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NOAA Technical Memorandum NOS ORCA 81

Empire Knight:

Assessing Environmental Risk

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noaa NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

National Ocean Service

Office of Ocean Resources Conservation and Assessment
National Ocean Service
National Oceanic and Atmospheric Administration
U.S. Department of Commerce

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Prepared for the United States Coast Guard District I

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The National Oceanic and Atmospheric Administration (NOAA) acts as a natural resource trustee on behalf of the public under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended. In this capacity, NOAA is responsible for protecting natural resources from the effects of hazardous substances released by human activity. The mercury in the wreck of the M/V *Empire Knight* is a CERCLA-listed hazardous substance. Despite the high probability that increased exposure to the environment by elemental mercury will not injure natural resources, such a consequence cannot be guaranteed. This report makes no interpretations of injury to natural resources or potential liability for damages to natural resources pursuant to CERCLA, nor does it address injuries or potential liabilities for damages that could result from human activities, such as salvage attempts at the wreck site.

This report documents the efforts of NOAA's Hazardous Materials Response and Assessment Division (HAZMAT) to evaluate the environmental risk from the *Empire Knight* site in Maine. HAZMAT has prepared this report at the request of the U.S. Coast Guard (USCG) Captain of the Port (COTP) as part of an ongoing evaluation of the potential environmental risks associated with the site.

INTRODUCTION

NOAA HAZMAT efforts were extensive and involved a team with broad expertise on mercury, toxicology, oceanography, and resource assessment; however, our evaluation is not a formal ecological risk assessment as would be conducted at a U.S. Environmental Protection Agency (EPA) Superfund site and is described by Cardwell 1993. (See Appendix C for a description on how a more complete ecological risk assessment could be undertaken at the *Empire Knight*.) We proceeded in a manner that closely resembles a typical ecological risk assessment, using the following six steps (taken from Cardwell 1993):

1. Problem definition
2. Source characterization
3. Exposure assessment
4. Ecological receptor and endpoint characterization
5. Risk characterization
6. Risk management

HAZMAT's technical evaluation, which is presented in this report, contributes to the first five steps of the above framework. In summer 1994 our findings were presented to the Federal On-Scene Coordinator (FOSC), who used this information to make a set of decisions comprising the risk management. Issues such as remediation and/or monitoring fall under the risk management sector and are not addressed in this report.

PROBLEM DEFINITION

The *Empire Knight* was a merchant cargo ship under the British flag that was wrecked in 1944 during a storm off the Maine Coast while en route from Canada to New York. Approximately one mile off Boon Island (seven miles from the mainland), the ship broke into two pieces. The bow section came to rest approximately one mile from the stern section (which contained the majority of the cargo holds) located at a depth of 80 meters (m). The *Empire Knight*'s cargo consisted of a variety of items, including locomotive and automobile parts, canned milk, copper coils, fertilizer (sulfate), and an estimated 7.3 metric tons (mt) of mercury shipped in 221 steel vials. Each vial measured approximately 10 inches by 5 inches and contained approximately 34 kilograms (kg) of mercury.

HAZMAT first became involved with the *Empire Knight* in March 1992, when we were asked to evaluate concerns related to a potential salvager who wished access to the wreck to salvage copper coils. The USCG COTP in Portland, Maine and other local government entities were concerned that salvage attempts might impact the distribution and availability of mercury that was believed to have been part of the ship's cargo. Prior to 1991, it was not known whether mercury contamination was a problem at the wreck, or whether marine organisms had been affected by such contamination, though the states of Maine and New Hampshire were concerned about actual and possible threats to commercial fisheries in the region.

Initial, unverified estimates of mercury in the cargo, came from the ship's stowage plan, which indicated that the cargo held 7.3 mt of mercury (thought to be in elemental form, but not specified in the stowage plan), packed in iron vials in hold #5. It was not known whether mercury remained in the original vials, or if these had been breached and mercury released. Other elements in the cargo that were potential contaminants included fertilizer (sulfate) and ordnance. (Subsequent investigations indicated that ordnance was unlikely to be active and that sulfate was unlikely to still be present.) Our initial task was to identify whether mercury contamination was present, and to what degree this contamination might pose a risk to the marine environment.

