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Potential Formation of PCDD/Fs in Triclosan Wastewater Treatment: An Overall Toxicity Assessment Under a Life Cycle Approach

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HIGHLIGHTS:

Potential formation of PCDD/Fs in triclosan wastewater treatment.

Toxicity assessment derived from electrooxidation of triclosan using LCA.

LCIA methods are not fully adapted to PCDD/Fs computation in wastewater treatment.

Increase in environmental impacts when 2,3,7,8-TCDD is included.

PCDD/Fs omission tends to un toxic emissions in many oxidation processes.

KEYWORDS: Emerging pollutants, Life Cycle Assessment, Electrochemical oxidation (EOX), Polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), EPA method, Toxicity.

ABSTRACT

Wastewater may contain a diverse group of unregulated pollutants known as emerging pollutants, such as pharmaceuticals and personal care products (PPCPs). Triclosan (TCS) is a personal care product widely used as an antiseptic or preservative in cosmetics, hand wash, toothpaste and deodorant soaps. Advanced oxidation processes (AOPs) have been used as effective and alternative treatments for complex wastewater. However, an important criterion for the assessment of AOPs and their operation conditions could be the potential formation of new toxic secondary products, such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), especially when emerging pollutants are present in the media. If these are omitted from environmental management studies, the real environmental impacts of a WWTPs (wastewater treatment plants) may be underestimated. Consequently, the current study aims to evaluate the environmental impacts derived from electrooxidation (EOX), one of the most effective oxidation technologies, of emerging pollutants using Life Cycle Assessment. The analyses were performed for the treatment of effluents containing TCS, firstly without considering the formation of PCDD/Fs and, thereafter, considering the effects of these compounds. Total toxicity, calculated through different methods and corresponding impact factors, were evaluated for each stage of the process when different electrolytes are used, including PCDD/Fs formation. Finally, a sensitivity analysis was carried out to study i) the effect of the TCS initial concentration on the environmental impacts associated to ecotoxicity for the different life cycle methods and ii) the influence of changing the organic pollutant on PCDD/Fs formation employing 2-chlorophenol (2-CP). As a result, LCIA methods demonstrate that they are not fully adapted to the computation of PCDD/Fs in the water compartment, since only 2,3,7,8-tetraclorodibenzo-p-dioxina (2,3,7,8-TCDD) is present as a substance in the impact categories assessed, ignoring the remaining list of PCDD/Fs.

1. Introduction

Domestic and industrial activities generate high amounts of wastewater, whose direct disposal to natural channels causes a negative impact to the environment (Tarpani and Azapagic, 2018; Vázquez-Rowe, 2020). Wastewater can contain, among others, a diverse group of unregulated pollutants, including pharmaceuticals and personal care products (PPCPs), which raises increasing concerns on the risks they pose to humans and the environment. These pollutants are known as emerging pollutants (Muñoz et al., 2008). PPCPs include anticonvulsants, contrast agents, hormones, nonsteroidal anti-inflammatory drugs, beta-blockers, lipid regulators, painkillers, preservatives, disinfectants, insect repellants, fungicides, soaps and detergents, fragrances, and sunscreen UVfilters (Awfa et al., 2018). Within PPCPs, triclosan (TCS), i.e., 5-chloro-2-[2,4 dichlorophenoxy] phenol, is a personal care product widely used as an antiseptic or preservative in cosmetics, hand wash, toothpaste and deodorant soaps, at concentrations ranging from 0.10 to 0.30% (Solá-Gutiérrez et al., 2018). However, given its toxicity, the United States Food and Drug Administration (USFDA) has banned its use in consumer soaps and other wash products (FDA, 2016).

These types of pollutants enter the wastewater, and then get transferred to wastewater treatment plants (WWTPs) (Wei et al., 2015, Thomaidi et al., 2017). In many cases, the effectiveness of these WWTPs for removing chemicals is limited by secondary treatment processes, such as biological filters and activated sludge. Therefore, a large number of organic contaminants escape to treatments becoming ubiquitous contaminants in the environment. Taking into consideration the limitations of treatments applied in WWTPs, additional processes are required for the elimination of these problematic compounds and, therefore, decrease their toxicity in the environment (Serna-Galvis et al., 2019). In this context, advanced oxidation processes (AOPs) have been used as effective and alternative treatments for complex wastewater, especially in the case of non-biodegradable compounds (Serna-Galvis et al., 2019). This kind of technologies constitute a set of techniques based on the powerful capability of hydroxyl radicals ($OH^{\bullet}$) to oxidize organic compounds. One of its main advantages includes fast degradation rates and non-selective oxidation, allowing the treatment of many pollutants at the same time, and potential to reduce the toxicity of contaminants (Fernández-Castro et al., 2015). Among them AOPs, electrochemical oxidation (EOX) has been demonstrated as an effective technology with good environmental performance (Solá-Gutiérrez et al., 2018).

A crucial issue when using AOPs is the fact that, when employed, other organic compounds may be produced from the degradation of the initial ones. In fact, in some occasions the secondary compounds formed are more acutely toxic than their parent compounds. Furthermore, due to their stability, they are not breakable in less-toxic molecules (Vallejo et al., 2013). According to the literature (Vallejo et al., 2015), an important criterion for the assessment of AOPs and their operation conditions could be the potential formation of new toxic secondary products, such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), especially when chlorinated organic compounds, as emerging pollutant, considered precursors of these compounds are present in the media. PCDD/Fs, also known as dioxins and furans, are a group of organic chemical substances that are classified as persistent organic pollutants (POPs). They are characterized by a particular combination of physical and chemical properties. Moreover, they persist for long periods in the environment, becoming widely distributed through different natural compartments. Wildlife and humans, when exposed, accumulate these highly toxic substances in their fatty tissue (Stockholm Convention, 2001) (More details are included in the Section 1 of the Supplementary Data – SD).

