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

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

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ABSTRACT

Petroleum refinery effluents (PRE) are wastewaters from industries associated with oil refining. Within EU, PREs are regulated through local discharge permits and receive significant treatment before emission. After treatment, PREs can still contain various pollutants potentially toxic to organisms. Earlier work, including whole-effluent toxicity assessments, has shown that toxicity of PREs is often limited. However, the extent to which PREs contribute to mixture pressure in the receiving environment is unknown. Therefore, our study aimed to assess the contribution of PREs to mixture effects 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 dilution factors, msPAF levels were computed for undiluted effluents at discharge points and diluted effluents downstream in receiving waters. Average msPAF-chronic and msPAF-acute levels of PREs at discharge points were 69% (P50) and 40% (P95), respectively. Levels were reduced substantially <5% downstream, indicating low to negligible toxicity of PREs in receiving environments. 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 background levels, suggesting that PREs were minor contributors to the toxic pressure in the environment.

Our results provide effluent and substance rankings, helping identify hotspots and take effective targeted action to remediate potential risks. We explicitly discuss the uncertainties for further refinement and development of the method.

KEYWORDS

Petroleum refinery effluents; petroleum hydrocarbons; multi-substance potentially affected fraction; environmental risk assessment

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SUMMARY

Petroleum refinery effluents (PRE) are wastewaters from industries associated with oil refining. Within EU, PREs are regulated through local discharge permits and receive significant treatment before emission. After treatment, PREs can still contain various pollutants potentially toxic to organisms. Previously conducted whole-effluent toxicity assessment works has shown that toxicity of PREs is often limited. However, the extent to which PREs contribute to mixture pressure in the receiving environment is unknown. Environmental risks of PREs on aquatic organisms depend on several factors, including effluent compositions and receiving water conditions.

This study aimed to assess the contribution of PREs to mixture effects in the environment, using the multi-substance potentially affected fraction of species (msPAF) as an indicator. The msPAF represents the estimated affected fraction of species at a certain chemical mixture exposure, derived from species sensitivity distributions (SSDs). The msPAF can be computed for both chronic and acute effects, interpreted as indicators for environmental protection (msPAF-chronic) and biodiversity impacts (msPAF-acute), respectively.

Based on measured chemical concentrations, compiled species sensitivity distributions (SSD) and dilution factors, msPAF levels were computed for undiluted effluents at discharge points and diluted effluents downstream in receiving waters. A scheme was developed to assess the contribution of PREs to mixture pressure in the environment. Dissolved concentrations of Total Petroleum Hydrocarbons (TPH) in PREs were determined using the PetroTox model. SSDs for petrochemicals were compiled, and the target lipid model (TLM) was applied to compute toxicity values for TPH. Based on concentrations and SSDs, the msPAF levels were calculated for 79 PREs at discharge points and 49 PREs downstream (after dilution in the recipient using actual dilution factors). Computed msPAF levels were compared with the background msPAF levels in European waters to assess the PRE contribution. Computed msPAF levels were also compared with measured toxicity from available whole effluent toxicity tests to assess the level of conservatism of the method.

Average msPAF-chronic and msPAF-acute levels of PREs at discharge points were 69% (P50) and 40% (P95), respectively. Levels were reduced substantially <5% downstream, indicating low to negligible toxicity of PREs in receiving environments. 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 background levels, suggesting that PREs were minor contributors to the toxic pressure in the environment.

Our results provide effluent and substance rankings, helping identify hotspots and take effective targeted action to remediate potential risks. Uncertainties for further refinement and development of the method are explicitly discussed.

1. INTRODUCTION

Petroleum refinery effluents (PRE) are wastewaters originating 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 being operated (e.g. distillation, thermal cracking) (Cote, 1976, Wake, 2005). In Europe, Concawe have collected 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 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 EU 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.

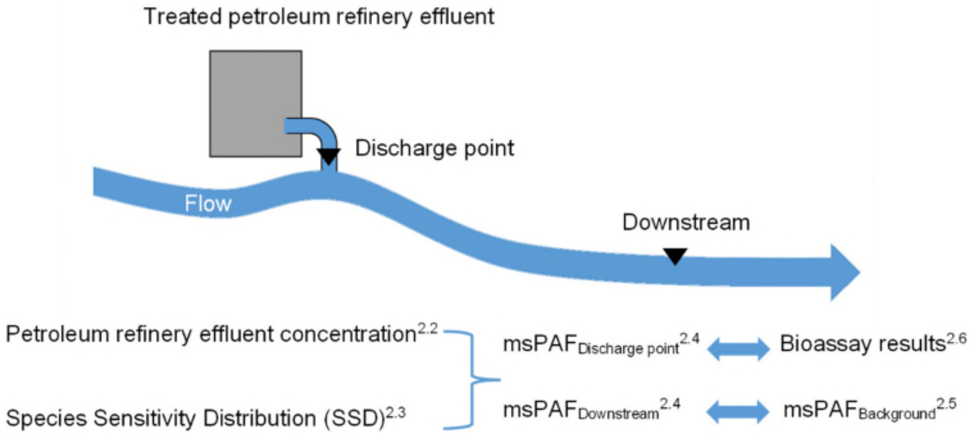
Traditionally, environmental effects of PREs have been assessed based on toxicity tests and field surveys (Concawe, 1979, Concawe, 1982), indicating that PREs have adverse impacts on aquatic organisms (Wake, 2005). However, the studies reviewed in Wake (2005) were mostly published before 2000, and the quality of PREs has significantly improved over the years (Hjort et al., 2021, Whale et al., 2022). Within EU, PREs are regulated through local discharge permits under the Industrial Emissions Directive (European Commission, 2010), receiving substantial treatment before emission takes place. Recent work, including whole effluent toxicity (WET) assessments, has shown that toxicity of 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 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).

Hence, the objective of the present study was to assess the contribution of treated refinery effluents to 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 **Figure 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, SSDs and dilution factors, chronic and acute msPAF levels were subsequently calculated for undiluted PREs at discharge points (msPAF_{DP}) and downstream after dilution by natural water flow (msPAF_{DS}) (Section 2.4). The computed 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 sensitivity of the method (Section 2.6).

Figure 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.



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. In line with Concawe's operating guidelines, PREs were coded and not represented by refinery names or locations. Effluent abbreviations, average discharge volumes and receiving environment descriptions are summarised in **Table A1** in the Supporting Information (Appendix).

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 of the PREs were taken from the Concawe survey data (2016 from Concawe (2016) and 2019 from unpublished data). 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 3**). Note that each effluent covers different measured parameters. In total, the 2016 and 2019 datasets consisted of 1,868 and 51,045 measurements, of which 394 and 8,319 were below the Limit of Quantification (LoQ), respectively.

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 shown **Table 1**.

Table 1. Empirical compositional fraction (± standard deviation) of individual constituents in BTEX and phenols

	Compositional fraction	Number of measurements
BTEX		
Benzene	0.19 (±0.08)	22
Toluene	0.26 (±0.11)	22
Ethylbenzene	0.16 (±0.09)	22
Xylenes	0.39 (±0.16)	22
Phenols[a]		
Phenol (C0-C3-alkyl-phenols)	0.88 (±0.10)	5
Butylphenol (C4-alkyl-phenols)	0.06 (±0.05)	5
Pentylphenol (C5-alkyl-phenols)	0.05 (±0.05)	5
Octylphenol (C6-C8-alkyl-phenols)	0.00 (±0.00)	5
Nonylphenol (C9-alkyl-phenols)	0.00 (±0.00)	5

[a] Concentrations for different phenol groups were only available for effluents from offshore oil extraction installations (i.e. without biological treatment). Concentrations after biological treatment were estimated based on computed biodegradation rate constants (Nolte et al., 2020), taking a hydraulic retention time of 8 hours and biomass of $10^{9\text{-}10}$ cells/L and assuming that variation in the concentration profiles between the effluents is sufficiently small as to not effectuate differing degrees in acclimation (i.e. a constant ‘active’ biomass).

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, Cdiss/Ctotal) at discharge points and downstream according to (Van der Kooij et al., 1991):

$$\frac{C_{diss}}{C_{total}} = \frac{1}{K_{pm/w} \cdot TSS \cdot 10^{-6} + 1} \tag{1}$$

where $K_{pm/w}$ 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 $K_{pm/w}$ were not available for PREs and all European waters, partitioning at both discharge points and downstream were assumed to be similar to levels in Dutch surface waters (values taken from Crommentuijn et al. (1997), **Table 2**). 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 2**.

