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Life Cycle Assessment of urban wastewater reuse with ozonation as tertiary treatment

A focus on toxicity-related impacts

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ABSTRACT

Life Cycle Assessment has been used to compare different scenarios involving wastewater reuse, with special focus on toxicity-related impact categories. The study is based on bench-scale experiments applying ozone and ozone in combination with hydrogen peroxide to a wastewater effluent from a Spanish sewage treatment plant. Two alternative characterisation models have been used to account for toxicity of chemical substances, namely USES-LCA and EDIP97. Four alternative scenarios have been assessed: wastewater discharge plus desalination supply, wastewater reuse without tertiary treatment, wastewater reuse after applying a tertiary treatment consisting on ozonation, and wastewater reuse after applying ozonation in combination with hydrogen peroxide. The results highlight the importance of including wastewater pollutants in LCA of wastewater systems assessing toxicity, since the contribution of wastewater pollutants to the overall toxicity scores in this case study can be above 90%. Key pollutants here are not only heavy metals and other priority pollutants, but also non-regulated pollutants such as pharmaceuticals and personal care products. Wastewater reuse after applying any of the tertiary treatments considered appears as the best choice from an ecotoxicity perspective. As for human toxicity, differences between scenarios are smaller, and taking into account the experimental and modelling uncertainty, the benefits of tertiary treatment are not so clear. From a global warming potential perspective, tertiary treatments involve a potential 85% reduction of greenhouse gas emissions when compared with desalination.

1. Introduction

According to the European Environment Agency, Spain is considered as a water-stressed country (European Environment Agency, 2005). The distribution of the resource is very heterogeneous and some Spanish regions, namely the Mediterranean region and the Balearic and Canary Islands suffer from water scarcity, mainly due to agriculture and tourism. Agriculture alone used 17,808 hm^3 in 2004, which represents more than 80% of total water use in Spain (Insituto Nacional de Estadística, 2008). The authorities have discarded large river transfers as a solution for water supply in water-deficient areas, and consider instead desalination and wastewater reuse as the main technological options to prevent water shortage. At present there are more than 700 operative desalination plants in Spain, with a production capacity above 800,000 m^3/day. According to official foresights, desalination capacity will be increased, leading to additional 621 hm^3/year (Ministerio de Medio Ambiente, 2007), this means a threefold increase as compared to current desalina-

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tion capacity. Concerning wastewater reuse, national statistics show that 1 hm^3/day, or 6.6% of the treated wastewaters, was reused in 2004 (Instituto Nacional de Estadística, 2008), although additional 133 hm^3/year are expected to be reused in drought-prone regions in the near future (Ministerio de Medio Ambiente, 2007). Nevertheless, the overall potential for wastewater reuse is much higher: according to Hochstrat et al. (2006), Spain is the European country with the highest reuse potential, with a maximum of 2000 hm^3/year, a figure an order of magnitude above the current situation.

Among the reasons why wastewater reuse has not received appropriate attention up to date, the potential effects in human health and the environment of trace contaminants, such as priority pollutants, pharmaceuticals and personal care products, etc., must be highlighted. Some of these compounds show little biodegradability, thus entering the environment via treated effluents from sewage treatment plants. For this reason, effective tertiary treatment technologies are needed in order to ensure that reclaimed wastewater is safely used. Available technologies for wastewater reclamation include from simple sand filtration until advanced oxidation processes and reverse osmosis. The choice of the most appropriate technology or combination of technologies will depend on the quality requirements and expected application of the reclaimed water.

Ozonation is a well established technology for water treatment, especially drinking water, and it has been the focus of attention in literature in the last few years as an option for advanced wastewater treatment (Pera-Titus et al. 2004). Ozone is an expensive oxidant, but its ability to mineralize organic matter, alone or in combination with hydrogen peroxide, may be attractive for wastewater reuse purposes (Rodríguez et al., 2008).

Although water reuse strategies are intended to address the problem of water scarcity, measures taken to solve this problem must not come at the price of aggravating other environmental problems, such as human health or global warming. In this context, the Life Cycle Assessment (LCA) methodology (Guinée et al., 2002) offers a holistic approach for environmental assessment, in which problem shifting is avoided, since impacts in different places and moments in time can taken into account. Up to date few LCA studies have focused on wastewater reuse, and in most cases, they have focused on energy and material requirements of the process, whereas toxicity related to trace elements in wastewater has not been heeded. Stokes and Horvath (2006) assessed water supply systems in energy terms, including desalination, imports, and recycling, being the latter the environmentally preferable option. Ortiz et al. (2007) compared the environmental impact of several membrane technologies for wastewater reclamation, including the indirect toxicity contribution from energy and infrastructure. Tangsubkul et al. (2005) assessed membranes and stabilisation ponds as reclamation technologies, including toxicity of trace pollutants in biosolids management, which appear to be an environmental hotspot, although the actual pollutants assessed are not shown. With regard to ozonation, it has been included in several LCAs of wastewater treatment (Nijdam et al., 1998; Pillay et al., 2002; Muñoz et al., 2005, 2006a, 2007), in which the fate of trace pollutants was excluded. On the other hand, Wenzel et al. (2008) assessed ozonation, sand filtration, and membranes, taking into account the toxicity of some priority and emerging pollutants in wastewater, but in the context of advanced treatment without subsequent wastewater reuse. In this work we aim to assess the life-cycle environmental impact of urban wastewater reuse for agricultural purposes, putting special emphasis on the potential toxicity of priority and emerging pollutants present in the effluents to be reused. The tertiary treatments assessed are ozonation and ozonation in combination with hydrogen peroxide, whereas desalination is chosen as the reference technology for water supply in a no-reuse scenario.

2. Experimental

LCA has been applied on the basis of bench-scale ozonation experiments and analytical work carried out with the effluent from a wastewater treatment plant (WWTP) in Alcalá de Henares (Madrid). This WWTP applies a physical pre-treatment, primary settling, secondary treatment by means of activated sludge with nitrogen removal, and secondary settling, after which the effluent is discharged to a river.

2.1. *Ozonation experiments*

Ozonation experiments were carried out in batch mode at 25 °C in a 5 L stirred tank at a speed of 1000 rpm with a four-blade turbine. Ozone was produced by an Ozomatic SWO 100 ozonisator (Baunatal, Germany) fed by oxygen (about 95% pure) produced by an AirSep AS-12 PSA oxygen generator unit (Buffalo, USA). The gas, a mixture of ozone and oxygen with a concentration of 45.9 g/Nm^3 ozone, was bubbled at a rate of 0.36 Nm^3/h. Cooling water flow was set at 0.5 L/min, and the total duration of the experiments was 30 min, during which samples were taken at 0, 5, 10, 20, and 30 min. Experiments using ozone in combination with hydrogen peroxide were carried out in the same conditions, and adding 0.15 mL of hydrogen peroxide (33% w/v) from Panreac (Barcelona, Spain) every 5 min.

2.2. *Analytical work*

Samples were analysed in order to determine the occurrence of 84 pollutants, including priority pollutants classified in the Water Framework Directive (EU, 2001), as well as pharmaceuticals and personal care products (PPCPs) frequently found in wastewater. Table 1 shows the pollutants analysed and summarizes the analytical methods employed. Further details on these analytical procedures can be found in Muñoz et al. (in press).