Taking into account that the removal of emerging pollutants is highly required, the implementation of AOPs needs exhaustive knowledge, not only regarding the removal efficiency of the target pollutants, but also concerning the environmental impacts linked to the technology and its operational conditions. A robust and standardized methodology to evaluate and quantify the environmental impacts along all the life cycle stages of a product, process or service, aiming to reduce the consumption of natural resources consumption and environmental burdens, is Life Cycle Assessment - LCA (Hellweg and Milà i Canals, 2014; García-Herrero, 2017). This methodology has experienced in recent years a continuous update in terms of life cycle modelling, in an effort to improve the life cycle inventory databases, as well as the robustness of the assessment methods. The latter has been attained either by including a more comprehensive list of substances that contribute to the generation of a particular environmental impact, or by improving the accuracy of their characterization factors (Saouter et al., 2017a, 2017b; Wender et al., 2018). Despite these efforts, LCA currently lacks full development, and shows certain limitations from a modelling approach (Zhao et al., 2018). For instance, it is highly susceptible to uncertainties and disparities in practice; a nontrivial interpretation step is necessary in order to deduce a meaningful outcome. Furthermore, Life Cycle Impact Assessment (LCIA) is not capable of covering the entire spectrum of anthropogenic consequences to the environment (Mayer et al., 2019).

The influence of anthropogenic activities on toxicity is a growing concern that requires outstanding attention, by either a merely scientific interest or its health or environmental importance. To date, a number of LCA studies have focused on the estimation of indirect toxicity contribution from energy, materials and infrastructure of wastewater treatment technologies, including different wastewater applications, such as greywater (Dominguez et al., 2018), urban (Ioannou-Ttofa et al., 2016) or industrial wastewater (Foteinis, et al., 2018). Likewise, direct toxicity related to some trace emerging pollutants , have been widely studied: including pharmaceuticals emissions such as ibuprofen, Naproxen, Diclofenac, Bisphenol-A and TCS, among others (Lorenzo-Toja et al., 2016), as well as pharmaceuticals, pharmaceutical metabolites, personal care products and personal care products metabolites (Muñoz et al., 2009) or active pharmaceutical ingredients (APIs) (Emara et al., 2019). However, there is a lack of LCA studies dealing with the toxicity posed by the formation of dioxins and furans during the treatment process, including those associated to AOPs. Taking the previous considerations together with the demonstrated significance of dioxins and furans formation in wastewater treatment (Solá-Gutiérrez et al., 2018), the omission of an accurate assessment could translate into an underestimation of the toxicity of the evaluated treatment processes, as well as the wrong operation conditions in which the technologies are operated. Therefore, the main objective of this study is to provide a life cycle modelling where the system boundaries are elongated to account for the potential formation of PCDD/Fs when wastewater containing precursor molecules of these compounds are treated by AOPs. Based on experimental framework this study has been established for the emerging organic pollutant TCS when EOX technology is applied. Moreover, a comparative analysis is performed across different assessment methods in LCIA to understand the influence that these inclusions may have when using different metrics. Results are intended to be of interest for the LCA community, considering the lack of accountability of secondary pollutants in wastewater treatment technologies, as well as for policy-makers, considering that the inclusion of these substances could potentially address the decision-making process.

2. Experimental framework

The experiments carried out in this study were performed in batch mode, employing a laboratory DiaCell system, with two regular electrodes composed of BDD as the anode, and titanium as the cathode.

2.1. EOX experiments

In order to treat the influent wastewater, the operation conditions that were considered are described in SD, Section 2, Table S2. In this context, TCS concentration can vary ten-thousand-fold, covering the range between a strongly polluted industrial waste (hundreds of mg L^{-1}) and the very small concentrations that can be found in the effluent of municipal WWTPs (usually measured in µg L^{-1}). In the current study, an average TCS concentration of 100.00 mg L^{-1} was employed in order to assess the potential formation of more toxic compounds after applying the EOX process. Table S2 shows the specific operation conditions for both EOX experiments carried out by Solá-Gutiérrez et al. (2018, 2019) for TCS experiment. In these works the influence of the variables of operation, electrolyte, initial concentration and presence of catalyst on the formation of highly chlorinated PCDD/Fs during the electrochemical oxidation of triclosan were analyzed. Under these conditions, the International Toxicity Equivalency Factor (I-TEF) was calculated. Finally, considering the information reported in literature, a mechanism describing the formation of low chlorinated PCDD/Fs from TCS oxidation reactions was proposed.

2.2. Analytical procedure

The concentration of TCS at the end of the experiment was quantified by high performance liquid chromatography (HPLC), using a Waters 2695 HPLC coupled to a photo diode array (PDA) detector. A replicate of the experiment was carried out.

PCDD/Fs were determined according to the Standard Method US EPA 1613 by isotope dilution and high-resolution gas chromatography/high resolution mass spectrometry (HRGC-HRMS) (US EPA, 1994). This method consists of a set of stages that requires a rigorous follow up of each step: three liquid-liquid extractions, three concentrations, an H_2SO_4 treatment, two filtrations and purification steps prior to the analysis by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-

HRMS). The preparation of each sample through all these stages takes approximately five days, and a large amount of different reagents is employed, which increases the final cost considerably. Different standard solutions have to be employed during the quantification and quality (QC/QA) assurance in the analysis of PCDD/Fs: labelled compound solution, LCS; precision and recovery solution, PAR; and internal standard solution, ISS. The main objective of the QC/QA is the verification of the accuracy, recovery rates recoveries and the absence of contamination during the analysis. When the results from the blank experiments show that the concentrations of native PCDD/Fs are below the detection limit, indicating the absence of contamination, and when average recoveries of labelled PCDD/Fs are in the range of the method, it can be concluded that the analytical methodology setup fulfils the acceptance criteria established by EPA 1613 Method. On the other hand, the recoveries obtained of the labelled standard compounds (1613 LCS) during the multiple steps followed to prepare the sample before the analysis were between 55.00 and 117.00%. The average recoveries were within the range established in the EPA 1613 method. Furthermore, blanks covering the whole sample preparation methodology showed that congeners were either not detected or below the detection limits, indicating the absence of contamination. The average detection limits (LOD) were within the range 1.77 - 0.03 pg for all the analysis (Solá-Gutiérrez et al., 2018, 2019).

3. Toxicity-related impacts under a life cycle approach

LCA followed the standards required by the UNE-EN ISO 14040:2006 and ISO 14044 international standards (ISO, 2006a, 2006b). Thereby, the analysis was performed following the LCA stages detailed in the preceding documents: definition of the goal and scope and functional unit and system boundaries, life cycle inventory (LCI) followed by the LCIA methods concluding with the interpretation of the results.

