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Biogeochemical benchmarks for source identification of contaminants from an offshore oil and gas industry

Repères biogéochimiques pour la détermination des sources de contaminants produits par des activités pétrolières et gazières extracôtières.

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ABSTRACT

Crude oils are complex mixtures of tens of thousands of compounds. Because numerous structures are possible, most compounds can only be characterised by their elemental composition, if they are known at all. Fortunately, compounds occur in classes or groups of similar compounds. Hence, a classification tree can be produced for crude oils and refined products that permits preliminary assessments to be made of their toxicity and physicochemical properties. For example, oils can be chemically separated into an aromatic fraction, which contains most of the toxic components, and a non-aromatic fraction, which is much less toxic. These two fractions may be further separated into boiling point ranges and thence into groups of compounds of similar structure. The order in which the classification is done is arbitrary and can be adjusted to fit the needs of the assessor.

Groups of compounds having similar structure often may be traced to common, naturally occurring precursors. Some members of such groups are known as biomarkers because of their biological origins. Useful biomarkers are biologically and chemically robust compounds that survive degradation when released into aquatic environments. These chemical biomarkers thus can be used to track petroleum products released into the ocean. The presence or absence of particular compounds usually cannot be used to distinguish among crude oils or their refined products, although such distinctions can occur. Rather, it is the compositional differences in biomarker compounds that allow one oil sample to be distinguished from another. Various analytical tools are available to produce biomarker "fingerprints," which like human fingerprints, can be visually compared. Nowadays, however, sophisticated computer-based statistical methods often are used to make comparisons for oil identification purposes.

A major complication in the source identification of oils through their biomarker fingerprints is the presence of a background of the same and similar compounds in the environment. The biological precursors of biomarkers in petroleum are produced continuously in the environment and undergo diagenic transformations in soils or sediments to give compounds nearly indistinguishable from those in petroleum. Eroding coal and shale oil deposits and underwater oil seeps also can introduce many of the same petroleum biomarkers into sediments, biota and seawater.

Having a measure or benchmark of the background biomarker profiles may be crucial for assessing the impact of a catastrophic spill or unequivocally assigning blame for the cumulative effect of many little spills. The *Exxon Valdez* oil spill has been the showcase for modern source identification studies using biomarkers and statistical methods. The source of petroleum in the spill zone and surroundings, however, is the subject of continuing debate and litigation. Papers are still being published on the impact of the spilled oil, some because no petroleum benchmark for the area was established prior to the spill event. This mistake can be avoided in the case of the Queen Charlotte basin.

During exploration and production drilling, waste muds and cuttings can be released into the marine environment. These wastes contain metals, petroleum and a number of additives whose fingerprint may be superimposed upon that of the natural background. Although volume and density considerations as well as experience indicate that the influence of these compounds would be limited and local, establishing a fingerprint for key compartments such as bottom sediments and surface microlayer would help to resolve future environmental questions.

Petroleum spills, big and little, and wastes from combustion processes and drilling are not the only sources of organic compounds and metals entering marine environments from an offshore oil and gas industry. Over the lifetime of an oil field, produced water may exceed recovered oil by as much as ten-fold. If produced water is not re-injected into oil depleted formations and instead is released at sea, it can represent a major source of organic and inorganic constituents. Source identification of these constituents is necessary to assess the environmental impact of produced water. As in the case of oil itself, the importance of establishing a benchmark for constituents found in produced water should not be underrated. In this regard, widespread alteration of the composition of the sea-surface microlayer is of particular concern.

RÉSUMÉ

Les pétroles bruts sont des mélanges complexes de dizaines de milliers de composés. Comme de nombreuses structures sont possibles, la plupart des composés, s'ils sont connus, ne peuvent être identifiés que par leur composition élémentaire. Heureusement, ces composés se répartissent en catégories ou groupes de composés similaires. Il est donc possible de produire un arbre de classification des pétroles bruts et des produits raffinés permettant une évaluation préliminaire de leur toxicité et de leurs propriétés physico-chimiques. Par exemple, les pétroles peuvent être divisés chimiquement en une fraction aromatique, qui contient la majeure partie des composantes toxiques, et une fraction non aromatique, beaucoup moins toxique. Ces deux fractions peuvent ensuite être divisées en intervalles de distillation et donc en groupes de composés de structure similaire. L'ordre dans lequel la classification est faite est arbitraire et peut être ajusté aux besoins de l'évaluateur.

Les groupes de composés de structure similaire peuvent souvent être rattachés à des précurseurs communs naturellement présents dans l'environnement. Certains membres de ces groupes constituent ce qu'on appelle des « biomarqueurs » en raison de leur origine biologique. Les composés plus robustes biologiquement et chimiquement, qui résistent à la dégradation lorsqu'ils se retrouvent dans des milieux aquatiques, constituent des biomarqueurs particulièrement utiles. Ils peuvent permettre de retracer l'origine de produits pétroliers trouvés dans l'océan. On ne peut ordinairement se fier sur la présence ou l'absence de composés particuliers pour distinguer différents pétroles bruts et leurs produits raffinés, quoique de telles distinctions puissent se faire. On se fonde plutôt sur leur composition en biomarqueurs. Divers outils d'analyse permettent de produire des « empreintes » de biomarqueurs qui, comme nos empreintes digitales, peuvent être comparées visuellement. De nos jours, toutefois, les comparaisons sont souvent effectuées à l'aide de méthodes statistiques informatisées, très perfectionnées.

Par ailleurs, la présence naturelle des mêmes biomarqueurs ou de composés similaires dans l'environnement crée un bruit de fond qui représente une difficulté majeure dans l'application de la méthode des empreintes. Les précurseurs biologiques des biomarqueurs contenus dans le pétrole sont continuellement produits dans l'environnement et sont transformés en composés pratiquement indistinguables de ceux du pétrole par les processus diagénétiques ayant lieu dans les sols et les sédiments. L'érosion des gisements de charbon et de schistes bitumineux et les suintements sous-marins de pétrole peuvent également entraîner l'introduction de bon nombre des mêmes biomarqueurs dans les sédiments, le biote et l'eau de mer.

Une mesure ou un repère définissant le profil des biomarqueurs du fond géochimique naturel pourrait être extrêmement utile pour évaluer l'impact d'un déversement majeur ou établir sans équivoque l'auteur ou les auteurs de nombreux petits déversements dont les effets sont cumulatifs. Le déversement de l'*Exxon Valdez* a donné l'occasion d'étudier de nouvelles approches de détermination de la source d'un déversement à l'aide de biomarqueurs et de méthodes statistiques. La question de la source du pétrole trouvé dans la zone d'un déversement et dans les environs demeure toutefois un sujet de discussions et de litiges. Des articles continuent d'être publiés sur l'impact du pétrole déversé, en partie à cause de l'absence de repères quant aux conditions qui existaient dans la zone avant le déversement. Il est possible d'éviter ce problème dans le cas du bassin Reine-Charlotte.

Les boues usées et les déblais de forage qui peuvent être libérés dans le milieu marin lors des forages d'exploration et de production contiennent des métaux, du pétrole et un certain nombre d'additifs dont l'empreinte peut se superposer à celle du fond géochimique naturel. Même si des considérations telles que le volume et la densité, aussi bien que l'expérience, indiquent que l'influence de ces composés serait limitée et locale, il serait utile d'établir l'empreinte des composantes importantes, telles que les sédiments de fond et la microcouche de surface, afin de faciliter le règlement de futures questions environnementales.

Les déversements de pétrole, gros ou petits, et les procédés de combustion et de forage ne sont pas les seules sources de composés organiques et de métaux introduits dans l'environnement marin par les activités pétrolières et gazières extracôtières. Au cours de la vie d'un champ pétrolifère, une grande quantité d'eau, pouvant dépasser jusqu'à dix fois la quantité de pétrole récupéré, est produite. Cette eau peut représenter une source majeure de composés organiques et inorganiques dans le milieu marin si elle est rejetée dans la mer plutôt qu'être réinjectée dans les formations exploitées. L'identification de l'origine de ces composés est nécessaire pour évaluer l'impact environnemental de l'eau produite. Tout comme pour le pétrole lui-même, il ne faut pas sous-estimer l'importance d'établir un repère pour les constituants de l'eau produite. À cet égard,

une modification à grande échelle de la composition de la microcouche de surface de la mer présente un intérêt particulier.

