







# Minimizing marine pollution transfer via ballast water: AOP-based chemical decontamination, efficiency comparison, and LCA study

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## ABSTRACT

Ballast water is a relevant vector for the dissemination of chemical and microbiological pollutants, raising concerns about its environmental impact on marine ecosystems; in this context, advanced oxidation processes (AOPs) is a promising alternative despite the high salinity of seawater. This study evaluates the performance of several AOPs (UVC, UVC/H<sub>2</sub>O<sub>2</sub>, UVC-driven photo-Fenton, O<sub>3</sub>, O<sub>3</sub>/UVC, and VUV irradiation) for the degradation of a representative mixture of six contaminants (phthalic acid, dihydroxybenzophenone, 2,4-dinitrophenol, bisphenol A, pentachlorophenol, and benzylparaben) in real matrices. Highest removal rates were obtained by ozone, reaching 100% of pollutant removal in less than 15 min; additionally, VUV and UVC/photo-Fenton showed good efficiency even in saline waters (80–90% removal), although longer irradiation times were required. A comprehensive life cycle assessment (LCA) was performed to compare the environmental sustainability of each treatment, which revealed that energy and reagent consumption were the key parameters. Significantly, VUV showed the lowest environmental impact in the scenario that involves using the excess of energy from the ship engines and N<sub>2</sub> reuse (decreasing 2–3 orders of magnitude between scenarios, c.a. 6.2·10<sup>-6</sup> g CO<sub>2</sub> eq). The integration of avoided toxicity analysis further confirmed the environmental benefits of treating ballast water. These findings support the implementation of photochemical AOPs as on-board ballast water treatment strategies, balancing efficacy and environmental sustainability.

## 1. Introduction

Maritime transport is one of the main means to move goods and people. During the voyage between ports, it is necessary to load and unload significant volumes of seawater to ensure the stability, manoeuvrability, and structural integrity of the vessels; this process is commonly known as ballasting, and the water involved as ballast water [1]. Ballasting/deballasting is a major vector of spreading chemical and microbiological contamination worldwide. For this reason, the International Maritime Organization (IMO) has responded with the *Ballast Water Management (BWM) Convention* (2004), which requires ships to install treatment systems to decrease such contamination and minimize the effect of invasive species when they discharge the water at another point [2].

According to IMO, most of the processes that can be implemented for

this purpose are divided in two main groups: The first one relates to primary treatments, mainly physical procedures such as filtration, to remove large organisms and suspended solids [3], while the second group is based on chemical techniques, such as the addition of biocides, mainly hypochlorite, or advanced oxidation processes (AOPs), including ozone (O<sub>3</sub>) and ultraviolet/H<sub>2</sub>O<sub>2</sub> [4,5].

Ultraviolet C radiation (UVC), which corresponds to photons, which wavelength is in the range 200–280 nm, is able to photolise chemicals that absorb in this region of the spectrum, while the combination of UVC with hydrogen peroxide (UVC/H<sub>2</sub>O<sub>2</sub>) enhances hydroxyl radical (·OH) generation, reaching higher removals in real matrices [6]. The UVC-driven photo-Fenton process (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UVC) further improves efficiency in complex effluents [7]. UVC irradiation is widely applied, but its efficiency may be limited in highly turbid or saline waters [8].

Vacuum ultraviolet irradiation (VUV) comprises radiation in the

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range 5–200 nm [9]. It is an emerging AOP that, in addition to photolyzing most molecules, is capable of decomposing  $O_2$  and  $H_2O$  into highly reactive species [10,11]; however, its penetration depth is limited in water [12,13]. Although the small emission band of mercury lamp at 185 nm is widely employed, xenon excimer lamps could be a more efficient alternative, as their main emission is centred at 172 nm [14].

Finally, ozonation is one of the most established chemical treatments [15,16]; furthermore, its combination with ultraviolet irradiation ( $O_3$ /UVC) enhances its efficiency, leading in some cases to nearly complete mineralization of persistent compounds in complex effluents [17–19].

Despite microbiological contamination might be more relevant when treating ballast water due to the potential introduction of invasive species, chemical contamination can also be a concern; for instance, antibiotics can lead to the development of antibiotic resistance genes [20,21]. For this reason, chemical decontamination is a meaningful goal in order to compare different processes in terms of efficiency or sustainability.

Information on the applicability of AOPs in highly saline environments remains limited [22], although several studies have explored their use for ballast water decontamination, mainly focused on disinfection [23–26]. However, their use for chemical decontamination, which is a more stringent goal [27], still encounters significant challenges due to high salinity or the presence of different types of organic matter, which results in scavenging of the reactive species or a competition with the pollutants or the oxidants. Nonetheless, the ability of AOPs to enable both disinfection and pollutant mineralization underscores their promise as an emerging, sustainable technology for ballast water treatment [28,29].

The presence of chemical pollutants found in ballast water mainly depends on the type of activities that are developed nearby the harbour where the water is loaded. Many substances such as pharmaceuticals, personal-care products, endocrine disruptors, pesticides, microplastics [30], and even heavy metals such as Fe ( $30\text{--}300\ \mu\text{g L}^{-1}$ ), Mn ( $10\text{--}80\ \mu\text{g L}^{-1}$ ), Cu ( $5\text{--}60\ \mu\text{g L}^{-1}$ ), Ni ( $2\text{--}25\ \mu\text{g L}^{-1}$ ), V ( $1\text{--}40\ \mu\text{g L}^{-1}$ ), Pb, Cd, and Zn have been detected [31]. The high salinity content of these matrices (ca.  $36\ \text{g L}^{-1}$ ;  $0.61\ \text{M}$  in the Mediterranean Sea) together with the high concentration of other anions ( $\text{Br}^- \approx 0.8\ \text{mM}$ ,  $\text{SO}_4^{2-} \approx 28\ \text{mM}$ ,  $\text{HCO}_3^- \approx 2\ \text{mM}$ ) means a threat to water treatment technologies [32]. These facts explain the complexity of implementing AOPs to deal with this problem and, consequently, the scarcity of available results, thus highlighting the importance of further exploring AOPs for treating real ballast water.

Alongside the development of increasingly innovative and high-performing technologies, attention has also shifted towards the sustainability of treatment processes, which should be carried out in such a way that efficiency is accompanied by a low environmental impact associated with the consumption of materials (e.g., chemicals) and energy [33,34]. Environmental sustainability assessments, whether applied to treatments designed to produce drinking water [35–37] or to manage wastewater [38–40], are primarily based on the Life Cycle Assessment (LCA) methodology, which allows the identification of the most environmentally preferable alternative and the detection of process hotspots. This also makes it a useful decision-making support tool to examine alternative scenarios of operation alongside and during strategic planning of the wastewater sector [41]. In fact, AOPs commonly involve significant energy demands, reagent addition, and the formation of secondary pollutants. LCA emerges as a powerful tool to quantify and compare the potential environmental impacts associated with different treatment strategies [42,43]. Applying LCA to ballast water enables the evaluation of carbon footprint, energy intensity, ecotoxicity, and resource depletion, contributing to the selection of the most sustainable and environmentally responsible technologies [44].

In parallel, the interest in the spread of emerging pollutants and their integration into LCA models has also increased. In this field, the objective of LCA is the identification of characterization factors (CFs) capable

of translating the emission or presence of a given contaminant into a potential environmental impact [45,46]. CFs makes use of a reference substance with a known effect on a particular impact category to estimate the potential impact of the studied pollutant [47]. This means that CFs must be available (in literature or libraries) to assess the environmental impact of an emission of a substance for each relevant impact category. Although CFs for common pollutants are now well established, this is not always true for substances that have only recently been recognized as environmentally relevant (e.g., emerging contaminants). This challenge is particularly acute for toxicity-related impact categories, which must account for complex cause-effect mechanisms, including transport, exposure, and effect pathways, while simultaneously addressing a very large number of substances within the assessment framework [47,48]. In this case, estimation of potential impacts based on the physicochemical properties of substances is needed and frameworks have been developed for this purpose, often integrated into life cycle-based tools such as USEtox [47]. However, further advancements are necessary to comprehensively address all types of emerging pollutants.

With this background, the aim of this work is to compare the efficiency of different AOPs, namely Fenton, UVC,  $\text{UVC}/\text{H}_2\text{O}_2$ , UVC-driven photo-Fenton (PF),  $\text{O}_3$ ,  $\text{O}_3/\text{UVC}$ , and VUV for the treatment of chemical pollutants in seawater. For this purpose, a mixture of six different pollutants has been employed, namely phthalic acid, dihydroxybenzophenone, 2,4-dinitrophenol, bisphenol A, pentachlorophenol, and benzylparaben. They have been chosen according to the results of recent samplings in three Spanish ports [48]. The treatments will not only be assessed by their ability to remove the pollutants, but also a detailed LCA study will be performed in order to estimate their environmental impacts.

## 2. Materials and methods

### 2.1. Reagents and reactions

Phthalic acid, dihydroxybenzophenone, 2,4-dinitrophenol, bisphenol A, pentachlorophenol, and benzylparaben were purchased from Sigma Aldrich as high-purity reagents. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 33% w/v) was supplied by PanReac AppliChem; sodium orthovanadate ( $\text{Na}_3\text{VO}_4$ ), heptahydrated iron(II) sulfate ( $\text{FeSO}_4 \cdot 7\ \text{H}_2\text{O}$ ), and copper(II) chloride ( $\text{CuCl}_2$ ) were purchased from Sigma Aldrich. High-purity  $\text{O}_2$  and  $\text{N}_2$ , used for the  $\text{O}_3$  and VUV experiments, respectively, were supplied by PraxAir.

In all experiments, an equimolecular mixture of six pollutants (phthalic acid, dihydroxybenzophenone, 2,4-dinitrophenol, bisphenol A, pentachlorophenol, and benzylparaben) at a concentration of  $5\ \mu\text{M}$  each was used as target solution ( $30\ \mu\text{M}$  in total). Two different water matrices were used, namely MilliQ® water and real seawater ( $\text{DOC} = 4.04\ \text{mg L}^{-1}$ ;  $[\text{NaCl}] = 35\ \text{g L}^{-1}$ ; conductivity =  $39.1\ \text{mS cm}^{-1}$ ; turbidity =  $5.09\ \text{NTU}$ ;  $\text{pH} = 7.89$ ). Seawater was sampled from the Mediterranean Sea (Les Palmeretes beach, near Valencia at the East of Spain).

