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# Combined Life Cycle Assessment and Life Cycle Costing of UV-based Treatment of Emerging Contaminants

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## ABSTRACT

UV-based methods were studied for the removal of mixture of steroid hormones (17 $\alpha$ -estradiol, 17 $\beta$ -estradiol, 17 $\alpha$ -dihydroequilin, 17 $\alpha$ -ethinyl estradiol, estriol, estrone, equilin, norgestrel, gestodene, trimegestrone, medrogestone and progesterone) in aqueous solution. Contribution and comparative life cycle assessment (LCA) study was applied to assist the decision making for the selection of the optimal treatment method from technological and environmental point of view. The results showed that chemically-assisted UV processes (e.g. UV/hydrogen peroxide, UV/persulfate) enhance not only degradation efficiency of these contaminants, but are more beneficial from environmental and economical point of view. Qualitative assessment was provided by eco-efficiency index (EEI). The most eco-efficient option was UV/persulfate, which had the lowest EEI (0.55), whereas the EEI for UV/hydrogen peroxide was 0.61.

**Keywords:** UV-photolysis, UV/hydrogen peroxide, UV/persulfate, steroid hormones, Life Cycle Assessment

## INTRODUCTION

Over past two decades photochemical technologies have become more attractive than conventional methods due to several reasons. It is simple and clean technology, cost-effective in many applications, which provide not only treatment of many organic contaminants but also disinfection (1). Ultraviolet (UV) based technologies belong to the class of advanced oxidation processes (AOP), which are primarily based on the generation of hydroxyl radicals ( $\bullet\text{OH}$ ), having an oxidation potential of 2.7 V. Hydroxyl radicals are formed through direct photolysis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or photo-induced processes such as photo-Fenton type reactions or photocatalysis. The persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ,  $E_0 = 2.01$  V) is another

strong oxidant that can be activated to generate an even stronger oxidant known as a sulfate radical ( $\text{SO}_4^{\bullet-}$ ,  $E_0 = 2.4$  V). The UV direct photolysis is restricted to those pollutants that exhibit large molar absorption coefficient and quantum yields, whereas the addition of photocatalyst or hydrogen peroxide makes the process to be less sensitive to the nature of treated compound (2). Continued advances of technology include (i) high efficiency for removal of wide range of compounds (due to unselectivity of  $\bullet\text{OH}$ ), (ii) simple reactor design, (iii) easy exploitation (3). The selection of UV system depends on the cost of equipment, operation and maintenance, which in turn, is affected by water quality, system design, and operation parameters (design flow rate, reagents doses, reaction pH, etc.).

The use of complex advanced technologies to remediation of persistent contaminants may pose risk to the environment and human health due to increased greenhouse gas emissions, higher demands for energy and releases of pollutants to the environment. Therefore, an optimization analysis must be performed to estimate the environmental impacts of the treatment technology, while the toxicological risks associated with contaminants are reduced. In this context, the LCA methodology can provide a holistic approach for environmental assessment, in which environmental and health impacts in different places and at different moments in time are taken into account (4). LCA could be used as a method to define and reduce the environmental burdens from a technological process by identifying and quantifying energy and materials usage, as well as waste emissions, assessing the impacts of these wastes on the environment and evaluating opportunities for environmental improvements over the whole life cycle (5). Because of its holistic approach, LCA is becoming an increasingly important decision-making tool in environmental management. Life Cycle Costing (LCC) is used to optimise the cost of acquiring, owning and operating of technology during its life. The methodology is similar to LCA and aims to identify and quantify all the significant costs involved in that life, using the present value technique (6). Therefore, the combination of LCA and LCC will ensure the adoption of the optimum technology.

The current study describes the technological aspects of the UV-based removal (UV-photolysis, UV/hydrogen peroxide and UV/persulfate) of steroid hormones mixture: 17 $\alpha$ -estradiol (17 $\alpha$ , 17 $\beta$ -estradiol (E2), 17 $\alpha$ -dihydroequilin, 17 $\alpha$ -ethinyl estradiol (EE2), estriol (E3), estrone (E1), equilin, norgestrel, gestodene, trimegestrone, medrogestone and progesterone. All three technologies were assessed by combined LCA and LCC to provide a comprehensive overview and to assist the decision making for the selection of the optimal treatment method.

## MATERIALS AND METHODS

### Chemicals and reagents

The following steroid hormones (minimal purity) were obtained from Sigma Aldrich or Steroids, Inc.: 17 $\alpha$ -estradiol (98%), 17 $\beta$ -estradiol (97.1%), 17 $\alpha$ -dihydroequilin (99.4%), 17 $\alpha$ -ethinylestradiol (99.1%), estrone (100%), estriol (100%), equilin (99.9%), gestodene, progesterone (99.1%), norgestrel (99.1%), and medrogestrone (99.1%), and 3-O meth-

yl estrone (internal standard, 98%). Methanol (HPLC grade), toluene (HPLC grade), and amber glass bottles were obtained from Fisher Scientific. Varian Bond Elut 3mL/500mg C-18 solid phase extraction (SPE) adsorbent cartridges were obtained from Varian Inc.