Table 2. Ratios of dissolved and total concentrations of metals (C_{diss}/C_{total}) applied in this study

Metal	$\log K_{pm/w}$ (L/kg)[a]	C_{diss}/C_{total} at discharge point[b]	C_{diss}/C_{total} downstream[c]
Arsenic (As)	4.00	0.87	0.77
Cadmium (Cd)	5.11	0.34	0.21
Chromium (Cr)	5.46	0.19	0.10
Cobalt (Co)	3.59	0.94	0.90
Copper (Cu)	4.70	0.57	0.40
Lead (Pb)	5.81	0.09	0.05
Mercury (Hg)	5.23	0.28	0.16
Nickel (Ni)	3.90	0.89	0.81
Selenium (Se)	2.77	0.99	0.98
Vanadium (V)	3.74	0.92	0.86
Zinc (Zn)	5.04	0.38	0.23

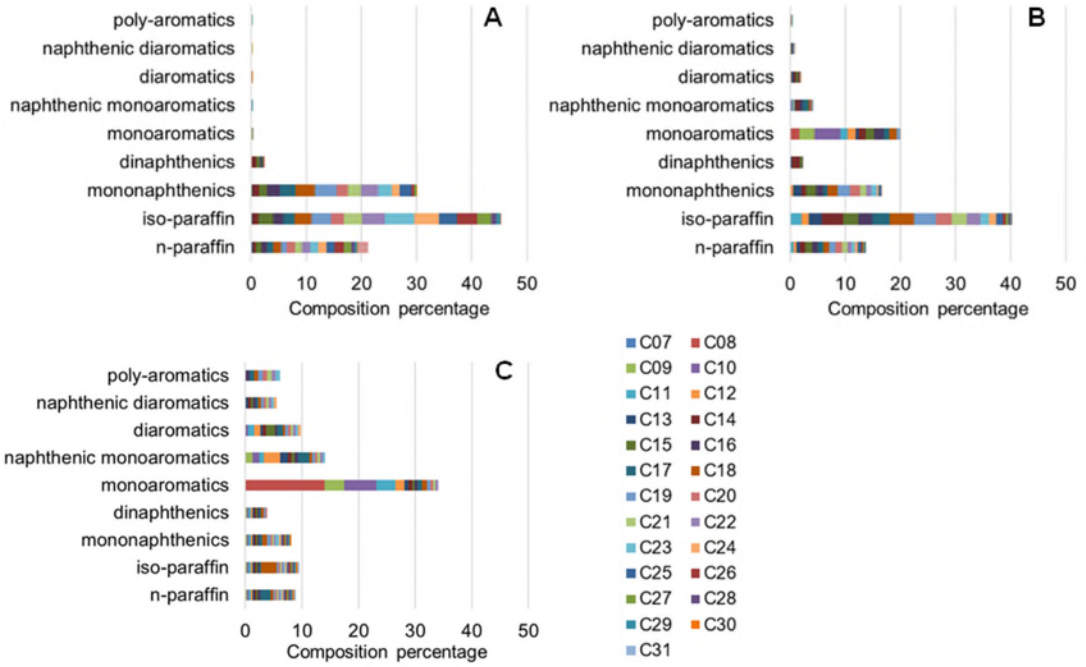
[a] Values taken from Crommentuijn et al. (1997).

[b] Calculated based on Eq. (1) with TSS equalling 15 mg/L as the average total suspended solid concentration of all effluents (Concawe, 2020a).

[c] Calculated based on Eq. (1) with TSS equalling 30 mg/L as the average total suspended solid concentration of receiving waters (Crommentuijn et al., 1997).

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. concentration of TPH 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 (**Figure 2**). The compositions were subsequently applied in PetroTox, assuming an experimental set-up with 10% headspace. Dissolved concentrations (mol/L) were computed for the 1,512 individual hydrocarbon constituents mapped to the hydrocarbon block format (Redman et al., 2012).

Figure 2. The least (A), average (B) and most (C) toxic relative composition of total petroleum hydrocarbon applied in the study, with each carbon number-chemical class combination. The carbon numbers per hydrocarbon group are indicated by C07, C08, etc.



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 (µg/L) were taken from the SSD database (Posthuma et al., 2019) (**Table 3**). The average SSD slope σ (µg/L) was adopted with a value of 0.7 for both acute and chronic endpoints (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 to compute acute and chronic median toxicity *HC50*-values (mmol/L) for hydrocarbon constituent *i*:

$$\log(HC50_{acute,i}) = E[\log(EC50_i)] = E[m] \cdot \log(\mathrm{K}_{OW,i}) + E[\log(\mathrm{C}_\mathrm{L}^*)] + \Delta \mathrm{c}_i \tag{2.1}$$

$$\log(HC50_{chronic,i}) = E[\log(NOEC_i)] = E[m] \cdot \log(\mathrm{K}_{OW,i}) + E[\log(\mathrm{C}_\mathrm{L}^*)] + \Delta \mathrm{c}_i - E[\log(\mathrm{ACR})] \tag{2.2}$$

where E[m] is the mean of universal narcosis slope (-0.940), $\mathrm{K}_{\mathrm{OW,i}}$ is the octanol-water partition coefficient for hydrocarbon i, $E[\log(\mathrm{C}_\mathrm{L}^*)]$ is the logarithmic mean of the critical target lipid body burden distribution (1.85 µmol/g octanol), $\Delta\mathrm{c}_\mathrm{i}$ 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 applies to hydrocarbons with log(K_{OW}) values up to 5.5 and 6 for acute and chronic toxicity, respectively (Redman et al., 2017). These upper limits were applied to hydrocarbons with log(K_{OW}) values higher than 5.5 and 6 in calculating acute and chronic toxicity, respectively, reducing the bioavailability of more hydrophobic components while allowing fractional contribution to the overall toxicity of the substance.

Table 3. Summary of SSD parameters for individual constituents in PREs applied in the msPAF calculations in the present study (values are log10-transformed)

	Acute μ (µg/L)	Chronic μ (µg/L)
Inorganics		
Ammonia	3.95	2.95
Sulphide	3.41	2.41
Metals		
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
Hydrocarbons		
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
Other organics		
Dichloromethane	5.40	4.40
Pentachlorobenzene	2.99	2.03
Phenols		
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)

2.4. 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 3). When calculating downstream concentrations, dilution factors (DF, unpublished data summarised in **Table A1**, available for 49 and 11 effluents in 2016 and 2019 datasets, respectively) 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 to freshwater and marine water, respectively, to assess the conservatism of the default values (**Table A1**). Bioavailability of metals and TPH downstream was corrected based on C_{DS}, following methods described in Section 2.2.2.

To allow 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), assuming that all chemicals act concentration additively (De Zwart and Posthuma, 2005):

$$HU = \sum(\frac{C_i}{10^{\mu_i}}) \tag{3.1}$$

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

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 3**), 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 of 1760 substances with high-quality SSD data (Posthuma et al., 2019). In the present study, these levels were considered as background levels, reflecting the mixture toxic pressure from other chemicals already present in receiving waters. In order to assess the contribution from PREs to mixture toxic pressure in the environment, we calculated the contribution ratio (logCR, 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:

$$logCR_i = \log_{10}(\frac{msPAF_{DS,i}}{msPAF_{Background,i}}) \tag{4}$$

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. Bioassays (toxicity tests) were performed on raw (unextracted) refinery effluent spot samples from three refineries (Whale et al., 2022) and were used in the present study. The bioassay data represented acute and chronic tests results for four different species (**Table 4**).

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 impacts estimated from chemical concentrations to the observed effects.

Table 4. Summary of bioassays (Whale et al., 2022) applied in the present study

Test species	Exposure duration	Endpoint	Classification
Bacteria (*Aliivibrio fischeri*)	Acute	EC_{50}	Acute EC_{50}
Algae (*Raphidocelis subcapitata*)	Chronic	EC_{10} growth	Chronic NOEC
Daphnids (*Daphnia magna*)	Chronic	LC_{50} mortality	Chronic EC_{50}
		EC_{10} reproduction	Chronic NOEC
Zebrafish embryos (*Danio rerio*)	Acute	EC_{50} malformation	Acute EC_{50}

