TEXTE
63/2022

Final report

Development of a chemical analysis concept for substances derived from coal and petroleum stream

Identification and quantification of PetCo constituents/constituent groups by means of comprehensive chromatographic analysis.

by:

Majbrit Dela Cruz, Josephine Susanne Lübeck, Jason Patrick Devers, and Jan Henning Christensen
Department of Plant and Environmental Sciences, University of Copenhagen, Copenhagen, Denmark

publisher:
German Environment Agency

German Environment Agency

Umwelt Bundesamt

TEXTE 63/2022

Ressortforschungsplan of the Federal Ministry for the Enviroment, Nature Conservation, Nuclear Safety and Consumer Protection

Project No. (FKZ): 3718 65 426 0

Report No. (UBA-FB): FB000736/ENG

Final report

Development of a chemical analysis concept for substances derived from coal and petroleum stream

Identification and quantification of PetCo constituents/constituent groups by means of comprehensive chromatographic analysis.

by

Majbrit Dela Cruz, Josephine Susanne Lübeck, Jason Patrick Devers, and Jan Henning Christensen

Department of Plant and Environmental Sciences, University of Copenhagen, Copenhagen, Denmark

On behalf of the German Environment Agency

Imprint

Publisher
Umweltbundesamt
Wörlitzer Platz 1
06844 Dessau-Roßlau
Tel: +49 340-2103-0
Fax: +49 340-2103-2285
buergerservice@uba.de
Internet: www.umweltbundesamt.de

/umweltbundesamt.de
/umweltbundesamt

Report performed by:
Department of Plant and Environmental Sciences, University of Copenhagen
Thorvaldsensvej 40
1871 Frederiksberg C
Denmark

Report completed in:
November 2021

Edited by:
Section IV 2.3 Chemicals
Dr. Ivo Schliebner und Dr. Eva-Maria Burkhardt (Fachbegleitung)

Publication as pdf:
http://www.umweltbundesamt.de/publikationen

ISSN 1862-4804

Dessau-Roßlau, June 2022

Abstract: Development of a chemical analysis concept for substances derived from coal and petroleum stream

Characterisation of petroleum and coal (PetCo) based substances and products is currently challenging due to the lack of standard analytical methods that can adequately address the complexity of the substances and products. The aim of this project was therefore to develop an analytical concept to be applied on a selection of PetCo products, to identify those constituents or constituent groups that might be of concern for the environment and human health. Three analytical platforms were developed and validated for a total of 128 constituents and 46 constituent groups representing saturates, aromatics, SPACs, OPACs, NPACs and acids. The three analytical platforms were GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS. The validation of the methods showed excellent results and all methods are applicable for constituents present at low ppb levels in PetCo products.

A literature review of PetCo products was conducted and five PetCo products were chosen that represented a wide spectrum of constituents and constituent groups present in PetCo products. The five PetCo products were asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil and a total of 24 samples were analysed by the three analytical platforms. The chemical analysis revealed great variability in chemical composition and total concentration of constituents and constituent groups, both within and between product types. The largest fraction of any sample that was quantified reached 36 % (w/w).

The recommendation from this project is to use both GC×GC-HRMS and SFC-ESI-HRMS for the quantification of target constituents and constituent groups in PetCo producst as these two methods combined will cover the largest number of constituents present in PetCo products.

Kurzbeschreibung: Entwicklung eines Analytik-Konzepts für Stoffe aus Erdöl- und Kohlefraktionen

Die Charakterisierung von erdöl- und kohlehaltigen Stoffen und Erzeugnissen ist derzeit herausfordernd, da keine standardisierten Analysemethoden verfügbar sind, die der Komplexizität der Stoffe und Produkte gerecht werden können. Ziel dieses Projekts war es daher, einen analytischen Ansatz zu entwickeln, der auf eine Auswahl von Erdöl- und Kohleprodukten angewendet werden kann und dabei diejenigen Konstituenten (engl. constituents) oder Konstituentengruppen (engl. constituents groups) zu identifizieren, die für die Umwelt und die menschliche Gesundheit besorgniserregend sein könnten. Es wurden drei Analyseplattformen verwendet und für insgesamt 128 Konstituenten und 46 Konstituentengruppen validiert. Die Gruppen repräsentieren gesättigte Kohlenwasserstoffe, Aromaten, schwefelhaltige polyaromatische Kohlenwasserstoffe (SPACs) sauerstoffhaltige (O)PACs, stickstoffhaltige (N)PACs und Säuren. Die drei analytischen Plattformen waren GC-MS/SIM, GC×GC-HRMS und SFC-ESI-HRMS. Die Validierung der Methoden ergab ausgezeichnete Ergebnisse, und alle Methoden eignen sich für Inhaltsstoffe, die in PetCo-Produkten in niedrigen ppb-Werten vorhanden sind.

Basierend auf einer detaillierten Literaturrecherche zu PetCo-Produkten wurden fünf PetCo-Produkte für weitere Analysen ausgewählt, die ein breites Spektrum von Konstiuenten und Konstiuentengruppen in PetCo-Produkten repräsentieren. Bei den fünf PetCo-Produkten handelte es sich um Asphalt, Autowachs/Politur, Kohlenteer, Schmieröl und Reifenpyrolyseöl. Insgesamt wurden 24 Proben mit Hilfe der drei Analyseplattformen untersucht. Die chemische Analyse ergab eine große Variabilität in der chemischen Zusammensetzung und der Gesamtkonzentration von Konstituenten und Konstituentengruppen, sowohl innerhalb als auch zwischen den Produkttypen. Die größte Fraktion, die in einer der Proben quantifiziert wurde, erreichte 36 %. (w/w).

Dieses Projekt empfiehlt GC×GC-HRMS als auch SFC-ESI-HRMS für die Quantifizierung von Konstituenten und Konstituentengruppen in PetCo-Produkten zu verwenden, da beide Methoden zusammen die größte Anzahl von Bestandteilen in PetCo-Produkten erfasst.

Table of content

List of figures

List of tables

List of abbreviations

Abbreviation	
ACN	Acetonitrile
AP	Analyte protectant
AspLub	Asphalt and lubricating oil mixture
C_x	Degree of alkylation, where x denotes the number of carbons in alkyl group
CTPO	Coal tar and tyre pyrolysis oil mixture
d_F	Film thickness
DCM	Dichloromethane
DL	Detection limit
EC	European Commission
ECHA	The European Chemical Agency
ESI	Electrospray ionisation
ESI^-	Negative electrospray ionisation
EURL	European Union reference laboratory
FID	Flame ionisation detection
GC	Gas chromatography
GC×GC	Comprehensive two-dimensional gas chromatography
HMW	High molecular weight
HPLC	High-performance liquid chromatography
HRMS	High-resolution mass spectrometry
IAF	Isomer abundance factor
ID	Internal diameter
IS	Internal standard
L	Length
LC	Liquid chromatography
LOQ	Limit of quantification
MeOH	Methanol
MS	Mass spectrometry
m/z	Mass-to-charge ratio
N/A	Not available

Abbreviation	
NIST	National Institute of Standards and Technology
NPAC	Nitrogen containing polycyclic aromatic constituent
ON	Oxygen- and nitrogen-containing constituents (F3)
OPAC	Oxygen containing polycyclic aromatic constituent
PAC	Polycyclic aromatic constituent
PAH	Polycyclic aromatic hydrocarbon
PBT	Persistent, bioaccumulative and toxic
PE	Polyethylene
PetCo	Petroleum and coal
PTFE	Polytetrafluoroethylene
Q1	First quartile
Q3	Third quartile
QC	Quality control
qTOF	Quadrupole time-of-flight (MS detector)
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RR	Relative response
SAR	Saturates, aromatics and resins
SAS	Saturates, aromatics and sulfur-containing constituents (F1+F2)
SCAN	Scan acquisition mode
SFC	Supercritical fluid chromatography
SIC	Selected ion chromatogram
SIM	Selected ion monitoring
SPAC	Sulphur containing polycyclic aromatic constituent
SVHC	Substance of very high concern
t_R	Retention time
UVCB	Unknown or variable composition, complex reaction products or biological material
vPvB	Very persistent and very bioaccumulative

Summary

The aim of this project was to develop an analytical strategy that can be applied to a wide range of petroleum and coal (PetCo) based products and substances, considering their complex chemical composition. This strategy was applied to five PetCo product types to identify and quantify constituents in these products of potential cause environmental and human health concern. The proposed strategy relies on the following three methods:

1) A one-dimensional gas chromatography mass spectrometry (GC-MS) method with selected ion monitoring (SIM)
2) A two-dimensional GC (GC×GC)-high resolution (HR) MS method to ensure improved selectivity and low detection limits
3) A supercritical fluid chromatography (SFC)-electrospray ionisation (ESI)-HRMS method to detect substances that are not easily analysed by gas chromatographic methods.

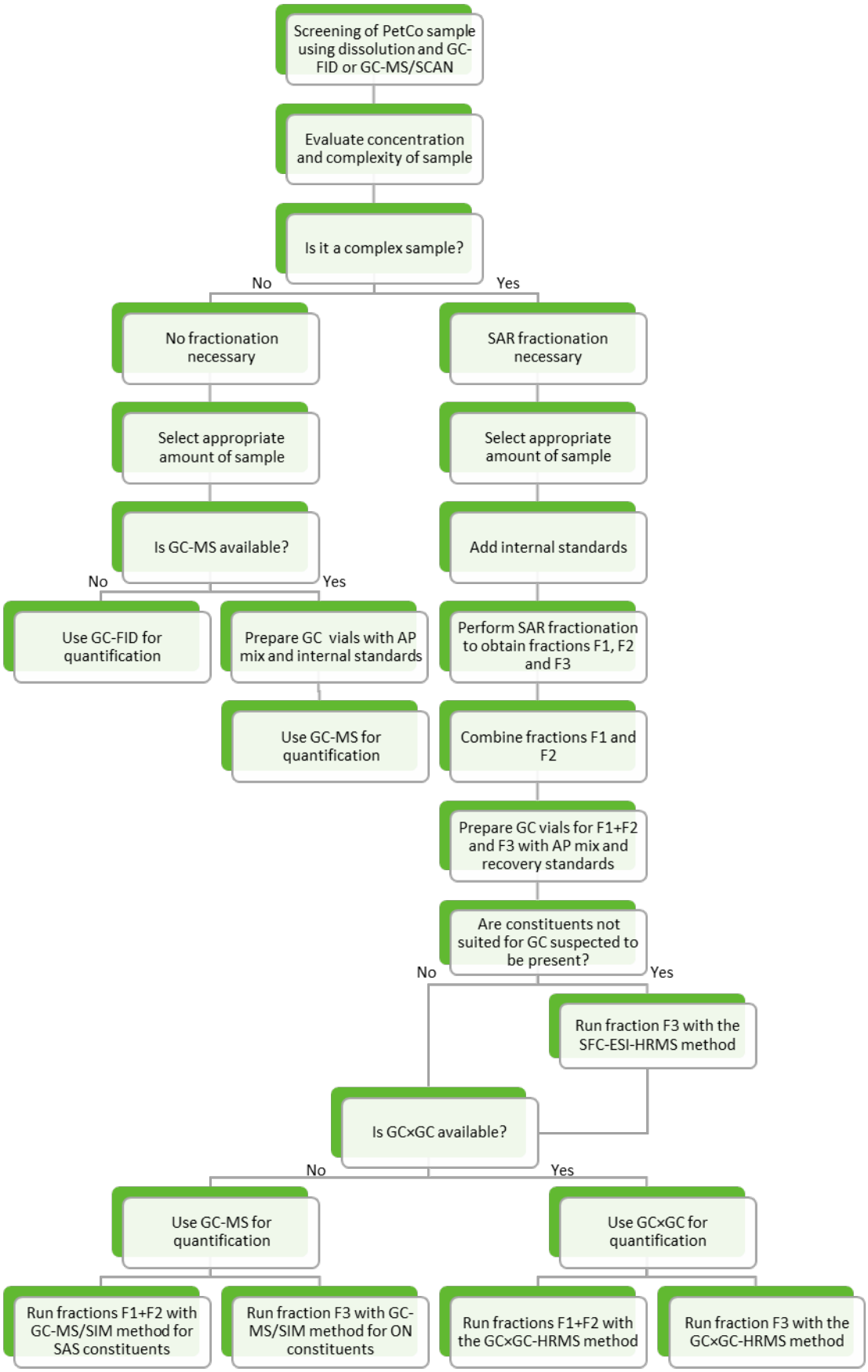
The three methods combined covered saturates, aromatics, N-, O-, S-heterocyclic polycyclic aromatic constituents (NPACs, OPACs and SPACs), and acids. In total, 128 constituents and 46 constituent groups were targeted by the three methods.

An overview of the analytical workflow is shown in Figure 1. The first step in analysis of a PetCo product is to screen the sample by GC-MS/SCAN (scan acquisition mode) or GC-FID (flame ionisation detector). The purpose of this screening is to evaluate the chemical complexity of the sample and the concentration range of the target constituents. If the sample does not appear to be chemically complex, the next step is to prepare the sample for the quantification of target constituents by GC-MS or GC-FID. The concentration range of the target constituents should be evaluated to select an appropriate amount of sample as well as to aid constructing calibration standards to fit the concentration range of the target constituents. If GC-MS is used, a mixture of analyte protectants (APs) and internal standards (IS) is added to the sample.

If the PetCo sample is chemically complex we recommend to fractionate the sample into saturates, aromatics and resins (SAR) prior to chemical analysis. As especially aromatics can constitute a large part of the constituents in PetCo products, they can confound the analysis of NPACs and OPACs, and SAR fractionation is therefore necessary. Based on the screening results, an IS mixture (at relevant concentration, based on screening results) is added to an appropriate amount of sample and the sample is prepared for SAR fractionation. Standards and AP mixture are subsequently added to each fraction, which is then preferably analysed by GC×GC-HRMS. In addition, if the sample contains constituents that cannot be analysed by GC, fraction F3 should be analysed by SFC-ESI-HRMS. The nature of the sample or the results of the screening step can be used to make a decision on the need to use SFC-ESI-HRMS.

For the analysis of a batch of samples, we recommend to prepare quality control (QC) samples that are a mixture of selected samples representing the batch. If the batch consists of similar samples, the samples for the QC mixture should be selected randomly. The QC samples are used to verify instrument stability during a sequence.

Figure 1: Flow diagram for sample preparation and chemical analysis of PetCo products



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

All methods were validated based on detection limit (DL), limit of quantification (LOQ), linearity, instrument precision, and QC precision and the GC-MS/SIM method was further validated based on accuracy, recovery, and method precision. Each of the three methods is applicable for constituents and constituent groups at the low ppb levels.

The three methods developed in this project were tested on 24 PetCo samples representing five types of PetCo products. The five types of PetCo products were: Coal tar, tyre pyrolysis oil, lubricating oil, car wax/polish, and asphalt. The products were selected to cover a wide range of chemical constituents that is expected to be present in PetCo products. The target constituents and constituent groups quantified herein cover a boiling range of 181 – 550 °C.

The highest concentration of target constituents and constituent groups was found in coal tar and tyre pyrolysis oil reaching a total concentration of up to 364 mg/g. The product type with the overall lowest concentration of target constituents and constituent groups was asphalt. A high variability in chemical constituents was observed for some product types, especially for lubricating oils.

It was further investigated if any of the samples contained constituents from the REACH candidate list in concentrations above 0.1 % (w/w). This was the case for anthracene, benzo[a]anthracene, chrysene, fluoranthene, phenanthrene and pyrene in CT4 and CT5 as well as benzo[ghi]perylene and benzo[k]fluoranthene in CT5. These two samples were also by far the samples with the highest total concentration of constituents and constituent groups.

Our analysis focused in particular on constituents and constituent groups that could lead to concern for the environment and human health. Most of the constituents of a sample therefore are not quantified. However, it was found that relevant knowledge about the composition of a PetCo substance for an assessment can be obtained using a combination of GC×GC-HRMS and SFC-ESI-HRMS. The combination of both methods allows the maximum possible number of constituents and constituent groups to be quantified.

Zusammenfassung

Ziel dieses Projekts war es, eine Analysestrategie zu entwickeln, die auf eine breite Palette von Produkten und Stoffen auf Erdöl- und Kohlebasis (PetCo) unter Berücksichtigung ihrer komplexen chemischen Zusammensetzung angewende werden kann. Diese Strategie wurde auf fünf PetCo-Produkttypen angewandt, um jene Konstituenten in diesen Produkten zu identifizieren und zu quantifizieren, die möglicherweise zu einer Besorgnis für die Umwelt und menschlichen Gesundheit führen könnten. Die vorgeschlagene analytische Strategie stützt sich auf die folgenden drei Methoden:

1) eindimensionale Gaschromatographie-Massenspektrometrie-Methode (GC-MS) im *Selected Ion Monitoring*-Modus (SIM)
2) zweidimensionale GC (GC×GC) in Kombination mit hochauflösender Massenspektrometrie (*high resulution mass sprectroscopy* HRMS), die eine verbesserte Selektivität und niedrigere Nachweisgrenzen gewährleistet
3) überkritische Flüssigkeitschromatographie (SFC)-in Kombination mit Elektrospray-Ionisation (ESI)-HRMS zum Nachweis von Substanzen, die mit gaschromatographischen Methoden nicht leicht zu analysieren sind

Die Kombination der drei Methoden zusammen erlaubten die Analyse gesättigter Kohlenwasserstoffe, Aromaten, N-, O- und S-heterozyklische polyzyklische aromatische Konstituenten (NPACs, OPACs und SPACs) und Säuren. Insgesamt wurden 128 Konstituenten und 46 Konstituentengruppen mit den drei Methoden untersucht. Eine Übersicht über den analytischen Arbeitsablauf ist in Abbildung 1 dargestellt. Der erste Schritt bei der Analyse eines PetCo-Produkts ist ein Screening der Probe mittels GC-MS/SCAN oder GC-FID (Flammenionisationsdetektor). Der Zweck dieses Screenings besteht darin, die chemische Komplexität der Probe und den Konzentrationsbereich der Zielbestandteile zu bewerten. Erweist sich die Probe als chemisch nicht komplex, besteht der nächste Schritt darin, die Probe für die Quantifizierung der Zielbestandteile mittels GC-MS oder GC-FID vorzubereiten. Der Konzentrationsbereich der Zielbestandteile sollte bewertet werden, um eine geeignete Probenmenge auszuwählen und Kalibrierstandards zu erstellen, die dem Konzentrationsbereich der Zielbestandteile entsprechen. Wenn GC-MS verwendet wird, wird der Probe eine Mischung aus Analytschutzmitteln (*Analyte Protectants* APs) und eine Mischung aus internen Standards (IS) zugesetzt.

Ist die PetCo-Probe chemisch komplex, empfehlen wir vor der chemischen Analyse eine Fraktionierung der Probe in gesättigte Kohlenwasserstoffe, Aromaten und Harze (SAR). Da insbesondere Aromaten meist für einen großen Teil der Konstituenten in PetCo-Produkten verantwortlich sind, können diese die Analyse von NPACs und OPACs verdecken und deshalb eine SAR-Fraktionierung erforderlich machen. Auf der Grundlage der Screening-Ergebnisse wird eine geeignete Menge der Probe einem IS-Gemisch zugesetzt. Die Probe wird mittels der SAR-Fraktionierung prozessiert. Standards und AP-Mix werden anschließend jeder Fraktion zugesetzt und vorzugweise mittels GC x GC – HRMS analysiert. Sollten die Proben Konstiuenten enthalten, die nicht mittels GC zu analysieren sind, ist die Fraktion F3 zudem mittels SFC-ESI-HRMS zu analysieren. Die Natur der Probe oder die Ergebnisse des Screening-Schrittes können für einen Entscheidung zur Notwendigkeit der SFC-ESI-HRMS Methode herangezogen werden.

Für die Analyse einer Probenserie wird empfohlen, Qualitätskontrollproben (QC-Proben) vorzubereiten, die aus einer Mischung ausgewählter Proben der Analyse-Sequenz bestehen. Wenn die Charge aus ähnlichen Proben besteht, sollten die Proben für den QC-Mix zufällig

ausgewählt werden. Die QC-Proben werden verwendet, um die Stabilität des Geräts während einer Sequenz zu überprüfen.

Alle Methoden wurden auf der Grundlage von Nachweisgrenze (DL), Bestimmungsgrenze (LOQ), Linearität, Gerätepräzision und QC-Präzision validiert, und die GC-MS/SIM-Methode wurde auf der Grundlage von Genauigkeit, Wiederfindung und Methodenpräzision weiter validiert. Jede der drei Methoden ist für Konstituenten und Konstituentengruppen im niedrigen ppb-Bereich anwendbar.

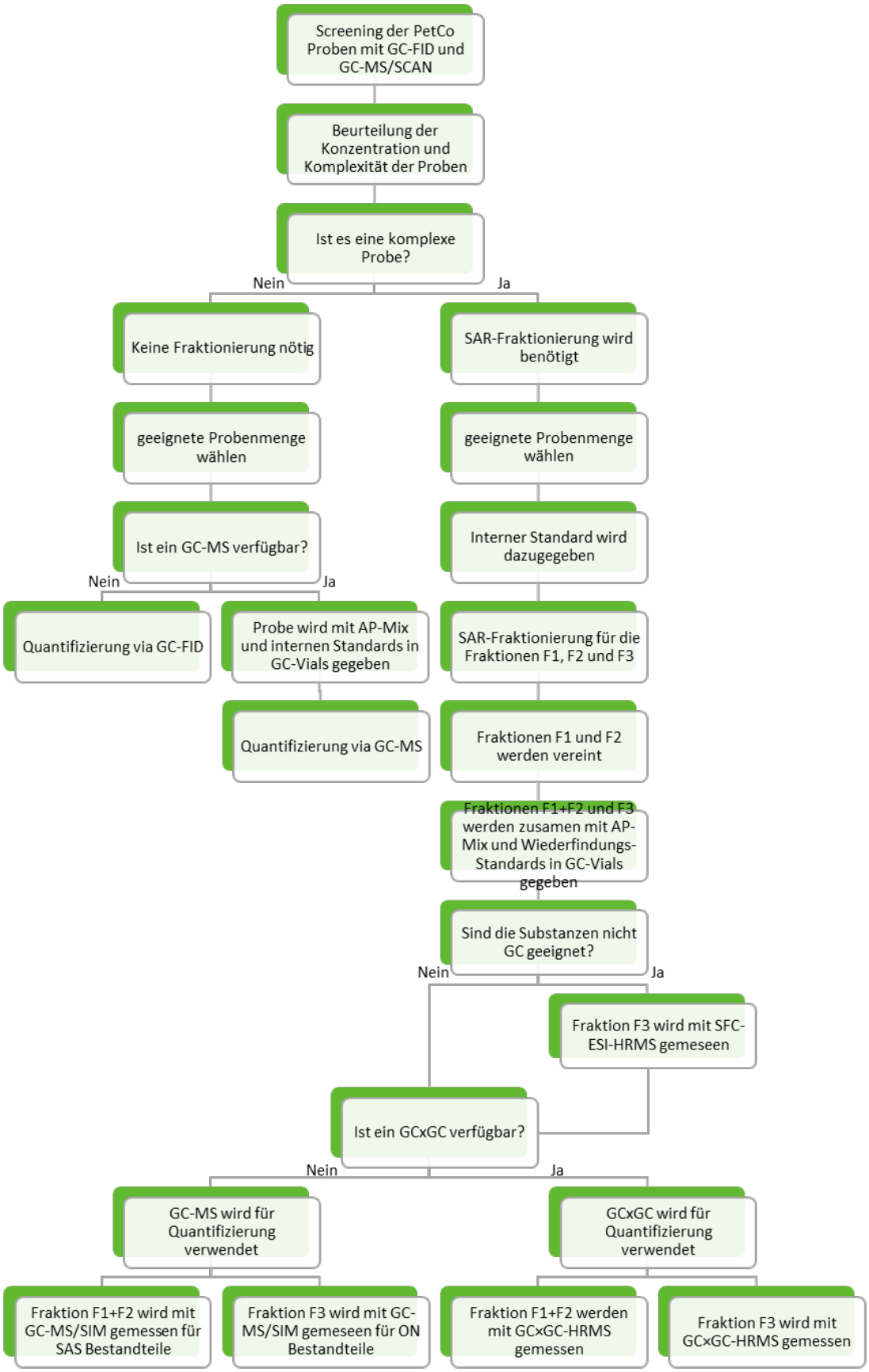
Die drei in diesem Projekt entwickelten Methoden wurden an 24 PetCo-Proben getestet, die fünf PetCo-Produkte repräsentieren. Die fünf PetCo-Produkte waren: Steinkohlenteer, Reifenpyrolyseöl, Schmieröl, Autowachs/Politur und Asphalt. Die Produkte wurden ausgewählt, um ein breites Spektrum an chemischen Konstituenten abzudecken, die in PetCo-Produkten zu erwarten werden. Die hier quantifizierten Konstituenten und -gruppen deckten einen Siedebereich von 181 - 550 °C ab.

Die höchste Konzentration an Zielkonstituenten und -gruppen wurde in Steinkohlenteer und Reifenpyrolyseöl gefunden, mit einer Gesamtkonzentration von bis zu 364 mg/g. Der Produkttyp mit der insgesamt niedrigsten Konzentration von Konstituenten und Konstituentgruppen war Asphalt. Bei einigen Produkttypen, insbesondere bei Schmierölen, wurde eine hohe Variabilität der chemischen Bestandteile beobachtet.

Es wurde weiter untersucht, ob eine der Proben Stoffe (Konstituent) der REACH-Kandidatenliste in Konzentrationen von über 0,1 % (w/w) enthielt. Dies wurde bestätigt sowohl für Anthracen, Benzo[a]anthracen, Chrysen, Fluoranthen, Phenanthren und Pyren in Proben CT4 und CT5, als auch für Benzo[ghi]perylen und Benzo[k]fluoranthen in CT5. Beiden Proben aus Steinkohlenteer wiesen die mit Abstand höchsten Gesamtkonzentration an untersuchten Konstituenten und Konstituentgruppen auf.

Unsere Analyse fokussierte sich insbesondere auf Konstituenten und Kostituentgruppen, die zu einem Besorgnis für die Umwelt und menschliche Gesundheit führen könnten. Demnach bleiben die meisten Konstituenten einer Probe nicht quantifiziert. Es zeigte sich jedoch, dass sich für eine Bewertung relevantes Wissen über die Zusammensetzung eines PetCo-Stoffes mittels einer Kombination aus GC×GC-HRMS und SFC-ESI-HRMS gewinnen lässt. Die Kombination beider Methoden erlaubt die höchstmögliche Anzahl an Konstituenten und Konstituentgruppen zu quantifizieren.

Abbildung 1: Flussdiagramm zur Probenvorbereitung und chemischen Analyse von PetCo-Produkten



Quelle: Eigene Darstellung, Institut für Pflanzen- und Umweltwissenschaften, Kopenhagen Universität.

1 Introduction

The European Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH, Regulation (EC) No 1907/2006) aims to improve the protection of both human health and the environment. Manufacturers and importers of chemicals must submit a registration dossier to The European Chemical Agency (ECHA) for all substances manufactured or imported in quantites greater than one tonne per company per year. In this dossier, companies must identify the risks linked to the substance as well as the management of the risks. Furthermore, for substances registered in quantities over 10 tonnes, a chemical safety assessment must be performed if, for example, it is known to contain a substance of very high concern (SVHC) at a concentration above 0.1% (w/w).

REACH ensures that the hazard posed by SVHCs are controlled and that SVHCs are replaced by alternatives where feasible. Substances may be identified as SVHC if they 1) are carcinogenic, mutagenic or toxic for reproduction, 2) are persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB), or 3) cause the equivalent level of concern as in 1) or 2) [1].

Once a substance is identified as a SVHC, it is included in the REACH candidate list for eventual inclusion in the authorisation procedure. ECHA may then prioritise the substance for inclusion in Annex XIV (list of substances subject to authorisation). Substances in the authorisation list are regulated. However, authorisation to use the substance may be granted by the European Commission (EC) if it can be verified that the substance can be adequately controlled or that the socio-economic benefits are greater than the risks to human health and the environment [1].

Substances of complex chemical composition can be difficult to register due to their sheer complexity and the fact that the exact chemical composition is unknown. Such substances can be classified as substances of unknown or variable composition, complex reaction products or biological materials (UVCB) [2]. Petroleum and coal (PetCo) based substances or products may be classified in this category. The identification of the individual substances in PetCo products is hampered by their chemical complexity. Practically, to ensure appropriate registration, it needs to be known whether a complex PetCo substance or product contains a SVHC at concentrations above 0.1% (w/w). If this is the case, then the entire complex PetCo susbtance or product would be designated as a SHVC. Such information on composition is rarely available in REACH registrations of complex PetCo substances or products.

PetCo products can be substances such as tyre pyrolysis oil, lubricating oils, car wax, and asphalt. The overall composition of some PetCo products are known. For example, asphalt is mainly composed of polar organic constituents of high molecular weight that contain a large number of heteroatoms [3], petroleum lubricants are usually rich in cyclic aliphatic hydrocarbons or branched alkanes [4], and waxes either consist mainly of straight-chained alkanes or branched and cyclic alkanes [5]. However, the composition of the individual constituents in the PetCo products is largely unknown.

Few standard methods exist for the detailed analysis of specific constituents in PetCo products. Concawe recommends methods for characterisation of petroleum UVCB substances for REACH registration purposes [6]. Here three methods are listed for the analysis of individual components with a maximum boiling point of 225 °C. All three methods are based on gas chromatography (GC).

Methods for quantitative analysis of, for example, polycyclic aromatic hydrocarbons (PAHs) can be found for various matrices [7], but to our knowledge no standard methods exist for

quantification of a larger range of individual organic constituents of different chemical classes with a boiling point >225 °C in PetCo products.

It is therefore necessary to expand the current analytical methods and introduce new ones to aid in the identification and quantification of relevant constituents in UVCB substances in general and in PetCo products or substances specifically. The aim of this study was to develop an analytical concept which can be applied to a wide spectrum of PetCo-based products or substances, considering their complex composition, and to identify and quantify constituents in the products which may pose a concern to environmental or human health.

This report describes the selection of five PetCo products (Chapter 2) and presents the sample preparation including the preparation of calibration standards, quality control samples and sequence set-up for chemical analysis (Chapter 3). Chapter 4 describes the analytical methods while method validation is presented in Chapter 5. A method comparison is carried out in Chapter 6 and the PetCo products are characterised in Chapter 7. Finally, Chapter 8 presents the concluding remarks and recommendations for the analysis of PetCo products.

2 Selection of PetCo products

A literature review was carried out where eleven products were identified that cover a wide range of PetCo products and their chemical composition (Table 1). The selection covered intermediate products (i.e. products that require further processing before arriving at the final consumer) and finished products (i.e. products that are available for the consumer). Of the eleven products, the following five selected PetCo products were included in this project:

- asphalt (semi-solid or highly viscous form of petroleum mixed with, for example, sand)
- car wax/polish (liquid or paste used for car mainetenance)
- coal tar (thick liquid formed as by-product from coke and coal gas production)
- lubricating oil (high boiling point petroleum based oil used to reduce friction)
- tyre pyrolysis oil (a fraction formed during pyrolysis of waste tyres)

The five PetCo products were chosen to limit the sample load as well as still representing a wide range of PetCo products and ensuring that product types with expected high concentrations of relevant constituents were available.

Table 1: Eleven PetCo products screened to cover the wide range of PetCo products and their chemical composition

Products highlighted in ***bold italic*** were selected for detailed analysis in this project.

Material of origin	Intermediate/finished product	Finished product
Petroleum or coal	***Coal tar***	***Lubricating oil***
	Recycled tyres/***tyre pyrolysis oil***	Resilient flooring material
	Bio-pyrolysis oil	***Car wax/polish***
		Asphalt/*bitumen*
		Plastic bag
		Food-contact material
		Motor oil

In total, 24 samples were acquired representing the five PetCo products with details given in Table 2. The sample set was comprised of five coal tars, one tyre pyrolysis oil, eight lubricating oils, five car waxes/polishes, and five asphalts.

Table 2: Sample set for quantitative analysis

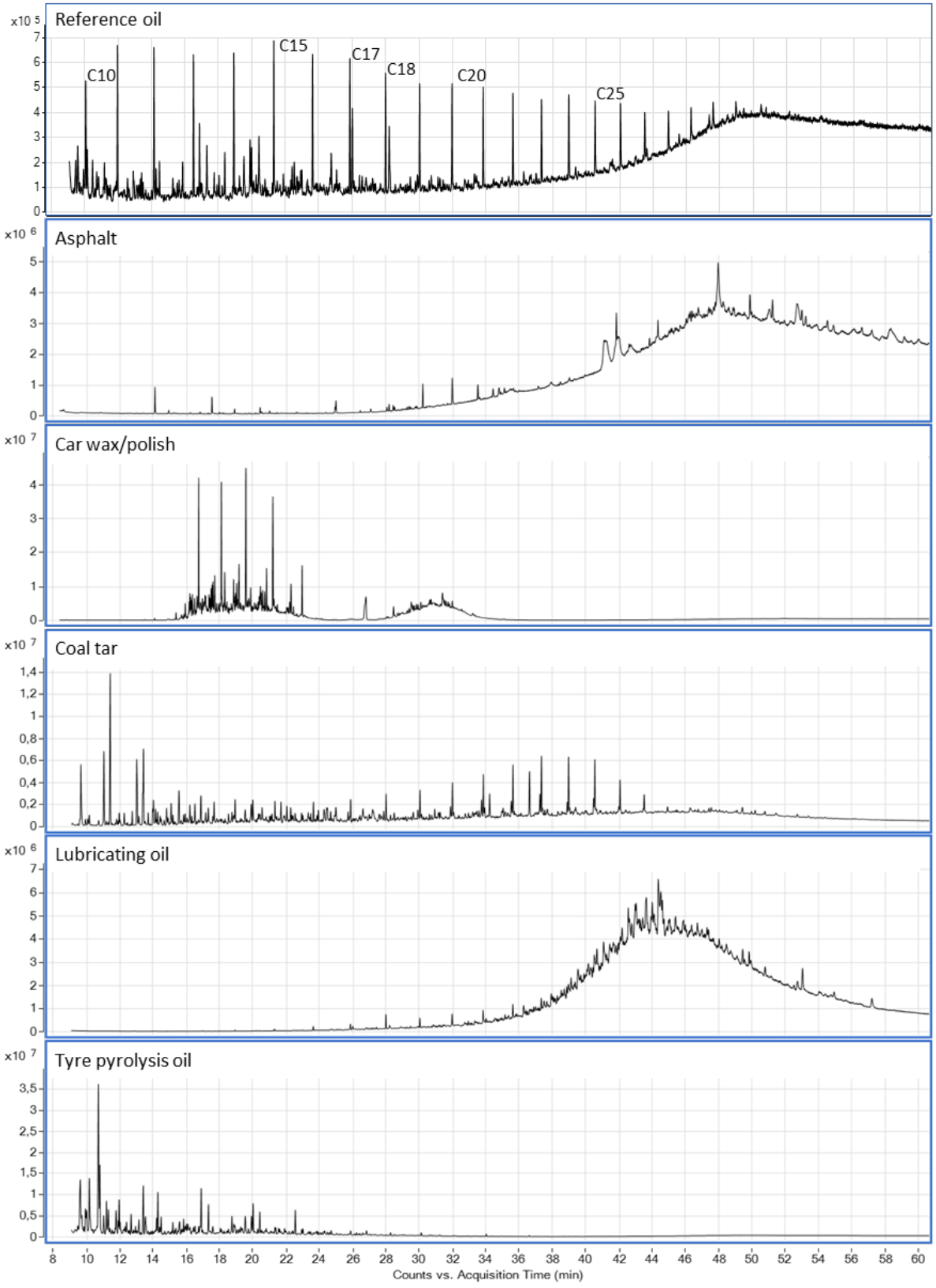
Product type	Abbreviation	Sample name	Producer	Provider
Asphalt	Asp1	Asphalt (Copenhagen)	N/A	Josephine Lübeck
Asphalt	Asp2	Asphalt (Berlin)	N/A	Josephine Lübeck
Asphalt	Asp3	Asphalt (Utterslev Mose)	N/A	Josephine Lübeck
Asphalt	Asp4	Asphalt (Finsensvej)	N/A	Josephine Lübeck
Asphalt	Asp5	Asphalt (Nydamvej)	N/A	Anita Sandager
Car wax/polish	CWP1	Meguiar´s Glass polishing	Meguiar's Inc., Mitchell South, CA, USA	Local shop in Frederiksberg, Denmark

Product type	Abbreviation	Sample name	Producer	Provider
Car wax/polish	CWP2	Sadolin slipol (abrasive polish)	AkzoNobel Deco A/S, København V, Denmark	Local shop in Frederiksberg, Denmark
Car wax/polish	CWP3	Bumper shine	Royal Dutch Shell Plc., The Hague, The Netherlands	Local shop in Frederiksberg, Denmark
Car wax/polish	CWP4	Top coat sealer	BASTA ACTIVE CAR CARE A/S, Kolding, Denmark	Local shop in Frederiksberg, Denmark
Car wax/polish	CWP5	Car wax	Royal Dutch Shell Plc., The Hague, The Netherlands	Local shop in Frederiksberg, Denmark
Coal tar	CT1	CHG.X.SB TR1 (unfiltered)	N/A	Haldor Topsøe A/S, Kongens Lyngby, Denmark
Coal tar	CT2	TT.X.LO.B2 TR2 (filtered)	N/A	Haldor Topsøe A/S, Kongens Lyngby, Denmark
Coal tar	CT3	Coal tar 2020593014	N/A	Haldor Topsøe A/S, Kongens Lyngby, Denmark
Coal tar	CT4	Coal tar 2020593025	N/A	Haldor Topsøe A/S, Kongens Lyngby, Denmark
Coal tar	CT5	Coal tar 2020593036	N/A	Haldor Topsøe A/S, Kongens Lyngby, Denmark
Lubricating oil	Lub1	Ship 9-0523	N/A	University of Copenhagen, København K, Denmark
Lubricating oil	Lub2	Comma X-Flow Type MF 15W-40	Moove Lubricants Limited, Kent, England	Bildeleshop.dk, Partex Global GmbH, Berlin, Germany
Lubricating oil	Lub3	10W-40 for Motorbike	LIQUI MOLY GmbH, Ulm, Germany	Bildeleshop.dk, Partex Global GmbH, Berlin, Germany
Lubricating oil	Lub4	Elf Evolution 500 Turbo Diesel 15W-40	Total SE, Paris la Défense cedex, France	Bildeleshop.dk, Partex Global GmbH, Berlin, Germany
Lubricating oil	Lub5	M342_2020_2101_4	N/A	Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg, Germany
Lubricating oil	Lub6	Shell Naturelle lS4 Gear Fluid 150	Royal Dutch Shell Plc., The Hague, The Netherlands	Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg, Germany
Lubricating oil	Lub7	Shell Naturelle HF-E32	Royal Dutch Shell Plc., The Hague, The Netherlands	Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg, Germany
Lubricating oil	Lub8	Shell Gadinia S340	Royal Dutch Shell Plc., The Hague, The Netherlands	Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg, Germany
Tyre pyrolysis oil	TP1	Tyre pyrolysis oil	Haldor Topsøe A/S, Kongens Lyngby, Denmark	Haldor Topsøe A/S, Kongens Lyngby, Denmark

The samples were screened to evaluate the complexity of the products. The screening was performed using a GC-MS/SCAN method with similar parameters as the GC-MS/SIM method described in Section 4.1, except SCAN mode was used, to provide spectral information for the constituents present. Examples of the screening results for each product type are shown in Figure 2 along with a reference oil with a number of n-alkanes marked for retention index comparison.

Figure 2: GC-MS/SCAN chromatograms of five PetCo products and a reference oil

The reference oil is marked with a number of alkanes for retention index comparison.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Based on the screening results, the overall composition of the five PetCo products was largely characterised (Table 3).

Table 3: Chemical characterisation of the five PetCo products based on screening by GC-MS/SCAN

*HMW – high molecular weight

	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
Aliphatic hydrocarbons	Low	High	High	High	Low
Aromatic hydrocarbons	High	Low	High	High (not HMW* PAHs)	High
Heterocyclic constituents	High	Low – Medium	High	Low – high	High

3 Sample preparation

Two sample preparation approaches are presented for the analysis of PetCo products: 1) sample dissolution and 2) SAR fractionation. The sample preparation and analytical methods target specific groups of constituents, i.e. saturates, aromatics, and heterocyclic polycyclic aromatic constituents (PACs) containing sulphur, oxygen, or nitrogen (SPACs, OPACs, and NPACs, respectively).

3.1 Chemicals and other materials

Solvents such as heptane, hexane, methanol (MeOH), and dichlorometane (DCM) were of high-performance liquid chromatography (HPLC) grade or better to reduce interferences. Ottawa sand and glassware (fractionation columns, vials, etc.) were heated overnight at 550 and 450 °C, respectively, before use to remove potential contamination. Silica 60 (0.063-0.200 mm) was activated for 15 h at 180 °C. Polyethylene (PE) frits were sonicated three times in DCM for 10 min and dried before use.

3.2 Sample dissolution

Dissolution with subsequent chemical analysis can be used to screen a PetCo product. Thus, the chemical complexity of the sample can be assessed and the amount of sample for SAR fractionation can be adjusted if necessary. In this way, the output from a quantitative analysis of the product can be optimised.

Screening of PetCo products can be performed by GC with either FID or MS detection in SCAN acquisition mode. The screening procedure has several purposes:

a) The PetCo products are screened for concentration ranges and whether the PetCo product needs to be diluted or enriched for the quantitative analysis.

b) It can be evaluated whether fractionation and/or GC×GC analysis is necessary, for example if a product's main composition is complex and contains hundreds of peaks, or if the chromatogram is relatively simple and peaks are easily separated. In addition, if it is suspected that the product contains non-volatile constituents that cannot be analysed by GC, alternative analytical methods such as liquid chromatrography (LC) or SFC might be more applicable. These methods can be utilised with the purpose of detecting constituents that are not GC-amenable.

c) When screening is performed by GC-MS/SCAN, a first estimate of the content of the PetCo product can be made by identification and matching of prominent peaks in a library (for example the National Institute of Standards and Technology (NIST) MS library). Thereby, the quantification method with GC-MS/SIM can be adapted by adding ions of interest to the method.

For sample dissolution, 12.5 mg of product was dissolved in 5 mL of DCM. Samples with low complexity where SAR fractionation is not necessary, for example samples in which the aromatic and resin fractions are only present as a few well-resolved constituents, may be diluted to 1.5 µL/mL in DCM and filtered (through a glass wool plug or 0.2 µM polytetrafluoroethylene (PTFE) filter). Subsequently, they can be directly injected in GC- or GC×GC systems coupled to MS or FID.

3.3 SAR fractionation

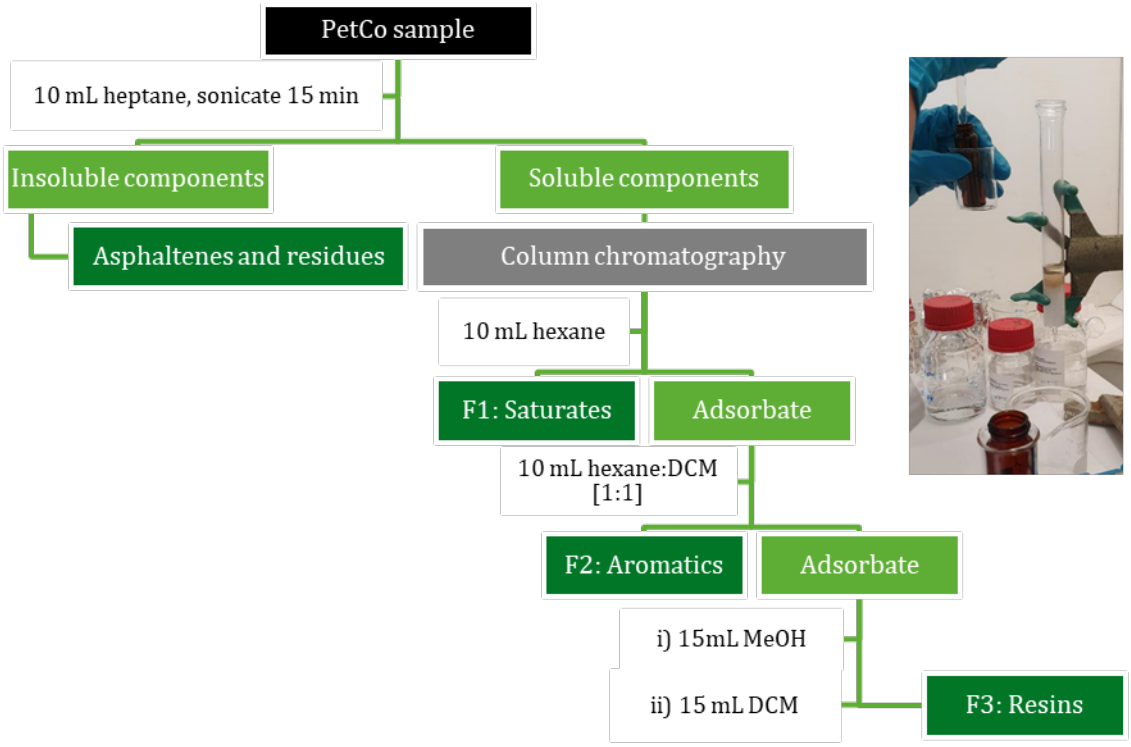
As PetCo products are usually highly chemically complex, it is recommended to perform SAR fractionation before the chromatographic analysis. By using solvents of different polarities, SAR fractionation may separate the sample into different constituent classes, namely saturates, aromatics, and resins.

The SAR fractionation procedure was based on the conventional ASTM D4124 method [8], but was modified and as described below. Figure 3 provides an overview of the SAR fractionation procedure used for the PetCo products. The SAR fractionation has the following steps:

1. **Open-column preparation**: The fractionation column (here: 17 mm i.d. × 137 mm L) is vertically and securely clamped in the ring stand. First, the cleaned PE frit is placed in the bottom, then 3 g of activated silica are added to the column, equally distributed and levelled to avoid channelling effects[1]. Finally, 2.5 g of Ottawa sand are added and properly packed.
2. **Sample Pre-treatment**: Approximately 0.1 to 1 g of the sample (PetCo product) is dissolved in 10 mL heptane and sonicated for 15 min. The amount of sample used depends on the type of PetCo product and its chemical complexity, which can be investigated with a preliminary screening. For asphalt, 5 g is dissolved in 10 mL DCM, sonicated and let stand overnight. The sample is then sonicated for another 10 min before 1 mL of the dissolved asphalt in DCM is combined with 9 mL heptane. For car wax/polish, 0.5 g of sample is mixed with 0.5 g of silica and evaporated overnight.
3. **Conditioning/Equilibration**: The column is equilibrated with 10 mL hexane.
4. **Sample Load**: The sample is added (10 mL in heptane or dry sample-silica mixture).
5. **Elution**: Once the sample is loaded and the solvent has cleared the top of the Ottawa sand, a collection vial is placed under the fractionation column. The collection vials are exchanged after each fraction: F1 – elution with 10 mL hexane; F2 – elution with 10 mL hexane:DCM (1:1 v/v); F3 – elution with a) 15 mL MeOH and b) 15 mL DCM into the same collection vial.
6. **Combination of fractions**: Fractions F1 and F2 are combined and contain the saturates, aromatics and SPACs (hereafter denoted the SAS fraction) while fraction F3 contains the resins, especially OPACs, NPACs, and acids (hereafter denoted the ON fraction).

[1] Channelling effects can be caused by heterogeneous flow velocities in the packed silica bed. Therefore, there is a preferential flow through the pathways with the lowest hydraulic resistance. which leads to potentially reduced recoveries.

Figure 3: Overview of the SAR fractionation procedure



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

3.4 Isotope labelled standards

Isotope dilution using a set of deuterated or ^{13}C-labelled internal standards (IS) is the gold standard for reliable quantification of individual constituents and are ideally applied to correct for variation in the chromatography and MS analysis as well as matrix effects. However, isotope labelled analytes are expensive, and it is impossible to cover all constituents in PetCo products with labelled internal standards. Thus, a selection of relevant internal isotope labelled standards for constituents in PetCo products is chosen that covers a wide range in size, volatility and polarity, especially for the SAS fraction. The choice of IS for each target constituent is presented in Appendices A.1, A.2, and A.3.

In addition to using isotope labelled standards to correct for variation in the analytical system, they are also suitable for correction of losses during sample preparation. Here it is advisable to choose an appropriate selection of isotope labelled standards as internal standards (added prior to sample preparation) while another group of labelled constituents is used as recovery standards (added prior to GC-MS analysis). As the aim of this study was to develop an analytical concept and not a sample preparation method, the addition of recovery standards was not implemented herein. A suggestion for which IS may be used as recovery standards for the GC-MS/SIM method for the SAS fraction is given in appendix A.1. As the method for the ON fraction only contains few analytes in the IS-mixture, it is not feasible to divide these into recovery and internal standards.

The screening of a sample as suggested in Section 3.2 can also be helpful here when determining what concentration of the recovery standards and IS to add.

3.5 Analyte protectant mixture

In general when analytes are quantified in pure solvent matrices and the responses are compared to the response in the samples, a bias is likely introduced due to matrix effects. Thus, matrix-matched calibrations are often performed where the sample matrix is spiked at different concentration levels of the analytes. Analyte protectants (Aps) are a mixture of constituents that mimic the matrix components and allow determination of matrix-matched calibration curves without running matrix-matched standards for all different matrices [9].

In addition, unwanted peak tailing of constituents of intermediate polarity (for example, carbazoles and phenols) can be challenging in GC analysis due to the presence of active sites on the nonpolar column surface. APs may decrease peak tailing on the GC column and the loss of analytes within the GC inlet by masking these active sites on the column and liner, respectively. The effect is also termed “matrix-induced signal enhancement” [9]. Constituents containing multiple hydroxy-groups, which can interact with active sites via hydrogen bonds, were found to be the most effective APs by the European Union reference laboratory (EURL) for pesticide analysis.

An AP mixture was prepared from sorbitol, D-(-)gluconic acid-δ-lactone, shikimic acid, and 3-ethoxy-1,2-propanediol following the EURL procedure [9]. Separate stock solutions were prepared for all except 3-ethoxy-1,2-propanediol by dissolving 500 mg of the constituent in acetonitrile (ACN) and water (60:40, %-vol) for a final volume of 10 mL. The AP mixture was subsequently constructed by adding 2 g of 3-ethoxy-1,2-propanediol, 2 mL of D-(-)gluconic acid-δ-lactone stock solution, and 1 mL each of sorbitol and shikimic acid stock solutions in ACN and water (60:40, %-vol) for a final volume of 10 mL.

3.6 Calibration standards

For the GC-MS platform, separate calibration stock solution mixtures were prepared for the saturates, aromatics, SPACs, OPACs, and NPACs, respectively, in addition to two IS stock solution mixtures. These were a:

1. GC-saturate stock solution mixture containing five saturates
2. GC-aromatic stock solution mixture containing 38 aromatics
3. GC-SPAC stock solution mixture with nine SPACs
4. GC-SAS-IS stock solution mixture containing 19 internal standards for saturates, aromatics and SPACs
5. GC-OPAC stock solution mixture with 15 OPACs
6. GC-NPAC stock solution mixture consisting of 24 NPACs
7. GC-ON-IS stock solution mixture comprising of five internal standards for OPACs and NPACs.

For GC×GC-HRMS, two calibration stock solution mixtures and one IS stock solution mixture were prepared. These were a:

1. GC×GC-OPAC stock solution mixture with 16 OPACs
2. GC×GC-NPAC stock solution mixture consisting of 25 NPACs
3. GC×GC-IS stock solution mixture comprising of seven internal standards for OPACs and NPACs.

For the SFC-ESI-HMS platform, four calibration stock solution mixtures and two IS stock solution mixtures were prepared. These were an:

1. SFC-OPAC1 stock solution mixture consisting of eight OPACs
2. SFC-OPAC2 stock solution mixture consisting of 14 OPACs
3. SFC-NPAC stock solution mixture with ten NPACs
4. SFC-acid stock solution mixture containing 16 acids
5. SFC-IS1 stock solution mixture comprising of three internal standards for OPACs, NPACs, and acids.
6. SFC-IS2 stock solution mixture comprising of five internal standards for OPACs, NPACs, and acids.

For each method, eight calibration standard solutions (L1 – L8) were prepared from the respective stock and IS solution mixtures. In addition, a null-level calibration standard (L0, only solvent, APs, and IS mixture) was prepared for each method to verify the purity of the calibration standards. Fresh calibration standard solutions were made for every batch.

The analytes in each stock solution mixture, the most appropriate IS for each analyte and the concentration of each analyte in each calibration standard are listed in Appendices A.1, A.2, and A.3 for GC-MS, GC×GC-HRMS, and SFC-ESI-HRMS, respectively. Notes on the preparation of the stock solution mixtures and calibration standards are given in Appendix A.4 and information on InchiKey, CAS no., vendor, purity, form when purchased, and solvent used for individual stock solution for each constituent is presented in Appendix A.5.

3.7 Further sample preparations

Prior to analysis of the SAS fraction (F1 + F2) by GC-MS/SIM, 30 µL AP mixture (see Section 3.5), 50 µL GC-SAS-IS mixture, and 220 µL ethanol were added to 700 µL of sample extract in a GC vial. For the ON fraction (F3), 30 µL AP mixture and 100 µL GC-ON-IS mixture were added to 870 µL of sample extract in a GC vial.

For GC×GC-HRMS and SFC-ESI-HRMS analysis of the ON fraction, 100 µL of GC×GC-ON-IS mixture was added to 900µL of sample extract in a GC vial and 100 µL of SFC-ON-IS1 and 50 µL of SFC-ON-IS2 mixture was added to 850 µL of sample extract in a GC vial, respectively.

3.8 Quality control samples

Quality control samples (QCs) were prepared for GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS, respectively. The QCs are used to verify stability of the instrument during a sequence and to calculate QC precision.

For GC-MS/SIM, the QC for the SAS fraction consisted of one part of each of four samples (CWP5, Lub4, Asp1, and TP1) and six parts of a 1:25 dilution of CT2. The QC for the ON fraction consisted of one part of each of the five samples (CWP5, Lub4, Asp1, TP1, and 1:25 dilution of CT2) and the same ON QC mixture was used for GC×GC-HRMS. For SFC-ESI-HRMS, the QC consisted of equal parts of TP1, Lub2, Lub8, a 1:3 dilution CWP1, and 1:3 dilution of CT2.

3.9 Sequence set-up

This section gives an example set up for a sequence (Table 4), but the general principle was followed for every sequence that was run during the study.

Sequences were set up so that a blank and QC sample were run approximately every ten injections. In between, a randomised selection of samples and calibration standards were analysed. We recommend a maximum of 50-60 samples for each sequence. Before running each sequence, instrument stability and suitability was verified, and for GC-MS/SIM sequences, a blank with APs and a QC were run as primers. It is important to note that a matrix-devoid sample may affect the response of the following sample making it less comparable to the remaining samples (see also Section 3.5 on APs).

Table 4: Example of sequence

Injection no.	Type	Injection no.	Type
1	Blank (primer)	25	Blank
2	QC (primer)	26	QC
3	Blank	27	Sample
4	QC	28	Sample
5	Sample	29	Calibration standard
6	Sample	30	Sample
7	Calibration standard	31	Sample
8	Sample	32	Calibration standard
9	Sample	33	Calibration standard
10	Calibration standard	34	Sample
11	Sample	35	Sample
12	Calibration standard	36	Blank
13	Sample	37	QC
14	Blank	38	Sample
15	QC	39	Calibration standard
16	Sample	40	Sample
17	Sample	41	Calibration standard
18	Calibration standard	42	Sample
19	Sample	43	Calibration standard
20	Sample	44	Sample
21	Calibration standard	45	Sample
22	Calibration standard	46	Sample
23	Sample	47	Blank
24	Sample	48	QC

4 Chemical analysis

Three platforms for chemical analysis were developed for quantification of target constituents and constituent groups in PetCo products: GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS. The GC-MS/SIM method was developed to cover SAS and ON constituents and constituent groups while the GC×GC-HRMS focused only on ON constituents and constituent groups, but SAS constituents and constituent groups can also be analysed by this method. The SFC-ESI-HRMS covered ON constituents as well as carboxylic acids.

4.1 GC-MS/SIM

Quantification of target analytes with MS detection is preferably performed in SIM mode since this mode offers high sensitivity (if the number of SIM ions is low). Two GC-MS/SIM methods were developed for the SAS and ON fraction, respectively. The methods were developed and validated using a 7890A GC system coupled to a 5975C MS detector (Agilent Technologies, Santa Clara, CA, USA).

4.1.1 Instrument parameters

The chromatographic conditions were the same for the two GC-MS/SIM methods and are presented in Table 5 together with the overall parameters for the MS.

Table 5: Instrument parameters for the GC-MS/SIM methods

Instrument part	Method parameter	Value	Unit
Inlet	Mode	Pulsed splitless	
	Temperature	300	°C
	Total flow	34	mL/min
	Septum purge flow	3	mL/min
	Injection pulse pressure (until 2 min)	45	psi
	Purge flow to split vent (at 1.9 min)	30	mL/min
	Injection volume	1	µL
Column	Type	HP5MS	
	Dimensions (L × ID, d_F)	60 × 0.25, 0.25	m × mm, µm
	Carrier gas	He	
Oven	Initial temperature	35	°C
	Equilibration Time	0.5	min
	Total flow	1.0	mL/min
	Average velocity	25.575	cm/s
	Programme: Hold at 35 °C Ramp to 150 °C Ramp to 315 °C Hold at 315 °C	7 15 5 13.4	min °C/min °C/min min
	Total run time	61.1	min
MSD Transfer Line	Temperature	315	°C
MS	Acquisition mode	SIM	

Instrument part	Method parameter	Value	Unit
	Solvent delay	12.3	min
	Emission	35	µA
	Energy	70	eV

4.1.2 SIM parameters for the SAS and ON fractions

Table 6 and Table 7 list the constituents and constituent groups that potentially can be covered by the GC-MS/SIM method for the SAS and ON fractions, respectively, along with their respective SIM group and ion used for quantification. The start times for the SIM groups are defined by the retention time of the listed n-alkane. Not all constituents and constituent groups listed in the tables were validated and quantified in the PetCo samples in this report. In addition, not all constituent groups are fully covered by these SIM parameters.

Table 6: Constituents and constituent groups covered by the GC-MS/SIM method for the SAS fraction

*) Each SIM group contains 13 ions

**) Cx. where x = 0, 1, 2, 3 etc. refers to the degree of alkylation: 0 = no alkyl, 1 = methyl, 2 = ethyl or dimethyl, 3 = trimethyl, methyl-dimethyl or propyl, etc.

Constituent/Constituent group	Isotope labelled standards	SIM group number*																Ion
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
	n-alkane (retention time of n-alkane used for group division)	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*23*	*24*	*25*	*27*	*32*	
Alkanes		×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	43
Alkylcyclopentanes, Alkylcyclohexanes		×	×	×	×	×	×	×	×										55
n-Alkylcyclohexanes		×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	82
	p-Xylene-d10	×																	98
Xylenes, Alkyltoluenes, Alkylbenzenes		×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	105
Sesquiterpanes		×	×	×	×	×	×	×	×	×	×	×							123
Naphthalene				×															128
Alkylated tetralins		×	×	×	×	×													131
Tetralin		×	×																132
Benzo[b]thiophene				×															134
C1-Adamantane**		×	×																135
Adamantane	Naphthalene-d8	×	×	×															136
Decalin		×																	138
C1-Naphthalenes					×														142
C1-Benzothiophenes	n-Butylbenzene-d14				×														148
C2-Adamantane			×	×															149
C1-Decalins, Acenaphthylene		×	×			×													152
Biphenyl, Acenaphthene					×	×	×												154
C2-Naphthalenes						×													156
	Acenaphthylene-d8					×													160
C2-Benzothiophenes						×													162
C3-Adamantane			×	×	×														163
	Acenaphthene-d10, Biphenyl-d10				×	×	×												164
C2-Decalins, Fluorene		×	×	×				×	×										166
C5-Biphenyls											×								167
C1-Biphenyls							×												168
C3-Naphthalenes							×	×											170
C3-Benzothiophenes	Fluorene-d10						×	×											176
Phenanthrene, Anthracene										×									178
C3-Decalins, C1-Fluorenes				×	×			×	×										180

Constituent/Constituent group	Isotope labelled standards	SIM group number*																Ion
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
	n-alkane (retention time of n-alkane used for group division)	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*23*	*24*	*25*	*27*	*32*	
C2-Biphenyls							×	×											182
C4-Naphthalenes, C0-Dibenzothiophene							×	×	×	×									184
	Phenanthrene-d10, Anthracene-d10								×	×									188
C4-Benzothiophenes								×	×										190
Tricyclic terpanes, Hopanes														×	×	×	×	×	191
C1-Phenanthrenes/ Anthracenes	Dibenzothiophene-d8								×	×	×								192
C4-Decalins, C2-Fluorenes					×	×				×	×	×							194
C3-Biphenyls								×	×	×									196
C1-Dibenzothiophenes										×	×	×							198
Fluoranthene, Pyrene											×	×	×						202
C2-Phenanthrenes/ Anthracenes												×	×						206
C3-Fluorenes										×	×	×	×						208
	n-Nonylbenzene-2,3,4,5,6-d5						×												209
C4-Biphenyls									×	×	×	×							210
C2-Dibenzothiophenes	Fluoranthene-d10, Pyrene-d10										×	×	×						212
C1-Fluoranthenes/ Pyrenes														×					216
Steranes													×	×	×	×	×	×	217
Steranes														×	×	×	×	×	218
C3-Phenanthrenes/ Anthracenes												×	×	×					220
C3-Dibenzothiophenes											×	×	×	×					226
Benzo[a]anthracene, Chrysene															×	×			228
C2-Fluoranthenes/ Pyrenes														×	×				230
Triaromatic steranes														×	×	×	×	×	231
C4-Phenanthrenes/ Anthracenes, Retene, Benzonaphtothiophene													×	×	×	×			234
C4-Dibenzothiophenes	Benz[a]anthracene-d12, Chrysene-d12												×	×	×	×			240
C1-Chrysenes																×	×		242
C3-Fluoranthenes/ Pyrenes	p-Terphenyl-d14												×		×	×			244
C1-Benzonaphtothiophenes															×	×	×		248
5 Rings PAHs																	×	×	252
C2-Chrysenes																	×		256
	Benzo[k]fluoranthene-d12, Benz[a]pyrene-d12, Perylene-d12																×	×	264
C3-Chrysenes																	×	×	270
6 Rings PAHs																		×	276
6 Rings PAHs																		×	278
	Indeno[1,2,3-c,d]pyrene-d12, Benzo[g,h,i]perylene-d12																	×	288

Table 7: Constituents and constituent groups covered by the GC-MS/SIM method for the ON fraction

*) Each SIM group contains 12 ions
**) C*x*, where x = 0, 1, 2, 3 etc. refers to the degree of alkylation: 0 = no alkyl, 1 = methyl, 2 = ethyl or dimethyl, 3 = trimethyl, methyl-dimethyl or propyl, etc.

Constituent/ Constituent group	Isotope labelled standards	SIM group number*													Ion
		1	2	3	4	5	6	7	8	9	10	11	12	13	
	n-alkane (retention time of n-alkane used for group division)	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*20*	*21*	*23*	*24*	*26*	*27*	
Palmitonitrile(s)							×	×	×	×	×				55
Phenol		×	×												94
	Phenol-d6	×													99
Benzonitrile		×	×												103
C5-, C6-, C7-, C8-, C9-Phenols**						×	×	×							107
C1-Phenols		×	×	×											108
C1-Benzonitriles, Indole		×	×	×	×										117
Benzofuran		×	×												118
C2-Phenols		×	×												122
	Indole-d7		×	×	×										123
Quinoline		×	×												129
C1-Indoles			×	×	×										130
C2-Benzonitriles, C1-, C2-, C3-, C4-Benzofurans		×	×	×	×										131
Benzothiazole, C4-Phenols		×	×	×	×										135
C3-Phenols		×	×	×											136
C1-Quinolines		×		×	×										143
C2-Indoles, Hydroxynaphthalene						×	×								144
C3-Benzonitriles				×	×	×									145
C1-Benzothiazoles				×	×										149
Naphthaldehyde						×									156
C2-Quinolines				×	×	×									157
C3-, C4-Indoles, C1- Hydroxynaphthalenes					×	×	×								158
C4-Benzonitriles					×	×	×								159
C1-Phthalamides				×	×										161
Carbazole							×	×							167
Dibenzofuran						×									168
Diphenylamine						×									169
C3-Quinolines						×	×								171
C2- Hydroxynaphthalenes							×	×							172
C2-Phthalamide	Carbazole-d8					×	×	×							175
	Dibenzofuran-d8					×									176
Benzoquinoline, Acridine								×							179
C2-Carbazoles									×						180
C1-Carbazoles								×							181
C1-Dibenzofurans, Hydroxyfluorene							×	×	×	×					182
C1-Diphenylamines							×	×							183
C3- Hydroxynaphthalenes							×	×	×	×					186
	Acridine-d9							×							188
C3-, C4-Acridines, C3-, C4-Benzoquinolines									×	×	×	×			192
C1-Acridines, C1-Benzoquinolines									×	×					193
Hydroxyphenanthrene									×	×	×				194
C2-Dibenzofurans, C1-Hydroxyfluorenes									×	×					196
C4- Hydroxynaphthalenes								×	×	×					200
C2-Acridines, C2-Benzoquinolines									×	×					207
C1-Hydroxyphenanthrenes											×	×			208
C3-Carbazoles									×	×	×				209
C3-Dibenzofurans, C2-Hydroxyfluorenes									×	×	×	×			210
Benzo[c]carbazole											×	×	×		217
Benzonaphthofuran + Hydroxypyrene											×	×	×		218
C2-Hydroxyphenanthrenes											×	×	×		222
C4-Carbazoles											×	×	×		223
C4-Dibenzofurans, C3-Hydroxyfluorenes										×	×	×			224

Constituent/ Constituent group	Isotope labelled standards	SIM group number*													Ion
		1	2	3	4	5	6	7	8	9	10	11	12	13	
	n-alkane (retention time of n-alkane used for group division)	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*20*	*21*	*23*	*24*	*26*	*27*	
Dibenzoquinoline, Benzoacridine											×	×			229
C1-Benzocarbazoles												×	×	×	231
C1-Benzonaphthofurans, C1-Hydroxypyrenes												×	×	×	232
C3-Hydroxyphenanthrenes												×	×	×	236
C1-Dibenzoquinoline, C1-Benzoacridines													×	×	243
C2-Benzocarbazoles													×	×	245
C2-Benzonaphthofurans, C2-Hydroxypyrenes													×	×	246
C2-Dibenzoquinolines, C2-Benzoacridines													×	×	257
C3-Benzocarbazoles													×	×	259
C3-Benzonaphthofurans, C3-Hydroxypyrenes														×	260
C3-Dibenzoquinolines, C3-Benzoacridines														×	271
Dibenz[a,h]acridine														×	279
C4-Dibenzoquinoline, C4-Benzoacridines														×	285

4.2 GC×GC-HRMS

GC×GC-HRMS provides a higher separation efficiency, peak capacity, and enhanced resolution power compared to one-dimensional GC [10, 11]. The systematic order of constituent groups with increasing degree of alkylation (similar to GC-MS) and the higher mass accuracy of HRMS instruments such as a quadrupole time-of-flight (qTOF) detector facilitate the identification of constituents in complex PetCo products. In GC×GC, constituents eluting from the first and long GC column (here, a nonpolar stationary phase; measured in minutes) are refocussed and released (so-called modulation) onto a second and shorter GC column (here, a polar stationary phase; measured in seconds). GC×GC has previously been applied for the analysis of petroleum hydrocarbons [12].

Herein, a method for the ON fraction of the SAR fractionated PetCo products was developed with GC×GC-HRMS using a 7890B GC×GC system coupled to a 7200 qTOF MS detector (Agilent Technologies, Santa Clara, CA, USA).

4.2.1 Instrument parameters

The instrument parameters for the GC×GC-HRMS method with scan acquisition mode is provided in Table 8. To obtain response factors with a higher sensitivity, the same inlet and oven programme as in Table 8 can be used for the analysis with GC×GC-FID.

Table 8: Instrument parameters for the GC×GC-MS method

Instrument part	Method parameter	Value	Unit
Inlet	Mode	Splitless	
	Temperature	300	°C
	Total flow	55	mL/min
	Septum purge flow	3	mL/min
	Purge flow to split vent (at 1 min)	50	mL/min
	Injection volume	1	µL

Instrument part	Method parameter	Value	Unit
Column	Type	^{1}D: ZB5 ^{2}D: ZB50	
	Dimensions (L × ID, d_F)	^{1}D: 60 × 0.25, 0.25 ^{2}D: 2.0 × 0.15, 0.15	m × mm, µm
	Carrier gas	He	
	Loop of ^{1}D (approximately)	0.7	m
Primary oven	Initial temperature	35	°C
	Equilibration Time	1.0	min
	Total flow	2.0	mL/min
	Average velocity	33.109	cm/s
	Programme: Hold at 35 °C Ramp to 150 °C Ramp to 315 °C Hold at 315 °C	5 7.5 5 13.4	min °C/min °C/min min
	Total run time	66.73	min
Secondary oven	Offset from primary oven	+30	°C
Cryogenic modulator	Type	Zoex® Corp	
	Modulation period	7.0	s
	Cold jets (N_2)	-70	°C
	Hot jets (N_2) – Offset from primary oven	+60	°C
	Hot jets (N_2) – On	750	ms
MSD Transfer Line	Temperature	315	°C
MS	Quadrupole temperature	150	°C
	Ion source temperature	230	°C
	Acquisition mode	SCAN	
	Acquisition range	60-500	Da
	Acquisition sampling frequency	25	spectra/s
	Solvent delay	10.3	min
	Emission	35	µA
	Energy	70	eV
	Mass calibration	Perfluorotributylamine	

4.2.2 Quantifier/qualifier ions

Table 9 lists the quantifier ion and up to 4 qualifier ions for the constituents and constituent groups that were covered by the GC×GC-HRMS method.

Table 9: GC×GC-HRMS quantifier and qualifier ions for constituents and constituent groups

Constituent/constituent group	Quantifier (Da)	Qualifier 1 (Da)	Qualifier 2 (Da)	Qualifier 3 (Da)	Qualifier 4 (Da)
Phenol	94.0419	66.0477			
Phenol-d6	99.0728	71.0782			
Benzonitrile	103.0422	76.0318			
o-Cresol	108.0575	108.0575	79.0549	77.0393	107.0509
C1-Phenols	108.0575	107.0509	77.0393	79.0549	108.0575
C1-Benzonitriles	117.0578	90.0469	116.0503		
Indole	117.0578	89.0399	90.0474	117.0578	
2,3-Benzofuran	118.0419	89.0400	63.0236		
C2-Phenols	122.0732	107.0508	77.0395	122.0732	
3,5-Dimethylphenol	122.0732	122.0732	107.0508	77.0395	
Indole-d7	123.0948	123.0963	95.0782		
1-hydroxynaphthalene-2,3,4,5,6,7,8-d7	123.1058	150.0950	151.1012		
(Tere)Phthalonitrile	128.0374	101.0269	75.0122		
Quinoline	129.0578	102.0473	76.0305		
C1-Indoles	130.0735	130.0735			
C2-Benzonitriles	131.0721	116.0492			
C1-Benzofurans	132.0575	131.0568	103.0550	77.0393	
3-Methylbenzofuran	132.0575	131.0568	103.0550	77.0393	
Indanols	134.0732	133.0677			
Benzothiazole	135.0143	108.0069	68.9803		
C3-Phenols	136.0888	121.0729	91.0553	107.0632	136.0888
C1-Quinolines	143.0735	115.0556			
1-Methylisoquinoline	143.0735	115.0556			
2-Hydroxynaphthalene	144.0575	115.0551	116.0619	144.0575	
2,3-Dimethylindole	145.0891	144.0832	130.0669		
C2-Indoles	145.0891	144.0832	130.0669		
C3-Benzonitriles	145.0892	116.0492			
C1-Benzothiazoles	149.0299	108.0040	68.9801		
C4-Phenols	150.1045	135.0819	91.0549	121.0669	150.1045
4-tert-Butylphenol	150.1045	135.0819	91.0549	121.0669	150.1045
Naphthaldehyde	156.0575	127.0555	128.0629	155.0508	
C2-Quinolines	157.0891	115.0571	157.0891		
C1-Hydroxynaphthalenes	158.0732	129.0707	157.0679	158.0732	
C3-Indoles	159.1048	159.1048			
C5-Phenols	164.1201	135.0814	121.0661	149.0973	164.1201
Carbazole	167.0735	139.0560	167.0735		
Dibenzofuran	168.0575	139.0553			
Diphenylamine	169.0891	83.5372	168.0818		
C3-Quinolines	171.1048	156.0825	170.0983		

Constituent/constituent group	Quantifier (Da)	Qualifier 1 (Da)	Qualifier 2 (Da)	Qualifier 3 (Da)	Qualifier 4 (Da)
4,6,8-Trimethylquinoline	171.1048	156.0825	170.0983		
C2-Hydroxynaphthalenes	172.0888	157.0660			
C4-Indoles	173.1204	158.0997	143.0748		
2-tert-Butyl-1H-indole	173.1204	158.0997	143.0748		
C4-Benzofurans	174.1045	131.0537			
2-n-Butylbenzofuran	174.1045	131.0537			
Carbazole-d8	175.1237	146.0951	87.5620	175.1237	
C3-Tetrahydroquinolines	175.1361	160.1163			
Dibenzofuran-d8	176.1077	146.0957			
C6-Phenols	178.1358	107.0505	77.0391	121.0656	178.1358
4-Hexylphenol	178.1358	107.0505	77.0391	121.0656	178.1358
Benzo[h]quinoline	179.0735	151.0554	89.0337	179.0735	
Acridine	179.0735	151.0554	89.0337	179.0735	
1-Methylcarbazole	181.0891	180.0833	152.0633	181.0891	
C1-Carbazoles	181.0891	180.0833	152.0633	181.0891	
2-Methyldibenzofuran	182.0732	152.0628	76.0313	181.0690	
C1-Dibenzofurans	182.0732	152.0628	76.0313	181.0690	
9-Hydroxyfluorene	182.0732	152.0630	181.0657	165.0709	182.0732
C1-Diphenylamines	183.1048	167.0734	91.0540		
Dibenzofuranols	184.0524	102.0463	155.0498	184.0524	
C4-Quinolines	185.1204	185.1204			
C3-Hydroxynaphthalenes	186.1047	171.0810			
Acridine-d9	188.1300	186.1164	93.0579	158.0977	188.1300
C7-Phenols	192.1514	107.0505	121.0656	135.0806	192.1514
C1-Acridines/Benzoquinolines	193.0891	192.0826	165.0708		
9-Methylacridine	193.0891	192.0826	165.0708		
9-Hydroxyphenanthrene	194.0732	165.0697	166.0765	194.0732	
9-Ethylcarbazole	195.1048	180.0869	195.1048		
C2-Carbazoles	195.1048	180.0869	195.1048		
Diethyl-a-naphthylamine	199.1361	184.1143			
C4-Hydroxynaphthalenes	200.1205	185.0966			
2,4-Di-tert-butylphenol	206.1671	121.0651	135.0806	107.0505	206.1671
C8-Phenols	206.1671	121.0651	135.0806	107.0505	206.1671
C1-Hydroxyphenanthrene	209.0966	208.0890			
1,4,8-Trimethylcarbazole	209.1204	194.0991	208.1149	209.1204	
C3-Carbazoles	209.1204	194.0991	208.1149	209.1204	
2,3,6-Trimethylcarbazole	209.1204	194.0991	208.1149	209.1204	
C5-Hydroxynaphthalenes	214.1357	199.1123			
11H-Benzo[a]carbazole	217.0891	217.0891	108.5454	189.0700	
C9-Phenols	220.1827	107.0501	121.0651	135.0814	220.1827

Constituent/constituent group	Quantifier (Da)	Qualifier 1 (Da)	Qualifier 2 (Da)	Qualifier 3 (Da)	Qualifier 4 (Da)
4-Nonylphenol	220.1827	107.0501	121.0651	135.0814	220.1827
C3-Acridines/Benzoquinolines	221.1204	221.1204			
C2-Hydroxyphenanthrene	223.1122	222.1049			
2,3,6,7-Tetramethylcarbazole	223.1361	208.1145	222.1304	223.1361	
C4-Carbazoles	223.1361	208.1145	222.1304	223.1361	
Hydroxypyrene-d9	227.1287	197.1199	227.1287		
Dibenzo[f,h]quinoline	229.0891	114.0411	228.0831		
Benzo[c]acridine	229.0891	200.0635	114.0416		
8-Methyl-11(H)-benzo[a]carbazole	231.1048	202.0787	230.0973	231.1048	
C1-Benzocarbazoles	231.1048	202.0787	230.0973	231.1048	
C4-Acridines/Benzoquinolines	235.1361	235.1361			
C1-Benzoacridines	243.1048	243.1048			
C2-Benzocarbazoles	245.1204	245.1204			
C2-Acridines/Benzoquinolines	257.1204	242.0980	127.0488		
8,10-Dimethyl-Benzo[a]acridine	257.1204	242.0980	127.0488		
C2-Benzoacridines	257.1204	242.0980	127.0488		
5-Ethyl-7-methyl-benzo[b]carbazole	259.1361	244.1138			
C3-Benzocarbazoles	259.1361	244.1138			
Dibenz[a,h]acridine	279.1043	139.0467			

4.3 SFC-ESI-HRMS

The use of supercritical fluid chromatography (SFC) allows for the determination of constituents that are not amenable to conventional GC-based methods due to their high polarity or high molecular mass and low volatility. For theory on SFC, please refer to [13] and [14]. The SFC method was developed for the ON fraction and is based on electrospray ionisation (ESI) coupled to a HRMS (qTOF). The development was based on the optimisation of the chromatography (incl. a chromatographic column screening, gradient steepness, additive type, and concentration) and the ionisation parameters (incl. capillary and cone voltages and desolvation temperature) in ESI negative mode (ESI^-). These parameters were previously identified as relevant in SFC-ESI-HRMS for OPACs and complex environmental samples [15, 16]. ESI is a soft ionisation technique. Thus, the molecular ion of a constituent can be preserved and characteristic fragments can be produced, facilitating constituent identification. The negative ionisation mode produces deprotonated ions $[M-H]^-$ and is useful for the ionisation of, for example, phenols or carboxylic acids.

