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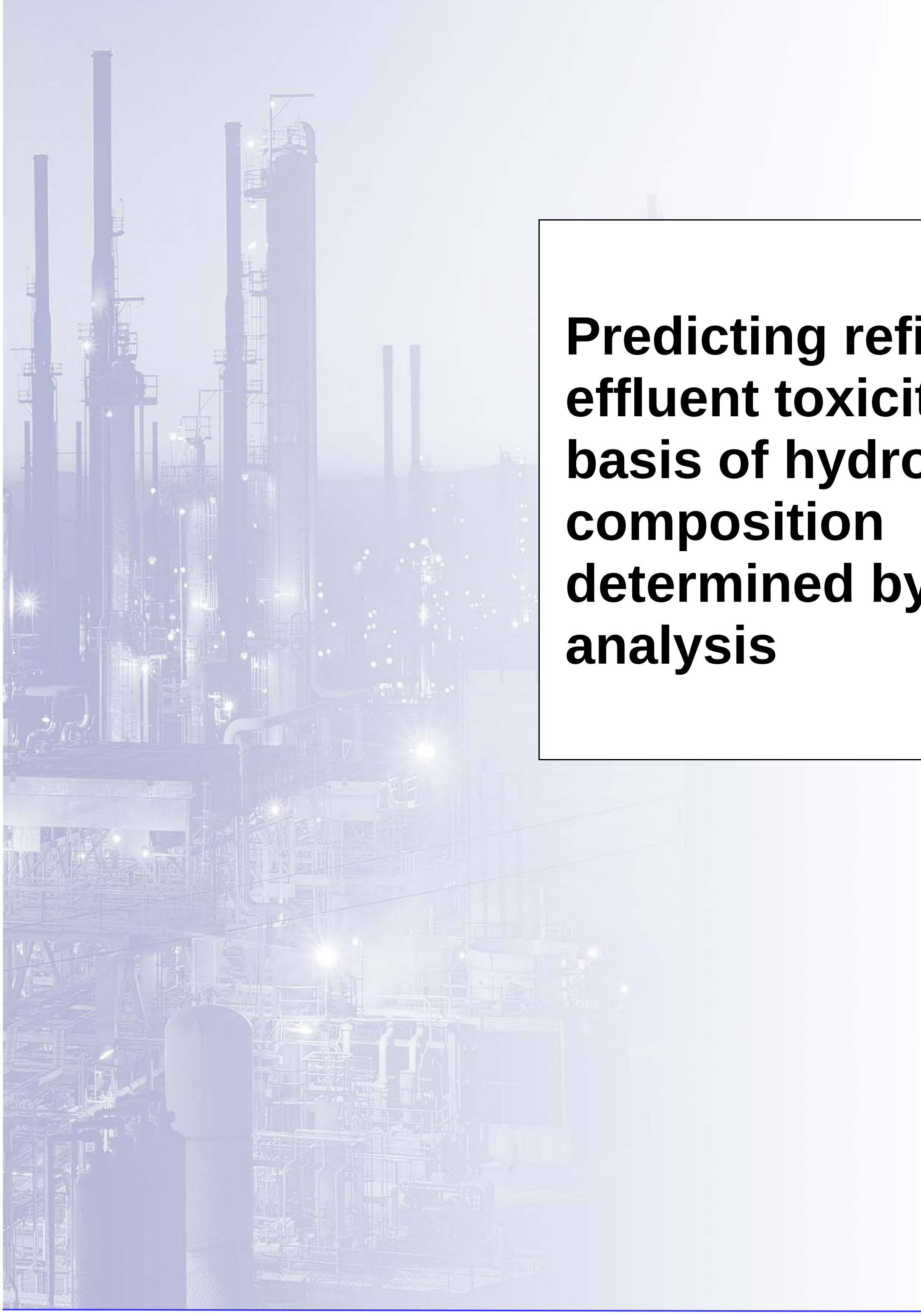

Predicting refinery effluent toxicity on the basis of hydrocarbon composition determined by GCxGC analysis

conservation of **c**lean **a**ir and **w**ater in **e**urope

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Predicting refinery effluent toxicity on the basis of hydrocarbon composition determined by GCxGC analysis

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ABSTRACT

A high resolution analytical method for determining hydrocarbon blocks in petroleum products by comprehensive two-dimensional gas chromatography (GCxGC) was used for the analysis of petroleum hydrocarbons extracted from refinery effluents. From 105 CONCAWE refineries in Europe 111 refinery effluents were collected in the period June 2008 to March 2009 (CONCAWE, 2010). The effluents were analysed for metals, standard effluent parameters (including Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), oil in water (OiW), GCxGC speciated hydrocarbons, BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) and volatile organic compounds.

This report describes the subsequent analysis of the GCxGC data, as described in hydrocarbon blocks, and uses the PETROTOX model, to predict the environmental toxicity (i.e. ecotoxicity) of the discharged effluents. A further analysis was undertaken to address the potential environmental impact of these predicted effects initially using default dilution factors and then, when necessary site specific factors.

The report describes all the methods used to arrive at the predictions, and shows that for the majority of refinery effluents direct toxicity effects in the effluents are not anticipated.

Furthermore, when applying either the EU Risk Assessment Technical Guidance Document (TGD) default dilution factors or site specific dilution factors, none of the refineries are predicted to exerting either acute or chronic toxicity to organisms in the receiving aquatic environment, based on their hydrocarbon composition present in the effluent samples.

KEYWORDS

Hydrocarbon blocks, refinery effluents, oil in water, GCxGC, REACH, Ecotoxicity

INTERNET

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SUMMARY

In this report the PETROTOX (Redman, *et al.*, 2012), model has been used to predict the ecotoxicity of the refinery effluent spot samples taken and analysed during a previously reported effluent speciation project (CONCAWE, 2010). Using the speciated hydrocarbon composition determined using high resolution GCxGC analytical techniques, the following conclusions can be drawn from the PETROTOX calculations:

- Assuming the REACH default dilution factor of 10 (ECHA, 2008), none of 58 refinery effluents discharged into the freshwater environment are predicted to cause acute or chronic toxic effects.
- Assuming the REACH default dilution factor of 100, none of the 41 refinery effluents discharged into the marine environment are predicted to cause acute or chronic toxic effects.
- The results indicate that 3 of the 12 effluents transferred for offsite treatment may raise concerns due to their predicted chronic toxicity. However, as this observation concerns the untreated effluents, no conclusions can be drawn with respect to environmental risk associated with the discharge of the treated effluent. Moreover, these refinery effluents are not anticipated to cause any adverse toxic effects in the receiving environment after treatment. This conclusion is based on knowledge regarding how such treatment facilities are operated, the fate of hydrocarbons present in refinery effluents and the fact that the discharges of these waste water treatment plants (WWTP) will be subject to dilution.

1. INTRODUCTION

In 2008 – 2009, a project to assess whether it was feasible to obtain detailed hydrocarbon composition of refinery effluents was undertaken and reported (CONCAWE, 2010). That report describes how a high resolution analytical method for speciating petroleum products into hydrocarbon blocks by comprehensive two-dimensional gas chromatography (GCxGC) was first transferred to a laboratory external to the petroleum industry (Institute for Environmental Studies (IVM) of the VU University of Amsterdam), and then validated and used for speciating and measuring hydrocarbon concentrations in refinery effluents.

Between June 2008 and March 2009, 111 samples of refinery effluents were received from 105 CONCAWE refineries in Europe. The parameters measured included standard effluent parameters as well as their speciated hydrocarbon composition, which could then be assigned to hydrocarbon blocks (HCBs) included in the Hydrocarbon Block Method (HBM). The HCBs for the refinery effluents determined by the aforementioned high resolution GCxGC analytical method were used to predict the ecotoxicity of the complex hydrocarbon mixtures present in refinery effluents with the PETROTOX model.

The HBM was originally developed to improve the environmental risk assessment of petroleum substances, which are typical examples of substances of unknown variable composition, complex reaction products or biological materials (UVCBs), as these consist of an unknown complex and variable composition of individual hydrocarbons. Petroleum substances typically contain hydrocarbons that exhibit large differences in physical-chemical and environmental fate properties. These properties alter the emissions and environmental distribution of the constituent hydrocarbons, and consequently it is not possible to define a unique predicted exposure concentration (PEC) for a petroleum substance. Furthermore, it also is not possible to directly apply conventional risk assessment guidance developed for individual substances to complex petroleum substances. To provide a sound technical basis to assess environmental exposure and risks of petroleum substances, CONCAWE devised the HBM in which constituent hydrocarbons with similar properties are treated as pseudo-components or "hydrocarbon blocks" for which PECs and predicted no effects concentrations (PNECs) can be determined (CONCAWE, 1996). Risks are then assessed by summing the PEC/PNEC ratios of the constituent blocks. This conceptual approach has been adopted by the EU as regulatory guidance (EU, 2003) and recent studies have demonstrated the utility of the HBM to gasoline (MacLeod et al, 2004; McGrath et al, 2004 & 2005; Foster et al, 2005). However, experience in applying this method to environmental samples such as effluents has been limited.