3. Application of LCA

3.1. *Goal and scenarios assessed*

The goal of this case study is to assess the environmental advantages and drawbacks of urban wastewater reuse in agriculture, mainly focusing on toxicity-related impact

Table 1 – Summary of target pollutants and analytical methods used

Compounds	Sample pre-treatment	Extraction method		Analytical method
		Technique	Solvent	
Pharmaceuticals: Acetaminophen, Indomethacine, Codeine, Mefenamic acid, Ketorolac, Naproxen, Ibuprofen, Diclofenac, Fenoprofen, Ketoprofen, Metronidazole, Sulfamethoxazole, Trimethoprim, Ciprofloxacin, Cefotaxime, Ofloxacin, Erythromycin, Fenofibrate, Bezafibrate, Gemfibrozil, Atenolol, Propranolol, Sotalol, Metoprolol, Fluoxetine, Paroxetine, Carbamazepine, Diazepam, Ranitidine, Omeprazole, Methylprednisolone, Nicotine, Furosemide, Hydrochlorothiazide, Salbutamol, Terbutaline, Caffeine, Mepivacaine. **Pharmaceuticals metabolites**: Carbamazepine 10,11-epoxide, Paraxanthine, Clofibric acid, Fenofibric acid, 4-methylaminoantipyrine (4-MAA), *N*-acetyl-4-aminoantipiryne (4-AAA), *N*-formyl-4-aminoantipiryne (4-FAA), 4-dimethylaminoantipiryne (4-DAA), 4-aminoantipiryne (4-AA), Antipyrine. **Personal care products**: Chlorophene. **Priority pollutants**: Atrazine, Chlorpyriphos methyl, Chlorfenvinphos, Diuron, Isoproturon, Simazine.	–Filtration –pH adjustment (pH 8)	Solid phase extraction	MeOH	Liquid chromatography–QTRAP-Mass Spectrometry
Personal care products: Celestolide, Phantolide, Traseolide, Galaxolide, Tonalide, Triclosan, Benzophenone-3. **Personal care products metabolites**: 2,7/2,8-dichloro-dibenzo-*p*-dioxin (2,7/2,8-DCDD). **Priority pollutants**: α-Endosulfan, β-Endosulfan, Endosulfan sulphate, 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (2,3,7,8-TCDD).	–No filtration –pH adjustement (pH 3) –NaCl Addition	Liquid–liquid extraction	Hexane	Gas chromatography–Mass Spectrometry/ Mass spectrometry
Organic priority pollutants: 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, Hexachloro 1,3-butadiene, Hexachlorobenzene, Pentachlorobenzene, α-Hexachlorocyclohexane, β-Hexachlorocyclohexane, γ-Hexachlorocyclohexane (Lindane), δ-Hexachlorocyclohexane, Alachlor, Tetrabromodiphenyl ether (TBDE), Pentabromodiphenyl ether (PBDE).	–No filtration. –pH adjustment (pH 3) –NaCl addition	Liquid–liquid extraction	Hexane	Gas chromatography–High Resolution–Mass spectrometry
Heavy metals: Cadmium, Lead, Nickel, Mercury.	–Filtration –1:2 dilution with 3% HNO_3	None	None	Inductively Coupled Plasma Mass Spectrometry

categories. For this purpose, the following scenarios have been included:

- No reuse: this scenario represents the situation in most Spanish WWTPs, in which treated wastewater is discharged to a natural water stream after secondary treatment.
- Direct reuse: this scenario involves reusing the treated effluent from the WWTP, but without any tertiary treatment.
- Ozone reuse: in this case wastewater is reused after applying a tertiary treatment consisting on ozonation.
- Ozone-peroxide reuse: wastewater is reused after applying a tertiary treatment consisting on ozonation in combination with hydrogen peroxide.

3.2. *Function and functional unit*

The function of the system under study can be considered twofold, being one of the functions disposal of a treated effluent (either in a river or in agricultural soil), and the second one supplying an agricultural production system with water for crop irrigation. This must be accounted for in the study, since only functionally equivalent alternatives can be fairly compared in LCA. All scenarios involving reuse fulfil the two functions, but the no-reuse scenario does not. For this reason, a system expansion approach (Ekvall and Weidema, 2004) has been applied, adding to the no-reuse scenario the environmental burdens of supplying irrigation water from an alternative source, namely seawater desalination. The functional unit chosen for comparing the scenarios is the supply of 1 m^3 for irrigation in agriculture.

3.3. *Up-scaling hypothesis*

The main limitation to perform this case study is the bench-scale at which ozonation experiments were carried out. Laboratory experiments do not represent optimized conditions, and although they may show effectiveness in removing pollution, they usually show a very low efficiency in energy and reagent use terms. In the case of ozonation, a full-scale reactor would work in continuous rather than in batch mode, and the efficiency in ozone use, i.e. the mass transfer efficiency from the gas to the liquid phase, would be much higher. Besides, residence time of wastewater in the reactor would probably be below 30 min. As a consequence, the actual conditions employed in the experiments cannot be directly used in the LCA, unless some kind of up-scaling estimation is applied in order to make them more representative of a full-

scale application. The approach taken in the study has been to calculate the actual ozone consumed (as opposed to produced) in the experiment for reaching an optimum pollution removal level, and next consider this ozone dose in a industrial-scale system. This procedure is further detailed in Section 3.5.

3.4. *Life Cycle Impact Assessment methodology*

Toxicity on both humans and ecosystems has been assessed in Life Cycle Impact Assessment (LCIA) with two different characterisation models, namely USES-LCA (Huijbregts et al., 2000a) and EDIP97 (Hauschild and Wenzel, 1998), the main features of which are summarised in Table 2.

USES-LCA is an integrated multimedia fate, exposure and effects model; potential toxicity of chemicals is measured as equivalents of a reference substance, namely 1,4-dichlorobenzene (DCB). From the set of impact categories available in this model, we have chosen to include freshwater aquatic ecotoxicity, terrestrial ecotoxicity, and human toxicity.

Toxicity of chemical substances in EDIP97 is based on independent key properties of substances, which are used to model fate, exposure, and effects, in a simple way, instead of

