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Oil Pollution in Water Bodies of Restricted Circulation

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Abstract

Coastal lagoons and embayments near urban centers around the world share many common characteristics and problems. Physical impediments to free water circulation (spits, barrier islands, internal islands, tombolos, submerged sills) often lead to water stagnation and, in the presence of excess nutrients, eutrophication. Urban and industrial activities provoke (usually accidental) spills of hazardous materials into these confined water bodies, such as crude petroleum and refined petroleum products, leading to difficulties for resident biota and potential hazards for human health. The sluggish turnover of these water bodies (or low-energy zones within them) may retard the natural attenuation of the spilled contaminants. The environmental forensics approach uses organic molecular fingerprinting to characterize spills and identify sources, as well as quantitatively monitor the progress of pollutant attenuation. Environmental nuisances and hazards may occasionally be turned to beneficial use, as with the attempt to harvest algal biomass from blooms as a biofuel feedstock and the use of anoxic deep water to sequester polluted sediments. Case studies from locations worldwide including Jamaica Bay (United States), Venice and Orbetello Lagoons (Italy), Lagoa dos Patos and Baía da Guanabara (Brazil), Pearl River Estuary (China), and Grisefjorden (Norway) illustrate these principles.

Key words. Coastal lagoon, stagnation, eutrophication, environmental forensics, petroleum spills, polycyclic aromatic hydrocarbons, Jamaica Bay, Venice, Lagoa dos Patos, Baía da Guanabara, Pearl River Estuary, Orbetello, Grisefjorden

I. Introduction

In the open ocean, currents circulate relatively freely, widely distributing well-oxygenated water. Aerobic organisms require adequate concentrations of dissolved oxygen in order to effectively scavenge and recycle the organic matter in the marine system, such as that created by primary producers in the photic zone. Unlike the open ocean, water bodies (whether saline or fresh) with restricted circulation are bounded laterally and/or vertically by physical impediments to free movement of water currents. If such a body of water were to receive excessive nutrients, particularly nitrogen and phosphorus, a condition known as eutrophication would develop (Segar, 2007; Cloern, 2013). Lacking a continual resupply of the well-oxygenated water, the activity of aerobic scavenging organisms would be suppressed. Therefore, under eutrophic conditions, organic matter produced within the system or entering it from outside would not be effectively recycled and would tend to accumulate in the water column and bottom sediments. If organic material entering a water body with restricted circulation were to include anthropogenic pollutants (for example, spilled crude petroleum or refined petroleum products), the contamination would likely fail to biodegrade efficiently, as aerobic scavengers would lack necessary oxygen. Furthermore, if the affected water body adjoins an urbanized zone, the pollution hazard would be of even greater concern.

Somewhat ironically, it should be noted that naturally-occurring, large-scale, oxygen-poor environments are necessary for the initial stage of petroleum formation (Demaison and Moore, 1980). This first step is the preservation and sedimentary burial of large amounts of microbial organic matter. This has occurred on multiple occasions and in multiple locations over geologic time and has ultimately given rise to Earth's commercial petroleum and natural gas deposits.

After first presenting an overview of environmental forensic methodologies, this review paper documents the impact of petroleum and related anthropogenic contamination on a number of coastal settings world-wide that are characterized by restricted circulation.
II. Principles of environmental forensics.

Environmental forensics is employed to quantitatively evaluate the molecular composition of contaminants, such as spilled petroleum, to determine their type and extent. This chemical "fingerprinting" ideally permits apportionment of blame for environmental damages incurred (Murphy, 2007; Wang et al., 2002). The methodology employed evolved from petroleum geochemistry, which oil companies developed in the latter part of the 20th century for oil-to-oil and oil-to-source rock correlations useful in petroleum exploration. Hundreds of compounds (mostly saturated and aromatic hydrocarbons) have been discovered in petroleum. Many of them strongly resemble common biological molecules, e.g., chlorophyll and cholesterol, and are hence termed biological markers or "biomarkers". Collectively these "molecular fossils" provide strong evidence for the ultimate biological origin of petroleum (Ourisson et al., 1984; Peters et al., 2005).

