



Petroleum refinery effluent contribution to chemical mixture toxic pressure in the environment

Jiaqi Wang^a, Mathijs G.D. Smit^{b,c}, Yves Verhaegen^c, Tom M. Nolte^a, Aaron D. Redman^{c,d}, A. Jan Hendriks^a, Markus Hjort^{c,*}

^a Department of Environmental Science, Radboud Institute for Biological and Environmental Sciences (RIBES), Radboud University, Heyendaalseweg 135, 6525 AJ, Nijmegen, the Netherlands

^b Shell Global Solutions International BV, The Hague, the Netherlands

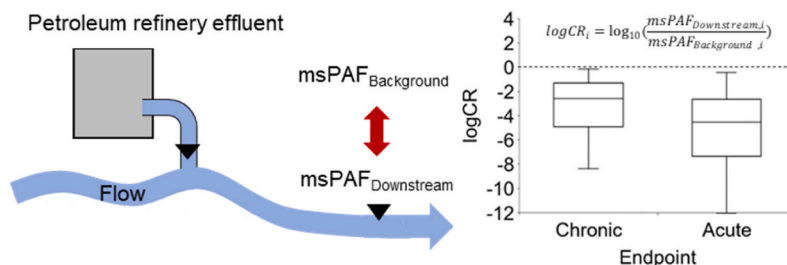
^c Concawe, Boulevard du Souverain 165, 1160, Brussels, Belgium

^d ExxonMobil Biomedical Sciences, Inc, Annandale, NJ, United States

HIGHLIGHTS

- We assessed petroleum refinery effluent (PRE) contribution to chemical pollution.
- 82% of PREs posed no significant toxic pressure in receiving environments.
- PREs were not major contributors to chemical pollution in the environment.
- Toxic pressure was mostly explained by aromatic constituents (C₁₀–C₁₅).

GRAPHICAL ABSTRACT



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ABSTRACT

Petroleum refinery effluents (PRE) are wastewaters from industries associated with oil refining. Within Europe, PREs are regulated through local discharge permits and receive substantial treatment before emission. After treatment, PREs can still contain low levels of various pollutants potentially toxic to organisms. Earlier work, including whole-effluent toxicity assessments, has shown that the toxicity of permitted PREs is often limited. However, the extent to which PREs contribute to chemical pollution already present in the receiving environment is unknown. Therefore, our study aimed to assess the contribution of PREs to mixture toxic pressure in the environment, using the multi-substance potentially affected fraction of species (msPAF) as an indicator. Based on measured chemical concentrations, compiled species sensitivity distributions (SSD) and a mechanistic solubility model, msPAF levels were estimated for undiluted effluents at discharge points and diluted effluents downstream in receiving waters. Median msPAF-chronic and msPAF-acute levels of PREs at discharge points were 74% (P50) and 40% (P95), respectively. The calculated msPAF levels were reduced substantially to <5% downstream for most effluents (82%), indicating low to negligible toxicity of PREs in receiving environments beyond the initial mixing zone. Regardless of differences in endpoints and locations, hydrocarbons (mainly total petroleum hydrocarbons) and inorganics (mainly ammonia) explained at least 85% of the mixture toxic pressure. The msPAF levels of PREs were on average 2.5–4.5 orders of magnitude lower than msPAF levels derived from background pollution levels, suggesting that PREs were minor contributors to the toxic pressure in the environment. This

* Corresponding author.

E-mail address: markus.hjort@concawe.eu (M. Hjort).

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study presents a generic methodology for quantifying the potential toxic pressure of PREs in the environment, identifying hotspots where more effective wastewater treatment could be needed. We explicitly discuss the uncertainties for further refinement and development of the method.

1. Introduction

Petroleum refinery effluents (PRE) are wastewaters from industries that extract crude oil and manufacture fuel, lubricants and other petroleum-based products (Singh and Shikha, 2019). PREs contain various pollutants, including hydrocarbons, ammonia, heavy metals, sulphides and phenols (Hoshina et al., 2008; Hjort et al., 2021). PRE compositions vary depending on the crude oil being processed and treatment processes (e.g. distillation, thermal cracking) (Cote, 1976; Wake, 2005). In Europe, Concawe¹ collects data on refinery discharges and investigates the impacts of the refining sector on the environment, inventorying discharge loads on a regular basis since 1969 (Concawe, 2020a).

Chemical mixtures can adversely impact human health and the environment (Bernhardt et al., 2017; Kortenkamp and Faust, 2018; Posthuma et al., 2020; Wang et al., 2021b). In order to quantify chemical mixture toxic pressure on the environment, the multi-substance potentially affected fraction of species (msPAF) can be applied. The msPAF represents the estimated fraction of species affected under a given chemical mixture exposure and is derived from species sensitivity distributions (SSDs) (Posthuma et al., 2001). As a standard indicator in risk assessment, the msPAF has been shown to be (cor)related to ecological indicators such as (mean) species abundance (Posthuma and De Zwart, 2012; Hoeks et al., 2020), the provision of ecosystem services (Wang et al., 2021b) and ecological status under the European Water Framework Directive (WFD) (Posthuma et al., 2020). Recently, as part of the EU project SOLUTIONS (<https://www.solutions-project.eu/>), toxic pressure due to existing chemicals in the environment (including 1760 chemicals of which exposure and high-quality hazard data were available) was estimated for European water bodies (Posthuma et al., 2019), indicated by msPAF values. The results indicate the potential environmental impacts of chemical mixtures.

Traditionally, environmental impacts of PREs have been assessed based on toxicity tests and field surveys (Concawe, 1979, 1982), indicating that PREs have adverse effects on aquatic organisms (Wake, 2005). However, the studies reviewed in Wake (2005) were mostly published before 2000, and the quality of PREs has significantly improved over the years (Hjort et al., 2021; Whale et al., 2022). Within Europe, PREs are regulated through local discharge permits under the Industrial Emissions Directive (European Commission, 2010) and receive substantial treatment before emission takes place. Recent work, including whole effluent toxicity (WET) assessments, has shown that the toxicity of permitted PREs is often limited (Comber et al., 2015; Concawe, 2015; Hughes et al., 2021; Whale et al., 2022). These evaluations mainly addressed contaminants introduced solely by refineries. However, it is largely unknown how much PREs would contribute to the overall mixture toxic pressure in the environment. Moreover, despite several attempts (Van der Oost et al., 2017; De Baat et al., 2021), results from effect-based methods (e.g. bioassays) for PREs are not directly comparable to msPAF levels in the environment, as estimated in Posthuma et al. (2019).

¹ Concawe was established as CONCAWE (CONservative of Clean Air and Water in Europe) in 1963 by a small group of leading oil companies to carry out research on environmental issues relevant to the petroleum refining industry. Its membership has broadened and currently includes most oil companies operating in EU-28, Norway and Switzerland, representing approximately 95% of petroleum refining capacity in those countries. In 2014, it became the Scientific Division of the European Fuel Manufacturers Association (formerly European Petroleum Refiners Association).

Hence, the objective of the present study was to assess the contribution of treated and permitted refinery effluents to the overall mixture toxic pressure in the environment, using the msPAF as the indicator. We also discussed the uncertainties in the analysis and identified focal points for further development of the method.

