1 **Characterisation of weathered hydrocarbon wastes at contaminated sites**

2 **by GC-simulated distillation and nitrous oxide chemical ionisation GC/MS,**

3 **with implications for bioremediation**

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15 **Contents list entry**

16 Weathered hydrocarbon wastes at five hydrocarbon-contaminated sites in Alberta are

17 characterised by preparative chromatography, GC-SIMDIS and CI GC/MS. Asphaltene and

18 polar classes predominate and recalitrant C_{14}-C_{22} 2-4 ring alicyclics, alkylbenzenes and

19 benzocycloparaffins dominate the saturate class composition. Implications for

20 bioremediation are discussed.

21

22 **Summary**

23 An extended analytical characterisation of weathered hydrocarbons isolated from historically

24 contaminated sites in Alberta is presented. The characterisation of soil extracts,

25 chromatographically separated into component classes, by GC-simulated distillation and

nitrous oxide (N_2O) chemical ionisation (CI) GC/MS provides new insights into the

composition of the residual oil at these sites, the principal partition medium for risk critical

components. The combined polar and asphaltene content of representative soil extracts

ranged from 40% ^{w}/w to 70% ^{w}/w of the oils encountered. An abundance of C_{14}-C_{22} 2-4 ring

alicyclics, alkylbenzenes and benzocycloparaffins is prevalent within the saturate fractions of

site soils. Implications for the partitioning of risk critical compounds at sites with weathered

hydrocarbons and the practical application of bioremediation technologies are discussed.

Introduction

The identification of soils that have become contaminated with hydrocarbons through

accidental spillage and gradual inventory loss often occurs when industrial facilities are

identified for decommissioning, sale or redevelopment[1-2]. The more toxic components of

hydrocarbon residues drive the health and environmental risk assessments that inform

decisions on site remediation[1, 3-4]. Historic hydrocarbon contamination long in the ground

will have often weathered through a range of physical, chemical and microbiological

processes. The complexity of weathered mid-distillate and heavy oil residues is widely

acknowledged[5-8] and is evidenced at sites where they are encountered by (i) the heterogeneity

of the oil-soil matrix; (ii) the extensive analytical cleanup procedures required for the

quantification of contaminants in these matrices; and (iii) the unresolved gas and ion

chromatograms that analytical chemists invariably elicit from soil extracts[7].

Research into heavy oils at contaminated sites has been sparse. Research efforts need

to extend beyond simply quantifying the concentrations of risk critical compounds (*e.g.* the

polynuclear aromatic hydrocarbons (PAH)) for risk assessment purposes to a broader analysis

of the oil matrix. This is because the partitioning behaviour that drives the environmental

fate of individual compounds is largely determined by the affinity of the residual weathered

oil for priority compounds; a property that changes with the type of oil (the 'source term')

and degree of weathering it experiences. In our attempts to better understand the

characteristics and environmental behaviour of these weathered hydrocarbon wastes in soils,

we have reported on the composition[9] and relative toxicities[10] of a range of chemical classes

isolated from soil extracts at petroleum and creosote-contaminated sites, the development of

tiered strategies for the analysis of weathered oils[11] and the performance of a suite of

biomarker indices as indicators of the source and progressive biotransformation of oily

wastes[12]. We have demonstrated (i) that the analysis of the class composition (*e.g.* saturates,

aromatics, polars, asphaltenes) of solvent extracts at hydrocarbon-contaminated sites provides

valuable insights into the potential biotreatability of oily wastes[9]; (ii) that the residual oil

phase is the principal partition medium for PAH in hydrocarbon-contaminated soils[13]; and

(iii) that biomarker indices comprising hopane pairs (*e.g.* the ratio of $17\alpha(H)21\beta(H)$-

norhopane to $17\alpha(H)21\beta(H)$-hopane) within the saturate class can be used (a) to track

biotransformation; or (b) as source identification indices for weathered oils[12].

Aim of investigation

Despite these and other insights and the frequent occurrence of weathered oils at

contaminated sites, our understanding of how weathered mid-distillate and heavy oils behave

in the environment remains incomplete. In part, this is a consequence of standardised

analytical procedures used for the analysis of priority substances in soils sampled during site

investigation, which tends not to require in-depth characterisation of the oil matrix in which

these substances reside. The unresolved complex mixtures (UCM) characteristic of

weathered mid-distillate and heavy oils[14-16] mask a complexity of composition rarely

elucidated using conventional electron impact (EI) gas chromatography/mass spectrometry

(GC/MS).

