

## REVIEW

# Molecular and Geochemical Tracers for the Precise Apportionment of Hydrocarbon Spills from Vessels in Critical Coastal Habitats

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## ABSTRACT

The danger of hydrocarbon spills from vessels presents long-term threats to vital coastal environments, such as mangroves, salt marshes, seagrass meadows, coral reef-related shorelines, and ecological sensitivity is coupled with maritime activities. The accurate source apportionment is necessary to perform impact assessment, remediation prioritization and regulatory enforcement, but it is still hard to achieve because of the complex source mixtures and fast post-release weathering. This is a review of molecular and geochemical tracer techniques to determine and apportion ship-produced hydrocarbons in coastal systems. We assess the forensic usefulness of diagnostic biomarkers (hopanes, steranes), n-alkanes and isoprenoids, polycyclic aromatic hydrocarbons, and explore the effects of evaporation, dissolution, photo-oxidation, and biodegradation on molecular fingerprints and their effect on interpretation. They are complementary geochemical evidence, such as stable carbon and hydrogen isotopes ( $\delta^{13}\text{C}$ ,  $\delta\text{D}$ ), radiocarbon limits separating fossil and modern carbon, and elemental indications and evidence of marine fuel and lubricants, including trace metals. The combinations of multi-tracer evidence and chemometric techniques and mixing models, with highlighting built-in discrimination between refined fuels, solving overlapping sources, and quantifying the uncertainty of the situation in complex coastal environments are mentioned. Lastly, we cover new directions of future development, such as high-resolution mass spectrometry, analysis of compound-specific isotopes, and machine learning, and the requirement of standardized protocols and libraries of weathered marine fuels. In combination, these developments can enhance defensible attribution of murderous tanker pollution and uphold protection of susceptible shoreline ecosystems.

**Keywords:** Hydrocarbon Forensics; Vessel Spills; Biomarkers; Compound-Specific Isotopes; Coastal Sediments

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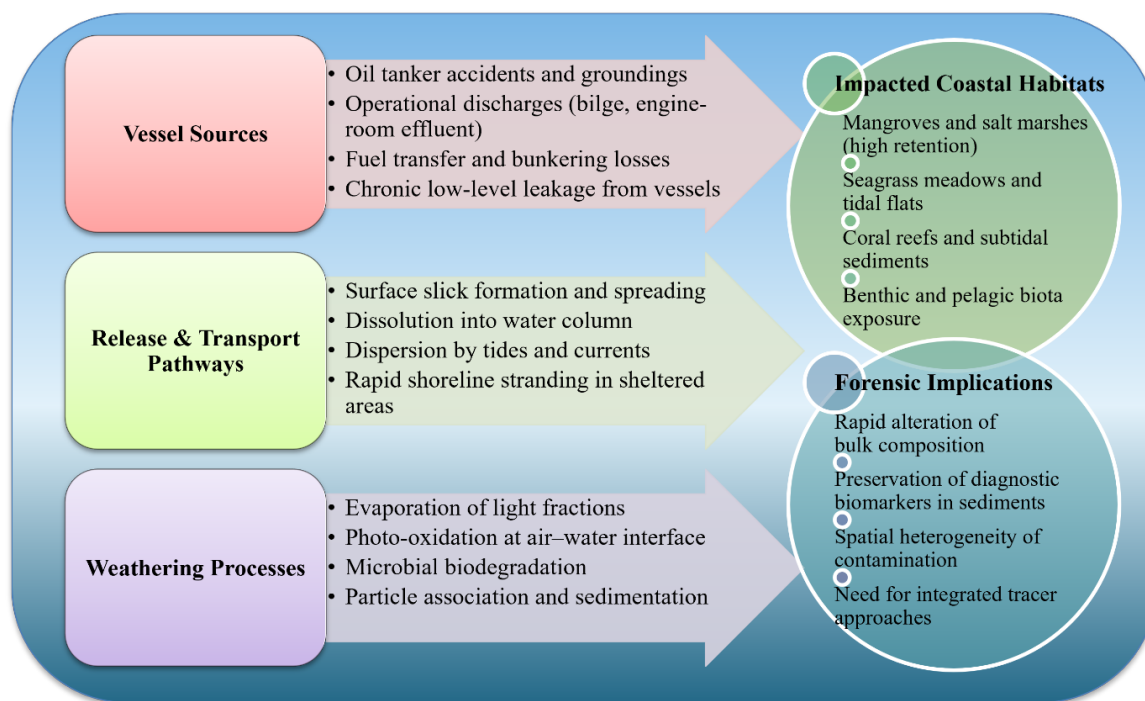
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## 1. Introduction

The coastal ecosystems are considered some of the most productive and ecologically valuable systems on Earth, but they are also being endangered by anthropogenic sources of hydrocarbon pollution<sup>[1]</sup>. Essential ecosystem services are offered by critical coastal habitats, which include mangroves, salt marshes, seagrass meadows, tidal flats, coral reefs, and estuaries, including stabilizing shorelines, nutrient

cycling, carbon sequestration, and nursery areas of marine organisms<sup>[2]</sup>. Their exposure to the major shipping routes, ports and anchorage areas, however, makes them especially susceptible to hydrocarbon inputs that are caused by maritime activities. Accidental and operational hydrocarbon spills of vessels are among them and form an ongoing and unrecognized source of contamination<sup>[3]</sup>. **Figure 1** provides a conceptual overview of the main vessel-related hydrocarbon input pathways to critical coastal habitats.



**Figure 1.** Conceptual diagram illustrating vessel-derived hydrocarbon inputs to critical coastal habitats, including acute spill events and chronic operational discharges, and their transport into surface waters, sediments, and biota.

