# *Assessment of Risks Associated with the Shipment and Transfer of LAPIO in the St. Johns River, Northern and Central Florida*

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# ASSESSMENT OF RISKS ASSOCIATED WITH THE SHIPMENT AND TRANSFER OF LAPIO IN THE ST. JOHNS RIVER, NORTHERN AND CENTRAL FLORIDA

## INTRODUCTION

The Jacksonville Electric Authority (JEA) recently proposed an amendment to their Oil Pollution Act of 1990 Facility Response Plan addressing their response strategy for spills of low API gravity fuel oils (LAPIO). LAPIO is defined as an oil having an API gravity less than 10° at 60°F, meaning that its specific gravity is less than or equal to 1.00 mg/L, the same as fresh water. Thus, LAPIO can float, be neutrally buoyant, or sink in water, depending on the properties of the specific oil and the salinity of the receiving waters. Electric utilities are exploring the use of this type of oil due to its relative low cost and high BTU value. JEA proposes to receive tankships of LAPIO at their Northside Generating Station bulk transfer facility adjacent to Blount Island on the St. Johns River. Although it is not being proposed at this time, it is also possible that LAPIO could be shipped to Florida Power and Light's facility at Sanford, as indicated in their facility response plan.

This report provides a detailed review of the chemical and physical properties of LAPIO, an analysis of the resources at risk within the St. Johns River system, and a review of the potential response considerations when dealing with spilled LAPIO. Case histories of LAPIO spills are also provided as examples of the diverse issues associated with an oil product of this nature.

## HOW AND WHY IS LAPIO DIFFERENT THAN #6 FUEL OIL

Conventional #6 fuel oil is a mixture of the heavy residual oil left after the lighter components of crude oil are removed through a refining process, which is then blended with lighter oils to meet specifications for viscosity, pour point, and API gravity. LAPIO is also a blend of heavy and light oils, but it generally contains more of the heavier components. Therefore, LAPIO could be considered as a very heavy #6 fuel oil. However, there are subtle differences that are important in assessing the behavior and effects of LAPIO in the event of a spill. LAPIO is not only heavier, but may differ in chemical composition. To understand these differences, it is necessary to understand how LAPIO is produced.

Residual oils used for blending are derived primarily from three sources (Campbell and Rahbany, 1991):

1. Atmospheric reduced crude. This oil is the residue left when crude oil is heated to boiling and the distillate collected, which is the simplest refining process. Few refineries still use this process.

2. Vacuum bottoms. This oil is the residue from vacuum distillation of the residuum from atmospheric reduced crude (listed above). These residues are the most common source of heavy oils since most refineries use the vacuum distillation process.

3. Heavy slurry oils. These are heavy aromatic oils produced as a byproduct from catalytic cracking. These oils have very different properties than the first two.

In the U.S., refiners have modified their process to include catalytic cracking which produces more of the light refined (and more valuable) fuels from crude oil. In fact, the amount of residual oil generated from a barrel of crude oil dropped from 12 percent in 1978 to 7 percent in 1984 (Campbell and Rahbany, 1991). As a result, less residual oil from the U.S. is available for sale to utilities. Much of the residual oil sold today is obtained from foreign refiners who have not upgraded their refining processes. For East Coast markets, common sources of residual oils are refineries in the Caribbean, South America, and east coast of Canada (Campbell and Rahbany, 1991). The lowest cost residual fuels will be the vacuum bottoms from heavy crudes, which also have high aromatic contents. Thus, LAPIO are likely to be chemically different than conventional crude oils, because of market-driven changes in source and production. Furthermore, there has been a shift in marketing of residual oils, in that oil jobbers now are the dominant suppliers, acting as middlemen who buy residual oils from refineries then blend them for resale on the spot market to electric utilities. Therefore, residual fuels today can vary even more widely in source and properties than before.

Another difference between #6 fuel oil and LAPIO is the amount and source of the cutter stock blended with the residual oil to meet client specifications. No 2 fuel oil is a common blending agent, used to reduce the viscosity of conventional #6 fuel oils. However, LAPIO is blended only to meet client specifications for viscosity, pour point, and sulfur, without having to meet a minimum API gravity requirement. The least expensive LAPIO would be compatible blends of any of the residual oils listed above without any light cutter stock. Again, this difference in blending can result in a very different chemical composition of LAPIO. Figure 1 shows a plot of viscosity versus API gravity for conventional #6 fuel oil and LAPIO. Viscosity increases as API gravity decreases, with the exception of heavy slurry oils. Electric utilities often have to make adjustments to their equipment and/or operating procedures to use LAPIO.

A third difference between #6 fuel oil and LAPIO is the stability and compatibility of the blended oil. Because #2 fuel oil (which is a good solvent for many blended residual fuel oils) is used as the cutter stock, #6 fuel oils are usually well-blended mixtures that are stable during long-term storage and do not tend to separate when spilled. The light component can be lost by evaporation, which is a change in the physical state, from a liquid to a gas. In contrast, problems arising from mixing of incompatible oils are often magnified with LAPIO. Utilities using LAPIO have to deal with problems of asphaltene precipitation during transportation and storage. Asphaltenes are kept in suspension in oil by the presence of aromatic compounds, and they precipitate and settle out when the aromatic content of the oil drops. Blending with a cutter stock that is low in aromatics or mixing incompatible oils in the same tank can cause asphaltene precipitation which leads to changes in the physical properties of the oil and problems during combustion. Of environmental concern, these oils can physically separate into components that float, sink, and/or become neutrally buoyant when spilled on the water. Samples of visually homogeneous oil will separate when simply poured into water in a beaker. This potential for physical separation appears to be unique to LAPIO.

Some people tend to think of LAPIO as similar to asphalt, but this is a poor analogy. Asphalt spills rapidly cool to form solid masses of product, whereas most LAPIO will remain liquid at ambient temperatures. Figure 2 is a plot of pour point versus API gravity for selected residual oils. Trends are difficult to discern because pour point is strongly influenced by the composition of the original crude oil. High paraffinic oils tend to have high pour points and high aromatic oils tend to have low pour points. Thus, when these types of oils are plotted together, there is no clear pattern. However, it is important to note that of the 26 LAPIO samples plotted in Figure 2, only four had relatively high pour points. Based on these data, most LAPIO spills in the St. Johns River will remain liquid, so they will act like fluids when spreading and are less likely to be sticky.

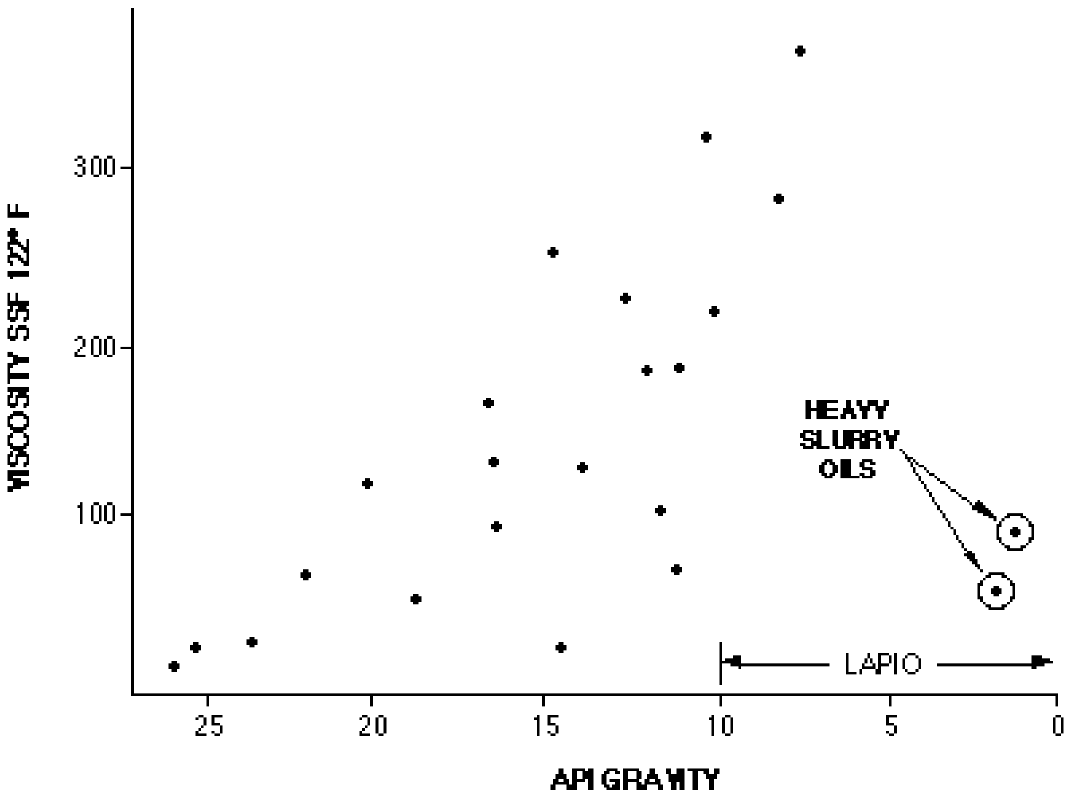


Figure 1. Plot of viscosity versus API gravity for selected residual oils used by utilities (from Campbell and Rahbary, 1991). In general, viscosity increases with API gravity, with the exception of heavy slurry oils.

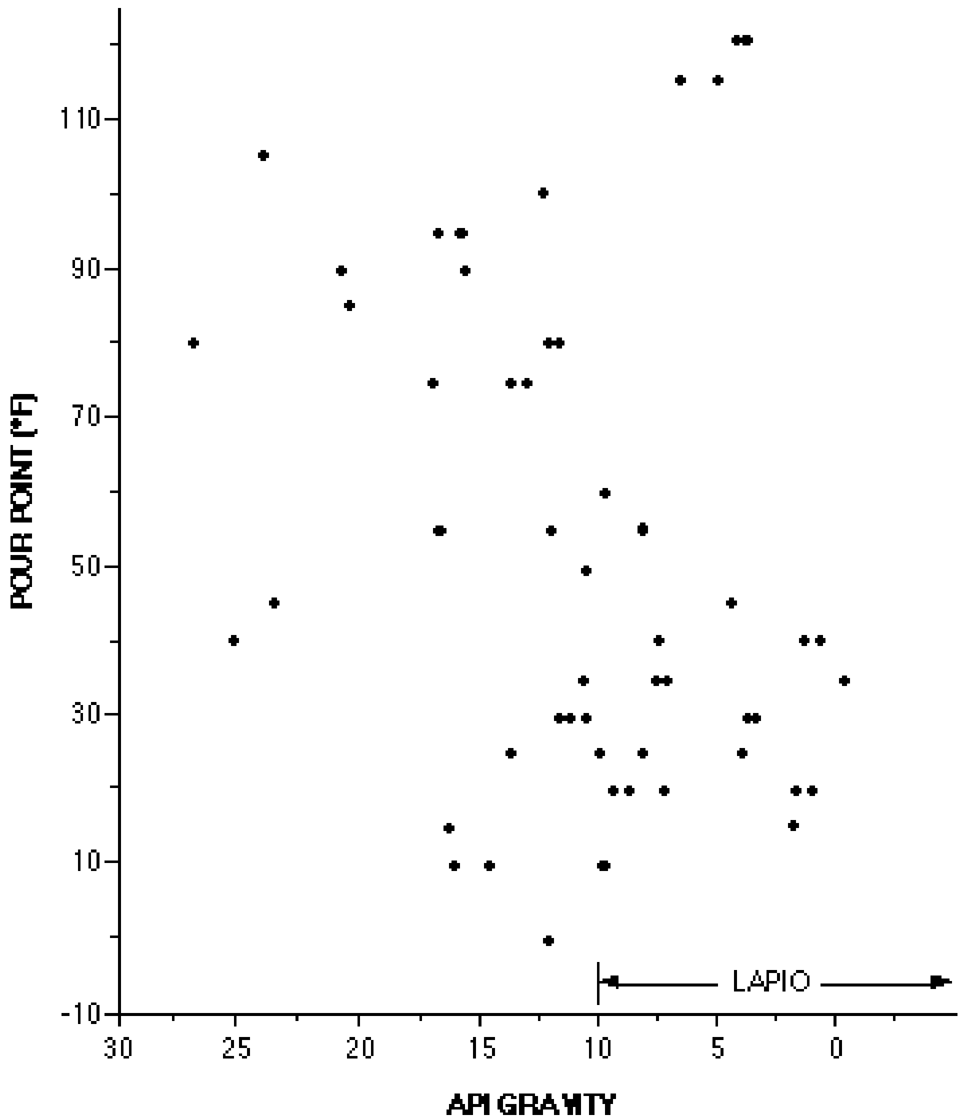


Figure 2. Plot of pour point versus API gravity for selected residual oils used by utilities (from Campbell and Rahbary, 1991). Trends are hard to see because the pour point is closely related to paraffin content of the source crude oil. Note that most LAPIOs have pour points below 45°F, meaning that they are liquid at most ambient seawater temperatures.