3.1. Functional unit and system boundaries

The function of the electrochemical oxidation is the reduction of the concentration of the different pollutants employed until they reach minimum values (i.e., a removal of at least 95.00%). Hence, the functional unit (FU) is defined based on the same treated volume of polluted water and the same amount of pollutant removed. Consequently, 1.00 m^3 of treated wastewater was selected as the FU, in line with other studies in the literature evaluating wastewater treatment technologies (Lorenzo-Toja et al., 2015). Therefore, all mass and energy inputs and outputs were referred to this FU. The use of a similar FU that considers the same treated water volume and a fixed reduction level of the contaminant have been previously reported in literature (Dominguez et al., 2018). Figure 1 shows the flow diagram and the system boundaries considered for each treatment. The analysis is going to follow a "cradle to gate" pathway considering water-energy-reagents-dioxins.

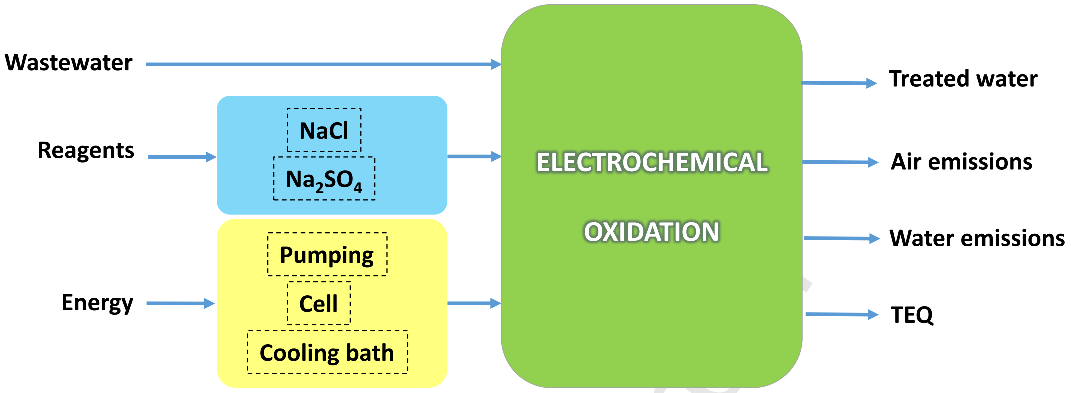


Figure 1. Graphical representation of the system boundaries of the systems under analysis. TEQ Equivalent Toxicity (Section 3.3).

3.2. Life cycle inventory

Reactants, energy and PCDD/Fs flows examined in this study were documented in the LCI, which collects the most relevant input and output data for the case under study in separate unit processes. The summary of data sources used in LCI are detailed in SD, Section 3, Table S3. The quality of the LCI per FU are detailed in Table 1. The main assumptions considered in the inventory phase of the LCA can be summarized as follows:

- For the estimation of energy consumption and reagents, a concentration of 100.00 mg L^{-1} of TCS is assumed to be implemented in a laboratory plant to treat synthetic wastewater.

- The electricity consumption corresponds to a treatment time required to remove at least 95.00% of the initial concentration of TCS in 1.00 L of wastewater for a period of 3.00 hours.

- To improve data quality and consider local characteristics, the electricity mix provided by the PE database was adapted to the characteristics of the Spanish mix in 2018, which contains 40.10% of renewable sources (hydro, wind, solar photovoltaic, solar thermal, among others) and 59.90% of non-renewable sources (pumped storage, nuclear, coal, fuel/gas, among others).

Table 1. LCI for TCS Input and Output.

INPUTS	UNIT	TCS: 100.00 mg L^{-1}	
Untreated water	m^3	1.00E-03	
Reagents			
NaCl	kg FU^{-1}	3.29	
Na_2SO_4	kg FU^{-1}	3.00	
Energy			
Pumping	MJ FU^{-1}	4.02	
Cell	MJ FU^{-1}	51.34	
Cooling bath	MJ FU^{-1}	10.26	
OUTPUTS	**UNIT**	**TCS: 100.00 mg L^{-1}**	
		NaCl	**Na_2SO_4**
TEQ	kg FU^{-1}	2.75E-10	5.31E-11
2,3,7,8-TCDD		1.71E-10	3.38E-11
1,2,3,7,8-PeCDD		1.71E-10	2.81E-11
1,2,3,4,7,8-HxCDD		3.08E-11	2.20E-12
1,2,3,6,7,8-HxCDD		7.86E-11	2.42E-11
1,2,3,7,8,9-HxCDD		2.04E-11	2.19E-12
1,2,3,4,6,7,8-HpCDD		4.30E-11	7.37E-12
OCDD		2.25E-11	6.05E-12
2,3,7,8-TCDF		2.00E-11	6.36E-12
1,2,3,7,8-PeCDF		2.15E-12	9.10E-13
2,3,4,7,8-PeCDF		4.30E-12	2.11E-12
1,2,3,4,7,8-HxCDF		1.73E-12	6.60E-13
1,2,3,6,7,8-HxCDF		1.39E-12	4.00E-13
1,2,3,7,8,9-HxCDF		3.60E-13	7.30E-13
2,3,4,6,7,8-HxCDF		6.44E-12	5.10E-13
1,2,3,4,6,7,8-HpCDF		3.41E-11	3.17E-11
1,2,3,4,7,8,9-HpCDF		5.10E-13	3.00E-13
OCDF		1.13E-12	3.11E-12
Treated water (95.00% removal)	m^3 FU^{-1}	1.00E-03	

3.3. Life cycle impact assessment – (LCIA) methods

Several commonly used LCIA assessment methods were chosen in order to obtain toxicity results. The International Reference Life Cycle Data System Handbook (JRC, 2011) determined that USEtox was the best available method for toxicity-related impact categories. Table S4 in the SD shows the impact categories that are contained in this method. This method is based on scientific consensus to identify and obtain human and eco-toxicological impacts values linking emissions to impact through three steps: environmental fate, exposure and effects (see Section 4 in SD for more information regarding USEtox) (Rosenbaum et al., 2007). However, despite this recommendation, the rationale behind selecting several assessment methods is justified on the fact that methods are generally experiencing updates and upgrades given the active development in LCIA.

CML 2001, created by the University of Leiden in the Netherlands in 2001, contains more than 1700 different flows (Guinée et al., 2002). The method is divided into baseline and non-baseline, the baseline being the most common impact categories used in LCA. Table S5 in the Section 4 of the SD shows the categories it contains. There are four impact categories derived from ecotoxicological effect factors and fate data that express the relative toxicity of each substance to a reference substance (i.e., 1,4-dichlorobenzene) (Ligthart et al., 2010): Human Toxicity, Freshwater Aquatic Ecotoxicity, Marine Aquatic Ecotoxicity and Terrestrial Ecotoxocity. Section 4 in the SD collects more information about CML 2001 method.

