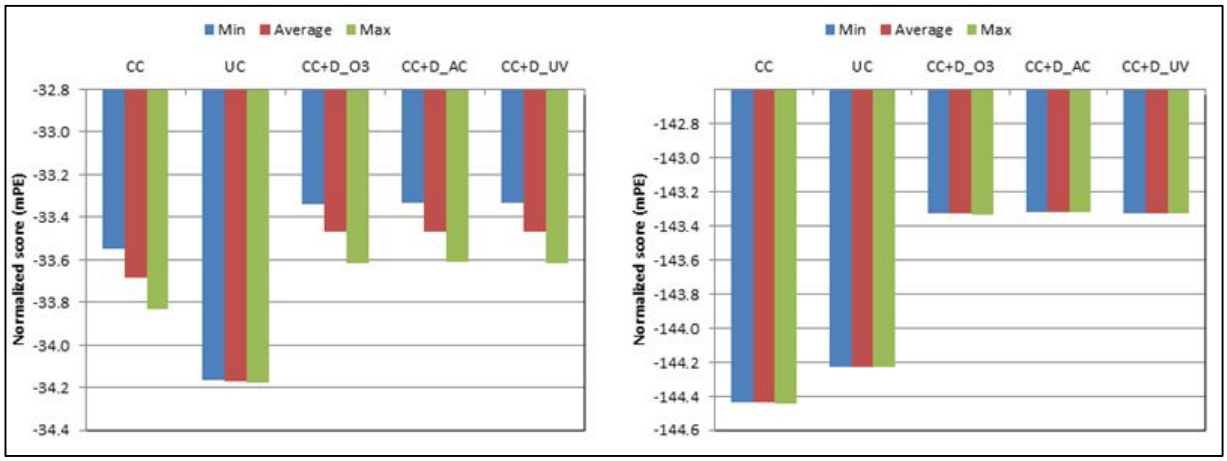

Figure 2: Comparison of net impact of global policy scenarios depending on removal rates of pharmaceuticals using EDIP (left) and ReCiPe+USEtox (right)

For each scenario, several datasets are obtained combining the possible removal rates for each unit process: 3 for scenario CC, 9 for scenario UC, 27 for scenario CC+D_O3, 9 for scenario CC+D_AC and 18 for scenario CC+D_UV. Only the minimum, the maximum and the average values are retained. The net impact is calculated using these 3 sets of removal rates for each scenario and displayed in Figure 2, using the two impact assessment methods described in the paper.

References

1. Miège C., Choubert J. M., Ribeiro L., Eusèbe M., Coquery M. (2009). Fate of pharmaceuticals and personal care products in wastewater treatment plants – conception of a database and first results. Environmental Pollution 157, 1721-1726.

2. Abegglen C., Escher B., Hollender J., Koepke S., Ort C., Peter A., Siegrist H., et al. (2009). Ozonung von gereinigtem Abwasser Schlussbericht Pilotversuch Regensdorf. Dübendorf, Eawag, Swiss 16. Juni 2009.

SI 6: Sensitivity analysis on operational data for scenario UC

Data for scenario UC were taken from two existing upgraded WWTPs: a German plant in Bad Sassesdorf, and a Swiss plant in Regensdorf[1]. While the biological treatment is modeled via the Ecoinvent tool[2] (as for scenario CC), the measured data on these two sites could be used for the operation of the ozonation unit. Similar values are observed but the Swiss plant invests a bit less treatment effort than the German one.

Table 6: Parameters for ozonation unit according to data from the upgraded plant in Bad Sassendorf or in Regensdorf

Parameter	Unit	Bad Sassendorf (DE)	Regensdorf (CH)
Energy consumption for O3	kWh/m3	0.06	0.04
Oxygen liquid	kg/m3	0.05	0.034
Transport	tkm/m3	0.005	0.003

From the previous data of Table 6, the generated impacts for scenario UC can be calculated for the both LCIA methods and are represented in Figure 3.

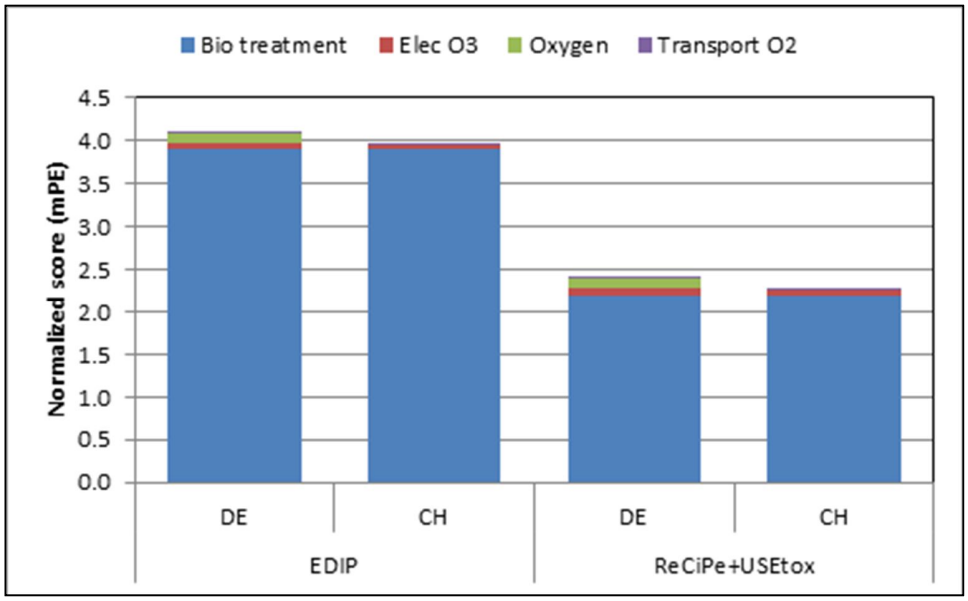

Figure 3: Comparison of generated impacts in function of data used

The small difference between the two data sources leads to similar conclusions when comparing the net impact of the 5 scenarios. In Figure 4, the net impact of the scenarios is compared to the one of scenarios UC, representing -100% (the absolute net impact of the scenarios are all negatives).

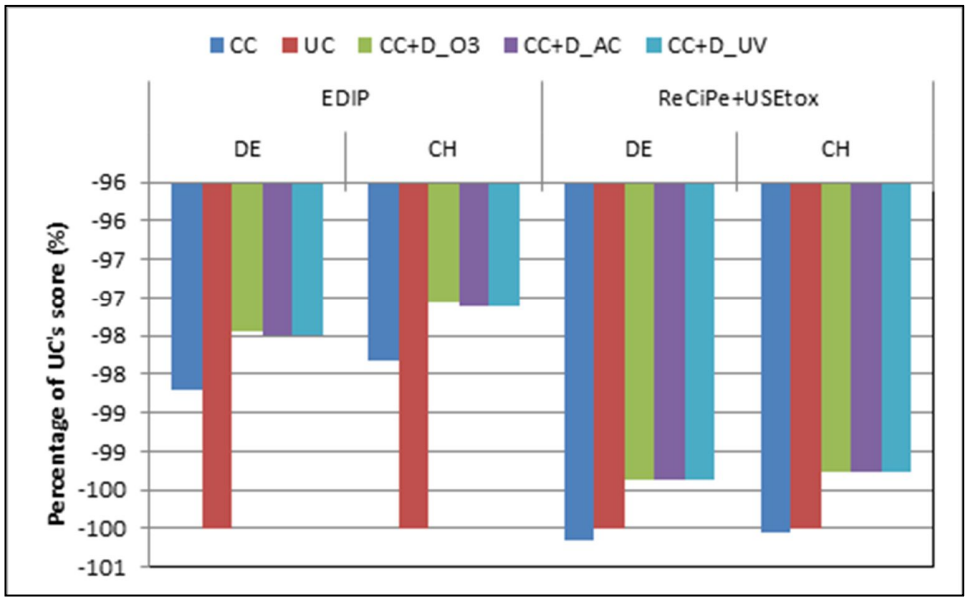

Figure 4: Comparison of net impact of global scenarios relative to normalized score of scenario UC

Additional hypothetical operational conditions were tested in order to identify the breakthrough points, where the ranking of the scenarios changes. The oxygen consumption is the determining parameter, as values of energy consumption and transport are correlated. In the case of EDIP, oxygen consumption was increased up to the point where the scenario UC show higher impact than CC. Using ReCiPe+USEtox, , the value was decreased until the scenario UC shows higher environmental performances than the other scenarios. The breakthrough points obtained are listed in Table 7.

Table 7: Breakthrough points for EDIP and ReCiPe+USEtox

Parameter	Unit	Breakthrough points - EDIP	Breakthrough points - ReCiPe+USEtox
Energy consumption for O3	kWh/m3	0.248	0.0036
Oxygen liquid	kg/m3	0.211	0.0031
Transport	tkm/m3	0.021	$3.1.10^{-4}$

For both the LCIA methods, the breakthrough points seem to be unrealistic, showing a variation of one order of magnitude as compared to the measured data. In the case of EDIP, high consumption of oxygen would be useless and induce side effects (e.g. formation of bromates). In the case of ReCiPe+USEtox, too low concentration of oxygen would lead to poor removal performances.

References

1. Abegglen C., Escher B., Hollender J., Koepke S., Ort C., Peter A., Siegrist H., et al. (2009). Ozonung von gereinigtem Abwasser Schlussbericht Pilotversuch Regensdorf. Dübendorf, Eawag, Swiss 16. Juni 2009.

2. Doka G. (2007). Life Cycle Inventories of Waste Treatment Services. ecoinvent report No. 13, Swiss Centre for Life Cycle Inventories, Dübendorf, December 2007.

SI 7: Sensitivity analysis on wastewater volume ratio between hospitals and other sources

The volume ratio between hospitals and other sources can vary in function of local conditions and this variation could lead to different results. Indeed, if a region has a high proportion of hospitals, the decentralized treatment could be more advantageous. The baseline results with Luxembourgish ratio have been compared to other possible volume ratios: French data in Limoges (2% of wastewater from hospitals), and a range between 5 and 20 hospital beds per inhabitant (from Swiss observations). The concentrations of pharmaceuticals in the virtual wastewater which would not receive hospital discharge have been recalculated and are presented in Table 7.

Table 8: Concentration of pharmaceuticals in wastewater excluding hospital source, according to the wastewater volume ratio between hospitals and other sources

Regional conditions	**LU**	**Limoges (FR)**	**5 B**	**10 B**	**15 B**	**20 B**
Volume from hospital	0.86%	2%	0.70%	1.41%	2.11%	2.82%
Beds/1000 inhabitants	6.09	14.19	5	10	15	20
Concentration of pharmaceuticals in wastewater excluding hospital source (mg/m^3)						
Atenolol	1.567	1.577	1.566	1.572	1.578	1.584
Carbamazepine	0.614	0.595	0.617	0.605	0.593	0.580
Ciprofloxacin	0.677	0.185	0.743	0.441	0.136	-0.176
Clarithromycin	1.230	1.097	1.248	1.166	1.083	0.999
Cyclophosphamide	0.006	0.001	0.007	0.004	0.001	-0.002
Diclofenac	2.010	1.919	2.022	1.966	1.910	1.852
Lidocaine	0.177	0.112	0.186	0.146	0.105	0.064
Paracetamol	254	257	254	255	257	259
Sulfamethoxazole	0.578	0.511	0.587	0.546	0.504	0.462
Trimethoprim	8.681	8.654	8.684	8.668	8.652	8.635

The net impact of the 5 scenarios is compared according to each volume ratio. In Figure 5, we observed that the ranking of scenarios is not affected and higher the fraction from hospital, higher the net impact of decentralized scenarios. Effectively, the generated impacts of decentralized treatment are higher than the avoided impacts from pharmaceuticals elimination.

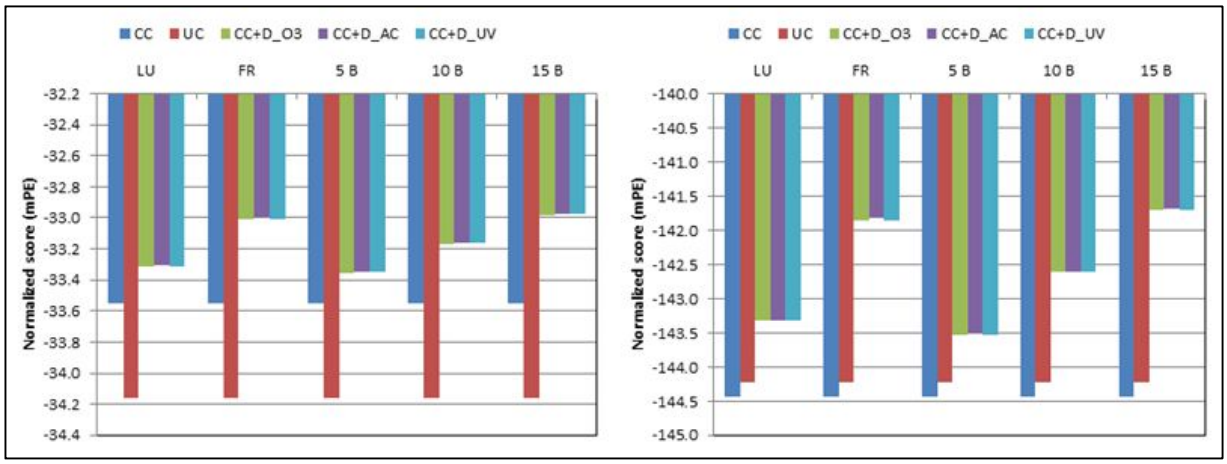

Figure 5: Comparison of net impact of global policy scenarios depending on regional conditions using EDIP (left) and ReCiPe+USEtox (right)

Comparative and integrative environmental assessment of advanced wastewater treatment processes based on an average removal of pharmaceuticals

Elorri Igos, Enrico Benetto, Silvia Venditti, Christian Köhler and Alex Cornelissen

ABSTRACT

Pharmaceuticals are normally barely removed by conventional wastewater treatments. Advanced technologies as a post-treatment, could prevent these pollutants reaching the environment and could be included in a centralized treatment plant or, alternatively, at the primary point source, e.g. hospitals. In this study, the environmental impacts of different options, as a function of several advanced treatments as well as the centralized/decentralized implementation options, have been evaluated using Life Cycle Assessment (LCA) methodology. In previous publications, the characterization of the toxicity of pharmaceuticals within LCA suffers from high uncertainties. In our study, LCA was therefore only used to quantify the generated impacts (electricity, chemicals, etc.) of different treatment scenarios. These impacts are then weighted by the average removal rate of pharmaceuticals using a new Eco-efficiency Indicator *EFI*. This new way of comparing the scenarios shows significant advantages of upgrading a centralized plant with ozonation as the post-treatment. The decentralized treatment option reveals no significant improvement on the avoided environmental impact, due to the comparatively small pollutant load coming from the hospital and the uncertainties in the average removal of the decentralized scenarios. When comparing the post-treatment technologies, UV radiation has a lower performance than both ozonation and activated carbon adsorption.