2. Materials and methods

A schematic overview of the assessment steps executed in this study is shown in Fig. 1. Chemical concentrations in PREs were first collected and converted into dissolved concentrations to account for the bioavailable fraction assumed to be directly related to the toxicity (Section 2.2). Next, a set of SSD data for all constituents of PREs was compiled (Section 2.3). Based on concentrations and SSDs, chronic and acute msPAF levels were subsequently calculated for both discharge points (msPAF_{DP}) and downstream (msPAF_{DS}) beyond the zone of initial mixing (Section 2.4). Next, the msPAF_{DS} levels were compared with estimated msPAF background levels in European waters (Posthuma et al., 2019) to assess the PRE contribution (Section 2.5). Lastly, the msPAF_{DP} levels were compared with observed toxicity (Whale et al., 2022) to evaluate the level of conservatism in the msPAF indicator (Section 2.6).

2.1. Description of treated petroleum refinery effluents

In total, 79 PREs were investigated from 67 refineries of varying types and complexities in 22 European countries, from Portugal in the southwest to Romania in the east and Norway in the north shown in Fig. S1 in the Supporting Information (SI 1). In line with Concawe's operating guidelines, PREs were coded and not represented by refinery names or locations. Nevertheless, effluent abbreviations, average discharge volumes and receiving environment descriptions (e.g. sea, river, estuary) are summarised in Table S1 (SI 1).

2.2. Environmental concentrations of treated petroleum refinery effluents

2.2.1. Data collection and treatment

2016 yearly average chemical concentrations for 79 PREs and 2019 granular concentrations (e.g. daily, monthly) for 14 PREs were taken from the Concawe survey data (2016 from Concawe (2020a) and 2019 from unpublished data from Concawe). For each effluent, a set of parameters were measured, including general water quality parameters (e.g. total suspended solids (TSS)) and concentrations of chemical constituents (Table 1). Note that each effluent covers different measured parameters. In total, the 2016 and 2019 datasets consisted of 1868 and 51,045 measurements, of which 394 and 8319 were below the Limit of Quantification (LoQ), respectively. Data are available upon request.

From the 2019 granular measurements, 50th (P50) and 95th percentile concentrations (P95) were calculated for each effluent parameter. Measurements below LoQ were included either as half the corresponding LoQ or as half of the median of non-zero measurements for the same analyte if the LoQ was not communicated. Chemicals for which all records fell below LoQ were discarded. To facilitate the calculation of mixture toxic pressure (i.e. the msPAF), we divided measured mixture concentrations of BTEX (benzene, toluene, ethylbenzene, and xylenes) and phenols (C0–C3, C4, C5, C6–C8 and C9 alkylphenols) into individual constituents by applying empirical compositional fractions (derived from Concawe (2020a), shown in Table S2 in SI 1). 2016 yearly average chemical concentration data (expressed as P50), and P50 and P95 concentration data from the 2019

granular measurements are shown in SI 2. Effluent concentrations are shown rather constant throughout the year, with the ratios between P95 and P50 for respective chemical on average less than six (SI 2).

2.2.2. Conversion to dissolved concentrations

Measured total concentrations of metals and total petroleum hydrocarbons (TPH) were converted to dissolved concentrations to correct bioavailability limitations to aquatic life. For metals, the equilibrium partitioning method was applied to calculate metal distributions (i.e. ratios between dissolved and total concentrations, $C_{\text{diss}}/C_{\text{total}}$) at discharge points and downstream according to (Van der Kooij et al., 1991):

$$\frac{C_{\text{diss}}}{C_{\text{total}}} = \frac{1}{K_{\text{pm/w}} \bullet \text{TSS} \bullet 10^{-6} + 1} \quad (1)$$

where $K_{\text{pm/w}}$ is the partition coefficient for metals between particulate matter and water (L/kg), TSS is the total suspended solids (mg/L) and 10^{-6} is the conversion factor (kg/mg). As values of $K_{\text{pm/w}}$ were not available for PREs and all European waters, partitioning at both discharge points and downstream was assumed to be similar to levels in Dutch surface waters (values taken from Crommentuijn et al. (1997), Table S3 in SI 1). Values of TSS at discharge points and downstream were taken as 15 mg/L (average TSS concentration of all PREs combined (Concawe, 2020a)) and 30 mg/L (average TSS concentration in Dutch surface waters (Van der Kooij et al., 1991)), respectively. Metal distributions in PREs are summarised in Table S3.

To determine dissolved concentrations profiles for TPH, the PetroTox model was applied to account for the variable solubility behaviour of petroleum hydrocarbons following Raoult's Law (Concawe, 2020b). The model requires product loading (i.e. TPH concentration in mg/L) and the corresponding high-resolution two-dimensional gas chromatography (GCxGC) compositional data in the hydrocarbon block format as input parameters. Each hydrocarbon block contains constituents of similar size and structure with similar environmental distribution and fate (King et al., 1996). However, compositional data were only available for ten single spot samples taken in 2015 and 2016 from 10 distinct refineries during stable running conditions (Hjort et al., 2021). In other words, hydrocarbon block compositional data were not available for all effluents and were not measured at the same time as for TPH. Nevertheless, these ten samples were from the same sites in the 2016 dataset and three samples from the same sites in the 2019 dataset. We determined the least, average and most toxic hydrocarbon block compositions among the ten samples (Figs. S2 and SI 1). The compositions were subsequently applied in PetroTox, assuming an experimental set-up with 10% headspace. Dissolved concentrations (mol/L) were computed for the 1512 individual hydrocarbon constituents mapped to the hydrocarbon block format (Redman et al., 2012).

Table 1

Summary of SSD parameters for individual constituents in PREs applied in the msPAF calculations (values are log10-transformed).

	Acute μ ($\mu\text{g/L}$)	Chronic μ ($\mu\text{g/L}$)
<i>Inorganics</i>		
Ammonia	3.95	2.95
Sulphide	3.41	2.41
<i>Metals</i>		
Arsenic	3.39	2.39
Cadmium	2.91	1.69
Chromium	3.89	2.89
Cobalt	3.62	1.74
Copper	2.26	1.34
Lead	3.55	2.55
Mercury	2.26	1.26
Nickel	3.38	2.38
Selenium	3.84	2.84
Vanadium	3.27	2.27
Zinc	3.22	1.92
<i>Hydrocarbons</i>		
Benzene	4.88	4.01
Toluene	4.65	3.35
Total Petroleum Hydrocarbons (in mmol/L)	Eq. (2.1)	Eq. (2.2)
Xylenes	4.00	3.04
<i>Other organics</i>		
Dichloromethane	5.40	4.40
Pentachlorobenzene	2.99	2.03
<i>Phenols</i>		
Phenol (C0–C3 alkylphenols)	4.31 ^a	3.24 ^a
Butylphenol (C4 alkylphenols)	3.65 ^b	2.65 ^b
Pentylphenol (C5 alkylphenols)	3.42 ^c	2.38 ^c
Octylphenol (C6–C8 alkylphenols)	2.47 ^d	1.68 ^d
Nonylphenol (C9 alkylphenols)	2.40 ^e	1.67 ^e

^a The average values of phenol, cresol, o-cresol, p-cresol, m-cresol and 2,4-xylenol in Posthuma et al. (2019).