INTRODUCTION

The aftermath of the *Exxon Valdez* oil spill in 1989 into waters off Alaska, B.C.'s northern neighbour provides a lesson on how not to do scientific investigations, despite the enviable accomplishments eventually attained. Few ecological data existed for the impacted area and, initially, sound scientific investigation fell victim to the process of litigation and damage recovery (Kaiser, 1999). Until 1991, "[b]arred by lawyers from both sides from sharing data, EXXON and government scientists carried out redundant studies. And many scientists outside Alaska who offered help were rebuffed" (Kaiser, 1999).

One contentious issue that is highly pertinent to this Research Document still continues. This issue turns on the origin of hydrocarbons in sediments before the spill and is being studied by academic, government and industry researchers. As noted by Mudge (2002) the "motivation for their work revolves around the likely toxicity of the pre-spill sediments based on their PAH content. This may relate to the level of fine imposed on Exxon." The issue could have been resolved years ago had their been an appropriate hydrocarbon benchmark for the Gulf of Alaska coastal area prior to the spill. Although one can argue that the time and place of oil spills from tankers is too unpredictable to justify developing petroleum benchmarks along their delivery routes, the zone encompassing an offshore oil and gas industry is relatively small and well defined. Prudent foresight would seem to be preferable to seemingly endless litigation.

This Research Document discusses the value of polycyclic terpanes and polycyclic aromatic hydrocarbons, as well as metals associated with metal-binding constituents of oil, for source identification of petroleum residues found in the marine environment before and after spill events. It touches upon the factors that produce compositional differences during the formation of petroleum oils and other source materials. Finally, this paper addresses transformations in petroleum that take place after burning or release into the marine environment, and it discusses the tracer potential of some other chemicals discharged to the environment during drilling and production.

CHEMICAL PROPERTIES OF PETROLEUM

CRUDE OIL

Crude oil is a mixture of compounds having simple to complex structures made up of combinations of carbon, hydrogen, oxygen, nitrogen, sulphur, trace metals and even mineral salts (Patin, 1999). Indeed, Hughey *et al*. (2002) report that a particular South America crude oil contains basic components having about 8000 different elemental compositions[1]. These authors' unpublished data indicate that the crude oil has a similar number of acidic components. Hydrocarbons, which contain only carbon and hydrogen, make up 80-90% of the mass of crude oils (Patin, 1999). The crude oil being analysed by Hughey *et al*. (2002) contains >85% hydrocarbons, and these authors estimate the number of compositionally distinct compounds could exceed 30,000. Because compounds can have the same elemental composition but different geometries, the total number of chemically distinct compounds in the oil could be some multiple of 30,000.

Hydrocarbons can have densities less than water's. Because such hydrocarbons often make up the bulk of a crude oil, crude oils tend to float on water. The density of individual hydrocarbons increases as their molecular weight increases and their volatility decreases. A weathered crude oil's density may exceed that of water, allowing it to sink.

Although crude oils are complex mixtures of compounds, the compounds may be grouped according to similarity of properties. The grouping can be done in a variety of ways, but for the purposes of this document it is convenient to first group the mixture into aromatic and non-aromatic compounds. Compounds are generally classified into these two groups for considerations of physico-chemical properties and source

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[1] Each elemental composition corresponds to all compounds (within the limits of the instrument and search algorithm used) having a common molecular formula of the type $C_cH_hN_nS_sO_o$ in which C, H, N, S, O are the common isotopes of the elements carbon (12), hydrogen (1), nitrogen (14), sulphur (32 and 34) and oxygen (16), respectively. The subscript letters correspond to the number of atoms of an isotope in the molecular formula (e.g., $C_{12}H_9N \equiv {}^{12}C_{12}{}^{1}H_9{}^{14}N_1$).

identification. For example, the non-aromatic compounds do not interact with visible light[2], and it is the aromatic compounds impart the colour to crude oils[3]. The aromatic compounds also are more water-soluble than the non-aromatic ones, on an equal molecular weight basis. Both groups contain compounds useful for source identification.

This classification also is useful for toxicity considerations. To a first approximation, the non-aromatic compounds are not inherently toxic. The toxic mode they exhibit in organisms is non-polar narcosis, and evidence suggests that similar molar concentrations of these compounds in organisms illicit that toxic effect (McCarty and Mackay, 1993; Gobas *et al*., 2001). The aromatic compounds can exhibit a variety of toxic modes that generally have distinct threshold concentrations. The thresholds form a hierarchy of concentrations in an organism, and some polycyclic aromatic compounds arguably could have a "threshold" of a single molecule (the single hit hypothesis) (McCarty and Mackay, 1993; Gobas, 2001).

The aromatic and non-aromatic compound groups can be further subdivided according to the volatility, solubility or molecular weight of their respective constituents. In general, the three properties vary together within each of these two groups, such that the lower molecular weight compounds are more volatile and soluble than the high molecular weight compounds. This correspondence is convenient for some purposes. For example, a group of hundreds of compounds may be considered as a single "pseudocomponent" (Stiver and Mackay, 1984; Reed *et al*, 1999) that has the average molecular weight, volatility and solubility of the members of the group. The oil then can be characterised as a mixture of a few pseudocomponents, instead of thousands of compounds. This artificial grouping is necessary, for example, to make computationally tractable oil-spill behaviour models (Reed *et al*, 1999) for use in forensic (source identification) or toxicity investigations (Stiver and Mackay, 1984), where the distribution of specific compounds is required.

Pseudocomponents are relevant to the source identification problem, because oil-spill behaviour and other fate models can, in principle, predict the environmental distribution (within a pseudocomponent grouping) of specific compounds whose relative composition can be used to distinguish one oil from another. Thus, in certain instances model results can be part of a source identification package.

Each pseudocomponent grouping can be divided further into resolved and unresolved fractions. This division, however, is an operationally defined one that depends on the resolving power of instruments used to physically partition oils into separate components. In general a gas chromatograph is used to separate oil samples in a capillary column from the most to least volatile constituents by gradually increasing the column's temperature. In gas chromatograms, obtained by recording the response of a device that detects the constituents as they exit the column, the resolved components stand out like spikes along a "hump" of unresolved compounds. The latter is commonly referred to as the unresolved complex mixture or UCM for short.

A perhaps more germane definition of the UCM in the context of source identification is: the chromatographic hump that remains after an oil sample has been substantially biodegraded. Indeed, the ratio of the resolved biodegradable compounds to the UCM is one way of telling the weathering history of spilled oils.

In the case of the non-aromatic compound group, despite its composition of many components, the UCM appears to consist predominantly of structurally similar, alkylated T-branched alkanes (Gough and Rowland, 1990). This UCM thus comprises many combinations of basic, biogenetically derived elements, according to a common theme. The aromatic UCM appears to be built of alkanes and cycloalkanes attached to aromatic moieties (Wharton *et al*, 1999; Smith *et al*, 2001). In either case, the resolved and unresolved components that remain after biodegradation and other weathering processes have potential for use in identifying sources of hydrocarbons found in the environment. Despite the structural similarities of UCM compounds, particularly with respect to the T-branched alkanes, the shear number of structural variations likely limits their utility for source identification.

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[2] The interaction refers to the absorption of visible light and the absorption of ultra-violet light and its re-emission as visible light by aromatic molecules. Thin films of oil interact with light to produce an interference pattern that appears as a rainbow-coloured sheen on water when the film thickness is about equal to the wavelengths of visible light. This phenomenon is a property of the film.

[3] In this context "aromatic" refers to all compounds containing aromatic systems that absorb visible light or absorb ultra-violet light and re-emit it as visible light. The designation includes aromatic hydrocarbons, aromatic resins, asphaltenes and petroporphyrins.

As noted, aromatic compounds tend to be inherently toxic. The resolved, degradable aromatic compounds can be isolated or synthesised. Their toxicities can be measured, and their modes of toxic action studied. However, the aromatic compounds of the UCM are not easily accessible and are only now gaining much attention for their toxicological properties (Smith *et al*, 2001; Rowland, *et al*., 2001). These studies demonstrate that the aromatic fraction of the UCM is widespread in coastal sediments adjacent to urban areas and that this aromatic UCM is toxic to biota. Accordingly, the aromatic UCM may be the major contaminant fraction contributing to observed impacts on biota during oil spills. Even if the toxicity of individual constituents of the UCM is relatively low (or even if only a small fraction of the compounds present are highly toxic), the concentrations of UCM present may cause a major impact.