Although molecular fingerprinting with biomarkers was initially employed in petroleum exploration, it was logical to extend its use to environmental studies, particularly if suspected contaminants are crude petroleum or refined petroleum products.

Figure 1 presents examples of several types of diagrams commonly used in environmental forensics. The data were generated using the standard analytical technique of gas chromatography/mass spectrometry (GC/MS), in which a complex mixture of hydrocarbons and other organic compounds was separated (ideally) into its individual constituents. These were subsequently identified and quantitated. Mass spectrometry, when combined with the power of gas chromatography to separate, conveniently permits the recognition and visualization of groups or "families" of similar compounds. For example, in Figure 1a, the peaks marked with a "+" are all straight-chain hydrocarbons (termed normal alkanes), with the number of sequentially linked carbon atoms increasing from 13 at the left side of the trace to 31 on the right. Among the longer chains (on
the right side) there is a noteworthy predominance of those comprised of an odd number of carbon atoms (25, 27, 29, 31) over the even (26, 28, 30). This is the hallmark of a contribution of waxes from land plants (Eglinton and Hamilton, 1967) and therefore obviously not a mark of contamination in itself. More worrisome is the pronounced hump or bulge under the right side of the trace labeled "UCM", i.e., "unresolved complex mixture". To produce this effect, an excessively large variety of hydrocarbons overwhelmed the ability of the chromatograph to separate ("resolve") them. This feature is characteristic of biodegraded petroleum and is a classic fingerprint of a contaminated soil or sediment in which the spilled petroleum is no longer fresh (Wang et al., 2002).

The scale of a trace may be expanded to reveal greater detail, as in Figure 1b, which displays only the region showing normal alkanes containing 16 to 19 carbons. Some of the other hydrocarbons are now more evident, in particular pristane (pr) and phytane (ph). These two branched-chain (isoprenoid) hydrocarbons are common indicators of the presence of spilled petroleum, with the forensic advantage of being resistant to biodegradation after a spill. Biomarkers with distinctive multi-ring structures, e.g., the hopane group (Fig. 1c), occur in trace amounts, but are among the most useful for fingerprinting purposes (Stout and Wang, 2007). They are persistent in the environment and are unambiguous indicators of the presence of petroleum. Determination of their relative proportions is a standard environmental forensic procedure (Daling et al., 2002; Stout and Wang, 2007).

A number of polycyclic aromatic hydrocarbons (PAHs) are deemed to be priority pollutants by the United States Environmental Protection Agency, the European Commission, and other governmental entities (Lerta, 2010). PAHs such as phenanthrene (Fig. 1d) are found in petroleum, but also occur in the environment as combustion products (Yunker et al., 2002). A common environmental forensics exercise is to ascertain whether the PAHs found in a contaminated soil or sediment sample are derived from spilled petroleum ("petrogenic") or from combustion soot ("pyrogenic"). A pyrogenic mixture of PAHs consists primarily of the parent compounds, i.e., those
with only the central structural skeleton and no appended methyl groups, such as the parent phenanthrene and anthracene in Figure 1d. In contrast, a petrogenic mixture also includes compounds with one, two, or more methyl groups (Bence et al., 2007), such as the clusters of methylphenanthrenes and dimethylphenanthrenes also seen in Figure 1d. It can be concluded that the subject sediment sample of Figure 1 was impacted by both petroleum and combustion-derived contamination.

For greater visual impact, a group of related compounds seen on a standard chromatographic trace may be plotted as a simple bar graph. For example, the series of normal alkanes, marked by "+" in Figure 2a, can be readily displayed as bars (Fig. 2b). The normal alkane data from another samples (Fig. 2c) can easily be compared with the first once it too has been presented in bar format (Fig. 2d). This presentation style is also used with other classes of compounds, including hopane biomarkers and PAHs (Daling et al., 2002).