As the methodology has developed, the approach for defining the HCBs been refined, and within CONCAWE it is now standardised across the petroleum products. These HBCs form the basis of the risk assessment model PETRORISK that utilises all the previous information and has been termed, and a toxicity model, PETROTOX. In both models the HCB-blocking scheme used was follows;

- All HCBs are based on 3 carbon numbers, thus blocks are C3, 4, 5, then C6, 7, 8 etc., up to the final block of >C30.
- The principal hydrocarbon classes used are paraffins, iso-paraffins, nC5-based cyclic and nC6- based cyclic mono-naphthenics, other single ring mono–naphthenics, di-naphthenics, n-olefins, iso-olefins, poly-naphthenics, mono-

aromatics, di-aromatics, naphthenic-mono-aromatics, naphthenic-di-aromatics, poly-aromatics and sulphur heterocyclics.

The methodology used is based on the analytical method of 2-dimensional Gas Chromatography or GCxGC, which has been outlined by Eadsforth et al, 2006, and described in more detail in the CONCAWE Risk Assessment Project (CONCAWE, 2005). In GCxGC, the petroleum sample is subjected to two independent (orthogonal) GC separations, providing far better discrimination of the numerous components than is possible by one dimensional GC. The first separation is based on volatility differences (i.e. carbon number) between the components whilst the second separation exploits differences in polarity (i.e. functionality). All components are quantified using the universal flame ionization detector (FID), so calibration standards of the individual components are not required for accurate quantitative analysis.

In the effluent speciation project the GCxGC methodology was used to determine the concentrations of speciated total petroleum hydrocarbons (TPH) present in refinery effluents (CONCAWE, 2010). In this report, the analytical data has been used to enable the HBM to be applied to the refinery effluents to predict the acute and chronic toxicity of refinery effluents. The toxicity data have been used to ascertain whether there are any concerns regarding the potential impact of refinery effluents in the environment into which they are discharged.

2. EFFLUENT ASSESSMENT METHODOLOGY

The blocking scheme for hydrocarbons in PETROTOX for the effluent GCxGC analytical methodology, is based on the blocks of 3 carbons and the following hydrocarbon classes (**Table 1**): n-paraffins, iso-paraffins, nC5- based cyclic and nC6- based cyclic mono-naphthenics, other single ring mono– naphthenics, di-naphthenics, poly-naphthenics, mono-aromatics, di-aromatics, naphthenic-mono-aromatics, naphthenic-di-aromatics, poly-aromatics, and poly-naphthenics. The n-olefins, iso-olefins, and sulphur containing compounds were not included as separate hydrocarbon classes in the effluent samples as they could not be separated from the other hydrocarbon groups with the current GCxGC settings and are likely present at low levels.

Table 1 Full HC block template used for PETROTOX as quantifiable in effluents in this study

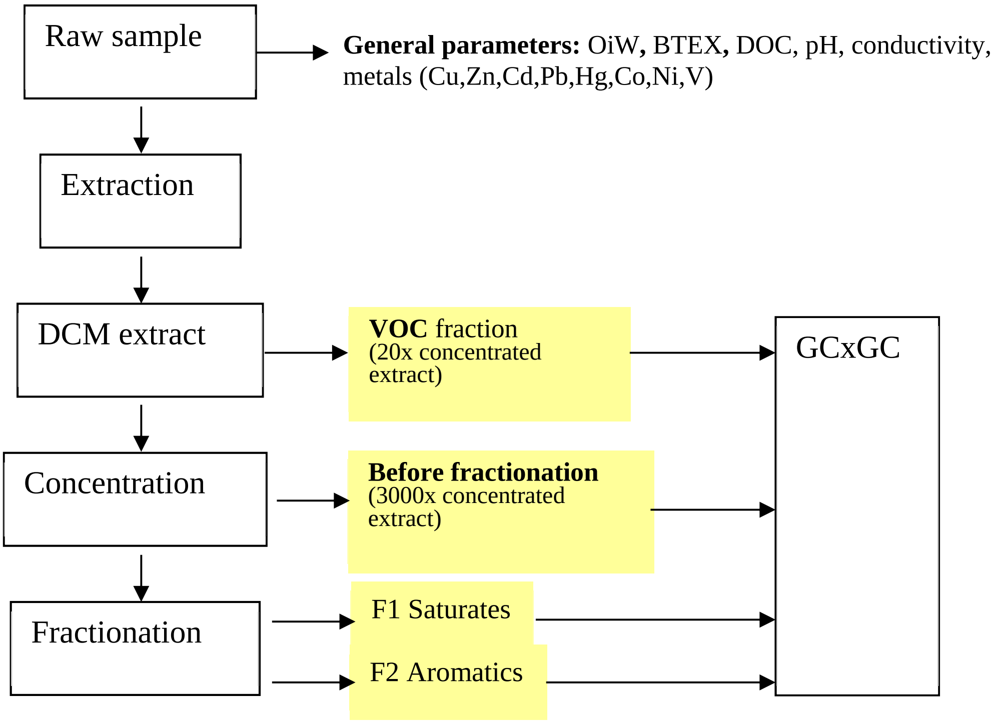
	normal paraffins	iso paraffins	mono naphthenes	di naphthenes	mono aromatics	naphthenic mono aromatics	di aromatics	naphthenic di aromatics	Poly aromatics	n-CC5 mono naphthenics	n-CC6 mono naphthenics	poly naphthenics
C6 - C8					x							
C9-C11	x	x	x	x	x	x	x		x	x	x	
C12-C14	x	x	x	x	x	x	x	x	x	x	x	
C15-17	x	x	x	x	x	x	x	x	x	x	x	
C18-20	x	x	x	x	x	x			x	x	x	x
C21-23	x	x	x							x	x	x
C24-26	x	x	x							x	x	x
C27-C29	x	x	x							x	x	x
C30-C40	x	x								x	x	x

The blocks marked X were observed in the ESP-study

An analytical GCxGC method developed by Shell (Eadsforth et al, 2006; CONCAWE, 2005) for the analysis of HC blocks in refinery products was implemented at the Institute for Environmental Studies, VU University (IVM). IVM initially set-up the Shell GCxGC method and analysed samples of diesel fuel, kerosene (jet fuel no. 6, JP-5), and refinery effluent samples. Based on the results of these analyses, the GCxGC method (GC temperature programme, injection mode, and type of second dimension column) was modified.

The full description of the transfer of the method and validation is given in CONCAWE, 2010. An overview of the steps taken in the effluent analysis project is presented in **Figure 1**.

Figure 1 Overview of steps taken in effluent analysis project



Before effluent sampling CONCAWE contacted and informed the refineries of the project and what they should expect. For each sampling a sample kit was prepared by IVM containing a background document prepared by CONCAWE, a sampling protocol, sampling bottles, safety material, and a sample information sheet. The sample protocol was optimised for the collection and determination of hydrocarbons (C9 and higher) and metals. Sample bottles were pre-cleaned according to protocols for metals (1 M nitric acid) and organic substance analysis (hot water, acetone, hot water, cold water, demineralised water, and drying step) before shipment.

The sample information sheet asked for information on sample time, date, location, type of effluent, and details of water treatment prior to the sample location (e.g. biological treatment, dissolved air floatation (DAF), interceptor etc.).

The effluent samples were collected from the refinery's usual sampling point (i.e. the one where samples for oil in water (OiW) analysis are collected), and were freshly collected spot samples. A 20 l sample for hydrocarbon analysis (HC blocks and OiW analysis) was collected in a stainless steel container with the addition of nitric acid (500 ml, 4% nitric acid) as preservation agent. A plastic bottle was used for metal analysis. All bottles were completely filled, leaving no headspace. The instructions were to avoid exposing the contents of the bottles to light or heat, and complete the sample information sheet. The bottles were returned as fast as possible by courier to the laboratory (IVM) for chemical analysis.

