EBULLITION-FACILITATED TRANSPORT OF MANUFACTURED GAS PLANT TAR FROM CONTAMINATED SEDIMENT

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Abstract—Manufactured gas plant (MGP) tar and wastewater solids historically were discharged into the Penobscot River, Maine, USA, via a sewer at the Bangor Landing site. The tar and wastewater solids accumulated in riverbed sediment over a 5-hectare area downstream from the sewer outfall. Much of the tarry sediment is a hardened mass at the bottom of the river, but in part of the tar deposit (the active zone), the tar remains unhardened. In the active zone, anaerobic biodegradation of organic matter generates methane and carbon dioxide; as gas accumulates and migrates upward, it entrains tar, eventually dragging the tar from the sediment to surface water. Understanding the migration mechanisms in different portions of the tar deposit is critical for modeling the risk posed by the tar at the Bangor Landing site, because during gas-facilitated tar migration, the tar is brought to the water surface, instead of remaining in the sediment. Tar migration from sediment poses a potential human health risk because of the high concentrations of polycyclic aromatic hydrocarbons in the tar. Migration from sediment to the water surface greatly increases the potential exposure of human and ecological receptors to tar that reaches the water surface. In order for tar to migrate from sediment to surface water, three conditions are necessary: the sediment must contain liquid tar, the sediment must produce gas bubbles, and the gas must come into contact with the tarry sediment. Failure to consider facilitated transport of MGP tar from sediment can cause underestimation of site risk and can lead to failure of remedial measures.

Keywords—Ebullition   Facilitated transport   Nonaqueous phase liquid   Sediment

INTRODUCTION

The Bangor Gas Works, a manufactured gas plant (MGP) in Bangor, Maine, USA, generated tar as a byproduct of the various gas manufacturing processes employed at the site (coal carbonization, carbureted water gasification, and oil gasification) during the period from the early 1850s to the early 1960s. Wastewater from the gas manufacturing process contained tar. The MGP and other industries discharged wastewater to a sewer that drained to the Penobscot River. Tar and other wastewater solids accumulated in the riverbed sediment over a 5-hectare area (the tar deposit) at Bangor Landing in Dunnett's Cove, (44°27′29″N, 68°46′17″W), a sheltered area in the river downstream from the sewer outfall. Figure 1 is a site plan that shows the tar deposit.

Oil and tar droplets have been observed floating up from the riverbed to the surface of the river along with gas bubbles at low tide over a 2-hectare portion of the tar deposit near the sewer outfall at least since the early 1970s. Eyewitness accounts indicate that tar migration from sediment was occurring at Bangor Landing prior to the 1970s. These observations are problematic, because the MGP tar is a dense nonaqueous phase liquid (DNAPL); once it is deposited in riverbed sediment, one typically would not expect it to float up from the riverbed to the water surface.

Tar characteristics

Manufactured gas plant tar is a complex mixture of hundreds of organic compounds, including monocyclic aromatic hydrocarbons (MAHs), such as benzene, and polycyclic

aromatic hydrocarbons (PAHs), such as benzo[a]pyrene [1]. All of these compounds have a low surface tension compared with that of water, are sparingly soluble in water (even though their individual solubilities vary by several orders of magnitude), and have a strong affinity for other organic compounds. Because of the properties of the individual compounds and the way that the compounds behave in solution with one another, MGP tar behaves in a hydrophobic fashion, forming a nonaqueous phase liquid (NAPL).

Tar and water have substantially different physical properties (as shown in Table 1), and these physical properties control the transport of tar from sediment. The first difference is that the density of MGP tar is usually greater than that of water [1]. As a result, tar carried into a surface water body as part of a wastewater stream will tend to be deposited on the bottom once the water decelerates enough to drop its suspended load. Because tar is denser than water, once it has been deposited, it is not possible for the tar to float up from the sediment through the water column unless the tar is acted upon by an outside force.

The second difference is that intermolecular forces for water and for PAHs (which comprise a large fraction of tar) are very dissimilar. For instance, water molecules are polar, whereas PAH molecules are nonpolar. These differences cause this mixture of PAHs to exhibit the general characteristic of hydrophobicity. The PAHs in contact with water will tend to seek out and attach themselves to other materials, including solids or gas bubble surfaces, rather than remain in water. For this reason, if a gas bubble formed in sediment contacts liquid tar, then the tar will be attracted to the gas bubble.