III. Case Studies

1. Jamaica Bay

The first case study presented is from Jamaica Bay, a relatively small (ca. 70 km²), shallow estuarine embayment in the boroughs of Brooklyn and Queens, New York, USA (Fig. 3a). The bay is protected from the open Atlantic Ocean by a long spit, with a single narrow channel on its southwest corner. The surrounding land is densely urbanized, with Kennedy International Airport along its northeastern margin. A number of tidal creeks and canals incise the shoreline, while the bay itself is dotted with small tidal marsh islands. With a vertical range of nearly 2 m, tidal currents are the principal force for circulation within the bay. The average water depth is only about 5 m but water mixing occurs slowly (Benotti and Brownawell, 2007). Water current circulation is poor,
particularly along the inner portion of the bay. The area nearest the airport is the deepest part of the bay, as it was dredged to provide fill for runway construction, and is afflicted with seasonal stratification, bottom water anoxia, and high (6-7%) organic carbon concentrations in the sediments (Ferguson et al., 2003). The main input of fresh water to the bay is from municipal wastewater treatment plants. After heavy rains, the antiquated combined storm and sanitary sewer systems overflow, discharging raw sewage to the bay. Several Jamaica Bay studies have focused on entrained pharmaceuticals and surfactants as marker compounds for wastewater (Benotti and Brownawell, 2007; 2009; Ferguson et al., 2003; Lara-Martin et al., 2010).

A sample of Jamaica Bay bottom sediment taken at the mouth of the channel (site 1, Fig. 3a) does not show the UCM hump characteristic of biodegraded petroleum on its GC/MS trace. Rather, it shows a pronounced odd over even carbon number predominance among normal alkanes with 24 to 32 carbon atoms (Fig. 2a, b) indicating organic matter derived from land plants. The isoprenoids and fatty acid suggest a contribution of algal debris (Micić et al., 2011). In contrast, the sediment taken from the Hendrix Street Canal on the north side of the bay (site 27, Fig. 3a) shows a distinct hump on its trace (Fig. 2c), evidence of petroleum contamination at this site, which likely overwhelms the input of land plant material, leading to a reduced odd carbon preference (Fig. 2d).

Stable carbon isotopic composition of individual PAHs provides another means to estimate the contribution of petroleum-derived contamination. Using this method, Yan and others (2006) noted summed concentrations of PAHs in Jamaica Bay sediments ranging from 3 to 40 mg/kg, of which about one third appears to derive from petroleum sources, with the remainder due to combustion products. Their PAH trend correlates well the observed presence of the UCM hump on chromatographic traces, which is the more commonly used petroleum indicator, as discussed above.

2. Laguna di Venezia
The Laguna di Venezia (Venice Lagoon) in Italy is protected from the Adriatic Sea by a chain of barrier islands and spits (Fig. 3b). With an area of about 550 km², it is much larger than Jamaica Bay. The average water depth is only about 1 m and the tidal range is a mere 0.3 m (Sfriso et al., 2005), considerably less than in Jamaica Bay. There are a number of islands, the largest of which is in the center of the lagoon and occupied by the city of Venice. There are three principal openings to the Adriatic, altered considerably by human engineering, notably by the ongoing construction of the MOSE floodgate system; circulation is primarily driven by tides and wind (Ghezzo et al., 2010). Major sources of pollutants include the industrial zone of Porto Marghera, agricultural runoff from countryside, urban wastewater from Mestre and other municipalities, and untreated sewage from Venice (Sfriso et al., 2003). Eutrophication events and attendant algal blooms have historically been problematic in the lagoon, although the situation has improved recently, in part due to stricter controls on nutrient inputs (Sfriso et al., 2003).