SOURCE CHARACTERIZATION

The main source of mercury contamination immediately around the wreck was assumed to have originated from the *Empire Knight* cargo. Concern quickly focused on mercury because of the suspected quantities on board the vessel, and because mercury is known to be toxic in aquatic environments and to accumulate in higher-level organisms.

Brief Background on Mercury

HAZMAT's scientific team has had experience with mercury contamination at several coastal sites. Most of these sites were in freshwater or estuarine environments, and all marine sites were nearshore (Beckvar et al. 1994). Before the *Empire Knight*, we had not been directly involved with an offshore, deep-water site with mercury contamination. Even in the extensive published scientific literature on mercury contamination, there are few examples of offshore marine sites. Most literature on mercury in marine environments consists of mercury levels in tissue of fish species caught offshore. It is even more unusual to find instances where elemental mercury (as opposed to an inorganic or organic form of mercury) is the original contaminant.

From our previous experience with mercury and extensive research in the scientific literature we knew the following about this metal:

☐ mercury's chemistry is very complex; the metal can change form in aquatic environments, becoming either more or less toxic;

☐ mercury's environmental fate and toxicity is strongly dependent on environmental conditions;

☐ mercury has the potential to bioaccumulate and biomagnify in higher trophic level organisms;

☐ mercury is a known neurotoxin to humans and other organisms;

☐ mercury pollution problems at well-studied sites have resulted from discharges with major sources of inorganic mercury (Lavaca Bay, Texas; Evans and Engel 1994) or organic mercury (Minimata Bay, Japan), not elemental mercury.

Thus, though mercury is always a concern as a contaminant in the environment, the case of the *Empire Knight* did not fit the profile of many problematic mercury sites (many of which are located on land or in fresh water). The two main differences at the *Empire Knight* from a contaminant perspective were 1) its location in a deepwater marine environment, and 2) the *Empire Knight* mercury was initially suspected to be in elemental form (this was later confirmed through chemical analysis). Whether mercury from the *Empire Knight* represented an environmental risk would need to be determined by its environmental fate in the deep-sea environment and by determining whether mercury was being accumulated by marine organisms.

Existing Contamination

The first task was to describe the conditions at the site and determine whether mercury could be found outside the *Empire Knight's* hold where it was originally stored during shipping. When HAZMAT first became involved, the only site-specific data was from a small number of sediment and biota samples collected by the State of Maine in 1991. These data consisted of 16 surface sediment samples, two sediment core samples, and a small number of biota samples. All were analyzed for total mercury (Tables 1 through 4).

Table 1. Sediment, scrape and water samples collected from the *Empire Knight* as of February 8, 1994.

Sample Type	Date	Number of Samples	Analysis Conducted	Dry Weight	Wet Weight	Facility
sediment	1991	9	total Hg % Fe, % Al	X		Texas A&M
sediment (6) cores (2)	1991	8	total Hg	X	X	Texas A&M
surface sediment	1993 Aug/Sep	22	total Hg	X	X	Battelle
surface sediment	9/13/93	47	total Hg % solids	X		Battelle
sediment from hold	9/18/93	2	Hg, Fe, Pb, Sn		X	Battelle
sediment cores	1993 Aug/Sep	3	total Hg (by depth 0-30 cm) % solids	X		Battelle
sediment cores	10/7/93	7	total Hg elemental Hg (by depth 0-10 cm) grain size	X		Battelle
cargo scrapes	10/7/93	6	total Hg elemental Hg % solids	X		Battelle
seawater (hydrovac)	10/93	2	total Hg suspended solids grain size	X		Battelle

Table 2. Biota sampled at the *Empire Knight* as of February 8, 1994.

Organism	Date	Number of Samples	Analysis Conducted	Dry Weight	Wet Weight	Facility
invertebrates	1991	11	total Hg	X		Texas A&M
fish	1991	5	total Hg	X	X	
fish (trawl)	1993- Aug/Sep	19	total Hg		X	Battelle
invertebrates		54	total Hg		X	
invertebrates from hold #5	1993- October	57	total Hg methyl Hg	X	X	Battelle
invertebrates from seafloor		32	total Hg methyl Hg	X	X	
fish (trawls)	?	34 ?	methyl Hg		?	FDA

Table 3. Sediment samples collected from the *Empire Knight* by the State of Maine, and analyzed by Texas A&M University.