All vessel-derived hydrocarbon releases represent a broad range of incidents, including disastrous tanker incidents to sustained, low-volume fuel mishandling, bilge water discharge, engine spillages, and unlawful dumping<sup>[4,5]</sup>. Small, poorly documented oil spills, unlike large and well-documented spills caused by commercial shipping, fishing vessels, and recreational boats, are often not immediately detected or reported but have cumulative effects on the ecology in sensitive nearshore settings. These inputs are mainly controlled by refined petroleum products, heavy fuel oils, marine diesel, and lubricating oils, the chemical compositions of which vary significantly from those of crude oils and onshore sources of petroleum. Proper identification and allocation of these inputs is thus very important in environ-

mental impact assessment, remedial planning, and enforcing maritime and environmental regulations.

The apportionment of hydrocarbons in the coastal sediments and biota using source apportionment is still a significant scientific and regulatory issue<sup>[6,7]</sup>. Complex blends of hydrocarbons of various sources, such as vessel traffic, riverine discharge, urban runoff, atmospheric deposition, and in some areas, natural hydrocarbon seeps, characterize coastal environments. Moreover, when petroleum hydrocarbons are discharged into the environment, they rapidly and selectively weather, including evaporation, dissolution, biodegradation, photo-oxidation, and sedimentation, changing their initial chemical structure. These reactions are especially vigorous in deep and sunlit and bioactive coastal areas, making the ef-

forts to trace perceived pollution to certain sources or spillage hard to determine.

Conventional methods of identifying oil spills have been based on bulk parameters, e.g., total petroleum hydrocarbons (TPH) or total polycyclic aromatic hydrocarbons ( $\Sigma$ PAHs), and on visual/operational data<sup>[8,9]</sup>. Although useful in a preliminary screening, these techniques are not as discriminating as needed to differentiate between numerous overlapping sources and between vessel-based sources and background contamination. In a legal and regulatory sense, these restrictions may undermine attribution of liability, postpone the remedial measures and deter the implementation of international conventions which regulate ship-related marine pollution.

In order to deal with these issues, molecular and geochemical tracer methods have become effective tools of hydrocarbon spill forensics<sup>[10,11]</sup>. The molecular tracers, especially the diagnostic biomarkers, including n-alkanes, isoprenoids, hopanes, steranes, and alkylated polycyclic aromatic hydrocarbons, store the source-discriminatory information that may remain even during the extensive weathering of the environment. The ratios and relative distributions of these compounds have been commonly used on fingerprints of petroleum products to distinguish between crude oil, refined fuels and biogenic hydrocarbon feedstock. These tracers are particularly useful in the context of spills of vessels to be able to differentiate between marine fuels and terrestrial petroleum sources, as well as to separate hydrocarbons produced naturally.

Supplementary and usually independent geochemical and isotopic tracers can supplement molecular fingerprinting to give a second and additional line of evidence for source apportionment<sup>[12,13]</sup>. A difference in feedstock source, refining and combustion can be represented by stable isotopic ratios of carbon and hydrogen ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ), whereas radiocarbon ( $^{14}\text{C}$ ) measurements can be used to establish a clear distinction between fossil-derived hydrocarbons and new biogenic organic matter. Auxiliary tracers that are proposed to be utilized to identify vessel-related contamination are trace metals and organometallic compounds linked to a particular fuel formula or engine wear. Such geochemical indicators, when combined with molecular data, can provide a large benefit in the strength and assurance of the source attribution, especially in those environments that are subject

to intricate source mixing.

Although it has made considerable progress in the last few decades, the use of molecular and geochemical tracers to vessel-generated hydrocarbon spills in sensitive coastal environments is still disjointed in interdisciplinary and case study-specific research<sup>[14]</sup>. Numerous of the reviews were done on oil spill forensics or petroleum geochemistry, but there was little specific attention to refined marine fuels or the special biogeochemical situation of coastal ecosystems. On the other hand, research on the subject of coastal contamination has tended to focus either on the ecological consequences or the remediation results, and little has been said about the forensic methodology that supports the source identification. Consequently, it is strongly desirable to have a synthesis that would combine molecular geochemistry, isotopic analysis, and applied environmental forensics, in practice, in the context of vessel-related hydrocarbon contributions to sensitive coastal environments.

In this review, the authors intended to fill this gap by performing a literature review on molecular and geochemical tracer methods to accurately apportion the hydrocarbon spills of vessels in key coastal ecosystems. First, we provide an overview of the chemical properties and behavior of the ship-generated hydrocarbons in the environment, including weathering and overlapping of sources. We then discuss major molecular tracers and biomarker methods applicable in fingerprinting ocean fuels and then discuss isotopic and elemental tracers which can be used to supplement the molecular evidence. Special attention is given to the combination of several tracer lines, the application of multivariate and chemometric methods to enhance the discrimination capability and the evaluation of uncertainty. We conclude with applications in real-life coastal environments, potential uses in environmental management and policy implementation, and future prospects of spill forensics, the occurrence of new analytical tools that can be used to further improve the same<sup>[15–18]</sup>.

This review aims to inform the formulation of more credible, consistent, and justifiable methods of assigning vessel-contributed hydrocarbon pollution in seashores by integrating existing information and establishing methodological strengths and weaknesses. These innovations are vital not only in enhancing the scientific knowledge on the fate and transport of hydrocarbons, but also in enlighten-

ing regulatory systems, remediation plans, and in ensuring the safeguarding of the delicate coastal ecosystems against current and future maritime contamination.

## 2. Characteristics of Vessel-Derived Hydrocarbon Inputs

Vessel-generated hydrocarbons contamination is chemically different than most other petroleum sources to the coastal environment, which represents variation in formulation of fuels, mode of operation, and release<sup>[19]</sup>. The basic idea of successfully using molecules and geochemical tracers to apportion the sources is their understanding. Refined petroleum products are usually dominant in vessel-derived hydrocarbons and have completely different compositions, weathering, and environmental behavior relative to crude oils and natural sources of hydrocarbons.