On the other hand, the main objective of the ReCiPe method is to provide a method that combines Eco-Indicator 99 and CML, in an updated version. ReCiPe distinguishes two levels of indicators: i) midpoint indicators, and ii) endpoint indicators with the following categories: damage to human health, damage to ecosystems and damage to resource availability. Table S6 in the Section 4 of the SD shows the impact categories for this method (Goedkoop et al., 2009).

Under LCA framework, the EPA method, as described in Section 1 of the SD, cannot be considered strictly an LCIA method. However, it includes an in-depth description on how to estimate the toxicity of complex mixtures containing PCDD/Fs. More specifically, the toxicity of the 2,3,7,8 congeners is related to that of the most toxic isomer, 2,3,7,8-TCDD, through the use of the international toxicity equivalency factors (I-TEFs). TEF values for PCDD/Fs are shown in the Table S1 in the Section 1 of the SD. The levels of the individual 2,3,7,8-PCDD/Fs are converted into one value of toxic equivalents (TEQ) of the isomer 2,3,7,8-TCDD. The TEQ value gives an idea of the potential toxicity of the sample and is calculated as the sum of the concentration of each congener multiplied by its TEF.

$$TEQ = \sum_i (PCDD_i \cdot TEF_i) + \sum_j (PCDF_j \cdot TEF_j) \quad (1)$$

Where $PCDD_i$ and $PCDF_j$ are the polychlorodibenzo-p-dioxin and polychlorodibenzofuran, a total of 17 congeners with the positions 2,3,7,8 chlorinated.

3.4. Characterization factors for PCDD/Fs

LCIA methods acknowledge 2,3,7,8-Tetrachlorodibenzo-p-dioxin as being one of the most relevant existing toxic substances. Consequently, it is included in all the impact categories assessed in the methods evaluated. However, a set of 16 additional PCDD/Fs are typically omitted from LCA studies due to the fact that characterization factors for them are yet to be computed. In the current study, two different approaches were considered. On the one hand, the LCIA methods evaluated (i.e., CML, ReCiPe and USEtox) were run including the emissions to water identified for the substances that are present in the three assessment methods. On the other hand, the TEF values from the EPA method for the different PCDD/Fs, which are shown in Table S1, were used to convert the environmental impacts of the remaining PCDD/Fs on the basis of the specific characterization factor of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in each category. The latter perspective allowed understanding the amount of potential environmental impacts that are being omitted in each impact category due to the lack of a comprehensive modelling of PCDD/Fs.

3.5. Scenario analysis

A scenario analysis was conducted to account for alternative approaches undergone in the experimental framework. Firstly, an alternative was varying the concentration of TCS in the wastewater. For this, beyond the baseline 100.00 mg L^{-1} scenario, concentrations of 10.00 and 150.00 mg L^{-1} were modelled in order to assess the potential formation of more toxic compounds after applying the EOX process using NaCl and Na_2SO_4 as electrolytes. The output LCIs per FU are detailed in Table S7 in the Section 5 of the SD.

A second scenario was assumed considering an alternative pollutant to TCS. Therefore, a priority pollutant, 2-chlorophenol (2-CP) was the substance selected to conduct additional experiments. If emerging pollutants are relatively new and not regulated, this is not the case of priority pollutants, which are mostly part of these, but are regulated at international and national levels due to their high risk to the aquatic biota and human health, hence their “priority” status (Teodosiu et al., 2018). Directive 2013/39/EU (EC, 2013) defines a list of 45-priority pollutants grouped as single or classes of substances, which contains pesticides, industrial additives and secondary products, pharmaceuticals, personal care products, steroid hormones, drugs of abuse, food additives, flame/fire retards, surfactants and others. Similarly, the United States Environmental Protection Agency regulates 126 priority pollutants, including heavy metals, organic chemicals, and their specific analytical test methods (US EPA, 2014). Chlorinated organic compounds, such as chlorophenols (CPs), are some of the categories that have been listed as priority pollutants (Vallejo et al., 2013). Out of this group of substances, 2-CP is worth mentioning as one of the most applied CPs. In addition, the high water solubility of 2-CP contributes to worsen the problem of its potential water pollution. A concentration of 2,000.00 mg L^{-1} was assumed for the correct assessment of the formed secondary products during the treatment. However, it should be noted that, in common situations, such an amount of 2-CP is rare to find in environmental samples. In fact, Terashima and colleagues (2002) have reported concentrations from 1.00 to 21.00 mg L^{-1} in various industrial effluents and municipal waste discharges, although higher concentrations of phenolic compounds have also been reported in wastewater from oil refineries and coking plants (i.e., from 500.00 to 1,500.00 mg L^{-1}) (El-Ashtoukhy et al., 2013). The concentration of 2-CP at the end of the experiment was quantified by high performance liquid chromatography (HPLC), using a Waters 2695 HPLC coupled to a photo diode array (PDA) detector. The electricity consumption that corresponds to a treatment time required to remove at least 95.00% of the initial concentration of 2-CP in 1.00 L of wastewater was determined as a 4.00 hour period. The input and output of the LCI per FU are detailed in Tables S8-S9 list in the Section 5 of the SD.

4. Results and discussion

4.1. PCDD/Fs toxicity assessment

4.1.1. Influence of PCDD/Fs on the toxicity LCIA methods

The PCDD/Fs toxicity assessment was carried out on the application of different life cycle methods for the evaluation of the environmental impacts associated to human toxicity and ecotoxicity. Figure 2a shows the influence the life cycle methods present on toxicity when NaCl is used as electrolyte in EOX processes. In the same way, Figure 2b shows the influence the life cycle methods present on toxicity when $NaSO_4$ is used as an alternate electrolyte in the EOX process. The absolute values are shown in Tables S10 and S11 in the Section 6 of the SD.