With intensive navigational activities, including transport of crude petroleum, and runoff from the adjacent urban and rural areas, the lagoon is continually at risk for hydrocarbon contamination. Petroleum hydrocarbons, chlorinated compounds, and fecal sterols from untreated sewage all accumulate in the fine-grained lagoonal sediments (Van Vleet et al., 1988). Within the city of Venice, Wetzel and Van Vleet (2003) sampled sediments from an interior canal, partially enclosed, and open harbor locations (zones marked 1, 2 and 3 respectively on Fig. 3c). They found that interior canal sediments from depths of 30-45 cm below the canal bottom were heavily contaminated, containing around 1200 mg/kg of hydrocarbons, while surface sediments (0-15 cm sediment depth) contained 400-500 mg/kg. Partially enclosed waterways yielded about 400 mg/kg of hydrocarbons, while those from open water locations had ca. 200 mg/kg, still cause for concern, although less extreme than the interior canal sediments. Chromatographic traces clearly show the UCM hump, particularly for the interior canal samples (Wetzel and Van Vleet, 2003). Their environmental forensic study also considered the PAHs in the sediments, which they concluded were
primarily combustion-derived, but with a direct admixture of unburned petroleum. They determined that the hydrocarbon contamination resulted from multiple non-point sources, rather than discrete major spill events. Mussels from the partially enclosed waters, as would be expected, showed higher levels of hydrocarbon contamination than those collected from the open water sites, while no mussels were found at the interior canal sites due to that zone's extreme toxicity (Wetzel and Van Vleet, 2004). In a broader biomonitoring study covering the full expanse of the lagoon, Ricciardi and others (2010) quantified the PAH concentrations in shore crabs, noting significantly higher amounts in animals caught near urban and industrial zones (Venice and Marghera).

3. Lagoa dos Patos

With a surface area of about 10,200 km$^2$, Brazil's Lagoa dos Patos is considerably larger than either Jamaica Bay or Laguna di Venezia. However, like the other two coastal lagoons, it is largely isolated from the open sea by a long, narrow strip of land (Fig. 3d) and is very shallow, with a mean water depth of only 1.7 m. The sole channel connecting the lagoon to the Atlantic Ocean is at its extreme southern end and thus only the southernmost tenth of the lagoon is estuarine (Schwochow and Zanboni, 2007). There are two major urban areas adjacent to the lagoon: Porto Alegre in the north and Rio Grande in the estuarine zone in the south. The long, narrow embayments near Rio Grande provide further impediments to water circulation and suffer episodes of cyanobacterial blooms (da Rosa et al., 2005). Medeiros and others (2005) examined estuarine sediments along the urbanized shore zone of Rio Grande and the mouth of the channel opening to the ocean for concentrations of petroleum hydrocarbons and PAHs (zones 1 and 2 respectively on Fig. 3e). They documented normal alkane and biomarker distributions characteristic of petroleum contamination predominating near the urbanized tip of the Rio Grande peninsula, transitioning to a signature characteristic of land plant and algal organic matter down the embayment to the west. Natural
organic matter predominated at the lagoon mouth. PAH concentrations were also highest in the most urbanized zone, in a distribution indicating contributions of both combustion debris and unburned hydrocarbons.

4. Baía da Guanabara

Unlike the three coastal lagoons discussed above, Brazil's Baía da Guanabara is connected to the open ocean via a narrow channel bisecting a coastal mountain range (Fig. 3f), accentuated by Rio de Janeiro's iconic Morro do Pão de Açúcar (Sugarloaf Mountain). To the north of the channel the bay widens, attaining a total surface area of about 380 km² and an average water depth of 7.7 m, with urban and industrial zones along its shoreline. There are also mangrove swamps, particularly in the northeastern margin (Farias et al., 2008), where they are discernible as darker gray patches on the satellite image (Fig. 3f). There is a deeper central channel amenable to navigation, in contrast to the broad shallow margin (< 5 m water depth) along the northern bay, with weaker current flow (Meniconi and Barbanti, 2007). This enclosed water body, a eutrophic, sub-tropical estuarine system (Carreira et al., 2004) has been afflicted by numerous instances of point and non-point source pollution.