### 2.1. Types and Composition of Vessel-Related Hydrocarbons

The main hydrocarbons emitted through vessels are heavy fuel oils, marine diesel oils, gas oils, and lubricating oil<sup>[20]</sup>. Heavy oil (typically used in large commercial ships) is a by-product of the petroleum refining process, and it is highly viscous, containing high amounts of sulfur as well

as the largest number of high-molecular-weight hydrocarbons. These fuels have a high level of biomarker compounds like hopanes and steranes, and complex blends of alkylated polycyclic aromatic hydrocarbons, which give important diagnostic information to forensic analyses<sup>[21]</sup>.

By comparison, marine diesel and gas oils are lighter and more refined and have lower viscosities with a higher content of low and mid-molecular-weight n-alkanes and aromatic hydrocarbons<sup>[22]</sup>. The ease with which they weather the environment due to their chemical simplicity compared to heavy fuel oils can also be detrimental in that they lessen the longevity of diagnostic molecular signatures. The lubricating oils that can be discharged by engines or in the course of maintenance procedures usually include unique additive packages, such as organometallic compounds and certain hydrocarbon distributions that might help identify them.

The chemical heterogeneity of these types of fuels gives a chance for source apportionment but also poses challenges. **Table 1** summarizes the major vessel-derived hydrocarbon types, their typical operational contexts, and the compositional features most relevant to forensic source apportionment. While refined fuels may exhibit characteristic molecular fingerprints, overlapping compositions among different products and manufacturers can complicate discrimination, particularly when multiple vessel types operate within the same coastal area<sup>[20]</sup>.

**Table 1.** Major vessel-derived hydrocarbon sources, typical operational contexts, dominant compositional characteristics, and key forensic considerations in coastal environments.

Vessel-Related Hydrocarbon Type	Common Operational Context	Dominant Composition	Forensic Strengths	Typical Complications in Coastal Settings
Heavy fuel oil (HFO; residual/bunker)	Large commercial vessels, shipping lanes, ports	High molecular weight (MW) unresolved complex mixture (UCM), abundant hopanes/steranes, alkyl-PAHs	Biomarkers often persist and remain diagnostic after weathering	High viscosity promotes sedimentation; strong sorption to organic-rich sediments; mixing with legacy residues
Marine diesel oil (MDO)/gas oil	Coastal shipping, ferries, workboats	Higher proportion of low-mid MW n-alkanes and lighter aromatics; fewer heavy fractions	Fresh releases can be distinguishable by light-end patterns	Rapid evaporation/dissolution; diagnostic n-alkanes/PAHs degrade quickly
Lubricating oils	Engine leakage, maintenance, bilge-related releases	Base oils plus additive packages; may include organometallic additives	Additive/elemental co-signatures can aid attribution	Additives vary by brand; weathering and dilution reduce detectability
Bilge/engine-room mixtures	Routine operations or illegal discharge	Mixed fuels, oils, detergents; variable UCM and polar compounds	“Mixture” signatures can indicate operational source	High heterogeneity; difficult to match to a single reference fuel

Table 1. Cont.

Vessel-Related Hydrocarbon Type	Common Operational Context	Dominant Composition	Forensic Strengths	Typical Complications in Coastal Settings
Fuel transfer/handling losses	Bunkering, refueling at docks	Depends on product; often less-weathered signatures initially	Good match potential if reference fuel is obtained	Rapid shoreline/sediment partitioning obscures time since release

## 2.2. Release Pathways and Spill Scenarios in Coastal Environments

The vessels are the sources of hydrocarbons that enter in a range of different ways, affecting the spatial distribution and chemical development of contaminants<sup>[23]</sup>. Acute releases, as caused by collisions, groundings, or fuel transfer accidents, may bring large amounts of hydrocarbons on short time scales, with the effect that there may be recognizable contamination patterns. Conversely, the chronic inputs relating to regular operations such as bilge water discharge, leakage of fuel tanks, and poor waste management practices would result in diffuse and chronic pollution that can remain unnoticed over a long period of time.

Local geomorphological and hydrodynamic conditions are highly affected in these release pathways in critical coastal habitats. High rates of sedimentation, low depths of water, and low circulation favor quick incorporation of hydrocarbons into the sediment, which could last years or decades. Plants like mangroves and salt marshes further improve the hydrocarbon retention ability through physical entrapment and organic interactions, which make them more likely to be exposed to ecological risk long term<sup>[24,25]</sup>.

The intermittent quality of most vessel-related spills, together with the continuous background contributions as a result of shipping traffic, frequently causes a complicated history of contaminations with overlapping indicators of multiple occurrences. This complexity is what ensures that tracers are required to solve subtle differences between different sources and release histories of hydrocarbons<sup>[26]</sup>.

## 2.3. Weathering Processes Affecting Vessel-Derived Hydrocarbons

After being emitted into the marine ecosystem, hydrocarbons emitted by vessels are exposed to a series of weathering processes that quickly change their chemical structure<sup>[27]</sup>. Low-molecular-weight hydrocarbons, especially of

the lighter fuels, are favored by evaporation, which, within hours to days of release, selectively removes them. Selective dissolution to the water column occurs in soluble aromatic compounds and photo-oxidation processes by solar radiation have the potential to convert hydrocarbons to more polar and oxygenated compounds.

Biodegradation is a prevailing set of transformations in coastal ecosystems that encourages the selective elimination of labile substances in the form of n-alkanes and low-ring aromatic hydrocarbons due to the presence of high microbial activity and nutrient levels<sup>[28]</sup>. With the further course of biodegradation, more recalcitrant components such as branched alkanes, hopanes, steranes, and high-molecular-weight polycyclic aromatic hydrocarbons are further impoverished in the remaining mixture. These mechanisms can also alter diagnostic molecular ratios greatly, and thus forget source signatures, unless they are accounted for. Sorption to organic material and fine particles has been shown to have further effects on the hydrocarbon fate in vegetated systems and sediment-rich environments, where it reduces bioavailability and slows the rate of degradation. These interactions will have the ability to maintain the molecular fingerprints over long durations, but may also incorporate the effects of the matrices that make the analysis of the results difficult<sup>[29]</sup>.