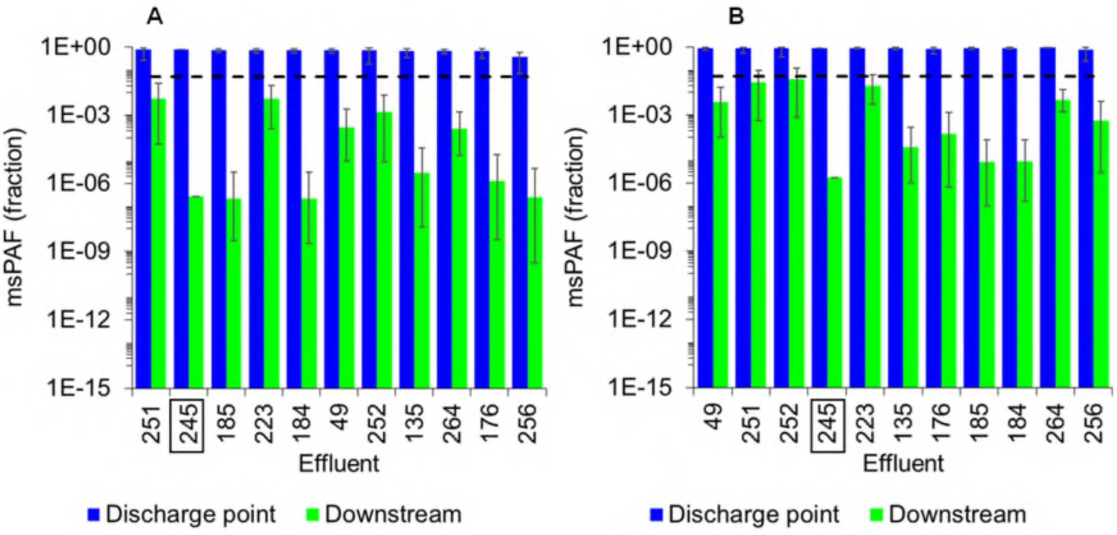
3. RESULTS AND DISCUSSION

3.1. MULTI-SUBSTANCE POTENTIALLY AFFECTED FRACTION

3.1.1. 2019 dataset

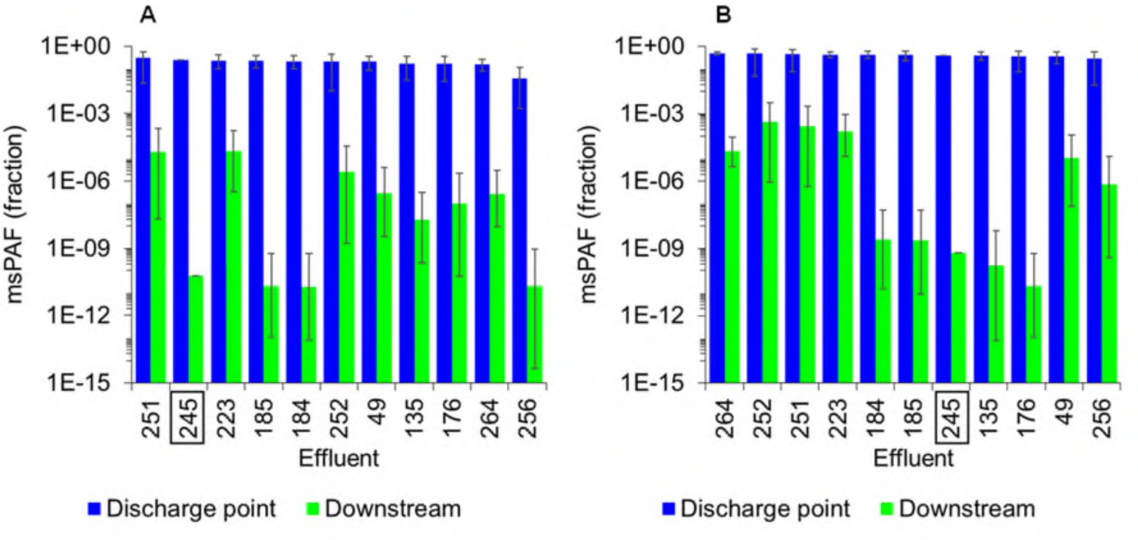
The chronic mixture toxic pressure (msPAF-chronic) of refinery effluents in the 2019 dataset is shown in **Figure 3**. Only effluents with actual dilution factors are discussed here (full results in **Table A2**). At discharge points, average msPAF-chronic levels were estimated to be 68.5% (±11.2%) and 85.9% (±3.8%), based on 50th (P50) and 95th percentile concentrations (P95), respectively. Average chronic pressure downstream decreased to 0.1% (±0.2%) and 0.9% (±1.3%), respectively (**Figure 3**).

Figure 3. The msPAF levels (fraction) at discharge points (blue) and downstream (green) for the chronic endpoint based on 50th (A) and 95th percentile concentrations (B) in the 2019 dataset. Bars show the range of msPAF levels based on the least and most toxic hydrocarbon block compositions (Figure 2). The black dashed line represents msPAF-chronic < 0.05, protecting 95% of the species against adverse effects. Total petroleum hydrocarbon concentrations were unavailable for effluents labelled with a box.



Average msPAF-acute levels at discharge points were estimated to be 19.7% (±6.8%) and 40.5% (±5.7%), based on P50 and P95 concentrations, respectively (**Figure 4**). Average acute pressure downstream was negligible, lower than 0.1%.

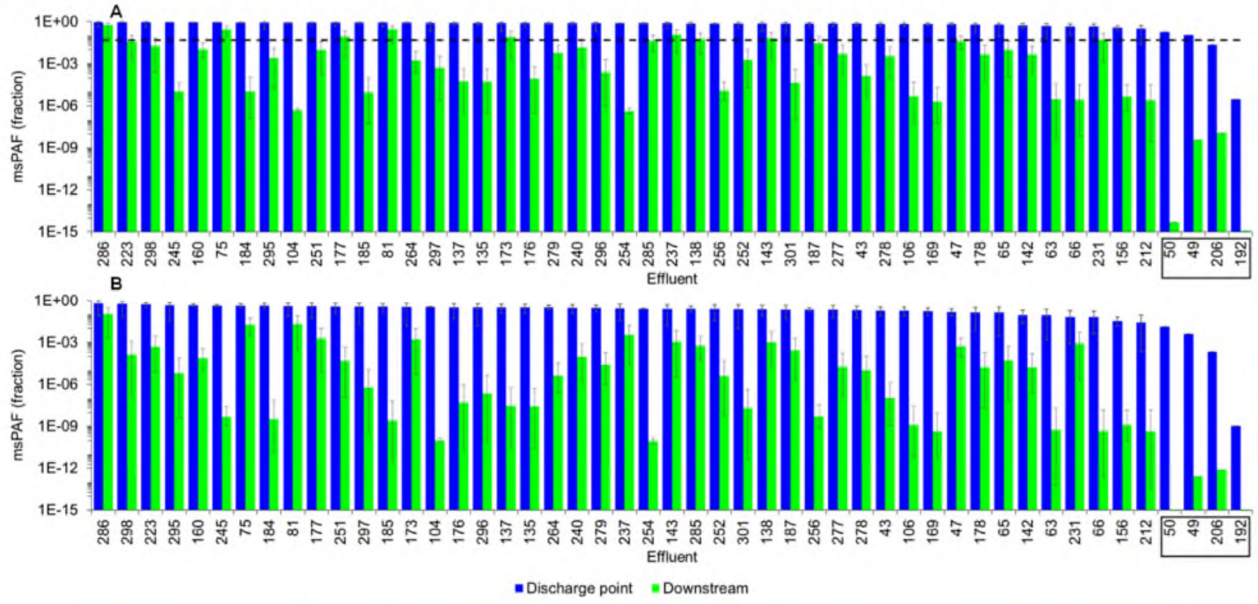
Figure 4. The msPAF levels (fraction) at discharge points (blue) and downstream (green) for the acute endpoint based on 50th (A) and 95th percentile concentration (B) in the 2019 dataset. Bars show the range of msPAF levels based on the least and most toxic hydrocarbon block compositions (Figure 2). Total petroleum hydrocarbon concentrations were unavailable for effluents labelled with a box.



3.1.2. 2016 dataset

Based on yearly average concentrations in 2016, average msPAF-chronic and msPAF-acute levels at discharge points were estimated to be 69.2% (±23.0%) and 26.2% (±15.7%), respectively (**Figure 5**). The pressure reduced to 3.8% (±9.8%) and 0.3% (±1.6%) downstream, respectively. When applying default dilution factors (DF), msPAF levels were on average three orders of magnitude higher than those with actual DFs (**Figure A1**, full results in **Table A3**).

Figure 5 The msPAF levels (fraction) at discharge points (blue) and downstream (green) for the chronic (A) and acute endpoint (B) based on the 2016 dataset. Bars show the range of msPAF values based on the least and most toxic hydrocarbon block compositions (Figure 2). The black dashed line represents msPAF-chronic < 0.05, protecting 95% of the species against adverse effects. Total petroleum hydrocarbon concentrations were unavailable for effluents labelled with a box



Based on both datasets, results showed that average msPAF-chronic and msPAF-acute levels of PREs at discharge points were approximately 69% (P50) and 40% (P95), respectively. Due to dilution, the mixture toxic pressure was 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 near the discharge, most effluents (82%) would not pose significant toxic pressure in the receiving environment with msPAF-chronic levels < 0.05. Nevertheless, additional analysis (e.g. bioavailability measurements such as BE-SPME in effluents and receiving waters, detailed chemistry for HCB compositions, targeted bioassays) should be done for the rest 18% of effluents with msPAF-chronic levels > 0.05.

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 the study from 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 dilution factors (DF, 10 and 100 for the freshwater and marine environment, respectively (ECHA, 2016)). While the default DF of 100 for marine areas seems adequate, DF of 10 for freshwater seems low when applied to large rivers and estuaries where most refineries are located (**Table A1**). For effluents discharging into freshwater, actual DFs were on average 650 times higher than default DFs (**Table A1**), resulting in msPAF levels several orders of magnitude lower (**Table A1**). Therefore, we recommend using effluent-specific DFs to improve the accuracy of risk estimates in the environment.

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 and 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 (**Figure 2**) based on spot samples. 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 (e.g. bars in **Figure** 5) may characterise the uncertainties due to unknown hydrocarbon compositions. The average toxic hydrocarbon block composition (**Figure 2B**) is close to the compositions based on measured median hydrocarbon block concentrations in 2008-2009 (Concawe, 2010) (**Figure A2**). 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). 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 was applied. 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 **Table A4**). 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 A4**).

Finally, we reviewed the treatment of measurements below Limit of Quantification (LoQ). With half of the LoQ of each chemical constituent as input concentrations, msPAF-chronic and msPAF-acute levels were 11% and 0.4%, respectively. Compared with the average msPAF levels at discharge points shown above (around 70% and 40%, respectively), the LoQ/2 data are considered non-significant contributors to the overall msPAF.

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) (**Figure A3**). The average contribution across effluents for different endpoints and locations was calculated (**Table 5**). 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 point (**Table 5**), with msPAF levels downstream closely related to the TPH concentrations downstream (i.e. TPH concentrations divided by DFs, **Figure A4**). 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 to algae, invertebrates and fish based on toxicity tests.

Table 5. Contribution of each chemical group to mixture toxic pressure (%)[a]

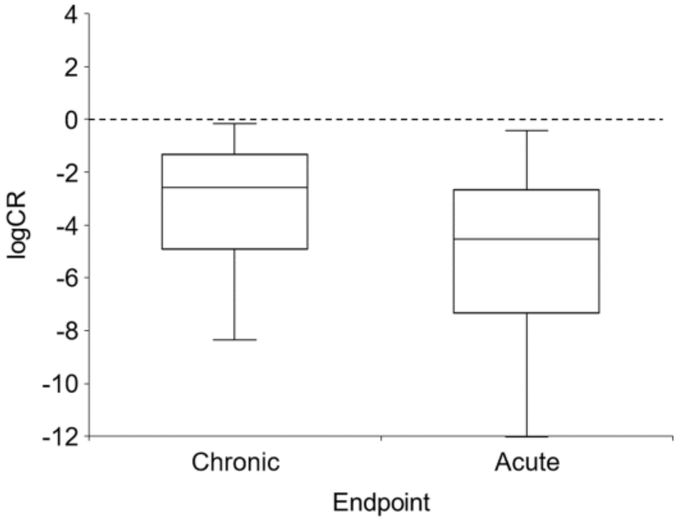
Endpoint	Location	Hydrocarbons[b]	Inorganics[c]	Metals[d]	Others[f]
Chronic	Discharge point	53.1 (±20.3)	32.3 (±20.8)	12.4 (±11.8)	2.2 (±5.5)
	Downstream	77.8 (±20.7)	16.4 (±18.6)	4.6 (±5.0)	1.2 (±3.5)
Acute	Discharge point	57.7 (±21.5)	30.6 (±20.8)	9.6 (±9.9)	2.1 (±5.4)
	Downstream	76.0 (±21.4)	18.4 (±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.