Both the non-aromatic and aromatic UCMs are recognised markers for contamination by petroleum (Jones *et al*., 1983), but the UCM, as a whole, is not of much use for source identification. However, there are several groups of highly stable non-aromatic and aromatic compounds that are useful markers for oil. These compounds originate from precursor materials synthesised by bacteria, plankton, plants and animals in both terrestrial and aquatic environments and are often referred to as biomarkers[4]. The relative abundances of these biomarkers vary from oil to oil and thus can be used to identify oils. The abundances provide characteristic "fingerprints" of different oils that, apart from their usefulness in source identification, hold information about the history of the oil. This history extends to the type of material from which a given oil was generated, allows geochemists to distinguish oils from marine and terrestrial sources, and in some cases identify the geological era when the oil was produced.

Although the plants and animals that formed crude oils may have looked different to those now existing, the biochemical processes through which they lived are much the same today. Some biomarkers that occur in crude oil, generally in somewhat modified form, are being generated in living organisms today. Accordingly, an important part of petroleum source identification includes distinguishing newly formed biomarkers from ancient ones. More will be said in the following section about the use of biomarkers in source identification of samples of oil and other materials.

Although nitrogen, sulphur and oxygen (NSO) containing compounds make up a minor fraction of a crude oil, they have a strong influence on its bulk properties. These NSO compounds occur in both the aromatic and non-aromatic fractions of the oil. The asphaltenes, resins and metalloporpyrins are important groups of aromatic NSO compounds, because they tend to concentrate at the interface between water and crude oil. Without them and other NSO containing compounds, oil would not spread to form a thin, iridescent sheen on water or produce water-in-oil emulsions (Canevari and Fiocco, 1997; Fingas *et al*., 1999). The asphaltenes and porphyrins tend to remain dissolved in oil and increase the size of the oil/water interface by stabilising a dispersion of water droplets in oil. The emulsions formed can contain up to about 90% water. Despite the high concentration of water, the oil remains the continuous phase in the mixture. The bulk properties of such emulsion are very different from the original crude oil; the emulsions have a different colour and are much more viscous than the oil from which they were formed.

The asphaltenes are very high molecular weight (MW >1000), polyaromatic NSO compounds. Asphaltenes have potential for oil-spill source identification and have been used for source identification for bitumens from the Queen Charlotte basin (Fowler *et al.*, 1988). Metallopophyrins have a ring system reminiscent of the active centres of chlorophyll and haemoglobin, from which they derive. Vanadium, nickel and other metals can replace the magnesium and iron as the central metals in petroleum. The metals' "fingerprint" has use in source identification, as discussed below.

NATURAL GAS

Crude oil deposits contain natural gas, although the reverse is not generally true. For example, unlike the Queen Charlotte basin the Tofino and Georgia basins off the B.C coast are thought to have natural gas potential, but no crude oil potential (Hannigan *et al.*, 2001). A crude oil pool under the pressure of the earth's crust will contain large amounts of dissolved natural gas that is released on extraction. Methane, which

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[4] These biomarkers are characteristic chemical compounds present in petroleum that have an origin in an identifiable biological precursor (e.g., steranes are modified and rearranged sterols). These biomarkers can be used as tracers for the fate of petroleum in the environment. These compounds are not the same as biomarkers defined in environmental studies as a change or variation in the state of an organism or ecosystem presumed to result from an anthropogenic stress (McCarty *et al.*, 2002).

contains one carbon atom in its molecule, is the simplest and generally the most abundant constituent of natural gas. About equal amounts of homologues with two to four carbons (ethane to butane), which are gaseous at the temperature and pressure of the earth's surface, co-occur with the methane that is associated with crude oil. According to Patin (1999), 25% of the natural gas associated with crude oil is flared off worldwide, because there is no infrastructure to deal with it. Microbial methanogenesis accounts for accumulations of nearly pure methane in the upper layers of the earth's crust (Patin, 1999) as well as in gas hydrates on the sea floor.

In general, the composition of petrogenic natural gas varies with depth, i.e., the deeper the deposit, the higher the content of larger molecules such as ethane, propane or butane (Patin, 1999). When the higher-carbon molecules are in much greater concentration than methane, the product is a gas condensate, which may contain appreciable concentrations of aromatic compounds (Patin, 1999). Carbon dioxide, nitrogen, hydrogen sulphide and inert gases are also found in association with natural gas. Hydrogen sulphide, a very toxic gas, is of particular concern. Patin (1999) mentions gas condensates with up to 30% hydrogen sulphide.

Natural gas hydrates can begin to form at combined depths of water and sediment of about 200 m and temperatures around 0 °C (Patin, 1999). Gas hydrates are ice with gases occupying cavities in the ice structure. The open structure of ice also accounts for its having a lower density than water at its freezing temperature. In the presence of a gas the ice forms a lattice with larger than usual cavities to accommodate the molecules of the "guest" gas (Kelland, 1994). Methane and the other constituents of natural gas and gas condensates have high solubilities in water and can achieve concentrations in water of toxicological importance, especially following blowouts (Patin, 1999).

Methane and the larger molecules present in natural gas and condensates have but transient use for source identification purposes. The presence of gas in seawater may indicate underwater seeps, while the composition can identify the seep source as methanogenic or petrogenic.

REFINED PRODUCTS

Crude oil is refined to produce a large variety of products used in society. A number of the products may be transported and spilled at sea. Hence, these products have the potential to complicate the source identification of hydrocarbon residues found in or under the sea. To a first approximation, refined products can be classified according to their boiling point ranges (Table 1). The ranges indicate only that given product will have a boiling point distribution somewhere within it. No. 2 heating oils and diesel oils are essentially the same product, except diesel-oil characteristics, such as cetane number, are specified (Schmidt, 1969). Bunker C fuel oil, which is used in some ships for fuel and has been the subject of some oil-spill studies, is equivalent to No 6 fuel oil. Persistent compounds that are useful for source identification generally have numbers of carbon atoms in their molecules that place them in the upper end of the heavy distillate range (i.e., $\gtrsim$ 400 °C)(Clarke and Brown, 1977). These low-volatility, persistent compounds are highly concentrated in Bunker oils and heavily weathered crude oils from spills and seeps.

CONJECTURES ABOUT THE COMPOSITION OF B. C. MARINE CRUDE OIL AND NATURAL GAS

No liquid oil has been discovered through past drilling activities in the Queen Charlotte basin (Hannigan *et al.*, 2001). Hence, no properties of liquid well oil have been described. Nevertheless, characterisations have been done on oils and tars from land seeps on the Queen Charlotte Islands (Hamilton, and Cameron, 1989). Land seeps at various locations could be expected to extend offshore (Cretney *et al.*, 2003). Bustin (1997) referred to Shouldice (1971) to note that oil-stained sandstones occurred in the Sockeye B-10 well drilled in Hecate Strait off Gwaii Haanas (Moresby Island). A number of oil, tar and bitumen samples that came from shows that were located onshore nearby to the Sockeye wells have been characterised for biomarkers (Fowler *et al.*, 1988).

Lloyd Snowdon, NRCAN, notes that "Martin Fowler and I have made a very tenuous connection between shows (especially in the Sockeye well) with a Sandilands Fm. source rock."(Snowdon, personal commun., 2002). These shows may provide clues to the properties of potential oils. At the same time, however, Snowdon cautions: "Predicting properties of potential oils might be better achieved through analysis of outcrop samples that might reasonably be expected to be present under Hecate Strait." He also advocates analysing sedimentary material to provide "both concentrations and fingerprints of bitumens … to establish a benchmark against which subsequent work can be measured to assess levels and sources of new impacts."

This assertion supports a major recommendation of this working paper to establish a hydrocarbon benchmark for sediments from the Queen Charlotte Sound - Hecate Strait area of the B.C coast.