### *Steroid hormones treatability study*

UV photolysis experiments were conducted to test the effect of retention time on steroid hormones degradation. Experiments were conducted at retention times of 20 and 10 minutes, corresponding to flow rates of 200 and 100 mL min<sup>-1</sup>, respectively. Different oxidizing agents (hydrogen peroxide and persulfate) were tested at various concentrations, with a retention time of 10 minutes. The concentrations of the oxidizing agents were 5 and 10 mg L<sup>-1</sup> for H<sub>2</sub>O<sub>2</sub>, and 2, 5, and 10 mg L<sup>-1</sup> for persulfate. For both UV/H<sub>2</sub>O<sub>2</sub> and UV/persulfate experiments, H<sub>2</sub>O<sub>2</sub> and persulfate were added to the working solution prior to UV exposure. The lamp intensity for these experiments was 7.9 mW cm<sup>-2</sup>.

The stock solution of hormones (100 mg L<sup>-1</sup>) was prepared in methanol and stored in silanized amber glass volumetric flask at 40C. Aqueous working solutions of steroid hormones (25  $\mu$ g L<sup>-1</sup>) were prepared by the addition of 1.25 mL of stock solution to 5 L deionized water. 250 mL samples were extracted using SPE and then analyzed using GC/MS/MS.

### *Analysis of steroid hormones with SPE Gas Chromatography (GC) – tandem Mass Spectrometry (MS)*

SPE was carried out using Varian Bond Elute C-18 SPE cartridges, which were initially activated using 3mL of methanol and rinsed with 3 mL of DI water. Samples were passed through SPE cartridges at a flow rate of 5 mL min<sup>-1</sup>. The cartridges were then rinsed twice with 3mL of DI water and eluted with 6mL of methanol. The eluent was collected in a clean, silanized test-tube and 1mL of internal standard was added. The eluent was then dried in a Genevac centrifugal evaporator at 40°C and 12mbar vacuum.

After drying, the samples were derivatized by the addition of 25 $\mu$ L of pyridine and 25 $\mu$ L of bis(trimethylsilyl) trifluoro-acetamide (BSTFA). After addition of pyridine and BSTFA, the sample was left to stand for 15 minutes at 26°C to enable sufficient reaction time. 250 $\mu$ L of toluene was then added, and the sample was vortexed. The sample was transferred into a 0.25mL silanized GC glass insert and was analyzed on GC/MS/MS.

GC/MS/MS analysis was performed using a Waters Quattro micro. Auto injections were made using split mode with a split ratio of 0.1, and an injection volume of 1.0  $\mu\text{L}$ . Injection temperature was 250°C. The initial temperature of the oven was 110°C. The temperature was ramped to 250°C at a rate of 20.0°C  $\text{min}^{-1}$ , and held for 8.0 minutes, then ramped to 265°C at a rate of 1.0°C  $\text{min}^{-1}$ , and finally ramped to 300°C at a rate of 7°C  $\text{min}^{-1}$  and held for 34 minutes. Transfer line to the MS was maintained at 300°C and the electron energy was 70eV (7).

## LCA METHODOLOGY

### Goal and scope definition

The goal of the study is to apply streamlined LCA to assess the UV-based treatment technologies (UV-photolysis, UV/hydrogen peroxide and UV/persulfate) for removal of mixture of steroid hormones. This assessment will highlight the critical sources of environmental impact in the process life cycle, and the areas where improvements should be made when implementing these techniques to a full scale. Therefore, primary goal of the current study is to assess the operation of aforementioned technologies for the removal of hormones. The secondary goal is to combine the obtained results with streamlined life cycle costing (LCC) study and to provide the comparative analysis according to the results.

The term “streamlined”, used in the LCA context refers to “simplified”. The border between detailed and streamlined LCA is not straightforward. However, the streamlined approach in LCA allows to perform LCA that reduce the scope, cost, and effort required for studies that use an LCA framework. The current study provides a streamlined LCA used for purposes of technology performance evaluation, which subsequent determining whether an additional study is needed and where that study should focus.

The main characteristics making this study a streamlined LCA are the following:

- Some life cycle stages

are left out, both upstream and downstream of the AOP.

- Uses the most readily available data. This is considered the key streamlining method in this particular study, referring to the fact that laboratory data is used as the basis for the inventory phase. In the case of the emerging technologies for the removal of ECs the bench -scale data is the most readily available to assess a chemical process, and this constitutes an advantage, but also an inconvenient: the advantage is that potential impacts and possibilities for improvement can be detected at the beginning of the R&D stage; on the other hand, the main inconvenient is that data is incomplete (this links with the first point) and represents the furthest situation for the process from being optimized.

### Functional unit and system boundaries

The function of the system has been defined in a wide sense as: “Degradation of the steroid hormones from 1m<sup>3</sup> of water.” System boundaries are presented in Figure 1 as general flow diagram. In this section, all processes (both included and excluded) considered in the study are identified, as well as the reasons for their inclusion or exclusion.