In this study, we apply preparative chromatography and specialist GC and GC/MS techniques to an extended characterisation of weathered oily wastes (Fig. 1). We present a qualitative analysis, using simulated distillation GC[17] (GC-SIMDIS) and nitrous oxide (N_2O) chemical ionisation GC/MS[18] (CI-GC/MS) of the chemical classes that comprise chromatographically separated fractions of soil extracts at five historically contaminated sites in Alberta, Canada. Simulated distillation GC allows the elucidation of the effective carbon number (EC_n) distribution of the component classes of contaminated soil extracts by using a non-polar GC column as a surrogate distillation column from which analytes are 'distilled' using a linear temperature profile. Chemical ionisation GC/MS, in which gaseous atoms of the analyte are bombarded in a mass spectrometer with ions produced from the electron bombardment of a reagent gas (here, N_2O), allows construction of parent (molecular) ion chromatograms and, with reference to our previous work[9, 11], the analysis of the 'fine' composition of individual chemical classes separated by preparative chromatography.

The results presented are relevant in the context of the recent interest in establishing soil assessment criteria for the heavier hydrocarbons and, more broadly, in setting realistic remediation objectives for hydrocarbon-contaminated sites[1-2]. Our analysis further informs the source characterisation of these difficult wastes and our understanding of their candidacy for bioremediation.

Materials and experimental procedures

Sample preparation and analysis were performed according to the schedule set out in Fig. 1.

Soil sampling and preparative soil extract fractionation

We have previously described the sampling of residual hydrocarbon contamination from soils at five historically contaminated hydrocarbon waste sites in Alberta[9]. Briefly, surficial (0-0.25m depth) soils (*ca.* 5kg) from the process areas of four former petroleum refineries

(site I-IV) and a former coal-tar creosote wood treatment facility (site V) were sampled using

a hand held soil auger, sieved to below 2.38mm (< ASTM No. 8) and stored at 4°C prior to

analysis. Air-dried (20±2°C, overnight), cone and quartered sub-samples (*ca.* 30g) of grab

sampled soils contained between 2.4%^{w}/w (typically ±0.2^w/w % RSD) and

5.4% ^{w}/w dichloromethane (HPLC grade DCM; 16h) extractable organic matter as

gravimetrically determined by Soxhlet extraction to exhaustion (Fig. 2).

DCM extracts were chromatographically separated (Fig. 2) into six component class

fractions (saturates, mono-, di- and polyaromatics, polars and asphaltenes) using an

established technique[11]; the fractions being designated S, A_m, A_d, A_p, P and A, respectively

(Fig. 2). Asphaltenes (A) were gravimetrically recovered from separate portions of DCM

extracts using *n*-pentane[9, 12] precipitation. A stainless steel chromatography column (137cm

x 0.94cm) was then pre-packed in its lower length with 42g Davidson grade 12 silica (28-200

BS mesh) activated at 250°C for 20h. The top half was packed with 47g Alcoa F-20 alumina

(80-200 BS mesh) activated at 400°C for 20h. Preparative class fractions were obtained and

quantified using the following series of eluents;

- for saturates (S): 150mL *n*-pentane;

- for monoaromtics (A_m): 250mL 5%^{v}/v toluene in *n*-pentane;

- for diaroamtics (A_d): 300 mL 30%^{v}/v toluene in *n*-pentane;

- for polyaromatics (A_p): 300mL 70%^{v}/v toluene in *n*-pentane; and

- for polars (P): 300mL 50%^{v}/v methanol in DCM.

Pre-weighed glass beakers were used to collect eluates. The solvent was then removed by

air-drying in a fume hood (16h) and the gravimetric recoveries (typically ±5%RSD[9]) for each

class fraction estimated (Fig. 2). A well characterized Athabasca bitumen reference material

(#82-02; Alberta Research Council, Edmonton, Canada) was fractionated for comparative

purposes.

Simulated distillation

Simulated distillation (GC-SIMDIS) of the S, A_m, A_d, A_p, and P class fractions of each soil

extract was undertaken using a modified ASTM method D2887-89[19]. Boiling point

distribution profiles for each class fraction, illustrated in Fig. 3 for soils extracts from sites I,

III and V, were obtained using a *n*-carbon number calibration curve extended to an

atmospheric equivalent boiling point of 720°C (nC$_{100}$). GC-SIMDIS was performed on a

Hewlett-Packard 5890 GC equipped with an on-column temperature-controlled injector and

an aluminum clad Quadrex column (8m x 0.53mm ID) coated with 5% phenyl silicone of

0.15μm thickness. An oven temperature programme of 55-420°C was employed at a linear

rate of 10°C/min.

