Analytical Characterization of Petroleum Substances - Summary and Conclusions, including further work TU283

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This poster is number 2 of a series of 5 posters on the risk assessment of petroleum substances. See also posters TU282, 284, 285 & 286.

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Abstract

CONCAWE has been conducting a programme assessing the risks of petroleum substances to man and the environment to comply with the REACH legislation. The substances have been grouped according to previously agreed categories for classification, with consolidation based on composition and intended use. The approach adopted for assessing the environmental fate and effects of these categories is based on the Hydrocarbon Block Method, which has been used for all categories. The poster will describe the

- Use of GCxGC to generate quantitative data on > 300 hydrocarbon groups and individual constituents
- More detailed characterisation of petroleum UVCB substances to support a revised category justification for REACH purposes
- Use of biomimetic extraction using SPME fibres to screen petroleum substances which have high levels of water soluble hydrocarbons (and hence ecotoxicity)

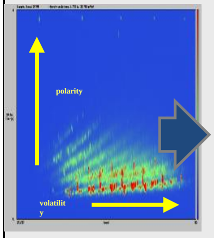
Introduction

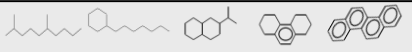
CONCAWE has been involved in the creation and submission of a number of technical dossiers on a wide range of petroleum substances to the European Chemicals Agency (ECHA). ECHA guidelines require the quantitative calculation of risk quotients for environmental and human exposure scenarios, which compare predicted exposure levels and reported "no adverse effect" concentrations. For complex UVCB materials such as petroleum substances, which may contain many thousands of individual constituents, these assessments are much more difficult. This can be circumvented by dividing the composition of these substances into groups of constituents (hydrocarbon blocks) having similar physical-chemical and/or ecotoxicological properties. Meaningful UVCB characterization requires detailed information on the chemical composition of the substances under examination. The range of analytical work carried out is shown below.

Analytical methodologies

Two-dimensional gas chromatography

Detailed two-dimensional gas chromatography (GCxGC) has been carried out on petroleum substances to provide compositional data to support the risk assessments of these substances (Forbes et al., 2006). Following HPLC fractionation of saturated and aromatic constituents, GCxGC was used to generate quantitative data on >300 hydrocarbon groups and individual constituents. This information was used to characterize the distribution of mass among the different chemical classes and carbon number intervals. Structures based on the CONCAWE library, were then used to define and populate the hydrocarbon blocks. The hydrocarbon blocks were subsequently employed in quantitative calculations (i.e. PETROTOX/PETRORISK) (see posters 3 and 4 in this series) to conduct hazard and risk assessments for environmental and human exposure scenarios of the petroleum substances. A wide range of petroleum substance samples collected by CONCAWE has been analyzed using GCxGC. The two-dimensional data set provides a great deal of structured information about hydrocarbon types and concentrations. GCxGC profiles were examined and templates constructed to group individual constituents into the appropriate carbon number (C_5-C_{30}) and hydrocarbon classes (see Figure below).





HB	C#	n-P	i-P	n-CC6	i-N	Di-N	Poly-N	MoAr	NMAr	DiAr	NDiAr	PolyAr
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
1	3-5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	6-8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	9-11	0.1	0.2	0.0	0.3	0.2	0.0	0.1	0.4	0.4	0.1	0.0
4	12-14	2.1	2.9	0.3	3.3	1.6	0.0	1.4	1.6	0.9	0.6	0.3
5	15-17	4.6	9.1	1.1	7.6	4.2	0.0	3.0	2.2	1.0	0.4	0.4
7	etc	"	"	"	"	"	"	"	"	"	"	"

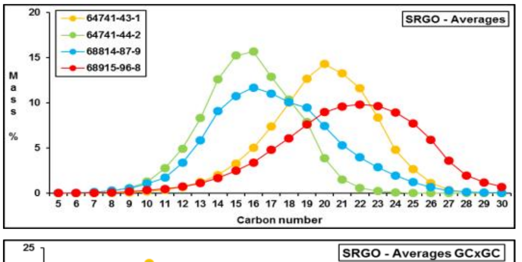
More detailed characterization

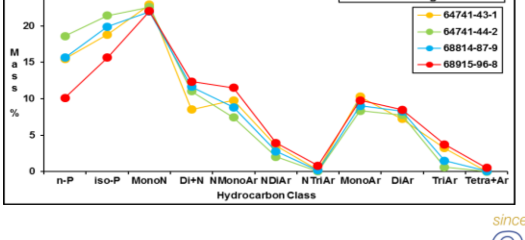
Samples of gas oils, bitumen and residual aromatic extracts (RAEs) have been characterized to identify the specific substances within these substance categories which will be proposed to ECHA for toxicity testing. This analytical work is aimed at supporting revised category justification documents on these substance categories. The analytical programme included:-

Gas oils : Simulated distillation GC (for boiling point and carbon number range), GCxGC (for chemical functionalities and carbon number), HPLC (aromatics) and detailed PAH and PAC analysis

Bitumen/RAE: Simulated distillation GC (for boiling point and carbon number range), detailed PAH analysis and TLC-FID (for saturates, aromatics, resins and asphaltenes).