### Excluded processes:

1. Infrastructure and equipment for the different treatments are not included in the LCA. Infrastructure and equipment used in the laboratory is not considered to be representative. Moreover, the current study focuses on the comparative study of the performance of three UV-based technologies, which

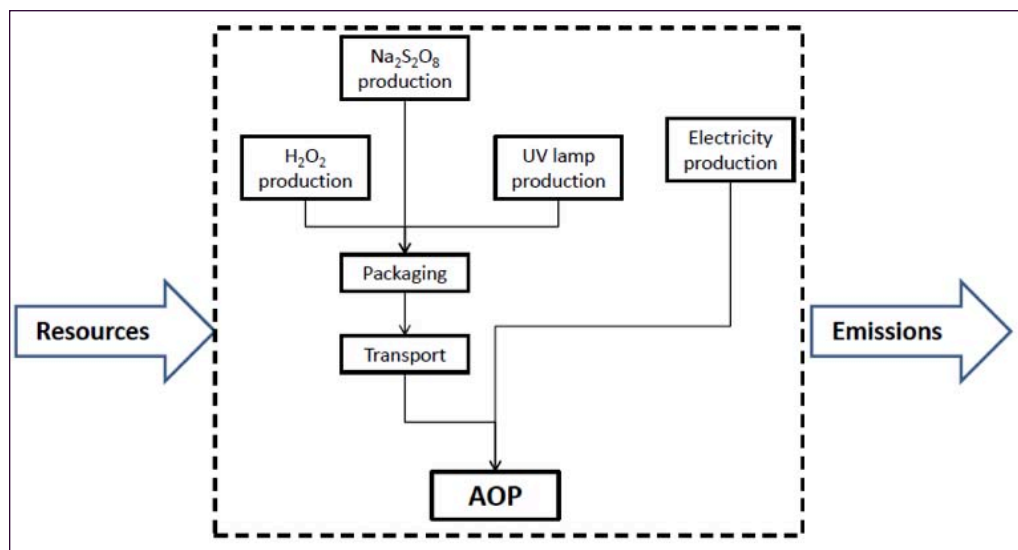


Figure 1. System boundaries

- will have relatively the same infrastructure.
- Any pre-treatment or post-treatment stages. The study focuses in AOPs, the functional unit has been defined in such a way that processes placed before and after the AOP can be excluded, as they are constant for all treatments.
  - CO<sub>2</sub> emissions produced by the mineralization of steroid hormones

*Included processes:*

- Production of electricity consumed by the treatment technologies. This sub-system comprises extraction of resources, transport, and electricity production, as well as production of the capital equipment required for these operations.
- Production of UV lamp, hydrogen peroxide and persulfate. This sub-system comprises extraction of resources, transport, packaging, production stage, transport to the wastewater treatment plant, and also production of capital goods.

**Inventory analysis**

The inventory analysis is a technical process of collecting data, in order to quantify the inputs and outputs of the system, as defined in the scope (8). Energy and raw materials consumed, emissions to air, water, soil, and solid waste produced by the system are calculated for the entire life cycle of the product or service.

The present study includes two types of data: the first-order corresponds to the data used to calculate the inputs from technosphere to the foreground system, and the second-order data corresponds to the data used to account for the environmental interventions related to those inputs from the background system. The main hypothesis and assumptions in the inventory phase of the LCA can be summarized as follows:

- Infrastructure and equipment for the different treatments are not included in the LCA. Infrastructure and equipment used in the laboratory is not considered to be representative.
- The energy used to run the US, UV, ozonator and pumps have been assumed to be electricity delivered from the US grid (medium voltage+ IMPORT).
- Hydrogen peroxide and persulfate are totally consumed during the reaction.
- UV lamp was included in the group of consumables and therefore, its life cycle was fully assessed. The end-of-life management concept is taken from the Guide for Waste managers, dealing with mercury lamp recycling (<http://www.swana.org/extra/lamp/lropmanualfinal.pdf>)

**IMPACT CATEGORIES AND IMPACT ASSESSMENT METHOD**

The method, used for the environmental impacts assessment is IMPACT 2002+. The IMPACT 2002+ methodology combines two approaches: the classical

**Table 1. Summary of data used in the inventory phase of the LCA/Life Cycle Inventory results**

Topic	Data Sources
Electricity (Eastern US grid )	Representative of year 2000 mix of fuels used for utility electricity generation in the Eastern U.S. Fuels include coals, fuel oil, nuclear, hydroelectric, and unconventional energy sources (US LCI, 2008).
Electricity consumption by the AOP technology and auxiliary equipment (e.g. pumps)	Data from laboratory experiments and equipment power
Hydrogen peroxide, H <sub>2</sub> O <sub>2</sub> (30%) Sodium persulfate, Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	Data from Ecoinvent, calculated using the methodology from ETH (2003). Total aggregated inventory.
Chemical products consumption by the AOP	Data from laboratory experiments
UV Lamp	Data from the manufacturer
Process water for cooling and washing	Raw materials (007732-18-5)
Ozone production	Total requirements per g ozone produced: 0.09 kWh
Transport, single unit truck, diesel powered/US	Data on fuel consumption and emissions from US LCI database from Franklin associates (2008)
Transport distances	Assumptions
Packaging	Data from US LCI database calculated using the methodology from Franklin associates (2008).

assessment methods, which restrict quantitative modeling to relatively early stages in the cause-effect chain to limit uncertainties and classify and characterize LCI results in so-called midpoint categories and damage oriented methods, which model the cause-effect chain up to the damage, sometimes with high uncertainties.