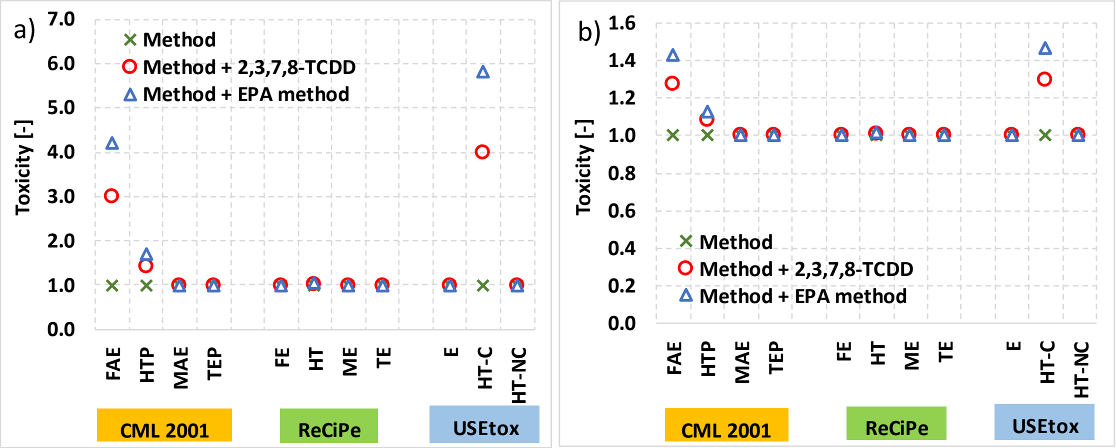


Figure 2. Influence on environmental impacts across different life cycle assessment methods when the EOX process is applied to TCS and a) NaCl reactant or b) Na_2SO_4 reactant.

FAE=Freshwater Aquatic Ecotoxicity, HTP=Human Toxicity Potential, MAE=Marine Aquatic Ecotoxicity, TEP=Terrestric Ecotoxicity Potential, FE=Freshwater Ecotoxicity, HT=Human Toxicity, ME=Marine Ecotoxicity, TE=Terrestrial Ecotoxicity, E=Ecotoxicity, HT-C=Human Toxicity-cancer, HT-NC= Human toxicity-non-cancer.

Figure 2a shows how the presence of 2,3,7,8-tetraclorodibenzo-p-dioxina (2,3,7,8-TCDD) has minimal influence on the results of the ReCiPe method when NaCl is used as a reactant in the EOX process. However, important differences can be identified when the CML 2001 and USEtox methods are applied. For CML, a threefold increase in environmental impacts is identified in freshwater ecotoxicity when the 2,3,7,8-TCDD is included within the system boundaries in the LCI, while a fourfold augmentation is visible whenever the EPA method TEFs are aggregated to the computation. Noticeable increases in both metrics are visible also for the human toxicity impact category, whereas increments are negligible for marine and terrestrial ecotoxicity. In the case of USEtox, the changes in environmental impact are very low for ecotoxicity and non-carcinogenic human toxicity, but impacts increase six fold when the impact category is coupled with the EPA method to account for all the PCDD/Fs present in the wastewater. If this same impact category is applied without accounting for these additional PCDD/Fs, the increase is fourfold with respect to an analysis that obviates the formation of these substances.

When Na_2SO_4 is used (see Figure 2b), the results show a very similar distribution across impact categories. However, the increase in environmental impacts when 2,3,7,8-TCDD are included, with or without coupling with the EPA method, is substantially lower.

4.1.2. Influence of PCDD/Fs on the toxicity in different interventions

Figures 3-5 summarize the results of applying the LCA models CML 2001, ReCiPe and USEtox to the effluent containing TCS, when EOX processes using NaCl and Na_2SO_4 as electrolytes treat this stream, and considering the impact categories analysed in the previous section. However, in contrast to the representation in Figure 2, the results are now disaggregated per life cycle intervention. As expected, based on the results shown in Section 4.1.1, 2,3,7,8-TCDDD represented the highest portion of environmental impacts in two specific impact categories when NaCl is used as an electrolyte: freshwater aquatic ecotoxicity in the CML 2001 method, and the human toxicity (carcinogenic) in the USEtox model. Furthermore, if these two categories are coupled with the EPA method, a slight increase in the relative values of PCDD/Fs (EPA method) is observed. In contrast, when Na_2SO_4 is used as the electrolyte, the relative importance of the electrolyte increases considerably, whereas the relative contribution of PCDD/Fs (2,3,7,8-TCDD and EPA method) decreases substantially. While the latter observation is valid across all the impact categories assessed, it is particularly relevant for human toxicity (carcinogenic) in USEtox, where the reactant becomes the main environmental impact, ahead of energy and PCDD/Fs. The reasons for this different behaviour when using Na_2SO_4 are mainly two. On the one hand, the toxicity of the electrolyte is much higher when using Na_2SO_4. On the other hand, the formation of PCDD/Fs is substantially lower when using this electrolyte rather than NaCl, as shown in Table 1. The absolute values are shown in Tables S12, S13 and S14 in the Section 6 of the SD.

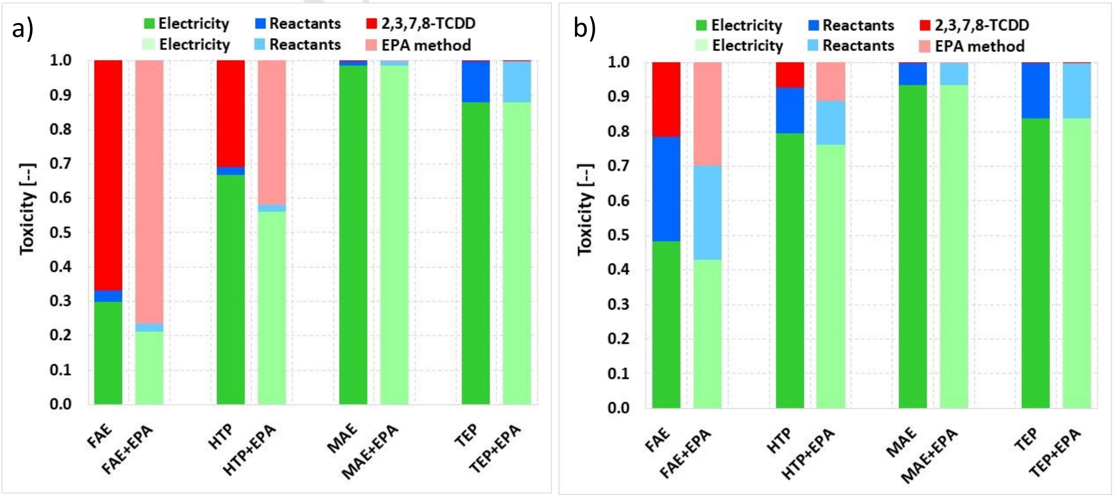


Figure 3. Environmental impacts for toxicity impact categories using the CML 2001 method disaggregated per inventory items. a) NaCl; b) Na_2SO_4.