Chemical ionisation GC/MS

S, A_m, A_d and A_p class fractions from individual soil extracts were analyzed by GC separation

(Carlo Erba HRGC 5160) on a DB-5 column (25m x 0.25mm ID x 0.32μm film thickness)

using a 2μL injection volume and linear temperature profile between 50-320°C at 10°C/min.

Subsequent mass spectrometric determination (m/z range 44-500) of the eluates employed

nitrous oxide ($N_2$0) chemical ionisation (CI) on a Finnigan Mat 4500 mass spectrometer

calibrated using standard reference oils (Alberta Research Council) used routinely for the

analysis of homologous hydrocarbon series in tar sands and heavy oils. CI spectra were

obtained using a Townsend discharge ionisation source (0.6 Torr $N_2$0 at 120°C). For each

class fraction the identification of the following class components: open chain and alicyclic

saturates, alkyl benzenes, benzo-, naphtho- and phenanthro- alicyclics and the homocyclic

polyaromatics was performed from reconstructed ion chromatograms by analysis of the raw

molecular ion data and by reference to the nominal masses of these hydrocarbons[20] and their

alkyl-substituted analogues (Fig. 1). Relative ring type and carbon number distributions for

these class components were constructed for each of the S, A_m, A_d and A_p class fractions, illustrated in Figure 4 for site III class fractions and Fig. 5 for the saturate fractions of sites I, II and V. Our results are necessarily qualitative since the CI-GC/MS of the polar and asphaltene class fractions was not possible and, for the remaining fractions, the interpretations of the relative distributions of chemical components in each class assumes (i) that the total ion count for each fraction equals the sum of intensities of all identified components; and (ii) equal response factors for all individual components. The resulting distributions (Fig. 4(a)-(c) and Fig. 5(a)-(c)) provide a relative abundance of homologous classes (*e.g.* the benzocycloalkanes) reporting in each of the S, A_m, A_d and A_p class fractions for selected site soils.

Results and discussion

Distillation profiles

The boiling point distribution of class fractions can be broadly related to their relative resistance to microbial degradation. In general, high molecular weight compounds are less easily biotransformed. GC-SIMDIS profiles for extract fractions from sites I, III, and V are illustrated in Fig 3 (a)-(c) with the reference plot of boiling point versus carbon number for *n*-alkanes C_4-C_{100} included for interpretive purposes. Differences in character between class fractions can be inferred by interrogating three aspects of these profiles: (1) The relative gradient of the boiling point curve indicates the boiling point range over which a class fraction is 'distilled' from the column, and by inference, the relative molecular weight distribution of that fraction. Steep curves have tight distributions; lower gradient curves have broader distributions. (2) The relative position of individual curves away from the y-axis allows a qualitative description of the distillation range of the class fraction (*e.g.* light, mid-

distillate, heavy). (3) The point above the temperature on the x axis obtained from

interpolating 25% cumulative weight distilled from the profile of an individual class fraction

represents the boiling point of the remaining $75\%^{w}/_w$ of the sample, and can be expressed in

terms of an equivalent n-saturate carbon number. For example, the saturate fraction at site I

(Fig. 3(a)) was $>75\%^{w}/_w$ in C_{25} equivalent compounds (402°C) and above, and the polar

fraction was $>75\%^{w}/_w$ in C_{42} equivalent compounds (534°C) and above. Similar results

obtained from the polars fraction of the remaining GC-SIMDIS plots for the samples enables

them to be ranked in terms of their boiling distribution: site I > (heavier than) site III ≈site II

> site IV> site V. This sequence is in agreement with the decreasing percentage

contributions of the polars fraction to site soil extracts obtained by preparative column

fractionation (Fig. 2), inferring that the polar fraction of these extracts dominates their

distillation behaviour on the GC column.

Site V (Fig. 3 (c)), the creosote soil extract, exhibited a distinct distillation profile

with narrower boiling point distributions and lower atmospheric equivalent boiling points for

all extract fractions except the polars and an anomalous portion of the monoaromatics

fraction. This indicates the extract is composed of a lower and narrower distillate, consistent

with the documented use of $N^{o.}$ 2 fuel oil as a diluent for coal tar creosote at this site. This

contrasts with the heavy oil residues observed at each of the petroleum sites (I, III), now

confirmed by their apparent molecular weight distribution by GC-SIMDIS analysis.