The midpoint impact categories provided by the method are: Carcinogens, Non-carcinogens, Respiratory inorganics, Ionizing radiation, Ozone layer depletion, Respiratory Organics (RO), Aquatic Ecotoxicity (AE), Terrestrial Ecotoxicity (TE), Terrestrial Acid/nutria (TA), Land Occupation (LO), Aquatic Acidification (AA), Aquatic Eutrophication (AEU), Global Warming (GW), Non-renewable Energy (NE), and Mineral Extraction (ME). These midpoint categories form the following end (damage) categories, which represent quality change to the environment: Human Health (HH), Ecosystem Quality (EQ), Climate Change (CC) and Resources (R).

## RESULTS AND DISCUSSION

### Degradation of steroid hormones

Two groups of steroid hormones were studied: (i) estrogens: 17  $\alpha$ - and  $\beta$ - estradiols, estrone, estriol, equilin, 17  $\alpha$ -dihydroequilin, 17  $\alpha$ -etinylestradiol, and (ii) progestins: trimegestone, progesterone, norgestrel, gestodene and medrogestone. Treatability experiments for all aforementioned steroid hormones were conducted in mixture by three UV-based technologies: UV photolysis, UV/hydrogen peroxide and UV/persulfate.

### UV photolysis

Previous studies on the photolysis of estrone and 17  $\beta$ -estradiol in aqueous solutions concluded that UVC (200-280nm) radiation was found to be much more effective than UVA-vis (315-700 nm) (9). However, steroid hormones have a UV absorption minima at approximately 250 nm, and therefore, the degradation of these compounds by exposure to low-pressure UV lamps (254 nm) is expected to be low (10).

UV photolysis experiments were performed at flow rates of 100 mL min<sup>-1</sup> and 200 mL min<sup>-1</sup>. Figure 2 shows the removal efficiencies for all hormones. The highest removal efficiencies (80-98%) were achieved for estrone, equilin, gestodene, progestodene and medrogestone. Low degradation efficiency of approximately 40% to 50% was observed for 17  $\alpha$ - and  $\beta$ -estradiols, estriol, 17  $\alpha$ -etinylestradiol, 17  $\alpha$ -dihydroequilin and trimegestone. The increase of retention time did not lead to

enhancement of degradation process. Overall, UV photolysis treatment was not very effective for mixture of steroid hormones. Despite the structural similarities, the behavior of these compounds differs. For example, estrone is photolysed at faster rate than 17  $\beta$ -estradiol which is in accordance with previous studies (11). The progestins in general demonstrate better ability to be photolysed than estrogens. This difference can be explained by reported quantum yields of these compounds as  $220 \times 10^{-2}$  of progesterone and  $4-5 \times 10^{-2}$  mol Einstein<sup>-1</sup> of estrogens (E2 and EE2) (9). In general, the photolytic degradation follows pseudo first-order rate order for all the compounds. It was suggested that the photolysis of E1 and E2 causes the rupture and oxidation of the benzene ring to produce compounds containing carbonyl groups (11).

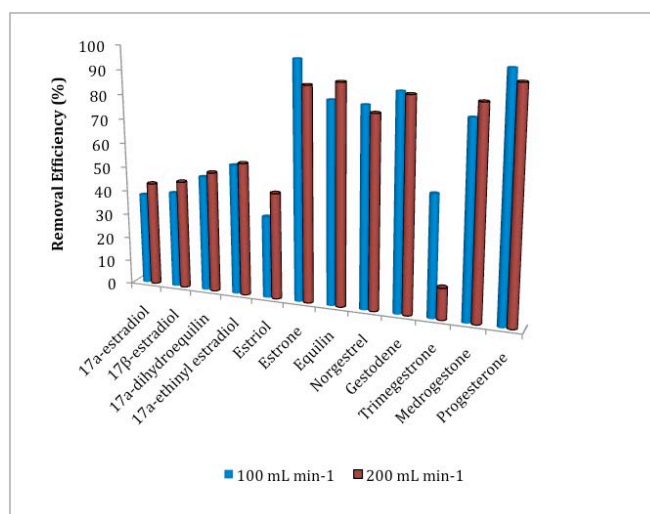


Figure 2. Removal efficiency of steroid hormones by UV-photolysis (254 nm, lamp intensity 7.9 mW cm<sup>-2</sup>, room temperature, circum neutral pH, retention time 10 and 20 min.)

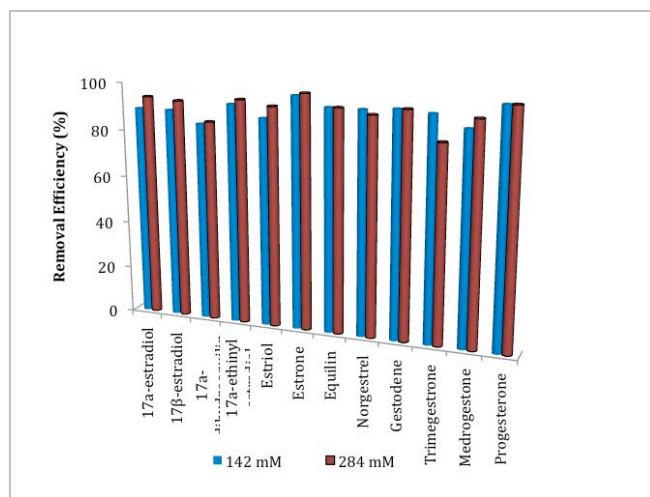


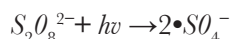
Figure 3. Effect of hydrogen peroxide concentration on the removal efficiency of steroid hormones by UV/hydrogen peroxide (254 nm, lamp intensity 7.9 mW cm<sup>-2</sup>, room temperature, circum neutral pH, retention time 10 min.)