## 2.4. Distinction from Non-Vessel Hydrocarbon Sources

One of the main issues in forensic work on coastal hydrocarbons is the identification of the contribution of vessels in relation to other sources of anthropogenic and natural origin<sup>[30]</sup>. Pollution of the urban runoff and river discharge, and in urban setups, can be characterized by the introduction of petroleum hydrocarbons due to road traffic, industries, and domestic waste, with combustion-related polycyclic aromatic hydrocarbons being introduced through atmospheric deposition. In other areas, there are natural seeps of hy-

drocarbons or biogenic sources of production in the marine organisms, which further complicate the background signal.

The hydrocarbons produced by vessels are typically rich in petrogenic compounds and have the molecular patterns of refined fuels, and not combustion products or biogenic lipids<sup>[31]</sup>. But massive weathering and mixing of the sources may obscure these differences, especially in long-affected coast systems. To be able to rely on source apportionment, the detection of strong tracers that can be considered diagnostic despite these conditions is thus necessary.

## 2.5. Implications for Source Apportionment in Critical Coastal Habitats

The chemical diversity, unpredictable release pathways, and quick weathering of vessel-based hydrocarbons all complicate the attempts to attribute contamination in coastal settings<sup>[32]</sup>. The above factors lead to the necessity of a subtle appreciation of fuel composition and environmental behavior when analyzing molecular and geochemical tracer information. Notably, the fact that some of the diagnostic compounds remain in sediments and biota has provided the possibility to identify the spills that happened in the past, even in situations when the visual evidence is no longer present.

Identifying the typical characteristics of the vessel-derived hydrocarbons offers a basis for the establishment of highly effective forensic tools, as will be mentioned in the following sections. Molecular and geochemical tracers can be better utilized to attain accurate and justifiable source apportionment of sensitive coastal environments by considering the process of compositional variability and environmental transformation.

## 3. Molecular Tracers for Hydrocarbon Source Apportionment

The molecular tracers are the foundation of petroleum spill forensics and have seen wide use in identifying and apportioning hydrocarbon contributions in the marine and coastal settings<sup>[11,33]</sup>. The principle underlying these tracers is that petroleum products have characteristic molecular compositions that are used to indicate their source materials and histories of refining. Molecular tracers are especially useful in the situation of vessel-derived hydrocarbon spills since most diagnostic compounds remain present in the en-

vironment even after bulk hydrocarbons have been modified or degraded by weathering.

### 3.1. Diagnostic Hydrocarbon Biomarkers

Biomarkers are molecules, fossils of organisms that have lived and which are retained in petroleum by the geologic processes of time and refining<sup>[34,35]</sup>. The source apportionment biomarkers most commonly used are hopanes and steranes, both of bacterial lipids and eukaryotic cells, respectively. The compounds are relatively stable physically, biodegradation resistant, and not readily altered by weathering in the short term, and thus, it makes them very dependable in demonstrating the presence of petroleum. Vessel fuels and especially heavy fuel oils and residual marine fuel are generally rich in hopanes and steranes that have characteristic homolog distributions and stereochemical structures. Isomer ratios between individual hopene and sterane isomers have been demonstrated to give strong fingerprints that can be compared between environmental samples and probable source fuels. These biomarkers are frequently found in sediments even under the advanced weathering conditions, which enables the retrospective detection of the contamination of vessels.

### 3.2. n-Alkanes and Isoprenoid Hydrocarbons

Another significant group of molecular tracers that can be utilized in hydrocarbon forensics is n-Alkanes and isoprenoid hydrocarbons<sup>[36]</sup>. The patterns of distribution of n-alkanes with the range of carbon numbers and the occurrence of odd and even numbers can give an understanding of the level of refinement and possible biogenic input. The refined marine fuels usually have a relatively sharp range of n-alkanes with little odd-even dominance, as opposed to the higher plant waxes, which are very strongly odd-carbon-number dominant.

Pristane and phytane are some of the isoprenoids that are more advantageous to interpret alongside the n-alkanes<sup>[37]</sup>. Pristane to n-C<sub>17</sub> and phytane to n-C<sub>18</sub> ratios have been extensively used as biodegradation and type of source indicators. These ratios in vessel-derived fuels frequently tend to lie in characteristic ranges that are different from both crude oils and biogenic organic matter. Nevertheless, due to the fact that n-alkanes and isoprenoids are

predominantly degraded by the environment, their diagnostic effectiveness decreases with time, so they should be interpreted carefully.

### 3.3. Polycyclic Aromatic Hydrocarbons as Source Indicators

Polycyclic aromatic hydrocarbons are relevant in separating petrogenic, pyrogenic, and mixed hydrocarbons<sup>[38]</sup>. New fuels derived or produced by vessels are usually high in alkylated low- to mid-molecular-weight PAHs, not because of high-temperature combustion but because of petroleum refining. The fact that alkylated and parent PAHs are relatively abundant, and the distributions of the homolog family, is overwhelming evidence of petrogenic contributions related to marine fuels. The principal molecular tracer classes used in vessel spill forensics, together with their diagnostic value and limitations, are summarized in **Table 2**.

Polycyclic aromatic hydrocarbons are relevant in separating petrogenic hydrocarbons and pyrogenic and mixed

hydrocarbons. New fuels derived or produced by vessels are usually high in alkylated low- to mid-molecular-weight PAHs, not because of high-temperature combustion but because of petroleum refining. The fact that alkylated and parent PAHs are relatively abundant, and the distributions of the homolog family, are overwhelming evidence of petrogenic contributions related to marine fuels<sup>[39]</sup>.