Table 2 – Summary of main features of the toxicity LCIA methods used

Feature	EDIP97	USES-LCA
Impact categories included	Human toxicity: –Human toxicicity potential via air –Human toxicity potential via water –Human toxicity potential via soil Ecotoxicity: –Ecotoxicity potential via water, acute –Ecotoxicity potential via water, chronic –Ecotoxicity potential via soil, chronic –Ecotoxicity potential in WWTP	Human toxicity: –Human toxicity potential Ecotoxicity: –Freshwater aquatic ecotoxicity potential –Freshwater sediment ecotoxicity potential –Marine aquatic ecotoxicity potential –Marine sediment ecotoxicity potential –Terrestrial ecotoxicity potential
Emissions to	Air, water, WWTP, and soil	Air, freshwater, seawater, agricultural soil, industrial soil
Media considered	Air, water, (porewater of) soil	Global scale: air, water, and soil. Continental scale: air, freshwater, seawater, natural soil, agricultural soil, industrial soil, freshwater sediment, and seawater sediment
Fate and exposure analysis	Partially included through substance key properties	Based on an integrated multi-media fate and exposure model
Effects analysis	Based on policy targets and animal testing	Based on policy targets and animal testing
Units used	Dilution volume: m^3 environmental compartment (air, water, soil) per g substance	Reference substance: kg 1,4-dichlorobenzene (DCB) equivalents per kg substance
Spatial differentiation	In the fate model: none In the characterisation factors: none in the 1997 version; included in the 2005 version	In the fate model: differentiation in three climatic zones and two geographical scales. In the characterisation factors: none
Default characterisation factors available	For 70–103 organic and inorganic substances	For 181 organic and inorganic substances
Pro's of the approach	Simplicity	Integrated multimedia fate and exposure model. Aggregation of human toxicity in a single impact category
Data requirements[a]	Physico-chemical properties: –Henry's law constant –Kow –pKa Degradation rates: –Atmospheric half life –Biodegradability Toxicological data: –Predicted no-effect concentration (PNEC) in water –PNEC in soil –Human reference concentration in air –Human reference dose	Physico-chemical properties: –Henry's law constant –Molecular weight –Kow –Melting point –Vapor pressure –Solubility in water –pKa Degradation rates: –Reaction half-life in air –Hydroxyl radical reaction in air –Biodegration in surface water –Biodegration in soil –Biodegradation in aerobic sediment –Biodegradation in anaerobic sediment Toxicological data: –PNEC in water –PNEC in soil –Human reference concentration in air –Human reference dose

Adapted from De Koning et al. (2002).

[a] For USES-LCA these are the minimum requirements. Refinement through further parameters is allowed, but not carried out in this work.

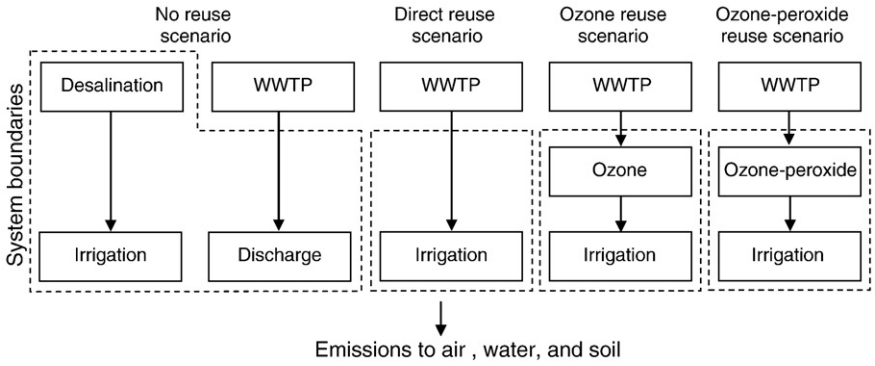

Fig. 1 – System under study and scenarios assessed.

using an integrated, quantitative model like USES-LCA. It has been judged interesting to use more than one model in order to check the robustness of the results and possible differences. The EDIP97 impact categories assessed in the case study are chronic ecotoxicity in water, chronic ecotoxicity in soil, while concerning human toxicity, EDIP97 gives the possibility of including up to three impact categories, corresponding to the main three exposure routes to humans: air, water, and soil. In this case study, the relevant exposure routes are water and soil, whereas human toxicity via air is excluded. Instead of using a reference unit, EDIP97 measures toxicity as a dilution volume of water or soil, depending on the environmental compartment of relevance; this can be interpreted as the volume of water or soil required to dilute the pollutants in order for the resulting environmental concentration to remain below the predicted no-effect concentration.

Characterisation factors for most target pollutants in Table 1 were initially lacking in these toxicity models, but have been recently calculated (Muñoz et al., in press).

Although the present study focuses on toxicity issues, the increasing concern about human-induced climate change and energy efficiency justifies the inclusion of Global Warming Potential (Forster et al., 2007), an impact category included in almost every LCA study. Results for other impact categories frequently included in LCA studies, such as acidification, stratospheric ozone depletion, and photochemical oxidants formation (Guinée et al., 2002) are not shown in this paper, since they follow the same pattern than global warming. This does not hold true for eutrophication, a relevant impact category in wastewater systems which is dominated by nutrient emissions in effluents (Muñoz et al., 2006b; Hospido et al., 2004). Modelling of nutrient-derived emissions is out of the scope of this study, and for this reason eutrophication is not discussed.

All impact categories have been assessed at the characterisation level, excluding the optional steps of normalization and weighing, since these should not be used in comparative assertions disclosed to the public, according to the ISO 14044 standard (ISO, 2006).

3.5. *Inventory analysis*

Fig. 1 shows the system under study and its boundaries for each scenario. As it can be seen, processes taking place in the WWTP until secondary treatment are excluded, as they are common to all the scenarios. Another common process excluded is the transport of reclaimed or desalinated water to the user. Infrastructure required for tertiary treatment (reactor, pumps, etc.) has also been excluded due to lack of data. Processes included in the system under study can be summarised as follows:

- Production of oxygen, electricity, and cooling water for ozone production
- Production of hydrogen peroxide
- Transport of chemicals to the plant site (assuming a distance of 100 km)
- Sea water desalination
- Emission of trace pollutants in wastewater either to a river (no reuse scenario), or to agricultural soil (remaining scenarios)

In order to calculate the material and energy inputs related to ozone production, first the minimum treatment time required has been determined. This has been done with Fig. 2, which plots the total concentration of target pollutants vs. time; this graph excludes the concentration of heavy metals (Ni, Cd, Hg, Pb), since they are not affected by ozone. It can be seen in this figure that it is during the first 5 min of advanced treatment, either with ozone only or in combination with hydrogen peroxide, when most of the pollution is removed, while for the rest of the experiment pollutant concentration remains almost constant. In fact, it is likely that most of this removal is achieved in 1 or 2 min, although we cannot prove this with the present data, as the first sample was taken after 5 min. Therefore, 5 min has been

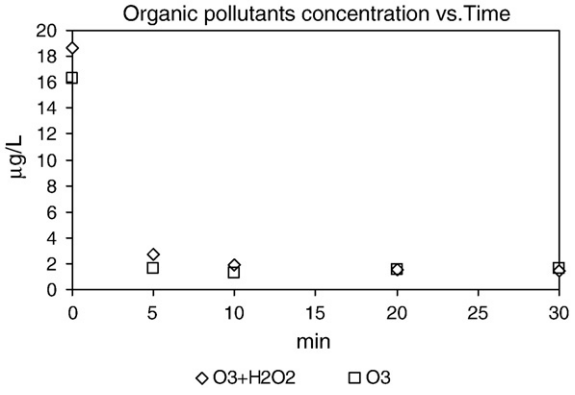

Fig. 2 – Total concentration of organic pollutants vs. treatment time.

used in both treatments to calculate the ozone injected, which is 1.38 g for the reactor containing 5 L wastewater. As for consumption, mass balance calculations allowed us to estimate that only 4.6% (12.7 mg ozone/L) of the ozone injected is actually transferred from gas bubbles to the liquid phase. On the other hand, a literature survey on full-scale ozone contactors reveals that efficiencies range from 80% to almost 100%, depending on reactor type and operating conditions (Morioka et al., 1997; Muroyama et al., 1999, 2005). In the present study we have assumed the conditions used by Muñoz et al. (2007), where an oxygen-fed ozonisator with a capacity of 1 kg ozone/h is used, along with a reactor having a gas-to-liquid transfer efficiency of 75%. These inventory data include the oxygen, cooling water, and power consumption to produce ozone, as well as power demand for pumping and residual ozone destruction.