SOURCE IDENTIFICATION IN CHEMICAL FATE STUDIES

PETROLEUM

A large number of different hydrocarbon-biomarker parameters have been developed by petroleum organic geochemists to correlate different oils, and determine their source, original depositional environment, maturation and amount of biodegradation (Peters, and Moldowan, 1993). In the last two decades many of these techniques have been utilised to identify the origins and degree of biodegradation of oils spilled in the marine environment (e.g., Barakat *et al.*, 1999; Boehm *et al.*, 1987; Cretney *et al.*, 1987; Volkman *et al.*, 1992; Wang and Fingas, 1994; Wang *et al.*, 1995; Zakaria *et al.*, 2000).

Recently, organic geochemistry has played a major role in assessments of the impact of the *Exxon Valdez* oil spill on the environment of Prince William Sound, Alaska, through the identification and quantification of the multiple petroleum sources in the spill area (Bence *et al.*, 1996). Oil seeps in the eastern Gulf of Alaska were first thought to be responsible for the background in Prince William Sound (Bence *et al.*, 1996), but coal has subsequently been championed as the major source by one group (Short *et al.*, 1999; Short *et al.*, 2000) and oil seepage and eroded shales by another (Boehm *et al.*, 2000; Boehm *et al.*, 2001; Page *et al.*, 1996; Page *et al.*, 1999). Recently, a multivariate statistical method known as Partial Least Squares (PLS) modelling has been applied to data sets from Gulf of Alaska and Prince William Sound (Mudge, 2002). For the data set with both non-aromatic and aromatic biomarkers, the analysis provided quantitative contributions to the variance in the data set from five different sources.

The environmental significance of source stems from whether the PAHs in the background come from coal, and thus may be of limited bioavailability, or from oil seepage and eroded shales and, therefore, may have greater bioavailability (Boehm *et al.*, 2001). The important question of bioavailability remains unresolved as this extended debate continues in the scientific literature (at least one paper has been recently submitted for review).

The *Exxon Valdez* spill provides the most relevant case study of how the problems of source identification can confound, or at least complicate, a study of the fate and effects of an oil spill when a benchmark does not exist. Identification and quantification of baseline petroleum hydrocarbons in the proposed Hecate Strait and Tofino basin exploration areas are essential to the evaluation of the fate, effects and weathering of oil in the event of a blow out or oil spill (cf. Bence *et al.*, 1996). Because these areas have a similar coal- and oil-rich geology to coastal Alaska, multiple natural sources of hydrocarbons can potentially contribute to the petroleum background through oil seeps and erosion of carbon-rich rock formations.

When chronic anthropogenic petroleum discharges are added to the mix, many of the same compounds expected in Queen Charlotte basin oils also will be present in contemporary sediments. Accordingly, methods that utilise a variety of molecular and isotopic techniques will be required. The hydrocarbon benchmark for the Queen Charlotte Basin will have to include sediments, potential petroleum source rocks, water and tissues from sessile and benthic animals (e.g., mussels and flatfish) and be established before exploratory drilling begins.

Fingerprinting petroleum

Fingerprinting methods, utilising multiple parameters sensitive to both source composition and degree of weathering, can be used to distinguish oil-spill hydrocarbons from petroleum sources unrelated to a spill in shoreline, subtidal sediment, and biological samples (e.g., Bence *et al.*, 1996). Methods used in such studies include measurements of total hydrocarbons and carbon isotopic compositions ($\delta^{13}C$) of sample extracts, and chromatographic and mass spectrometric analyses of aliphatic (the non-aromatic alkanes, tricyclic terpanes, hopanes and steranes) and aromatic (benzene derivatives, PAHs and mono- and triaromatic steranes) biomarkers (Table 2). Carbon isotope measurements have proved to be a valuable method for distinguishing *Exxon Valdez* residues on Prince William Sound shorelines from tars that can be traced to production from southern California oil fields (Bence *et al.*, 1996). The presence or absence of selected hopane biomarkers and characteristic ratios of different hopanes and steranes also can be invaluable for distinguishing oils from different sources (Barakat *et al.*, 1999; Peters and Moldowan, 1993; Volkman *et al.*, 1992; Zakaria *et al.*, 2000). Distributions of 2- to 6-ring polycyclic aromatic hydrocarbons (PAH), dibenzothiophenes and aromatic steranes have proved to be particularly effective for distinguishing *Exxon Valdez* oil and its weathered residues from oil seep or coal hydrocarbons in the modern sediments of Prince William Sound

(Bence *et al.*, 1996; Boehm *et al.*, 2001; Douglas *et al.*, 1996; Short and Heintz, 1997; Short *et al.*, 1999). The single-ring aromatics (benzene, toluene, ethylbenzene, xylene), which are of significant environmental concern, are highly volatile, dissipate rapidly, and are of little value in the identification of hydrocarbon sources (Bence *et al.*, 1996).

Because no real knowledge exists about the composition of Queen Charlotte Basin oil, should there be any, benchmark studies should consist of detailed examinations of the concentrations and carbon isotopic compositions of alkane and PAH biomarkers in representative samples from Hecate Strait and the surrounding shoreline. The identification and quantification of the background hydrocarbons with both natural and anthropogenic sources is necessary to make meaningful fate and effects assessments, should there be an oil spill during drilling or production. A more detailed description of the parameters that should be measured and what they mean in terms of identifying spilled oil against a pre-existing hydrocarbon background follows.

Alkanes and cycloalkanes

Petroleum-derived alkanes in marine environmental samples are frequently degraded to the point where they are not discernible from the biogenic background (e.g., Bence *et al.*, 1996; Wang and Fingas, 1994). Accordingly, the measurement of total petroleum hydrocarbons (Table 2) is valuable only in the initial stages following an oil spill and is normally of little value for long term fate and effects studies. In contrast, the tricyclic terpane, hopane and sterane biomarkers (Table 3) are refractory enough to persist in the environment for extended periods of time.

Hopanes and steranes are stable 5- and 4-ring hydrocarbons whose respective precursors in living organisms are the hopanols produced by bacteria and the sterols produced by algal and terrestrial plants (Mackenzie *et al.*, 1982; Ourisson *et al.*, 1979; Ourisson *et al.*, 1987). The precursors of the tricyclic terpanes are less well established but bacteria or primitive alga are likely possibilities (Ourisson *et al.*, 1982; Peters and Moldowan, 1993; Simoneit *et al.*, 1990). Heat and pressure diagenetically modify all these compounds from the "biological" configuration into forms with higher thermodynamic stability as organic matter is converted into petroleum or coal over geological time scales. The modifications occur in predictable ways resulting in well defined and characteristic series of the rearranged, diagenetic isomers of these hopane and sterane biomarkers in organic rich sediments and sedimentary rocks, petroleum source rocks, crude oils, coals, etc. (Peters and Moldowan, 1993). Because these biomarkers are more stable than other petroleum components such as the resolved alkanes, the hopanes and steranes serve as conservative indicators (and tracers) of petroleum that has entered the marine environment *via* oil seeps or the erosion of bitumens, organic-rich rocks or coals (e.g., Bieger *et al.*, 1996; Hostettler *et al.*, 1999; Prince *et al.*, 1994; Volkman *et al.*, 1992; Yunker *et al.*, 1993).

The tricyclic terpanes, hopanes and steranes are absent from refined products such as gasoline, but they are present in crude and heavy oils, motor oils, asphalt and coal (e.g., Barrick *et al.*, 1984; Bieger *et al.*, 1996; Peters and Moldowan, 1993). Because the bioavailability of contaminants such as the PAHs differs dramatically between these various matrices, the exact petroleum source(s) must be established to predict the impact of this petroleum on biota (e.g., Short *et al.*, 1999). The polycyclic biomarkers are more resistant to weathering than are the alkanes and 2- and 3-ring PAH.

Oils, bitumens, asphalts, etc. from different locations, geological periods, or maturities in the Western Canada sedimentary basin of Alberta (the source of much of the oil used in BC) contain different (and often characteristic) proportions of hopane and sterane biomarkers (Creaney and Allan, 1992; Creaney *et al.*, 1994). There also are composition differences between the oils of many of these basins and the oils from Alaska (Bence *et al.*, 1996). However, hopane distributions for most Alberta and Alaska basins lack any characteristic triterpane biomarkers that can provide a definitive identification, and the consideration of more subtle features such as the ratios of selected hopanes or steranes is necessary for identification of an oil.