Sample type	Date sampled	Station	Total mercury µg/g dry weight (ppb)
surface sediment	Aug 29, 1991	1	58
		2	712
		3	63
		4	32
		5	22
		6	18
		7	17
		8	33
		9	30
	Sep 5, 1991	10	25
		11	21
		12	22
		13	17
		14	32
		15	28
		16	31
sediment cores (analyzed by 1-cm increments)	Sep 5, 1991	2A1	47
		2A2	47
		2A3	65
		2A4	40
		2A5	43
		6B1	20
		6B2	16
		6B3	18
		6B4	15
		6B5	12

Table 4. Mercury concentrations in tissue samples collected from the *Empire Knight* by the State of Maine, and analyzed by Texas A&M University. All samples were collected on September 5, 1991.

Sample type	Station	Total mercury µg/g dry weight (ppb)	Total mercury µg/g wet weight (ppb)
worms	2A	176	
bivalve		118	
brittle star		7	
crustacean		95	
worm/bivalve		180	
worms	6A	651	
bivalve			
brittle star		24	
crustacean (amphipod)		33	
worm/bivalve		436	
dogfish	near wreck	423	101
		389	93
cod	control site	198	37
		194	37
pollock		142	25

Concentrations of total mercury in surface sediment ranged from 17 to 712 parts per billion (ppb) dry weight. However, 25 out of 26 samples had values less than 100 ppb. Since no samples were collected to specifically represent "background" conditions, the sediment samples farthest from the ship were used to represent background. This value, approximately 25 ppb total mercury, is typical of continental shelf sediments (Young et al. 1973). Compared with this background, 9 of the 16 surface sediment samples could be considered to have elevated mercury concentrations. However, since small differences between samples may not be meaningful, for initial screening purposes, we looked for values that were at least an order of magnitude greater than background. Using this approach, only one sample (Station 2, at 712 ppb) stands out. Since Station 2 is closest to the ship, this indicated that mercury contamination might be very localized near the wreck. These results also indicated that mercury contamination in sediment could be distributed very unevenly, a situation that can be difficult to sample and characterize.

The 1991 data showed that mercury had contaminated sediment outside the wreck, but that this contamination appeared to be localized near the wreck. Contamination also appeared to be very patchy with "hotspots" located next to samples measuring near background.

Biological organisms appeared to have taken up mercury in relatively low quantities, but more comprehensive sampling was needed to verify this.

EXPOSURE ASSESSMENT

To assess exposure at the *Empire Knight*, we examined the fate, transport, and chemical pathways of mercury at the site. (Potential uptake by biological organisms will be addressed in the section on ecological receptors.) Since the 1991 data indicated that at least some mercury had been released from the ship, we needed to determine the extent of this contamination and how mercury was being transported from the hold to the surrounding environment. Determining the chemical pathways of the mercury at the site is a fundamental part of this risk assessment process because it indicates whether the mercury has, or will in the future, change from its original elemental form into one of the more bioavailable forms of mercury (inorganic or organic). Additional sampling sponsored by the USCG in September and October 1993 was designed to answer the following questions about sediment contamination and chemical pathways of mercury at the site:

☐ What were the baseline conditions for mercury contamination at the wreck site when removal and sampling efforts began in 1993?

☐ How widespread was the sediment contamination? Was there a gradient of decreasing concentration with distance from the ship?

☐ What form of mercury was in the sediments (i.e., had elemental mercury undergone a chemical transformation to an inorganic or organic form)?

☐ Was there evidence that methylation of mercury was occurring at the site?