3.3. PETROLEUM REFINERY EFFLUENT CONTRIBUTION TO MIXTURE TOXIC PRESSURE IN THE ENVIRONMENT

In general, PREs were estimated to contribute less than the sum of other pollution sources, as all logCR values were below 0 (**Figure 6**). 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 **Table A5**). Of all effluents, effluent 286 had the highest logCR values of -0.15 (chronic) and -0.44 (acute), indicating that its msPAF levels downstream were 71% ($10^{-0.15}$) and 36% ($10^{-0.44}$) of msPAF$_{background}$ for chronic and acute endpoints, respectively. This is due to effluent's relatively high msPAF levels, ranking first among all effluents (**Figure 5**).

Figure 6. Refinery effluent contribution to mixture toxic pressure in the environment. logCR is the log10-transformed contribution ratio between msPAF levels of PREs downstream 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.



Our results suggested that refinery effluents are minor contributors to the toxic pressure in the environment. The chemical pollution 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 dilutions or was not observed in the 100% effluent (**Table 6**), 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 to be conservative compared to the observed toxicity (**Table 6**). On the basis of the expected dilution in the receiving environment, msPAF 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 6**).

Table 6. 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[a]	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)	0.08	>45	>100	>100	19.4	>100	0.059	0.087	33.1	6.8
C (16)	0.06	>45	>100	69.6	<10	>100	0.056	0.084	33.1	6.7
D (23)	0.22	>45	29	>100	>100	>100	0.049	0.067	28.5	5.1

[a] Final raw effluent code consistent 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 EC$_{10}$ 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.

3.5. IMPLICATION FOR REGULATORY RISK MANAGEMENT

Since the environment and humans are constantly exposed to multiple chemicals, the Mixture Assessment Factor (MAF) was proposed to be implemented under the EU regulation for the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), accounting for potential combined effects of chemicals after emissions (KEMI, 2015). 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 refinery effluents are minor contributors compared to other chemicals. This could better support science-based decisions on informing focused regulations for environmental risks from multiple chemicals by identifying chemical groups estimated to drive the toxic pressure in a given receiving water. Furthermore, it would be a better approach than the proposed use of a generic MAD, as it has been noted as 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 MAF to all substances is not scientifically justified and 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 as it is the result of the emissions occurred due to the processing of multiple substance types in refineries. REACH deals with the registration of single substances. In the present study, we 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. In general, while generally low, the calculated msPAFs were explained mostly by the aromatic constituents (C_{10}-C_{15}).

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 ambient msPAF estimated in the receiving waters (Posthuma et al., 2019) and were found to be approximately 2-4 orders of magnitude lower. This suggested that PREs were not major contributors to the toxic pressure in the environment. This methodology can identify the relative contributions of different chemical stressors and develop targeted regulatory and industrial activities to mitigate environmental risks.

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APPENDIX: SUPPORTING INFORMATION

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

Table A1. Description of petroleum refinery effluents investigated in this study

Effluent id	Discharge volume (m^3/y)[a]	Receiving environment type[b]	Receiving basin type	Year of data collection	Actual dilution Factor (n/a = not available)	Default dilution factor[c]
16	1.10E+06	marine	lagoon	2016	n/a	100
17	1.13E+07	freshwater	lagoon	2016	n/a	10
42	3.48E+06	marine	sea	2016	n/a	100
43	4.70E+06	freshwater	river	2016	2044	10
44	4.36E+06	freshwater	estuary	2016	n/a	10
47	1.82E+07	marine	estuary	2016	50	100
49	2.84E+06	freshwater	river	2016, 2019	1554	10
50	1.20E+05	freshwater	river	2016	44903	10
56	1.13E+06	marine	estuary	2016	n/a	100
58	7.24E+06	freshwater	canal	2016, 2019	n/a	10
59	5.60E+06	marine	estuary	2016	n/a	100
60	1.90E+06	marine	estuary	2016	n/a	100
63	1.38E+06	freshwater	river	2016	4570	10
65	2.34E+06	freshwater	river	2016	218	10
66	1.52E+06	freshwater	river	2016	3116	10
75	4.98E+06	freshwater	river	2016	40	10
76	4.55E+06	marine	sea	2016	n/a	100
77	3.57E+06	marine	sea	2016	n/a	100
81	6.04E+06	freshwater	river	2016	57	10
88	3.26E+04	freshwater	canal	2016	n/a	10
100	3.17E+06	marine	sea	2016	n/a	100
104	7.13E+05	freshwater	river	2016	14683	10
106	3.20E+06	freshwater	river	2016	6690	10
113	1.06E+06	freshwater	river	2016	n/a	10
124	1.29E+07	marine	sea	2016	n/a	100
127	2.22E+06	marine	sea	2016	n/a	100
135	1.77E+06	freshwater	estuary	2016, 2019	8870	10
137	1.25E+06	freshwater	estuary	2016	8870	10
138	2.38E+06	freshwater	canal	2016	101	10
141	8.44E+05	marine	sea	2016, 2019	n/a	100
142	8.31E+06	marine	estuary	2016	145	100
143	9.90E+06	marine	estuary	2016	145	100
146	1.40E+06	marine	sea	2016	n/a	100
153	1.24E+06	marine	sea	2016	n/a	100
154	4.23E+06	freshwater	river	2016	n/a	10
155	5.49E+06	marine	sea	2016	n/a	100
156	1.83E+06	freshwater	canal	2016	828	10

Effluent id	Discharge volume (m^3/y)[a]	Receiving environment type[b]	Receiving basin type	Year of data collection	Actual dilution Factor (n/a = not available)	Default dilution factor[c]
160	1.83E+06	freshwater	river	2016	648	10
164	2.90E+06	marine	sea	2016	n/a	100
169	1.60E+06	freshwater	river	2016	6690	10
171	2.26E+06	marine	sea	2016	n/a	100
173	3.38E+06	freshwater	canal	2016	267	10
175	5.09E+06	freshwater	canal	2016	n/a	10
176	2.77E+06	freshwater	river	2016, 2019	11519	10
177	6.53E+05	freshwater	river	2016	305	10
178	2.72E+06	marine	estuary	2016	338	100
184	5.65E+05	freshwater	river	2016, 2019	23553	10
185	9.88E+05	freshwater	river	2016, 2019	23553	10
187	3.08E+06	marine	sea	2016	200	100
192	3.32E+08	marine	sea	2016	200	100
201	4.20E+06	marine	sea	2016	n/a	100
202	1.15E+06	marine	sea	2016	n/a	100
205	8.96E+05	freshwater	river	2016, 2019	n/a	10
206	2.00E+07	marine	canal	2016	290	100
207	8.93E+06	marine	sea	2016	n/a	100
211	3.02E+06	marine	estuary	2016	n/a	100
212	2.43E+05	freshwater	canal	2016	1429	10
223	9.97E+06	marine	estuary	2016, 2019	448	100
231	9.72E+04	marine	canal	2016	24	100
237	7.52E+06	marine	canal	2016	86	100
240	3.17E+06	freshwater	estuary	2016	954	10
245	5.08E+06	marine	estuary	2016, 2019	10001	100
248	2.31E+06	freshwater	canal	2016	n/a	10
251	9.92E+06	marine	estuary	2016, 2019	1413	100
252	2.65E+06	marine	estuary	2016, 2019	1413	100
254	1.50E+07	freshwater	river	2016	10487	10
256	6.01E+06	freshwater	river	2016, 2019	3837	10
262	1.81E+06	marine	sea	2016	n/a	100
264	2.40E+06	freshwater	river	2016, 2019	973	10
277	1.70E+06	freshwater	river	2016	562	10
278	4.05E+07	freshwater	river	2016	562	10
279	1.05E+07	freshwater	river	2016	562	10
285	1.55E+06	marine	sea	2016	100	100
286	3.17E+04	marine	sea	2016	100	100
295	3.64E+03	freshwater	river	2016	8167	10
296	1.53E+06	freshwater	river	2016	8167	10
297	2.33E+05	freshwater	river	2016	8167	10
298	2.51E+05	freshwater	river	2016	8167	10
301	8.76E+06	freshwater	river	2016	8273	10

[a] Average discharge volume measured in 2016. [b] Differentiation between freshwater and marine is based on the IPIECA definition/limit of 2000 mg/L total dissolved solids (IPIECA, 2014). [c] Based on ECHA (2016).