The triterpanes 18α(H)-oleanane and 17α(H),18α(H),21β(H)-28,30-bisnorhopane hold special interest for the fate and effects studies of *Exxon Valdez* oil (Bence *et al.*, 1996). Oleanane is an angiosperm (flowering plant) biomarker whose presence generally indicates Cretaceous (105-65 Ma) or younger petroleum reservoirs (Moldowan *et al.*, 1994; Murray *et al.*, 1997; Peters and Moldowan, 1993; Rullkötter *et al.*, 1994). Oleanane is absent in oils from Cook Inlet (Bence *et al.*, 1996), Western Canada (Creaney, 1992; Creaney, 1994; Martin Fowler, personal commun., 1999) and the Alaska North Slope (Bence *et al.*, 1996). 28,30-Bisnorhopane also does not occur at detectable levels in oils from the Alaska North Slope, but it is present in some Western Canada oils including the heavy oils from the Athabasca tar sands (Brooks *et al.*, 1988). In contrast, oleanane[5] occurs in Tertiary oil shows and bitumen samples from the Queen Charlotte Islands and seep oils from the eastern Gulf of Alaska, and both oleanane and bisnorhopane are present in southern California tars (Bence *et al.*, 1996; Fowler *et al.*, 1988).

Polycyclic aromatic hydrocarbons and aromatic steranes

PAHs can induce biological effects (Canadian Council of the Ministers of the Environment, 1998). Accordingly, PAHs of concern as environmental contaminants should be measured along with PAHs with potential utility as source indicators (Table 4).

The dibenzothiophene content of crude oils varies from trace levels to more than 30% of the alkyl PAH total (Requejo *et al.*, 1996) and is not always correlated with the sulphur content (Hughes *et al.*, 1995). It has recently been established that the ratio of the dibenzothiophenes to the phenanthrenes is characteristic of the depositional environment where a crude oil was formed (Hughes *et al.*, 1995; Requejo *et al.*, 1996) and can be used to distinguish petroleum sources in the environment (Bence *et al.*, 1996; Douglas *et al.*, 1996). Ratios can be based either on the totals for all homologues (e.g., C_0 - C_2 sum), and thereby improve the detectability of the ratio (Requejo *et al.*, 1996), or on the ratios of specific homologues (e.g., C_2), and reduce the sensitivity of the ratio to petroleum weathering (Douglas *et al.*, 1996).

PAH ratios of C_2-dibenzothiophene/C_2-phenanthrene (D2/P2) and C_3-dibenzothiophene/C_3-phenanthrene (D3/P3) are particularly useful for distinguishing oils (Bence *et al.*, 1996). These ratios, which vary among oils having different sulphur contents, remain relatively constant as spilled oil weathers and may be used to identify oil sources when the residues are heavily degraded (Douglas *et al.*, 1996). Biodegradation experiments using *Exxon Valdez* crude oil in soil (Douglas *et al.*, 1996) show that the D2/P2 and D3/P3 ratios remain relatively unchanged even when the individual components have been degraded by more than 95% and total PAH has been reduced by more than 98%.

In contrast, the C_3-chrysenes exhibit little depletion even in the advanced stages of crude oil weathering and the ratio of C_3-dibenzothiophene/C_3-chrysene (D3/C3) provides a measure the degree of weathering of a sample of crude oil collected from the environment (Douglas *et al.*, 1996).

Combustion products are distinguished from all oils by the dominance of 4- to 6-ring PAH over the lower molecular weight 2- to 3-ring PAH and by the dominance of the unsubstituted compound over the alkylated homologues particularly for the four-ring and higher homologous PAH series. PAH alkyl homologue series maxima at C_1 and higher usually can be taken as a sign of mature organic matter or petroleum, whereas a maximum at C_0 usually indicates combustion (Laflamme and Hites, 1978; Sporstøl *et al.*, 1983; Wakeham *et al.*, 1980). For example, the alkyl phenanthrene/anthracene (P) series for petroleum has an essentially linear concentration increase to higher homologues, whereas wood, brown coal and coal combustion maxima generally are at C_0 for the alkyl P plus the naphthalenes (N), fluoranthene/pyrenes (FP) and benz[*a*]anthracene/chrysenes (C)(Grimmer *et al.*, 1985; Grimmer *et al.*, 1983; Schauer *et al.*, 2001; Simoneit, 1985).

The mono- and triaromatic steranes are produced by the aromatization of steranes as petroleum matures (Peters and Moldowan, 1993). The aromatic steranes are highly resistant to degradation and these compounds will preserve oil source profiles even in heavily biodegraded samples (Boehm *et al.*, 2001; Peters and Moldowan, 1993; Short *et al.*, 1999). A ratio of two refractory constituents of crude oils, the triaromatic steroids to the methylchrysenes, can be used to distinguish crude oils from coals in Prince William Sound (Boehm *et al.*, 2001; Short *et al.*, 1999).

METALS

Crude oils, drilling muds and produced water can all have distinctive concentrations of heavy metals or other inorganic constituents that have the potential to be tracers for the identification of sources of contamination from the offshore oil and gas industry.

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[5] Nytoft *et al.* (2002) report that 18α(H)-oleanane and lupane, which coelute on non-polar gas chromatography columns, may have been misidentified in some publications, even though lupane has three characteristic mass fragments not in common with oleanane. These authors believe that lupane or a mixture of oleanane and lupane may have been reported as oleanane. The work on the Queen Charlotte basin samples by Fowler *et al.* (1988) is free of this error, however.

Crude oils

That crude oils can have high concentrations of V and Ni is well known, and for V in particular, the concentrations can show much variation from one source oil to another (Yen, 1975). Concentration ranges reported by Yen for a series of crude oils are from 0.09 mg/kg to 1.2 g/kg for V and 0.23 mg/kg to 100 mg/kg for Ni. These metals exist in the oils as metalloporphyrin complexes as well as nonporphyrin complexes and their concentrations generally increase with increasing asphaltic content of the oils, i.e., higher metal concentrations in heavier crude oils. Because these two metals exhibit large concentration ranges and are actual components of the oils, not just contaminants associated with, for example, clay particles, they have potential as tracers for crude oils from different source environments. It is noteworthy that measurements of the inorganic composition of terrestrial surface hydrocarbon occurrences in the Queen Charlotte Islands (Hamilton and Cameron, 1989) show concentrations of V and Ni that are much lower than the North American crude oil averages.

In recent years, attempts to 'fingerprint' oil and oil residues tend to have focused primarily on the biomarker and PAH data (see sections above). Unequivocal identification of hydrocarbon sources based on these compounds, however, is not always straightforward (see, e.g. Prince William Sound controversy described above). So, there continues to be a potential for usefulness of measurements of V concentrations or V/Ni ratios as an independent marker of hydrocarbons from different sources.

Drilling muds and cuttings

Ba is clearly the most important tracer of drilling muds in the environment because barite ($BaSO_4$) can make up 80-90% of the mud. Although drilling muds are recovered before cuttings are discharged, cutting/mud residues in sediments adjacent to offshore drilling rigs can have as much as several hundred g Ba/kg of sediment (Carr *et al*., 1996; Kennicutt *et al*., 1996; Olsgard and Gray, 1995). Pure drilling mud may contain as much as 500 g/kg of Ba. Fine-grained continental-shelf sediments normally contain some hundreds of mg/kg of Ba, and sandy sediments, much less, so the potential for an enrichment factor of the order of 1000:1 clearly exists. Not surprisingly, as drill cuttings are rather course and barite rather dense, Ba concentrations in sediments decrease rather rapidly with distance from the drill sites. Ba concentrations usually decrease to background levels within 1000 m of a drill site (Kennicutt *et al*., 1996; Daan and Mulder, 1996). Other metals that are associated with drill cuttings (Cd, Cu, Hg, Pb, Zn, etc.) can show very similar distribution patterns in sediments near rigs and strong covariances with Ba (Carr *et al*., 1996; Kennicutt *et al*., 1996, Olsgard and Gray, 1995).

Because all these metals are naturally occurring components of sediments that exhibit natural variability, optimum use of Ba or other heavy metal tracers in sediments depends to a great extent on our understanding of these natural distributions. One of the most important factors in determining heavy-metal concentrations in sediments is the grain size of the sediments. Heavy-metal concentrations in shelf sediments generally increase in a rather predictable fashion with decreasing grain size of the sediments. Although several geochemical tracers (Al, Fe, Li) for normalising heavy metal concentrations for this grain size effect have been proposed, Li seems to work best (Loring, 1990, 1991). Subtraction of background concentrations of Ba (or other heavy metal tracers) based on Li-normalised concentrations substantially increases the sensitivity of Ba (or another heavy metal) as a drilling mud tracer. It is thus important to include measurements of at least one of these grain-size normalisers (preferably Li) in any surveys of metal concentrations in sediments in the vicinity of drilling operations.

