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Sedimentary Impact of Dredging the Delaware Estuary:

Geochemical Impacts and Natural Radionuclide Tracers

A White Paper Report

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by

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Executive Summary

The proposed plan of the U.S. Army Corps of Engineers (USACE) to deepen the channel of the Delaware River from the existing 40 feet to 45 feet has raised concerns regarding the impacts of dredging activity and upland disposal of dredge materials on the water quality of the channel, the bay, and the region's groundwaters. Major concerns arise from the possible release and remobilization of several hazardous chemical species, including heavy metals, radionuclides, pesticides, and other organic chemicals from the sediments and their subsequent return to the human population through consumption of seafood or contaminated water.

In order to respond to such concerns and provide authoritative answers to the related questions, USACE researchers have analyzed the quality of the Delaware channel waters and sediments with respect to heavy metals and pesticides. They have also researched the leaching characteristics of such sediments by the river water and studied the possibility of aquifer contamination through leachate generation and recharge into local groundwaters.

The objective of this report is to compile the results of other similar studies documented in the published literature or as internal reports of agencies like the U.S. Geological Survey (USGS), the Environmental Protection Agency (EPA), and their contractors, which address the question of safety in dredging activities through comparison of data and modeling. The primary resource for this work was the published literature on the topic, identified through the University of Delaware's library holdings and searchable electronic databases. Through these searches, several studies on the abundances of heavy metals and pesticides in the Delaware river and bay waters and sediments were identified. Limited data were found on the leaching characteristics of these chemicals from sediments by fresh or saline waters. Data on the abundances of a few radionuclides of the uranium and thorium series in the aqueous phase of the channel and the bay and in their sediments were primarily obtained by our own research group at the University of Delaware.

Based on the results of these studies, the "no significant impact" conclusion propounded in the USACE's Supplemental Environmental Impact Statement (SEIS 1997) is criticized on several accounts. Our conclusions are supported through a critical analysis of the available information and the results of new modeling.

Concentrations of several heavy metals, including lead and mercury, in Delaware River waters are below the Delaware River Basin Commission's recommended chronic criteria (DRBC 1994) and are similar to their concentrations in other East Coast rivers. Levels of arsenic pose some concern, as it is feared that its levels in river waters will often exceed DRBC criteria. However, reduced and methylated forms of arsenic are not the dominant species in these waters. For the suspended load of the Delaware River, lead is the most enriched element compared to similar rivers elsewhere in the nation. Sediment concentrations of polychlorinated biphenyls (PCBs), PCB congeners, polycyclic aromatic hydrocarbons (PAHs), dichloro-diphenyl-trichloro-ethane (DDT), chromium, copper, nickel, lead, zinc, and mercury increase by factors of 5 to 10 from Egg Island Point, NJ, to the Walt Whitman Bridge in Philadelphia. Throughout the estuary, a widespread presence of PCBs is found in the sediments. At least one study has warned that, through food-chain transfer, the bioavailability of these contaminants may result in adverse impacts to organisms that biomagnify the toxins and may pose potential health risks to humans who consume fish from the estuary (Arthur D. Little, Inc. 1994). The USACE found much lower levels of these contaminants in sediments collected mainly from the navigational channel of the Delaware River.

The risk arising from the biofixation of polonium (^{210}Po) by marine organisms such as fish, molluscs, and crustaceans and their consumption by humans is shown to be small given the ^{210}Po concentrations in the Delaware Estuary as reported by Church and Sarin (1995) and the average annual per capita consumption of seafood. However, factors such as elevated concentrations of ^{210}Po in the waters, higher-than-average consumption of seafood, and the status of certain individuals (e.g., smokers or those living in dwellings with high radon concentrations) could drastically alter these risk estimates.

Heavy metal concentrations of groundwaters in the Delmarva Peninsula are generally below the EPA's potable water limits. Concentrations of iron and radon often exceed EPA limits in the groundwaters of New Castle County, DE. The USGS suggests that the local groundwater recharge in Gloucester and Salem counties, NJ, is small, and contaminant travel times are on the order of 50 to 100 years, which virtually eliminates the possibility of well contamination through leachate generation from upland disposal of dredge spoils. However, at two Delaware agricultural sites used in corn and soybean farming, another report showed the existence of common herbicides in the shallow groundwaters, suggesting accelerated local recharge in some areas. Model-based calculations suggest that the leaching action of rain on upland-disposed dredge spoils from the annual maintenance dredging of the 45-foot channel alone could potentially cause contaminant concentrations in groundwaters to exceed allowed limits.

For more accurate assessments of risks to the human population, either from consumption of seafood or use of groundwater, data on radionuclide concentrations in the local waters, biota, and sediments are also essential. Similarly, heavy metal leaching characteristics of the dredge spoils by rainwater, and their adsorption/desorption characteristics in local soil-water systems, are central to evaluating groundwater contamination by heavy metals and pesticides.