FAE=Freshwater Aquatic Ecotoxicity, HTP=Human Toxicity Potential, MAE=Marine Aquatic Ecotoxicity, TEP=Terrestric Ecotoxicity Potential.

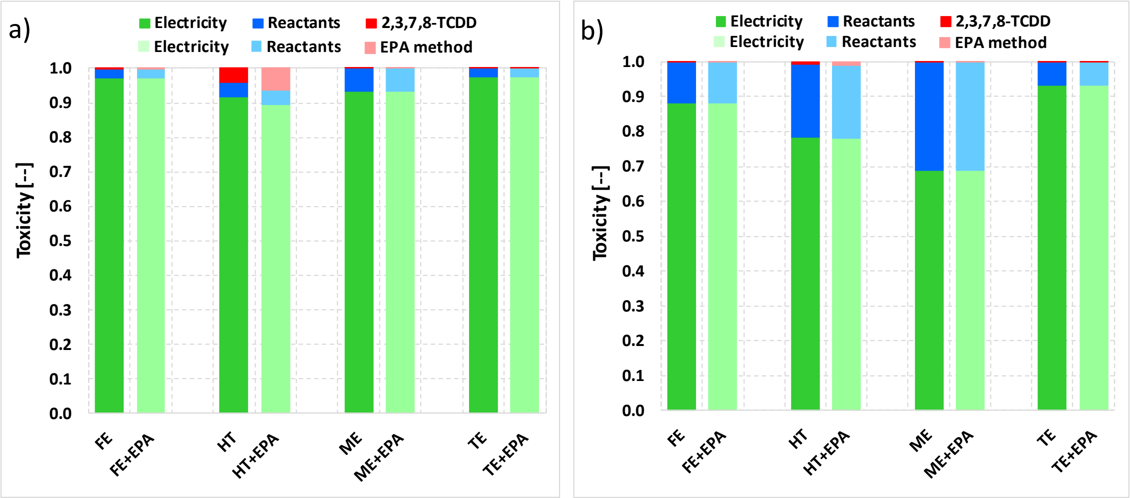


Figure 4. Environmental impacts for toxicity impact categories using the ReCiPe method disaggregated per inventory items. a) NaCl; b) Na_2SO_4.

FE=Freshwater Ecotoxicity, HT=Human Toxicity, ME=Marine Ecotoxicity, TE=Terrestrial Ecotoxicity.

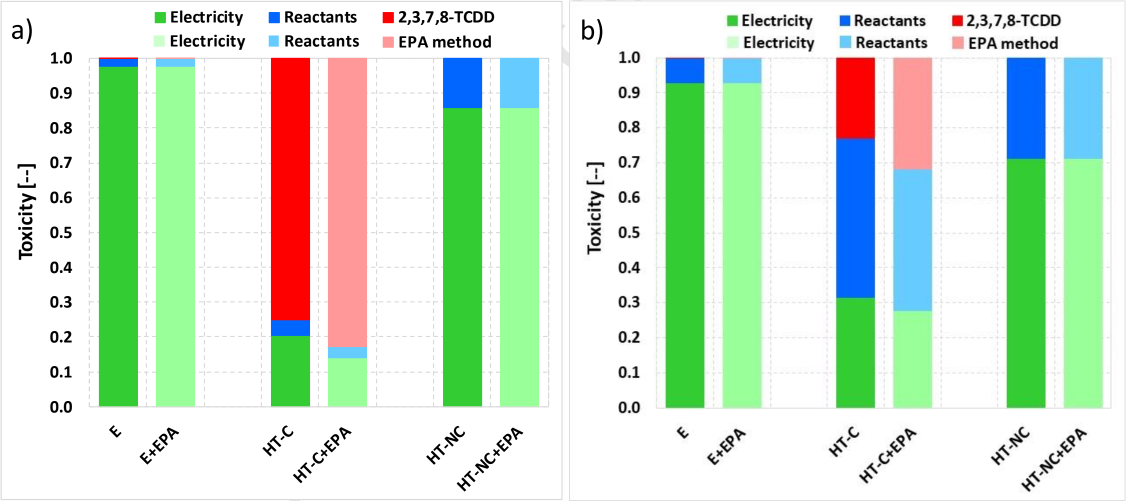


Figure 5. Environmental impacts for toxicity impact categories using the USEtox method disaggregated per inventory items. a) NaCl; b) Na_2SO_4.

E=Ecotoxicity, HT-C=Human Toxicity-cancer, HT-NC= Human toxicity-non-cancer.

4.1.3. Electrolyte influence on toxicity

The importance of the electrolyte in the final toxicity is further represented in Figure 6 after applying the LCA models CML 2001, ReCiPe and USEtox to the effluent containing TCS when this stream is treated using EOX processes, comparing the environmental impacts of using one of the two reactants. The absolute values are shown in Table S15 in the Section 6 of the SD.