Class components in individual class fractions at weathered hydrocarbon sites

The boiling point and the general resistance of heavy oils to microbial degradation is a

function of their chemical structure and molecular weight distribution[5-6]. Among the saturate

class components found in petroleum residues, the isoprenoid alkanes (pristane, phytane) and

the polycyclic alkanes (hopanes, steranes) are recognized as refractory compounds[21-23].

1   Detailed analysis of the total ion data by examining the nominal molecular masses[20]

2 for homologous aliphatic, alicyclic and aromatic groups provides useful information on the

3 relative composition of each component class by equivalent carbon number. In Fig. 4 (a) to

4 (c), the progressive representation of linear, alicyclic, alkyl benzene, benzocycloparaffin,

5 naphthalene and phenanthrene class components is illustrated in successive class fractions of

6 the soil extract. In each case the carbon number range suggests the extent of alkyl

7 substitution of the parent structure. Significant 'carry over' is observed, with identical class

8 components reporting in more than one class fraction. The class composition of individual

9 fractions from different soils can be compared using this approach. The saturate class

10 composition from sites I, II, and V, for example (Fig. 5 (a) to (c)), is presented as distribution

11 of component type and carbon number. Extract fractions identifiable by CI GC-MS show

12 hydrocarbon distributions typical of mid- to high distillate residues (C_{13}-C_{27}). In general, the

13 saturate fractions are dominated by the 2-4 ring alicyclics, recognised as resistant to

14 biotransformation.

15   A tentative assessment of the extent of weathering experienced by these samples may

16 also be obtained from the C_{17} open chain/pristane and C_{18} open chain/phytane ratios[24];

17 pristane and phytane being regarded generally as more resistant to microbial degradation than

18 the equivalent *n*-alkanes, though this indicator has recognised limitations[25, 12]. From the raw

19 molecular ion data, these ratios were calculated, respectively as: site I (0.3,0.3); site II

20 (0.5,0.5); site III (0.5,0.7); site IV (1.2, 1.1); and site V (6.9. 4.9). Hence, residual

21 contamination can be ranked according to its apparent relative weathered state: site I > (more

22 weathered than) site II ≈ site III > site IV > site V. This sequence is in close agreement with

23 the GC-SIMDIS profile and %^{w}/w polars contribution data (Fig. 2), lending additional support

24 to these indicators as surrogates for distinguishing between the extent of weathering of the

25 hydrocarbons at these sites. Hydrocarbon contamination at the creosote site (site V) was

markedly different in its characteristics from that encountered at petroleum sites (Fig. 3(c))

and was significantly less weathered in composition. Sites I-III were characteristic of

significantly weathered oils and site IV (not shown) characteristic of a mid-distillate residue.

Significant contributions come from alkyl benzenes, which report in the saturate class in

cases where extensive alkyl- substitution overrides ring aromaticity as a determinant of

polarity. Likewise, some of the benzocycloparaffins (also resistant to biotransformation)

report in this class.

Implications for bioremediation

Many hydrocarbon-contaminated sites (former refineries, coal carbonisation plants, and

integrated steelworks) contain (i) oils that are weathered because the source term has aged

significantly since release; (ii) heavy fuel oil residues such as Nos. 4, 5 and 6 fuel oil used in

commercial boilers or heavy diesel engines; and/or (iii) viscous tars and solid bituminous

process residues that are difficult to treat biologically. In contrast to lighter gasoline (petrol),

diesel and aviation fuels, the literature on heavy oil wastes is not extensive and the risks to

human health are not well characterised. Understanding the physicochemical and

toxicological characteristics of contaminants in these wastes is critical because these factors

drive the design of analytical strategies, our understanding of exposure and the selection and

operation of remediation technologies.

Our previous studies[13] have shown that compositional changes during weathering

affect the partitioning behaviour of risk critical components (*e.g.* the PAHs) prior to, during

and following biological soil treatment. The data presented in this study provides additional

insight into the composition of weathered hydrocarbon wastes and the residual oil that form

the principal partition medium for risk critical components. We have shown that taken

together, the recalcitrant polar and asphaltene content of soil extracts from these sites

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contributes between 40%^{w}/w and 70% ^{W}/w of the oils encountered (Fig. 1), with the polars

determining the distribution profile of the soil extracts. With respect to the class composition

of chromatographically-separated fractions, the abundance of C_{14}-C_{22} 2-4 ring alicyclics (Fig.