Background inventory data for production of oxygen, electricity from the Spanish grid, hydrogen peroxide and road transport have been obtained from the Ecoinvent database version 2.0 (Frischknecht et al., 2007), whereas desalination has been modelled with data from a recent study (Muñoz and Rodríguez, 2008). Water for ozonisator cooling has been assumed to be produced by desalination, since the latter is considered as the marginal production technology in this study. Table 3 shows the inventory of technosphere processes for each scenario, whereas Table 4 shows the concentration of pollutants in wastewater. Desalinated water is assumed not to have any of the pollutants displayed in Table 4.

4. Results and discussion

4.1. *Toxicity modelled with USES-LCA*

Fig. 3 shows the life-cycle impact scores obtained for each scenario with the multimedia fate, exposure and effects model USES-LCA. From a freshwater ecotoxicity point of view (Fig. 3a), the worst scenario is not reusing wastewater, since all the pollutants in the WWTP effluent end up in the aquatic environment. If wastewater is instead reused, the impact is up to 2 orders of magnitude lower, due to the fact that the aquatic ecosystem no longer receives this pollution load, which is transferred to agricultural soil, and only a fraction of the initial pollution reaches freshwater through soil runoff, percolation, etc. The lowest impact on aquatic ecotoxicity corresponds to reusing wastewater after ozone treatment. According to USES-LCA, the main substances causing aquatic ecotoxicity in the WWTP effluent are the PPCPs ciprofloxacin and triclosan.

With regard to terrestrial ecotoxicity (Fig. 3b), direct reuse is the worst option, since all the pollutants in the WWTP effluent are being emitted to soil. On the other hand, no direct pollution is being emitted to soil in the no-reuse scenario, as here water for irrigation comes from desalination, in which chemical pollutants have been assumed to be absent. The environmental impact of ozone-peroxide is higher than that of not reusing, but in the same order of magnitude, whereas the lowest impact is attributed to reuse after ozonation. The pollutants with highest contribution to this impact category in the WWTP effluent are ciprofloxacin and mercury.

As for human toxicity (Fig. 3c), all scenarios score in the same order of magnitude. The worst case is no-reuse, mainly due to the indirect toxicity caused by the desalination process, and to some extent by human exposure to pollutants discharged to the river. Toxicity from desalination is originated by several substances emitted to air during electricity and ferric chloride production, especially hydrogen fluoride, chromium VI, PAHs, and arsenic. Differences between reuse scenarios are very small, and a higher impact is observed when an advanced treatment is applied, due to: 1) the indirect toxicity of producing auxiliary materials and energy, and 2) human toxicity from reclaimed water does not decrease as compared to the untreated water. The latter is caused by the concentrations of cadmium and hexachlorobenzene, which, as can be seen in Table 4, are not effectively removed neither by ozone nor by ozone-peroxide. Cadmium is not a target pollutant for advanced oxidation, and although hexachlorobenzene is, our experimental data show that it was not degraded in the 30-min experiment.

Table 3 – Inventory of material and energy requirements for each scenario

Inputs from technosphere	Scenario				Comments
	No reuse	Direct reuse	Ozone reuse	Ozone-peroxide reuse	
Electricity (kWh)	0	0	0.27	0.27	Total requirements per kg ozone produced: 15.85 kWh (12.8 kWh from ozonisator, 2.2 kWh from main pump, 1.55 kWh from recirculation pump, 0.1 kWh from ozone destructor). Ozone required: 12.7 g/m^3 × 1.33 = 16.9 g/m^3. Dataset includes extraction of energy resources, transport, energy conversion and grid distribution, assuming the spanish electricity consumption profile. Consumed at medium voltage.
Oxygen (kg)	0	0	0.14	0.14	Total requirements per kg ozone produced: 8.3 kg oxygen. Ozone required: 12.7 g/m^3 × 1.33 = 16.9 g/m^3. Dataset includes electricity for process, cooling water and infrastructure for air separation plant.
Hydrogen peroxide, pure (kg)	0	0	0	0.011	0.15 mL hydrogen peroxide (33% w/v, 1.11 g/mL) per 5 L: 0.011 kg pure hydrogen peroxide/m^3. Dataset includes material and energy input, waste and emissions for production by the anthrachinone process.
Water from desalination (L)	1000	0	34	34	Ozonisator uses 2000 L per kg ozone produced. Ozone required: 12.7 g/m^3 × 1.33 = 16.9 g/m^3. Includes plant infrastructure, chemicals, electricity requirements, and membrane replacement. Water distribution excluded.
Road transport (kg km)	0	0	14	17	100 km by 3.5 to 16 tonne lorry. Includes lorry production, fuel use, emissions, maintenance and disposal. Road life cycle is also included.

Table 4 – Occurrence of pollutants during experiments (ng/L)

Substances	Ozonation (min)					Ozonation in combination with hydrogen peroxide (min)				
	0	5	10	20	30	0	5	10	20	30
2,7/2,8-DCDD	298	203	321	209	195	162	310	150	224	369
4-AAA	2163					2065				
4-FAA	1096					1029				
4-MAA	22					22				
Alfa-hexachlorocyclohexane	1.3	1.3	1.1	0.9	1.6	1.4	1.8	1.9	2.5	2.4
Antipyrine	20					21				
Atenolol	849	8				717				
Bezafibrate	139					126				
Caffeine	61	873	233	133	56	38	316	309	207	169
Carbamazepine	65	2				61	2			
Carbamazepine Epoxide	14					13				
Cd	4300	6400	5100	4800	4500	7500	8400	7900	7400	9800
Cefotaxime										
Celestolide	10					10				
Ciprofloxacin	741	70	44	50	49	572	6	6	9	10
Clofibric acid	18	590	477	116	75	18	184	310	308	186
Codeine	329					351				
Delta-hexachlorohexane	2.8	2.2	1.6	1.4	2.1	2.6	2.4	2.8	2.9	2.9
Diazepam	3					2				
Diclofenac	369					216				
Diuron	9					15				
Erythromycin	126					120				
Fluoxetine	54	15	3			135				
Furosemide	101					71				
Galaxolide	6666	610	547	728	432	5329	523	271	609	654
Gemfibrozil	608					618				
Hexachlorobenzene	3.4	3.9	3.3	3.2	3.7	4.6	4.5	6.1	5.8	6.7
Hg	650									200
Hydrochlorothiazide	1301	15				1470				
Indomethacine	47					40				
Ketoprofen	346					335				
Ketorolac	40					42				
Mefenamic Acid	85					71				
Mepivacaine	5					5				
Metoprolol	18					16				
Metronidazole	212					188				
Naproxen	389					334				
Nicotine	96	107	85	79	37	56	95	44	45	43
Ofloxacin	565	33				464				
Omeprazole	181					164				
Paraxanthine			28	28						
Pb	13,400	9180	7050	6820	5670	6450	6130	8350	7050	4840
PBDE						0.4				
Propanolol hydrochloride	30					27				
Ranitidine	297	7				224				
Salbutamol	6					5				
Sotalol	13					11				
Sulfamethoxazole	150					117				
TBDE	1.1	0.9	0.6	0.5	3.2	0.7	0.7	0.8	0.8	0.8
Tonalide	754	121	107	134	536	675	133	86	111	132
Traseolide						9				
Triclosan	254	83	58	61	42	212	73	45	19	12
Trimethoprim	69					59				

Note: Blank cells correspond to concentrations below limit of detection or limit of quantification. Considered as zero in the LCA calculations.