Produced water

Produced water is by far the largest volume waste from production platforms. It is generally discharged to the sea after its hydrocarbon content has been reduced below regulatory limits by hydrocycloning or similar removal processes. Produced waters comprising formation water from the oil bearing geological structure, water injected to improve oil recovery and any chemicals added to improve oil separation or prevent corrosion, can have very high, but very variable, concentrations of salt, heavy metals, ammonia, silica, and radionuclides. Any of these components has the potential for being tracers of discharges from the platform, but their utility depends greatly on two factors: 1) the variability in time and space of produced water composition, and 2) the chemical reactions that occur when produced water mixes with seawater.

Produced waters are invariably hot and devoid of oxygen. The content of other chemicals, however, varies from concentrations that are similar to, or even lower than, those in seawater to concentrations that are as much as 100,000 times those in seawater. Observed concentration ranges based on data available from the literature for a number of these are listed in Table 5 together with some estimates of concentrations expected in seawater from the B.C. north coast. Neff (2002) provides a recent list of produced-water concentrations.

His compilation gives similar, but somewhat broader concentration ranges for most of the metals in Table 5 and includes numerous references to grey literature unavailable to others. In both cases, the numbers are taken from a wide diversity of sources, so to some extent the variability may represent differences in analytical techniques, but to a large extent the variation is real. The large ranges in concentrations limit our ability to reach general conclusions about the usefulness of these chemicals as tracers. Most of the variability indicated in Table 5 represents spatial variability in the concentrations, i.e. variability in conditions from one formation to another. There is also, however, variability with time in an individual field. Measurements made over very short time scales (a few days) indicate a definite consistency in the concentrations (e.g. Utvik, 1999), but over longer time scales concentrations would be expected to change as a field ages and petroleum is pumped from different locations within it. Introduction of water to improve the petroleum flow also can alter metal concentrations as injection water mixes with formation water. Any serious assessment of potential chemical tracers must depend on measurements of the concentrations and variability in the specific fields in the area of interest.

Most measurements of produced waters from offshore platforms find highly saline waters (2-6 times seawater salinity). These high salinities can be used as a tracer for the produced water discharged to inshore environments (Woodall *et al.*, 2001). The other common feature of these high-salinity produced waters is consistently very high concentrations of Ba, Fe, Mn, and Al. These elements all precipitate on contact with oxygenated seawater; Fe, Mn and Al form hydroxides/oxides and Ba forms a sulphate. For low-salinity produced waters that will be buoyant and remain at the ocean's surface, these precipitates can be used as a visual tracer of the produced-water plume. A study of a mine-water discharge provides an example. Yeats *et al.* (1998) report that mine water, which was similar to produced water in most chemical characteristics but not highly saline, as it was pumped into the ocean from Cape Breton coal mines produced a visibly turbid surface plume (Fe hydroxides) that could be followed for several kilometres. The concentrations of these metals, however, are generally lower in low-salinity produced waters, so more sensitive techniques such as quasi-continuous real-time sampling with a pump on a towed surface sled coupled with ship-board heavy metal determination (e.g. Volpe *et al.*, 2001; Esser and Volpe, 2002; Volpe, 2002) may be necessary. Established techniques for following a sub-surface plume generated by the denser highly saline produced waters based on monitoring of Fe concentrations don't exist. There are, however, intruments for in-situ measurement of heavy metals (e.g. Coale *et al.*, 1991) that could be adapted for use on a towed sub-surface sled.

The potential utility of other metals (Cd, Cu, Pb, Zn, etc.) as plume tracers must depend on the chemical characteristics of the produced water in any particular field and also on the temporal variability in the concentrations. Of these elements, only Pb and Zn appear to have consistently elevated concentrations. Even for these two, the concentration factors over concentrations in seawater are not generally as high as those for Fe, Mn and Ba. Fe, Mn and Ba look like the best bets as general inorganic tracers of produced waters. For Ba, it may be difficult to separate signals arising from produced water from those arising from drilling muds. Other metals may be useful for specific fields with very high concentrations of the particular metal. One example is the apparent contamination of water, sediments and biota with Hg released from natural gas wells in the Gulf of Thailand having exceptionally high concentrations of produced water Hg (Fegan, 1996).

A number of naturally occurring radionuclides can be found in produced waters. These include ^{226}Ra, ^{228}Ra, ^{89}Sr, ^{90}Sr, ^{212}Bi, ^{214}Bi, ^{228}Ac, ^{210}Pb, ^{212}Pb and ^{214}Pb (Neff, 2002). The two Ra isotopes are found in by far the highest concentration and have the greatest potential as tracers. They are derived from the decay of U (^{226}Ra) and Th (^{228}Ra) contained in the rocks of the hydrocarbon reservoirs. As with many of the other metals, concentrations of ^{226}Ra and ^{228}Ra show considerable variability (see Table 5) and concentration factors compared to seawater that range from ~10 to 300,000. Rabalais *et al.* (1992) assessed the usefulness of Ra and Pb isotopes as tracers of produced waters in an inshore Gulf of Mexico environment. They found that the produced water plume could be followed farther by Ra anomaly than by salinity anomaly and that elevated ^{210}Pb could be detected in sediments at least a kilometre from the discharge.

The chemical changes that occur when produced water mixes with seawater will also be important. The main chemical reaction will be the precipitation of Fe and Mn oxides or hydroxides and precipitation of $BaSO_4$. Other metals will coprecipitate with these, including the Ra isotopes with $BaSO_4$. These reactions will separate the inorganic chemicals in the produced water that are initially all in the dissolved phase into two components, those that remain in solution and are transported and diluted with the produced water plume and those that precipitate. Because the produced water also contains oil, a third buoyant component comprising oil droplets and inorganic precipitates that adhere to the droplets will also be generated. Ideally, tracers for each of these phases will be available. The hydrocarbons will likely be the best tracers for the buoyant particles but finding suitable inorganic tracers for the other two phases will present a problem.

Because most produced water is highly saline, the initial discharge will sink until its density is reduced to that of seawater by mixing, or it reaches the bottom. It will subsequently continue to mix with seawater as it is transported more or less horizontally with the ambient currents.

Potential tracers for this predominantly dissolved flow include NH_3 and SiO_2, although both of these micronutrients are subject to biological uptake, as well as Ba, Ra, or other heavy metals that have high concentrations in produced water. But all of these metals are likely to be involved in precipitation reactions. Because of this reactivity none of these constituents are ideal tracers. Effective trace metal tracers must be ones with low reactivity, i.e. with low particulate:dissolved partitioning coefficients, and long residence time. But, metals such as U, Mo or V that meet this requirement for low reactivity tend to have low concentrations in produced water. Temperature, salinity or the major-ion content of the produced water (the ratios of major ions in produced water will be different from those in seawater) may end up being the best tracers for the dissolved component of these highly saline produced waters.

Fe and Mn hydroxides/oxides and coprecipitating metals will settle from a produced water plume as they are generated. Ba and Ra sulphates will also precipitate and settle. The most distinctive characteristic of these precipitates will be their Fe content, which could be as much as 50% depending on the actual Fe compounds that precipitate and the other materials that are coprecipitating.

Laboratory measurements done at BIO (Yeats, unpublished) of the material precipitating from produced water/seawater mixtures indicate 20-40% Fe content. Coastal sediments should have 5% Fe or less, so produced water precipitates have at least a 4-8-fold enrichment. Most of the metals showing large enrichments compared to seawater are associated with these precipitate particles in one way or another. Depending on the actual concentrations in the produced water in question, any or all of them have potential as tracers of produced water precipitates in the benthic boundary layer or in fine, easily mobilised surficial sediments.

Measurements of the chemical content of the produced water from the oil fields of the Queen Charlotte basin will be required before potential chemical tracers (if any) for this basin can be identified. As was indicated in the discussion of the identification of drilling mud tracers, establishing the natural background concentrations (i.e. normalising for grain size, etc. using Li) will be important when identifying any produced water precipitate signals in the sediments or boundary layer particulates.