Introduction

The U.S. Army Corps of Engineers (USACE) has proposed to deepen the channel of the Delaware River from the existing 40 feet to 45 feet at mean low water, with an allowable dredging overdepth of 1 foot. The dredging is expected to have major cost benefits in transporting commodities in and out of Philadelphia-area ports via more efficient vessel loadings. Since 1910, the main navigation channel of the Delaware Estuary has been dredged repeatedly, altering the former 18- to 23-foot controlling depths to the present 40-foot depth (DiLorenzo et al. 1993).

The modified channel will extend from the Philadelphia harbor to the mouth of Delaware Bay, with little or no change in the channel width. Approximately 33 million cubic yards of material would be removed in the initial phase of the project, and more than 6 million cubic yards of annual dredging would be required for the maintenance of the 45-foot channel. The spoils are proposed to be disposed at the nine active upland disposal sites and four new sites identified as 17G, 15D, 15G, and Racoon Island. The new sites are located in Delaware and Gloucester counties. The USACE proposes to use the dredged material for wetland restoration at Egg Island Point, NJ, and Kelly Island, DE. The corps also proposes stockpiling of sand for later beach nourishment work at Slaughter and Broadkill beaches in Delaware. Dredge spoils from maintenance dredging are proposed to be deposited at the existing open-water site at Buoy 10 in the Delaware Bay (SEIS 1997).

Sediments often act as sinks for a host of chemical species that include natural radioelements, i.e., uranium and thorium series radionuclides, such as isotopes of thorium, lead, and polonium (Anderson 1987; Heussner et al. 1990; Barnes and Cochran 1993; Sarin and Church 1994) as well as anthropogenic substances like polychlorinated biphenyls (PCBs), heavy metals, and high-molecular-weight organic compounds (LaFlamme and Hites 1978; Tanabe et al. 1987; Johnson and Sims 1991) Estuaries, the saline mixing zones between fresh and open ocean water, process dissolved natural and contaminant reactants along the salinity gradient and eliminate these substances from the suspended loads (Church and Scudlark 1998). Many of these substances are potential carcinogens and pose significant health hazards to humans and animals.

Major concerns in dredging (which may remobilize several of such adsorbed species from the sediments) and upland disposal of the dredge materials include the following:

- release of contaminants from resuspended sediments during the dredging process and subsequent focusing and return higher up the food chain via fish and shellfish;
- mobilization and transport of upland-disposed dredge spoils and contaminants into environmental pathways through biogeochemical, hydrodynamical, or wind-driven processes; and
- mobilization of contaminants from the dredge spoils and transport to other locations via leachate generation and seepage to subsurface water resources.

Remobilization of hazardous species from the dredge spoils and their return to humans via food and water resources is a serious concern. The purpose of this study is to gather the available data on the abundances of radionuclides, heavy metals, and PCBs in sediments from the Delaware river and estuary, model their release characteristics from sediment resuspension or via dredge-spoil leachates, and assess the impact of their return to humans via seafood and groundwaters.

Project Objectives

Specific objectives of this project are to

- summarize existing information on the abundances of radionuclides, heavy metals, and PCBs in Delaware river and estuary sediments and determine if they are within safe disposal limits for the residential disposal of spoils,
- assess contaminant leaching characteristics in resuspension during dredging operations and estimate the risks from their biofocusing and return via seafood,
- assess the extent of leaching of upland-disposed dredge spoils and its impact on groundwater quality via infiltration, and

- identify exposure pathways for contaminants and determine if the environmental risks associated with an environmental dredging and disposal project are acceptable.

Findings of our studies, modeling, and understanding are presented in this report. No experiments or actual analyses have been carried out. Only the existing published literature and data from various reports of agencies like the U.S. Geological Survey (USGS), the Environmental Protection Agency (EPA), Artesian Water, the USACE, and their contractors have been used. Some modeling has been carried out for impact assessments. The University of Delaware Library was a major resource in this study. The collection of reports at the Delaware Geological Survey at the University of Delaware was another significant source of data. Several electronic search engines, such as Web of Science, FirstSearch, WorldCat, ISI-Citation, Government Document Catalogue Service, UnCover, and Current Contents Connect, were used to gather the information and modeling parameters reported here. These searches were carried out using the standard techniques of choosing appropriate keywords, authors, and subject titles. Cross references in various publications and reports provided further leads to continue data accumulation and to compare results from more than one institution. Unpublished and generally unavailable reports from contractors to the EPA and USACE were obtained by making specific requests to the agencies. All of these agencies were very cooperative and generous in providing the required assistance or advice.

Status of the Delaware River

General water quality conditions in the Delaware Estuary are controlled largely by municipal and industrial discharges located upstream in the Delaware River. Various segments of the river, from Philadelphia to the sea, are influenced differently by the existing local conditions. For example, the segment of the Delaware River between Torresdale, PA, and the Walt Whitman Bridge is influenced by municipal discharges, combined sewer and stormwater overflows, industrial discharges, and nonpoint sources. Numerous petroleum refineries are situated along the segment from the Walt Whitman Bridge to Marcus Hook. The segment from Marcus Hook to the south of Pea Patch Island (north of the Chesapeake and Delaware Canal) contains the turbidity maximum and represents a hydrodynamic transition zone. This segment also contains major chemical industries and a major railway site. It receives municipal discharges from Wilmington, DE, and flows from the Christina River. The remaining segment of the Delaware River, especially between Stony Point, NJ, and Egg Island Point, NJ, has been historically less contaminated than the rest of the river (Arthur D. Little, Inc. 1994).