5), alkylbenzenes and the benzocycloparaffins is prevalent within the saturate (S) class

fractions of site soil extracts. These hydrophobic, recalcitrant compounds, together with the

polar and extended hetero-polyaromatic asphaltene structures in these oils[26] comprise the

partitioning medium for PAHs in weathered oil wastes into which between 71-96%^{w}/w of PAH

in the creosote-contaminated soils is partitioned (84% ^{W}/w for benzo[a]pyrene)[13]. Under

these conditions, the availability of PAHs to pose human health risk may be substantially

reduced.

Bioremediation is used internationally for sites contaminated with fossil fuel

hydrocarbons, organic wood-preserving wastes and high volume industrial organics (*e.g.*

polychlorinated biphenyls, tetrachloroethylene). Its application to hydrocarbon wastes,

principally as *ex-situ* engineered biopiling, has been assisted in the US by a shift to risk-

based, remedial objective-led remediation which has forced a scientific rigour on site

investigation, remedial design and technology verification. The move towards risk-based

corrective action has been slow in the UK and, whilst some progress has been made in

integrating aspects of analysis, exposure assessment and technology verification[3], there tends

to be a lack of synthesis between these aspects of risk management. Indeed, bioremediation

performance tends to be evaluated by reductions in hydrocarbon load[27-28] rather than

combined reductions in toxicity, chemical mass and risk. Studies that integrate these aspects

are essential if risk-based decision-making is to become the basis for the management of

contaminated land.

Conclusions

The data in this study further inform our understanding of the nature of oily wastes at weathered hydrocarbon sites and the extent to which bioremediation might practically progress for these wastes. Bioremediation technologies express operational limits beyond which, because of the composition and recalcitrance of the partition medium for risk critical compounds and the strength of association between, say PAH, and the weathered source term, prolonged bioremediation is futile in terms of progressive risk reduction. A key factor is to recognise the partitioning behaviour of contaminants like PAHs into recalcitrant heavy oil residues. One research challenge is to now demonstrate the optimisation of bioremediation (*e.g.* biopiling) processes by reference to risk reduction and to identify the practical limits of this technology using knowledge gained on the composition of weathered hydrocarbons.