The third difference is that the viscosity of tar is very sensitive to temperature. Tar will tend to behave as a near-solid at low temperatures near 0°C and as a much less viscous
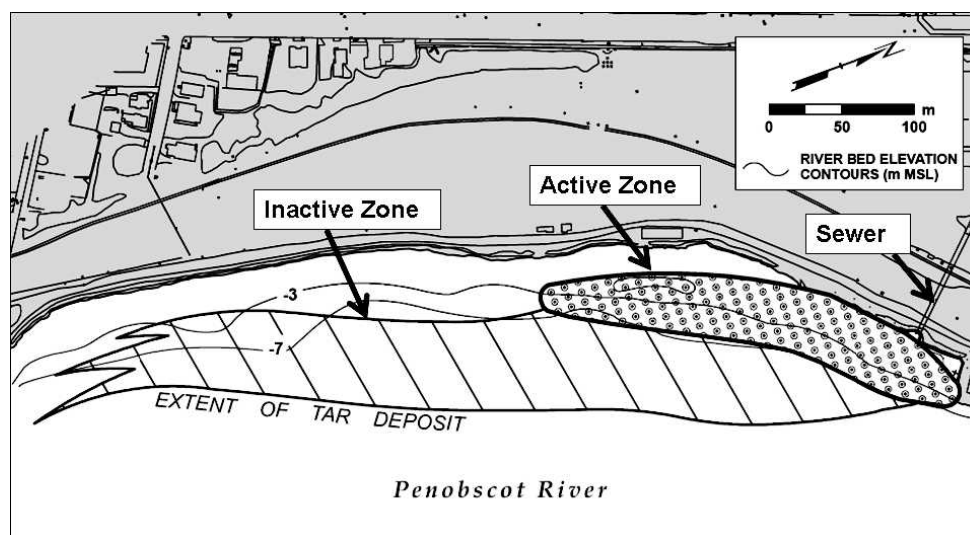
Fig. 1. Zone of the tar deposit and riverbed elevation of the Penobscot River in Maine, USA. Ebullition and tar migration occur only in the active zone, where the riverbed elevation is greater than 7 m mean sea level (MSL; water depth of less than 5.5 m). Only 2 hectare of the 5-hectare area of the tar deposit produces gas and tar from sediment.

liquid at summertime temperatures (temperature range in the Penobscot River is from near-freezing in the winter to approximately 24°C in summer at Bangor, based on measurements collected during the present study). As a result, the potential for tar migration is less during the colder months of the year, when the tar is more viscous, than in the summer, when it is less viscous.

The fourth major difference is that the surface tension of tar is much less than that of water. As a result, once a droplet of tar reaches the water's surface, the water will tend to draw back together beneath the droplet and suspend the tar at the water surface, even though the tar is denser than water. The low surface tension of the tar relative to water and its hydrophobic character drive the tar to spread out on the water surface and form a sheen (a visible microlayer of NAPL that has an iridescent, partially reflective luster). This spreading action vastly increases the surface area to volume ratio of the tar and so increases the potential for human and environmental receptors to come into direct contact with the tar.

Previous studies

A substantial body of literature has been developed on NAPL migration in saturated and unsaturated terrestrial systems, but relatively little research has been devoted to NAPL migration from sediments. The studies that have been performed are typically site-specific contamination investigations [2–6].

Different aspects of facilitated migration of contaminants from sediments have been evaluated by earlier investigators, in particular the generation of gas from sediment. Gas migration from sediment was found to be a function of changes in air pressure at Mirror Lake in New Hampshire, USA [7]. Changes in hydrostatic pressure due to changing tide also were found at several field sites to influence rates of gas migration [8]. Sediment temperature was found to influence gas migration from sediment in Lake Sawa, Japan, on a seasonal basis [9]. Long-term trends for methane mass in water were evaluated at Onondaga Lake in New York, USA, and it was found that methane increased through the spring and summer, peaked in early fall, and rapidly decreased in late fall to winter [10]. Sediment samples from Lake Mendota, Wisconsin, USA, were found to be capable of producing gas under laboratory conditions at temperatures ranging from 4 to 45°C [11]. The formation of gas in sediment was found to decrease the sediment's cohesive strength and enhance its potential for erosion [12].

Facilitated migration of petroleum has been studied at naturally occurring oil seeps in many locations, commonly as part of oil exploration. In particular, petroleum migration at the Coal Oil Point Seep Field, California, USA, has been evaluated through a series of field studies [13].

Much work has been done to evaluate the physical properties and migration behavior of MGP tars and similar DNAPLs in the terrestrial environment [1,14]. A broad survey of MGP tar contaminant transport research is summarized in

Table 1. Comparison of properties of manufactured gas plant (MGP) tar and water

Property	Units	Water		MGP tar		References
Temperature	°C	0	25	0	25	
Density	g/cm^3	1	0.997	1.152	1.15	MGP tar estimate[a]; water[b]
Surface tension	dyn/cm^2	76	72	No data	36–42	MGP tar[c]; water[b]
Kinematic viscosity	cSt[e]	1.8	0.9	250	50	MGP tar[d]; water[b]

[a] Kong [32].
[b] Lide [33].
[c] Mercer and Cohen [34].
[d] Ripp et al. [1].
[e] cSt = centistoke.

Birak and Miller [15]. This work has focused primarily on three-phase systems (water–soil–NAPL). The formation of interfacial films in two-phase (water–NAPL) systems has been evaluated for a number of different NAPLs, particularly coal tar [16].