### 2.2. Reactions and analysis

#### 2.2.1. In tank experiments (dark Fenton)

In-tank treatments were carried out in dark conditions using a cylindrical glass reactor loaded with 1 L of the solution to be treated. The stoichiometric amount of  $\text{H}_2\text{O}_2$  required to mineralize the pollutants was employed ( $0.61\ \text{mM}$ ). This is a procedure commonly employed to ensure that there is enough amount of oxidant and to work under comparable conditions [49–52]. In the Fenton process, Fe(II) was added as sulphate salt, to reach a concentration of  $5\ \text{mg L}^{-1}$ . In some experiments, Cu(II), added as  $\text{CuCl}_2$ , was used instead of Fe(II) at the same concentration ( $5\ \text{mg L}^{-1}$ ). Eventually, further additions of  $\text{H}_2\text{O}_2$  ( $0.61\ \text{mM}$ ) were done. Magnetic stirring (700 rpm) was kept throughout the reaction; experiments were carried out at room temperature (ca.  $25^\circ\text{C}$ ).

### 2.2.2. UVC-driven processes

UVC irradiations were carried out using a 15 W low-pressure mercury lamp (Heraeus Noblelight) emitting nearly monochromatic radiation at 254 nm, protected by a quartz envelope and placed axially in a closed glass reactor (8 cm diameter, 25 cm height). The system was refrigerated using an outer water jacket (see Fig. 1a). The reactor was loaded with 0.5 L of the solution to be treated. In the H<sub>2</sub>O<sub>2</sub> and PF process, the same concentrations of H<sub>2</sub>O<sub>2</sub> and Fe(II) were employed. Magnetic stirring was kept during the irradiation at 700 rpm at room temperature (25°C).

### 2.2.3. VUV experiments

VUV irradiations were carried out using a 4 W xenon excimer lamp (UV-Consulting Peschl) emitting nearly monochromatic radiation at 172 nm. In order to protect the electronic components, N<sub>2</sub> was continuously flown through the lamp to prevent O<sub>3</sub> formation. The reactor has an optical path of 3 mm and a reactor surface of 45 × 100 mm, and the irradiated volume was 13.5 mL. The walls of the reactor are made of high-purity quartz to allow penetration of photons with  $\lambda < 200$  nm. A 0.1 L volume of solution was used in each experiment. The system was operated by continuously recirculating the solution from a reservoir to the reactor and then back to the reservoir, by using a peristaltic pump at a constant flow of 1.15 L h<sup>-1</sup> (see Fig. 1b). This flow rate was selected to ensure complete mixing and sufficient exposure of the recirculated volume to VUV irradiation according to preliminary tests conducted at different flow rates (data not shown); furthermore, higher flow rates resulted in minor leakage due to pressure build-up in the recirculation circuit. Samples were taken throughout the experiment for analysis (1 mL each time, 8 mL in total). Magnetic stirring was kept in the reservoir at 700 rpm during the whole experiment.

### 2.2.4. Ozonation experiments

The ozonation tests were performed in a cylindrical glass reactor (see Fig. 1c). Ozone was supplied by a generator (Ozogas, T.R.C.E. 4000) capable of producing 8 g h<sup>-1</sup> when fed with oxygen. The ozone production was adjusted to the desired experimental conditions (0.1 g h<sup>-1</sup>) selected based on previous studies. The reactor was loaded with 0.2 L of the solution to be treated, and the experiment was kept for 2 h. The gas was bubbled from the bottom of the reactor, ensuring homogeneous mixing conditions. Also, the combination of UVC with ozone was tested by placing axially the UVC lamp described in Section 2.2.2 (see Fig. 1d). Initial pH values were 4.7 for distilled water and 8.0 for real seawater; the pH was not adjusted to maintain the natural conditions of the matrices used in the study. Adjusting the pH of large volumes of seawater (m<sup>3</sup> scale) would require significant amounts of chemicals and energy, which is not feasible in a realistic operational scenario. Experiments were carried out at room temperature (ca. 25°C).

### 2.2.5. Chemical analysis

Pollutant concentrations were monitored by HPLC (Hitachi Chromaster chromatograph; VWR). A Prevail Hichrom column (C18-Select; 250 × 4.6 mm; 5 μm) was employed as stationary phase. The mobile phase consisted of a mixture of two compounds, Milli-Q water (A) and acetonitrile (B) which composition was: i) a linear gradient set to reach 25% of B in 10 min, ii) 27 min more to reach 75% of B, and iii) 5 min were needed for re-equilibration to the initial conditions (100% A) at a flow rate of 1 mL min<sup>-1</sup>. The device was equipped with a UV-vis detector. Five different wavelengths were used: 220 nm for phthalic acid and pentachlorophenol, 300 nm for dihydroxybenzophenone, 368 nm for 2,4-dinitrophenol, 226 nm for bisphenol A, and 258 nm for benzylparaben. Identification and quantification of target molecules were

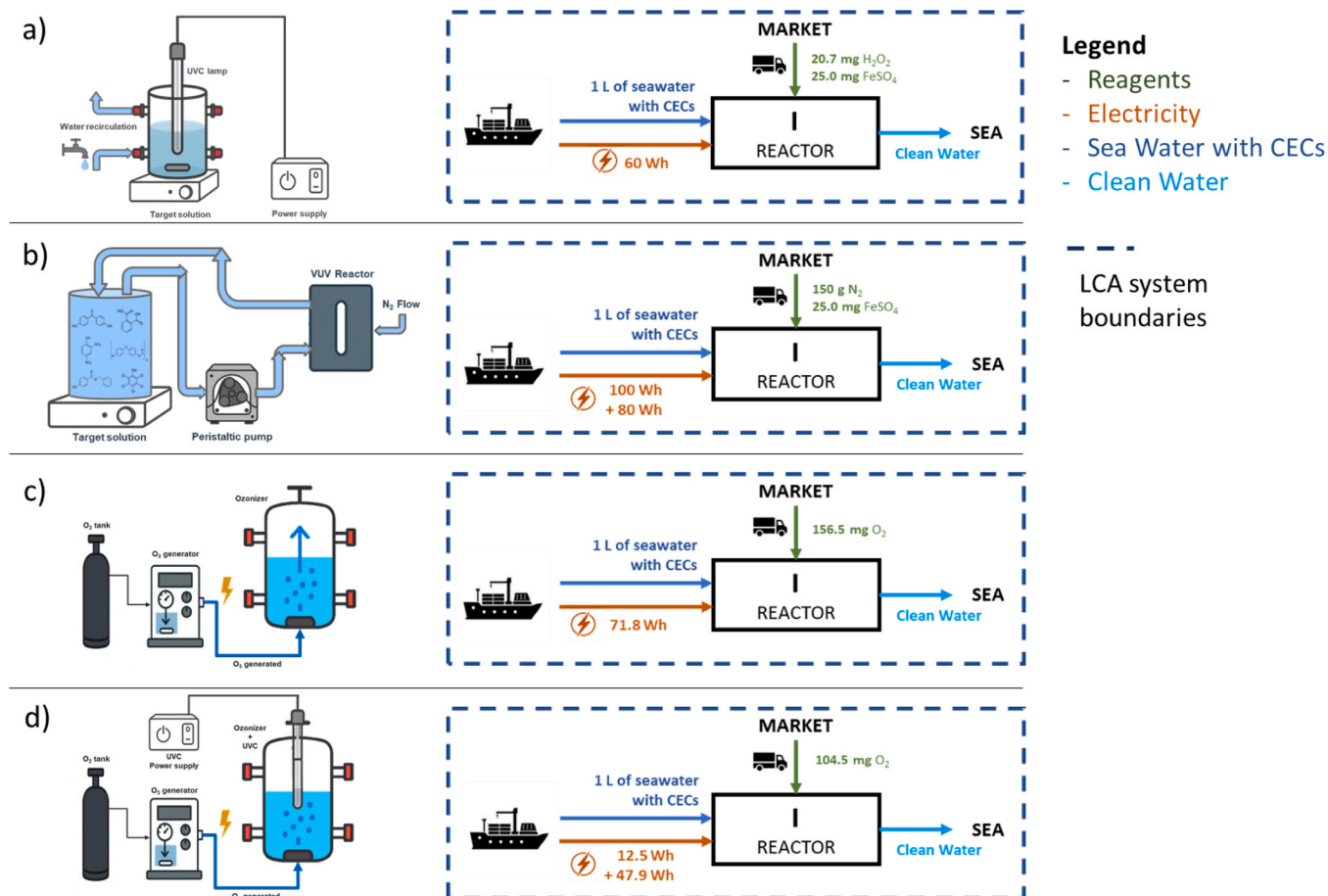


Fig. 1. Mass and energy flow diagram of each AOP: a) UVC, b) VUV, c) O<sub>3</sub>, and d) O<sub>3</sub>/UVC.

performed by comparison with standards.

The concentration of the H<sub>2</sub>O<sub>2</sub> generated during VUV irradiation was determined using a Hitachi-UH5300 spectrophotometer using the metavanadate method described elsewhere [53].

Excitation emission matrices (EEMs) from the ESI file were measured in a Horiba PTI Quanta Master 400 spectrofluorometer, equipped with a Xe arc lamp, employing an excitation range of 250–400 nm (recorded with 5 nm intervals), and emission range from 300 to 600 nm (recorded within 2.5 nm intervals). Absorbance spectra for inner filter effect corrections were measured with the Hitachi-UH5300 spectrophotometer described above. During the EEM preprocessing, the regions corresponding to the primary Rayleigh scatter were suppressed (white zone in the EEM plots).

### 2.3. Life cycle assessment (LCA)

LCA were performed according to the international ISO standards 14040:2006/Amd 1:2020 and 14044:2006/Amd 1:2017 + Amd2:2020 [54–56]. The common LCA framework applies well-regarded scientific mechanisms and characterization models and consists of 4 main phases: i) Goal and scope definition; ii) Life Cycle Inventory (LCI); iii) Life Cycle Impact Assessment (LCIA); and iv) Interpretation. These four phases are described below with reference to the system under investigation.