4.2. *Toxicity modelled with EDIP97*

Fig. 4 shows the Life Cycle Impact Assessment results obtained for toxicity impacts modelled with EDIP97. Not reusing wastewater is again the worst option for aquatic ecotoxicity (Fig. 4a), although tertiary treatments score worse than direct reuse, due to the impact of producing ozone, oxygen, etc. It is also observed in Fig. 4a that desalination is responsible of 40% of the overall score in the no-reuse scenario, a much higher share as compared to results with

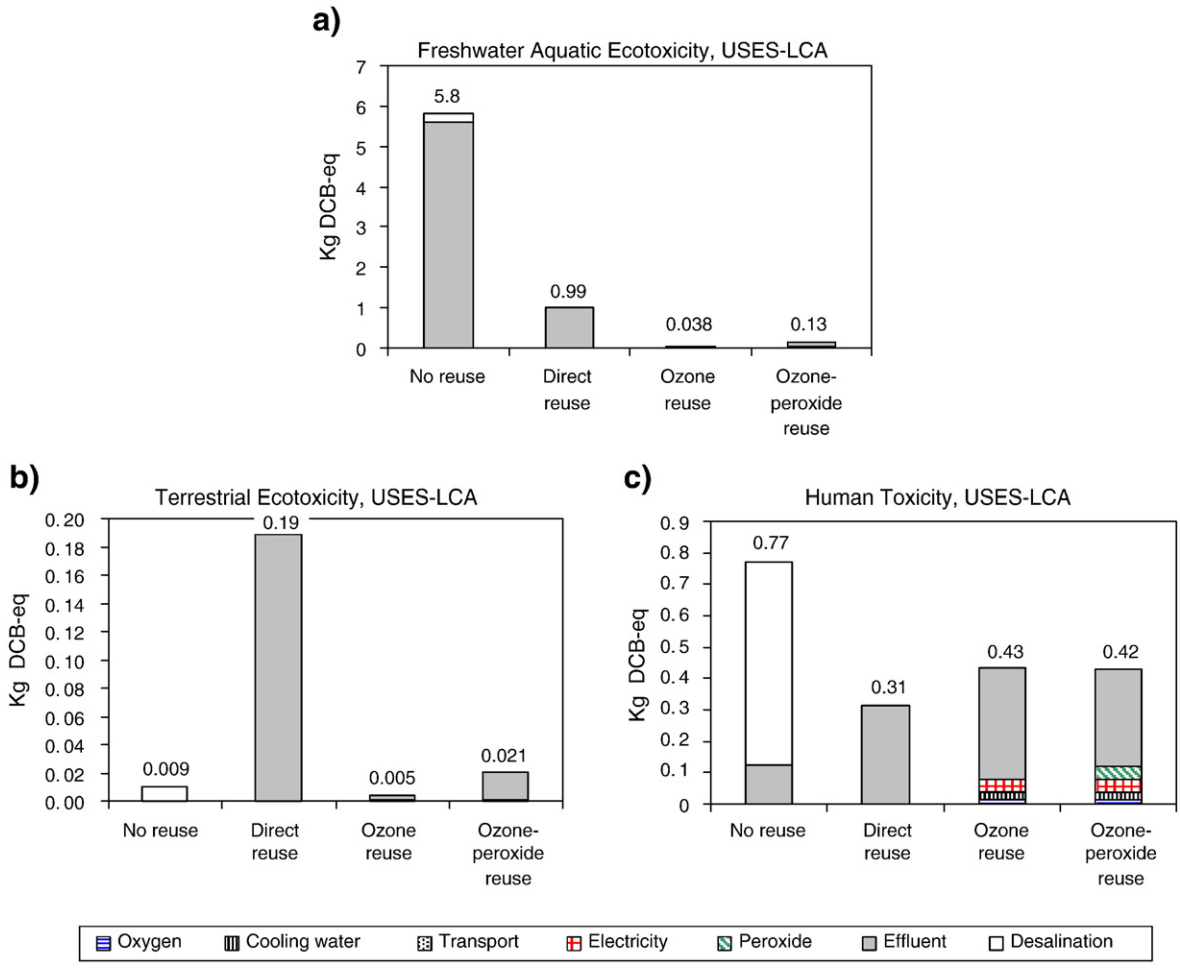

Fig. 3 – Life Cycle Impact Assessment results per functional unit for toxicity-related impact categories, modelled with USES-LCA.

USES-LCA, where it is responsible of less than 5% of the total score. The substances causing the highest aquatic ecotoxicity in the WWTP effluent are the same highlighted by USES-LCA, namely ciprofloxacin and triclosan, but also including Cadmium.

The overall picture in terrestrial ecotoxicity (Fig. 4b) does not differ significantly when compared to results from USES-LCA. Direct reuse is the worst option, being ciprofloxacin the most important substance (it is responsible of more than 95% of the total contribution).

With regard to human toxicity, two graphs are displayed (Fig. 4c and d), since EDIP97 does not aggregate all exposure routes in a single human toxicity category, but assesses them separately. Human toxicity through soil (Fig. 4c) displays a ranking of scenarios which can be considered very similar to that in human toxicity from USES-LCA, but here direct reuse appears to be the worst option along with no reuse. The most critical substances causing toxicity through reclaimed water in soil are gemfibrozil, mercury, nicotine, and cadmium, while toxicity from desalination is mainly caused by airborne emissions of benzene and arsenic associated to electricity and ferric chloride production. Finally, human toxicity through water exposure (Fig. 4d) highlights no-reuse as the worst scenario, with a toxicity three orders of magnitude above direct reuse, and two orders of magnitude above both tertiary treatments, which have the same impact score. This toxicity is mostly caused by the pollutants present in the WWTP effluent, especially mercury, gemfibrozil, and cadmium.

4.3. *Global warming potential*

Impact on global warming through emission of greenhouse gases is shown in Fig. 5. As it can be seen, this impact category is not affected by water pollutants, but by material and energy requirements of each scenario. Direct reuse of the WWTP effluent does not require any treatment, thus it appears as a zero-emission scenario. Emissions related to seawater desalination are close to 2 kg CO_2-eq./m^3, while ozone and ozone-peroxide imply almost the same emissions, around 0.3 kg CO_2-eq./m^3, that is, 85% less than the no-reuse scenario. Nevertheless, the "climate-friendliness" of ozone treatments for wastewater reuse would change in different contexts. In Spain reverse osmosis desalination is positioning itself as the reference technology in water-stressed regions, and it is known to be the most energy-intensive technology for drinking water production, but according to the Ecoinvent database (Althaus et al., 2007), the average production of drinking water in Western Europe, including waterworks and the supply network, implies 0.31 kg CO_2-eq./m^3, which would make tertiary treatment appear as a