Summary of Existing Information

Significant literature exists on the concentrations of heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), PCB congeners, and dichloro-diphenyl-trichloroethane (DDT) in the sediments as well as the aqueous phase of the Delaware River and the estuary. Much of the information about the concentrations of these species in groundwaters of the Delmarva Peninsula is in the form of reports from the USGS. Limited data exist on the distribution of radium isotopes in Delaware Bay (Elsinger and Moore 1983). Limited data also exist on the distribution of uranium isotopes ($^{238,234}U$) in the dissolved and particulate fractions of a lower Delaware Bay salt marsh in Canary Creek (Church et al. 1996) as well as thorium, lead, and polonium in the tidal phases of the Delaware Estuary (Church and Sarin 1995) and a Delaware salt marsh (Church et al. 1986). Leaching characteristics of these radionuclide species from sediments by river water or rainwater are unavailable. However, Riedel and Sanders (1998) report results on the leaching characteristics of arsenic, cadmium, copper, chromium, lead, nickel, selenium, and zinc from Delaware River suspensions by weak hydrochloric acid (1N HCl). Inquiries with the USACE (Philadelphia District) have revealed that experiments on the heavy metal leaching characteristics of dredge spoils by a series of solvents are under way in their laboratories and the results were expected to be out in mid-1999 (John Brady, personal communication). Results of these studies are central to assessing the impact from the upland disposal of dredge spoils on local groundwater resources.

One of the original objectives of this report was to provide an annotated bibliography of the work reported in the literature or unpublished reports. However, during the literature search, it became apparent that a large volume of literature is available on heavy metal and pesticide distributions in Delaware River waters, sediments, and local groundwaters. Such data are easily accessible through electronic catalogs and data searches, making an annotated bibliography redundant. Therefore, for better presentation of results and for purposes of easy comparison, the available information on heavy metal and PCB concentrations for Delaware River waters, sediments, and suspended matter is divided into three groups. The first group consists of the published data reported in peer-reviewed journals or books; the second group is from the report of Arthur D. Little, Inc., a contractor to the EPA; and the third group is from the work of the USACE reported in their 1997 Supplemental Environmental Impact Statement (SEIS 1997). The latter two sources are put into separate groups because of the contrasts in their data, evaluation strategies, and conclusions.

Group I: Peer-Reviewed Literature

(Sharp et al. 1982, 1984; Biggs et al. 1983; Church et al. 1988; Riedel and Sanders 1998)

Heavy metal data in the tidal freshwater of the Delaware River and seston mass are reported in these studies. Samples cover the length of the river from Fieldsboro to Marcus Hook. Except for arsenic and copper, other heavy metal concentrations (antimony, cadmium, chromium, lead, mercury, nickel, selenium, silver, and zinc) in the river waters were found to be below the Delaware River Basin Commission's recommended chronic criteria (DRBC 1994) and also in line with similar results from other rivers on the U.S. East Coast. Arsenic showed significant sources in the Philadelphia area (30–50% higher dissolved concentrations below the Benjamin Franklin Bridge). The sources of arsenic appear to be fixed-point sources (i.e., the flux of arsenic remains unchanged in all seasons). Reduced and methylated forms of arsenic are not dominant in Delaware River waters. Phytoplankton are among some of the most sensitive organisms to reduced arsenic, due to its chemical similarity to phosphate. Noting that arsenic is a human carcinogen when ingested through fish and water, these studies warn that the prevailing concentrations of arsenic in the Delaware River often exceed the DRBC criterion for arsenic and may pose a health threat. Copper concentrations were often higher in the river below Philadelphia, suggesting a source of copper in the region. A minimum of 30–60% of the copper is found to be complexed by organic matter, making it less toxic and bioavailable.

Concentrations of all trace elements in the suspended matter show lead to be the most enriched element compared to similar rivers. Levels of arsenic, cadmium, and zinc suggest minor elevations. Speciation experiments suggest that most trace elements in the suspended load are present in acid-labile form and may be bioavailable (Luoma and Bryan 1978). In 1N HCl leaches, cadmium, zinc, lead, and copper showed greater than 90% mobilization, with nickel and arsenic slightly less. Results on fresh or saline water leaching characteristics of the channel sediments could not be found in the published literature.

Group II: The Little Report

(Arthur D. Little, Inc. 1994)

With a view to determine the spatial distributions of toxic chemical contaminant concentrations in the sediments, biota, and waters of the Delaware river and estuary, the Delaware Estuary Program asked the environmental consulting firm Arthur D. Little, Inc. to compile the historical data on sediments and biota and also to measure these parameters experimentally in an effort to fill important data gaps and assess the bioavailability of sediment-bound organic chemical contaminants. Sixteen sampling sites along the Delaware river and bay were chosen for sediment characterization studies. The design strategy was intended to provide extensive spatial coverage for the industrial and municipal point and nonpoint sources of pollutants along the length of Delaware River.