### Effect of H<sub>2</sub>O<sub>2</sub> as an oxidizing agent

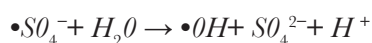
The enhancement of the UV-photolysis can be achieved via production of •OH radicals. In such hybrid technologies the efficiency of the oxidation process strongly depends on experimental conditions (12). For practical application an understanding of the photo-degradation mechanism is very important to achieve improvements in the yield and the efficiency of these processes. Figure 3 shows the impact of the hydrogen peroxide concentration on the removal efficiency of steroid hormones mixture. Addition of H<sub>2</sub>O<sub>2</sub> significantly increased the removal efficiencies for of all steroid hormones in comparison with UV-photolysis. With the addition of 5 mg L<sup>-1</sup> (142 mM) of hydrogen peroxide, the observed hormones removal was more than 90% for nine of the steroid hormones. Further increase of the dose up to and with 10 mg L<sup>-1</sup> (284 mM) lead to the enhanced removal for almost all steroid hormones up to 95%. Similar observations were also made by (10, 13), who found that the addition of peroxide removed up to 90% of both 17β-estradiol and 17α-ethinyl estradiol, which was a significant increase in comparison to UV photolysis. However, with subsequent increase in the dosage of hydrogen peroxide from 142 mM to 284 mM the removal efficiency of trimegestone slightly decreased.

### Effect of persulfate as an oxidizing agent

Similar to hydroxyl radicals, sulfate anion radicals may react with wide range of organic compounds (14). It is a strong oxidant with comparable reactivity to hydroxyl radical (oxidation potential 2.4 and 2.7 V, respectively). Sulfate radical anion itself could be generated by the scission of the peroxide bond of persulfate. In previous studies, the persulfate degradation has been performed by photolysis at wavelengths from 248 to 351 nm (15). The photolysis of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> has been postulated to result in the formation of two SO<sub>4</sub><sup>-•</sup> radicals:



Moreover, sulfate radical anion can react with water to form hydroxyl radicals :



The optimization of applied persulfate doses of 2 -10 mg L<sup>-1</sup> (8-42 mM) is shown in Figure 4. The average removal of steroid hormones was 89, 92 and 95%, respectively. It was observed that an increase in persulfate concentration results in a higher removal for most

of the steroids compounds, as can be seen in Figure 4. With 5 mg L<sup>-1</sup> (21 mM) of persulfate, removal efficiency reached above 90% for ten of the twelve hormones, however with double of the initial persulfate dose up to 10 mg L<sup>-1</sup> (42 mM) removal reached above 95% for ten of the hormones, nine of which reached above 98% removal. Interestingly, the increase in the dose of persulfate lead to a slight decrease of the removal of trimegestone, which is consistent with its behavior during UV/H<sub>2</sub>O<sub>2</sub> treatment.

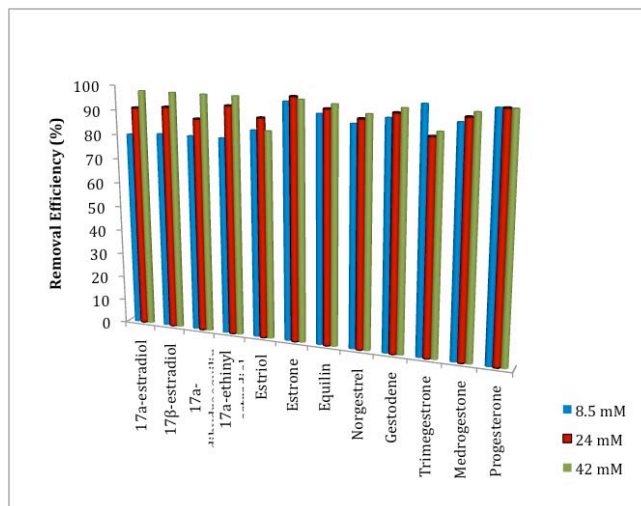


Figure 4. Effect of persulfate concentration on the removal efficiency of steroid hormones by UV/persulfate (254 nm, lamp intensity 7.9 mW cm<sup>-2</sup>, room temperature, circum neutral pH, retention time 10 min.)

### LIFE CYCLE ASSESSMENT

The two types of LCA studies performed were: contribution and comparative LCA. This approach is aimed not only to compare the different treatments, but also to identify the critical subsystems for each treatment and impact category. For this purpose the characterization results are used, disaggregating them so that the contribution of the chemical products, electricity and transports can be analyzed.

### Contribution analysis

The contribution analysis shows the environmental impacts of each component of the system. This analysis is universal regardless the functional unit as it gives the general idea on the contribution of various subsystems to the general system. Figure 5 (a, b and c) shows these relative contributions for each treatment (UV, UV/hydrogen peroxide, UV/persulfate, respectively). Every impact indicator is expressed as 100%, being the contribution of a sub-system a fraction of this figure.