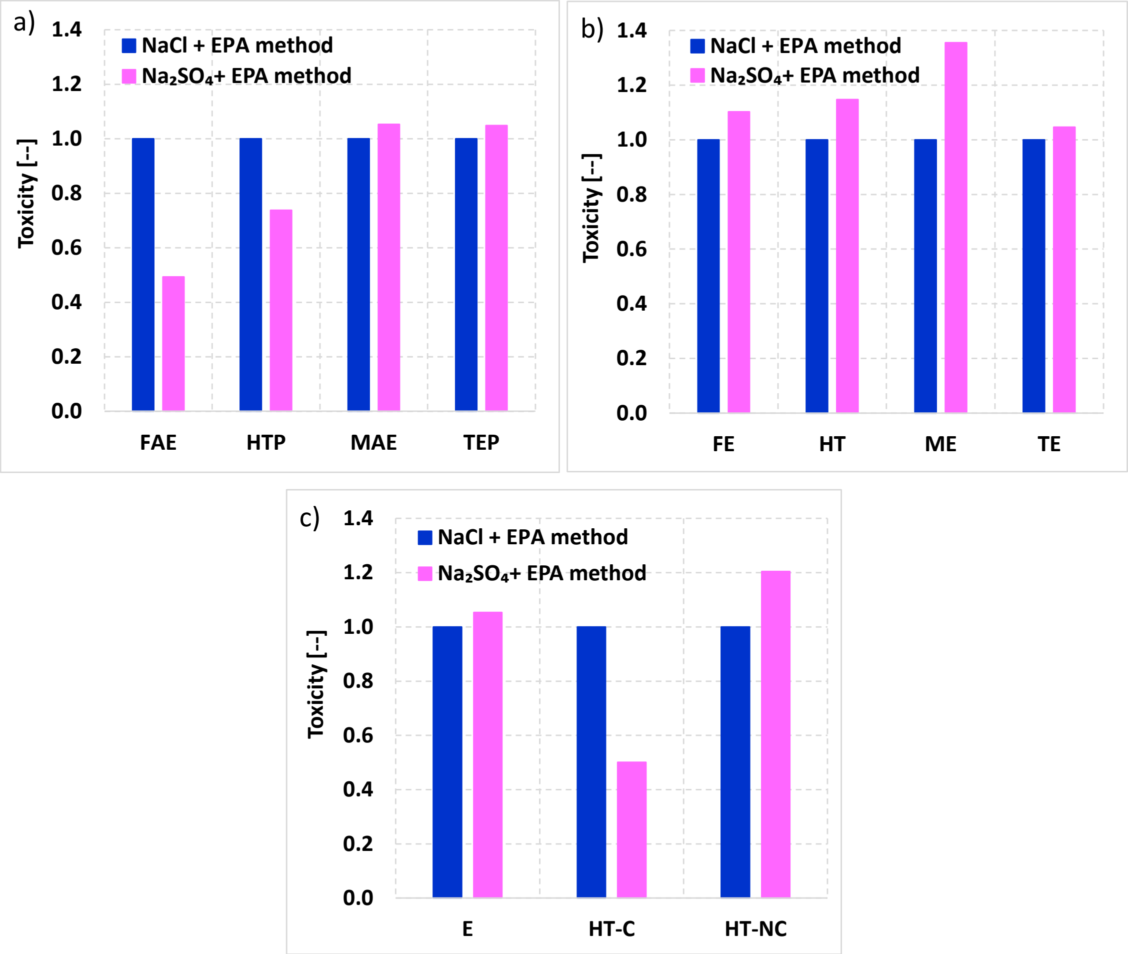


Figure 6. Graphical representation of the influence of the electrolyte choice on the environmental impacts for a) CML 2001 method, b) ReCiPe method, and c) USEtox method.

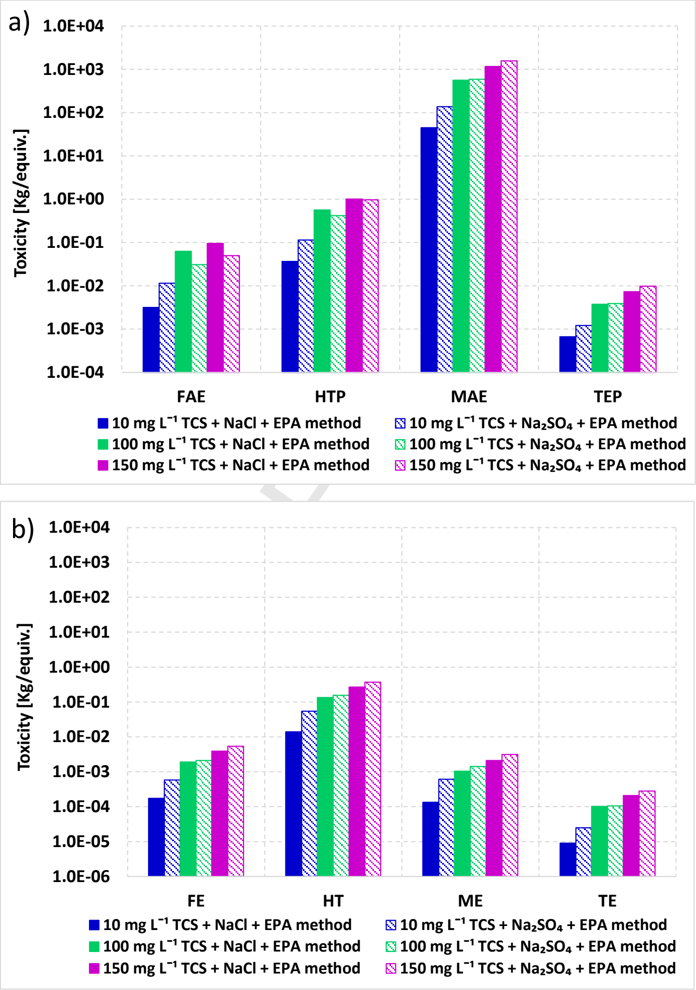
FAE=Freshwater Aquatic Ecotoxicity, HTP=Human Toxicity Potential, MAE=Marine Aquatic Ecotoxicity, TEP=Terrestric Ecotoxicity Potential, FE=Freshwater Ecotoxicity, HT=Human Toxicity, ME=Marine Ecotoxicity, TE=Terrestrial Ecotoxicity, E=Ecotoxicity, HT-C=Human Toxicity-cancer, HT-NC= Human toxicity-non-cancer.

In those impact categories in which PCDD/Fs represent a low relative contribution to environmental impacts, an increase in total toxicity can be observed when using Na_2SO_4. In the CML 2001 method, these impact categories are Marine Aquatic and Terrestric Ecotoxicity (Figure 6a), in the ReCiPe method, all impact categories (Figure 6b) and in the USEtox method, ecotoxicity and human toxicity (cancer) (Figure 6c). In contrast, when PCDD/Fs emissions represent a high proportion of total toxicity, the use of Na_2SO_4 decreases the impacts noticeably as compared to the use of NaCl. This situation is especially decisive in the freshwater aquatic ecotoxicity impact category of the CML 2001 method (Figure 6a) and the human toxicity (carcinogenic) impact category of the USEtox method (Figure 6c).

4.2. Sensitivity assessment

4.2.1. Concentration influence

A sensitivity analysis was carried out to study the effect of the TCS initial concentration on the environmental impacts associated to ecotoxicity for the different life cycle methods, in order to assess if the initial concentration of this pollutant gives rise to higher toxicity in the residual effluent to be treated (see Figure 7).