#### 2.3.1. Goal and scope definition

The study aims to estimate the environmental impacts associated with four treatments, carried out at laboratory scale (UVC, VUV, O<sub>3</sub>, and O<sub>3</sub>/UVC) aimed at reducing the presence of contaminants of emerging concern (CECs) in real seawater. More details about the conditions were reported in Section 2.2. The functional unit (FU) was defined as the amount of energy and reagents required to achieve a 60% removal in the concentration of the CECs in the seawater matrix, to ensure a consistent basis for comparing the different treatments.

The system boundaries include upstream phases of materials and energy involved (i.e., extraction of raw materials, manufacturing, and supply) and the core operations. The release of treated water into the environment is not included in the reference model. However, considerations on the possible environmental benefits of removing contaminants before water is released back into the environment are addressed in Section 3.2.3.

The infrastructural components have been excluded from the evaluation, assuming that their environmental cost is amortized over an extensive number of usage cycles. Accordingly, in the reference model, a *cradle-to-gate* approach has been adopted. No allocation criteria were applied in the study.

The application of the four treatment pathways, each involving different reagents, is expected to lead to the formation of distinct degradation by-products, depending on the specific process conditions. Experimental analyses aimed at specifically identifying or quantifying these compounds were not conducted. Nevertheless, qualitative and quantitative estimates of potential emissions were derived through stoichiometric calculations (see Tables S1, S2, and S3 of the ESI). These emissions were not included in the initial comparative assessment but are subsequently discussed in Section 3.2.2. The laboratory set-ups and flowsheets of the four alternatives are depicted in Fig. 1.

#### 2.3.2. Life cycle inventory (LCI)

The inventory of the CECs removal system was modelled according to the primary data obtained experimentally in the laboratory from an ad hoc experimental campaign. Electricity consumption was estimated by multiplying the laboratory equipment's power rating (W) by its operating time. This assumption is likely to represent an overestimation, as the equipment does not typically operate at full power [57]. Nevertheless, the estimate is considered valid, as it is highly conservative. Background information related to input materials and energy was drawn from the ecoinvent 3.11 database [58]. The proxy representing

the electricity generation was “Electricity, high voltage {CH}| heat and power co-generation, diesel, 200 kW electrical, SCR-NOx reduction | Cut-off, U”, since the equipment is predicted to be installed directly on board the ships, which is fed by diesel. Reagents, materials, equipment and energy flows involved in each step of the system and the associated ecoinvent proxies were reported in Table 1. The product system was modelled on SimaPro 10.2 (PRé Consultants, SimaPro v.10.2, Amersfoort, Netherland, 2025).

#### 2.3.3. Life cycle impact assessment (LCIA)

Results are reported according to the Environmental Footprint (EF) v. 3.1 LCIA method [59]. The selected procedure was developed by the Joint Research Centre (JRC) and is a standardized LCA framework adopted across Europe to measure environmental impacts. The method provides a comprehensive estimation of the interactions between the system under scrutiny and the environment for a set of 16 categories, ensuring alignment with ISO 14044:2006, which recommends considering a reasonably broad spectrum of impact categories. The choice of the EF method was also driven by its ability to calculate results in terms of the endpoint Single Score (micro-points,  $\mu\text{P}$ ) through a transparent process of characterization, normalization, and weighting. The considered midpoint categories are: Acidification (AC, mol H<sup>+</sup> eq), Climate Change (CC, kg CO<sub>2</sub> eq), Ecotoxicity (ECOTOX, CTUe), Particulate Matter (PM, kg PM 2.5 eq), Marine Eutrophication (MEU, kg N eq), Freshwater Eutrophication (FEU, kg P eq), Terrestrial Eutrophication (TEU, kg N eq), Human carcinogenic Toxicity (HTOX\_c, CTUe), Human non-carcinogenic Toxicity (HTOX\_nc, CTUe), Ionizing Radiation (IR, kg U<sup>235</sup> eq), Land Use (LU, Pts), Ozone Depletion (ODP, kg CFC<sup>-11</sup> eq), Fossil Resources Depletion (FRD, MJ), Mineral Resources Depletion (MRD, kg Sb eq), Water Use (WU, m<sup>3</sup>). In addition, the results are also presented in terms of single score (micro-point,  $\mu\text{P}$ ).

#### 2.3.4. Sensitivity and uncertainty analysis

In a sensitivity analysis, the parameters affected by the assumptions considered most relevant, or the outcomes of the hotspot analysis, were taken as a reference to test the robustness of the model created and enable identification and quantification of the influence of the main exogenous parameters on the environmental impact of the entire system [60]. As anticipated in Section 2.3.1, electricity consumption was conservatively estimated by multiplying the maximum power demand of the equipment by the process operating time. However, since the equipment is expected to be installed directly on board the ships, electricity can reasonably be assumed to be generated by the vessels' excess power. Accordingly, this flow was assumed to be negligible under optimized onboard operating conditions. The second flow selected for the sensitivity analysis was the amount of N<sub>2</sub> used in the VUV system, as its quantity was measured in the laboratory without considering potential optimizations (e.g., recovery) that would likely occur at an industrial scale. In the sensitivity scenario, electricity consumption and nitrogen use were assumed to be negligible under optimized onboard operating conditions, such as the availability of excess power from ship generators and the implementation of nitrogen recovery systems. Fig. 1 represents a valid depiction for both scenarios, as the involved flows do not change in terms of function or magnitude. Only the underlying assumptions differ: electricity is assigned no environmental burdens, as it is assumed to be generated anyway through the vessel's propulsion-related mechanisms, while nitrogen is considered to be fully recovered (100%). This scenario represents a best-case operational assumption rather than a universal onboard condition, and it is intended to explore the potential environmental performance of the investigated processes under optimized and technologically feasible configurations rather than to reflect all real-world operating situations.

Uncertainty evaluation was performed at the midpoint level. In general, as discussed above, the LCA model for the system under scrutiny was entered with primary data obtained by laboratory experiments. As such, input data related to material flows can be considered very

**Table 1**

Data inventory of the processes involved in the degradation of CECs. The amount of chemicals and energy are normalized to the functional unit.

UVC	Input Flow	Amount/ FU	Unit	Proxy
	Hydrogen peroxide	20.66	mg	Hydrogen peroxide, without water, in 50% solution state {RER}   market for hydrogen peroxide, without water, in 50% solution state   Cut-off, U
	Iron Sulfate	25.00	mg	Iron sulfate {GLO}   market for   Cut-off, U
	Electricity	60.00	Wh	Electricity, high voltage {CH}   heat and power co-generation, diesel, 200 kW electrical, SCR-NOx reduction   Cut-off, U
VUV	Input Flow	Amount	Unit	Proxy
	Iron Sulphite	25.00	mg	Iron sulfate {GLO}   market for   Cut-off, U
	Nitrogen	150.00	g	Nitrogen, liquid {RER}   market for nitrogen, liquid   Cut-off, U
	Electricity (pump)	100.00	Wh	Electricity, high voltage {CH}   heat and power co-generation, diesel, 200 kW electrical, SCR-NOx reduction   Cut-off, U
	Electricity (UVC)	80.00	Wh	
O <sub>3</sub>	Input Flow	Amount	Unit	Proxy
	Oxygen	156.50	mg	Oxygen, liquid {RER}   market for oxygen, liquid   Cut-off, U
	Electricity (Ozonizer)	71.88	Wh	Electricity, high voltage {CH}   heat and power co-generation, diesel, 200 kW electrical, SCR-NOx reduction   Cut-off, U
O <sub>3</sub> / UVC	Input Flow	Amount	Unit	Proxy
	Oxygen	104.50	mg	Oxygen, liquid {RER}   market for oxygen, liquid   Cut-off, U
	Electricity (UVC)	12.50	Wh	Electricity, high voltage {CH}   heat and power co-generation, diesel, 200 kW electrical, SCR-NOx reduction   Cut-off, U
	Electricity (Ozonizer)	47.92	Wh	

reliable and fulfil the highest scores for data quality criteria commonly applied in LCA, such as, for instance, geographical, temporal, and technological representativeness. To the electricity flows, more severe uncertainty scores were assigned to the assumption associated with its estimation. In general, the pedigree matrix was taken as a reference for the uncertainty assigned [58,61]. Pedigree Scores and Monte Carlo results are reported in Table S4 and Table S5 of the ESI.

### 2.3.5. Estimation of the avoided toxicity

The prevented release of such pollutants into the environment was

$$ED_{50, \text{ing}} \left[ \frac{\text{kg}}{\text{pers} \cdot \text{lifetime}} \right] = \frac{ED_{50, \text{chronic, oral}} \left( \frac{\text{mg}}{\text{kg} \cdot \text{day}} \right) \cdot \text{Body Weight (kg)} \cdot \text{Lifetime (years)} \cdot 365 \left( \frac{\text{days}}{\text{year}} \right)}{AFa \cdot 10^6 \left( \frac{\text{mg}}{\text{kg}} \right)} \quad (2)$$

estimated by extending the system boundaries to include the release stage, introducing the avoided release of the six CECs investigated as avoided emissions. However, CFs for 2,4-dinitrophenol, dihydroxybenzophenone, benzylparaben, and pentachlorophenol are not available in the current version of EF 3.1 and USEtox methods imported in SimaPro. Therefore, the USEtox tool (version 2.13) was downloaded and adopted to estimate the potential impacts related to ECOTOX and HTOXc and HTOXnc. The estimation of the midpoint impact by means of USEtox consists, synthetically, in the multiplication of the Fate Factor, the Exposure Factor and the Effect Factor, which are consistently calculated by knowing specific physico-chemical properties [62]. The list of properties and the relative values (both already available in the tool and ad hoc calculated) for the 6 CECs is reported in Table S6 of the ESI. The calculation of the avoided impacts proposed assumes a 60% degradation of the six investigated CECs, in line with the FU (i.e., the avoided impacts are computed by multiplying the initial mass of each CEC by a factor of 0.6).