Hot-water vents

Mineral water issuing from underwater vents in the Queen Charlotte Basin could complicate the use of inorganic tracers for oil and gas industry activities. Possible hot-water vents have been identified by sidescan sonar off Hotspring Island east of central Moresby Island (http://parkscan.harbour.com/gwaii/marineconservation.htm). No other real or potential hot-water vents have been shown to exist in the seafloor of the Queen Charlotte basin.

The SEAMAP (Seabed Resource Mapping Program) initiative may identify other potential hot -water vents. The Queen Charlotte Basin has regional program priority. Although the only hotsprings known to exist on the Queen Charlotte Islands are on Hotspring Island, a large number of hotsprings are located along mainland coastal inlets. Underwater hot-water vents should be considered as possible in the Queen Charlotte Basin.

The Hotspring Island springs are among the hottest in Canada. One spring is reported to have a water temperature of 76 ^{o}C (McDonald *et al.*, 1978). The springs' salinities are about 10% of seawater's (Clark, 1985). The SiO_2 concentration in the spring water is about 6-fold larger than the SiO_2 concentration given for produced water in Table5 (Clark, 1985). For the metals reported in Table 5 and in Clark (1985), Al concentrations fall in the produced-water range, Fe and Mn concentrations are 6- and 4-fold less than the lower limits in their produced-water ranges, and the Ba concentration is the same as its lower limit in produced water.

The flow from the springs on Hotspring Island is reported as 153 l/min (McDonald *et al.*, 1978), which is equivalent to 220 m^3/day. Patin (1999, p. 279) reports that produced-water discharges from a platform can reach 2000-7000 m^3/day. Underwater hot-water vents of similar flow to the Hotspring Island springs could affect the use of inorganic tracers for produced water plumes, at least in the far field.

Biota:

So far the discussion has focused on concentrations of metals in water and sediments that are derived from petroleum, drilling muds/cuttings and/or produced water. The potential has been recognised for bioaccumulation of metals from these sources. Neff (2002) recently reviewed the literature on the accumulation of metals from produced water by organisms near oilrigs in the Gulf of Mexico. This review indicated that no accumulation of As, Ba, Cd, Hg, Cr, Cu, Pb, Zn or Ra occurred. Accumulation of Ba from drilling muds, however, has been observed. Levels of these metals in the Gulf of Mexico produced waters were found to be generally rather low except for Ba, Zn and Ra. Trefry *et al*. (1996) did identify isolated instances of bioaccumulation of Pb and Ba that could be related to produced water discharges, and high Zn concentrations were observed in oysters near in-shore Louisiana production facilities. Elsewhere in the world, where metal levels in produced water might be higher, bioaccumulation such as that observed for Hg near natural gas wells in the Gulf of Thailand (Fegan, 1996) might be important. However, no potential for any of these to be a tracer of oil field discharges has been identified.

SUMMARY OF KNOWLEDGE AND KNOWLEDGE GAPS

There is a profound lack of knowledge about organic and inorganic tracer substances in seawater, biota and surface sediments in Queen Charlotte basin. A good data set, however, is available for terrestrial petroleum shows on the Queen Charlotte Islands. This data set is now somewhat dated, but it contains both metal and hydrocarbon fingerprints suitable for comparisons. A similar data set is lacking for submarine petroleum, oil shale and coal shows.

Such data are necessary for a number of reasons. Source identification of petroleum from future releases requires an established benchmark. In addition, the impact of future petroleum releases may be demonstrable only because the influence of the natural and pre-existing petroleum residues is known. Marine organisms may be adapted to, or even be feeding on, these residues. An adequate database may help in delineating the spatial extent of the influence of pre-existing petroleum residues as well. The distribution of identified residues may confirm transport pathways suggested, for example, by modelling water or transport.

Certain heavy metals and other inorganic substances have potential as tracers for drilling and production activities of an offshore oil and gas industry. At present no database is available for the submarine concentrations of these substances in the Queen Charlotte basin. Nor is there at present any database for geochemical tracers that may be used for normalising the sedimentary concentrations of inorganic industrial substances to minimise the grain-size effect and provide reliable chemical fingerprints. If numbers of hot-water vents exist, their presence may complicate the use of inorganic tracers for produced-water plumes and contribute to the variability of sedimentary concentrations of metals in sediments.

Naturally occurring radionuclides have potential as tracers of produced water. Formation waters may contain very high concentrations of certain radionuclides compared to seawater. As with petroleum seeps, natural seepage of formation waters may result in local zones of elevated radionuclides. Hence, a rationale exists to map pre-existing levels of radionuclides before oil and gas industry activities in the Queen Charlotte basin.

Although petroleum oil because of its buoyant nature may be expected to affect the organic composition of the sea-surface microlayer, an emerging issue is the effect on the microlayer of the transfer of inorganic substances associated with buoyant oil particles in produced water. This pathway has the potential to change the concentrations of metals in the surface microlayer over large areas. This change may have consequences to larval forms of animals that concentrate at the sea surface. The potential for such a change underscores the value in obtaining a benchmark for metals, as well as hydrocarbons, in the surface microlayer.

RECOMMENDATIONS

- A guideline document must be prepared for the establishment of benchmarks for petroleum biomarkers and metals to permit source identification of acute and chronic emissions from an offshore oil and gas industry in B.C.;
- Guidelines should refer to, but not be limited to, the petroleum compounds and chemical elements discussed in this report;
- Guidelines should recognise that source identification methods are evolving and that new or refined procedures are likely to be available when work begins to establish petroleum benchmarks;
- Preparation of adequate benchmarks will require advance survey work to characterise the existing petroleum signatures in sediments, seawater and biota in areas where new drilling is likely; and,
- Baseline studies must be completed and the benchmark profiles must be established prior to the commencement of drilling activities.

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TABLES

Table 1. Boiling point ranges for products refined from crude oil[1]

Boiling-point range under atmospheric pressure (°C)	Products
30-205	gasoline
65-150	naphtha
150-280	kerosene
160-400	No. 2 heating and diesel oils, jet fuels
315-540 [2]	No. 5 and No. 6 fuel oils, light and heavy lubricating oils, paraffin waxes
>540 [3]	No. 6 fuel oil, petroleum grease, asphalts, wood preservatives)

[1] summarised from Clarke and Brown, (1977) and Schmidt (1969). [2] reduced crude, used as feed stock for vacuum distillation, thermal and catalytic cracking to produce gasoline and No. 2 distillate [3] vacuum bottoms, which can be blended with lighter stock to make a No. 6 fuel oil.

Table 2. Fingerprinting methods for petroleum in the marine environment[1]

Fraction	Parameter	Environmental persistence	Method [2]	Source specificity [3]	Level of effort/cost [4]
Whole oil	Total petroleum hydrocarbons	Low/moderate	Infrared, ultraviolet, and fluorescence spectrometry; flame ionisation; gravimetric	Low	Low
	Carbon isotopes ($\delta^{13}C$)	Moderate/high	Isotope ratio mass spectrometry	Moderate/high	Low/moderate
Aliphatic	Normal and isoalkanes (C_8-C_{35} +)	Low/moderate	GC/FID	Low/moderate	Low/moderate
	Saturate biomarkers (tricyclic terpanes, hopanes and steranes)	High	GC-MS (SIM)	High	High
Aromatic	Benzene, ethylbenzene, toluene, xylene, (BTEX)	Very low	Purge and trap GC/FID	Low	Moderate
	Polycyclic aromatic hydrocarbons (PAH)	Low/moderate/ high	GC-MS (SIM)	Moderate/high	High
	Mono- and triaromatic steranes	High	GC-MS (SIM)	High	High

[1] Table adapted from Bence *et al*. (1996) [2] GC = gas chromatography; FID = flame ionisation detection; MS = mass spectrometry; SIM = selective ion monitoring. [3] The ability to resolve two or more sources of petroleum hydrocarbons in a sample depends upon many factors, including: 1) initial compositional differences of the sources; and 2) the degree of weathering and the extent to which the identifying constituents are still present and resolvable; and 3) relative concentrations of the sources. [4] Level of effort and cost are determined primarily by two factors: 1) time and labour involved in processing and analysing the sample, and 2) costs of purchasing and maintaining the instrumentation.