^b The average values of 4-tert-butylphenol and 2-tert-butylphenol in Posthuma et al. (2019).

^c The values of 4-tert-pentylphenol in Posthuma et al. (2019).

^d The average values of 4-tert-octylphenol and 4-hexylphenol in Posthuma et al. (2019).

^e The values of 4-(7-methyloctyl)phenol in Posthuma et al. (2019).

2.3. Species sensitivity distribution parameters

Species sensitivity distribution (SSD) parameters include μ (the population average of log10-transformed toxicity values with equal weight per taxon) and σ (i.e. the SSD slope, the population standard deviation of log10-transformed toxicity data without considering taxon weight) (Posthuma et al., 2001). Both chronic and acute endpoints were included. For chemicals except for TPH, values of μ ($\mu\text{g/L}$) were taken from the SSD database in Posthuma et al. (2019) (Table 1). While only freshwater species were included in the database, previous studies

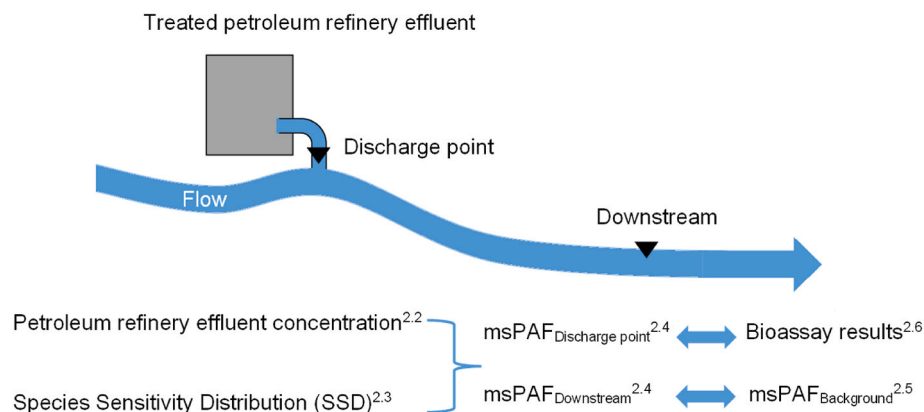


Fig. 1. Scheme for assessing petroleum refinery effluent contribution to chemical mixture toxic pressure in the environment. The numbers in superscript represent corresponding sections in the text.

showed that sensitivity to chemicals between freshwater and marine species are similar (Xin et al., 2015; McGrath et al., 2018). The average SSD slope σ ($\mu\text{g/L}$) was adopted with a value of 0.7 for both acute and chronic effects (Posthuma et al., 2019), assuming that all chemical constituents act via the same mode of action and act concentration additively. This is similar to the frequent practice of water quality assessments for mixtures (Posthuma et al., 2019).

For TPH, the target lipid model (TLM) (McGrath et al., 2018) was applied, including sensitivity of both freshwater and marine species. We computed acute and chronic median toxicity $HC50$ -values (mmol/L, identical to μ but different units) for hydrocarbon constituent i according to:

$$\log(HC50_{acute,i}) = E[\log(EC50_i)] = E[m] \bullet \log(K_{OW,i}) + E[\log(C_L^*)] + \Delta c_i \quad (2.1)$$

$$\log(HC50_{chronic,i}) = E[\log(NOEC_i)] = E[m] \bullet \log(K_{OW,i}) + E[\log(C_L^*)] + \Delta c_i - E[\log(ACR)] \quad (2.2)$$

where $E[m]$ is the mean of universal narcosis slope (-0.940), $K_{OW,i}$ is the octanol-water partition coefficient for hydrocarbon i , $E[\log(C_L^*)]$ is the logarithmic mean of the critical target lipid body burden distribution ($1.85 \mu\text{mol/g}$ octanol), Δc_i is the chemical class correction (0 for aliphatics, -0.025 for monocyclic aromatic hydrocarbons and -0.364 for polycyclic aromatic hydrocarbons), and $E[\log(ACR)]$ is the logarithmic mean of the acute-to-chronic ratio distribution (0.718). All parameters were derived from McGrath et al. (2018). The TLM framework was performed with toxicity cut-off at $\log(K_{OW})$ values higher than 5.5 (acute) and 6 (chronic), generally correlated with empirically observed reduced toxicity of very hydrophobic hydrocarbon constituents (Redman et al., 2017; McGrath et al., 2018).

2.4. The multi-substance potentially affected fraction of aquatic species

msPAF levels were calculated based on chemical concentrations in PREs at discharge points (C_{DP}) and downstream (C_{DS}) and SSD parameters (Table 1). When calculating downstream concentrations, dilution factors (DF), unpublished data from Concawe summarised in Table S1, available for 49 effluents (out of 79) in the 2016 dataset and 11 effluents (out of 14) in the 2019 dataset) were applied to effluents according to $C_{DS} = \frac{C_{DP}}{DF}$. Additionally, default DFs of 10 and 100 (ECHA, 2016) were applied to effluents discharging into freshwater and marine water, respectively, to assess the conservatism of the default values (Table S1). Bioavailability of metals and TPH downstream was corrected based on C_{DS} , following methods described in Section 2.2.2.

To allow a direct comparison with background msPAF levels calculated by Posthuma et al. (2019) for European water bodies, we applied the same approach as Posthuma et al. (2019). This approach assumed that all chemicals act concentration additively (De Zwart and Posthuma, 2005):

$$HU = \sum \left(\frac{C_i}{10^{\mu_i}} \right) \quad (3.1)$$

$$msPAF = NORMDIST(\log_{10}(HU), 0, 0.7, 1) \quad (3.2)$$

where HU is the hazard unit (dimensionless), C_i is the (dissolved) concentration and μ_i is the SSD midpoint for the chemical i (Table 1), NORMDIST is the normal distribution function in Microsoft Excel, and 0.7 is the average SSD slope in the SSD database (Posthuma et al., 2019).

2.5. Comparison with background msPAF levels

Recently, msPAF levels were estimated for European water bodies based on predicted exposure concentrations for 1760 substances with high-quality SSD data (Posthuma et al., 2019). In the present study,

these levels were considered background levels, reflecting the mixture toxic pressure from other chemicals already present in receiving water bodies. In order to assess the contribution from PREs to mixture toxic pressure in the environment, we calculated the contribution ratio ($\log CR$, Eq. (4)), where we divided the msPAF of effluent i downstream ($msPAF_{DS,i}$) by the background level in the corresponding basin ($msPAF_{Background,i}$) and then applied the logarithm:

$$\log CR_i = \log_{10} \left(\frac{msPAF_{DS,i}}{msPAF_{Background,i}} \right) \quad (4)$$

Contribution ratios >0 indicate the mixture toxic pressure contribution towards refinery effluents, whereas ratios <0 indicate contribution towards other chemicals already present in the environment.