**2.3.5.1. Human toxicity.** While for the calculation of ECOTOX, it is sufficient to integrate the required substance properties into the tool, which can be retrieved from databases such as CompTox, the primary reference used in this study. Conversely, information related to human toxicity is often more complex to obtain and is frequently unavailable in a format suitable for direct implementation in the tool. First, in the present case study, the only two compounds lacking such data were

dihydroxybenzophenone and benzylparaben. These two CECs were not classified as carcinogenic, so the research has been limited only to the estimation of the HTOXnc factor. To the best of our knowledge, only rat oral LD<sub>50</sub> values have been found in the literature and on websites. Therefore, Eq. 1 was applied to convert LD<sub>50</sub> values into ED<sub>50</sub>, followed by the application of Eq. 2 to translate the rat-based data into human-equivalent values [63].

$$ED_{50}(\text{chronic}) = LD_{50}/26 \quad (1)$$

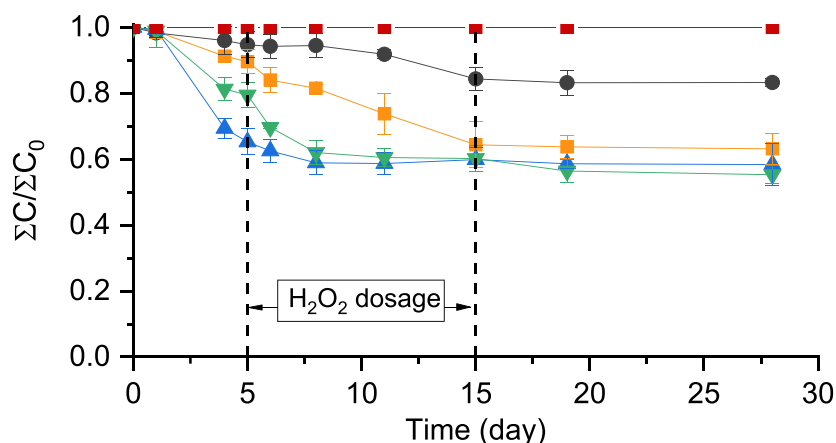
In Eq. 2, average body weight is assumed to be 70 kg, the lifetime 70 years, and the AF<sub>a</sub>, which is the conversion factor rat-human, is equal to 4.1 [62]. Since only the ingestion LD<sub>50</sub> are reported in the found documents, the inhalation effect is not considered for these two molecules. This assumption is discussed in detail in Section 2.3.3. In Table S7, the employed LD<sub>50</sub> values of dihydroxybenzophenone, benzylparaben, and phthalic acid are reported with the relative web source. 2,4-dinitrophenol, bisphenol A, and pentachlorophenol were contaminants already included in the list of substances provided by the USEtox tool. For this reason, it has been possible to estimate the midpoint impacts without doing further research.

## 3. Results and discussion

### 3.1. Experimental results

#### 3.1.1. In-tank strategy: Fenton and related processes

First of all, in-tank strategy was studied to test whether it was possible to eliminate chemical pollutants during navigation. For this purpose, Fenton treatment was applied in real seawater. Degradation of target pollutants was represented as the summation of the relative concentration of each pollutant at a given time ( $\sum C/\sum C_0$ ), where C is the concentration of each pollutant at the sampling time, and C<sub>0</sub> is the initial concentration.



**Fig. 2.** Remaining relative concentration ( $\Sigma C/\Sigma C_0$ ) of a mixture of 6 target pollutants (30  $\mu\text{M}$ ) using real seawater under different dark conditions: Fenton (0.61 mM  $\text{H}_2\text{O}_2$  + 5 mg  $\text{L}^{-1}$  Fe(II); pH = 3) (■), Fenton (0.61 mM  $\text{H}_2\text{O}_2$  + 5 mg  $\text{L}^{-1}$  Fe(II) + 3 mg  $\text{L}^{-1}$  V; pH = 3) (●), Fenton (0.61 mM  $\text{H}_2\text{O}_2$  + 5 mg  $\text{L}^{-1}$  Cu(II); pH = 3) (▲) and (0.61 mM  $\text{H}_2\text{O}_2$  + 5 mg  $\text{L}^{-1}$  Cu(II); pH = 8) (▼).

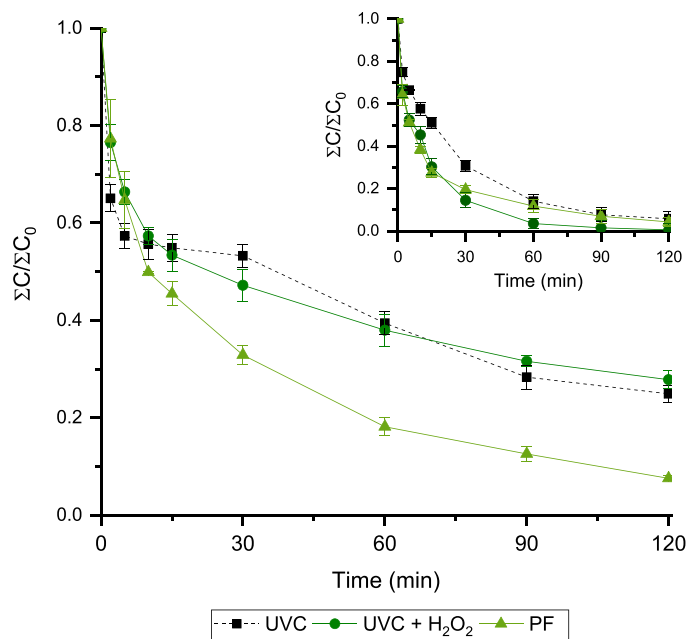
As can be seen in Fig. 2, Fenton treatment at natural pH (ca. 8) did not result in any pollutant degradation. This is a logical result as this pH is far away from the optimum value and the presence of chlorides is detrimental for the process. For this reason, the treatment was applied at pH = 3, within the optimum pH range [64]. Under these conditions, 40% pollutant degradation was observed after 15 days, but the reaction was then stopped, most probably due to iron inactivation. However, this treatment should be disregarded as pH variation in such huge volumes of seawater is not realistic and using higher iron concentrations might result in eutrophication.

One possibility is combining ballast water with a highly acidic effluent generated on the ship, namely, scrubber water. Scrubber water is formed by bubbling combustion gases to prevent the emission of sulfur oxides (SOx) and other particulate matter to the atmosphere. Thus, it contains traces of hydrocarbons, inorganic acidic compounds, and heavy metals such as vanadium, with a highly acidic pH [1,3]. Scrubber water was simulated by adding 3 mg  $\text{L}^{-1}$  of vanadium (selected as a representative of heavy metals produced in fuel combustion) to the Fenton mixture and adjusting the pH to 3 with sulphuric acid. However, results show no degradation under these conditions and seem to point to an inhibitory role of vanadium ion; anyway, mixing these streams does not seem convenient.

Finally, copper has been demonstrated to be able to drive Fenton-like processes at mild pH and highly saline water [65]. For this purpose, the reaction was driven using Cu(II) instead of Fe(II). The percentages of removal were ca. 40% after 10 days at both tested pHs, 3 and 8, but then, the reaction was stopped even when further  $\text{H}_2\text{O}_2$  addition was made, showing that there was an inactivation of copper (day 10). However, although this approach could be interesting for some niche applications, the addition of copper is not meaningful for ballast water.

### 3.1.2. UVC-based processes

UVC irradiation was tested as an intensive process for pollutant removal. UVC photolysis was tested, as well as UVC/ $\text{H}_2\text{O}_2$  and PF. Fig. 3 shows the plot of ( $\Sigma C/\Sigma C_0$ ) vs. time obtained for all three treatments in seawater, while the same process in distilled water is shown as an inset. In distilled water, nearly complete removal was reached in all cases (above 90%) after 120 min of irradiation, with negligible differences among them. In the case of seawater, degradation rates decrease significantly as the matrix becomes more complex [66], achieving 60% degradation in the case of UVC and UVC/ $\text{H}_2\text{O}_2$  and 90% for PF. The higher relative efficiency of PF vs. the other treatments in seawater can be explained by considering the ability of dissolved organic matter (DOM) to complex iron and to extend the applicability of this process



**Fig. 3.** Remaining relative concentration ( $\Sigma C/\Sigma C_0$ ) of 6 target pollutants (30  $\mu\text{M}$ ) using real seawater (pH = 8.05) by UVC (■), UVC +  $\text{H}_2\text{O}_2$  (●), and PF (▲). The inset represents the same conditions in distilled water (pH = 4.65).

towards milder pH values [67–71]. In fact, a DOC of ca. 4 mg  $\text{L}^{-1}$  was measured for seawater and a fluorescence analysis by means of excitation-emission matrices (see Figure S1) showed the typical fingerprints of humic-like (excitation at 330–340 nm, emission at 440–450 nm) and fulvic substances (excitation at 260–300 nm, emission at 390–420 nm) [70]. However, DOM is also responsible for absorbing light, as an absorbance of 0.026 was obtained at 254 nm, thus decreasing the number of photons reaching pollutants or  $\text{H}_2\text{O}_2$ . Furthermore, DOM and chlorides can act as scavengers of the reactive species involved in the process, such as hydroxyl radicals [71,72].