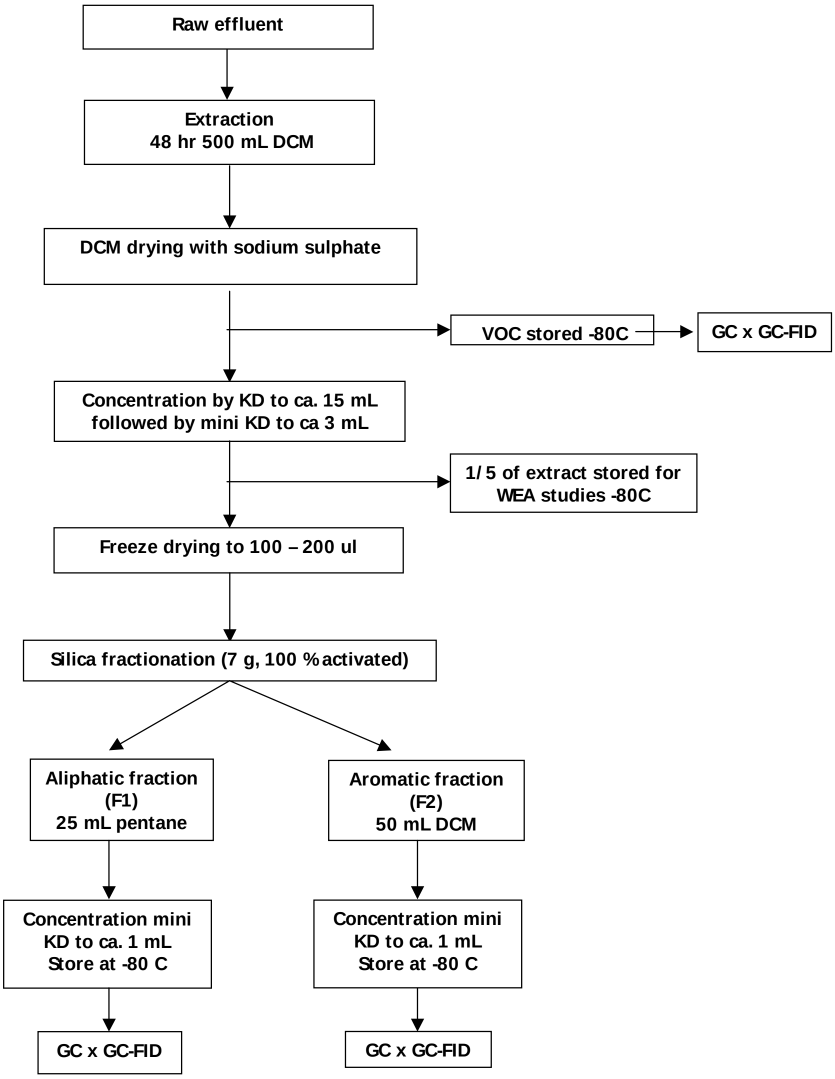
Returned samples were split in samples for OiW, HC blocks determination with GCxGC, BTEX and chlorinated aliphatic analysis which were taken from the stainless steel container. Subsamples for metals and other inorganic parameters (pH, conductivity, BOD, COD, TOC and DOC) were taken from the plastic bottle. The IVM laboratory determined the HC blocks, pH and conductivity. The OiW, BTEX, metals, and other inorganic parameters were determined by Omegam laboratories (Amsterdam) which is accredited according to NEN-EN-ISO/IEC 17025.

2.1. HYDROCARBON SPECIATION BY GCXGC

A full description of the methods used can be found in CONCAWE, 2010. The following descriptions are given to allow the data and their interpretation to be better understood.

For the speciation of HC blocks the effluent was extracted in two 5 l glass bottles each containing 250 ml dichloromethane (DCM). The bottles were closed without headspace. The effluent was stirred for 48 hours. Next, the DCM layer was separated from the effluent, and dried with sodium sulphate. An aliquot of the extract (1 ml) was stored in a GC vial at -80ºC (this fraction was labelled VOC (volatile organic carbon) fraction, see **Figure 2**).

Figure 2 Schematic diagram of the sample treatment steps for the full hydrocarbon speciation analysis



The remaining DCM extract was carefully evaporated with a 250 ml Kuderna Danish (KD) system to 10-15 ml. The extract was transferred to a mini KD system and carefully reduced to 1-3 ml. An aliquot (~20% of the extract) was stored in a glass vial and stored at -80ºC for additional whole effluent assessment (WEA) studies. One ml of pentane was added to the residual extract and transferred to a glass vial, covered with aluminium foil, and cooled to –80ºC. The cooled extract was freeze-dried to reduce the volume to 100 to 200 µl.

Two ml of pentane was added and fractionated with silica gel according to the protocol described above. An aliphatic fraction and an aromatic fraction were collected and evaporated to 0.5 to 1 ml with KD, and analysed by GCxGC. All extracts were weighed to be able to calculate the final concentrations of hydrocarbons. An Agilent 7890A gas chromatograph (GC) with capillary flow technology as modulator, and flame ionisation detection (FID) with a scan speed of 200 Hz was used as GCxGC system. The FID detector was operated at 300ºC. One µl of the final extract was splitless injected at 300ºC.

As a first dimension column a DB-1MS (30 m x 0.25 mm x 0.1 µm) and as second dimension column a HP-Innowax (5 m x 0.25 mm x 0.1 µm) were used. For the analysis of the aliphatic fraction the GC temperature programme started at 40ºC for 1 min, followed by an increase of 2.5ºC/min to 270ºC and kept for 35 min. The second GC column was placed in a second GC oven that was programmed 20ºC higher than the first oven, but following the same ramps and hold times.

For the determination of the n-C5 based cyclic, n-C6 based cyclic, and other mono-naphthenic compounds a reduced temperature programme was used to increase the separation of the naphthenics from the paraffins. Naphthenic analysis started at 40ºC for 1 min, followed by an increase of 1.5ºC/min to 270ºC and kept for 70 min, the second GC oven followed the first oven without an additional temperature setting. The aromatic fraction was analysed with a GC programme starting at 40ºC for 1 min, followed by an increase of 4.5ºC/min to 270ºC and kept for 18 min, without the use of a second GC oven.

For quantification of the hydrocarbon blocks an external calibration with 2,3-dimethylnaphthalene was applied as this compound has an average response factor. Integration and peak labelling was performed with the software package GC Image version 1.9 (Zoex). HC blocks were marked in the GCxGC chromatogram based on analytical standards (n-paraffins, iso-paraffins, naphthenes, olefins, naphthenic-mono-aromatics, mono-aromatics, di-aromatics, poly-aromatics, polynaphthenics), diesel and kerosene. A template for HC blocks was prepared for every new GC sequence. For actual effluent samples, the background of the GCxGC chromatogram was subtracted and the individual compounds of a HC block were identified, marked and labelled according to the template, and manually verified.

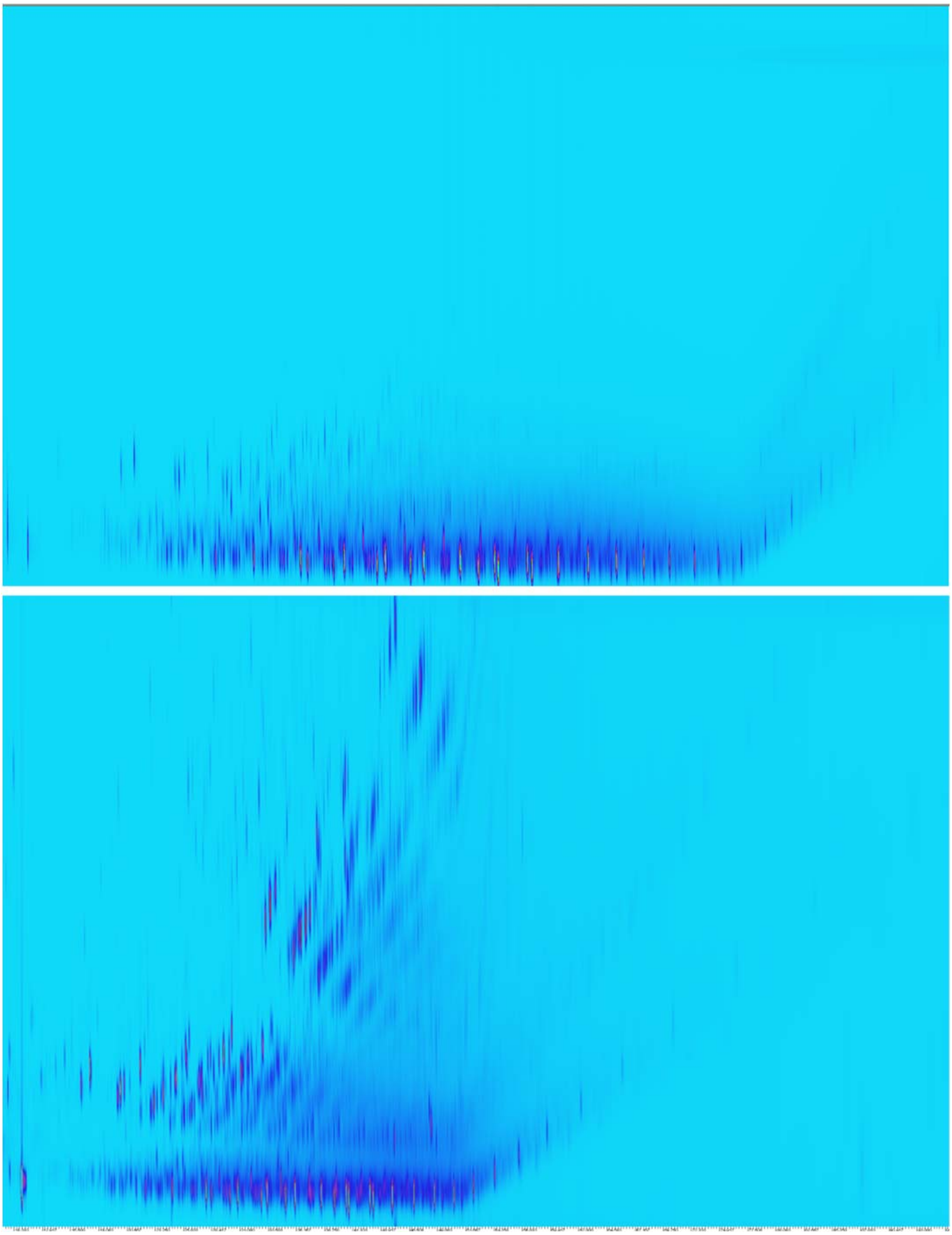
With the current method quantification of olefins was not possible as these compounds interfered with the naphthenes.