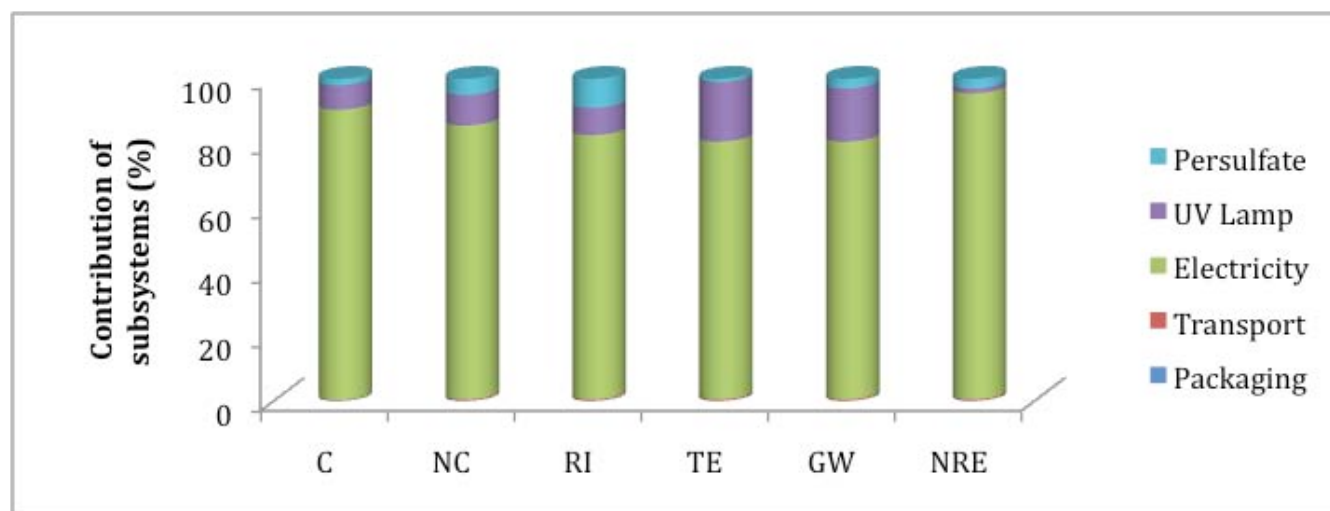
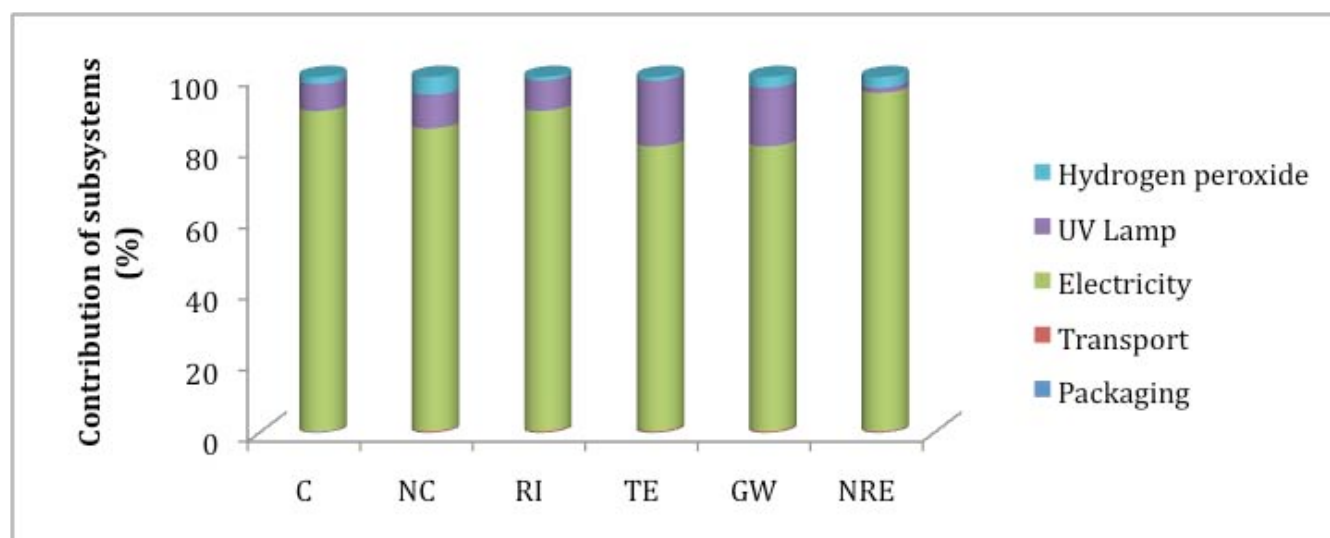
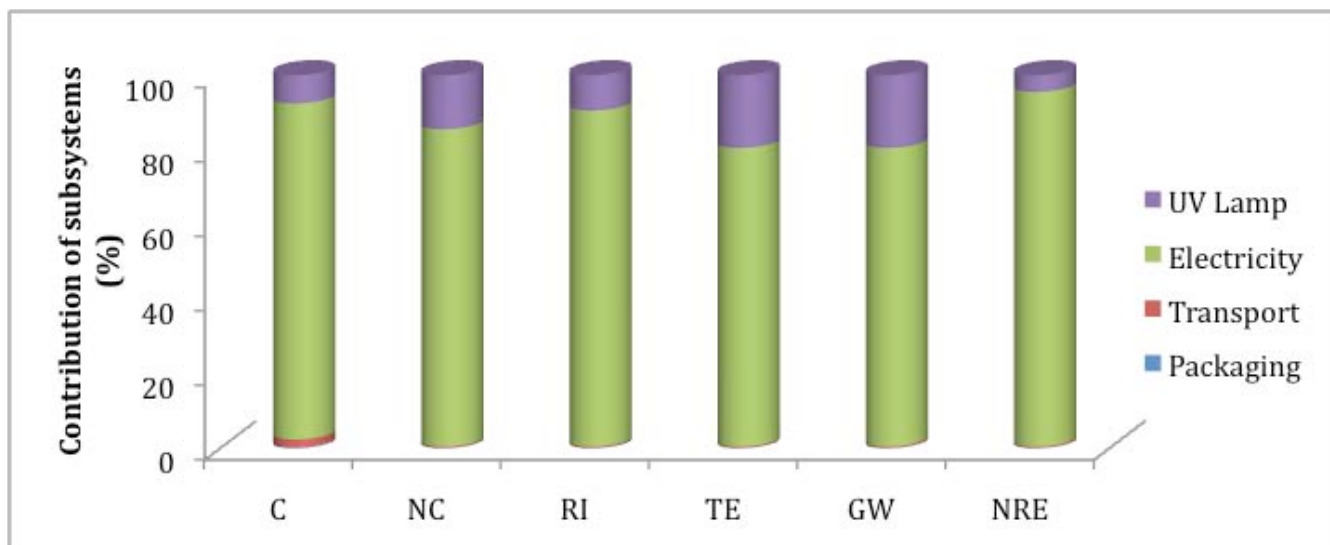