Fig. 4 shows the behaviour of each pollutant during the process and very significant differences among them can be found. In UVC photolysis, reactivity varied in the order benzylparaben > bisphenol A > dihydroxibenzophenone > pentachlorophenol > 2,4-dinitrophenol > phthalic acid; this order might be ruled by the direct UVC photon absorption and the quantum yield of the reaction of this species with the

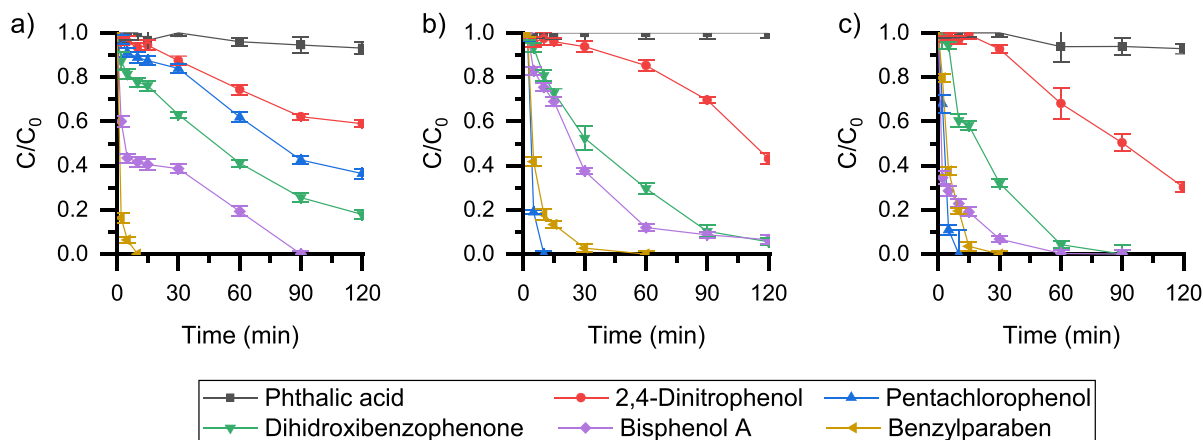


Fig. 4. Remaining relative concentration ( $C/C_0$ ) of 6 target pollutants ( $5 \mu\text{M}$  of each one) under different conditions in real seawater: a) UVC, b) UVC +  $\text{H}_2\text{O}_2$ , c) PF. Pollutants: phthalic acid (■), 2,4-dinitrophenol (●), pentachlorophenol (▲), dihydroxybenzophenone (▼), bisphenol A (◆), and benzylparaben (◄).

Table 2

Report of the bimolecular rate constants ( $\text{L mol}^{-1} \text{s}^{-1}$ ) found in the literature of the selected pollutants with the main reactive species involved in the investigated AOPs ( $\cdot\text{OH}$ ,  $\text{O}_3$ , and  $\cdot\text{Cl}$ ), together with the measured absorbance at 254 nm in real seawater. Values were taken from the indicated references. The symbol “-” indicates that no reliable kinetic data were found in the literature for the corresponding reaction.

Pollutant (CAS Number)	$k_{\text{OH}}$	$k_{\text{Cl}}$	$k_{\text{Cl}_2}$	$k_{\text{O}_3}$	Absorbance in seawater( $\lambda = 254 \text{ nm}$ )
Phthalic acid (88–99–3)	$1.2 \cdot 10^9$ [73]	-	-	$1.2 \cdot 10^6$ [66]	0.090
2,4-dinitrophenol (51–28–5)	$2.82 \cdot 10^9$ [66]	-	-	$2.4 \cdot 10^6$ [66]	0.380
Bisphenol A (80–05–7)	$8.77 \cdot 10^9$ [73]	$1.82 \cdot 10^{10}$ [74]	$5.82 \cdot 10^8$ [74]	$2.1 \cdot 10^6$ [66]	0.038
Pentachlorophenol (87–86–5)	$9.00 \cdot 10^9$ [66]	-	-	$3.0 \cdot 10^6$ [66]	0.353
Benzylparaben (94–18–8)	$4.80 \cdot 10^9$ [75]	$1.52 \cdot 10^{10}$ [74]	$1.61 \cdot 10^8$ [74]	$1.5 \cdot 10^6$ [66]	0.540
Dihydroxybenzophenone (131–56–6)	$6.25 \cdot 10^9$ [73]	-	-	$2.2 \cdot 10^6$ [66]	0.292

oxidant (e.g. oxygen), and therefore its efficiency shows some correlation with the molar absorption coefficients of the compounds at 254 nm (Table 2) and slight discrepancies might be explained by the specific quantum yield. Interestingly, the order changes in the other treatments as the oxidation of some pollutants is greatly enhanced. When  $\text{H}_2\text{O}_2$  is added (UVC/ $\text{H}_2\text{O}_2$  or PF, the process becomes predominantly driven by  $\cdot\text{OH}$ , and degradation rates are more closely associated with the bimolecular rate constants for  $\cdot\text{OH}$  and pollutants. This is even more evident for PF, where the order of reactivity changes to pentachlorophenol > benzylparaben > bisphenol A > dihydroxybenzophenone > 2,4-dinitrophenol > phthalic acid. Table 2 summarizes the bimolecular rate constants ( $k$ ) for the pollutants with the  $\cdot\text{OH}$  and the  $\text{O}_3$ . The higher values for  $k_{\text{OH}}$  are attributed to pentachlorophenol and bisphenol A, while for  $k_{\text{O}_3}$  is reported for pentachlorophenol. Those pollutants with higher constant values are expected to experience faster degradation compared to those with lower reactivity.

### 3.1.3. Ozonation

Samples were also treated with  $\text{O}_3$  and the combination of  $\text{O}_3/\text{UVC}$ , in both distilled water and seawater. For those experiments, the pH of the matrices was maintained at its natural value, around pH 8.1 for real seawater and 4.7 for distilled water, as modifying pH in large volumes of seawater would not be practical or realistic in an operational scenario, as it would involve high economic and environmental costs. Fig. 5 shows that, in sharp contrast with the  $\text{H}_2\text{O}_2$ -driven processes,  $\text{O}_3$  was able to reach a very fast removal of the pollutants in both water matrices (complete abatement was achieved in 15 min). Coupling  $\text{O}_3/\text{UVC}$  does not seem to enhance the process significantly, as the high direct ozone reactivity and rapid pollutant depletion limit the additional contribution

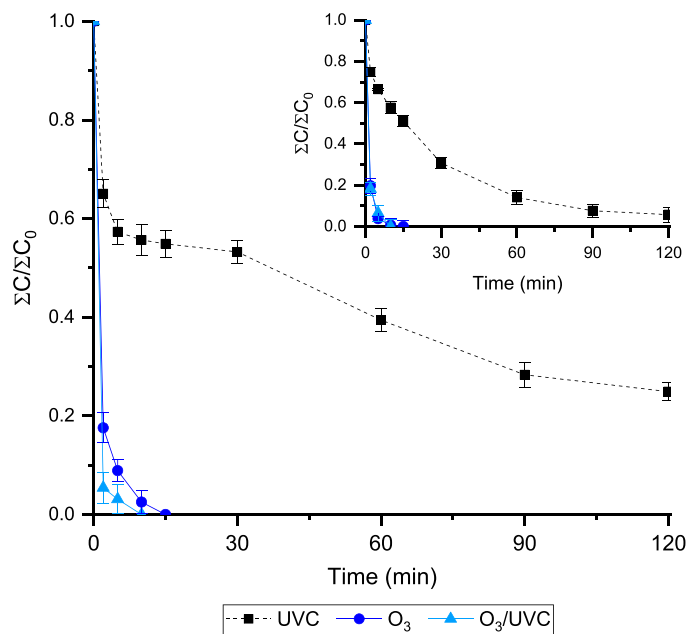
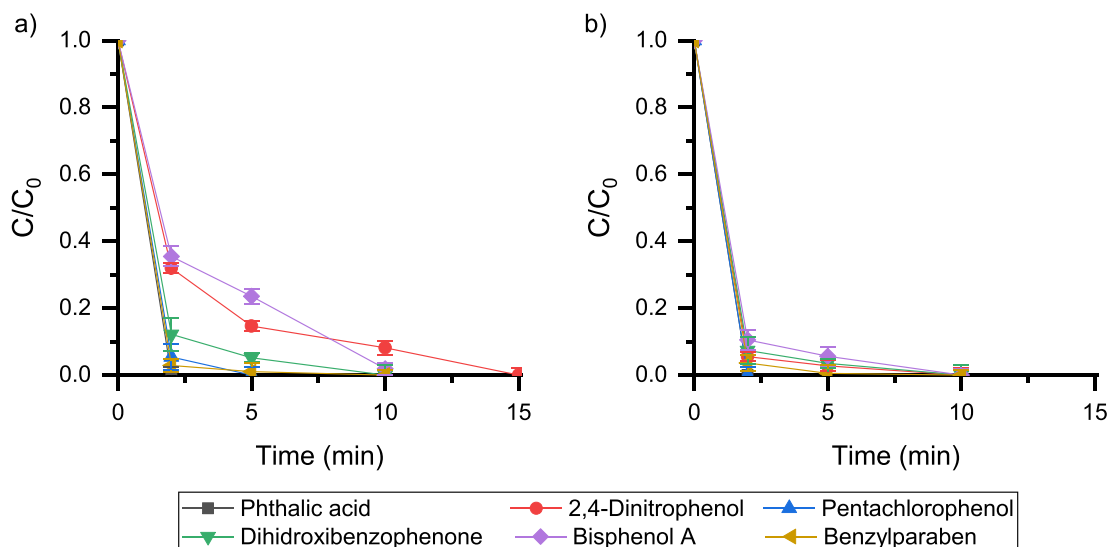


Fig. 5. Remaining relative concentration ( $\Sigma C/\Sigma C_0$ ) of 6 target pollutants ( $30 \mu\text{M}$ ) using real sea water (pH = 8.05) by UVC (■),  $\text{O}_3$  (●) and  $\text{O}_3/\text{UVC}$  (▲). The inset represents the same conditions in distilled water (pH = 4.65).



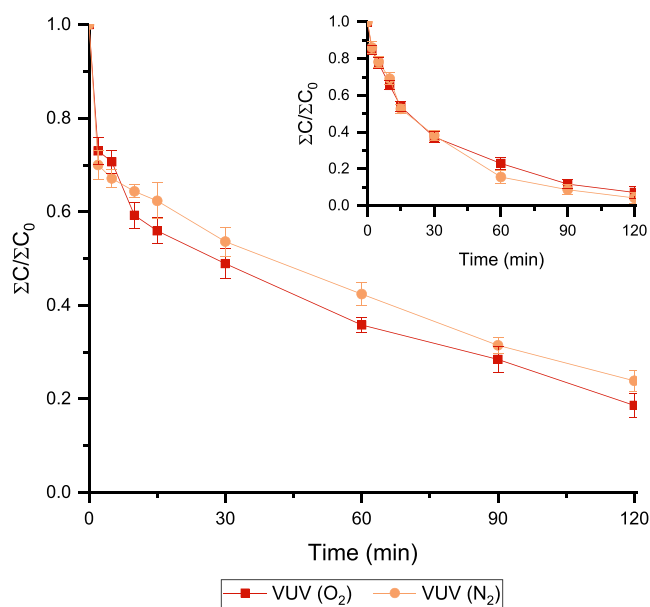
**Fig. 6.** Remaining relative concentration ( $C/C_0$ ) of 6 target pollutants ( $5 \mu\text{M}$  of each one) under different conditions in real seawater: a)  $\text{O}_3$ , and b)  $\text{O}_3/\text{UVC}$ . Pollutants: phthalic acid (■), 2,4-dinitrophenol (●), pentachlorophenol (▲), dihydroxybenzophenone (▼), bisphenol A (◆), and benzylparaben (◄).

of UV-induced radical formation. However, in the more complex seawater matrix, some enhancement can be found [76–78].