Quantification of the n-CC5 based cyclic and n-CC6 based cyclic peaks showed that a complete overlap between n-CC5 and n-CC6 for the C15-C17 group, the C18-C20 group, and for the C30-C40 group exists. For the other n-CC5 and n-CC6 based cyclic compounds the effluents showed in general equal concentrations for n-CC5 and n-CC6. Therefore, the concentrations of n-CC5 and of n-CC6 for the HC blocks C15-C17, C18-C20, and C30-C40 was set at half of the concentration of the sum of n-CC5+n-CC6.

Limited information is available on the separation and identification of poly-naphthenics in hydrocarbon products. Frysinger and Gaines (2001) studied the separation and identification of petroleum biomarkers using GCxGC. They identified a number of steranes, tri-terpenes, and tri-aromatic steranes in crude oil. In cooperation with Shell and the use of a number of poly-naphthenic standards (17b(H)-21b(H) hopane 5-a-chlolestane, prednisolone), the HC blocks of the poly-naphthenics were marked in the GCxGC chromatograms. The test of the standards showed that some HC chain lengths overlap, e.g. some C21 poly-naphthenics elute in the retention area of C20 poly-naphthenics. A more extensive study will be needed to further separate and identify the peaks in the poly-naphthenic area to get a reliable quantification method. Further, due to a limited number of analytical standards identification is partly hindered. Therefore, the results of the poly-naphthenics are only semi-quantitative.

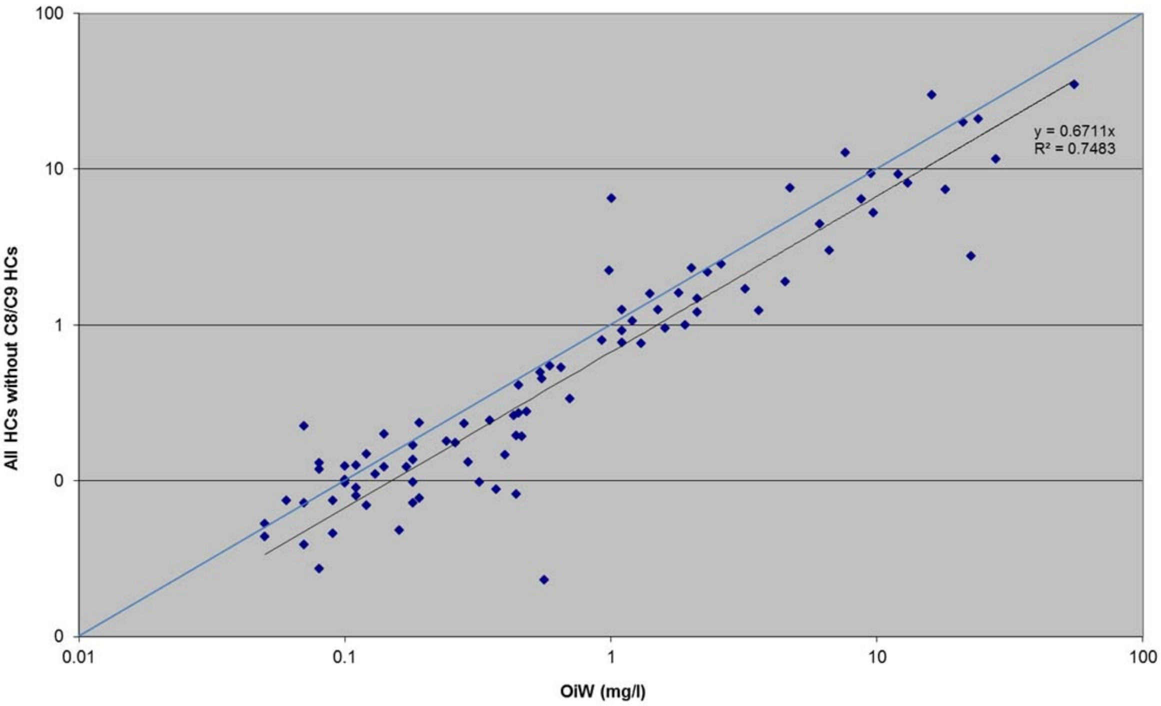
A typical GCxGC chromatogram, taken from CONCAWE report 3/10 (CONCAWE, 2010), is shown in **Figure 3** demonstrating the complexity of the analytical technique and the assignment and quantitation of the HCBs.

Figure 3 GCxGC-FID chromatograms of an effluent sample (6.6 mg/l OiW) using the full hydrocarbon speciation method. The upper figure shows the first aliphatic fraction and the lower figure the second aromatic fraction. (The X-axis shows the retention time of GC-1 and the Y-axis the orthogonal retention time of GC-2)



The levels of oil in water (OiW) and concentrations of hydrocarbons quantified in all effluents using the HC block speciation method are shown in **Figure 4**. In this figure, it can be seen that the OiW concentrations positively correlated with the concentrations of all GCxGC HC blocks. The difference in concentration between the OiW and full HC speciation GCxGC method is probably due to the differences in analytical and quantification methods used for both approaches, including the range of carbon numbers determined, different clean-up methods (florisil vs. silica) and different calibration standards are used for OiW (mixture of hydrocarbons) and GCxGC methods (2,3-dimethylnaphthalene) respectively.

Figure 4 Concentrations of all HC blocks determined by GCxGC vs. OiW concentrations. The black line is the regression line based on the samples and a forced intercept through zero. The blue line has a regression coefficient of 1.



2.2. OTHER PARAMETERS

2.2.1. BTEX

The benzene, toluene, ethylbenzene and xylenes, (BTEX), were determined by a method based on NEN-EN-ISO 15680 (NEN, 2003). The sample is purged by helium, and the helium stream was cooled in an adsorption tube to trap the VOCs. The adsorption tube was heated and transferred to a GC-MS system, where the determinations are carried out.

2.2.2. BOD, COD & TOC

Chemical oxygen demand (COD) was determined with a titrimetric method according to NEN 6633 (NEN, 2006). The effluent was refluxed for 2 hours with potassium chromate in sulphuric acid. The used potassium chromate was titrimetrically determined. Biological oxygen demand (BOD) was determined by adding a mixture of salts and microorganism and measuring the oxygen demand before and after an inoculation period of 5 days at 20ºC according to NEN-EN-1899. Total organic carbon (TOC) was analysed by measuring the carbon dioxide evolved at a high temperature (950ºC) combustion, using IR-spectrometry according to the NEN-EN 1484 method.

3. PETROTOX

PETROTOX (Redman et al, 2012) is a spreadsheet-based programme that is designed to calculate the toxicity of petroleum substances and products to aquatic organisms, using the HBM. Petroleum substances are complex mixtures of hydrocarbons that exert a narcotic mode of toxic action, which is assumed to be additive. This model calculates the solubility of a petroleum product and then uses the Target Lipid Model (TLM) (Di Toro et al, 2000) and toxic unit theory of additivity to calculate the toxicity or environmental risk limits of these mixtures.

The spread sheet uses a three-phase (air, water, free product) oil solubility calculation (McGrath et al, 2004) that is coupled with a database of physical and chemical properties of typical petroleum hydrocarbons to calculate the distribution of petroleum hydrocarbons among the exposure water, headspace and free product phases. The properties database was developed by CONCAWE and contains physical-chemical properties such as boiling point, solubility and octanol-water partition coefficients (Kow) for 1512 hydrocarbon structures that are possibly found in petroleum products. The PETROTOX model performs the solubility and toxicity calculations with physical-chemical properties derived from the database for each hydrocarbon block (PETROTOX Users Guide PETROTOX v3.06).

The computed dissolved hydrocarbon concentrations are then used by the TLM to calculate aquatic toxicity. A modification to the TLM is the use of membrane-water partition coefficients (KMW) rather than KOW to describe the partitioning between the water phase and the organism. This modification is critical for petroleum products that have very hydrophobic compounds (log(KOW) > 6.0) (PETROTOX Users Guide PETROTOX v3.06).

3.1. COMPOSITION AND MAPPING

As described above in Section 3, the mass distribution for up to 16 chemical classes is obtained and entered into a mass matrix made up of 3 carbon numbers. The total mass derived from the GCxGC analyses is then used as a loading for the PETROTOX input.

The library structures are assigned to a hydrocarbon block and the mass fraction given to that block is evenly distributed among all of the assigned structures. For example, if a hydrocarbon block in the paraffin class is assigned a mass fraction of 5.0% with an initial carbon number interval of C9-C11, there will be 3 structures within the paraffin class that are described. The mass fraction of this hydrocarbon block (5.0%) is evenly distributed among the candidate structures so that each has 1.67% of the total mass. The mass fraction that is assigned to each structure is later used to determine the mole fraction of a given hydrocarbon, which impacts the aqueous solubility of that structure.