In one particularly egregious incident (in January, 2000) a pipeline ruptured spilling 1600 m³ of marine fuel oil near the mangrove swamps on the northeast (Fig. 3f). It produced a large oil slick on the bay surface, which then spread eastward towards the mangroves. After intensive sediment sampling and environmental forensic (PAH and biomarker) analyses conducted immediately following the spill and again three years later, Meniconi and Barbanti (2007) determined that January 2000 spill had little lasting impact on the bay sediments, a finding that supported their preliminary conclusions (Meniconi et al., 2002). Instead, the observed lagoon sediment contamination appeared to be the result of multiple spills and non-point source input over time. However, the Suruí
mangrove (S on Fig. 3f) suffered significant vegetation mortality after the spill. Extensive PAH and biomarker data from samples collected there over several years indicated a strong and lasting impact from the spill (Farias et al., 2008). These latter authors found that while surface hydrocarbon contamination attenuated rapidly over several years, there was downward migration of the contaminants to the vegetation's root zones, where they predicted it will degrade more slowly due to the lack of oxygen. Brito and co-workers (2009) studied the bacterial populations at the mangrove oil spill site in an attempt to harness appropriate microbes to accelerate the degradation of the contaminants. The effects of hydrocarbon contamination upon marine animals, particularly those harvested for food, are of great concern. Soares-Gomes and others (2010) monitored mangrove animals after a smaller spill of diesel fuel in 2005, observing that PAH concentrations in barnacle tissues returned to background levels several months after the spill. They conclude that barnacles appeared to be among the best candidates for a sentinel species in the Guanabara mangrove environment.

The general trends of sediment contamination by hydrocarbons and sewage in Guanabara Bay show an overall increase to the west, in the direction of the Rio de Janeiro metropolitan area (Carreira et al., 2004; Meniconi and Barbanti, 2007; Christensen et al., 2010). The sluggish, narrow, malodorous Canal do Fundão (CF in Figure 3f), separating the Ilha do Fundão from the mainland, was plagued by multiple forms of contamination for many years. As the canal is adjacent to the campus of the Federal University of Rio de Janeiro and to the main access route from the international airport to the city, its revitalization became an important objective. In a major public works project, 3 million m³ of canal sediments have been dredged. Using an innovative solution, the sediments have been placed in large "geotextile" bags, dewatered, and buried on the island to form new parkland (Pereira, 2012; SEA, 2013).

5. Pearl River Estuary.
The Pearl River Estuary lies at the mouth of one of the largest river systems in China, in a highly populous region that has been undergoing rapid urbanization and industrialization (Fig. 3g). PAH contamination is prevalent in the estuary sediments, with a predominantly petroleum-derived signature, likely due to multiple spills related to transportation (Chau, 2006). An example of such a spill impacted a mangrove forest in Hong Kong's New Territories on the southern shore of Shenzhen Bay (site 1, Fig. 3g). Mangroves develop in quiet, shallow-water conditions with relatively poor water circulation and, as was noted in the example above from Bahía da Guanabara, are vulnerable to oil spills. In this case, mangrove trees were dying mysteriously, prompting an environmental forensic investigation by Tam and coworkers (2005). Quantities of total petroleum hydrocarbons and the unresolved complex mixture were considerably greater those in sediments from uncontaminated mangroves in the region. They noticed a distribution of normal alkanes in the diesel fuel carbon number range (C_{14} to C_{20}) when the spill was relatively fresh, as well as pristane and phytane. They concluded that the spill was likely due to an illegal discharge by fuel smugglers operating on ships offshore. As law enforcement brought the smuggling under control, hydrocarbon analysis confirmed the attenuation of the spilled fuel contamination and a recovery of the mangrove was noted.

In another incident, an oil spill impacted a mangrove swamp in a small estuarine embayment on Hong Kong's Lantau Island (site 2, Fig. 3g). In this case, there was accidental leak of about 270 m^3 of crude oil from a ship in the Pearl River Estuary, heavily contaminating the foreshore zone of the swamp. Ke and others (2002) undertook an environmental forensic study of the affected zone, limited only to analysis of parent PAHs in sediments repeatedly sampled over several months. They noted a reduction in the petroleum pollution which they attributed largely to tidal washing and photo-oxidation.