The firm's analyses suggest more widespread, acute sediment toxicity in the Delaware Estuary than previously documented, especially in the more urbanized and industrialized portion of the upper river (between Torresdale and Marcus Hook). Sediment concentrations of PAHs, PCBs, PCB congeners, DDT, chromium, copper, nickel, lead, zinc, and mercury increase by factors ranging from 5 to as much as 10 from Egg Island Point, NJ, to the Walt Whitman Bridge. Widespread existence of PCBs was found in sediments throughout the estuary, with concentrations exceeding sediment effect levels (no observed effect level, or NOEL) at 14 of the 16 stations sampled.

Concentrations of DDT and its related DDE and DDD metabolites exceeded sediment effect levels (effect range-low, or ER-L) at 15 stations. Concentrations of dieldrin, another chlorinated pesticide, exceeded sediment effect levels (ER-L) at seven stations. PAH concentrations strongly correlated with toxicity across the 16 stations and exceeded sediment effect levels (ER-L) at 10 stations. The heavy metals chromium, copper, mercury, lead, and zinc all exceeded sediment effect levels at stations between Torresdale and Marcus Hook. Although chromium did not follow a concentration gradient, the other metals exhibited a decreasing concentration gradient from the upper reaches of the river to its lower reaches (Cohansey River). Sediment-bound PCBs, DDT-related pesticides, and, to a lesser extent, PAHs are bioavailable to benthic organisms. Arthur D. Little, Inc. suggests that "through food-chain transfer, the bioavailability of these toxic contaminants may result in adverse impacts to organisms that biomagnify these contaminants and may pose potential health risk to humans who consume fish from the estuary."

The report published by Arthur D. Little, Inc. (1994) provides elaborate descriptions of sampling stations and methods, field quality controls, analyses and measurement details, and quality controls for the data. Its conclusions are conservative.

Group III: The Corps Report

(SEIS 1997)

To evaluate the quality of sediments that would be disturbed during dredging and disposal and their potential impact on aquatic resources, the U.S. Army Corps of Engineers (USACE) measured the abundances of heavy metals (antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, vanadium, and zinc) as well as a series of other organic contaminants (pesticides, PCBs, PAHs, etc.) in Delaware river and bay waters as well as sediments along the entire river length (from the Walt Whitman Bridge to Egg Island Point). Results and conclusions were reported in a Supplemental Environmental Impact Statement (SEIS 1997). Through their bulk analyses of sediment samples, USACE researchers did not identify high concentrations of organic contaminants within the channel or bend-widening locations. PCBs were detected only in two samples. PAHs were detected in channel bends between Philadelphia Harbor and Artificial Island but were absent in the Delaware Bay portion of the project area.

The USACE also found heavy metals widely distributed throughout the project area. Concentrations in the sandy lower Delaware Bay were lower than up-river. However, the USACE suggested that there were no apparent contamination trends. To assess the potential human health impacts associated with the disposal of channel sediments, the corps used the New Jersey Department of Environmental Protection (NJDEP) Residential and Nonresidential Criteria. A total of 91 chemical parameters were compared to the NJDEP criteria. The corps concluded that all 91 parameters from the entire length of the river met the NJDEP criteria without exception. The pesticide toxaphene and the heavy metals thallium and cadmium, which were found close to the NJDEP limits, were further analyzed in more samples and shown to be within safe limits. However, when compared to the ER-L criteria, USACE data suggest that some of the measured chemical parameters exceeded recommended limits. Among these were the heavy metals arsenic, cadmium, mercury, silver, and zinc, which were above ER-L values, as well as a few PAHs. The USACE concludes that overall concentrations of the contaminants in channel sediments are considered to be low, making the sediments "sufficiently clean" to be dredged and used for beneficial uses such as beach nourishment.

The USACE also carried out elutriate analyses of the sediments by dispersing the sediments in Delaware River waters and studying the release characteristics of the heavy metals and pesticides. All heavy metals showed significant release characteristics, whereas the release of organic contaminants in the sediment elutriates was limited. PCBs were not detected, and pesticides were detected in only three of the 107 samples. Based on their elutriate analyses, USACE researchers concluded that dredging and dredged material disposal operations would not significantly impact water quality within the Delaware River.

Concentrations of PCBs reported by the USACE are lower by factors of 8 to 28 than those reported by Arthur D. Little, Inc. (1994) in the Delaware River sediments. The USACE report contends that these differences are due to spatial differences in the concentration levels within the channel. The navigational channel, where the corps carried out its sampling, has much lower concentrations than the shallow regions of the river and bay, where Arthur D. Little, Inc. is said to have carried out its sampling. The USACE concludes that sediments dredged from the navigational channel are harmless and can effectively be used for the construction of wetlands and beach nourishment projects.

The "No Significant Impact" Conclusion of USACE: How Accurate?