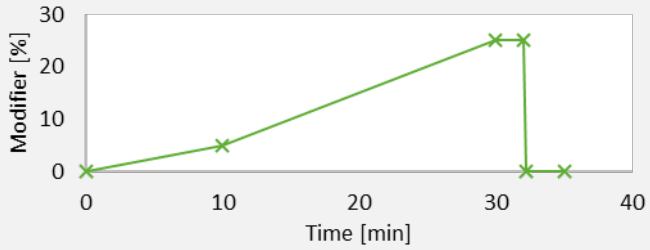
The development of the SFC-ESI-HRMS method was performed on an Acquity UPC^2 (SFC) coupled to a Synapt G2-Si HDMS from Waters (Milford, Massachusetts, USA). A so-called tool-free ESI probe from Waters was installed as the ionisation source.

4.3.1 Instrument parameters

The instrument parameters for the ON fraction of the PetCo products are summarised in Table 10. To ensure accurate mass measurements, every 30 s during the chromatographic run, a mass

calibration was performed with leucine-enkephalin as the reference constituent (mass: 554.2615 Da).

Table 10: Instrument parameters for the SFC-ESI-HRMS

Instrument part	Method parameter	Value	Unit
Column	Brand/ Chemistry	Acquity Torus 1-AA	
	Dimensions (L × ID), particle size	100 × 3, 1.7	mm × mm, µm
	Particle shape	Spherical	
	Pore size	130	Å
Pre-column	Brand/ Chemistry	Acquity Torus 1-AA	
	Dimensions (L × ID), particle size	5 × 2.1, 1.7	mm × mm, µm
Mobile phase	A-solvent	CO_2 (≥ 99.998%)	
	Modifier (B-solvent)	MeOH	
	Additive type (in modifier)	Ammonium formate	
	Additive concentration (in modifier)	5	mM
	Make-up solvent	MeOH	
	Additive type (in make-up solvent)	Formic acid	
	Additive concentration (in make-up solvent)	10	mM
Gradient programme			
	Flow rate	1.5	mL/min
	Make-up solvent flow rate	0.1	mL/min
	Total run time	35	min
Injection	Injection volume	1	µL
	Injection solvent	MeOH:DCM, 1:1	
	Weak needle wash (Isopropanol)	600	µL
	Strong needle wash (H_2O:MeOH, 1:4)	200	µL
Others	Column temperature	40	°C
	Automated backpressure regulator	140	bar
	UV range (photo-diode array detector)	220 - 500	nm
MS	Polarity	ESI^-	
	Capillary voltage	2.3	kV
	Cone voltage (Function 1)	10	V
	Cone voltage (Function 2, ramp)	10-40	V
	Desolvation temperature	500	°C
	Desolvation gas flow	1000	L/hr
	Source temperature	120	°C
	Mass range	50 – 1200	Da
	Scan rate	0.25	scans/s
	Acquisition mode	Continuum	

4.3.2 Quantifier ions

The quantifier ions for the constituents targeted by SFC-ESI-HRMS are listed in Table 11.

Table 11: SFC-ESI-HRMS quantifier ions for target constituents

Constituent	Quantifier (Da)
Phenol	93.0346
Phenol-d6	93.0346
o-Cresol	107.0502
Indole	116.0506
3,5-Dimethyl phenol	121.0659
Indole-d7	123.0945
3-Methylindole	130.0662
5-Methylindole	130.0662
1-Hydroxynaphthalene	143.0502
2-Hydroxynaphthalene	143.0502
2,3-Dimethylindole	144.0819
1,2,3,4-Tetrahydro-1-hydroxynaphthalene	147.0815
1-Hydroxynaphthalene (13C6)	149.0703
4-tert-Butylphenol	149.0972
2-Methyl-1-hydroxynaphthalene	157.0660
1,7-Dihydroxynaphthalene	159.0452
Carbazole	166.0660
1-Naphthoic acid	171.0452
2-Naphthoic acid	171.0452
2-tert-Butyl-1H-indole	172.1132
Carbazole-d8	174.1164
1,2,3,4-Tetrahydro-2-naphthoic acid	175.0764
4-Hexylphenol	177.1285
1-Adamantane carboxylic acid	179.1077
1-Methylcarbazole	180.0819
2-Hydroxyfluorene	181.0659
3-Hydroxyfluorene	181.0659
9-Hydroxyfluorene	181.0659
1-Hydroxy-2-naphthoic acid	187.0401
2-Hydroxyfluorene (13C6)	187.0855
1-Hydroxyphenanthrene	193.0659
2-Hydroxyphenanthrene	193.0659
3-Hydroxyphenanthrene	193.0659
4-Hydroxyphenanthrene	193.0659
9-Hydroxyphenanthrene	193.0659
9-Ethylcarbazole	194.0975

Constituent	Quantifier (Da)
4-Hydroxyphenanthrene (13C6)	197.0793
Lauric acid	199.1698
2,4-Di-tert-butylphenol	205.1598
1,4,8-Trimethylcarbazole	208.1131
2,3,6-Trimethylcarbazole	208.1131
1-Hydroxypyrene	217.0659
4-Nonylphenol	219.1754
2-Phenanthrene carboxylic acid	221.0608
Phenanthrene carboxylic acids	221.0608
3,5,7-Trimethyladamantane-1-carboxylic acid	221.1547
2,3,6,7-Tetramethylcarbazole	222.1288
Hydroxypyrene-d9	226.1224
9-Anthracene-d9-carboxylic acid	230.1173
Pentadecanoic acid	241.2173
1-Pyrene carboxylic acid	245.0608
Pyrenecarboxylic acids	245.0608
Palmitoleic acid	253.2173
3-Hydroxybenzo[a]pyrene	267.0815
3-Chrysene carboxylic acid	271.0764
Chrysene carboxylic acids	271.0764
Linolenic acid	277.2173
Linoleic acid	279.2330
Oleic acid	281.2486
Stearic acid	283.2643

5 Method validation

The focus of the project was the development of an analytical strategy applying GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS methods. All three methods were validated in terms of detection limit (DL), limit of quantification (LOQ), linearity of the calibration curves and precision of both the lowest available standard (instrument precision) and the QC sample (QC precision). The chemical analysis was carried out as according to Section 4 and the data analysis as described in Appendix B.1.

In addition, a separate method validation experiment was carried out for the GC-MS/SIM method which included accuracy, recovery, and method precision as well as the aforementioned validation parameters. The information on the sample preparation for the separate validation experiment for the GC-MS/SIM validation is given in Appendix B.2 and an overview of the additional GC-MS/SIM method validation values for DL, LOQ, R^2, and instrument and QC precision are given in Appendix B.3. The separate method validation for GC-MS/SIM was based on combinations of products to reduce the work load and hence asphalt and lubricating oil were combined (AspLub) and coal tar and tyre pyrolysis oil were combined (CTPO). Car wax was not mixed with another product type. The sample preparation, i.e. the SAR fractionation was evaluated based on recovery and method precision.

5.1 Analyte protectants

As part of the method development and validation, the use of APs was investigated.

Matrix effects were assessed by comparing the peak areas of the calibration standards analysed in

1) a solvent matrix (*Solvent*)
2) a solvent matrix (*Solvent*) with AP mixture added (*AP*)
3) a sample matrix (*CTPO*)
4) a sample matrix (*CTPO*) with AP mixture added (*CTPO+AP*)

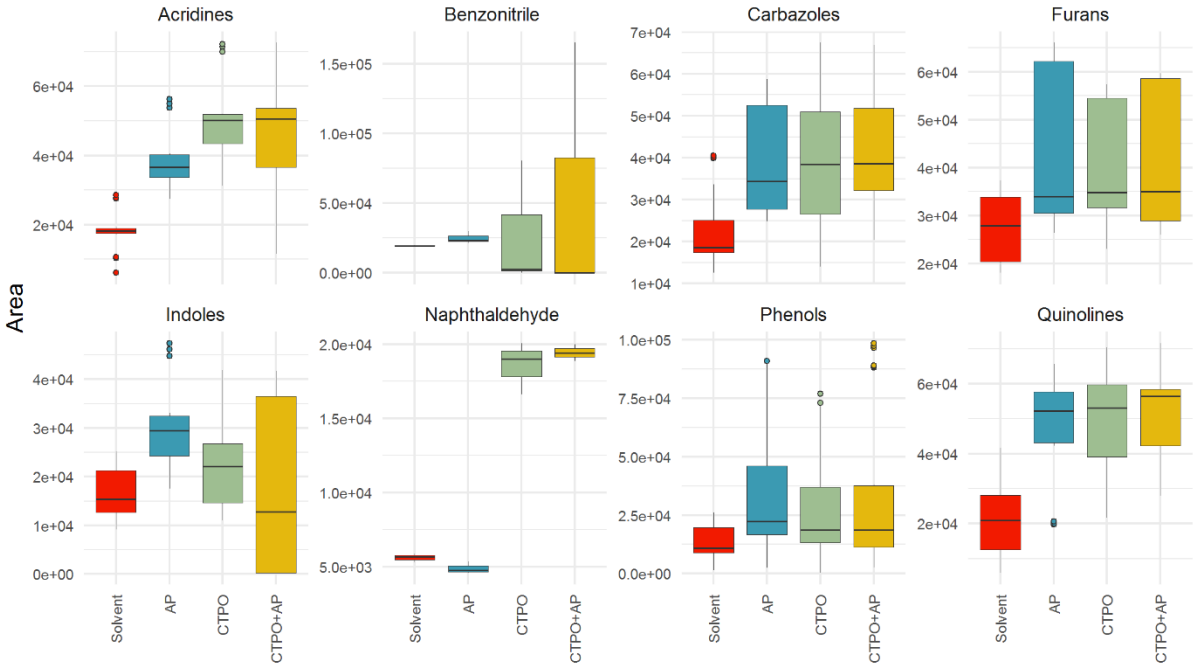
Each matrix was spiked with a standard containing SAS constituents and a standard containing ON constituents reaching an average concentration of 175 ng/mL and 380 ng/mL for SAS and ON constituents, respectively. Each spiked sample was subtracted the average of three corresponding non-spiked samples and prior to this each spiked and non-spiked sample was subtracted a solvent blank in order to assess the analytes based solely on the spiking level response.

Figure 4 and Figure 5 illustrate the effect of the different matrices on the absolute peak areas of the standards, grouped according to constituent types for ON and SAS analytes, respectively. Both figures show a general trend for matrix-induced signal enhancement for most of the constituent types compared to the solvent matrix (with the exception of benzonitrile, indoles, naphthaldehyde, adamantanes, cycloalkanes, and naphthalenes). The peak areas of the constituents were typically increased in the AP-, CTPO-, and CTPO+AP-matrices compared to the pure solvent matrix. However, there is no effect of APs on peak areas in the CTPO matrix compared to the CTPO matrix without APs. The matrix in itself is here acting as its own analyte protectant. The main effect is that there is an AP-induced signal enhancement for the constituents in AP matrix and that this enhancement equalises the AP matrix with the CTPO and CTPO+AP matrices when evaluating peak ares making these matrices more comparable. Furthermore, the effect of APs and sample matrix was more dominant for the ON analytes than

for the SAS analytes, which is due to a higher polarity of the ON analytes than the SAS analytes and thus, a higher susceptibility towards active sites in the liner and on the GC column.

Figure 4: Effect of matrices on peak area of ON standards

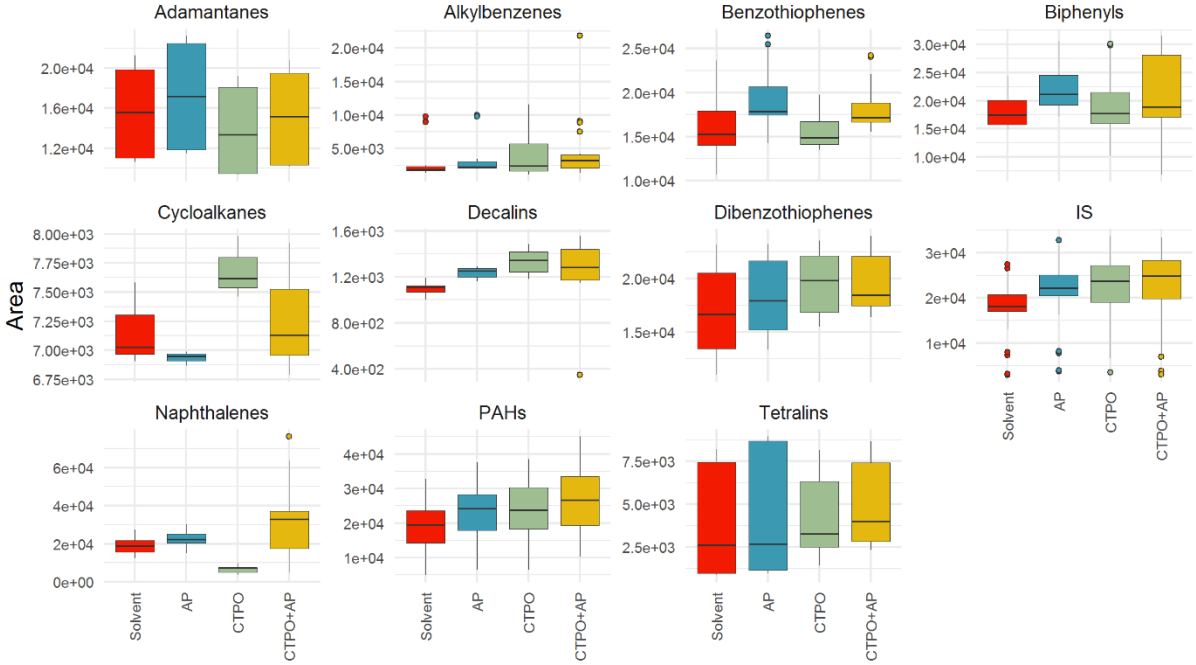
Solvent – DCM:MeOH [1:1], *AP* – *Solvent* with added AP mixture (30 µL/mL), *CTPO* – Coal tar and tyre pyrolysis oil matrix (1:1 diluted with *Solvent*), *CTPO+AP* – *CTPO* with added AP mixture (30 µL/mL).
Boxplots representing the minimum, first quartile (Q1), median, third quartile (Q3), and maximum. Coloured circles represent outliers defined as 1.5 · (Q3-Q1) below Q1 or above Q3.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure 5: Effect of matrices on peak area of SAS standards

Solvent – Hexane:DCM [3:2], *AP* – *Solvent* with added AP mixture (30 µL/mL), *CTPO* – Coal tar and tyre pyrolysis oil matrix (50:1 diluted with *Solvent*), *CTPO+AP* – CTPO with added AP mixture (30 µL/mL).
Boxplots representing the minimum, first quartile (Q1), median, third quartile (Q3), and maximum. Coloured circles represent outliers defined as 1.5 · (Q3-Q1) below Q1 or above Q3.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

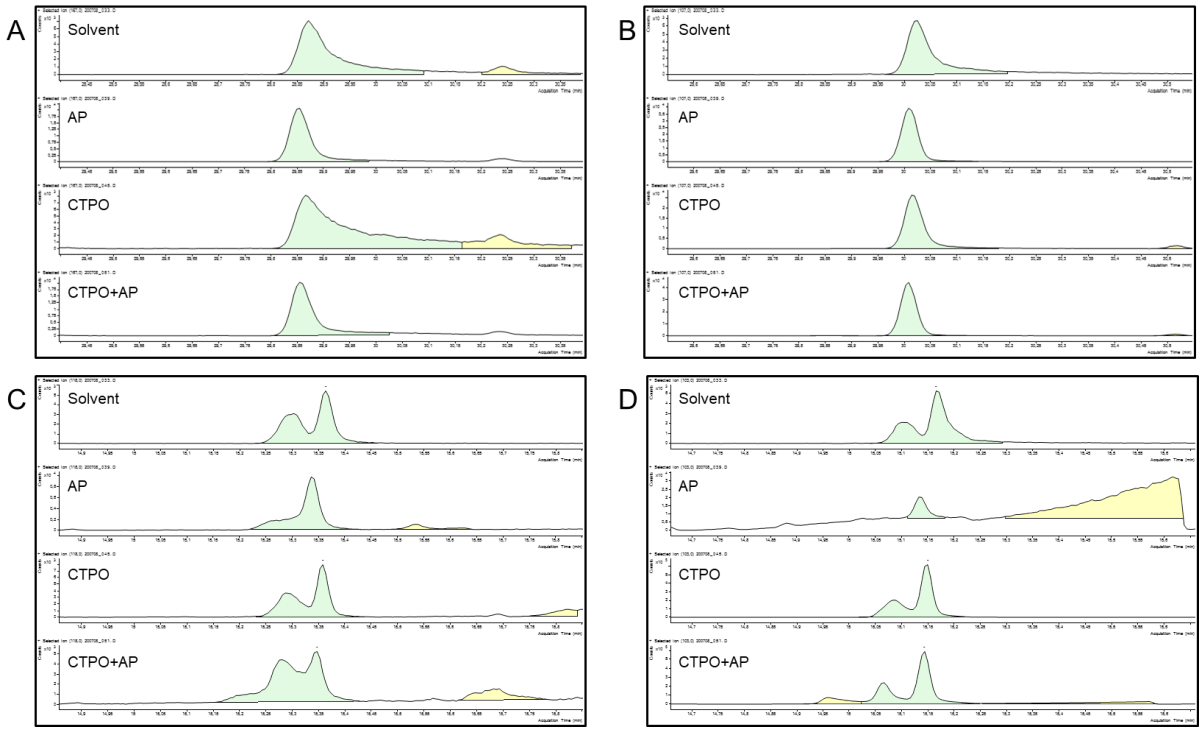
In addition to signal enhancement, the peak shapes of some analytes were positively affected by the presence of APs. Some examples of the effect on peak shapes for ON constituents are shown in Figure 6. For some analytes there was a clear improvement by adding APs, for example carbazole and 4-nonylphenol, while for others, for example 2,3-benzofuran and benzonitrile, the effect was less clear, but not necessarily negative (Figure 6). The improvement of peak shape by adding APs was seen to a lesser degree for the SAS constituents and only for the solvent matrix with APs compared to the pure solvent matrix. However, the peak shapes of the SAS analytes in the solvent matrix with APs more closely resembled the analyte peak shapes in the CTPO and CTPO+AP than the analytes in the pure solvent matrix. This could lead to more accurate calibration curves and quantification compared to using calibration standards made in pure solvents without APs.

Some of the early eluting analytes co-elute with the APs, (phenol, benzonitrile, and 2,3-benzofuran) and the AP mixture introduces more peaks in the early part of the chromatograms due to break down or reactions in the liner. In addition, some indoles were negatively affected by the combination of the CTPO sample matrix and APs.

Addition of APs gives an overall signal enhancement and positive effects on the peak shape of the analytes, especially ON analytes. Thus, addition of APs lowers the DLs and LOQs and improves the quality of peak integrations, which increases the precision of the method. Improved peak shape also leads to increased peak resolution, which should improve the method accuracy, although this has not been evaluated in the absence and presence of APs in this report.

Based on these results, the use of APs was added to the sample preparation method, and APs were used with each sample and all standards for the validation and quantification acquired with GC-MS/SIM.

Figure 6: Effect of matrix on peak shape of the ON constituents A) carbazole, B) 4-nonylphenol, C) 2,3-benzofuran, and D) benzonitrile



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

5.2 Validation parameters for target constituents

5.2.1 GC-MS/SIM method validation

A total of 52 constituents were targeted in the SAS fraction of which five were saturates, 38 were aromatics and nine were SPACs. In the ON fraction, 39 constituents were targeted with 15 being OPACs and 24 NPACs. For each constituent, DL, LOQ, linearity of the standard curve, instrument precision, and QC precision are listed in Appendix B.4. A summary of the values is shown in Table 12. For QC precision, only values above LOQ were included. Hence, 41 out of 52 constituents in the SAS fraction and 10 out of 39 constituents in the ON fraction were included.

Table 12: Range and median value (in parentheses) of DL, LOQ, linearity, and instrument and QC precision for saturates, aromatics, SPACs, OPACs and NPACs analysed by GC-MS/SIM

Chemical class	DL (ng/mL)	LOQ (ng/mL)	Linearity (R^2)	Instrument precision (%)	QC precision (%)
Saturates	0.2 – 3.0 (1.3)	0.7 – 12 (5.2)	0.9993 – 0.9999 (0.9996)	0.5 – 9 (3.7)	4.8 – 11 (5.1)

Chemical class	DL (ng/mL)	LOQ (ng/mL)	Linearity (R^2)	Instrument precision (%)	QC precision (%)
Aromatics	0.3 – 14 (0.81)	1.2 – 58 (3.0)	0.9856 – 1.000 (0.9998)	0.6 – 13 (2.5)	0.2 – 10 (1.8)
SPACs	0.6 – 1.9 (1.3)	2.3 – 7.9 (2.7)	0.9987 – 0.9999 (0.9997)	1.2 – 6.0 (1.9)	0.7 – 6 (2.8)
OPACs	0.5 – 278 (2.0)	2.0 – 546 (7.5)	0.9246 – 0.9997 (0.9923)	1.9 – 18 (5.9)	2.6 – 11 (4.3)
NPACs	0.5 – 4.8 (1.6)	1.9 – 16 (6.7)	0.9803 – 0.9997 (0.9952)	1.8 – 26 (7.3)	1.9 – 21 (3.6)

Median DL values for saturates, aromatics, SPACs, OPACs, and NPACs were <2.0 ng/mL and for 85 out of the 91 target constituents, DL was <10 ng/mL, corresponding to a DL <0.8 – 1.2 µg/g product (ca. 0.25g of product was fractionated into 20 mL for SAS constituents and 30 mL for ON constituents). The median values for linearity of the calibration curves were >0.992 for all five chemical classes and instrument precision and QC precision were within the ranges of 0.5 – 26 % and 0.2 – 21 %, respectively.

Overall, DL, LOQ, linearity, instrument precision, and QC precision for the target constituents analysed by GC-MS/SIM were deemed to be acceptable.

An overview of accuracy, recovery and intermediate method precision from the separate method validation experiment for GC-MS/SIM is given in Table 13.

Table 13: Range and median value (in parentheses) of accuracy, recovery and intermediate method precision for saturates, aromatics, SPACs, OPACs and NPACs analysed by GC-MS/SIM

Chemical class	Accuracy (%)	Recovery (%)	Intermediate method precision (%)		
			AspLub	CTPO	Car wax
Saturates	-12 – 2.8 (-6.0)	54 – 95 (61)	5.7 – 7.4 (6.5)	3.6 – 26 (9.1)	60 – 102 (79)
Aromatics	-243 – 43 (-4.9)	68 – 171 (101)	5.9 – 27 (10)	2.6 – 24 (7.5)	9.7 – 173 (33)
SPACs	-17 – 13 (1.4)	45 – 111 (100)	6.2 – 38 (7.6)	3.8 – 21 (7.7)	20 – 33 (27)
OPACs	-34 – 259 (-5.5)	5.2 – 12 (7.3)	1.8 – 24 (11)	3.3 – 44 (10)	25*
NPACs	-16 – 21 (1.6)	3.8 – 14 (8.5)	2.0 – 74 (8.2)	2.4 – 59 (12)	N/A

Accuracy was generally high with median values for all five chemical classes in the range of -6.0 – 1.6 % (Table 13). Four ON constituents were below DL and hence left out (phenol, 2,3-benzofuran, naphthaldehyde, and benzonitrile). Two constituents (2,2,5,7-tetramethyltetralin and 9-hydroxyphenanthrene) were not accurately measured with accuracies of -243 % and 259 %, respectively. All accuracy values are presented in appendix B.3.3.

Recoveries for aromatics and SPACs were close to 100% with median values of 101 % and 100 %, respectively. The saturates had a median recovery of 61 %. For the ON constituents, the median values were 7.3 % for OPACs and 8.5 % for NPACs (Table 13). All recovery values are

presented in appendix B.3.3. It should be noted that for 13 out of 39 constituents in the ON fraction, the concentration in the spiked blank sample was below DL. For the remaining ON constituents, the recovery values are likely confounded by a relatively high uncertainty as many of the low concentration levels were close to or below the LOQ.

The intermediate method precision for saturates, aromatics, and SPACs was in the range of 5.7 – 38 % for AspLub, 2.6 – 26 % for CTPO, and 9.7 – 173 % for Car wax with median values in the range of 6.5 – 10 %. For OPACs and NPACs, the range for the intermediate method precision was 1.8 – 74 % for AspLub, 2.4 – 59 % for CTPO, while only one constituent was quantifiable in Car wax with a method precision of 25 %. The median values for AspLub and CTPO were 11 and 10 % for OPACs and 8.2 and 12 % for NPACs, respectively (Table 13). All method precision values for SAS and ON constituents are listed in Appendix B.3.4.

The method precision values show that there were differences between the product types where car wax had the lowest precision. This may be because that this was the only product type that was loaded on the SAR fractionation column in dry condition.

The method precision is based on constituents with concentrations >LOQ. The number of SAS and ON constituents quantifiable out of 52 and 39 constituents, respectively, in each product type for each block is listed in Table 14. The samples were not spiked and the method precision values were therefore only quantifiable for those constituents that were present in the samples.

Table 14: Number of SAS and ON constituents quantified by GC-MS/SIM in each product type for each extraction block

Product type	SAS constituents		ON constituents	
	Block I	Block II	Block I	Block II
AspLub	41	38	6	9
CTPO	48	45	24	26
Car wax	13	13	0	1

Overall, accuracy and method precision for the target constituents analysed by GC-MS/SIM were acceptable while recovery was acceptable for the SAS fraction, but not for the ON fraction.

5.2.2 GC×GC-HRMS method validation

For GC×GC-HRMS a total of 45 constituents were targeted of which 18 were OPACs and 27 were NPACs. An overview of DL, LOQ, linearity, instrument precision and QC precision is given in Table 15. Values for each constituent are listed in Appendix B.5. For the QC precision, 25 out of 45 constituents were included while the remainder were below LOQ.

Table 15: Range and median values (in parentheses) of DL, LOQ, linearity, instrument precision, and QC precision for OPACs and NPACs analysed by GC×GC-HRMS

Chemical class	DL (ng/mL)	LOQ (ng/mL)	Linearity	Instrument precision (%)	QC precision (%)
OPACs	1.4 – 64 (9.2)	4.7 – 182 (23)	0.9762 – 0.9999 (0.9982)	2.2 – 25 (19)	0.91 – 35 (6.6)
NPACs	0.8 – 111 (2.6)	2.7 – 245 (7.7)	0.9826 – 0.9995 (0.9972)	2.8 – 53 (11)	2.0 – 32 (7.0)

Median DL values for OPACs and NPACs were 9.2 and 2.6 ng/mL, respectively. Of the 45 constituents, 34 had DLs <10 ng/mL, corresponding to <1.2 µg/g product. Linearity was in the range of 0.9762 – 0.9999 with 38 out of 45 constituents showing linearity above 0.99. Instrument and QC precision were in the ranges of 2.2 – 53 % and 0.91 – 35 % for OPACs and NPACs, respectively.

Overall, DL, LOQ, linearity, instrument precision, and QC precision for the target constituents analysed by GC×GC-HRMS were acceptable.

5.2.3 SFC-ESI-HRMS method validation

For SFC-ESI-HRMS a total of 47 target constituents were targeted. Of these, 21 were OPACs, ten were NPACs, and 16 were acids. An overview of DL, LOQ, linearity, instrument precision, and QC precision is given in Table 16, while values for each constituent are provided in Appendix B.6. For QC precision, only values above LOQ were included which led to exclusion of 24 out of 47 constituents.

Table 16: Range and median value (in parentheses) of DL, LOQ, linearity, instrument precision, and QC precision for OPACs and NPACs analysed by SFC-ESI-HRMS

Chemical class	DL (ng/mL)	LOQ (ng/mL)	Linearity	Instrument precision (%)	QC precision (%)
OPACs	0.4 – 175 (10)	1.0 – 796 (24)	0.8046 – 0.9984 (0.9919)	0.4 – 173 (9.0)	3.3 – 62 (11)
NPACs	2.5 – 28 (10)	12 – 103 (31)	0.9701 – 0.9971 (0.9929)	3.8 – 35 (12)	3.0 – 24 (13)
Acids	5.6 - 359 (13)	10 – 1174 (53)	0.6780 – 0.9981 (0.9889)	2.9 – 94 (10)	4.5 – 26 (11)

Median values for DL were 10 ng/mL for OPACs, 10 ng/mL for NPACs, and 13 ng/mL for acids. Out of the 47 constituents, 40 constituents had DL values <50 ng/mL, corresponding to <6 µg/g product. The majority of constituents (28) had R^2 values >0.99 while 42 out of the 47 constituents had R^2 values >0.95. For instrument precision, the median values were 9.0 % for OPACs, 12 % for NPACs, and 10 % for acids. The median values for QC precision were <13 %. Only one analyte had a QC precision >50 %.

It was not possible to calculate instrument precision for 1,2,3,4-tetrahydro-1-hydroxynaphthalene as the replicate analysis of the lowest standards did not give a response for the constituent.

Overall, DL, LOQ, linearity, instrument precision, and QC precision for the majority of the target constituents analysed by SFC-ESI-HRMS were acceptable.

5.3 Validation parameters for constituent groups

Quantification of constituent groups is more laborious than quantification of target constituents and a high selectively for the constituent groups is important to obtain a reliable quantification. The retention time range, quantifier and potential qualifier ions for GC-MS/SIM analysis can be defined based on:

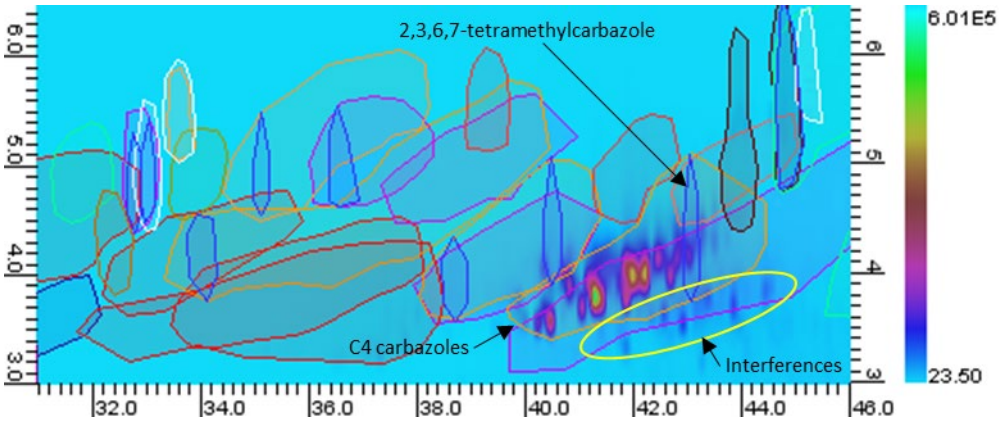
1. Available data, for example from articles where these constituent groups have previously been defined

2. Relative retention behaviour
3. GC×GC-HRMS data
4. Available commercial standards within the constituent groups

The basis for the definition of the constituent groups quantified here by GC-MS/SIM is given in Appendix B.7. In this data set, one quantifier ion was used to define and quantify the constituent groups. Suggestions for qualifier ions for each constituent and constituent group quantified by GC-MS/SIM are presented in Appendix B.8. However, due to differences in fragmentation pattern between different types of alkylation, it may be necessary to include more than one qualifier ion for some constituent groups.

In contrast, in GC×GC analysis, the constituent groups are defined based on HRMS data with one quantifier and one to four qualifier ions. GC×GC-HRMS offers higher selectivity and most interferences can be eliminated. For constituent groups that overlap in the first column dimension, fragments from, for example, a C4 constituent group may be erroneously caught in the corresponding C3 constituent group as the masses will be the same. This kind of misassignment can potentially be overcome if constituent groups can be separated in the second dimension. An example of interferences in the first dimension for C4-carbazoles for GC×GC-HRMS data is presented in Figure 7. These interferences would be included in quantification of C4-carbazoles by one-dimensional GC but is due to separation in the second dimension not included in the quantification by GC×GC-HRMS.

Figure 7: GC×GC image of C4-carbazoles, the standard 2,3,6,7-tetra methylcarbazole, and interferences extracted at high resolution of 223.1361±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

From the definition of the constituent groups it was clear that other constituents or interferences were included in the quantification of constituent groups by GC-MS/SIM and it was also evident that some constituent groups were not fully covered by the GC-MS/SIM method. In general, quantification of constituent groups by GC×GC-HRMS is more reliable than by GC-MS/SIM. This is due to a combination of higher chance of excluding interfering constituents in a group and fully covering a group. The quantification of constituent groups in GC×GC-HRMS is assissted by the well-known structure in GC×GC data where isomers elute close in the 2D space and groups with increasing degree of alkylation (C0, C1, C2, C3, etc.) varies systematically in the 2D space.

When quantifying constituent groups, either by GC-MS/SIM or GC×GC-HRMS, the calibration curves are not based on the entire group, but only on the available standard for that constituent class. If no standard for a particular constituent group exists, the best available standard is

chosen. For example, 2,6-dimethylnaphthalene was used for C3- and C4-naphthalenes. It is not feasible to have analytical standards for each constituent, as the number of alkylated isomers within the same group can be high (for example C1-naphthalenes consist of two isomers, C2-naphthalenes of 14, and C3-naphthalenes of more than 30 possible isomers). Furthermore, standards for each type of alkylation are not commercially available (i.e. trimethyl vs. methyl-ethyl vs. propyl vs. isopropyl for C3-alkylated constituents). This necessary compromise has effects on the accuracy of the quantification, since even closely related isomers can have large variations (with more than a factor of ten) in response factors when using GC-MS/SIM. Unfortunately, there are no certified reference materials available that can be used to provide accurate quality control of these quantifications.

The determination of DL and LOQ values for constituent groups, is also based on the single standard calibration curve. The DL and LOQ values for the standard should then be multiplied with the number of expected resolved isomers in the constituent group. However, not all isomers are present in equal amounts and instead an isomer abundance factor (IAF) can be applied. The IAF is the number of isomers that are above a specified level, for example three times the baseline [17]. This approach works well if samples are quite similar. For quantification of different types of samples as in this case, we have decided to set the threshold level as the baseline plus 1/10 the height of the tallest peak in the constituent group to avoid an overestimation of the IAF. This threshold still poses challenges as constituent group patterns can vary between the different products and it would be advisable to evaluate the IAF for each product type in more detail for future constituent group quantifications. The IAF should be determined from a sample with a high concentration of that particular constituent group. Applying the IAF will provide a better estimate of the DL and LOQ values especially for the highly alkylated constituent group.

When quantifying a constituent group based on a single standard calibration curve, there is a great chance that the area of the constituent group is larger than the highest concentration of the single standards. Therefore, the area of the constituent group is divided by the IAF before the concentration is calculated and the calculated concentration is then multiplied by the IAF. This approach will have an impact on the calculated concentration if the calibration curve is not forced through zero or is not linear. If only a response factor is applied, the division and later multiplication with the IAF has no effect.

5.3.1 GC-MS/SIM method validation

In the SAS fraction, 30 constituent groups were targeted while 23 were targeted in the ON fraction. The best available standard and the IAF for each constituent group as well as DL, LOQ and QC precision values for constituent groups analysed by GC-MS/SIM are listed in Appendix B.7. An overview of DL, LOQ and QC precision is provided in Table 17. For QC precision, values for one saturate, two SPAC, five OPAC, and ten NPAC constituent groups were below LOQ and hence excluded.

Table 17: Range and median values (in parentheses) for DL, LOQ, and QC precision for saturate, aromatic SPAC, OPAC, and NPAC constituent groups analysed by GC-MS/SIM

Chemical class	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
Saturates	21 – 145 (102)	36 – 416 (242)	2.2 – 2.6 (2.4)
Aromatics	2.2 – 59 (14)	5.1 – 79 (43)	0.2 – 3.1 (1.3)

Chemical class	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
SPACs	5.2 – 57 (24)	12 – 171 (96)	0.5 – 4.9 (0.8)
OPACs	5.3 – 497 (43)	14 – 3841 (322)	1.1 – 11 (5.4)
NPACs	8.1 – 110 (51)	49 – 1500 (310)	2.7 – 14 (8.1)

DL for SAS constituent groups ranged from 2.2 to 145 ng/mL while DL for the ON constituents groups were higher ranging from 5.3 to 497 ng/mL (Table 17). For 37 out of the 43 constituents groups, DL was <100 ng/mL, corresponding to <8 – 12 µg/g product. The median value for the QC precision was <2.4 % and <8.1 % for SAS and ON constituents groups, respectively.

5.3.2 GC×GC-HRMS method validation

A total of 46 constituent groups was targeted by GC×GC-HRMS. Of these 19 were OPACs and 27 were NPACs. An overview of DL, LOQ, and QC precision is given in Table 18. Values for each constituent group are listed in Appendix B.10. For QC precision, six OPAC constituent groups and 14 NPAC constituent groups were included as the remainder values were below LOQ and hence excluded.

Table 18: Range and median values (in parentheses) for DL, LOQ, and QC precision for OPAC and NPAC constituent groups analysed by GC×GC-HRMS

Chemical class	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
OPAC constituent groups	2.6 – 502 (75)	9.4 – 1915 (168)	2.7 – 7.8 (7.0)
NPAC constituent groups	1.4 – 142 (27)	4.7 – 572 (94)	1.1 – 24 (6.6)

The median DL values for OPAC and NPAC constituent groups were 75 ng/mL and 27 ng/mL, respectively. Out of the 46 constituent groups, 35 had DL values <100 ng/mL, corresponding to <12 µg/g product. Median values for QC precision was 7.0 % and 6.6 % for OPAC and NPAC constituent groups, respectively. QC precision was <10 % for 17 out of 20 constituent groups.

6 Method comparison

An overview of the three methods considering the potential for separation of constituents and constituent groups, the transfer of methods to other laboratories, the potential for standardisation, and a rough estimate of instrument procurement and running costs is given in Table 19.

Table 19: Comparison between GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS

Parameter	GC-MS/SIM	GC×GC-HRMS	SFC-ESI-HRMS
Potential for separation of constituents and constituent groups	• Good with SAR fractionation • Risk of interference in constituent group quantification	• Excellent with SAR fractionation • Limited risk of interference due to high peak capacity and MS detection	• Excellent with SAR fractionation • Limited risk of interference • Soft ionisation methods (ESI) and MSMS possibilities
Transfer of method to other laboratories	• Fairly straightforward • Equipment is available	• Challenging due to an increase in complexity. However, GC×GC-FID is available in several labs • Investment in GC×GC-MS equipment necessary	• SFC used in high-throughput pharmaceutical labs • Quantification is more dependent on available standards due to suppression effects in ESI
Potential for standardisation	• Challenge with interference especially f unknown products/sample matric • Confirmation of constituent group purity required by GCxGC	• Equipments have been commercially available for >15 years and standard setups are available • Data processing is a much larger challenge than for GC-MS	• Fairly high (pharmaceutical labs) • Robust equipment available for > 5 years • Data processing is a larger challenge than for GC-MS
Costs	• Relatively cheap as methods are extensions standard methods and equipment is available	• High procurement costs (0.2-0.5 M Euros) • Higher running-costs than GC-MS/SIM • Use of Low-resolution MS can reduce costs.	• High procurement costs (0.3-0.5 M Euros) • Higher running-costs than GC-MS/SIM

Generally, the GC-MS/SIM instrument is likely the most available instrument in industries as it has been commercially available for a longer time than GC×GC-HRMS and SFC-ESI-HRMS. In addition, it also has the lowest procurement costs of the three instruments. Therefore, any transfer of methods to other laboratories should be straightforward. GC×GC has been becoming increasingly common over the past 15 years while we believe that the availability of the SFC is still limited within industry. However, there may be a need to upgrade GC×GC detectors to MS or HRMS.

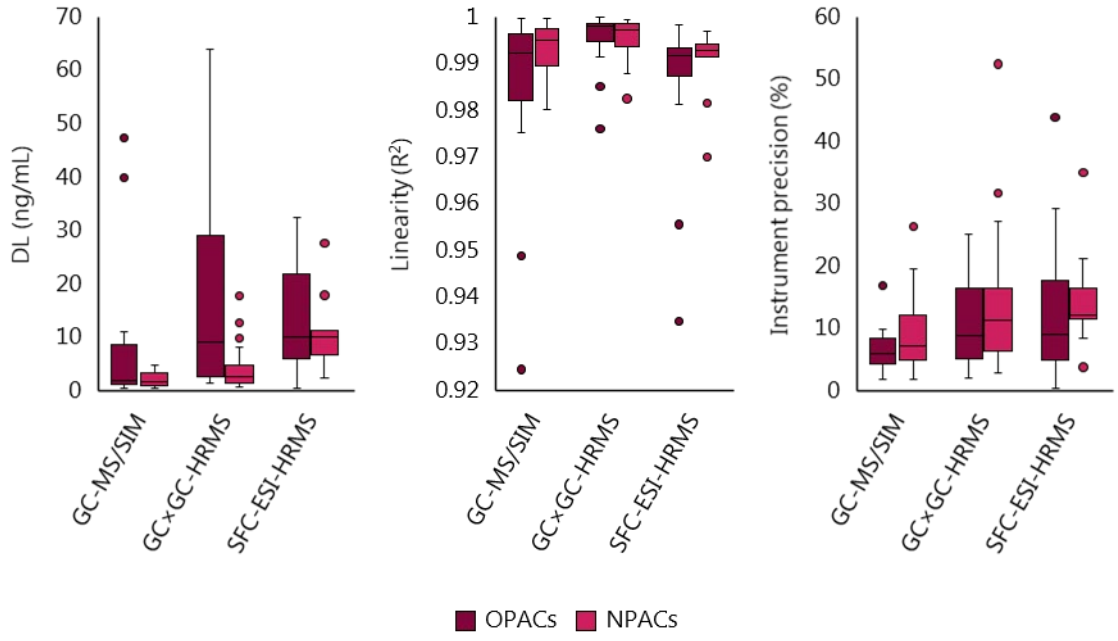
There is a risk of challenges with interfering constituents when using GC-MS due to the low resolution of the MS, both in target constituent quantification and in quantification of constituent groups. Here the HRMS offers better resolution and coupled to a GC×GC, which has increased peak capacity compared to the GC, the risk of challenges with interfering constituents can be minimised. The SFC-ESI-HRMS used herin offers the one-dimensional chromatographic separation as the GC-MS/SIM method but has the advantage of the higher resolution on the detector side due to the HRMS. The SFC, however, has the advantage that it is useful for compounds that are not easily analysed by GC.

Comparison of the performance of the three methods used within this project based on the parameters DL, linearity, and precision obtained from the validation is shown in Figure 8. Only OPACs and NPACs were quantified using all three methods, hence the comparison is limited to these constituents. While there were differences in the included OPACs and NPACs between the three methods, the comparison can still provide a general overview of the performance of the three methods.

DLs are generally lowest for the GC-MS/SIM method and highest for SFC-ESI-HRMS and DLs for OPACs are more variable than for NPACs. For linearity, performance is best for the GC×GC-HRMS method while the median values for GC-MS/SIM and SFC-ESI-HRMS are fairly similar. However, the variability is higher for the GC-MS/SIM than for the SFC-ESI-HRMS. Instrument precision is best for the GC-MS/SIM method compared to GC×GC-HRMS and SFC-ESI-HRMS, both in terms of median values and variability. The performance of the GC×GC-HRMS and SFC-ESI-HRMS in regards to instrument precision is similar, though with less variability for the NPACs analysed by SFC-ESI-HRMS compared to GC×GC-HRMS (Figure 8).

Figure 8: Overview of DL, linearity, and instrument precision for OPACs and NPACs analysed by GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS

Boxplots representing the minimum, first quartile (Q1), median, third quartile (Q3), and maximum. Coloured circles represent outliers defined as 1.5 · (Q3-Q1) below Q1 or above Q3.
For better representation of the figure, the y-axis for DL has been limited to 70 ng/mL, the y-axis for linearity hase been limited to the range 0.92 – 1.00, and the y-axis has been limited to 60 % for instrument precision. Twelve data points are thus not represented in the figure.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

For constituent groups, DLs for OPAC constituent groups are generally lower when analysed by GC-MS/SIM than by GC×GC-HRMS while the opposite is the case for NPAC constituent groups (Table 17 and Table 18, Section 5.3), however, twice as many constituent groups were included in the GC×GC-HRMS analysis than in the GC-MS/SIM analysis.

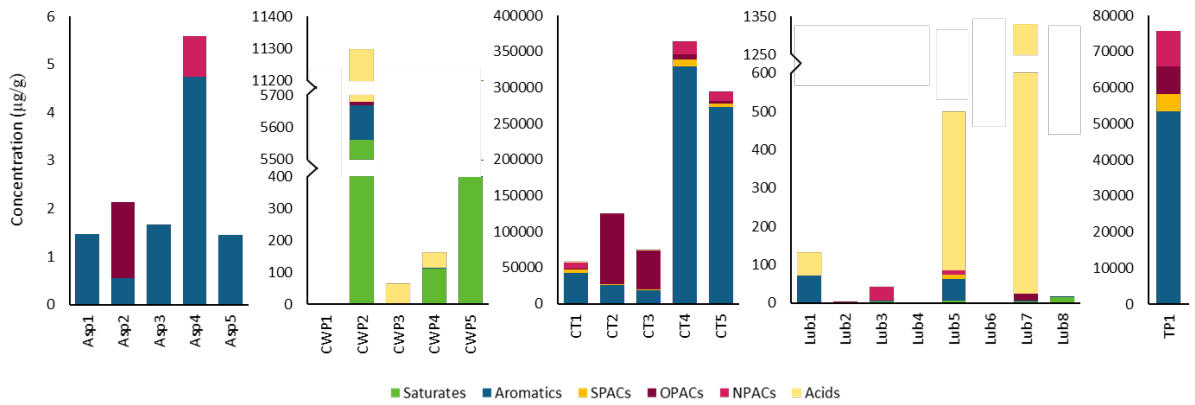
Standard methods for detailed analysis of specific substances in PetCo products focus on constituents with a maximum boiling point of 225 °C and are GC based [6]. The GC based methods developed herein focus on constituents with a boiling point range of ca. 182 – 550 °C while the SFC-ESI-HRMS method can cover the same range of constituents but also constituents that are not usually amenable to GC. Thus, the herein developed methods are an expansion of the current standard methods and will allow for extended detailed analysis of specific constituents in PetCo products. The combined analysis of PetCo products by GC×GC-HRMS and SFC-ESI-HRMS will give the maximum knowledge about the PetCo products and will allow for an improved knowledge based decision on the hazard properties of a PetCo product.

7 Product characterisation

Based on the quantitative data of the 24 PetCo samples from the three platforms, an overall product characterisation is given here. The entire data set from the quantification can be seen in Appendix C. As mentioned in the method comparison, the most reliable data is from the GC×GC-HRMS platform and therefore GC×GC-HRMS data has been used for the constituents that are in common between the three platforms.

Figure 9 gives an overview of the distribution and total content of saturates, aromatics, SPACs, OPACs, NPACs, and acids in aspalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil. Clearly, the lowest concentration of constituents and constituent groups is seen in asphalts while the highest is in coal tar and tyre pyrolysis oil. It is also evident that the variability within a product type can be high. The total concentration of constituents and constituent groups varied between 1.5 and 5.6 µg/g for asphalt, between 0 and 11.3 mg/g for car wax/polish, between 57 and 364 mg/g for coal tar and tyre pyrolysis oil, and between 0.6 and 1329 µg/g for lubricating oil. The highest concentration of constituents and constituent groups in any sample was found in CT4, reaching 364 mg/g (Figure 9). Thereby the maximum explained mass of the included samples reached 36 % (w/w).

Figure 9: Distribution and concentration of saturates, aromatics, SPACs, OPACs, NPACs, and acids in asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Table 3 in Section 2 presented a chemical characterisation based on a screening of samples of the selected product types. This characterisation is confirmed here with the addition of acids (Table 20). The content of aliphatic hydrocarbons in coal tar and lubricating oil was evaluated to be high on the basis of the screening results and this was not confirmed by the quantification. However, this is mainly due to the fact that only few aliphatic hydrocarbon were included in the methods. For example, alkanes were not quantified by any of the methods.

Table 20: Chemical characterisation of asphalt, car wax/polish, coal tar, lubrication oil, and tyre pyrolysis oil

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
Aliphatic hydrocarbons	Low	High	Low (high in screening)	Low (high in screening)	Low

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
Aromatic hydrocarbons	High	Low	High	Medium	High
Heterocyclic constituents	High	Low	High	Medium	High
Acids	Low	High	Low	High	Low

The asphalt samples were mainly characterised by high molecular weight (HMW) aromatics and a few OPACs and NPACs, but generally very few constituents and constituent groups were quantified in these samples. Car wax/polish contained mainly saturates and acids at low concentrations. However, one car wax/polish sample (CWP2) was substantially higher in total concentration than the remaining car wax/polish samples. Coal tar and tyre pyrolysis oil were mainly characterised by aromatics but variability was seen within the coal tar samples where CT2 and CT3 had a proportionally higher concentration of OPACs than aromatics compared to CT1, CT4, and CT5. The lubricating oil was the product type where most variability in chemical composition between the samples were seen. Some samples were rich in acids and to some extent aromatics, while other samples were mainly characterised by OPACs or saturates (Figure 9, Table 20).

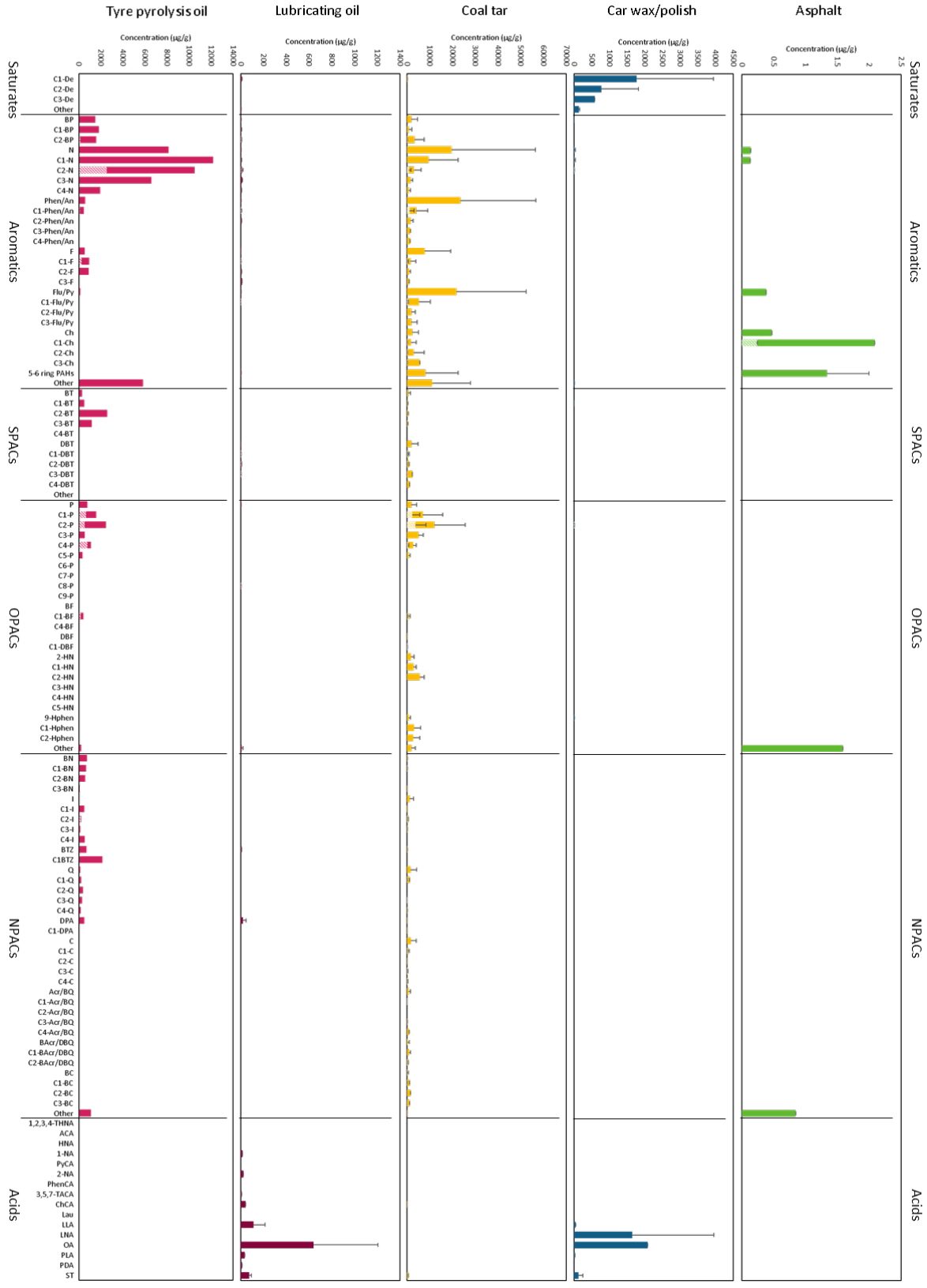
A more detailed overview of the chemical composition of the product types can be seen in Figure 10 while the detailed chemical composition of each sample is presented in Appendix C.3. The list of abbreviations for the constituents and constituent groups is found in Table C.36 in Appendix C.3.

Generally, only few constituents and constituent groups were quantified in asphalt, car wax/polish and lubricating oils at low concentrations. Coal tar and tyre pyrolysis oil were, by far, the product types with the highest number of quantified constituents and constituent groups.

As mentioned in the introduction, it needs to be known for REACH registration if a PetCo product contains a SVHC at a concentration above 0.1 % (w/w) [1]. This indicates that a constituent with a concentration above 1000 µg/g would surpass the limit of 0.1 % (w/w). For compounds listed in the candidate list, this was the case for anthracene, benzo[a]anthracene, chrysene, fluoranthene, phenanthrene and pyrene in CT4 and CT5 as well as benzo[ghi]perylene and benzo[k]fluoranthene in CT5. A number of constituents and constituent groups that are not listed in the candidate list also surpassed the limit of 0.1 % (w/w). In total, 78 constituents and constituent groups surpassed the limit of 0.1 % (w/w) in at least one sample. For 74 of the 78 constituents and constituent groups, the limit was surpassed in only coal tar and tyre pyrolysis oil while the remaining four constituents and constituent groups surpassed the limit of 0.1 % (w/w) in other samples, but not in coal tar and tyre pyrolysis oil. Considering that the concentration of constituents and constituent groups were not corrected for losses during sample preparation, the number of constituents, especially ON constituents, that surpass levels of 0.1 % (w/w) may be higher than reported here.

Figure 10: Chemical composition (average per product type) of asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil

Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

8 Concluding remarks

The aim of this project was to develop an analytical concept for the quantification and identification of constituents in PetCo products. Three analytical methods were developed for quantification of individual constituents and constituent groups in PetCo products: GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS. SAR fractionation was used for sample preparation.

While sample preparation is an essential step in any chemical analysis, the SAR fractionation utilised herein was not in focus and this step was therefore not further optimised. The sample preparation step was evaluated based on recovery of target constituents as well as the method precision. The aromatics and SPACs showed excellent recovery with median values of 101 % and 100 %, respectively, while it was lower for the saturates (median value of 61 %). The recovery of OPAC and NPAC constituents was very low (median values of 7.3 and 8.5 %, respectively) and with such a low recovery the quantification of the constituents becomes challenging. To correct for losses in sample preparation, the addition of internal standards in the sample preparation step is advised. Fractionation of the samples will be necessary as the SAS constituents otherwise will mask the ON constituents, as they are often present in high concentrations. It was also evident from the method precision that the included product types differ substantially and it is unknown how much the matrix of the different PetCo products will influence recovery and method precision of the constituents. It is essential to optimise and validate the SAR fractionation for a range of product types to have a sample preparation method that works for a wide range of PetCo products.

The method validation of the GC-MS/SIM method showed that this method is generally well-suited for the analysis of the saturates, aromatics, SPACs, OPACs, and NPACs included herein as evaluated based on DL, LOQ, linearity, accuracy and instrument precision. SAS constituents were generally more easily analysed than the ON constituents were, which is likely due to the low polarity of the former constituents.

The validation data for GC×GC-HRMS showed that the OPAC and NPACs constituents included herein are also generally well-suited for this analytical platform. Saturates, aromatics, and SPACs were not quantified by GC×GC-HRMS, but it is well-known that these constituents are also well-suited for analysis by GC×GC-HRMS [18, 19]. Most of the OPAC, NPAC, and acid constituents could be analysed by SFC-ESI-HRMS. The use of SFC-ESI-HRMS extended the chemical space covered by the methods to include non-volatile and polar constituents. A few constituents were not performing well when evaluated based on DL, linearity and instrument precision and the quantification of the acids was difficult due to a high number of isomers and co-elution in the samples. Currently, we therefore recommend that further optimisation of the SFC-ESI-HRMS method is undertaken.

Quantification of constituent groups by GC×GC-HRMS is more reliable than by GC-MS/SIM, which is due to less co-coelution within constituent groups and more evident grouping. The quantification of constituent groups in GC×GC-HRMS is assissted by the well-known feature in GC×GC data where isomers elute close in the 2D space and groups with increasing degree of alkylation (C0, C1, C2, C3, etc.) varies systematically in the 2D space.

The quantification of constituent groups by GC-MS/SIM and GC×GC-HRMS is based on a single isomer standard curve even though it is known that relative response factors can vary greatly among isomers. This decreases the accuracy, but it is not feasible to have true analytical standards for each constituent, as the number of alkylated isomers within the same group can be high. For harmonisation of results, it is key that laboratories use the same standards. Overall, GC×GC-HRMS is superior to GC-MS/SIM in regards to constituent group quantification and we

recommend that the constituent groups are quantified with the internal standards described herein to allow for comparability between analysis of PetCo products by different analytical laboratories.

For GC×GC-HRMS, both quantifier and qualifier ions were included for the quantification of target constituents and constituent groups. For target and constituent group quantification by GC-MS/SIM, including qualifier ions can improve the reliability of the quantification, however it will be at the cost of sensitivity as more ions need to be included in the individual SIM windows in the GC-MS/SIM method, thereby lowering the dwell time for the individual ions. In GC×GC-HRMS and SFC-ESI-HRMS analysis full spectral data over a wider mass range is routinely acquired, and has less impact on sensitivity with these analytical platforms. Inclusion of qualifier ions in GC-MS/SIM could potentially aid in the quantification of constituents such as the alkylbenzenes where specific quantifier and qualifier ions could be chosen to more selectively target the individual types of alkylation than can be done with the current GC-MS/SIM method. The addition of qualifier ions will, however, not help in the resolution of isomers such as chrysene and triphenylene and it may not be feasible to always include a qualifier ion for PAHs, as these constituents do not fragment much. For the quantification of constituent groups, using a qualifier ion can minimise the inclusion of interfering constituents in the quantification results and thus more accurate results can be obtained. However, due to differences in fragmentation pattern between different types of alkylation, it may be necessary to include more than one qualifier ion for some constituent groups.

For the GC-MS/SIM method, the use of APs was applied. An AP mixture is a mixture of constituents that mimics matrix components and this will allow for matrix-matched calibration curves without running matrix-matched standards for different matrices. The application of APs showed an enhanced peak intensity and improved peak shape especially for ON constituents. The ON analytes have a higher polarity than the SAS analytes and are therefor more susceptible to active sites in the liner and on the GC column. The APs will occupy these active sites allowing for an improved analysis of the analytes. It should be noted that the effect of APs will not be sufficient if the GC-MS system is not kept clean, for example regular change of liner and column. It is therefore recommended to always verify system stability and especially liner and column integrity before analyzing PetCo products. An optimisation of the AP mixture could be relevant as the current AP mixture was developed for pesticides and more suitable APs may exist for the analysis of saturates, aromatics, SPACs, OPACs, NPACs and acids. The inclusion of the AP mixture for the GC×GC-HRMS and SFC-ESI-HRMS methods was not implemented herein, but it is expected that the AP mixture will also be beneficial for quantification of constituents and constituent groups by these methods.

The product characterisation showed that the chosen product types were different which was expected based on the literature review carried out in the beginning of the project, as well as the screening of the products. The product characterisation based on the screening results was confirmed with the quantified data and updated with the presence of acids. The presence of aliphatic hydrocarbons was not confirmed by the quantification data, which was due to the fact that only a few aliphatic hydrocarbons were quantified. Clearly, the product characterisation also showed that there is still a large fraction of the constituents in the samples that remain unknown and are not quantified. With the current methods, 128 constituents and 46 constituent groups were quantified. An inclusion of more constituent and constituent groups may decrease the fraction of unknown composition. Further optimisation of the SFC-ESI-HRMS method, as mentioned before, may also decrease this fraction of unknown constituents as potentially a larger fraction of the HMW constituents may be quantified by this method.

In conclusion, we recommend to use both GC×GC-HRMS and SFC-ESI-HRMS for the quantification of target constituents and constituent groups in PetCo producst as these two methods combined will cover the largest number of constituents possible.

9 List of references

[1] European Commission (2006): Regulation (EC) No 1907/2006 of the European parliament and of the council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. In: Official Journal of the European Union, L 396, 30 December 2006.

[2] European Chemicals Agency (2017): Guidance in a nutshell – Identification and naming of substances under REACH and CLP. Version 2, European Chemcicals Agency, p. 1 – 10.

[3] Speight JG (2016): Asphalt materials science and technology. Elsevier, Amsterdam, Boston, Heidelberg, London, New York, Oxford, Paris, San Diego, San Francisco, Singapore, Sydney, Tokyo, Chapter 6.

[4] Uhler AD, Stout SA, Douglas GS, Healey EM, Emsbo-Mattingly SD (2016): Chemical character of marine heavy fuel oils and lubricants. In: Stout SA, Wang Z [eds.]: Standard handbook of oil spill environmental forensics: Fingerprinting and source identification, 2nd edition, Elsevier, Amsterdam, Boston, Heidelberg, London, New York, Oxford, Paris, San Diego, San Francisco, Singapore, Sydney, Tokyo, Chapter 13.

[5] Speight JG, (2015): Handbook of petroleum product analysis. John Wiley & Sons, Inc., Hoboken, New Jersey.

[6] Concawe (2012): Guidance to Registrants on Methods for the Characterisation of Petroleum UVCB Substances for REACH Registration Purposes. Concawe, p. 1 – 29.

[7] Lerda D, (2011): Polycyclic Aromatic Hydrocarbons (PAHs) factsheet – 4th edition. European Commission, JRC 66955, Joint Research Centre, Institute for Reference Materials and Measurements, p. 1 – 27.

[8] ASTM International (2018): ASTM D4124 – 09(2018) – Standard Test Method for Separation of Asphalt into Four Fractions. ASTM Internation, p. 1 – 8.

[9] EURL-SRM (2013): Use of Analyte Protectants in GC-Analysis – a way to improve peak shape and reduce decomposition of susceptible constituents. https://www.eurl-pesticides.eu/library/docs/srm/EURL_Observation-APs.pdf (23.10.2020).

[10] Muscalu AM, Górecki T (2018): Comprehensive two-dimensional gas chromatography in environmental analysis. In: Trends Anal Chem, 2018, 106, p. 225-245. DOI: 10.1016/j.trac.2018.07.001.

[11] Górecki T, Harynuk J, Panić O (2004): The evolution of comprehensive two-dimensional gas chromatography (GC×GC). In: J Sep Sci, 2004, 27, (5-6). p. 359-379. DOI: 10.1002/jssc.200301650.

[12] Blomberg J, Schoenmakers PJ, Beens J, Tijssen R (1997): Comprehensive two-dimensional gas chromatography (GC×GC) and its applicability to the characterization of complex (petrochemical) mixtures. In: J High Resolut Chromatogr, 1997, 20 (10). p. 539-544. DOI: 10.1002/jhrc.1240201005.

[13] Fountain, K. J., Grumbach, E. S., McCabe, D. R., Anwer, P., Young, B., Beginner's Guide to Convergence Chromatography. Waters Corporation, Milford, MA USA 2014.

[14] Nováková, L., Grand-Guillaume Perrenoud, A., Francois, I., West, C., Lesellier, E., Guillarme, D., Modern analytical supercritical fluid chromatography using columns packed with sub-2 mum particles: a tutorial. Anal Chim Acta 2014, 824, 18-35 DOI: 10.1016/j.aca.2014.03.034.

[15] Lübeck, J. S., Malmquist, L. M. V., Christensen, J. H., Supercritical fluid chromatography for the analysis of oxygenated polycyclic aromatic constituents in unconventional oils. J Chromatogr A 2019, 1589, 162-172 DOI: 10.1016/j.chroma.2018.12.056.

[16] Lübeck, J. S., Christensen, J. H., Tomasi, G., Nontarget screening of sediments using ultra-high-performance supercritical fluid chromatography – high-resolution mass spectrometry (UHPSFC-HRMS). Optimisation by D-optimal design. (To be submitted) 2021.

[17] Grung M, Meland S, Ruus A, Ranneklev S, Fjeld E, Kringstad A, Rundberget JT, Dela Cruz M, Christensen JH (2021): Occurrence and trophic transport of organic constituents in sedimentation ponds for road runoff. In: Sci Total Environ, 2021, 141808, p. 1-11. DOI: 10.1016/j.scitotenv.2020.141808.

[18] Nelson RK, Kile BM, Plata DL, Sylva SP, Xu L, Reddy CM, Gaines RB, Frysinger GS, Reichenbach SE (2006): Tracking the weathering of an oil spill with comprehensive two-dimensional gas chromatography. In: Environ Forensics, 2006, 7, 33 – 44.

[19] Tran TC, Logan GA, Grosjean E, Ryan D, Marriott PJ (2010): Use of comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry for the characterization of biodegradation and unresolved complex mixtures in petroleum. In: Geochim Cosmochim Ac, 2010, 74, 6468 – 6484.

[20] Dolan J (2009): Calibration Curves. Part V: Curve Weighting. https://www.chromatographyonline.com/view/calibration-curves-part-v-curve-weighting (30.10.2020).

[21] Bonn-OSINet (2011): CEN/TR 15522-2:2012 Oil spill identification. Waterborne petroleum and petroleum products Analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses. Version 2, Bonn-OSINet, p. 1 – 138.

[22] Trolio R, Grice K, Fisher SJ, Alexander R, Kagi RI (1999): Alkylbiphenyls and alkyldiphenylmethanes as indicators of petroleum biodegradation. In: Organic Geochemistry, 1999, 30, 1241-1253.

[23] Bennett B, Bowler BFJ, Larter, SR (1996): Determination of C0-C3 alkylphenols in crude oils and waters. In: Analytical Chemistry, 1996, 68, p. 3697-3702.

[24] Li M, Wang T, Zhong N, Zhang W, Sadik A, Li H (2013): Ternary diagram of fluorenes, dibenzothiophenes and dibenzofurans: Indicating depositional environment of crude oil source rocks. In: Energy exploration and exploitation, 2013, 31, 4, 569-588.

[25] Zhang G, Yang C, Serhan M, Koivu G, Yang Z, Hollebone B, Lambert P, Brown CE (2018): Characterization of nitrogen-containing polycyclic aromatic heterocycles in crude oils and refined petroleum products. In: Sheppard C [ed.]: Advances in Marine Biology, 81, Elsevier Ltd, London, Oxford, San Diego, Cambridge (MA).

[26] Wang Z, Yang C, Hollebone B, Fingas M (2006): Forensic Fingerprinting of diamondoids for correlation and differentiation of spilled oil and petroleum products. In: Environmental Science and Technology, 2006, 40, 18, p. 5636-5646.

[27] Mössner SG, Lopez de Alda MJ, Sander LC, Lee ML, Wise SA (1999): Gas chromatographic retention behavior of polycyclic aromatic sulfur heterocyclic compounds, (dibenzothiophene, naphtho[b]thiophenes, benzo[b]naphthothiophenes and alkylsubstituted derivatives) on stationary phases of different selectivity. In: Journal of Chromatography A, 1999, 841, 207-228.

A Calibration standards

Appendix A provides additional information on the analytes in the calibration standards, how the calibration standards were prepared and the concentration of the individual constituents in the calibration standards for GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS.

A.1 Calibrations standards for GC-MS/SIM

The concentrations of analytes in stock solution mixtures and calibration levels L0 – L8 for GC-MS/SIM are listed Table A.1.