Key words | eco-efficiency, Life Cycle Assessment, pharmaceuticals, statistical tests, USEtox, wastewater treatment

Elorri Igos
Enrico Benetto (corrreponding author)
Silvia Venditti
Christian Köhler
Alex Cornelissen
Public Research Centre Henri Tudor (CRPHT)/ Resource Centre for Environmental Technologies (CRTE) - 66,
rue de Luxembourg – P.B. 144, L-4002,
Esch-sur-Alzette,
Luxembourg
E-mail: *enrico.benetto@tudor.lu*

LIST OF ABBREVIATIONS

AC	Activated carbon
CC	Conventional centralized
CH	Switzerland
CI	Confidence interval
CO_2	Carbon dioxide
COD	Chemical oxygen demand
D	Decentralized
DE	Germany
EFI	Eco-efficiency Indicator
EU	European
FU	Functional unit
I	Normalized Impact
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
MBR	Membrane biological reactor
O3	Ozonation
P	Phosphorus
PE	Person equivalent
R	Removal
UC	Upgraded centralized
UV	Ultraviolet
WWTP	Wastewater treatment plant

INTRODUCTION

The removal of pharmaceuticals in a conventional wastewater treatment plant (WWTP) has already been

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investigated and shown to be mostly ineffective due to the extreme resistance of these compounds to biological degradation processes (Heberer 2002; Ternes & Joss 2006). The release of pharmaceuticals into the environment engenders detrimental effects on the receiving ecosystem (Kümmerer 2004; Fent *et al.* 2006; Jolibois & Guerbert 2006). Thus, the application of several advanced treatments may be adopted to improve the quality of the treated water and therefore reduce the impact of the pharmaceuticals on the water body (Hollender *et al.* 2009; Köhler *et al.* 2012). In recent studies, Life Cycle Assessment (LCA) has been used as the selected methodology to evaluate the overall environmental balance of different treatment options downstream of a standard WWTP (Larsen *et al.* 2009, 2010). In the European project PILLS (Interreg IVb program), we compared different advanced treatment technologies through a comprehensive LCA of centralized and decentralized (i.e. at the hospital) treatment scenarios (Igos *et al.* 2012). The selected functional unit (FU) was the treatment of one cubic meter of wastewater. The overall environmental impact of an advanced post-treatment was calculated as the difference between the generated impacts (related to treatment effort in terms of consumption of electricity, chemicals, etc.) and the avoided impacts (i.e. the benefit arising from the removal of pollution) over the life cycle of the treatment process. The evaluation of the scenarios was achieved using the EDIP97 (Hauschild & Wenzel 1998) and USEtox (Rosenbaum *et al.* 2008) methodologies. Nevertheless, the environmental impact generated by pharmaceutical emissions and the avoided impact due to the advanced treatments was negligible compared with the impact caused by phosphorous emissions. Furthermore, the results were affected by high uncertainties based on the limitations of the ecotoxicity characterization factors available. As a result, the comparison of the advanced technologies by using the net environmental impact was not conclusive. Similar conclusions were drawn in the NEPTUNE FP6 project (Larsen *et al.* 2010), in which the authors also reported a high variation in the avoided impacts of pharmaceutical emissions depending on the risk assessment approach used for the calculation of the characterization factors.

Based on the assessment results from Igos *et al.* (2012), this study focuses on the comparative assessment of the same technologies but from a different perspective. Instead of considering the differential 'generated minus avoided' of the various impacts (as in Igos *et al.* 2012), where the avoided impacts are comprised of the reduction in pharmaceutical emissions (which varies depending on the technology), this study deals with the quantification of an 'average removal of pharmaceuticals' for a specific technology. Using this novel approach, the different technologies can now be characterized, and thereafter compared, by quantifying the generated impact per unit of 'average removal of pharmaceuticals'. The values obtained can be described as: the treatment effort needed per unit of average pharmaceutical removal, i.e. the eco-efficiency of the treatment. Therefore, the comparison perspective adopted here is completely different from the one of Igos *et al.* (2012). A similar approach is described in Ferreira *et al.* (2011), where treatment alternatives are compared using the ratio of the costs and an environmental performance indicator which is based on chemical oxygen demand (COD) removal exclusively. No previous attempt to adopt a similar approach to LCA results was found in the literature. A limited number of LCA studies included a FU including not only the treated volume, but also the associated load considering COD, phosphorous and nitrogen concentrations (Foley *et al.* 2010) or person equivalents (PE) (which is normally derived from the COD) as implemented by Tillman *et al.* (1998) and Gallego *et al.* (2008).

This paper is structured as follows. In the first place, the different technological options and related treatment scenarios are briefly outlined by referring to the previous publication (Igos *et al.* 2012) which is far too detailed to be repeated here. Secondly, the methodology calculating the 'average removal' is presented in detail. Finally, the results from the new comparison of the technological treatment options are discussed.

MATERIALS AND METHODS

Goal and scope definition

Three wastewater treatment scenarios are considered. The first one represents the most common situation: a conventional centralized WWTP (scenario CC). Wastewater collected within a geographic area is treated at a WWTP through primary and secondary treatments. An advanced post-treatment may be used for upgrading a centralized plant (scenario UC). Finally, an advanced post-treatment may be implemented in a decentralized plant, at a hospital (i.e. the main source of pharmaceuticals). In the latter scenario, wastewater effluents from houses or industrial sites are still treated by a conventional plant (CC), whereas three different advanced post-treatments for the concentrated effluent from hospitals are considered: ozonation (scenario

CC + D_O3), activated carbon (scenario CC + D_AC) and UV (scenario CC + D_UV). At the hospital site a treatment including a screen and a Membrane Biological Reactor (MBR) is assumed. The FU corresponds to the treatment of 1 m^3 of wastewater. However, the FU is mainly used as the reference flow to which the eco-efficiency indicator is scaled and the scenarios (or advanced post-treatments studied in the decentralized scenario) are compared. The infrastructure of the treatment plants are not included and were assumed to be negligible (Doka 2007; Lassaux *et al.* 2007).

Life Cycle Inventory

Generated impact

The Ecoinvent tool for wastewater treatment (Doka 2007) has been used to calculate, for the specific input composition of a Luxemburgish local WWTP, the inventory data for the conventional WWTP scenario. For the UC scenario, the consumption of electricity, liquid oxygen and transport were collected from two existing plants at Bad Sassendorf (DE) and at Regensdorf (CH) (Abegglen *et al.* 2009). Data for the decentralized plants were collected by the partners of the PILLS project at demonstration facilities located in Germany, Luxembourg, the Netherlands and Switzerland (Igos *et al.* 2012). Due to the variability of the data sources, electricity consumption for ozonation varies by one order of magnitude and hydrogen peroxide usage during UV radiation by three orders of magnitude. Hence, minimum and maximum values are used in the inventory. Furthermore, MBR electricity consumption doubles in the case of non-optimized operation. Therefore, both optimized and non-optimized operational conditions are considered.

Removal of pharmaceuticals

Ten pharmaceuticals with high eco-toxicities, known to be excreted in high amounts in the hospital locations investigated, are considered in the current case study (Table 1). The observed removal rates are very similar and most of them were retrieved from measurements at Luxembourg's local WWTP and at the hospital pilot (Venditti *et al.* 2011). The removal rates for four out of the 10 pharmaceuticals (carbamazepine, clarithromycin, cyclophosphamide and lidocaine) were considered equal to zero within their experimental errors and uncertainty for scenario CC. These pharmaceuticals are usually not removed by biological treatment (Giger *et al.* 2003; Clara *et al.* 2005; Joss *et al.* 2005). Table 1 illustrates for a few scenarios, including a decentralized treatment, that the removal rate is not significant. For example, carbamazepine is not removed by a conventional treatment, whereas in scenario D_O3 the elimination is 99%. As the hospital effluent flow is very low (0.86% of the total WWTP influent flow), the avoided amount of carbamazepine is very small from a catchment perspective and the overall removal rate is only 3%. Moreover, for other substances i.e. atenolol, paracetamol and trimethoprim, the separate treatment of hospital wastewater has a negligible influence on the total load at catchment level because of contributions from other sources. As a result, no effect is observed by the addition of a decentralized treatment. On the contrary, for some pharmaceuticals (cyclophosphamide and lidocaine) a net improvement of

Table 1 | Removal rates of pharmaceuticals for each scenario

	Scenarios					Advanced post-treatments of the decentralized scenario		
% Pharmaceuticals	CC	UC	CC + D_O3	CC + D_AC	CC + D_UV	D_O3	D_AC	D_UV
Atenolol	48	98	48	48	48	99	94	98
Carbamazepine	0	99	3	3	3	99	97	97
Ciprofloxacin	65	97	74	77	76	91	99	96
Clarithromycin	0	97	8	7	8	99	88	93
Cyclophosphamide	0	58	24	35	30	64	95	80
Diclofenac	7	99	11	11	11	100	98	99
Lidocaine	0	100	22	21	20	100	94	93
Paracetamol	98	100	98	98	98	100	100	100
Sulfamethoxazole	53	100	53	53	53	99	93	91
Trimethoprim	9	97	10	10	10	98	97	57

the removal rate is observed by adding a decentralized treatment. These substances are normally present at very low concentrations in urban wastewater, which makes the removal rate very sensitive to an additional advanced treatment at a hospital. The removal rate for CC ranges from 0% (for four different compounds) to 98% (for paracetamol). Conversely, decentralized treatments and scenario UC obtain similar values in terms of pharmaceutical removal rates (almost all are above 90%).

Life cycle impact assessment

EDIP2003

This method (Potting & Hauschild 2005) has been used in Larsen *et al.* (2010) and Igos *et al.* (2012) to assess the impact generated by wastewater treatment. Life Cycle Inventory (LCI) data are used to evaluate 14 midpoint impact categories (climate change, land use, eutrophication, etc.), expressed by a reference unit per category (kg CO_2 eq, m^2, kg P eq., etc.). Thereafter, these midpoint categories are further aggregated into a single score by means of normalization. This approach consists of scaling the generated impact to a normalization factor, representing the average impact, per category, generated by a PE. The latter is obtained by the ratio between the total impact for the specific category, calculated for a particular reference area and time period, and the relative number of persons living in the catchment during the period considered. EDIP2003 uses the European inventory for the year 2004 to calculate the normalization factors (Laurent *et al.* 2011). This normalization approach is questionable as it implicitly weights to a lesser extent (i.e. gives a lesser preference) those impact categories that showed a higher total impact in the 2004 situation at an EU level. Thus, in the further aggregation, the generated impacts corresponding to that category have a reduced contribution to the total aggregated impact. Through normalization, one implicitly gives more importance to the results of the impact categories which had lower impacts in the 2004 situation at EU level, i.e. normalization seeks to protect the categories which are currently less affected.

ReCiPe

Developed in 2008, ReCiPe (Goedkoop *et al.* 2009) assesses the environmental impact at the midpoint (16 categories) and at the endpoint (damage on human health, ecosystems and resources) levels. Endpoint results are further aggregated into a single score by weighting the three damages (40, 40 and 20% respectively). For the sake of comparability with EDIP2003, midpoint results from ReCiPe are normalized in PE as well. Normalization factors are based on the LCI of Europe for the year 2000 (Sleeswijk *et al.* 2008) and are developed considering different cultural perspectives (individualist, hierarchist and egalitarian). The hierarchist factors are used in this study to comply with 'the view that impacts can be avoided with proper management, and that the choice on what to include in the model is based on the level of (scientific) consensus' (Goedkoop *et al.* 2009). Normalization factors differ from those in EDIP because of a different inventory and a different number of persons (different years), but also due to the fact that different substances are characterized by the two methods.

Eco-efficiency indicator

Statistical tests are often used in the field of wastewater treatment, for example to quantify the improvement of nitrate removal due to a new wetland treatment (Tegegne *et al.* 2008) or to compare mercury concentrations in domestic wastewater (Berthouex & Brown 2002). The use of confidence intervals (CI) allows the discussion of results and the inference of conclusions which are statistically significant. In this study, a statistical approach based on paired *t*-tests is used to evaluate a consistent average removal of pharmaceuticals and the related CI. Furthermore, an independent *t*-test is used to compare alternative treatment technologies based on a novel eco-efficiency indicator.

Translating the treatment effort of each scenario per unit of average removal of pharmaceuticals:

$$EFI = \frac{I}{\overline{R}}$$

where *EFI*: Eco-efficiency Indicator (PE), *I*: normalized environmental impact of the treatment (PE) and $\overline{R}$: average removal of pharmaceuticals (dimensionless).