Table A2. Summary of msPAF results for the 2019 dataset (NA = not available)

Endpoint	Percentile	Effluent	msPAF$_{\text{discharge point}}$ (fraction)	msPAF$_{\text{downstream}}$_actual dilution factor (fraction)	msPAF$_{\text{downstream}}$_default dilution factor (fraction)
Chronic	P50	49	7.18E-01	2.82E-04	3.13E-01
Chronic	P50	58	6.73E-01	NA	2.73E-01
Chronic	P50	135	6.64E-01	2.81E-06	2.67E-01
Chronic	P50	141	6.90E-01	NA	4.09E-02
Chronic	P50	176	6.57E-01	1.23E-06	2.61E-01
Chronic	P50	184	7.31E-01	2.02E-07	3.05E-01
Chronic	P50	185	7.41E-01	2.16E-07	3.12E-01
Chronic	P50	205	5.95E-01	NA	2.19E-01
Chronic	P50	223	7.35E-01	5.23E-03	4.52E-02
Chronic	P50	245*	7.76E-01	2.59E-07	1.53E-02
Chronic	P50	251	7.81E-01	5.36E-03	1.55E-01
Chronic	P50	252	7.06E-01	1.37E-03	6.94E-02
Chronic	P50	256	3.73E-01	2.38E-07	6.87E-02
Chronic	P50	264	6.58E-01	2.46E-04	2.10E-01
Chronic	P95	49	8.45E-01	3.63E-03	5.12E-01
Chronic	P95	58	8.03E-01	NA	4.91E-01
Chronic	P95	135	8.56E-01	3.87E-05	4.66E-01
Chronic	P95	141	8.77E-01	NA	1.52E-01
Chronic	P95	176	8.27E-01	1.45E-04	5.45E-01
Chronic	P95	184	8.82E-01	8.67E-06	5.41E-01
Chronic	P95	185	8.67E-01	8.15E-06	5.27E-01
Chronic	P95	205	8.28E-01	NA	5.61E-01
Chronic	P95	223	8.82E-01	1.92E-02	1.13E-01
Chronic	P95	245*	8.73E-01	1.74E-06	3.73E-02
Chronic	P95	251	8.70E-01	2.85E-02	3.28E-01
Chronic	P95	252	8.69E-01	3.79E-02	3.33E-01
Chronic	P95	256	7.65E-01	5.79E-04	4.62E-01
Chronic	P95	264	9.13E-01	4.65E-03	5.28E-01
Acute	P50	49	2.03E-01	2.92E-07	2.45E-02
Acute	P50	58	1.71E-01	NA	1.78E-02
Acute	P50	135	1.65E-01	2.00E-08	1.70E-02
Acute	P50	141	1.87E-01	NA	5.14E-04
Acute	P50	176	1.62E-01	1.03E-07	1.63E-02
Acute	P50	184	2.16E-01	1.87E-11	2.31E-02
Acute	P50	185	2.23E-01	2.05E-11	2.42E-02
Acute	P50	205	1.23E-01	NA	1.12E-02
Acute	P50	223	2.29E-01	2.06E-05	6.42E-04
Acute	P50	245*	2.52E-01	5.65E-11	1.65E-04
Acute	P50	251	3.07E-01	1.94E-05	5.81E-03
Acute	P50	252	2.16E-01	2.52E-06	1.26E-03
Acute	P50	256	3.73E-02	2.07E-11	1.27E-03
Acute	P50	264	1.56E-01	2.68E-07	1.10E-02

Endpoint	Percentile	Effluent	$\text{msPAF}_{\text{discharge point}}$ (fraction)	$\text{msPAF}_{\text{downstream_}}$actual dilution factor (fraction)	$\text{msPAF}_{\text{downstream_}}$default dilution factor (fraction)
Acute	P95	49	3.65E-01	1.11E-05	7.86E-02
Acute	P95	58	3.21E-01	NA	7.21E-02
Acute	P95	135	3.80E-01	1.74E-10	6.26E-02
Acute	P95	141	4.24E-01	NA	5.58E-03
Acute	P95	176	3.66E-01	2.05E-11	9.65E-02
Acute	P95	184	4.27E-01	2.56E-09	9.06E-02
Acute	P95	185	4.01E-01	2.28E-09	8.45E-02
Acute	P95	205	3.70E-01	NA	1.05E-01
Acute	P95	223	4.29E-01	1.67E-04	3.35E-03
Acute	P95	245*	3.87E-01	6.47E-10	6.62E-04
Acute	P95	251	4.55E-01	2.74E-04	2.73E-02
Acute	P95	252	4.72E-01	4.41E-04	2.80E-02
Acute	P95	256	2.87E-01	7.32E-07	6.26E-02
Acute	P95	264	4.86E-01	2.12E-05	8.50E-02

*Total petroleum hydrocarbon concentrations were unavailable.

Table A3. Summary of msPAF results for the 2016 dataset (NA = not available)

Endpoint	Effluent	$\text{msPAF}_{\text{discharge point}}$ (fraction)	$\text{msPAF}_{\text{downstream_}}$actual dilution factor (fraction)	$\text{msPAF}_{\text{downstream_}}$default dilution factor (fraction)
Chronic	16	7.52E-01	NA	8.70E-02
Chronic	17	8.79E-01	NA	5.00E-01
Chronic	42	8.56E-01	NA	1.86E-01
Chronic	43	7.13E-01	1.38E-04	2.97E-01
Chronic	44	9.20E-01	NA	6.52E-01
Chronic	47	6.60E-01	3.96E-02	1.52E-02
Chronic	49*	1.16E-01	3.74E-09	1.17E-02
Chronic	50*	1.85E-01	4.91E-15	5.80E-03
Chronic	56	7.64E-01	NA	7.41E-02
Chronic	58	7.62E-01	NA	3.41E-01
Chronic	59	4.19E-01	NA	3.05E-03
Chronic	60	4.34E-01	NA	3.16E-03
Chronic	63	5.24E-01	2.93E-06	1.66E-01
Chronic	65	6.11E-01	1.02E-02	2.49E-01
Chronic	66	4.72E-01	2.61E-06	1.40E-01
Chronic	75	8.92E-01	2.76E-01	5.43E-01
Chronic	76	9.28E-01	NA	1.77E-01
Chronic	77	9.90E-01	NA	5.06E-01
Chronic	81	8.38E-01	2.97E-01	5.83E-01
Chronic	88	8.50E-01	NA	4.39E-01
Chronic	100	9.57E-01	NA	4.33E-01
Chronic	104	8.61E-01	4.74E-07	3.51E-01
Chronic	106	6.92E-01	4.85E-06	2.64E-01
Chronic	113	9.60E-01	NA	6.72E-01

Endpoint	Effluent	msPAF$_{\text{discharge point}}$ (fraction)	msPAF$_{\text{downstream}}$_actual dilution factor (fraction)	msPAF$_{\text{downstream}}$_default dilution factor (fraction)
Chronic	124	8.31E-01	NA	1.59E-01
Chronic	127	9.23E-01	NA	2.04E-01
Chronic	135	8.07E-01	5.16E-05	4.50E-01
Chronic	137	8.13E-01	5.62E-05	4.55E-01
Chronic	138	7.62E-01	6.28E-02	3.68E-01
Chronic	141	7.83E-01	NA	7.66E-02
Chronic	142	5.33E-01	4.59E-03	8.69E-03
Chronic	143	7.40E-01	6.59E-02	9.53E-02
Chronic	146	5.83E-01	NA	2.01E-02
Chronic	153	7.50E-01	NA	7.51E-02
Chronic	154	6.49E-01	NA	2.94E-01
Chronic	155	6.12E-01	NA	1.60E-02
Chronic	156	3.65E-01	4.71E-06	4.19E-02
Chronic	160	9.02E-01	1.10E-02	5.29E-01
Chronic	164	6.99E-01	NA	3.45E-02
Chronic	169	6.77E-01	2.01E-06	2.25E-01
Chronic	171	8.07E-01	NA	1.91E-01
Chronic	173	8.05E-01	8.18E-02	5.49E-01
Chronic	175	7.80E-01	NA	4.42E-01
Chronic	176	8.03E-01	8.43E-05	5.12E-01
Chronic	177	8.43E-01	8.80E-02	5.86E-01
Chronic	178	6.21E-01	4.81E-03	2.94E-02
Chronic	184	8.75E-01	1.08E-05	5.47E-01
Chronic	185	8.39E-01	9.16E-06	5.20E-01
Chronic	187	7.31E-01	2.81E-02	6.67E-02
Chronic	192*	2.81E-06	1.21E-15	3.50E-14
Chronic	201	9.18E-01	NA	2.61E-01
Chronic	202	8.78E-01	NA	2.94E-01
Chronic	205	7.85E-01	NA	5.02E-01
Chronic	206*	2.21E-02	1.15E-08	4.17E-07
Chronic	207*	5.99E-01	NA	3.82E-03
Chronic	211	9.34E-01	NA	3.14E-01
Chronic	212	3.24E-01	2.46E-06	5.32E-02
Chronic	223	9.23E-01	3.90E-02	6.79E-01
Chronic	231	4.71E-01	5.42E-02	7.99E-03
Chronic	237	7.70E-01	1.23E-01	1.14E-01
Chronic	240	7.96E-01	1.41E-02	8.88E-02
Chronic	245	9.03E-01	1.07E-05	7.71E-02
Chronic	248	6.43E-01	NA	2.14E-01
Chronic	251	8.46E-01	9.75E-03	1.91E-01
Chronic	252	7.49E-01	1.88E-03	8.38E-02
Chronic	254	7.87E-01	3.92E-07	2.77E-01
Chronic	256	7.53E-01	1.17E-05	2.65E-01
Chronic	262	8.36E-01	NA	2.24E-01