As stated in the SEIS (1997), the USACE has concluded that "no significant impact" will result from either dredging or disposal of dredged materials within the channel or in upland disposal facilities. This conclusion appears to be in contrast with conclusions based on other studies. Among the numerous instances in which the conclusions drawn in the SEIS seem doubtful are the following:

1. The disagreement between the USACE and Arthur D. Little, Inc. (ADL) on the heavy metal and pesticide concentrations of the Delaware River sediments are on the order of 800–2,800% for similar parts of the river (ADL values being higher than USACE values). Temporal variations in the concentrations of these measured species at any given location are generally within 30%. ADL values show agreement with other published results (e.g., Church et al. 1988; Riedel and Sanders 1998). The USACE (SEIS 1997) contends that ADL conducted its studies primarily in the shoal habitats and at stations which were often located in the mouths of major tributaries to the Delaware River, whereas the USACE took its samples from the main navigational channel. The USACE further contends that since the shoal habitats are not truly representative of the dredged material, concerns from its disposal are unwarranted. However, according to the ADL report (1994), 25% of ADL's samples were taken from the navigation channel, while only 20% were taken from the mouths of major tributaries to the Delaware River. The report's section on sampling design states, "The field sampling program featured a design strategy intended to (1) provide extensive spatial representation along portions of the Delaware River potentially influenced by industrial and municipal point and nonpoint sources of pollutants and (2) include sampling stations

within the Delaware Bay that could serve as reference stations that reflect baseline conditions in the estuary."

2. The ADL report (1994) is very elaborate in its station documentation and descriptions of sampling methods, field quality controls, analyses and measurement details, and quality controls for the data. The conclusions are very conservative and well within the domain of what is derivable from the data. In contrast, the data from the USACE (SEIS 1997) is often lacking many of the details or appropriate references provided by ADL, which a normal research report provides. Thus the conclusions appear doubtful.
3. In the SEIS (1997), it is hard not to notice the application of different standards to show that the disposal of spoils would remain within "safe limits," based upon the perceived use of that disposal facility. For example, in discussing the disposal site selection criteria, the USACE report says, "Background sample HTRW-13 in area 15G had an arsenic content of 22 ppm, which slightly exceeded the NJDEP Residential Cleanup Criteria of 20 ppm. Sample HTRW-7 in area 17G had a Toxicity Characteristic Leaching Procedure lead level of 6 ppm, which slightly exceeds the Federal Regulatory level of 5 ppm set for toxicity characterization. Sample HTRW-10 in area 17G had a benzopyrene content of 674 ppb which slightly exceeds the NJDEP Non-residential Cleanup Criteria of 660 ppb." If the NJDEP Residential Cleanup Criteria were uniformly applied, these contents would not "slightly exceed" but very significantly exceed the criteria.
4. Little or no available data is often regarded by the USACE as no evidence to suggest concern. The authority of indulgence is very strong in its conclusions. For example, in a statement of "no concern" regarding the disposal of hazardous, toxic, and radioactive waste in dredged material disposal, the USACE concludes, "Based upon the literature search and subsequent chemical testing, the minimal exceedance of the stated regulatory levels, and the proposed use of the area as a dredged material disposal site, no additional testing or remediation of these areas is required" (SEIS 1997).

Geochemistry of Polonium and Possible Exposure

Marine organisms such as fish, molluscs, and crustaceans are well known to accumulate the radioactive isotope of polonium, ^{210}Po. Concentration factors for ^{210}Po in seafood are on the order of 10^3 to 10^4 (Cherry and Heyraud 1982; Carvalho and Fowler 1993; Bangera and Rudran 1995). Because they may be eaten, these organisms can provide a direct radiological dose to humans. During the course of dredging, as the bottom sediments are resuspended, much of the polonium adsorbed on sediments may potentially be remobilized in the aqueous phase. Such bioavailable polonium may then pose the threat of being passed up the food chain. With that in mind, we did some calculations to assay the radiation dose from ^{210}Po via consumption of seafood.

Biomagnification of ^{210}Po and Radiation Dose from Seafood

The dissolved ^{210}Po concentrations of the bay are between 6 and 10 Bacquerrals per cubic meter (Bq m^{-3}) under normal circumstances (Bacon et al. 1976; Church and Sarin 1995; Hussain et al. 1998). According to Aarkrog et al. (1977), the annual radiation dose received by eating an average of 15 kg per year of seafood taken from such waters can vary from 2 to about 40 micro-Sievards (≰Sv). Many bays and shallow coastal waters may have higher ^{210}Po concentrations, which would increase the dose proportionately if the catch came from those regions. If the ^{210}Po concentration of the water further increases by a factor "f" due to ^{210}Po release from sediment resuspension, the dose would increase by the same factor. Determinations of the bioavailability of ^{210}Po to the aqueous phase are therefore important.

The radiation received by eating seafood containing ^{210}Po is focused in varying degrees in different body tissues. Hunt and Allington (1993) have shown, for example, that the gut absorption factor of ^{210}Po in humans is on the order of 0.8 (with a factor of 1.0 indicating complete absorption). This suggests that for these body parts, the dose estimates due to ingestion of food carrying ^{210}Po need to be increased. Calculations show such increases would be on the order of 250–400%, which would increase the normal dose of 2–40 ≰Sv to about 5–150 ≰Sv.