Figure 5. Contribution of subsystems in the characterization results for (a) UV, (b) UV/hydrogen peroxide, (c) UV/persulfate. The impact categories abbreviations: Carcinogens (C), Non-carcinogens (NC), Respiratory inorganics (RI), Terrestrial ecotoxicity (TE), Global warming (GW), Non-renewable energy (NE) and Mineral extraction (ME).

The impact categories affected by the UV-based treatment were: Carcinogens (C), Non-carcinogens (NC), Respiratory inorganics (RI), Terrestrial ecotoxicity (TE), Global warming (GW), Non-renewable energy (NE) and Mineral extraction (ME) (Figure 5).

From Figure 5 it is seen that electricity production is by far the most critical sub-system, accounting for at least 75% of the contribution to all impact categories in all treatments. In some cases electricity is responsible of almost 100% of the contribution. This noticeable impact is caused by the energy intensity of the AOPs and the characteristics of the Eastern US grid for electricity production, which relies to a considerable extent on fossil fuels, coals, fuel oil, nuclear, hydroelectric, and unconventional energy sources.

The contribution of chemical reagents (e.g. hydrogen peroxide and persulfate) as well as production of UV lamp is low, only up to 10% for all the technologies. Transporting the chemicals to the wastewater plant implies a relatively low impact in comparison to the contribution of other components of the studied systems (e.g. electricity production).

In a summary, it can be stated that the AOPs are mainly energy-intensive, which means that the environmental impact is proportional to the overall energy consumption for each treatment.

### Comparative analysis

In this section the different treatments are compared

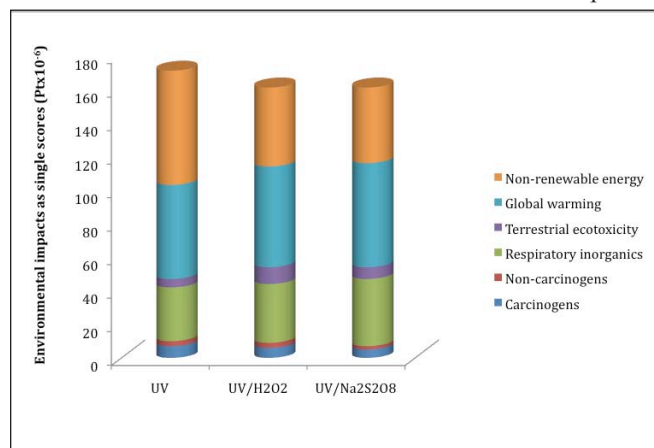


Figure 6. Environmental impact as a Single scores ( $\mu\text{Pt}$ ) for UV-based technologies

under the baseline scenario conditions. Figure 6 shows environmental performance for all the systems as single scores (Pt). The relative pattern in the other impact cat-

egories is very similar.

The single scores for all UV-based technologies were small due to small functional unit, however, the streamlined assessment revealed that all of the processes contribute in the following categories: Carcinogens (C), Non-carcinogens (NC), Respiratory inorganics (RI), Terrestrial ecotoxicity (TE), Global warming (GW), Non-renewable energy (NE) and Mineral extraction (ME).

As shown in Figure 6, the total score for UV-photolysis was higher. Therefore, it becomes evident that the enhanced removal efficiency promoted by addition of hydrogen peroxide and persulfate is the main factor responsible in the reduction of the non-renewable energy impact score.

### Streamlined Life Cycle Costing

The UV-based treatment systems were also assessed from an economic point of view. Streamlined LCC does not provide the information on the cost of the technology, but it can give a comparison between options under study. The main focus of the LCA is the exploitation of UV-based technologies, therefore, capital costs were excluded. Table 2 shows the operation cost in  $\$ \text{m}^{-3}$  wastewater contaminated with steroid hormones treated with each of the UV-based technology.