Regarding the individual behaviour of each pollutant (Fig. 6), it has to be observed that removal was very fast in all cases (less than 15 min are required for complete abatement in the worst scenario), and there were small differences among them in both  $\text{O}_3$  and  $\text{O}_3/\text{UVC}$ . This is in agreement with the very similar bimolecular rate constant with ozone ( $k_{\text{O}_3}$ ) reported in literature for all six pollutants (Table 2), which range between  $1.2 \cdot 10^6$  and  $3.0 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ .

### 3.1.4. VUV irradiation

Xenon excimer lamps emitting at VUV (172 nm) were also used as



**Fig. 7.** Remaining relative concentration ( $\Sigma C/\Sigma C_0$ ) of 6 target pollutants ( $30 \mu\text{M}$ ) real sea water ( $\text{pH} = 8.05$ ) by VUV ( $\text{O}_2$ ) (■) and VUV ( $\text{N}_2$ ) (●). The inset represents the same conditions in distilled water ( $\text{pH} = 4.65$ ).

irradiation source. Photons with this wavelength are able to reach photolysis of a wide range of species, including the pollutants, but also  $\text{H}_2\text{O}$  or  $\text{O}_2$  [79]. For this reason, penetration of light is scarce, and the reactor had an optical path of 3 mm. Thus, 100 mL were recirculated from a reservoir to the reactor and then back to the reservoir.

First, the effect of dissolved  $\text{O}_2$  was determined by irradiating at aerated conditions (dissolved oxygen =  $8.5 \text{ mg L}^{-1}$ ) and under  $\text{N}_2$  atmosphere. Fig. 7 shows that the effect of dissolved oxygen was very scarce (around 5% of difference on removal rate) and working under  $\text{N}_2$  atmosphere should be disregarded. The water matrix had a remarkable influence, as while complete pollutant removal could be achieved in distilled water after 120 min of irradiation, in the case of seawater it was in the 70%–80% range. The complexity of the system and the very scarce information available on the application of VUV in saline environments and seawater in particular, does not allow for obtaining a definite explanation for this behaviour [79]. However,  $\text{Cl}^-$  is reported to have a strong absorption in the VUV region, forming  $\text{Cl}^\cdot$  and  $\text{Cl}_2^\cdot$ , which might minimize pollutants photolysis and that are less reactive than the  $\cdot\text{OH}$  formed from water photolysis (see Table 2) [80]. As can be seen, the highest degradation was reached when using distilled water (97% removal) in comparison with seawater (76%), probably due to the presence of higher turbidity and DOM, as it is known that they can act as scavengers [81].

Finally, Fig. 8 shows the reactivity of each pollutant in the process. Interestingly, trends are very similar to the UVC/ $\text{H}_2\text{O}_2$  driven experiments, including the reluctance of phthalic acid (pentachlorophenol > dihydroxybenzophenone > benzylparaben > bisphenol A > 2,4-dinitrophenol > phthalic acid). This is consistent with the  $\cdot\text{OH}$  generated from water photolysis playing a major role in the process. In fact, formation of  $\text{H}_2\text{O}_2$  has been measured after 120 min of irradiation (ca.  $3.7 \text{ mg L}^{-1}$ ), which can be explained by recombination of the formed  $\cdot\text{OH}$ .

## 3.2. Life cycle assessment results

### 3.2.1. Comparison among the treatments

Although experimental conditions (reactor volume, irradiation time, and configuration) differ among treatments, the LCA comparison is normalized through the FU (60% CECs removal in seawater), ensuring comparability at the environmental performance level. Dark Fenton and

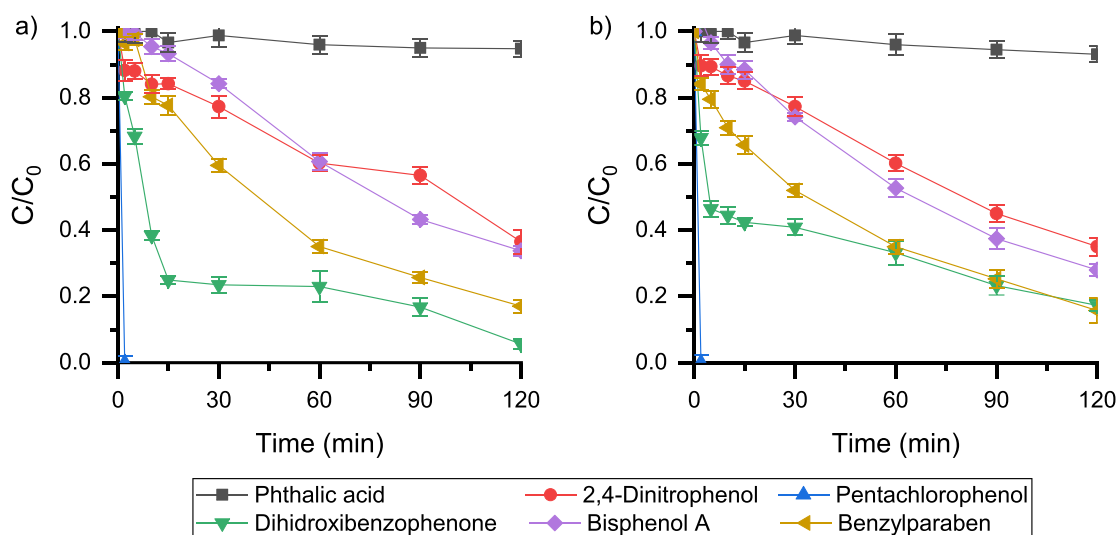


Fig. 8. Remaining relative concentration (C/C<sub>0</sub>) of 6 target pollutants (5 μM of each one) with VUV irradiation in real seawater in two different atmospheres: a) O<sub>2</sub>, and b) N<sub>2</sub>. Pollutants: phthalic acid (■), 2,4-dinitrophenol (●), pentachlorophenol (▲), dihydroxybenzophenone (▼), bisphenol A (◆), and benzylparaben (◇).

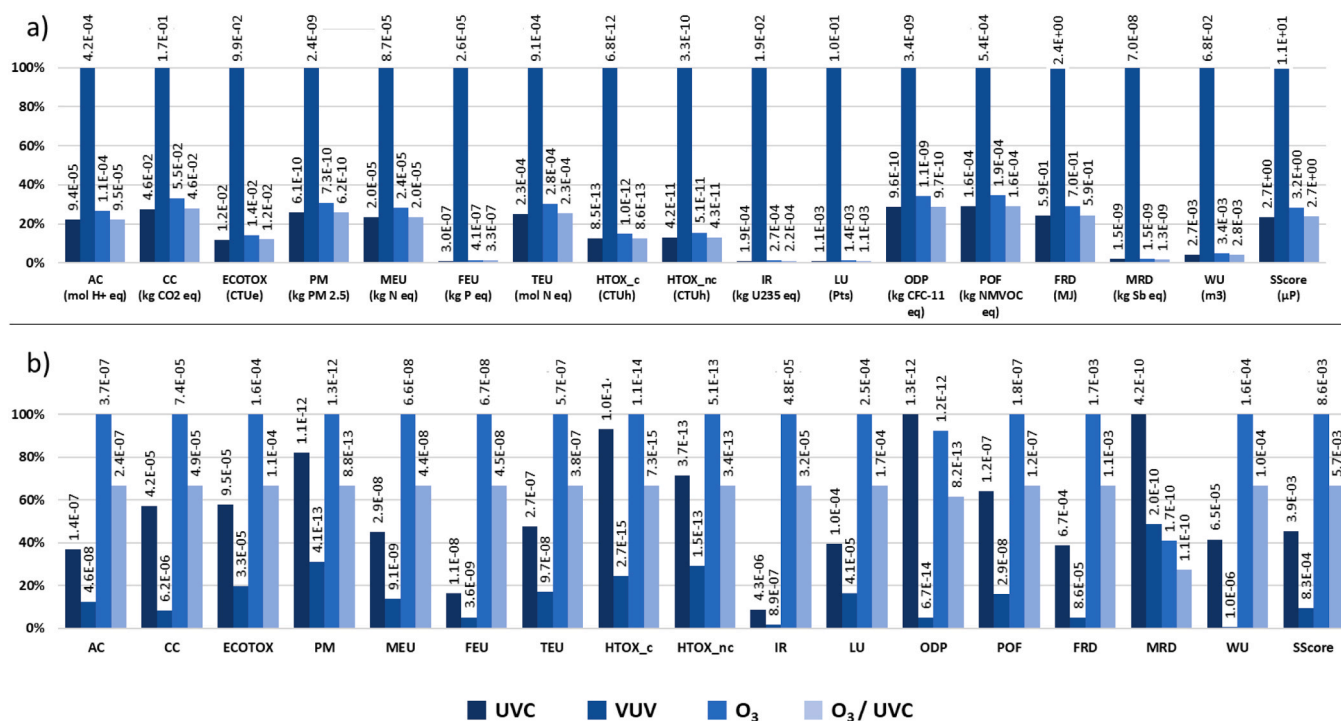


Fig. 9. LCIA results of the four alternatives estimated with the method Environmental Footprint 3.1, including a) energy and nitrogen consumption, and b) considering only chemicals. Acidification (AC), Climate Change (CC), Ecotoxicity (ECOTOX), Particulate Matter (PM), Marine Eutrophication (MEU), Freshwater Eutrophication (FEU), Terrestrial Eutrophication (TEU), Human carcinogenic Toxicity (HTOX<sub>c</sub>), Human non-carcinogenic Toxicity (HTOX<sub>nc</sub>), Ionizing Radiation (IR), Land Use (LU), Ozone Depletion (ODP), Fossil Resources Depletion (FRD), Mineral Resources Depletion (MRD), Water Use (WU).