Our searches did not yield any data on ^{210}Po concentrations in the upper parts of the Delaware River. Our proposal to study the abundances of several radioelements including ^{210}Po in the Delaware River, estuarine sediments, and groundwaters in New Castle County, was declined funding by the Sea Grant College Program. Under the circumstances, this section will deal with limits on the dose estimates from seafood consumption in the Delaware Valley, or such estimates will be based upon the limited ^{210}Po data of Church and Sarin (1995) in the Delaware Bay.

Effective Dose Estimates

The Annual Limit on Intake (ALI) of radionuclides for occupational exposure as prescribed by the Nuclear Regulatory Commission (NRC, at http://www.nrc.gov/NRC/CFR/PART020/part020-appb.html) is 50 mSv for whole body exposure. About 4 mSv are received by an average individual in the continental U.S. as a background dose (from radon, consumer products, miscellaneous environmental sources, medical X-rays, etc.). This value is calculated by summing the annual collective effective dose equivalents and dividing by the total population (NCRP 1987a, 1987b). This is therefore only a reference, and large deviations based on local existing conditions are expected. For example, smokers and those living in dwellings with high radon concentrations could receive background doses as much as 10 to 50 times higher.

As stated above, the maximum dose a person should receive from the consumption of seafood in the Delaware Valley under normal circumstances is less than 1 mSv per year. It would appear that the risk of exceeding the ALI is minimal. However, if ^{210}Po concentrations in the Delaware estuary are higher by a factor of 10 than the earlier reported values of 6–10 Bq m^{-3}, or the level of bioavailable ^{210}Po in waters increases due to resuspension and leaching of sediments, or individuals consume more than 15 kg of seafood per year, or they smoke or live in dwellings with high levels of radon, the consequent risk arising from radiation exposure could be significant. It is interesting to note that recent articles in the Philadelphia *Inquirer* (August 31, 1998) reported PCB concentrations in the Delaware River that were higher than EPA limits and raised cautions about consuming Delaware River fish, since fish and other seafood tend to focus these chemicals in their tissues and return them up the food chain. Strong association of ^{210}Po with organic matter (Harada et al. 1989; Hussain et al. 1995) suggests that polonium may follow a similar fate.

Groundwater Impacts from Dredging

The origin of groundwater is basically from surface runoff infiltrating the ground or recharge at points of discontinuity in subsurface geological formations. Bachman and Ferrari (1995) observe, "New Castle County is undergoing rapid residential, industrial, and commercial growth. From 1995 to 2020, the population in that part of the county south of the C & D Canal is expected to be increased by more than 153%, with a corresponding increase of more than 169% in the number of housing units. This area has the lowest population density in the county, 113 people per square mile as compared to a county-wide total of 1,067 people per square mile. It also has been an area of active and continued expansion of commercial, industrial, and residential development.

"Southern New Castle County relies exclusively on groundwater for its water supply because surface-water resources are limited. The expansion of groundwater supply systems associated with population growth and development could cause declining water levels and water-quality degradation. Knowledge of the distribution of potable groundwater and of the geochemical controls on water quality are essential to develop and manage dependable groundwater supplies in the area south of the C & D Canal."

Groundwater quality can be degraded by several processes and human activities. Wastewater disposal, spray irrigation of treated wastewater, salt from de-icing roads, and releaching and subsequent mobilization of several hazardous species from dredge spoils could all affect groundwater quality. A proper analysis of the extent of any contamination of groundwater would require information about the adsorption/desorption characteristics of the hazardous species in soil-groundwater systems (Hussain and Krishnaswami 1980, 1982; Krishnaswami et al. 1982) and also the transit times of groundwater recharge (Hussain 1984). Denver (1993) detected several common herbicides in shallow groundwaters at two agricultural sites in Delaware, which are used in corn and soybean farming. One of these sites is in northern Delaware (termed the Vandyke site), and the other is in southern Delaware (the Fairmount site). Although the detected herbicide levels in groundwaters at these sites were generally below the EPA's maximum contaminant or health advisory levels, the study establishes the recent connection between surface leaching and local groundwater recharge. Again, before we can talk about the possibility of groundwater contamination from leaching of dredge spoils with any authority, we need information about the leaching characteristics of heavy metals from the spoils by rainwater as well as their adsorption/desorption characteristics in the local soil-water system. Personnel at the USACE's Philadelphia District office confirmed in October 1998 that studies of the leaching characteristics of sediments from the Delaware river and estuary by rainwater and a host of other fluids with varying geochemistries were under way at the USACE (John Brady, personal communication). Results of these analyses and discussion were expected to be available during mid-1999.

Major Aquifer System of the Study Area

The study area is underlain mainly by unconsolidated sands and clays of cretaceous, tertiary, and quaternary age (Benson and Spoljaric 1996). The unconsolidated formations dip to the southeast. Major aquifer formations along the Delaware River include the Potomac-Raritan-Magothy, Cape May, and Columbia formations. The Cape May and Columbia formations cover practically all of Delaware and parts of southern New Jersey.