3.2. THREE-PHASE FATE (SOLUBILITY) MODEL

The PETROTOX model utilises a multi-phase (petroleum product, water, air) dissolution model that considers the changes in product volume and composition as a result of dissolution, to simulate a toxicity study. The full description of the derivation of the equations used can be found in the PETROTOX Users Guide (PETROTOX Users Guide PETROTOX v3.06).

The conditions used in this study were that of an exposure system made up of 0.9 litre of water and 0.1 litre of overlying air.

3.3. TARGET LIPID MODEL

For the risk assessment of petroleum-derived products, it is accepted that the mode of action of petroleum related hydrocarbon components is narcosis (CONCAWE, 1996). Chemicals that act via narcosis are referred to as narcotics. It has been demonstrated experimentally that the effects of narcotics are additive, and shown that such a model is a reasonably conservative approach (Olmstead and LeBlanc, 2005; McGrath and Di Toro, 2009; Engraff et al, 2011). The toxic unit (TU) approach is used to express the toxicity of mixtures with components that exert a similar mode of action. Recently, the TLM (Di Toro et al, 2000) and the TU concept have been adopted for use in computing environmental risk limits for mineral oil (Verbruggen, 2004), a complex petroleum substance.

The TLM predicts the aquatic toxicity of narcotic chemicals to a variety of aquatic species, including fish, algae and invertebrates. It is based on the inverse relationship observed between the log(LC50) (lethal concentration to 50% of test organisms) and log(Kow) and the observation by McCarty et al, 1991 that this relationship can be understood as the result of a constant body burden of narcotic chemical that causes adverse effects. In the TLM a single universal slope for the log (LC50)-log (K_{ow}) relationship has been demonstrated, independent of the species. The TLM equation for computing the LC50 (mmol/L) for a particular chemical for a specific species is

$$\log(\mathrm{LC50}) = -0.936 \log(\mathrm{K_{ow}}) + \Delta c_\ell + \log(\mathrm{C_L^*}) \qquad (1)$$

where Δc_ℓ is the chemical class correction factor for chemicals that were found to be slightly more potent than baseline chemicals (e.g., Polyaromatic Hydrocarbons), -0.936 is the universal slope, and C_L^* is the species-specific critical target lipid body burdens (CTLBB) for narcosis effects (μmol/g octanol). These parameters are provided in the worksheet labelled 'CTLBB' for 42 organisms including daphnia's, fish, algae and other species. The parameters include the CTLBB, universal narcosis slope, chemical class corrections and their associated standard errors. The acute-to-chronic ratio can also be applied to calculate chronic effect concentrations.

For application to petroleum products/effluents the term LL50 (lethal loading concentration) is used instead of the LC50 due to their low water solubility. Additionally, for application to petroleum products/effluents, the KMW is used in place of KOW as follows

$$\log(K_{\mathrm{MW}}) = \log(K_{\mathrm{OW}}); \mathrm{for Structures with} \log(K_{\mathrm{OW}}) <= 6.0 \qquad (2)$$

and,

$$\log(K_{\mathrm{MW}}) = b_2 + 0.037 \log(K_{\mathrm{OW}}); \mathrm{for Structures\ with} \log(K_{\mathrm{OW}}) > 6.0 \qquad (3)$$
$$b_2 = cutoff - slope * cutoff = 6.0 - 0.037 * 6.0 = 5.78$$

The toxicity of a hydrocarbon mixture can be expressed using the concept of TUs (Sprague and Ramsay, 1965). A TU is defined as the ratio of the exposure concentration of the freely dissolved chemical to the effect concentration for a specific medium (e.g. water). A toxic unit posed by each specific hydrocarbon block i in a mixture is computed as

$$TU_i = \frac{C_{D,i}}{LC50_i} \quad (4)$$

where $C_{D,i}$ is the aqueous freely dissolved concentration of the hydrocarbon block (mmol/L) and LC50i is the aqueous effect concentration (mmol/L) for that block for a specific species. To compute the toxicity of the mixture, the TUs for all hydrocarbon components in the mixture are summed. When the sum of the TUs for the mixture equals one, the mixture is expected to be toxic to 50% of the organisms.

Loading data are not required for the model to calculate median acute or chronic effect endpoint (e.g., LL50). However, to calculate the TUs of a sample, the loading is required, and for this exercise, the concentration of hydrocarbons in each sample, determined by GCxGC was used.

3.4. DATA INPUT

To enable the TUs in each effluent to be calculated the data generated in the Effluent Speciation project (as reported in CONCAWE, 2010) were treated as follows:

- Firstly the data was assessed to convert those hydrocarbon blocks reported to be present at less than the Limit of Detection (LoD) to a concentration of ½ that of the LoD.
- Secondly the concentrations of all the hydrocarbon blocks for which concentrations were reported (including those present at less than the LoD) were summed to generate a total hydrocarbon concentration for the sample. This includes the BTEX analysed separately, which is included in the C6-8 mono-aromatics block.
- Thirdly the concentration data were expressed as percentages by normalising the data for each hydrocarbon block against the total hydrocarbons data.
- Finally the TUs, both acute and chronic to the invertebrate *Daphnia magna* were calculated using the percentage composition data (as the composition of a mixture) and the loading (based on the total hydrocarbon concentration).

3.5. RISK ASSESSMENT FOR EFFLUENTS

In the final treatment of the data, those effluents that were being discharged directly to the environment were divided by the default dilution factors, as specified in the official guidance (ECHA, 2008), which states: “The default dilution factor for sewage from municipal treatment plants emitted to a freshwater environment is 10. A default dilution factor for discharges to a coastal zone (marine environment) of 100 is assumed to be representative for a realistic worst case”. Using these factors the final figure thus obtained is a worst case assumption of the likely toxicity of the refinery effluents.

A further consideration in understanding these data, is that the GCxGC analytical approach is based on liquid solvent extraction and thus may overestimate the freely dissolved fraction of hydrocarbons in the various fractions based on partitioning to particulate and dissolved organic carbon. In the current analysis TOC and DOC are excluded (only three phases are considered in exposure calculations - oil, water and air) despite the fact that TOC and DOC are present in the effluent. As a result of this assumption, the approach used in this study is conservative in describing bioavailability/toxicity of effluent hydrocarbons.

4. RESULTS

The distribution of the effluents with their toxic units has been summarised in **Figures 4 to 9**. A more comprehensive summary of the data on which these figures are based including refinery codes, of oil in water measurements, GCxGC hydrocarbons and the acute and chronic toxicity predictions is provided in **Appendix 1**.

In line with the previous report, the samples of the refineries were classified in discharging their effluents to i) freshwater, ii) marine waters, or iii) to an off-site waste water treatment plant (WWTP).

4.1. PREDICTED TOXIC UNITS OF EFFLUENTS DISCHARGED TO FRESHWATER

The following figures summarise the frequency of refineries (y-axis) with predicted acute or chronic toxic units that discharge to freshwater. The values for the toxic units are before the default REACH dilution factors of 10 or 100 are applied to address the potential for effects in the receiving Fresh water or Marine environment, respectively.

Figure 4 Predicted acute toxic units for refinery effluents discharging to the freshwater environment

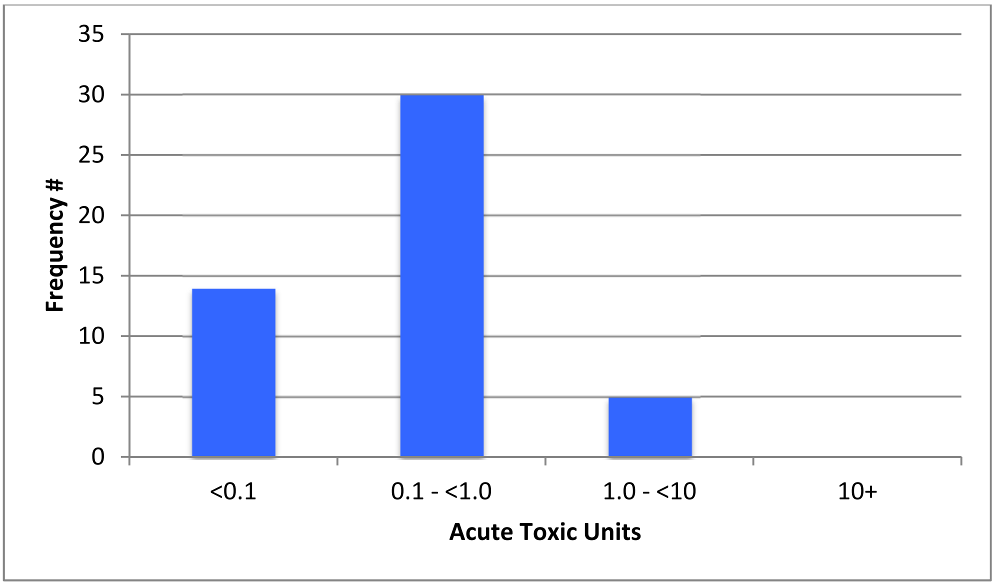
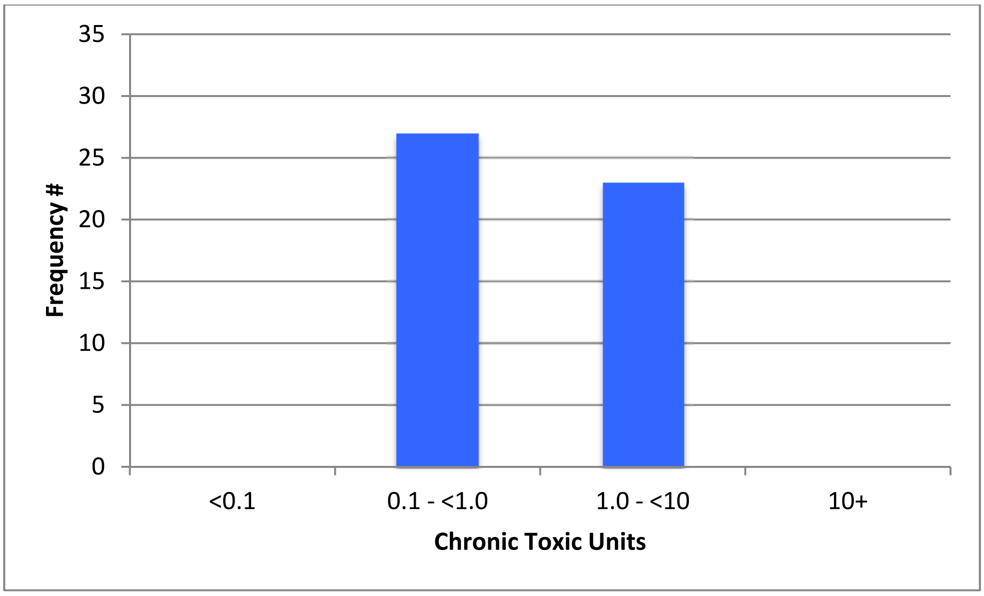