Table A.1: Concentrations of analytes in stock solution mixtures and calibration levels of standards for GC-MS/SIM

The concentrations are not corrected for the purity of the constituents listed in Table A.9
*IS suggested to be used as recovery standard

Stock solution mix	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
GC-saturate	1,3-Dimethyladamantane	Adamantane-d16	4.192	0	13	21	50	84	168	210	419	629
GC-saturate	1-Methyldecalin	Adamantane-d16	4.000	0	12	20	48	80	160	200	400	600
GC-saturate	2-Isopropyldecalin	n-Nonylbenzene-2,3,4,5,6-d5	4.000	0	12	20	48	80	160	200	400	600
GC-saturate	Adamantane	Adamantane-d16	5.248	0	16	26	63	105	210	262	525	787
GC-saturate	Butylcyclohexane	n-Butylbenzene-d14	4.293	0	13	21	52	86	172	215	429	644
GC-aromatic	1,3,6-Trimethylchrysene	Chrysene-d12	2.000	0	10	20	48	80	160	200	400	600
GC-aromatic	1-Methylfluorene	Fluorene-d10	2.713	0	14	27	65	109	217	271	543	814
GC-aromatic	1-Methylnaphthalene	Naphthalene-d8	2.240	0	11	22	54	90	180	224	448	672
GC-aromatic	1-Methylpyrene	Pyrene-d10	2.015	0	10	20	48	81	161	201	403	604
GC-aromatic	1-Phenylheptane	n-Nonylbenzene-2,3,4,5,6-d5	2.139	0	11	21	51	86	171	214	428	642
GC-aromatic	1-Phenylnonane	n-Nonylbenzene-2,3,4,5,6-d5	2.120	0	11	21	51	85	170	212	424	636
GC-aromatic	1-Phenyloctane	n-Nonylbenzene-2,3,4,5,6-d5	2.014	0	10	20	48	81	161	201	403	604
GC-aromatic	2,2,5,7-Tetramethyltetralin	n-Nonylbenzene-2,3,4,5,6-d5	2.000	0	10	20	48	80	160	200	400	600
GC-aromatic	2,6-Dimethylnaphthalene	Naphthalene-d8	2.059	0	10	21	49	82	165	206	412	618
GC-aromatic	2-Methylnaphthalene	Naphthalene-d8	1.578	0	8	16	38	63	126	158	316	473
GC-aromatic	2-Methylphenanthrene	Phenanthrene-d10	1.996	0	10	20	48	80	160	200	399	599
GC-aromatic	3,3',5,5'-Tetramethylbiphenyl	Biphenyl-d10	2.080	0	10	21	50	83	166	208	416	624
GC-aromatic	3,3'-Dimethylbiphenyl	Biphenyl-d10	2.140	0	11	21	51	86	171	214	428	642
GC-aromatic	4-Methylchrysene	Chrysene-d12	1.654	0	8	17	40	66	132	165	331	496
GC-aromatic	4-n-Pentylbiphenyl	Biphenyl-d10	2.000	0	10	20	48	80	160	200	400	600
GC-aromatic	6-Ethylchrysene	Chrysene-d12	2.000	0	10	20	48	80	160	200	400	600
GC-aromatic	Acenaphthene	Acenaphthene-d10	2.205	0	11	22	53	88	176	220	441	661
GC-aromatic	Acenaphthylene	Acenaphthylene-d8	1.858	0	9	19	45	74	149	186	372	557
GC-aromatic	Anthracene	Anthracene-d10	2.667	0	13	27	64	107	213	267	533	800
GC-aromatic	Benzo[a]anthracene	Benz[a]anthracene-d12	1.912	0	10	19	46	76	153	191	382	574
GC-aromatic	Benzo[a]pyrene	Benz[a]pyrene-d12	2.300	0	12	23	55	92	184	230	460	690
GC-aromatic	Benzo[b]fluoranthene	Benzo[k]fluoranthene-d12	1.929	0	10	19	46	77	154	193	386	579
GC-aromatic	Benzo[e]pyrene	Benz[a]pyrene-d12	2.054	0	10	21	49	82	164	205	411	616
GC-aromatic	Benzo[g,h,i]perylene	Benzo[g,h,i]perylene-d12	2.149	0	11	21	52	86	172	215	430	645

Stock solution mix	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
GC-aromatic	Benzo[k]fluoranthene	Benzo[k]fluoranthene-d12	1.734	0	9	17	42	69	139	173	347	520
GC-aromatic	Biphenyl	Biphenyl-d10	1.906	0	10	19	46	76	152	191	381	572
GC-aromatic	Butylbenzene	n-Butylbenzene-d14	1.928	0	10	19	46	77	154	193	386	578
GC-aromatic	Chrysene	Chrysene-d12	1.921	0	10	19	46	77	154	192	384	576
GC-aromatic	Dibenzo[a,h]anthracene	Benzo[g,h,i]perylene-d12	1.883	0	9	19	45	75	151	188	377	565
GC-aromatic	Fluoranthene	Fluoranthene-d10	2.146	0	11	21	52	86	172	215	429	644
GC-aromatic	Fluorene	Fluorene-d10	2.004	0	10	20	48	80	160	200	401	601
GC-aromatic	Hexylbenzene	n-Butylbenzene-d14	2.006	0	10	20	48	80	161	201	401	602
GC-aromatic	Indeno[1,2,3-c,d]pyrene	Indeno[1,2,3-c,d]pyrene-d12	1.775	0	9	18	43	71	142	178	355	533
GC-aromatic	Naphthalene	Naphthalene-d8	1.982	0	10	20	48	79	159	198	396	595
GC-aromatic	Perylene	Benz[a]pyrene-d12	1.868	0	9	19	45	75	149	187	374	560
GC-aromatic	Phenanthrene	Phenanthrene-d10	1.901	0	10	19	46	76	152	190	380	570
GC-aromatic	Pyrene	Pyrene-d10	2.162	0	11	22	52	86	173	216	432	649
GC-aromatic	Tetralin	Naphthalene-d8	2.216	0	11	22	53	89	177	222	443	665
GC-SPAC	1-Benzothiophene	Naphthalene-d8	4.240	0	13	21	51	85	170	212	424	636
GC-SPAC	2,3,4-Trimethylbenzothiophene	Fluorene-d10	3.960	0	12	20	48	79	158	198	396	594
GC-SPAC	2-Methylbenzothiophene	Naphthalene-d8	4.577	0	14	23	55	92	183	229	458	687
GC-SPAC	3-Methylbenzothiophene	Naphthalene-d8	5.328	0	16	27	64	107	213	266	533	799
GC-SPAC	4,6-Dimethyldibenzothiophene	Dibenzothiophene-d8	3.978	0	12	20	48	80	159	199	398	597
GC-SPAC	4-Ethyl-6-methyldibenzothiophene	Dibenzothiophene-d8	3.880	0	12	19	47	78	155	194	388	582
GC-SPAC	4-Methyldibenzothiophene	Dibenzothiophene-d8	4.092	0	12	20	49	82	164	205	409	614
GC-SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	Chrysene-d12	4.000	0	12	20	48	80	160	200	400	600
GC-SPAC	Dibenzothiophene	Dibenzothiophene-d8	3.824	0	11	19	46	76	153	191	382	574
GC-OPAC	2,3-Benzofuran	Dibenzofuran-d8	4.432	0	13	22	66	133	222	443	886	1330
GC-OPAC	2-Hydroxynaphthalene	Dibenzofuran-d8	4.064	0	12	20	61	122	203	406	813	1219
GC-OPAC	2-Methyldibenzofuran	Dibenzofuran-d8	3.920	0	12	20	59	118	196	392	784	1176
GC-OPAC	2-n-Butylbenzofuran	Dibenzofuran-d8	4.000	0	12	20	60	120	200	400	800	1200
GC-OPAC	3,5-Dimethylphenol	Phenol-d6	4.784	0	14	24	72	144	239	478	957	1435
GC-OPAC	3-Methylbenzofuran	Dibenzofuran-d8	5.472	0	16	27	82	164	274	547	1094	1642
GC-OPAC	4-Hexylphenol	Phenol-d6	3.984	0	12	20	60	120	199	398	797	1195
GC-OPAC	4-Nonylphenol	Phenol-d6	4.288	0	13	21	64	129	214	429	858	1286
GC-OPAC	4-tert-Butylphenol	Phenol-d6	3.552	0	11	18	53	107	178	355	710	1066
GC-OPAC	9-Hydroxyfluorene	Dibenzofuran-d8	4.112	0	12	21	62	123	206	411	822	1234
GC-OPAC	9-Hydroxyphenanthrene	Dibenzofuran-d8	3.648	0	11	18	55	109	182	365	730	1094
GC-OPAC	Dibenzofuran	Dibenzofuran-d8	4.368	0	13	22	66	131	218	437	874	1310
GC-OPAC	Naphthaldehyde	Dibenzofuran-d8	6.832	0	20	34	102	205	342	683	1366	2050
GC-OPAC	o-Cresol	Phenol-d6	5.712	0	17	29	86	171	286	571	1142	1714
GC-OPAC	Phenol	Phenol-d6	4.584	0	14	23	69	138	229	458	917	1375
GC-NPAC	1,4,8-Trimethylcarbazole	Carbazole-d8	3.232	0	10	16	48	97	162	323	646	970
GC-NPAC	11H-Benzo[a]carbazole	Acridine-d9	3.936	0	12	20	59	118	197	394	787	1181
GC-NPAC	1-Methylcarbazole	Carbazole-d8	3.183	0	10	16	48	95	159	318	637	955
GC-NPAC	1-Methylisoquinoline	Carbazole-d8	6.592	0	20	33	99	198	330	659	1318	1978
GC-NPAC	2,3,6,7-Tetramethylcarbazole	Carbazole-d8	3.840	0	12	19	58	115	192	384	768	1152
GC-NPAC	2,3,6-Trimethylcarbazole	Carbazole-d8	3.392	0	10	17	51	102	170	339	678	1018
GC-NPAC	2,3-Dimethylindole	Indole-d7	4.192	0	13	21	63	126	210	419	838	1258

Stock solution mix	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
GC-NPAC	2-tert-Butyl-1H-indole	Indole-d7	3.500	0	11	18	53	105	175	350	700	1050
GC-NPAC	3-Methylindole	Indole-d7	5.392	0	16	27	81	162	270	539	1078	1618
GC-NPAC	4,6,8-Trimethylquinoline	Carbazole-d8	4.000	0	12	20	60	120	200	400	800	1200
GC-NPAC	5-Ethyl-7-methylbenzo[b]carbazole	Acridine-d9	4.000	0	12	20	60	120	200	400	800	1200
GC-NPAC	5-Methylindole	Indole-d7	5.088	0	15	25	76	153	254	509	1018	1526
GC-NPAC	8,10-Dimethyl-Benzo[a]acridine	Acridine-d9	3.472	0	10	17	52	104	174	347	694	1042
GC-NPAC	8-Methyl-11[H]-benzo[a]carbazole	Acridine-d9	4.000	0	12	20	60	120	200	400	800	1200
GC-NPAC	9-Methylacridine	Acridine-d9	4.080	0	12	20	61	122	204	408	816	1224
GC-NPAC	Acridine	Acridine-d9	3.795	0	11	19	57	114	190	379	759	1138
GC-NPAC	Benzo[c]acridine	Acridine-d9	3.888	0	12	19	58	117	194	389	778	1166
GC-NPAC	Benzo[h]quinoline	Acridine-d9	4.944	0	15	25	74	148	247	494	989	1483
GC-NPAC	Benzonitrile	Carbazole-d8	3.648	0	11	18	55	109	182	365	730	1094
GC-NPAC	Carbazole	Carbazole-d8	4.352	0	13	22	65	131	218	435	870	1306
GC-NPAC	Dibenzo[a,h]acridine	Acridine-d9	4.800	0	14	24	72	144	240	480	960	1440
GC-NPAC	Dibenzo[f,h]quinoline	Acridine-d9	4.640	0	14	23	70	139	232	464	928	1392
GC-NPAC	Indole	Indole-d7	4.192	0	13	21	63	126	210	419	838	1258
GC-NPAC	Quinoline	Carbazole-d8	4.145	0	12	21	62	124	207	414	829	1243
GC-SAS-IS	Acenaphthene-d10		4.014	201	201	201	201	201	201	201	201	201
GC-SAS-IS	Acenaphthylene-d8*		4.108	205	205	205	205	205	205	205	205	205
GC-SAS-IS	Adamantane-d16		3.920	196	196	196	196	196	196	196	196	196
GC-SAS-IS	Anthracene-d10*		4.124	206	206	206	206	206	206	206	206	206
GC-SAS-IS	Benzo[a]anthracene-d12*		3.976	199	199	199	199	199	199	199	199	199
GC-SAS-IS	Benzo[a]pyrene-d12*		4.265	213	213	213	213	213	213	213	213	213
GC-SAS-IS	Benzo[g,h,i]perylene-d12		4.123	206	206	206	206	206	206	206	206	206
GC-SAS-IS	Benzo[k]fluoranthene-d12		3.709	185	185	185	185	185	185	185	185	185
GC-SAS-IS	Biphenyl-d10		3.640	182	182	182	182	182	182	182	182	182
GC-SAS-IS	Chrysene-d12		3.564	178	178	178	178	178	178	178	178	178
GC-SAS-IS	Dibenzothiophene-d8		4.467	223	223	223	223	223	223	223	223	223
GC-SAS-IS	Fluoranthene-d10*		3.559	178	178	178	178	178	178	178	178	178
GC-SAS-IS	Fluorene-d10		2.156	108	108	108	108	108	108	108	108	108
GC-SAS-IS	Indeno[1,2,3-c,d]pyrene-d12*		3.992	200	200	200	200	200	200	200	200	200
GC-SAS-IS	Naphthalene-d8		3.564	178	178	178	178	178	178	178	178	178
GC-SAS-IS	n-Butylbenzene-d14		3.920	196	196	196	196	196	196	196	196	196
GC-SAS-IS	n-Nonylbenzene-2,3,4,5,6-d5		3.920	196	196	196	196	196	196	196	196	196
GC-SAS-IS	Phenanthrene-d10		4.328	216	216	216	216	216	216	216	216	216
GC-SAS-IS	Pyrene-d10		4.055	203	203	203	203	203	203	203	203	203
GC-ON-IS	Acridine-d9		4.000	400	400	400	400	400	400	400	400	400
GC-ON-IS	Carbazole-d8		3.720	372	372	372	372	372	372	372	372	372
GC-ON-IS	Dibenzofuran-d8		1.000	100	100	100	100	100	100	100	100	100
GC-ON-IS	Indole-d7		4.023	402	402	402	402	402	402	402	402	402
GC-ON-IS	Phenol-d6		3.776	378	378	378	378	378	378	378	378	378

A.2 Calibration standards for GC×GC-HRMS

The concentrations of analytes in stock solution mixtures and calibration levels L0 – L8 are listed in Table A.2.

Table A.2: Concentrations of analytes in stock solution mixtures and calibration levels of standards for GC×GC-HRMS

The concentrations are not corrected for the purity of the constituents listed in Table A.9

Stock solution mixture	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
GC×GC-OPAC	2,3-Benzofuran	Dibenzofuran-d8	4.432	0	13	22	66	133	222	443	886	1330
GC×GC-OPAC	2,4-Di-tert-butylphenol	Phenol-d6	3.792	0	11	19	57	114	190	379	758	1138
GC×GC-OPAC	2-Hydroxynaphthalene	1-Napthol-2,3,4,5,6,7,8-d7	4.064	0	12	20	61	122	203	406	813	1219
GC×GC-OPAC	2-Methyldibenzofuran	Dibenzofuran-d8	3.920	0	12	20	59	118	196	392	784	1176
GC×GC-OPAC	2-n-Butylbenzofuran	Dibenzofuran-d8	4.000	0	12	20	60	120	200	400	800	1200
GC×GC-OPAC	3,5-Dimethylphenol	Phenol-d6	4.784	0	14	24	72	144	239	478	957	1435
GC×GC-OPAC	3-Methylbenzofuran	Dibenzofuran-d8	5.472	0	16	27	82	164	274	547	1094	1642
GC×GC-OPAC	4-Hexylphenol	Phenol-d6	3.984	0	12	20	60	120	199	398	797	1195
GC×GC-OPAC	4-Nonylphenol	Phenol-d6	4.288	0	13	21	64	129	214	429	858	1286
GC×GC-OPAC	4-tert-Butylphenol	Phenol-d6	3.552	0	11	18	53	107	178	355	710	1066
GC×GC-OPAC	9-Hydroxyfluorene	Dibenzofuran-d8	4.112	0	12	20	62	123	205	411	823	1233
GC×GC-OPAC	9-Hydroxyphenanthrene	Dibenzofuran-d8	3.648	0	11	19	55	109	183	365	729	1095
GC×GC-OPAC	Dibenzofuran	Dibenzofuran-d8	4.368	0	13	22	66	131	218	437	874	1310
GC×GC-OPAC	Naphthaldehyde	Dibenzofuran-d8	6.832	0	20	34	102	205	342	683	1366	2050
GC×GC-OPAC	o-Cresol	Phenol-d6	5.712	0	17	29	86	171	286	571	1142	1714
GC×GC-OPAC	Phenol	Phenol-d6	4.584	0	14	23	69	138	229	458	917	1375
GC×GC-NPAC	1,4,8-Trimethylcarbazole	Carbazole-d8	3.232	0	10	16	48	97	162	323	646	970
GC×GC-NPAC	11H-Benzo[a]carbazole	Carbazole-d8	3.936	0	12	20	59	118	197	394	787	1181
GC×GC-NPAC	1-Methylcarbazole	Carbazole-d8	3.183	0	10	16	48	95	159	318	637	955
GC×GC-NPAC	1-Methylisoquinoline	Carbazole-d8	6.592	0	20	33	99	198	330	659	1318	1978
GC×GC-NPAC	2,3,6,7-Tetramethylcarbazole	Carbazole-d8	3.840	0	12	19	58	115	192	384	768	1152
GC×GC-NPAC	2,3,6-Trimethylcarbazole	Carbazole-d8	3.392	0	10	17	51	102	170	339	678	1018
GC×GC-NPAC	2,3-Dimethylindole	Indole-d7	4.192	0	13	21	63	126	210	419	838	1258
GC×GC-NPAC	2-tert-Butyl-1H-indole	Indole-d7	3.500	0	11	18	53	105	175	350	700	1050
GC×GC-NPAC	3-Methylindole	Indole-d7	5.392	0	16	27	81	162	270	539	1078	1618
GC×GC-NPAC	4,6,8-Trimethylquinoline	Carbazole-d8	4.000	0	12	20	60	120	200	400	800	1200
GC×GC-NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	Carbazole-d8	4.000	0	12	20	60	120	200	400	800	1200
GC×GC-NPAC	5-Methylindole	Indole-d7	5.088	0	15	25	76	153	254	509	1018	1526
GC×GC-NPAC	8,10-Dimethyl-Benzo[a]acridine	Acridine-d9	3.472	0	10	17	52	104	174	347	694	1042
GC×GC-NPAC	8-Methyl-11(H)-benzo[a]carbazole	Carbazole-d8	4.000	0	12	20	60	120	200	400	800	1200
GC×GC-NPAC	9-Ethylcarbazole	Carbazole-d8	3.840	0	12	19	58	115	192	384	768	1152
GC×GC-NPAC	9-Methylacridine	Acridine-d9	4.080	0	12	20	61	122	204	408	816	1224
GC×GC-NPAC	Acridine	Acridine-d9	3.795	0	12	19	57	114	190	379	759	1139
GC×GC-NPAC	Benzo[c]acridine	Acridine-d9	3.888	0	12	19	58	117	194	389	778	1166
GC×GC-NPAC	Benzo[h]quinoline	Acridine-d9	4.944	0	15	25	74	148	247	494	989	1483
GC×GC-NPAC	Benzonitrile	Carbazole-d8	3.648	0	11	18	55	109	182	365	730	1094
GC×GC-NPAC	Carbazole	Carbazole-d8	4.352	0	13	22	65	131	218	435	870	1306

Stock solution mixture	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
GC×GC-NPAC	Dibenz[a,h]acridine	Acridine-d9	4.800	0	14	24	72	144	240	480	960	1440
GC×GC-NPAC	Dibenzo[f,h]quinoline	Acridine-d9	4.640	0	14	23	70	139	232	464	928	1392
GC×GC-NPAC	Indole	Indole-d7	4.192	0	13	21	63	126	210	419	838	1258
GC×GC-NPAC	Quinoline	Carbazole-d8	4.145	0	12	21	62	124	207	414	829	1243
GC×GC-IS	1-Napthol-2,3,4,5,6,7,8-d7		0.200	20	20	20	20	20	20	20	20	20
GC×GC-IS	Acridine-d9		4.000	400	400	400	400	400	400	400	400	400
GC×GC-IS	Carbazole-d8		3.720	372	372	372	372	372	372	372	372	372
GC×GC-IS	Dibenzofuran-d8		1.000	100	100	100	100	100	100	100	100	100
GC×GC-IS	Hydroxypyrene-d9		4.000	400	400	400	400	400	400	400	400	400
GC×GC-IS	Indole-d7		4.023	402	402	402	402	402	402	402	402	402
GC×GC-IS	Phenol-d6		3.780	378	378	378	378	378	378	378	378	378

A.3 Calibrations standards for SFC-ESI-HRMS

The concentrations of analytes in stock solution mixtures and calibration levels L0 – L8 are listed in Table A.3.

Table A.3: Concentrations of analytes in stock solution mixtures and calibration levels of standards for SFC-ESI-HRMS

The concentrations are not corrected for the purity of the constituents listed in Table A.9

Stock solution mixture	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
SFC-OPAC2	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	None	11.025	0	11	24	55	95	252	551	1103	-
SFC-OPAC2	1,7-Dihydroxynaphthalene	Hydroxypyrene-d9	10.973	0	11	24	55	94	251	549	1097	-
SFC-OPAC1	1-Hydroxynaphthalene	1-Hydroxynaphthalene (13C6)	19.760	0	20	198	494	988	1976	4940	9880	16796
SFC-OPAC1	1-Hydroxyphenanthrene	4-Hydroxyphenanthrene (13C6)	0.933	0	0.9	9.3	23	47	93	233	466	793
SFC-OPAC2	1-Hydroxypyrene	Hydroxypyrene-d9	10.622	0	11	23	53	91	243	531	1062	-
SFC-OPAC2	2,4-Di-tert-butylphenol	None	10.949	0	11	23	55	94	250	547	1095	-
SFC-OPAC1	2-Hydroxyfluorene	2-Hydroxyfluorene (13C6)	0.948	0	0.9	9.5	24	47	95	237	474	806
SFC-OPAC2	2-Hydroxynaphthalene	1-Hydroxynaphthalene (13C6)	11.466	0	11	25	57	98	262	573	1147	-
SFC-OPAC1	2-Hydroxyphenanthrene	4-Hydroxyphenanthrene (13C6)	0.101	0	0.1	1	2.5	5	10	25	50	86
SFC-OPAC2	2-Methyl-1-hydroxynaphthalene	1-Hydroxynaphthalene (13C6)	11.037	0	11	24	55	95	252	552	1104	-
SFC-OPAC2	3,5-Dimethylphenol	None	11.302	0	11	24	57	97	258	565	1130	-
SFC-OPAC1	3-Hydroxybenzo[a]pyrene	Hydroxypyrene-d9	1.000	0	1	10	25	50	100	250	500	850
SFC-OPAC1	3-Hydroxyfluorene	2-Hydroxyfluorene (13C6)	0.500	0	0.5	5	12	25	50	125	250	425
SFC-OPAC1	3-Hydroxyphenanthrene	4-Hydroxyphenanthrene (13C6)	0.945	0	0.9	9.4	24	47	94	236	472	803
SFC-OPAC2	4-Hexylphenol	None	11.504	0	12	25	58	99	263	575	1150	-
SFC-OPAC1	4-Hydroxyphenanthrene	4-Hydroxyphenanthrene (13C6)	1.016	0	1	10	25	51	102	254	508	863
SFC-OPAC2	4-Nonylphenol	None	11.256	0	11	24	56	96	257	563	1126	-
SFC-OPAC2	4-tert-Butylphenol	None	11.189	0	11	24	56	96	256	559	1119	-
SFC-OPAC2	9-Hydroxyfluorene	2-Hydroxyfluorene (13C6)	10.516	0	11	23	53	90	240	526	1052	-
SFC-OPAC2	9-Hydroxyphenanthrene	4-Hydroxyphenanthrene (13C6)	10.836	0	11	23	54	93	248	542	1084	-
SFC-OPAC2	o-Cresol	None	11.246	0	11	24	56	96	257	562	1125	-
SFC-OPAC2	Phenol	None	10.830	0	11	23	54	93	248	542	1083	-
SFC-NPAC	1,4,8-Trimethylcarbazole	Carbazole-d8	10.605	0	11	23	53	91	242	530	1061	-
SFC-NPAC	1-Methylcarbazole	Carbazole-d8	10.658	0	11	23	53	91	244	533	1066	-
SFC-NPAC	2,3,6,7-Tetramethylcarbazole	Carbazole-d8	10.710	0	11	23	54	92	245	535	1071	-
SFC-NPAC	2,3,6-Trimethylcarbazole	Carbazole-d8	11.130	0	11	24	56	95	254	556	1113	-
SFC-NPAC	2,3-Dimethylindole	None	11.004	0	11	24	55	94	252	550	1100	-
SFC-NPAC	2-tert-Butyl-1H-indole	None	10.565	0	11	23	53	91	241	528	1057	-
SFC-NPAC	3-Methylindole	None	10.615	0	11	23	53	91	243	531	1062	-
SFC-NPAC	5-Methylindole	None	10.684	0	11	23	53	92	244	534	1068	-
SFC-NPAC	Carbazole	Carbazole-d8	11.424	0	11	24	57	98	261	571	1142	-
SFC-NPAC	Indole	None	11.004	0	11	24	55	94	252	550	1100	-
SFC-acid	1,2,3,4-Tetrahydro-2-naphthoic acid	None	11.067	0	11	24	55	95	253	553	1107	-
SFC-acid	1-Adamantane carboxylic acid	None	10.915	0	11	23	55	94	249	546	1091	-
SFC-acid	1-Hydroxy-2-naphthoic acid	None	10.915	0	11	23	55	94	249	546	1091	-
SFC-acid	1-Naphthoic acid	9-Anthracene-d9-carboxylic acid	10.495	0	10	22	52	90	240	525	1050	-

Stock solution mixture	Constituent	Assigned IS	Concentration in stock solution mixture (µg/mL)	Concentration in calibration levels (ng/mL)								
				L0	L1	L2	L3	L4	L5	L6	L7	L8
SFC-acid	1-Pyrene carboxylic acid	9-Anthracene-d9-carboxylic acid	10.920	0	11	23	55	94	250	546	1092	-
SFC-acid	2-Naphthoic acid	9-Anthracene-d9-carboxylic acid	11.508	0	12	25	58	99	263	575	1151	-
SFC-acid	2-Phenanthrene carboxylic acid	9-Anthracene-d9-carboxylic acid	11.180	0	11	24	56	96	256	559	1118	-
SFC-acid	3,5,7-Trimethyladamantane-1-carboxylic acid	None	11.025	0	11	24	55	95	252	551	1103	-
SFC-acid	3-Chrysene carboxylic acid	9-Anthracene-d9-carboxylic acid	11.134	0	11	24	56	95	254	557	1113	-
SFC-acid	Lauric acid	None	11.148	0	11	24	56	96	255	557	1115	-
SFC-acid	Linoleic acid	None	11.089	0	11	24	55	95	253	554	1109	-
SFC-acid	Linolenic acid	None	11.089	0	11	24	55	95	253	554	1109	-
SFC-acid	Oleic acid	None	11.497	0	11	25	57	99	263	575	1150	-
SFC-acid	Palmitoleic acid	None	10.550	0	11	23	53	90	241	527	1055	-
SFC-acid	Pentadecanoic acid	None	11.458	0	11	25	57	98	262	573	1146	-
SFC-acid	Stearic acid	None	10.588	0	11	23	53	91	242	529	1059	-
SFC-IS1	1-Hydroxynaphthalene (13C6, 99%)		5.000	500	500	500	500	500	500	500	500	500
SFC-IS1	2-Hydroxyfluorene (13C6, 99%)		0.500	50	50	50	50	50	50	50	50	50
SFC-IS1	4-Hydroxyphenanthrene (13C6, 99%)		0.500	50	50	50	50	50	50	50	50	50
SFC-IS2	9-Anthracene-d9-carboxylic acid		1.100	55	55	55	55	55	55	55	55	55
SFC-IS2	Acridine-d9		1.019	51	51	51	51	51	51	51	51	51
SFC-IS2	Carbazole-d8		1.023	51	51	51	51	51	51	51	51	51
SFC-IS2	Indole-d7		2.000	100	100	100	100	100	100	100	100	100
SFC-IS2	Phenol-d6		1.044	52	52	52	52	52	52	52	52	52

A.4 Preparation of calibration standards

The stock solution mixtures for GC-MS/SIM and GC×GC-HRMS contained approximately 4 µg/mL of each individual analyte, except for the GC-aromatic stock solution mixture which were approximately 2 µg/mL. For SFC, the concentration of the individual analytes in the SFC-OPAC2, SFC-NPAC and SFC-Acid stock solution mixtures was approximately 11 µg/mL. In the SFC-OPAC1, SFC-IS1, and SFC-IS2 stock solution mixtures, the concentration of the individual analytes was approximately 1 µg/mL, except for 1-hydroxynaphthalene that had a concetration of 20 µg/mL.

From the stock solution mixtures, eight calibration standards (L1-L8) and a null-level calibration standard (L0, only solvent, APs, and IS mixture) were prepared for a final volume of 5 mL according to Table A.4 and Table A.5 for GC-MS/SIM and Table A.6 for GC×GC-HRMS.

For SFC-ESI-HRMS, two sets of calibration standards were prepared, one which included SFC-OPAC1, SFC-IS1, and SFC-IS2 (calibration curve 1) and one which included SFC-OPAC2, SFC-NPAC, SFC-acid, and SFC-IS2 (calibration curve 2). For the latter, the SFC-OPAC2, SFC-NPAC, and SFC-acid solution mixtures were combined at equal volumes to one SFC-combined stock solution mixture. The calibration standards were prepared in 1 mL vials and it was necessary to prepare dilutions of the stock solution mixtures to avoid adding very small volumes. Table A.7 and Table A.8 presents the preparation of calibration curve 1 and calibration curve 2, respectively.

For the preparation of calibration standards, it should be noted that miscibility issues can occur due to the different solvents used for the individual stock solutions. It is therefore advisable that the addition of stock solution mixtures and solvents are added in the order they are listed in the tables.

Table A.4: Overview of calibration level composition (L0-L8) for SAS constituents analysed by GC-MS/SIM

	L0	L1	L2	L3	L4	L5	L6	L7	L8
GC-saturate stock solution mixture (µL)	0	15	25	60	100	200	250	500	750
GC-aromatic stock solution mixture (µL)	0	25	50	120	200	400	500	1000	1500
GC-SPAC stock solution mixture (µL)	0	15	25	60	100	200	250	500	750
GC-SAS-IS stock solution mixture (µL)	250	250	250	250	250	250	250	250	250
AP mixture (µL)	150	150	150	150	150	150	150	150	150
Ethanol (µL)	500	500	500	500	500	500	500	500	500
Dichloromethane (µL)	4100	4045	4000	3860	3700	3300	3100	2100	1100
Average analyte concentration (ng/mL)	0	11	21	49	82	165	206	412	618
Average IS concentration (ng/mL)	193	193	193	913	193	193	193	193	193

Table A.5: Overview of calibration level composition (L0-L8) for ON constituents analysed by GC-MS/SIM

	L0	L1	L2	L3	L4	L5	L6	L7	L8
GC-OPAC stock solution mixture (µL)	0	15	25	75	150	250	500	1000	1500
GC-NPAC stock solution mixture (µL)	0	15	25	75	150	250	500	1000	1500
GC-ON-IS stock solution mixture (µL)	500	500	500	500	500	500	500	500	500
AP mixture (µL)	150	150	150	150	150	150	150	150	150
Ethanol (µL)	500	500	500	500	500	500	500	500	500
Dichloromethane (µL)	3850	3820	3800	3700	3550	3350	2850	1850	850
Average analyte concentration (ng/mL)	0	13	21	64	129	214	429	857	1286
Average IS concentration (ng/mL)	330	330	330	330	330	330	330	330	330

Table A.6: Overview of calibration level composition (L0-L8) for constituents analysed by GC×GC-HRMS

	L0	L1	L2	L3	L4	L5	L6	L7	L8
GC×GC-OPAC stock solution mixture (µL)	0	15	25	75	150	250	500	1000	1500
GC×GC-NPAC stock solution mixture (µL)	0	15	25	75	150	250	500	1000	1500
GC×GC-IS stock solution mixture (µL)	500	500	500	500	500	500	500	500	500
Dichloromethane (µL)	4500	4470	4450	4350	4200	4000	3500	2500	1500
Average analyte concentration (ng/mL)	0	13	21	64	129	214	428	857	1286
Average IS concentration (ng/mL)	296	296	296	296	296	296	296	296	296

Table A.7: Overview of calibration level composition (L0-L8) for constituents analysed by SFC-ESI-HRMS (calibration curve 1)

	L0	L1	L2	L3	L4	L5	L6	L7	L8
SFC-OPAC1 stock solution mixture diluted 1:10 (µL)	0	10	100	250	500	0	0	0	0
SFC-OPAC1 stock solution mixture (µL)	0	0	0	0	0	100	250	500	850
SFC-IS1 stock solution mixture (µL)	100	100	100	100	100	100	100	100	100
SFC-IS2 stock solution mixture (µL)	50	50	50	50	50	50	50	50	50
Dichloromethane (µL)	500	500	500	500	350	500	500	350	0
Methanol (µL)	350	340	250	100	0	250	100	0	0
Average analyte concentration, except 1-hydroxynaphthalene (ng/mL)	0	1	9	21	43	86	214	428	727
Concentration of 1-hydroxynaphthalene (ng/mL)	0	2	24	61	122	243	608	1215	2066
Average IS concentration (ng/mL)	114	114	114	114	114	114	114	114	114

Table A.8: Overview of calibration level composition (L0-L8) for constituents analysed by SFC-ESI-HRMS (calibration curve 2)

	L0	L1	L2	L3	L4	L5	L6	L7	L8
SFC-combined stock solution mixture diluted 1:10 (µL)	0	70	150	350	0	0	0	0	-
SFC-combined stock solution mixture (µL)	0	0	0	0	60	160	350	700	-
SFC-IS1 stock solution mixture (µL)	100	100	100	100	100	100	100	100	-
SFC-IS2 stock solution mixture (µL)	50	50	50	50	50	50	50	50	-
Dichloromethane (µL)	500	500	500	500	350	500	500	150	-
Methanol (µL)	350	280	200	0	440	190	0	0	-
Average analyte concentration (ng/mL)	0	11	23	55	94	251	548	1097	-
Average IS concentration (ng/mL)	114	114	114	114	114	114	114	114	-

A.5 Constituent information

Information on InchiKey, CAS no., vendor, purity, form when purchased, and solvent used for individual stock solution for all target constituents is presented in Table A.9.

Table A.9: Information for target constituents

Chemical class	Constituent name	InchiKey	CAS no.	Vendor	Purity	Form when purchased	Solvent for individual stock solution
Saturate	1,3-Dimethyladamantane	CWNOIUTVJRWADX-BKUVIOGVSA-N	702-79-4	Sigma Aldrich	99.4	Liquid	Isooctane
Saturate	1-Methyldecalin	NHCREQREVZBOCH-UHFFFAOYSA-N	2958-75-0	Chiron	89.1	Liquid	Isooctane
Saturate	2-Isopropyldecalin	RIVBBHMGRSGNTJ-UHFFFAOYSA-N	861642-00-4	Chiron	N/A	N/A	Isooctane
Saturate	Adamantane	ORILYTVJVMAKLC-UHFFFAOYSA-N	281-23-2	Sigma Aldrich	99.9	Solid	Isooctane
Saturate	Butylcyclohexane	GGBJHURWWWLEQH-UHFFFAOYSA-N	1678-93-9	Sigma Aldrich	99.8	Liquid	Isooctane
Aromatic	1,3,6-Trimethylchrysene	UGLPREDFUVNEMJ-UHFFFAOYSA-N	N/A	N/A	N/A	N/A	Isooctane
Aromatic	1-Methylfluorene	GKEUODMJRFDLJY-UHFFFAOYSA-N	1730-37-6	Sigma Aldrich	98.9	Solid	Isooctane
Aromatic	1-Methylnaphthalene	QPUYECUOLPXSFR-UHFFFAOYSA-N	90-12-0	Sigma Aldrich	99.8	Liquid	Isooctane
Aromatic	1-Methylpyrene	KBSPJIWZDWBDGM-UHFFFAOYSA-N	2381-21-7	Sigma Aldrich	98.4	Solid	Isooctane
Aromatic	1-Phenylheptane	LBNXAWYDQUGHGX-UHFFFAOYSA-N	1078-71-3	Sigma Aldrich	99.4	Liquid	MeOH
Aromatic	1-Phenylnonane	LIXVMPBOGDCSRM-UHFFFAOYSA-N	1081-77-2	Sigma Aldrich	98.3	Liquid	MeOH
Aromatic	1-Phenyloctane	CDKDZKXSXLNROY-UHFFFAOYSA-N	2189-60-8	Sigma Aldrich	99.8	Liquid	MeOH
Aromatic	2,2,5,7-Tetramethyltetralin	LPZOMHQRIWIZSX-UHFFFAOYSA-N	23342-25-8	Chiron	N/A	N/A	Isooctane
Aromatic	2,6-Dimethylnaphthalene	YGYNBBAUIYTWBF-UHFFFAOYSA-N	581-42-0	Sigma Aldrich	99.9	Solid	Isooctane
Aromatic	2-Methylnaphthalene	QIMMUPPBPVKWKM-UHFFFAOYSA-N	91-57-6	Sigma Aldrich	98.6	Solid	Isooctane
Aromatic	2-Methylphenanthrene	KANLOADZXMMCQA-UHFFFAOYSA-N	2531-84-2	N/A	N/A	N/A	Isooctane
Aromatic	3,3',5,5'-Tetramethylbiphenyl	CMZYGFLOKOQMKF-UHFFFAOYSA-N	25570-02-9	Sigma Aldrich	N/A	Solid	MeOH
Aromatic	3,3'-Dimethylbiphenyl	LSKSXPUNSGPDLU-UHFFFAOYSA-N	612-75-9	Sigma Aldrich	99.2	Liquid	Isooctane
Aromatic	4-Methylchrysene	BLVHWJCLSMYFMT-UHFFFAOYSA-N	3351-30-2	N/A	N/A	N/A	Isooctane
Aromatic	4-n-Pentylbiphenyl	IFUOTAQBVGAZPR-UHFFFAOYSA-N	7116-96-3	Chiron	96.4	Liquid	Isooctane
Aromatic	6-Ethylchrysene	ZJSYTTGSPQNXKT-UHFFFAOYSA-N	2732-58-3	N/A	N/A	N/A	Isooctane
Aromatic	Acenaphthene	CWRYPZZKDGJXCA-UHFFFAOYSA-N	83-32-9	Ceriliant	99.0	Solid	Isooctane
Aromatic	Acenaphthylene	HXGDTGSAIMULJN-UHFFFAOYSA-N	208-96-8	Dr. Ehrenstorfer GmbH	>98.0		Isooctane
Aromatic	Anthracene	MWPLVEDNUUSJAV-UHFFFAOYSA-N	120-12-7	Sigma Aldrich	99.3	Solid	Isooctane
Aromatic	Benzo[a]anthracene	DXBHBZVCASKNBY-UHFFFAOYSA-N	56-55-3	Dr. Ehrenstorfer GmbH	>99.0	N/A	Isooctane

Chemical class	Constituent name	InchiKey	CAS no.	Vendor	Purity	Form when purchased	Solvent for individual stock solution
Aromatic	Benzo[a]pyrene	FMMWHPNWAFZXNH-UHFFFAOYSA-N	50-32-8	Bie&Berntsen	N/A	N/A	Isooctane
Aromatic	Benzo[b]fluoranthene	FTOVXSOBNPWTSH-UHFFFAOYSA-N	205-99-2	Bie&Berntsen	N/A	N/A	Isooctane
Aromatic	Benzo[e]pyrene	TXVHTIQJNYSSKO-UHFFFAOYSA-N	192-97-2	Dr. Ehrenstorfer GmbH	>99.0	N/A	Isooctane
Aromatic	Benzo[g,h,i]perylene	GYFAGKUZYNFMBN-UHFFFAOYSA-N	191-24-2	Dr. Ehrenstorfer GmbH	99.5	Solid	Isooctane
Aromatic	Benzo[k]fluoranthene	HAXBIWFMXWRORI-UHFFFAOYSA-N	207-08-9	Supelco	99.9	Solid	Isooctane
Aromatic	Biphenyl	ZUOUZKKEUPVFJK-UHFFFAOYSA-N	92-52-4	Sigma Aldrich	99.72	Solid	Isooctane
Aromatic	Butylbenzene	OCKPCBLVNKHBMX-UHFFFAOYSA-N	104-51-8	Sigma Aldrich	99.9	Liquid	MeOH
Aromatic	Chrysene	WDECIBYCCFPHNR-UHFFFAOYSA-N	218-01-9	VWR Chemicals	99.8	Solid	Isooctane
Aromatic	Dibenzo[a,h]anthracene	LHRCREOYAASXPZ-UHFFFAOYSA-N	53-70-3	Dr. Ehrenstorfer GmbH	>99.0	N/A	Isooctane
Aromatic	Fluoranthene	GVEPBJHOBDJJJI-UHFFFAOYSA-N	206-44-0	Bie&Berntsen	N/A	N/A	Isooctane
Aromatic	Fluorene	NIHNNTQXNPWCJQ-UHFFFAOYSA-N	86-73-7	Ceriliant	99.0	Solid	Isooctane
Aromatic	Hexylbenzene	LTEQMZWBSYACLV-UHFFFAOYSA-N	1077-16-3	Sigma Aldrich	99.9	Liquid	MeOH
Aromatic	Indeno[1,2,3-c,d]pyrene	SXQBHARYMNFBPS-UHFFFAOYSA-N	193-39-5	Dr. Ehrenstorfer GmbH	>99.0	N/A	Isooctane
Aromatic	Naphthalene	UFWIBTONFRDIAS-UHFFFAOYSA-N	91-20-3	Sigma Aldrich	99.9	Solid	Isooctane
Aromatic	Perylene	CSHWQDPOILHKBI-UHFFFAOYSA-N	198-55-0	Dr. Ehrenstorfer GmbH	>99.0	N/A	Isooctane
Aromatic	Phenanthrene	YNPNZTXNASCQKK-UHFFFAOYSA-N	85-01-08.	Dr. Ehrenstorfer GmbH	99.0	Solid	Isooctane
Aromatic	Pyrene	BBEAQIROQSPTKN-UHFFFAOYSA-N	129-00-0	Ceriliant	98.5	Solid	Isooctane
Aromatic	Tetralin	CXWXQJXEFPUFDZ-UHFFFAOYSA-N	119-64-2	Sigma Aldrich	100.0	Liquid	Isooctane
SPAC	1-Benzothiophene	FCEHBMOGCRZNNI-UHFFFAOYSA-N	95-15-8	Merck KGaA	100.0	Solid	MeOH
SPAC	2,3,4-Trimethylbenzothiophene	N/A	80421-98-3	Chiron	N/A	N/A	Isooctane
SPAC	2-Methylbenzothiophene	BLZKSRBAQDZAIX-UHFFFAOYSA-N	1195-14-8	Sigma Aldrich	99.5	Solid	Isooctane
SPAC	3-Methylbenzothiophene	SEBRPHZZSLCDRQ-UHFFFAOYSA-N	1455-18-1	Sigma Aldrich	98.0	Liquid	Isooctane
SPAC	4,6-Dimethyldibenzothiophene	MYAQZIAVOLKEGW-UHFFFAOYSA-N	1207-12-1	Sigma Aldrich	98.1	Solid	Isooctane
SPAC	4-Ethyl-6-methyldibenzothiophene	INNOFEYMWASPFP-UHFFFAOYSA-N	132034-90-3	Alfa Aeser	N/A	N/A	Isooctane
SPAC	4-Methyldibenzothiophene	NICUQYHIOMMFGV-UHFFFAOYSA-N	7372-88-5	Sigma Aldrich	96.8	Solid	Isooctane
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	CKOZCPVQNQOFGX-UHFFFAOYSA-N	24964-09-8	Chiron	99.9	Liquid	Isooctane
SPAC	Dibenzothiophene	IYYZUPMFVPLQIF-UHFFFAOYSA-N	132-65-0	Dr. Ehrenstorfer GmbH	>99.0	N/A	Isooctane
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	JAAJQSRLGAYGKZ-UHFFFAOYSA-N	529-33-9	Sigma Aldrich	N/A	N/A	MeOH
OPAC	1,7-Dihydroxynaphthalene	ZUVBIBLYOCVYJU-UHFFFAOYSA-N	575-38-2	Acros Organics	99.6	Solid	MeOH

Chemical class	Constituent name	InchiKey	CAS no.	Vendor	Purity	Form when purchased	Solvent for individual stock solution
OPAC	1-Hydroxynaphthalene	JCVRFUGPWSIIH-UHFFFAOYSA-N	90-15-3	Sigma Aldrich	100.0	Solid	ACN
OPAC	1-Hydroxyphenanthrene	GTBXZWADMKOZQJ-UHFFFAOYSA-N	2433-56-9	Dr. Ehrenstorfer GmbH	99.8	Solid	ACN
OPAC	1-Hydroxypyrene	BIJNHUAPTJVVNQ-UHFFFAOYSA-N	5315-79-7	Sigma Aldrich	99.2	Solid	ACN
OPAC	2,3-Benzofuran	IANQTJSKSUMEQM-UHFFFAOYSA-N	271-89-6	Sigma Aldrich	99.5	Liquid	MeOH
OPAC	2,4-Di-tert-butylphenol	ICKWICRCANNIBI-UHFFFAOYSA-N	96-76-4	Sigma Aldrich	99.7	Solid	MeOH
OPAC	2-Hydroxyfluorene	ZDOIAPGLORMKTR-UHFFFAOYSA-N	2443-58-5	Sigma Aldrich	99.8	Solid	ACN
OPAC	2-Hydroxynaphthalene	JWAZRIHNYRIHIV-UHFFFAOYSA-N	135-19-3	Chiron	99.9	Solid	ACN
OPAC	2-Hydroxyphenanthrene	YPWLZGITFNGGKW-UHFFFAOYSA-N	605-55-0	Dr. Ehrenstorfer GmbH	94.0	Liquid	ACN
OPAC	2-Methyl-1-hydroxynaphthalene	SRJCJJKWVSSELL-UHFFFAOYSA-N	7469-77-4	Sigma Aldrich	98.6	Solid	MeOH
OPAC	2-Methyldibenzofuran	VTKMFJSESAHMLR-UHFFFAOYSA-N	7320-51-6	Chiron	N/A	N/A	Isooctane
OPAC	2-n-Butylbenzofuran	OVJKFJDEVKABNF-UHFFFAOYSA-N	4265-27-4	Chiron	N/A	N/A	Isooctane
OPAC	3,5-Dimethylphenol	TUAMRELNJMMDMT-UHFFFAOYSA-N	108-68-9	Sigma Aldrich	99.9	Solid	MeOH
OPAC	3-Hydroxybenzo[a]pyrene	SPUUWWRWIAEPDB-UHFFFAOYSA-N	13345-21-6	N/A	N/A	N/A	ACN
OPAC	3-Hydroxyfluorene	PVUBSZGNXLNTLX-UHFFFAOYSA-N	6344-67-8	Cambridge Isotope Laboratories	98.0	Liquid	Toluene
OPAC	3-Hydroxyphenanthrene	NGPOABOEXMDQBT-UHFFFAOYSA-N	605-87-8	Dr. Ehrenstorfer GmbH	99.5	Solid	ACN
OPAC	3-Methylbenzofuran	ZRXHLJNBNWVNIM-UHFFFAOYSA-N	21535-97-7	Sigma Aldrich	98.7	Liquid	MeOH
OPAC	4-Hexylphenol	SZWBRVPZWJYIHI-UHFFFAOYSA-N	2446-69-7	Sigma Aldrich	98.1	Solid	MeOH
OPAC	4-Hydroxyphenanthrene	SIMYIUXARJLHEA-UHFFFAOYSA-N	7651-86-7	DR. Ehrenstorfer GmbH	99.5	Solid	ACN
OPAC	4-Nonylphenol	IGFHQQFPSIBGKE-UHFFFAOYSA-N	104-40-5	Sigma Aldrich	99.9	Solid	MeOH
OPAC	4-tert-Butylphenol	QHPQWRBYOIRBIT-UHFFFAOYSA-N	98-54-4	Sigma Aldrich	99.3	Solid	MeOH
OPAC	9-Hydroxyfluorene	AFMVESZOYKHDBJ-UHFFFAOYSA-N	1689-64-1	Acros Organics	99.8	Solid	ACN
OPAC	9-Hydroxyphenanthrene	DZKIUEHLEXLYKM-UHFFFAOYSA-N	484-17-3	Sigma Aldrich	93.9	Solid	ACN
OPAC	Dibenzofuran	TXCDCPKCNAJMEE-UHFFFAOYSA-N	132-64-9	Fluka Analytical	99.9	Solid	MeOH
OPAC	Naphthaldehyde	SQAINHDHICKHLX-UHFFFAOYSA-N	66-77-3	Alfa Aeser	99.3	Liquid	MeOH
OPAC	o-Cresol	QWVGKYWNOKOFNN-UHFFFAOYSA-N	95-48-7	Sigma Aldrich	99.8	Liquid	MeOH
OPAC	Phenol	ISWSIDIOOBJBQZ-UHFFFAOYSA-N	108-95-2	Sigma Aldrich	99.5	Solid	MeOH
NPAC	1,4,8-Trimethylcarbazole	DKMJSUBUAMUZAJ-UHFFFAOYSA-N	N/A	N/A	N/A	N/A	MeOH
NPAC	11H-Benzo[a]carbazole	MYKQKWIPLZEVOW-UHFFFAOYSA-N	239-01-0	Sigma Aldrich	N/A	Solid	MeOH
NPAC	1-Methylcarbazole	HIAGSPVAYSSKHL-UHFFFAOYSA-N	N/A	N/A	N/A	N/A	MeOH

Chemical class	Constituent name	InchiKey	CAS no.	Vendor	Purity	Form when purchased	Solvent for individual stock solution
NPAC	1-Methylisoquinoline	PBYMYAJONQZORL-UHFFFAOYSA-N	1721-93-3	Sigma Aldrich	99.4	Liquid	MeOH
NPAC	2,3,6,7-Tetramethylcarbazole	HWDNKGBOXICHLW-UHFFFAOYSA-N	N/A	N/A	N/A	N/A	MeOH
NPAC	2,3,6-Trimethylcarbazole	BPIBYEJKQUCBHG-UHFFFAOYSA-N	N/A	N/A	N/A	N/A	MeOH
NPAC	2,3-Dimethylindole	PYFVEIDRTLBMHG-UHFFFAOYSA-N	91-55-4	N/A	N/A	N/A	MeOH
NPAC	2-tert-Butyl-1H-indole	WVPGIDWFLXGCLA-UHFFFAOYSA-N	1805-65-8	Chiron	99.7	Solid	MeOH
NPAC	3-Methylindole	ZFRKQXVRDFCRJG-UHFFFAOYSA-N	83-34-1	Sigma Aldrich	99.9	Solid	MeOH
NPAC	4,6,8-Trimethylquinoline	HNCYZWOTJQPKTQ-UHFFFAOYSA-N	88565-88-2	Chiron	99.5	Liquid	Isooctane
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	QMQBZYPNTIWQGW-UHFFFAOYSA-N	4133-22-6	Chiron	99.9	Liquid	Toluene
NPAC	5-Methylindole	YPKBCLZFIYBSHK-UHFFFAOYSA-N	614-96-0	N/A	N/A	N/A	MeOH
NPAC	8,10-Dimethyl-Benzo[a]acridine	QJPFZQCEUDMYTG-UHFFFAOYSA-N	53-69-0	N/A	N/A	Solid	MeOH
NPAC	8-Methyl-11(H)-benzo[a]carbazole	ZABDXPYMQDDAFD-UHFFFAOYSA-N	21064-33-5	Chiron	99.9	Liquid	Toluene
NPAC	9-Ethylcarbazole	PLAZXGNBGZYJSA-UHFFFAOYSA-N	86-28-2	Sigma Aldrich	99.9	Solid	MeOH
NPAC	9-Methylacridine	FLDRLXJNISEWNZ-UHFFFAOYSA-N	611-64-3	Chiron	98.5	Solid	MeOH
NPAC	Acridine	DZBUGLKDJFMEHC-UHFFFAOYSA-N	260-94-6	Alfa Aeser	99.4	Solid	MeOH
NPAC	Benzo[c]acridine	OAPPEBNXKAKQGS-UHFFFAOYSA-N	225-51-4	Sigma Aldrich	N/A	Solid	MeOH
NPAC	Benzo[h]quinoline	WZJYKHNJTSNBHV-UHFFFAOYSA-N	230-27-3	Alfa Aeser	98.7	Solid	MeOH
NPAC	Benzonitrile	JFDZBHWFFUWGJE-UHFFFAOYSA-N	100-47-0	Fluka Analytical	N/A	N/A	MeOH
NPAC	Benzothiazole	IOJUPLGTWVMSFF-UHFFFAOYSA-N	95-16-9	Sigma Aldrich	99.4	Liquid	N/A
NPAC	Carbazole	UJOBWOGCFQCDNV-UHFFFAOYSA-N	86-74-8	Sigma Aldrich	99.3	Solid	MeOH
NPAC	Dibenzo[a,h]acridine	JNCSIWAONQTVCF-UHFFFAOYSA-N	226-36-8	European Commission Community Bureau of Reference	99.92	Solid	MeOH
NPAC	Dibenzo[f,h]quinoline	RIYPENPUNLHEBK-UHFFFAOYSA-N	217-65-2	Sigma Aldrich	87.75	Solid	MeOH
NPAC	Indole	SIKJAQJRHWYJAI-UHFFFAOYSA-N	120-72-9	Sigma Aldrich	99.7	Solid	MeOH
NPAC	Quinoline	SMWDFEZZVXVKRB-UHFFFAOYSA-N	91-22-5	Acros Organics	98.9	Liquid	MeOH
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	NTAGXJQHJQUOOA-UHFFFAOYSA-N	53440-12-3	Sigma Aldrich	99	Solid	MeOH
Acid	1-Adamantane carboxylic acid	JIMXXGFJRDUSRO-UHFFFAOYSA-N	828-51-3	Sigma Aldrich	99.7	Solid	Acetone
Acid	1-Hydroxy-2-naphthoic acid	SJJCQDRGABAVBB-UHFFFAOYSA-N	86-48-6	Sigma Aldrich	99.8	Solid	Acetone
Acid	1-Naphthoic acid	LNETULKMXZVUST-UHFFFAOYSA-N	86-55-5	Alfa Aeser	99.7	Solid	Acetone
Acid	1-Pyrene carboxylic acid	HYISVWRHTUCNCS-UHFFFAOYSA-N	19694-02-1	Sigma Aldrich	98.2	Solid	MeOH

Chemical class	Constituent name	InchiKey	CAS no.	Vendor	Purity	Form when purchased	Solvent for individual stock solution
Acid	2-Naphthoic acid	UOBYKYZJUGYBDK-UHFFFAOYSA-N	93-09-4.	Sigma Aldrich	99.4	Solid	Acetone
Acid	2-Phenanthrene carboxylic acid	QTWYUOSZMIWHJV-UHFFFAOYSA-N	40452-20-8	N/A	N/A	Solid	MeOH
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	DHIIUPVOLLOORM-YXSUXZIUSA-N	281-23-2	Sigma Aldrich	N/A	Solid	Acetone
Acid	3-Chrysene carboxylic acid	VQQQKLBIQBNFOY-UHFFFAOYSA-N	96403-20-2	N/A	N/A	Solid	MeOH
Acid	Lauric acid	POULHZVOKOAJMA-UHFFFAOYSA-N	143-07-7	Sigma Aldrich	98.8	Solid	Acetone
Acid	Linoleic acid	OYHQOLUKZRVURQ-HZJYTTRNSA-N	60-33-3	Sigma Aldrich	99.0	Liquid	Acetone
Acid	Linolenic acid	DTOSIQBPPRVQHS-PDBXOOCHSA-N	463-40-1	Sigma Aldrich	99.0	Liquid	Acetone
Acid	Oleic acid	BOWVQLFMWHZBEF-KTKRTIGZSA-N	112-80-1	Sigma Aldrich	99.2	Liquid	Acetone
Acid	Palmitoleic acid	SECPZKHBENQXJG-FPLPWBNLSA-N	373-49-9	Sigma Aldrich	99.0	Liquid	Acetone
Acid	Pentadecanoic acid	WQEPLUUGTLDZJY-UHFFFAOYSA-N	1002-84-2	Sigma Aldrich	98.8	Solid	MeOH:Ethyl acetate (9:1)
Acid	Stearic acid	QIQXTHQIDYTFRH-UHFFFAOYSA-N	57-11-4.	Sigma Aldrich	99.5	Solid	MeOH:Ethyl acetate (9:1)
IS	1-Hydroxynaphthalene (13C6, 99%)	N/A	N/A	Cambridge Isotope Laboratories	99.8	Liquid	Toluene
IS	1-napthol-2,3,4,5,6,7,8-d7	KJCVRFUGPWSIIH-GSNKEKJESA-N	124251-84-9	Chiron	99.0	Liquid	Isooctane
IS	2-Hydroxyfluorene (13C6, 99%)	N/A	N/A	Cambridge Isotope Laboratories	99.7	Liquid	Toluene
IS	4-Hydroxyphenanthrene (13C6, 99%)	N/A	N/A	Cambridge Isotope Laboratories	100.0	Liquid	Toluene
IS	9-Anthracene-d9-carboxylic acid	N/A	1219803-78-7	CDN Isotopes	99.0	Solid	MeOH
IS	Acenaphthene-d10	CWRYPZZKDGJXCA-WHUVPORUSA-N	15067-26-2	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	Acenaphthylene-d8	HXGDTGSAIMULJN-PGRXLJNUSA-N	93951-97-4	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	Acridine-d9	DZBUGLKDJFMEHC-LOIXRAQWSA-N	34749-75-2	Chiron	99.5	Liquid	Toluene
IS	Adamantane-d16	ORILYTVJVMAKLC-IHRGUYRUSA-N	30470-60-1	Chiron	99.8	Liquid	Isooctane
IS	Anthracene-d10	MWPLVEDNUUSJAV-LHNTUAQVSA-N	1719-06-8	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	Benzo[a]anthracene-d12	DXBHBZVCASKNBY-AQZSQYOVSA-N	1718-53-2	Cambridge Isotope Laboratories	98.6	Solid	Isooctane
IS	Benzo[a]pyrene-d12	FMMWHPNWAFZXNH-AQZSQYOVSA-N	63466-71-7	Sigma Aldrich	98.4	Solid	Isooctane
IS	Benzo[g,h,i]perylene-d12	GYFAGKUZYNFMBN-AQZSQYOVSA-N	93951-66-7	Dr. Ehrenstorfer GmbH	99.0	Solid	Isooctane
IS	Benzo[k]fluoranthene-d12	HAXBIWFMXWRORI-AQZSQYOVSA-N	93952-01-3	Dr. Ehrenstorfer GmbH	99.9	Solid	Isooctane
IS	Biphenyl-d10	ZUOUZKKEUPVFJK-LHNTUAQVSA-N	1486-01-7	Chiron	99.7	Solid	Isooctane
IS	Carbazole-d8	UJOBWOGCFQCDNV-PGRXLJNUSA-N	97960-57-1	Chiron	99.2	Solid	MeOH
IS	Chrysene-d12	WDECIBYCCFPHNR-AQZSQYOVSA-N	1719-03-5	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	Dibenzofuran-d8	TXCDCPKCNAJMEE-PGRXLJNUSA-N	93952-04-6	Chiron	99.9	Liquid	Isooctane

Chemical class	Constituent name	InchiKey	CAS no.	Vendor	Purity	Form when purchased	Solvent for individual stock solution
IS	Dibenzothiophene-d8	IYYZUPMFVPLQIF-PGRXLJNUSA-N	33262-29-2	Cambridge Isotope Laboratories	99.4	Solid	Isooctane
IS	Fluoranthene-d10	GVEPBJHOBDJJJI-LHNTUAQVSA-N	93951-69-0	Cambridge Isotope Laboratories	N/A	Solid	Isooctane
IS	Fluorene-d10	NIHNNTQXNPWCJQ-QNNBDYQESA-N	81103-79-9	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	Hydroxypyrene-d9	BIJNHUAPTJVVNQ-LOIXRAQWSA-N	132603-37-3	N/A	N/A	N/A	Isooctane
IS	Indeno[1,2,3-c,d]pyrene-d12	SXQBHARYMNFBPS-AQZSQYOVSA-N	203578-33-0	Cambridge Isotope Laboratories	98.1	Solid	Isooctane
IS	Indole-d7	SIKJAQJRHWYJAI-HOSXNMPPSA-N	73509-20-3	Sigma Aldrich	99.5	Solid	MeOH
IS	Naphthalene-d8	UFWIBTONFRDIAS-PGRXLJNUSA-N	1146-65-2	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	n-Butylbenzene-d14	OCKPCBLVNKHBMX-GQMPCAPXSA-N	7116-96-3	Chiron	99.8	Liquid	Isooctane
IS	n-Nonylbenzene-2,3,4,5,6-d5	LIXVMPBOGDCSRM-VDUBJQOGSA-N	634897-78-2	Chiron	99.6	Liquid	Isooctane
IS	Phenanthrene-d10	YNPNZTXNASCQKK-LHNTUAQVSA-N	1517-22-2	Cambridge Isotope Laboratories	N/A	N/A	Isooctane
IS	Phenol-d6	ISWSIDIOOBJBQZ-QNKSCLMFSA-N	13127-88-3	Sigma Aldrich	99.9	Solid	EtOH
IS	Pyrene-d10	BBEAQIROQSPTKN-LHNTUAQVSA-N	1718-52-1	Cambridge Isotope Laboratories	98.0	Solid	Isooctane

B Method validation

Appendix B gives additional information for the GC-MS/SIM method validation including detection limit, limit of quantification, linearity, accuracy, recovery, and precision for the individual analytes.

B.1 Data analysis

The GC-MS/SIM data was evaluated with MassHunter Workstation GC-MS Software Quantitative Analysis (version B.07.00). Calibration curves were set up in MassHunter for target constituents using weighted least squares regression (with a weight of 1/x, where x is the concentration). Thus equal importance is given to all calibration levels throughout the curve as the absolute variation tends to be higher at higher concentrations than at the lower end of the curve (so-called heteroscedasticity) [20]. Constituent groups were defined using MassHunter, MSD ChemStation (version D.03.00.611) and GC Image (version 2.9R1.1). Integration of the constituent groups was conducted in Masshunter. For some groups, two standards were available and here the averages of the slopes for the individual calibration curves were used for the calculation of DL and LOQ.

GC×GC-HRMS data was evaluated using GC Image, via the application of an area template including both target constituents and constituent groups. Linear calibration curves were created and evaluated within GC Image for the target constituents.

The softwares used for SFC-ESI-HRMS data analysis and quantification was MassLynx (v4.1) and TargetLynx (v4.1), respectively, with the calibration curves set up and evaluated in the latter.

Calibration curves were for all analytical methods based on eight levels with the intercept defined by the software (i.e. not forced through zero). For determination of instrument DL and LOQ replicate analysis of the standard with the lowest detectable concentration was used.

The formulae used to calculate DL (Eq. 1) and LOQ (Eq. 2) were:

$$DL_x = \frac{(\overline{RR}_{Blank} + t \cdot s) - b}{Slope} \cdot C_{IS} \qquad \text{(Eq. 1)}$$

$$LOQ_x = \frac{(\overline{RR}_{Blank} + 10 \cdot s) - b}{Slope} \cdot C_{IS} \qquad \text{(Eq. 2)}$$

where $\overline{RR}_{Blank}$ is the average relative response of three extraction blanks; t is the t-value based on α=0.95 and 4 degrees of freedom; s is the standard deviation of triplicate measurements of calibration solution levels L1, L2 or the QC sample; b is the intercept; $Slope$ is the slope of the calibration curve; and C_{IS} is the concentration of the respective internal standard.

The b-value was not included in the equation for GC-MS/SIM and GC×GC-HRMS to prevent calculation of negative DL and LOQ values.

All DL and LOQ values are for sample extracts in 1 mL. To obtain DL and LOQ values per g product, values should be divided by 0.25 g/mL (sample weight per mL of extract).

For the separate method validation for the GC-MS/SIM method, a four-level calibration curve was set up based on the lowest four levels of the calibration standards. The null-level calibration standard was used to visually inspect if the calibration curve should have an off-set. If the null-level calibration standard clearly showed a peak for the constituent in question, an intercept was included in the calibration curve. For constituents were there was no visible peak in the null-

level calibration standard, the intercept for the calibration curve was forced through zero. The analytes for which the calibration curve included an intercept are marked with an asterisk in Appendix B.3.1. For a few constituents, it was necessary to exclude a calibration standard due to deviation from linearity (2,2,5,7-tetramethyltetralin, phenol, o-cresol, and 9-hydroxyphenanthrene).

DL and LOQ were determined per analyte based on triplicate measurements of calibration standard L1. DL and LOQ were calculated for each of the two extraction blocks.

Accuracy was determined based on three post-spiked samples, i.e. fractionated blank samples (from extraction block II) that were spiked prior to GC-MS/SIM analysis (see Appendix B.2). The spiking level was 5 – 14 ng/mL which was below the lowest calibration level. Therefore a four-level calibration curve based on the lowest four levels of the calibration standards was set up to focus the calibration curve in the concentration range of the samples and therefore get a better estimation of the accuracy. The null-level calibration standards were used to visually inspect if the calibration curve should have an off-set or not. If the null-level calibration standards clearly showed a peak for the constituent in question, the calibration curve was set up to include an intercept. For constituents where there was no visible peak in the null-level calibration standard, the intercept for the calibration curve was set to zero.

Accuracy was calculated based on the formula (Eq. 3):

$$Accuracy = \frac{average\ concentration\ found - known\ concentration}{known\ concentration} \cdot 100 \qquad \text{(Eq. 3)}$$

Recovery was calculated based on three spiked blank samples that were fractionated in extraction block II and three fractionated blank samples that were spiked post extraction and prior to GC-MS/SIM analysis (post-spiked samples, see appendix B.2). Blank subtraction was performed and the relative response (RR) for the analytes in the spiked blank samples was then compared to the post-spiked samples according to this formula (Eq. 4):

$$Recovery = \frac{RR\ of\ analyte\ in\ spiked\ blank\ sample}{RR\ of\ analyte\ in\ post-spiked\ blank\ sample} \cdot 100 \qquad \text{(Eq. 4)}$$

Method precision was determined based on triplicate analysis of three product combinations in each of the two extraction blocks and therefore describes how close together samples lie that have undergone the entire process from sample preparation to quantification. The method precision for each block was calculated as the relative standard deviation of the triplicate analyte concetration in the sample extract determined on an eight level calibration curve. The intermediate method precision was the relative standard deviation of all six replicates.

B.2 Sample preparation for separate GC-MS/SIM validation experiment

Five samples representing each of the five product types were used for method validation of the GC-MS/SIM method. Briefly, the sample preparation followed the description in Section 3.3, but in order to have enough volume for triplicates, the solvent volume for sample pre-treatment was doubled. Prior to SAR fractionation, the coal tar and tyre pyrolysis oil were combined 1:1 (CTPO) and the asphalt and lubricating oil were likewise combined 1:1 (AspLub). The car wax/polish was not mixed with another sample. Two sets of samples were prepared on different days,

denoted Extraction Block I and Extraction Block II. The same asphalt dissolved in DCM was used for the two extraction block. The samples were further processed as according to Section 3.7.

Three blank samples and three spiked blanks were SAR fractionated per extraction block according to Section 3.3. The blank samples consisted of 10 mL heptane while the spiked blank samples were 10 mL of heptane spiked with 500 µL of each of the OPAC, NPAC and aromatics stock solution mixtures and 250 µL of each of the saturates and SPAC stock solution mixtures. The blank and the spiked blank samples were further processed as according to Section 3.7. Three post-spiked samples were prepared for the SAS fraction and consisted of 1400 µL of each of F1 and F2 (from the SAR fractionated blank sample), 120 µL AP mixture, 200 µL SAS-IS mixture, 20 µL aromatics stock solution mixture, 10 µL of each of saturates and SPAC stock solution mixtures, 210 µL ethanol and 630 µL DCM. Likewise, three post-spiked samples for the ON fraction were prepared from 5.22 mL of F3 (from the SAR fractionated blank sample, diluted 1:4 with DCM:MeOH (1:1) to have enough volume), 180 µL AP mixture, 480 µL ON-IS mixture, and 10 µL of each of OPAC and NPAC stock solution mixtures. The spiked blank and post-spiked samples thus contained different concentrations of the standards and IS which is taken into account when comparing the samples. Due to human error, all blank, spiked blank, and post-spiked ON samples were preconcentrated in extraction block I. Only extraction block II samples were therefore used for calculating recovery and accuracy for both SAS and ON constituents.

QC samples were prepared by combining equal parts of CTPO, AspLub, and car wax. A set of calibration standards was prepared for each extraction block consisting of eight calibration standards (L1 – L8), a null-level calibration standard, and triplicates of calibration standards L1, L2 and L6.

Due to human error, the mass-to-charge ratio (*m/z*) for the ON internal standards phenol-d6 and indole-d7 were not included in the GC-MS/SIM method. Instead, C0-C4 indoles and C0-C9 phenols were assigned carbazole-d8 and dibenzofuran-d8 as internal standards, respectively.

B.3 Validation parameters from separate GC-MS/SIM validation experiment

B.3.1 Detection limit, limit of quantification, and linearity

Detection limit (DL), limit of quantification (LOQ) and linearity from extraction block I and extraction block II in the separate GC-MS/SIM validation experiment are presented in Table B.1.

Table B.1: DL, LOQ, and linearity for target constituents analysed in the separate GC-MS/SIM validation experiment

*Calibration curve was not forced through zero

Chemical class	Constituent	DL (ng/mL)		LOQ (ng/mL)		Linearity (R^2)	
		Block I	Block II	Block I	Block II	Block I	Block II
Saturate	1,3-Dimethyladamantane	2.2	0.8	7.8	2.9	0.9985	0.9976
Saturate	1-Methyldecalin	0.2	3.1	0.6	11	0.9995	0.9939
Saturate	2-Isopropyldecalin	0.7	7.4	2.4	27	0.9995	0.9991
Saturate	Adamantane	1.5	0.5	5.2	1.7	0.9996	0.9989
Saturate	Butylcyclohexane	0.8	0.4	2.7	1.5	0.9995	0.9996
Aromatic	1,3,6-Trimethylchrysene	2.5	1.2	8.9	4.3	0.9935	0.9961
Aromatic	1-Methylfluorene	0.8	0.8	2.9	2.8	0.9900	0.9945
Aromatic	1-Methylnaphthalene	0.7	0.5	2.7	1.8	0.9999	0.9998
Aromatic	1-Methylpyrene	2.6	0.2	9.2	0.5	0.9996	0.9996
Aromatic	1-Phenylheptane*	3.1	-3.1	11	2.3	0.9999	0.9997
Aromatic	1-Phenylnonane	1.1	11	3.8	16	0.9997	0.9998
Aromatic	1-Phenyloctane	0.9	1.6	3.4	5.8	0.9999	0.9997
Aromatic	2,2,5,7-Tetramethyltetralin*	27	-19	95	-2.2	0.9998	0.9995
Aromatic	2,6-Dimethylnaphthalene	1.6	3.3	3.0	6.9	0.9933	0.9974
Aromatic	2-Methylbenzothiophene	0.9	0.7	1.9	1.4	0.9997	0.9998
Aromatic	2-Methylphenanthrene	0.9	0.6	3.3	2.1	0.9995	0.9995
Aromatic	3,3',5,5'-Tetramethylbiphenyl	0.1	0.3	0.3	1.3	0.9977	0.9974
Aromatic	3,3'-Dimethylbiphenyl	0.3	0.2	1.0	0.7	0.9998	0.9996
Aromatic	4-Methylchrysene	1.6	0.4	5.8	1.4	0.9999	0.9998
Aromatic	4-n-Pentylbiphenyl	0.0	0.3	0.1	1.2	0.9976	0.9977
Aromatic	6-Ethylchrysene	1.6	0.9	5.8	3.4	0.9999	0.9997
Aromatic	Acenaphthene	3.5	2.0	4.9	3.0	0.9996	0.9997
Aromatic	Acenaphthylene	0.2	0.3	0.8	1.0	0.9988	0.9985
Aromatic	Anthracene	2.3	1.0	8.1	3.4	0.9761	0.9923
Aromatic	Benzo[a]anthracene	1.7	1.0	6.3	3.6	0.9998	0.9995
Aromatic	Benzo[a]pyrene	1.6	1.6	5.7	5.8	0.9996	0.9996
Aromatic	Benzo[b]fluoranthene*	1.7	0.6	3.6	1.9	0.9986	0.9978
Aromatic	Benzo[e]pyrene	4.3	0.3	15	1.1	0.9997	0.9998
Aromatic	Benzo[g,h,i]perylene	1.1	1.8	3.4	5.7	0.9998	0.9997
Aromatic	Benzo[k]fluoranthene	3.1	1.4	11	5.1	0.9991	0.9991

Chemical class	Constituent	DL (ng/mL)		LOQ (ng/mL)		Linearity (R^2)	
		Block I	Block II	Block I	Block II	Block I	Block II
Aromatic	Biphenyl*	0.9	0.8	2.9	1.6	0.9998	0.9998
Aromatic	Butylbenzene	0.1	1.8	0.3	6.5	0.9996	0.9998
Aromatic	Chrysene	2.1	1.0	7.5	3.5	0.9995	0.9997
Aromatic	Dibenz[a,h]anthracene	1.8	0.8	6.3	2.4	0.9997	0.9996
Aromatic	Fluoranthene	0.9	0.3	2.5	0.9	0.9997	0.9996
Aromatic	Fluorene	0.5	0.1	1.7	0.4	0.9998	0.9997
Aromatic	Hexylbenzene	0.8	1.2	2.9	4.5	0.9992	0.9996
Aromatic	Indeno[1,2,3-c,d]pyrene	2.8	0.3	9.9	0.8	0.9996	0.9998
Aromatic	Naphthalene*	1.0	0.4	1.9	1.0	0.9997	0.9997
Aromatic	Perylene	1.2	1.4	4.3	5.0	0.9995	0.9997
Aromatic	Phenanthrene	1.7	1.0	4.5	2.4	0.9998	0.9995
Aromatic	Pyrene	1.0	0.4	3.5	1.2	0.9998	0.9995
Aromatic	Tetralin*	1.2	1.5	2.3	2.8	0.9998	0.9997
SPAC	1-Benzothiophene	0.8	0.8	3.0	2.9	0.9997	0.9993
SPAC	2,3,4-Trimethylbenzothiophene	2.2	2.7	8.0	9.6	0.9997	0.9997
SPAC	2-Methylnaphthalene	0.1	0.3	0.3	0.7	0.9970	0.9915
SPAC	3-Methylbenzothiophene*	4.4	2.9	5.2	3.5	0.9993	0.9997
SPAC	4,6-Dimethyldibenzothiophene	0.5	0.2	1.7	0.9	0.9990	0.9988
SPAC	4-Ethyl-6-methyldibenzothiophene	0.7	0.5	2.4	1.8	0.9990	0.9995
SPAC	4-Methyldibenzothiophene	0.2	0.4	0.5	1.4	0.9993	0.9988
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	3.0	0.9	11	3.4	0.9995	0.9993
SPAC	Dibenzothiophene*	3.3	2.2	6.5	3.8	0.9996	0.9993
OPAC	2,3-Benzofuran	1.6	7.7	4.1	12	0.9970	0.9903
OPAC	2-Hydroxynaphthalene*	1.0	3.0	2.8	4.5	0.9935	0.9951
OPAC	2-Methyldibenzofuran	0.8	0.3	2.5	0.7	0.9954	0.9972
OPAC	2-n-Butylbenzofuran	0.5	0.2	1.2	0.6	0.9976	0.9993
OPAC	3,5-Dimethylphenol*	8.9	4.0	10	19	0.9982	0.9978
OPAC	3-Methylbenzofuran	1.4	1.2	2.1	2.4	0.9965	0.9975
OPAC	4-Hexylphenol	0.2	2.4	0.2	6.0	0.9961	0.9969
OPAC	4-Nonylphenol	3.6	2.1	11	7.0	0.9954	0.9991
OPAC	4-tert-Butylphenol	1.9	0.9	2.3	3.4	0.9974	0.9980
OPAC	9-Hydroxyfluorene	4.1	1.4	12	4.1	0.9946	0.9977
OPAC	9-Hydroxyphenanthrene	0.0	6.7	0.0	24	0.9843	0.9761
OPAC	Dibenzofuran*	0.8	2.5	4.5	4.1	0.9970	0.9978
OPAC	Naphthaldehyde	8.8	40	32	75	0.9876	0.9589
OPAC	o-Cresol	45	40	45	46	0.9967	0.9985
OPAC	Phenol*	243	57	671	149	0.9937	0.9637
NPAC	1,4,8-Trimethylcarbazole	2.2	0.7	6.7	2.0	0.9988	0.9997
NPAC	11H-Benzo[a]carbazole	2.6	1.4	8.5	4.7	0.9971	0.9989

Chemical class	Constituent	DL (ng/mL)		LOQ (ng/mL)		Linearity (R^2)	
		Block I	Block II	Block I	Block II	Block I	Block II
NPAC	1-Methylcarbazole	0.9	0.5	3.1	1.8	0.9982	0.9997
NPAC	1-methylisoquinoline	2.1	1.2	6.7	4.2	0.9979	0.9987
NPAC	2,3,6,7-Tetramethylcarbazole	3.7	0.8	12	1.9	0.9952	0.9943
NPAC	2,3,6-Trimethylcarbazole	1.4	1.0	4.3	3.6	0.9956	0.9962
NPAC	2,3-Dimethylindole	22	7.6	39	16	0.9971	0.9978
NPAC	2-tert-Butyl-1H-indole	0.1	0.7	0.4	2.4	0.9981	0.9983
NPAC	3-Methylindole	0.8	3.7	2.1	8.4	0.9964	0.9987
NPAC	4,6,8-Trimethylquinoline	0.6	1.6	1.6	5.0	0.9979	0.9995
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	3.1	1.3	9.5	3.0	0.9979	0.9987
NPAC	5-Methylindole	2.1	0.2	3.1	0.7	0.9982	0.9987
NPAC	8,10-Dimethyl-Benzo[a]acridine	4.0	1.3	13	3.6	0.9958	0.9976
NPAC	8-Methyl-11(H)-benzo[a]carbazole	3.9	1.2	13	3.9	0.9970	0.9989
NPAC	9-Methylacridine	2.0	3.0	7.0	10	0.9982	0.9991
NPAC	Acridine	0.4	0.6	1.1	2.0	0.9987	0.9996
NPAC	Benzo[c]acridine	2.6	1.2	8.5	4.0	0.9973	0.9985
NPAC	Benzo[h]quinoline*	1.3	3.3	1.6	6.4	0.9985	0.9990
NPAC	Benzonitrile	14	11.0	37	40	0.9938	0.9972
NPAC	Carbazole	0.6	0.9	1.0	3.3	0.9981	0.9997
NPAC	Dibenzo[a,h]acridine	6.7	3.6	22	9.7	0.9930	0.9961
NPAC	Dibenzo[f,h]quinoline	2.6	1.2	7.9	3.4	0.9981	0.9990
NPAC	Indole	1.8	0.9	4.7	3.3	0.9971	0.9981
NPAC	Quinoline	3.0	1.6	7.7	5.7	0.9974	0.9522

B.3.2 Instrument and QC precision

Instrument and QC precision for extraction block I and extraction block II from the separate GC-MS/SIM validation experiment listed in Table B.2.