Endpoint	Effluent	msPAF$_{\text{discharge point}}$ (fraction)	msPAF$_{\text{downstream}}$_actual dilution factor (fraction)	msPAF$_{\text{downstream}}$_default dilution factor (fraction)
Chronic	264	8.34E-01	1.82E-03	3.98E-01
Chronic	277	7.30E-01	5.01E-03	3.87E-01
Chronic	278	7.09E-01	3.48E-03	5.94E-01
Chronic	279	7.99E-01	5.90E-03	3.90E-01
Chronic	285	7.73E-01	4.16E-02	4.16E-02
Chronic	286	9.25E-01	5.68E-01	5.68E-01
Chronic	295	8.63E-01	2.54E-03	6.75E-01
Chronic	296	7.91E-01	2.46E-04	5.19E-01
Chronic	297	8.15E-01	5.10E-04	5.69E-01
Chronic	298	9.16E-01	1.85E-02	7.96E-01
Chronic	301	7.32E-01	4.42E-05	4.11E-01
Acute	16	2.58E-01	NA	1.90E-03
Acute	17	3.91E-01	NA	9.12E-02
Acute	42	4.04E-01	NA	8.12E-03
Acute	43	1.93E-01	1.06E-07	2.18E-02
Acute	44	5.27E-01	NA	1.56E-01
Acute	47	1.51E-01	5.38E-04	1.15E-04
Acute	49*	4.15E-03	2.55E-13	1.10E-04
Acute	50*	1.32E-02	5.91E-20	5.83E-05
Acute	56	2.63E-01	NA	1.46E-03
Acute	58	2.28E-01	NA	2.77E-02
Acute	59	4.48E-02	NA	8.11E-06
Acute	60	5.04E-02	NA	9.09E-06
Acute	63	8.76E-02	5.25E-10	6.37E-03
Acute	65	1.37E-01	5.24E-05	1.47E-02
Acute	66	6.53E-02	4.68E-10	4.84E-03
Acute	75	4.44E-01	1.87E-02	9.10E-02
Acute	76	5.23E-01	NA	7.67E-03
Acute	77	8.26E-01	NA	7.61E-02
Acute	81	3.93E-01	2.17E-02	1.17E-01
Acute	88	3.52E-01	NA	5.23E-02
Acute	100	6.62E-01	NA	5.21E-02
Acute	104	3.46E-01	9.42E-11	3.21E-02
Acute	106	1.86E-01	1.20E-09	1.71E-02
Acute	113	6.34E-01	NA	1.61E-01
Acute	124	3.63E-01	NA	5.93E-03
Acute	127	5.22E-01	NA	1.01E-02
Acute	135	3.18E-01	2.60E-08	5.74E-02
Acute	137	3.27E-01	2.93E-08	5.94E-02
Acute	138	2.45E-01	1.06E-03	3.41E-02
Acute	141	2.79E-01	NA	1.55E-03
Acute	142	8.92E-02	1.67E-05	4.93E-05
Acute	143	2.54E-01	1.15E-03	2.23E-03
Acute	146	1.17E-01	NA	1.57E-04

Endpoint	Effluent	$\text{msPAF}_{\text{discharge point}}$ (fraction)	$\text{msPAF}_{\text{downstream\_actual dilution factor}}$ (fraction)	$\text{msPAF}_{\text{downstream\_default dilution factor}}$ (fraction)
Acute	153	2.44E-01	NA	1.44E-03
Acute	154	1.65E-01	NA	2.11E-02
Acute	155	1.23E-01	NA	1.13E-04
Acute	156	3.27E-02	1.27E-09	5.85E-04
Acute	160	4.58E-01	7.17E-05	8.43E-02
Acute	164	1.91E-01	NA	4.00E-04
Acute	169	1.71E-01	4.10E-10	1.25E-02
Acute	171	3.54E-01	NA	8.49E-03
Acute	173	3.50E-01	1.69E-03	9.99E-02
Acute	175	2.84E-01	NA	5.46E-02
Acute	176	3.31E-01	4.87E-08	8.14E-02
Acute	177	3.90E-01	1.91E-03	1.18E-01
Acute	178	1.40E-01	1.64E-05	2.88E-04
Acute	184	4.22E-01	3.36E-09	9.44E-02
Acute	185	3.67E-01	2.56E-09	8.32E-02
Acute	187	2.28E-01	2.71E-04	1.21E-03
Acute	192[*]	1.08E-09	4.14E-21	2.21E-19
Acute	201	5.24E-01	NA	1.63E-02
Acute	202	4.62E-01	NA	2.10E-02
Acute	205	3.16E-01	NA	7.77E-02
Acute	206[*]	2.21E-04	8.00E-13	7.52E-11
Acute	207[*]	1.06E-01	NA	1.70E-05
Acute	211	5.76E-01	NA	2.46E-02
Acute	212	2.63E-02	4.16E-10	7.89E-04
Acute	223	5.44E-01	4.81E-04	1.79E-01
Acute	231	6.56E-02	8.14E-04	3.57E-05
Acute	237	2.80E-01	3.57E-03	3.18E-03
Acute	240	3.00E-01	9.28E-05	2.03E-03
Acute	245	4.50E-01	4.90E-09	1.87E-03
Acute	248	1.46E-01	NA	1.11E-02
Acute	251	3.84E-01	4.86E-05	8.48E-03
Acute	252	2.49E-01	4.00E-06	1.76E-03
Acute	254	2.60E-01	8.73E-11	2.13E-02
Acute	256	2.26E-01	5.17E-09	1.80E-02
Acute	262	3.94E-01	NA	1.17E-02
Acute	264	3.14E-01	4.33E-06	4.07E-02
Acute	277	2.25E-01	1.83E-05	4.03E-02
Acute	278	2.03E-01	1.07E-05	1.19E-01
Acute	279	2.92E-01	2.53E-05	4.03E-02
Acute	285	2.52E-01	5.65E-04	5.65E-04
Acute	286	6.23E-01	1.10E-01	1.10E-01
Acute	295	4.64E-01	6.25E-06	1.87E-01
Acute	296	3.27E-01	2.16E-07	8.53E-02
Acute	297	3.68E-01	6.07E-07	1.11E-01

Endpoint	Effluent	msPAF$_{\text{discharge point}}$ (fraction)	msPAF$_{\text{downstream\_actual}}$ dilution factor (fraction)	msPAF$_{\text{downstream\_default}}$ dilution factor (fraction)
Acute	298	5.98E-01	1.35E-04	3.34E-01
Acute	301	2.46E-01	2.04E-08	4.63E-02

*Total petroleum hydrocarbon concentrations were unavailable.

Table A4. Summary of SSD parameters for individual constituents in PREs applied in the complex approach[a] (values of µ and σ are log10-transformed)

	Typical concentrations (µg/L)	Acute		Chronic		TMoA
		µ (µg/L)	σ (µg/L)	µ(µg/L)	σ (µg/L)	
Inorganics						
Ammonia	2000.00	3.95	1.04	2.95	1.04	Ammonia
Sulphide	0.00	3.41	0.62	2.41	0.62	Sulphide
Metals						
Arsenic	0.00	3.39	0.86	2.39	0.86	Arsenic
Cadmium	1.02	2.91	1.13	1.69	1.02	Cadmium
Chromium	0.00	3.89	1.09	2.89	1.10	Chromium
Cobalt	0.00	3.62	1.13	1.74	1.17	Cobalt
Copper	0.00	2.26	0.70	1.34	0.45	Copper
Lead	0.56	3.55	0.78	2.55	0.78	Lead
Mercury	1.13	2.26	0.98	1.26	0.98	Mercury
Nickel	10.72	3.38	1.17	2.38	1.17	Nickel
Selenium	0.00	3.84	0.60	2.84	0.60	Selenium
Vanadium	46.19	3.27	0.75	2.27	0.75	Vanadium
Zinc	0.00	3.22	0.78	1.92	0.68	Zinc
Hydrocarbons						
Anthracene	-	1.27	0.69[b]	0.27	0.70[b]	Non-polar narcosis
Benzene	3.80	4.88	0.69[b]	4.01	0.70[b]	Non-polar narcosis
Benzo(a)pyrene	-	1.48	0.69[b]	0.52	0.70[b]	Non-polar narcosis
Benzo(b)fluoranthene	-	0.57	0.69[b]	-0.13	0.70[b]	Non-polar narcosis
Benzo(g,h,i)perylene	-	-0.33	0.69[b]	-1.32	0.70[b]	Non-polar narcosis
Benzo(k)fluoranthene	-	0.97	0.69[b]	-0.13	0.70[b]	Non-polar narcosis
Ethylbenzene	-	4.24	0.69[b]	3.23	0.70[b]	Non-polar narcosis
Fluoranthene	-	2.13	0.69[b]	1.48	0.70[b]	Non-polar narcosis
Indeno(1,2,3-cd)pyrene	-	1.08	0.69[b]	0.08	0.70[b]	Non-polar narcosis
Naphthalene	-	3.62	0.69[b]	3.17	0.70[b]	Non-polar narcosis
Toluene	5.28	4.65	0.69[b]	3.35	0.70[b]	Non-polar narcosis
Total Petroleum Hydrocarbons (TPH)	1400.00	Eq. (2.1)	0.69[b]	Eq. (2.2)	0.70[b]	Non-polar narcosis
Xylenes	7.73	4.00	0.69[b]	3.04	0.70[b]	Non-polar narcosis
Other organics	0.00					
Dichloromethane	0.00	5.40	0.69[b]	4.40	0.70[b]	Non-polar narcosis
Pentachlorobenzene		2.99	0.69[b]	2.03	0.70[b]	Non-polar narcosis
Phenols						

	Typical concentrations (μg/L)	Acute		Chronic		TMoA
		μ (μg/L)	σ (μg/L)	μ(μg/L)	σ (μg/L)	
Phenol (C0-C3 alkylphenols)	70.35	4.31[c]	0.80[d]	3.24[c]	0.84[d]	Polar narcosis
Butylphenol (C4 alkylphenols)	5.12	3.65[e]	0.80[d]	2.65[e]	0.84[d]	Polar narcosis
Pentylphenol (C5 alkylphenols)	4.22	3.42[f]	0.80[d]	2.38[f]	0.84[d]	Polar narcosis
Octylphenol (C6-C8 alkylphenols)	0.30	2.47[g]	0.80[d]	1.68[g]	0.84[d]	Polar narcosis
Nonylphenol (C9 alkylphenols)	0.01	2.40[h]	0.80[d]	1.67[h]	0.84[d]	Polar narcosis

[a] The msPAF was first calculated for each chemical group j with similar TMoA, using concentration addition method as an approximation of effects assuming log-normal distributions (De Zwart and Posthuma, 2005): $msPAF_j = NORMDIST(\log_{10}(\sum(\frac{C_i}{10^{\mu_i}}), 0, \sigma_j, 1)$. The response addition method was then applied to predict the mixture toxicity across the groups of chemicals (De Zwart and Posthuma, 2005): $msPAF_{overall} = 1 - \prod_{j=1}^{15}(1 - msPAF_j)$. Individual hydrocarbons of anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, ethylbenzene, fluoranthene, indeno(1,2,3-cd)pyrene and naphthalene were not included in the calculation.