Table 3. Typical tricyclic terpanes, hopanes, steranes and diasteranes determined for petroleum fingerprinting and fate and effects studies

Terpanes	Steranes and Diasteranes[1]
Tricyclic Terpanes	*Steranes (m/z 217)*
C_{23}-Tricyclic terpane	20S-13β(H),17α(H)-Cholestane (diasterane)
C_{24}-Tricyclic terpane	20R-13β(H),17α(H)-Cholestane (diasterane)
C_{25}-Tricyclic terpane	20S-5α(H),14α(H),17α(H)-Cholestane
C_{24}-Tricyclic terpane	20R-5α(H),14β(H),17β(H)-Cholestane
Diagenetic (Rearranged) Hopanes	24-ethyl-20S-13β(H),17α(H)-Cholestane (diasterane)
18α(H)-22,29,30-Trisnorneohopane (Ts)	20S-5α(H),14β(H),17β(H)-Cholestane
17α(H)-22,29,30-Trisnorhopane (Tm)	20R-5α(H),14α(H),17α(H)-Cholestane
17α(H),18α(H),21β(H)-28,30-bisnorhopane	24-ethyl-20R-13β(H),17α(H)-Cholestane (diasterane)
17α(H),21β(H)-30-Norhopane	24-methyl-20R-5α(H),14α(H),17α(H)-Cholestane
17β(H),21α(H)-30-Normoretane	24-ethyl-20S-5α(H),14α(H),17α(H)-Cholestane
17α(H),21β(H)-Hopane	24-ethyl-20R-5α(H),14β(H),17β(H)-Cholestane
22S and 22R-17α(H),21β(H)-Homohopane	24-ethyl-20S-5α(H),14β(H),17β(H)-Cholestane
22S and 22R-17α(H),21β(H)-Bishomohopane	24-ethyl-20R-5α(H),14α(H),17α(H)-Cholestane
22S and 22R-17α(H),21β(H)-Trishomohopane	24-propyl-20S-5α(H),14α(H),17α(H)-Cholestane
Biogenic Hopanes	24-propyl-20R-5α(H),14β(H),17β(H)-Cholestane
22,29,30-Trisnorhop-17(21)-ene	24-propyl-20S-5α(H),14β(H),17β(H)-Cholestane
17β(H)-22,29,30-Trisnorhopane	24-propyl-20R-5α(H),14α(H),17α(H)-Cholestane
Neohop-13(18)-ene	*Steranes (m/z 218)*
17β(H),21β(H)-30-Norhopane	20R-5α(H),14β(H),17β(H)-Cholestane
17β(H),21β(H)-Hopane	20S-5α(H),14β(H),17β(H)-Cholestane
Diploptene (hop-22(29)-ene)	24-methyl-20R-5α(H),14β(H),17β(H)-Cholestane
Terpanes	24-methyl-20S-5α(H),14β(H),17β(H)-Cholestane
18α(H)-Oleanane	24-ethyl-20R-5α(H),14β(H),17β(H)-Cholestane
	24-ethyl-20S-5α(H),14β(H),17β(H)-Cholestane
	24-propyl-20R-5α(H),14β(H),17β(H)-Cholestane
	24-propyl-20S-5α(H),14β(H),17β(H)-Cholestane

[1] These steranes are only a subset of the compounds present, but they are the compounds that in most cases can be reliably quantified without GC-MS-MS. Sterane derivatives such as the monoaromatic and triaromatic steranes (m/z 253 and 231, respectively) also can be valuable petroleum source indicators particularly for biodegraded oils (Peters and Moldowan, 1993; Short *et al.*, 1999).

Table 4. Parent and alkyl PAH parameters required for petroleum fate and effects studies

PAH	Molecular Mass	Parent PAH Abbreviation	Alkyl PAH Abbreviation
Naphthalene	128	Na	N0
C_1-Naphthalenes	142		N1
C_2-Naphthalenes	156		N2
C_3-Naphthalenes	170		N3
C_4-Naphthalenes	184		N4
Biphenyl	154	Bp	
Acenaphthylene	152	Ayl	
Acenaphthene	154	Aen	
Fluorene	166	F	F0
C_1-Fluorenes	180		F1
C_2-Fluorenes	194		F2
C_3-Fluorenes	208		F3
Dibenzothiophene	184	DBT	D0
C_1-Dibenzothiophenes	198		D1
C_2-Dibenzothiophenes	212		D2
C_3-Dibenzothiophenes	226		D3
Phenanthrene	178	Pn	P0
Anthracene	178	An	
C_1-Phenanthrene/anthracenes	192		P1
C_2-Phenanthrene/anthracenes	206		P2
C_3-Phenanthrene/anthracenes	220		P3
C_4-Phenanthrene/anthracenes	234		P4
Fluoranthene	202	Fl	FP0
Pyrene	202	Py	
C_1-Fluoranthene/pyrenes	216		FP1
C_2-Fluoranthene/pyrenes	230		FP2
C_3-Fluoranthene/pyrenes	244		FP3
Benz[*a*]anthracene	228	BaA	C0
Chrysene/triphenylene	228	Ch	
C_1-Benz[*a*]anthracene/chrysenes	242		C1
C_2-Benz[*a*]anthracene/chrysenes	256		C2
C_3-Benz[*a*]anthracene/chrysenes	270		C3
Benzo[*b/j/k*]fluoranthene	252	BF	
Benzo[*e*]pyrene	252	BeP	
Benzo[*a*]pyrene	252	BaP	
Perylene	252	Per	
Dibenz[*a,h*]anthracene	278	DhA	
Indeno[1,2,3-*cd*]pyrene	276	IP	
Benzo[*ghi*]perylene	276	Bghi	

Table 5. Inorganic chemical composition of produced water

	Produced water	Seawater	References
Salinity	1-225 ‰	27.1-34.1 ‰	3,4,5,7,8,9,10,11,12,15,16,27
NH3	0-14 mM	No data	4,5,9,11,27
SiO2	250 µM	0.6-80.3 µM	8,27
Al	0.07-2.3 mg/L	30-130 ng/L	2,3,4,6,23
Fe	0.12-680 mg/L	4-140 ng/L	2,3,4,6,8,10,15,17,21
Mn	0.11-11 mg/L	50-70 ng/L	2,4,6,15,21
Ba	0.2-342 mg/L	4-20 µg/L	2,3,4,5,6,7,11,15,16,17,22
Cd	0.05-190 µg/L	0.8-100 ng/L	1,2,4,7,11,13,14,15,21
Cu	0.2-800 µg/L	0.08-0.13 µg/L	1,2,4,6,7,11,13,14,15,16,21
Hg	0.01-7 µg/L	0.5 ng/L	2,3,4,7,9,14,15,17,24
Pb	0.1-840 µg/L	3-9 ng/L	1,2,3,5,7,11,13,14,15,21
Zn	0.26-69000 µg/L	4-500 ng/L	1,2,3,4,5,6,7,8,11,13,15,16,17,21
Ra-226	0.1-1565 pCi/L	0.03-0.045 pCi/L	1,3,7,18,19,25,26
Ra-228	0.6-1509 pCi/L	0.006 pCi/L	1,3,7,18,19,25,26

References for produced water studies: 1) Stephenson, 1992; 2) Jacobs *et al*., 1992; 3) Rogers *et al*., 1992; 4) Tibbetts *et al*., 1992; 5) Schiff *et al*., 1992; 6) Higashi *et al*., 1992; 7) Neff *et al*., 1992; 8) Janks and Cadena, 1992; 9) Tellez and Nirmalakhandan, 1992; 10) Atkinson *et al*., 1992; 11) Roe *et al*., 1996; 12) Flynn *et al*., 1996; 13) Karman *et al*., 1996; 14) Buffagni *et al*., 1996; 15) Trefrey *et al*., 1996; 16) Somerville *et al*., 1987; 17) Utvik, 1999; 18) Mulino and Rayle, 1992; 19) Kraemer and Reid, 1984.

References for seawater studies: 21) Martin *et al*., 1989; 22) Chung, 1980; 23) Orians and Bruland, 1986; 24) Fitzgerald *et al*., 1983; 25) Chung and Craig, 1980; 26) Nozaki, 1991, 27) Ocean Science and Productivity (OSAP) Division archive, IOS, data for Queen Charlotte Basin area (water depth < 400 m).