# SUMMARY OF RECENT SPILLS WHERE THE OIL SANK

Most of our knowledge regarding petroleum spills is derived from experience with lighter-than-water oils. There is very little information available that deals with response to oils that have a density which allows them to sink or exist in a neutrally buoyant state in the water column. Each documented case to date has been unique and highly problematic. There have been several spills in the U.S. that involved LAPIO or oils that behaved like LAPIO: the SS SANSINENA spill in 1976 (Hutchison and Simonsen, 1979; White and Kopeck, 1979); the MOBILOIL spill in 1984 (Kennedy and Baca, 1984); the Tampa Bay spill in August 1993; and most recently the MORRIS J. BERMAN spill in San Juan, Puerto Rico in January 1994. Brief summaries of these case histories are provided to identify the spill response issues of concern when dealing with LAPIO and LAPIO-like oils.

## *SS SANSINENA, Los Angeles, California, 1976*

The Tanker SS SANSINENA exploded while berthed at Pier 46 in the process of loading more than 30,000 barrels (bbls) of bunker fuel oil on 17 December 1976. The bunker fuel oil had an API gravity between 7.9° to 8.8° and a viscosity of approximately 180 (units reported) at 60°F. Approximately 200 bbls of oil was reported to be floating on the water surface, however, the majority of the oil sank. Divers reported large pools of oil on the harbor bottom, where the oil had settled into depressions along the bottom's uneven surface and collected in pools up to nine feet deep in places. By December 29, divers from the California Department of Fish and Game (CDF&G) found the oil "to have a wrinkled surface with algae growing on it" (White and Kopeck, 1979). The oil was stationary and not affected by tidal action.

Initial recovery operations included using vacuum trucks and separation tanks mounted on a barge. An air eductor was used to further boost the suction of the vacuum trucks. This method was abandoned because the divers were having great difficulty moving the suction along the bottom. Next, diver-guided hydraulic pumps were used. The divers were immediately covered in oil after reaching the bottom, so they had to direct the pumps by "feel". This method of recovery was terminated after the thick accumulations close to the pier were removed, because it was slow and limited by the crane boom reach. Specially designed pumping units consisting of a prime mover and hydraulic pumps mounted on a barge were then used to collect oil from various depressions on the bottom. However, this method was only marginally successful once the large oil pockets had been recovered. In total, nearly 16,000 bbls of the sunken oil were recovered during the initial recovery operations.

Eventually, a suction head device and pump was designed on-site for recovery of the large quantities of oil still remaining on the bottom. This device had to be operated using directions from a diver because some of the oil pools had become silted over and even had marine life living in the silt, making the oil difficult to locate. After using this specialized suction device for nearly sixty days, an additional 10,000 bbls of the oil were recovered from the harbor bottom.

After a third survey, divers estimated that approximately 100 bbls of oil remained on the bottom. However, after another month of continuous effort with the modified suction head device, 250-300 bbls of oil were recovered. By 1 March 1978, all recovery efforts were halted when CDF&G divers reported that recovery efforts were ineffective and that the remaining oil was unrecoverable. CDF&G divers reported a "healthy benthic community" on the harbor bottom.

In total, nearly 33,000 bbls of the oil were recovered over a sixteen month period, indicating that most of the spilled oil was recovered. Multiple recovery techniques were required to recover the spilled oil at a cost of more than three million dollars.

### *MOBILOIL, Columbia River, Oregon/Washington, 1984*

On 19 March 1984, the tank ship MOBILOIL grounded on the Columbia River near St. Helens, Oregon. The tanker was carrying five different oils, including an industrial fuel oil with an API gravity of 5.5° and a pour point of 30°F. The river currents in the spill vicinity dispersed this LAPIO throughout the water column and along the river bottom. Some of the oil sank directly to the bottom, where it was transported downstream by strong river currents at nearly the same rate as the floating oil slick. In the lower river sections, the bottom oil slowed as it became caught up in the salt wedge circulation pattern. The sunken oil was difficult to locate and track. Sorbent pads wrapped around anchors were used to search for bottom oil.

The majority of the floating slicks was flushed from the river within several days. Some of the oil that spilled had pooled behind the vessel in an area protected from the river currents. When the vessel was moved, this pooled oil quickly dispersed and within a day or so, no pooled oil remained in the vicinity of the grounding. Oil suspended in the water column remained for up to one week. The oil on the river bottom was predicted to be present in the river for a period of several weeks (Kennedy and Baca, 1984).

### *BOUCHARD 155, Tampa Bay, Florida, August 1993*

On 10 August 1993, a collision involving three vessels at the entrance to Tampa Bay, Florida resulted in the release of an estimated 325,000 gallons (gal) of #6 fuel oil. Cleanup efforts were successful in removing a significant amount of the floating oil slicks and oil stranded on the shoreline. However, thick mats of submerged oil were found in the nearshore subtidal habitats. It is important to note that this oil was not a LAPIO-type oil as defined, and it also weathered on the water surface for nearly five days before it can ashore. However, it is a good example of the problems to be addressed in recovery of sunken oil.

Submerged oil occurred on the intertidal and shallow subtidal flats fronting a small island just inside an inlet. This oil was successfully removed using vacuum transfer units mounted on barges and grounded on the flat at low tide. However, removal rates were extremely slow, particularly where the oil had stranded in and between mangroves.

Divers conducted surveys of the offshore areas along nearly 6 miles of shoreline and found mobile tarballs on the bottom with a frequency ranging from 1 per 10 square feet to 1 per 100 square feet. They also found a mat of submerged oil that was 150-200 feet long, 10-20 feet wide, and 2 inches thick. Three such mats were observed from aerial surveys. The volume of oily material in the mats was estimated to be 7,800 gal, although the oil contained 37-60 percent water. The oil contained about 2.6 percent sand by volume and had a density of 1.17 g/mL. Thus, it was determined that the oil sank because it had picked up sediment suspended in the water column or after stranding onshore. The submerged oil remained on the bottom and did not re-float. The submerged oil was highly viscous, with a consistency similar to peanut butter.

Attempts to remove the submerged offshore oil had very low success rates. Various vacuum-pumping strategies, including air injection, failed because of the high viscosity of the oil. Very large amounts of contaminated water were generated for very small amounts of oil recovered. Six possible removal techniques were evaluated, with manual removal determined the most feasible option for this spill (Michel and Benggio, 1993). Manual removal of the submerged oil by divers was successfully conducted in a dead-end, seawalled bay. The offshore mats were never removed, and oil continued to wash ashore for at least six months following the spill.

### *MORRIS J. BERMAN, San Juan, Puerto Rico, January 1994*

On 7 January, the towline to the MORRIS J. BERMAN barge parted, and the barge grounded within a few hundred yards of shore off San Juan. The cargo was a LAPIO-type oil (API gravity of 9.5°). Although much of the oil floated, responders reported submerged oil within the first 24 hours, and eventually extensive amounts of submerged oil were found in both offshore areas and in sheltered bays. This submerged oil was not emulsified and remained fluid enough to flow (described as having the consistency of maple syrup). It also tended to re-float during the afternoon. It is thought that this was due, at least in part, to a phenomenon whereby sand mixed with the oil slowly migrated down through the oil, thus allowing the surface layer to refloat. Where the water was very clear and shallow, the areas of submerged oil were readily located. Most of the identified patches were in protected lagoons, embayments, or on the landward side of reefs.

The submerged oil caused many difficult cleanup issues. Shoreline cleanup could not be completed until the submerged oil was removed, because of the continued re-floating of the submerged oil and re-oiling of the adjacent shoreline. Although the submerged oil was being effectively removed by diver-directed vacuuming, the process was extremely slow. Because of the need to open the beaches as soon as possible, it was decided that both large and small dredges would be used to remove the oil more quickly. Dredges generate large amounts of contaminated water and sediment. Four settling pools were used to handle these volumes. Fortunately, the submerged oil was close to shore and in very limited areas, thus all removal operations could be shore-based, greatly decreasing the logistics and costs. Even so, removal cost estimates as of 18 February 1994, including divers, dredging, and miscellaneous support, but excluding treatment and disposal, were $35-$45 per gallon of recovered oil. The degree of emulsification of the recovered product has not been determined, but is assumed to be low.

## BEHAVIORAL MODELS FOR SPILLED LAPIO

Based on an understanding of the general physical and chemical properties of LAPIO and observations during spills, the following behavioral models are proposed for spills of LAPIO. These are descriptive, qualitative models which attempt to predict how spills of LAPIO might behave when spilled in coastal settings. These predicted behavioral models for LAPIO are used in the next section to assess the likely resources at risk during spills.

### Model 1: Oil Remains Liquid, Majority Floats

Under these conditions, a LAPIO would behave in a manner similar to conventional #6 fuel oils. At 60°F, oils with an API gravity of about 6.5° would still be lighter than full strength sea water. Many LAPIOs are likely to float and remain liquid during the early stages of a spill. The light fractions will be lost by evaporation, and the floating oil will initially form contiguous slicks. Eventually the slicks will break up into widely scattered fields of pancakes and tarballs, which could persist over large distances and can concentrate in convergence zones.

### Model 2: Oil Remains Liquid, Majority Does Not Float

In this case, the oil has a specific gravity greater than the receiving water. Some of the oil will float, but the majority does not. As the oil mixes in the water column, it will form small drops. This oil is not expected to adhere to debris or vegetation in the water column. When oil encounters water-wet surfaces, it generally does not stick to them. Where currents are greater than about 0.1 knots, the oil droplets will be kept in suspension. An oil with an API gravity of 0.0° at 60°F has a specific gravity of 1.076, so even very heavy oils can be suspended by alongshore currents. Thus, in most nearshore coastal settings, the oil is not likely to accumulate on the bottom because the currents are strong enough to mobilize the oil. The size of the oil drops is likely to range from 0.5 microns to one millimeter or so. Weathering processes such as evaporation and photo-oxidation will be slower relative to floating slicks, but the drops should eventually weather faster than floating tarballs because of their smaller size.