The standard deviation in the *EFI* can be derived from the standard deviations in the numerator and denominator. The one affecting the impact result (σ_1) could not be calculated due to the lack of data. Therefore, only the standard deviation of the removal rate (σ_R) is considered here:

$$\sigma_{EFI} = \sqrt{\theta_I^2\sigma_I^2 + \theta_R^2\sigma_R^2} = \frac{I}{\overline{R}^2}\sigma_R$$

$$\text{With } \theta_I = \frac{\partial EFI}{\partial I} = \frac{1}{R}, \theta_R = \frac{\partial EFI}{\partial R} = -\frac{1}{R^2}, \sigma_1 = 0,$$

$$\sigma_R = \sqrt{\frac{\sum_{i=1}^{10}(R_i - \overline{R})^2}{10-1}} \Big/ \sqrt{10}$$

It can be observed that the standard deviation of the average removal of pharmaceuticals does not reflect an uncertainty per se. Instead, it represents the variability of the treatment performance with respect to the different targeted pharmaceuticals. A larger standard deviation reflects a situation where the treatment performs very well for some pharmaceuticals and not so well for others. For each treatment scenario, *EFI* is calculated together with a 95% CI estimated at $2\sigma_{EFI}$. The scenarios are then compared pairwise using an independent *t*-test, testing the null hypothesis that the difference between the average values is zero (Berthouex & Brown 2002). The pooled variance of the difference between two averages is:

$$S^2_{pool} = \frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1+n_2-2}$$

where n_1: size of sample 1, n_2: size of sample 2, s_1: variance of sample 1, and s_2: variance of sample 2. The standard error is therefore equal to:

$$s_{\overline{y}_1-\overline{y}_2} = s_{pool}\sqrt{\frac{1}{n_1}+\frac{1}{n_2}}$$

Student's *t* distribution is then used to determine the 95% CI. If the latter includes zero, there is no persuasive evidence that the two samples are different and that one of the two scenarios generated a higher environmental impact per unit of average removal rate of pharmaceuticals. The magnitude of the standard deviation on the removal of pharmaceuticals plays an essential role in the comparison and takes into consideration the variability of the performance of the treatment with respect to the targeted pharmaceuticals. If the treatment performs evenly for most of the pharmaceuticals, the comparison is most likely to be conclusive. Otherwise, if the treatment performance is scattered, the treatment scenarios are likely to be impossible to differentiate.

RESULTS

Scenario CC is affected by a high variability, which propagates to scenarios CC+D_O3, CC+D_AC and CC+D_UV. On the contrary, the upgraded plants obtain high removal rates for all pharmaceuticals leading to a low standard deviation. The same conclusion is observed for the decentralized scenarios (Figure 1). When the error bars for the comparison of *EFI*s are examined (Figure 2), a positive CI is observed when comparing UC and CC. This shows a clear preference for the upgraded plant. The larger standard error affecting the conventional plant does not allow any conclusion for a preference regarding the decentralized treatment scenarios, even when considering optimal

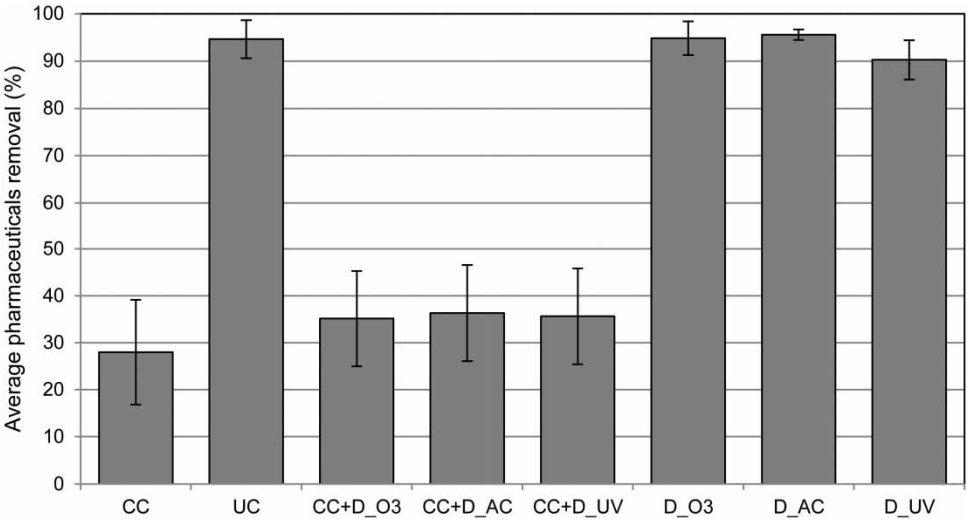

Figure 1 | Average removal of pharmaceuticals and their 95% confidence intervals for the different scenarios.

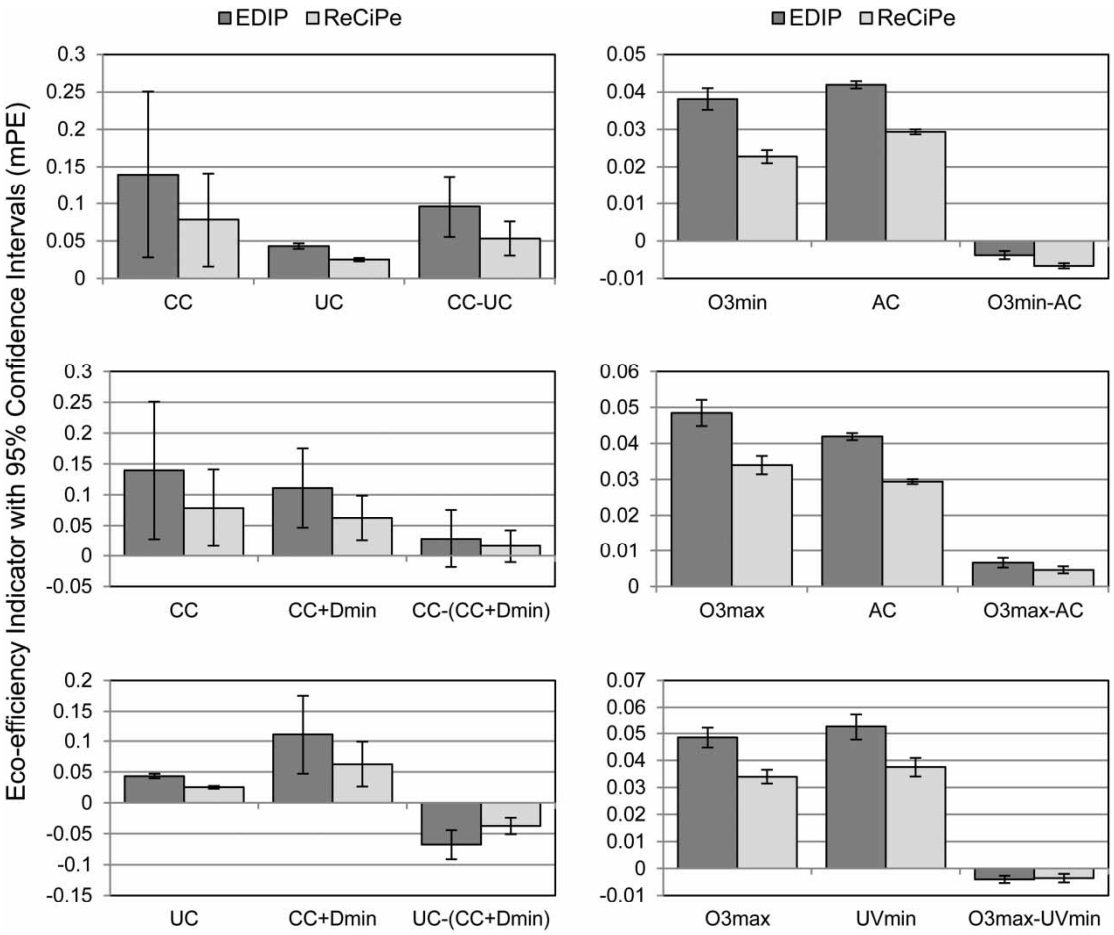

Figure 2 | Pairwise comparison of global (on the left) and decentralized scenarios (on the right) based on *EFI*.

operational conditions (scenario Dmin considering optimized MBR and ozonation with minimal electricity consumption). When comparing the advanced technologies, UV radiation underperforms relative to all the other scenarios. Additionally, while using a low dosage of hydrogen peroxide (UVmin), this phenomenon can be observed. The comparison between ozonation and AC adsorption provides different conclusions, depending on the electricity consumption of ozonation (O3min or O3max). The normalized score calculated with ReCiPe is always slightly lower than the one obtained with EDIP, except for the activated carbon scenario. The lower values of ReCiPe are mainly associated with the lower impacts on ecotoxicity and human toxicity as a result of direct emissions from the WWTP (sludge digester).

Infrastructures are not included in this study. The construction of a new sewer system could be required when considering decentralized treatment. In Lassaux *et al.* (2007) the sewer system contributed to 8% of the total impact. However, even by increasing the impact generated by decentralized scenarios to 10%, the conclusion of the comparison between the *EFI*s is not affected.

DISCUSSION AND CONCLUSION

In the present study, advanced post-treatments to remove pharmaceuticals from urban and hospital wastewater were compared using a newly developed eco-efficiency indicator. The indicator represents the overall environmental impact generated by the treatment, evaluated using LCA methodology per unit of average removal. The new approach allows the comparison of treatment technologies as well as their implementation from an integrated perspective, while not losing the information contained in the variability of the pollutant removal rates. When only pharmaceutical removal is considered, *EFI* clearly indicates a preference for the upgraded centralized WWTP. Furthermore, the use

of the *EFI* has highlighted the comparatively reduced performance of the UV technologies when matched to other advanced post-treatments. The alleged added value of the decentralized treatment option at the hospital is negligible due to the relative low volume of wastewater treated when compared with the overall volume. Furthermore, the results from the decentralized scenarios are affected by high uncertainties. The pertinence of including paracetamol in the calculations could be questioned as its removal rate is always higher than 98%. Therefore, it may introduce a bias in the CI for the conventional WWTP which is far less efficient for other pharmaceuticals. This substance is easily removed during biological treatment and, therefore, its importance is minimal when considering post-treatments. If paracetamol is not included in the calculations, the *EFI* of scenarios CC and CC + D is 30% higher, while a 1% increase is observed for scenario UC and the decentralized scenarios.

Nevertheless, the change does not affect the outcome of the overall comparison. As a result, the environmental performances of decentralized treatments are not competitive compared with upgraded centralized WWTPs. Therefore, the decentralized approach does not appear to be a suitable option to remove pharmaceuticals from the urban water cycle. Nonetheless, it should be taken into account that other, possibly highly valuable, beneficial effects of decentralized treatment, for instance on the local ecosystem, cannot be quantified in LCA. LCA's primary function is to provide an overall assessment at a global level. Furthermore, it should be noted that only a limited selection of pharmaceuticals was considered in this study. Additionally, specific phenomena as the formation of transformation products (and their relative impacts) and the presence of antiresistant bacteria in the urban water systems were not with in the scope of this study. Therefore, the specific results of the scenario comparisons must be interpreted cautiously, as also discussed in Igos *et al.* (2012). In addition to the more conventional comparison approach based on the differential 'generated minus avoided' impacts (used in Igos *et al.* 2012), the *EFI* is a promising approach which can provide complementary decision-making support on the choice and development of treatment technologies as well as their implementation approaches within the urban water cycle. The characteristics of the selected pollutants are not considered in this paper. Further developments of the indicator will include the possibility to consider a much higher number of pollutants, which could be attributed a different weight as a function of their relevance and importance for the decision-making process.

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Development of USEtox characterisation factors for dishwasher detergents using data made available under REACH

Elorri Igos [a,*], Ruth Moeller [a], Enrico Benetto [a], Arno Biwer [a], Mélanie Guiton [a], Philippe Dieumegard [b]

[a] Public Research Centre Henri Tudor (CRPHT), Resource Centre for Environmental Technologies (CRTE), 6A, Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg
[b] Chemolux, McBride Group, Rue de l'Industrie, L-3895 Foetz, Luxembourg

HIGHLIGHTS

- Impacts of three generations of dishwasher detergents are studied through LCA.
- Novel characterisation factors for (eco)toxicity have been developed within USEtox.
- Up-to-date data submitted by companies under REACH have been used.
- Results show the importance of removing phosphate-based ingredients.
- Combining REACH and LCA improves data availability.

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ABSTRACT

Because of the more and more stringent regulations and customer demand, dishwasher detergent manufacturers are constantly improving the composition of the products towards better environmental performances. In order to quantify the pros and cons of these changes on the lifecycle of detergents, as compared to conventional products, the use of Life Cycle Assessment (LCA) is a meaningful opportunity. However, the application of the methodology is hampered by the lack of Characterisation Factors (CFs) relative to the specific chemical substances included in the detergents composition, which cannot be included in the impact assessment of the effluent discharge. In this study we have tackled this problem, taking advantage of the specific case of three dishwasher detergents produced by the Chemolux/McBride group: phosphate-based, eco-labelled and phosphate-free formulations. Nine CFs for freshwater ecotoxicity and seven CFs for human toxicity have been developed, using the USEtox methodology and data made available under the REACH regulation. As a result, the dishwasher effluent composition could be characterised by more than 95% for freshwater ecotoxicity whereas for human toxicity the percentage was less than 36%, due to the lack of adequate and reliable repeated dose toxicity studies. The main contributing substances to freshwater ecotoxicity were found to be sodium percarbonate and sodium triphosphate, the latter confirming the pertinence of phosphates banning in the detergent industry. Regarding human toxicity, zinc shows the highest contribution. Further comparison to previous studies and sensitivity analysis substantiated the robustness of these conclusions.