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site soils, *ca.* 5kg

cone and quartered sub-sample, 30g

soil extract, DCM, 16h
SOIL EXTRACTS

n-pentane $precip^n$. of asphaltenes

preparative chromatography
CLASS FRACTIONS

S A_m A_d A_p P   A

GC-SIMDIS Simulated distillation

CI-GC/MS

Open chain

Alkylbenzenes

CLASS COMPONENTS
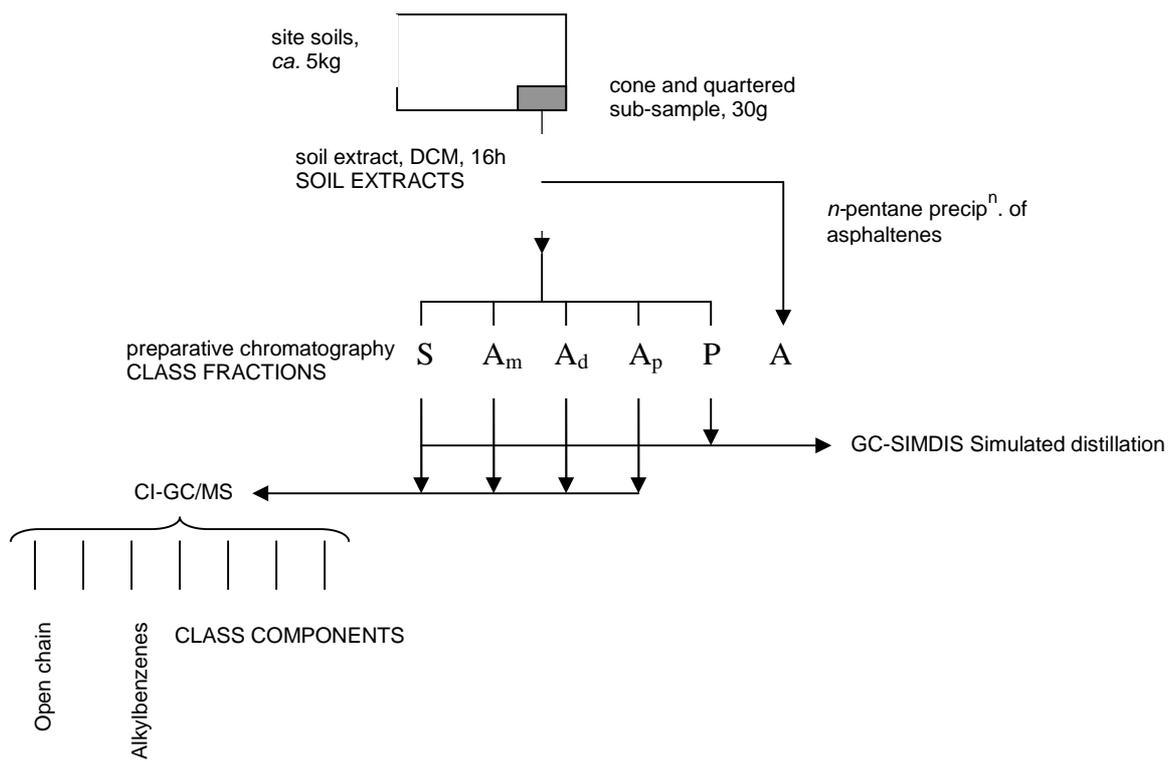
1