In low-flow zones (less than about 0.1 knots), the suspended oil could sink and accumulate on the bottom. Direct sinking in low-flow areas was observed during the SANSINENA and the MOBILOIL spills. Thus, it is possible that suspended oil could settle out and accumulate in estuaries in locations similar to those where fine-grained sediments are deposited during slack periods of the tide. However, oil drops are expected to be readily re-mobilized by tidal currents, so long-term accumulation is likely only in areas little affected by tidal or riverine currents. Examples of such areas would include abandoned channels, dredged channels or pits, depressions adjacent to piers caused by prop wash of anchoring vessels, dead-end canals, and in the lee of man-made structures. The oil drops will re-coalesce into pools of liquid oil, which can be up to feet thick, although it can also spread into a thin layer when there are no depressions.

### *Model 3: Oil Remains Liquid, Initially Floats, But Sinks After Picking Up Sand*

This behavior was observed recently during the Tampa Bay and Puerto Rico spills. The oil behaves very much like a conventional #6 fuel oil at first, including rapid loss of the light fractions by evaporation and an increase in viscosity. However, when the oil is transported into shallow water, it is more likely to be temporarily mixed into the water column by wave turbulence because it is heavy. Where the bottom is sandy, the sand is also suspended in the water column by the waves, and some sand is mixed with the oil. The specific gravity of quartz is 2.65 and calcium carbonate is 2.71, so it only takes about 2-3 percent sand by weight mixed into oil with a specific gravity of 1.00 to make it heavier than seawater. The oil/sand mixture is deposited in relatively sheltered areas where it can form extensive, thick layers of oil on the bottom. In Puerto Rico, submerged oil was found in sheltered pockets in the lee of offshore rocks in an otherwise relatively high wave energy setting.

It appears that oil sinks in this manner only when it is mixed with sand. There have been several spills where oil has picked up sand after being stranded on sand beaches. (e.g., Ixtoc 1, Alvenus). After being eroded from the beach by wave action, the oil/sand mixture was deposited at the toe of the beach or just offshore in the form of tarmats. However, during the Tampa Bay and Puerto Rico spills was the first time that sinking of oil caused by oil mixing with sand in the surf zone, prior to contact with the beach was documented.

Submerged oil can form thick, continuous deposits that are hundreds of feet long, or small tarballs. Where there is current activity, especially generated by waves, the oil/sand mixture can form cigar-shaped “rollers” which can be scattered on the bottom or accumulated into mats. These rollers pick up more sand and shell fragments as they move, making them heavier. They can eventually be deposited on adjacent beaches after storms. The extent to which the oil weathers prior to sedimentation has a profound effects on the viscosity and character of the resulting oil/sediment mixture.

Submerged oil can refloat, as was observed during the Puerto Rico spill. There are three possible mechanisms for refloating: 1) the sand can separate from the oil; 2) wave-generated currents can loosen and resuspend pieces of oil from the bottom; and 3) increases in water and/or oil temperature can make the oil more buoyant.

### *Summary of LAPIO Behavior*

Spills of LAPIO-type oils can have complex behavioral patterns, depending on the API gravity of the oil, the homogeneity of the mixture, the density of the receiving water, and the physical setting of the spill site. Oil is only likely to sink straight to the bottom where the currents are very low. Also, denser-than-water oil is expected to mix in the water column as oil drops rather than large, cohesive mats. Only when oil that initially floats mixes with sediment are thick mats formed on the seafloor. Oil can accumulate on the bottom under calm currents, so releases of very heavy oil in harbors with dredged channels and berths in canals could readily sink and form pools of oil on the bottom. Releases in areas subject to tidal and riverine flow are likely to be kept in suspension the water column by currents. If the oil is poorly mixed or unstable, the spill could separate into fractions which can float, suspend, and sink simultaneously.

## RESOURCES AT RISK

The St. Johns River and estuary system provides drainage for nearly one-sixth of the total area of Florida (9,562 square miles). This system extends northward from just south of Melbourne to the river's mouth in Mayport, northeast of Jacksonville (Fig. 3).

This ecologically diverse system is composed of a variety of habitats along its 248 mile route, including: freshwater wetlands, estuarine wetlands, tidal flats, subtidal substrates and habitats, fine-grained sand beaches, mixed sand and gravel beaches, and man-made structures. Due to the natural zonation of the St. Johns River, we have divided the river system into three sections: the marine and estuarine component which extends from Mayport to the Duval/Clay County Line just south of the Jacksonville Naval Air Station at Plummers Cove; the riverine component which extends from Plummers Cove to Sastuma; and the lacustrine component which is upstream of Sastuma (Fig. 3). In evaluating the resources at risk within each section, the information will be presented by river component below.

## MARINE AND ESTUARINE HABITAT RESOURCES AT RISK

### *Shoreline Habitats*

The marine and estuarine portion of the St. Johns River extends from the river mouth at Mayport to the Clay and Duval County line (Fig. 4). Tidal currents in the St. Johns River as far as Jacksonville, are less than one knot on average with a tidal range of 1.2 feet. The

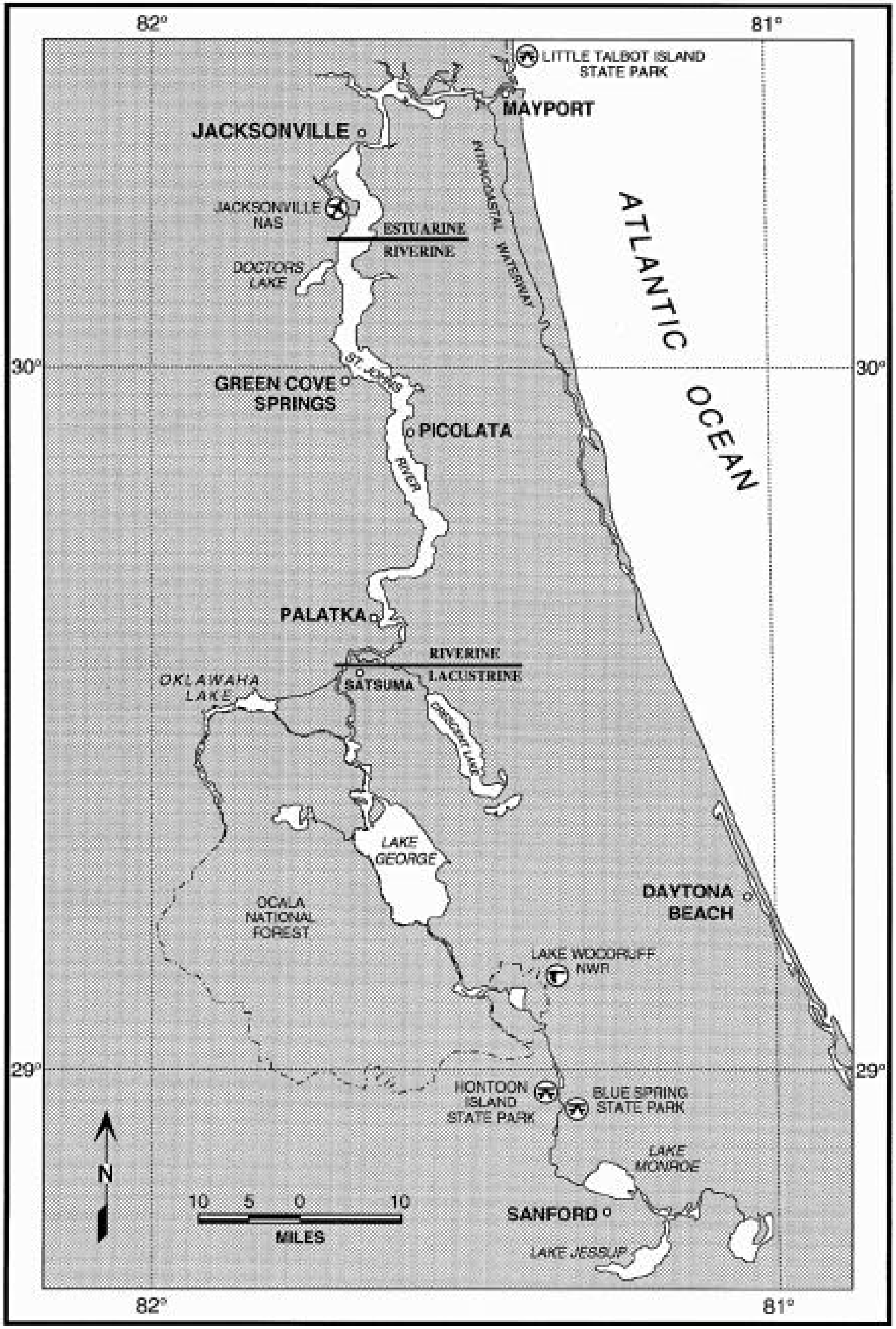


Figure 3. Location map of the St. Johns River.

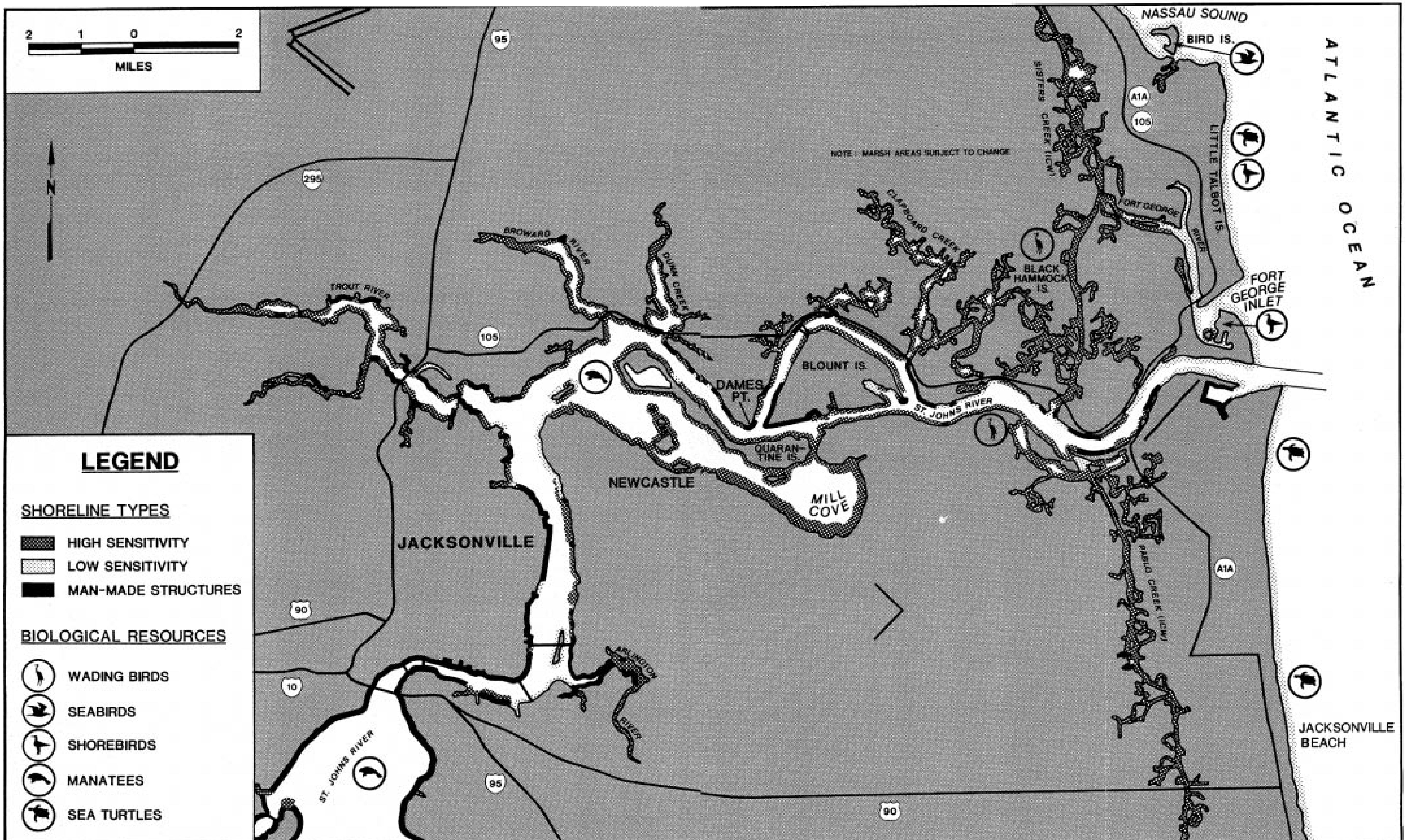


Figure 4. Environmental areas of special concern in the Jacksonville area.

salinity of the upper estuarine portion of the St. Johns River varies with wind action: at low water with westerly winds, the brackish water limit may be at Jacksonville; with a northeasterly wind, brackish water may extend as far upriver as Palatka (NOAA, 1989).