### 3.4. Weathering Effects on Molecular Fingerprints

Environmental weathering has a significant impact on molecular tracer signatures, and it is a significant issue in spill forensics. This results in the progressive enrichment of high-molecular-weight and branched hydrocarbons, varying the relative abundance of many common tracers of use. Consequently, there is continuous evolution of molecular fingerprints after release, and comparison of environment samples and fuels of origin should consider variations in weathering conditions<sup>[40]</sup>.

**Table 2.** Molecular tracer classes commonly applied in vessel-derived hydrocarbon spill forensics, including representative compounds, forensic applications, resistance to weathering, and key interpretive limitations.

Molecular Tracer Class	Examples/Targets	Primary Forensic Use	Weathering Resistance	Key Interpretive Cautions
Biomarkers (terpanes/steranes)	Hopanes (e.g., C <sub>30</sub> hopane), steranes (C <sub>27</sub> –C <sub>29</sub> )	High-specificity matching between field samples and candidate fuels	High	Requires comparable analytical methods and quality assurance (QA)/quality control (QC); overlap possible among similar residual fuels
n-Alkanes & isoprenoids	n-C <sub>10</sub> –n-C <sub>35</sub> ; pristane, phytane	Fuel type indication; biodegradation state; biogenic vs. petrogenic screening	Low–moderate	Rapid loss of light ends; plant wax inputs can confound unless carbon preference index (CPI)/odd–even patterns considered
PAHs (parent + alkylated)	Naphthalenes, phenanthrenes, dibenzothiophenes; alkyl homolog series	Petrogenic vs. pyrogenic; product discrimination (especially alkyl patterns)	Moderate	Photo-oxidation/biodegradation shift ratios; combustion sources elevate parent PAHs
UCM and resolved/unresolved patterns	Gas chromatography–flame ionization detector (GC-FID) UCM “hump” vs. resolved peaks	Residual fuel indication; chronic contamination assessment	High	UCM is not uniquely diagnostic; legacy contamination may resemble fresh residuals
Polar/oxygenated products (emerging)	Oxidized PAHs, sulfur/oxygen heteroatom classes (high-resolution mass spectrometry, HRMS)	Weathered spill tracking; extended “fingerprint” beyond classic targets	Variable	Method-dependent comparability; reference libraries often lacking

Weathering-dependent alterations may cause the obscuration or degradation of the simplest molecular markers, e.g., light n-alkanes and low-ring-number PAHs, and preserve more resistant biomarkers fairly intact. Accordingly, to ensure stable compounds, multi-level analytical approaches are necessary in any old contamination case where source apportionment is required. Experiments and reference libraries of weathered fuels in laboratories have gained importance in understanding the molecular data of coastal sediments and biota<sup>[41]</sup>.

### 3.5. Strengths and Limitations of Molecular Tracer Approaches

Molecular tracers offer several advantages for the apportionment of vessel-derived hydrocarbon spills, including high source specificity, compatibility with established analytical techniques, and applicability across a wide range of environmental matrices<sup>[11,42]</sup>. When appropriately selected and interpreted, these tracers can provide compelling evidence linking contamination to specific fuel types or spill events.

However, molecular approaches also have inherent limitations. Overlapping compositions among refined fuels, extensive environmental weathering, and mixing of multiple sources can reduce discriminatory power. In addition, reliance on a single class of compounds may lead to ambiguous conclusions in complex coastal systems. These limitations highlight the importance of integrating molecular tracer data with complementary geochemical and isotopic indicators, as discussed in the following section, to achieve more robust and defensible source apportionment outcomes<sup>[43]</sup>.

## 4. Geochemical and Isotopic Tracers

These geochemical and isotopic tracers are a fundamental supplement to the molecular fingerprinting in the process of forensic apportionments of vessel-generated hydrocarbon spills<sup>[44]</sup>. Although molecular biomarkers contain considerable information on the composition of petroleum, there are geochemical pointers that provide autonomous restrictions on the derivation, pathway of change, and fusion of sources of hydrocarbons. This should be particularly true in complicated coastal settings where molecular signatures can be lost, or even merged between fuel types, by weathering

or other sources of confusion, where isotopic and elemental tracers can help make the attribution of sources much more confident and robust.

### 4.1. Stable Carbon and Hydrogen Isotope Signatures

Carbon and hydrogen isotope ratios have been extensively used to identify the source of hydrocarbons in the marine and coastal environment<sup>[45]</sup>. Isotopic composition of petroleum hydrocarbons. Petroleum hydrocarbons contain carbon that is isotopically equivalent to their original organic material and the geologic processes of hydrocarbon production and refining. Vessel-derived fuels commonly have  $\delta^{13}\text{C}$  values in a fairly limited range typical of fossil petroleum, and are therefore distinguishable (in some instances) by biogenic organic matter and in other cases by separate sources of crude oil.

The isotope ratios of hydrogen ( $\delta\text{D}$ ) give the extra source discrimination dimension, because these ratios both depend on the original deposition environment of the source organic material, and are modified by later refining. A technique has been found especially potent, namely the compound-specific isotope analysis of the individual hydrocarbons; it will retain source data when bulk isotope values are influenced by mixing or degradation. In vessel spill studies,  $\delta^{13}\text{C}/\delta\text{D}$  data should be utilized to differentiate between refined marine fuels and terrestrial petroleum sources as well as natural hydrocarbon seeps<sup>[44,46]</sup>.

### 4.2. Radiocarbon Approaches to Source Differentiation

Radiocarbon is a sure way of distinguishing between fossil hydrocarbons and contemporary organic carbon<sup>[47]</sup>. Since petroleum products contain no radiocarbon because of their geological age, measurements of the  $^{14}\text{C}$  are reliable in showing that petroleum fuels were being contaminated in a setting where other organic materials were being produced. This method particularly comes in handy in vegetated coastal environments where biogenic hydrocarbons of plants and microorganisms can obscure petroleum in bulk chemical measurements.