In a typical river basin, groundwater generally will flow toward the river. However, the groundwater regime in the project area, specifically on the New Jersey side of the river, has been disturbed by urbanization (SEIS 1997 and reports quoted therein). Estimates suggest that about 70 million gallons of water per day are leaking from the Delaware River into the Potomac-Raritan-Magothy aquifer system, mainly due to overpumping of the aquifer (Phillips 1987). Prior to municipal and industrial pumping, water in the aquifer flowed toward the river. Recharge of the aquifer directly from the river poses further concerns about the quality of the river water and the groundwater. Remobilized hazardous species in the channel could find an easy route to the groundwater under the present pumping conditions. Although deepening the channel would tend to reduce the reverse flow of groundwaters, the extent of contamination would depend upon future pumping levels as well as the extent of remobilization of hazardous species from the sediments into the channel fluids.

Groundwater Quality Impacts

Riedel and Sanders (1998) have shown that between 80–98% of most heavy metals (arsenic, cadmium, chromium, copper, lead, nickel, and zinc) from the suspended matter of the Delaware River are leachable by 1N HCl. Although one would not expect rainwater to be as strong a leachant as 1N HCl, it may leach some heavy metals from the dredge spoils at the 25–50% level, largely because of its acidic character.

Using the heavy metal data of Arthur D. Little, Inc. (1994) for the sediments of the Delaware River that will be dredged and disposed upland, we estimated a worst-case scenario for the total amount of heavy metals that could leach out of the dredge spoils and become available for groundwater recharge. For these calculations, we used only the annual maintenance dredging volume of spoils from the 45-foot channel (which is at least a factor of 7 to 10 lower than the amount that would be dredged in the initial deepening of the channel). We also assumed that the contaminants contained in the leachate will reach the Potomac aquifer and be thoroughly mixed in the total volume of water in the aquifer (approximately 10^{13} liters). We then compared our calculated levels of these heavy metals in the groundwater with the EPA's current drinking water standards (obtained at http://www.epa.gov/safewater/wot/appa.html). According to our calculations, only zinc, copper, and chromium would remain a factor of 2 to 10 below the EPA's Maximum Contaminant Level *(MCL)*, which is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system. Arsenic, cadmium, nickel, and antimony would be within 20% of the MCL, while lead and selenium would exceed the MCL by factors of 3.5 and 2 respectively. When our calculations are compared to the EPA's more stringent Maximum Contaminant Level Goal (MCLG), which is the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur and which allows for an adequate margin of safety, arsenic, nickel, and antimony would exceed these limits by very significant margins. It must be noted that these deductions are based on zero initial concentrations of these species in the aquifer waters, which may be unrealistic. Many of these species will have their initial concentrations above zero in groundwaters. In the following, we will further analyze the situation in New Castle County where data on the groundwater concentrations of these species exist.

It must also be recognized that these are estimates based on several assumptions where actual data are not available. For example, data on the leaching characteristics of all these species from dredge spoils by the action of rainwater are essential for precise calculations. Data on the retention characteristics of these species in the local soil-water system, which will enable calculations of the exact fluxes of the leached nuclides to the groundwaters, are also essential. Then, one needs the residence times of these species in the groundwater to know how their concentrations in the groundwater will vary over time. Without such data, the estimates have large uncertainties associated with them. Without such data, these calculations can be regarded only as a guide and cannot be depended upon for policy matters. Thus, in the present case, all reported concentration levels of the heavy metals which are a factor of 2 below MCL, may actually exceed MCL. On the other hand, if reactive species like lead, arsenic, and nickel are removed actively on the soil surfaces, their resulting concentrations in the groundwaters could be below MCL. It should also be noted that the above estimates are based only on contaminant releases from the annual spoil volumes from maintenance dredging, which could be a factor of 7 to 10 lower than the amount of dredge spoils from the main channel deepening project (from 40 to 45 feet).

Data on the concentrations of heavy metals in groundwaters in Delaware could not be found in the published literature. However, a large volume of such data exists in the internal, and sometimes confidential, reports of institutions like the EPA, the USGS, and local water companies. Artesian Water Company of New Castle County, Judith Denver at the USGS in Dover, DE, and Betsy Marchand at the USGS in Baltimore, MD, have all provided significant help in obtaining some data on the groundwater concentrations of heavy metals within New Castle County in particular and the Delmarva Peninsula in general. Data presented in reports included that from Denver (1986), Hamilton et al. (1993), and Senior (1996). Unpublished data provided by Betsy Marchand (personal communication) was very valuable in this assessment. We have been advised not to present or publish this data in any form. Thus we will only state our conclusions.

In many counties within the Delmarva Peninsula, concentrations of several heavy metals in regional groundwaters are very close to the EPA's potable water limits. Bachman and Ferrari (1995) reported that levels of iron in most groundwater samples from confined aquifers in southern New Castle County exceeded MCL by as much as a factor of 70. Any constituents leached from dredge spoils by the action of rainwater that reach the groundwater could potentially push their concentrations above tolerable limits, unless they are effectively removed by the action of soil adsorption prior to reaching the aquifer systems. Information about the adsorption/desorption characteristics of these species in the regional soil-water geochemical settings is not available.