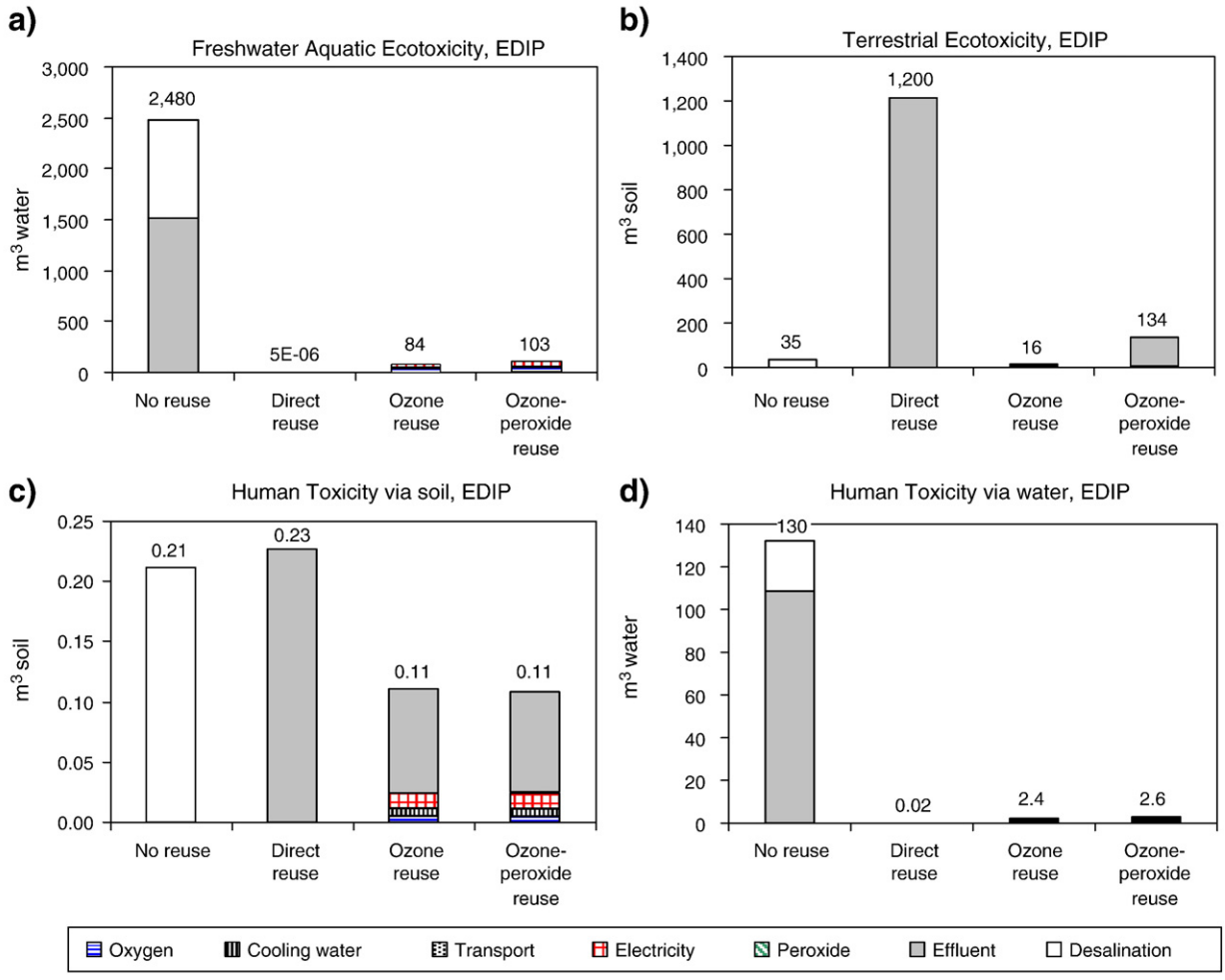

Fig. 4 – Life Cycle Impact Assessment results per functional unit for toxicity-related impact categories, modelled with EDIP97.

less favourable option in places (also in Spain) where conventional drinking water production technologies are used. Furthermore, previous LCA studies have shown that desalination can substantially reduce its environmental impact when renewable energy sources are used to drive the process (Raluy et al., 2005). According to these studies, CO_2 emissions of wind-powered reverse osmosis desalination can go as low as 0.12 kg per m^3, and 0.35 kg per m^3 when photovoltaic energy is used.

4.4. *Uncertainty considerations*

Uncertainty in these results is considered to be large, as it is common when a focus is put on toxicity impact categories (Geisler et al., 2005). Pre-eminent factors contributing to this uncertainty are discussed below:

- Experimental uncertainty: by experimental uncertainty we mean the variability and stochastic error due to all the measurements carried out, from wastewater sampling in the WWTP until the concentrations in Table 4 are obtained with laboratory equipment. First of all, there is the variability in the occurrence of the different compounds in wastewater. Our experience in wastewater monitoring is that PPCP concentrations can vary up to 2 orders of magnitude in 24-h integrated samples collected in different months. It is important to bear this in mind, since variations in the concentration of key substances may involve important

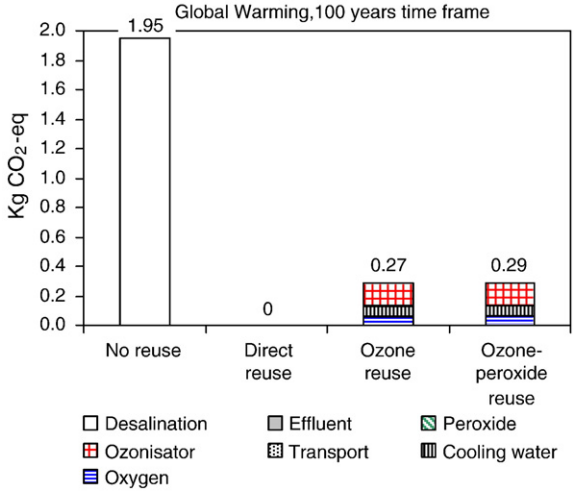

Fig. 5 – Life Cycle Impact Assessment results per functional unit for Global Warming, measured for a time frame of 100 years.

changes in the final LCIA scores. Concerning analytical work, there is always a certain degree of uncertainty, especially if the target substances occur at such a low level as ng/L. This can be seen in Table 3, where sometimes concentrations of pollutants are found to be higher during the course or at the end of the experiments (the clearest examples are caffeine, clofibric acid, and mercury), something which is actually not possible and attributed to experimental error. A possible reason explaining this is the higher concentration of organic matter in the initial samples, leading to a higher suppression of the MS/MS detector signal (Gómez et al., 2006); as chemical oxidation proceeds, the lower concentration of organic matter results in a clearer MS/MS signal.

- Up-scaling: this study has shown at the laboratory scale that urban wastewater can be properly reclaimed by means of ozonation and ozonation in combination with hydrogen peroxide. It is then assumed that this could be also achieved at full-scale, but with a higher efficiency in the use of energy and reagents. A conservative value of 75% ozone transfer efficiency in a full-scale reactor has been used, although published studies claim to achieve values above 90%.
- Toxicity modelling: uncertainty related to LCIA modelling is considered at least as important as that related to inventory analysis (Frischknecht et al., 2007), and especially when the focus is on toxicity-related impact categories (Geisler et al., 2005). The uncertainty of characterisation factors obtained with USES-LCA was investigated by Huijbregts et al. (2000a,b, 2001) for some substances, concluding that toxicity potentials may deviate from 1.5 to 6 orders of magnitude, mostly due to limited substance-specific data. Nevertheless, as Huijbregts (1998) points out, these large uncertainties in characterisation factors do not necessarily imply a large influence on the results of an LCA study.