Abbreviations: 4Na HEDP, tetrasodium (1-hydroxyethylidene)bisphosphonate; AE C8-10, alcohols C8-C10 ethoxylated; AE C11, alcohols C11 ethoxylated, propoxylated; CF, characterisation factor; EC50, effect concentration which affects 50% of a tested population; ED50, effect dose which causes a disease with a probability of 50%; EL, eco-labelled tablet; EDIP97, environmental design of industrial products – 1997 version; kedgA, degradation rate in air; kdegSd, degradation rate in sediment; kdegSl, degradation rate in soil; kdegW, degradation rate in water; Kow, partitioning coefficient between octanol and water; LCA, Life Cycle Assessment; LCIA, life cycle impact assessment; MW, molecular weight; Na-carbonate, sodium carbonate; Na-percarbonate, disodium carbonate compound with hydrogen peroxide; Na-silicate, silicic acid sodium salt; NOAEL, No Observed Adverse Effect Level; PAF, potentially affected fraction of species; PB, phosphate-based tablet; PEG, polyethylene glycol; PF, phosphate-free soluble bag; Pvap25, vapour pressure at 25; QSAR, Quantitative Structure Activity Relationship; REACH, Regulation (EC) No 1907/2006 concerning the registration, evaluation, authorisation and restriction of chemicals; Sol25, solubility at 25 °C; STP, pentasodium triphosphate; TAED, N,N′-ethylenebis[N-acetylacetamide]; USES-LCA, uniform system for the evaluation of substances adapted for LCA purposes; WWTP, waste water treatment plant.

* Corresponding author. Tel.: +352 42 59 91 3351; fax: +352 42 59 91 555.
E-mail address: elorri.igos@tudor.lu (E. Igos).

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1. Introduction

Due to the more and more stringent regulations and customer demand, detergents manufacturers are constantly striving to improve the environmental performances of their products, e.g. by banning phosphate ingredients in the formulations or by developing products which undergo the eco-labelling certification scheme. As long as environmental improvements are communicated to third parties, these have to be correctly quantified through scientifically sound and proven approaches. Life Cycle Assessment (LCA) methodology, standardised by ISO 14040-44 standards (2006), has been widely used to this aim. Concerning laundry detergents, previous studies have particularly focused on the assessment of aquatic eco-toxicity potential of the effluent discharge after washing, due to the lack of Characterisation Factors (CFs) for specific ingredients and to the high contribution of wastewater treatment discharge to the detergents lifecycle. Saouter et al. (2002) and Van Hoof et al. (2003) calculated CFs as the inverse of the effect concentration given by the Detergent Ingredient Database list (European Commission, 2007). The latter was further improved in Pant et al. (2004) and Dewaele et al. (2006) by applying the cause-effect chains of LCIA models (USES-LCA, EDIP97, Impact2002, CML92 and Uses2.0) and thus considering several key properties of the assessed substances. Finally, Van Hoof et al. (2011) used the USEtox model, developed under the umbrella of the United Nations Environment Program (UNEP) and the Society for Environmental Toxicology and Chemistry (SETAC) Life Cycle Initiative (Rosenbaum et al., 2008), to retrieve CFs for freshwater ecotoxicity (in PAF m^3 d kg^{-1}). The USEtox model, which also characterises human toxicity (in cases kg^{-1}), combines three assessment steps: (1) "fate assessment", described by a multimedia model based on the physic-chemical properties of the substance; (2) "exposure assessment" expressing the fraction dissolved in freshwater and transferred to the human population (through drinking water, inhaling air, food chain, etc.); and (3) "effect characterisation" evaluating the toxicity potential for aquatic organisms and human health.

Continuing this line of research, this paper aims at characterising the ecotoxicity and human toxicity potential of effluent discharge from dishwashers, after treatment in waste water treatment plant. Three dishwasher detergents produced by the Chemolux/McBride group were considered: phosphate-based (PB), eco-labelled (EL) and phosphate-free (PF) formulations. Information collected and published under the European REACH framework (Regulation (EC) 1907/2006) was used in the identification of relevant endpoints for effect characterisation. The link between REACH and LCA has already been pointed out in literature (e.g. Askham, 2012) and, in this paper, the potential synergies between CFs development and REACH screening are further explored. The impacts of effluent discharges for the dishwasher detergents are then compared and further interpreted through sensitivity analysis on the USEtox model parameters and cross-analysis with the results from Van Hoof et al. (2011), to evaluate the overall assessment robustness. These results are part of the complete LCAs of the three dishwasher detergents, aiming at quantifying the environmental benefits associated to recent detergent formulation improvements, which will not be detailed here.

2. Materials and methods

2.1. Goal and scope

The aim of the study is to assess the freshwater ecotoxicity and human toxicity impacts of the dishwasher effluent composition after partial treatment in a Waste Water Treatment Plant (WWTP). The focus here is on the effluent composition, i.e. the lifecycle steps of detergent production, use and the functioning of the WWTP are not included in this study. The functional unit (FU) is "one washing cycle, considering a standard program of a modern dishwasher (water temperature around 50–60 °C) using one detergent unit (tablet or bag)". Chemolux/McBride performed analytical measurements of the composition of dishwasher effluent samples for the three detergents under study and the FU. A few substances were characterised and related to the corresponding detergent ingredients, e.g. zinc from dissociation of zinc diacetate and citric acid from sodium citrate. For the other ingredients, the amounts included in the formulations of the detergents are considered for the effluent characterisation as these substances (or related dissociation elements) could not be detected by the analytical measurements. The inventory of the composition of the effluent discharge is therefore calculated based on the dishwasher effluent composition and the WWTP removal performances (HERA, 2004, 2009a; Dewaele et al., 2006; UNEP, 2002; Saouter and Van Hoof, 2001). Since a large number of substances are included in the detergent products, only the ones whose mass percentage is above 0.1% are considered in the study, for a total of 32 compounds. The environmental relevance of the excluded substances was however checked for sake of consistency of the assessment. Among the inventoried components, **citric acid** (CAS 77-92-9) (representing citric acid and/or sodium citrate in the formulation), **glycerol** (CAS 56-81-5), **acrylic acid** (CAS 79-10-7) and **zinc** (CAS 7440-66-6) are already included by USEtox, despite for the former two human toxicity characterisation is missing. Furthermore, the existing CFs are labelled as "interim" because of the high uncertainties affecting the assessment.

In this study, the development of novel CFs has focused on citric acid and glycerol (for human toxicity), and on eleven other components representing more than 1% of at least one formulation (for both freshwater ecotoxicity and human toxicity): alcohols C11 ethoxylated propoxylated (hereafter called **AE C11**), alcohols C8-C10 ethoxylated (**AE C8-10**), disodium carbonate compound with hydrogen peroxide (**Na-percarbonate**), N,N′-ethylenebis[N-acetylacetamide] (**TAED**), pentasodium triphosphate (**STP**), polyethylene glycol (**PEG**), silicic acid sodium salt (**Na-silicate**), sodium carbonate (**Na-carbonate**), tetrasodium (1-hydroxyethylidene) bisphosphonate (**4Na HEDP**), acrylic/sulphonic polymer (**Acry/sulf poly**) and polymer acrylic/maleic (**Acry/mal poly**). The exact composition of the latter two polymeric compounds is not available because of confidentiality reasons, and their potential degradation to the individual components is unknown. Therefore, a worst case approach has been followed by choosing for the inventory the most hazardous known component of the polymers. In the case of **Acry/sulf poly**, acrylic acid is assumed to be the most harmful since it is classified as very toxic to aquatic organisms (contrarily to sodium sulphide) and the ecotoxicity and toxicity profiles indicate higher toxicity for the relevant endpoints. For **Acry/mal poly**, the CF provided by USEtox for freshwater ecotoxicity of maleic acid is lower than the one for acrylic acid. Data made available under REACH also indicate less toxicity for maleic acid. For human toxicity the opposite is observed, i.e. maleic acid has higher toxicity potential than acrylic acid. Thus, **Acry/mal poly** is characterised by the freshwater ecotoxicity of acrylic acid and the human toxicity of maleic acid.

2.2. Fate assessment

The fate model estimates the residence time of a pollutant by calculating the mass balance under steady state conditions. For five of the studied substances (the organic ones), only eight parameters out of the twelve inputs normally required by USEtox are sufficient for the characterisation under the assumptions of the Quantitative

Structure Activity Relationship (QSAR) model: (1) molecular weight (MW), (2) partitioning coefficient between octanol and water (Kow), (3) vapour pressure at 25 °C (Pvap25), (4) solubility at 25 °C (Sol25), (5) degradation rate in air (kdegA), (6) degradation rate in water (kdegW), (7) degradation rate in sediment (kdegSd) and (8) degradation rate in soil (kdegSl). Four substances are inorganic: **Na-percarbonate**, **STP**, **Na-carbonate** and **Na-silicate**. USEtox has known limitations concerning the applicability to inorganic chemicals which are flagged with "interim" factors (Huijbregts et al., 2010) and currently only metallic compounds are characterised. However, the data required for the assessment of inorganics are not available for the four ingredients studied here. The model was thus applied to the inorganic ingredients by using only the eight parameters required for organics, for which data could be estimated, keeping in mind the uncertainties embedded in the calculation. This approach has been cross-checked with the USEtox developers (Rosenbaum, 2012). The physic-chemical properties were retrieved from the HERA (Human and Environmental Risk Assessment) reports on ingredients of household cleaning products (HERA, 2002a,b; 2003, 2005a,b, 2009b). In the case no experimental data were available the EPI Suite™ model (USEPA, 2009) was used. Degradation rates are equal to ln(2) divided by half-life values. **Na-percarbonate** and **Na-silicate** were not present in the database of EPI Suite™ model. **Na-percarbonate** was assumed to have similar properties as **Na-carbonate**, while **Na-silicate** parameters were set to zero as in Van Hoof et al. (2011) (see Table 1).

2.3. Exposure assessment

The dissolved fraction in freshwater is calculated using the parameters collected for fate analysis. For human exposure, seven pathways are included: air inhalation, drinking water, exposed produce, unexposed produce, meat, dairy products and fish. Each of them has a different formula and the user can provide degradation rate in above-ground plant tissues and bioaccumulation factors for the assessed chemical. QSAR was applied to estimate these values for the nine studied substances.

2.4. Ecotoxicology effect assessment

The ecotoxicity effect factor is based on the chronic EC50, i.e. the effect concentration affecting 50% of the tested population. In the case of acute values, a time extrapolation factor of two is applied. EC50s are collected per species and should ideally reflect the three trophic levels, using a specific time duration (e.g. 48 h for acute tests with crustacean) and standard species (e.g. *Daphnia magna* for crustacean) as recommended by USEtox. The average of the logarithm values of the geometric mean of the single species EC50s are the required input data. In this study, the European Chemicals Agency portal (http://echa.europa.eu/) was consulted to collect the best available data for substances registered under REACH: **Na-percarbonate**, **TAED**, **STP**, **Na-silicate**, **Na-carbonate** and **4Na HEDP**. The reliability of the studies underlying the endpoint is indicated by the Klimisch-score (Klimisch et al., 1997), ranging from 1 (reliable without restrictions) to 4 (not assignable). For sake of reliability, all the tests with a Klimisch-score of 3 (not reliable) were excluded from the analysis. Data were then double-checked with other databases: eChem Portal (OECD, 2013), PAN Pesticide Database (Kegley et al., 2011) and ChemIDplus (U.S. National Library of Medicine, 2010). For **4Na HEDP**, the ECHA file is based on a read-across, where data for all the substances of the category (phosphonic acid compounds group 2) have been considered for the single substance. This grouping approach is also used for this study. For **AE C11**, only predicted values from the ECOSAR model of EPI Suite™ could be extracted, which classifies the chemical in the class of "neutral organics" and calculates the effect concentrations via linear regressions based on the Kow coefficient only. This rough estimation from a large group of chemicals adds significant uncertainty to the assessment. For **AE C8-10**, experimental data for 17 ethoxylated alcohols with a carbon chains length from C8 to C11 (whereas the ethoxy unit has a length between 0 and 10) from HERA (2009b) were used. Although the chain length and the degree of ethoxylation of the substances vary, the acute EC50 values spread over one order of magnitude only. Therefore, the derived EC50 are considered to be close enough to the true value for **AE C8-10**. Finally, **PEG** data were found in the PAN Pesticide Database. All the ecotoxicity data are listed in Table A1 of the Supporting information (SI). Out of the 67 EC50 values reported, only three come from chronic tests since EC50s are not commonly reported in chronic studies. About half of the 67 EC50s were performed on the standard species as indicated by USEtox. For **Na-percarbonate**, **TAED**, **PEG** and **4Na HEDP**, the three trophic levels could not be covered because of the lack of data, although three of them are registered under REACH.

2.5. Human toxicology effect assessment

Human toxicity characterisation considers chronic effects to reflect a life time duration of the environmental exposure to chemicals, and distinguishes between carcinogenic and non-carcinogenic effects. The carcinogenicity potential was verified despite they are classified as consumer products. None of the ingredients was found in the Carcinogenicity Potency Database (Gold et al., 2013), which is consulted by USEtox. **PEG** and **Na-silicate** have been notified with a carcinogenicity potential in the Classification and Labelling Inventory hold by ECHA. However, in both cases, only one company classified the substance and no reliable data are available in the public databases to evaluate the pertinence of this self-classification for carcinogenicity notified by industry. Carcinogenic effects of the detergents ingredients have therefore not been characterised. Regarding non-carcinogenic effects, USEtox considers for humans the endpoint ED50 (i.e. Effect Dose which causes a disease with a probability of 50%), usually extrapolated from animal tests

Table 1
Data sources for fate assessment.