Facilitated migration of NAPL from sediment has been observed at several other field sites where tarry sediment has accumulated, including the St. Louis River/Interlake/Duluth Tar Superfund Site in Minnesota, USA [3], the McCormick and Baxter Creosoting Superfund Site in Oregon, USA (yosemite.epa. gov/r10/CLEANUP.NSF/6ea33b02338c3a5e882567ca005d382f/ 5b51fb13cffbfb008825651a005e0c66/$FILE/McCormick-Baxter-5YrReview.pdf), the Thea Foss Waterway portion of the Commencement Bay Superfund Site in Washington, USA [4], the Pine Street Barge Canal Superfund Site in Vermont, USA [5], and Bubbly Creek in Illinois, USA [6,17]. At all of these sites, gas bubbles and tar droplets have been observed migrating from sediment to the surface of the water body, and the investigators developed conceptual models that link NAPL migration and gas migration.

At several sites, gas migration from sediment has confounded or complicated remedial measures. For example, at the Pine Street Barge Canal site, a sand cap was placed over contaminated sediment to control tar migration from sediment to the overlying surface water. After construction of the cap, ongoing gas migration from sediment facilitated the transport of MGP tar upward through the sand layer, so that the tar continued to the water surface [5]. At the McCormick and Baxter site, the sand cap that was initially placed over sediment contaminated with creosote failed to control NAPL migration to the river surface, so organoclay layers were installed over portions of the sand cap to increase the sorption of NAPL (yosemite.epa.gov/r10/ CLEANUP.NSF/6ea33b02338c3a5e882567ca005d382f/5b51fb13c ffbfb008825651a005e0c66/$FILE/McCormick-Baxter-5YrReview. pdf). At the Anacostia River site in Washington, DC, USA, gas generation in the sediment caused a test section of a low-permeability cap to uplift and rupture, allowing gas to erupt from beneath the cap [18].

Several investigators have begun recently to study the effect of ebullition on the flux of contaminants from sediment in a series of laboratory experiments [17,19,20]. In general, these investigators found that ebullition has the potential to increase the flux of inorganic and organic contaminants from sediment relative to purely diffusive or advective fluxes, but none of them has focused on the effect of ebullition on enhancing the migration of a separate-phase NAPL. Recent laboratory studies indicate that ebullition has the potential to facilitate migration of NAPL through model sand layers under laboratory conditions [21].

At the Bangor Landing site, density, hydrophobicity, viscosity, and surface tension combine to facilitate the deposition of tar in the river sediment, the transport of tar from the river sediment to the surface of the river via ebullition, and the subsequent formation of sheens on the surface water. Figure 2 is a photograph of a droplet of DNAPL (MGP tar) floating on the surface of the water in a glass. The tar droplet was collected initially as it floated on the surface of the Penobscot River. When the surface tension of the water was disrupted, the tar droplet fell through the water to the bottom of the glass.

At the Bangor Landing site, tar droplets and sheens commonly accumulate on the river surface at low tide. The tar droplets and sheens, as well as the riverbed sediment,
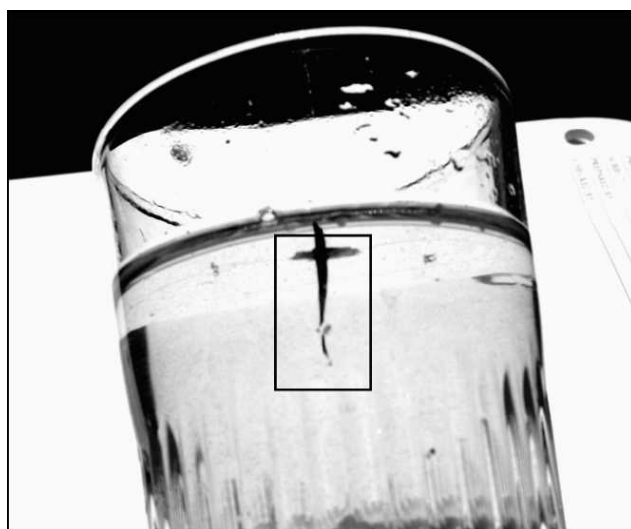

Fig. 2. Dense nonaqueous phase liquid tar droplet suspended at the water surface due to surface tension. Tar droplet floating at water surface is approximately 1 cm long and 0.3 cm wide at water surface, outlined in the box. Droplet shaped like a roofing nail; reflection of tail of the tar droplet appears to extend upward. Tar droplet fell through water column when surface tension was disrupted.

contain total PAH concentrations that range up to several tens of thousands of mg/kg, based on data collected during the present study. When the MGP tar migrates from the riverbed and forms sheens on the surface of the river, the surface area of a tar droplet may increase from an estimated 1 cm^2 to as much as a 1 m^2, as the tar droplet spreads on the water, based on field and laboratory observations in the present study. Under some conditions of tide and wind, individual sheens can coalesce on the river surface and cover areas of a hectare or more at Dunnett's Cove. Sheens containing high concentrations of PAHs at the surface of the river pose a potentially significant pathway for human exposure to tar constituents because of the large affected surface area. The risk assessment for the site indicated that the risk from dermal contact and incidental ingestion of the sheens (9×10^{-3}) was an order of magnitude greater than the risk posed by tarry sediment in situ (1×10^{-3}) (Maine Department of Environmental Protection, Augusta, Maine, 2005, Uncontrolled Hazardous Substances Site Program Decision Document, Bangor Landing, aka Dunnett's Cove, August 17, 2005, unpublished manuscript).

The purpose of the present study is to describe the process of tar migration in a field setting. Understanding the contaminant migration process is critical for modeling the pathways for human and environmental receptors that may be exposed to the MGP tar. In addition, understanding the facilitated migration of the NAPL process is necessary to formulate remedies to reduce the risk from the tarry sediment. This understanding is applicable at other sites where facilitated migration of NAPL from sediment to surface water is occurring.

MATERIALS AND METHODS

To determine the mechanism of tar migration, it is necessary to know the dimensions of the deposit of tarry sediment; the subarea where bubbling and tar migration occur; the physical conditions in the river affected by tar migration and ebullition; and the chemistry of tar, sheens, and gas.

The dimensions of the tar deposit at Bangor Landing were determined based on the results of a field sampling program that included over 130 observation points evaluated over a 5-year period during the present study. Sediment cores were collected using a split-spoon sampler and a rotary drilling rig equipped with hollow-stemmed augers, as well as a barge-mounted vibratory coring drilling rig. Split-spoon samples were collected typically in accordance with American Society for Testing and Materials (ASTM) Method 1586 [22]. In addition, shallow sediment samples were collected by a diver using hand tools. Sediment samples were logged in the field using the Unified Soil Classification System, ASTM Method D2488 [23], paying special attention to the presence or absence of tarry material in the samples. In situ sediment observations also were made with an underwater video camera. Selected sediment samples were analyzed at various commercial laboratories for MAHs and PAHs using U.S. Environmental Protection Agency (U.S. EPA) Method 8260 [24]; www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8260b.pdf and U.S. EPA Method 8270 [25]; www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8270d.pdf. Sediment samples also were submitted to META Environmental Laboratories in Watertown, Massachusetts, USA, for forensic analysis to verify that the tarry material observed in sediment from the site was MGP tar and not another hydrocarbon product rich in PAHs (for example, crude oil). Total organic carbon as a percentage of organic material in sediment was determined by measuring the residual that remained after heating at CT Laboratories in Baraboo, Wisconsin, USA (Methods of Soil Analysis 29-4) [26]. Tar density was determined using ASTM Method D70 [27], and viscosity was determined using ASTM Method D445 [28], at Harris Testing Laboratories in Houston, Texas, USA. A differential global positioning system (GPS) (Trimble) unit was used to determine the locations of sediment borings.

Tar droplets and sheen samples were collected directly from the river surface. Samples of the hydrocarbon sheen on the river surface were collected using Teflon® nets designed for collecting oil spill samples (Model 5080; General Oceanics) The tar droplets and sheens were submitted to META Environmental Laboratories for forensic analysis and for quantitation of PAHs and MAHs. Gas samples were collected in shallow water (depth less than 1 m) from the surface of the river at low tide, in focused areas as gas bubbled up from the sediment, using an inverted 10-L transparent polyethylene tub; the tub had an open area of approximately 45 cm by 60 cm. Gas bubbles were trapped in the tub as they migrated up from the river sediment through the water column. Gas production rates were on the order of 20 to 50 ml/min. When the volume of gas trapped in the tub was sufficient to allow an accurate reading to be taken (~1 L), the gas composition (carbon dioxide, methane, and oxygen) was measured in the field with a portable infrared spectrophotometer (Model GA-90; Land-tec).

The extent of the area of gas bubbling and tar migration was determined from 370 direct observations of tar and gas migration collected in the river on more than 30 occasions from 2001 to 2004. Project scientists paddled to the area of tar migration in the river, noted the time, recorded their location using a hand-held GPS unit, and made observations of the field conditions, the water depth, the surface and deep water temperatures, and the intensity of ebullition and tar migration at low tide. Most of these observations were made during spring tides, the time at which ebullition and tar migration are most vigorous.

Historical flow information in the river was retrieved from the staff gauge at Eddington, upriver from Bangor (waterdata.usgs.gov/me/nwis/peaks/?site_no=01036390&agency_cd=USGS). The bathymetry of the riverbed in the cove was determined using a lead line survey and a differential GPS unit during the present study. In addition, other survey information made available by the city of Bangor was used.

Several physical experiments were performed as part of the present study to assess aspects of ebullition-facilitated tar migration. The rate at which bubbles migrated upward through a water column was evaluated by injecting small volumes of air (~50 cm at a time) into the base of a 3-m tall, 20-cm diameter, water-filled Plexiglas® column. By injection of air at different rates, bubbles of different diameters were generated. Bubbles were generated with a diameter of between 1 and 3 cm at the base of the column. The time required for a bubble to migrate from the base of the column to the surface was measured.

Sheen formation from tar was assessed by a combination of laboratory observations and direct field observations of tar migration and by evaluation of videotapes of tar migration from sediment in the field. From field observations during the present study, tar droplets that migrate to the river surface tend to have a surface area of approximately 1 cm². By examination of videotapes of tar migrating from sediment to the water surface, the amount of sheen generated by a single droplet of tar was estimated. These field observations were reproduced in the laboratory by examining sheen formation from droplets of laboratory-grade coal tar applied to the surface of a water-filled tray at 20°C.