Table B.2: Instrument and QC precision for block I and block II from the separate GC-MS/SIM validation experiment

Chemical class	Constituent	Instrument precision (%)		QC precision (%)	
		Block I	Block II	Block I	Block II
Saturate	1,3-Dimethyladamantane	1.4	2.3	5.6	2.6
Saturate	1-Methyldecalin	1.9	8.7	2.4	3.5
Saturate	2-Isopropyldecalin	11	18	N/A	N/A
Saturate	Adamantane	1.3	1.1	11	16
Saturate	Butylcyclohexane	4.4	1.2	4.6	2.3
Aromatic	1,3,6-Trimethylchrysene	8.7	4.1	6.8	2.5
Aromatic	1-Methylfluorene	1.4	2.1	4.6	1.6
Aromatic	1-Methylnaphthalene	2.0	1.6	0.1	0.5
Aromatic	1-Methylpyrene	7.8	0.5	1.9	2.3
Aromatic	1-Phenylheptane	12	5.2	N/A	N/A
Aromatic	1-Phenylnonane	3.2	6.0	N/A	N/A
Aromatic	1-Phenyloctane	5.5	5.3	N/A	N/A
Aromatic	2,2,5,7-Tetramethyltetralin	20	6.6	N/A	30
Aromatic	2,6-Dimethylnaphthalene	1.7	5.0	0.3	0.6
Aromatic	2-Methylnaphthalene	0.3	0.8	0.5	0.7
Aromatic	2-Methylphenanthrene	2.6	2.2	1.3	1.3
Aromatic	3,3',5,5'-Tetramethylbiphenyl	0.3	1.2	N/A	3.2
Aromatic	3,3'-Dimethylbiphenyl	0.8	0.6	1.4	0.6
Aromatic	4-Methylchrysene	7.4	1.8	7.0	0.4
Aromatic	4-n-Pentylbiphenyl	0.1	1.2	0.6	5.5
Aromatic	6-Ethylchrysene	8.4	3.5	3.3	9.3
Aromatic	Acenaphthene	1.0	1.3	0.5	0.3
Aromatic	Acenaphthylene	0.8	1.1	1.3	1.2
Aromatic	Anthracene	3.8	2.6	11	5.4
Aromatic	Benzo[a]anthracene	5.2	4.1	2.3	2.8
Aromatic	Benzo[a]pyrene	3.0	5.5	1.6	3.8
Aromatic	Benzo[b]fluoranthene	1.7	1.8	1.0	2.1
Aromatic	Benzo[e]pyrene	7.8	1.0	2.6	2.4
Aromatic	Benzo[g,h,i]perylene	2.5	5.4	1.1	0.7
Aromatic	Benzo[k]fluoranthene	9.7	6.1	1.5	3.3
Aromatic	Biphenyl	1.9	1.0	0.3	0.5
Aromatic	Butylbenzene	2.3	6.9	4.4	5.3
Aromatic	Chrysene	4.8	3.6	4.6	2.7
Aromatic	Dibenz[a,h]anthracene	6.4	2.7	8.4	9.2

Chemical class	Constituent	Instrument precision (%)		QC precision (%)	
		Block I	Block II	Block I	Block II
Aromatic	Fluoranthene	1.0	0.7	1.1	1.8
Aromatic	Fluorene	0.9	0.4	0.3	1.3
Aromatic	Hexylbenzene	21	4.1	N/A	N/A
Aromatic	Indeno[1,2,3-c,d]pyrene	9.2	0.7	5.4	4.3
Aromatic	Naphthalene	0.9	0.8	0.0	1.6
Aromatic	Perylene	9.6	5.9	8.6	5.7
Aromatic	Phenanthrene	2.6	2.1	0.4	0.9
Aromatic	Pyrene	1.6	1.1	0.6	0.7
Aromatic	Tetralin	3.0	1.6	2.3	1.0
SPAC	1-Benzothiophene	1.7	2.5	1.8	2.8
SPAC	2,3,4-Trimethylbenzothiophene	7.0	8.1	12	5.4
SPAC	2-Methylbenzothiophene	1.0	0.7	0.5	1.3
SPAC	3-Methylbenzothiophene	0.8	0.6	1.0	1.6
SPAC	4,6-Dimethyldibenzothiophene	1.6	0.8	2.2	0.5
SPAC	4-Ethyl-6-methyldibenzothiophene	3.8	1.7	4.2	1.6
SPAC	4-Methyldibenzothiophene	0.4	1.2	1.2	1.4
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	7.9	3.1	5.8	5.1
SPAC	Dibenzothiophene	4.0	2.2	1.8	2.4
OPAC	2,3-Benzofuran	2.8	4.9	N/A	12
OPAC	2-Hydroxynaphthalene	2.2	1.9	20	14
OPAC	2-Methyldibenzofuran	2.3	0.5	N/A	N/A
OPAC	2-n-Butylbenzofuran	1.0	0.5	55	N/A
OPAC	3,5-Dimethylphenol	3.2	13	9.7	17
OPAC	3-Methylbenzofuran	0.7	1.1	N/A	N/A
OPAC	4-Hexylphenol	0.0	4.2	22	N/A
OPAC	4-Nonylphenol	9.4	6.7	N/A	N/A
OPAC	4-tert-Butylphenol	0.5	3.2	21	N/A
OPAC	9-Hydroxyfluorene	8.9	3.5	N/A	N/A
OPAC	9-Hydroxyphenanthrene	0.0	12	6.4	6.2
OPAC	Dibenzofuran	4.1	1.9	N/A	N/A
OPAC	Naphthaldehyde	21	21	N/A	N/A
OPAC	o-Cresol	0.1	1.4	3.6	1.8
OPAC	Phenol	27	13	12	11
NPAC	1,4,8-Trimethylcarbazole	7.1	2.1	9.9	5.6
NPAC	11H-Benzo[a]carbazole	8.3	4.6	14	12
NPAC	1-Methylcarbazole	3.2	2.0	0.8	1.1
NPAC	1-mMthylisoquinoline	6.8	4.1	N/A	N/A
NPAC	2,3,6,7-Tetramethylcarbazole	11	1.4	N/A	N/A
NPAC	2,3,6-Trimethylcarbazole	4.4	3.8	N/A	N/A

Chemical class	Constituent	Instrument precision (%)		QC precision (%)	
		Block I	Block II	Block I	Block II
NPAC	2,3-Dimethylindole	14	6.7	N/A	9.6
NPAC	2-tert-Butyl-1H-indole	0.4	2.1	N/A	N/A
NPAC	3-Methylindole	1.3	3.6	0.4	N/A
NPAC	4,6,8-Trimethylquinoline	1.2	4.3	N/A	N/A
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	8.7	2.3	N/A	N/A
NPAC	5-Methylindole	0.9	0.5	13	3.9
NPAC	8,10-Dimethyl-Benzo[a]acridine	15	3.9	N/A	N/A
NPAC	8-Methyl-11(H)-benzo[a]carbazole	13	3.8	13	12
NPAC	9-Methylacridine	7.3	9.5	N/A	N/A
NPAC	Acridine	0.9	2.0	5.8	7.1
NPAC	Benzo[c]acridine	8.6	4.0	15	5.0
NPAC	Benzo[h]quinoline	0.4	3.2	6.5	2.0
NPAC	Benzonitrile	32	33	30	3.5
NPAC	Carbazole	0.4	2.7	1.7	2.9
NPAC	Dibenzo[a,h]acridine	20	7.2	N/A	N/A
NPAC	Dibenzo[f,h]quinoline	6.4	2.5	N/A	N/A
NPAC	Indole	4.8	2.4	114	N/A
NPAC	Quinoline	6.3	5.5	5.2	1.6

B.3.3 Recovery and accuracy

The recovery and accuracy of target constituents from extraction block II from the separate GC-MS/SIM validation experiment are listed in Table B.3.

Table B.3: Recovery and accuracy of target constituents from extraction block II

Chemical class	Constituent	Recovery (%)	Accuracy (%)
Saturate	1,3-Dimethyladamantane	61	-12
Saturate	1-Methyldecalin	54	-3.3
Saturate	2-Isopropyldecalin	58	2.8
Saturate	Adamantane	62	-9.2
Saturate	Butylcyclohexane	95	-6.0
Aromatic	1,3,6-Trimethylchrysene	84	27
Aromatic	1-Methylfluorene	98	-5.9
Aromatic	1-Methylnaphthalene	108	-2.9
Aromatic	1-Methylpyrene	108	-10
Aromatic	1-Phenylheptane	68	42
Aromatic	1-Phenylnonane	76	43
Aromatic	1-Phenyloctane	90	5.0
Aromatic	2,2,5,7-Tetramethyltetralin	85	-243
Aromatic	2,6-Dimethylnaphthalene	123	-19
Aromatic	2-Methylnaphthalene	108	-32
Aromatic	2-Methylphenanthrene	104	16
Aromatic	3,3′,5,5′-Tetramethylbiphenyl	98	-11
Aromatic	3,3′-Dimethylbiphenyl	100	-7.5
Aromatic	4-Methylchrysene	103	11
Aromatic	4-n-Pentylbiphenyl	108	-12
Aromatic	6-Ethylchrysene	101	12
Aromatic	Acenaphthene	104	-6.6
Aromatic	Acenaphthylene	100	1.0
Aromatic	Anthracene	139	-1.0
Aromatic	Benzo[a]anthracene	85	-9.1
Aromatic	Benzo[a]pyrene	99	-5.2
Aromatic	Benzo[b]fluoranthene	91	-7.1
Aromatic	Benzo[e]pyrene	79	3.8
Aromatic	Benzo[g,h,i]perylene	90	-2.4
Aromatic	Benzo[k]fluoranthene	102	-16
Aromatic	Biphenyl	109	-11
Aromatic	Butylbenzene	159	35
Aromatic	Chrysene	92	24
Aromatic	Dibenz[a,h]anthracene	171	-46
Aromatic	Fluoranthene	94	1.2

Chemical class	Constituent	Recovery (%)	Accuracy (%)
Aromatic	Fluorene	98	-1.8
Aromatic	Hexylbenzene	104	-3.8
Aromatic	Indeno[1,2,3-c,d]pyrene	93	-11
Aromatic	Naphthalene	107	-4.6
Aromatic	Perylene	107	-13
Aromatic	Phenanthrene	104	-7.1
Aromatic	Pyrene	94	1.7
Aromatic	Tetralin	121	-19
SPAC	1-Benzothiophene	108	-0.5
SPAC	2,3,4-Trimethylbenzothiophene	86	6.2
SPAC	2-Methylbenzothiophene	111	7.9
SPAC	3-Methylbenzothiophene	109	1.4
SPAC	4,6-Dimethyldibenzothiophene	100	-13
SPAC	4-Ethyl-6-methyldibenzothiophene	108	-17
SPAC	4-Methyldibenzothiophene	99	-8.1
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	45	13
SPAC	Dibenzothiophene	97	1.8
OPAC	2,3-Benzofuran	N/A	N/A
OPAC	2-Hydroxynaphthalene	8.2	12
OPAC	2-Methyldibenzofuran	12	-7.0
OPAC	2-n-Butylbenzofuran	5.6	-20
OPAC	3,5-Dimethylphenol	9.6	-34
OPAC	3-Methylbenzofuran	6.5	-15
OPAC	4-Hexylphenol	6.3	-1.1
OPAC	4-Nonylphenol	N/A	1.4
OPAC	4-tert-Butylphenol	5.2	-5.7
OPAC	9-Hydroxyfluorene	7.1	-5.2
OPAC	9-Hydroxyphenanthrene	N/A	259
OPAC	Dibenzofuran	9.0	-4.1
OPAC	Naphthaldehyde	N/A	N/A
OPAC	o-Cresol	7.4	-21
OPAC	Phenol	N/A	N/A
NPAC	1,4,8-Trimethylcarbazole	N/A	-2.1
NPAC	11H-Benzo[a]carbazole	N/A	5.3
NPAC	1-Methylcarbazole	3.8	-7.4
NPAC	1-Methylisoquinoline	14	-4.3
NPAC	2,3,6,7-Tetramethylcarbazole	N/A	-9.4
NPAC	2,3,6-Trimethylcarbazole	N/A	-5.2
NPAC	2,3-Dimethylindole	8.4	17
NPAC	2-tert-Butyl-1H-indole	4.2	-9.0

Chemical class	Constituent	Recovery (%)	Accuracy (%)
NPAC	3-Methylindole	8.5	-5.1
NPAC	4,6,8-Trimethylquinoline	8.3	0.2
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	11	2.0
NPAC	5-Methylindole	4.6	-16
NPAC	8,10-Dimethyl-Benzo[a]acridine	11	3.5
NPAC	8-Methyl-11(H)-benzo[a]carbazole	N/A	2.5
NPAC	9-Methylacridine	11	1.4
NPAC	Acridine	8.6	2.2
NPAC	Benzo[c]acridine	8.1	6.0
NPAC	Benzo[h]quinoline	N/A	9.9
NPAC	Benzonitrile	N/A	N/A
NPAC	Carbazole	N/A	-5.9
NPAC	Dibenz[a,h]acridine	12	3.1
NPAC	Dibenzo[f,h]quinoline	6.2	1.6
NPAC	Indole	9.9	21
NPAC	Quinoline	8.6	3.4

B.3.4 Method precision

Method precision values for extraction block I and extraction block II as well as the intermediate precision for target constituents in AspLub, CTPO, and car wax are listed in Table B.4.

Table B.4: Method precision (%) for target constituents in AspLub, CTPO, and car wax listed as extraction block I, extraction block II, and intermediate precision

Chemical class	Constituent	Extraction block I			Extraction block II			Intermediate		
		AspLub	CTPO	Car wax	AspLub	CTPO	Car wax	AspLub	CTPO	Car wax
Saturate	1,3-Dimethyladamantane	N/A	2.7	67	N/A	4.2	6.6	N/A	3.6	60
Saturate	1-Methyldecalin	6.1	2.0	69	6.6	3.6	17	5.7	11	79
Saturate	2-Isopropyldecalin	7.4	26	N/A	N/A	N/A	N/A	7.4	26	N/A
Saturate	Adamantane	N/A	0.9	88	N/A	6.0	35	N/A	7.0	102
Saturate	Butylcyclohexane	N/A	N/A	71	N/A	N/A	31	N/A	N/A	79
Aromatic	1,3,6-Trimethylchrysene	6.1	1.8	N/A	N/A	2.4	N/A	6.1	12	N/A
Aromatic	1-Methylfluorene	14	3.5	91	5.7	6.7	N/A	9.7	5.5	123
Aromatic	1-Methylnaphthalene	12	4.6	15	4.6	3.5	26	8.9	3.8	24
Aromatic	1-Methylpyrene	11	3.4	N/A	7.7	5.3	N/A	8.8	11	N/A
Aromatic	1-Phenylheptane	N/A	32	N/A	N/A	3.1	27	N/A	24	27
Aromatic	1-Phenylnonane	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Aromatic	1-Phenyloctane	4.5	N/A	N/A	18	N/A	N/A	18	N/A	N/A
Aromatic	2,2,5,7-Tetramethyltetralin	N/A	3.4	N/A	N/A	N/A	N/A	N/A	3.4	N/A
Aromatic	2,6-Dimethylnaphthalene	12	4.7	9.7	5.9	3.0	N/A	9.1	3.8	9.7
Aromatic	2-Methylbenzothiophene	32	5.2	N/A	2.3	4.2	N/A	27	4.3	N/A

Chemical class	Constituent	Extraction block I			Extraction block II			Intermediate		
		AspLub	CTPO	Car wax	AspLub	CTPO	Car wax	AspLub	CTPO	Car wax
Aromatic	2-Methylphenanthrene	12	3.9	N/A	5.7	3.3	N/A	9.4	6.7	N/A
Aromatic	3,3',5,5'-Tetramethylbiphenyl	16	5.0	N/A	4.0	5.1	N/A	11	4.6	N/A
Aromatic	3,3'-Dimethylbiphenyl	12	6.4	N/A	5.1	3.8	17	9.3	4.8	37
Aromatic	4-Methylchrysene	13	2.2	N/A	5.5	1.7	N/A	11	11	N/A
Aromatic	4-n-Pentylbiphenyl	11	6.3	N/A	15	7.0	N/A	12	14	N/A
Aromatic	6-Ethylchrysene	22	10	N/A	13	3.3	N/A	16	7.8	N/A
Aromatic	Acenaphthene	6.9	3.2	N/A	2.0	4.9	N/A	5.9	4.3	N/A
Aromatic	Acenaphthylene	23	3.6	N/A	14	3.0	N/A	21	3.1	N/A
Aromatic	Anthracene	14	4.2	N/A	6.7	4.6	N/A	11	7.2	N/A
Aromatic	Benzo[a]anthracene	13	1.1	N/A	6.6	3.5	N/A	9.0	16	N/A
Aromatic	Benzo[a]pyrene	12	9.0	N/A	6.4	4.3	N/A	9.0	11	N/A
Aromatic	Benzo[b]fluoranthene	12	2.9	N/A	6.4	2.5	N/A	9.0	12	141
Aromatic	Benzo[e]pyrene	14	3.9	N/A	6.7	3.2	N/A	13	10	N/A
Aromatic	Benzo[g,h,i]perylene	14	1.7	N/A	4.5	3.0	N/A	9.8	12	N/A
Aromatic	Benzo[k]fluoranthene	13	6.1	N/A	6.2	6.6	N/A	9.8	13	N/A
Aromatic	Biphenyl	11	4.9	17	4.6	3.4	11	8.1	4.0	13
Aromatic	Butylbenzene	N/A	N/A	N/A	N/A	7.5	33	N/A	7.5	33
Aromatic	Chrysene	16	0.8	N/A	7.1	1.3	N/A	13	9.7	N/A
Aromatic	Dibenz[a,h]anthracene	14	6.6	N/A	7.3	3.0	N/A	12	15	N/A
Aromatic	Fluoranthene	14	3.7	N/A	4.5	2.2	N/A	10	8.7	N/A
Aromatic	Fluorene	15	3.2	173	4.5	2.6	N/A	10	2.6	173
Aromatic	Hexylbenzene	N/A	5.7	N/A	N/A	N/A	N/A	N/A	5.7	N/A
Aromatic	Indeno[1,2,3-c,d]pyrene	15	7.4	N/A	3.8	N/A	N/A	12	7.4	N/A
Aromatic	Naphthalene	12	4.9	35	5.4	3.8	27	8.5	4.1	33
Aromatic	Perylene	13	6.1	N/A	5.7	3.8	N/A	11	13	N/A
Aromatic	Phenanthrene	13	4.2	N/A	5.2	3.2	N/A	9.2	7.5	80
Aromatic	Pyrene	14	3.9	N/A	6.9	3.6	N/A	10	8.5	N/A
Aromatic	Tetralin	9.4	6.6	37	19	2.7	30	14	7.1	33
SPAC	1-Benzothiophene	N/A	4.2	N/A	N/A	4.2	33	N/A	4.1	33
SPAC	2,3,4-Trimethylbenzothiophene	N/A	12	N/A	N/A	1.6	N/A	N/A	7.7	N/A
SPAC	2-Methylnaphthalene	12	4.8	20	5.2	3.6	24	8.4	3.8	20
SPAC	3-Methylbenzothiophene	3.6	4.5	N/A	N/A	4.1	N/A	38	3.9	N/A
SPAC	4,6-Dimethyldibenzothiophene	10	4.7	N/A	3.9	3.1	N/A	6.9	11	N/A
SPAC	4-Ethyl-6-methyldibenzothiophene	9.1	4.5	N/A	2.4	2.1	N/A	6.3	10	N/A
SPAC	4-Methyldibenzothiophene	12	4.9	N/A	4.2	3.2	N/A	21	8.8	N/A
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	N/A	0.9	N/A	N/A	8.5	N/A	N/A	21	N/A
SPAC	Dibenzothiophene	7.0	5.3	N/A	6.9	1.3	N/A	6.2	7.4	N/A
OPAC	2,3-Benzofuran	N/A	N/A	N/A	N/A	12	25	N/A	12	25
OPAC	2-Hydroxynaphthalene	4.2	4.1	N/A	1.7	2.5	N/A	11	3.7	N/A
OPAC	2-Methyldibenzofuran	N/A	N/A	N/A	N/A	3.3	N/A	N/A	3.3	N/A
OPAC	2-n-Butylbenzofuran	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	3,5-Dimethylphenol	N/A	6.2	N/A	N/A	1.7	N/A	N/A	18	N/A

Chemical class	Constituent	Extraction block I			Extraction block II			Intermediate		
		AspLub	CTPO	Car wax	AspLub	CTPO	Car wax	AspLub	CTPO	Car wax
OPAC	3-Methylbenzofuran	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	4-Hexylphenol	N/A	0.0	N/A	N/A	3.3	N/A	N/A	12	N/A
OPAC	4-Nonylphenol	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	4-tert-Butylphenol	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	9-Hydroxyfluorene	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	9-Hydroxyphenanthrene	30	16	N/A	19	47	N/A	24	44	N/A
OPAC	Dibenzofuran	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	Naphthaldehyde	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
OPAC	o-Cresol	2.1	7.9	N/A	0.9	2.2	N/A	1.8	6.3	N/A
OPAC	Phenol	N/A	10	N/A	N/A	1.3	N/A	N/A	8.1	N/A
NPAC	1,4,8-Trimethylcarbazole	16	16	N/A	7.1	42	N/A	5.9	36	N/A
NPAC	11H-Benzo[a]carbazole	N/A	16	N/A	N/A	5.9	N/A	N/A	11	N/A
NPAC	1-Methylcarbazole	7.1	7.6	N/A	7.1	10	N/A	11	10	N/A
NPAC	1-Methylisoquinoline	N/A	1.1	N/A	N/A	3.0	N/A	N/A	2.4	N/A
NPAC	2,3,6,7-Tetramethylcarbazole	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NPAC	2,3,6-Trimethylcarbazole	N/A	5.0	N/A	N/A	17	N/A	N/A	20	N/A
NPAC	2,3-Dimethylindole	N/A	8.2	N/A	2.0	6.3	N/A	2.0	7.8	N/A
NPAC	2-tert-Butyl-1H-indole	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NPAC	3-Methylindole	N/A	4.9	N/A	N/A	6.3	N/A	N/A	5.1	N/A
NPAC	4,6,8-Trimethylquinoline	N/A	N/A	N/A	N/A	13	N/A	N/A	13	N/A
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	N/A	N/A	N/A	N/A	N/A	N/A	12	N/A	N/A
NPAC	5-Methylindole	N/A	17	N/A	N/A	N/A	N/A	N/A	17	N/A
NPAC	8,10-Dimethyl-Benzo[a]acridine	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NPAC	8-Methyl-11(H)-benzo[a]carbazole	N/A	15	N/A	4.9	13	N/A	4.9	13	N/A
NPAC	9-Methylacridine	N/A	8.1	N/A	N/A	12	N/A	N/A	16	N/A
NPAC	Acridine	13	11	N/A	N/A	4.7	N/A	13	8.7	N/A
NPAC	Benzo[c]acridine	N/A	15	N/A	5.7	10	N/A	5.7	14	N/A
NPAC	Benzo[h]quinoline	N/A	17	N/A	N/A	1.5	N/A	N/A	11	N/A
NPAC	Benzonitrile	N/A	5.9	N/A	N/A	5.1	N/A	N/A	6.6	N/A
NPAC	Carbazole	43	9.4	N/A	4.7	3.6	N/A	74	8.6	N/A
NPAC	Dibenz[a,h]acridine	N/A	9.2	N/A	N/A	55	N/A	N/A	51	N/A
NPAC	Dibenzo[f,h]quinoline	N/A	7.8	N/A	N/A	47	N/A	N/A	59	N/A
NPAC	Indole	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NPAC	Quinoline	N/A	11	N/A	N/A	2.6	N/A	N/A	12	N/A

B.4 GC-MS/SIM: Target constituent validation parameters

The target constituent validation parameters DL, LOQ, linearity, instrument precision, and QC precision for each target constituent analysed by GC-MS/SIM are listed in Table B.5.

Table B.5: DL, LOQ, linearity, instrument precision and QC precision for the individual target constituents analysed by GC-MS/SIM

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity (R^2)	Instrument precision (%)	QC precision (%)
Saturates	1,3-Dimethyladamantane	0.4	1.6	0.9999	1.3	4.8
Saturates	1-Methyldecalin	3.0	10	0.9996	7.8	N/A
Saturates	2-Isopropyldecalin	2.9	12	0.9993	9.3	N/A
Saturates	Adamantane	0.2	0.7	0.9998	0.5	11
Saturates	Butylcyclohexane	1.3	5.2	0.9993	3.7	5.1
Aromatic	1,3,6-Trimethylchrysene	0.8	3.1	0.9995	3.1	N/A
Aromatic	1-Methylfluorene	1.4	3.3	0.9992	1.8	2.0
Aromatic	1-Methylnaphthalene	0.6	1.9	0.9999	1.5	0.5
Aromatic	1-Methylpyrene	0.7	3.0	0.9999	3.0	0.9
Aromatic	1-Phenylheptane	11	16	0.9967	5.4	6.5
Aromatic	1-Phenylnonane	1.8	7.2	0.9994	6.0	2.1
Aromatic	1-Phenyloctane	1.6	6.5	0.9992	6.2	N/A
Aromatic	2,2,5,7-Tetramethyltetralin	14	58	0.9863	13	10
Aromatic	2,6-Dimethylnaphthalene	0.4	1.7	0.9999	1.7	0.5
Aromatic	2-Methylnaphthalene	0.6	1.3	0.9999	1.3	0.2
Aromatic	2-Methylphenanthrene	0.9	3.2	0.9996	2.9	1.8
Aromatic	3,3',5,5'-Tetramethylbiphenyl	0.7	2.9	0.9997	2.9	N/A
Aromatic	3,3'-Dimethylbiphenyl	0.5	1.9	0.9999	1.8	1.9
Aromatic	4-Methylchrysene	0.5	2.1	0.9997	2.5	0.9
Aromatic	4-n-Pentylbiphenyl	1.0	4.2	0.9997	4.4	N/A
Aromatic	6-Ethylchrysene	0.8	3.2	0.9995	3.3	N/A
Aromatic	Acenaphthene	1.9	2.5	0.9998	0.8	3.8
Aromatic	Acenaphthylene	0.3	1.3	0.9999	1.4	1.8
Aromatic	Anthracene	0.4	1.7	0.9994	1.3	3.2
Aromatic	Benzo[a]anthracene	0.4	1.6	0.9998	1.6	3.8
Aromatic	Benzo[a]pyrene	1.3	5.2	0.9996	4.7	1.1
Aromatic	Benzo[b]fluoranthene	0.7	1.7	0.9999	1.3	1.3
Aromatic	Benzo[e]pyrene	0.3	1.2	0.9999	1.2	1.4
Aromatic	Benzo[g,h,i]perylene	0.9	3.5	0.9991	3.2	3.5
Aromatic	Benzo[k]fluoranthene	0.5	2.2	0.9999	2.5	1.9
Aromatic	Biphenyl	1.9	3.2	0.9999	1.7	1.0
Aromatic	Butylbenzene	7.8	32	0.9856	13	N/A
Aromatic	Chrysene	1.0	4.2	0.9999	4.3	3.2
Aromatic	Dibenzo[a,h]anthracene	0.8	3.4	0.9999	4.1	6.8
Aromatic	Fluoranthene	1.1	2.3	0.9999	1.5	0.5
Aromatic	Fluorene	0.5	1.7	0.9997	1.5	1.1
Aromatic	Hexylbenzene	1.1	4.4	0.9945	3.8	N/A

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity (R^2)	Instrument precision (%)	QC precision (%)
Aromatic	Indeno[1,2,3-c,d]pyrene	0.6	2.3	0.9999	2.6	3.3
Aromatic	Naphthalene	1.5	2.0	1.0000	0.6	0.4
Aromatic	Perylene	0.4	1.6	0.9995	1.8	4.5
Aromatic	Phenanthrene	2.5	5.6	0.9998	4.4	1.6
Aromatic	Pyrene	0.7	1.3	1.0000	0.7	1.0
Aromatic	Tetralin	2.7	3.9	1.0000	1.3	1.1
S-PAC	1-Benzothiophene	0.6	2.3	0.9999	1.9	2.8
S-PAC	2,3,4-Trimethylbenzothiophene	1.9	7.9	0.9997	6.0	5.7
S-PAC	2-Methylbenzothiophene	1.2	2.5	0.9999	1.2	0.7
S-PAC	3-Methylbenzothiophene	1.8	3.3	0.9998	1.3	0.7
S-PAC	4,6-Dimethyldibenzothiophene	1.3	5.5	0.9989	4.6	3.4
S-PAC	4-Ethyl-6-methyldibenzothiophene	1.5	6.3	0.9987	5.3	N/A
S-PAC	4-Methyldibenzothiophene	0.6	2.3	0.9994	1.8	4.8
S-PAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	0.7	2.7	0.9995	2.4	N/A
S-PAC	Dibenzothiophene	1.5	2.7	0.9998	1.4	2.3
OPAC	2,3-Benzofuran	2.3	9.3	0.9889	8.4	N/A
OPAC	2-Hydroxynaphthalene	2.9	9.4	0.9952	8.4	3.8
OPAC	2-Methyldibenzofuran	0.8	2.5	0.9984	2.2	4.3
OPAC	2-n-Butylbenzofuran	1.3	5.3	0.9997	5.0	N/A
OPAC	3,5-Dimethylphenol	6.2	26	0.9754	18	2.6
OPAC	3-Methylbenzofuran	1.5	5.9	0.9909	4.4	N/A
OPAC	4-Hexylphenol	1.4	5.7	0.9972	5.9	N/A
OPAC	4-Nonylphenol	0.5	2.0	0.9958	1.9	N/A
OPAC	4-tert-Butylphenol	11	16	0.9923	4.4	N/A
OPAC	9-Hydroxyfluorene	2.0	7.5	0.9959	7.0	N/A
OPAC	9-Hydroxyphenanthrene	0.9	3.6	0.9490	6.5	N/A
OPAC	Dibenzofuran	2.0	6.1	0.9994	4.2	N/A
OPAC	Naphthaldehyde	47	69	0.9246	9.9	N/A
OPAC	o-Cresol	40	62	0.9920	5.8	4.8
OPAC	Phenol	278	546	0.9753	17	11
NPAC	1,4,8-Trimethylcarbazole	1.1	4.6	0.9984	5.2	N/A
NPAC	11H-Benzo[a]carbazole	0.5	1.9	0.9977	1.8	N/A
NPAC	1-Methylcarbazole	1.6	6.6	0.9994	7.2	3.6
NPAC	1-Methylisoquinoline	3.8	14	0.9803	11	N/A
NPAC	2,3,6,7-Tetramethylcarbazole	1.7	6.9	0.9896	7.3	N/A
NPAC	2,3,6-Trimethylcarbazole	1.5	6.1	0.9934	7.3	N/A
NPAC	2,3-Dimethylindole	0.8	3.3	0.9931	3.1	8.5
NPAC	2-tert-Butyl-1H-indole	3.3	14	0.9853	19	N/A
NPAC	3-Methylindole	3.6	15	0.9954	12	N/A
NPAC	4,6,8-Trimethylquinoline	3.4	14	0.9949	13	N/A
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	1.5	6.3	0.9976	5.7	N/A
NPAC	5-Methylindole	4.8	16	0.9858	14	N/A

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity (R^2)	Instrument precision (%)	QC precision (%)
NPAC	8,10-Dimethyl-Benzo(a)acridine	0.9	3.8	0.9972	4.4	N/A
NPAC	8-Methyl-11(H)-benzo[a]carbazole	0.9	3.7	0.9971	3.6	N/A
NPAC	9-Methylacridine	2.0	8.1	0.9978	8.0	N/A
NPAC	Acridine	3.0	12	0.9897	11	N/A
NPAC	Benzo[c]acridine	1.1	4.7	0.9973	4.7	N/A
NPAC	Benzo[h]quinoline	3.6	15	0.9950	12	N/A
NPAC	Benzonitrile	1.1	4.3	0.9914	6.3	3.0
NPAC	Carbazole	1.1	4.4	0.9997	3.5	1.9
NPAC	Dibenzo[a,h]acridine	1.5	6.2	0.9973	5.1	N/A
NPAC	Dibenzo[f,h]quinoline	3.5	14	0.9975	13	N/A
NPAC	Indole	3.2	13	0.9838	20	N/A

B.5 GC×GC-HRMS: Target constituent validation parameters

The constituent validation parameters DL, LOQ, linearity, instrument precision and QC precision for the individual target constituents analysed by GC×GC-HRMS are listed in Table B.6.

Table B.6: DL, LOQ, linearity, instrument precision, and QC precision for the individual target constituents analysed by GC×GC-HRMS

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity	Instrument precision (%)	QC precision (%)
OPAC	2,3-Benzofuran	15	29	0.9986	7.1	6.0
OPAC	2,4-Di-tert-butylphenol	2.9	9.2	0.9989	12	18
OPAC	2-Hydroxynaphthalene	31	67	0.9994	21	15
OPAC	2-Methyldibenzofuran	1.8	5.1	0.9970	5.0	6.5
OPAC	2-n-Butylbenzofuran	1.4	4.7	0.9988	4.1	N/A
OPAC	3,5-Dimethylphenol	7.4	20	0.9879	11	0.9
OPAC	3-Methylbenzofuran	43	71	0.9955	9.9	35
OPAC	4-Hexylphenol	2.1	6.2	0.9915	7.3	N/A
OPAC	4-Nonylphenol	2.6	7.2	0.9988	7.7	N/A
OPAC	4-tert-Butylphenol	10	25	0.9991	12	6.8
OPAC	9-Hydroxyfluorene	35	85	0.9995	22	N/A
OPAC	9-Hydroxyphenanthrene	45	104	0.9999	23	8.9
OPAC	Dibenzofuran	2.7	6.8	0.9944	2.2	N/A
OPAC	Dibenzofuranols	64	182	0.9984	18	N/A
OPAC	Indanols	19	72	0.9984	25	4.5
OPAC	Naphthaldehyde	3.3	7.3	0.9762	2.3	3.8
OPAC	o-Cresol	8.6	16	0.9988	5.8	8.6
OPAC	Phenol	23	30	0.9970	3.1	3.7
NPAC	(Tere)Phthalonitrile	3.2	9.4	0.9970	22	32
NPAC	1,4,8-Trimethylcarbazole	0.8	2.7	0.9880	6.6	N/A

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity	Instrument precision (%)	QC precision (%)
NPAC	11H-Benzo[a]carbazole	1.7	6.5	0.9972	15	N/A
NPAC	1-Methylcarbazole	1.0	3.5	0.9933	9.6	N/A
NPAC	1-Methylisoquinoline	4.9	15	0.9984	11	8.1
NPAC	2,3,6,7-Tetramethylcarbazole	1.1	3.9	0.9892	9.1	N/A
NPAC	2,3,6-Trimethylcarbazole	1.2	3.5	0.9878	8.5	N/A
NPAC	2,3-Dimethylindole	1.3	4.5	0.9986	6.1	15
NPAC	2-tert-Butyl-1H-indole	1.6	4.8	0.9935	6.2	24
NPAC	4,6,8-Trimethylquinoline	1.3	4.4	0.9991	5.2	7.0
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	2.0	7.6	0.9852	14	N/A
NPAC	8,10-Dimethyl-Benzo[a]acridine	10	25	0.9988	23	N/A
NPAC	8-Methyl-11(H)-benzo[a]carbazole	1.8	6.9	0.9962	13	N/A
NPAC	9-Ethylcarbazole	1.1	3.7	0.9981	5.3	N/A
NPAC	9-Methylacridine	2.6	10	0.9983	18	N/A
NPAC	Acridine	2.4	7.7	0.9995	10	5.9
NPAC	Benzo[c]acridine	5.1	17	0.9957	15	N/A
NPAC	Benzo[h]quinoline	3.5	12	0.9981	13	N/A
NPAC	Benzonitrile	18	29	0.9963	9.1	19
NPAC	Benzothiazole	13	19	0.9991	53	7.0
NPAC	Carbazole	3.2	8.9	0.9940	4.5	1.9
NPAC	Dibenzo[a,h]acridine	111	245	0.9993	32	N/A
NPAC	Dibenzo[f,h]quinoline	8.1	23	0.9985	15	N/A
NPAC	Diethyl-a-naphthylamine	2.8	6.1	0.9978	32	5.5
NPAC	Diphenylamine	1.6	4.9	0.9994	27	7.9
NPAC	Indole	4.6	8.8	0.9972	2.8	4.5
NPAC	Quinoline	4.2	10	0.9986	5.9	5.8

B.6 SFC-ESI-HRMS: Target constituent validation parameters

The constituent validation parameters DL, LOQ, linearity, instrument precision and QC precision for the individual target constituents analysed by SFC-ESI-HRMS are listed in Table B.7.

Table B.7: DL, LOQ, linearity, instrument precision, and QC precision for the individual target constituents analysed by SFC-ESI-HRMS

* No response for replicate analysis of the lowest standard, DL and LOQ are estimated based on the calibration curve.

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity	Instrument precision (%)	QC precision (%)
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene*	8.3	8.3	0.9556	N/A	10
OPAC	1,7-Dihydroxynaphthalene	10	12	0.9920	2.1	11
OPAC	1-Hydroxynaphthalene	124	362	0.9945	8.6	14
OPAC	1-Hydroxyphenanthrene	1.0	1.5	0.9966	0.4	5.7
OPAC	1-Hydroxypyrene	9.7	16	0.9923	5.2	3.3
OPAC	2,4-Di-tert-butylphenol	6.4	21	0.9935	8.5	N/A
OPAC	2-Hydroxyfluorene	4.9	14	0.9897	6.0	17
OPAC	2-Hydroxynaphthalene	22	84	0.9880	29	7.4
OPAC	2-Hydroxyphenanthrene	0.4	1.0	0.9952	4.2	4.4
OPAC	2-Methyl-1-hydroxynaphthalene	27	74	0.9919	44	N/A
OPAC	3,5-Dimethyl phenol	175	796	0.8046	173	23
OPAC	3-Hydroxybenzo[a]pyrene	18	29	0.9350	12	N/A
OPAC	3-Hydroxyfluorene	5.9	18	0.9910	17	26
OPAC	3-Hydroxyphenanthrene	1.8	2.6	0.9984	0.6	4.7
OPAC	4-Hexylphenol	15	52	0.9923	20	N/A
OPAC	4-Hydroxyphenanthrene	1.1	1.8	0.9967	0.5	5.8
OPAC	4-Nonylphenol	13	41	0.9873	15	N/A
OPAC	4-tert-Butylphenol	32	131	0.9814	5.1	28
OPAC	9-Hydroxyfluorene	6.2	28	0.9852	12	62
OPAC	9-Hydroxyphenanthrene	13	24	0.9931	9.4	4.4
OPAC	o-Cresol	163	665	0.9886	87	13
NPAC	1,4,8-Trimethylcarbazole	11	30	0.9971	13	N/A
NPAC	1-Methylcarbazole	6.2	12	0.9954	3.8	9.4
NPAC	2,3,6,7-Tetramethylcarbazole	10	28	0.9938	12	N/A
NPAC	2,3,6-Trimethylcarbazole	10	21	0.9943	8.6	N/A
NPAC	2,3-Dimethylindole	18	48	0.9914	21	16
NPAC	2-tert-Butyl-1H-indole	9.1	28	0.9926	12	N/A
NPAC	3-Methylindole	2.5	32	0.9816	12	24
NPAC	5-Methylindole	5.8	34	0.9915	12	N/A
NPAC	Carbazole	11	42	0.9932	17	N/A
NPAC	Indole	28	103	0.9701	35	3.0
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	7.1	13	0.9960	4.2	N/A
Acid	1-Adamantane carboxylic acid	5.6	19	0.9832	7.6	N/A
Acid	1-Hydroxy-2-naphthoic acid	7.4	73	0.9647	22	N/A
Acid	1-Naphthoic acid	8.0	25	0.9981	10	N/A

Chemical class	Constituent	DL (ng/mL)	LOQ (ng/mL)	Linearity	Instrument precision (%)	QC precision (%)
Acid	1-Pyrene carboxylic acid	15	38	0.9927	18	N/A
Acid	2-Naphthoic acid	7.6	23	0.9966	9.3	N/A
Acid	2-Phenanthrene carboxylic acid	9.0	21	0.9971	8.5	N/A
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	10	18	0.9870	5.5	N/A
Acid	3-Chrysene carboxylic acid	6.0	10	0.9942	2.9	N/A
Acid	Lauric acid	215	666	0.6780	94	N/A
Acid	Linoleic acid	74	216	0.9857	87	26
Acid	Linolenic acid	50	147	0.9953	87	N/A
Acid	Oleic acid	359	1174	0.8881	87	11
Acid	Palmitoleic acid	38	101	0.9907	19	N/A
Acid	Pentadecanoic acid	23	67	0.9860	11	N/A
Acid	Stearic acid	115	295	0.6866	5.7	4.5

B.7 Definition of constituent groups

A total of 17 constituent group families have been defined for GC-MS/SIM analysis. These are decalins, naphthalenes, biphenyls, fluorenes, phenanthrenes/anthracenes, fluoranthenes/pyrenes, chrysenes, benzothiophenes, dibenzothiophenes, phenols, hydroxynaphthalenes, dibenzofurans, hydroxyphenanthrenes, quinolines, indoles, carbazoles, and benzocarbazoles. For each constituent group family the relative retention behaviour is shown by selected ion chromatograms (SICs) and for each constituent group a more detailed example of the group is given based on a high concentration samples. The blue line indicates the isomer abundance factor (IAF) threshold, for each constituent group with more than two isomers.

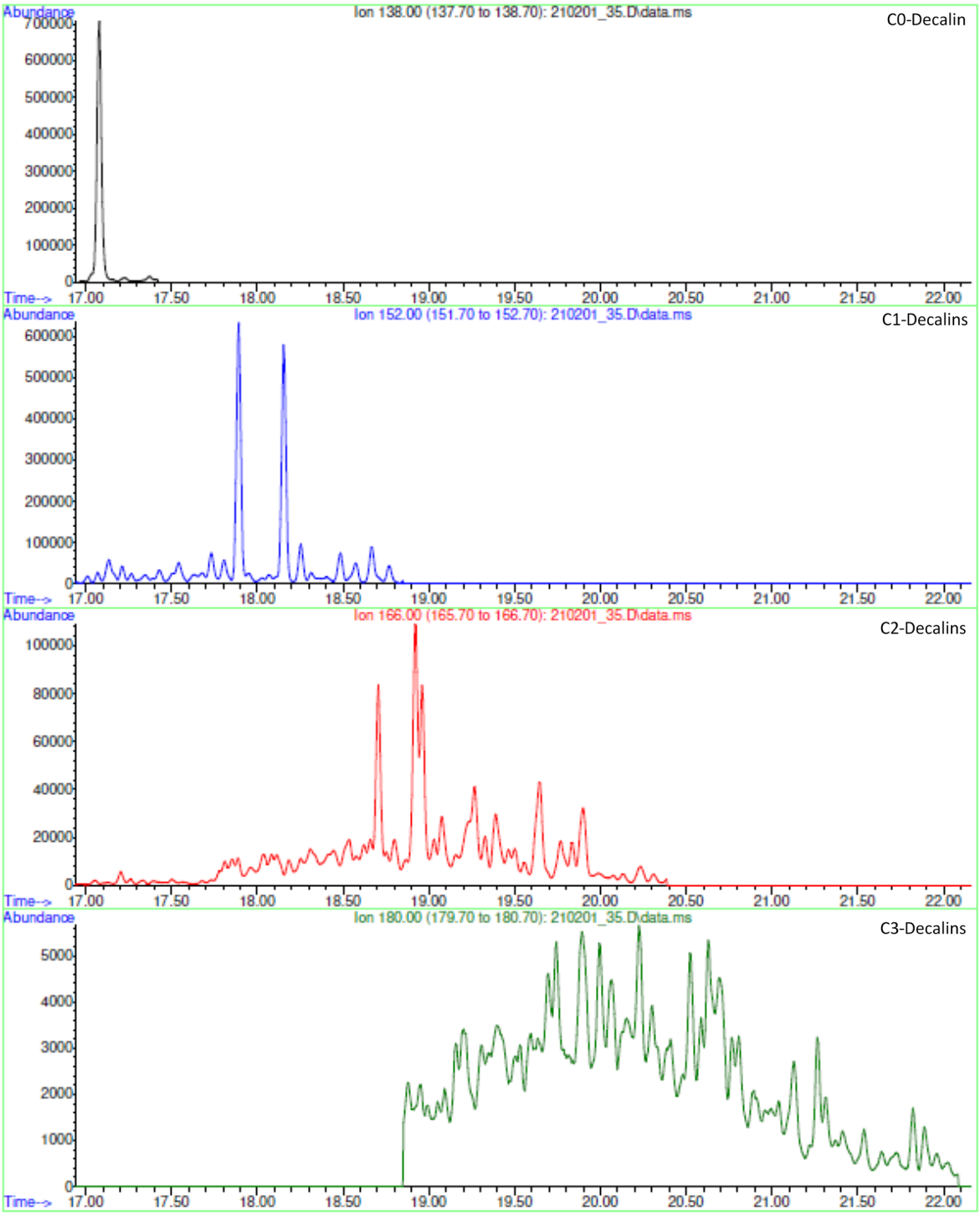
Furthermore, for each constituent group relative retention behaviour, articles, standards, or GC×GC data is given where available. Where available, the calibration standard is also given. The articles that were used in the identification of the constituent groups are given under their respective constituent group.

Besides the 17 constituent group families, ten further constituent group families were evaluated, but deemed too unreliable for quantification by GC-MS/SIM due to difficulties identifying the groups or too low concentrations in the samples to identify the groups. These are alkylcyclohexanes, alkylbenzenes, adamantanes, tetralins, benzonaphthothiophenes, benzonitriles, benzofurans, hydroxyfluorenes, acridines/benzoquinolines, and benzoacridines/dibenzoquinolines.

Decalins

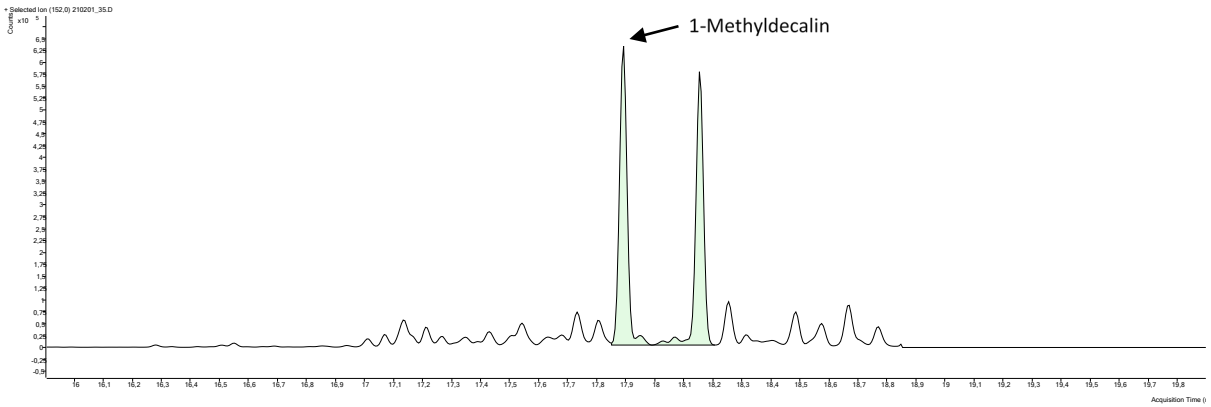
The definition of the decalin constituent groups is based on relative retention behaviour, one article [21], and standard for C1- and C3-decalins. GC×GC data was not available. Below is the relative retention behaviour for C0-C3-decalins (Figure B.1) and detailed chromatograms of the constituent groups C1-decalins (Figure B.2), C2-decalins (Figure B.3), and C3-decalins (Figure B.4).

Figure B.1: Relative retention behaviour for C0-C3-decalins illustrated by SICs at *m/z* 138, 152, 166, and 180



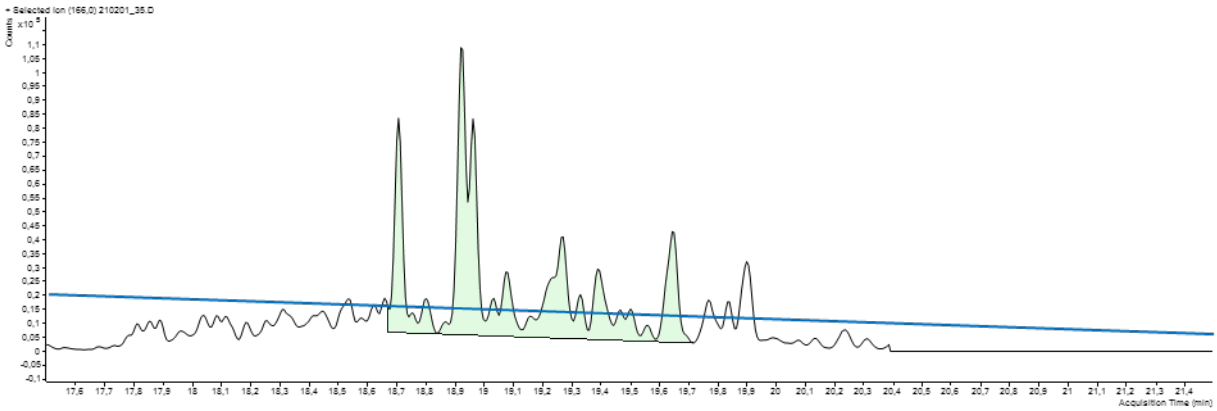
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.2: SIC at *m/z* 152 for C1-decalins (green area) with the standard 1-methyldecalin shown



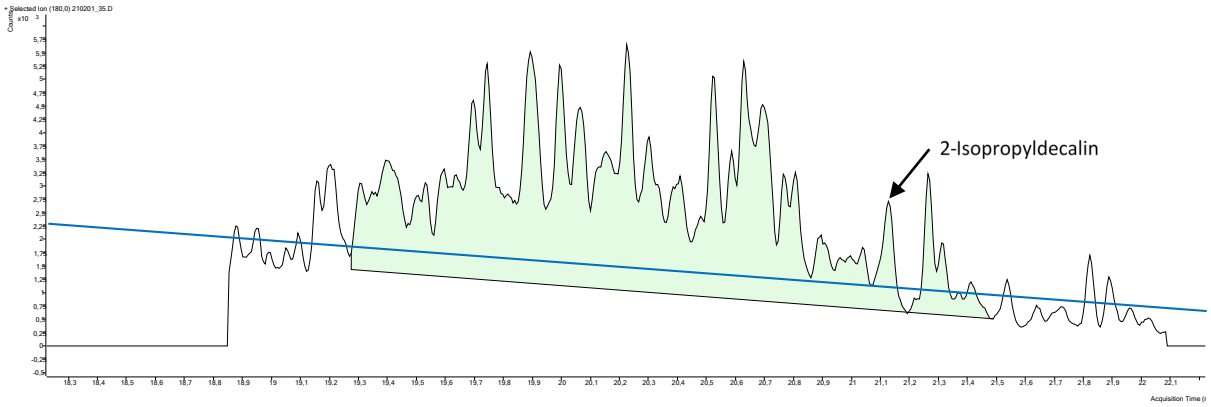
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.3: SIC at *m/z* 166 for C2-decalins (green area). The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.4: SIC at *m/z* 180 for C3-decalins (green area). The blue line indicates the threshold for determining the IAF

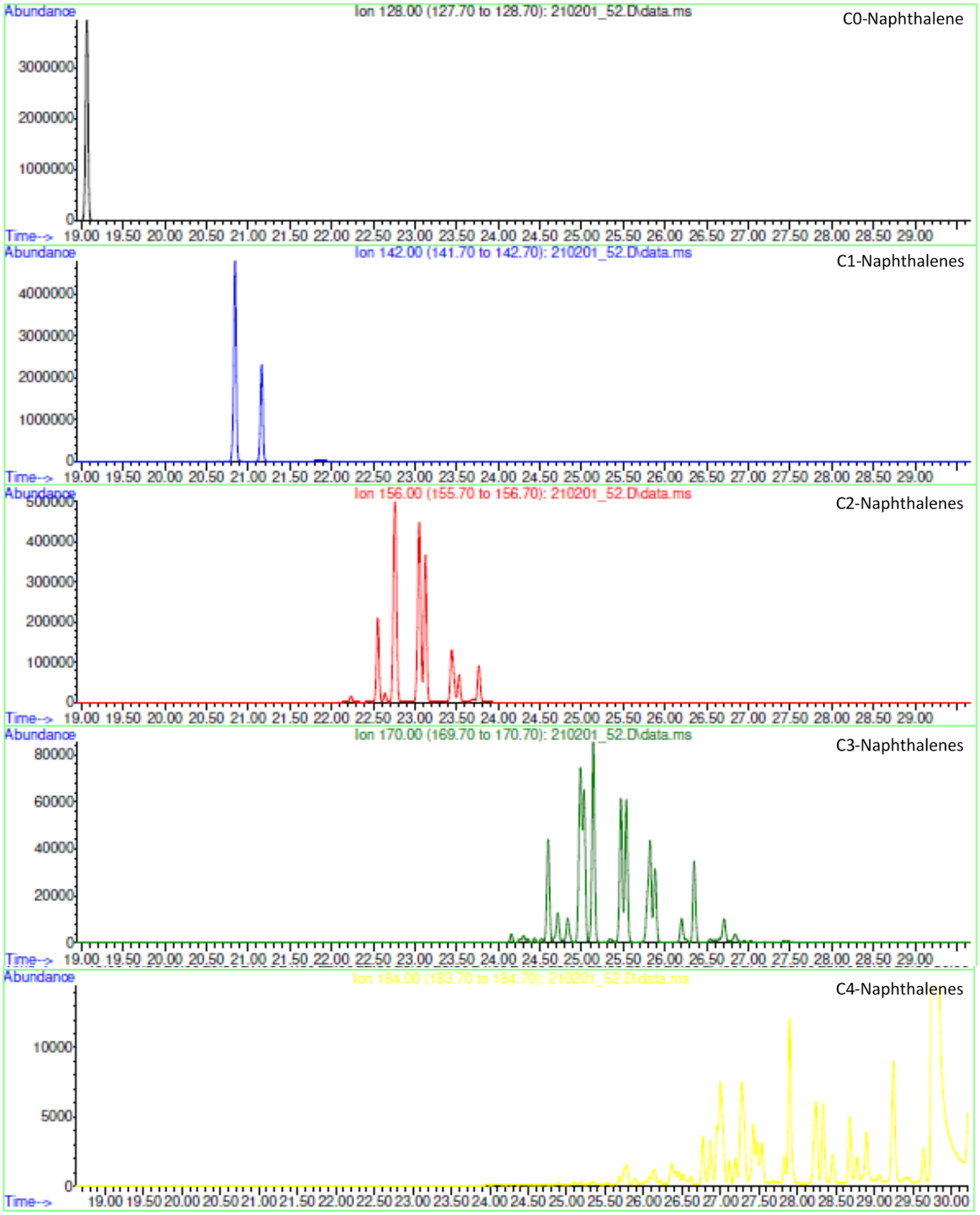


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Naphthalenes

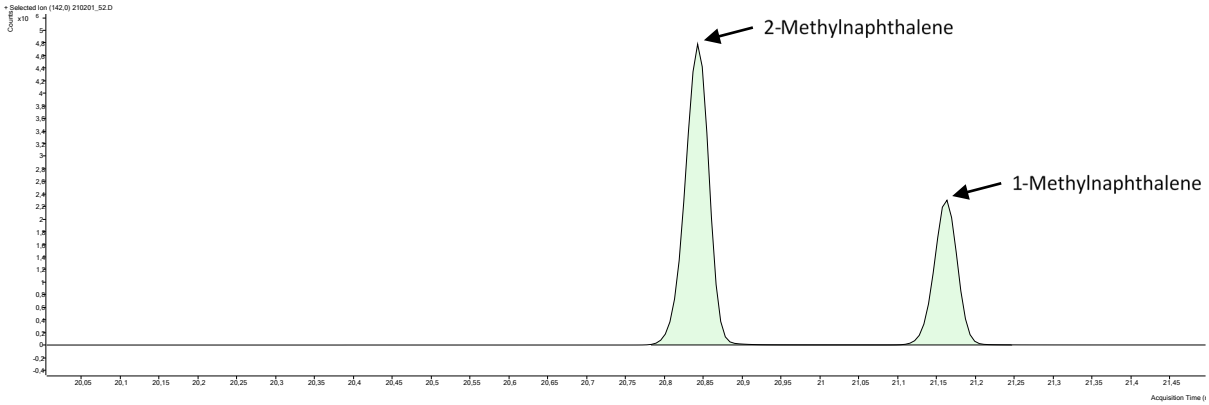
The definition of the naphthalene constituent groups is based on relative retention behaviour, one article [21], and standard for C0-C2-naphthalenes. GC×GC data was not available. Below is the relative retention behaviour for C0-C4-naphthalenes (Figure B.5) and detailed chromatograms of the constituent groups C1-naphthalenes (Figure B.6), C2-naphthalenes (Figure B.7), C3-naphthalenes (Figure B.8), and C4-naphthalenes (Figure B.9).

Figure B.5: Relative retention behaviour for C0-C4-naphthalenes illustrated by SICs at *m/z* 128, 142, 156, 170, and 184



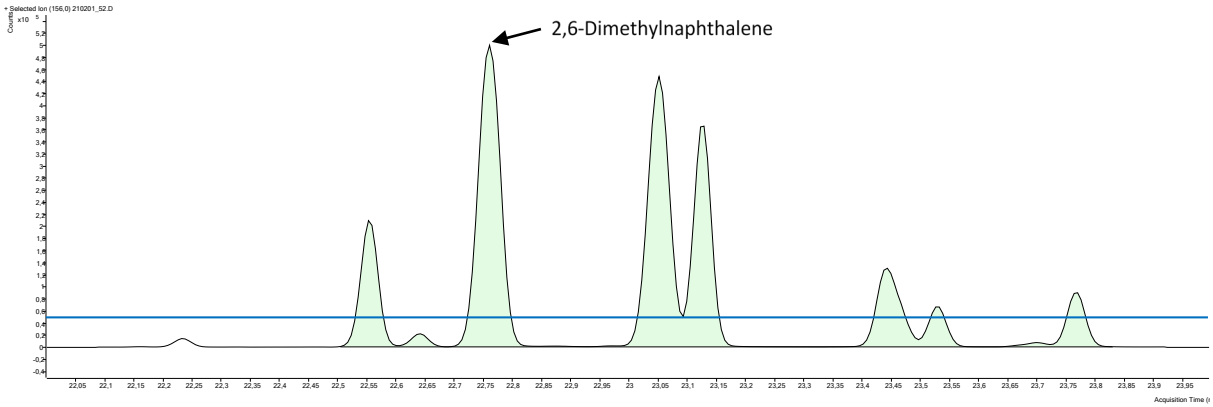
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.6: SIC at *m/z* 142 for C1-naphthalenes (green area) with the two standards 2-methylnaphthalene and 1-methylnaphthalene shown



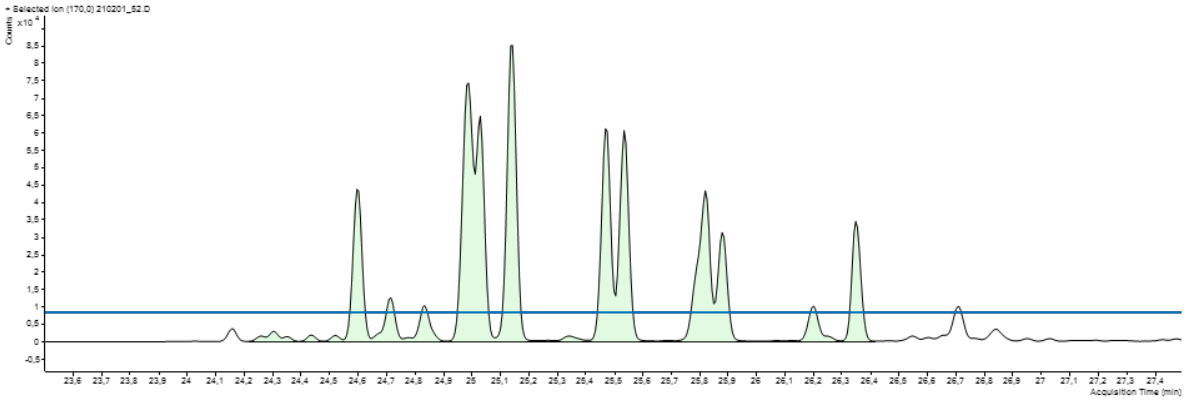
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.7: SIC at *m/z* 156 for C2-naphthalenes (green area) with the standards 2,6-dimethylnaphthalene shown. The blue line indicates the threshold for determining the IAF



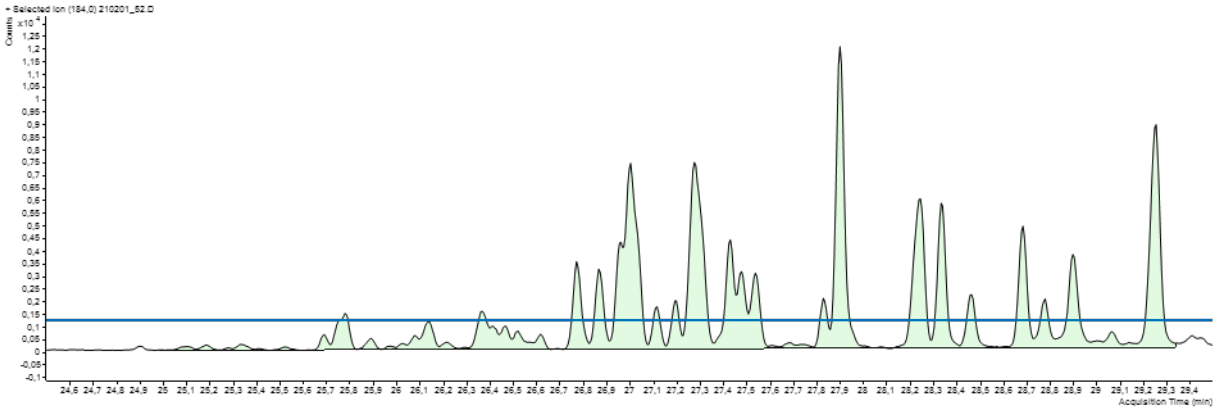
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.8: SIC at *m/z* 170 for C3-naphthalenes (green area). The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.9: SIC at *m/z* 184 for C4-naphthalenes (green area). The blue line indicates the threshold for determining the IAF

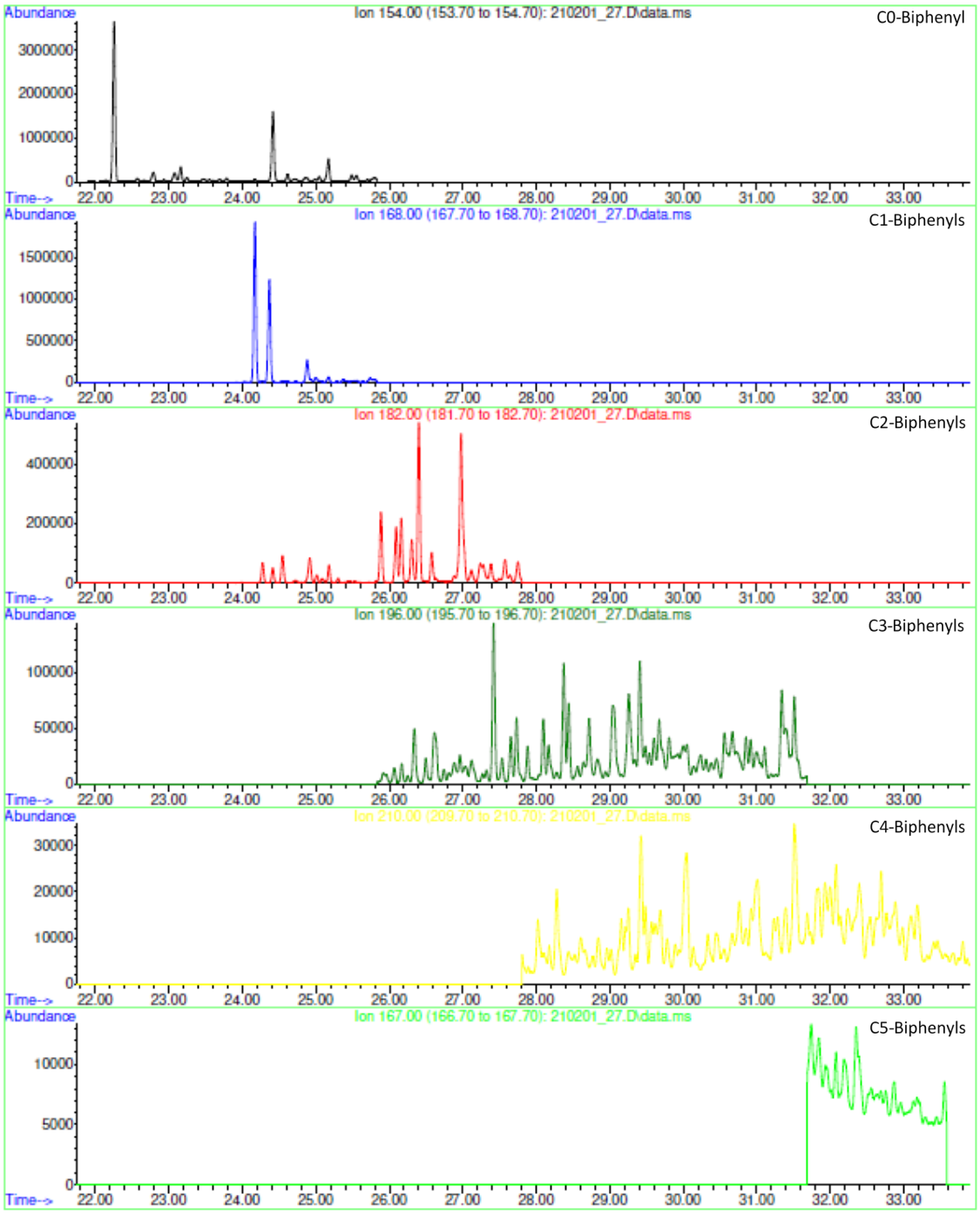


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Biphenyls

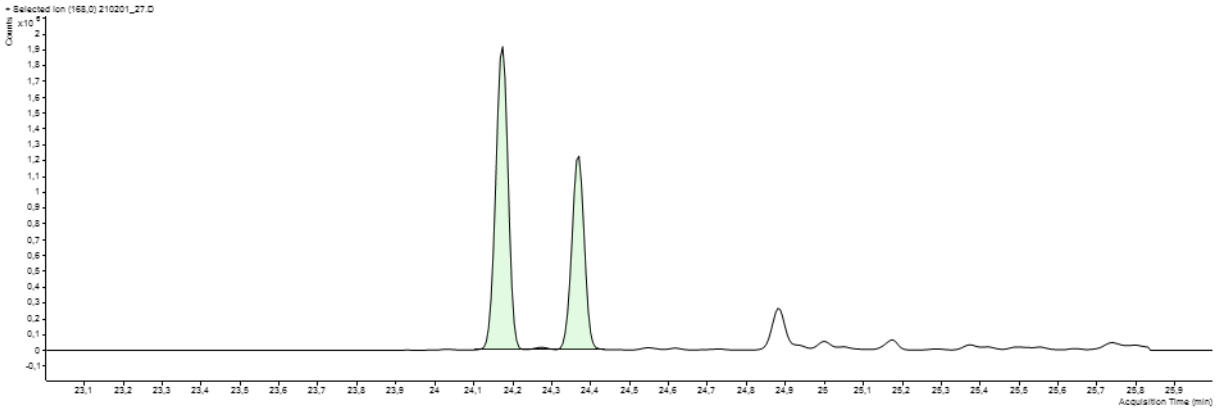
Biphenyl constituent groups are defined based on relative retention behaviour, on articles for C1-C3-biphenyls [22], and standards for C0-, C2-, C4-, and C5-biphenyls. GC×GC data was not available. The C3-C5-biphenyls were too populated or too low in concentration to identify the regions. Below is the relative retention behaviour for C0-C5-biphenyls (Figure B.10) and detailed chromatograms of the constituent groups C1-biphenyls (Figure B.11) and C2 -biphenyls (Figure B.12).

Figure B.10: Relative retention behaviour for C0-C5-biphenyls illustrated by SICs at *m/z* 154, 168, 182, 196, 210, and 167



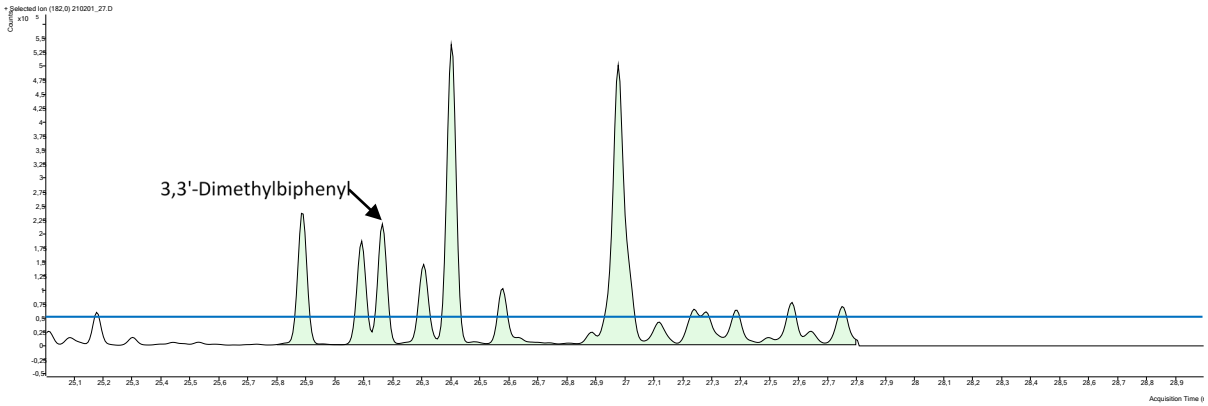
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.11: SIC at *m/z* 168 for C1-biphenyls (green area)



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.12: SIC at *m/z* 182 for C2-biphenyls (green area) with the standard 3,3'-dimemethylbiphenyl shown. The blue line indicates the threshold for determining the IAF

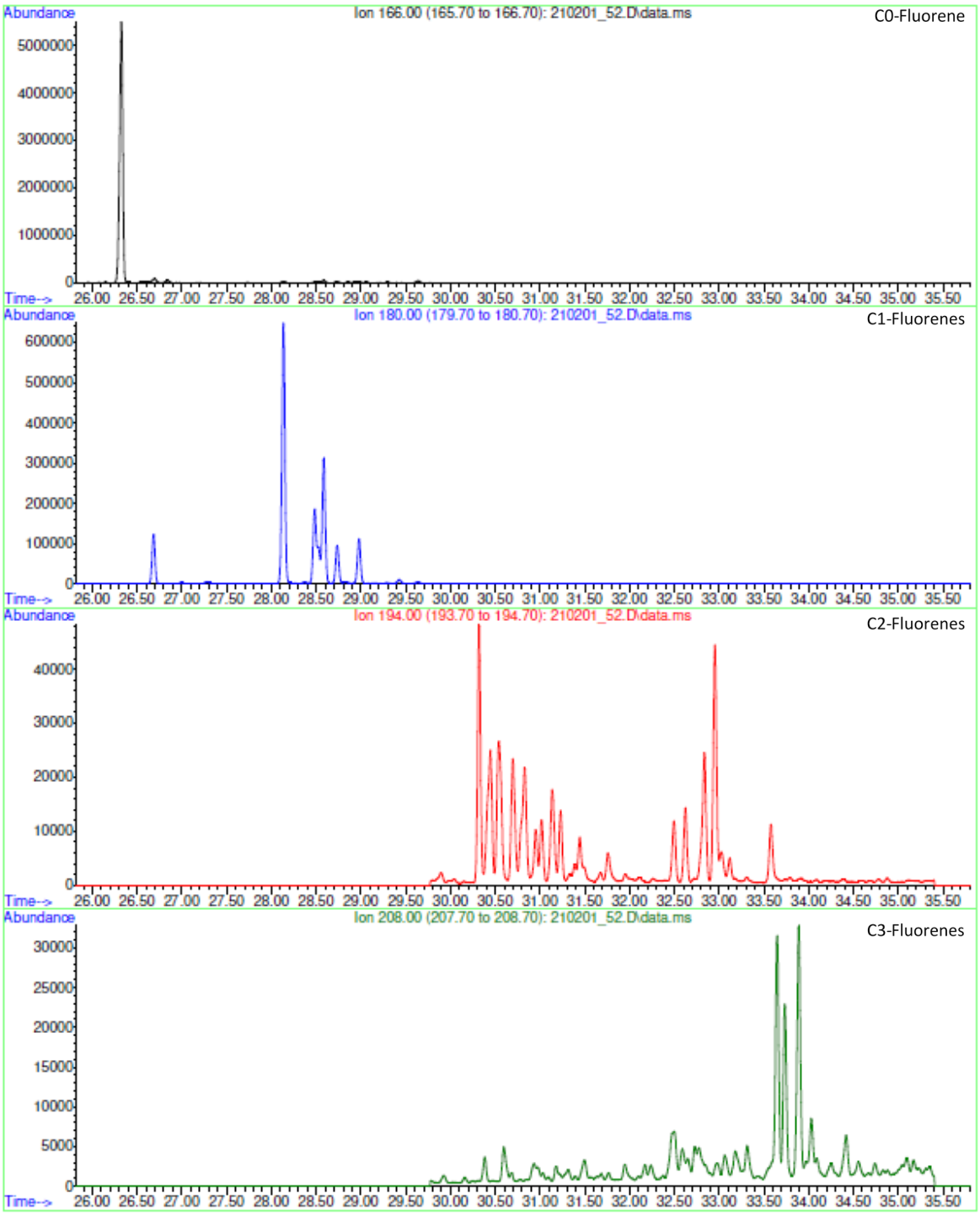


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Fluorenes

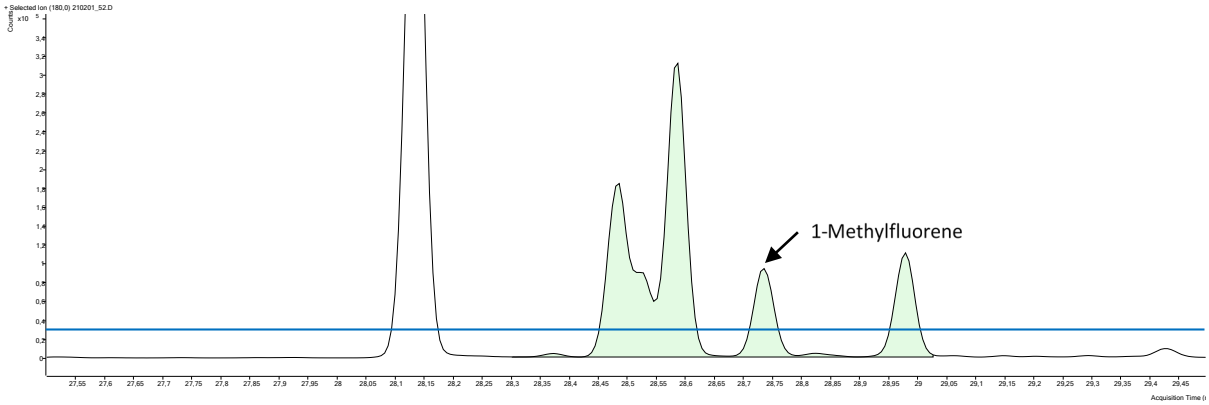
The definition of the fluorene constituent groups is based on relative retention behaviour, one article [21], and standards for C0- and C1-fluorenes. GC×GC data was not available. Below is shown the relative retention behaviour for C0-C3-fluorenes (Figure B.13) and detailed chromatograms of the constituent groups C1-fluorenes (Figure B.14), C2-fluorenes (Figure B.15), and C3-fluorenes (Figure B.16).