2.6. Comparison with effect-based method data

In order to increase the validity of the method, we compared the msPAF estimations to observed toxicity. Routine chemical characterisation and bioassays (toxicity tests) of refinery effluents are conducted according to permit or regulatory conditions (Whale et al., 2022). The present study provides a unique combination of detailed chemical composition, mechanistic toxicity modelling and bioassays on a subset of three refineries that were sampled as part of this study in 2015 and 2016 (Whale et al., 2022). The effluents were wastewaters from production units and oily runoff (Hjort et al., 2021), collected using a sampling protocol previously developed (Concawe, 2010). Bioassays were conducted following several guidelines (ISO, 1998; ISO, 2012; OECD, 2012; OECD, 2013), representing acute test results for bacteria (*Aliivibrio fischeri*) and zebrafish embryos (*Danio rerio*) and chronic results for algae (*Raphidocelis subcapitata*) and daphnids (*Daphnia magna*) (Tables S4 and SI 1). All details on bioassays were described in Whale et al. (2022).

We calculated msPAF levels for the three effluents tested in the bioassays, following the procedure described in Sections 2.3 and 2.4, but based on corresponding chemical concentrations and GCxGC hydrocarbon block compositional data from Hjort et al. (2021). We qualitatively compared the environmental impacts estimated from chemical concentrations to the observed effects.

3. Results and discussion

3.1. Multi-substance potentially affected fraction

3.1.1. 2019 dataset

For effluents of which actual DFs are available, median msPAF-chronic levels at discharge points were estimated to be 71.8% (95% CI: 51.5%, 77.9%) and 86.9% (79.6%, 89.7%) based on 50th (P50) and 95th percentile concentrations (P95), respectively (Fig. S3 and full results in Tables S5 and SI 1). Median msPAF-acute levels at discharge points were estimated to be 21.6% (9.7%, 27.9%) and 40.1% (32.6%, 47.9%) based on P50 and P95 concentrations, respectively. Median chronic and acute pressure downstream was negligible, lower than 0.1%.

3.1.2. 2016 dataset

Based on yearly average concentrations in 2016, median msPAF-chronic and msPAF-acute levels at discharge points were estimated to be 77.0% (95% CI: 14.3%, 91.1%) and 25.4% (0.8%, 51.2%), respectively (Fig. 2 and full results in Tables S6 and SI 1). Average pressure reduced to $<0.2\%$ downstream. When applying default DFs, msPAF levels were on average three orders of magnitude higher than those with actual DFs (Figs. S4 and SI 1).

Based on both datasets, median msPAF-chronic levels of PREs at discharge points were approximately 74% based on P50 concentrations, and median msPAF-acute levels were approximately 40% based on P95

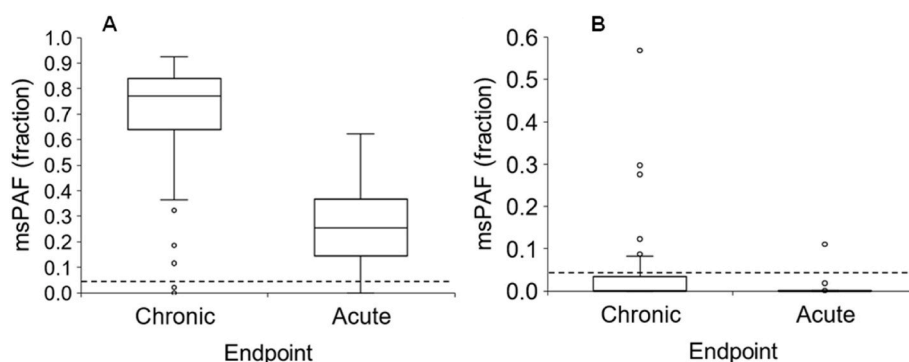


Fig. 2. The msPAF levels (fraction) at discharge points (A) and downstream (B) based on the 2016 dataset. The black dashed line represents msPAF <0.05, protecting 95% of the species against adverse effects.

concentrations. Due to dilution, the mixture toxic pressure reduced substantially to <5% in the receiving environment. In a regulatory context, the msPAF can be distinguished for protection targets (msPAF-chronic) and biodiversity impacts (msPAF-acute), and sufficient protection relates to msPAF-chronic = 0.05 protecting 95% of the species against adverse effects (Posthuma et al., 2019). In other words, our results suggested that while PREs may be toxic to organisms living within the initial mixing zone, most effluents (82%) would not pose significant toxic pressure in the receiving environment beyond the mixing zone with msPAF-chronic levels <0.05. Nevertheless, additional analysis (e.g. bioavailability measurements such as biomimetic solid phase micro extraction (BE-SPME) in effluents and receiving waters, detailed chemistry for hydrocarbon block compositions, targeted bioassays) could be suggested as a follow-up for the rest 18% of effluents of which msPAF-chronic levels >0.05 outside the initial mixing zone.

As our study is the first to assess the ecological risks of PREs to the aquatic community using msPAF as an indicator, a direct comparison of our results with other studies is difficult. Nevertheless, our results showed good agreement with Hughes et al. (2021), showing that regulatory compliance was met for most PREs in North America after dilution (i.e. downstream), with most whole effluent toxicity (WET) tests passing the established criteria by large margins. Additionally, our results are consistent with Comber et al. (2015), concluding that effluent toxicity is not a major concern to the environment.

Our results further suggested the conservatism of default DFs (10 and 100 for the freshwater and marine environment, respectively) (ECHA, 2016). While the default DF of 100 for marine areas seems adequate, the DF of 10 for freshwater seems low when applied to large rivers and estuaries where most refineries are located (Table S1). For effluents discharging into freshwater, actual DFs were on average 650 times higher than default DFs (Table S1), resulting in msPAF levels several orders of magnitude lower (Fig. S4). Therefore, we recommend using effluent-specific DFs to improve the accuracy of risk estimates in the environment, corroborating the study of Finckh et al. (2022).

3.1.3. Uncertainties

Several uncertainties should be considered when interpreting our results. First, some chemical constituents that may be present in PREs but were not measured were not considered in the analysis. For instance, naphthenic acids were reported as key contributors to the toxicity of heavy oil refining effluents (Pinzón-Espinosa and Kanda, 2020). Additionally, chloride was shown to be the primary stressor for the chemical and paper/wood processing sectors driving risks to aquatic life (De Zwart et al., 2018), and it can be present in crude oil as an emulsified solution of salt even after the desalting process (Chambers et al., 2011). Consequently, constituents not included in the existing analytical data could result in higher msPAF levels than estimated.

Secondly, the PetroTox model requires detailed hydrocarbon block compositional data to calculate the dissolved fraction of TPH. Due to the

lack of GCxGC compositional data for effluents involved, we assumed that all effluents have the same toxic compositions in TPH (Fig. S2) based on effluent spot samples. However, as spot samples were taken from wastewater treatment plants of different types and treatments (Hjort et al., 2021), we envision that the variability in the msPAF (bars in Figs. S3 and S4) may characterise the uncertainties due to unknown hydrocarbon compositions. Therefore, while the actual risks of a specific refinery effluent may vary, they are most likely to be within the range calculated based on the least and most toxic compositions.