2   Fig. 1 Analytical strategy and terminology employed in this study
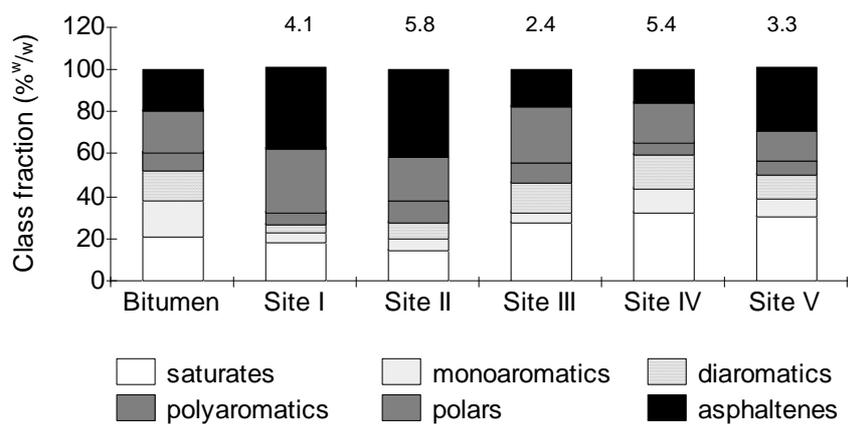
Fig. 2 Normalised composition of soil extracts from Sites I-V by class fraction (bar labels showing %^{w}/w DCM-extractable matter in sample, ± 0.2 ^{w}/w % RSD).
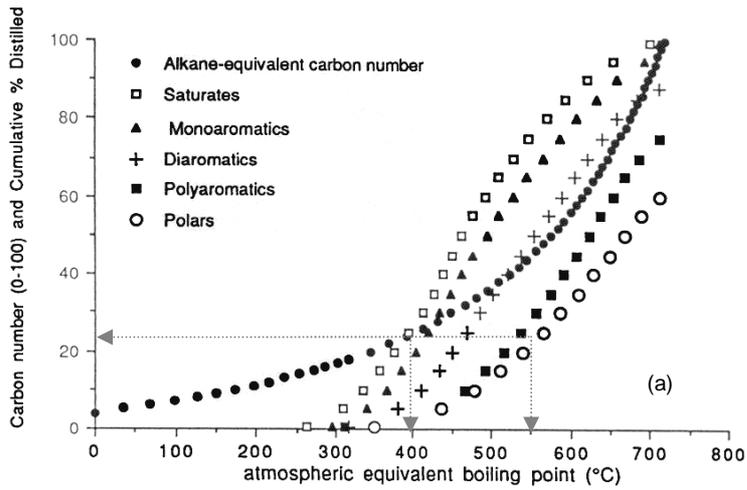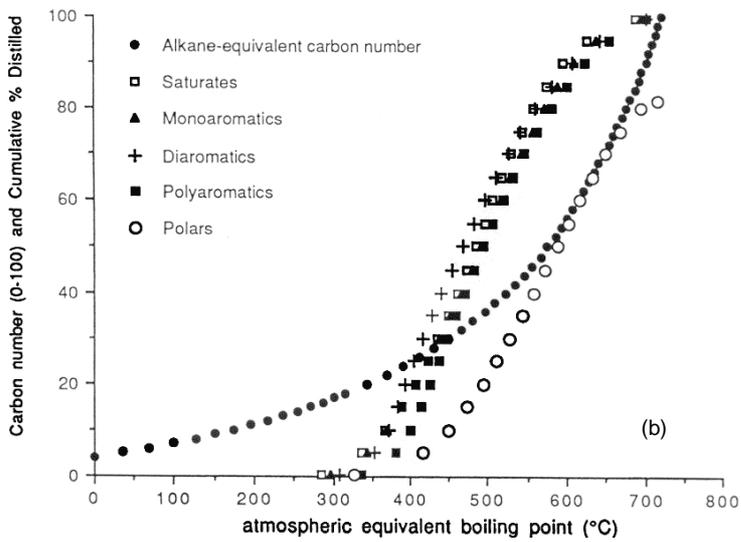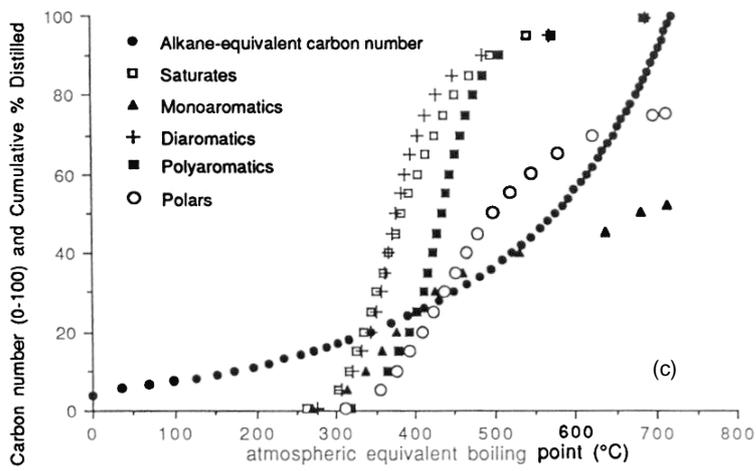