Besides variability due to measurement and model uncertainty, other sources of uncertainty are the (un)appropriateness of the background data used, and the omission of flows (Frischknecht et al., 2007). In the present case study, the background data used (Ecoinvent datasets and desalination data) is considered to be of good quality and representative of the Spanish situation. As for the omission of flows, only the infrastructure of the ozone reactor has been excluded due to lack of data, although the potential influence of this omission in the outcome of the study is judged to be of minor importance.

4.5. *Limitations of LCA as a tool for assessing toxicity-related impacts*

Although assessing toxic effects in LCA has traditionally been inspired by the methodology of Risk Assessment, it should be stressed that environmental impacts assessed by means of LCA are considered as "potential" impacts rather than actual impacts or risks, due to the fact that emissions are typically not specified in space and time (ISO, 1999). As a consequence, the results of this case study do not indicate if the treated effluent has sufficient quality to be discharged, or used in agriculture. They indicate instead the potential impact of the studied alternatives, from a life cycle perspective. In order to determine the "actual" impact in a given specific location, a Risk Assessment should be conducted, taking into account such elements as the nature of soils used for irrigation and the character of surface water into which there is discharge.

Another limitation refers to leaving out of the assessment one or more critical substances, such as important metabolites. It can be the case that a parent compound is degraded during the treatment, but a more toxic metabolite appears; if this metabolite is not analysed in the samples or taken into account in the LCA, its impact will be omitted. This is important, since previous studies have shown that degradation products may increase ecotoxicity of wastewater treated with ozone and other Advanced Oxidation Processes (Vogna et al., 2004; Gagné et al., 2008). Furthermore, the fact that impacts in LCA are obtained as the sum of individual contributions from substances, implies that synergistic and antagonistic effects are not taken into account. These are indeed limitations of LCA as compared to toxicity assays, since the latter always reflect the integrated effect of all substances present in water. The strength of LCA lies in its ability to not only address direct toxicity in water, but also indirect toxic releases in upstream/downstream processes of the life cycle.

Concerning the difficulty in taking into account all possible metabolites, and synergistic/antagonistic effects, LCA is in practice not different from Environmental Risk Assessment, which typically focuses on Predicted Environmental Concentration (PEC) and Predicted No-Effect Concentration (PNEC) of individual (parent) compounds, excluding metabolites, as can be seen in Santos et al. (2007) and Grung et al. (2008).

5. Conclusions

LCA has been used to compare different scenarios involving wastewater reuse for agricultural purposes in Spain, with special focus on environmental impacts related to ecotoxicity and human toxicity. Two alternative characterisation methods have been used to model toxicity of chemical substances, namely USES-LCA and EDIP97. Four alternative scenarios have been assessed: wastewater discharge plus desalination supply, wastewater reuse without tertiary treatment, wastewater reuse after applying a tertiary treatment consisting on ozonation, and wastewater reuse after applying ozonation in combination with hydrogen peroxide. None of these scenarios has been found to be simultaneously the best choice under all environmental impact categories, but the results allow us to draw some general conclusions, as well as to identify their environmental advantages and drawbacks.

The first aspect to highlight is the importance of including wastewater pollutants in LCA of wastewater systems assessing toxicity. In this case study, the contribution of wastewater pollutants to the overall toxicity scores can be above 90% in some impact categories. Key pollutants here are not only heavy metals and other priority pollutants, but also non-regulated pollutants such as pharmaceuticals and personal care products.

In ecotoxicity, results obtained with USES-LCA and EDIP97 suggest that scenarios involving wastewater reuse after tertiary treatment appear as preferable options from an integrated aquatic and terrestrial ecotoxicity perspective, since the no-reuse scenario involves a very high impact in aquatic

ecotoxicity, whereas direct reuse performs similarly from a terrestrial ecotoxicity perspective. When tertiary treatments are compared to each other, it is observed that ozonation obtains lower toxicity scores than ozone-peroxide, although differences are small and at the same time uncertainty is high.

Concerning human toxicity, the results are not as conclusive as those obtained for ecotoxicity, since differences between scenarios are smaller, and the uncertainty is judged to be high. According to USES-LCA, scenarios involving wastewater reuse are better, specially if no advanced treatment is applied. According to EDIP97, wastewater reuse is also a better option, but the choice of a specific reuse scenario depends on whether human toxicity is assessed via soil or via water. The former suggests advanced treatments being better, and the latter suggests direct reuse as the preferable option. Differences between ozone and ozone-peroxide as tertiary treatments are not significant. It is also important to highlight that in the no-reuse scenario, the indirect contribution of desalination to eco- and human toxicity through energy and auxiliary materials demand is important.

Besides impacts on ecotoxicity and human toxicity, global warming potential has also been investigated. Direct reuse of wastewater is the best option, since neither tertiary treatment nor an alternative water production technology is needed. Both ozone and ozone-peroxide involve an 85% reduction of emissions as compared to desalination. Nevertheless, these reductions would not apply in regions where less energy-intensive drinking water production technologies are used, or if desalination is powered by renewable energies.

LCA is a useful tool to assess different scenarios from a global perspective, but it has its limitations. Therefore, it cannot substitute other tools like Risk Assessment and experimental toxicity assays, which are also needed in order to have all the relevant information for decision making.

Finally, it must be borne in mind the fact that this case study disregards other issues which may be of importance when comparing the advantages and drawbacks of the scenarios assessed. Water conservation, for example, has not been assessed, and should be the first priority for farmers, industry, and householders. Another important aspect is microbiological quality requirements, under which probably direct reuse is not an acceptable option for certain applications involving human exposure, such as irrigation of freshly-consumed food crops, public gardens, etc. In this context, a tertiary treatment using ozone would be useful not only for removal of chemical pollutants, but also for disinfection.

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REFERENCES

Althaus H-J, Chudacoff M, Hischier R, Jungbluth N, Osses M, Primas A. Life cycle inventories of chemicals. Final report ecoinvent data v2.0, No. 8, Swiss Centre for Life Cycle Inventories, Duebendorf, Switzerland; 2007.

De Koning, A., Guinée, J., Pennington, D., Sleeswijk, A., Hauschild, M., Molander, S., et al. (2002). Methods and typology report Part A: Inventory and classification of LCA characterisation methods for assessing toxic releases. Contribution to Workpackage 7 of the Omniitox project as part of appropriate Deliverable 11.

Ekvall T, Weidema BP. System boundaries and input data in consequential life cycle inventory analysis. Int J Life Cycle Assess 2004;9(3):161–71.

EU. Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Off J 2001;L 331:0001–5 15/12/2001.

European Environment Agency, 2005. The European environment: state and outlook. Part A: integrated assessment. http://reports.eea.europa.eu/state_of_environment_report_2005_1/en.

Forster P, Ramaswamy V, Artaxo P, Berntsen T, Betts R, Fahey DW, et al. Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, editors. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press; 2007.

Frischknecht R, Althaus H-J, Doka G, Dones R, Heck T, Hellweg S, et al. Overview and methodology. Final report ecoinvent v2.0 No. 1, Swiss Centre for Life Cycle Inventories, Duebendorf, Switzerland; 2007.