RESULTS AND DISCUSSION

Sediment texture

The Penobscot River near Bangor is a large river with daily average flows of 400 m³/s and peak flows that can exceed 4,000 m³/s (waterdata.usgs.gov/me/nwis/peaks/?site_no=01036390&agency_cd=USGS). The estimated velocity at the riverbed varied between 0 at slack tide to nearly 2 m/s during extremely high flow, and the observed velocity during a site-specific acoustic Doppler profiling survey varied from 0.3 to 1 m/s (G. Stewart, U.S. Geological Survey, unpublished data.) As a result of the high river velocity, there is very little sediment deposition in the main channel of the Penobscot River near Bangor Landing. A bulkhead at the upstream edge of Dunnett's Cove creates a large eddy where the river velocity is much less than in the main channel of the river, resulting in some fine-grained sediment deposition in the lee of the bulkhead. The vast majority of the tar deposit falls within the eddy line in Dunnett's Cove. The sediment textures in different areas of the river reflected their environment of deposition: Well to poorly graded gravel was observed in the high-energy environment of the main channel of the river, and silty sand to well graded gravel were observed in the lower-energy zone in the lee of the bulkhead. Similar findings were reported by the U.S. Geological Survey during their study of sediment texture in the Penobscot River directly upstream from Bangor [29].

The macroscopic organic material identified in sediment in the lee of the bulkhead included sawdust, leaves, aquatic plants, wood, coal, and MGP tar. Total organic material

Table 2. Summary of hydrocarbon ratios in sediment in and near Bangor Landing, Bangor, Maine, USA

Area	No. of sediment samples	Geometric mean LMW PAH/total PAH ratio in sediment[a]
Active zone of tar deposit	25	0.70
Inactive zone of tar deposit	17	0.56
Unaffected by tar deposit	38	0.33

[a] LMW = lower molecular weight (two- and three-ring compounds); PAH = polycyclic aromatic hydrocarbon; total PAH = 16 priority pollutant PAHs, plus 1- and 2-methylnaphthalene.

averaged 11% in samples from the active zone. Macroscopic organic material in the main channel of the river was almost exclusively tar and was more sparse than it was in the sediment in the lee of the bulkhead. Total organic material averaged 0.6% in samples from sediment in the main channel of the river.

Tar characteristics in the active and inactive zones

The tar within sediment of the active zone is less weathered than tar in sediment in downstream portions of the tar deposit. Unweathered tar is a viscous liquid with a glossy texture and a characteristic naphthalene odor, is tacky to the touch, and is generally present in a massive deposit (a sediment layer more than 0.3 m in thickness). The tar becomes glossier, more aromatic, and tackier as river temperature increases from near-freezing in the winter and spring to summertime river temperatures that can exceed 24°C. Tar downstream from the active zone is a pliable solid that commonly has a hardened surface layer, and hardened chunks of tar may be disseminated in a matrix of uncontaminated river sediment. The precise mechanism of tar hardening is not well understood at this time, although it is likely that much of the tar hardening is associated with the development of interfacial films on the tar surface, as described in Luthy et al. [16]. Weathered or hardened tar also has a much lower tendency to form sheens when exposed to air and water than unweathered tar, based on observations during the present study. Because the physical characteristics of the weathered tar make it much less likely to migrate, weathered tar poses less of a human health risk than does unweathered tar.

On the basis of PAH analyses, the tarry sediment in the inactive zone has a chemical fingerprint very similar to that of the tar in the active zone, but it is slightly depleted with regard to low-molecular-weight (LMW) PAHs relative to total PAHs. Background PAHs are even more depleted with regard to LMW PAHs in this area, as shown in Table 2.

Tarry sediment near the sewer outfall that was not exposed to air was typically weathered only slightly and contained oily, aromatic tar that was not hardened. Tar from this area contained a higher proportion of more soluble fractions of MGP tar, the LMW PAHs (two- and three-ring compounds, such as naphthalene or acenaphthene) and MAHs. Hardened and weathered tarry sediment from the distal portions of the tar deposit contained proportionately lesser amounts of MAHs and LMW PAHs and also was more viscous. In the distal portions of the tar deposit, the tarry sediment was covered with a rind of weathered tar overlying less-weathered tar. In addition to the depletion of soluble constituents due to
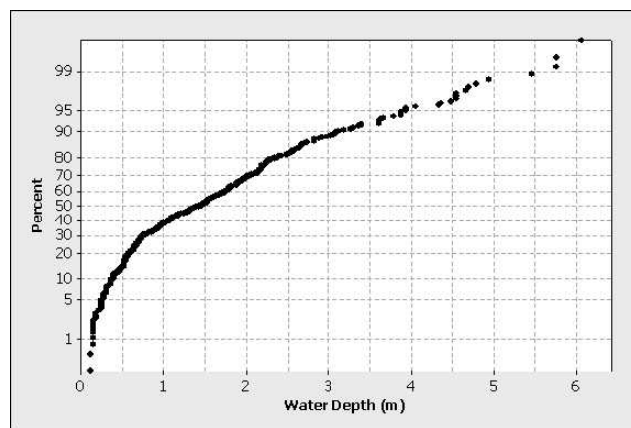

Fig. 3. Probability plot of water depth at locations where ebullition was observed. Fifty percent of bubbling was observed at depths of less than 1.5 m, and 99% was observed at water depths of less than 5.5 m.

leaching, the differences between fresh tar and weathered tar are thought to be related to the formation of interfacial films that form between tar and tar-like materials and water, as discussed earlier. The lesser degree of weathering increases the mobility and the toxicity of tarry sediment in the area near the sewer outfall relative to tar from other portions of the tar deposit.