Substance	Data from HERA	Data from EPI Suite™	Other assumptions
AE C11		All	
AE C8-10		All	
Na-percarbonate	MW, Sol25		Others: same values as Na-carbonate
TAED	MW, Kow, Sol25	Pvap25, half-lives	
STP	MW, Sol25	Kow, Pvap25, half-lives	
PEG		All	
Na-silicate	MW, Sol25		Others values equal to 1E-20 (same assumption than Van Hoof et al., 2011)
Na-carbonate	MW, Sol25	Kow, Pvap25, half-lives	
4Na HEDP		All	

and differentiated according to the exposure route j (inhalation or ingestion):

$$ED50_{h,j} = \left(ED50_{a,t,j} \cdot BW \cdot LT \cdot N\right) / \left(AF_a \cdot AF_t \cdot 10^6\right)$$

$ED50_{a,t,j}$, ED50 for animal a, time duration t and exposure route j (mg kg^{-1} d^{-1}); BW, body weight of humans (70 kg); LT, average lifetime of humans (70 years); N, number of days per year (365 d year^{-1}); AF_a, extrapolation factor for interspecies differences (e.g. 4.1 for rat and 7.3 for mouse); AF_t, extrapolation factor for differences in time of exposure (2 for subchronic to chronic and 5 for subacute to chronic).

ED50s for repeated dose toxicity are normally not available from routine toxicity studies. They need to be derived from the No Observed Adverse Effect Level (NOAEL) by applying, according to USEtox, a default extrapolation factor of 9 to express the difference of observed effects. Public available data have been evaluated against their reliability (i.e. Klimisch score 3 was excluded), adequacy and relevance for the exposure scenario. The most sensitive endpoint (i.e. lowest ED50 value) was retained for further calculation in USEtox. Whenever an ED50 was not available for a specific exposure route, the same value was applied to both ingestion and inhalation, as specified by USEtox. Among the screened chemicals, NOAELs could be retrieved for **AE C8-10**, **Na-silicate**, **4Na HEDP**, maleic acid (**Acry/mal poly**), **TAED**, **glycerol**, and **citric acid**, only for ingestion route except for **glycerol** (NOAELs found for both routes), and based on grouping approach for the first three after verifying the toxicological profiles of the categories. For **AE C8-10** the grouping approach from HERA (2009b) was followed, as it was the case for ecotoxicity. The NOAEL considered was derived from chronic feeding studies reflecting an overall NOAEL of alcohol ethoxylates for subchronic and chronic exposure. The REACH registration dossier of **Na-silicate** refers to the SIDS Initial Assessment Report for the Screening Information Assessment Meeting of the category "soluble silicates" (SIAM 18, 2004). The lowest NOAEL of the category, i.e. subchronic study on sodium metasilicate, was used for the assessment. For the assessment of **4Na HEDP** the category approach (OECD category "phosphonic acid compounds group 2") as submitted with the REACH registration dossier was used to extract the toxicity endpoint, as for ecotoxicity. The lowest chronic NOAEL of a sodium salt (disodium etidronate) was considered. The ECHA database was used for **TAED** and **maleic acid** to derive a NOAEL from the registration dossier (subchronic and chronic study, respectively). For **glycerol**, the NOAELs for oral route and inhalation were retrieved from the ECHA database of registered substances, the latter based on local effects in the respiratory tract. For **citric acid**, the NOAEL selected as most reliable endpoint in OECD SIDS file has been taken into account, although reliability of the study has been questioned (Klimisch 4: not assignable). However, no reliable study has been submitted so far to ECHA. The calculation for each chemical is described in the SI (Table A2), providing the value and source of the used endpoint.

3. Results and discussion

3.1. Results

The CFs of the main detergents ingredients are listed in Table 2. For both ecotoxicity and human toxicity, **zinc** shows the highest CF, in particular for human toxicity. However, the characterisation for this metal suffers of high uncertainties, especially linked to the intrinsic limitations of the fate model regarding inorganic substances. The same limitations do apply to **Na-percarbonate**, **STP**, **Na-silicate** and **Na-carbonate**. Considering the newly calculated CFs, the overall impact of the effluent discharge was assessed, covering more than 95% and less than 36% of the effluent composition, for freshwater ecotoxicity and human toxicity respectively. The impact is compared in Fig. 1 to the impact of the entire lifecycle of the detergents, calculated for the three main countries where the detergents are sold (Germany, France and United Kingdom), to account for geographical specificities, e.g. the national electricity mix. Regarding ecotoxicity, the effluent impact represents 50–80% of the total impact and is dominated by the emission of **Na-percarbonate**. **Acrylic acid**, which has been used as proxy for all the polymers, **Na-carbonate, STP, Na-silicate** and **zinc** also show a significant contribution. Because of the uncertainties intrinsic to the USEtox assessment, these results shall be interpreted in the aim of identifying the main impacting substances but not to rank them. When comparing the detergents, the impact of PB tablet effluent is around 40% higher than one of EL and PF, mainly due to **STP** emissions. While **Na-silicate** contributes to increase the impact of EL, **zinc** emission disadvantages the PF's ecotoxicity profile. From the ecotoxicity results, it can be concluded that phosphates removal from the detergent formulation results in a proven environmental benefit. At the opposite, eco-label requirements do not seems to bring clear added value, as the EL effluent has only 5% lower ecotoxicity potential than the PF one. Regarding human toxicity, the effluent impact represents between 5% and 10% of the total impact for PB and PF detergents while the effluent contribution is negligible for EL tablet (less than 0.3%). This is mainly due to the lack of reliable hazard data and to the high CF of **zinc**, which is present in the PB and PF discharge as both formulations include the ingredient zinc diacetate. These results confirm the importance of developing new CFs for specific pollutants, especially for freshwater ecotoxicity.

3.2. Comparison with previous studies

Van Hoof et al. (2011) presented two studies on laundry detergents from the manufacturers Unilever and Procter&Gamble (P&G), including newly developed CFs for freshwater ecotoxicity using USEtox. Seven substances are in common with the present study: five for which new CFs were developed and three for which default USEtox CFs were used. The parameters underlying the calculations and the comparison between the different CFs are presented in the Annex 3 of the SI (Table A3 lists the parameters values and Fig. A3 shows the differences among the calculated CFs). When comparing the CFs from Van Hoof et al. (2011) and the ones calculated in the present study, the range of variation is of one order of magnitude at the most, and many CFs are very close to each other. We can thus conclude that there is a general agreement among the studies. Also, the ranking of the most hazardous substances is quite similar, indicating **glycerol** as the less harmful chemical and **Na-percarbonate**, **Na-silicate**, **Na-carbonate** and **4Na HEDP** as the most hazardous substances. However, as discussed in Van Hoof et al. (2011), the variability of the resulting CFs (which is the highest for **glycerol** and **Na-carbonate**) is related to the sensitivity of the model to the data source and to the practitioner choices. Therefore, the similarity between the values obtained is insufficient to guarantee the reliability of the assessment.

3.3. Sensitivity analysis

Sensitivity analysis was performed on the CF for freshwater ecotoxicity, by varying each of the model parameters at a time. The ecotoxicity effect (avlogEC50) was found to be the most sensitive parameter. The rationale is the direct relation to the CF, while the other parameters, mostly background parameters to calculate the fate/exposure matrix, have eventually an indirect effect. The variation of the CFs is inversely proportional to the avlogEC50 variation and follows the inverse of the function $y = 10\hat{}x$. Regarding the physic-chemical parameters, the calculated CF is mainly

Table 2
CFs of the main substances present in the effluent of the three dishwasher detergents.

Substance	CAS number	CF for ecotoxicity (PAF m^3 d kg^{-1})	CF for human toxicity without carcinogenic effects (cases kg^{-1})	Included in
AE C8-10	71060-57-6	4.05E02[a]	1.28E−07[a]	PB, PF
AE C11	68154-97-2	1.14E04[a]	–	PB, PF
Na-percarbonate	15630-89-4	1.01E03[a]	–	PB, PF, EL
TAED	10543-57-4	1.96E01[a]	2.30E−07[a]	PB, PF, EL
STP	7758-29-4	2.02E02[a]	–	PB
PEG	25322-68-3	8.40E00[a]	–	PB, PF, EL
Na-silicate	1344-09-8	4.05E02[a]	5.17E−07[a]	EL
Na-carbonate	497-19-8	5.11E01[a]	–	PB, PF, EL
4Na HEDP	3794-83-0	9.09E01[a]	2.06E−07[a]	PB, PF
Acry/sulf poly		1.98E02[b, d]	1.47E−07[b, d]	PB, PF, EL
Acry/mal poly	52255-49-9	1.98E02[b, d]	3.03E−7[a, c]	PB
Glycerol	56-81-5	2.13E−01[d]	6.09E−10[a]	EL
Citric acid	77-92-9	2.20E01[d]	2.52E−9[a]	EL, PF
Zinc	7440-66-6	3.86E04[d]	1.28E−3[d]	PB, PF

[a] CF developed by the authors.
[b] Proxy acrylic acid.
[c] Proxy maleic acid.
[d] CF already defined by USEtox.

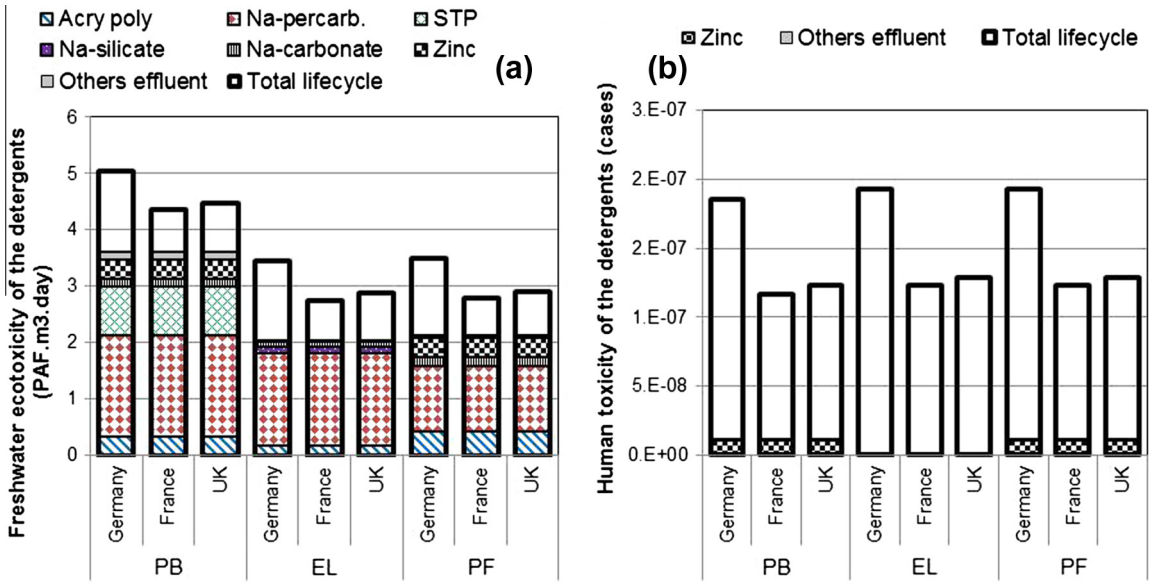

Fig. 1. Impact of the detergent lifecycle and the related effluent discharge on (a) freshwater ecotoxicity and (b) human toxicity (non-carcinogenic effects) for the eco-labelled (EL), phosphate-free (PF) and phosphate-based (PB) products used in France, Germany and United Kingdom (UK).

sensitive to the degradation rate in water (kdegW). This is in accordance with the conclusions from Birkved and Heijungs (2011), who observed that the most important fate pathway is the compartment-specific degradation process in the emission compartment (e.g. degradation in air by emission to air). The CF and kdegW follow opposite trends: the higher the degradation rate, the lower is the persistence of the substance in the environment and the lower is the CF. For the other model inputs, the CF variation is lower than 3% even if the studied parameter is multiplied by 100. This is not the case for the two ethoxylated alcohols, for which significant variations of the CFs are observed also when varying the parameters Kow and Sol25. Indeed, the values of these two parameters for the alcohols are different from the others by several orders of magnitude (due to their relative high bioaccumulation potential), leading to more important changes.

3.4. Limitations affecting the CFs

A first limitation concerns the fate assessment, which is not reliable for inorganic substances because of the missing data and vagueness of the methodology for applicability (as discussed in Van Hoof et al., 2011). In the present study, the fate of inorganic substances was modelled using the parameters of organics, estimated using EPI Suite™. Such approach adds significant uncertainty to the calculation because of the intrinsic limitations of EPI Suite™ and its use outside the domain of validity. Fortunately, as highlighted in Section 3.3, USEtox showed little sensitivity with respect to these physic-chemical parameters and therefore their uncertainty is not likely to have significant repercussions to the impact results.

Concerning the effect assessment, the main obstacle is the availability and suitability of toxicity data, as already discussed in Igos et al. (2012). While chronic EC50 and ED50 values are required by USEtox model, most often only EC50/ED50 based on acute tests are reported. Substances registered under REACH provide, on average, a better data basis. Nevertheless, registrants do not always completely fulfill the data requirements and the studies are often poorly documented, which question the reliability or restricts the data usability. The direct consequence may be a poor representativeness of the assessment (e.g. less than three trophic

levels can be covered) and the need to use extrapolation factors in most of these cases, implying additional uncertainty.