Operation cost is dominated by electricity, which is consistent with characteristics of AOP technologies as they are energy intensive processes. The most costly technology for the removal of steroid hormones is direct photolysis. This is mainly caused by the highest power consumption and the lowest efficiency. Therefore, this option is the least economically feasible for the treatment of wastewater contaminated with steroid hormones. The cheapest alternative is UV/persulfate, due to higher efficiency of treatment, which is consistent with the impacts for both technologies. However, several aspects, which can increase the operational costs such as maintenance and personnel, were excluded from the present study.

### Combined results of LCA and LCC as eco-efficiency index (EEI)

The eco-efficiency index (EEI) has been defined under basic premises: eco-efficiency is considered as the result of minimizing the binomial impact-cost, and environmental and economic aspects must receive the same weighting. This means that decreasing the magnitude



Table 2. Calculation of the Eco-efficiency Index (EEI) for UV-based technologies

EEI parameters	UV	UV/hydrogen peroxide	UV/persulfate
LCIA	171x10 <sup>-6</sup> Pt/ m <sup>3</sup>	161x10 <sup>-6</sup> Pt/ m <sup>3</sup>	163x10 <sup>-6</sup> Pt/ m <sup>3</sup>
LCC	10.5x10 <sup>-2</sup> \$/ m <sup>3</sup>	3.02\$/ m <sup>3</sup>	1.46\$/ m <sup>3</sup>
LCIA <sub>REL</sub>	1	0.94	0.95
LCC <sub>REL</sub>	1	0.29	0.14
EEF <sub>E</sub>	0.5	0.47	0.48
EEF <sub>C</sub>	0.5	0.14	0.07
EEI	1	0.61	0.55

of impacts is as important as decreasing costs (16). Taken into account these premises, EEI is expressed as:

$$EEI = EEF_E + EEF_C; \quad 0 \leq EEI \leq 1$$

where: EEF<sub>E</sub> is the environmental factor of EEI, and EEF<sub>C</sub> is the cost factor of EEI expressed as following:

$$EEF_E = \frac{LCIA_{REL}}{2}$$

$$EEF_C = \frac{LCC_{REL}}{2}$$

LCIA<sub>REL</sub> is the life cycle impact of an alternative, relative to the alternative under study with the highest impact; and LCC<sub>REL</sub> is the life cycle cost of an alternative, relative to the alternative under study with the highest life cycle cost. Therefore, these entities can be expressed as following:

$$LCIA_{REL} = \frac{LCIA}{LCIA_{MAX}}$$

$$LCC_{REL} = \frac{LCC}{LCC_{MAX}}$$

where:

LCIA is the life cycle impact of an alternative (Pt m<sup>-3</sup>)

LCIAMAX is the life cycle impact of the alternative entailing the highest impact from the set of alternatives under study (Pt m<sup>-3</sup>),

LCC is the life cycle cost of an alternative (\$ m<sup>-3</sup>), and

LCCMAX is the life cycle cost of the most expensive alternative under study (\$ m<sup>-3</sup>).

The life cycle impact of an alternative is obtained in the LCA as a normalized set of six indicator scores, namely the environmental profile. Nevertheless, in the EEI environmental impact is defined as unidimensional. Therefore normalization and weighting must be applied, in order to obtain a single impact score in (Pt m<sup>-3</sup>). Table 2 shows the detailed calculation of all the parameters leading to EEI for UV-based technologies under study.

From an integrated environmental-economic point of view, great differences appear between the alternatives for estrogen hormones treatment. The least eco-efficient option is direct photolysis, which reaches the highest EEI score, 1. That means that it is at the same time the most expensive and least environmentally friendly alternative. The most eco-efficient option is UV/persulfate, which has the lowest EEI (0.55), whereas the EEI for UV photolysis combined with hydrogen peroxide was 0.61.

## CONCLUSION

UV-based treatment systems (e.g. UV-photolysis, UV/hydrogen peroxide and UV/persulfate) were studied for the removal of mixture of steroid hormones (17 $\alpha$ -estradiol, 17 $\beta$ -estradiol, 17 $\alpha$ -dihydroequilin, 17 $\alpha$ -ethinyl estradiol, estriol, estrone, equilin, norgestrel, gestodene, trimegestrone, medrogestone and progesterone) in aqueous solution. The technological efficiency of the chemically- assisted processes (UV/hydrogen peroxide and UV/persulfate) was higher than UV-photolysis only. Further, combined Life Cycle Assessment and Life Cycle Costing (LCA&LCC) methodology was applied to identify optimal UV-based technology (UV-photolysis, UV/hydrogen peroxide and UV/persulfate) for removal of steroid hormones from aqueous solution. UV-photolysis was found as the least efficient option not only from technological, but also from environmental point of view. UV-based technologies have the environmental impacts in the

following categories: Carcinogens (C), Non-carcinogens (NC), Respiratory inorganics (RI), Terrestrial ecotoxicity (TE), Global warming (GW), Non-renewable energy (NE) and Mineral extraction (ME). The contribution of various subsystems in several impact categories was also assessed. The results of combined LCA&LCC have been summarized as eco-efficiency index (EEI). The results showed that the most eco-efficient option is UV/persulfate, which has the lowest EEI (0.55), the EEI for UV photolysis combined with hydrogen peroxide was 0.61, whereas the EEI for UV-photolysis was 1.

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