Tar deposit geometry

A comprehensive picture of the tar deposit was assembled using sediment probes, an underwater video survey, descriptions of sediment cores and grab samples, and chemical analysis of sediment samples. As shown in Figure 1, the tar deposit is elongated in the predominant downstream direction of river flow, extending more than 500 m downstream from the outfall, ranging between 50 and 80 m in width. The tar deposit is thickest and least weathered at the upstream end of Dunnett's Cove, near the sewer outfall. Up to 4 m of tarry sediment was encountered at the sewer outfall; 400 m downriver from the outfall, more than 1 m of tarry sediment was present in the central portion of the tar deposit. The thickness of the tarry sediment decreases and tarry sediment becomes discontinuous and interbedded with nontarry sediment at the lateral edges and in the distal portions of the tar deposit.

Direct observation of ebullition and NAPL migration

The location of the area of ebullition and NAPL migration (the active zone) was defined based on surface observations as discussed earlier. Special care was taken to avoid false-positive and false-negative errors regarding the presence or absence of NAPL sheens in the field [30]. Gas migration observations were made at low tide, when current was at a minimum in the river, so that relatively little error was introduced as a result of lateral displacement as the bubbles rose through the water column. At the Bangor Landing site, 50% of the observed ebullition occurred in water depths of less than 1.5 m, and 99% occurred in depths of less than 6 m (Fig. 3).

In the laboratory, gas bubbles similar in size to those observed at Bangor Landing rose through a 3-m water column at a rate of roughly 30 cm/s, and the observed surface water flow rates in the river at low tide were on the order of 30 cm/s. As a result, the offset between the riverbed locations from which bubbles were migrating was within 3 m of the location

of the bubbles surfacing on the river. In addition, the accuracy of the hand-held GPS units was generally on the order of 10 m or less during the time of measurement. Hence, the error associated within any given measurement was on the order of ≤ 13 m. This level of accuracy was sufficient for initial definition of site conditions at the field scale.

The composition of the gas generated from sediment in the tar deposit was measured in the field with a hand-held infrared spectrophotometer on several occasions. The gas consisted of 50 to 90% methane, 0.3% carbon dioxide, and 34 to 50% other. The composition of the undetermined portion of the gas is unknown; it likely includes some form of nitrogen gas and volatile organic compounds. Gas bubbles from sediment of the tar deposit are generated by anaerobic degradation of organic matter, consisting of organic material in the riverbed (sawdust and other detritus), as well as LMW PAHs in tar, as discussed by Viana et al. [17] and Godsy et al. [31].

Tar migration to surface water was observed only in areas where both ebullition and tarry sediment were observed. Ebullition occurred only in a portion of the tar deposit in which the water was relatively shallow (less than 6 m) and in which sufficient organic matter was observed in the sediment (active zone, total organic material in sediment averaged 11%; main channel, total organic material in sediment averaged 0.6%). Note that ebullition is a dynamic equilibrium among the degradation of organic carbon, water depth, and sediment strength, such that no one parameter will control gas bubble generation.

Comparison of PAH composition in sheens, droplets, and sediment

The chemical fingerprint of the PAHs at the surface of the tar deposit was quite uniform and was characteristic of petroleum tar (water gas tar or oil gas tar). Near the outfall, the surface petroleum tar fingerprint was underlain by sediment with a MGP coal gas tar fingerprint. This is consistent with the operational history of the MGP, which produced coal gas from the 1850s to 1926 and then carbureted water gas and oil gas until the 1960s. The composition of PAHs in the sediment of the tar deposit was very similar to the composition of the tar droplets and tar sheens found on the river surface. Total PAH concentrations (16 priority pollutant PAHs plus 1- and 2-methylnaphthalene) in all of these phases (tarry sediment, sheens, and droplets) were similar (up to tens of thousands of mg/kg, with approximately 60% of the total PAHs consisting of LMW [two- and three-ring] species). The similarity in total PAH concentrations among the different phases (tar in sediment, tar droplets, and tar sheens) illustrates that when migration of tar from sediment occurs there is very little attenuation of the total PAH concentration.

Mechanism of tar migration

Gas is generated constantly in the sediment by anaerobic degradation of organic material, although at different rates as the sediment warms and cools with the changing seasons. When gas migrates upward through tarry sediment, the gas bubbles entrain tar or become entrained in tar, as observed in the field and under laboratory conditions. When the volume of gas in a tar droplet changes, it will change the density of the tar droplet containing the gas. If the volume of gas in a tar droplet increases sufficiently, then it may reduce the density of the gassy tar droplet to less than that of water. As a result, a gas-containing tar droplet can become lighter than water, even though the tar in the droplet is denser than water. This change in density can facilitate the transport of tar to the surface of the river. As an example, a 1-cm³ droplet of tar with a starting density of 1.1 g/cm³ would require a gas bubble of only 0.15 cm³ to change the net density of the tar droplet/bubble system to 0.96, less than that of the water in the river. The change in density can be sufficient to cause DNAPL tar droplets to float. However, other factors also affect tar transport.