Uncertainties also remain regarding bioavailability and fate processes. For metals, we assumed the partitioning of metals to suspended solids ($K_{pm/w}$) similar to Dutch standard values (Crommentuijn et al., 1997), and total suspended solid (TSS) levels in other EU water systems similar to the Dutch average level (Van der Kooij et al., 1991). However, $K_{pm/w}$ shows great variability depending on physicochemical factors such as solid compositions, water pH and dissolved organic carbon (Van der Kooij et al., 1991; Wang et al., 2021a). Balasubramanian et al. (2020) showed a global mean of 30.7 mg/L for TSS, ranging from 0.1 to 2626.8 mg/L. While the Dutch average TSS level of 30 mg/L appears to represent other receiving locations, marine environments tend to have lower TSS levels than freshwater sources (Czuba et al., 2011), resulting in a higher fraction of metals available for incorporation into organisms (i.e. higher bioavailability). Therefore, we recommend improving bioavailability assessments using specific $K_{pm,w}$ and TSS values for sites close to the screening thresholds (i.e. msPAF-chronic = 0.05). For TPH, especially for heavier fractions, partitioning to suspended solids would reduce the bioavailability and thus toxicity (Parkerton et al., 2018), which was not considered in the PetroTox model. Additionally, potential loss processes (e.g. (bio)degradation) that lighter TPH fractions may be susceptible to upon discharge were ignored in the PetroTox, resulting in overestimated field exposures. However, Stepnowski et al. (2002) showed that TPH in the wastewater underwent slow degradation in time. Al-Hawash et al. (2018) summarised that the limited availability of microorganisms in the environment is likely to restrict the biodegradability of TPH. Therefore, impacts of such fate processes can be considered minor.

In the present study, to allow a fair comparison with background msPAF levels calculated by Posthuma et al. (2019), we applied a similar approximation approach assuming that all chemicals act via the same toxic mode of action (TMoA) and thus act concentration additively (simplified approach). In practice, a generic SSD slope of 0.7 for both acute and chronic data was applied in this study. However, complex chemical mixtures as in PREs are expected to have different TMoAs and exert effects based on response addition (complex approach, SSD parameters and detailed calculation in Tables S7 and S11). Therefore, we applied both approaches to a typical PRE (average chemical concentrations in 2016 (Concawe, 2020a)) to gain insights on the influence: msPAF levels using the complex approach (87.0% and 53.6% for chronic and acute endpoints, respectively) were 10% higher than those using the

simplified approach (76.4% and 43.3%, respectively). This is contrary to empirical evidence that concentration addition overestimates the toxicity (i.e. worst-case approximation) (KEMI, 2015; Van Broekhuizen et al., 2017), and can be mainly explained by the exceedingly flat SSD curve for ammonia with an SSD slope of 1.04 (Table S7). Consequently, it is recommended to consult the estimated msPAF levels from both simplified and complex approaches.

3.2. Hazardous unit contribution

The contribution of each chemical group to mixture toxic pressure was examined for 36 effluents of which inorganics, metals and hydrocarbons were all measured in the effluent, expressed as % of hazardous unit (HU) (Figs. S5 and SI 1). The average contribution across effluents for different endpoints and locations was calculated (Table 2). Regardless of differences in endpoints and locations, hydrocarbons (mainly TPH) and inorganics (mainly ammonia) were always the key constituents explaining at least 85% of the mixture toxic pressure. The relative contribution of hydrocarbons (mainly TPH) became more prominent downstream than at discharge points (Table 2), with msPAF levels downstream closely related to the TPH concentrations downstream (i.e. TPH concentrations divided by DFs, Fig. S6 in SI 1). Due to low solubility limits of 'heavy' substances, dissolved petroleum hydrocarbons and associated HU follow a non-linear (asymptotic) function of TPH concentrations (Redman et al., 2014). Therefore, compared to other chemicals whose dissolved concentrations and HUs decreased linearly downstream, TPH becomes more prominent in determining the msPAF levels downstream. Within TPH, low-molecular-weight monoaromatic hydrocarbons (MAH) and polycyclic aromatic hydrocarbons (PAH), generally with lower carbon numbers (C_{10} – C_{15}) and $\log K_{OW}$ values, had higher HUs due to their relatively high water solubility and thus bioavailability (Varjani et al., 2017; Honda and Suzuki, 2020). The contribution of other organics, including phenols, was negligible. Our findings are consistent with an earlier study addressing offshore produced water discharges, indicating that hydrocarbons and ammonia were the main contributors to toxicity based on estimated cumulative risks (Parkerton et al., 2018). Moreover, our results also support the findings from Wake (2005) that PAHs and ammonia in refinery effluents are the most likely cause of toxic effects on algae, invertebrates and fish based on toxicity tests.

3.3. Petroleum refinery effluent contribution to mixture toxic pressure in the environment

In general, permitted PREs were estimated to contribute less than the sum of other pollution sources, as all logCR values were below 0 (Fig. 3).

Table 2
Contribution of each chemical group to mixture toxic pressure (%).^a

Endpoint	Location	Hydrocarbons ^b	Inorganics ^c	Metals ^d	Others ^e
Chronic	Discharge point	53.1 (±20.3)	32.3 (±20.8)	12.4 (±11.8)	2.2 (±5.5)
	Downstream	77.8 (±20.7)	16.4 (±18.6)	4.6 (±5.0)	1.2 (±3.5)
Acute	Discharge point	57.7 (±21.5)	30.6 (±20.8)	9.6 (±9.9)	2.1 (±5.4)
	Downstream	76.0 (±21.4)	18.4 (±19.7)	4.3 (±4.9)	1.3 (±3.9)

^a The average contribution (±1 standard deviation) across 36 petroleum refineries.

^b Hydrocarbons include total petroleum hydrocarbons and individual hydrocarbons (benzene, toluene and xylenes).

^c Inorganics include ammonia and sulphide.

^d Metals include arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, vanadium and zinc.

^e Others include dichloromethane, pentachlorobenzene and phenols.

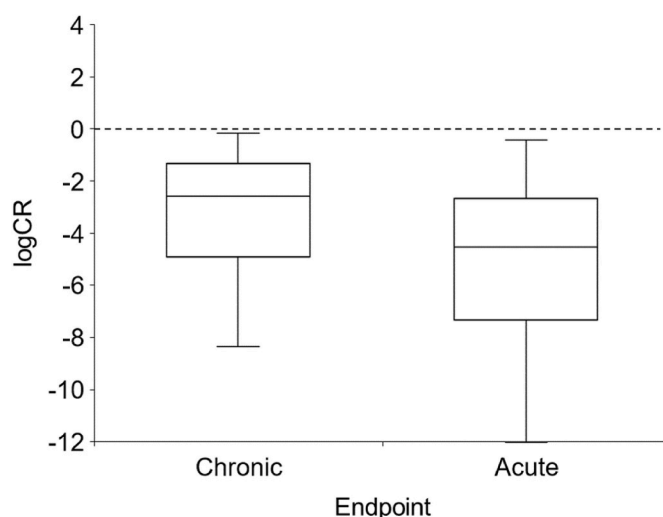


Fig. 3. Refinery effluent contribution to mixture toxic pressure in the environment. logCR is the log10-transformed contribution ratio between median msPAF levels of PREs downstream in the 2016 dataset and those in receiving environments (Posthuma et al., 2019). logCR = 0 (dashed line) indicates refinery effluents contribute the same as existing chemicals to mixture toxic pressure in the environment. logCR > 0 indicates the mixture toxic pressure contribution towards refinery effluents, whereas logCR < 0 indicate contribution towards existing chemicals in the environment.

msPAF levels of PREs were on average 2.5 and 4.5 orders of magnitude lower than background levels for chronic and acute endpoints, respectively (full results in Tables S8 and SI 1).