The dominant shoreline habitats within the marine and estuarine areas consist of salt marshes, sheltered and exposed tidal flats, fine-grained sand beaches, mixed sand and gravel beaches, and man-made structures (Fig. 4). Due to the possibility of LAPIO sinking, subtidal habitats are considered as habitats at risk.

Salt marshes are the most common habitat in this section of the river and consist primarily of black needlerush (*Juncus roemerianus*; high marsh—exposed only to irregular tidal inundation) and smooth cordgrass (*Spartina alterniflora*; low marsh—regularly flooded by tidal action). Salt marshes provide important nursery and foraging habitats for many species of birds, shellfish, and fish. For example, "anadromous saltwater fish spawning upstream use these areas to begin the gradual osmotic changes necessary for survival in fresher waters" (SJRWMD, 1993). LAPIO spills affecting salt marsh habitats are of special concern because of the increased likelihood of oil persistence in the marsh sediments. Floating oil slicks usually adhere to the vegetation and seldom strand on the sediments. Instead, the oil is usually lifted off the water-saturated substrate by the rising tide. Floating and neutrally buoyant LAPIO could pick up enough sediment in the marshes to accumulate on the sediment surface and not re-float during high tide. Efforts to remove oil stranded on soft, muddy, vegetated sediments would likely cause extensive additional disruption of roots, mix oil deeper into the sediments, and prolong recovery. Oil effects in marshes are greatest for spills where the sediments have been contaminated.

Salt marshes are often associated with tidal flats, both exposed and sheltered. Species associated with these habitats include oysters, fiddler crabs, snails, and other invertebrates. Higher oil concentrations and longer persistence in marsh sediments would increase the risk of oil exposure, via contact and ingestion, to these animals. Thick accumulations of oil could smother sessile organisms in the immediate vicinity, as well as be a source of chronic oil releases as the oil is mobilized by natural removal processes.

Floating oil slicks are usually lifted off tidal flats with the rising tide. LAPIO could strand on the flats during low water and pick up enough sediment to prevent re-floating, especially on sand flats where the water drained out of the sand during low water. Penetration is likely to be very low because of the high oil viscosity. However, currents would erode the oil/sand mixture from the flat, possibly forming rollers in the adjacent channels. Cleanup of stranded oil from sandy tidal flats is possible, although oil could be mixed deeper into the sediment by foot traffic. Removal of heavy, viscous oil from soft, muddy flats would be extremely difficult, and natural removal rates very slow.

Fine-grained sand beaches and mixed sand and shell beaches comprise the majority of the St. Johns River shoreline from the Intra-Coastal Waterway to the river mouth and outer beaches. LAPIO is not expected to behave idfferently than other heavy fuel oil spills on beaches. Coastal structures are also prevalent along the river, including exposed and sheltered coastal structures and riprap. Biota associated with seawalls and riprap are typically limited to barnacles, oysters, algae, and other smaller invertebrates. Because these structures are steep or vertical, the only different effect might be the formation of a heavier coating of oil if the floating LAPIO is more viscous and sticky.

### Submerged Aquatic Vegetation Habitat

Beds of submerged aquatic vegetation (SAV) are important primary producers and nursery habitats along the St. Johns River (DeMort, 1991). Wigeon grass (*Ruppia maritima*), the most common species in SAV habitat in the estuarine portion of the St. Johns River, is only found in areas with stable substrate (SJRWMD, 1993). The SAV provides a stable habitat for numerous species of invertebrates and fish as well as important nursery habitat for many marine and estuarine organisms. This habitat also provides seasonal foraging grounds for manatees (SJRWMD, 1993). During most oil spills, seagrass habitats are not generally considered to be at great risk, unless the beds are intertidal. However, based on observations of submerged and neutrally buoyant oil in seagrass habitats at the recent Puerto Rico oil spill, sinking LAPIO spills are likely to: adhere to the seagrass blades; affect the animals and plants that are associated with the SAV; become buried in areas exposed to some currents and mobile, sandy substrates; and be a source of shoreline contamination as the submerged oil is refloated when disturbed.

Removal of oil from seagrass beds will be very difficult and likely to result in extensive damage to the vegetation. Removal of buried oil or large mats would require intrusive techniques such as vacuum and dredging. During the Puerto Rico spill, divers used snares to wipe oil from the blades and pick up oil scattered among the vegetation and in the sediment. This effort was very labor intensive and of limited effectiveness.

## RIVERINE HABITAT RESOURCES AT RISK

The vegetation along the St. Johns River consists primarily of freshwater wetlands. The freshwater habitats are composed predominantly of:

- Bottomland hardwood forests (bald cypress, red maple, ash, willow, and several oak species) that border the river and its tributaries from the southern portions of the basin northward to the brackish streams in Duval County;
- Freshwater marshes (cattails and bulrushes) and floating-leaved plants (water shield, spatterdock, and water hyacinth) in areas with direct sunlight; and
- Submerged aquatic vegetation (SAV), eelgrass (*Vallisneria americana*), and coontail (*Ceratophyllum demersum*) in freshwater reaches (DeMort, 1991; SJRWMD, 1993).

Of the freshwater wetland habitats, the SAV would incur the most extensive impacts from exposure to LAPIO that sank, either initially or after weathering or mixing with sediment. SAV provides important nursery habitats for estuarine and freshwater organisms, as well as seasonal foraging grounds for manatees (DeMort, 1991; SJRWMD, 1993).

Most of the riverine portion of the St. Johns River is bordered by freshwater marshes, which provide important nursery and foraging habitats for many species of birds, shellfish, and fish. However, compared to saltwater marshes, there is less likelihood of oil penetrating deep into freshwater wetlands from a spill in the river because of very slow water currents and only very small changes in water level under normal conditions. There could be heavy oil contamination along the wetland fringe, in side channels with significant river flow, and in river bends where the oil may accumulate. However, only during high-water conditions would there be enough current to transport the oil into the wetland more than a few feet.

The bottomland hardwood forests that border the river and its tributaries are considered least at risk from exposure to LAPIO. For the most part, the plants associated with this habitat have deep root systems. Any coating of the exposed portion of these plants is unlikely to result in injury other than stress. If the leaf matter is coated, the plant's photosynthetic abilities might be impaired resulting in defoliation of the affected areas on the plants.

Of greatest concern in freshwater habitats along the river would be the increased likelihood for a LAPIO spill to sink. The St. Johns River drops only 25 feet along the 300 miles from source to mouth, amounting to a 1 percent slope (DeMort, 1991). Currents are weak and spilled LAPIO will tend to sink to the bottom. Most of the tributaries and main channel of the St. Johns are characterized by soft mud and silt bottoms (DeMort, 1991), making location and recovery of spilled oil very difficult.

## LACUSTRINE HABITAT RESOURCES AT RISK

The southernmost portion of the St. Johns River system is composed primarily of eight shallow lakes and a main channel that varies widely in width and degree of meandering. Some lakes have recommended draft limits of less than three feet (NOAA, 1989). Due to the Florida Manatee Sanctuary Act, motor boats are required to regulate their speeds and operations within critical areas of manatee concentrations between 15 November and 31 March. The confluence of the St. Johns River with Blue Springs Run is one such area (Fig. 3). This regulated zone requires that....“boat operators shall reduce their speed to “slow” or “idle”, and no person shall intentionally or negligently annoy, molest, harass, disturb, collide with, injure, or harm manatees” (NOAA, 1989).

LAPIO spills are most likely to sink in the lacustrine stretches of the St. Johns River. Under weak currents, the oil would be less likely to migrate, so the effects would be very localized. Visibility in the tannin-rich waters could make tracking the oil in the water column and on the sediments difficult.

## BIOLOGICAL RESOURCES AT RISK

Many of the resources considered to be at risk from exposure to LAPIO are the animals themselves. Many species utilize multiple habitats, and therefore can be found in various areas within the three zones during different life stages. As such, the information provided for the different biological resources at risk is not divided by river zone. Instead, the various factors that are important to each species are discussed in terms of preferred habitat and life-stage data. The general species categories considered at risk include birds, fish, shellfish, reptiles, and marine mammals.

### *Birds*

The habitats along the St. Johns River are host to numerous bird species, including seabirds, shorebirds, wading birds, waterfowl, gulls and terns, raptors, and songbirds. Dabbling ducks and diving ducks are found throughout the coastal zone on a year-round basis. Additionally, the St. Johns River serves as a migratory route and overwintering area for a wide variety of birds. Two endangered species, the bald eagle (*Haliaeetus leucocephalus*) and wood stork (*Mycteria americana*), are known to forage within the area (USFWS, 1980).

There are several known nesting and congregating sites for shorebirds, wading birds, seabirds, waterfowl, raptors, and songbirds within the marine and estuarine portion of this system, including: Bird Island, Little Talbot Island Park, and the Mayport jetty at the mouth of the St. Johns River; Black Hammock Island as a nesting site for egrets and an adult concentration areas for wood ibis; a general wading bird nesting site just east of the Fort Caroline National Memorial; and a migratory route and overwintering area for shorebirds, wading birds, diving and dabbling ducks along the Atlantic coastline (Fig. 4) (USFWS, 1980; RPI, 1985).

In general, the degree and extent of injury from exposure to LAPIO is dependent on each species' feeding and nesting behavior (RPI, 1988). Shorebirds (e.g., oyster-catchers, plovers) and wading birds (e.g., herons, egrets, wood storks) forage at the water's edge, in wetlands, and on tidal flats. Historically, these birds have been only moderately affected during oil spills because they do not tend to immerse their bodies in the water. Oil can cause loss of their preferred prey items, and external coating of legs, feet, and bills during foraging efforts. Effects on these birds from LAPIO spills are likely to be similar to #6 fuel oil spills, or even lower if most of the oil sinks. The only increase in impact may be where a LAPIO spill contaminated the sediments on tidal flats where the birds rest and forage.

Waterfowl, gulls and terns, and seabirds, by their very nature, are more likely to be affected by floating LAPIO in ways expected during usual oil spills. These birds are closely associated with the water surface in feeding and resting activities and, as such, there is the potential for these birds to become oiled and die from hypothermia or loss of buoyancy (RPI, 1988). It is not known if these birds may experience additional oil exposure when diving for prey if the LAPIO is mostly mixed into the water column and not floating on the surface. Suspended LAPIO is not expected to be sticky, but some birds spend so much time underwater searching for food (e.g. cormorants) that they may have some risk of exposure.