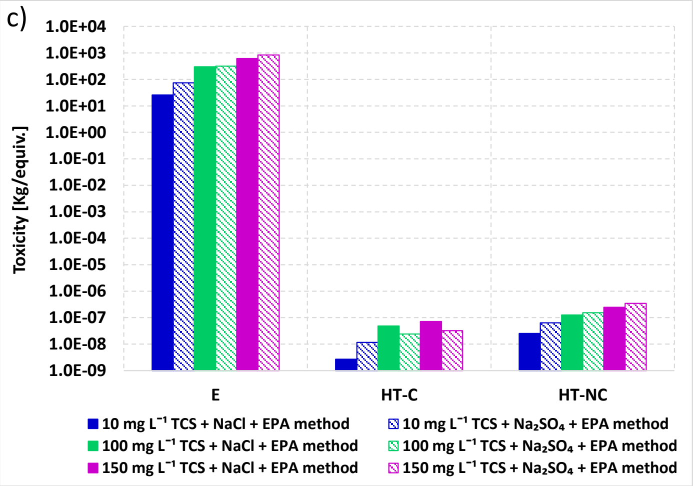


Figure 7. TCS initial concentration influence on toxicity from a) CML 2001 method, b) ReCiPe method, c) USEtox method.

Figure 7 shows higher toxicity rates for both electrolytes as the initial concentration of TCS is increased after applying the LCIA. According to previous results, employing the TCS initial concentrations of 100.00 and 150.00 mg L^{-1} and using Na_2SO_4 as the electrolyte increases the toxicity more than when NaCl is used as electrolyte, except for the freshwater aquatic ecotoxicity and human toxicity impact categories of the CML 2001 method and human toxicity cancer impact category of the USEtox method. In the latter situation, the values of PCDD/Fs provided by the EPA method are more important than the Na_2SO_4 reactant, as seen in Section 4.1.2. However, when applying initial TCS concentrations below 100.00 mg L^{-1} (i.e., 10.00 mg L^{-1}), opposing results are observed in these impact categories. In these scenarios, the values of PCDD/Fs are higher than the toxicity of the reactants. This behaviour may be due to the amount of electrolyte used is the same for TCS initial concentrations studied. On the other hand, the lower PCDD/Fs formation occurs when TCS initial concentration employed is lower, as observed in the experimental results (Table S7 in the Section 5 of the SD).

4.2.2. Organic pollutant influence

In order to determine the influence of changing the organic pollutant on PCDD/Fs formation, 2-CP toxicity was calculated when NaCl and $NaSO_4$ are used as electrolytes in the EOX process. The results, which are shown in Figures 8a and 8b, suggest that the influence on toxicity when including PCDD/Fs is minimal, only noticeable for USEtox and two impact categories in the CML 2001 method (i.e., freshwater eco-toxicity and, to a lesser extent, human toxicity) when NaCl is used as an electrolyte. These results are linked to the lower generation of PCDD/Fs as a result of the oxidation of 2-CP. In fact, 2,3,7,8-TCDD is not found when the EOX process is applied using both electrolytes (see Table S9 in the Section 5 of the SD). However, the light differences that can be identified when the CML 2001 and USEtox methods are applied employing NaCl as the electrolyte and the EPA method is included within the system boundaries, are linked to the contribution of additional 2,3,7,8-PCDD/Fs obtained experimentally with both electrolytes.

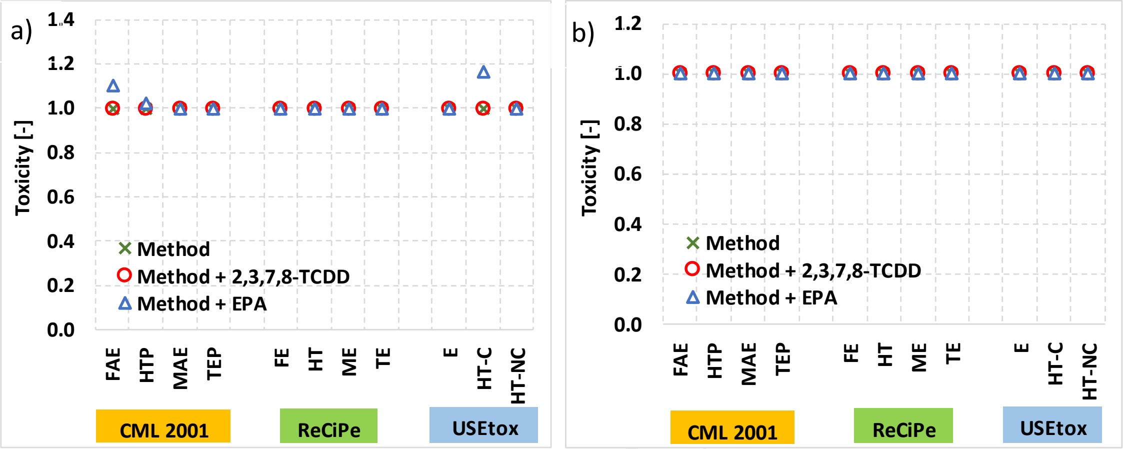


Figure 8. Influence of the life cycle methods when EOX process is applied to 2-CP and a) NaCl reactant and b) Na_2SO_4 reactant.

FAE=Freshwater Aquatic Ecotoxicity, HTP=Human Toxicity Potential, MAE=Marine Aquatic Ecotoxicity, TEP=Terrestric Ecotoxicity Potential, FE=Freshwater Ecotoxicity, HT=Human Toxicity, ME=Marine Ecotoxicity, TE=Terrestrial Ecotoxicity, E=Ecotoxicity, HT-C=Human Toxicity-cancer, HT-NC= Human toxicity-non-cancer.

5. Conclusions

Results obtained in the current study delve into the lack of comprehensiveness of LCIs whenever EOX processes are considered in life cycle methods, given the lack of data and, therefore, omission of secondary pollutants that are generated in the treatment process.

LCIA methods demonstrate that they are not fully adapted to the computation of PCDD/Fs in the water compartment, since only 2,3,7,8-TCDD is present as a substance in the impact categories assessed, ignoring the remaining list of PCDD/Fs. Therefore, we consider that future research should focus on two main issues. On the one hand, there is a need to develop characterization factors in the mainstream LCIA methods to account for a wider range of PCDD/Fs in the water compartment. Their omission, as proved in this study, tends to underestimate the toxic emissions in many production processes. On the other hand, the analysis of the emissions of PCDD/Fs should be deepened in the LCA literature, in order to understand the full extent of their toxic performance in the natural environment.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract