Working Memo #S-336

MEMORANDUM

June 28, 2010 DATE:

TO: Division of Shellfish Sanitation Staff

FROM:

Robert E. Croonenberghs, PhD, Director Division of Shellfish Sanitation Robert W. Hicks, Director Office of Environmental Services

THROUGH: Robert W. Hicks, Director Office of Environmental Services

Contingency Plan for Petroleum Hydrocarbon Contamination of Shellfish SUBJECT:

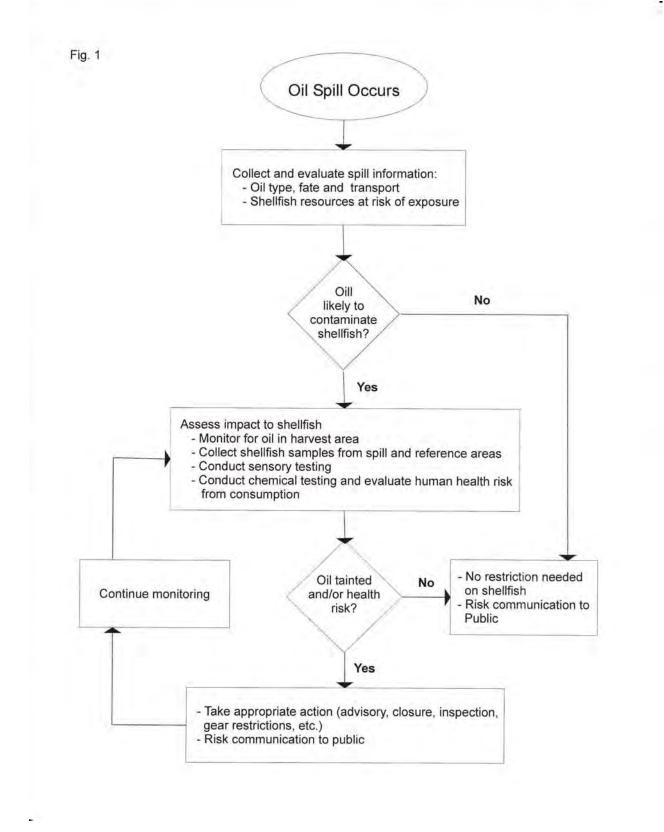
Purpose:

The purpose of this protocol is to establish the Department of Health, Division of Shellfish Sanitation's (VDH/DSS) protocol for responding to oil contamination of Virginia's shellfish waters. The objective of such a response would be to protect consumers of Virginia shellfish and crab meat from oil contamination with the least reasonable impact upon the fisheries. The primary emphasis of this working memo pertains to oil spills of potential, widespread contamination.

Introduction:

The US Department of Commerce, National Ocean and Atmospheric Administration (NOAA), and the US Food and Drug Administration (FDA) have developed two documents to guide states and federal agencies in their response to oil spills: Protocol for interpretation and use of sensory testing and analytical chemistry results for re-opening oil-impacted areas closed to seafood harvesting, 6/18/2010¹ (FDA/NOAA Protocol), and Managing Seafood Safety after an Oil Spill, 2002². These documents are currently being used by Gulf States in their response to the ongoing Deepwater Horizon oil spill, and form the basis for many of the procedures outlined in this working memo.

Since there is no current "incident" concerning a major oil spill, this working memo will be part of a contingency plan for the Commonwealth. However, should a large spill impact or threaten Virginia shellfish waters, DSS's efforts would likely be part of a larger Incident Action Plan that would involve state and federal agencies. Figure 1 shows the generic decision process that would be used by VDH/DSS to manage shellfish safety in such a situation.



Modified from reference 2.

Background:

Types, Components and Properties of Oils

"Oil type and properties strongly influence whether seafood is exposed and contaminated. Crude oils and the refined products derived from them are complex and variable mixtures of hydrocarbons of different molecular weights and structures. They can contain hundreds of different compounds. All crude oils contain lighter fractions similar to gasoline, as well as heavier tar or wax fractions. Because of these differences in composition, different oils vary considerably in their physical and chemical properties. For example, consistencies of different crude oils vary, ranging from a light volatile fluid to a viscous semi-solid. Such differences in properties influence behavior of spilled oil and subsequent cleanup operations.

The petroleum hydrocarbons that comprise oil are composed primarily of hydrogen and carbon, but also can contain varying amounts of sulfur, nitrogen, oxygen, and trace metals. The three main fractions of hydrocarbon compounds in oils are saturates, aromatics, and polar compounds. The properties and relative abundance of each fraction in different types of oil products are summarized in Table 1. Note that toxicity differs among different hydrocarbons and, therefore, different oils" (ref. 2, page 6.).

Group	Sub-groups (alternate name)	Selected Characteristics	Typical Content in Oil (%)
Saturates	 Alkanes (aliphatics): n- alkanes (paraffins) are straight- chained; isoalkanes are branching Cyclo-alkanes (cyclo- paraffins or naphthenes): saturated ring structures Waxes: larger saturate compounds 	High rate of microbial degradation up to C22; Low water solubility; Low aquatic toxicity	Gasoline: 50-60 Diesel: 65-95 Light crude: 55-90 Heavy crude: 25-80 Heavy fuel oil: 20-30
Aromatics	1. Monoaromatics (BTEX): single benzene ring 2. Polycyclic aromatic hydrocarbons (PAH): 2-6 benzene rings	Slower rate of microbial degradation than saturates; Higher water solubility; High aquatic toxicity	Gasoline: 25-40 Diesel: 5-25 Light crude: 10-35 Heavy crude: 15-40 Heavy fuel oil: 30-50
Polar Compounds	1. Resins: smaller compounds that bond with S, N, or O 2. Asphaltenes: very large compounds	Very slow microbial/ physical degradation; Very low water solubility/aquatic toxicity	Gasoline: 0 Diesel: 0-2 Light crude: 1-15 Heavy crude: 5-40 Heavy fuel oil: 10-30

Table 1.

"Seafood contamination can result from exposure to the dissolved fraction of oil, dispersed oil droplets, or an oil coating. With regard to the dissolved fraction, the aromatic fraction of the oil poses the greatest exposure risk because aromatics are relatively more soluble than the other components in oil. Saturates are a major component of oil, but they have lower solubility and higher volatility compared to aromatics of the same molecular weight. Furthermore, Heras et al. (1992)⁴ has concluded that saturates are virtually odorless and tasteless, and do not contribute to tainting.

Of the aromatic hydrocarbons, the mono-aromatic hydrocarbons, such as benzene, toluene, ethyl benzene, xylene (known collectively as BTEX), other substituted benzenes, and the 2- to 3-

ringed PAHs (naphthalene, fluorene, dibenzothiophene, anthracene and their substituted homologues, referred to as low-molecular weight PAHs) comprise over 99 percent of the water-soluble fraction (McAuliffe 1987)⁵. The distribution of these compounds in the spilled oil is one measure of the potential for contamination of seafood from water exposure. Most crude oils are composed of a wide range of compounds, including the PAHs of concern.

Compounds in petroleum-derived oils have a general pattern of increasing abundance with higher level of substitution of a benzene ring (e.g., unsubstituted parent naphthalene is less abundant than C1-naphthalene, which is less abundant than C2-naphthalene). This pattern indicates that the PAHs are "petrogenic," that is, they are from petroleum oils. The PAH pattern is very different for hydrocarbons produced from the combustion of fossil fuels ("pyrogenic" hydrocarbons), in that the parent PAHs are by far the dominant compounds in hydrocarbons of pyrogenic origin. Also, it is important to note that crude oils contain very low concentrations of the high-molecular weight PAHs (e.g., 4- and 5-ringed compounds such as pyrene, chrysene, and benzo[a]pyrene) that are associated with combustion by-products. These differences in relative PAH abundance are key components of fingerprinting analysis."

"For exposure via ingestion of whole oil droplets or contaminated sediments, the highmolecular weight PAHs pose greater risk of contamination. These compounds have low water solubility and are more lipophilic. In organisms with relatively limited capability to metabolize PAHs, such as bivalve mollusks, the high-molecular weight compounds are more likely to accumulate in tissues and persist for longer periods, compared to the low-molecular weight PAHs, which are more rapidly eliminated (Meador et al. 1995)⁶. Finfish and some crustaceans, however, readily metabolize and eliminate all of these compounds rapidly" (ref. 2, page 8). Crabs have a reduced capacity to metabolize oil constituents (ref. 2, page 19).