The bald eagle, osprey, and peregrine falcon are common residents within the river system. Osprey are at risk of being directly oiled because they feed on live fish; eagles and flacons are subject to secondary contamination through the consumption of oiled food, such as oiled dead birds or rodents. Raptors are thought to be affected byLAPIO in ways expected during usual oil spills.

### *Fish*

There are some 170 species representing 55 families of fish known to inhabit the waters of the St. Johns River (Tagatz, 1968). Most of the fish reported occur within the lower basin and their distribution depends on seasonal migrations and salinity tolerances. Many marine fish utilize the estuarine habitats along the river as nursery sites for their larvae to young-of-year. The lower St. Johns River supports an extensive recreational fishery of national prominence, including largemouth bass (*Micropterus salmoides*), black crappie (*Pomoxis nigromaculatus*), and bream (*Lepomis spp*.) (SJRWMD, 1993).

There is also a year-round commercial fishery associated with the St. Johns River. Blue crab (*Callinectes sapidus*), white and channel catfish (*Ictalurus spp*.), bullheads, the American eel (*Anguilla rostrata*), and shad (*Alosa spp*.) provide the bulk of the fishery.

Floating oil spills usually have limited impacts on adult and juvenile fish, as most oils have very low water-soluble fractions, and the mobile fish are able to avoid petroleum products (RPI, 1987). Larval stages that float at the water surface are at greatest risk. Non-floating oil spills are likely to have dramatically <u>different</u> impacts to fish. During the Puerto Rico spill, diving scientists observed dead fish, living fish with lesions and tumors, and many lethargic fish in nearshore areas, primarily for territorial species, that is, they tend to stay in and defend their preferred location (Vincente, 1994). Mobile species may be able to move to uncontaminated areas, thus reducing these impacts. Sinking oil can smother and kill bottom feeders and their food, though impacts would be localized. In addition, oils that sink or suspend in the water column could have greater impacts to water-column organisms because more of the water-soluble fraction of the oil could actually dissolve rather than be lost by evaporation, which usually is the dominant process for floating slicks. These oils are often high in aromatics, which are the primary source of both acute and chronic toxicity to aquatic organisms. The naphthalene compounds, which are two-ringed aromatics, have been shown to be more toxic than the light weight aromatics such as benzene and toluene (Anderson et al., 1987). If only the water-soluble fraction is considered, bunker C is rated as toxic as diesel (Markarian et al. 1993). Thus, even though heavy residual oils are not usually considered to be acutely toxic to fish, spills that mix into the water column without first weathering (by evaporation) on the water surface may increase the amount of oil that dissolves and the acute toxicity to fish.

### *Shellfish*

The St. Johns River provides important nursery habitat for commercially important shellfish, including blue crab (*Callinectes sapidus*), white shrimp (*Penaeus setifierus*), brown shrimp (*P. aztecus*), and pink shrimp (*P. duorarum*). This system is unique in that it has an extended estuary—minimum salinities are reached between Green Cove Springs and Palatka but then increase again upstream due to saline groundwater inflows (Fig. 3). Thus blue crabs, larval shrimp, and several estuarine fish species can inhabit areas up to 200 miles from the ocean (SJRWMD, 1993).

The blue crab migrates up the St. Johns River from fall to winter to mate. The female carries the eggs back out into the ocean where the eggs hatch. The planktonic larvae eventually are transported back into the river where they grow into adults (Tagatz, 1968; Durako et al., 1988). Blue crab can be found in the marine and estuarine portion of the river year-round.

The commercially important shrimp species enter the river as juveniles, where they mature into early adult stages. These species are known to migrate extensive distances upstream. Therefore, various life stages of shrimp are present throughout the estuarine and marine portions of the river. Joyce (1965) found that pink shrimp juveniles were not found any further than Green Cove Springs; brown shrimp juveniles migrate as far as Rice Creek; while white shrimp juveniles could be found along the river as far upstream as Lake George (Fig. 3).

These species of shellfish are primarily bottom dwellers that scavenge the substrate for food items. Floating oil spills usually have limited impacts to these organisms (RPI, 1989). In contrast, sinking LAPIO spills are expected to have direct impacts to crabs and shrimp, due to both acute toxicity from the water-soluble fraction and ingestion. The aquatic toxicity of oil for shrimp is closely related to the naphthalene content (Anderson et al., 1987), so anything which tends to increase the amounts of these compounds in the water would increase the impacts to shrimp.

There have been several spills of heavy oil that sank in the Delaware River where oiled crabs were found in crab pots many miles downstream of the spill. Crabs and shrimp are described as "opportunistic omnivores" (Lassuy, 1983; Perry and McIlwain, 1986), meaning that they eat almost anything they can catch, and they will attempt to feed on oil, oiled prey, and oiled sediments. Thus, even though heavy oils are not normally considered to be biologically available to most marine organisms, crabs and shrimp may be more susceptible than other organisms because of their benthic scavenging habits.

### *Reptiles*

Within the St. Johns River system there are sea turtles, alligators, and terrestrial turtles that have the potential to be affected by LAPIO spills in their preferred habitats. The outer beaches at the mouth of the St. Johns River are nesting beaches for loggerhead turtles in spring and summer. Other turtle species which may be encountered less frequently include green turtles, hawksbill turtles, Atlantic Ridley's turtles, and leatherback turtles (SJRWMD, 1993). It is assumed that offshore LAPIO spills are likely to be difficult to recover and thus result in a larger percentage of the spill forming persistent tarballs that will eventually concentrate in convergence zones where turtles also concentrate to feed. Thus, adult and juvenile turtles could be affected by LAPIO spills through ingestion of tarballs, having tarballs stuck in their mouths, and/or having tarballs adhering to their flippers and shells (Vargo et al., 1986). These risks are similar to those from #6 fuel oil.

LAPIO stranded on sand beaches is less likely to penetrate the sand than more fluid oil because of its viscosity. However, oil that sank offshore could provide a source of episodic oiling during the nesting season as the submerged oil is re-mobilized during storms, weeks to months after cleanup of stranded oil was completed.

The American alligator and other endangered terrestrial turtles are unlikely to come in contact with spilled LAPIO, as they are typically found along the river system in areas removed from direct tidal influence (Moler, 1992). Although they use both the water surface and the water column, impacts from a spill of LAPIO are not likely to be much different than floating oil spills.

### *Marine Mammals*

The marine mammal of importance within the St. Johns River system is primarily the West Indian manatee. Dolphins are also common residents of the waters near and within the river mouth, however, they are not considered at risk within this system. At present, there is a population of 88 manatee that inhabit the river. This population has been increasing in number (Joe Kenner, Blue Springs State Park, pers. comm., 1994). In warm weather, the majority of the manatees can be found congregating in and around Lake George and Lake Monroe. However, when water temperatures drop below 72°F, (typically from November through mid-March) the manatee population migrates to Blue Springs (Fig. 3). Manatees can also be found congregating in warm-water power plant outflows (O'Shea and Ludlow, 1992).

Impacts to manatees from spilled petroleum products are virtually unknown. They are thought to suffer skin irritation from direct contact, irritation of mucosal membranes of the nose and mouth from volatile fractions, and coating of the mouth and flippers through contact during feeding and grooming activities (St. Aubin and Lounsbury, 1990). Manatees spend most of their time under water or resting on the bottom, but how they would be affected by LAPIO which sunk or mixed into the water column is unknown. The greatest concern would be a spill during winter when they are concentrated at warm-water outflows, regardless of whether the oil floated or not.

## RESPONSE ISSUES FOR LOCATION, CONTAINMENT, AND RECOVERY

### Location

Spills of LAPIO that sink or become neutrally buoyant are likely to be difficult to locate and assess. The options for locating sunken oil include aerial observations in clear water, diver transects, underwater video, and sonar equipment, such as the Roxann system used during the Tampa Bay spill. All remote observations have to be verified with diver surveys. Diving conditions can be very difficult because the divers are likely to grossly contaminated whenever they are in the vicinity of LAPIO. During the MORRIS J. BERMAN spill in Puerto Rico, divers had to undergo extensive decon after each assessment and removal dive. For oil that is neutrally buoyant and suspended in the water column, there are no proven techniques for locating the oil.

### Containment

Historically, sunken oil was not actually contained but instead tended to accumulate in natural collection areas. Any oil that was mobilized by currents was not contained. Although bottom booms have been proposed, it is not likely that they will be effective in any kind of bottom currents, or even properly deployed on the bottom in an effective location. Realistically, the only likely containment will occur naturally as the oil accumulates in low areas at the spill site.

Containment of oil that is suspended or mixed into the water column is feasible only where the currents are very weak. Options include silt curtains or fine-mesh nets coupled with a surface boom to contain the floating or re-floating fraction of the oil. The only known case where this kind of curtain boom was used was in Louisiana to isolate leaking, abandoned barges in a dead-end canal. The use of the curtain boom was successful until local vessel traffic disrupted it. Use of silt curtains may be promising, and there would be contractors experienced in the proper deployment and maintenance in the region because of the extensive dredging. However, it should be noted that effectiveness would drop rapidly with any currents. Fishing nets would have to be attached to floating booms on the surface and heavy weights along the bottom. It would be difficult to modify existing rigging into an effective containment system.

### Recovery

Recovery of sunken oil has proven to be very difficult and expensive. During the Tampa Bay oil spill, various options for recovery of the submerged oil were researched and evaluated. Options included and discussed below are:

- Manual removal by divers
- Removal by pump and vacuum systems
- Dredging
- Use of robotic systems

Manual removal involves the collection of the oil by divers into bags or containers. The advantages of manual removal are:

1. The volume of material removed is the lowest of all options. Little additional water or sediment would be removed, thus there will be no need to treat oily water or dispose of large amounts of oiled sediment.
2. Divers will be able to pick up relatively small pieces, which may be widely scattered over large areas.
3. The recovered oil can be placed directly into suitable containers for disposal. There would be less need for intermediate storage or transfers.

The biggest disadvantage of manual removal is the slow rate of recovery. The potential for the oil to spread to other areas may force a more rapid recovery strategy.

Removal by pump and vacuum systems have historically been the most successful removal strategy for sunken oil. Such systems can include vacuum trucks, units mounted on barges, and submersible pumps. They often are diver-directed and the suction head modified so that the diver manually opens and closes the valve. The oil must be liquid to be pumped. Because large volumes of oily water are generated, there must be facilities for oil/water separation and discharge of the separated water back into the water. Separation can be very problematic for some LAPIOs, especially when they are only slightly heavier than water and part of the oil tends to re-float. During the MORRIS J. BERMAN spill, vacuum removal was effective but very slow.

Dredging is the fastest method for removing sunken oil from the bottom, but is likely to generate very large volumes of oily water and sediment that must then be handled, treated, and disposed of. Pumping rates of 1,000 gallons per minute are typical of small dredges. Even under careful control, dredges will remove the top two feet of material, removing and contaminating a large amount of clean sediment. Logistics and costs are reduced if the material can be handled on land, compared to using barges or temporary storage and separation. Time can be of concern because oil that is still fluid could be re-mobilized by storm waves, increased river flow following heavy rains, or ship traffic.

Recovery of oil that is suspended in the water column poses the greatest challenges. Fish nets have not been very successful for recovery of firm tarballs; they are likely to be even less effective with liquid oil droplets. The net mesh size would have to be matched to the droplet size. Heavy accumulations would clog the nets, resulting in breakage or failure. Liquid oil could drain from the nets as they were lifted from the water. The nets could be used only once then disposed of.

Another important consideration is that the contractors involved in location, containment, and recovery phases of the cleanup of LAPIO spills must meet all federal training requirements for workers and supervisors involved in hazardous material operations.

## CONCLUSIONS

Because LAPIO can float, sink, become neutrally buoyant, or fractionate and possess all three characteristics, it poses significantly different risks to natural resources, compared to floating oil spills, for the following reasons.

1. Neutrally buoyant or sinking LAPIO weathers very slowly by evaporation, a process which tends to remove the more toxic fractions from floating oil slicks and greatly reduces the acute toxicity of the spilled oil. As a result, the toxic components of a LAPIO spill are introduced directly into the water column at concentrations greater than traditional spills. Animals in the water column, such as fish, shellfish, and marine mammals, can be exposed to these higher concentrations.

2. LAPIO that is denser than the receiving waters is not expected to sink immediately to the bottom and remain there. More likely, it will be suspended in the water column by tidal and riverine currents, eventually exiting the river system with the net outflow of water. Accumulation of oil on the bottom is expected only in zones of low flow, such as dredged channels, dead-end waterways, and abandoned channels. Natural removal rates by physical flushing would be very slow for spills in the lacustrine section of the St. Johns River system.

3. Benthic organisms are seldom at risk from floating oil spills. However, with heavier-than-water spills, additional impacts to benthic resources are likely to occur from smothering as well as increased exposure to residual oil that was not recovered. As a corollary impacts to shoreline habitats and animals that use both the shoreline and water surface should be less for sinking oil spills.

4. Containment and removal efforts for sinking oil will have low effectiveness. As recently experienced during the San Juan, Puerto Rico oil spill, removal of submerged oil is very slow, and usually generates large volumes of contaminated water and sediment. In fact, removal of the submerged oil in Puerto Rico was conducted only where the oil was contained by natural or existing features. Oil sank in other areas, but tidal currents dispersed the oil over large areas, making it impractical to recover.

5. Containment and removal efforts for neutrally buoyant oil will likely be ineffective. There are no proven techniques for containing oil in the water column, or for removing oil from such large volumes of water.

6. Even standard techniques for location, containment, and recovery will fail unless conducted by contractors experienced in the proper deployment and maintenance of the equipment and the special requirements of oil-spill response.

The potential for spilled LAPIO on the water surface, in the water column, and on the river bottom will tend to affect a broad range of resources (e.g., fish, shellfish, manatees, birds, etc.) in the St. Johns River. Manatees (a protected species) are unlikely to be found in the lower river segments in any great numbers, only as single individuals traveling to and from preferred habitats upstream. Woodstorks (endangered) are also unlikely to be affected as they prefer to roost in trees and wade in upland freshwater marshes—areas unlikely to be oiled. Additional injuries to fishery and shellfish resources are more likely to occur. Present response technology is ill-equipped to deal with the potential water-column and benthic habitat impacts from a spill of LAPIO.

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# APPENDIX: CHEMISTRY

# RESULTS OF CHEMICAL ANALYSIS OF TWO SAMPLES PROVIDED BY JACKSONVILLE ELECTRIC AUTHORITY

This report provides a chemical characterization of two LAPIO samples (#932118 and #932089) provided to the Louisiana State University (LSU) Environmental Studies Institute. LSU is part of NOAA's scientific support team and is responsible for environmental characterization of oil spills. The objective of this evaluation was to develop a prospective of the two LAPIO samples submitted relative to "typical" heavy residual fuel oils such as Bunker C. The samples were received in good condition on 7 December 1993. Each sample was prepared as bulk oil reference standard and as a water-accommodated fraction. The water-accommodated fraction includes that part of the oil which is water soluble as well as very small droplets that suspend in the water after gentle mixing. Each was analyzed by gas chromatography/mass spectrometry (GC/MS) for target aromatic hydrocarbons and compared to a typical residual fuel oil to assess relative similarities. Target aromatic hydrocarbons include those of environmental concern because of their acute and chronic toxicity. The GC/MS values are attached as an addendum.

## *Summary*

The two LAPIO samples submitted were very different in appearance and chemical composition when compared to each other. Sample #932118 was brown in color and characterized by a very low abundance of asphaltenes and a high abundance of the 3 and 4 ring aromatic hydrocarbons such as phenanthrenes, naphthobenzothiophenes, pyrenes, and chrysenes. Sample #932089 was a black oil with a high concentration of naphthalenes. When poured on deionized water with a density of 1.00 g/mL both samples separated with most of the oil sinking and some floating. Both samples have many similarities to residual fuel oils. The water-accommodated fractions produced by both oils are typical for heavy residual fuel oils. Both were enriched in target aromatic hydrocarbons relative to "typical" residual fuel oils and North Slope crude (NSC) oil, but lower in target aromatic hydrocarbons than coal tar and creosote oils. The chemical composition of LAPIO is similar to heavily weathered oil initially; therefore, biological degradation of spilled LAPIO will be very slow. The bulk of the LAPIO will sink. Beach impacts are still possible because of migrating tar balls formed from the spilled oil.

## *Residual Fuel Oil and Crude Oil*

Residual fuel oils such as No. 6 fuel oil and Bunker C are blended from a variety of refinery residuals left over from the production of highly refined products such as gasoline. Residual fuel oils encompass a wide range of chemical and physical properties, depending on the source crude oil and the refining process. Residual fuel oils have only trace concentrations of the more volatile benzene and alkylated benzene compounds which are abundant in crude oil. The relative concentration of 2, 3, 4, and 5 ring aromatic hydrocarbons in residual fuel oils is greater than crude oils. Figure 1 shows a histogram profile of the aromatic hydrocarbons of North Slope crude oil compared to a “typical” residual fuel oil. The “typical” residual fuel oil shown is the mean value of four different heavy fuel oils which were spilled over the last year including oil from the recent Tampa Bay incident (BOUCHARD B155). The sum of the aromatic hydrocarbon compounds in the residual fuel oil is approximately twice that in North Slope crude oil, 3.3 percent compared to 1.6 percent by weight. The acute toxicity of residual fuel oils are generally associated with the 2-ring naphthalenes.

## *LAPIO Bulk Oil GC/MS Characterization*

Figures 2 and 3 show Total Ion Chromatogram (TIC) comparisons for the two LAPIO oil samples and North Slope crude oil. Sample #932089 is dominated by aromatic hydrocarbons while the crude oil sample is dominated by normal alkanes. Sample #932118 has a highly pronounced unresolved complex mixture and appears as a heavily weathered oil initially. Figures 4 and 5 show a comparison of LAPIO samples #932089 and #932118 to typical residual fuel oil. Sample #932089 is similar in composition to the typical residual fuel oil, but 3 times higher in overall abundance of the target aromatic hydrocarbons, 9.8 percent compared to 3.3 percent by weight. The distribution pattern of the targeted aromatic hydrocarbons looks like that expected for a highly weathered heavy fuel oil, and the overall abundance of aromatic hydrocarbons is twice that of a typical residual oil. The total amount of aromatic hydrocarbons for both LAPIO samples, while relatively high, may be considered within acceptable values for a residual fuel oil (there are no known standards that define an upper limit for aromatic hydrocarbons in residual fuel oil).

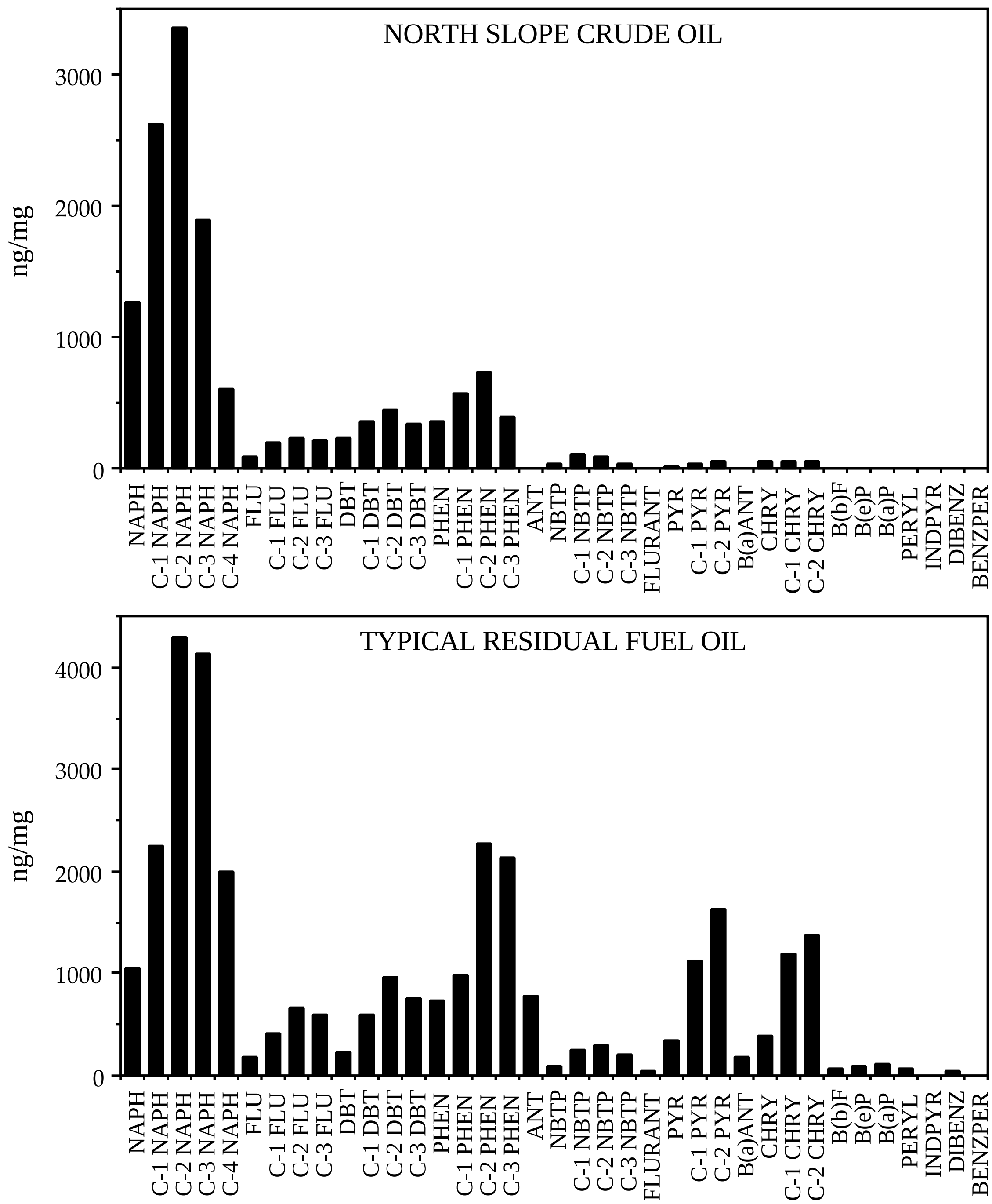


Figure 1. Histograms comparing the aromatic hydrocarbons profile for North Slope crude oil and a typical residual fuel oil (mean values of 4 recently spilled oils).