Fig. 3 SIMDIS GC profiles for DCM extracts from Sites (a) I; (b) III; and (c) V
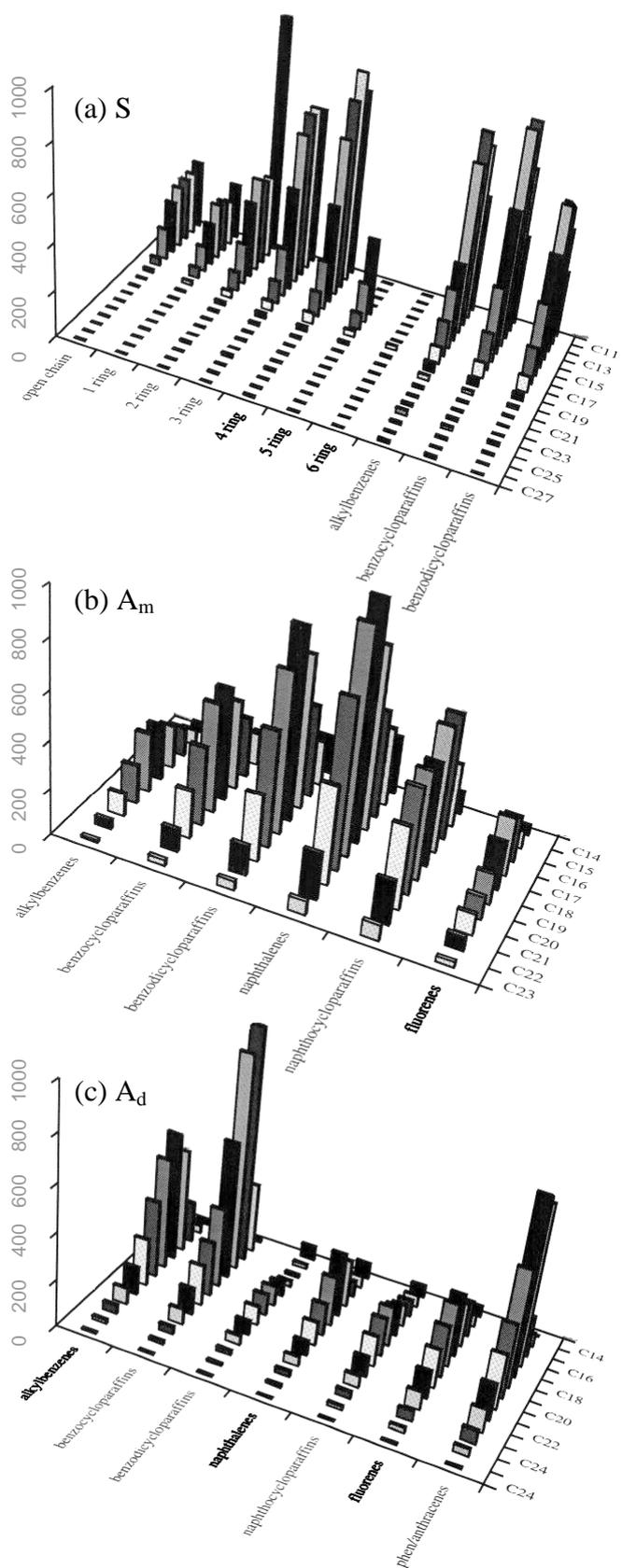
Fig. 4   Relative composition of site III soil extract fractions by class component, carbon number and relative ion count (unitless)
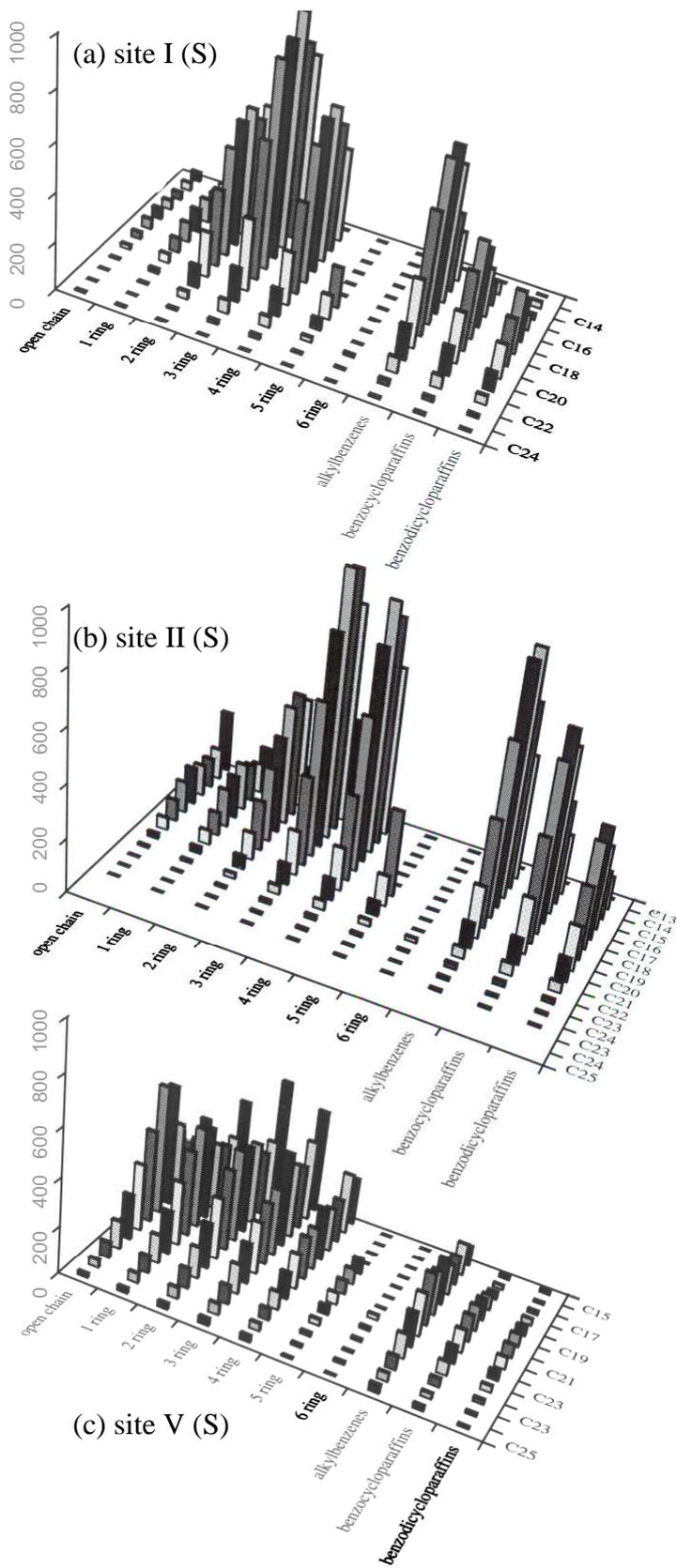
Fig. 5 Relative composition of site extract saturate (S) fractions by class component, carbon number and relative ion count (unitless)