The physical properties of tar (especially low water solubility and low surface tension) also affect transport by making the tar hydrophobic; these properties tend to attract tar to the surface of migrating gas bubbles. Consequently, a gas bubble also can facilitate migration of tar by accumulating the hydrophobic, mobile tar at the gas bubble surface as the gas bubble migrates through water-saturated sediment. In effect, the migrating gas bubbles drag the tar upward with them as they migrate through the sediment and then through the overlying water column to the water surface.

Tar migration has been observed especially during extreme low tides when the river water is warm and gas generation is most vigorous at Bangor Landing. When a gas bubble with entrained tar reaches the river surface and the gas bubble pops, some portion of the entrained tar often remains at the surface of the water, held up by surface tension, even though the tar is denser than water.

When the tar droplets reach the surface of the river, they commonly form sheens that spread out as a thin layer on the river surface. The sheens spread because the surface tension of the tar is much less than the surface tension of the water. The spreading action is very important when evaluating the health risk associated with migrating tar. Field and laboratory observations during the present study have shown that a single tar droplet with a surface area of 1 cm² can spread at the river surface to cover areas of thousands of square centimeters, depending on site conditions. The increase in surface area of the tar increases the potential for dermal exposure to human and environmental receptors.

At Bangor Landing, the tar at the bottom of the river was denser than water (specific gravity of 1.3 from the present study). For the tar droplets to migrate from the riverbed to the river surface, they need to have a net density of less than 1 g/cm³. The tar at the bottom of the river became light enough to float to the surface of the river, because enough gas became entrained in the tar that the net density of the tarry sediment was slightly less than 1 g/cm³. After enough gas diffused out of the floating tar droplet, the tar droplets were no longer lighter than water, and the tar once again sank to the bottom of the river.

Alternatively, tar droplets can become entrained with migrating gas bubbles and be dragged along with the gas to the water surface; the tar can be left behind at the water surface due to the high surface tension of the water when the gas bubbles pop. These tar droplets can be redeposited on the riverbed when the surface tension of the water is disrupted. The cycle of tar floating up from sediment to the river surface and then sinking back through the water column to the sediment was observed in the laboratory as well as in the field.

Change in volume of gas over a tidal cycle

Tar migration was qualitatively observed to increase with the rate of gas bubbling from the river bottom, and that tar
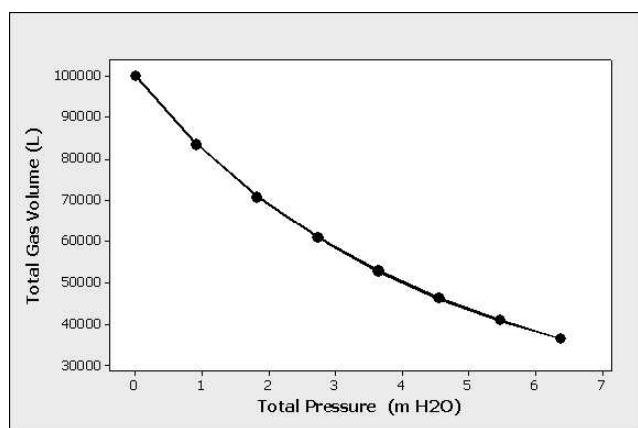
Fig. 4. Plot of gas volume in sediment versus pressure. As the pressure decreases from 6.6 to 0 m water, the estimated volume of the gas in the tar deposit increases from 35,000 to 100,000 L.

migration was more vigorous in the warmer months, when river temperatures ranged from 15 to 24°C. This temporal variation in gas production rate from sediment with temperature is common at field sites [8–11]. On the basis of field observations, ebullition was most vigorous at low tide in the near-shore portions of the tar deposit, in the lee of the bulkhead, where organic material had a chance to accumulate and the maximum water depth at low tide was less than 6 m. Ebullition was controlled by the hydrostatic pressure over the riverbed. The pressure dependence of gas bubble generation also has been commonly observed at field sites [7,8]. Ebullition slowed down and eventually ceased when the tide came in, because the depth of water, and hence the pressure, over the tar deposit increased by 4 m to more than 6 m of water (0.36 to 0.63 atmosphere). The change in pressure affects both the solubility of gas and the size of the gas bubbles. Figure 4 shows that for a site with a 6-m tidal range, the volume of gas in the sediment could vary by nearly 70% over the course of a tide cycle. As organic matter degrades, the tar deposit builds up gas, and then, with each tide cycle, the volume of the gas within the tar deposit changes. This change in the volume of the tar deposit is thought to disrupt the grain-to-grain

structure of the sediment and to decrease the cohesive strength of the sediment. The change in strength of sediment with increasing gas pressure also was simulated in the laboratory by others [12]. The cyclic change in pressure due to the tides decreases the strength of the sediment and thus enhances the ability of gas and tar to migrate.