4. Conclusions

This study has provided a comprehensive toxicity impact characterisation of the effluent from three dishwasher detergents, covering around 95% and 36% of the effluent composition, respectively for freshwater ecotoxicity and human toxicity. The contribution of the dishwasher effluent to the overall freshwater ecotoxicity impact of the detergent lifecycle was found to be significant. The main impacting substances identified are **Na-carbonate**, **zinc**, **Na-percarbonate**, **polymers** (for which acrylic and maleic acids used as a proxy), **Na-silicate** and **STP**. The STP is definitively a major contributor to the overall impact of the PB tablet, which is the less performing amongst the compared detergents. This result corroborates the current efforts made by producers to remove the phosphate-based ingredients in the novel formulations and more generally the decision of the European Commission to ban phosphorous as detergent ingredient in all Member States as of January 2017 (European Commission, 2011). Interestingly, the eco-labelled formulation does not present a net advantage as compared to the phosphate-free product. This result is important for the producer's strategy as it shows that the effort to be undertaken to comply to the eco-label requirements do not seems to pay off considered the superior environmental and technical performances of the PF tablet.

Despite the interest and pertinence of the development of novel CFs, several limitations affecting the USEtox approach were stressed. The main points to be considered for correct interpretation of the results are the intrinsic limitations of the fate model for inorganic compounds and the use of extrapolation factors for effect endpoints due to the mismatch between the data available under REACH and the ones required by USEtox. However, as LCA it is preferable to use uncertain CFs than to exclude *a priori* substances from characterisation, the approach adopted seems to be fully justified. The comparison of the CFs for freshwater ecotoxicity calculated in this study with the ones published in literature showed that USEtox is quite stable. The most sensitive parameter is the effect factor based on EC50 values. This result shows the importance of choosing the most relevant endpoints and the possible role that REACH could play to this aim, especially after 2014 when the next large set of data will become available. Beyond the need for additional data, the harmonisation between the experimental data as provided under REACH and the data required for toxicity assessment in LCA shall be further researched.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.11.041.

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Development of USEtox characterization factors for dishwasher detergents using data made available under REACH

Elorri Igos[1*], Ruth Moeller[1], Enrico Benetto[1], Arno Biwer[1], Mélanie Guiton[1], Philippe Dieumegard[2]

[1]Public Research Centre Henri Tudor (CRPHT) / Resource Centre for Environmental Technologies (CRTE) – 6A, avenue des Hauts-Fourneaux – L-4362 Esch-sur-Alzette, Luxembourg

[2]Chemolux / McBride Group – Rue de l'Industrie, L-3895 Foetz, Luxembourg

*Corresponding author: elorri.igos@tudor.lu, +352 42 59 91 - 3351

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Annex 1: Ecotoxicity data

Table A1: Ecotoxicity data used for the effect assessment of the studied substances

Substance						AE C11
avlogEC50						-0.723
Number of species						3
Trophic levels covered						3
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
unknown	*Fish*	Fish	96h	0.344	Acute	EPI Suite™
unknown	*Daphnid*	Invertebrate	48h	0.301	Acute	EPI Suite™
unknown	*Green algae*	Algae	96h	0.522	Acute	EPI Suite™
Substance						AE C8-10
avlogEC50						0.731
Number of species						11
Trophic levels covered						3
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
2	*Sleletonema costatum*	Algae	72 h	43.72	Acute	HERA (2009b)
2	*Scenedesmus subspicatus*	Algae	72 h	14	Acute	HERA (2009b)
2	*Scenedesmus subspicatus*	Algae	72 h	45	Acute	HERA (2009b)
2	*Selenastrum capricornutum*	Algae	72 h	2.7	Acute	HERA (2009b)
2	*Selenastrum capricornutum*	Algae	72 h	1.4	Acute	HERA (2009b)
2	*Selenastrum capricornutum*	Algae	72 h	47	Acute	HERA (2009b)
4	*Hyalella azteca*	Invertebrate	10 d	14	Acute	HERA (2009b)
4	*Chironomus tentans*	Invertebrate	10 d	5.7	Acute	HERA (2009b)
4	*Mysidopsis bahia*	Invertebrate	48 h	5.6	Acute	HERA (2009b)
4	*Daphnia magna*	Invertebrate	24 h	71	Acute	HERA (2009b)
2	*Acartia tonsa*	Invertebrate	48 h	17.2	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	3.85	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	8.5	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	2.5	Acute	HERA (2009b)
2	*Crangon crangon*	Invertebrate	96 h	9.9	Acute	HERA (2009b)
4	*Daphnia magna*	Invertebrate	48 h	5.1	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	5.3	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	96 h	17	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	12	Acute	HERA (2009b)
1	*Daphnia magna*	Invertebrate	48 h	9	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	0.7	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	13.4	Acute	HERA (2009b)
2	*Daphnia magna*	Invertebrate	48 h	13.4	Acute	HERA (2009b)

4	*Zebra fish*	Fish	96 h	38	Acute	HERA (2009b)
2	*Pimephales promelas*	Fish	96 h	1.8	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	8	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	6	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	4.2	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	7.5	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	11.5	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	8.5	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	23.7	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	12	Acute	HERA (2009b)
2	*Salmo gairdneri*	Fish	96 h	20.9	Acute	HERA (2009b)
Substance						Na-percarbonate
avlogEC50						0.969
Number of species						2
Trophic levels covered						2
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
1	*Daphnia pulex*	Invertebrate	48 h	4.9	Acute	ECHA (1989)
2	*Pimephales promelas*	Fish	96 h	70.7	Acute	ECHA (1989)
Substance						TAED
avlogEC50						3.000
Number of species						1
Trophic levels covered						1
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
1	*Daphnia magna*	Invertebrate	21d	1000	Chronic	ECHA (2008)
Substance						STP
avlogEC50						1.988
Number of species						5
Trophic levels covered						3
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
2	*Danio rerio*	Fish	96 h	10	Chronic	ECHA (Sinha and Kanamadi,2000)
4	*Cladoceran dubia*	Invertebrate	48 h	276.61	Acute	ECHA (Warne and Schifko, 1999)
3	*Ceriodaphnia dubia*	Invertebrate	24 h	290.2	Acute	ECHA (2004)
3	*Daphnia magna*	Invertebrate	50h	1089	Acute	IUCLID (Huber, 1987)
2	*Desmodesmus subspicatus*	Algae	96 h	160	Acute	ECHA (1985)
Substance						PEG
avlogEC50						3.048
Number of species						2

Trophic levels covered						1
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
unknown	*Carassius auratus*	Fish	24 h	5000	Acute	PAN (Bridie et al., 1979)
unknown	*Salmo salar*	Fish	96 h	1000	Acute	PAN (Wildish, 1974)
Substance						Na-silicate
avlogEC50						2.249
Number of species						7
Trophic levels covered						3
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
2	*Oncorhynchus mykiss*	Fish	96 h	285	Acute	ECHA (Maruyama et al., 1989)
1	*Danio rerio*	Fish	96 h	1108	Acute	ECHA (1988)
2	*Danio rerio*	Fish	96 h	210	Acute	OECD SIDS (Richterich and Mühlberg, 2001)
4	*Lepomis macrochirus*	Fish	96 h	389.5	Acute	ECHA (1991)
2	*Daphnia magna*	Invertebrate	48 h	1700	Acute	ECHA (1997)
4	*Daphnia magna*	Invertebrate	96 h	231.5	Acute	ECHA (Dowden and Bennett, 1965)
2	*Lymnaea sp. eggs*	Invertebrate	96 h	632	Acute	ECHA (Dowden and Bennett, 1965)
2	*Hyallela sp.*	Invertebrate	96 h	160	Acute	ECHA (Dowden and Bennett, 1965)
2	*Desmodesmus subspicatus*	Algae	72 h	207	Acute	ECHA (1995)
Substance						Na-carbonate
avlogEC50						2.265
Number of species						8
Trophic levels covered						3
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
2	*Lepomis macrochirus*	Fish	96 h	300	Acute	ECHA (Cairns and Scheier, 1959)
2	*Gambusia affinis*	Fish	96 h	740	Acute	ECHA (Wallen et al., 1957)
4	*Mollienesia latipinna*	Fish	96 h	297	Acute	ECHA (Dowden and Bennett, 1965)
4	*Lepomis macrochirus*	Fish	96 h	385	Acute	ECHA (Dowden and Bennett, 1965)

2	*Ceriodaphnia sp.*	Invertebrate	48 h	213.5	Acute	ECHA (Warne and Schifko, 1999)
4	*Daphnia magna*	Invertebrate	48 h	265	Acute	ECHA (Dowden and Bennett, 1965)
4	*Dugesia sp.*	Invertebrate	48 h	360	Acute	ECHA (Dowden and Bennett, 1965)
4	*Culex sp.*	Invertebrate	48 h	600	Acute	ECHA (Dowden and Bennett, 1965)
4	*Nitzschia sp.*	Algae	120 h	242	Chronic	IUCLID (Patrick et al., 1968)
Substance						4Na HEDP
avlogEC50						2.014
Number of species						2
Trophic levels covered						1
Reliability	**Species**	**Trophic level**	**Duration**	**EC50 (mg/L)**	**Type**	**Source**
2	*Daphnia magna*	Invertebrate	48 h	527	Acute	ECHA (1981)
2	*Crassostrea virginica*	Invertebrate	96h	81	Acute	ECHA (1977)

Annex 2: Human toxicity data

Table A2: Toxicity data for the effect assessment of the studied substances

Substance	NOAEL ingestion (mg/kg bw/day)	NOAEL inhalation (mg/m^3)	Exposure time	Tested animal	Source	Calculated ED50 (kg/person/ lifetime)
AE C8-10	50		Chronic	Rat	HERA (2009b)	196.3
TAED	90		Subchronic	Rat	ECHA (1987)	176.7
Na-silicate	260		Subchronic	Mouse	ECHA/OECD SIDS (Sawai et al. 1980)	286.7
4Na HEDP	24		Chronic	Rat	ECHA/OECD SIDS (1979)	94.22
Maleic acid	10		Chronic	Rat	ECHA (1983)	39.26
Glycerol	10000		Subchronic	Rat	ECHA/OECD SIDS (Hine, 1953)	19630
Glycerol		167	Subchronic	Rat	ECHA/OECD SIDS (Renne, 1992)	60.88
Citric acid	1200		Chronic	Rat	OECD SIDS (Horn et al, 1957)	4711

For the NOAEL measured for the inhalation route expressed in mg/m^3, the body weight factor BW in the formula of paragraph 2.5 of the manuscript is replaced by the average human inhalation rate defined by USEtox (16 m^3/day).

Annex 3: Comparison of the studies

Table A3: Comparison of the calculation of CF for freshwater ecotoxicity performed by Unilever, Procter&Gamble P&G (Van Hoof et al., 2011) and Chemolux-McBride. A star refers to default values from USEtox.

Name	CAS number	Study	MW (g/mol)	Kow (-)	Pvap25 (Pa)	Sol25 (mg/L)	KdegA (s^{-1})	KdegW (s^{-1})	KdegSd (s^{-1})	KdegSl (s^{-1})	avlogEC50 (mg/L)	CF (PAF.m3.day/kg)
Citric acid	77-92-9	Unilever	258	2.29E-02	4.90E-08	5.92E+07	3.51E-06	9.30E-07	1.03E-07	4.65E-07	2.17	3.87E+01
		P&G*	192	2.29E-02	2.21E-06	5.92E+05	5.27E-06	9.25E-07	1.03E-07	4.63E-07	2.42	2.20E+01
		Chemolux*	192	2.29E-02	2.21E-06	5.92E+05	5.27E-06	9.25E-07	1.03E-07	4.63E-07	2.42	2.20E+01
Glycerine (or glycerol)	56-81-5	Unilever	92	1.74E-02	2.24E-02	1.00E+06	2.81E-05	9.30E-07	1.03E-07	4.65E-07	3.70	1.14E+00
		P&G	92	1.07E-02	2.20E-02	1.00E+06	2.81E-05	5.37E-07	2.67E-06	2.67E-07	3.60	2.30E+00
		Chemolux*	92	1.74E-02	2.24E-02	1.00E+06	1.41E-05	9.25E-07	1.03E-07	4.63E-07	4.43	2.13E-01
Na-carbonate	497-19-8	Unilever	106	6.46E-07	1.32E-14	2.15E+05	1.00E-20	1.00E-20	1.00E-20	1.00E-20	2.22	4.37E+02
		P&G	106	6.46E-07	6.56E-05	2.20E+05	1.00E-20	1.00E-20	1.00E-20	1.00E-20	2.10	8.50E+02
		Chemolux	106	6.46E-07	1.32E-14	2.15E+05	1.93E-09	5.35E-07	5.94E-08	2.67E-07	1.99	5.11E+01
Na-percarbonate	15630-89-4	Unilever	314	6.46E-07	1.32E-14	1.30E+05	8.02E-06	1.60E-06	1.60E-05	1.60E-05	1.20	2.15E+02
		P&G	314	1.00E-01	1.00E-20	1.40E+05	1.00E-20	1.00E-20	1.00E-20	1.00E-20	2.43	2.60E+02
		Chemolux	314	6.46E-07	1.32E-14	1.40E+05	1.93E-09	5.35E-07	5.94E-08	2.67E-07	0.97	1.01E+03
Na-silicate	1344-09-8	Unilever	122	1.00E-20	1.00E-20	2.10E+05	1.00E-20	1.00E-20	1.00E-20	1.00E-20	2.21	4.42E+02
		P&G	184	1.00E-20	1.00E-20	2.10E+05	1.00E-20	1.00E-20	1.00E-20	1.00E-20	2.36	3.10E+02
		Chemolux	184	1.00E-01	1.00E-20	2.10E+05	1.00E-20	1.00E-20	1.00E-20	1.00E-20	2.30	3.59E+02
TAED	10543-57-4	Unilever	228	4.37E-03	1.97E-06	1.57E+05	5.97E-05	8.91E-07	4.46E-07	4.46E-07	2.67	1.26E+01
		P&G	228	1.58E-01	1.97E-06	1.50E+03	2.98E-05	1.27E-06	2.38E-08	1.07E-07	2.43	1.60E+01
		Chemolux	228	1.58E-01	1.97E-06	1.50E+03	2.99E-05	2.14E-07	2.38E-08	1.07E-07	3.00	1.96E+01
4Na HEDP	3794-83-0	Unilever	294	5.25E-13	7.72E-11	1.00E+06	2.92E-04	2.03E-08	5.83E-08	1.78E-07	2.30	2.85E+02
		Chemolux	294	5.25E-13	7.72E-11	1.00E+06	1.46E-04	5.35E-07	5.94E-08	2.70E-07	2.01	9.09E+01