Fenton-like processes, which were initially explored as in-tank options, should be excluded from the LCA due to operational and environmental constraints. Thus, the study was applied to UVC, VUV, O<sub>3</sub>, and O<sub>3</sub>/UVC.

Two scenarios have been considered for LCA calculations; one includes all inputs (reference scenario), and the second one excludes electricity and nitrogen required to protect VUV electronic components from oxidation (sensitivity scenario). The choice has been made

because, in the case of ballast water, electricity can be drawn from the excess generated by the ships' generators, and N<sub>2</sub> can be recirculated rather than continuously flown, as it is not consumed. Fig. 9a presents the results of the reference scenario, which includes energy and nitrogen consumption by the configurations. Fig. 9b, conversely, illustrates the results of the sensitivity scenario, considering only the chemicals used for contaminant degradation. The first noticeable aspect is the decrease

of two to three orders of magnitude for all impact categories between the reference scenario and the one generated through the sensitivity analysis. This is due to the high impacts associated with electricity and nitrogen. For electricity, impacts are strongly influenced by the energy source (diesel fuel), as confirmed by the production and supply network analysis. Since the experiments were conducted at laboratory scale, energy consumption is likely affected by scale effects that may be reduced at larger operational scales [62]. Similarly, nitrogen-related impacts are mainly linked to its production and supply, with scale effects expected to play a role. These considerations prompted the modelling of a sensitivity scenario, assuming the use of surplus on-board electricity and optimized nitrogen utilization, which is considered more representative of real-scale conditions. This highlights the significant influence of electricity and nitrogen consumption within the processes. In addition to the general decrease, a notable variation in the ranking of the alternatives can be observed when the two flows are excluded, particularly for the impact categories most affected by them. Specifically, VUV is always the worst option in the reference scenario, while the remaining configurations compete to rank as the best choice. Conversely, upon removal of the energy and nitrogen contributions, VUV emerges as the least impacting configuration across all assessed impact categories. In contrast, the highest impact values are associated with  $O_3$  (14 out of 16 midpoint categories) and  $O_3$ /UVC (2 categories, POF and WU, out of 16 midpoint categories). The single score, which integrates all impact values observed across the midpoint categories, is consistent with the previously described trend, showing a higher impact for the VUV option ( $11.3 \mu\text{P}$ ) in the scenario that includes electricity consumption. VUV is followed by  $O_3$  ( $3.2 \mu\text{P}$ ),  $O_3$ /UVC ( $2.7 \mu\text{P}$ ) and UVC ( $2.7 \mu\text{P}$ ). In the scenario where electricity is excluded from the assessment (Fig. 9b), VUV emerges as the preferable option ( $8.3 \cdot 10^{-4} \mu\text{P}$ ), while  $O_3$  is associated with the highest impact ( $8.3 \cdot 10^{-3} \mu\text{P}$ ).

Since CC is a widely recognised and well-understood indicator, globally, easily applicable for researchers, companies, and authorities to evaluate the carbon intensity of products, processes, and activities, it was selected as a reference for visualization and further analysis. In this category, electricity represents the most contributing flow in the reference scenario (Fig. 10a), affecting the impacts of almost 100% in UVC ( $0.046 \text{ kg CO}_2 \text{ eq/FU}$ ),  $O_3$  ( $0.055 \text{ kg CO}_2 \text{ eq/FU}$ ), and  $O_3$ /UVC ( $0.046 \text{ kg CO}_2 \text{ eq/FU}$ ). The impact of VUV ( $0.166 \text{ kg CO}_2 \text{ eq/FU}$ ) is instead due to both electricity (83%) and nitrogen (17%). If electricity and nitrogen are neglected (sensitivity scenario, Figure 10b),  $O_3$  ranks as the most impactful option ( $7.4 \cdot 10^{-5} \text{ kg CO}_2 \text{ eq/FU}$ ). This is due to the oxygen demand, which is in turn converted into  $O_3$  by means of the ozonizer. The contribution of  $O_2$  dominates  $O_3$ /UVC (total CC impact estimated at

$4.9 \cdot 10^{-5} \text{ kg CO}_2 \text{ eq/FU}$ ), also, while UVC CC impact ( $4.2 \cdot 10^{-5} \text{ kg CO}_2 \text{ eq/FU}$ ) derives from the 85% from the  $\text{H}_2\text{O}_2$  consumption and from the 15% from the  $\text{Fe}(\text{SO}_4)$ . VUV ranks as the best alternative, since the CC value of  $6.2 \cdot 10^{-6} \text{ g CO}_2 \text{ eq}$  is only due to the  $\text{Fe}(\text{SO}_4)$  consumption.

### 3.2.2. The influence of degradation products

As anticipated in the goal and scope section, the degradation of organic pollutants entails the formation of degradation products, which represent emissions that may potentially cause environmental harm. Since the main objective of this work was to compare the degradation processes and their respective efficiencies, the formation of byproducts after the four treatments has not been experimentally qualified nor quantified and is not considered within the LCA system boundaries. However, the potential release of those into the aquatic environment has been estimated stoichiometrically by assuming a complete oxidation of the degraded amount of the target CECs (see Tables S1, S2, and S3 of the ESI for these data). The emissions reported in Table S1 correspond to the release of non-degraded CECs, accounting for 40% of the total. The amount of this fraction was estimated to be  $3.68 \cdot 10^{-1} \text{ mg}$  for the 2,4-dinitrophenol,  $4.28 \cdot 10^{-1} \text{ mg}$  of dihydroxibenzophenone,  $4.56 \cdot 10^{-1} \text{ mg}$  of bisphenol A,  $4.56 \cdot 10^{-1} \text{ mg}$  of benzylparaben,  $5.32 \cdot 10^{-1} \text{ mg}$  of pentachlorophenol, and  $3.32 \cdot 10^{-1} \text{ mg}$  of phthalic acid. It is specified that this emission is not included in the evaluation.

The total amount of released  $\text{CO}_2$  resulting from the degradation of 60% of the CECs is always  $8.68 \cdot 10^{-6}$  for all 4 options. The results of the scenario that considers electricity consumption are not significantly affected by the inclusion of product degradation in the model, as no impact increases greater than 1% were observed. Instead, if only reagents are included in the evaluation, the CC impacts of UVC, VUV,  $O_3$ , and  $O_3$ /UVC may potentially increase by +21%, +104%, +12%, and +18%, respectively. It is highlighted that the notable contribution is also dependent on the relatively low CC value estimated for the sensitivity scenario, which reflects a low burden treatment. The remaining substances predicted to be emitted into the marine environment due to the degradation of CECs are  $\text{HNO}_3$ , deriving from the 2,4-dinitrophenol;  $\text{HCl}$ , generated in all the cases by the pentachlorophenol;  $\text{H}_2\text{SO}_4$ , obtained in UVC and VUV after the application of  $\text{Fe}(\text{SO}_4)$ ; and  $\text{Fe}(\text{OH})_3$ , for the same reason. The only predicted gaseous emission, in addition to  $\text{CO}_2$ , would be  $\text{NO}_2$ , again resulting from ozonization of 2,4-dinitrophenol. Despite the modest amount of  $0.28 \text{ mg L}^{-1}$  emitted, the impact associated with its formation is estimated to be the main contributor to the values observed for PM, MEU, TEU and POF (Table S8 and S9 of the ESI). Such an increase is justified by the CFs assigned to the molecule (Table 3). As previously anticipated, this estimate is dependent

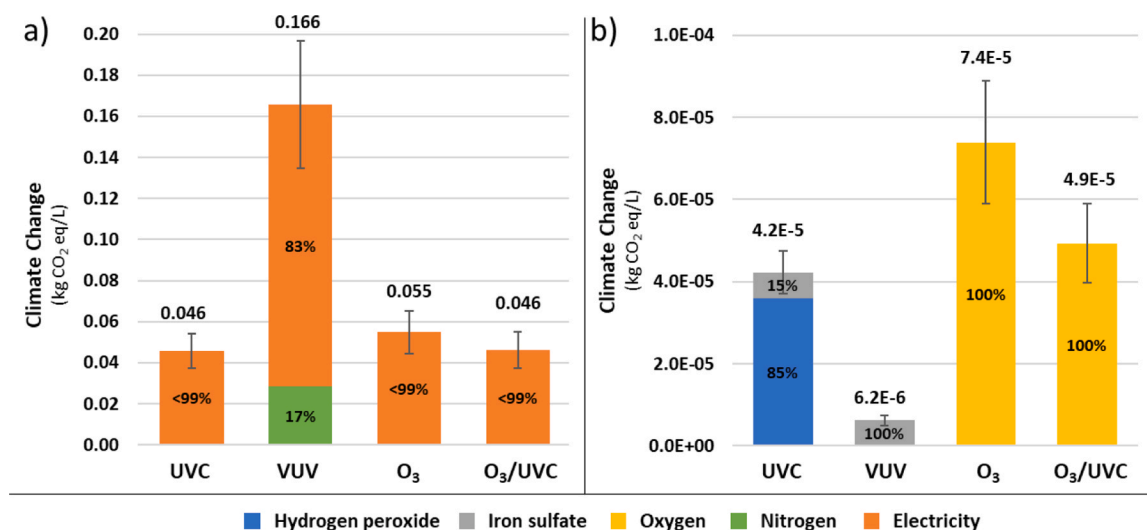


Fig. 10. Climate Change impacts with contribution analysis for a) reference scenario and b) sensitivity scenario.

**Table 3**

Characterisation factors of the degradation by-products emitted after the treatments according to the EF 3.1 LCIA method [59].