In the portion of the tar deposit located in deeper water, tar did not migrate to the surface of the river at low tide, even in areas in which several feet of tarry sediment were present and total PAH concentrations were very high (tens of thousands of mg/kg). Tar did not migrate from deeper water, because the sediment did not accumulate enough gas to cause the tar to become lighter than water and float to the surface or to produce bubbles that might entrain tar. In the main channel of the river, the pressure is always greater than 5 m of water. In this area, either the gas bubbles never formed because the pressure stayed too high or the gas was being dissolved at a rate such that the bubbles could not accumulate to the extent that the tar became lighter than water. Where there was no observed ebullition, there was no observed tar migration.

Conceptual model of MGP tar migration

The conceptual model for tar migration is shown in Figure 5. Tar and other wastewater solids accumulated in sediment near the outfall of the sewer. Anaerobic biodegradation of the organic matter generates methane and carbon dioxide in sediment. Gas builds up in the sediment as the organic matter degrades. As gas bubbles migrate through the sediment, the bubbles become entrained in, and also entrain, particles of tar. The tar migrates upward through the sediment with the gas and eventually through the water column. At the river surface, hydrocarbons disperse from the tar droplets and form sheens. Some droplets remain at the surface due to surface tension and due to trapped gas. As gas leaks from the floating tar droplets, they become denser than water again, and the droplets sink to the bottom of the river. In addition, if the surface of the water is disturbed, tar droplets held up by surface tension can fall back to the bottom, because the surface tension of the water is insufficient to keep the tar afloat. The release of gas from the sediment facilitates migration of MGP tar from the riverbed to the water surface.
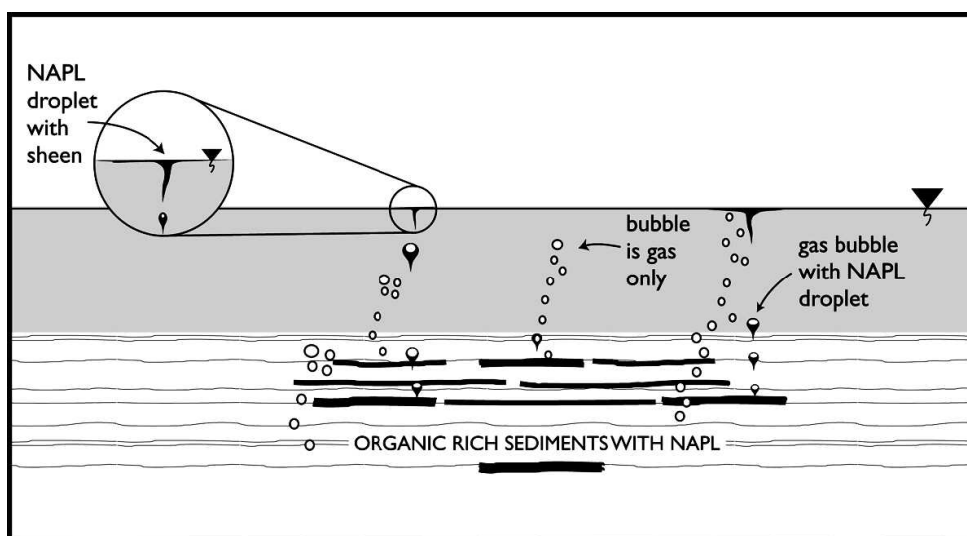

Fig. 5. Conceptual model of nonaqueous phase liquid (NAPL) migration. Note that gas generation can come from biodegradation of organic wastewater solids and sawdust in the sediment and not just from degradation of the NAPL.

CONCLUSION

For NAPL to migrate from sediment to surface water at Bangor Landing, three conditions appear to be necessary: the sediment must contain liquid tar, the sediment must produce gas bubbles at a rate to increase the buoyancy of the tar or otherwise facilitate the transport of the DNAPL tar upward through the sediment and then through the water column, and the gas must come into contact with tarry sediment. The migration of MGP tar from sediment at the bottom of the river to the surface of the river is controlled by anaerobic biodegradation of organic matter. In portions of the tar deposit in which the river was shallow (less than 6 m at Bangor Landing) and sufficient organic matter was present to generate gas, gas bubbles formed and accumulated in the tarry sediment, and the tar migrated with the gas to the surface of the river. In portions of the tar deposit in which the river was 6 m deep or greater, gas bubbles did not form at a rate sufficient to accumulate and cause gas to migrate from the tarry sediment, and the tar remained at the bottom of the river. The in-depth understanding of gas-facilitated NAPL migration is useful for evaluating the risk for sites with MGP tar in sediment, because the formation of sheens from tar droplets increases the surface area of the NAPL without reducing the exposure concentrations. This greatly increases the potential for exposure of human and environmental receptors to NAPL. In addition, at the Bangor Landing site, successful control of NAPL migration from sediment will entail successful control of the gas that is transporting the NAPL. Remedy development at other sites in which NAPL migration from sediment is occurring needs to take into account the mechanisms of migration; otherwise, it runs the risk of failure.

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