Figure B.13: Relative retention behaviour for C0-C3-fluorenes illustrated by SICs at *m/z* 166, 180, 194, and 208



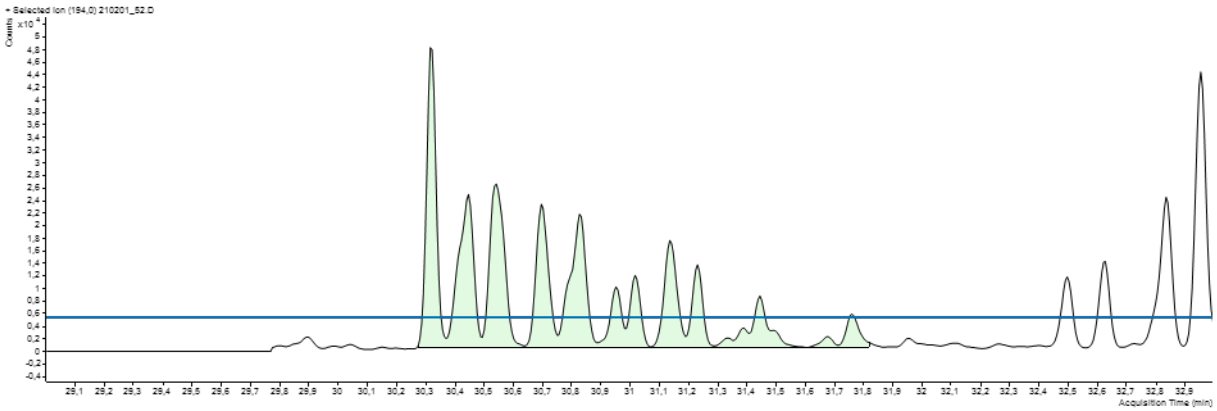
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.14: SIC at *m/z* 180 for C1-fluorenes (green area) with the standard 1-methylfluorene shown. The blue line indicates the threshold for determining the IAF



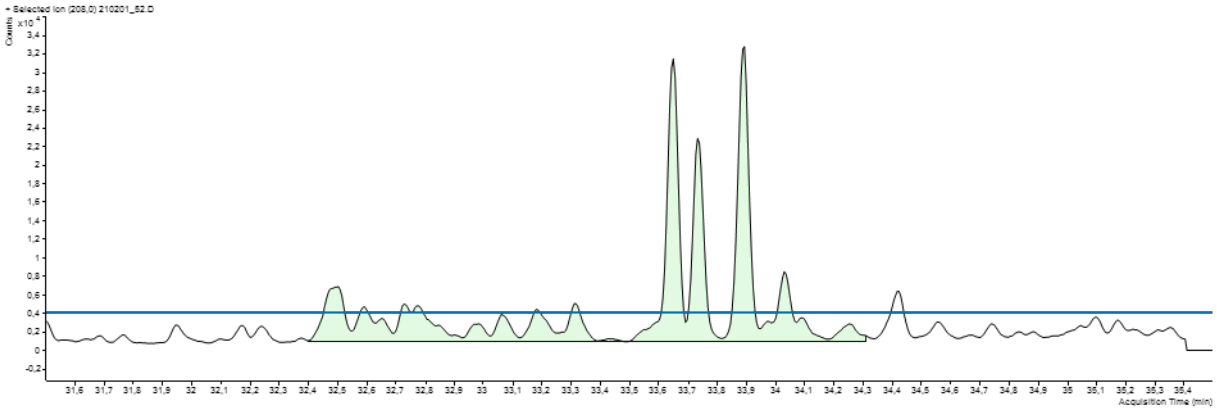
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.15: SIC at *m/z* 194 for C2-fluorenes (green area). The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.16: SIC at *m/z* 208 for C3-fluorenes (green area). The blue line indicates the threshold for determining the IAF

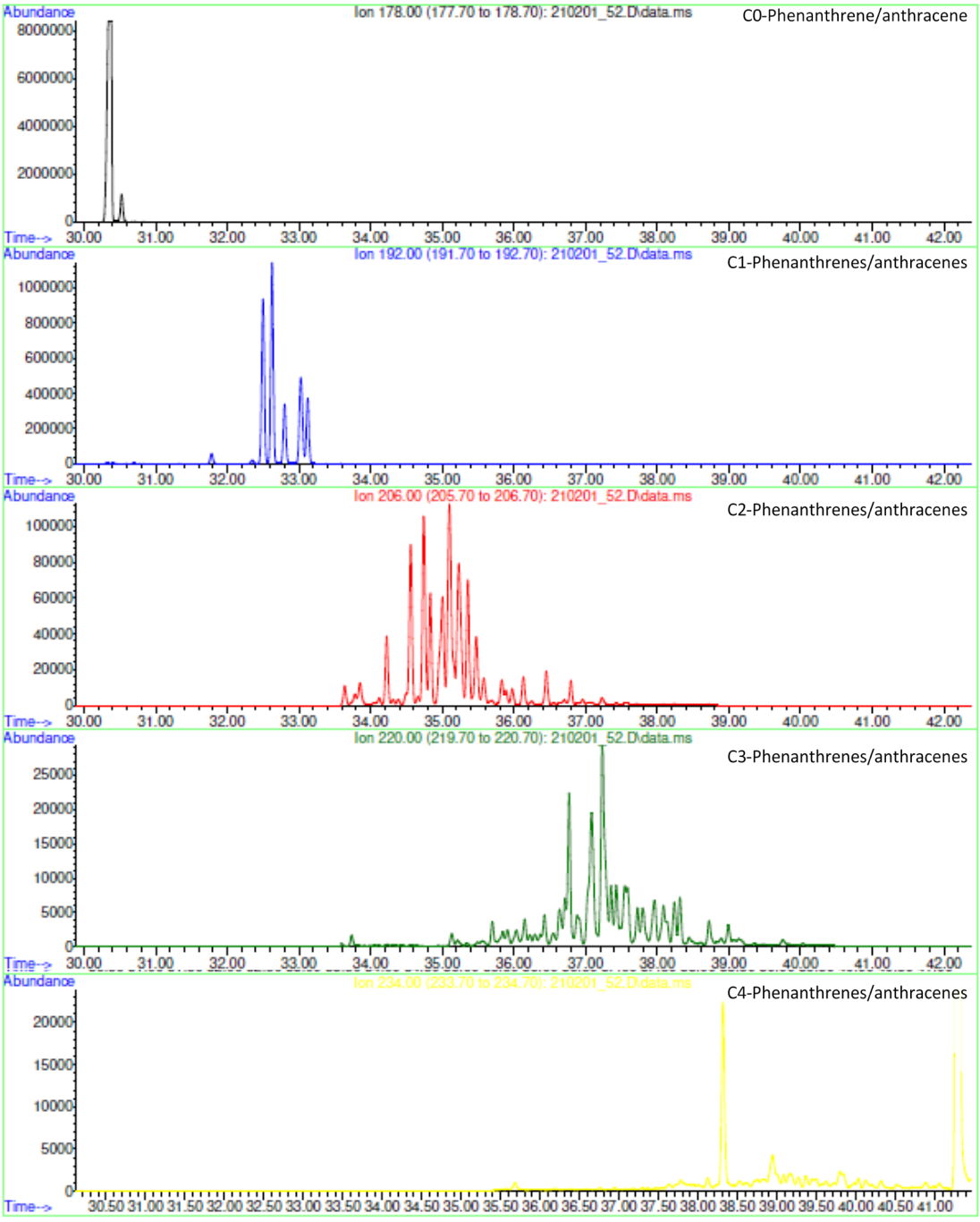


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Phenanthrenes/Anthracenes

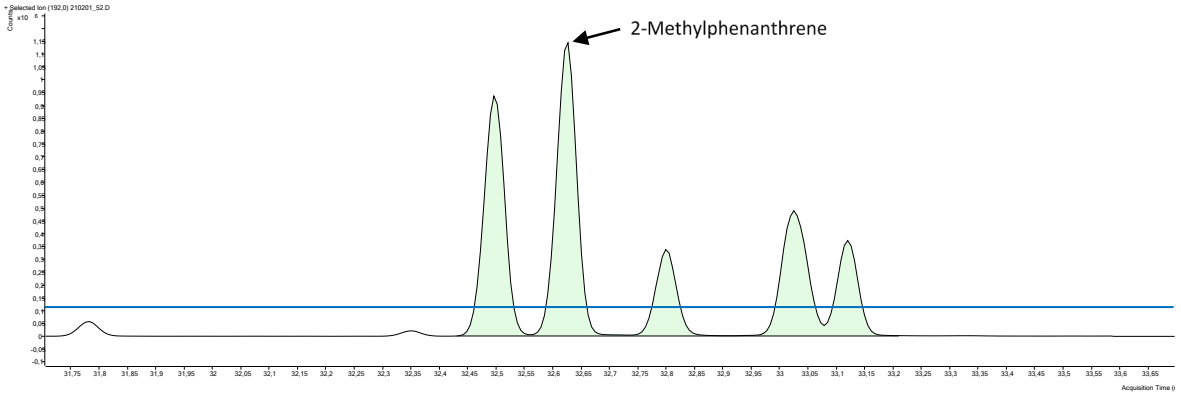
Phenanthrene/Anthracene constituent groups were defined based on relative retention behaviour, one article [21], and standards for C0- and C1-phenanthrenes and C0-anthracene. GC×GC data was not available. Below is shown relative retention behaviour for C0-C4-phenanthrenes/anthracenes (Figure B.17) and detailed chromatograms of the constituent groups C1-phenanthrenes/anthracenes (Figure B.18), C2-phenanthrenes/anthracenes (Figure B.19), C3-phenanthrenes/anthracenes (Figure B.20), and C4-phenanthrenes/anthracenes (Figure B.21).

Figure B.17: Relative retention behaviour for C0-C4-phenanthrenes/anthracenes illustrated by SICs at *m/z* 178, 192, 206, 220, and 234



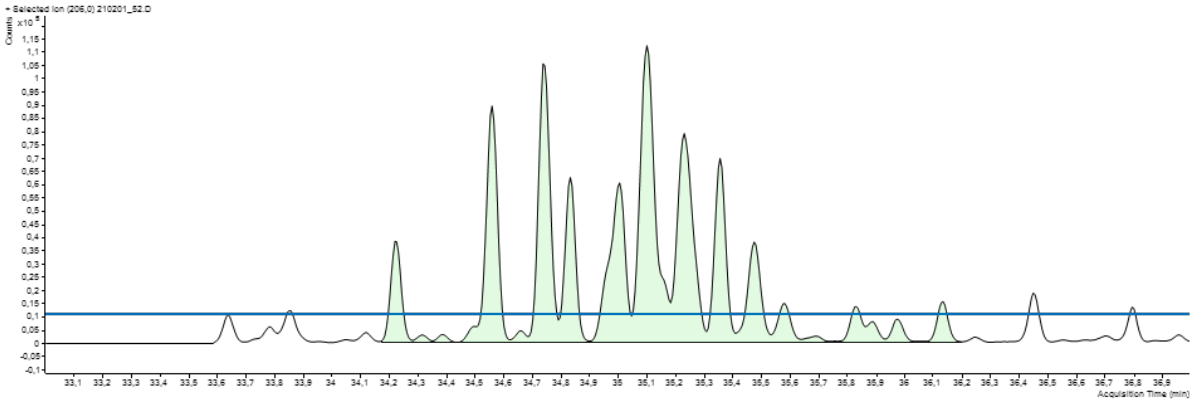
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.18: SIC at *m/z* 192 for C1-phenanthrenes/anthracenes (green area) with the standard 2-methylphenanthrene shown. The blue line indicates the threshold for determining the IAF



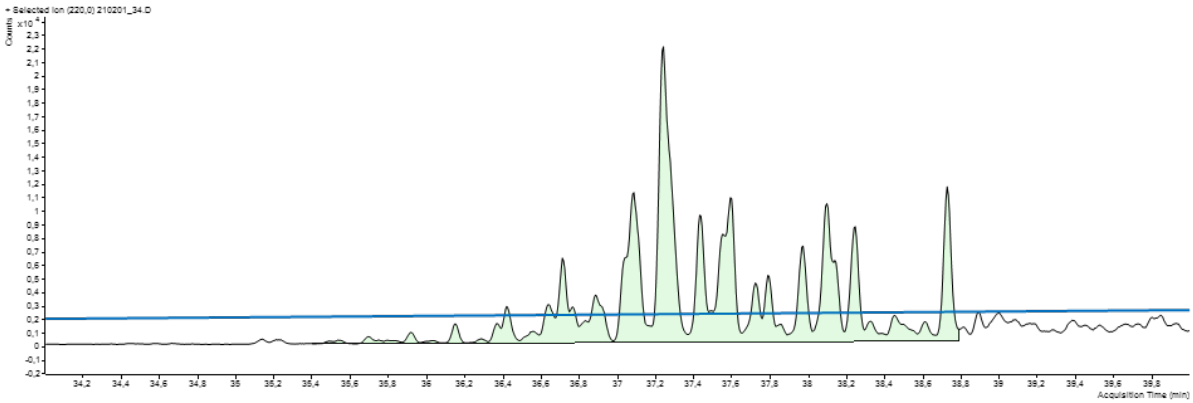
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.19: SIC at *m/z* 206 for C2-phenanthrenes/anthracenes (green area). The blue line indicates the threshold for determining the IAF



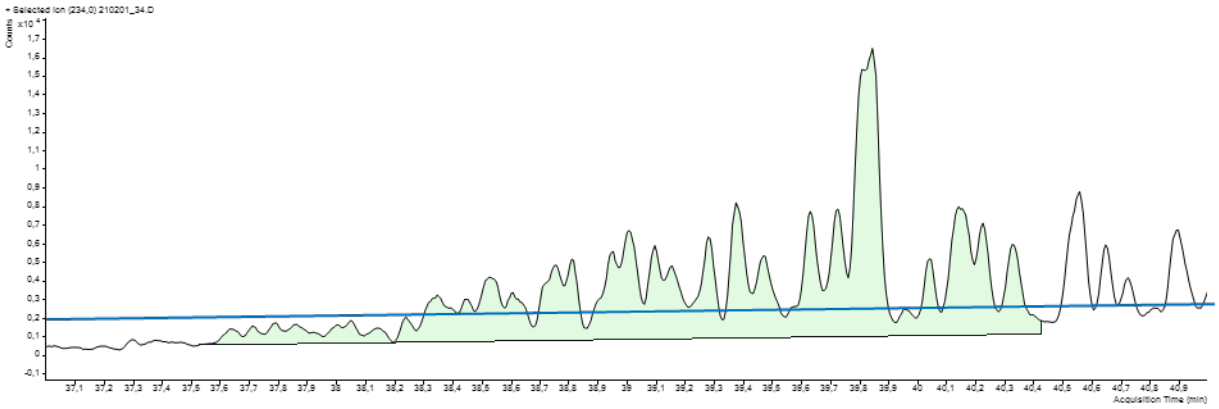
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.20: SIC at *m/z* 220 for C3-phenanthrenes/anthracenes (green area). The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.21: SIC at *m/z* 234 for C4-phenanthrenes/anthracenes (green area). The blue line indicates the threshold for determining the IAF

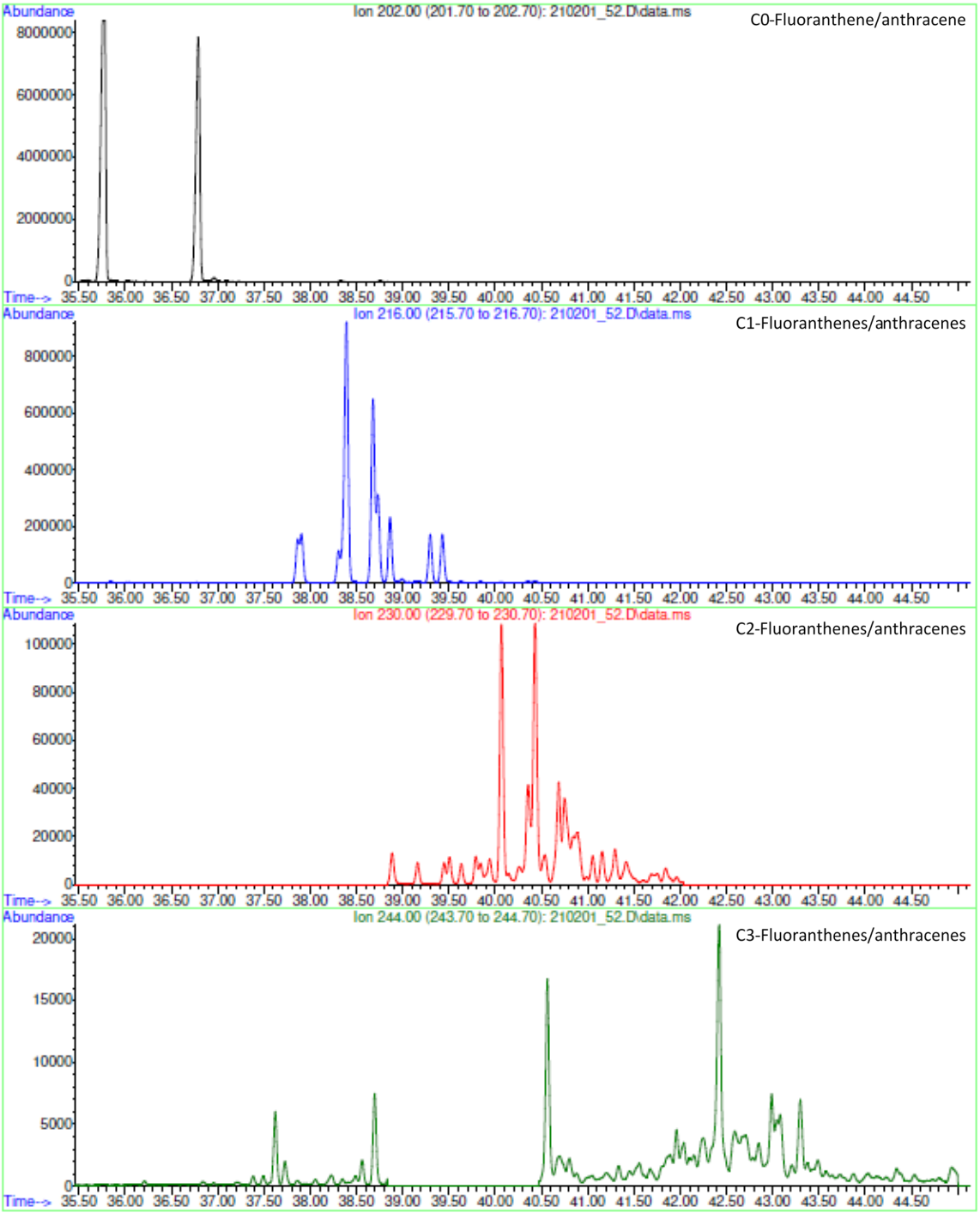


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Fluoranthenes/Pyrenes

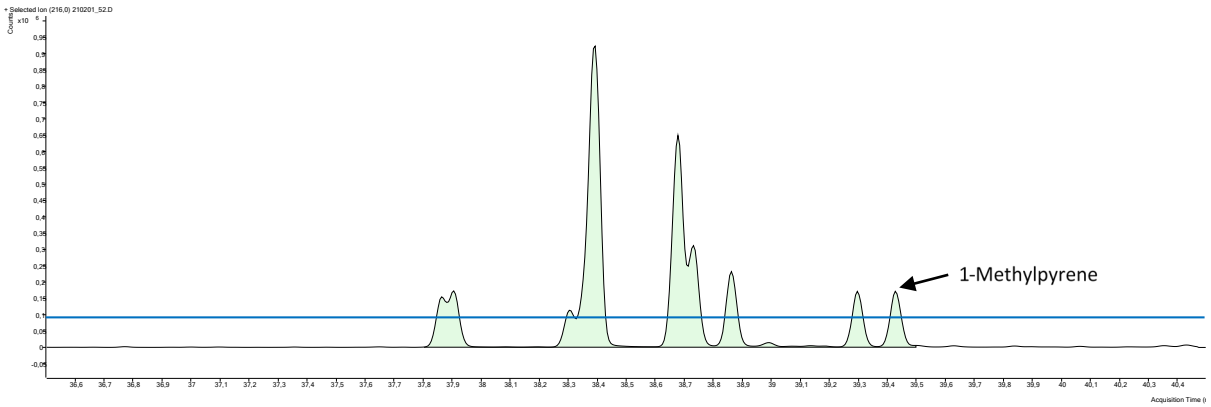
Fluoranthene/Pyrene constituent groups were defined based on relative retention behaviour, one article [21], and standards for C0-fluoranthene and C0- and C1-pyrenes. GC×GC data was not available. Below is shown the relative retention behaviour for C0-C3-fluoranthenes/pyrenes (Figure B.22) and detailed chromatograms for the constituent groups C1-fluoranthenes/pyrenes (Figure B.23), C2-fluoranthenes/pyrenes (Figure B.24), and C3-fluoranthenes/pyrenes (Figure B.25).

Figure B.22: Relative retention behaviour for C0-C3-fluoranthenes/pyrenes illustrated by SICs at *m/z* 202, 216, 230, and 244



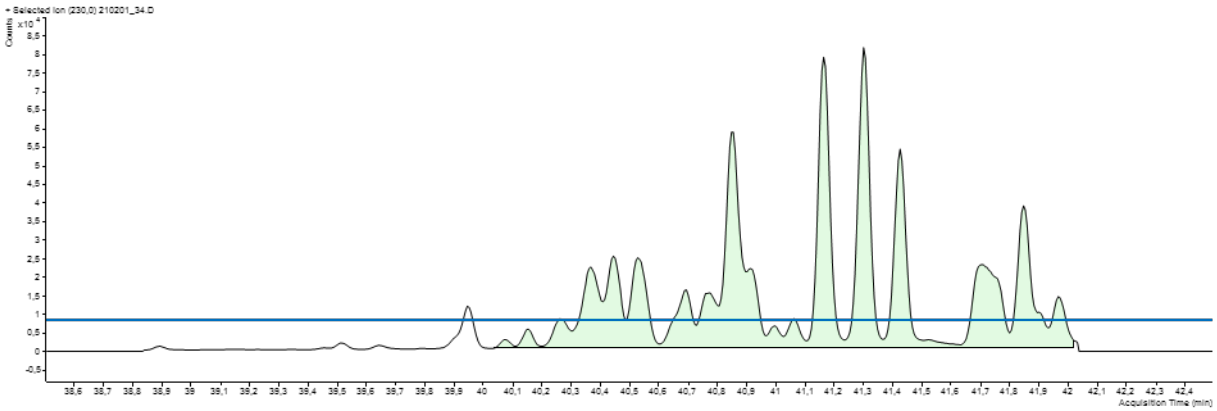
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.23: SIC at *m/z* 216 for C1-fluoranthenes/pyrenes (green area) with the standard 1-methylpyrene shown. The blue line indicates the threshold for determining the IAF



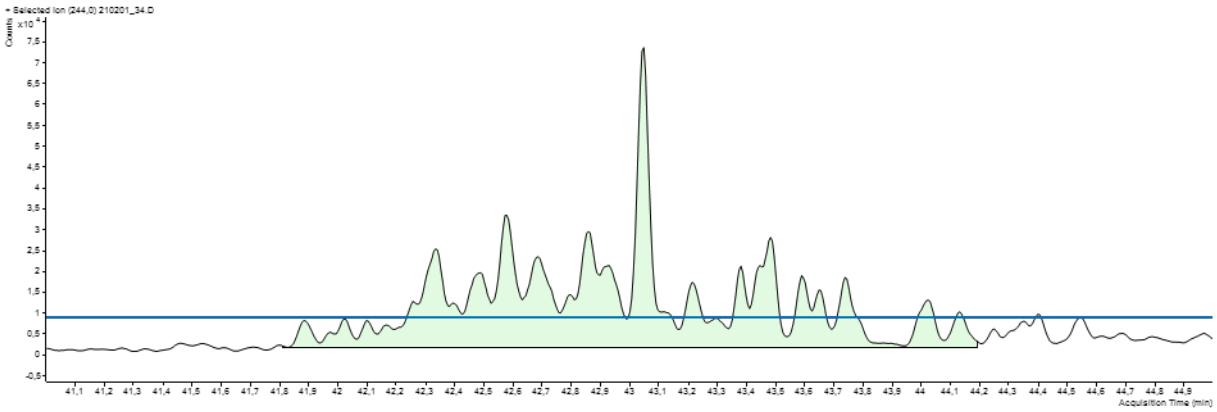
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.24: SIC at *m/z* 230 for C2-fluoranthenes/pyrenes (green area). The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.25: SIC at *m/z* 244 for C3-fluoranthenes/pyrenes (green area). The blue line indicates the threshold for determining the IAF

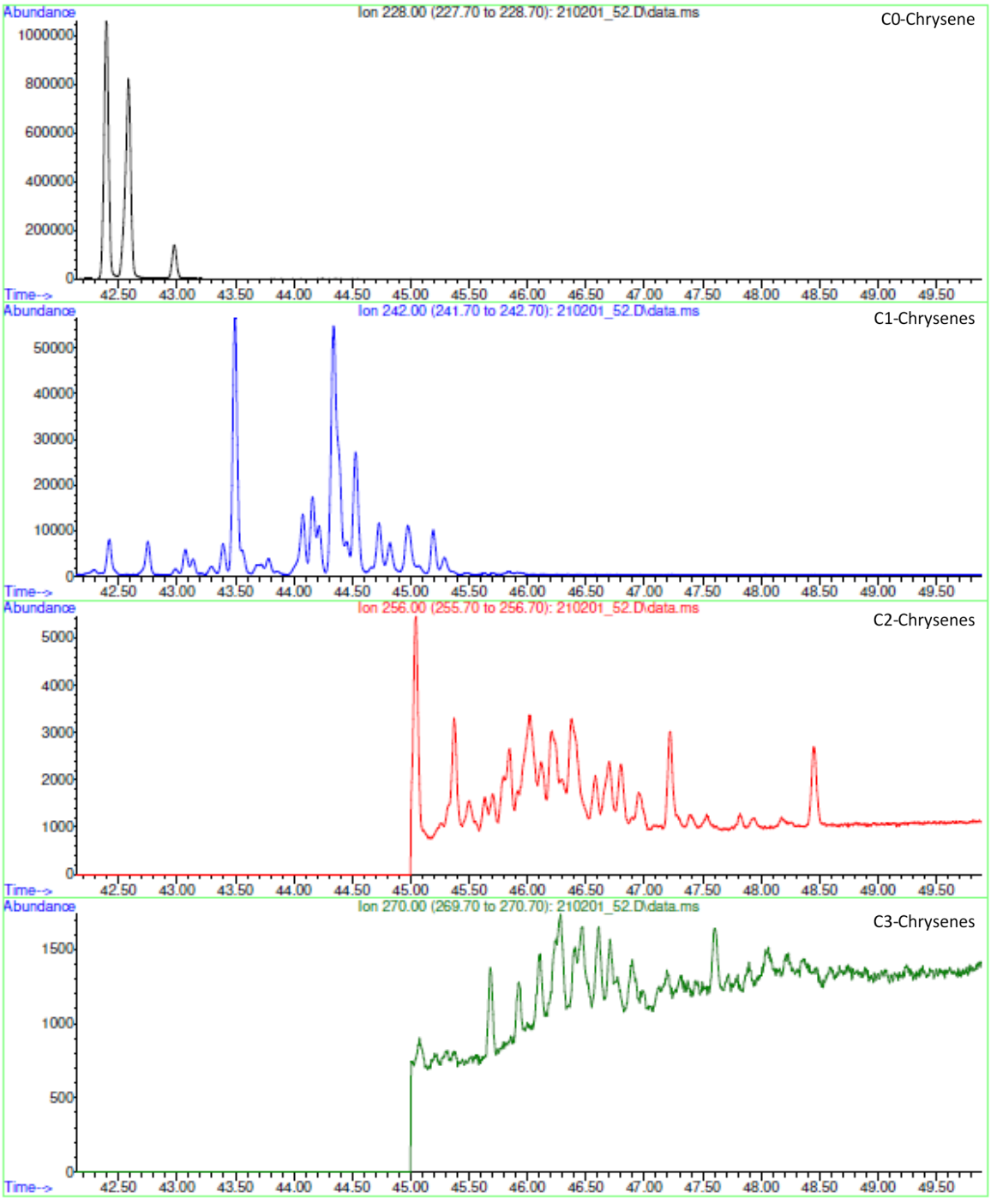


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Chrysenes

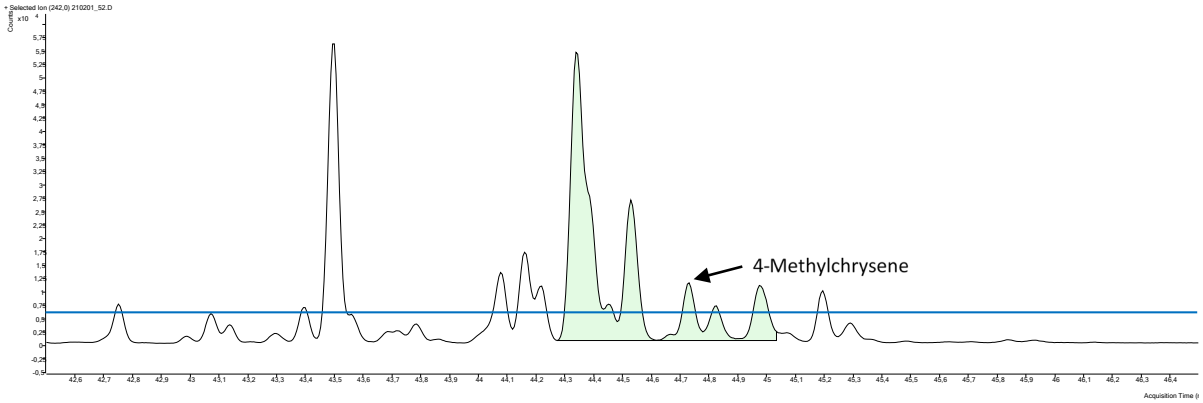
The definition of chrysene constituent groups is based on relative retention behaviour, one article [21], and standards for C0-, C1-, C2-, and C3-chrysenes. GC×GC data was not available. Below is the relative retention behaviour for C0-C3-chrysenes (Figure B.26) and detailed chromatograms for the constituent groups C1-chrysenes (Figure B.27), C2-chrysenes (Figure B.28), and C3-chrysenes (Figure B.29). The C2-chrysenes are mainly defined based on the article and the standard 6-ethylchrysene is outside constituent group retention range (at 45.65min).

Figure B.26: Relative retention behaviour for C0-C3-chrysenes illustrated by SICs at *m/z* 228, 242, 256, and 270



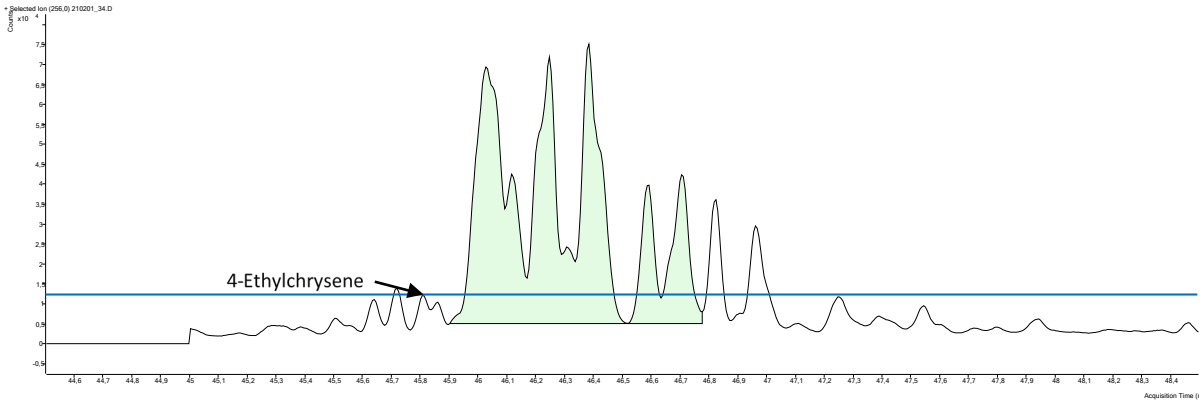
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.27: SIC at *m/z* 242 for C1-chrysenes (green area) with the standard 4-methylchrysene shown. The blue line indicates the threshold for determining the IAF



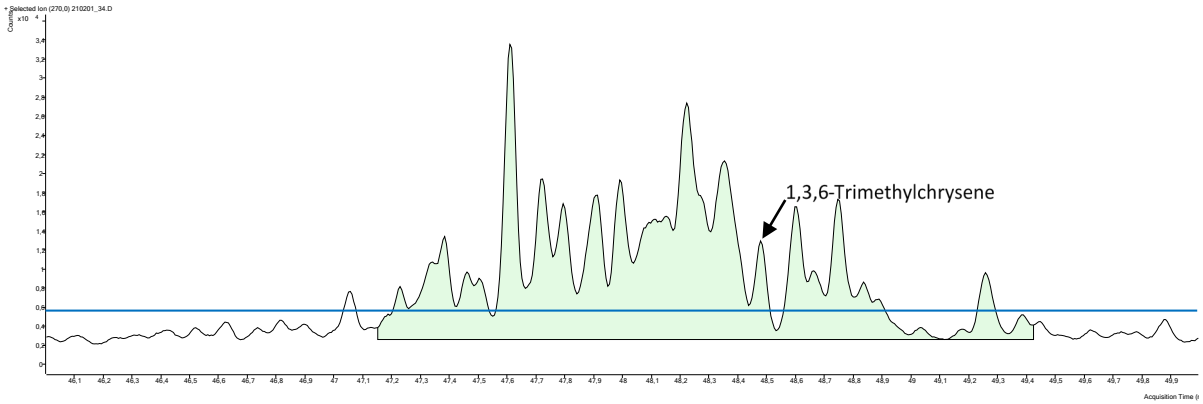
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.28: SIC at *m/z* 256 for C2-chrysenes (green area) with the standard 4-ethylchrysene shown outside constituent group retention time range (at 45.65 min). The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.29: SIC at *m/z* 270 for C3-chrysenes (green area) with the standard 1,3,6-trimetylchrysene shown. The blue line indicates the threshold for determining the IAF

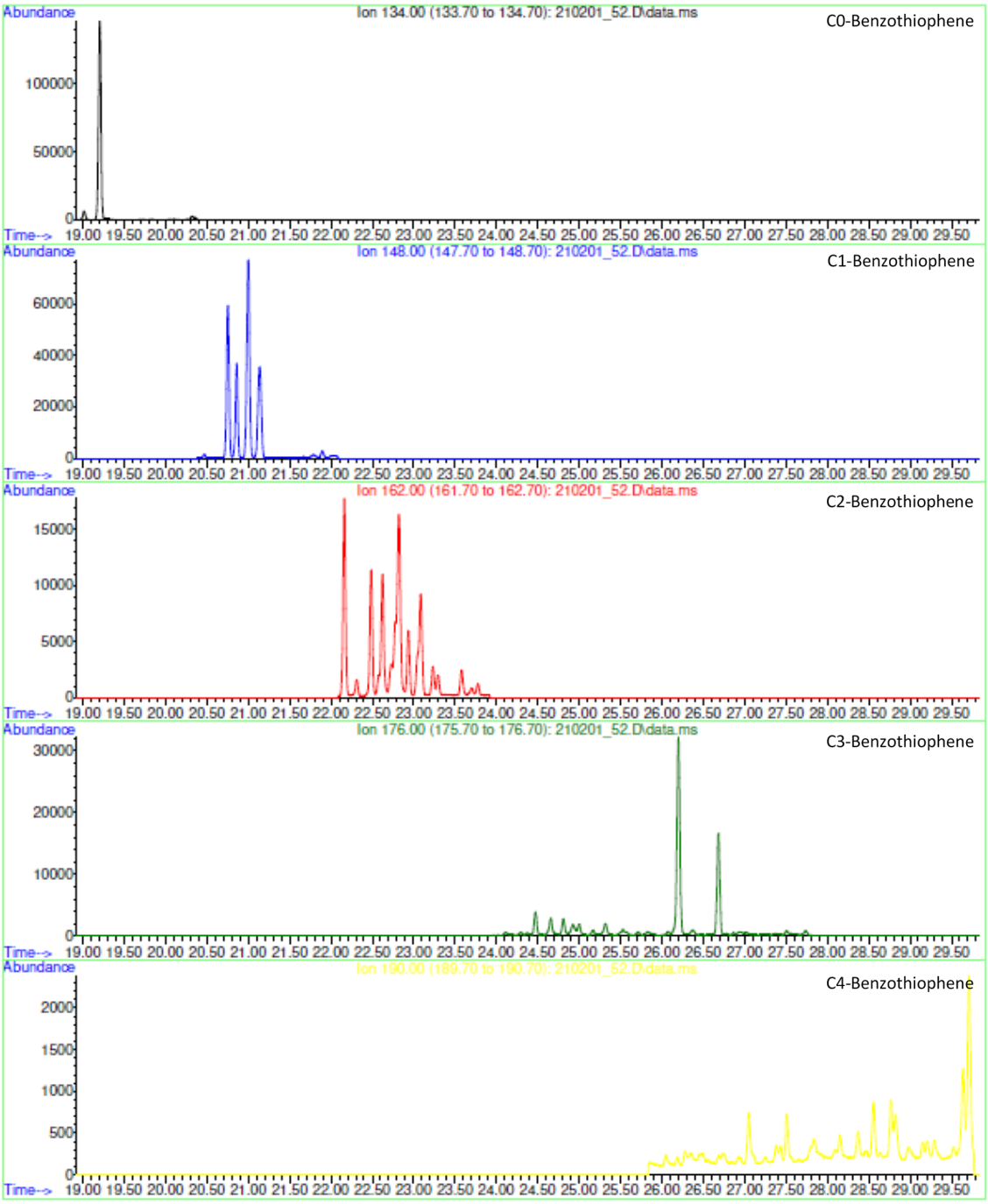


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Benzothiophenes

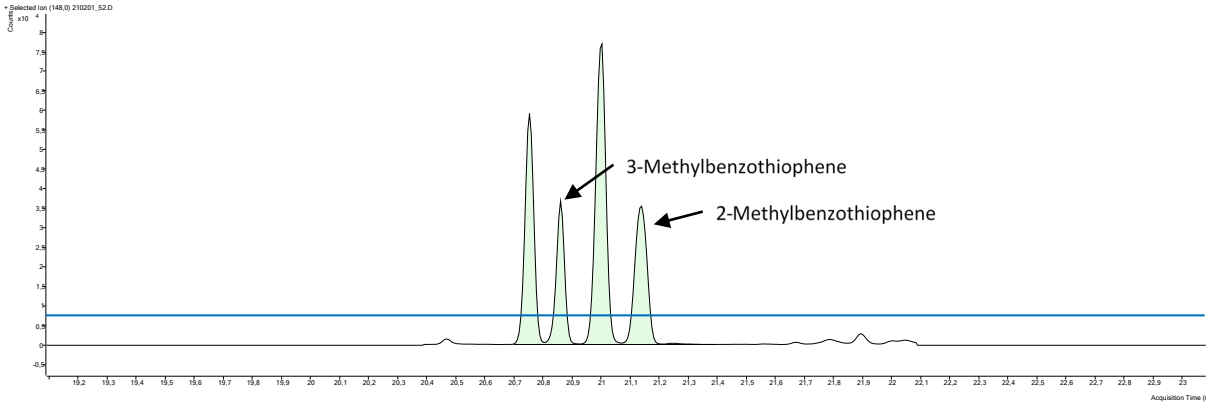
Benzothiophene constituent groups were defined based on relative retention behaviour, one article [21], and standards for C0-, C1-, and C3-benzothiophenes. GC×GC data was not available. Below is shown the relative retention behaviour (Figure B.30) and detailed chromatograms of the constituent groups C1-benzothiophenes (Figure B.31), C2-benzothiophenes (Figure B.32), C3-benzothiophenes (Figure B.33), and C4-benzothiophenes (Figure B.34). The constituent group for C3-benzothiophenes is shortened due to interference and the standard 2,3,4-trimethylbenzothiophene is outside the constituent group retention range (at 26.34min).

Figure B.30: Relative retention behaviour for C0-C4-benzothiophenes illustrated by SICs at *m/z* 134, 148, 162, 176, and 190



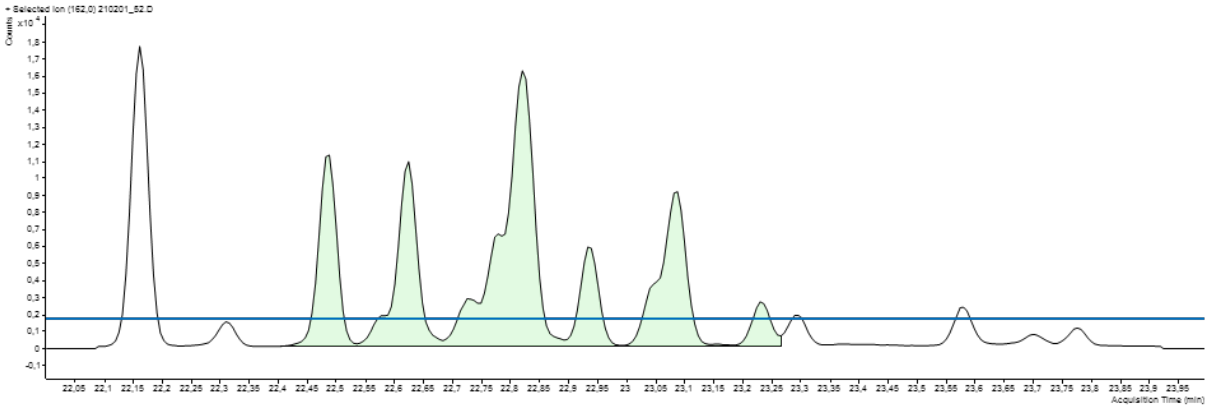
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.31: SIC at *m/z* 148 for C1-benzothiophenes with the two standards 3-methylbenzothiophene and 2-methylbenzothiophenes shown. The blue line indicates the threshold for determining the IAF



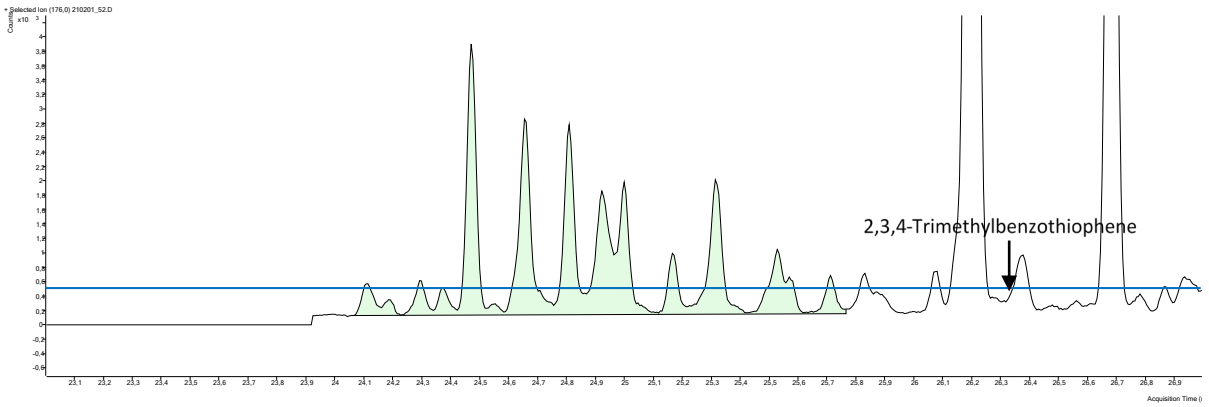
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.32: SIC at *m/z* 162 for C2-benzothiophenes (green area). The blue line indicates the threshold for determining the IAF



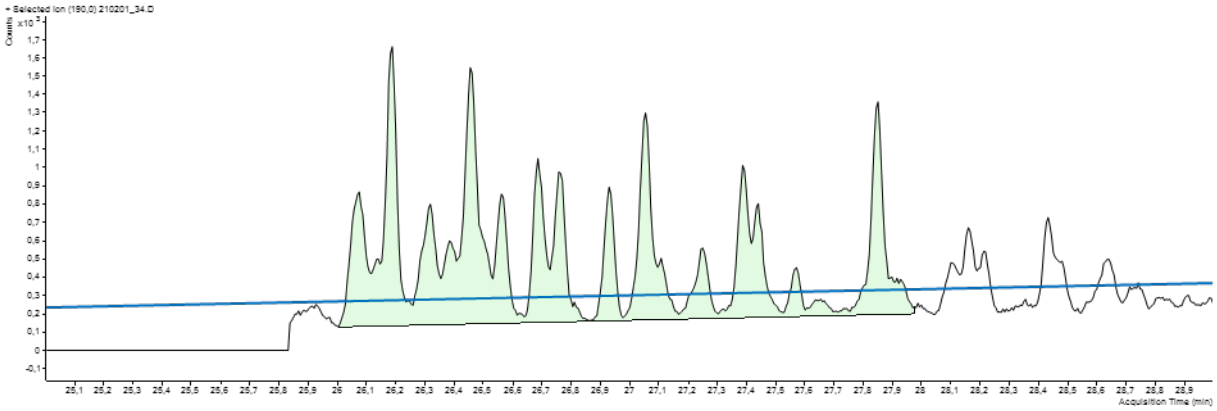
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.33: SIC at *m/z* 176 for C3-benzothiophenes (green area) with the standard 2,3,4-trimethylbenzothiophene shown outside the constituent group retention time range. The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.34: SIC at *m/z* 190 for C4-benzothiophenes (green area). The blue line indicates the threshold for determining the IAF

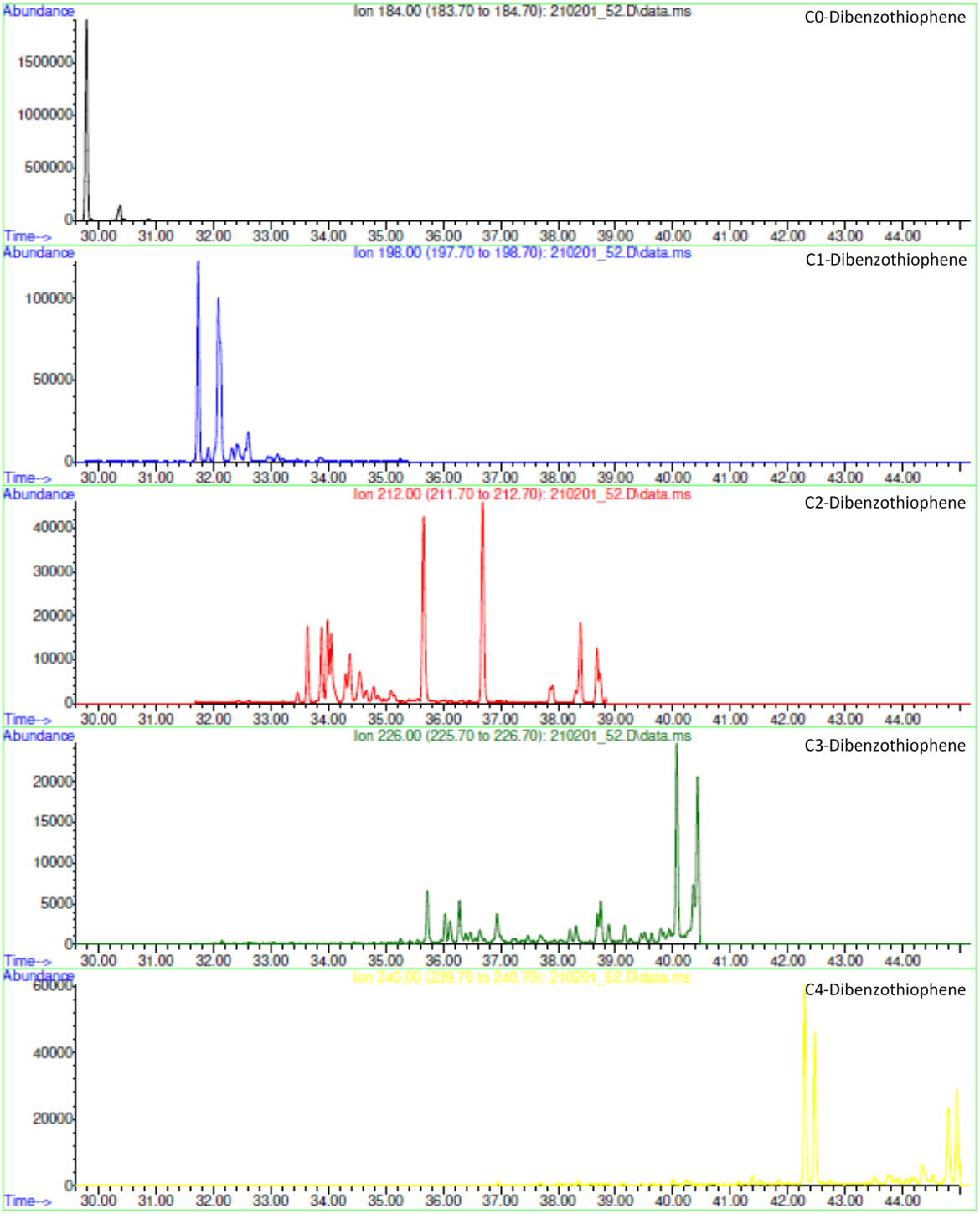


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Dibenzothiophenes

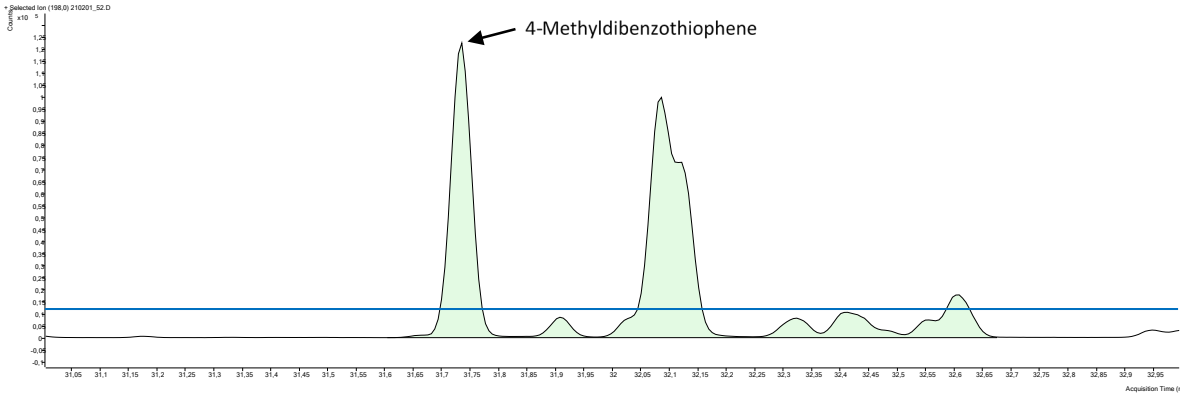
Dibenzothiophene constituent groups are defined based on relative retention behaviour, one article [21], and standards for C0-C3-dibenzothiophenes. GC×GC data was not available. Below is the relative retention behaviour for C0-C4-dibenzothiophenes (Figure B.35) and detailed chromatograms for C1-dibenzothiophenes (Figure B.36), C2-dibenzothiophenes (Figure B.37), C3-dibenzothiophenes (Figure B.38), and C4-dibenzothiophenes (Figure B.39).

Figure B.35: Relative retention behaviour for C0-C4-dibenzothiophenes illustrated by SICs at *m/z* 184, 196, 212, 226, and 240



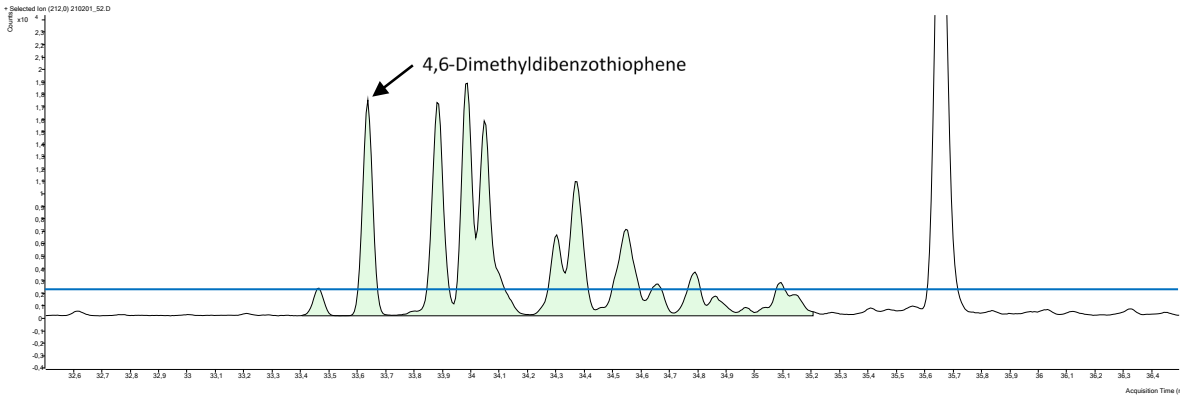
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.36: SIC at *m/z* 198 for C1-dibenzothiophenes (green area) with the standard 4-methyldibenzothiophene shown. The blue line indicates the threshold for determining the IAF



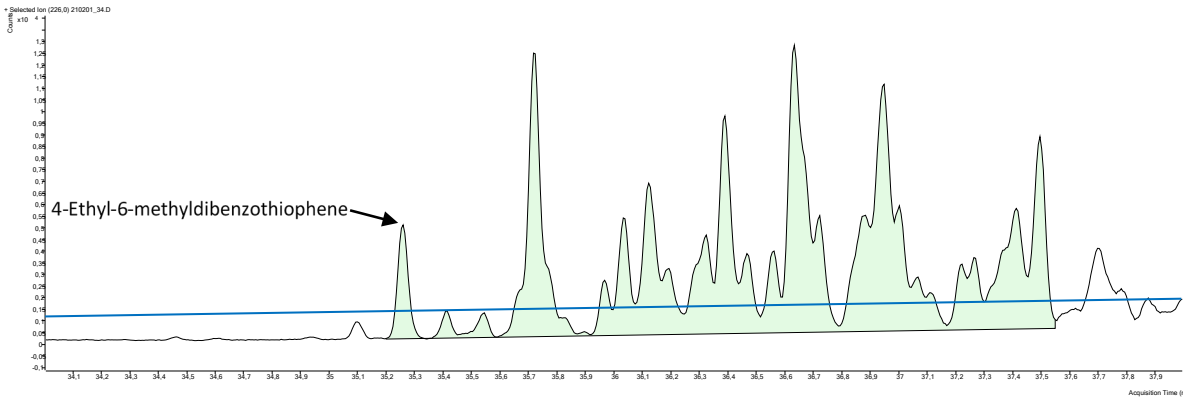
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.37: SIC at *m/z* 212 for C2-dibenzothiophenes (green area) with the standard 4,6-dimethyldibenzothiophene shown. The blue line indicates the threshold for determining the IAF



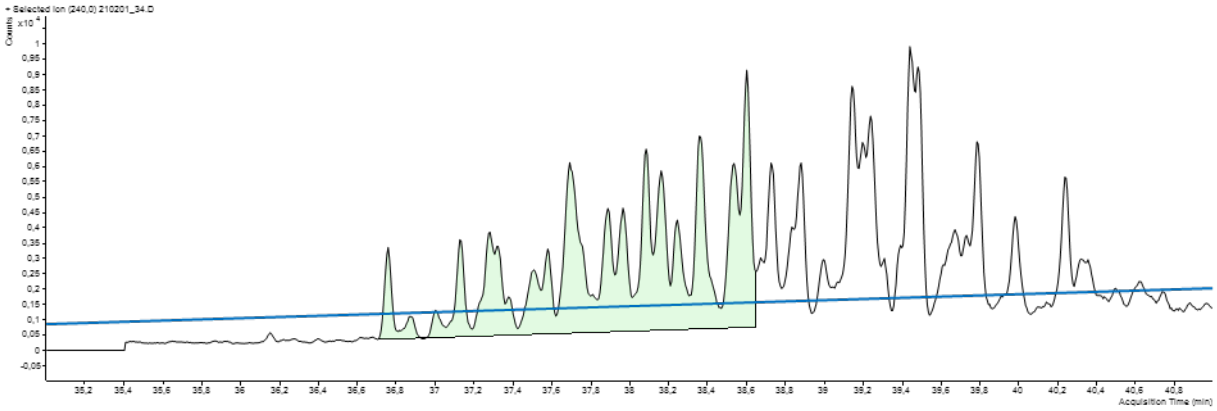
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.38: SIC at *m/z* 226 for C3-dibenzothiophenes (green area) with the standard 4-ethyl-6-methyldibenzothiophene shown. The blue line indicates the threshold for determining the IAF



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.39: SIC at *m/z* 240 for C4-dibenzothiophenes (green area). The blue line indicates the threshold for determining the IAF

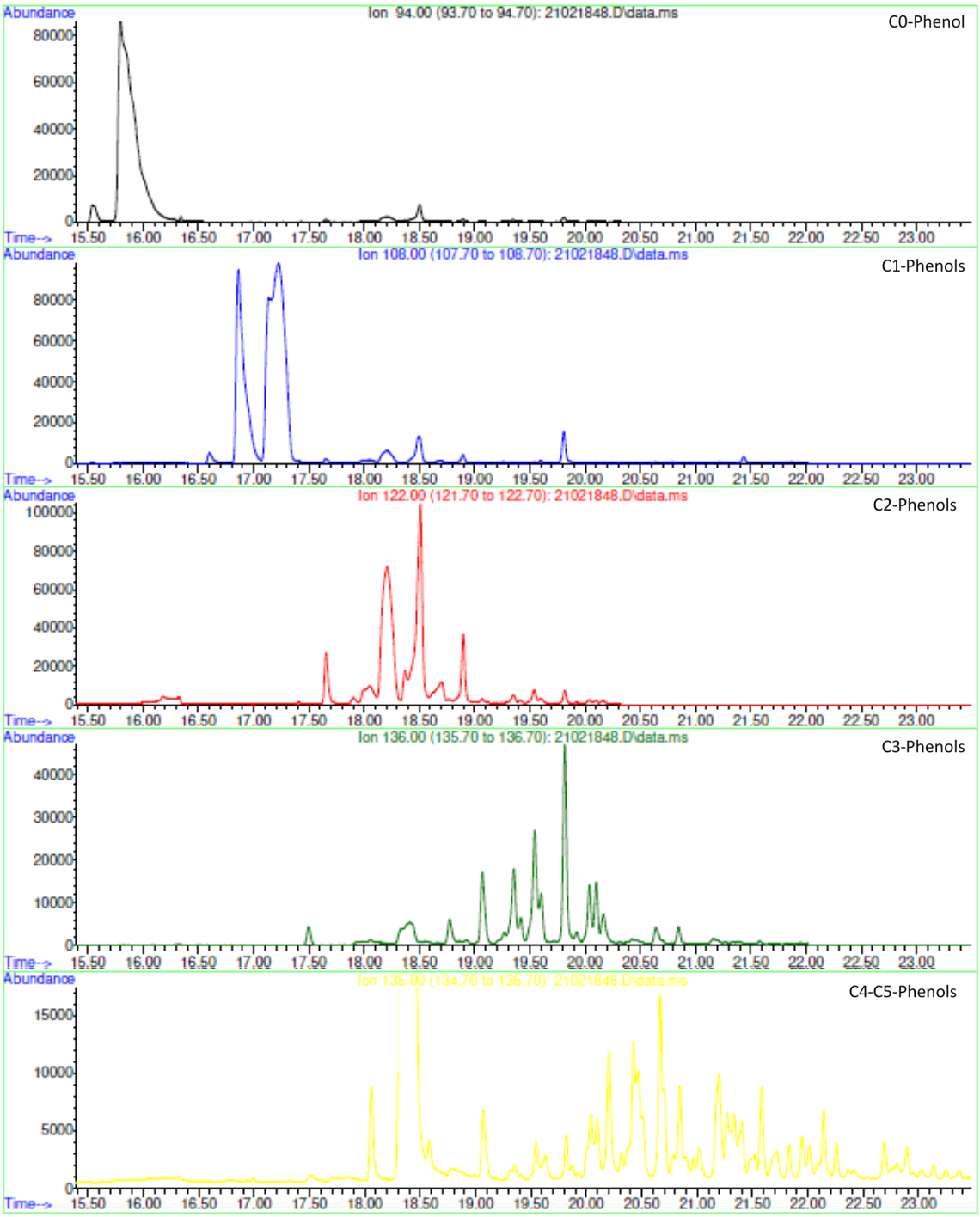


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Phenols

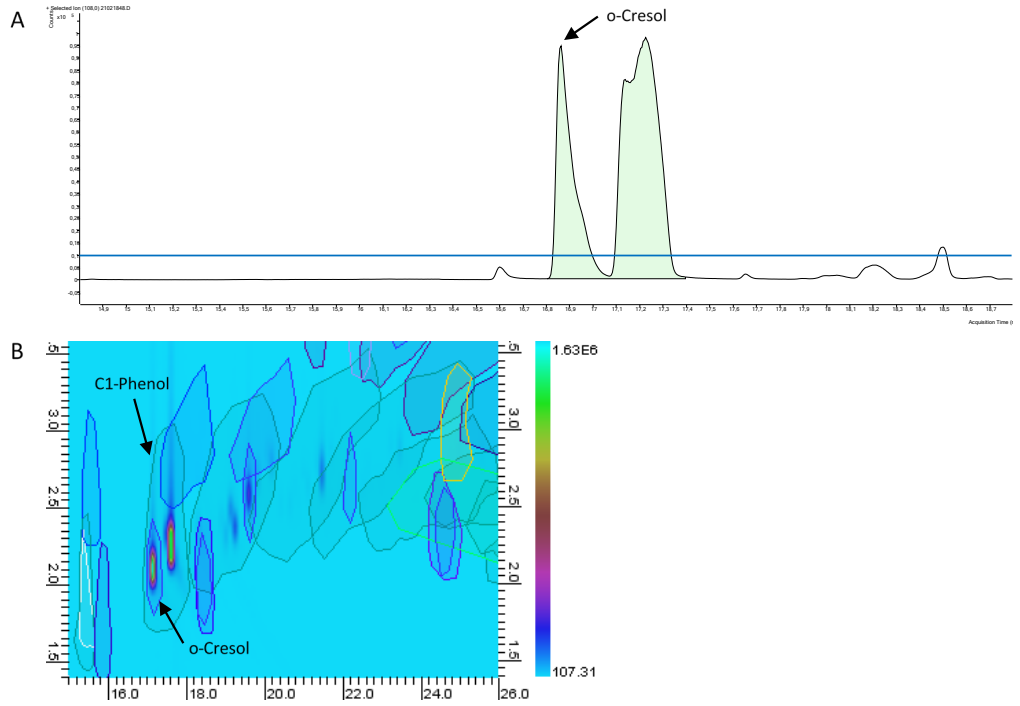
Phenol constituent groups were defined based on relative retention behaviour, one article [23], standard for C1-, C2- and C4-phenols, and GC×GC data. Below is the relative retention behaviour for C0-C5-phenols (Figure B.40), and detailed chromatograms and GC×GC data of the constituent groups C1-phenols (Fiigure B.41), C2-phenols (Figure B.42), C3-phenols (Figure B.43), and C4-C5-phenols (Figure B.44). It was not possible to define C6-C9-phenols as these were too low in concentration. The C6-phenols are further not fully covered by the GC-MS/SIM method.

Figure B.40: Relative retention behaviour for C0-C5-phenols illustrated by SICs at *m/z* 94, 108, 122, 136, and 135



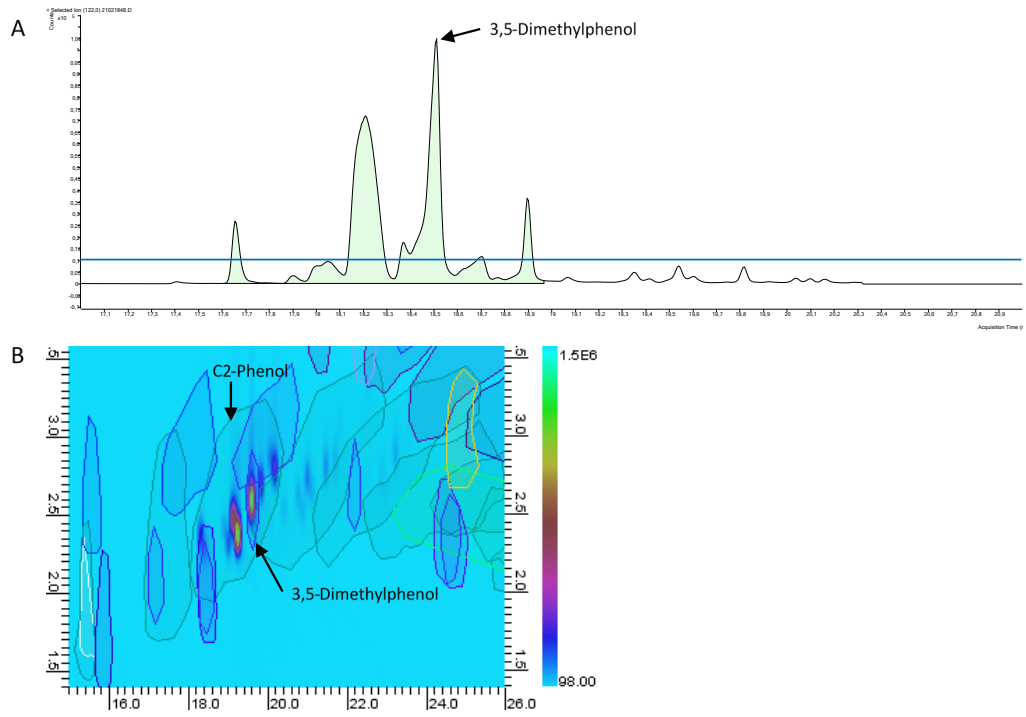
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.41: **A: SIC at *m/z* 108 for C1-phenols (green area) with the standard o-cresol shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-phenols and the standard o-cresol extracted at high resolution of 108.0575±0.0500**



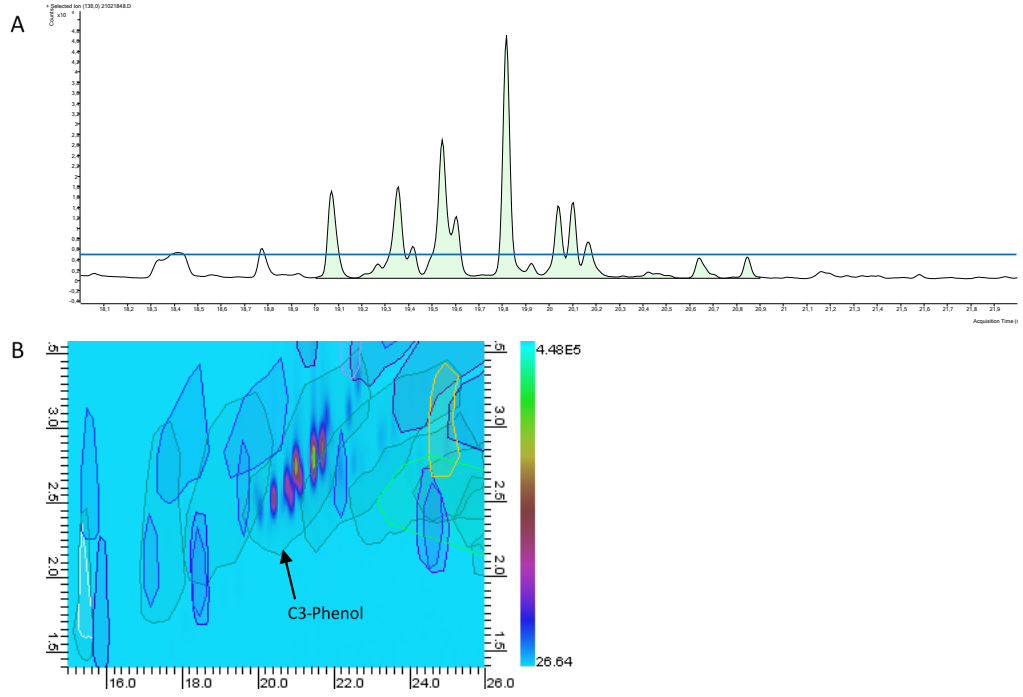
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.42: **A: SIC at *m/z* 122 for C2-phenols (green area) with the standard 3,5-dimethylphenol shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-phenols and the standard 3,5-dimethylphenol extracted at high resolution of 122.0732±0.0500**



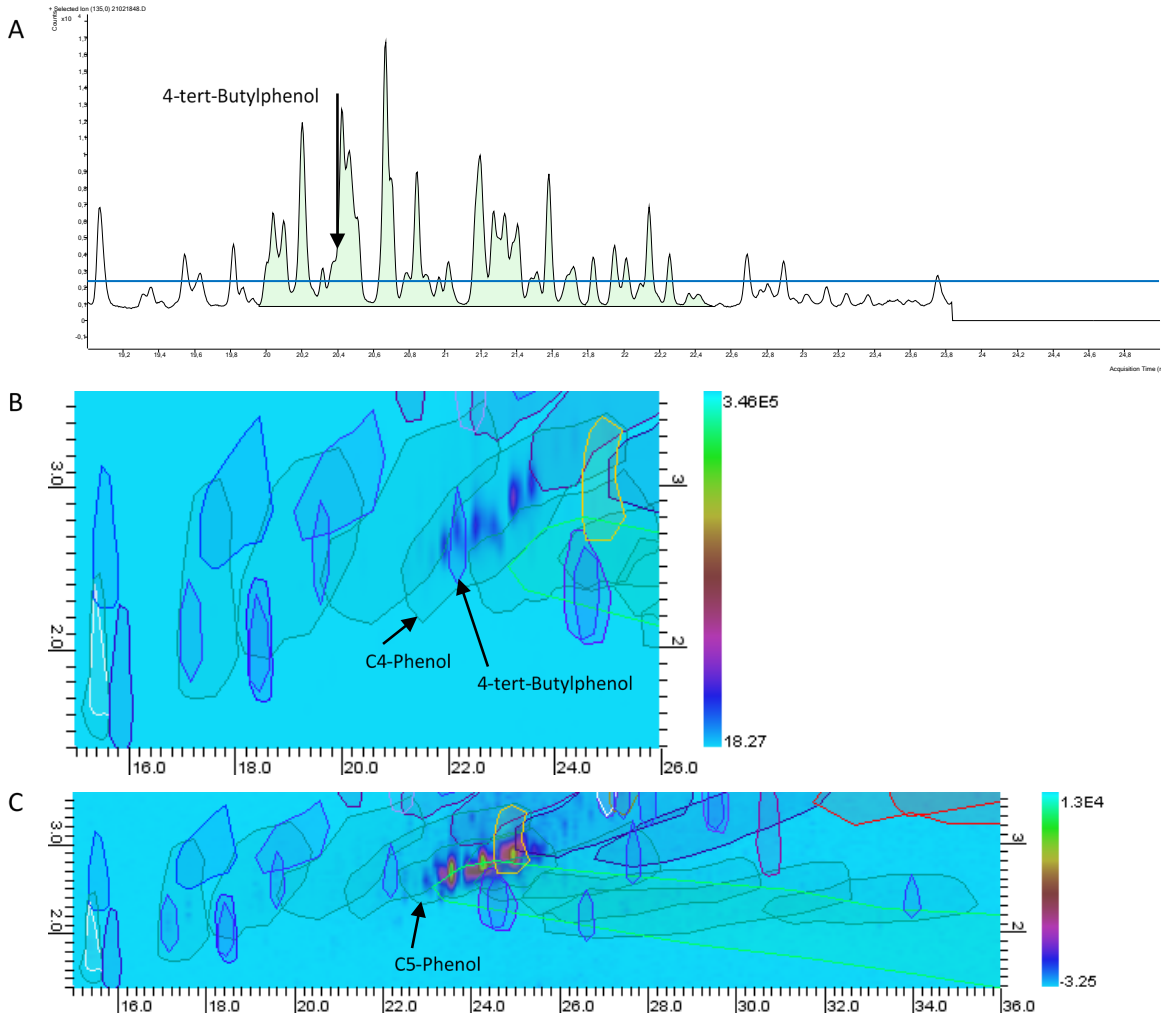
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.43: A: SIC at *m/z* 136 for C3-phenols (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C3-phenols extracted at high resolution of 136.0888±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.44: **A: SIC at *m/z* 135 for C4-C5-phenols (green area) with the retention of the standard 4-tert butylphenol shown, though possibly not present in the sample. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C4-phenols and the standard 4-tert butylphenol extracted at high resolution of 150.1045±0.0500. C: GC×GC image of C5-phenols extracted at high resolution of 164.1201±0.0500**

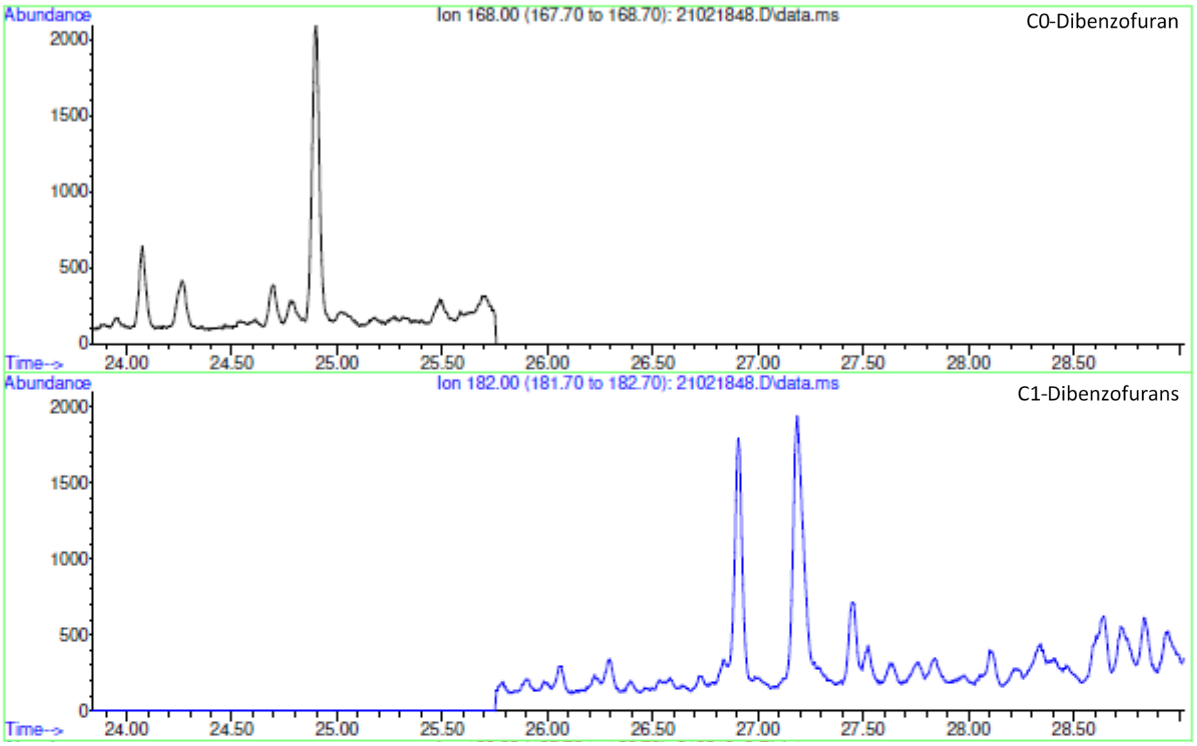


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Dibenzofurans

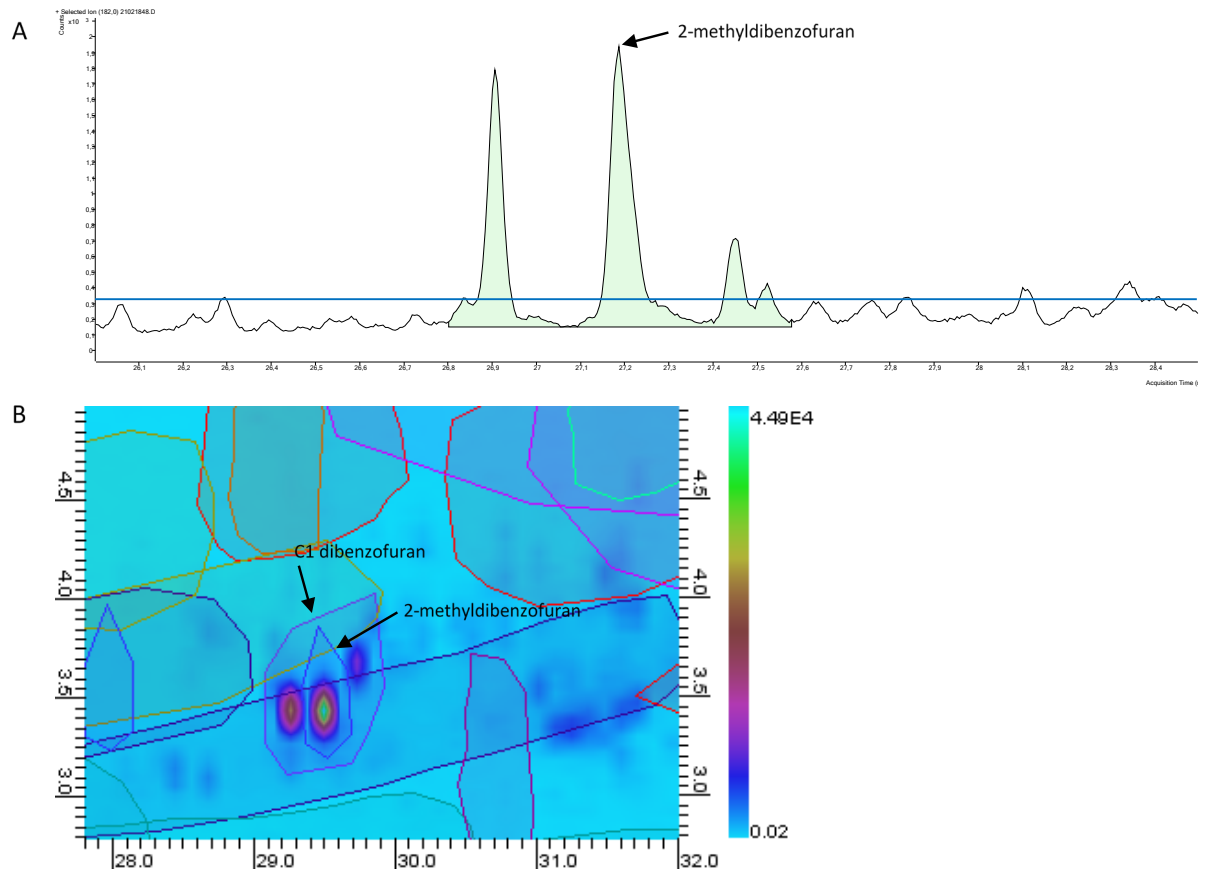
Dibenzofurans were defined based on limited relative retention behaviour, one article for C0-C2-dibenzofurans [24], standards for C0- and C1- dibenzofurans, and available GC×GC data. Below is the relative retention behaviour for C0-C1-dibenzofurans (Figure B.45) and detailed chromatograms and GC×GC data of the constituent group C1-dibenzofurans (Figure B.46).