6. Laguna di Orbetello
Situated on Italy's western coast, the Laguna di Orbetello has an unusual configuration, bounded by two tombolos connecting Monte Argentario to the mainland, isolating the lagoon from the Tyrrhenian Sea (Fig. 3h), which can only be reached by three narrow navigational canals. The historical town of Orbetello lies on the narrow spit which nearly bisects the lagoon. The water body is shallow (average depth < 1 m) covering about 25 km² and suffers from eutrophication, due to its restricted water circulation and high nutrient (P, N) contents from urban, agricultural, and aquacultural inputs (Bastianoni et al., 2008; Lenzi et al., 2003). The resulting nuisance algal blooms have inspired research into the potential beneficial use of its algal biomass as a feedstock for biofuel production (Bastianoni et al., 2008; Migliore et al., 2012).

While there has fortunately been no major petroleum spill in the lagoon to date, nonetheless environmental forensic analyses of the PAH distributions were undertaken (Perra et al., 2009; Specchiulli et al., 2011). Both studies concluded that the overall concentrations of PAHs in the lagoon sediments were considerably lower than those in more heavily industrialized sites around the world, and therefore the lagoon's fisheries are not threatened. The PAH fingerprints indicated a predominance of combustion sources over unburned petroleum input. The greater environmental concern remains the recurring dystrophic crises.

7. Grisefjorden

In southern Norway, a sequential chain of four narrow fjords links the municipality of Flekkefjord to the North Sea (Fig. 3i). The fjords are separated from one another by shallow sills, which form barriers to free flow of bottom waters (Fig. 3j). Of these fjords, Oug (1989) reported that Grisefjorden was particularly contaminated. While no major oil spills occurred, Grisefjorden nonetheless received significant input of sewage, shipyard, and tannery discharges. Bottom
sediments were described as dark, anoxic, organic-rich silt. The water column had high biological oxygen demand and at depth was lifeless, with abundant hydrogen sulfide. Thus Grisefjorden provides a model of limited water circulation different from the cases discussed above, as the impediment to water movement is at the bottom of the water body, rather than on the lateral margins. An essentially separate stagnant, anoxic water mass is present below a depth of about 12 m (Fig. 3j).

Sødal (2003) reported that the legacy of the tannery discharges included a very high chromium burden in the sediment, as well as high PAH concentrations, although a detailed forensic study was not performed. The present plan for the site is to take advantage of the stagnant bottom water conditions and leave the fjord untouched, rather than attempt to remediate the sediments. The toxic, sulfidic bottom waters will prevent biota from entering the zone and there will thus be no uptake of the contaminants into the food chain. Ironically, if the conditions of the water column were to improve, then organism could colonize the sediment and begin to mobilize the pollutants (Løvland, 2013).

IV. Conclusions

Coastal lagoons and embayments near urban centers around the world share some common characteristics and problems. Physical impediments to free water circulation (spits, barrier islands, internal islands, tombolos, submerged sills) often lead to stagnation and eutrophication, particularly in the presence of excess nutrients. Urban and industrial activities provoke (usually accidental) spills of hazardous materials into these confined water bodies, such as crude petroleum and refined petroleum products, leading to difficulties for resident biota and potential hazards for human health. The sluggish turnover of these water bodies (or low-energy zones within them) may retard the natural attenuation of the spilled contaminants. The environmental forensics approach uses organic molecular fingerprinting to characterize spills and identify sources, as well as quantitatively monitor
the progress of pollutant attenuation. Environmental nuisances and hazards may occasionally be
turned to useful purposes, as with the attempt to use algal biomass from blooms as a biofuel
feedstock and the use of anoxic deep water to isolate and sequester polluted sediments.

V. References

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hydrocarbon (PAH) contamination in a mangrove swamp in Hong Kong following an oil spill.


Figure and table captions.
Table 1. Locations of the examples presented.