[b] The average values of all chemicals whose toxic mode of action was via non-polar narcosis in Posthuma et al. (2019).

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

[d] The average values of all chemicals whose toxic mode of action was via polar narcosis in Posthuma et al. (2019).

[e] The average values of 4-tert-butylphenol and 2-tert-butylphenol in Posthuma et al. (2019).

[f] The values of 4-tert-pentylphenol in Posthuma et al. (2019).

[g] The average values of 4-tert-octylphenol and 4-hexylphenol in Posthuma et al. (2019).

[h] The values of 4-(7-methyloctyl)phenol in Posthuma et al. (2019).

Table A5. Summary of petroleum refinery effluent contribution to mixture toxic pressure in the environment

Effluent	msPAF-chronic$_{PRE}$	msPAF-chronic$_{env}$	logCR	msPAF-acute$_{PRE}$	msPAF-acute$_{env}$	logCR
286	5.68E-01	8.12E-01	-0.15	1.10E-01	3.02E-01	-0.44
81	2.97E-01	8.13E-01	-0.44	2.17E-02	2.45E-01	-1.05
75	2.76E-01	7.64E-01	-0.44	1.87E-02	1.75E-01	-0.97
138	6.28E-02	2.84E-01	-0.65	1.06E-03	1.49E-02	-1.15
177	8.80E-02	6.06E-01	-0.84	1.91E-03	8.43E-02	-1.64
237	1.23E-01	8.59E-01	-0.84	3.57E-03	3.11E-01	-1.94
143	6.59E-02	5.85E-01	-0.95	1.15E-03	6.59E-02	-1.76
173	8.18E-02	8.17E-01	-1.00	1.69E-03	2.26E-01	-2.13
231	5.42E-02	5.85E-01	-1.03	8.14E-04	6.59E-02	-1.91
187	2.81E-02	3.09E-01	-1.04	2.71E-04	1.65E-02	-1.79
47	3.96E-02	4.92E-01	-1.09	5.38E-04	1.56E-01	-2.46
285	4.16E-02	8.12E-01	-1.29	5.65E-04	3.02E-01	-2.73
223	3.90E-02	8.59E-01	-1.34	4.81E-04	2.74E-01	-2.76
298	1.85E-02	4.67E-01	-1.40	1.35E-04	5.39E-02	-2.60
65	1.02E-02	4.90E-01	-1.68	5.24E-05	4.11E-02	-2.89
240	1.41E-02	8.03E-01	-1.75	9.28E-05	1.99E-01	-3.33
160	1.10E-02	7.54E-01	-1.84	7.17E-05	1.52E-01	-3.33
279	5.90E-03	4.33E-01	-1.87	2.53E-05	2.92E-02	-3.06
251	9.75E-03	7.76E-01	-1.90	4.86E-05	1.67E-01	-3.54

Effluent	msPAF-chronic$_{PRE}$	msPAF-chronic$_{env}$	logCR	msPAF-acute$_{PRE}$	msPAF-acute$_{env}$	logCR
277	5.01E-03	4.32E-01	-1.94	1.83E-05	2.90E-02	-3.20
142	4.59E-03	5.85E-01	-2.11	1.67E-05	6.59E-02	-3.60
295	2.54E-03	4.67E-01	-2.27	6.25E-06	5.39E-02	-3.94
178	4.81E-03	9.62E-01	-2.30	1.64E-05	5.71E-01	-4.54
278	3.48E-03	8.40E-01	-2.38	1.07E-05	2.67E-01	-4.40
264	1.82E-03	7.09E-01	-2.59	4.33E-06	1.22E-01	-4.45
252	1.88E-03	7.75E-01	-2.62	4.00E-06	1.66E-01	-4.62
297	5.10E-04	4.67E-01	-2.96	6.07E-07	5.39E-02	-4.95
296	2.46E-04	4.67E-01	-3.28	2.16E-07	5.39E-02	-5.40
43	1.38E-04	4.33E-01	-3.50	1.06E-07	2.95E-02	-5.45
176	8.43E-05	3.66E-01	-3.64	4.87E-08	2.02E-02	-5.62
137	5.62E-05	4.44E-01	-3.90	2.93E-08	3.02E-02	-6.01
135	5.16E-05	4.44E-01	-3.93	2.60E-08	3.02E-02	-6.06
301	4.42E-05	4.21E-01	-3.98	2.04E-08	2.75E-02	-6.13
256	1.17E-05	5.29E-01	-4.65	5.17E-09	5.04E-02	-6.99
184	1.08E-05	4.90E-01	-4.66	3.36E-09	3.93E-02	-7.07
245	1.07E-05	5.85E-01	-4.74	4.90E-09	6.59E-02	-7.13
106	4.85E-06	3.81E-01	-4.89	1.20E-09	2.32E-02	-7.29
156	4.71E-06	4.27E-01	-4.96	1.27E-09	3.14E-02	-7.39
185	9.16E-06	9.76E-01	-5.03	2.56E-09	5.93E-01	-8.36
63	2.93E-06	4.88E-01	-5.22	5.25E-10	4.05E-02	-7.89
66	2.61E-06	4.58E-01	-5.24	4.68E-10	3.52E-02	-7.88
169	2.01E-06	3.81E-01	-5.28	4.10E-10	2.32E-02	-7.75
212	2.46E-06	6.22E-01	-5.40	4.16E-10	9.09E-02	-8.34
104	4.74E-07	4.94E-01	-6.02	9.42E-11	4.20E-02	-8.65
254	3.92E-07	5.29E-01	-6.13	8.73E-11	5.04E-02	-8.76
206*	1.15E-08	8.59E-01	-7.87	8.00E-13	2.74E-01	-11.53
49*	3.74E-09	8.59E-01	-8.36	2.55E-13	2.74E-01	-12.03
50*	4.91E-15	4.92E-01	-14.00	5.91E-20	1.56E-01	-18.42
192*	1.21E-15	3.09E-01	-14.41	4.14E-21	1.65E-02	-18.60

*Total petroleum hydrocarbon concentrations were unavailable.

Figure A1. The msPAF levels (fraction) downstream based on actual (green) and default dilution factors (yellow) for the chronic (A) and acute endpoint (B) based on the 2016 dataset. Bars show the range of msPAF values based on the least and most toxic hydrocarbon block compositions (Figure 2). The black dashed line represents msPAF-chronic < 0.05, protecting 95% of the species against adverse effects. Total petroleum hydrocarbon concentrations were unavailable for effluents labelled with a box.

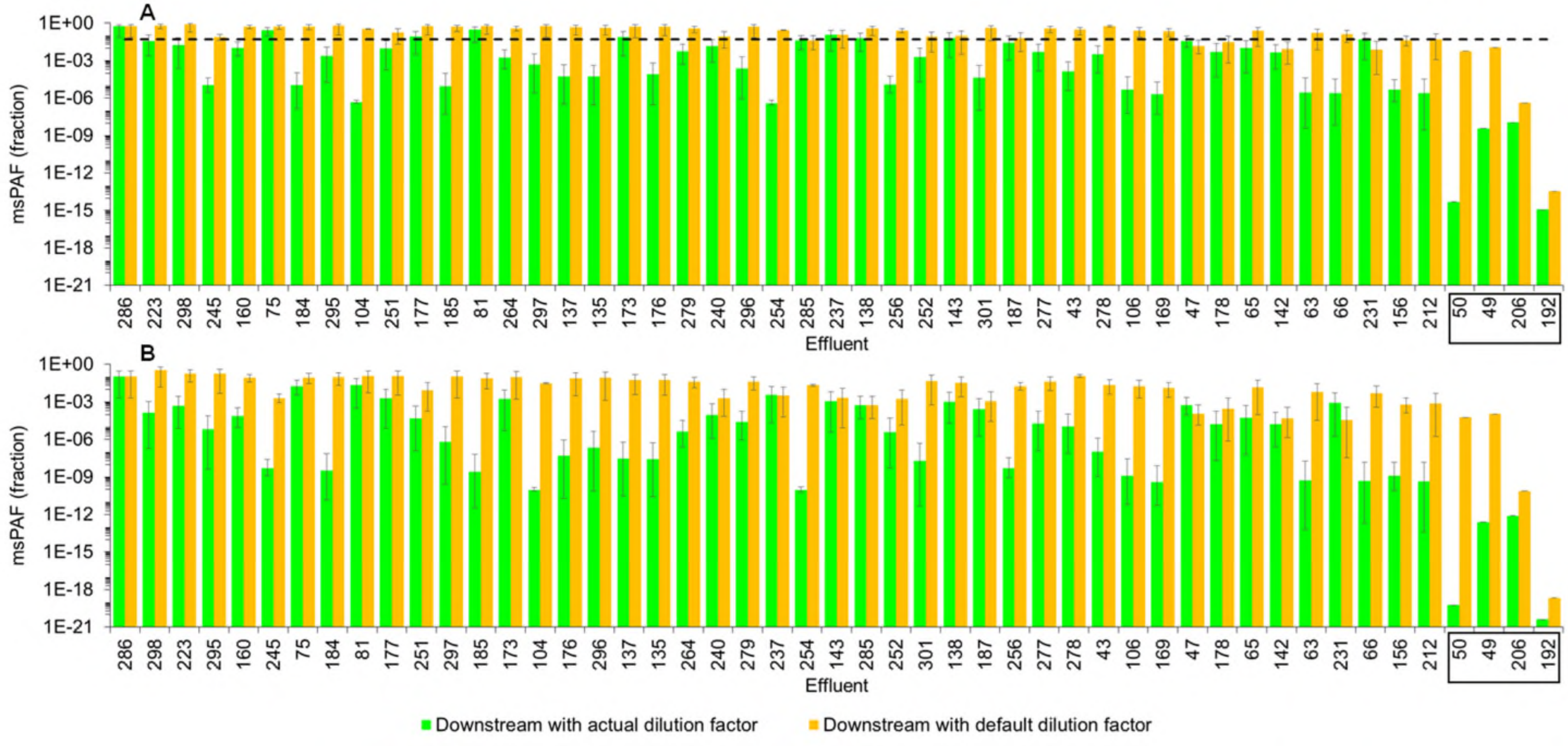


Figure A2. The average toxic relative composition of hydrocarbon block applied in the study (A), average composition of hydrocarbon block for effluents discharging into freshwater (B) and marine water (C) measured in 2008-2009 (Concawe, 2010). Indicated are the carbon chain length and the different classes of hydrocarbons.