Figure B.45: Relative retention behaviour for C0-C1-dibenzofurans illustrated by SICs at *m/z* 168 and 182



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.46: A: SIC at *m/z* 182 for C1-dibenzofurans (green area) with the standard 2-methyldibenzofuran shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-dibenzofurans and the standard 2-methyldibenzofuran extracted at high resolution of 182.0732±0.0100

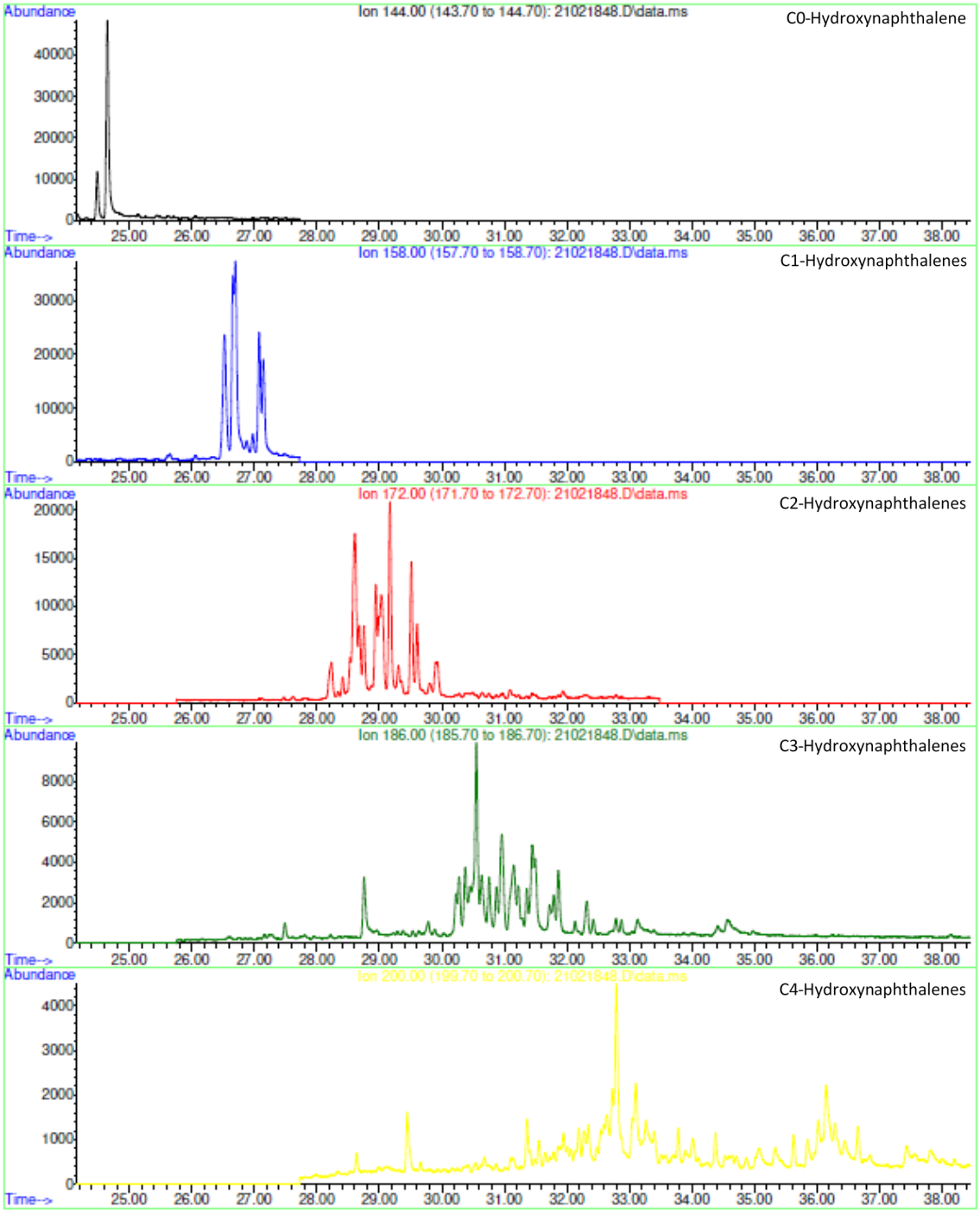


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Hydroxynaphthalenes

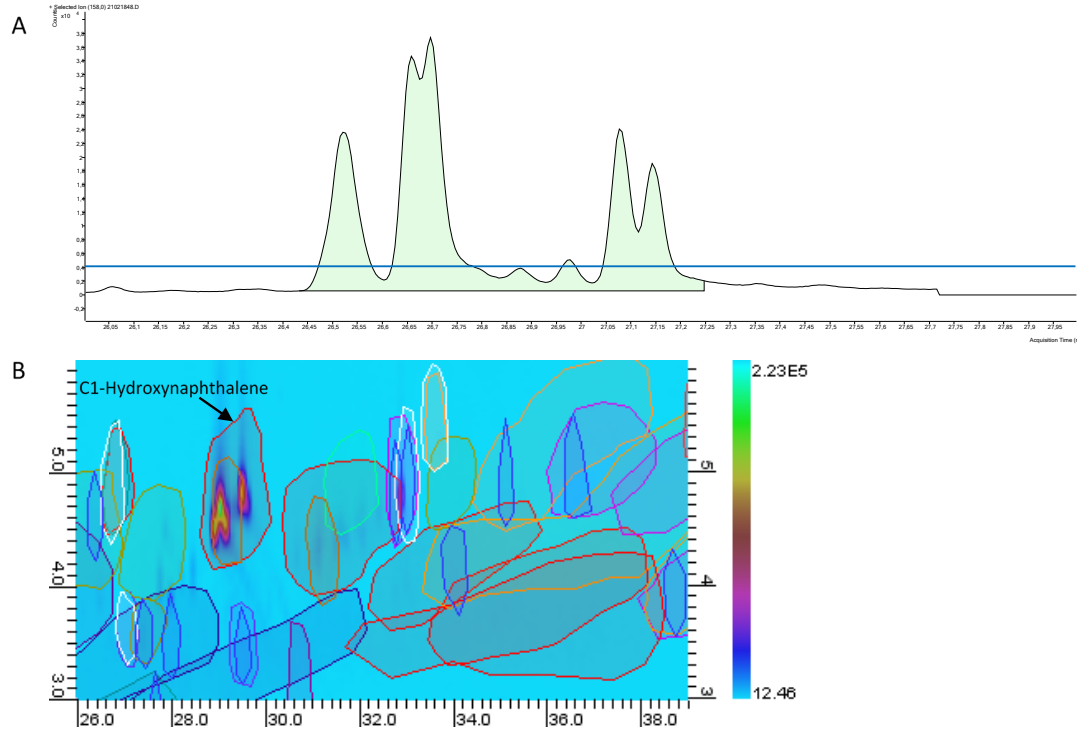
Hydroxynaphthalenes were defined by relative retention behaviour, standard for C0-hydroxynaphthalene, and available GC×GC data. Articles have not been found for the hydroxynaphthalene constituent groups. Below is shown the relative retention behaviour for C0-C4-hydroxynaphthalenes (Figure B.47) and detailed chromatograms and GC×GC data of the constituent groups C1-hydroxynaphthalenes (Figure B.48), C2-hydroxynaphthalenes (Figure B.49), C3-hydroxynaphthalenes (Figure B.50), and C4-hydroxynaphthalenes (Figure B.51).

Figure B.47: Relative retention behaviour for C0-C4-hydroxynaphthalenes illustrated by SICs at *m/z* 144, 158, 172, 186, and 200



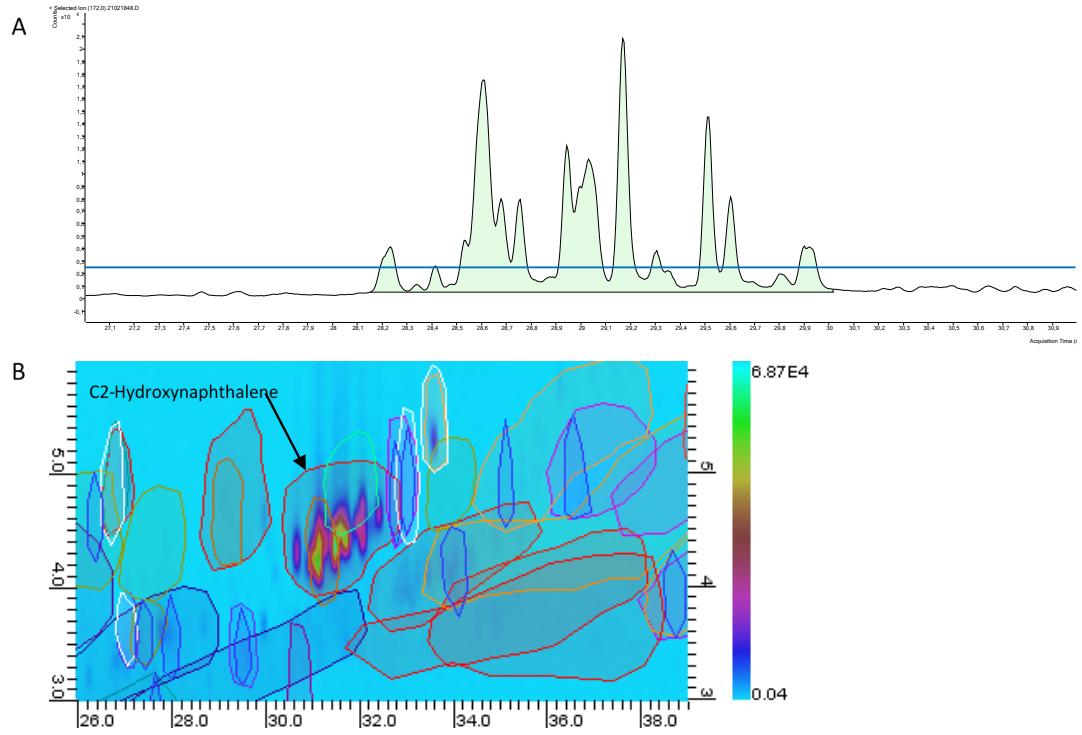
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.48: A: SIC at *m/z* 158 for C1-hydroxynaphthalenes (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-hydroxynaphthalenes extracted at high resolution of 158.0732±0.0500



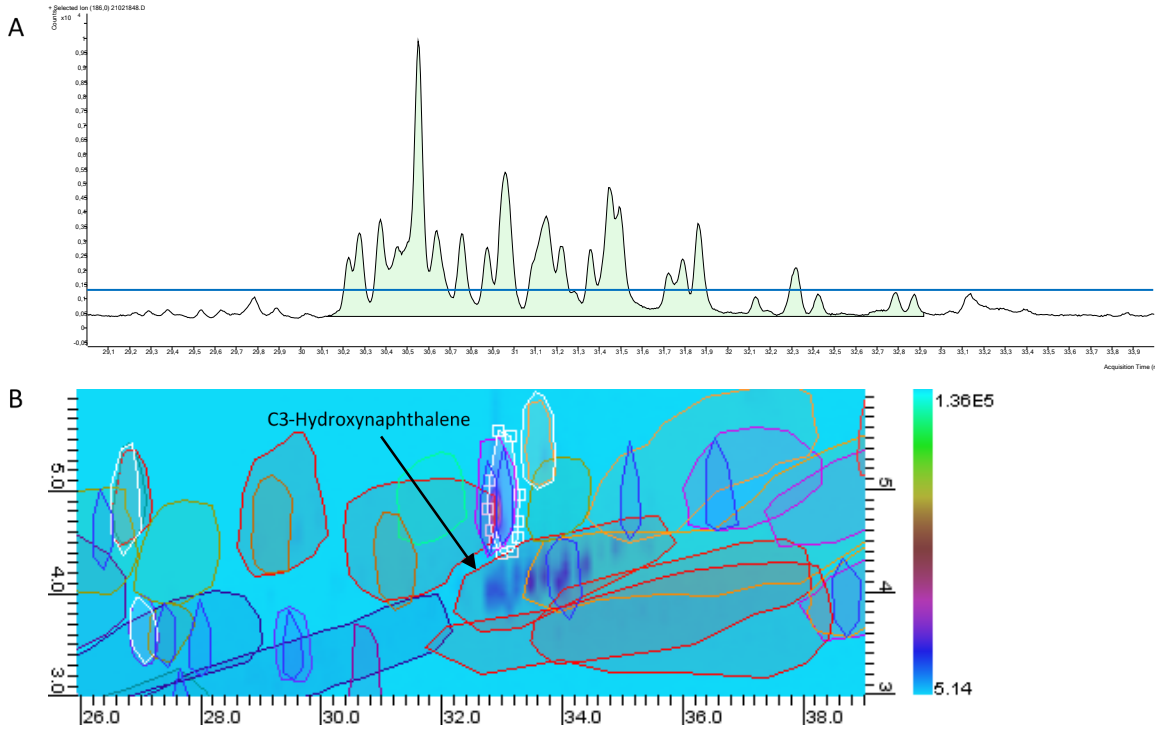
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.49: A: SIC at *m/z* 172 for C2-hydroxynaphthalenes (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-hydroxynaphthalenes extracted at high resolution of 172.0888±0.0500



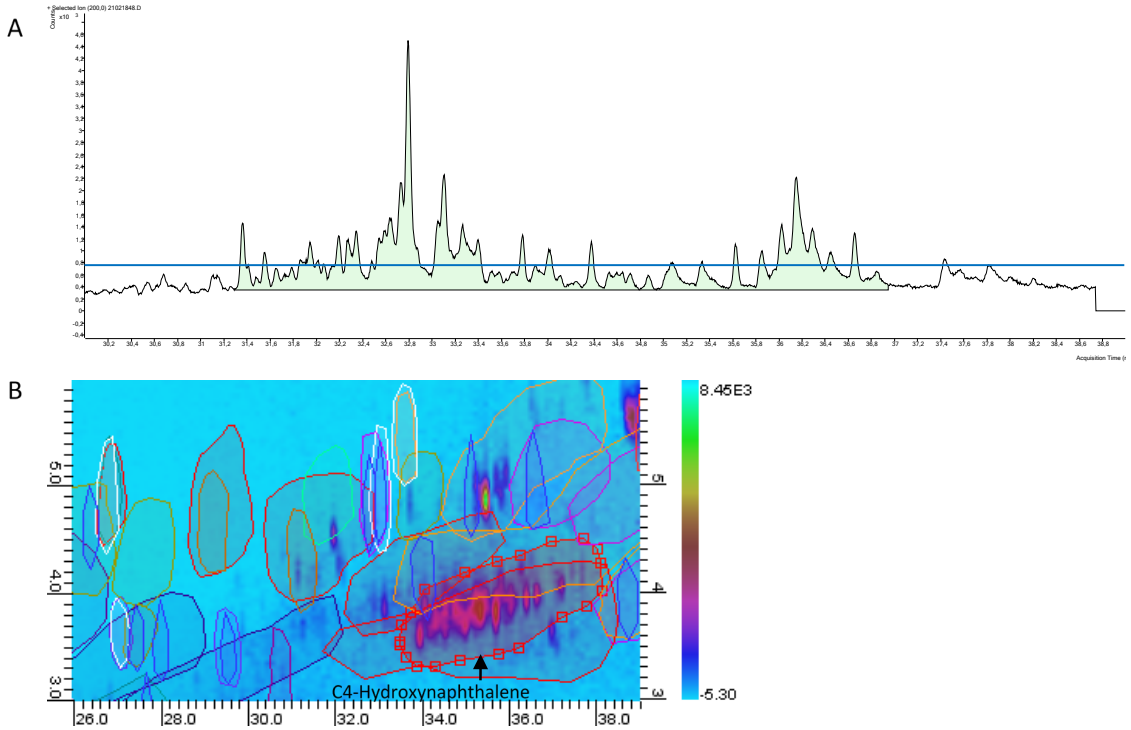
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.50: A: SIC at *m/z* 186 for C3-hydroxynaphthalenes (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C3-hydroxynaphthalenes extracted at high resolution of 186.1047±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.51: A: SIC at *m/z* 200 for C4-hydroxynaphthalenes (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C4-hydroxynaphthalenes extracted at high resolution of 200.1205±0.0500

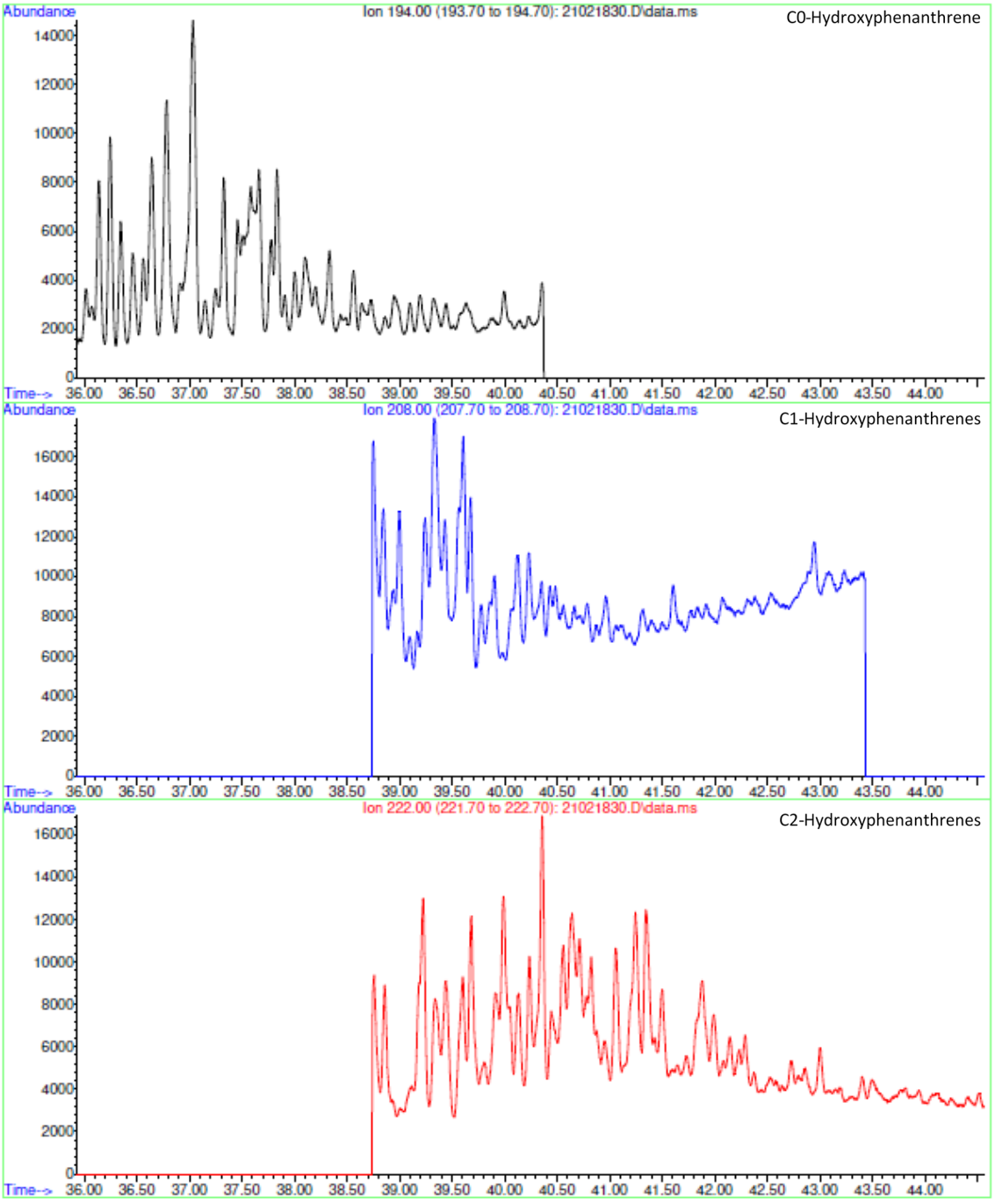


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Hydroxyphenanthrene

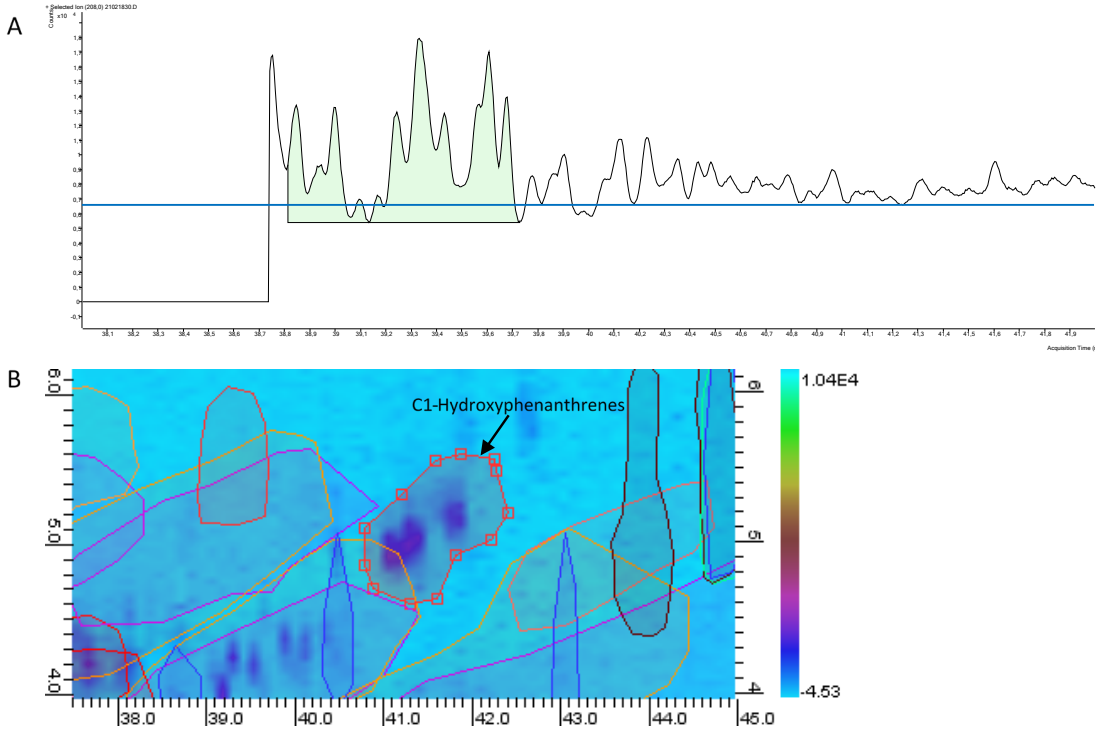
The regions for the hydroxyphenanthrenes are very populated and the constituent groups were based on limited relative retention behaviour, the standard for C0-hydroxyphenanthrene, which is though difficult to identify, and available GC×GC data. Articles have not been found for the hydroxyphenanthrene constituent groups. Below is shown the relative retention behaviour for C0-C2-hydroxyphenanthrenes (Figure B.52) and detailed chromatograms and GC×GC data of the constituent groups C1-hydroxyphenanthrenes (Figure B.53) and C2-hydroxyphenanthrenes (Figure B.54). C1-hydroxyphenanthrenes is not fully covered by the GC-MS/SIM method.

Figure B.52: Relative retention behaviour for C0-C2-hydroxyphenanthrenes illustrated by SICs at *m/z* 194, 208, and 222



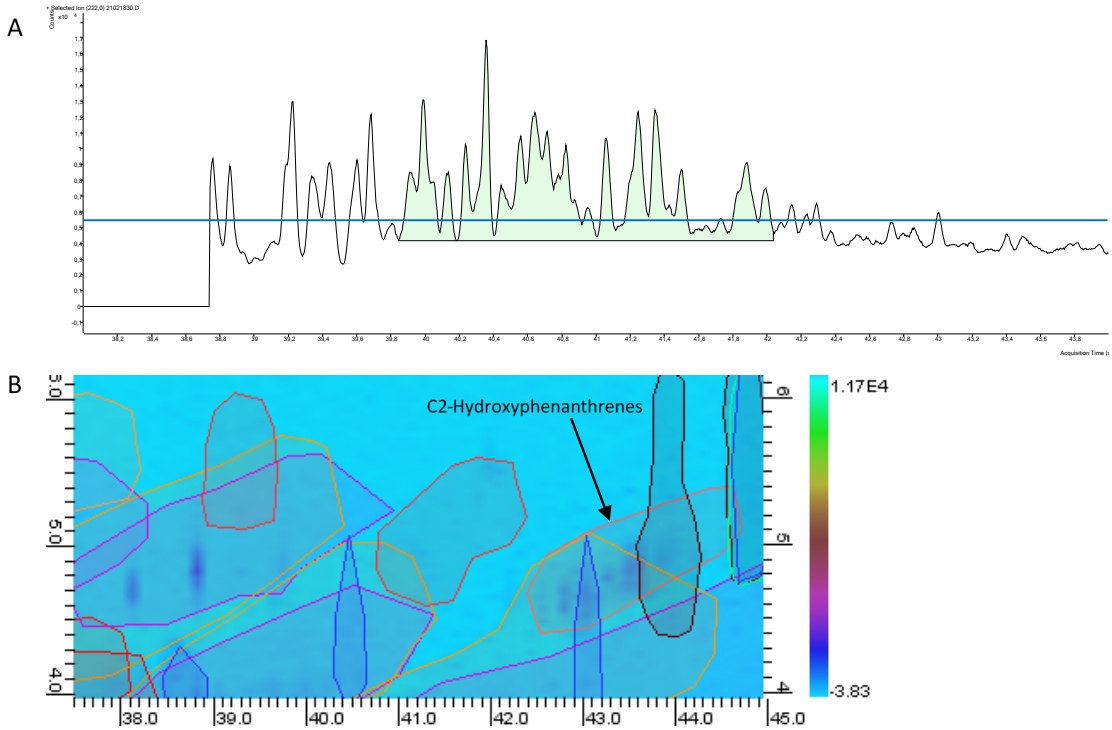
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.53: A: SIC at *m/z* 208 for C1-hydroxyphenanthrenes (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-hydroxyphenanthrenes extracted at high resolution of 208.0890±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.54: A: SIC at *m/z* 222 for C2-hydroxyphenanthrenes (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-hydroxyphenanthrenes extracted at high resolution of 222.1049±0.0500

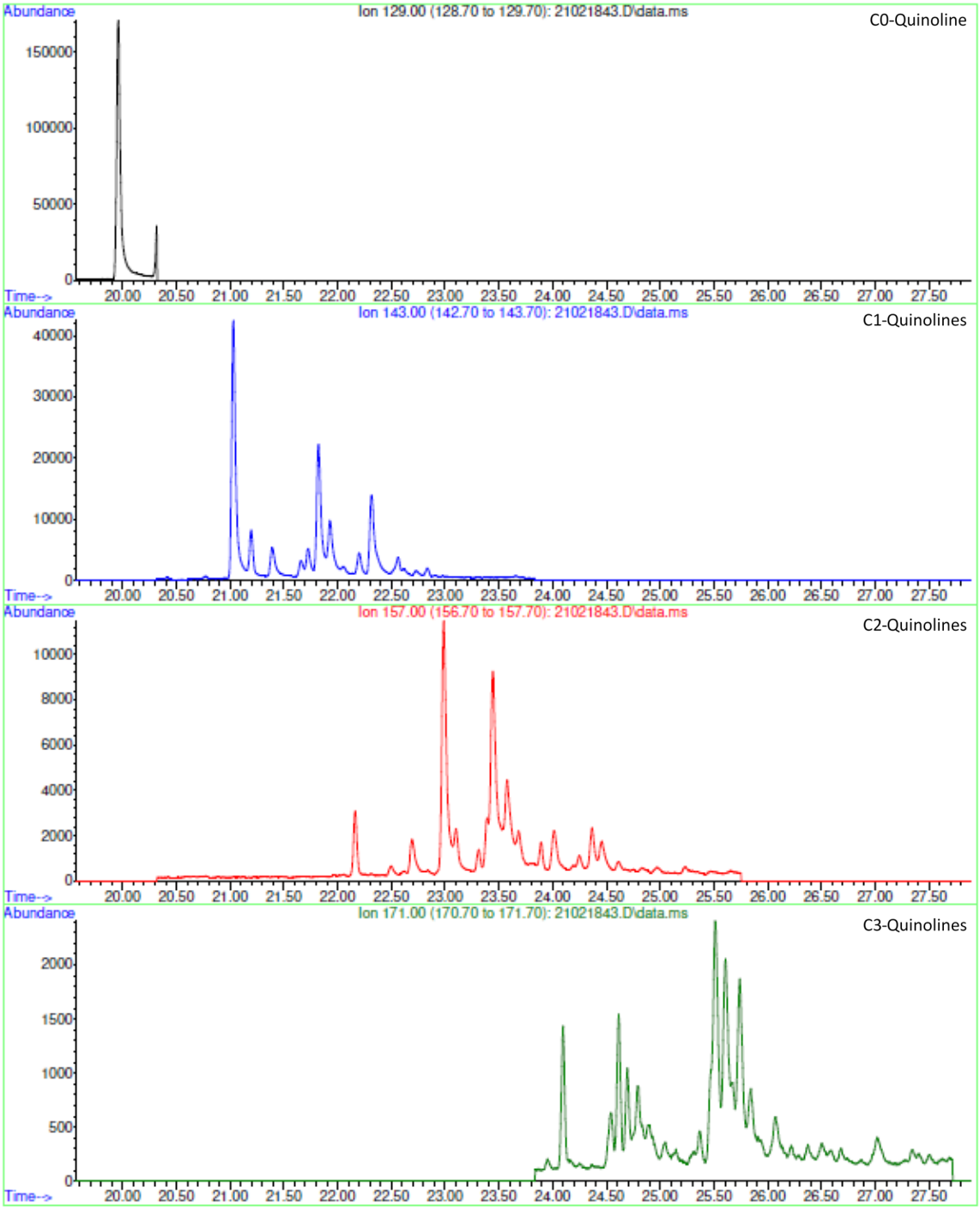


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Quinolines

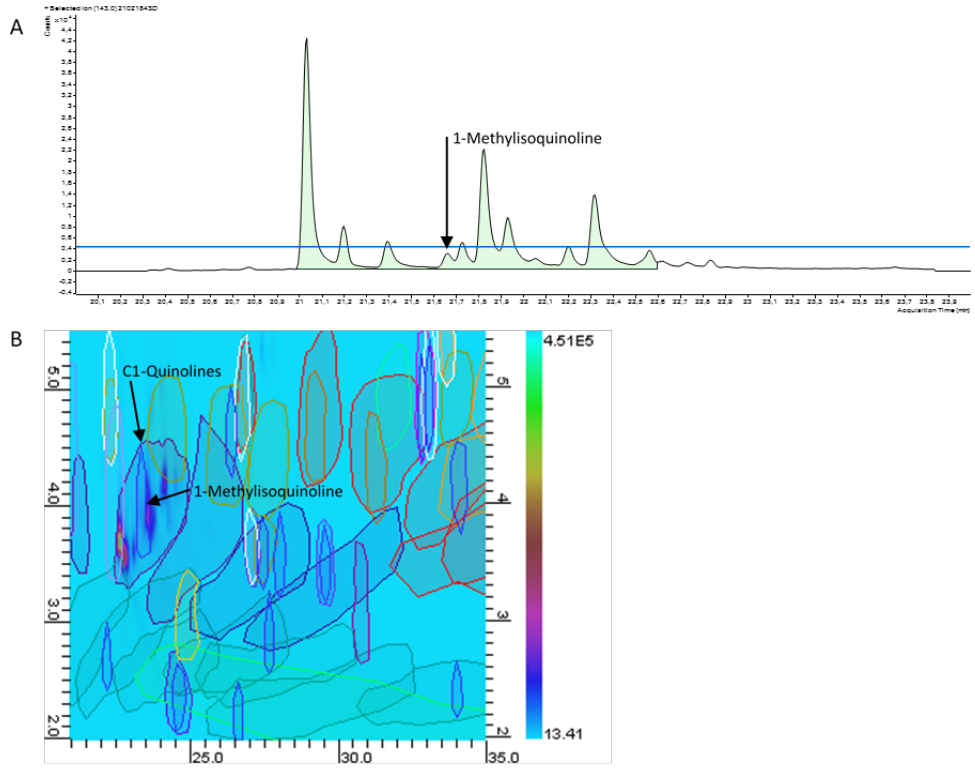
The quinoline constituent groups were defined based on relative retention behaviour, standard for C0-, C1- and C3-quinolines, and available GC×GC data. Articles have not been found for the quinoline constituent groups. Below is shown the relative retention behaviour for C0-C3-quinolines (Figure B.55) and detailed chromatograms and GC×GC data of the constituent groups C1-quinoline (Figure B.56), C2-quinoline (Figure B.57), and C3-quinoline (Figure B.58). The C3-quinolines starts approximately 1min earlier, but this is not covered by the GC-MS/SIM method.

Figure B.55: Relative retention behaviour for C0-C3-quinolines illustrated by SICs at *m/z* 129, 143, 157, and 171



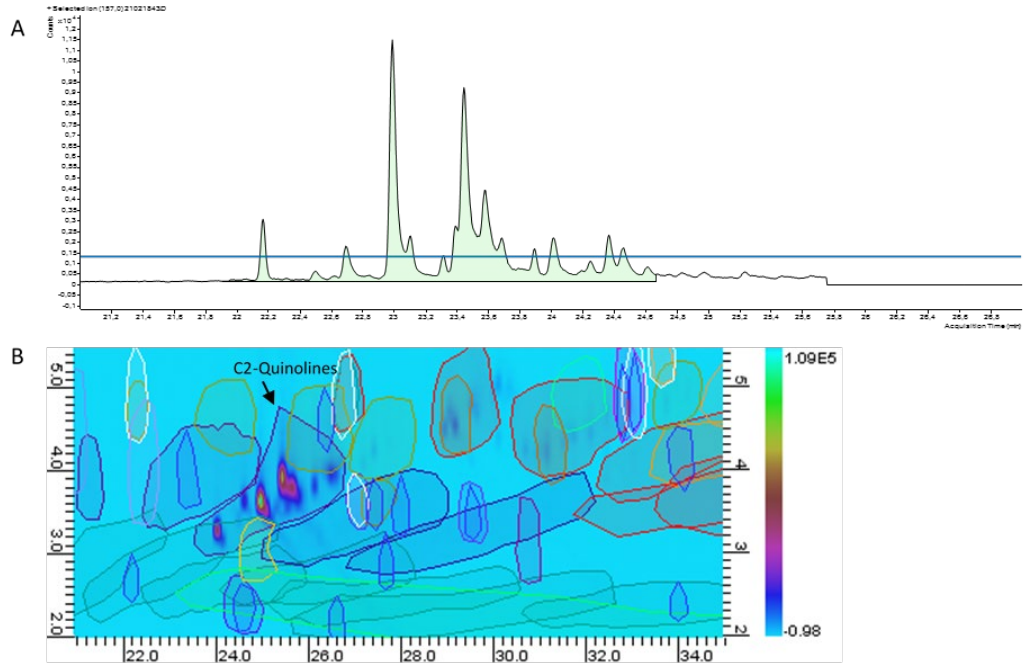
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.56: A: SIC at *m/z* 143 for C1-quinolines (green area) with the standard 1-methylisoquinoline shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-quinolines and the standard 1-methylisoquinoline extracted at high resolution of 143.0735±0.0500



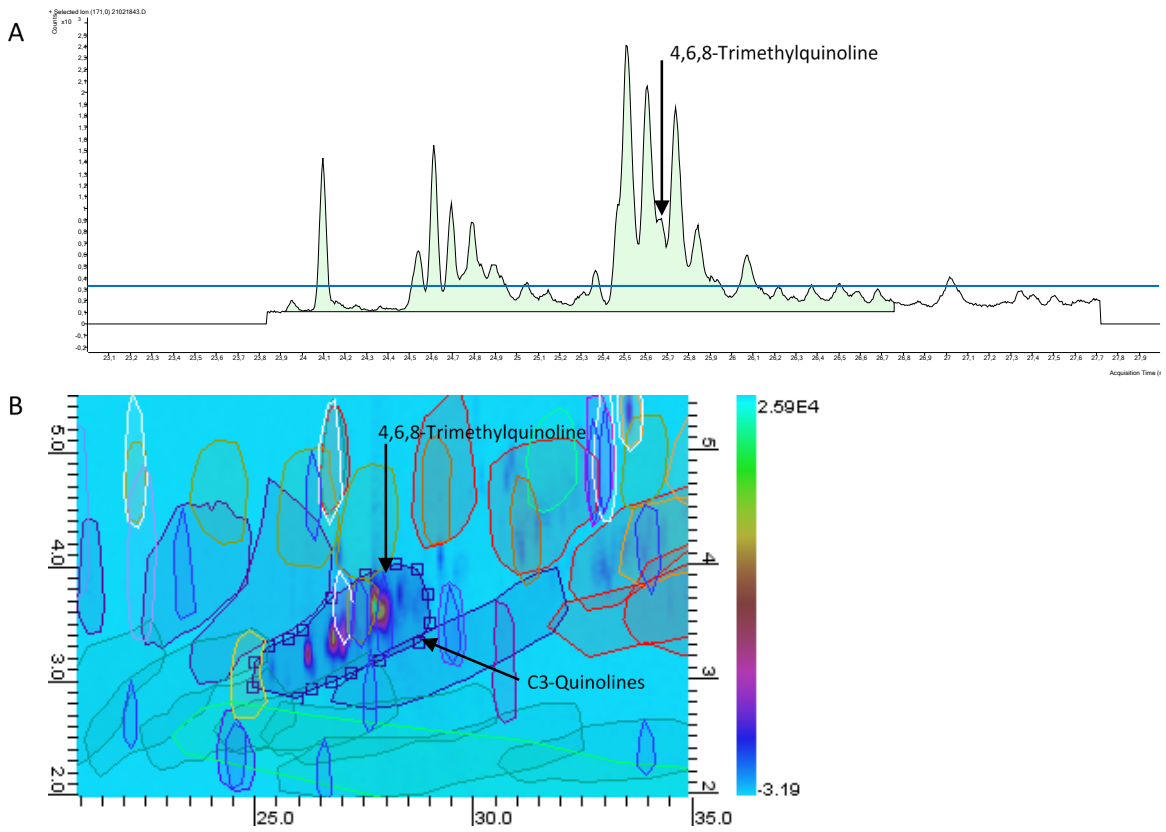
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.57: A: SIC at *m/z* 157 for C2-quinolines (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-quinolines extracted at high resolution of 157.0891±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.58: A: SIC at *m/z* 171 for C3-quinolines (green area) with the standard 4,6,8-trimethylquinoline shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C3-quinolines and the standard 4,6,8-trimethylquinoline extracted at high resolution of 171.1048±0.0500

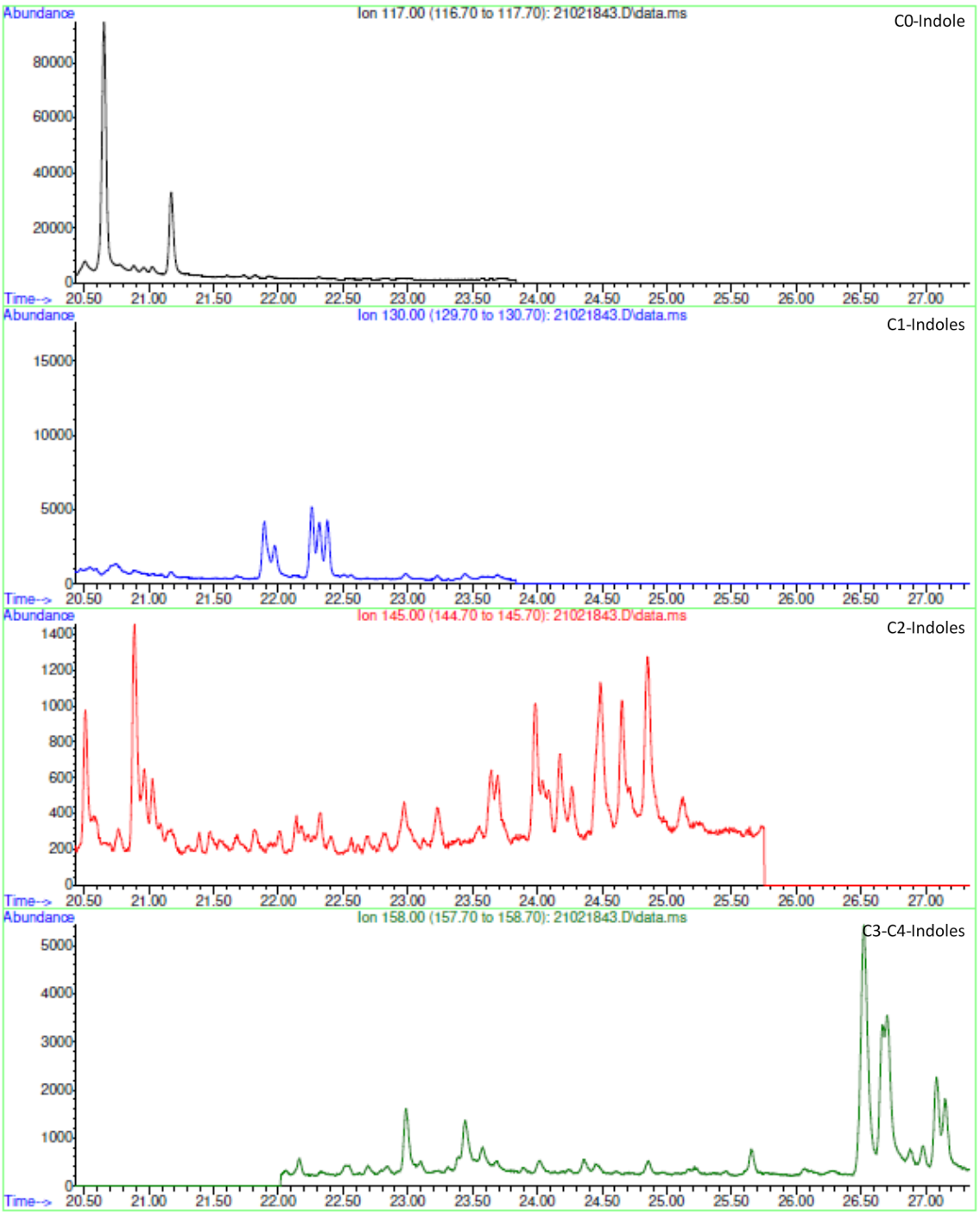


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Indoles

The definition of indole constituent groups was based on relative retention behaviour, standards available for C0-, C1-, C2-, and C4-indoles, and available GC×GC data. Articles have not been found for the indole constituent groups. The C3- and C4-indoles were not definable due to too low amount in the sample to set up group quantification. Below is shown relative retention behaviour for C0-C4-indoles (Figure B.59) and detailed chromatograms and GC×GC data of the constituent groups C1-indoles (Figure B.60) and C2-indoles (Figure B.61).

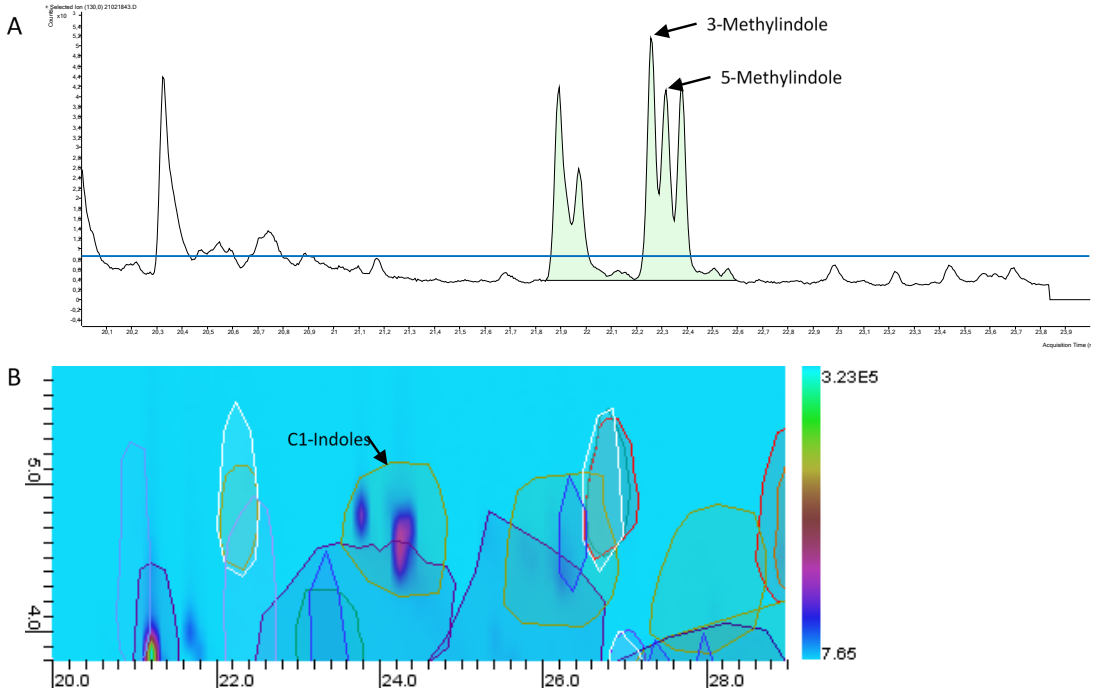
Figure B.59: Relative retention behaviour for C0-C4-indoles illustrated by SICs at *m/z* 117, 130, 145, and 158. C1-hydroxynaphthalenes are visible in the SIC for C3-C4-indoles



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

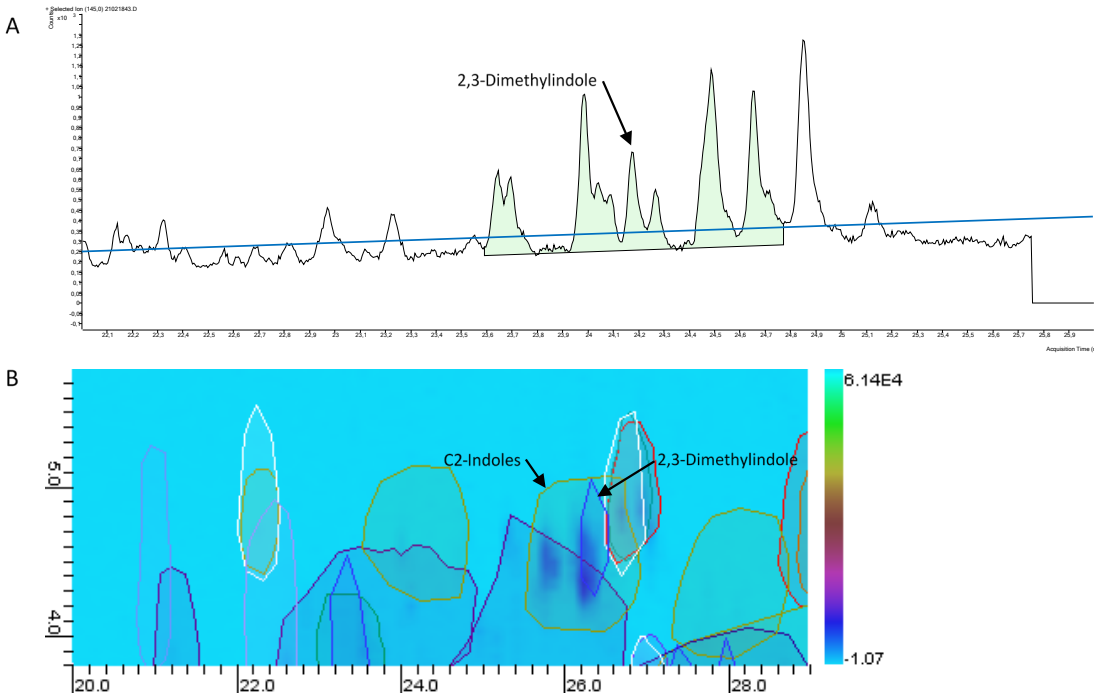
Figure B.60: A: SIC at *m/z* 130 for C1-indoles (green area) with the standards 3-methylindole and 5-methylindole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-indoles extracted at high resolution of 130.0735±0.0500.

The standards 3-methylindole and 5-methylindole co-elute in GC×GC and are therefore not defined



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.61: A: SIC at *m/z* 145 for C2-indoles (green area) with the standard 2,3-dimethylindole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-indoles and the standard 2,3-dimethylindole extracted at high resolution of 145.0891±0.0500

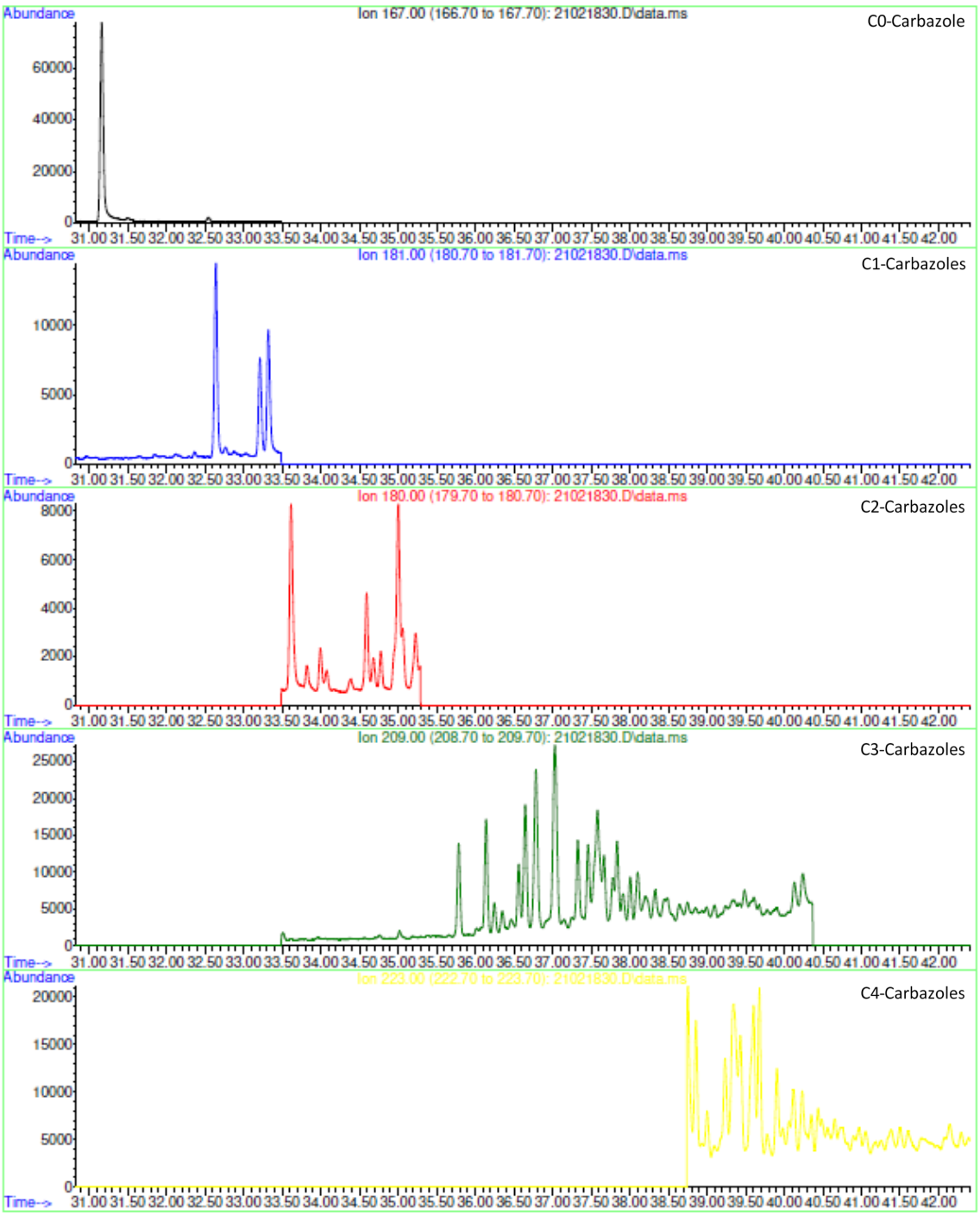


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Carbazoles

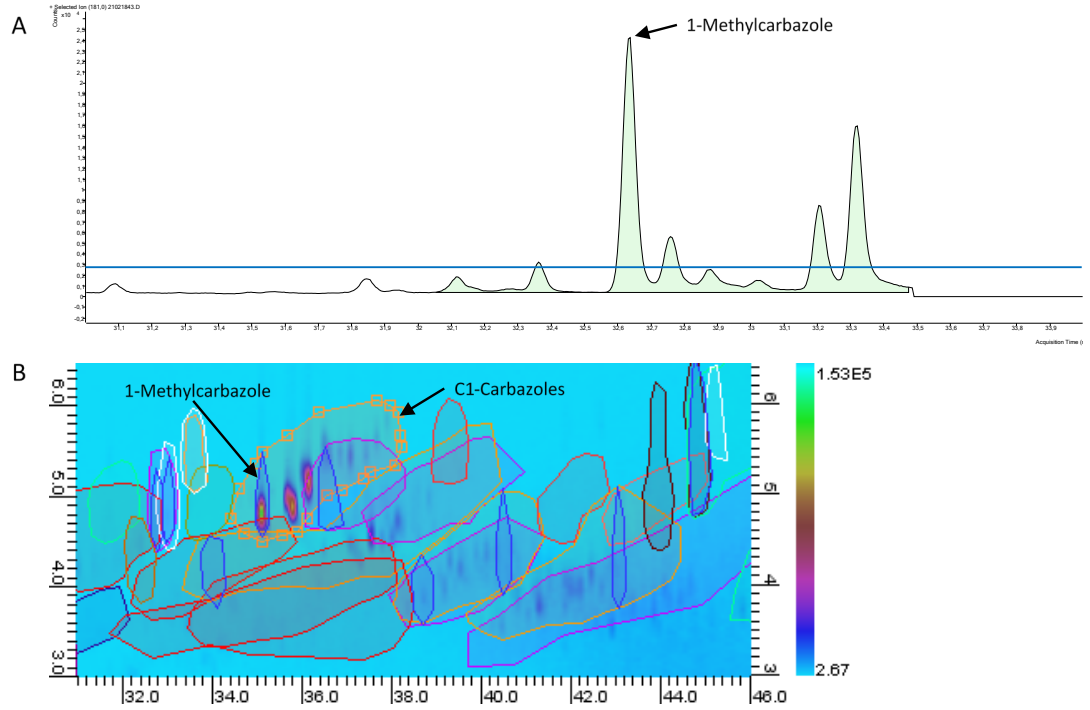
The carbazole constituent groups were defined based on relative retention behaviour, one article [25], standards available for C0-, C1-, C3-, and C4-carbazoles, and available GC×GC data. Below is shown the relative retention behaviour for C0-C4-carbazoles (Figure B.62) and detailed chromatograms and GC×GC data of the constituent groups C1-carbazoles (Figure B.63), C2-carbazoles (Figure B.64), C3-carbazoles (Figure B.65), and C4-carbazoles (Figure B.66). The C1-, C2-, and C4-carbazole constituent groups are not fully covered by the GC-MS/SIM method.

Figure B.62: Relaive retention behaviour for C0-C4 carbazoles illustrated by SICs at *m/z* 167, 181, 180, 209, 223



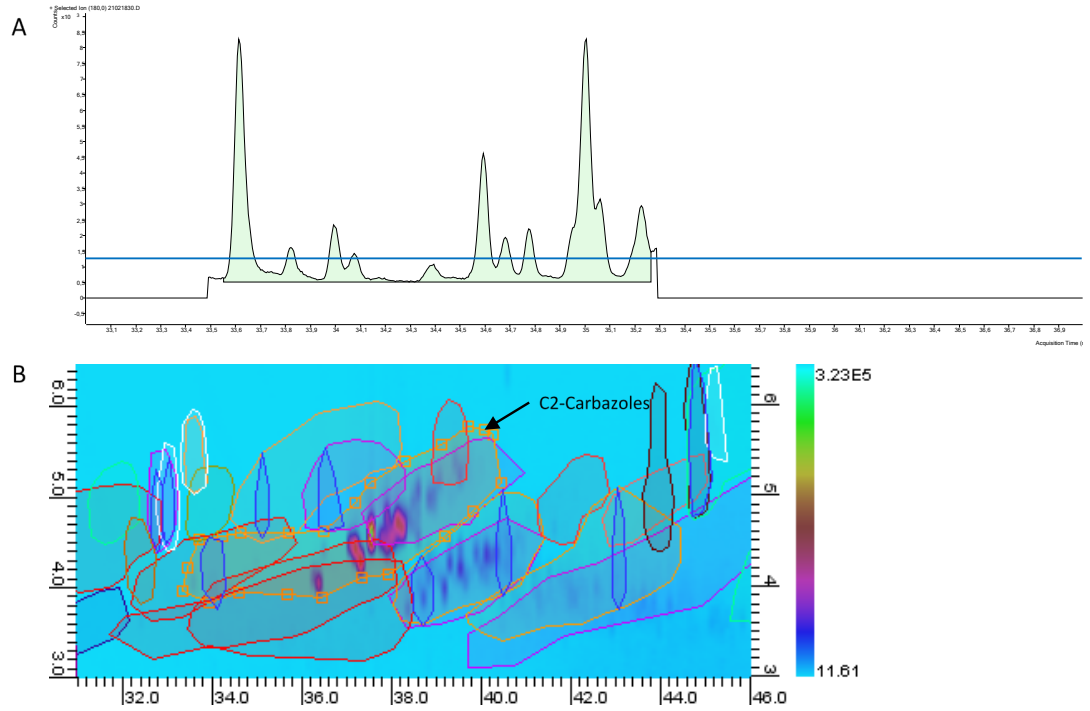
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.63: A: SIC at *m/z* 181 for C1-carbazoles (green area) with the standard 1-methylcarbazole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-carbazoles and the standard 1-methylcarbazole extracted at high resolution of 181.0891±0.0500



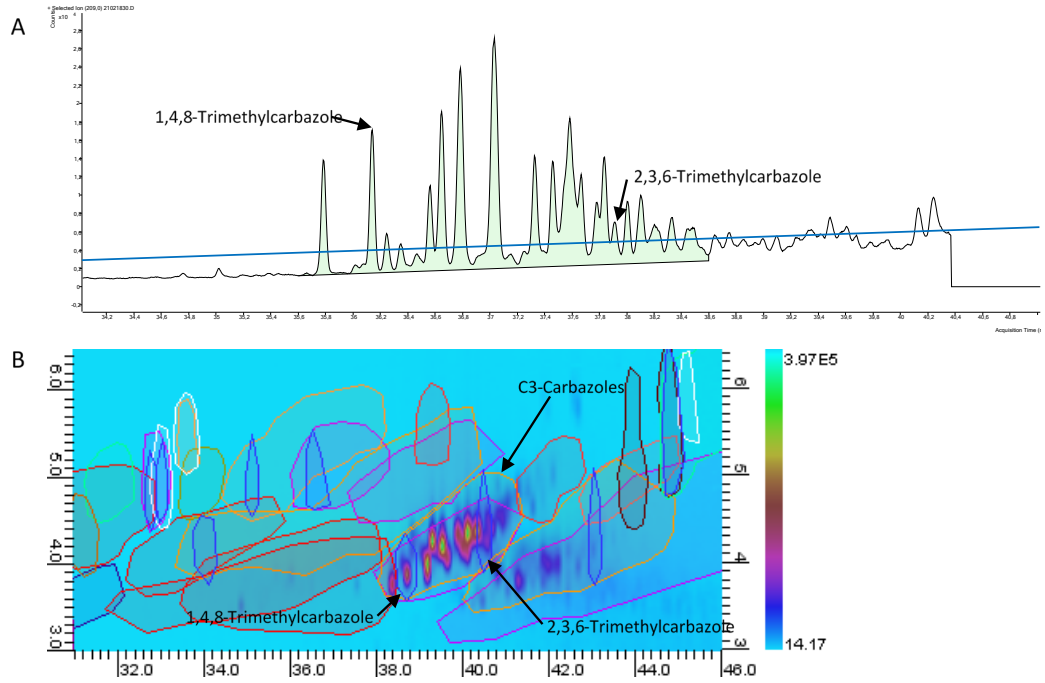
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.64: A: SIC at *m/z* 180 for C2-carbazoles (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-carbazoles extracted at high resolution of 195.1048±0.0500



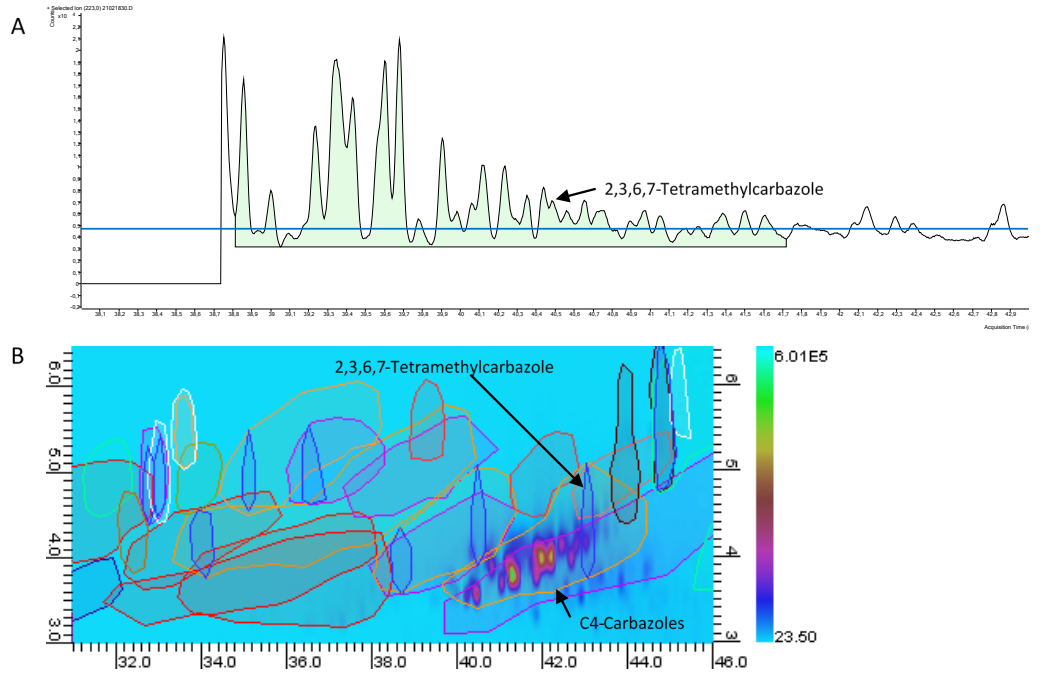
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.65: A: SIC at *m/z* 209 for C3-carbazoles (green area) with the standards 1,4,8-trimethylcarbazole and 2,3,6-trimethylcarbazole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C3-carbazoles and the standards 1,4,8-trimethylcarbazole and 2,3,6-trimethylcarbazole extracted at high resolution of 209.1204±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.66: A: SIC at *m/z* 223 for C4-carbazoles (green area) with the standard 2,3,6,7-tetramethylcarbazole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C4-carbazoles and the standard 2,3,6,7-tetra methylcarbazole extracted at high resolution of 223.1361±0.0500

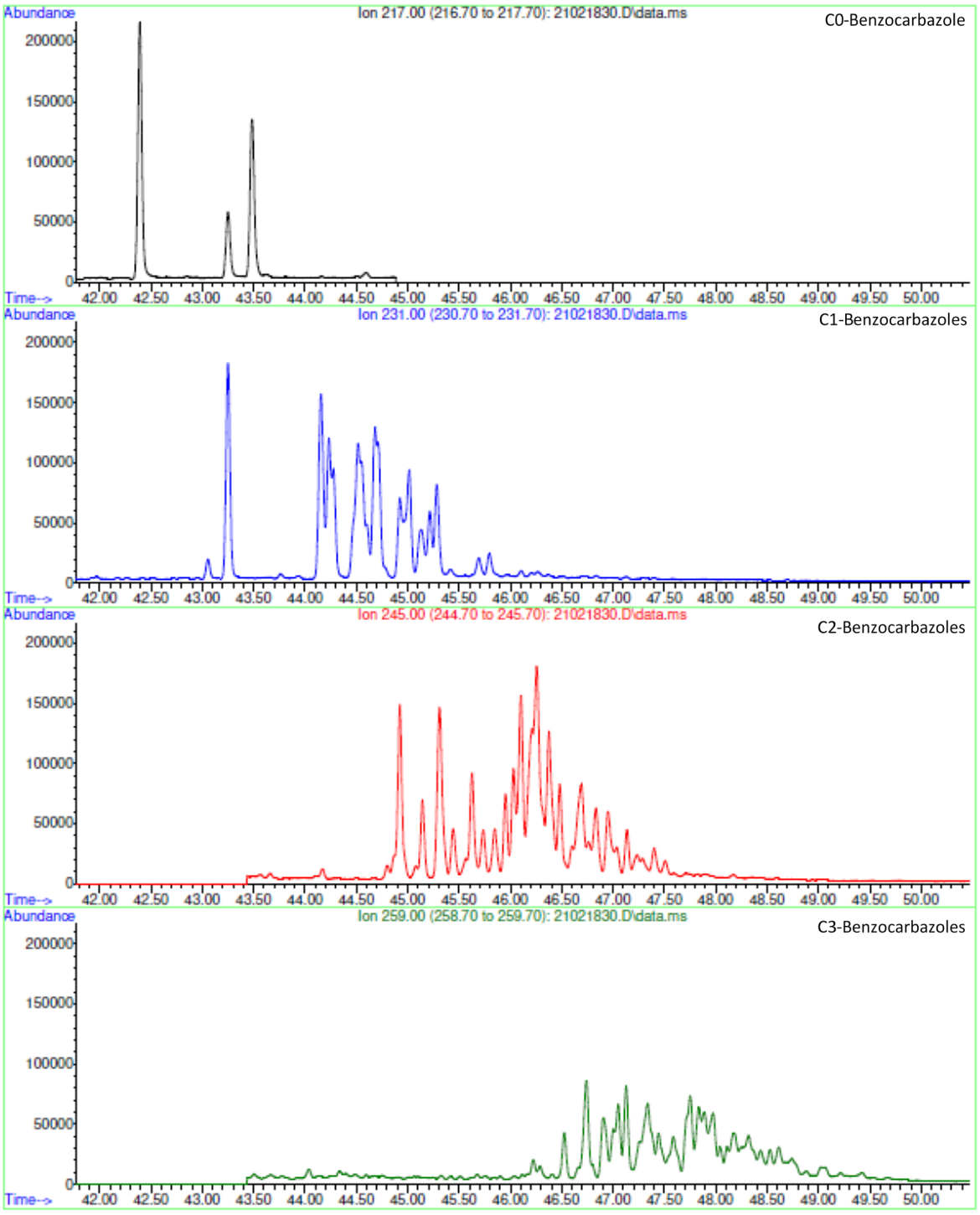


Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Benzocarbazoles

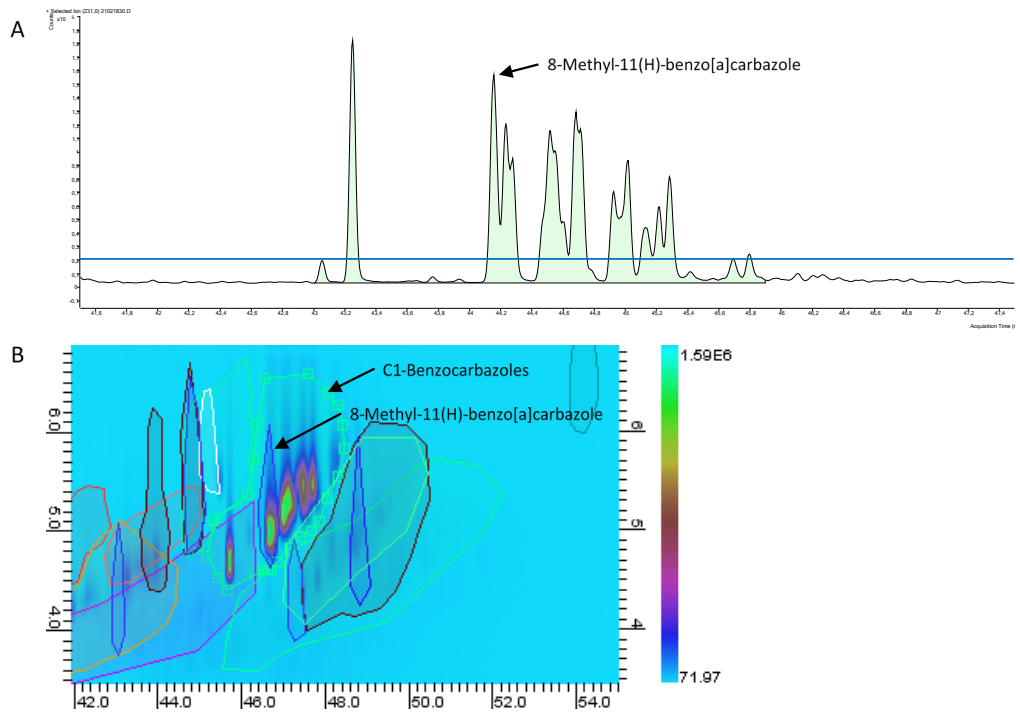
Benzocarbazole constituent groups were defined based on relative retention behaviour, one article [25], standards for C0-, C1- and C3-benzocarbazoles, and available GC×GC data. Below are relative retention behaviour for C0-C3-benzocarbazoles (Figure B.67) and detailed chromatograms and GC×GC data of the constituent groups C1-benzocarbazoles (Figure B.68), C2-benzocarbazoles (Figure B.69), and C3-benzocarbazoles (Figure B.70).