Amount = 1 kg	AC (mol H <sup>+</sup> eq)	ECOTOX (CTUe)	PM (kg PM 2.5)	MEU (kg N eq)	TEU (mol N eq)	HTOX <sub>nc</sub> (CTUh)	POF (kg NMVOC eq)
NO <sub>2</sub>	5.20·10 <sup>-2</sup>	/	1.60·10 <sup>-6</sup>	3.89·10 <sup>-1</sup>	8.77·10 <sup>-1</sup>	/	1.00
HNO <sub>3</sub>	/	2.77·10 <sup>-6</sup>	/	/	/	1.95·10 <sup>-13</sup>	/
HCl	/	2.16·10 <sup>-9</sup>	/	/	/	/	/
H <sub>2</sub> SO <sub>4</sub>	/	5.18·10 <sup>-8</sup>	/	/	/	5.51·10 <sup>-13</sup>	/
Fe(OH) <sub>3</sub>	/	3.41·10 <sup>-19</sup>	/	/	/	/	/

**Table 4**

List of midpoint CFs estimated by means of USEtox 2.13 and correlated with the avoided emission of CECs (i.e., 60% of the initial amount).

	[CEC](mg L <sup>-1</sup> )	HTOXc (cases)	HTOXnc (cases)	ECOTOX (PAF/ m <sup>3</sup> ·day)
2,4-dinitrophenol	5.53·10 <sup>-1</sup>	/*	2.19·10 <sup>-15</sup>	6.41·10 <sup>-12</sup>
Dihydroxybenzophenone	6.43·10 <sup>-1</sup>	/*	7.26·10 <sup>-16</sup>	1.92·10 <sup>-10</sup>
Bisphenol A	6.85·10 <sup>-1</sup>	/*	6.98·10 <sup>-9</sup>	4.12·10 <sup>-10</sup>
Benzylparaben	6.85·10 <sup>-1</sup>	/*	3.97·10 <sup>-17</sup>	2.07·10 <sup>-21</sup>
Pentachlorophenol	7.99·10 <sup>-1</sup>	5.13·10 <sup>-13</sup>	1.12·10 <sup>-12</sup>	4.02·10 <sup>-10</sup>
Phthalic acid	4.99·10 <sup>-1</sup>	/*	/	8.27·10 <sup>-16</sup>
Total		5.13·10 <sup>-13</sup>	6.98·10 <sup>-9</sup>	1.01·10 <sup>-9</sup>

on the assumption of complete degradation of by-products. Nevertheless, these findings highlight that the conversion of the contaminant into other chemical species represents a relevant process that should be properly accounted for in the overall assessment.

### 3.2.3. The avoided toxicity

Avoided toxicity values should not be interpreted as direct environmental impacts, but as potential benefits associated with preventing contaminant release. The midpoint CFs estimated with the approach described in 2.3.5 are reported in Table 4. From the obtained results, it can be observed that although the removal of CECs is evaluated as a whole, the removal of bisphenol A appears to provide the greatest benefits. In particular, the removal of 6.85·10<sup>-1</sup> mg/L of bisphenol A corresponded to the reduction of the 6.98·10<sup>-9</sup> cases for the HTOXnc impact and of the 4.12·10<sup>-10</sup> PAF/m<sup>3</sup>·day for the ECOTOX. These values correspond to at least three orders of magnitude higher than those of the other compounds in the HTOXnc category and at least two (up to eleven) orders of magnitude higher in the ECOTOX category. Bisphenol A is followed by pentachlorophenol, resulting in a potential impact of 5.13·10<sup>-13</sup> for HTOXc, of 1.12·10<sup>-12</sup> cases for HTOXnc and 4.02·10<sup>-10</sup> PAF/m<sup>3</sup>·day for ECOTOX. Dihydroxychlorobenzophenone showed an ECOTOX impact close to bisphenol A (i.e., 1.92·10<sup>-10</sup> PAF/m<sup>3</sup>·day) but a much lower HTOXnc impact (7.26·10<sup>-16</sup> cases). The lowest effects have been observed for 2,4-dinitrophenol (2.19·10<sup>-15</sup> cases for HTOXnc and 6.41·10<sup>-12</sup> PAF/m<sup>3</sup>·day for ECOTOX) and Benzylparaben (3.97·10<sup>-17</sup> cases for HTOXnc and 2.07·10<sup>-21</sup> PAF/m<sup>3</sup>·day for ECOTOX). In any case, the sum of the representative values for the six CECs was 5.08·10<sup>-10</sup> PAF/m<sup>3</sup>·day for ECOTOX, 3.49·10<sup>-9</sup> cases for HTOXnc, and 2.58·10<sup>-13</sup> cases for HTOXc.

The estimated values must be contextualized within the impact of the examined treatment processes, in order to assess the actual benefit associated with pollutant removal. This requires integrating both the burdens related to the set of activities involved in the treatment and aimed at pollutant removal, and the benefits resulting from the avoided emissions of these pollutants. In the case of ECOTOX, the total value of 1.01·10<sup>-9</sup> PAF/m<sup>3</sup>·day is significantly lower than the impacts estimated for both the reference and the sensitivity scenario (7 and 4 orders of magnitude, respectively). However, this result was expected since the emission occurs in the marine water compartment, while the category evaluates the impacts associated with the freshwater toxicity. So, the value is attributed only to the fraction of the CEC that potentially

reaches freshwater bodies after being emitted in the sea. The HTOXc value, instead, even if it derives only from the pentachlorophenol, which is the only carcinogenic species among the investigated, represents the 60% of the UVC and O<sub>3</sub>/UVC scenarios, the 8% of the VUV and the 50% of the O<sub>3</sub>, demonstrating that, for this impact category, the environmental burden associated with the application of the treatment exceeds the benefits derived from the avoided emissions. However, switching to the sensitivity scenario, which is the most realistic situation, the avoided emission presents a potential impact two orders of magnitude higher than the applied treatment, highly justifying the removal. Finally, in the case of HTOXnc, the avoided impacts are estimated to be lower by about two orders of magnitude in the reference scenario and about four orders of magnitude in the sensitivity scenario, still reflecting an environmental gain due to the treatment application.

### 3.2.4. Limitations of the study and future perspectives

Among the limitations of the approach described in Section 3.2.3, the first aspect to emphasise is that, despite the transparent calculation procedure provided, it represents an estimate constrained by the specific version of the tool. Given these premises, the aim of this study is not to provide a definitive value of the avoided impact, but rather to propose a methodological approach that enables the integration of treatment-related impacts with the potential environmental benefits. As an additional premise, the authors wish to emphasise that the USEtox framework, in its version 2.13, does not allow for the estimation of impacts associated with the marine water toxicity category, but only those related to ECOTOX, HTOXc, and HTOXnc. Since the present study concerns the marine environment, this may imply another significant limitation. Nonetheless, although the emissions considered occur directly in the marine environment, the USEtox model allows for the simulation of the environmental distribution of a given emitted substance, thereby enabling the estimation of its presence in the atmosphere, freshwater, and soil as a consequence of an initial marine release. As anticipated in 2.3.5, since no data related to the effect due to inhalation of dihydroxybenzophenone and benzylparaben have been found, only ingestion has been considered for estimations. An additional consideration concerns the selection of ED<sub>50</sub> (or LD<sub>50</sub>) values employed in the assessment. In line with the conservative approach typically adopted in LCA studies, when multiple values are available, the lowest one, representing the most conservative estimate since able to predict higher impacts, is generally preferred [62]. However, when the midpoint CFs derived from these values are used to estimate avoided impacts rather than direct impacts, the overall interpretation of the results shifts from a conservative to an optimistic perspective. As an alternative to the approach adopted in this study, the methodology also suggests using an average value rather than the most conservative one. Such an approach would likely be more appropriate when dealing with avoided emissions, as it may provide a more balanced representation of the expected benefits.

Regarding Section 3.2.2, as anticipated in the goal and scope, the amount of degradation products generated was estimated stoichiometrically. Therefore, the exact quantity released into the environment is not precisely known, and the estimation of the associated environmental impacts may be affected by this approximation. However, this phase has been excluded from the system boundaries in order not to affect results

due to this approximation, since this work aims to highlight the importance of including the formation of degradation products in the assessment, indicating their potential relative significance with respect to the overall impact.

Finally, building on the aspects discussed above concerning the transfer of pollutants from one port to another, it is worth noting that a future comprehensive evaluation could also address the issue of harmful and non-indigenous species, which may similarly induce environmental impacts [82,83]. Such species transfers, often associated with maritime activities, could represent an additional and non-negligible source of ecological pressure that deserves to be considered alongside chemical contamination.

#### 4. Conclusions

The comparative study of AOPs for ballast water treatment demonstrates the feasibility of applying oxidative strategies to remove pollutants under real seawater. Despite the improved performance for in-tank treatment at circumneutral pH, the intentional addition of Cu(II) to ballast water raises environmental concerns that outweigh its advantages. Moreover, in-tank approach showed limited degradation performance and practical constraints, supporting its exclusion in favor of more effective intensive processes such as UVC-based, ozonation, and VUV systems. Among the studied intensive processes, ozonation proved to be the most effective option for treating the contaminant mixture in seawater (15 min of treatment). Additionally, a modest but measurable enhancement is observed when coupling O<sub>3</sub>/UVC due to its synergistic effect (10 min). Conversely, VUV irradiation, despite its moderate degradation rates, was identified as the most environmentally sustainable solution under optimized operational assumptions. Integrating LCA and avoided toxicity analysis provided an extensive view of the trade-offs between process efficacy and environmental impacts, reinforcing the need for multi-criteria evaluation when designing on-board ballast water treatment systems. These insights can guide the implementation of effective and sustainable technologies for marine pollution control. Overall, the results highlight that process selection for ballast water treatment should rely on integrated performance–sustainability criteria rather than removal efficiency alone. Future work should focus on the inclusion of disinfection efficiency and invasive species translocation potential in AOP assessments, alongside the application of LCA under more realistic operational conditions and larger treatment volumes to validate scalability and confirm the environmental advantages observed at laboratory scale.

#### CRedit authorship contribution statement

**A. Arques:** Writing – review & editing, Supervision, Project administration, Formal analysis, Conceptualization. **D. Cespi:** Supervision, Conceptualization. **L. Santos-Juanes:** Writing – review & editing, Supervision, Conceptualization. **A.M. Amat:** Resources, Conceptualization. **F. Arfelli:** Writing – original draft, Investigation, Data curation. **R. López-Timoner:** Writing – original draft, Investigation, Data curation.

#### Declaration of Competing Interest

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.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2026.122301.

#### Data availability

Data will be made available on request.

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