Figure 5 Predicted chronic toxic units for refinery effluents discharging to the freshwater environment



4.2. PREDICTED TOXIC UNITS OF EFFLUENTS DISCHARGED TO MARINE ENVIRONMENT

The following figures summarise the frequency of refineries (y-axis) with predicted acute or chronic toxic units that discharge to the marine environment. The values for the toxic units are before a default dilution factor (100) is applied to address the potential for effects in the receiving environment.

Figure 6 Predicted acute toxic units for refinery effluents discharging to the marine environment

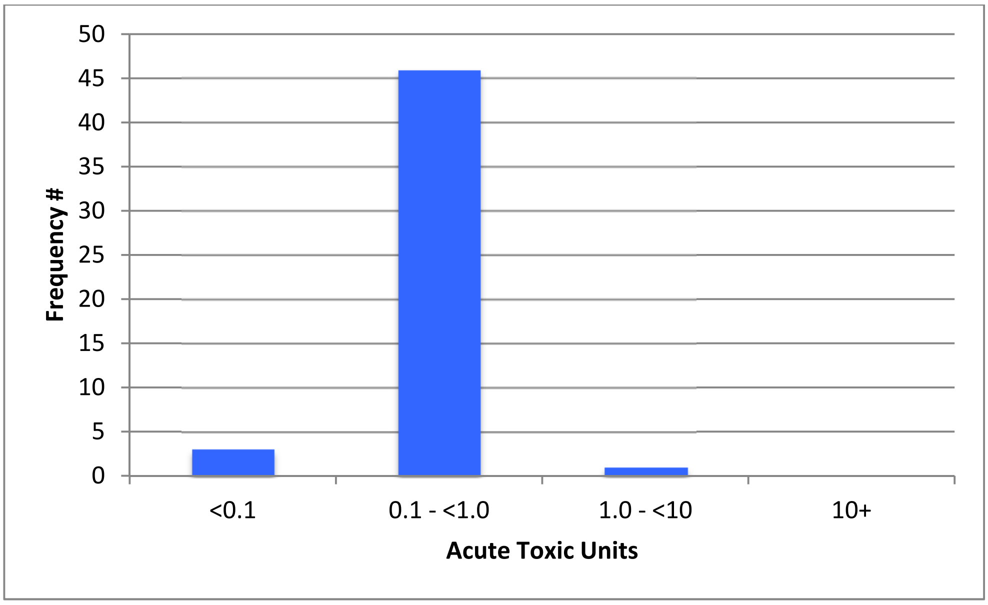
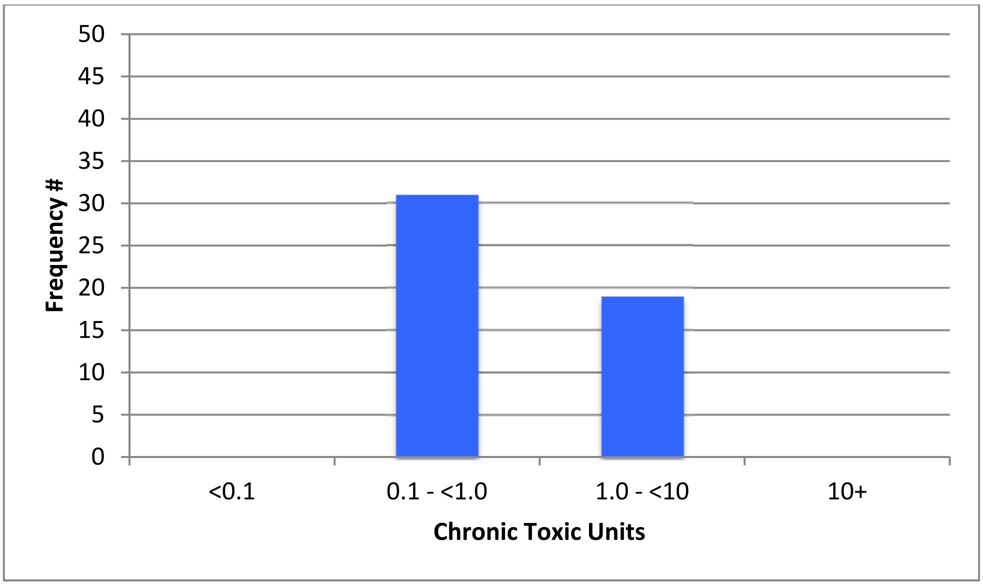


Figure 7 Predicted chronic toxic units for effluents discharging to marine waters



4.3. PREDICTED TOXIC UNITS OF EFFLUENTS DISCHARGED TO EXTERNAL TREATMENT PLANTS

The following figures summarise the frequency of refineries (y-axis) with predicted acute or chronic toxic units that discharge to external treatment plants.

Figure 8 Predicted acute toxic units for effluents discharging to external WWTPs

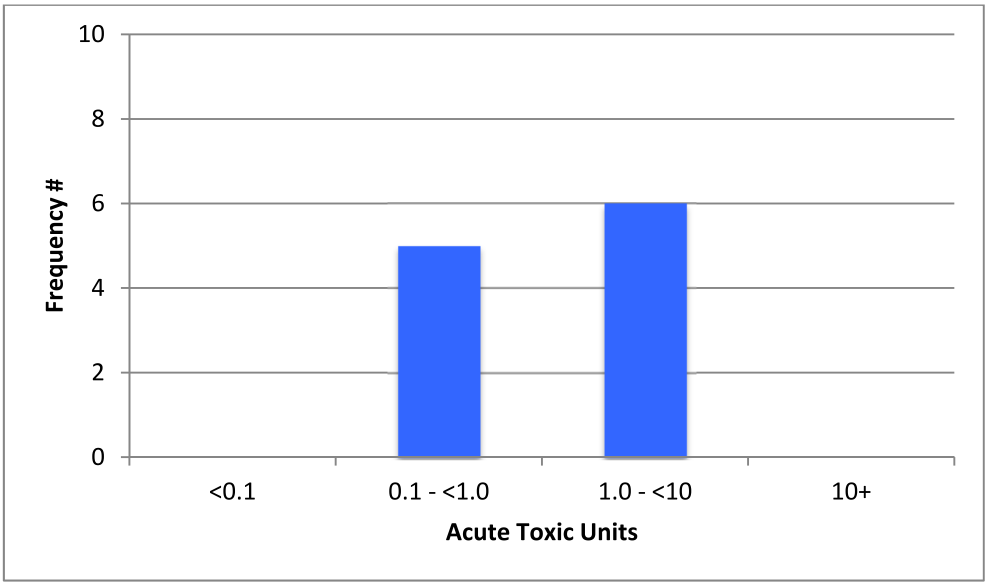
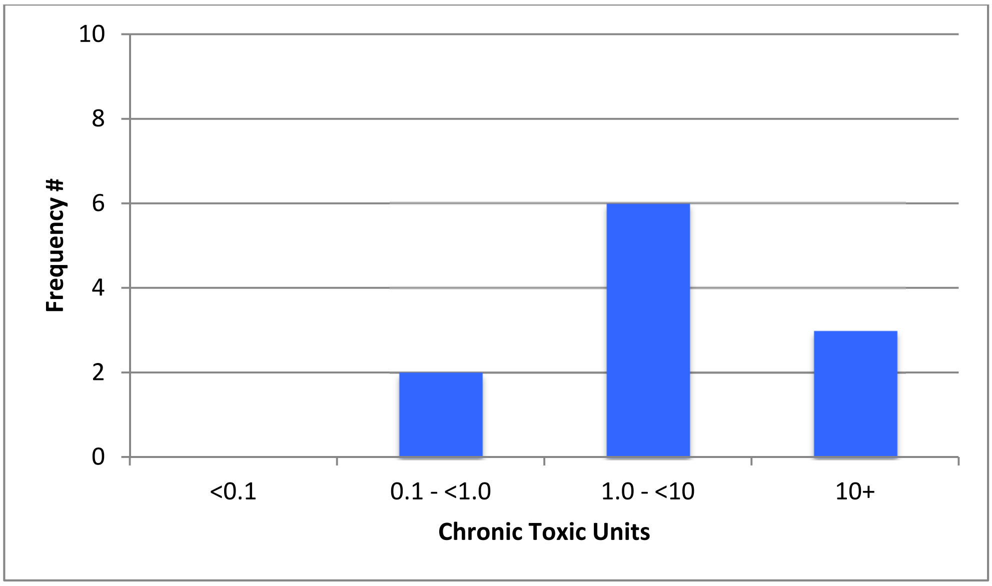