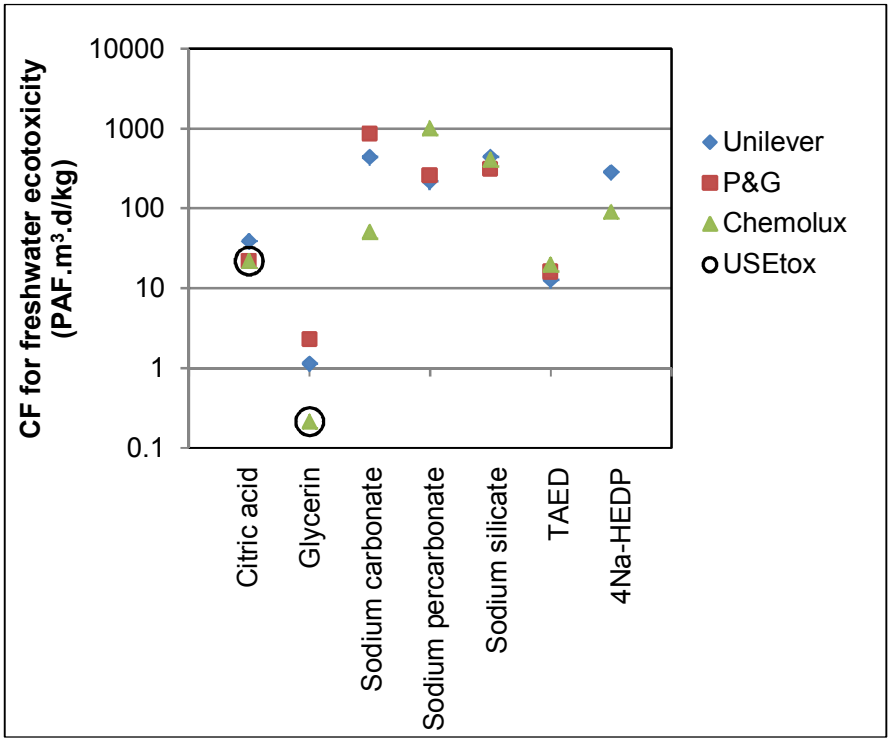

Figure A3: Comparison of the CFs for freshwater ecotoxicity obtained from the different studies: Unilever, P&G (Van Hoof et al., 2011) and Chemolux (the present study). Values which have been taken from USEtox are encircled in black.

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6. SYNTHESIS

The continuous improvement of the wastewater management systems is necessary to adapt to society behaviours and to mitigate water pollution. Technological solutions need however to comply with sustainable development, since the first aim of WWTP is to preserve the environment. LCA methodology fits to this objective by providing a holistic and comprehensive evaluation of the environmental impacts of systems along their life cycle. The main part of this research work consisted in performing a comparative LCA study of advanced treatment solutions for pharmaceuticals removal. The outcomes aimed at supporting decisions regarding their design (UV technology configuration types), the choice of the treatment step (comparison of ozonation, UV and activated carbon) and their implementation policy (centralized or decentralized treatment).

The assessment approach followed by previous authors based on net impacts calculation seemed very promising to consider the environmental benefits obtained from pollutants elimination and compare solutions in a consistent manner. The methodology from literature, normalization of net impacts calculated from EDIP method, was therefore applied to compare UV treatment options. For the sake of better representativeness, human toxicity potential was also considered for the avoided impacts characterization, while previous studies only included ecotoxicity indicator (Hoibye et al, 2008; Hospido et al, 2010; Larsen et al, 2010). This first assessment aimed at identifying hotspots and potential limitations of the LCA common practice. Regarding UV design, LCA outcomes were consistent with the cost-benefit analysis based on degradation kinetics: low pressure lamps represented the best configuration (high removal rates and low energy consumption). However, the improvement factor was lower with LCA assessment. This quite simple evaluation showed the added value of LCA in process development but highlighted also the difficulty to obtain good quality data, both for operation inventory and (eco)toxicity characterization (in particular toxic endpoints to calculate PNEC values). Also in this study, only pharmaceuticals were taken into account for the avoided impacts, which induced positive net impacts (i.e. wastewater treatment would not be beneficial for the environment!). Additional compounds (as well as impact categories such as eutrophication) need to be considered for the treatment benefits to get a more representative picture of the system environmental profile. Also, to fully support decisions for the eco-design of UV irradiation, an economic criterion should be included since it is a major argument for stakeholders to favour a specific configuration type.

For the comparison of advanced technologies and policy scenarios, a deeper environmental analysis was made. The common practice (net impacts based on EDIP method) was compared to other assessments, in particular to better consider elimination benefits. First, USEtox consensus was applied for the avoided impacts characterization (freshwater ecotoxicity and human toxicity), in combination with the more recent method ReCiPe for generated impacts. As for the previous assessment, environmental impacts were normalized in person-equivalent (which needed to be calculated for USEtox categories). Then, an eco-efficiency indicator was developed to weigh the treatment efforts (generated impacts based on EDIP and ReCiPe methods) by the average removal efficiency. In total, the same scenarios were compared with four types of assessment.

Regarding the choice of treatment process at the decentralized plant in hospital, all the outcomes showed ozonation and activated carbon as the preferred options (no significant differences between the two, in particular due to electricity consumption variability for ozonation treatment). Even with similar removal efficiencies, UV irradiation treatment was penalised by hydrogen peroxide consumption. The differences between policy scenarios was much less clear with slight advantage of the upgraded centralized plant, except for the assessment based on the net impacts with ReCiPe and USEtox (slight preference for CC scenario). Regarding pharmaceutical elimination, a significant increase of efficiency was observed with advanced treatment: measured rates were mostly higher than 90% while conventional treatment only removes efficiently paracetamol. On one hand, significant improvements of sewer system efficiency were observed for pharmaceuticals such as cyclophosphamide and lidocaine. On the other hand, some substances were not mainly consumed in hospitals (domestic use of atenolol, paracetamol or trimethoprim), therefore limiting the added value of source-separated treatment. Furthermore, the high variability of performances among pharmaceuticals for conventional treatment made the comparison not conclusive between CC and CC+D scenarios. After LCIA characterization for net impact assessment, the contribution of pharmaceuticals impacts was found negligible except when evaluating post-treatment with EDIP method. For the other assessments, phosphorous removal was largely dominated the avoided score (decrease of eutrophication effects). The increased generated impacts due to the installation of advanced treatment (especially for decentralized plants) also contributed to the lack of overall environmental advantages of the CC+D or UC systems. These outcomes from the four assessments are however not sufficient to conclude that advanced treatment is not necessary from an environmental perspective in current wastewater systems. The reasons are that very similar results were obtained between policy scenarios (less than 3% for net impact assessments), a small number of pharmaceuticals were considered (10 substances) and significant uncertainties were embedded in the LCA models.

Indeed, a significant part of this research work was dedicated to the discussion of uncertainty and limitations of the LCA outcomes. First, at the inventory level, technology operational data were treated by considering minimum and maximum values collected from PILLS partners. Some parameters were observed highly variable such as hydrogen peroxide consumption with a variation of three orders of magnitude. Unfortunately, the lack of data points (maximum three values collected from partners) did not allow the advanced characterization of inventory uncertainty, e.g. via probability distribution. The implementation of uncertainty distribution for the inventory could have been considered in the calculation of the confidence interval of the EFI indicator (instead of being based only on elimination efficiency variability between compounds). Regarding the WWTP operation, the ecoinvent tool (Doka, 2007) allowed calculating inventory data based on different influent quality. However, it can be argued that the modelling remains quite simple (e.g. default process chain cannot be changed) and based on Swiss data. The retrieved removal rates for pharmaceuticals also highlighted the difficulty of considering all interaction effects between pharmaceuticals. Indeed, negative numbers were obtained which gave evidence of reactions between compounds (leading to formation of transformed products or metabolites). A large number of substances should be monitored to

understand all these mechanisms. For sake of simplicity, the removal rate for these pharmaceuticals was set to zero.

Despite the embedded uncertainties, the assessments were based on transparent foreground data (influent quality, removal rates and consumption data) to ensure reliability and replicability of the study. Also, to cope with operational data variability, sensitivity analysis was performed by testing different values (from literature and partners measurements) of pharmaceuticals removal rates, post-ozonation treatment operation in WWTP and wastewater volume from hospitals. This recommended practice in LCA is used to check the validity of the outcomes in relation with inputs uncertainties. The results for net impacts (both for EDIP and ReCiPe + USEtox characterization) showed that the ranking of scenarios was not affected by the parameters variations. Indeed, the environmental profiles are largely driven by phosphorous avoided impacts and therefore not sensitive to other inputs. This outcome could question the relevance of normalization, and in more general impact indicators aggregation, in LCA. For example, with ReCiPe + USEtox calculation, the pharmaceuticals impacts were found even smaller than with EDIP because the ecotoxicity normalization factor includes emissions to soil, not taken into account in EDIP method. The ecotoxicity impact per person equivalent was therefore higher leading to lower net impact score. With normalization step, decision makers loose this information but easily interpret the results. This debate on aggregation trade-off is still ongoing in LCA community: Kägi et al (2016) and Kim et al (2012) highlighted the importance of the references (geographical and temporal delimitation) used for normalization.

The second investigation focus of this research work was done on toxicity assessment. Within the assessment of pharmaceutical treatment solutions, new CFs were developed using EDIP and USEtox methods. With the first one, a limited number of inputs were required and a conservative approach was followed, using the highest CF obtained, therefore based on the lowest PNEC derived from different toxicity endpoints (collected from Wikipharma database[5], ChemID plus Advance database[6] and ECOSAR model from EPI Suite™[7]). The sensitivity analysis on PNEC value revealed very high variations on the calculated CF (up to six orders of magnitude). In order to check their validity, CFs values were also compared with previous literature (Muñoz et al, 2008; Larsen et al, 2010) in a transparent way (detailed data and source for each substance). Some differences were identified because of different endpoints chosen to derive PNEC value. This could be partly explained by an updated list of toxicity tests, with more sensitive species. Therefore, most of the generated CFs within this work were found higher (lower PNEC calculated) than literature. This high sensitivity is in accordance with findings from Hoibye et al (2008), Wenzel et al (2008), Muñoz et al (2008) and Larsen et al (2010). The use of geometric mean of EC50 endpoints in USEtox method can tackle this effect because the CF can remain more stable if updated toxicity tests are available. However, one can argue that the approach is less conservative.

With both (eco)toxicity impact characterization, several limitations were underlined related to the use of toxicity tests. First, these latter are not always representative of the panel of

[5] http://www.wikipharma.org/api_data.asp
[6] http://chem.sis.nlm.nih.gov/chemidplus/chemidheavy
[7] http://www.epa.gov/opptintr/exposure/pubs/episuite.htm

potential effects. Indeed, high substance concentration is often applied while long-term low-level exposure acting on the physiological control systems (central nervous system, hormones, reproductive system, immune system and genes) is addressed to a limited extent. Also, specific effects such as endocrine disrupting or bacteria resistance (observed for antibiotics such as ciprofloxacin and clarithromycin) are barely reflected. Then, the lack of compatible data, in particular endpoints from chronic exposure tests (both for ecotoxicity and human toxicity), raises the issue of extrapolation from acute to chronic scenario (not recommended from a toxicological point of view). Also, the information found in database is also not always transparent, which can question their reliability and relevance. Finally, the allometric factor used in USEtox to extrapolate animal toxicity data to human value does not consider differences between species (e.g. metabolism). These uncertainties of (eco)toxicity assessment were already discussed in the published LCAs which included pharmaceuticals impacts (Hoibye et al, 2008; Wenzel et al, 2008; Muñoz et al, 2008; Larsen et al, 2010) and in general in the LCA field (Geisler et al, 2005; Larsen & Hauschild, 2007).

The last part of this research work tackled some of the above mentioned barriers by relying on data made available under REACH regulation. The idea was to use official European information in order to limit uncertainties of toxicity parameters. Ecotoxicity and human toxicity CFs were developed based on USEtox method for 13 detergent ingredients (among which ecotoxicity CFs were already available for two substances) to compare the dishwasher effluent impacts using three types of detergents. Similar limitations than for pharmaceuticals characterization were observed because of the limited number of registered substances (six ingredients out of 13) and because of the mismatch of required information between REACH regulation and USEtox. Despite the regulatory framework, registrants not always fulfil data requirements. These limiting factors led to poor representativeness of toxicity endpoints (e.g. three out of 67 based on chronic tests, about 50% testing standard species from USEtox and the three trophic levels could not be covered for four substances even if three of them were registered) and the use of extrapolation factors. The (eco)toxicity characterization was however refined by excluding test with a Klimisch-score of 3 (not reliable) and by cross-checking data from ECHA portal with other databases: HERA reports, eChem Portal[8], PAN Pesticide Database[9] and ChemIDplus. Predicted values from ECOSAR model were only used if no other data source could be found (ecotoxicity of alcohols C11 ethoxylated, propoxylated). Indeed, this approach is based on linear regression from the partitioning coefficient octanol-water after chemical classification. Related results are very uncertain.