Radiocarbon methods have been less widely used on the compound-specific level because of the complexities in-

volved in the analysis and are costly, but the development of accelerator mass spectrometry has increased their applicability in environmental forensics. Radiocarbon information, when combined with molecular biomarkers, can give powerful limitations on the input of vessel-of-hydrocarbon-

generated sedimentary organic carbon pools, even in systems with a large amount of source mixing<sup>[48]</sup>. **Table 3** provides an overview of geochemical and isotopic tracers commonly employed to complement molecular fingerprinting in coastal hydrocarbon source apportionment.

**Table 3.** Overview of geochemical and isotopic tracers used in hydrocarbon spill forensics, their primary diagnostic value, optimal application contexts, and major interpretive constraints.

Tracer Category	Measurement Type	What It Helps Distinguish	Best-Use Scenario	Limitations/Controls Needed
Stable carbon isotopes	Bulk $\delta^{13}\text{C}$ or compound-specific $\delta^{13}\text{C}$	Differentiation among petroleum types; separation from biogenic organic matter (OM)	Mixed-source sediments; corroborating molecular matches	Mixing can mask differences; fractionation during biodegradation requires caution
Stable hydrogen isotopes	Bulk $\delta\text{D}$ or compound-specific $\delta\text{D}$	Adds discrimination axis; can separate similar $\delta^{13}\text{C}$ sources	When biomarker patterns overlap among fuels	Environmental exchange effects are limited for many hydrocarbons but method QA is critical
Radiocarbon	Bulk $^{14}\text{C}$ (and emerging compound-specific $^{14}\text{C}$ )	Fossil vs. modern carbon; petroleum vs. biogenic inputs	Vegetated habitats with strong natural OM background	Cost/availability; compound-specific $^{14}\text{C}$ remains technically demanding
Trace metals	V, Ni, Fe (and others depending on fuel/additives)	Residual fuels and lubricant/additive co-signatures	Supporting evidence for HFO/lube impacts	Metal mobility affected by redox/mineralogy; need background baselines and sediment normalization
Multi-element signatures	Elemental ratios, enrichment factors	Strengthens discrimination when combined with organics	Port/industrial settings with multiple anthropogenic sources	Non-fuel industrial metals can confound; requires careful source-context evaluation

### 4.3. Trace Metals and Elemental Signatures

The other type of geochemical tracers that may have forensic applications are trace metals connected to marine fuels and vessel operations<sup>[49]</sup>. Heavy fuel oils usually contain elements like vanadium, nickel and iron, which are enriched due to their association with porphyrin structures in crude oil and concentration during the refining process. The relative abundance of these metals and their ratios are also used as auxiliary fuel type and origin indicators.

Lubricating oils contain organometallic additive packages (e.g., Zn, Ca, P from Zinc Dialkyl Dithiophosphate—ZDDP and detergents) that are absent in unadditized fuels. These additives persist in environmental samples and provide diagnostic ratios (e.g., Zn/Ca, P/Zn) capable of distinguishing operational discharges from fuel spills. For example, used crankcase oils typically exhibit elevated Zn and P with Zn/Ca > 0.5, while fuel oils show negligible additive signals. Such signatures remain detectable in weathered slicks and sediment extracts, enhancing source apportionment reliability. Besides fuel-based metals, metals that may be vessel-based include elemental products related to wear of engine and lu-

bricating oils additives, as well as antifouling coatings<sup>[50,51]</sup>. Even though these tracers are hardly diagnostic, when used together with petroleum hydrocarbons, they can be used to enhance source attribution when viewed in a greater molecular and isotopic context. Redox conditions and the sediment composition are some environmental factors that may affect metal mobility and bioavailability, so that post-depositional processes should be considered carefully.

### 4.4. Isotopic Effects of Weathering and Biodegradation

The process of environmental transformations may change the isotopic building of hydrocarbons, making the interpretation of sources more difficult<sup>[14]</sup>. In particular, biodegradation can tend to be isotopically fractionated, with the remaining hydrocarbons enriched in heavier isotopes as the lighter isotopes are selectively used by microorganisms. Isotopic shifts may also be induced by photo-oxidation and volatilization, but the effects are usually smaller.

The pattern of these fractionation patterns is important in the interpretation of the isotopic data of weathered

spills. Compound-specific isotope analysis has proven itself useful in the differentiation of source-related isotopic variation and environmental processing. Isotopic trends in several compounds with different degradation rates allow the determination of the origin of weathering as well as the degree of weathering of vessel-origin hydrocarbons in coastal environments<sup>[52]</sup>.

#### 4.5. Integration of Geochemical Tracers in Forensic Investigations

The most powerful feature of geochemical and isotopic tracers is that they are combined with molecular fingerprinting techniques<sup>[53,54]</sup>. These independent lines of evidence can be used to determine ambiguities that might be caused by taking one line of analysis. To illustrate, digital information such as isotopic data can be used to support molecular matches between the environment and the suspected source fuels, whereas trace metal signals can be used to provide contextual data about the type of fuel used and the activity of vessels.

In regulations and laws, defining multiple and complementary tracers increases the defensibility of source apportionment findings<sup>[55]</sup>. These combined methods have been widely accepted as best practice in the hydrocarbon spill forensics sector, especially in delicate coastal systems, where mixing of sources and vast weathering is widespread. With further development of analytical tools, the systematic use of molecular and geochemical tracers should be seen to occupy a more prominent role in the quantitative attribution of vessel-generated hydrocarbon contamination.

### 5. Integrated Forensic Approaches and Applications in Coastal Habitats

Hydrocarbon pollution in coastal areas is complicated enough to be subject to a combination of several methods in analysis to obtain a sound apportionment of sources. All the molecular, geochemical, and isotopic tracers present a unique but complementary type of information, and a combination of all three tracers has become more of a focal point in hydrocarbon spill forensics of the present day<sup>[56]</sup>. Integrated forensic approaches can be important in the context of

vessel-generated spills in essential coastal environments due to overlapping sources, modeling environmental change, and coming up with a defensible response to scientific, regulatory, and legal purposes.