### *Characterization of the Water-accommodated Fraction LAPIO*

The water-accommodated fraction of both LAPIO samples was characterized by placing 3 milliliters (mL) of sample into a beaker with 300 mL of deionized water. The water temperature was 68°F. The beaker was placed on a magnetic stirrer. The speed was set such that a vortex formed near the surface. When the oil was added to the water, it initially floated, although the oil's density suggests the oil should sink immediately. Surface tension may have kept the oil floating until the magnetic spin bar was turned on. Eventually, most of the oil sank, but thick oil remained on the surface for both oils tested. The oil/water mixture was stirred for 2 hours. After an additional 2 hours of sitting, 100 ml of water were sampled from the center of the beaker and extracted into a solvent. Sample #932089 was accidentally heated to 110°F (the heater element was found on). At that temperature, very tiny neutrally buoyant oil droplets were visible. The water-accommodated fraction for this sample was enriched in the more water-soluble naphthalenes and aromatic hydrocarbons as a result of the dispersion of tiny oil droplets. The water-accommodated fraction for sample #932118 indicated a profile very different than the bulk oil. The naphthalenes are the most water-soluble and were expected to dominate the water-accommodated fraction. However, the presence of some bulk oil or dispersed oil is apparent in the water-accommodated fraction, although no oil droplets were visible. Figures 6 and 7 compare the distribution of a water-accommodated fraction of original bulk oils and the water-accommodated fraction produced. The distribution of a water-accommodated fraction for the floating oil was similar to the bulk oil as shown in Figure 8 for sample #932118.

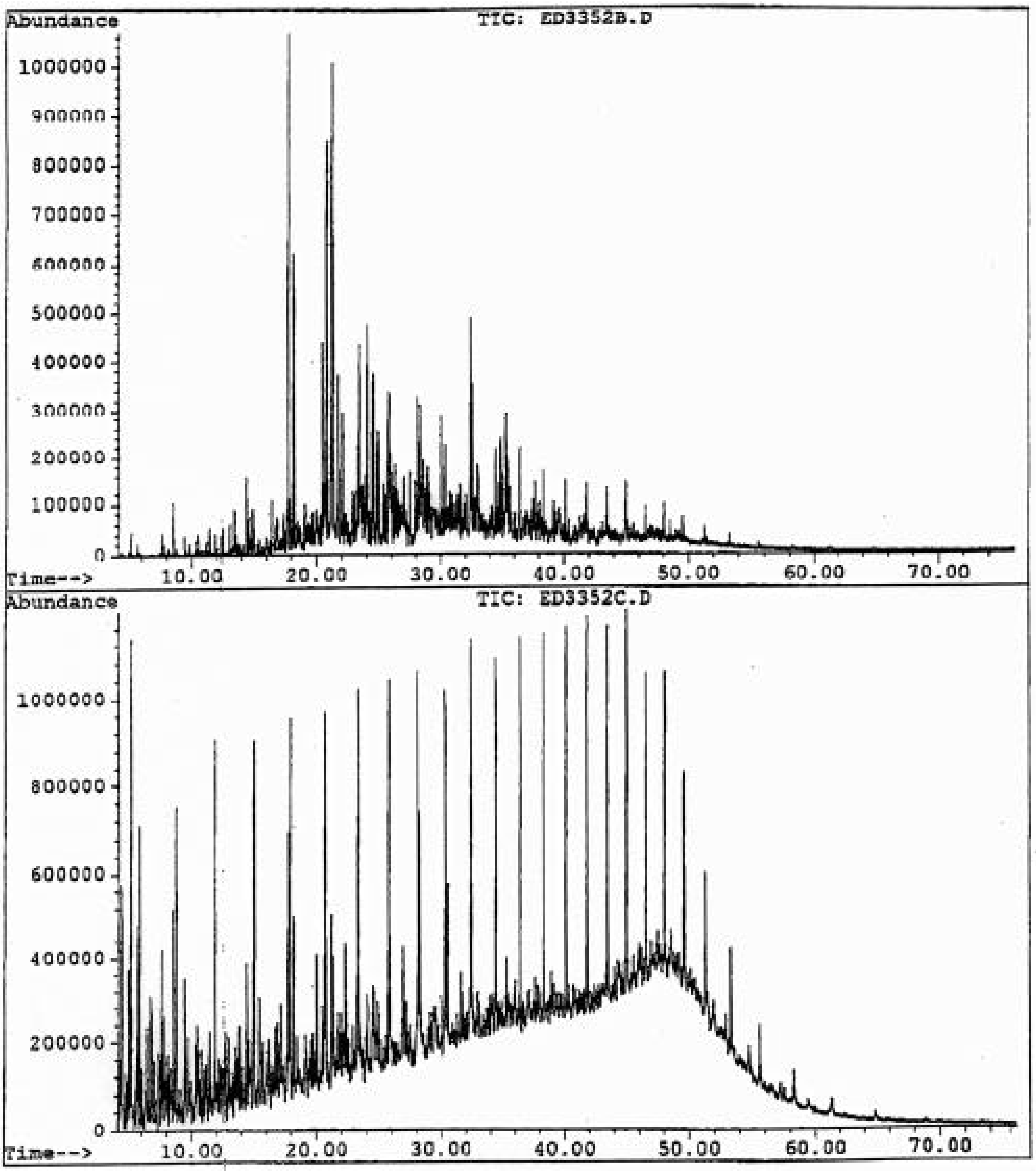


Figure 2.TIC of LAPIO sample #932089 (top) and North Slope crude oil (bottom).

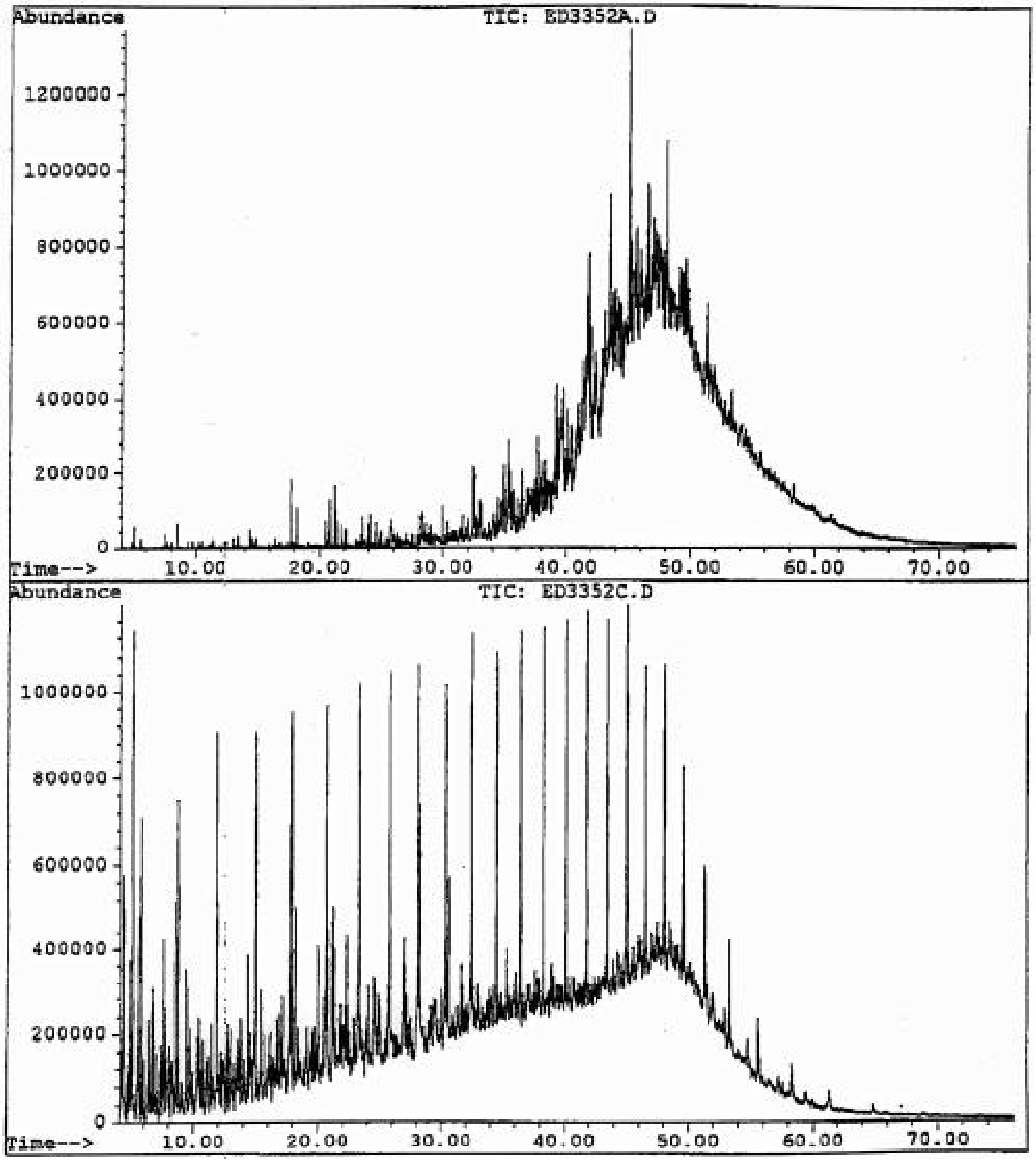


Figure 3.TIC of LAPIO sample #932118 (top) and North Slope crude oil (bottom).

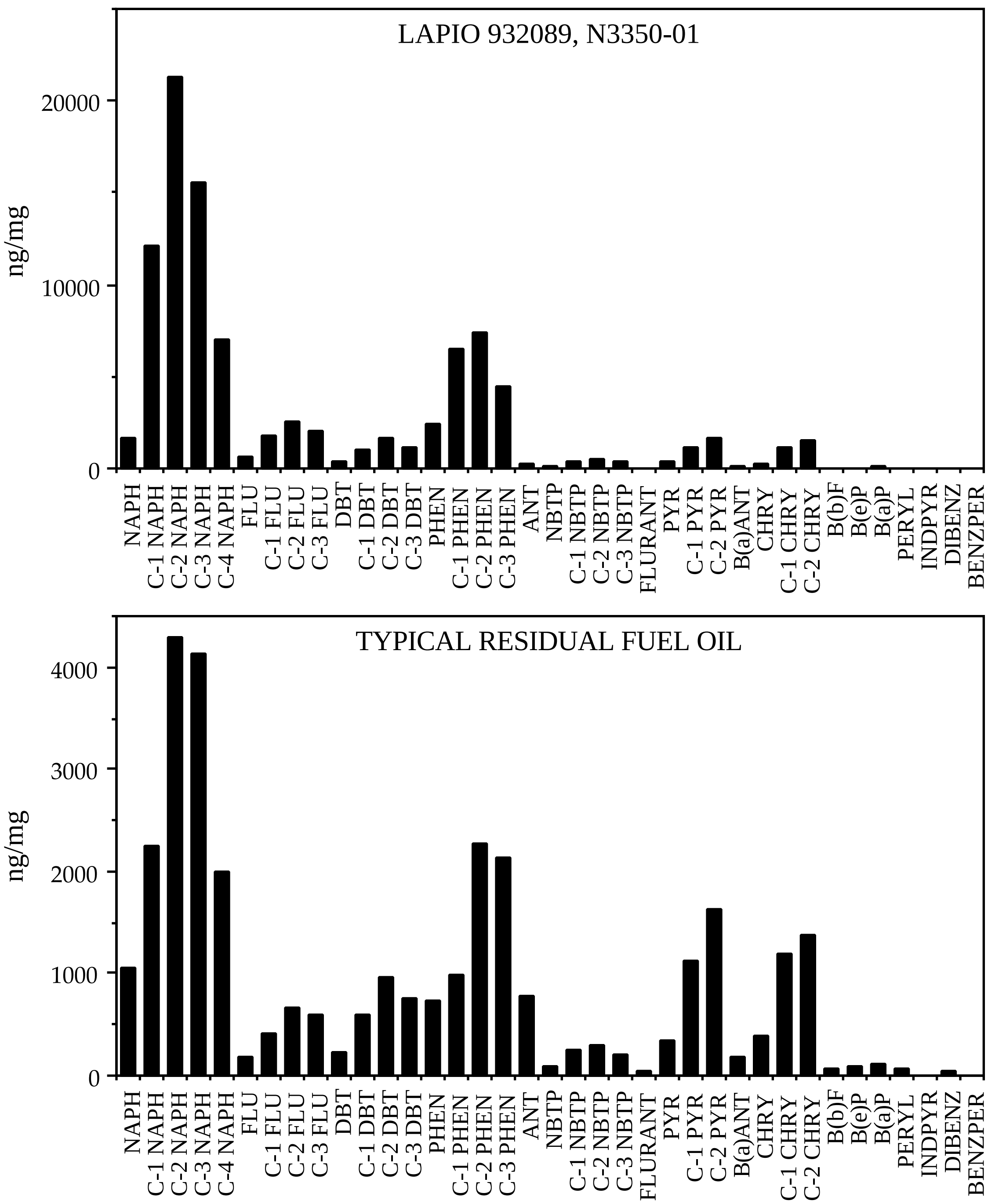


Figure 4. Histograms comparing the aromatic hydrocarbons profile for LAPIO sample #932089 and a typical residual fuel oil (mean values of 4 recently spilled oils). This LAPIO sample is similar in composition to a typical No. 6 fuel oil, but the total amount of aromatic hydrocarbons measured was three times higher (note difference in scale).