Regarding the fate assessment, parameters could be retrieved from HERA reports and EPI Suite™. However, four ingredients were inorganic substances for which USEtox shows a limited applicability (until now only metallic compounds are included in USEtox with "interim" status). Required parameters were missing and thus uncertain assumptions were made: use of EPI Suite™ model outside the validity domain or values set to zero such as in Van Hoof et al (2011). Significant uncertainties are therefore related to the CF of inorganic compounds and the methodology applicability remains vague even after discussions with USEtox developers.

[8] http://www.echemportal.org/echemportal/propertysearch/page.action?pageID=0
[9] http://www.pesticideinfo.org

When applying the developed CFs to the effluents composition (based on producer measurements and WWTP removal efficiency from literature and HERA reports), the contribution of effluent impacts to product lifecycle was found significant for ecotoxicity (50% to 80%) but minor for human toxicity (5% to 10% for phosphate-based and phosphate-free formulations and less than 0.3% for ecolabel tablet which does not contain zinc). The first result proved the usefulness of investigating the effects of detergent ingredients when released into water (and therefore generating new CFs). The human toxicity outcome could be partly explained by the lack of CFs for this indicator. Among the 13 studied substances, only seven CFs could be developed due to lack of data for the others, resulting in a coverage of 36% of effluent composition. For ecotoxicity, the main impacting substances could be identified however, results were too uncertain to rank them. The outcomes showed a major advantage of removing pentasodium triphosphate in detergent formulation which is in accordance with European Commission ban of phosphate (European Commission, 2011b).

In order to check the reliability of the CFs, a comparative assessment was performed with the results from Van Hoof et al (2011). Differences of ecotoxicity CFs for seven common substances were found reasonable, with one order of magnitude at the most and very similar values for several compounds. The variability was explained by factor sensitivity to data source and practitioner choice. The similarity between results does not however guarantee their reliability. The second step consisted into a sensitivity analysis, i.e. varying each parameter of USEtox one-at-the-time within a defined range. The ecotoxcitiy factor was mostly sensitive to the ecotoxicity effect factor (inversely proportional), while physic-chemical parameters were much less influencing, except for the degradation rate in water (in accordance with Birkved and Heijungs, 2011), as well as the partitioning coefficient octanol-water and the solubility for the ethoxylated alcohols (specifically high values for these substances).

This study showed that efforts are still needed in developing (eco)toxicity modelling in LCA. This is why all the sources for each parameter were provided and data for ecotoxicity and human toxicity endpoints were detailed in supporting information, for future use. Even if uncertainties are still large, it was concluded that it is better to have uncertain CFs that no characterization at all. Also, the mismatch between REACH and USEtox data raised the question of a potential harmonisation between these two communities.

To conclude, this research work showed the interest and potential barriers of LCA methodology to steer decision for wastewater management. The further decision process needs however other criteria to get a complete sustainability picture of advanced treatment implementation for pharmaceuticals removal. Indeed, LCA shows only part of the problem and local analysis (risk assessment, bacterial resistance, etc.) needs to be performed. All the performance indicators (e.g. local risk, environmental, economic and social impacts) could be then integrated in a multicriteria decision approach.

7. PERSPECTIVES

The use of net impacts represents a consistent approach to easily compare wastewater treatment solutions. Avoided impacts need nevertheless to be better characterized, by including as many pollutants as possible and by improving the (eco)toxicity assessment. Regarding the latter point, the presented work tried to reduce uncertainties by using data made available under REACH regulation. Better data quality was implemented but only in a limited extent due to lack of available information. Therefore, this approach is not sufficient to guarantee the reliability of the (eco)toxicity characterization but USEtox method is continuously improving (last version 2.01 released in February 2016) and more representative models can be expected in the future.

The proposed EFI indicator can avoid the issue related to (eco)toxicity characterization but pollutants are treated with the same weight, which can be questionable. The principle could be further developed to weigh the environmental impacts generated with LCA assessment by the technical performances of the studied system. In the present work and in Igos et al (2013), these latter corresponded to the improvement of water quality, but performances could also reflect the improvement of materials properties, of consumer comfort, etc. LCA methodology is sometimes criticized because it focuses on negative impacts. With the declination of EFI approach, the benefits of the product or process could be better represented in the results and the consideration of standard deviation also supports unbiased comparisons.

The interest of this work also consisted in comparing the same scenarios with four different approaches. These assessments showed similar conclusions regarding the technological and policy choice for pharmaceuticals elimination from wastewater. However, the outcomes should be less uncertain to really support stakeholders in their decision process. Even if this LCA study was not conclusive, this work made available data, both for treatment technologies inventory (consumption and efficiency) and for (eco)toxicity characterization (pharmaceuticals and detergents compounds), which could be reused in the LCA community for further analysis. It is very important to ensure the transparency of LCA studies because this methodology is based on many assumptions (definition of system boundaries, modelling of background processes, etc.) which can be easily manipulated to obtain the desired conclusions. LCA methodology awareness is increasing, for example by being required to support the development of innovative technologies in H2020 calls defined by the European Commission[10]. Scholars need therefore to invest efforts to make sure the related results are trustful and well interpreted.

In order to really progress through a more sustainable management of wastewater systems, two perspectives are further discussed here. First, LCA methodology needs to be improved to provide reliable outcomes to decision makers regarding the choice of technology and policy. Then, new management strategy should be thought with a circular economy approach in order limit pollution and valorise waste.

[10] https://ec.europa.eu/programmes/horizon2020/

7.1. Increasing LCA methodology reliability to better support decisions

This research work mainly focused on three methodological issues to improve LCA results reliability: definition of the functional unit, LCIA modelling and management of data quality and uncertainty.

With the complexity of certain product or process systems, as well as the enlargement of the LCA scope, the definition of functional unit becomes more and more difficult to consistently compare scenarios. For the LCA of wastewater systems, it was observed that the common practice of "the treatment of 1 m^3 of wastewater" was not sufficient to include the treatment properties (influent quality and removal efficiency). However, it was possible to consider these latter within the results by calculating the net impacts (generated minus avoided) or the defined eco-efficiency indicator. In this way, the properties of the system are not considered as usual in the functional unit definition but in the formulation of the environmental indicator. Maybe the vagueness of the functional unit is necessary to facilitate the comparison of alternatives. It could be the case for example for territorial of organizational LCA studies, which are spreading out. "Product properties" correspond here to a complex provision of services and products, which are translated with difficulty into a function. It could be therefore easier to consider these system outputs in a weighted performance score (e.g. in financial or social welfare terms), similarly to EFI indicator. Territories or organizations (or one of this system at different periods) could be compared even if they do not provide exactly the same panel of functions. In any cases, the performances specificities of the system should be considered in the LCA model in order to avoid the communication of inequitable results to decision makers.

Ecotoxicity and human toxicity characterization was found very uncertain, which can bias the outcomes of a LCA study. According to the ILCD handbook (European Commission, 2011a), many other categories need also improvement to better reflect environmental effects, such as ionising radiation, photochemical ozone formation, acidification, eutrophication, land use or resources depletion. LCA practitioners most often use the related LCIA methods "as is", without taking the time to confront results from different methods. Within this study, two LCIA characterizations were compared and sensitivity analysis was performed to analyse the influence of (eco)toxicity evaluation parameters on the final results. This was possible thanks to the transparency of the methods (through user manual and Excel tool). However, LCIA developers rarely propose such tools to the practitioners, limiting the generation of new CFs and the in-depth analysis of results.

Also, as highlighted in this research work, the reliability of LCIA models could increase with their spatialisation. Many efforts are currently investigated in this field for categories sensitive to local specificities, such as water stress (Pfister et al, 2009), toxicity (Kounina et al, 2014), eutrophication (Azevedo et al, 2013), acidification (Roy et al (2014) or land use (Saad et al, 2011). Maps or tables of CFs are generated at different scales, from half-degree cell to region or country, or for archetypes considering local parameters such as precipitation level, soil properties or population density. The LCA practitioner can therefore apply the factor specific to the location of the study. If this approach seems feasible to get more reliable results for the foreground system, it seems much more complicated for background processes because of

inadequacy with inventory precision. Besides the lack of regionalised data for the inventory, the refinement of the geographical dimension of LCIA methods can also lead to an additional variability in LCA, which might confuse decision makers. As highlighted by Mutel et al (2012), methods developer should define the appropriate scale, satisfying the trade-off between applicability and accuracy. Similar trends are observed for the consideration of temporal aspects in LCIA models.

The quality of data is of major importance in LCA methodology. The case studies on wastewater treatment for pharmaceuticals elimination showed that it could be challenging to collect inventory data for technologies, in particular when they are in development phase. To tackle this issue, minimum and maximum scenarios were considered and sensitivity analysis was performed. These types of uncertainty treatment remain quite basic and many LCA scholars (e.g. in Geisler et al, 2005; Heijungs & Lenzen, 2014; Tan, 2008; Clavreul et al, 2013; de Koning et al; 2010) are currently focusing on more advanced techniques to propagate uncertainty in LCA models (via uncertainty analysis) and understand its effects on results (via sensitivity analysis). The first step is the characterization of uncertainty, via intervals or probability distribution. Again, the LCA practitioner can face the issue of data availability. The definition of probability distribution based on data quality via Pedigree matrix (used by ecoinvent database, Frischknecht et al., 2007) can cope with this problem. Unfortunately, this technique is not very spread even if some LCA software tools recently included a functionality to facilitate this characterization.

Uncertainty analysis can rely on sampling methods such as Monte Carlo or Latin Hypercube, analytical methods (Taylor series expansion) or fuzzy approach. The outcomes define the uncertainty of the results. If the LCIA models would allow it, it could be possible to also propagate uncertainties from LCIA models. Even if communicating uncertainty can represent a barrier for decision makers, it should be a common practice to ensure scientifically-based results and reliable comparisons. Regarding sensitivity analysis, global approaches (variance decomposition based on analytical approach, Sobol or Fourier series) aim at exploring the uncertainty ranges of inputs to determine their contribution to results uncertainty. Also, the analysis of interaction effects between variables allows a better understanding of LCA models and therefore a better interpretation. Uncertainty and sensitivity analyses contribute to the iterative procedure of LCA methodology. If results are not conclusive due to high uncertainty ranges of results, sensitivity analysis can identify the main responsible parameters, for the practitioner to further refine them. The cited advanced approaches are however barely implemented in LCA software tools, limiting their application, besides the required effort in terms of data collection.

7.2. Implementing circularity for resources management

At the beginning of this research work, the technological challenge of WWTP to face new types of pollution was highlighted. Wastewater systems play a key role in mitigating impacts on ecosystems and humans. Innovation in this field should therefore always keep this sustainability advantage (environmental benefits higher than required efforts). Circular

economy approach seems very promising to develop new technologies with limited impacts (re-use of waste) and high added value (generation of co-products). It is also compliant with life-cycle thinking from LCA methodology, as far as the recycling efforts are lower than the related benefits.

Regarding the presence of pharmaceuticals in wastewater, it will not be possible to recover the substances into a valuable form. However, looking at the pharmaceutical cycle, efforts could be undertaken towards more reasonable consumption and more eco-friendly disposal route. The European project noPILLS (http://www.no-pills.eu), follow-up of PILLS project, aimed at identifying these potential "levers for intervention" towards the reduction of pharmaceutical ingress into the aquatic environment. In particular, the project conclusions showed the need of society engagement at different levels (patients, physicians, distribution channel and pharmaceutical industry) to limit the over-use of medication and the potential implementation of measures for source segregation at hospitals (e.g. urine collection bags in specific departments for incineration).

The decentralization of wastewater treatment at source shows benefits to increase removal efficiency (thanks to the concentration of pollutants) but scaling effects can disadvantage this management, e.g. regarding energy efficiency or economic costs. The implementation of decentralized plant should therefore be investigated on a case-to-case basis and supported by sustainability indicators. Several research works (e.g. Hamburg Water Cycle®) focus in particular on the separate treatment of blackwater (from toilets), greywater (other household flows, e.g. shower, sinks, washing machine, etc.) and rainwater. Blackwater contains high concentration of organic compounds, which can be valorised through the production of fertilising material or of energy. This development corresponds to the circular economy approach, where waste becomes valuable product. The results of section 3 showed the important environmental contribution of nutrients removal in wastewater treatment profile, in particular phosphorous elimination. The recovery of this compound, for example in the form of struvite from urine treatment (e.g. Lind et al, 2000; Wilsenach et al, 2007; Tilley et al, 2008), would represent significant benefits, both for reducing eutrophication effects in water bodies and for limiting the production of chemical fertilizers, considering that phosphorous is a non-renewable resource.

This transition to circular economy needs to be supported by policy makers. Recent actions are very encouraging, in particular with the Circular Economy Package adopted by the European Commission in December 2015 and including the revision of legislative proposals on waste to promote recycling and mitigate pollution. The deployment of the related action plan should encourage innovation for the development of sustainable supply chains. Also, as observed in section 5, the ban of phosphate in detergent formulations proposed by the European Commission (2011b) was proven to lead to significant environmental benefits. This type of decision can push industry towards eco-design of their products. In addition, subsidies schemes could be imagined to favour the market introduction of products generated from waste or compensate additional costs of innovative technologies until these latter achieve a mature and competitive state. Finally, as discussed in the introduction, the revision of the Water Framework Directive could contribute to better management of water systems. In particular, the potential inclusion of emerging substances would need to be discussed. Of

course, scientific results should highlight this necessity. To conclude this work, it is clear the transition to sustainable development of our economy and society will require the involvement of all actors, from the large public, scientists to industrial and policy stakeholders.

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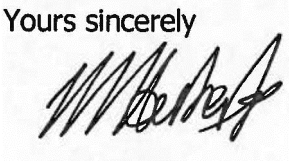

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