Figure 9 Predicted chronic toxic units for effluents discharging to external WWTPs

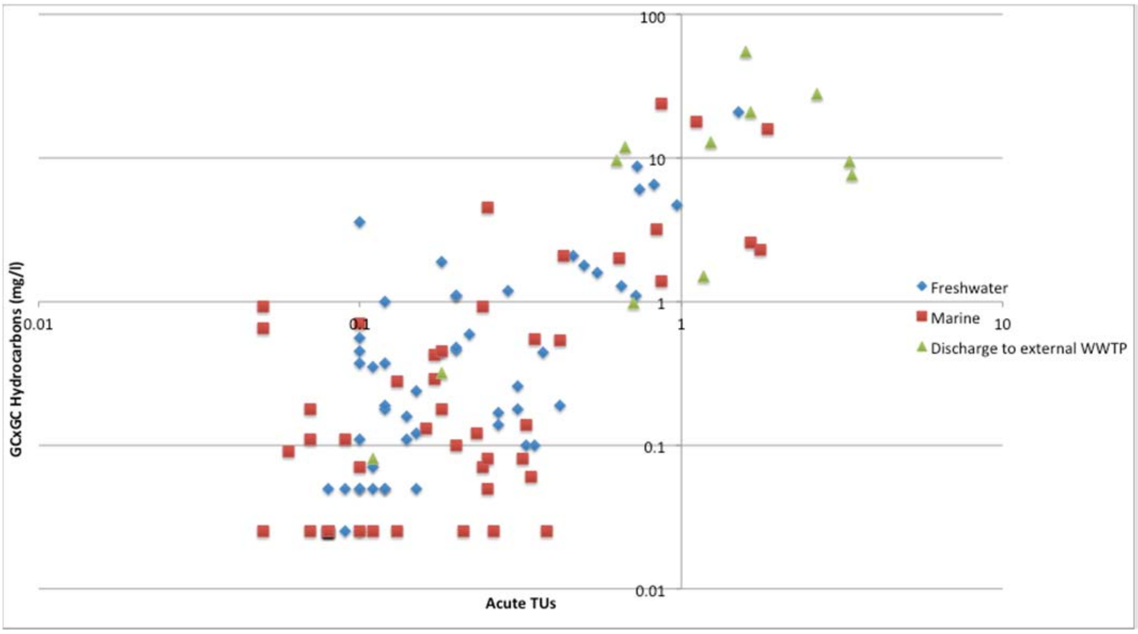


4.4. PREDICTED TOXIC UNITS VERSUS GCXGC HYDROCARBONS

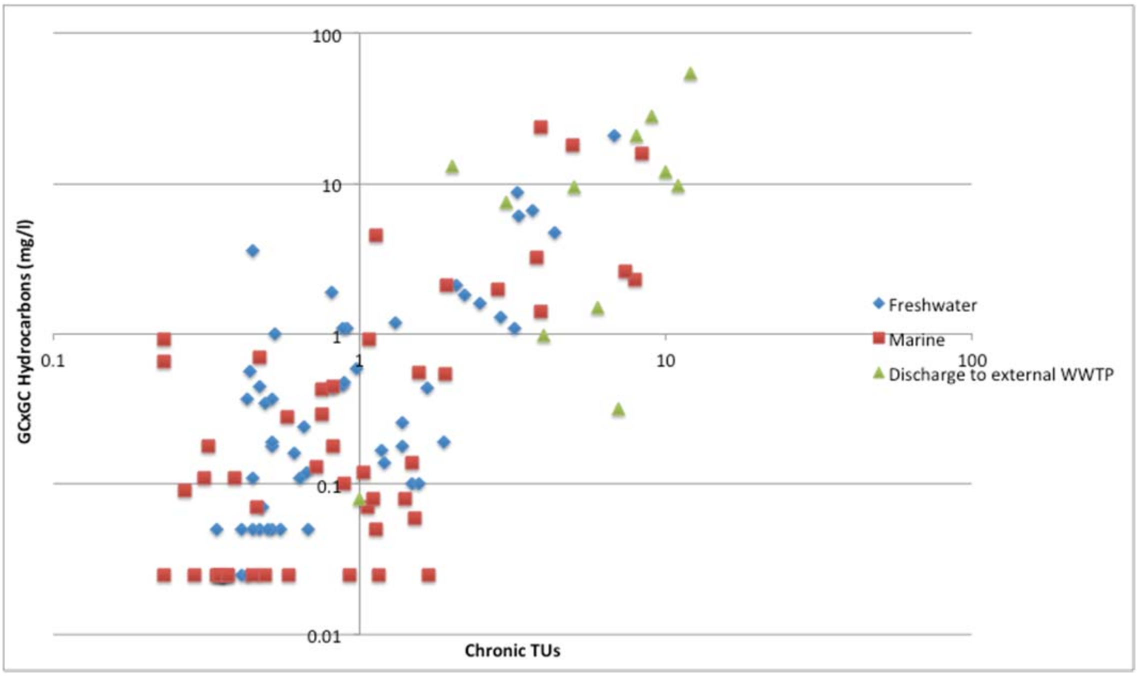
Acute TUs v GCxGC Hydrocarbons

The two graphs below demonstrate that there is a very weak relationship between the bulk parameter of hydrocarbons measured by GCxGC and the sum of TUs as calculated by PETROTOX. This is supported by the view that measuring hydrocarbons is a non-discriminative parameter, whereas the TU-estimation looks at the respective blocks present and their individual contributions to the estimated effects. For example, an effluent with a high concentration of aliphatics C10-C12 will have a higher predicted TU than an effluent comprising of mainly C20-C30 aliphatics, even when the measured hydrocarbon concentrations in the effluent are the same. These graphs represent a tier 0 assessment as no dilution has been applied to the predicted TUs in the effluents.

Acute TUs v GCxGC Hydrocarbons



Chronic TUs v GCxGC Hydrocarbons



5. CONCLUSIONS

The results of the current study, in which the PETROTOX model has been used to predict the toxicity of the refinery spot samples on the basis of their hydrocarbon composition determined using high resolution GCxGC analytical techniques, allow drawing the following conclusions:

1. Assuming the default dilution factor of 10, none of the 58 refinery effluents discharging to the fresh water environment are predicted to cause acute or chronic toxic effects that can be assigned to the Oil in Water present.

2. Assuming the default dilution factor of 100, none of the 41 refinery effluents discharging to the marine environment are predicted to cause acute or chronic toxic effects that can be assigned to the Oil in Water present.

3. The results indicate that three of the twelve effluents transferred to an offsite WWTP may be of concern due to their predicted chronic toxicity. This toxicity is based on the aquatic invertebrate *Daphnia magna*. Therefore, this may not be applicable for the environment that receives this effluent after treatment. This assumption has been based on the following:-

   a. As a condition of permitting procedures, WWTP operators will be aware of the waste streams they take and responsible operators would have ensured that their WWTP will be effective at reducing parameters such as COD and BOD of the waste waters they treat.

   b. The bacteria in the WWTP will not be exposed to the concentrations reported as prior to treatment the refinery effluents are mixed with those of the other customers of the treatment installation under consideration.

   c. WWTP discharges themselves will be subject to a further minimal default dilution factor of 10.

   d. Previous studies have shown that constituents of refinery effluents are biodegradable and that biodegradation will result in a reduction of toxicity (Leonards et al, 2011).

   These assumptions are supported by the observations of one installation, within the refining sector is treating its own effluent (8.04N) and that which is transferred from a neighbouring installation (8.04S). The latter, has a predicted acute TU content of 3.35 and a chronic TU content of 15, which is transferred to the WWTP of 8.04N. After BAT compliant treatment at 8.04N and including the influents of this installation, the predicted acute TU and chronic TU contents of the effluent is estimated to have become 0.12 and 0.52, respectively.