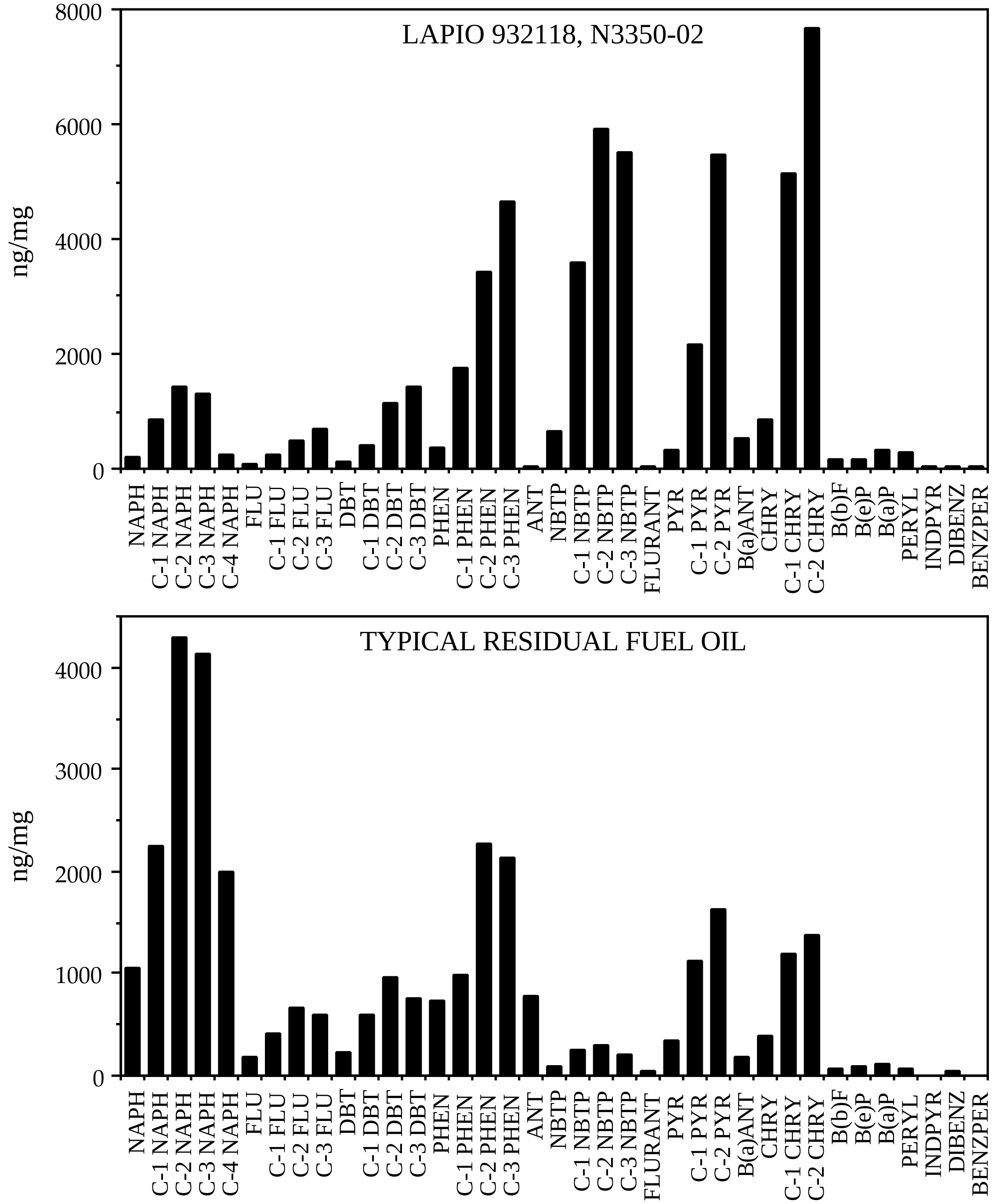


Figure 5. Histograms comparing the distribution of aromatic hydrocarbons for LAPIO sample #932118 and a typical residual fuel oil (mean values of 4 recently spilled oils). This LAPIO sample was very different; the distribution of aromatic hydrocarbons looked like that expected for a highly weathered No. 6 fuel oil.

# ADDENDUM

# GC/MS RESULTS

## ADDENDUM: GC/MS RESULTS

| MS FILE NAME: | ED3354C* | ED3354D* | - | - | - | - | - |
|---|---|---|---|---|---|---|---|
| LABORATORY ID: | N3350-02 | N3350-01 | x-02 WAF | x-01 WAF | x-02 sheen | WAF Blank | T.R.F.O. |
| SAMPLE NAME: | #932118 | #932089 | #932118 | #932089 | #932118 | - | |
| - | - | - | | | | | |
| COMPOUND | ng/mg | ng/mg | ng/uL | ng/uL | ng/mg | ng/uL | ng/mg |
| NAPH | 217.34 | 1607.32 | 0.0243 | 0.2395 | 0.9270 | 0.0001 | 1049.2559 |
| C-1 NAPH | 876.36 | 12120.99 | 0.0303 | 0.7184 | 4.1199 | 0.0000 | 2256.5194 |
| C-2 NAPH | 1431.01 | 21254.69 | 0.0156 | 0.6613 | 6.6948 | 0.0000 | 4296.6210 |
| C-3 NAPH | 1307.21 | 15544.46 | 0.0061 | 0.5110 | 6.6948 | 0.0000 | 4123.8172 |
| C-4 NAPH | 245.54 | 7025.41 | 0.0018 | 0.1353 | 3.9139 | 0.0000 | 2006.9255 |
| FLU | 68.29 | 674.50 | 0.0013 | 0.0261 | 0.3565 | 0.0000 | 178.9622 |
| C-1 FLU | 246.91 | 1796.03 | 0.0013 | 0.0404 | 1.2122 | 0.0000 | 408.6565 |
| C-2 FLU | 494.33 | 2540.72 | 0.0013 | 0.0541 | 2.7096 | 0.0000 | 655.1376 |
| C-3 FLU | 694.47 | 2101.57 | 0.0008 | 0.0379 | 3.4939 | 0.0000 | 588.8414 |
| DBT | 107.68 | 423.37 | 0.0011 | 0.0130 | 0.5211 | 0.0000 | 235.1873 |
| C-1 DBT | 413.88 | 1022.80 | 0.0013 | 0.0221 | 2.1537 | 0.0000 | 586.6005 |
| C-2 DBT | 1124.45 | 1684.07 | 0.0013 | 0.0287 | 5.9054 | 0.0000 | 952.9655 |
| C-3 DBT | 1413.80 | 1145.46 | 0.0010 | 0.0188 | 8.3371 | 0.0000 | 753.7685 |
| PHEN | 377.42 | 2448.87 | 0.0034 | 0.0696 | 1.9343 | 0.0001 | 744.1911 |
| C-1 PHEN | 1745.40 | 6514.08 | 0.0046 | 0.1391 | 8.8307 | 0.0001 | 982.6808 |
| C-2 PHEN | 3424.48 | 7438.72 | 0.0040 | 0.1311 | 18.0819 | 0.0000 | 2267.7712 |
| C-3 PHEN | 4634.44 | 4528.04 | 0.0034 | 0.0722 | 24.8101 | 0.0000 | 2137.3754 |
| ANT | 50.97 | 310.03 | 0.0004 | 0.0075 | 0.3112 | 0.0000 | 788.8187 |
| NBTP | 648.29 | 96.29 | 0.0004 | 0.0015 | 3.1611 | 0.0000 | 82.7031 |
| C-1 NBTP | 3582.05 | 381.95 | 0.0022 | 0.0077 | 18.4110 | 0.0000 | 257.0936 |
| C-2 NBTP | 5933.44 | 522.50 | 0.0028 | 0.0091 | 31.6114 | 0.0000 | 292.5311 |
| C-3 NBTP | 5497.58 | 437.93 | 0.0024 | 0.0086 | 29.8745 | 0.0000 | 213.1093 |
| FLURANT | 24.38 | 62.16 | 0.0001 | 0.0022 | 0.1868 | 0.0000 | 39.0000 |
| PYR | 310.97 | 370.69 | 0.0003 | 0.0079 | 1.6275 | 0.0000 | 334.3300 |
| C-1 PYR | 2160.18 | 1153.35 | 0.0025 | 0.0197 | 11.4723 | 0.0000 | 1118.9783 |
| C-2 PYR | 5460.15 | 1596.93 | 0.0043 | 0.0294 | 29.3478 | 0.0000 | 1624.2047 |
| B(a)ANT | 549.71 | 138.37 | 0.0005 | 0.0034 | 3.0682 | 0.0000 | 176.8645 |
| CHRY | 864.81 | 256.18 | 0.0008 | 0.0049 | 4.6023 | 0.0000 | 381.5354 |
| C-1 CHRY | 5125.96 | 1176.62 | 0.0038 | 0.0191 | 27.3068 | 0.0000 | 1198.5239 |
| C-2 CHRY | 7681.73 | 1533.75 | 0.0050 | 0.0259 | 42.9545 | 0.0000 | 1378.3846 |
| B(b)F | 168.64 | 37.18 | 0.0001 | 0.0010 | 0.8422 | 0.0000 | 65.0066 |
| B(e)P | 175.82 | 48.23 | 0.0011 | 0.0010 | 0.9034 | 0.0000 | 87.2340 |
| B(a)P | 342.40 | 73.40 | 0.0002 | 0.0014 | 1.8739 | 0.0000 | 126.1964 |
| PERYL | 281.62 | 18.15 | 0.0002 | 0.0006 | 1.5791 | 0.0000 | 58.7356 |
| INDPYR | 25.69 | 7.47 | 0.0000 | 0.0000 | 0.1029 | 0.0000 | 1.1250 |
| DIBENZ | 44.97 | 16.58 | 0.0001 | 0.0006 | 0.4008 | 0.0000 | 47.8888 |
| BENZPER | 46.64 | 12.07 | 0.0000 | 0.0006 | 0.2332 | 0.0000 | 8.5000 |
| Total PAH: | 57799.03 | 98120.94 | 0.1300 | 3.0708 | 310.5678 | 0.0007 | 32506.0405 |

Values valid to 2 significant figures only.