Overview of Cancer Risk Calculations for PAHs in Seafood

"Most seafood risk assessments conducted after oil spills in the U.S. have followed an approach used by the U.S. Food and Drug Administration (USFDA) in 1990 after the *Exxon Valdez* oil spill in Prince William Sound, Alaska. At the request of the Alaska Oil Spill Health Task Force, a group established after the spill to conduct a survey and assess the impact of the spill on subsistence food supplies, USFDA conducted a risk assessment and provided an advisory opinion on the safety of aromatic hydrocarbon residues in subsistence seafood in the spill area (Bolger et al. 1996⁷; Bolger and Carrington 1999⁸). This approach uses a set of calculations to determine finfish or shellfish PAH tissue concentrations, expressed in benzo[a]pyrene (BaP) equivalents (µg/kg), above which an acceptable risk level for cancer is exceeded. The values for several variables in these calculations can be adjusted on a case-by-case basis, depending on local seafood consumption levels of the exposed population, average body weight of the exposed population, estimates of exposure time for a particular spill, and the cancer risk level deemed acceptable. This approach to calculating seafood advisory or action levels has since been used after several other oil spills, including the *North Cape* spill in Rhode Island, the *Julie N* spill in Maine, the *Kure* spill in California, and the *New Carissa* spill in Oregon" (ref. 2, page 38).

Sensory Testing of Seafood

"Tainted seafood is defined as containing abnormal odor or flavor not typical of the seafood itself (ISO 1992⁹). Under this definition, the odor or flavor is introduced into the seafood from external sources and excludes any natural by-products from deterioration due to aging during

storage, decomposition of fats, proteins, or other components, or due to microbial contamination normally found in seafood. Taint is detected through sensory evaluation, which has been defined as "the scientific discipline used to evoke, measure, analyze and interpret those reactions to characteristics of foods and materials as perceived through the senses of sight, smell, taste, touch and hearing" (Food Technology Sensory Evaluation Division 1981¹⁰)" (ref. 2, page 31).

Correlation between Taint and Body Burden

"The specific compounds responsible for petroleum taint in seafood have not been unequivocally determined. Consequently, results of chemical analysis cannot yet be used to predict presence or absence of taint. Nevertheless, results from recent spills where both chemical and sensory testing have been conducted indicate a high degree correlation between presence of taint and presence of measured petroleum contaminants, or conversely, absence of both. The relationship, as well as tainting threshold, may vary somewhat depending on species, oil type, exposure pathway, and other unknown factors. Within a series of experiments using the same oil type and species, sensory panels can correctly rank the degree of taint with both tissue concentrations and exposure water concentrations" (ref. 2, page 26).

Discussion:

Size of Spill

The size of an oil spill in Virginia waters dictates to a significant degree the type of response required. The Virginia Department of Environmental Quality (DEQ) has responsibility for responding to oil spills in Virginia waters. For small spills affecting relatively small areas, no condemnation of shellfish beds may be needed, and detection of tainting of shellfish by harvesters, buyers and consumers can provide adequate public health protection. For more significant spills that require a condemnation, detecting the tainting of shellfish by the public has generally been used to protect public health; however VDH may decide to condemn areas for the harvesting of shellfish and may conduct chemical testing. Widespread oil spills would likely involve state and federal agencies, with condemnations of shellfish growing waters followed by sensing and testing water, sediment and/or shellfish.

Limits of Statutory Authority

An oil spill could occur within Virginia's Coastal Waters, which are within the 3-mile limit, or approach Virginia from federally-regulated waters farther offshore. Virginia has the authority to close its internal and Coastal Waters to recreational and commercial fishing. NOAA has the authority to close federal waters to commercial fishing³. FDA has several mandatory safety programs for seafood that stem from its authority based in the Federal Food, Drug and Cosmetic Act and thus can legally exert a considerable amount of control over the interstate shipment of seafood.