Our results suggested that under the current regulations and permit conditions, refinery effluents are minor contributors to the overall toxic pressure in the environment. This overall pressure is attributed to relatively few compounds (15 chemicals explaining nearly 99.5% of the mixture exposure effects), characterised by high production mass, ubiquitous use, and high hazard classifications (e.g. Bisphenol-A, Chlorpyrifos) (Posthuma et al., 2019). In addition to the uncertainties of msPAF calculations for PREs outlined in Section 3.1.3, one should note the uncertainties of background levels in Posthuma et al. (2019). Background levels were quantified based on the P95 chemical concentration of a year (i.e. exposures lasting more than 18 days were included (P95-year = 18 d)). However, the spatiotemporal variability of exposures is largely unknown. In other words, it is uncertain if all chemicals would co-occur in time and space, which was implicitly assumed in Posthuma et al. (2019). Additionally, due to the choice of P95 data, peak exposures (e.g. of pesticides) lasting less than 18 days were not included. Moreover, chemical concentrations were estimated based on water body-level exposure data; thus, impacts of point source pollution (e.g. wastewater treatment plants) were not included. Given the above factors, msPAF background levels may differ from those shown in Posthuma et al. (2019). Yet, since msPAF levels of PREs were estimated to be 2.5–4.5 orders of magnitude lower than background levels, we envision that the variabilities and uncertainties would only result in marginal differences in results (i.e. the very low contribution of PREs to mixture effects in the environment).

3.4. Comparison with effect-based method data

Bioassays showed that toxicity in the final effluent mainly occurred at high effluent concentrations or was not observed in the 100% effluent (Table 3), indicating low to negligible toxicity to aquatic organisms and their receiving environments (Whale et al., 2022). We compared our msPAF results with bioassays. Estimated msPAFs at discharge points seemed conservative compared to the observed toxicity (Table 3). On the basis of the expected dilution in the receiving environment, msPAF

Table 3

Comparison of bioassay data (Whale et al., 2022) and estimated msPAF based on chemical concentrations (TPH = total petroleum hydrocarbons; TU = toxic units of TPH estimated by Whale et al. (2022); HU = hazardous units of TPH estimated in the present study).

Effluent	Effluent TPH (mg/L)	Bacteria	Algae	Daphnia	Zebrafish embryos	TU-acute	HU-acute	msPAF-chronic (%)	msPAF-acute (%)
		Acute EC50 ^b	Chronic NOEC ^b	Chronic EC50 ^b	Chronic NOEC ^b	Acute EC50 ^b			
A (4) ^a	0.08	>45	>100	>100	19.4	>100	0.059	0.087	33.1
C (16) ^a	0.06	>45	>100	69.6	<10	>100	0.056	0.084	33.1
D (23) ^a	0.22	>45	29	>100	>100	>100	0.049	0.067	28.5
									5.1

^a The effluent code is consistent with that in Whale et al. (2022).

^b Effect concentrations from bioassays were expressed in % volume of effluents causing specific adverse effects on the test organism (L(E)C_R values). For instance, a 21 d EC₁₀ reproduction = 25% means that a 4-fold dilution (100%/25% = 4) of the refinery sample would cause 10% reproduction loss for the species after 21 d exposure to the effluent.

levels downstream would be many times lower than those at discharge points. Therefore, it is possible to say that these three final effluents would not cause adverse effects in receiving environments, consistent with the low toxic units (TU) and observed effects in effluent testing. Our estimates further showed that the effluent A(4) had the highest HUs and msPAFs, consistent with the ranking of observed toxicity in chronic tests and estimated TUs (Table 3).

3.5. Implication for (regulatory) risk management

Our study presented a novel methodology to estimate the mixture toxic pressure of PRE in the environment, combining toxicity tools (PetroTox and SSD) for complex petrochemicals and explaining the results using bioassay data. With sufficient data, our method could be applied to assess potential environmental risks of any PRE of interest. The results help identify pollution hotspots and take effective targeted actions to mitigate potential risks.

Since the environment and humans are constantly exposed to multiple chemicals, the Mixture Assessment Factor (MAF) was proposed to be implemented under the European regulation for the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), accounting for the potential combined effects of chemicals after emission. The MAF represents the reduction of environmental concentrations of individual chemicals to be acceptable to occur in a mixture, provided that the sum of risk quotients does not exceed 1 (KEMI, 2015). While using a single generic value of MAF (5, 10, 20 or other) might be helpful for data-poor chemicals, it has aroused debate on its scientific justification and the use of hypothetical exposures (Batke et al., 2022).

In the present study, msPAF levels for PREs, calculated based on chemical concentrations and hazard data, were compared to those for other chemicals in receiving waters. The major conclusion is that PREs are minor contributors compared to other chemicals. Our approach could better support science-based decisions on informing focused regulations for multiple chemicals by identifying chemical groups estimated to drive the toxic pressure in a given receiving water. This would be a more targeted and effective approach than the proposed use of a generic MAF, as it has been noted that there are generally only a few constituents that drive the estimated toxic pressure in most receiving waters (KEMI, 2015; Posthuma et al., 2019; Rorije et al., 2022). A broad application of a MAF to all substances may result in unnecessary changes to regulatory or manufacturing approaches.

It is noted that TPH, as shown to be the primary stressor in PREs driving risks to aquatic life, is not a substance that would be registered under the REACH regulation. REACH deals with the registration of single substances. The present study applied the hydrocarbon block method, dividing TPH into blocks representing the constituents based on chemical classes (e.g. aromatics) and carbon numbers, and correlated petroleum substances' environmental hazards with physicochemical properties. While generally low, the calculated msPAFs were mostly explained by the aromatic constituents (C₁₀–C₁₅).

4. Conclusions

We presented a generic methodology to assess the PRE contribution to mixture toxic pressure in the environment, using the msPAF as an indicator. We estimated the msPAFs for PREs using SSDs and a mechanistic solubility model to estimate the bioavailable fraction of TPH. The results showed that most PREs (82%) would not pose significant toxic pressure in the receiving environment with msPAF-chronic levels <0.05. The estimated msPAFs for the remaining PREs can be further refined using more detailed chemistry, bioavailability measurements or targeted bioassays. The msPAFs for PREs were also compared to the background msPAFs estimated for receiving waters (Posthuma et al., 2019) and were approximately 2–4 orders of magnitude lower. This result suggested that PREs were not major contributors to the toxic pressure in the environment. Our methodology can help identify the pollution hotspots, understand the relative contributions of different chemical groups and develop targeted regulatory and industrial activities to mitigate environmental risks.

Credit author statement

Jiaqi Wang: Investigation, Formal analysis, Writing - Original Draft, Data Curation. **Mathijs G.D. Smit:** Conceptualization, Methodology, Writing - Review & Editing. **Yves Verhaegen:** Project administration, Writing - Review & Editing, Data Curation. **Tom M. Nolte:** Formal analysis. **Aaron D. Redman:** Writing - Review & Editing, Methodology. **A. Jan Hendriks:** Supervision, Writing - Review & Editing. **Markus Hjort:** Project administration, Supervision, Investigation, Writing - Review & Editing, Data Curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Markus Hjort and Yves Verhaegen works for Concawe, which represents the European fuel manufacturing industry, whose members operate the refinery sites included in the study. Concawe is a non-profit scientific organisation established in 1963 to conduct research on environmental issues relevant to the European fuel manufacturing industry.