Figure 1. Example of mass chromatograms generated by pyrolysis-GC/MS of a contaminated sediment. a) Normal alkane (+) distribution and unresolved complex mixture (UCM) shown on the m/z 71 trace. b) Detail of the n-C16 to n-C19 region on the trace in Figure 1a showing the
distributions of the isoprenoids pristane (pr) and phytane (ph). c) Norhopane and hopane biomarkers on the m/z 191 trace from the same sample. d) Phenanthrene, anthracene and alkylphenanthrene distributions from the same sample on a composite m/z 178, 192 and 206 trace. Sediment core sample (Core 37, sediment depth 49-54 cm) collected upstream of the Dundee Dam on the Passaic River, New Jersey, USA. Pyrolysis-GC/MS conditions: Dry, homogenized sediment, CDS 2000 Pyroprobe, 610 °C, 20 s, He carrier. Thermo Finnigan Focus DSQ GC/MS, 30 m J&W DB-1MS column, 0.25 mm i.d., film thickness 0.25 μm, 50 °C for 5 min., 50 to 300 °C at 5 °C min⁻¹, 300 °C for 5 min., 50-500 Da, 1.08 scans s⁻¹.

Figure 2. Molecular fingerprinting examples comparing two surface sediment samples from Jamaica Bay, New York, USA. See Figure 3a for sampling site locations. Numerals: normal alkane carbon numbers, +: normal alkanes, A16: n-hexadecanoic acid, P1: prist-1-ene, P2: neophytadiene, P3: phytene, X: phthalate inadvertently introduced during sample handling. Pyrolysis-GC/MS conditions as in Figure 1. a) m/z 71 trace of sediment from site 1 showing the distribution of normal alkanes and other aliphatic compounds. b) quantitated values of normal alkanes for site 1 sediments derived from the m/z 71 trace in Figure 2a. c) m/z 71 trace of sediment from site 27 showing the distribution of normal alkanes and other aliphatic compounds. d) quantitated values of normal alkanes for site 27 sediments derived from the m/z 71 trace in Figure 2c. Contribution of the interfering phthalate compound (X) estimated by mass spectrometry and subtracted from the n-C25.  

Figure 3. Maps showing locations discussed in the text. Scales are variable. Base maps employ 1999 and 2000 Landsat imagery (https://earthexplorer.usgs.gov). See Table 1 for location details. a) Jamaica Bay. Sample sites 1 and 27 discussed in text. b) Laguna di Venezia. PM: Porto Marghera industrial zone. c) Enlargement showing the city of Venice and the 3 sampling zones discussed in the text. d) Lagoa dos Patos. e) Enlargement of the Rio Grande area and the bay mouth showing sampling zones mentioned in the text. f) Baía da Guanabara. CF: Canal do Fundão. S: Suruí mangrove. g) Pearl River estuary, Shenzhen Bay and Hong Kong's New Territories with the two discussed sampling zones indicated. h) Laguna di Orbetello. i) Chain of fjords near Flekkefjord. j) Depth profile for Grisefjorden indicating water depth below mean sea level (MSL). Dashed line indicates top of anoxic water mass. After Oug (1989).
Table 1. Locations of case studies.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Site</th>
<th>Locality</th>
<th>Latitude</th>
<th>Longitude</th>
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<td>Veneto, Italy</td>
<td>45.42 °N</td>
<td>12.35 °E</td>
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<td>3d, e</td>
<td>Lagoa dos Patos</td>
<td>Rio Grande do Sul, Brazil</td>
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</tbody>
</table>
a

Region enlarged in b below

b

m/z 71

m/z 71

m/z 191

norhopane

hopane

m/z 178

m/z 192

m/z 206

phenanthrene

methylphenanthrenes
dimethylphenanthrenes

Figure 1
Figure 2
Figure 3 (part 1)
Figure 3. Maps showing locations discussed in the text. Scales are variable. Base maps employ 1999 and 2000 Landsat imagery (https://earthexplorer.usgs.gov). See Table 1 for location details.  

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d) Lagoa dos Patos.  
e) Enlargement of the Rio Grande area and the bay mouth showing sampling zones mentioned in the text.  
g) Pearl River estuary, Shenzhen Bay and Hong Kong's New Territories with the two discussed sampling zones indicated.  
h) Laguna di Orbetello.  
i) Chain of fjords near Flekkefjord.  