Gagné F, André C, Cejka P, Hausler R, Fournier M, Blaise C. Immunotoxic effects on freshwater mussels of a primary-treated wastewater before and after ozonation: a pilot plant study. Ecotoxicol Environ Saf 2008;69(3):325–584.

Geisler G, Hellweg S, Hungerbuhler K. Uncertainty analysis in life cycle assessment (LCA): case study on plant-protection products and implications for decision making. Int J Life Cycle Assess 2005;10(3):184–92.

Gómez MJ, Petrovic M, Férnandez-Alba AR, Barceló D. Determination of pharmaceuticals of various therapeutic classes by solid-phase extraction and liquid chromatography-tandem mass spectrometry analysis in hospital effluent wastewaters. J Chromatogr A 2006;1114:224–33.

Grung M, Källqvist T, Sakshaug S, Skurtveit S, Thomas KV. Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline. Ecotoxicol Environ Saf 2008;71(2):328–40.

Guinée JB, Gorree M, Heijungs R, Huppes G, Kleijn R, Udo de Haes HA, et al. Life cycle assessment. An operational guide to ISO standards.Volume 1, 2, 3. The Netherlands: Centre of Environmental Science, Leiden University (CML); 2002.

Hauschild M, Wenzel H. Environmental assessment of products. Vol. 2: Scientific background. Chapman & Hall; 1998.

Hochstrat R, Wintgens T, Melin T, Jeffrey P. Assessing the European wastewater reclamation and reuse potential—a scenario analysis. Desalination 2006;188(1–3):1–8.

Hospido A, Moreira MT, Fernández-Couto M, Feijoo G. Environmental performance of a municipal wastewater treatment plant. Int J Life Cycle Assess 2004;10(5):336–45.

Huijbregts MAJ. Application of uncertainty and variability in LCA, Part II: Dealing with parameter uncertainty and uncertainty due to choices in life-cycle assessment. Int J Life Cycle Assess 1998;5:343–51.

Huijbregts MAJ, Thissen U, Guinée JB, Jager T, Kalf D, van de Meent D, et al. Priority assessment of toxic substances in life cycle assessment. Part I: Calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES-LCA. Chemosphere 2000a;41(4):541–73.

Huijbregts MAJ, Thissen U, Jager T, van de Meent D, Ragas AMJ. Priority assessment of toxic substances in life cycle assessment. Part II: Assessing parameter uncertainty and human variability in the calculation of toxicity potentials. Chemosphere 2000b; 41(4):575–88.

Huijbregts MAJ, Guinee JB, Reijnders L. Priority assessment of toxic substances in life cycle assessment. III: Export of potential impact over time and space. Chemosphere 2001;44(1):59–65.
Instituto Nacional de Estadística. 2008. Anuario Estadístico de España 2007. Madrid.
ISO. ISO 14042: Environmental management—life cycle assessment—Life cycle impact assessment. Switzerland: Geneva; 1999.
ISO. ISO 14044: Environmental management—life cycle assessment—requirements and guidelines. Switzerland: Geneva; 2006.
Ministerio de Medio Ambiente, 2007. Programa AGUA. http://www.mma.es/secciones/agua/entrada.htm.
Morioka T, Kato Y, Hoshikawa H, Okada M, Moniwa T. Study of the reactor with downflow injection on the characteristics of ozonation. Water Sci Technol 1997;36(12):367–74.
Muñoz I, Rieradevall J, Domènech X, Peral J, Torrades F. Environmental assessment of different solar driven advanced oxidation processes. Solar Energy J 2005;79(4):369–75.
Muñoz I, Rieradevall J, Domènech X, Peral J, Torrades F. Environmental assessment of different advanced oxidation processes applied to a bleaching kraft mill effluent. Chemosphere 2006a;62(1):9–16.
Muñoz I, Peral J, Ayllon JA, Malato S, Passarinho P, Domènech X. Life cycle assessment of a coupled solar photocatalytic-biological process for wastewater treatment. Water Res 2006b;40:3533–40.
Muñoz I, Peral J, Ayllon JA, Malato S, Martin MJ, Perrot JY, et al. Life cycle assessment of a coupled advanced oxidation-biological process for wastewater treatment. Comparison with granular activated carbon adsorption. Environ Eng Sci 2007;24(5):638–51.
Muñoz I, Rodríguez A. Reducing the environmental impacts of reverse osmosis desalination by using brackish groundwater resources. Water Res 2008;42:801–11.
Muñoz I, Gómez, MJ, Molina-Díaz, A, Huijbregts, MAJ, Fernández-Alba, AR, García-Calvo, E. Ranking potential impacts of priority and emerging pollutants in urban wastewater through life cycle impact assessment. Chemosphere in press. doi:10.1016/j.chemosphere.2008.09.029.
Muroyama K, Noriega T, Morioka A, Tsuji T. Hydrodynamics and computer simulation of an ozone oxidation reactor for treating drinking water. Chem Eng Sci 1999;54:5285–92.
Muroyama K, Yamasaki M, Shimizua M, Shibutania E, Tsuji T. Modeling and scale-up simulation of U-tube ozone oxidation reactor for treating drinking water. Chem Eng Sci 2005;60:6360–70.
Nijdam D, Blom J, Boere JA. Environmental Life Cycle Assessment (LCA) of two advanced wastewater treatment techniques. Stud Surf Sci Catal 1998;120 B:763–75.
Ortiz M, Raluy RG, Serra L, Uche J. Life cycle assessment of water treatment technologies: wastewater and water-reuse in a small town. Desalination 2007;204(1–3):121–31.
Pera-Titus M, García-Molina V, Baños MA, Giménez J, Esplugas S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. Appl Catal B: Environ 2004;47:219–56.
Pillay SD, Friedrich E, Buckley CA. Life Cycle Assessment of an industrial water recycling plant. Water Sci Technol 2002; 46(9):55–62.
Raluy G, Serra L, Uche J. Life Cycle Assessment of desalination technologies integrated with renewable energies. Desalination 2005;183:81–93.
Rodríguez A, Rosal R, Perdigón-Melón JA, Mezcua M, Agüera A, Hernando MD, et al. Ozone-based technologies in water and wastewater treatment. The handbook of environmental chemistry, Vol. 5. Berlin Heidelberg: Springer-Verlag; 2008.
Santos JL, Aparicio I, Alonso E. Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). Environment International 2007;33(4):596–601.
Stokes J, Horvath A. Life cycle energy assessment of alternative water supply systems. Int J Life Cycle Assess 2006;11(5):335–43.
Tangsubkul N, Beavis P, Moore SJ, Lundie S, Waite TD. Life Cycle Assessment of water recycling technology. Water Resour Manag 2005;19:521–37.
Vogna D, Marotta R, Andreozzi R, Napolitano A, d'Ischia M. Kinetic and chemical assessment of the UV/H2O2 treatment of antiepileptic drug carbamazepine. Chemosphere 2004; 54(4):497–505.
Wenzel H, Larsen HF, Clauson-Kaas J, Høibye L, Jacobsen BN. Weighing environmental advantages and disadvantages of advanced wastewater treatment of micro-pollutants using environmental life cycle assessment. Water Sci Technol 2008;57(1):27–32.