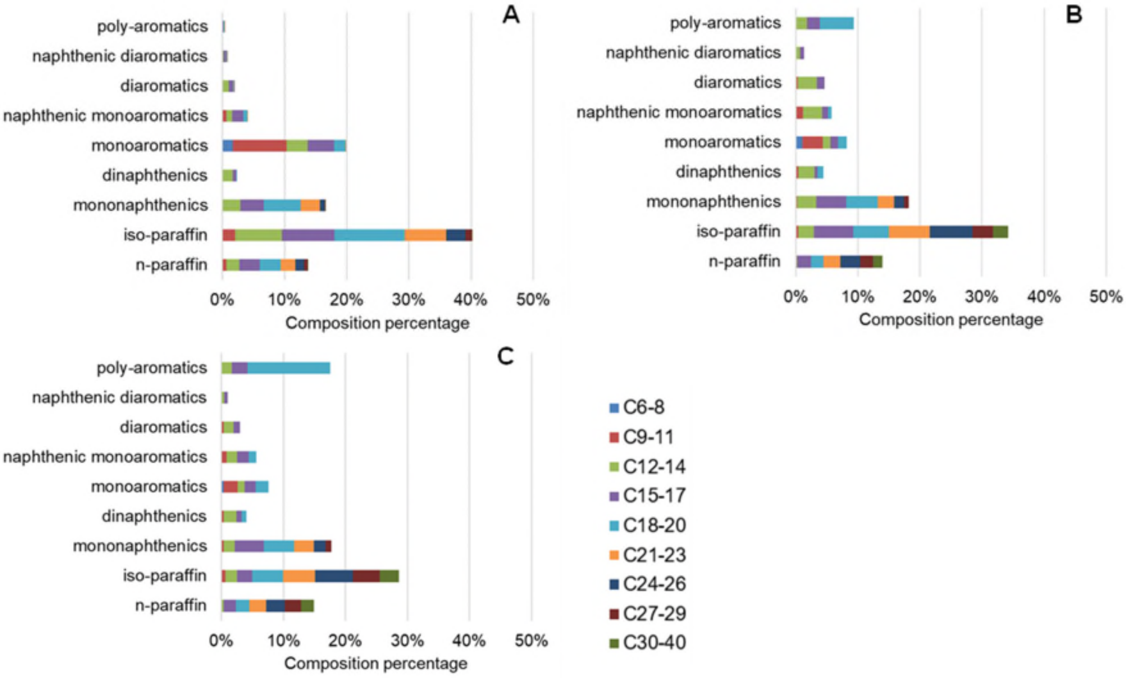


Figure A3. Contribution of each chemical group to msPAF-chronic levels at discharge points (A) and downstream (B), and to msPAF-acute levels at discharge points (C) and downstream (D), expressed as % of hazardous unit. Colours represent different chemical groups.

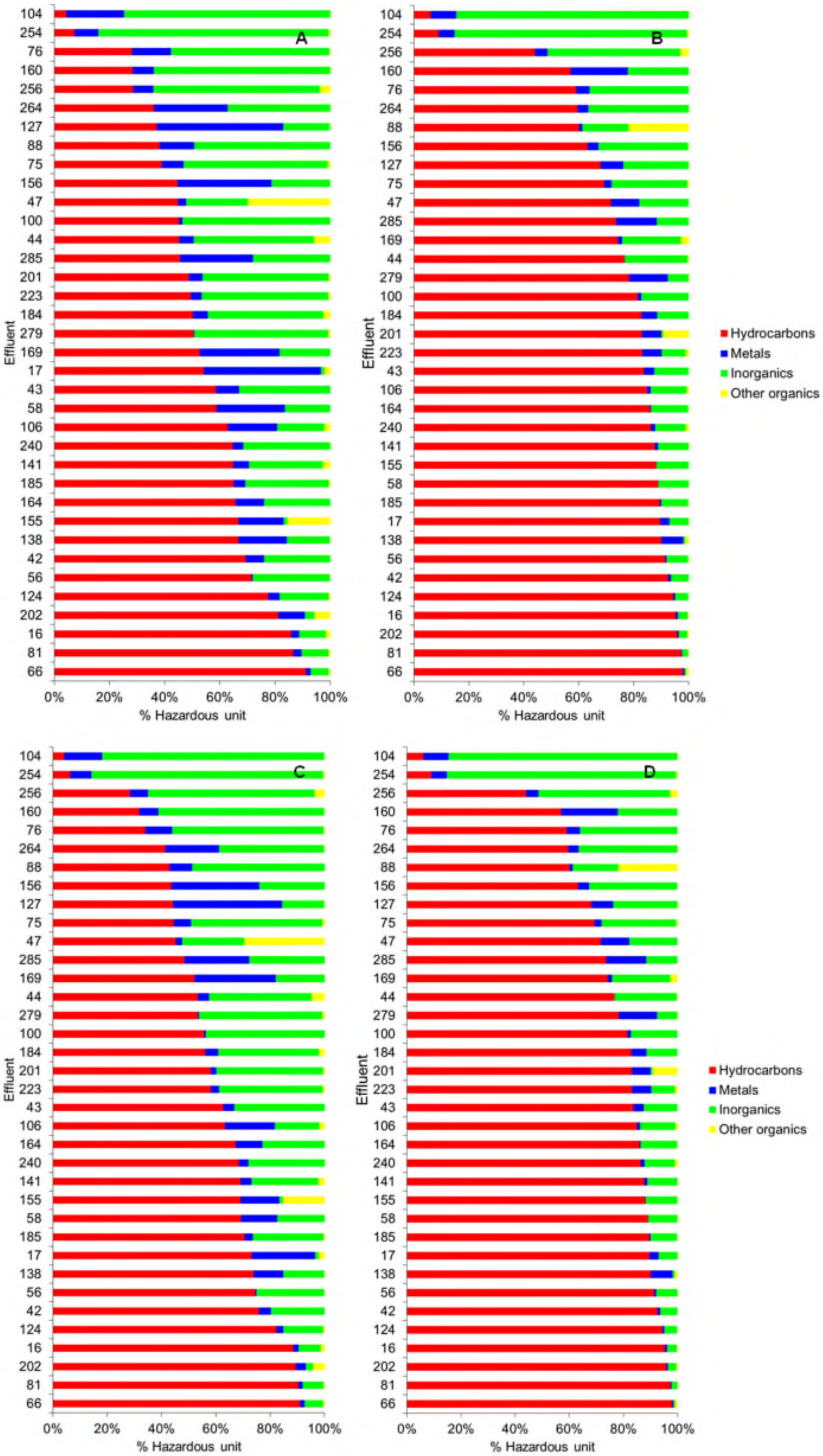
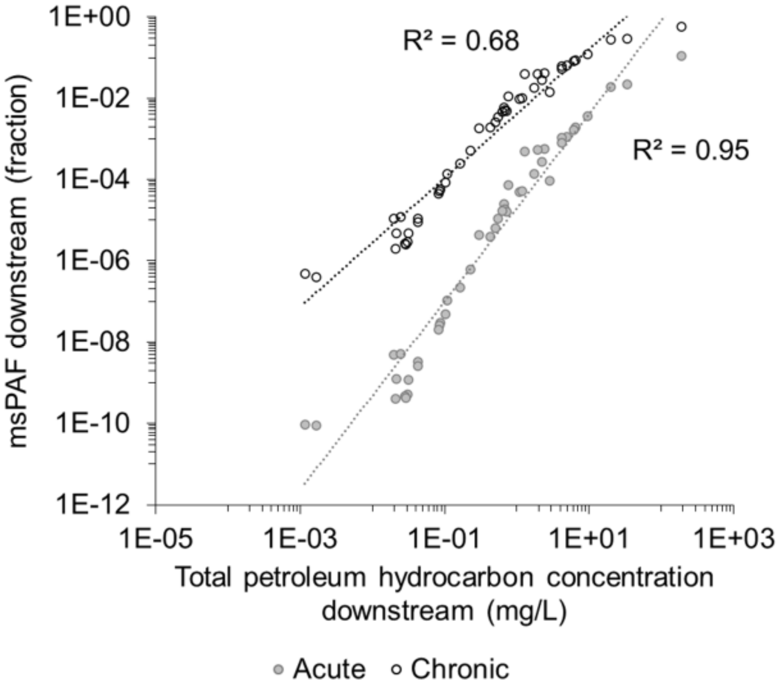


Figure A4. Relationships between total petroleum hydrocarbon concentrations downstream (mg/L) and msPAF levels downstream (fraction). Black and grey dotted lines represent regressions of msPAF downstream to total petroleum hydrocarbon concentrations downstream for the chronic and acute endpoints, respectively. Colours represent msPAF levels for different endpoints.



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