GCxGC can be used to separate hydrocarbons up to approximately C_{30} making it suitable for the characterisation of gas oils (such as OGO, VHGO and SRGO). Carbon number and hydrocarbon class profiles are similar for the various gas oil substances and support the read-across between these substances. Such testing is deemed necessary to confirm that that the test samples (and their CAS numbers) are aligned with the categories assigned to them. It has also assisted in identifying the "worst case" samples from the various gas oil sub-categories. The average carbon number profile and average hydrocarbon class profile for straight run gas oils (SRGO) using GCxGC is shown below.





Characterization for REACH purposes

CONCAWE has undertaken scientific and technical work to assess the feasibility and potential benefit of characterizing petroleum UVCB substances beyond the recommendations issued by CONCAWE for the substance identification of petroleum substances under REACH. This is based on Member Company experience of the chemical analysis of such substances in support of REACH registration undertaken in 2010.

CONCAWE (2012) proposed that a structured analytical approach be employed for the characterization of petroleum UVCB substances. It has recommended certain analytical techniques (such as GC, SIMDIS GC, HPLC or LC, NMR) are sufficient to characterize materials in each substance category. It is considered that there is no further benefit in applying the full suite of Annex VI analytical techniques

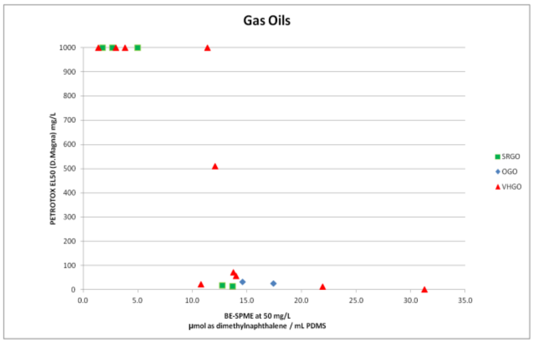
Screening

As part of the CONCAWE test programmes, a biomimetic extraction technique (Parkerton et al., 2001) has proved to be a successful ecotoxicity screening method for Heavy Fuel Oil (HFO) and Aromatic Extract samples enabling the identification of samples with high levels of water-soluble hydrocarbons (i.e. highest toxicity) from those with lower levels or non-detectable amounts (i.e. no/low toxicity)(CONCAWE, 2011). For HFO samples, the available BE-SPME screening data correlated better with the daphnia EC_{50} data than with the algae E_rL50 data.

Samples of gas oils, bitumen and RAEs from the same set used for category justifications were also used to generate biomimetic extraction (BE) data using solid phase microextraction (SPME) fibres. The aims are:

- to confirm that SPME data correlate to Toxic Units predicted by the PETROTOX model using GCxGC compositional data as input
- to strengthen the linkage between composition, SPME data and aquatic toxicity. This would provide a technical basis for further use of SPME as a more practical characterization tool for addressing the influence of variation in substance composition on aquatic toxicity within categories.

A plot of gas oil toxicity determined by BE-SPME versus PETROTOX predictions (based on GCxGC analysis) is shown below. The aim of this screening work was to identify "worst case" gas oil samples for subsequent ecotoxicity testing.



Conclusion

GCxGC is a very powerful technique for the detailed characterization of complex hydrocarbon mixtures. Individual constituents are separated based on both their relative volatility (~25 individual carbon numbers) and polarity (15 different chemical functionalities). GCxGC can provide accurate quantitative information on >300 hydrocarbon groups and individual constituents present in middle-distillate fuels. This is an ideal technique for (a) defining and populating the hydrocarbon blocks which underpin the risk assessments of petroleum substances and (b) identifying the worst case" samples from various petroleum substance categories for subsequent testing.

References

- CONCAWE (2011) "Acute aquatic toxicity of heavy fuel oils: summary of relevant test data", report 7/11, Brussels.
- CONCAWE (2012) "REACH – Analytical characterization of petroleum UVCB substances", Report 7/12, Brussels.
- Forbes et al. (2006) "Application of comprehensive two-dimensional gas-chromatography (GCxGC) for the detailed compositional analysis of gas oils and kerosines". Poster presentation, SETAC Europe, Annual Meeting, The Hague.
- Parkerton et al. (2001) "Biomimetic extraction s a cost-effective analytical tool for determining the aquatic toxicity hazard of complex petroleum products". Poster presentation, SETAC Europe, Annual Meeting, Madrid.