Concawe's operating principles aim to publish all research publicly, either on the Concawe website (<https://www.concawe.eu>) or as open access papers in scientific journals. Concawe has a long history of publications. Our mechanism to avoid bias is to publish our work, publish our data and methods so that the research community can reproduce and build on our findings.

Mathijs G.D. Smit and Aaron D. Redman works for Shell and ExxonMobil, respectively, which are Concawe member companies. As this study was funded by Concawe these co-authors are bound to follow the mission and operating principles of Concawe.

Jiaqi Wang, Tom M. Nolte, A. Jan Hendriks are employed by

Radboud University and have received research funding from Concawe for conducting this study. Their research group independently carries out studies financed by university, governmental, commercial and other funding that is published in peer review journals.

Data availability

Shared data as Supplementary Material

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.137127>.

References

- Al-Hawash, A.B., Dragh, M.A., Li, S., Alhujaili, A., Abbood, H.A., Zhang, X., Ma, F., 2018. Principles of microbial degradation of petroleum hydrocarbons in the environment. *Egypt. J. Aquatic Res.* 44, 71–76.
- Balasubramanian, S.V., Pahlevan, N., Smith, B., Binding, C., Schalles, J., Loisel, H., Gurlin, D., Greb, S., Alikas, K., Randa, M., Bunkei, M., Moses, W., Nguyễn, H., Lehmann, M.K., O'Donnell, D., Ondrusek, M., Han, T.-H., Fichot, C.G., Moore, T., Boss, E., 2020. Robust algorithm for estimating total suspended solids (TSS) in inland and nearshore coastal waters. *Rem. Sens. Environ.* 246, 111768.
- Batke, M., Damm, G., Foth, H., Freyberger, A., Gebel, T., Gundert-Remy, U., Hengstler, J., Mangerich, A., Partosch, F., Röhl, C., Schupp, T., Wollin, K.M., 2022. The EU chemicals strategy for sustainability: critical reflections on proposed regulatory changes for endocrine disruptors and mixture toxicity. *Arch. Toxicol.* 96, 1133–1135.
- Bernhardt, E.S., Rosi, E.J., Gessner, M.O., 2017. Synthetic chemicals as agents of global change. *Front. Ecol. Environ.* 15, 84–90.
- Chambers, B., Srinivasan, S., Yap, K.M., Yunovich, M., 2011. Corrosion in crude distillation unit overhead operations: a comprehensive review. *Corrosion* 11360, 5011–5021.
- Comber, M.H.I., Gurling, A., den Haan, K.H., Whale, G., 2015. Oil refinery experience with the assessment of refinery effluents and receiving waters using biologically based methods. *Integrated Environ. Assess. Manag.* 11, 653–665.
- Concawe, 1979. The Environmental Impact of Refinery Effluents. Concawe, Brussels. Report. 5/79.
- Concawe, 1982. Ecological Monitoring of Aqueous Effluents from Petroleum Refineries. Concawe, Den Haag.
- Concawe, 2010. Concawe Effluent Speciation Project. Report no. 3/10. Concawe Brussels.
- Concawe, 2015. Stream Studies: Evaluation of Whole Effluent Bioassays for Assessment of Hydrocarbon Ecotoxicity - Phase III Stream Study Report. Concawe, Brussels. Report no. 7/15.
- Concawe, 2020a. 2016 Survey of Effluent Quality and Water Use at European Refineries. Report no. 10/20, Brussels.
- Concawe, 2020b. PetroTox Version 4.0 User Manual. Concawe, Brussels. Report no. 7/20.
- Cote, R., 1976. The Effects of Petroleum Industry Liquid Wastes on Aquatic Life with Special Emphasis on the Canadian Environment. National Research Council of Canada, Canada.
- Crommentuijn, T., Polder, M., van de Plassche, E.J., 1997. Maximum Permissible Concentrations and Negligible Concentrations for Metals, Taking Background Concentrations into Account. RIVM Report 601501001. RIVM, Bilthoven.
- Czuba, J.A., Magirl, C.S., Czuba, C.R., Grossman, E.E., Curran, C.A., Gendaszek, A.S., Dinicola, R.S., 2011. Sediment Load from Major Rivers into Puget Sound and its Adjacent Waters. Fact Sheet, Reston, VA.
- De Baat, M.L., Pronk, T.E., Van den Berg, S.J.P., Van der Oost, R., 2021. Kalibratie van de risicogrenzen voor interpretatie van bioassays. Versie 1, 21 december 2021. KIWK-Toxiciteit Notitie. Amersfoort, Nederland. Kennis Impuls Water Kwaliteit.
- De Zwart, D., Adams, W., Galay Burgos, M., Hollender, J., Junghans, M., Merrington, G., Muir, D., Parkerton, T., De Schamphelaere, K.A.C., Whale, G., Williams, R., 2018. Aquatic exposures of chemical mixtures in urban environments: approaches to impact assessment. *Environ. Toxicol. Chem.* 37, 703–714.
- De Zwart, D., Posthuma, L., 2005. Complex mixture toxicity for single and multiple species: proposed methodologies. *Environ. Toxicol. Chem.* 24, 2665–2676.
- ECHA, 2016. Guidance on Information Requirements and Chemical Safety Assessment. Chapter R.16: Environmental exposure assessment [Online]. Available: <https://echa.europa.eu/en/information-on-chemicals/doc/default-source/chemical-safety-assessment/guidance-on-information-requirements-and-chemical-safety-assessment.pdf>.
- European Commission, 2010. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions (Integrated Pollution Prevention and Control).
- Finckh, S., Beckers, L.-M., Busch, W., Carmona, E., Dulio, V., Kramer, L., Krauss, M., Posthuma, L., Schulze, T., Slootweg, J., Von der Ohe, P.C., Brack, W., 2022. A risk based assessment approach for chemical mixtures from wastewater treatment plant effluents. *Environ. Int.* 164, 107234.
- Hjort, M., den Haan, K.H., Whale, G., Koekkoek, J., Leonards, P.E.G., Redman, A.D., Vaioiopolou, E., 2021. Conventional and high resolution chemical characterization to assess refinery effluent treatment performance. *Chemosphere*, 130383.
- Hoeks, S., Huijbregts, M.A.J., Douziech, M., Hendriks, A.J., Oldenkamp, R., 2020. Mean species abundance as a measure of ecotoxicological risk. *Environ. Toxicol. Chem.* 39, 2304–2313.
- Honda, M., Suzuki, N., 2020. Toxicities of polycyclic aromatic hydrocarbons for aquatic animals. *Int. J. Environ. Res. Publ. Health* 17, 1363.
- Hoshina, M.M., de Angelis, D.d.F., Marin-Morales, M.A., 2008. Induction of micronucleus and nuclear alterations in fish (*Oreochromis niloticus*) by a petroleum refinery effluent. *Mutat. Res., Genet. Toxicol. Environ. Mutagen.* 656, 44–48.
- Hughes, S.A., Maloney, E.M., Bejarano, A.C., 2021. Are vertebrates still needed in routine whole effluent toxicity testing for oil and gas discharges? *Environ. Toxicol. Chem.* 40, 1255–1265.
- ISO, 1998. Water Quality: Determination of the Inhibitory Effect of Water Samples on the Light Emission of *Vibrio Fischeri* (Luminescent Bacteria Test). Method Suring Liquid-Dried Bacteria. ISO.
- ISO, 2012. International Standards Organisation Water Quality – Fresh Water Algal Growth Inhibition Test with Unicellular Green Algae. ISO (8692:2012) guidelines.
- KEMI, 2015. An Additional Assessment Factor (MAF)—A Suitable Approach for Improving the Regulatory Risk Assessment of Chemical Mixtures? Report 5/15. T. Backhaus to the Swedish Chemicals Agency, Stockholm, Sweden.
- King, D., Lyne, R., Gurling, A., Peterson, D., Stephenson, R., Short, D., 1996. Environmental risk assessment of petroleum substances: the hydrocarbon block method. Report 96, 52.
- Kortenkamp, A., Faust, M., 2018. Regulate to reduce chemical mixture risk. *Science* 361, 224–226.
- McGrath, J.A., Fanelli, C.J., Di Toro, D.M., Parkerton, T.F., Redman, A.D., Paumen, L.L., Comber, M., Eadsforth, C.V., den Haan, K., 2018. Re-evaluation of target lipid model-derived HCS predictions for hydrocarbons. *Environ. Toxicol. Chem.* 37, 1579–1593.
- OECD, 2012. Guidelines for the Testing of Chemicals, Section 2 Effects on Biotic Systems Test No. 211: Daphnia Magna Reproduction Test. Adopted: 2nd October 2012.
- OECD, 2013. Guidelines for the Testing of Chemicals, Section 2 Effects on Biotic Systems Test No. 236: Fish Embryo Acute Toxicity (FET) Test. Adopted 26th July 2013.
- Parkerton, T.F., Bok, M., Ireland, A.W., Prosser, C.M., 2018. An evaluation of cumulative risks from offshore produced water discharges in the Bass Strait. *Mar. Pollut. Bull.* 126, 610–621.
- Pinzón-Espinosa, A., Kanda, R., 2020. Naphthenic acids are key contributors to toxicity of heavy oil refining effluents. *Sci. Total Environ.* 729, 138119.
- Posthuma, L., De Zwart, D., 2012. Predicted mixture toxic pressure relates to observed fraction of benthic macrofauna species impacted by contaminant mixtures. *Environ. Toxicol. Chem.* 31, 2175–2188.
- Posthuma, L., Suter II, G.W., Traas, T.P., 2001. Species Sensitivity Distributions in Ecotoxicology. CRC press.
- Posthuma, L., van Gils, J., Zijp, M.C., van de Meent, D., de Zwart, D., 2019. Species sensitivity distributions for use in environmental protection, assessment, and management of aquatic ecosystems for 12 386 chemicals. *Environ. Toxicol. Chem.* 38, 905–917.
- Posthuma, L., Zijp, M.C., De Zwart, D., Van de Meent, D., Globevnik, L., Koprivsek, M., Focks, A., Van Gils, J., Birk, S., 2020. Chemical pollution imposes limitations to the ecological status of European surface waters. *Sci. Rep.* 10, 14825.
- Redman, A.D., Parkerton, T.F., Leon Paumen, M., Butler, J.D., Letinski, D.J., den Haan, K., 2017. A re-evaluation of PETROTOX for predicting acute and chronic toxicity of petroleum substances. *Environ. Toxicol. Chem.* 36, 2245–2252.
- Redman, A.D., Parkerton, T.F., Letinski, D.J., Manning, R.G., Adams, J.E., Hodson, P.V., 2014. Evaluating toxicity of heavy fuel oil fractions using complementary modeling and biomimetic extraction methods. *Environ. Toxicol. Chem.* 33, 2094–2104.
- Redman, A.D., Parkerton, T.F., McGrath, J.A., Di Toro, D.M., 2012. PETROTOX: an aquatic toxicity model for petroleum substances. *Environ. Toxicol. Chem.* 31, 2498–2506.
- Rorije, E., Wassenaar, P.N.H., Slootweg, J., van Leeuwen, L., van Broekhuizen, F.A., Posthuma, L., 2022. Characterization of ecotoxicological risks from unintentional mixture exposures calculated from European freshwater monitoring data: forwarding prospective chemical risk management. *Sci. Total Environ.* 822, 153385.
- Singh, S., Shikha, 2019. Treatment and recycling of wastewater from oil refinery/petroleum industry. In: SINGH, R.L., SINGH, R.P. (Eds.), *Advances in Biological Treatment of Industrial Waste Water and Their Recycling for a Sustainable Future*. Springer Singapore, Singapore.
- Stepnowski, P., Siedlecka, E.M., Behrend, P., Jastorff, B., 2002. Enhanced photo-degradation of contaminants in petroleum refinery wastewater. *Water Res.* 36, 2167–2172.
- Van Broekhuizen, F., Posthuma, L., Traas, T., 2017. Addressing Combined Effects of Chemicals in Environmental Safety Assessment under REACH-A Thought Starter.
- Van der Kooij, L., Van De Meent, D., Van Leeuwen, C., Bruggeman, W., 1991. Deriving quality criteria for water and sediment from the results of aquatic toxicity tests and product standards: application of the equilibrium partitioning method. *Water Res.* 25, 697–705.