Evaluation of Conditions for Potential Closure of Shellfish Harvesting Areas

In situations where large areas may be contaminated by oil, it may not be entirely clear where the oil has or has not drifted. Furthermore, oil from remote areas may enter Virginia's waters simply as weathered tar balls. Currently along the Gulf Coast, some state waters are being severely impacted, while Texas's primarily are not. The Texas shellfish program is closing waters to harvest when an oil sheen has been seen in an area, but it is not closing waters when a few tar balls wash up on the shore (personal communication with Kirk Wiles, TX). Texas personnel have received sensory training from NOAA, and evaluate shellfish to ensure their lack of taint in particular areas. This seems to be a prudent approach that protects public health without unduly burdening the shellfish industry.

DSS has been in contact with several state agencies and educational institutions, and intends to implement the following plan in Virginia should its waters be threatened by widespread oil contamination. DSS will participate with DEQ, most likely in an Incident Command System as either a group or a unit of a group in Operations. DSS will collect shellfish samples from potentially impacted areas, if needed, and Virginia Tech's Hampton Agricultural Research and Extension Center (Va Tech) will conduct sensory evaluations. Va Tech will try to arrange sensory evaluation training from NOAA for a number of people in Virginia. Shellfish may also be sent to the Virginia Institute of Marine Science (VIMS) for PAH analysis, though a funding source for these analyses will need to be determined. DSS will collect bivalve molluscan shellfish samples from the mouth of the Chesapeake Bay and the seaside of the Eastern Shore to serve as baseline data. In the event of oil potentially impacting an area, the state will need to know whether measured PAH concentrations in shellfish represent an increase above background concentrations or not.

Conclusions:

Whether an oil spill were of sufficient magnitude to require a response simply by the state or by both state and federal authorities, certain principles in the FDA/NOAA Protocol¹ would need to be followed. VDH will implement these policies in the following manner:

- Once significant amounts of oil or chemical contaminants are visually observed on the surface of shellfish growing waters, the waters will be closed until free of sheen, and subsequent testing has been completed to confirm that shellfish from affected areas are wholesome and safe for human consumption. However, the presence of a few scattered tar balls will not necessarily be deemed sufficient to close the waters.
- After the initial closure, evaluation to determine whether the area can be reopened should involve both organoleptic analysis of shellfish (*i.e.*, sensory testing), and if found to be acceptable, then to be followed by chemical analysis.
- Shellfish closure areas will include a precautionary buffer zone around known contaminated waters to account for uncertainty, such as areas where oil was predicted, but never occurred or difficult-to-detect sub-surface plumes of oil may have drifted. After confirming through subsequent evaluation (*e.g.*, water quality sampling, remote sensing) that oil did not enter the buffer zone, the area may be re-opened without subjecting seafood samples to evaluation under this protocol. This protocol is an added layer of protection to be applied to shellfish only in areas known to have been contaminated.

References Cited:

1) Protocol for interpretation and use of sensory testing and analytical chemistry results for reopening oil-impacted areas closed to seafood harvesting, 6/18/2010.

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http://response.restoration.noaa.gov/book_shelf/963_seafood2.pdf

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4) Heras, H., R.G. Ackman, and E.J. MacPherson. 1992. Tainting of Atlantic salmon (Salmo salar) by petroleum hydrocarbons during a short-term exposure. Marine Pollution Bulletin 24:310-315.

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7) Bolger, M., S.H. Henry, and C.D. Carrington. 1996. Hazard and risk assessment of crude oil contaminants in subsistence seafood samples from Prince William Sound. American Fisheries Symposium 18:837-843.

8) Bolger, M. and C. Carrington. 1999. Hazard and risk assessment of crude oil in subsistence seafood samples from Prince William Sound: lessons learned from the Exxon Valdez. In L. Jay Field et al. (eds.). Evaluating and Communicating Subsistence Seafood Safety in a Cross-Cultural Context: Lessons Learned from the Exxon Valdez Oil Spill. Pensacola: Society of Environmental Toxicology and Chemistry. pp. 195-204.

9) International Standards Organization (ISO). 1992. Sensory Analysis – Methodology – Vocabulary. Report ISO 5942. Geneva: ISO.

10) Food Technology Sensory Evaluation Division. 1981. Sensory evaluation guide for testing food and beverage products. Food Technology 35(11):50-59.