Figure B.67: Relative retention behaviour for C0-C3-benzocarbazoles illustrated by SICs at *m/z* 217, 231, 245, and 259



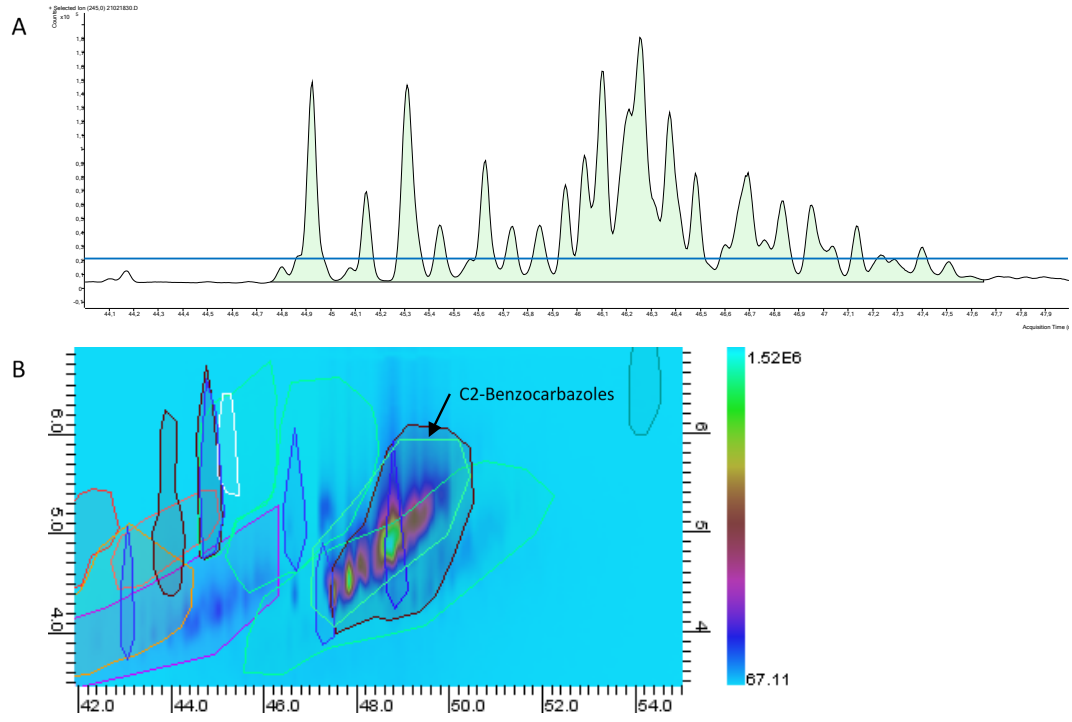
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.68: A: SIC at *m/z* 231 for C1-benzocarbazoles (green area) with the standard 8-methyl-11(H)-benzo[a]carbazole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C1-benzocarbazoles and the standard 8-methyl-11(H)-benzo[a]carbazole extracted at high resolution of 231.1048±0.0500



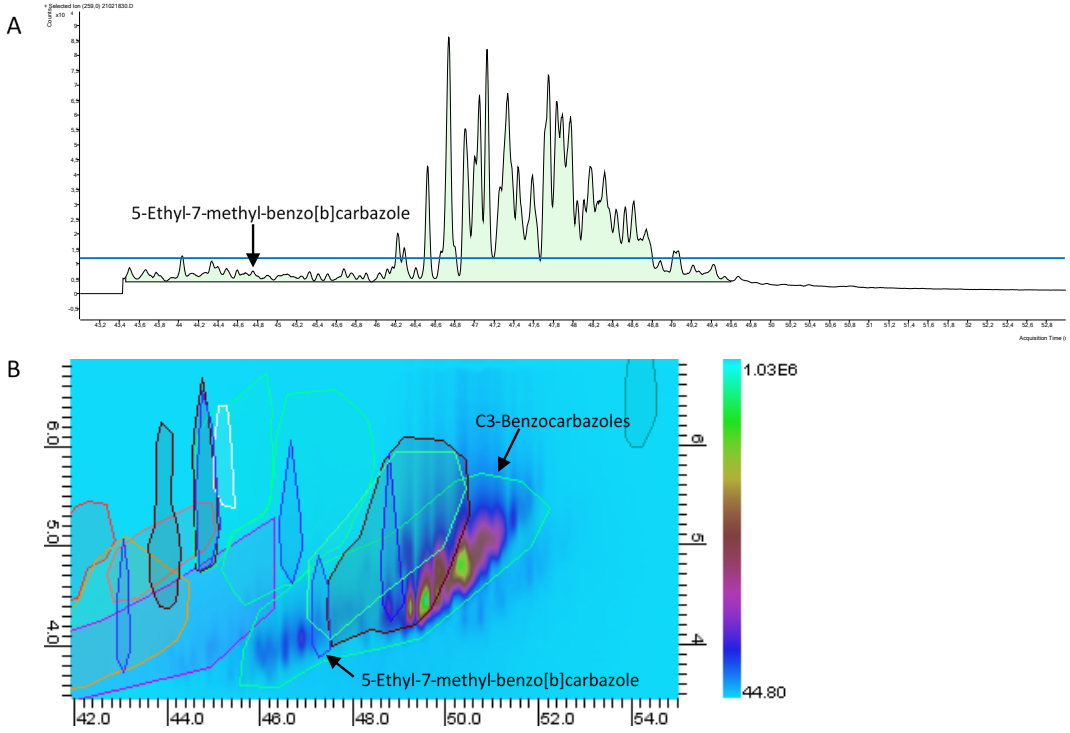
Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.69: A: SIC at *m/z* 245 for C2-benzocarbazoles (green area). The blue line indicates the threshold for determining the IAF. B: GC×GC image of C2-benzocarbazoles extracted at high resolution of 245.1204±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure B.70: A: SIC at *m/z* 259 for C3-benzocarbazoles (green area) with the standard 5-ethyl-7-methyl-benzo[b]carbazole shown. The blue line indicates the threshold for determining the IAF. B: GC×GC image of C3-benzocarbazoles and the standard 5-ethyl-7-methyl-benzo[b]carbazole extracted at high resolution of 259.1361±0.0500



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Alkylcyclohexanes

Alkylcyclohexane constituent groups were not defined as the regions were too populated and there was no distinct relative retention behaviour to identify the constituent groups. Standard is only available for C4-cyclohexanes and there was no GC×GC data available. Articles have not been searched for these constituent groups.

Alkylbenzenes

Alkylbenzene constituent groups were not defined as the regions were too populated and there was no distinct relative retention behaviour to identify the constituent groups Standard are available for C4- and C6-benzenes, and there was no GC×GC data available. Articles have not been searched for these constituent groups.

Adamantanes

Definition of adamantane constituent groups was not possible due to the regions being too populated and there was no distinct relative retention behaviour to identify the adamantane constituent groups. Standards are available for C0- and C2-adamantanes, one article was found [26] and GC×GC data was not available.

Tetralins

Tetralin constituent groups were not defined due to too populated regions and no relative retention behaviour to identify the tetralin constituent groups. Standards are available for C0- and C4-tetralin, and no GC×GC data was available. Articles have not been searched for these constituent groups.

Benzonaphthothiophenes

Definition of benzonaphthothiophene constituent groups was not possible due to too low amount in the samples and relative retention behaviour was not visible. One article was found [27] and one standard for C1-benzonaphthothiophenes is available. GC×GC data was not available.

Benzonitriles

Benzonitriles were not defined due to limited relative retention behaviour and limited GC×GC data. Standard is only available for C0-benzonitrile. Articles have not been searched for these constituent groups.

Benzofurans

Benzofurans were not defined due to limited relative retention behaviour and low concentrations for the constituent groups. Standards are available for C0-, C1- and C4-benzofuran while GC×GC data was only available for C1- and C4-benzofurans. Articles have not been searched for these constituent groups.

Hydroxyfluorenes

The definition of hydroxyfluorenes was not possible due to too low concentrations in the samples, limited relative retention behaviour and no available GC×GC data. Standard is only available for C0-hydroxyfluorene. C1-C3-hydroxyfluorenes are possibly not fully covered by the GC-MS/SIM method. Articles have not been searched for these constituent groups.

Acridines/Benzoquinolines

Acridines/Benzoquinolines constituent groups were not possible to define due to too low concentrations in the samples, limited relative retention behaviour, and limited GC×GC data. Standard is available for C0- and C1-acridines and C0-benzoquinoline. Articles have not been searched for these constituent groups.

Benzoacridines/ Dibenzoquinolines

Benzoacridines/dibenzoquinolines were not defines as the regions were too populated to identify the constituent groups. There was limited relative retention behaviour and GC×GC data. Standard is available for C0-benzoacridine, C0-dibenzoquinoline and C2-benzoacridines. C1-benzoacridines/dibenzoquinolines is possibly not covered completely by the GC-MS/SIM method. Articles have not been searched for these constituent groups.

B.8 Quantifier/qualifier ions for GC-MS/SIM

A suggestion for use of quantifier and qualifier ions for GC-MS/SIM analysis is presented in Table B.8 for target constituents and Table B.9 constituent groups. The suggestions are based on fragmentation patterns from the NIST MS library (version 2.3) or the quantifier/qualifier ions listed for the GC×GC-HRMS method. For some constituents and constituent groups, this data was not available.

Table B.8: GC-MS/SIM quantifier and qualifier ions for target constituents

Chemical class	Constituent	Quantifier ion (Da)	Qualifier ion (Da)
Saturate	1,3-Dimethyladamantane	149	93
Saturate	1-Methyldecalin	152	137
Saturate	2-Isopropyldecalin	180	
Saturate	Adamantane	136	93
Saturate	Butylcyclohexane	55	83
Aromatic	1,3,6-Trimethylchrysene	270	
Aromatic	1-Methylfluorene	180	165
Aromatic	1-Methylnaphthalene	142	115
Aromatic	1-Methylpyrene	216	215
Aromatic	1-Phenylheptane	105	92
Aromatic	1-Phenylnonane	105	92
Aromatic	1-Phenyloctane	105	92
Aromatic	2,2,5,7-Tetramethyltetralin	131	
Aromatic	2,6-Dimethylnaphthalene	156	141
Aromatic	2-Methylnaphthalene	142	115
Aromatic	2-Methylphenanthrene	192	191
Aromatic	3,3',5,5'-Tetramethylbiphenyl	210	195
Aromatic	3,3'-Dimethylbiphenyl	182	167
Aromatic	4-Methylchrysene	242	120
Aromatic	4-n-Pentylbiphenyl	167	
Aromatic	6-Ethylchrysene	256	241
Aromatic	Acenaphthene	154	153
Aromatic	Acenaphthylene	152	153
Aromatic	Anthracene	178	176
Aromatic	Benzo[a]anthracene	228	226
Aromatic	Benzo[a]pyrene	252	250
Aromatic	Benzo[b]fluoranthene	252	250
Aromatic	Benzo[e]pyrene	252	250
Aromatic	Benzo[g,h,i]perylene	276	138
Aromatic	Benzo[k]fluoranthene	252	250
Aromatic	Biphenyl	154	153
Aromatic	Butylbenzene	105	92
Aromatic	Chrysene	228	226

Chemical class	Constituent	Quantifier ion (Da)	Qualifier ion (Da)
Aromatic	Dibenzo[a,h]anthracene	278	279
Aromatic	Fluoranthene	202	200
Aromatic	Fluorene	166	165
Aromatic	Hexylbenzene	105	92
Aromatic	Indeno[1,2,3-c,d]pyrene	276	138
Aromatic	Naphthalene	128	129
Aromatic	Perylene	252	126
Aromatic	Phenanthrene	178	176
Aromatic	Pyrene	202	200
Aromatic	Tetralin	132	104
SPAC	1-Benzothiophene	134	89
SPAC	2-Methylbenzothiophene	148	147
SPAC	2,3,4-Trimethylbenzothiophene	176	161
SPAC	3-Methylbenzothiophene	148	147
SPAC	4,6-Dimethyldibenzothiophene	212	211
SPAC	4-Ethyl-6-methyldibenzothiophene	226	
SPAC	4-Methyldibenzothiophene	198	197
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	248	247
SPAC	Dibenzothiophene	184	139
OPAC	2,3-Benzofuran	118	89
OPAC	2-Hydroxynaphthalene	144	115
OPAC	2-Methyldibenzofuran	182	152
OPAC	2-n-Butylbenzofuran	131	174
OPAC	3,5-Dimethylphenol	122	107
OPAC	3-Methylbenzofuran	131	132
OPAC	4-Hexylphenol	107	178
OPAC	4-Nonylphenol	107	220
OPAC	4-tert-Butylphenol	135	150
OPAC	9-Hydroxyfluorene	182	152
OPAC	9-Hydroxyphenanthrene	194	165
OPAC	Dibenzofuran	168	139
OPAC	Naphthaldehyde	156	127
OPAC	o-Cresol	108	79
OPAC	Phenol	94	66
NPAC	1,4,8-Trimethylcarbazole	209	194
NPAC	11H-Benzo[a]carbazole	217	109
NPAC	1-Methylcarbazole	181	180
NPAC	1-Methylisoquinoline	143	115
NPAC	2,3,6,7-Tetramethylcarbazole	223	208
NPAC	2,3,6-Trimethylcarbazole	209	194

Chemical class	Constituent	Quantifier ion (Da)	Qualifier ion (Da)
NPAC	2,3-Dimethylindole	145	144
NPAC	2-tert-Butyl-1H-indole	158	173
NPAC	3-Methylindole	130	131
NPAC	4,6,8-Trimethylquinoline	171	156
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	259	244
NPAC	5-Methylindole	130	131
NPAC	8,10-Dimethyl-Benzo[a]acridine	257	242
NPAC	8-Methyl-11(H)-benzo[a]carbazole	231	202
NPAC	9-Methylacridine	193	192
NPAC	Acridine	179	151
NPAC	Benzo[c]acridine	229	200
NPAC	Benzo[h]quinoline	179	151
NPAC	Benzonitrile	103	76
NPAC	Carbazole	167	139
NPAC	Dibenzo[a,]acridine	279	139
NPAC	Dibenzo[f,h]quinoline	229	114
NPAC	Indole	117	89
NPAC	Quinoline	129	102
IS	Acenaphthene-d10	164	162
IS	Acenaphthylene-d8	160	
IS	Acridine-d9	188	186
IS	Adamantane-d16	152	
IS	Anthracene-d10	188	184
IS	Benzo[a]anthracene-d12	240	
IS	Benzo[a]pyrene-d12	264	
IS	Benzo[g,h,i]perylene-d12	288	
IS	Benzo[k]fluoranthene-d12	264	
IS	Biphenyl-d10	164	
IS	Carbazole-d8	175	146
IS	Chrysene-d12	240	236
IS	Dibenzofuran-d8	176	146
IS	Dibenzothiophene-d8	192	
IS	Fluoranthene-d10	212	
IS	Fluorene-d10	176	
IS	Indeno[1,2,3-c,d]pyrene-d12	288	
IS	Indole-d7	123	95
IS	Naphthalene-d8	136	134
IS	n-Butylbenzene-d14	98	
IS	n-Nonylbenzene-2,3,4,5,6-d5	209	
IS	Phenanthrene-d10	188	184

Chemical class	Constituent	Quantifier ion (Da)	Qualifier ion (Da)
IS	Phenol-d6	99	71
IS	Pyrene-d10	212	

Table B.9: GC-MS/SIM quantifier and qualifier ions for constituent groups

Chemical class	Constituent group	Quantifier ion (Da)	Qualifier ion (Da)
Saturate	C1-De	152	137
Saturate	C2-De	166	
Saturate	C3-De	180	
Aromatic	C1-N	142	115
Aromatic	C2-N	156	141
Aromatic	C3-N	170	155
Aromatic	C4-N	184	141
Aromatic	C1-BP	168	167
Aromatic	C2-BP	182	167
Aromatic	C1-F	180	165
Aromatic	C2-F	194	179
Aromatic	C3-F	208	165
Aromatic	C1-Phen/An	192	191
Aromatic	C2-Phen/An	206	191
Aromatic	C3-Phen/An	220	189
Aromatic	C4-Phen/An	234	189
Aromatic	C1-Flu/Py	216	215
Aromatic	C2-Flu/Py	230	215
Aromatic	C3-Flu/Py	244	
Aromatic	C1-Ch	242	120
Aromatic	C2-Ch	256	241
Aromatic	C3-Ch	270	
SPAC	C1-BT	148	147
SPAC	C2-BT	162	147
SPAC	C3-BT	176	147, 161
SPAC	C4-BT	190	
SPAC	C1-DBT	198	197
SPAC	C2-DBT	212	211
SPAC	C3-DBT	226	
SPAC	C4-DBT	240	
OPAC	C1-P	108	79
OPAC	C2-P	122	107
OPAC	C3-P	136	121
OPAC	C4-C5-P	135	150

Chemical class	Constituent group	Quantifier ion (Da)	Qualifier ion (Da)
OPAC	C1-DBF	182	152
OPAC	C1-HN	158	129
OPAC	C2-HN	172	157
OPAC	C3-HN	186	171
OPAC	C4-HN	200	185
OPAC	C1-HPhen	208	209
OPAC	C2-HPhen	222	223
NPAC	C1-Q	143	115
NPAC	C2-Q	157	115
NPAC	C3-Q	171	156
NPAC	C1-I	130	131
NPAC	C2-I	145	144
NPAC	C1-C	181	180
NPAC	C2-C	180	195
NPAC	C3-C	209	194
NPAC	C4-C	223	208
NPAC	C1-BC	231	202
NPAC	C2-BC	245	
NPAC	C3-BC	259	244

B.9 GC-MS/SIM: Constituent group parameters

Abbreviation, choice of standard, isomer abundance factor (IAF), DL, LOQ, and QC precision for each constituent group analysed by GC-MS/SIM is given in Table B.10.

Table B.10: Abbreviation, available standard, IAF, DL, LOQ, and QC precision for the constituent groups analysed by GC-MS/SIM

Chemical class	Abreviation	Constituent group	Standard	IAF	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
Saturate	C1-De	C1-Decalins	1-Methyldecalin	2	215	36	N/A
Saturate	C2-De	C2-Decalins	1-Methyldecalin	13	145	242	5
Saturate	C2-De	C3-Decalins	2-Isopropyldecalin	35	102	416	5
Aromatic	C1-N	C1-Naphthalenes	Average of 2-methylnaphthalene and 1-methylnaphthalene	2	3.6	5.1	0
Aromatic	C2-N	C2-Naphthalenes	2,6-Dimethylnaphthalene	7	59	67	1
Aromatic	C3-N	C3-Naphthalenes	2,6-Dimethylnaphthalene	12	32	47	1
Aromatic	C4-N	C4-Naphthalenes	2,6-Dimethylnaphthalene	21	24	50	1
Aromatic	C1-BP	C1-Biphenyls	3,3'-Dimethylbiphenyl	2	2.2	5.5	1
Aromatic	C2-BP	C2-Biphenyls	3,3'-Dimethylbiphenyl	12	9.8	27	1
Aromatic	C1-F	C1-Fluorenes	1-Methylfluorene	5	7.1	17	1
Aromatic	C2-F	C2-Fluorenes	1-Methylfluorene	12	20	42	3
Aromatic	C3-F	C3-Fluorenes	1-Methylfluorene	12	21	43	1

Chemical class	Abreviation	Constituent group	Standard	IAF	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
Aromatic	C1- Phen/An	C1-Phenanthrenes/Anthracenes	2-Methylphenanthrene	5	6.3	18	1
Aromatic	C2- Phen/An	C2-Phenanthrenes/Anthracenes	2-Methylphenanthrene	14	17	48	1
Aromatic	C3- Phen/An	C3-Phenanthrenes/Anthracenes	2-Methylphenanthrene	19	14	57	1
Aromatic	C4-Phen/An	C4-Phenanthrenes/Anthracenes	2-Methylphenanthrene	26	20	79	2
Aromatic	C1-Flu/Py	C1-Fluoranthenes/Pyrenes	1-Methylpyrene	9	7.1	27	1
Aromatic	C2-Flu/Py	C2-Fluoranthenes/Pyrenes	1-Methylpyrene	18	13	54	2
Aromatic	C3-Flu/Py	C3-Fluoranthenes/Pyrenes	1-Methylpyrene	23	17	69	2
Aromatic	C1-Ch	C1-Chrysenes	4-Methylchrysene	7	3.5	14	2
Aromatic	C2-Ch	C2-Chrysenes	6-Ethylchrysene	11	8.7	36	1
Aromatic	C3-Ch	C3-Chrysenes	1,3,6-Trimethylchrysene	22	17	71	2
SPAC	C1-BT	C1-Benzothiophenes	Average of 3-methylbenzothiophene and 2- methylbenzothiophene	4	8.3	14	1
SPAC	C2-BT	C2-Benzothiophenes	3-Methylbenzothiophene	10	13	28	1
SPAC	C3-BT	C3-Benzothiophenes	2,3,4-Trimethylbenzothiophene	13	57	135	1
SPAC	C4-BT	C4-Benzothiophenes	2,3,4-Trimethylbenzothiophene	19	44	157	1
SPAC	C1-DBT	C1-Dibenzothiophenes	4-Methyldibenzothiophene	4	5.2	12	3
SPAC	C2-DBT	C2-Dibenzothiophenes	4,6-Dimethyldibenzothiophene	11	15	60	2
SPAC	C3-DBT	C3-Dibenzothiophenes	4-Ethyl-6-methyldibenzothiophene	27	43	171	4
SPAC	C4-DBT	C4-Dibenzothiophenes	4-Ethyl-6-methyldibenzothiophene	21	32	132	6
OPAC	C1-P	C1-Phenols	o-Cresol	3	89	2835	4
OPAC	C2-P	C2-Phenols	3,5-Dimethylphenol	7	497	3841	5
OPAC	C3-P	C3-Phenols	3,5-Dimethylphenol	9	43	319	4
OPAC	C4-C5-P	C4-C5-Phenols	4-tert-Butylphenol	30	212	1593	5
OPAC	C1-DBF	C1-Dibenzofurans	2-Methyldibenzofuran	5	5.3	14	7
OPAC	C1-HN	C1-Hydroxynaphthalenes	2-Hydroxynaphthalene	6	16	142	4
OPAC	C2-HN	C2-Hydroxynaphthalenes	2-Hydroxynaphthalene	16	37	322	3
OPAC	C3-HN	C3-Hydroxynaphthalenes	2-Hydroxynaphthalene	19	125	1158	5
OPAC	C4-HN	C4-Hydroxynaphthalenes	2-Hydroxynaphthalene	33	83	729	5
OPAC	C1-HPhen	C1-Hydroxyphenanthrenes	9-Hydroxyphenanthrene	11	9.7	35	11
OPAC	C2-HPhen	C2-Hydroxyphenanthrenes	9-Hydroxyphenanthrene	24	36	146	7
NPAC	C1-Q	C1-Quinolines	1-Methylisoquinoline	8	110	1500	20
NPAC	C2-Q	C2-Quinolines	1-Methylisoquinoline	13	89	1201	14
NPAC	C3-Q	C3-Quinolines	4,6,8-Trimethylquinoline	19	77	1069	12
NPAC	C1-I	C1-Indoles	Average of 3-methylindole and 5-methylindole	5	56	879	7
NPAC	C2-I	C2-Indoles	2,3-Dimethylindole	11	73	310	2
NPAC	C1-C	C1-Carbazoles	1-Methylcarbazole	5	8.1	53	3
NPAC	C2-C	C2-Carbazoles	1-Methylcarbazole	10	16	106	8
NPAC	C3-C	C3-Carbazoles	Average of 1,4,8-trimethylcarbazole and 2,3,6-trimethylcarbazole	21	16	49	N/A
NPAC	C4-C	C4-Carbazoles	2,3,6,7-Tetramethylcarbazole	30	52	358	N/A
NPAC	C1-BC	C1-Benzocarbazoles	8-Methyl-11(H)-benzo[a]carbazole	16	14	53	8
NPAC	C2-BC	C2-Benzocarbazoles	8-Methyl-11(H)-benzo[a]carbazole	25	23	83	6
NPAC	C3-BC	C3-Benzocarbazoles	5-Ethyl-7-methyl-benzo[b]carbazole	32	49	310	N/A

B.10 GC×GC-HRMS: Constituent group parameters

The choice of calibration standard, IAF, DL, LOQ, and QC precision for OPAC and NPAC constituent groups analysed by GCxGC-HRMS are liste in Table B.11.

Table B.11: Abbreviation, available standard, IAF, DL, LOQ, and QC precision for the constituent groups analysed by GCxGC-HRMS

Chemical class	Abreviation	Constituent group	Standard	IAF	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
OPAC	C1-P	C1-Phenols	o-Cresol	3	28	51	7.8
OPAC	C2-P	C2-Phenols	3,5-Dimethylphenol	7	52	142	2.7
OPAC	C3-P	C3-Phenols	3,5-Dimethylphenol	9	57	173	7.5
OPAC	C4-P	C4-Phenols	4-tert-Butylphenol	6	79	171	4.9
OPAC	C5-P	C5-Phenols	4-tert-Butylphenol	6	75	168	7.0
OPAC	C6-P	C6-Phenols	4-Hexylphenol	12	21	70	N/A
OPAC	C7-P	C7-Phenols	4-Hexylphenol	12	20	70	N/A
OPAC	C8-P	C8-Phenols	2,4-Di-tert-butylphenol	8	21	71	N/A
OPAC	C9-P	C9-Phenols	4-Nonylphenol	7	18	51	N/A
OPAC	C1-BF	C1-Benzofurans	3-Methylbenzofuran	2	100	157	6.9
OPAC	C4-BF	C4-Benzofurans	2-n-Butylbenzofuran	2	2.6	9.4	N/A
OPAC	C1-DBF	C1-Dibenzofurans	2-Methyldibenzofuran	5	7.3	24	N/A
OPAC	C1-HN	C1-Hydroxynaphthalenes	2-Hydroxynaphthalene	6	108	324	N/A
OPAC	C2-HN	C2-Hydroxynaphthalenes	2-Hydroxynaphthalene	16	213	790	N/A
OPAC	C3-HN	C3-Hydroxynaphthalenes	2-Hydroxynaphthalene	19	236	921	N/A
OPAC	C4-HN	C4-Hydroxynaphthalenes	2-Hydroxynaphthalene	33	407	1598	N/A
OPAC	C5-HN	C5-Hydroxynaphthalenes	2-Hydroxynaphthalene	10	153	514	N/A
OPAC	C1-Hphen	C1-Hydroxyphenanthrenes	9-Hydroxyphenanthrene	11	240	888	N/A
OPAC	C2-Hphen	C2-Hydroxyphenanthrenes	9-Hydroxyphenanthrene	24	502	1915	N/A
NPAC	C1-BN	C1-Benzonitriles	Benzonitrile	3	17	51	7.3
NPAC	C2-BN	C2-Benzonitriles	Benzonitrile	6	27	94	3.2
NPAC	C3-BN	C3-Benzonitriles	Benzonitrile	1	7.3	19	3.1
NPAC	C1-Q	C1-Quinolines	1-Methylisoquinoline	8	37	121	1.1
NPAC	C2-Q	C2-Quinolines	1-Methylisoquinoline	13	57	195	10
NPAC	C3-Q	C3-Quinolines	4,6,8-Trimethylquinoline	19	22	80	3.8
NPAC	C4-Q	C4-Quinolines	4,6,8-Trimethylquinoline	9	11	38	5.9
NPAC	C1-I	C1-Indoles	Average of 3-methylindole and 5-methylindole (not separated in GC×GC)	5	37	139	22
NPAC	C2-I	C2-Indoles	2,3-Dimethylindole	11	13	48	16
NPAC	C3-I	C3-Indoles	2,3-Dimethylindole	4	4.8	18	5.9
NPAC	C4-I	C4-Indoles	2-tert-Butyl-1H-indole	5	9.0	25	24
NPAC	C1-Acr/BQ	C1-Acridines/Benzoquinolines	9-Methylacridine	19	104	407	N/A

Chemical class	Abreviation	Constituent group	Standard	IAF	DL (ng/mL)	LOQ (ng/mL)	QC precision (%)
NPAC	C2-Acr/BQ	C2-Acridines/Benzoquinolines	9-Methylacridine	4	21	85	N/A
NPAC	C3-Acr/BQ	C3-Acridines/Benzoquinolines	9-Methylacridine	10	62	222	N/A
NPAC	C4-Acr/BQ	C4-Acridines/Benzoquinolines	9-Methylacridine	27	142	572	N/A
NPAC	C1-C	C1-Carbazoles	1-Methylcarbazole	5	9.5	35	N/A
NPAC	C2-C	C2-Carbazoles	9-Ethylcarbazole	10	15	58	N/A
NPAC	C3-C	C3-Carbazoles	Average of 1,4,8-trimethylcarbazole and 2,3,6-trimethylcarbazole	21	119	471	N/A
NPAC	C4-C	C4-Carbazoles	2,3,6,7-Tetramethylcarbazole	3	28	114	N/A
NPAC	C1-BAcr	C1-Benzoacridines	Benzo[c]acridine	6	28	100	N/A
NPAC	C2-BAcr	C2-Benzoacridines	8,10-Dimethyl-Benzo[a]acridine	10	94	241	N/A
NPAC	C1-BC	C1-Benzocarbazoles	8-Methyl-11(H)-benzo[a]carbazole	16	27	108	N/A
NPAC	C2-BC	C2-Benzocarbazoles	8-Methyl-11(H)-benzo[a]carbazole	25	42	168	N/A
NPAC	C3-BC	C3-Benzocarbazoles	5-Ethyl-7-methyl-benzo[b]carbazole	32	60	239	N/A
NPAC	C1-BTZ	C1-Benzothiazoles	Indole	2	6.2	15	6.0
NPAC	C1-DPA	C1-Diphenylamines	2,3-Dimethylindole	1	1.4	4.7	7.3
NPAC	C3-THQ	C3-Tetrahydroquinolines	2-n-Butylbenzofuran	1	1.4	4.8	8.7

C Quantification of constituents in PetCo substances

A total of 24 PetCo samples were analysed by GC-MS/SIM, GC×GC-HRMS, and SFC-ESI-HRMS. Calibration curves were based on eight levels as previously described and the evaluation of whether analyte concentrations were above or below DL and LOQ, was performed based on the relative responses. It was not evaluated whether the analyte concentrations were within the calibration curve range, thus in some cases the calibration curve has been extrapolated. Furthermore, correction for recoveries of the constituents were not included in the data analysis. Thus, constituent concentrations in the products are conservative, and will likely be higher than reported here. Blank subtraction has been carried out for all platforms and all analytes.

C.1 Quality of analysis

C.1.1 GC-MS/SIM target constituents

The number of each chemical class quantified for each product type is given in Table C.1. Clearly most constituents were quantified in the coal tar and least in the asphalt.

Table C.1: Total number of quantified saturates, aromatics, SPACs, OPACs, and NPACs in asphalts, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil by GC-MS/SIM

The number in parentheses by the chemical class indicates the total number of constituents targeted of that class

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
Saturates (5)	0	5	1	2	0
Aromatics (38)	9	7	31	17	17
SPACs (9)	0	1	7	4	4
OPACs (15)	0	0	6	1	1
NPACs (24)	0	1	19	2	3
Total (91)	9	14	64	26	25

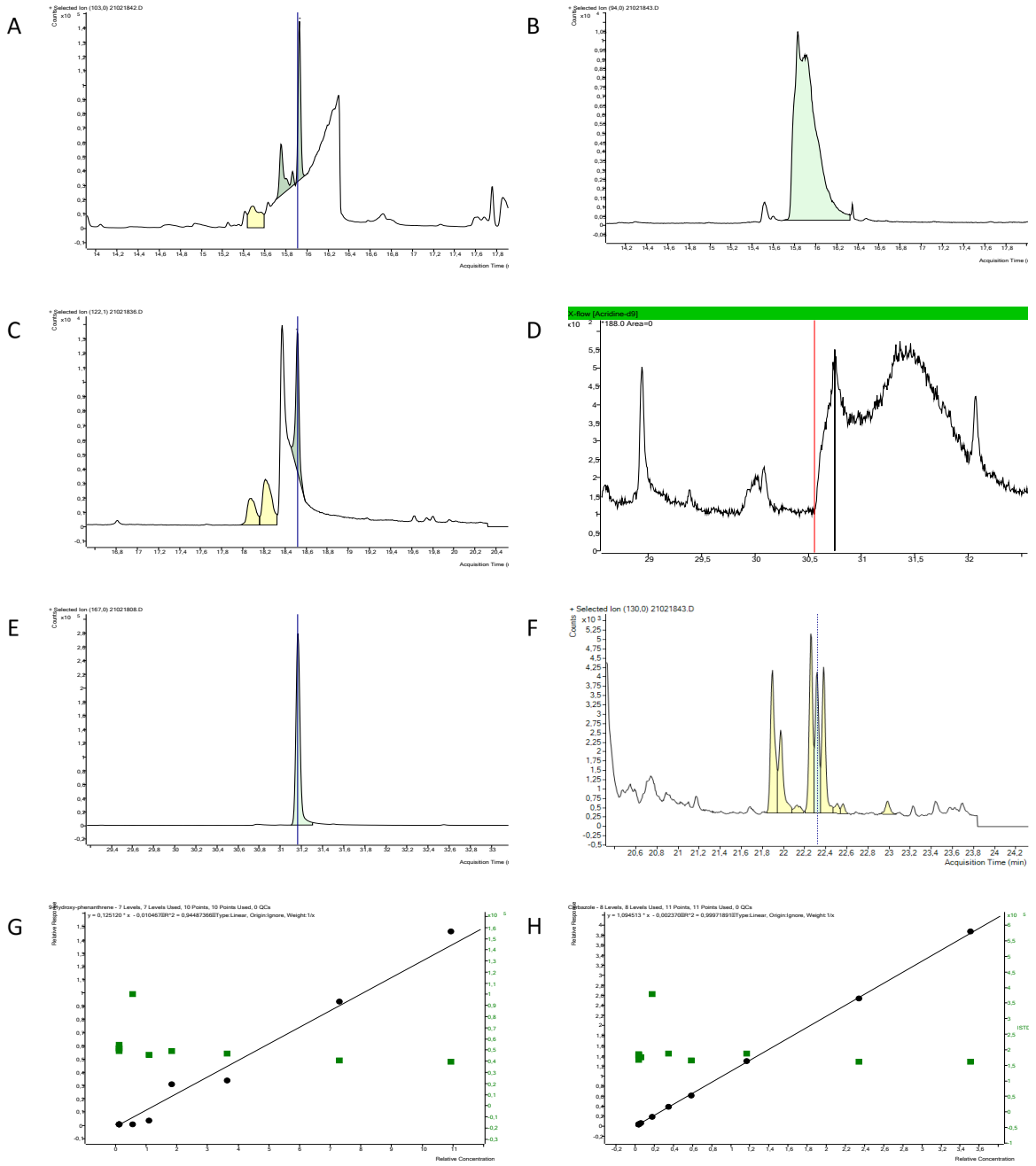
In the SAS fraction it should be noted that chrysene is well-known to co-elute with triphenylene using a ZB5 GC column and the concentrations are therefore the sum of chrysene and triphenylene. In one sample (CWP2), the area for the IS n-butylbenzene-d14 was substantially higher than for the other samples and co-elution with another constituent should be considered. This IS is used for butylcyclohexane, butylbenzene, and hexylbenzene. The area for the IS adamantane-d16 in one sample (CWP2) was slightly higher than for the other samples and co-elution with another constituent cannot be excluded, but it could also be due to instrument drift. Adamantane-d16 is used as IS for all saturates except butylcyclohexane. As the deviation in area for n-butylbenzene-d14 and adamantane-d16 was only seen in one sample (CWP2), it was decided not to change the IS for the mentioned constituents but instead the reported concentrations of saturates, butylbenzene and hexylbenzene should be taken with care in this sample.

It was clear from the ON data evaluation that not all internal standards were stable during the analysis and consequently only carbazole-d8 and dibenzofuran-d8 were used as internal

standards. Dibenzofuran-d8 was used as IS for all OPACs while carbazole-d8 was used as IS for all NPACs. The instability may have been caused by a combination of column deterioration and product type as the instability was most pronounced in some of the lubricating oils and that the inclusion of the AP mixture was not enough to counteract wear and tear of the GC system.

Quantification of 9-hydroxyphenanthrene was difficult as this constituent appeared to be positively affected by the matrix compared to the standards in AP solutions. The peak for 9-hydroxyphenanthrene in the standards was very broad and sometimes lost in the standards with low concentration. In contrast, the peak appeared to be well-behaved in the samples, i.e. it was narrow and separated from other constituents. It should also be noted that the peaks of benzonitrile, phenol, 2,3-benzofuran, o-cresol, 3-methylbenzofuran, dibenzofuran and 2-methyldibenzofuran split at high concentrations and the current AP mixture coelutes with phenol, benzonitrile and 2,3-benzofuran which requires that these constituents are manually integrated. More examples of the challenges with the analysis of ON constituents are given in Figure C.1.

Figure C.1: **A) Splitting of benzonitrile in high concentration standard, B) poor chromatography of phenol in a coal tar, C) 3,5-dimethylphenol in medium concentration standard, D) loss of acridine-d9 in a lubricating oil, E) carbazole peak in a coal tar, F) 5-methylindole in a coal tar, G) poor standard curve for 9-hydroxyphenanthrene, H) decent standard curve for carbazole**



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

C.1.2 GC×GC-HRMS target constituents

The number of each chemical class quantified in each product type by GC×GC-HRMS is listed in Table C.2. Coal tar and tyre pyrolysis oil were clearly the product types where most constituents were quantified.

Table C.2: Total number of quantified OPACs and NPACs in asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil by GC×GC-HRMS

The number in parentheses by the chemical class indicates the total number of targeted constituents of that class

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
OPACs (18)	0	2	12	2	15
NPACs (27)	1	0	23	2	16
Total (45)	1	2	35	4	31

C.1.3 SFC-ESI-HRMS target constituents

The number of each chemical class quantified in each product type by SFC-ESI-HRMS is listed in Table C.3. The highest number of quantified constituents was in coal tar (26 out of 47) while lubricating oil had the highest number of quantified acids (9 out of 16).

Table C.3: Total number of OPACs, NPACs and acids quantified in asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil by SFC-ESI-HRMS

The number in parentheses by the chemical class indicates the total number of targeted constituents of that class

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
OPACs (21)	3	0	15	5	4
NPACs (10)	0	0	9	0	6
Acids (16)	0	5	2	9	0
Total (47)	3	5	26	14	10

Phenol was originally intended to be analysed by SFC-ESI-MS, but it was not possible to produce a standard curve due to poor separation in this part of the chromatogram and the constituent was therefore left out of the analysis. It was difficult to obtain reproducible standard curves for aliphatic acids due to continuous background signals at the low-end concentrations. Furthermore, quantification of the acids was difficult due to high number of isomers and co-elution in the samples.

C.1.4 GC-MS/SIM constituent groups

The number of constituent groups quantified in each product type by GC-MS/SIM is given in Table C.4, clearly showing that the highest number of constituent groups quantified was in coal tar.

Table C.4: Total number of quantified saturate, aromatic, SPAC, OPAC and NPAC constituent groups in asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil by GC-MS/SIM

The number in parentheses by the chemical class indicates the total number of targeted constituent groups of that class

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
Saturate constituent groups (3)	0	3	1	1	0
Aromatic constituent groups (19)	1	2	19	11	9
SPAC constituent groups (8)	0	0	7	2	3
OPAC constituent groups (11)	0	0	8	0	0
NPAC constituent groups (12)	0	0	8	0	1
Total (53)	1	5	43	14	13

C.1.5 GC×GC-HRMS constituent groups

The total number of constituent groups quantified in the five product types by GC×GC-HRMS is listed in Table C.5. Coal tar and tyre pyrolysis oil were the only two product types where constituent groups could be quantified.

Table C.5: Total number of OPAC and NPAC constituent groups quantified in asphalt, car wax/polish, coal tar, lubricating oil, and tyre pyrolysis oil by GC×GC-HRMS

The number in parentheses by the chemical class indicates the total number of targeted constituent groups of that class

Chemical class	Asphalt	Car wax/polish	Coal tar	Lubricating oil	Tyre pyrolysis oil
OPAC constituent groups (19)	0	0	11	0	11
NPAC constituent groups (27)	0	0	19	0	14
Total (46)	0	0	30	0	25

C.2 Concentrations of constituents in PetCo substances

C.2.1 GC-MS/SIM target constituents

Concentrations of individual constituents of saturates, aromatics, SPACs, OPACs, and NPACs are listed for asphalt in Table C.6, for car wax/polish in Table C.7, for coal tar in Table C.8, for lubricating oil in Table C.9 and Table C.10, and for tyre pyrolysis oil in Table C.11.

Table C.6: Concentrations (µg/g) of saturates, aromatics, SPACs, OPACs, and NPACs in asphalt samples analysed by GC-MS/SIM

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
Saturate	1,3-Dimethyladamantane	<DL	<DL	<DL	<DL	<DL
Saturate	1-Methyldecalin	<DL	<DL	<DL	<DL	<DL
Saturate	2-Isopropyldecalin	<DL	<DL	<DL	<DL	<DL
Saturate	Adamantane	<DL	<DL	<DL	<DL	<DL
Saturate	Butylcyclohexane	<DL	<DL	<DL	<DL	<DL
Aromatic	1,3,6-Trimethylchrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Methylfluorene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	1-Methylnaphthalene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	1-Methylpyrene	<LOQ	<DL	<DL	<LOQ	<DL
Aromatic	1-Phenylheptane	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Phenylnonane	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Phenyloctane	<DL	<DL	<DL	<DL	<DL
Aromatic	2,2,5,7-Tetramethyltetralin	<DL	<DL	<DL	<DL	<DL
Aromatic	2,6-Dimethylnaphthalene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	2-Methylnaphthalene	0.13	<DL	<DL	<DL	<DL
Aromatic	2-Methylphenanthrene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	3,3',5,5'-Tetramethylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	3,3'-Dimethylbiphenyl	<LOQ	<DL	<DL	<DL	<DL
Aromatic	4-Methylchrysene	<LOQ	<LOQ	<DL	0.24	<DL
Aromatic	4-n-Pentylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	6-Ethylchrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	Acenaphthene	<DL	<DL	<DL	<DL	<DL
Aromatic	Acenaphthylene	<DL	<DL	<LOQ	<DL	<DL
Aromatic	Anthracene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	Benzo[a]anthracene	<LOQ	<LOQ	<DL	<LOQ	<DL
Aromatic	Benzo[a]pyrene	<DL	<DL	<DL	<LOQ	<DL
Aromatic	Benzo[b]fluoranthene	0.23	<LOQ	<LOQ	0.24	<LOQ
Aromatic	Benzo[e]pyrene	0.25	0.17	0.49	0.54	0.56
Aromatic	Benzo[g,h,i]perylene	<LOQ	<LOQ	0.70	0.45	0.36
Aromatic	Benzo[k]fluoranthene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	Biphenyl	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
Aromatic	Butylbenzene	<DL	<DL	<DL	<DL	<DL
Aromatic	Chrysene	<LOQ	<LOQ	<LOQ	0.47	<LOQ
Aromatic	Dibenzo[a,h]anthracene	<DL	<DL	<DL	<LOQ	<DL
Aromatic	Fluoranthene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	Fluorene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	Hexylbenzene	<DL	<DL	<DL	<DL	<DL
Aromatic	Indeno[1,2,3-c,d]pyrene	<LOQ	<DL	<LOQ	<LOQ	<LOQ
Aromatic	Naphthalene	0.14	<DL	<DL	<DL	<DL
Aromatic	Perylene	0.35	0.37	0.48	0.94	0.53
Aromatic	Phenanthrene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	Pyrene	0.38	<LOQ	<LOQ	<LOQ	<LOQ
Aromatic	Tetralin	<DL	<DL	<DL	<DL	<LOQ
SPAC	1-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	2-Methylbenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	2,3,4-Trimethylbenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	3-Methylbenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	4,6-Dimethyldibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	4-Ethyl-6-methyldibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	4-Methyldibenzothiophene	<LOQ	<DL	<DL	<LOQ	<DL
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	<DL	<DL	<DL	<DL	<DL
SPAC	Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo[a]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	Dibenzo[a,]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Indole	<DL	<DL	<DL	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL	<DL

Table C.7: Concentrations (µg/g) of saturates, aromatics, SPACs, OPACs, and NPACs in car wax/polish samples analysed by GC-MS/SIM

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
Saturate	1,3-Dimethyladamantane	<DL	8.6	<DL	<DL	2.3
Saturate	1-Methyldecalin	<DL	2140	<DL	15	125
Saturate	2-Isopropyldecalin	<DL	54	<DL	<DL	<DL
Saturate	Adamantane	<DL	6.1	<DL	0.50	3.9
Saturate	Butylcyclohexane	<DL	154	<DL	112	116
Aromatic	1,3,6-Trimethylchrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Methylfluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Methylnaphthalene	<DL	20	<DL	0.28	0.20
Aromatic	1-Methylpyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Phenylheptane	<DL	10	<DL	<DL	<DL
Aromatic	1-Phenylnonane	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Phenyloctane	<DL	<DL	<DL	<DL	<DL
Aromatic	2,2,5,7-Tetramethyltetralin	<DL	<DL	<DL	<DL	<DL
Aromatic	2,6-Dimethylnaphthalene	<DL	1.5	<DL	<LOQ	<LOQ

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
Aromatic	2-Methylnaphthalene	<DL	27	<DL	0.38	0.35
Aromatic	2-Methylphenanthrene	<DL	<DL	<DL	<DL	<DL
Aromatic	3,3',5,5'-Tetramethylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	3,3'-Dimethylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	4-Methylchrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	4-n-Pentylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	6-Ethylchrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	Acenaphthene	<DL	<DL	<DL	<DL	<DL
Aromatic	Acenaphthylene	<DL	<DL	<DL	<DL	<DL
Aromatic	Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	Benzo[a]anthracene	<DL	<LOQ	<DL	<DL	<DL
Aromatic	Benzo[a]pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	Benzo[b]fluoranthene	<DL	<DL	<DL	<DL	<DL
Aromatic	Benzo[e]pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	Benzo[g,h,i]perylene	<DL	<DL	<DL	<DL	<DL
Aromatic	Benzo[k]fluoranthene	<DL	<DL	<DL	<DL	<DL
Aromatic	Biphenyl	<LOQ	2.4	<DL	<DL	<DL
Aromatic	Butylbenzene	<DL	<DL	<DL	<DL	<DL
Aromatic	Chrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	Dibenz[a,h]anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	Fluoranthene	<DL	<DL	<DL	<DL	<DL
Aromatic	Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	Hexylbenzene	<DL	<DL	<DL	<DL	<DL
Aromatic	Indeno[1,2,3-c,d]pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	Naphthalene	<DL	43	<DL	0.63	3.2
Aromatic	Perylene	<DL	<DL	<DL	<DL	<DL
Aromatic	Phenanthrene	<DL	<DL	<DL	<DL	<DL
Aromatic	Pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	Tetralin	<DL	303	<DL	1.4	4.5
SPAC	1-Benzothiophene	<DL	<DL	<DL	<DL	<LOQ
SPAC	2-Methylbenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	2,3,4-Trimethylbenzothiophene	<DL	0.30	<DL	<DL	<DL
SPAC	3-Methylbenzothiophene	<DL	<LOQ	<DL	<DL	<DL
SPAC	4,6-Dimethyldibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	4-Ethyl-6-methyldibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	4-Methyldibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	<DL	<DL	<DL	<DL	<DL
SPAC	Dibenzothiophene	<LOQ	<DL	<DL	<DL	<DL
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo[a]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	Dibenzo[a,]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Indole	<DL	<DL	4.28	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL	<DL

Table C.8: Concentrations (µg/g) of saturates, aromatics, SPACs, OPACs, and NPACs in coal tar samples analysed by GC-MS/SIM

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
Saturate	1,3-Dimethyladamantane	<DL	<DL	<DL	<DL	<DL
Saturate	1-Methyldecalin	35	32	<DL	<DL	<DL
Saturate	2-Isopropyldecalin	<DL	<DL	<DL	<DL	<DL
Saturate	Adamantane	<DL	<DL	<DL	<DL	<DL
Saturate	Butylcyclohexane	<DL	<DL	<DL	<DL	<DL
Aromatic	1,3,6-Trimethylchrysene	112	<DL	<LOQ	<DL	<DL
Aromatic	1-Methylfluorene	24	239	176	654	160
Aromatic	1-Methylnaphthalene	84	947	624	9760	3269
Aromatic	1-Methylpyrene	482	146	102	709	486
Aromatic	1-Phenylheptane	<DL	90	109	<DL	<DL
Aromatic	1-Phenylnonane	<DL	<DL	<DL	<DL	<DL
Aromatic	1-Phenyloctane	<DL	<DL	<DL	<DL	<DL
Aromatic	2,2,5,7-Tetramethyltetralin	<DL	<DL	<DL	<DL	<DL
Aromatic	2,6-Dimethylnaphthalene	52	571	368	2469	768
Aromatic	2-Methylnaphthalene	179	1541	944	21522	8156
Aromatic	2-Methylphenanthrene	146	187	149	4268	1397
Aromatic	3,3',5,5'-Tetramethylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	3,3'-Dimethylbiphenyl	<LOQ	51	36	340	94
Aromatic	4-Methylchrysene	326	31	25	49	89
Aromatic	4-n-Pentylbiphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	6-Ethylchrysene	113	<LOQ	<LOQ	<DL	<LOQ
Aromatic	Acenaphthene	188	130	93	38413	596
Aromatic	Acenaphthylene	18	35	16	207	15270
Aromatic	Anthracene	133	347	245	3777	10298
Aromatic	Benzo[a]anthracene	611	134	108	3306	6602
Aromatic	Benzo[a]pyrene	291	82	59	201	4940
Aromatic	Benzo[b]fluoranthene	167	93	87	392	4400
Aromatic	Benzo[e]pyrene	371	59	49	176	3225
Aromatic	Benzo[g,h,i]perylene	50	62	49	49	3468
Aromatic	Benzo[k]fluoranthene	67	55	45	320	4225
Aromatic	Biphenyl	35	86	97	6540	2377
Aromatic	Butylbenzene	<DL	<DL	<DL	<DL	<DL
Aromatic	Chrysene	1200	109	100	3343	6576
Aromatic	Dibenz[a,h]anthracene	44	18	14	<LOQ	669
Aromatic	Fluoranthene	204	201	188	40295	22595
Aromatic	Fluorene	177	293	236	26278	11772
Aromatic	Hexylbenzene	<DL	<DL	<DL	<DL	<DL
Aromatic	Indeno[1,2,3-c,d]pyrene	21	27	25	33	2361

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
Aromatic	Naphthalene	224	792	585	11380	84948
Aromatic	Perylene	111	38	34	125	3779
Aromatic	Phenanthrene	472	277	246	68967	32711
Aromatic	Pyrene	420	243	197	27634	16232
Aromatic	Tetralin	<DL	25	15	<DL	<DL
SPAC	1-Benzothiophene	14	32	19	471	2294
SPAC	2-Methylbenzothiophene	<LOQ	<DL	<DL	<DL	<DL
SPAC	2,3,4-Trimethylbenzothiophene	38	22	13	227	81
SPAC	3-Methylbenzothiophene	8.1	24	15	185	58
SPAC	4,6-Dimethyldibenzothiophene	100	<LOQ	<DL	80	<LOQ
SPAC	4-Ethyl-6-methyldibenzothiophene	76	<DL	<DL	<DL	<DL
SPAC	4-Methyldibenzothiophene	89	<DL	<DL	481	128
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	<DL	<DL	<DL	<DL	<DL
SPAC	Dibenzothiophene	71	15	8.1	6766	2448
OPAC	2,3-Benzofuran	<DL	<LOQ	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	3482	2043	1062	343
OPAC	2-n-Butylbenzofuran	<DL	42	<DL	<LOQ	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	3.2	9828	7712	343	130
OPAC	4-Hexylphenol	<DL	354	171	<DL	<DL
OPAC	4-Nonylphenol	<DL	<LOQ	<LOQ	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	3.5	780	406	<LOQ	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<LOQ	<DL
OPAC	Dibenzofuran	29	2019	835	889	319
OPAC	Naphthaldehyde	<DL	33	<DL	29	<LOQ
OPAC	o-Cresol	<LOQ	<LOQ	<LOQ	1239	<LOQ
OPAC	Phenol	<DL	1177	835	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	1.6	<LOQ	<LOQ	378	86
NPAC	11H-Benzo[a]carbazole	3.0	7206	4197	197	308
NPAC	1-Methylcarbazole	3.5	5431	3402	174	762
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	17	14	<LOQ	<LOQ	<DL
NPAC	2,3,6-Trimethylcarbazole	88	<LOQ	<DL	125	596
NPAC	2,3-Dimethylindole	6.0	17	<LOQ	287	55
NPAC	2-tert-Butyl-1H-indole	<DL	81	56	102	<DL
NPAC	3-Methylindole	17	<LOQ	<LOQ	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	24	21	<LOQ	<LOQ	<DL

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<LOQ	53	26	24	<DL
NPAC	5-Methylindole	<DL	<LOQ	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo[a]acridine	0.73	34	16	33	<LOQ
NPAC	8-Methyl-11(H)-benzo[a]carbazole	31	<LOQ	<DL	<DL	<DL
NPAC	9-Methylacridine	60	<LOQ	<DL	<DL	<LOQ
NPAC	Acridine	224	26	<LOQ	<LOQ	46
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<LOQ	<DL	<DL	38	<LOQ
NPAC	Benzonitrile	5.7	<LOQ	<DL	595	398
NPAC	Carbazole	21	<LOQ	<DL	68	425
NPAC	Dibenzo[a,]acridine	3.6	<DL	<DL	1052	302
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL	268
NPAC	Indole	<DL	<DL	258	<DL	<DL
NPAC	Quinoline	53	49	27	3234	5234

Table C.9: Concentrations (µg/g) of saturates, aromatics, SPACs, OPACs, and NPACs in lubricating oils (Lub1 – Lub4) analysed by GC-MS/SIM

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
Saturate	1,3-Dimethyladamantane	<DL	<DL	<DL	<DL
Saturate	1-Methyldecalin	<DL	<LOQ	2.7	<LOQ
Saturate	2-Isopropyldecalin	<DL	<DL	<DL	<DL
Saturate	Adamantane	<DL	<DL	<DL	<DL
Saturate	Butylcyclohexane	<DL	<DL	<LOQ	<DL
Aromatic	1,3,6-Trimethylchrysene	<DL	<DL	<DL	<DL
Aromatic	1-Methylfluorene	0.74	<DL	<DL	<DL
Aromatic	1-Methylnaphthalene	3.5	<DL	<DL	<DL
Aromatic	1-Methylpyrene	<LOQ	<DL	<DL	<DL
Aromatic	1-Phenylheptane	<DL	<DL	<LOQ	<DL
Aromatic	1-Phenylnonane	<DL	<DL	<DL	<DL
Aromatic	1-Phenyloctane	<DL	<DL	<DL	<DL
Aromatic	2,2,5,7-Tetramethyltetralin	<DL	<DL	<DL	<DL
Aromatic	2,6-Dimethylnaphthalene	4.0	<LOQ	<DL	<LOQ
Aromatic	2-Methylnaphthalene	4.6	<LOQ	<DL	<LOQ
Aromatic	2-Methylphenanthrene	1.3	<DL	<DL	<DL
Aromatic	3,3',5,5'-Tetramethylbiphenyl	<DL	<DL	<DL	<DL
Aromatic	3,3'-Dimethylbiphenyl	1.3	<LOQ	<DL	<DL
Aromatic	4-Methylchrysene	<DL	<DL	<DL	<DL
Aromatic	4-n-Pentylbiphenyl	<DL	<DL	<DL	<DL
Aromatic	6-Ethylchrysene	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
Aromatic	Acenaphthene	<LOQ	<DL	<DL	<DL
Aromatic	Acenaphthylene	<DL	<DL	<DL	<DL
Aromatic	Anthracene	<LOQ	<DL	<DL	<DL
Aromatic	Benzo[a]anthracene	<DL	<DL	<LOQ	<DL
Aromatic	Benzo[a]pyrene	<DL	<DL	<DL	<DL
Aromatic	Benzo[b]fluoranthene	<DL	<DL	<DL	<DL
Aromatic	Benzo[e]pyrene	<DL	<DL	<DL	<DL
Aromatic	Benzo[g,h,i]perylene	<DL	<DL	<DL	<DL
Aromatic	Benzo[k]fluoranthene	<DL	<DL	<DL	<DL
Aromatic	Biphenyl	1.7	<DL	<DL	<DL
Aromatic	Butylbenzene	<DL	<DL	<DL	<DL
Aromatic	Chrysene	<DL	<DL	<DL	<DL
Aromatic	Dibenz[a,h]anthracene	<DL	<DL	<LOQ	<DL
Aromatic	Fluoranthene	<DL	<DL	<DL	<DL
Aromatic	Fluorene	0.59	<LOQ	<DL	<DL
Aromatic	Hexylbenzene	<DL	<DL	<DL	<DL
Aromatic	Indeno[1,2,3-c,d]pyrene	<DL	<DL	<DL	<DL
Aromatic	Naphthalene	0.21	<DL	<DL	<DL
Aromatic	Perylene	<DL	1.1	1.6	0.71
Aromatic	Phenanthrene	1.5	<DL	<DL	<DL
Aromatic	Pyrene	0.23	<DL	<DL	<DL
Aromatic	Tetralin	<DL	<DL	<DL	<DL
SPAC	1-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	2-Methylbenzothiophene	<DL	<DL	<DL	<DL
SPAC	2,3,4-Trimethylbenzothiophene	<DL	<DL	<DL	<DL
SPAC	3-Methylbenzothiophene	<DL	<DL	<DL	<DL
SPAC	4,6-Dimethyldibenzothiophene	<LOQ	<LOQ	<DL	<LOQ
SPAC	4-Ethyl-6-methyldibenzothiophene	<DL	<LOQ	<DL	<DL
SPAC	4-Methyldibenzothiophene	<LOQ	<LOQ	<DL	<LOQ
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	<DL	<DL	<DL	<DL
SPAC	Dibenzothiophene	<DL	<DL	<DL	<DL
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<LOQ	<DL	<LOQ
NPAC	3-Methylindole	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo[a]acridine	<DL	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL
NPAC	Dibenzo[a,h]acridine	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL
NPAC	Indole	<DL	<DL	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL

Table C.10: Concentrations (µg/g) of saturates, aromatics, SPACs, OPACs, and NPACs in lubricating oils (Lub5 – Lub8) analysed by GC-MS/SIM

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
Saturate	1,3-Dimethyladamantane	<DL	<DL	<DL	<LOQ
Saturate	1-Methyldecalin	2.8	<DL	2.1	9.0
Saturate	2-Isopropyldecalin	<DL	<DL	<DL	<DL
Saturate	Adamantane	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
Saturate	Butylcyclohexane	0.74	<DL	<DL	<DL
Aromatic	1,3,6-Trimethylchrysene	<DL	<DL	<DL	<DL
Aromatic	1-Methylfluorene	1.3	<LOQ	<DL	<LOQ
Aromatic	1-Methylnaphthalene	1.3	<DL	0.73	<LOQ
Aromatic	1-Methylpyrene	0.44	<DL	<DL	<LOQ
Aromatic	1-Phenylheptane	<DL	<DL	<DL	<DL
Aromatic	1-Phenylnonane	<DL	<DL	<DL	<DL
Aromatic	1-Phenyloctane	<DL	<DL	<DL	<DL
Aromatic	2,2,5,7-Tetramethyltetralin	<DL	<DL	<DL	<DL
Aromatic	2,6-Dimethylnaphthalene	1.1	<DL	0.41	0.28
Aromatic	2-Methylnaphthalene	1.7	<LOQ	1.4	0.16
Aromatic	2-Methylphenanthrene	0.53	<DL	<DL	<LOQ
Aromatic	3,3',5,5'-Tetramethylbiphenyl	<DL	<DL	<DL	<DL
Aromatic	3,3'-Dimethylbiphenyl	0.95	<LOQ	<LOQ	<DL
Aromatic	4-Methylchrysene	<DL	<DL	<DL	<DL
Aromatic	4-n-Pentylbiphenyl	<DL	<DL	<DL	<DL
Aromatic	6-Ethylchrysene	<DL	<DL	<DL	<DL
Aromatic	Acenaphthene	<LOQ	<DL	<DL	<DL
Aromatic	Acenaphthylene	<LOQ	<DL	<LOQ	<DL
Aromatic	Anthracene	<LOQ	<DL	<DL	<DL
Aromatic	Benzo[a]anthracene	<DL	<DL	<DL	<DL
Aromatic	Benzo[a]pyrene	<DL	<DL	<DL	<DL
Aromatic	Benzo[b]fluoranthene	<DL	<DL	<DL	<DL
Aromatic	Benzo[e]pyrene	<DL	<DL	<DL	0.17
Aromatic	Benzo[g,h,i]perylene	0.58	<DL	<LOQ	1.2
Aromatic	Benzo[k]fluoranthene	<DL	<DL	<DL	<DL
Aromatic	Biphenyl	0.82	<DL	<LOQ	<DL
Aromatic	Butylbenzene	<DL	<DL	<DL	<DL
Aromatic	Chrysene	<LOQ	<DL	<DL	<DL
Aromatic	Dibenz[a,h]anthracene	<DL	<DL	<DL	0.64
Aromatic	Fluoranthene	0.29	<DL	<DL	<DL
Aromatic	Fluorene	0.36	<DL	<DL	<LOQ
Aromatic	Hexylbenzene	<DL	<DL	<DL	<DL
Aromatic	Indeno[1,2,3-c,d]pyrene	<DL	<DL	<DL	<DL
Aromatic	Naphthalene	1.4	<DL	0.10	0.57
Aromatic	Perylene	<DL	<DL	<DL	<DL
Aromatic	Phenanthrene	0.70	<DL	<DL	<DL
Aromatic	Pyrene	2.0	<DL	0.30	<LOQ
Aromatic	Tetralin	<DL	<DL	<DL	<DL
SPAC	1-Benzothiophene	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
SPAC	2-Methylbenzothiophene	<DL	<DL	<DL	<DL
SPAC	2,3,4-Trimethylbenzothiophene	<LOQ	<DL	<DL	<DL
SPAC	3-Methylbenzothiophene	<DL	<DL	<DL	<DL
SPAC	4,6-Dimethyldibenzothiophene	1.5	<DL	<DL	0.60
SPAC	4-Ethyl-6-methyldibenzothiophene	0.85	<DL	<DL	<LOQ
SPAC	4-Methyldibenzothiophene	1.3	<DL	<LOQ	0.48
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	<DL	<DL	<DL	<DL
SPAC	Dibenzothiophene	0.34	<LOQ	<LOQ	<LOQ
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	5.24	<LOQ	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<LOQ	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<LOQ	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<LOQ
NPAC	5-Methylindole	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo[a]acridine	<DL	<DL	<DL	<LOQ
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
NPAC	Benzo[c]acridine	<DL	<DL	174	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL
NPAC	Dibenzo[a,h]acridine	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	3.8	<LOQ
NPAC	Indole	<DL	<DL	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL

Table C.11: Concentrations (µg/g) of saturates, aromatics, SPACs, OPACs, and NPACs in tyre pyrolysis oil analysed by GC-MS/SIM

Chemical class	Constituent	TP1
Saturate	1,3-Dimethyladamantane	<LOQ
Saturate	1-Methyldecalin	<DL
Saturate	2-Isopropyldecalin	<DL
Saturate	Adamantane	<DL
Saturate	Butylcyclohexane	<DL
Aromatic	1,3,6-Trimethylchrysene	<DL
Aromatic	1-Methylfluorene	262
Aromatic	1-Methylnaphthalene	4879
Aromatic	1-Methylpyrene	<LOQ
Aromatic	1-Phenylheptane	<DL
Aromatic	1-Phenylnonane	<DL
Aromatic	1-Phenyloctane	<DL
Aromatic	2,2,5,7-Tetramethyltetralin	<DL
Aromatic	2,6-Dimethylnaphthalene	2528
Aromatic	2-Methylnaphthalene	7314
Aromatic	2-Methylphenanthrene	104
Aromatic	3,3',5,5'-Tetramethylbiphenyl	<DL
Aromatic	3,3'-Dimethylbiphenyl	116
Aromatic	4-Methylchrysene	<DL
Aromatic	4-n-Pentylbiphenyl	<DL
Aromatic	6-Ethylchrysene	<DL
Aromatic	Acenaphthene	678
Aromatic	Acenaphthylene	152
Aromatic	Anthracene	156
Aromatic	Benzo[a]anthracene	<LOQ
Aromatic	Benzo[a]pyrene	<DL
Aromatic	Benzo[b]fluoranthene	<DL

Chemical class	Constituent	TP1
Aromatic	Benzo[e]pyrene	<DL
Aromatic	Benzo[g,h,i]perylene	<DL
Aromatic	Benzo[k]fluoranthene	<DL
Aromatic	Biphenyl	1478
Aromatic	Butylbenzene	<DL
Aromatic	Chrysene	<LOQ
Aromatic	Dibenz[a,h]anthracene	<DL
Aromatic	Fluoranthene	39
Aromatic	Fluorene	541
Aromatic	Hexylbenzene	5006
Aromatic	Indeno[1,2,3-c,d]pyrene	<DL
Aromatic	Naphthalene	8137
Aromatic	Perylene	<DL
Aromatic	Phenanthrene	401
Aromatic	Pyrene	94
Aromatic	Tetralin	456
SPAC	1-Benzothiophene	310
SPAC	2-Methylbenzothiophene	<DL
SPAC	2,3,4-Trimethylbenzothiophene	251
SPAC	3-Methylbenzothiophene	227
SPAC	4,6-Dimethyldibenzothiophene	<DL
SPAC	4-Ethyl-6-methyldibenzothiophene	<DL
SPAC	4-Methyldibenzothiophene	<LOQ
SPAC	7-Methylbenzo[b]naphtho[2,3-d]thiophene	<DL
SPAC	Dibenzothiophene	49
OPAC	2,3-Benzofuran	<DL
OPAC	2-Hydroxynaphthalene	<LOQ
OPAC	2-Methyldibenzofuran	<DL
OPAC	2-n-Butylbenzofuran	<DL
OPAC	3,5-Dimethylphenol	<DL
OPAC	3-Methylbenzofuran	<DL
OPAC	4-Hexylphenol	<DL
OPAC	4-Nonylphenol	<DL
OPAC	4-tert-Butylphenol	<DL
OPAC	9-Hydroxyfluorene	<DL
OPAC	9-Hydroxyphenanthrene	<DL
OPAC	Dibenzofuran	<DL
OPAC	Naphthaldehyde	<DL
OPAC	o-Cresol	1571

Chemical class	Constituent	TP1
OPAC	Phenol	<LOQ
NPAC	1,4,8-Trimethylcarbazole	<DL
NPAC	11H-Benzo[a]carbazole	<DL
NPAC	1-Methylcarbazole	<DL
NPAC	1-Methylisoquinoline	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL
NPAC	2,3-Dimethylindole	41
NPAC	2-tert-Butyl-1H-indole	<DL
NPAC	3-Methylindole	<LOQ
NPAC	4,6,8-Trimethylquinoline	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL
NPAC	5-Methylindole	<DL
NPAC	8,10-Dimethyl-Benzo[a]acridine	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL
NPAC	9-Methylacridine	<DL
NPAC	Acridine	<LOQ
NPAC	Benzo[c]acridine	<DL
NPAC	Benzo[h]quinoline	<DL
NPAC	Benzonitrile	5649
NPAC	Carbazole	<LOQ
NPAC	Dibenzo[a,h]acridine	<DL
NPAC	Dibenzo[f,h]quinoline	<DL
NPAC	Indole	<DL
NPAC	Quinoline	276

C.2.2 GC×GC-HRMS target constituents

Concentrations of the individual constituents in each sample analysed by GCxGC-HRMS are listed in Table C.12 for asphalt, in Table C.13 for car wax/polish, in Table C.14 for coal tar, in Table C.15 and Table C.16 for lubricating oil, and in Table C.17 for tyre pyrolysis oil.

Table C.12: Concentrations (µg/g) of OPACs and NPACs in asphalt analysed by GCxGC-HRMS

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	Dibenzofuranols	<DL	<DL	<DL	<DL	<DL
OPAC	Indanols	<DL	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<DL	<DL	<LOQ	<DL
NPAC	(Tere)Phthalonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<LOQ	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<LOQ	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo(a)acridine	<DL	<DL	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<LOQ	<DL
NPAC	9-Ethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	Benzothiazole	<DL	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<LOQ	<DL
NPAC	Dibenz[a,h]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Diethyl-a-naphthylamine	<DL	<DL	<DL	0.85	<DL
NPAC	Diphenylamine	<DL	<DL	<DL	<DL	<DL
NPAC	Indole	<DL	<DL	<DL	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL	<DL

Table C.13: Concentrations (µg/g) of OPACs and NPACs in car wax/polish analysed by GCxGC-HRMS

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<LOQ	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<LOQ	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	6.9	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<LOQ	<LOQ
OPAC	4-Hexylphenol	<LOQ	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<LOQ	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	10	<DL	<DL	<DL
OPAC	Dibenzofuran	<LOQ	<DL	<DL	<DL	<DL
OPAC	Dibenzofuranols	<DL	<DL	<DL	<DL	<DL
OPAC	Indanols	<DL	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<LOQ	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<LOQ	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<DL	<DL	<DL	<DL
NPAC	(Tere)Phthalonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<LOQ	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<LOQ	<DL	<DL	<DL

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<LOQ	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<LOQ	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo(a)acridine	<DL	<LOQ	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	9-Ethylcarbazole	<LOQ	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	Benzothiazole	<DL	<DL	<DL	<DL	<DL
NPAC	Carbazole	<LOQ	<DL	<DL	<DL	<DL
NPAC	Dibenz[a,h]acridine	<DL	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	Diethyl-a-naphthylamine	<DL	<DL	<DL	<DL	<DL
NPAC	Diphenylamine	<DL	<DL	<DL	<DL	<DL
NPAC	Indole	<LOQ	<DL	<DL	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL	<DL

Table C.14: Concentrations (µg/g) of OPACs and NPACs in coal tar analysed by GCxGC-HRMS

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
OPAC	2,3-Benzofuran	<DL	<LOQ	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	3482	2043	1062	343
OPAC	2-Methyldibenzofuran	<DL	42	<DL	<LOQ	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	3.2	9828	7712	343	130
OPAC	3-Methylbenzofuran	<DL	354	171	<DL	<DL
OPAC	4-Hexylphenol	<DL	<LOQ	<LOQ	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	3.5	780	406	<LOQ	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<LOQ	<DL
OPAC	9-Hydroxyphenanthrene	29	2019	835	889	319
OPAC	Dibenzofuran	<DL	33	<DL	29	<LOQ

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
OPAC	Dibenzofuranols	<LOQ	<LOQ	<LOQ	1239	<LOQ
OPAC	Indanols	<DL	1177	835	<DL	<DL
OPAC	Naphthaldehyde	1.6	<LOQ	<LOQ	378	86
OPAC	o-Cresol	3.0	7206	4197	197	308
OPAC	Phenol	3.5	5431	3402	174	762
NPAC	(Tere)Phthalonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	17	14	<LOQ	<LOQ	<DL
NPAC	11H-Benzo[a]carbazole	88	<LOQ	<DL	125	596
NPAC	1-Methylcarbazole	6.0	17	<LOQ	287	55
NPAC	1-Methylisoquinoline	<DL	81	56	102	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	17	<LOQ	<LOQ	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	24	21	<LOQ	<LOQ	<DL
NPAC	2,3-Dimethylindole	<LOQ	53	26	24	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<LOQ	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	0.73	34	16	33	<LOQ
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	31	<LOQ	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo(a)acridine	60	<LOQ	<DL	<DL	<LOQ
NPAC	8-Methyl-11(H)-benzo[a]carbazole	224	26	<LOQ	<LOQ	46
NPAC	9-Ethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<LOQ	<DL	<DL	38	<LOQ
NPAC	Acridine	5.7	<LOQ	<DL	595	398
NPAC	Benzo[c]acridine	21	<LOQ	<DL	68	425
NPAC	Benzo[h]quinoline	3.6	<DL	<DL	1052	302
NPAC	Benzonitrile	<DL	<DL	<DL	<DL	268
NPAC	Benzothiazole	<DL	<DL	258	<DL	<DL
NPAC	Carbazole	53	49	27	3234	5234
NPAC	Dibenz[a,h]acridine	58	<DL	<DL	<DL	<LOQ
NPAC	Dibenzo[f,h]quinoline	62	<LOQ	<DL	180	502
NPAC	Diethyl-a-naphthylamine	3.1	59	44	<LOQ	<DL
NPAC	Diphenylamine	<LOQ	<LOQ	<LOQ	38	<LOQ
NPAC	Indole	13	29	<LOQ	3673	985
NPAC	Quinoline	14	59	39	6231	1570

Table C.15: Concentrations (µg/g) of OPACs and NPACs in lubricating oil (Lub1 – Lub4) analysed by GCxGC-HRMS

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<LOQ	1.6	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	Dibenzofuranols	<DL	<DL	<DL	<DL
OPAC	Indanols	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL
OPAC	Phenol	<DL	<DL	<DL	<DL
NPAC	(Tere)Phthalonitrile	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo(a)acridine	<DL	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	9-Ethylcarbazole	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL
NPAC	Acridine	<DL	<DL	<DL	<DL
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL
NPAC	Benzothiazole	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL
NPAC	Dibenz[a,h]acridine	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL
NPAC	Diethyl-a-naphthylamine	<DL	<DL	<DL	<DL
NPAC	Diphenylamine	<DL	0.55	37	<LOQ

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
NPAC	Indole	<DL	<LOQ	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL

Table C.16: Concentrations (µg/g) of OPACs and NPACs in lubricating oil (Lub5 – Lub8) analysed by GCxGC-HRMS

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
OPAC	2,3-Benzofuran	<DL	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<LOQ	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	2-Methyldibenzofuran	<DL	<DL	<DL	<DL
OPAC	2-n-Butylbenzofuran	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL
OPAC	3-Methylbenzofuran	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	Dibenzofuranols	<DL	<DL	<DL	<DL
OPAC	Indanols	<DL	<DL	<DL	<DL
OPAC	Naphthaldehyde	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL
OPAC	Phenol	1.9	<DL	<DL	<DL
NPAC	(Tere)Phthalonitrile	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	11H-Benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylisoquinoline	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL
NPAC	4,6,8-Trimethylquinoline	<DL	<DL	<DL	<DL
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL	<DL	<DL	<DL
NPAC	8,10-Dimethyl-Benzo(a)acridine	<DL	<DL	<DL	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL	<DL	<DL	<DL
NPAC	9-Ethylcarbazole	<DL	<DL	<DL	<DL
NPAC	9-Methylacridine	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
NPAC	Acridine	<DL	<DL	<DL	<DL
NPAC	Benzo[c]acridine	<DL	<DL	<DL	<DL
NPAC	Benzo[h]quinoline	<DL	<DL	<DL	<DL
NPAC	Benzonitrile	<DL	<DL	<DL	<DL
NPAC	Benzothiazole	5.5	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL
NPAC	Dibenz[a,h]acridine	<DL	<DL	<DL	<DL
NPAC	Dibenzo[f,h]quinoline	<DL	<DL	<DL	<DL
NPAC	Diethyl-a-naphthylamine	<DL	<DL	<DL	<DL
NPAC	Diphenylamine	<LOQ	<DL	<LOQ	<DL
NPAC	Indole	<DL	<DL	<DL	<DL
NPAC	Quinoline	<DL	<DL	<DL	<DL

Table C.17: Concentrations (µg/g) of OPACs and NPACs in Tyre pyrolysis oil analysed by GCxGC-HRMS

Chemical class	Constituent	TP1
OPAC	2,3-Benzofuran	18
OPAC	2,4-Di-tert-butylphenol	9.4
OPAC	2-Hydroxynaphthalene	28
OPAC	2-Methyldibenzofuran	2.3
OPAC	2-n-Butylbenzofuran	0.60
OPAC	3,5-Dimethylphenol	548
OPAC	3-Methylbenzofuran	157
OPAC	4-Hexylphenol	0.99
OPAC	4-Nonylphenol	<DL
OPAC	4-tert-Butylphenol	778
OPAC	9-Hydroxyfluorene	25
OPAC	9-Hydroxyphenanthrene	<LOQ
OPAC	Dibenzofuran	1.4
OPAC	Dibenzofuranols	<LOQ
OPAC	Indanols	15
OPAC	Naphthaldehyde	5.3
OPAC	o-Cresol	643
OPAC	Phenol	761
NPAC	(Tere)Phthalonitrile	415
NPAC	1,4,8-Trimethylcarbazole	0.33
NPAC	11H-Benzo[a]carbazole	<DL
NPAC	1-Methylcarbazole	1.2
NPAC	1-Methylisoquinoline	14

Chemical class	Constituent	TP1
NPAC	2,3,6,7-Tetramethylcarbazole	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL
NPAC	2,3-Dimethylindole	154
NPAC	2-tert-Butyl-1H-indole	63
NPAC	4,6,8-Trimethylquinoline	11
NPAC	5-Ethyl-7-methyl-benzo[b]carbazole	<DL
NPAC	8,10-Dimethyl-Benzo(a)acridine	<DL
NPAC	8-Methyl-11(H)-benzo[a]carbazole	<DL
NPAC	9-Ethylcarbazole	<LOQ
NPAC	9-Methylacridine	<LOQ
NPAC	Acridine	11
NPAC	Benzo[c]acridine	<LOQ
NPAC	Benzo[h]quinoline	4.3
NPAC	Benzonitrile	727
NPAC	Benzothiazole	710
NPAC	Carbazole	9.0
NPAC	Dibenz[a,h]acridine	<DL
NPAC	Dibenzo[f,h]quinoline	<LOQ
NPAC	Diethyl-a-naphthylamine	611
NPAC	Diphenylamine	506
NPAC	Indole	37
NPAC	Quinoline	139

C.2.3 SFC-ESI-HRMS target constituents

Concentrations of the individual constituents in each sample analysed by SFC-ESI-HRMS are listed in Table C.18 for asphalt, in Table C.19 for car wax/polish, in Table C.20 for coal tar, in Table C.21 and Table C.22 for lubricating oil, and in Table C.23 for tyre pyrolysis oil.