- Van der Oost, R., Sileno, G., Suárez-Muñoz, M., Nguyen, M.T., Besselink, H., Brouwer, A., 2017. SIMONI (Smart Integrated Monitoring) as a novel bioanalytical strategy for water quality assessment: Part I—model design and effect-based trigger values. *Environ. Toxicol. Chem.* 36, 2385–2399.
- Varjani, S.J., Gnansounou, E., Pandey, A., 2017. Comprehensive review on toxicity of persistent organic pollutants from petroleum refinery waste and their degradation by microorganisms. *Chemosphere* 188, 280–291.
- Wake, H., 2005. Oil refineries: a review of their ecological impacts on the aquatic environment. *Estuar. Coast Shelf Sci.* 62, 131–140.
- Wang, J., Koopman, K.R., Collas, F.P.L., Posthuma, L., de Nijs, T., Leuven, R.S.E.W., Hendriks, A.J., 2021a. Towards an ecosystem service-based method to quantify the filtration services of mussels under chemical exposure. *Sci. Total Environ.* 763, 144196.
- Wang, J., Lautz, L.S., Nolte, T.M., Posthuma, L., Koopman, K.R., Leuven, R.S.E.W., Hendriks, A.J., 2021b. Towards a systematic method for assessing the impact of chemical pollution on ecosystem services of water systems. *J. Environ. Manag.* 281, 111873.
- Whale, G., Hjort, M., Di Paolo, C., Redman, A., Postma, J., Legradi, J., Leonards, P., 2022. Assessment of oil refinery wastewater and effluent integrating bioassays, mechanistic modelling and bioavailability evaluation. *Chemosphere* 287, 132146.
- Xin, Z., Wencho, Z., Zhenguang, Y., Yiguo, H., Zhengtao, L., Xianliang, Y., Xiaonan, W., Tingting, L., Liming, Z., 2015. Species sensitivity analysis of heavy metals to freshwater organisms. *Ecotoxicology* 24, 1621–1631.