Hussain and Krishnaswami (1982) evaluated the residence time of lead by measuring the activity ratio of $^{214}Pb/^{222}Rn$ in groundwaters from Gujarat, India. Their estimates suggested very fast removal of lead from the aqueous phase (on the order of a few minutes). If similar removal rates of lead and, by proxy, some other heavy metals are applicable in the soil-water systems of the Delmarva Peninsula, contamination of groundwaters from the recharge of dredge spoil leachates could be discounted. However, the fact that the concentrations of such contaminants in groundwaters from the Delmarva Peninsula are already rather high suggests that their removal rates from the aqueous phase onto soil surfaces must be small.

Work done by the USGS in 1995 for a subcontract to the USACE, and reported in "Evaluation of Groundwater Flow from Dredged Material Disposal Sites in Gloucester and Salem Counties, New Jersey" (SEIS 1997), showed that since the disposal sites provide a very small, local aquifer recharge and the potential contaminant travel times were on the order of 50 to 100 years, the possibility of well contamination is very remote. One exception at site 15G was noted. However, the USACE, citing their own investigation, responded, "The proposed site 15G and existing Oldmans disposal areas are in the contributing area to these wells. Oldmans disposal area is centrally located among the sites between areas 15G and Pedricktown North. This site has been used for over 40 years by the Corps of Engineers for disposal of maintenance material from the existing Delaware River 40-foot project. Recently, a detailed groundwater investigation of the Oldmans disposal area has been completed by the Corps of Engineers. The investigation concluded that potential environmental impacts to this site should not preclude further expansion and continued use of this site as a dredged material disposal area." What is not clear is whether the study implies "no significant impact" or is an argument similar to the one used by the USACE earlier: "In the light of minimal exceedance of the stated regulatory levels, and the proposed use of the area as a dredge material disposal site, no additional testing or remediation of these areas is required" (SEIS 1997).

Conclusions

A literature survey of the sedimentary geochemical environment of the Delaware Estuary was conducted, with a view toward evaluating the impact of proposals to deepen the shipping channel by 5 feet. This yielded significant information about the sediments of the Delaware river and estuary, including the sedimentary provinces and dynamics, and the geochemical constituency for natural and anthropogenic contaminants. Only limited data were found on the distribution and geochemical behavior of radionuclides in the river and estuarine waters or sediments. Much of the data on the concentrations of these species in local groundwater are in the form of reports from the USGS.

Concentrations of heavy metals (antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc) in the Delaware River and estuarine waters are below the Delaware River Basin Commission's recommended chronic criteria and presently pose no threat to human health. However, arsenic levels are very close to the recommended limits. The source of arsenic to the Delaware River, in the vicinity of Philadelphia, remains a cause for concern because arsenic levels in the river water can often exceed the DRBC criterion and pose a threat via food-chain transfer.

In suspended matter from the Delaware River, lead is the most enriched element compared to its distribution in the suspended loads of other rivers, while arsenic, cadmium, and zinc show minor enrichments. Sediment concentrations of pesticides, PAHs, PCBs, PCB congeners, DDT, and the metals chromium, copper, nickel, lead, zinc, and mercury increase by factors ranging from 5 to as much as 10 from Egg Island Point, NJ, to the Walt Whitman Bridge. A widespread persistence of PCBs in sediments throughout the estuary has been reported. Concentration levels of these contaminants exceed sediment effect levels at nearly 85% of the river length. Dredging-related activities aside, Arthur D. Little, Inc. (1994) suggests that the bioavailability of these toxic contaminants may result in adverse impacts to organisms that biomagnify them through food-chain transfer and pose potential health risks to humans who consume fish from the estuary.

Conclusions of the U.S. Army Corps of Engineers as presented in the Supplemental Environmental Impact Statement (SEIS 1997) may be criticized on several accounts. Although the data collected by the USACE is recognized to be the most extensive, measurements of heavy metal and pesticide concentrations in the sediments reported by the corps are on the low side in most cases when compared with other published and nonpublished results. The corps' conclusion of "no significant impact" does not appear to be completely supported by its reported analytical results.

The risk arising from biofixing of ^{210}Po by marine organisms such as fish, molluscs, and crustaceans and their consumption by humans is small under the assumed conditions of normal ^{210}Po concentrations in Delaware river or estuarine waters (6–10 Bq m^{-3}) and an average annual per person consumption of seafood of 15 kg. Elevated concentrations of ^{210}Po in the waters, higher consumption of seafood, and the status of individuals (e.g., smokers or those living in dwellings with high radon levels) could significantly alter the risk estimates.

Because most heavy metals in dredge spoils are leachable quantitatively by the action of mild acidifications, the leaching that results from acid rain or oxidized sulfide in dredge spoils may help mobilize these species into shallow aquifers. Thus, the leaching of constituents by the action of rain on upland-disposed dredge spoils from the annual maintenance dredging of the 45-foot channel alone could potentially raise concentrations in shallow groundwaters above allowed limits. Better information about the adsorption/desorption characteristics of these constituents in local soil-water systems is needed to make these estimates more precise.

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