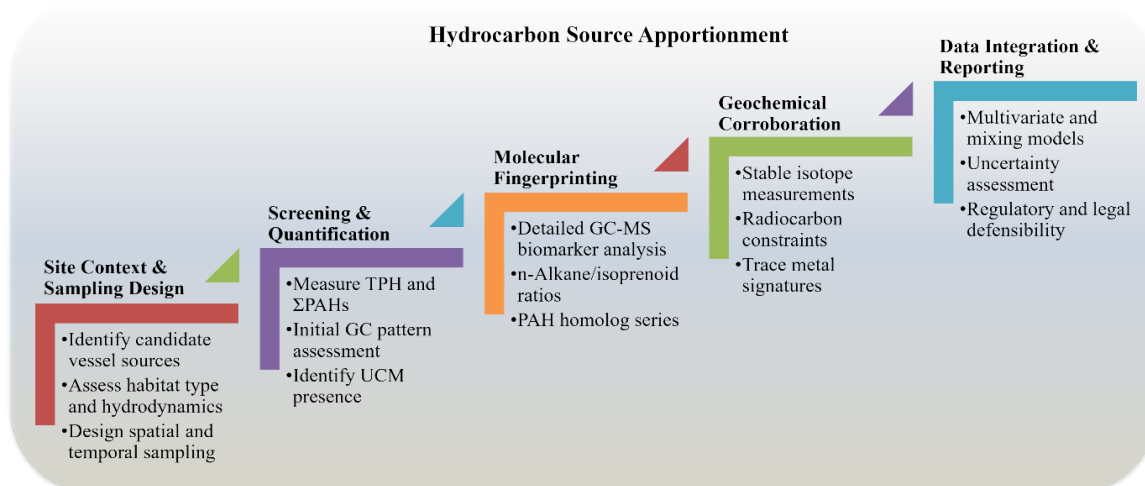
#### 5.1. Multivariate and Chemometric Approaches to Tracer Integration

The integration of diverse tracer datasets is often achieved through multivariate and chemometric techniques that enable objective comparison among samples and sources<sup>[57]</sup>. An end-to-end integrated forensic workflow for vessel spill apportionment in coastal habitats is presented in **Figure 2**. Principal component analysis, hierarchical clustering, and discriminant analysis are statistical techniques that have been extensively used on molecular and geochemical data to draw patterns and groupings that suggest common origins. Such methods come in especially handy when one is working with complicated data that encompasses more than just a few classes of hydrocarbons, isotopic markers, and elemental formulas<sup>[58]</sup>.

Chemometric tools can improve the differentiation between fuels generated by vessels and other hydrocarbon resources by better data dimensionality reduction and the relationship between variables. A recommended integrated workflow for applying these tools to vessel spill investigations in coastal habitats is outlined in **Table 4**. They also facilitate the identification of subtle differences among refined fuel types and degrees of weathering. Importantly, the use of multivariate approaches allows uncertainty to be quantified and visualized, providing a transparent framework for interpreting forensic evidence in complex coastal settings.

#### 5.2. Case Studies of Vessel-Derived Spill Apportionment

Integration of forensic methods in practical coastal settings is successful in the ascertainment of the source of hydrocarbon contamination to a particular vessel. Port, estuary, and nearshore case examples often depict the difficulties of various complex overlapping contributions and higher-order weathering. Here, molecular biomarkers can be used to be able to suggest the potentially petrogenic origin, and isotopic and elemental tracers further narrow down on the likely type of fuel and source<sup>[11,59]</sup>.



**Figure 2.** Integrated workflow for vessel-derived hydrocarbon spill forensics in coastal environments, from sampling design and molecular analysis to data integration, source apportionment, and regulatory application.

**Table 4.** Recommended integrated forensic workflow for apportioning vessel-derived hydrocarbon contamination in critical coastal habitats, from site assessment through regulatory interpretation.

Workflow Stage	Key Actions	Recommended Data Streams	Typical Outputs	Decision/Quality Checkpoints
Site context & sampling design	Identify candidate sources, habitat type, hydrodynamics; design spatial/temporal sampling	Field observations; AIS/shipping logs (if available); sediment/biota matrices	Sampling map; candidate source list	Adequate controls and background sites; chain-of-custody documentation
Screening & quantification	Quantify TPH/ΣPAHs; basic GC patterns; identify presence of UCM	TPH, ΣPAHs; GC-FID/Gas chromatography–mass spectrometry (GC-MS) screening	Presence/absence; contamination intensity	Detection limits; matrix blanks; replicate consistency
Molecular fingerprinting	Detailed GC-MS biomarkers, n-alkanes/isoprenoids, PAH homolog series	Hopanes/steranes; n-alkanes; alkyl-PAHs; UCM metrics	Similarity assessment to candidate fuels	Weathering state assessment; avoid single-ratio conclusions
Geochemical corroboration	Add isotopes and elemental signatures to resolve ambiguities	δ <sup>13</sup> C/δD (bulk or compound-specific); <sup>14</sup> C where needed; trace metals	Independent support for source class and mixing	Baseline correction; normalization (grain size/total organic carbon—TOC for metals)
Data integration & apportionment	Multivariate statistics; mixing models; uncertainty quantification	Principal component analysis (PCA)/Hierarchical cluster analysis (HCA)/Discriminant analysis (DA); Bayesian or mass-balance mixing models; sensitivity tests	Source grouping; contribution estimates with confidence bounds	Model assumptions explicit; end-member characterization; error propagation reported
Reporting & defensibility	Transparent methods, QA/QC, reproducible plots/tables	Full method details; reference fuel metadata; uncertainty statements	Defensible attribution narrative	Clear statement of confidence level; alternative sources considered and ruled out

These reports underscore the significance of context information on the site, such as shipping activity, hydrodynamic conditions, and historical records of contamination. The integrated tracer analysis may give compelling evidence

when environmental samples are directly compared to reference fuels available on the suspected vessels, that contamination is related to particular spillage events or even to operational discharge. On the other hand, lack of regular tracer signatures also serves to rule out some sources, and this highlights the importance of forensic methods in both attribution and source elimination<sup>[33,60]</sup>.