Table C.18: Concentrations (µg/g) of OPACs, NPACs, and acids in asphalt analysed by SFC-ESI-HRMS

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	1,7-Dihydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	1-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	1-Hydroxyphenanthrene	<DL	0.51	<DL	<DL	<LOQ
OPAC	1-Hydroxypyrene	<DL	<LOQ	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<LOQ	<DL	<DL	<DL
OPAC	2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyl-1-hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	3-Hydroxybenzo[a]pyrene	<DL	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyphenanthrene	<DL	0.51	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-Hydroxyphenanthrene	<DL	0.56	<DL	<DL	<LOQ
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL	<LOQ
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL	<LOQ
NPAC	Indole	<DL	<DL	<DL	<DL	<DL
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Adamantane carboxylic acid	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent	Asp1	Asp2	Asp3	Asp4	Asp5
Acid	1-Hydroxy-2-naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Pyrene carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	2-Naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	2-Phenanthrene carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	3-Chrysene carboxylic acid	<DL	<DL	<DL	<DL	<LOQ
Acid	Lauric acid	<DL	<DL	<DL	<DL	<DL
Acid	Linoleic acid	<DL	<DL	<DL	<DL	<DL
Acid	Linolenic acid	<DL	<DL	<DL	<DL	<DL
Acid	Oleic acid	<DL	<DL	<DL	<DL	<DL
Acid	Palmitoleic acid	<DL	<DL	<DL	<DL	<DL
Acid	Pentadecanoic acid	<DL	<DL	<DL	<DL	<DL
Acid	Stearic acid	<DL	<DL	<DL	<DL	<DL

Table C.19: Concentrations (µg/g) of OPACs, NPACs, and acids in car wax/polish analysed by SFC-ESI-HRMS

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	1,7-Dihydroxynaphthalene	<LOQ	<DL	<DL	<DL	<DL
OPAC	1-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<LOQ
OPAC	1-Hydroxypyrene	<LOQ	<DL	<DL	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	2-Methyl-1-hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	3-Hydroxybenzo[a]pyrene	<DL	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<LOQ
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent	CWP1	CWP2	CWP3	CWP4	CWP5
OPAC	o-Cresol	<DL	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<LOQ	<LOQ	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL	<LOQ
NPAC	Indole	<DL	<DL	<DL	<DL	<DL
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Adamantane carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Hydroxy-2-naphthoic acid	<DL	<DL	<DL	<DL	<LOQ
Acid	1-Naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Pyrene carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	2-Naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	2-Phenanthrene carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	3-Chrysene carboxylic acid	<LOQ	<DL	<DL	<DL	<DL
Acid	Lauric acid	<DL	<DL	<DL	<DL	<DL
Acid	Linoleic acid	<DL	33	43	<DL	<LOQ
Acid	Linolenic acid	<DL	3277	23	<DL	<LOQ
Acid	Oleic acid	<DL	2081	<LOQ	<DL	<LOQ
Acid	Palmitoleic acid	<DL	18	<DL	<DL	<DL
Acid	Pentadecanoic acid	<DL	<DL	<DL	<DL	<LOQ
Acid	Stearic acid	<DL	209	<DL	48	<DL

Table C.20: Concentrations (µg/g) of OPACs, NPACs, and acids in coal tar analysed by SFC-ESI-HRMS

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	<DL	710	257	<DL	<DL
OPAC	1,7-Dihydroxynaphthalene	<DL	29	19	7.6	<DL
OPAC	1-Hydroxynaphthalene	<DL	1636	1177	351	<LOQ
OPAC	1-Hydroxyphenanthrene	<LOQ	48	23	68	25
OPAC	1-Hydroxypyrene	<LOQ	46	23	59	59
OPAC	2,4-Di-tert-butylphenol	<DL	<LOQ	<LOQ	<DL	<DL
OPAC	2-Hydroxyfluorene	<LOQ	68	56	373	84

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
OPAC	2-Hydroxynaphthalene	<DL	317	190	170	204
OPAC	2-Hydroxyphenanthrene	0.14	32	20	17	3.0
OPAC	2-Methyl-1-hydroxynaphthalene	<DL	<LOQ	<DL	<LOQ	<DL
OPAC	3,5-Dimethylphenol	<DL	4504	2431	<DL	<DL
OPAC	3-Hydroxybenzo[a]pyrene	<DL	<LOQ	<DL	<DL	<DL
OPAC	3-Hydroxyfluorene	<DL	60	48	91	14
OPAC	3-Hydroxyphenanthrene	0.73	216	145	97	16
OPAC	4-Hexylphenol	<DL	<LOQ	<LOQ	<DL	<DL
OPAC	4-Hydroxyphenanthrene	<LOQ	53	25	74	27
OPAC	4-Nonylphenol	<DL	<LOQ	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<DL	<DL	8177	<LOQ	<LOQ
OPAC	9-Hydroxyphenanthrene	<LOQ	289	182	154	30
OPAC	o-Cresol	<DL	11019	5217	<LOQ	<LOQ
NPAC	1,4,8-Trimethylcarbazole	26	25	<LOQ	20	<LOQ
NPAC	1-Methylcarbazole	14	46	24	651	206
NPAC	2,3,6,7-Tetramethylcarbazole	7.8	<LOQ	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	3.6	<DL	<LOQ	<DL	<DL
NPAC	2,3-Dimethylindole	7.0	200	91	327	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	69	25	395	60
NPAC	5-Methylindole	<DL	34	20	121	<LOQ
NPAC	Carbazole	64	61	27	4225	8494
NPAC	Indole	<LOQ	<LOQ	<DL	3778	979
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Adamantane carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Hydroxy-2-naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Naphthoic acid	<DL	<DL	<DL	<DL	<DL
Acid	1-Pyrene carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	2-Naphthoic acid	<DL	<LOQ	<LOQ	<LOQ	<DL
Acid	2-Phenanthrene carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	<DL	<DL	<DL	<DL	<DL
Acid	3-Chrysene carboxylic acid	1.5	<DL	<LOQ	<LOQ	<LOQ
Acid	Lauric acid	<DL	<DL	<DL	<DL	<DL
Acid	Linoleic acid	<DL	<DL	<DL	<DL	<DL
Acid	Linolenic acid	<DL	<DL	<DL	<DL	<DL
Acid	Oleic acid	<DL	<DL	<DL	<DL	<DL
Acid	Palmitoleic acid	<DL	<DL	<LOQ	<DL	<DL
Acid	Pentadecanoic acid	<DL	<LOQ	<LOQ	<DL	<DL

Chemical class	Constituent	CT1	CT2	CT3	CT4	CT5
Acid	Stearic acid	<DL	<LOQ	516	<LOQ	<LOQ

Table C.21: Concentrations (µg/g) of OPACs, NPACs, and acids in lubricating oil (Lub1 – Lub4) analysed by SFC-ESI-HRMS

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	1,7-Dihydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	1-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	1-Hydroxyphenanthrene	<LOQ	<DL	<DL	<DL
OPAC	1-Hydroxypyrene	<DL	<LOQ	<DL	<DL
OPAC	2,4-Di-tert-butylphenol	<DL	<DL	<DL	<DL
OPAC	2-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<LOQ	<DL	<DL
OPAC	2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	2-Methyl-1-hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL
OPAC	3-Hydroxybenzo[a]pyrene	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyphenanthrene	<DL	0.42	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL
OPAC	4-Hydroxyphenanthrene	<DL	0.42	<DL	<DL
OPAC	4-Nonylphenol	<DL	<DL	<DL	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	<LOQ	<DL	<DL	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<DL	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL
NPAC	Indole	<DL	<DL	<DL	<DL
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	<DL	<DL	<DL	<DL
Acid	1-Adamantane carboxylic acid	<DL	<DL	<DL	<DL
Acid	1-Hydroxy-2-naphthoic acid	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub1	Lub2	Lub3	Lub4
Acid	1-Naphthoic acid	<DL	<DL	<DL	<DL
Acid	1-Pyrene carboxylic acid	<DL	<DL	<DL	<DL
Acid	2-Naphthoic acid	<DL	<DL	<DL	<DL
Acid	2-Phenanthrene carboxylic acid	<DL	<DL	<DL	<DL
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	<DL	<DL	<DL	<DL
Acid	3-Chrysene carboxylic acid	<DL	<DL	<DL	<DL
Acid	Lauric acid	<DL	<DL	<DL	<DL
Acid	Linoleic acid	<DL	<DL	<DL	<DL
Acid	Linolenic acid	<DL	<DL	<DL	<DL
Acid	Oleic acid	<DL	<DL	<DL	<DL
Acid	Palmitoleic acid	<DL	<DL	<DL	<DL
Acid	Pentadecanoic acid	<LOQ	<DL	<DL	<DL
Acid	Stearic acid	61	<DL	<DL	<DL

Table C.22: Concentrations (µg/g) of OPACs, NPACs, and acids in lubricating oil (Lub5 – Lub8) analysed by SFC-ESI-HRMS

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	1,7-Dihydroxynaphthalene	<DL	<DL	9.4	<DL
OPAC	1-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	1-Hydroxyphenanthrene	<DL	<LOQ	<DL	<LOQ
OPAC	1-Hydroxypyrene	<DL	<DL	9.0	<DL
OPAC	2,4-Di-tert-butylphenol	<LOQ	<DL	<LOQ	<DL
OPAC	2-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	2-Hydroxyphenanthrene	<DL	<LOQ	<LOQ	<DL
OPAC	2-Methyl-1-hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	3,5-Dimethylphenol	<DL	<DL	<DL	<DL
OPAC	3-Hydroxybenzo[a]pyrene	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyfluorene	<DL	<DL	<DL	<DL
OPAC	3-Hydroxyphenanthrene	<LOQ	0.56	<DL	<DL
OPAC	4-Hexylphenol	<DL	<DL	<DL	<DL
OPAC	4-Hydroxyphenanthrene	<DL	<LOQ	<DL	<LOQ
OPAC	4-Nonylphenol	<DL	<DL	<LOQ	<DL
OPAC	4-tert-Butylphenol	<DL	<DL	<DL	<DL
OPAC	9-Hydroxyfluorene	10	<DL	<LOQ	<DL
OPAC	9-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	o-Cresol	<DL	<DL	<DL	<DL

Chemical class	Constituent	Lub5	Lub6	Lub7	Lub8
NPAC	1,4,8-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	1-Methylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6,7-Tetramethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL	<DL	<DL	<DL
NPAC	2,3-Dimethylindole	<DL	<DL	<DL	<DL
NPAC	2-tert-Butyl-1H-indole	<DL	<DL	<DL	<DL
NPAC	3-Methylindole	<DL	<DL	<LOQ	<DL
NPAC	5-Methylindole	<DL	<DL	<DL	<DL
NPAC	Carbazole	<DL	<DL	<DL	<DL
NPAC	Indole	<DL	<DL	<DL	<DL
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	<DL	<DL	<LOQ	<DL
Acid	1-Adamantane carboxylic acid	<DL	<DL	<DL	<DL
Acid	1-Hydroxy-2-naphthoic acid	<DL	<DL	<DL	<DL
Acid	1-Naphthoic acid	<DL	<DL	13	<DL
Acid	1-Pyrene carboxylic acid	<DL	<DL	<LOQ	<DL
Acid	2-Naphthoic acid	<DL	<DL	22	<DL
Acid	2-Phenanthrene carboxylic acid	<DL	<DL	<DL	<DL
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	<DL	<DL	6.9	<DL
Acid	3-Chrysene carboxylic acid	<DL	<DL	41	<LOQ
Acid	Lauric acid	<DL	<DL	<DL	<DL
Acid	Linoleic acid	42	<DL	182	<DL
Acid	Linolenic acid	<DL	<DL	<LOQ	<DL
Acid	Oleic acid	240	<DL	1040	<DL
Acid	Palmitoleic acid	34	<DL	<LOQ	<DL
Acid	Pentadecanoic acid	12	<DL	<LOQ	<DL
Acid	Stearic acid	86	<DL	<LOQ	<DL

Table C.23: Concentrations (µg/g) of OPACs, NPACs, and acids in tyre pyrolysis oil analysed by SFC-ESI-HRMS

Chemical class	Constituent	TP1
OPAC	1,2,3,4-Tetrahydro-1-hydroxynaphthalene	166
OPAC	1,7-Dihydroxynaphthalene	<DL
OPAC	1-Hydroxynaphthalene	<DL
OPAC	1-Hydroxyphenanthrene	<LOQ
OPAC	1-Hydroxypyrene	<DL
OPAC	2,4-Di-tert-butylphenol	4.8
OPAC	2-Hydroxyfluorene	<DL
OPAC	2-Hydroxynaphthalene	<DL

Chemical class	Constituent	TP1
OPAC	2-Hydroxyphenanthrene	<DL
OPAC	2-Methyl-1-hydroxynaphthalene	<DL
OPAC	3,5-Dimethylphenol	<DL
OPAC	3-Hydroxybenzo[a]pyrene	<DL
OPAC	3-Hydroxyfluorene	<DL
OPAC	3-Hydroxyphenanthrene	<LOQ
OPAC	4-Hexylphenol	<DL
OPAC	4-Hydroxyphenanthrene	<LOQ
OPAC	4-Nonylphenol	<DL
OPAC	4-tert-Butylphenol	375
OPAC	9-Hydroxyfluorene	<DL
OPAC	9-Hydroxyphenanthrene	<DL
OPAC	o-Cresol	2297
NPAC	1,4,8-Trimethylcarbazole	<DL
NPAC	1-Methylcarbazole	3.1
NPAC	2,3,6,7-Tetramethylcarbazole	<DL
NPAC	2,3,6-Trimethylcarbazole	<DL
NPAC	2,3-Dimethylindole	93
NPAC	2-tert-Butyl-1H-indole	<DL
NPAC	3-Methylindole	49
NPAC	5-Methylindole	7.9
NPAC	Carbazole	11
NPAC	Indole	122
Acid	1,2,3,4-Tetrahydro-2-naphthoic acid	<DL
Acid	1-Adamantane carboxylic acid	<DL
Acid	1-Hydroxy-2-naphthoic acid	<DL
Acid	1-Naphthoic acid	<DL
Acid	1-Pyrene carboxylic acid	<DL
Acid	2-Naphthoic acid	<DL
Acid	2-Phenanthrene carboxylic acid	<DL
Acid	3,5,7-Trimethyladamantane-1-carboxylic acid	<LOQ
Acid	3-Chrysene carboxylic acid	<DL
Acid	Lauric acid	<LOQ
Acid	Linoleic acid	<DL
Acid	Linolenic acid	<DL
Acid	Oleic acid	<DL
Acid	Palmitoleic acid	<DL
Acid	Pentadecanoic acid	<LOQ
Acid	Stearic acid	<LOQ

C.2.4 GC-MS/SIM constituent groups

Concentrations of the individual constituent groups in each sample are listed for asphalt in Table C.24, for car wax/polish in Table C.25, for coal tar in Table C.26, for lubricating oil in Table C.27 and Table C.28, and for tyre pyrolysis oil in Table C.29.

Table C.24: Concentrations (µg/g) of individual constituent groups in asphalt analysed by GC-MS/SIM

Chemical class	Constituent group	Asp1	Asp2	Asp3	Asp4	Asp5
Saturate	C1-Decalin	<DL	<DL	<DL	<DL	<DL
Saturate	C2-Decalin	<DL	<DL	<DL	<DL	<DL
Saturate	C3-Decalin	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Naphthalene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Naphthalene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Naphthalene	<DL	<DL	<DL	<DL	<DL
Aromatic	C4-Naphthalene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Biphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Biphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Phenanthrene/Anthracene	<LOQ	<DL	<DL	<DL	<DL
Aromatic	C2-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	C4-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Fluoranthene/Pyrene	<DL	<DL	<DL	<LOQ	<LOQ
Aromatic	C3-Fluoranthene/Pyrene	<DL	<DL	<LOQ	<LOQ	<LOQ
Aromatic	C1-Chrysene	<LOQ	<LOQ	<LOQ	2.1	<LOQ
Aromatic	C2-Chrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Chrysene	<DL	<DL	<DL	<DL	<DL
SPAC	C1-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C2-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C3-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C4-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C1-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C2-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C3-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C4-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<DL	<LOQ	<LOQ	<DL	<DL
OPAC	C3-Phenol	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Asp1	Asp2	Asp3	Asp4	Asp5
OPAC	C4-C5-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL	<DL

Table C.25: Concentrations (µg/g) of individual constituent groups in car wax/polish analysed by GC-MS/SIM

Chemical class	Constituent group	CWP1	CWP2	CWP3	CWP4	CWP5
Saturate	C1-Decalin	<DL	3301	<DL	<DL	247
Saturate	C2-Decalin	<DL	1511	<DL	<LOQ	28
Saturate	C3-Decalin	<DL	580	<DL	<DL	<DL
Aromatic	C1-Naphthalene	<DL	47	<DL	0.55	0.48
Aromatic	C2-Naphthalene	<DL	6.4	<DL	<DL	<DL
Aromatic	C3-Naphthalene	<DL	<DL	<DL	<DL	<DL
Aromatic	C4-Naphthalene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Biphenyl	<DL	<LOQ	<DL	<DL	<DL
Aromatic	C2-Biphenyl	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Fluorene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent group	CWP1	CWP2	CWP3	CWP4	CWP5
Aromatic	C4-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Chrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	C2-Chrysene	<DL	<DL	<DL	<DL	<DL
Aromatic	C3-Chrysene	<DL	<DL	<DL	<DL	<DL
SPAC	C1-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C2-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C3-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C4-Benzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C1-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C2-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C3-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
SPAC	C4-Dibenzothiophene	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<LOQ	<LOQ	<DL	<LOQ	<LOQ
OPAC	C3-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C4-C5-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<LOQ	<DL	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Indole	<LOQ	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL	<DL

Table C.26: Concentrations (µg/g) of individual constituent groups in coal tar analysed by GC-MS/SIM

Chemical class	Constituent group	CT1	CT2	CT3	CT4	CT5
Saturate	C1-Decalin	64	168	<DL	<DL	<DL
Saturate	C2-Decalin	<DL	<DL	<DL	<DL	<DL
Saturate	C3-Decalin	<DL	<DL	<DL	<DL	<DL
Aromatic	C1-Naphthalene	260	2484	1569	31192	11396
Aromatic	C2-Naphthalene	193	2936	1998	8392	1987
Aromatic	C3-Naphthalene	208	2471	1873	2360	473
Aromatic	C4-Naphthalene	153	1527	1158	434	<DL
Aromatic	C1-Biphenyl	21	183	154	3021	877
Aromatic	C2-Biphenyl	111	1438	1048	10579	3172
Aromatic	C1-Fluorene	83	793	567	5531	1144
Aromatic	C2-Fluorene	173	874	603	1780	<DL
Aromatic	C3-Fluorene	305	804	472	1119	<DL
Aromatic	C1-Phenanthrene/Anthracene	487	1259	898	12864	4355
Aromatic	C2-Phenanthrene/Anthracene	999	1511	1076	3448	950
Aromatic	C3-Phenanthrene/Anthracene	1528	1459	1172	1004	<LOQ
Aromatic	C4-Phenanthrene/Anthracene	1390	1304	1194	<LOQ	<DL
Aromatic	C1-Fluoranthene/Pyrene	2585	1281	891	12695	8428
Aromatic	C2-Fluoranthene/Pyrene	4849	1142	735	2182	1065
Aromatic	C3-Fluoranthene/Pyrene	4753	772	504	<LOQ	<DL
Aromatic	C1-Chrysene	5734	333	267	707	1546
Aromatic	C2-Chrysene	8180	345	263	<DL	<DL
Aromatic	C3-Chrysene	5555	<DL	<DL	<DL	<DL
SPAC	C1-Benzothiophene	69	93	52	1160	435
SPAC	C2-Benzothiophene	288	230	177	675	<LOQ
SPAC	C3-Benzothiophene	342	<LOQ	<DL	<DL	<DL
SPAC	C4-Benzothiophene	<LOQ	<DL	<DL	<DL	<DL
SPAC	C1-Dibenzothiophene	317	119	82	1475	385
SPAC	C2-Dibenzothiophene	977	<DL	<DL	<LOQ	<LOQ
SPAC	C3-Dibenzothiophene	2340	<DL	<DL	<DL	<DL
SPAC	C4-Dibenzothiophene	1236	<DL	<DL	<DL	<DL
OPAC	C1-Phenol	<LOQ	22999	13107	<LOQ	<LOQ
OPAC	C2-Phenol	<LOQ	12685	<LOQ	<LOQ	<LOQ
OPAC	C3-Phenol	<LOQ	5269	3099	<LOQ	<DL
OPAC	C4-C5-Phenol	<LOQ	<LOQ	<LOQ	<LOQ	<DL
OPAC	C1-Dibenzofuran	<DL	132.3	<DL	<LOQ	<DL
OPAC	C1-Hydroxynaphthalene	<LOQ	4764	3268	659	<LOQ
OPAC	C2-Hydroxynaphthalene	<LOQ	4331	2950	<LOQ	<DL
OPAC	C3-Hydroxynaphthalene	<LOQ	<LOQ	<LOQ	<LOQ	<DL

Chemical class	Constituent group	CT1	CT2	CT3	CT4	CT5
OPAC	C4-Hydroxynaphthalene	<DL	<LOQ	<LOQ	<LOQ	<LOQ
OPAC	C1-Hydroxyphenanthrene	607	3997	2112	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	864	6515	3309	<LOQ	<DL
NPAC	C1-Quinoline	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
NPAC	C2-Quinoline	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
NPAC	C3-Quinoline	<LOQ	<LOQ	<LOQ	<LOQ	<DL
NPAC	C1-Indole	<DL	<LOQ	<DL	<LOQ	<LOQ
NPAC	C2-Indole	<LOQ	908	<LOQ	<LOQ	<DL
NPAC	C1-Carbazole	38.9	968	550	1982	732
NPAC	C2-Carbazole	39.6	<LOQ	<LOQ	665	<LOQ
NPAC	C3-Carbazole	159.4	397	<DL	<DL	<DL
NPAC	C4-Carbazole	240	<LOQ	<LOQ	<DL	<DL
NPAC	C1-Benzocarbazole	1392	885	393	213	595
NPAC	C2-Benzocarbazole	1934	<DL	<DL	<DL	<LOQ
NPAC	C3-Benzocarbazole	2265	<DL	<DL	<DL	<LOQ

Table C.27: Concentrations (µg/g) of individual constituent groups in lubricating oil (Lub1 – Lun4) analysed by GC-MS/SIM

Chemical class	Constituent group	Lub1	Lub2	Lub3	Lub4
Saturate	C1-Decalin	<DL	<DL	4.0	<DL
Saturate	C2-Decalin	<DL	<DL	<DL	<DL
Saturate	C3-Decalin	<DL	<DL	<DL	<DL
Aromatic	C1-Naphthalene	7.9	<DL	<DL	<DL
Aromatic	C2-Naphthalene	15	<DL	<DL	<DL
Aromatic	C3-Naphthalene	14	<LOQ	<DL	<DL
Aromatic	C4-Naphthalene	7.4	<DL	<DL	<DL
Aromatic	C1-Biphenyl	4.7	<LOQ	<DL	<LOQ
Aromatic	C2-Biphenyl	7.0	<LOQ	<LOQ	<LOQ
Aromatic	C1-Fluorene	1.7	<DL	<DL	<DL
Aromatic	C2-Fluorene	<LOQ	<DL	<DL	<DL
Aromatic	C3-Fluorene	<DL	<DL	<DL	<DL
Aromatic	C1-Phenanthrene/Anthracene	4.5	<DL	<DL	<DL
Aromatic	C2-Phenanthrene/Anthracene	5.1	<DL	<DL	<DL
Aromatic	C3-Phenanthrene/Anthracene	<LOQ	<DL	<DL	<DL
Aromatic	C4-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL
Aromatic	C1-Fluoranthene/Pyrene	<LOQ	<DL	<DL	<DL
Aromatic	C2-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL
Aromatic	C3-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL
Aromatic	C1-Chrysene	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Lub1	Lub2	Lub3	Lub4
Aromatic	C2-Chrysene	<DL	<DL	<DL	<DL
Aromatic	C3-Chrysene	<DL	<DL	<DL	<DL
SPAC	C1-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C2-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C3-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C4-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C1-Dibenzothiophene	<DL	<DL	<DL	<DL
SPAC	C2-Dibenzothiophene	<DL	<DL	<DL	<DL
SPAC	C3-Dibenzothiophene	<DL	<DL	<DL	<DL
SPAC	C4-Dibenzothiophene	<DL	<DL	<DL	<DL
OPAC	C1-Phenol	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<LOQ	<LOQ	<LOQ	<LOQ
OPAC	C3-Phenol	<DL	<DL	<DL	<DL
OPAC	C4-C5-Phenol	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<LOQ	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<LOQ	<LOQ	<LOQ
NPAC	C2-Indole	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL

Table C.28: Concentrations (µg/g) of individual constituent groups in lubricating oil (Lub5 – Lub8) analysed by GC-MS/SIM

Chemical class	Constituent group	Lub5	Lub6	Lub7	Lub8
Saturate	C1-Decalin	4.5	<DL	4.0	15
Saturate	C2-Decalin	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Lub5	Lub6	Lub7	Lub8
Saturate	C3-Decalin	<DL	<DL	<DL	<DL
Aromatic	C1-Naphthalene	2.8	<DL	2.0	<LOQ
Aromatic	C2-Naphthalene	5.0	<DL	<DL	<DL
Aromatic	C3-Naphthalene	4.8	<DL	<DL	<LOQ
Aromatic	C4-Naphthalene	4.4	<DL	<DL	<DL
Aromatic	C1-Biphenyl	2.3	<LOQ	<LOQ	<LOQ
Aromatic	C2-Biphenyl	5.3	<LOQ	<DL	<LOQ
Aromatic	C1-Fluorene	2.9	<DL	<DL	<DL
Aromatic	C2-Fluorene	8.3	<DL	<DL	<DL
Aromatic	C3-Fluorene	12	<DL	<DL	<DL
Aromatic	C1-Phenanthrene/Anthracene	2.9	<DL	<DL	<LOQ
Aromatic	C2-Phenanthrene/Anthracene	<LOQ	<DL	<DL	<LOQ
Aromatic	C3-Phenanthrene/Anthracene	<LOQ	<DL	<DL	<LOQ
Aromatic	C4-Phenanthrene/Anthracene	<DL	<DL	<DL	<DL
Aromatic	C1-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL
Aromatic	C2-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL
Aromatic	C3-Fluoranthene/Pyrene	<DL	<DL	<DL	<DL
Aromatic	C1-Chrysene	<DL	<DL	<DL	<DL
Aromatic	C2-Chrysene	<DL	<DL	<DL	<DL
Aromatic	C3-Chrysene	<DL	<DL	<DL	<DL
SPAC	C1-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C2-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C3-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C4-Benzothiophene	<DL	<DL	<DL	<DL
SPAC	C1-Dibenzothiophene	2.68	<DL	<DL	<DL
SPAC	C2-Dibenzothiophene	7.41	<DL	<DL	<LOQ
SPAC	C3-Dibenzothiophene	<LOQ	<DL	<DL	<LOQ
SPAC	C4-Dibenzothiophene	<DL	<DL	<DL	<LOQ
OPAC	C1-Phenol	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<DL	<DL	<DL	<DL
OPAC	C3-Phenol	<DL	<DL	<DL	<DL
OPAC	C4-C5-Phenol	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Lub5	Lub6	Lub7	Lub8
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<LOQ
NPAC	C2-Indole	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL

Table C.29: Concentrations (µg/g) of individual constituent groups in tyre pyrolysis oil analysed by GC-MS/SIM

Chemical class	Constituent group	TP1
Saturate	C1-Decalin	<DL
Saturate	C2-Decalin	<DL
Saturate	C3-Decalin	<DL
Aromatic	C1-Naphthalene	12110
Aromatic	C2-Naphthalene	10511
Aromatic	C3-Naphthalene	6573
Aromatic	C4-Naphthalene	1925
Aromatic	C1-Biphenyl	1807
Aromatic	C2-Biphenyl	1578
Aromatic	C1-Fluorene	920
Aromatic	C2-Fluorene	884
Aromatic	C3-Fluorene	<DL
Aromatic	C1-Phenanthrene/Anthracene	451
Aromatic	C2-Phenanthrene/Anthracene	<LOQ
Aromatic	C3-Phenanthrene/Anthracene	<LOQ
Aromatic	C4-Phenanthrene/Anthracene	<DL
Aromatic	C1-Fluoranthene/Pyrene	<LOQ
Aromatic	C2-Fluoranthene/Pyrene	<DL
Aromatic	C3-Fluoranthene/Pyrene	<DL
Aromatic	C1-Chrysene	<DL
Aromatic	C2-Chrysene	<DL
Aromatic	C3-Chrysene	<DL
SPAC	C1-Benzothiophene	804
SPAC	C2-Benzothiophene	2575

Chemical class	Constituent group	TP1
SPAC	C3-Benzothiophene	1188
SPAC	C4-Benzothiophene	<LOQ
SPAC	C1-Dibenzothiophene	<LOQ
SPAC	C2-Dibenzothiophene	<DL
SPAC	C3-Dibenzothiophene	<DL
SPAC	C4-Dibenzothiophene	<DL
OPAC	C1-Phenol	<LOQ
OPAC	C2-Phenol	<LOQ
OPAC	C3-Phenol	<LOQ
OPAC	C4-C5-Phenol	<LOQ
OPAC	C1-Dibenzofuran	<DL
OPAC	C1-Hydroxynaphthalene	<DL
OPAC	C2-Hydroxynaphthalene	<DL
OPAC	C3-Hydroxynaphthalene	<DL
OPAC	C4-Hydroxynaphthalene	<DL
OPAC	C1-Hydroxyphenanthrene	<DL
OPAC	C2-Hydroxyphenanthrene	<DL
NPAC	C1-Quinoline	<LOQ
NPAC	C2-Quinoline	4814
NPAC	C3-Quinoline	<LOQ
NPAC	C1-Indole	<DL
NPAC	C2-Indole	<DL
NPAC	C1-Carbazole	<DL
NPAC	C2-Carbazole	<DL
NPAC	C3-Carbazole	<DL
NPAC	C4-Carbazole	<DL
NPAC	C1-Benzocarbazole	<DL
NPAC	C2-Benzocarbazole	<DL
NPAC	C3-Benzocarbazole	<DL

C.2.5 GC×GC-HRMS constituent groups

Concentrations of the individual constituent groups in each sample analysed by GCxGC-HRMS are listed in Table C.30 for asphalt, in Table C.31 for car wax/polish, in Table C.32 for coal tar, in Table C.33 and Table C.34 for lubricating oil, and in Table C.35 for tyre pyrolysis oil.

Table C.30: Concentrations (µg/g) of individual constituent groups in asphalt analysed by GCxGC-HRMS

Chemical class	Constituent group	Asp1	Asp2	Asp3	Asp4	Asp5
OPAC	C1-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C3-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C4-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C5-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C6-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C7-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C8-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C9-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Benzofuran	<DL	<DL	<DL	<DL	<LOQ
OPAC	C4-Benzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C5-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Asp1	Asp2	Asp3	Asp4	Asp5
NPAC	C4-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzoacridine	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzoacridine	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzothiazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Diphenylamine	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Tetrahydroquinolines	<DL	<DL	<DL	<DL	<DL

Table C.31: Concentrations (µg/g) of individual constituent groups in car wax/polish analysed by GCxGC-HRMS

Chemical class	Constituent group	CWP1	CWP2	CWP3	CWP4	CWP5
OPAC	C1-Phenol	<LOQ	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<DL	<DL	<DL	<LOQ	<DL
OPAC	C3-Phenol	<DL	<DL	<DL	<LOQ	<DL
OPAC	C4-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C5-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C6-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C7-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C8-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C9-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Benzofuran	<DL	<DL	<DL	<DL	<LOQ
OPAC	C4-Benzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C5-Hydroxynaphthalene	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzonitrile	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Benzonitrile	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent group	CWP1	CWP2	CWP3	CWP4	CWP5
NPAC	C1-Quinoline	<DL	<LOQ	<DL	<DL	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Quinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Indole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzoacridine	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzoacridine	<DL	<LOQ	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Benzothiazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Diphenylamine	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Tetrahydroquinolines	<DL	<DL	<DL	<DL	<DL

Table C.32: Concentrations (µg/g) of individual constituent groups in coal tar analysed by GCxGC-HRMS

Chemical class	Constituent group	CT1	CT2	CT3	CT4	CT5
OPAC	C1-Phenol	14	19123	13523	851	1509
OPAC	C2-Phenol	<LOQ	28757	17258	1213	861
OPAC	C3-Phenol	<DL	6470	3417	<LOQ	<DL
OPAC	C4-Phenol	<LOQ	3614	1787	<LOQ	<DL
OPAC	C5-Phenol	<LOQ	1156	476	<DL	<DL
OPAC	C6-Phenol	<DL	<LOQ	<DL	<DL	<DL
OPAC	C7-Phenol	<DL	<LOQ	<DL	<DL	<DL
OPAC	C8-Phenol	<LOQ	<LOQ	<DL	<DL	<DL
OPAC	C9-Phenol	<DL	<DL	<DL	<DL	<DL
OPAC	C1-Benzofuran	<DL	1206	289	<DL	<DL
OPAC	C4-Benzofuran	<DL	<DL	<DL	<DL	<DL

Chemical class	Constituent group	CT1	CT2	CT3	CT4	CT5
OPAC	C1-Dibenzofuran	<DL	95	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	3780	2126	<LOQ	<DL
OPAC	C2-Hydroxynaphthalene	<DL	6925	4298	<LOQ	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<LOQ	<LOQ	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<LOQ	<DL	<DL	<DL
OPAC	C5-Hydroxynaphthalene	<LOQ	<LOQ	<LOQ	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	400	6284	2400	<LOQ	<DL
OPAC	C2-Hydroxyphenanthrene	689	4732	<LOQ	<DL	<DL
NPAC	C1-Benzonitrile	<DL	<LOQ	<LOQ	<DL	160
NPAC	C2-Benzonitrile	<DL	<LOQ	<DL	<LOQ	<DL
NPAC	C3-Benzonitrile	<DL	<LOQ	<LOQ	69	<LOQ
NPAC	C1-Quinoline	<DL	<LOQ	<LOQ	1202	<LOQ
NPAC	C2-Quinoline	<DL	<LOQ	<LOQ	<LOQ	<DL
NPAC	C3-Quinoline	<LOQ	<LOQ	<LOQ	<LOQ	<DL
NPAC	C4-Quinoline	8.8	223	<LOQ	<LOQ	<DL
NPAC	C1-Indole	<DL	<LOQ	<DL	-56	<LOQ
NPAC	C2-Indole	<DL	513	<LOQ	<LOQ	<LOQ
NPAC	C3-Indole	<LOQ	166	<LOQ	<DL	<DL
NPAC	C4-Indole	<LOQ	<LOQ	<LOQ	<LOQ	<DL
NPAC	C1-Acridine/Benzoquinoline	<LOQ	<DL	<DL	<LOQ	<DL
NPAC	C2-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL	<DL
NPAC	C3-Acridine/Benzoquinoline	173	<DL	<DL	<DL	<DL
NPAC	C4-Acridine/Benzoquinoline	877	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	31	<LOQ	<LOQ	985	490
NPAC	C2-Carbazole	24	<LOQ	<DL	<LOQ	<DL
NPAC	C3-Carbazole	434	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	380	<LOQ	<DL	<DL	<DL
NPAC	C1-Benzoacridine	1429	586	<LOQ	537	1375
NPAC	C2-Benzoacridine	589	<LOQ	<DL	<DL	<LOQ
NPAC	C1-Benzocarbazole	1086	<LOQ	<DL	<DL	<LOQ
NPAC	C2-Benzocarbazole	1521	<LOQ	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	1201	<DL	<DL	<DL	<DL
NPAC	C1-Benzothiazole	<DL	<DL	<DL	<DL	<DL
NPAC	C1-Diphenylamine	0.78	<LOQ	<DL	54	<DL
NPAC	C3-Tetrahydroquinolines	<DL	<LOQ	<LOQ	<DL	<DL

Table C.33: Concentrations (µg/g) of individual constituent groups in lubricating oil (Lub1 – Lub4) analysed by GCxGC-HRMS

Chemical class	Constituent group	Lub1	Lub2	Lub3	Lub4
OPAC	C1-Phenol	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<DL	<DL	<DL	<DL
OPAC	C3-Phenol	<DL	<DL	<DL	<DL
OPAC	C4-Phenol	<DL	<DL	<DL	<DL
OPAC	C5-Phenol	<DL	<DL	<DL	<DL
OPAC	C6-Phenol	<DL	<DL	<DL	<DL
OPAC	C7-Phenol	<DL	<DL	<DL	<DL
OPAC	C8-Phenol	<DL	<DL	<LOQ	<DL
OPAC	C9-Phenol	<DL	<DL	<DL	<DL
OPAC	C1-Benzofuran	<DL	<DL	<DL	<DL
OPAC	C4-Benzofuran	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C5-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
NPAC	C1-Benzonitrile	<DL	<DL	<DL	<DL
NPAC	C2-Benzonitrile	<DL	<DL	<DL	<DL
NPAC	C3-Benzonitrile	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<DL	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL
NPAC	C4-Quinoline	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<DL
NPAC	C2-Indole	<DL	<DL	<DL	<DL
NPAC	C3-Indole	<DL	<DL	<DL	<DL
NPAC	C4-Indole	<DL	<LOQ	<DL	<DL
NPAC	C1-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C2-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C3-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C4-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Lub1	Lub2	Lub3	Lub4
NPAC	C1-Benzoacridine	<DL	<DL	<DL	<DL
NPAC	C2-Benzoacridine	<DL	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C1-Benzothiazole	<DL	<DL	<DL	<DL
NPAC	C1-Diphenylamine	<DL	<DL	<DL	<DL
NPAC	C3-Tetrahydroquinolines	<DL	<DL	<DL	<DL

Table C.34: Concentrations (µg/g) of individual constituent groups in lubricating oil (Lub5 – Lub8) analysed by GCxGC-HRMS

Chemical class	Constituent group	Lub5	Lub6	Lub7	Lub8
OPAC	C1-Phenol	<DL	<DL	<DL	<DL
OPAC	C2-Phenol	<DL	<DL	<DL	<DL
OPAC	C3-Phenol	<DL	<DL	<DL	<DL
OPAC	C4-Phenol	<DL	<DL	<DL	<DL
OPAC	C5-Phenol	<DL	<DL	<DL	<DL
OPAC	C6-Phenol	<DL	<DL	<DL	<DL
OPAC	C7-Phenol	<DL	<DL	<DL	<DL
OPAC	C8-Phenol	<DL	<DL	<DL	<DL
OPAC	C9-Phenol	<DL	<LOQ	<DL	<DL
OPAC	C1-Benzofuran	<DL	<DL	<DL	<DL
OPAC	C4-Benzofuran	<DL	<DL	<DL	<DL
OPAC	C1-Dibenzofuran	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C3-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C4-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C5-Hydroxynaphthalene	<DL	<DL	<DL	<DL
OPAC	C1-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
OPAC	C2-Hydroxyphenanthrene	<DL	<DL	<DL	<DL
NPAC	C1-Benzonitrile	<DL	<DL	<DL	<DL
NPAC	C2-Benzonitrile	<DL	<DL	<DL	<DL
NPAC	C3-Benzonitrile	<DL	<DL	<DL	<DL
NPAC	C1-Quinoline	<DL	<DL	<DL	<DL
NPAC	C2-Quinoline	<DL	<DL	<DL	<DL
NPAC	C3-Quinoline	<DL	<DL	<DL	<DL
NPAC	C4-Quinoline	<DL	<DL	<DL	<DL
NPAC	C1-Indole	<DL	<DL	<DL	<DL

Chemical class	Constituent group	Lub5	Lub6	Lub7	Lub8
NPAC	C2-Indole	<DL	<DL	<DL	<DL
NPAC	C3-Indole	<DL	<DL	<DL	<DL
NPAC	C4-Indole	<DL	<DL	<DL	<DL
NPAC	C1-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C2-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C3-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C4-Acridine/Benzoquinoline	<DL	<DL	<DL	<DL
NPAC	C1-Carbazole	<DL	<DL	<DL	<DL
NPAC	C2-Carbazole	<DL	<DL	<DL	<DL
NPAC	C3-Carbazole	<DL	<DL	<DL	<DL
NPAC	C4-Carbazole	<DL	<DL	<DL	<DL
NPAC	C1-Benzoacridine	<DL	<DL	<DL	<DL
NPAC	C2-Benzoacridine	<LOQ	<DL	<DL	<DL
NPAC	C1-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C2-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C3-Benzocarbazole	<DL	<DL	<DL	<DL
NPAC	C1-Benzothiazole	<DL	<DL	<DL	<DL
NPAC	C1-Diphenylamine	<DL	<DL	<DL	<DL
NPAC	C3-Tetrahydroquinolines	<DL	<DL	<DL	<DL

Table C.35: Concentrations (µg/g) of individual constituent groups in tyre pyrolysis oil analysed by GCxGC-HRMS

Chemical class	Constituent group	TP1
OPAC	C1-Phenol	1557
OPAC	C2-Phenol	2447
OPAC	C3-Phenol	554
OPAC	C4-Phenol	1114
OPAC	C5-Phenol	326
OPAC	C6-Phenol	47
OPAC	C7-Phenol	47
OPAC	C8-Phenol	51
OPAC	C9-Phenol	16
OPAC	C1-Benzofuran	399
OPAC	C4-Benzofuran	<LOQ
OPAC	C1-Dibenzofuran	4.3
OPAC	C1-Hydroxynaphthalene	<LOQ
OPAC	C2-Hydroxynaphthalene	<DL
OPAC	C3-Hydroxynaphthalene	<DL
OPAC	C4-Hydroxynaphthalene	<DL

Chemical class	Constituent group	TP1
OPAC	C5-Hydroxynaphthalene	<LOQ
OPAC	C1-Hydroxyphenanthrene	<DL
OPAC	C2-Hydroxyphenanthrene	<DL
NPAC	C1-Benzonitrile	664
NPAC	C2-Benzonitrile	560
NPAC	C3-Benzonitrile	109
NPAC	C1-Quinoline	204
NPAC	C2-Quinoline	363
NPAC	C3-Quinoline	282
NPAC	C4-Quinoline	171
NPAC	C1-Indole	500
NPAC	C2-Indole	229
NPAC	C3-Indole	115
NPAC	C4-Indole	526
NPAC	C1-Acridine/Benzoquinoline	<LOQ
NPAC	C2-Acridine/Benzoquinoline	<DL
NPAC	C3-Acridine/Benzoquinoline	<LOQ
NPAC	C4-Acridine/Benzoquinoline	<DL
NPAC	C1-Carbazole	<LOQ
NPAC	C2-Carbazole	<LOQ
NPAC	C3-Carbazole	<DL
NPAC	C4-Carbazole	<DL
NPAC	C1-Benzoacridine	<LOQ
NPAC	C2-Benzoacridine	<DL
NPAC	C1-Benzocarbazole	<DL
NPAC	C2-Benzocarbazole	<DL
NPAC	C3-Benzocarbazole	<DL
NPAC	C1-Benzothiazole	2139
NPAC	C1-Diphenylamine	21
NPAC	C3-Tetrahydroquinolines	60

C.3 Chemical composition of the samples

The chemical composition of the samples are presented in Figure C.2 for asphalt, in Figure C.3 for car wax/polish, in Figure C.4 for coal tar, in Figure C.5 and Figure C.6 for lubricating oil, and in Figure C.7 for tyre pyrolysis oil. The constituent abbreviations are listed in Table C.36.

Table C.36: List of abbreviations for constituents and constituent groups

Chemical class	Abbreviation	Constituent/constituent groups
Saturate	C1-De	C1-Decalins
Saturate	C2-De	C2-Decalins
Saturate	C3-De	C3-Decalins
Saturate	Other	Other saturates (1,3-dimethyladamantane, adamantane, and butylcyclohexane)
Aromatic	BP	Biphenyl
Aromatic	C1-BP	C1-Biphenyl
Aromatic	C2-BP	C2-Biphenyl
Aromatic	N	Naphthalene
Aromatic	C1-N	C1-Naphthalene
Aromatic	C2-N	C2-Naphthalene
Aromatic	C3-N	C3-Naphthalene
Aromatic	C4-N	C4-Naphthalene
Aromatic	Phen/An	Phenanthrene + Anthracene
Aromatic	C1-Phen/An	C1-Phenanthrene/anthracene
Aromatic	C2-Phen/An	C2-Phenanthrene/anthracene
Aromatic	C3-Phen/An	C3-Phenanthrene/anthracene
Aromatic	C4-Phen/An	C4-Phenanthrene/anthracene
Aromatic	F	Fluorene
Aromatic	C1-F	C1-Fluorene
Aromatic	C2-F	C2-Fluorene
Aromatic	C3-F	C3-Fluorene
Aromatic	Flu/Py	Fluoranthene + Pyrene
Aromatic	C1-Flu/Py	C1-Fluoranthene/pyrene
Aromatic	C2-Flu/Py	C2-Fluoranthene/pyrene
Aromatic	C3-Flu/Py	C3-Fluoranthene/pyrene
Aromatic	Ch	Chrysene
Aromatic	C1-Ch	C1-Chrysene
Aromatic	C2-Ch	C2-Chrysene
Aromatic	C3-Ch	C3-Chrysene
Aromatic	5-6 ring PAHs	5-6 ring PAHs (benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[g,h,i]perylene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-c,d]pyrene, perylene)
Aromatic	Other	Other aromatics (tetralin, 1-phenylheptane, 1-phenylnonane, 1-phenyloctane, 2,2,5,7-tetramethyltetralin, 3,3',5,5'-tetramethylbiphenyl, 4-n-pentylbiphenyl, acenaphthene, acenaphthylene, butylbenzene, hexylbenzene)
SPAC	BT	1-Benzothiophene

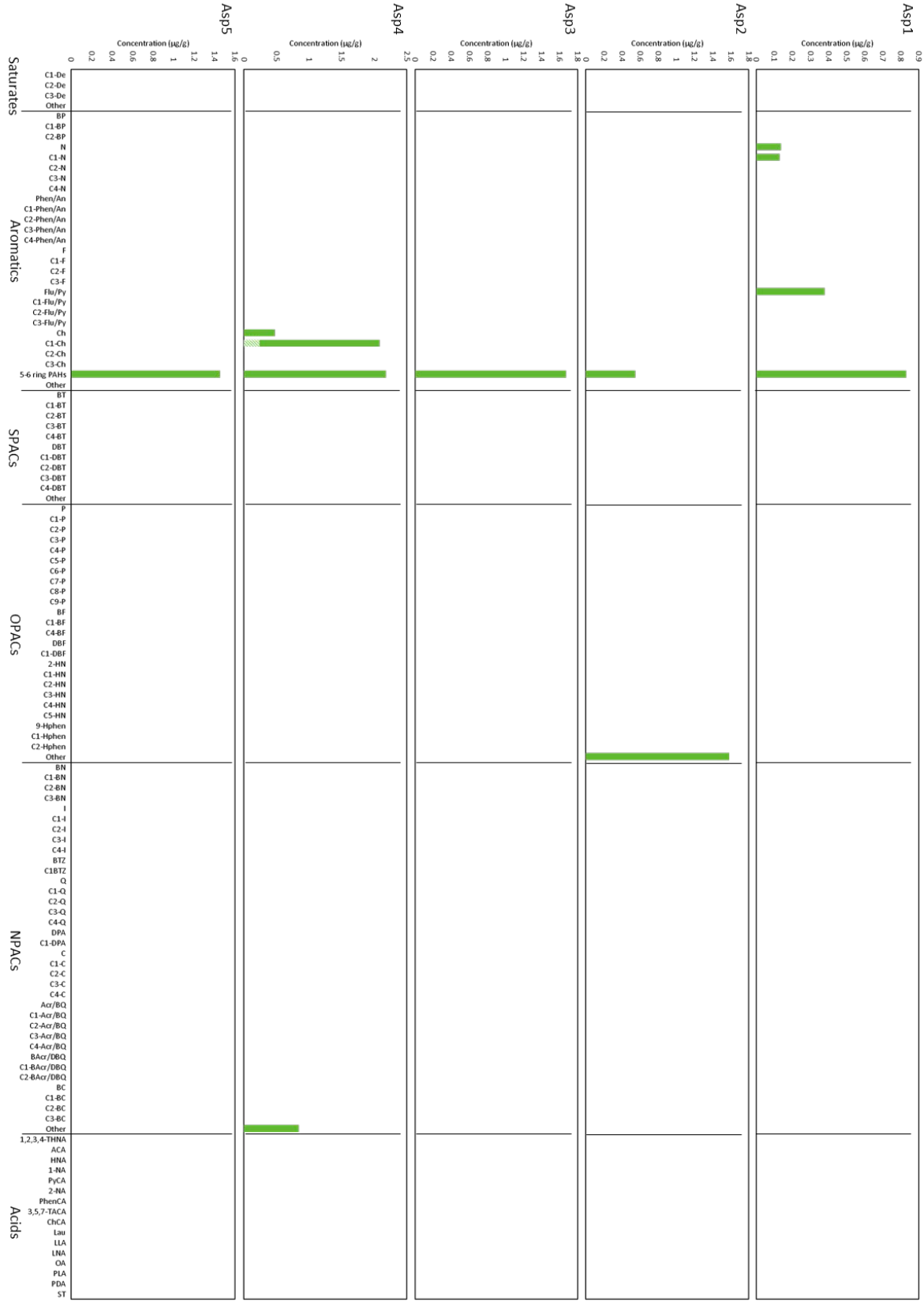
Chemical class	Abbreviation	Constituent/constituent groups
SPAC	C1-BT	C1-Benzothiophene
SPAC	C2-BT	C2-Benzothiophene
SPAC	C3-BT	C3-Benzothiophene
SPAC	C4-BT	C4-Benzothiophene
SPAC	DBT	Dibenzothiophene
SPAC	C1-DBT	C1-Dibenzothiophene
SPAC	C2-DBT	C2-Dibenzothiophene
SPAC	C3-DBT	C3-Dibenzothiophene
SPAC	C4-DBT	C4-Dibenzothiophene
SPAC	Other	Other SPACs (7-methylbenzo[b]naphtho[2,3-d]thiophene)
OPAC	P	Phenol
OPAC	C1-P	C1 Phenols
OPAC	C2-P	C2 Phenols
OPAC	C3-P	C3 Phenols
OPAC	C4-P	C4 Phenols
OPAC	C5-P	C5 Phenols
OPAC	C6-P	C6 Phenols
OPAC	C7-P	C7 Phenols
OPAC	C8-P	C8 Phenols
OPAC	C9-P	C9 Phenols
OPAC	BF	2,3-Benzofuran
OPAC	C1-BF	C1 Benzofurans
OPAC	C4-BF	C4 Benzofurans
OPAC	DBF	Dibenzofuran
OPAC	C1-DBF	C1 Dibenzofurans
OPAC	2-HN	2-hydroxynaphthalene
OPAC	C1-HN	C1 Hydroxynaphthalenes
OPAC	C2-HN	C2 Hydroxynaphthalenes
OPAC	C3-HN	C3 Hydroxynaphthalenes
OPAC	C4-HN	C4 Hydroxynaphthalenes
OPAC	C5-HN	C5 Hydroxynaphthalenes
OPAC	9-Hphen	9-hydroxyphenanthrene
OPAC	C1-Hphen	C1 Hydroxyphenanthrenes
OPAC	C2-Hphen	C2 Hydroxyphenanthrenes
OPAC	Other	Other OPACs (1,2,3,4-tetrahydro-1-hydroxynaphthalene, dibenzofuranols, indanols, naphthaldehyde, 1-hydroxynaphthalene, 1,7-dihydroxynaphthalene, 2-methyl-1-hydroxynaphthalene, 1-hydroxyphenanthrene, 1-hydroxypyrene, 2-hydroxyfluorene, 3-hydroxybenzo[a]pyrene, 3-hydroxyfluorene, 2-hydroxyphenanthrene, 3-hydroxyphenanthrene, 4-hydroxyphenanthrene, 9-hydroxyfluorene)
NPAC	BN	Benzonitrile
NPAC	C1-BN	C1 Benzonitriles

Chemical class	Abbreviation	Constituent/constituent groups
NPAC	C2-BN	C2 Benzonitriles
NPAC	C3-BN	C3 Benzonitriles
NPAC	I	Indole
NPAC	C1-I	C1 Indoles
NPAC	C2-I	C2 Indoles
NPAC	C3-I	C3 Indoles
NPAC	C4-I	C4 Indoles
NPAC	BTZ	Benzothiazole
NPAC	C1-BTZ	C1 Benzothiazoles
NPAC	Q	Quinoline
NPAC	C1-Q	C1 Quinolines
NPAC	C2-Q	C2 Quinolines
NPAC	C3-Q	C3 Quinolines
NPAC	C4-Q	C4 Quinolines
NPAC	DPA	Diphenylamine
NPAC	C1-DPA	C1 Diphenylamines
NPAC	C	Carbazole
NPAC	C1-C	C1 Carbazoles
NPAC	C2-C	C2 Carbazoles
NPAC	C3-C	C3 Carbazoles
NPAC	C4-C	C4 Carbazoles
NPAC	Acr/BQ	Acridine + Benzo[h]quinoline
NPAC	C1-Acr/BQ	C1 Acridines/Benzoquinolines
NPAC	C2-Acr/BQ	C2 Acridines/Benzoquinolines
NPAC	C3-Acr/BQ	C3 Acridines/Benzoquinolines
NPAC	C4-Acr/BQ	C4 Acridines/Benzoquinolines
NPAC	BAcr/DBQ	Benzo[c]acridine + Dibenzo[f,h]quinoline
NPAC	C1-BAcr/DBQ	C1 Benzoacridines
NPAC	C2-BAcr/DBQ	C2 Benzoacridines
NPAC	BC	11H-Benzo[a]carbazole
NPAC	C1-BC	C1 Benzocarbazoles
NPAC	C2-BC	C2 Benzocarbazoles
NPAC	C3-BC	C3 Benzocarbazoles
NPAC	Other	Other NPACs ((Tere)phthalonitrile, C3-tetrahydroquinolines, dibenzo[a,h]acridine, diethyl-a-naphthylamine)
Acid	1,2,3,4-THNA	1,2,3,4-Tetrahydro-2-naphthoic acid
Acid	ACA	1-Adamantane carboxylic acid
Acid	HNA	1-Hydroxy-2-naphthoic acid
Acid	1-NA	1-Naphthoic acid
Acid	PyCA	1-Pyrene carboxylic acid
Acid	2-NA	2-Naphthoic acid

Chemical class	Abbreviation	Constituent/constituent groups
Acid	PhenCA	2-Phenanthrene carboxylic acid
Acid	3,5,7-TACA	3,5,7-Trimethyladamantane-1-carboxylic acid
Acid	ChCA	3-Chrysene carboxylic acid
Acid	Lau	Lauric acid
Acid	LLA	Linoleic acid
Acid	LNA	Linolenic acid
Acid	OA	Oleic acid
Acid	PLA	Palmitoleic acid
Acid	PDA	Pentadecanoic acid
Acid	ST	Stearic acid

Figure C.2: Detailed chemical composition of asphalt samples

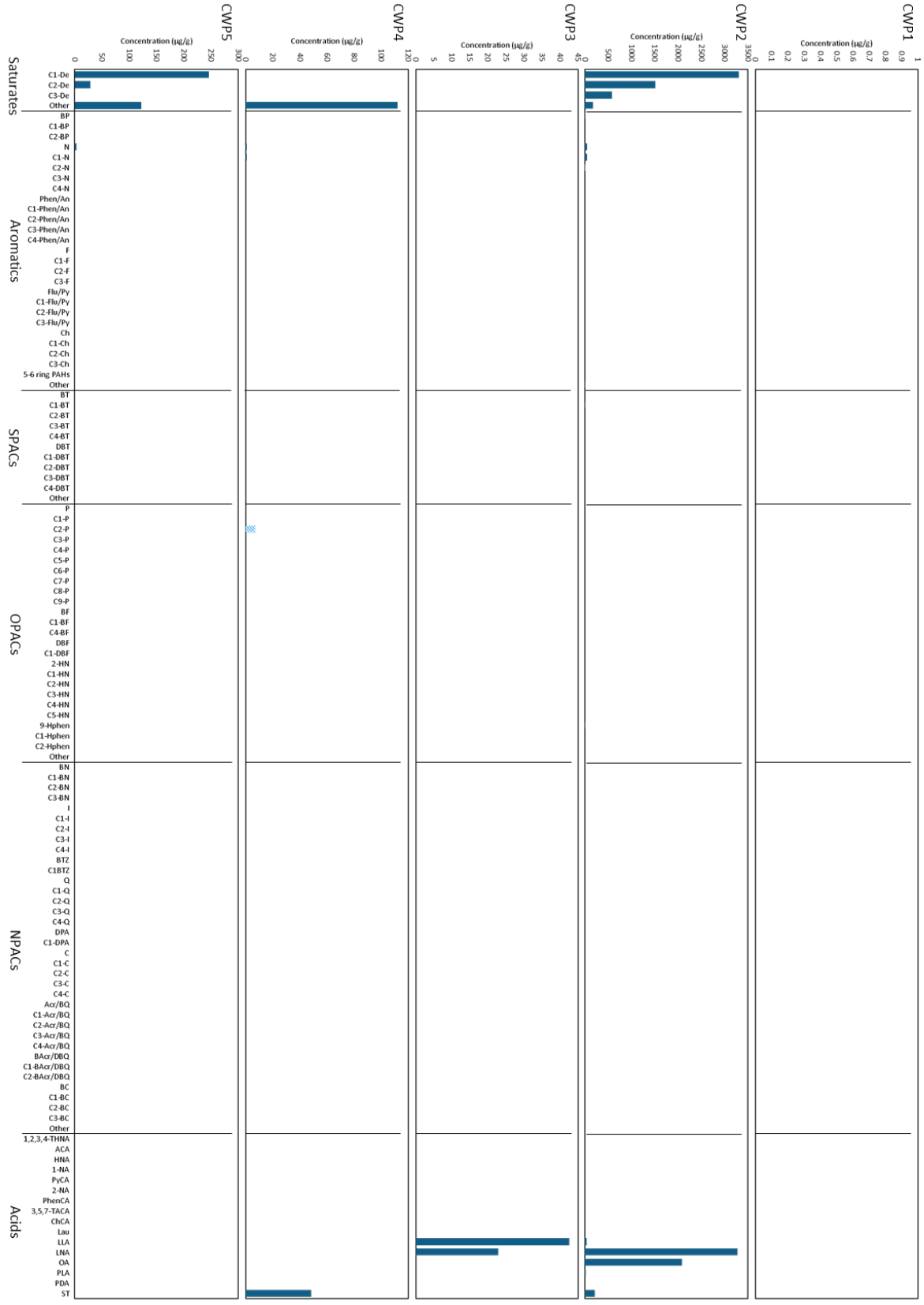
Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure C.3: Detailed chemical composition of individual car wax/polish samples

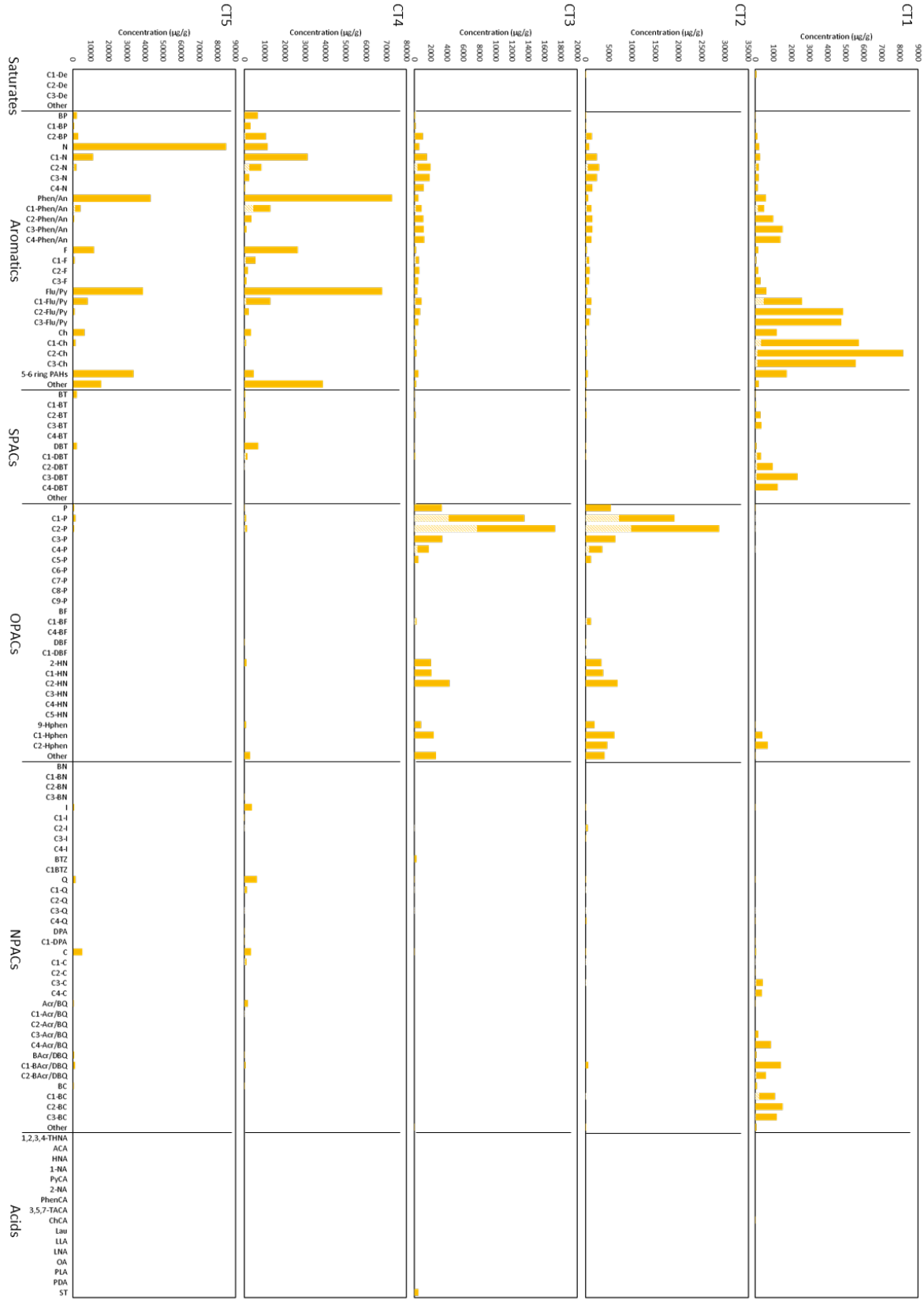
Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure C.4: Detailed chemical composition of individual coal tar samples

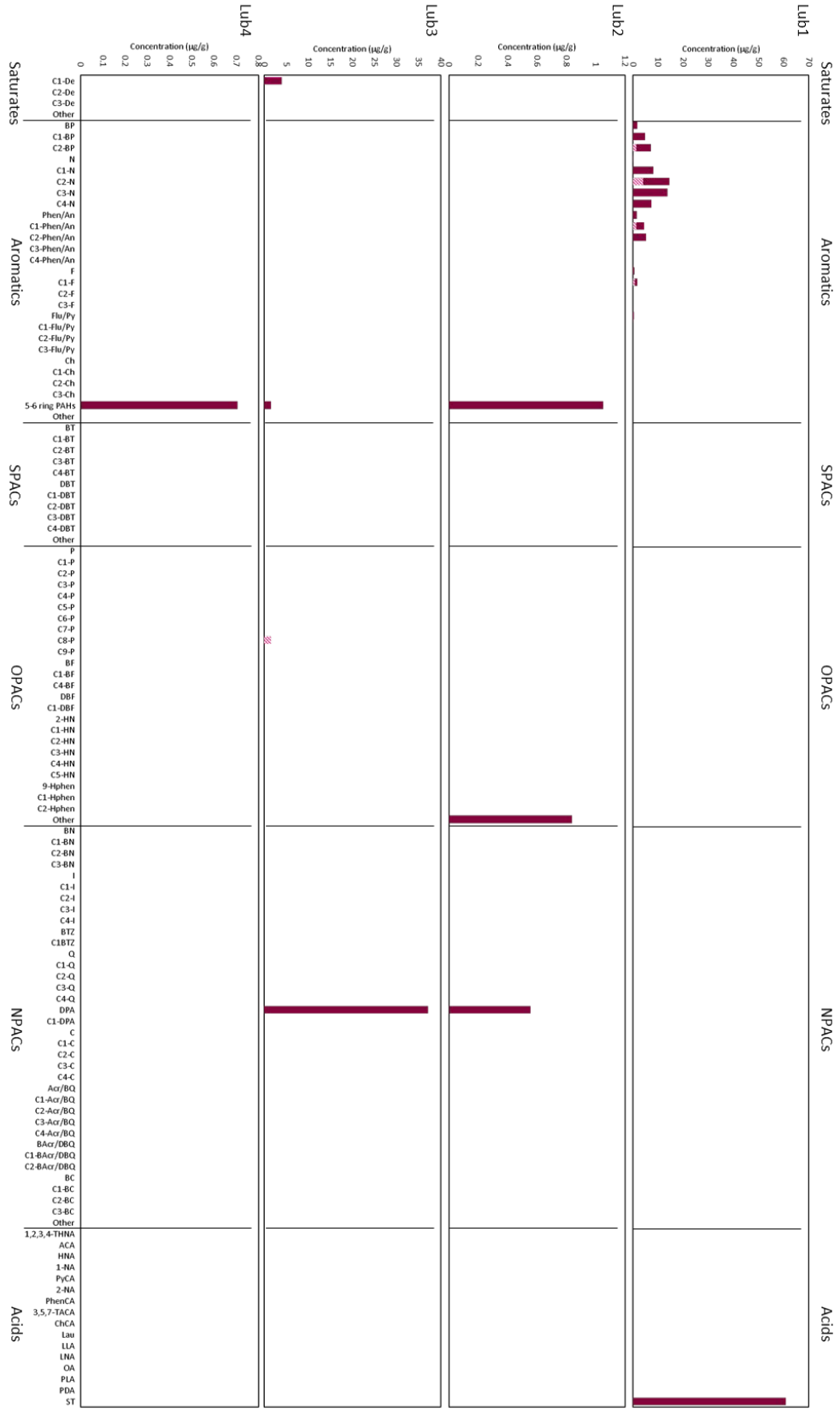
Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure C.5: Detailed chemical composition of individual lubricating oil samples (Lub1 – Lub4)

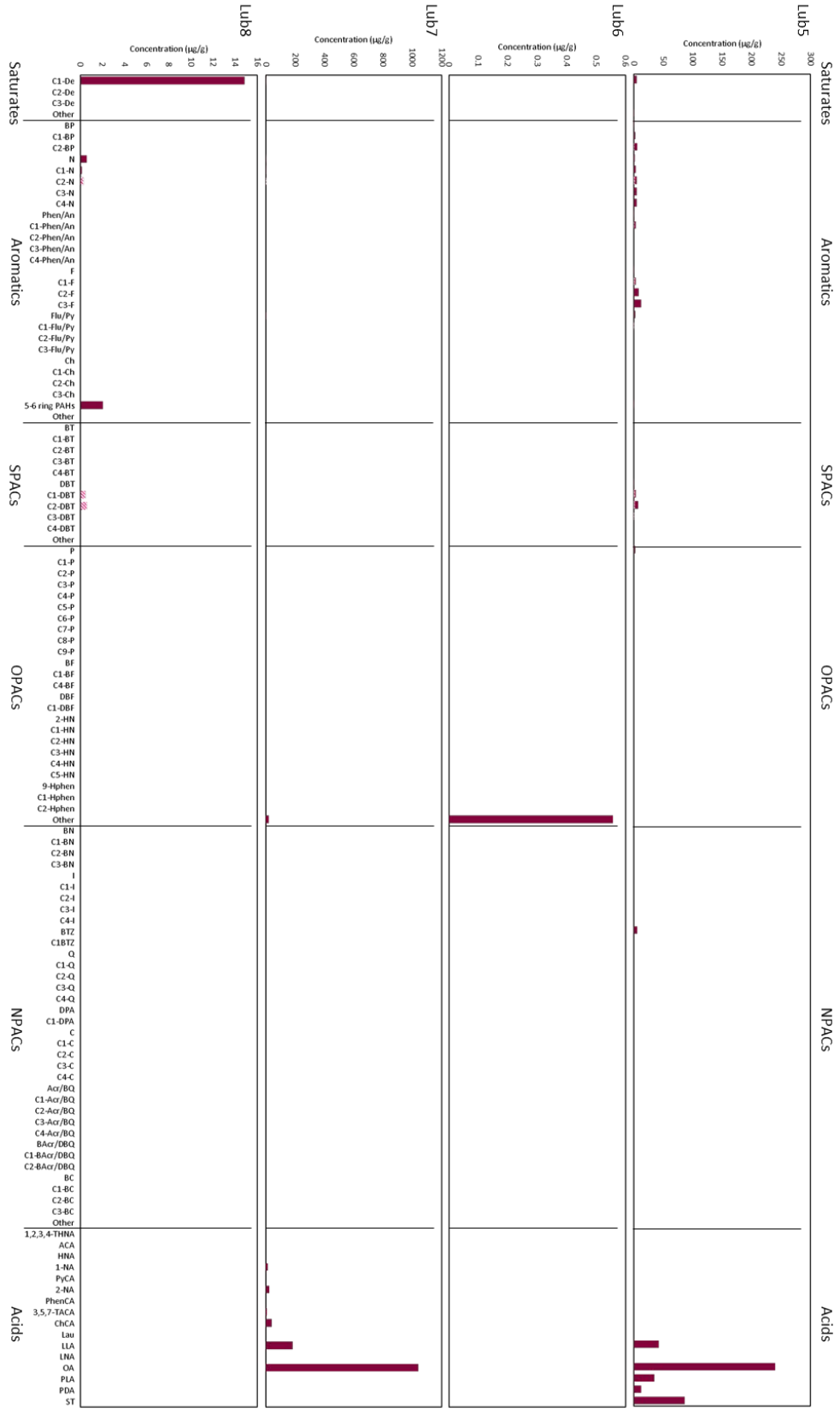
Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure C.6: Detailed chemical composition of individual lubricating oil samples (Lub5 – Lub8)

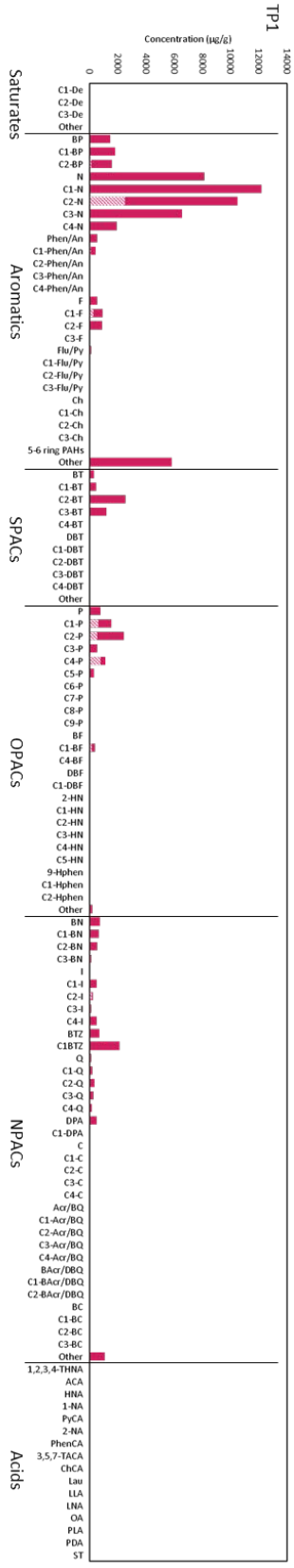
Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.

Figure C.7: Detailed chemical composition of the tyre pyrolysis sample sample

Coloured bars represent concentrations of constituents or constituent groups. Shaded coloured bars represent concentrations of individual constituents within a group. In some cases, concentrations of individual constituents within a group are higher than the concentration of the constituent group due to differences in detection limits.



Source: Own illustration, Department of Plant and Environmental Sciences, University of Copenhagen.