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7. GLOSSARY

BAT	Best Available Technique
BOD	Biochemical Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
COD	Chemical Oxygen Demand
CONCAWE	Conservation of Clean Air and Water in Europe
DAF	Dissolved Air Floatation
DCM	DiChloroMethane
DOC	Dissolved Organic Carbon
GCxGC	A research analytical method utilising two Gas Chromatographic columns to first separate hydrocarbons by boiling point and then by polarity (or functional group).
GC-MS	Gas Chromatography with Mass Spectrometric detection
GC-FID	Gas-Chromatography with Flame Ionisation Detection
HCB	Hydrocarbon Block
HBM	Hydrocarbon Block Method a method on which the toxicity of hydrocarbon mixtures can be predicted
LoD	Limit of Detection
OiW	Oil in Water
PEC	Predicted Environmental Concentration
PETRORISK	An Excel© based model that uses petroleum product use and emission data and composition to predict the PEC and PNEC of the constituent hydrocarbon blocks and thus the potential risk arising from their use of petroleum products in the environment.
PETROTOX	A model that predicts the ecotoxicity effects of hydrocarbon mixtures based on analytical data or boiling ranges. The model assumes additivity of the molecules contributing to toxicity and that they act via a non-specific mode of action.
PNEC	Predicted No Effect Concentration
REACH	Registration, Evaluation, Authorisation & restriction of Chemicals
TGD	Technical Guidance Document
TOC	Total Organic Carbon

TU	Toxic Unit
TLM	Target Lipid Model
UVCB	Substance of unknown variable composition, complex reaction products or biological materials
VOC	Volatile Organic Carbons
WEA	Whole Effluent Assessment
WWTP	Waste Water Treatment Plant

Abbreviations for Hydrocarbon blocks used in PETROTOX:

n-P	paraffins
i-P	iso-paraffins
n-CC5	nC5 - based cyclic mono-naphthenics
n-CC6	nC6- based cyclic mono-naphthenics
i-N	other single ring mono– naphthenics
Di-N	di-naphthenics
Poly-N	poly-naphthenics
AIS	Sulphur containing aliphatic molecules
MoAr	mono-aromatics
DiAr	di-aromatics
NMAr	naphthenic-mono-aromatics
NDiAr	naphthenic-di-aromatics
PolyAr	Poly-aromatics
ArS	Sulphur containing aromatic molecules.

8. ACKNOWLEDGEMENTS

The role of the refineries is acknowledged, as without their support and responsiveness to the supply of samples and additional information this project could not have succeeded.

APPENDIX 1

Table A1.1: Toxic Units calculated for refinery effluents discharging into freshwater bodies

Refinery code	OIW	Sum GCxGC Hydrocarbons	Acute T.U.	Chronic T.U.
	mg/l	mg/l		
2.01	<0.05	0.16	0.26	1.15
2.04	0.09	0.12	0.06	0.27
5.03	2.3	4.2	1.76	7.89
5.04	3.2	1.99	0.84	3.77
5.04_2	0.29	0.16	0.17	0.75
5.06	0.12	0.26	0.23	1.03
5.08	0.43	0.28	0.17	0.75
6.01	<0.05	0.12	0.07	0.29
6.04	0.11	0.12	0.07	0.31
6.05	<0.05	0.03	0.08	0.37
6.08N	<0.05	0.05	0.08	0.34
6.08V	<0.05	0.16	0.08	0.35
6.11	0.05	0.31	0.25	1.13
6.12	0.65	0.58	0.05	0.23
6.14	<0.05	0.17	0.21	0.93
6.15	<0.05	0.077	0.13	0.59
6.170	0.92	0.98	0.24	1.07
6.171	0.92	0.58	0.05	0.23
6.18	0.28	0.27	0.13	0.58
6.23	<0.05	0.21	0.11	0.49
6.26	0.11	0.13	0.09	0.39
6.27	0.13	0.13	0.16	0.72
8.01	0.18	0.17	0.07	0.32
8.02	<0.05	0.12	0.38	1.68
8.12	2	2.9	0.64	2.84
8.13	0.7	0.4	0.1	0.47
8.16	0.45	0.48	0.18	0.82
8.18D	18	8.4	1.11	4.97
8.18F	2.1	1.9	0.43	1.93
9.00	<0.05	0.16	0.08	0.36
9.04-R	0.54	0.57	0.42	1.9
9.04-C	0.1	0.14	0.2	0.89
11.09	4.5	2.3	0.25	1.13

Refinery code	OIW	Sum GCxGC Hydrocarbons	Acute T.U.	Chronic T.U.
	mg/l	mg/l		
12.00	<0.05	0.05	0.08	0.35
12.03	0.07	0.19	0.1	0.46
13.02-S	2.6	3.2	1.65	7.36
13.02-N	0.06	0.1	0.34	1.51
13.02-R	16	34.1	1.86	8.32
13.13	24	23.5	0.87	3.91
14.00	0.18	0.19	0.18	0.82
14.01	1.4	2.9	0.87	3.89
17.00	0.07	0.26	0.24	1.06
21.00	0.08	0.86	0.25	1.11
21.03	0.55	0.73	0.35	1.57
23.00	<0.05	0.065	0.05	0.23
24.03	<0.05	0.035	0.08	0.37
24.04	0.08	0.17	0.32	1.41
25.00	<0.05	0.047	0.1	0.45
27.03	0.14	0.15	0.33	1.48

Table A1.2: Toxic Units calculated for refinery effluents discharging into Marine environment or coastal water bodies

Refinery code	OIW	Sum GCxGC Hydrocarbons	Acute T.U.	Chronic T.U.
	mg/l	mg/l		
2.00	1.1	1.41	0.72	3.2
2.03	0.44	0.09	0.18	0.82
3.01	0.05	0.013	0.1	0.47
4.01	<0.05	0.076	0.09	0.41
5.00	0.1	0.14	0.33	1.48
5.02	0.05	0.06	0.12	0.55
5.05	1.3	1.19	0.65	2.89
5.1	0.14	0.24	0.27	1.2
5.11	1.2	1.1	0.29	1.31
5.12	0.35	0.3	0.11	0.49
5.15	0.07	0.093	0.11	0.48
5.16	0.37	0.22	0.1	0.43
6.10	3.6	1.384	0.1	0.45
6.22	0.18	0.08	0.12	0.52

Refinery code	OIW	Sum GCxGC Hydrocarbons	Acute T.U.	Chronic T.U.
	mg/l	mg/l		
7.00	0.05	0.012	0.1	0.45
7.01	2.1	1.24	0.46	2.06
7.03	0.11	0.05	0.14	0.64
8.03	0.17	0.155	0.27	1.18
8.04-S	0.19	0.21	0.12	0.52
8.07	0.18	0.16	0.31	1.38
8.09	0.05	0.08	0.08	0.34
8.14	<0.05	0.09	0.1	0.43
8.20	1.0	9.03	0.12	0.53
9.01	1.9	1.23	0.18	0.81
9.03R	4.7	8.53	0.97	4.32
10.00	0.44	0.26	0.37	1.67
10.02	1.1	0.96	0.2	0.91
11.00	6.1	4.92	0.74	3.3
11.01	21	24.4	1.51	6.75
11.02	0.37	0.12	0.12	0.52
11.03	0.11	0.16	0.1	0.45
11.04	0.46	0.3	0.2	0.88
11.05	0.12	0.08	0.15	0.67
11.06	0.05	0.02	0.12	0.52
11.07	0.59	0.62	0.22	0.98
12.01	0.24	0.21	0.15	0.66
12.02	0.48	0.31	0.2	0.89
12.04	0.56	0.04	0.1	0.44
13.00A	0.1	0.48	0.35	1.56
13.00B	0.26	0.24	0.31	1.38
13.01	1.6	1.05	0.55	2.48
13.05	0.19	0.26	0.42	1.88
13.07	6.6	3.3	0.82	3.66
13.10	0.05	0.045	0.09	0.41
13.11	0.16	0.057	0.14	0.61
13.12	0.05	0.065	0.15	0.68
13.14	8.7	6.7	0.73	3.27
15.01	0.45	0.31	0.1	0.47
16.00	1.8	1.73	0.5	2.21
24.00	0.05	0.065	0.11	0.5
28.01	1.1	0.88	0.2	0.88

Table A1.3: Toxic Units calculated for refinery effluents discharging to external WWTPs (before the final external treatment)

Refinery code	**OIW**	**Sum GCxGC Hydrocarbons**	**Acute** T.U.	**Chronic** T.U.
	mg/l	mg/l		
1.00	0.08	0.053	0.11	0.5
3.00	13	9.45	1.23	5.49
6.241	7.6	18.64	3.4	15.1
6.242	0.98	3.09	0.71	3.19
8.04-N	9.5	38.3	3.35	14.99
8.15	55	53.3	1.59	7.1
9.02	1.5	2.08	1.17	5.24
9.11	0.32	0.13	0.18	0.8
13.04	21	18.7	1.64	7.32
21.01	28	17.7	2.65	11.84
21.02	12	10.6	0.67	3.01
24.02	9.7	6.55	0.63	2.81

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