### **5.3. Source Mixing and Apportionment Models**

In most of the systems at the coast, the pollution of hydrocarbons indicates the combination of various sources, not the result of one spillage. To measure the relative contribution of various inputs using molecular and isotopic data, source apportionment models have thus been designed. Mixing models with mass balance principles can use the specific concentrations of components and the ratio of the isotopes to determine the source components, assuming that the end-member compositions are sufficiently described<sup>[61]</sup>.

The variability of fuel and weathering must be put in mind when using such models for contamination of vessels. Model outputs may propagate uncertainty in end-member definitions and transformation processes, which has an impact on the confidence of quantitative estimates. However, with strong tracer selection and sensitivity, source apportionment models provide a worthy tool for converting forensic records into a practical form of information that can be used to manage the environment and make remediation planning.

### **5.4. Implications for Environmental Assessment and Regulatory Enforcement**

The implications of integrated forensic methodologies on environmental damage assessment and enforcement of regulations on coastal areas are great. Accurate source attribution of hydrocarbon contamination is vital in measuring the liability, response and cleanup operations as well as enforcing international and national laws of marine pollution. In sensitive habitats, where contamination at low levels has disproportionate effects on the ecological system, proper source identification is vital in modifications of mitigation efforts<sup>[62,63]</sup>.

The fact that various and independent tracer lines are used adds more credibility to the forensic results in the context of law and policy. Regulatory authorities are becoming

more and more dependent on combined molecular and geochemical evidence to facilitate enforcement procedures as well as to assess the adherence to pollution prevention efforts. In this respect, technological improvements in forensic techniques will directly aid in better environmental management and preservation of the vulnerable coastal environments.

### **5.5. Challenges and Emerging Directions in Integrated Forensics**

Although integrated forensic approaches have proven useful, there are still a number of challenges that they are experiencing despite their usefulness. Their frequent use, especially in regular surveillance schemes, may be restricted by data accessibility, analytical expense, and the fact that it requires specialized skills. Moreover, the interpretation of multicenter, multitrace datasets should have standardized procedures and reporting to achieve inter-study reproducibility and comparability<sup>[11,64]</sup>.

As analytical methods, such as high-resolution mass spectrometry, compound-specific radiocarbon analysis, and machine learning-based classification, have proven to be promising, the possibilities of further expansion of the source apportionment capabilities exist. It is hoped that these developments will lead to better sensitivity, less uncertainty and the ability to examine more complicated contamination cases. Integrated forensic approaches are still being developed and their use in important coastal habitats will be central to not only creating scientific knowledge but also practical management of hydrocarbon pollution that derives from vehicles<sup>[65,66]</sup>.

## **6. Conclusions**

Vessel-based hydrocarbon spills are a longstanding and multifaceted source of pollution in sensitive coastal ecosystems that are a nexus of ecological sensitivity, intensive anthropogenic and dynamic biogeochemical processes. Proper distribution of such inputs is imperative towards comprehending environmental effects, remediation policies, and enforcement of regulations. This review has summarized what is known of the molecular and geochemical tracers with regard to identifying and distinguishing vessel-derived hydrocarbons, and also the strengths of each of them, as well as their overall merits when used as part of an integrated

forensic system.

Detailed compositional fingerprints which indicate fuel type, refining history, environmental transformation are provided by molecular tracers, especially diagnostic biomarkers, n-alkanes, isoprenoids and polycyclic aromatic hydrocarbons. Their tenacity in the sediment and biota renders them extremely vital in the retrospective identification of a spill, even when the weathering is highly advanced. Nevertheless, the vulnerability of certain molecular indicators to degradation and the overlapping nature of compositions between refined fuels highlight the shortcomings of using any one type of compound as a source indicator.

Molecular evidence can be reinforced and supported by important isotopic tracers and geochemical tracers. Radiocarbon measurements, stable isotope ratios and elemental signatures are independent constraints on hydrocarbon origin, source mixing and the pathways of hydrocarbon transformation. These tracers, when used in the context of environmental processes, are able to clear ambiguities associated with molecular fingerprinting and increase the assurance of forensic inferences in complex coastal systems.

A combination of molecular, geochemical, and isotopic data, with the backing of multivariate analysis and source apportionment models, is found to be the best practice for the specific attribution of vessel-contributed hydrocarbon contamination. Critical coastal habitats may benefit especially from such integrated methods, as numerous sources and severe weathering tend to blur original spill indications. The case studies considered above show that integration of various strands of evidence not only enhances source discrimination but also offers clear and justifiable grounds in regard to environmental assessment and regulation decision-making.

In the future, more sensitive and discriminatory power should be obtained by further development of analytical instrumentation, such as high-resolution mass spectrometry and compound-specific isotope techniques. Implementation of new data-driven methods, including machine learning, can provide further possibilities to handle complex data and measure uncertainty in a more rigorous way. In order to enjoy these advantages in their entirety, a standardized approach to methodology, reference material of good character and more synergy between science research and regulation practice seems to be essential.

To sum up, molecular and geochemical tracers represent a sound and dynamic instrumentation for the exact allocation of hydrocarbon spills by vessels in essential coastal ecosystems. Future studies have the potential to enhance the scientific appeal of attributing spills by working together with integrated methods and fostering consistency in methods, enhancing environmental stewardship, and adding to the long-term sustainability of fragile coastal ecosystems in a rapidly used marine ecosystem.

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The author declares no conflict of interest.

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