Sediment Sampling and Mercury Removal

Sediment sampling was conducted in accordance with EPA protocols by a commercial diving operation contracted by the USCG from August 31 through September 13, 1993 (USCG 1993). (For a summary of all *Empire Knight* data collected, see Tables 1 and 2.) In addition to collecting samples, extensive efforts were made to remove visible pools of elemental mercury from cargo holds and other surfaces inside the wreck, using a diver-held vacuum pump apparatus. The mercury collected was stored in special vials onboard the support ship and was eventually disposed onshore as hazardous waste. When operations were halted in October 1993 due to deteriorating seasonal weather, approximately 544 kg (less than 8% of initial load) of elemental mercury had been removed from the wreck. By the end of the operation, divers reported seeing less and less of the visible mercury in readily accessed areas. Divers were also able to locate the mercury vials, and by the end of the operation had removed 221 vials, which were all in a deteriorated condition (Pascoe 1994).

Mercury distribution

Our initial hypotheses about the patterns of mercury contamination were confirmed by the 1993 sediment data: highest concentrations were found closest to the wreck, and the overall distribution of mercury was very patchy. At a few stations, mercury concentrations varied by an order of magnitude or more from subsamples taken from the same sediment sample (especially stations 12, 13, 22, and 24; Table 5). Descriptions from the divers give a plausible explanation for this type of patchiness—they described seeing small, shiny spots of mercury in discrete pools inside the #5 cargo hold. Elemental mercury beads up because of its very high surface tension and forms droplets. Thus, very high levels of mercury could result from a subsample that included a pool of elemental mercury, whereas another subsample taken only centimeters away could measure at background levels. Similar patchiness has been observed with tributyltin and copper paint chips from shipyards in sediment samples.

Mean values from surface sediment samples, including the top layer of three core samples, were plotted for 27 stations (Table 5; Figure 1). Stations with similar mercury concentrations were connected, forming isopleths showing mercury concentration gradients (Figure 1). These isopleths form an ellipse around the wreck, with highest contamination closest to the ship and decreasing contamination with distance away from the ship. The steepest contamination gradient is seen along the stern, where a few high values quickly drop to background concentrations. In contrast, along the mid-section of the wreck where the bow broke from the vessel, the contamination spreads out for a longer distance, before gradually decreasing to background. We do not have direct evidence to confirm the chemical or physical pathway by which mercury was transported from hold #5 to the surrounding sediments, but three pathways are discussed in detail in a later section.

Table 5. Mercury concentrations in surface sediment samples collected near the *Empire Knight* in 1993. Values represent sub-samples taken from the same sample bottle and analyzed separately. (*Values marked with an asterisk are from the first 1-5 cm layer of a core sample. Mean values are in bold type.)

Station	Total Mercury µg/g dry weight (ppb)	Date sampled
1	37	Aug-Sep 93
	8.5	
	23	**mean**
2	42	Aug-Sep 93
3	66	Aug-Sep 93
	41	
	54	**mean**
4	99	Aug-Sep 93
	40	
	70	**mean**
5	146	Aug-Sep 93
	25	
	86	**mean**
6	76	Aug-Sep 93
	48	
	62	**mean**
7	36	Aug-Sep 93
	35	
	36	**mean**
8	46	Aug-Sep 93
	10	
	28	**mean**
9	26	Aug-Sep 93
	14	
	20	**mean**
10	44	Aug-Sep 93
	13	
	29	**mean**
11	180	Aug-Sep 93
	130	
	155	**mean**
12	290	Aug-Sep 93
	86	
	188	**mean**
13	1606	Aug-Sep 93
	48	
	827	**mean**
14	63	Aug-Sep 93
	18	
	41	**mean**

Table 5 continued

Station	Total mercury µg/g dry weight (ppb)	Date sampled
15	43 15 **29**	Aug-Sep 93 **mean**
16	39 29 **34**	Aug-Sep 93 **mean**
17	27 12 **20**	Aug-Sep 93 **mean**
18	26 8.2 **17**	Aug-Sep 93 **mean**
19	23 10 **17**	Aug-Sep 93 **mean**
20	17 11 **14**	Aug-Sep 93 **mean**
21	398 445 **422**	Aug-Sep 93 **mean**
22	240 36 **138**	Aug-Sep 93 **mean**
23	97 43 **70**	Aug-Sep 93 **mean**
24	290 37 **164**	Aug-Sep 93 **mean**
1A	10*	Aug-Sep 93
2A	22*	Aug-Sep 93
3A	22*	Aug-Sep 93

* value used is upper 1-5 cm layer of core sample

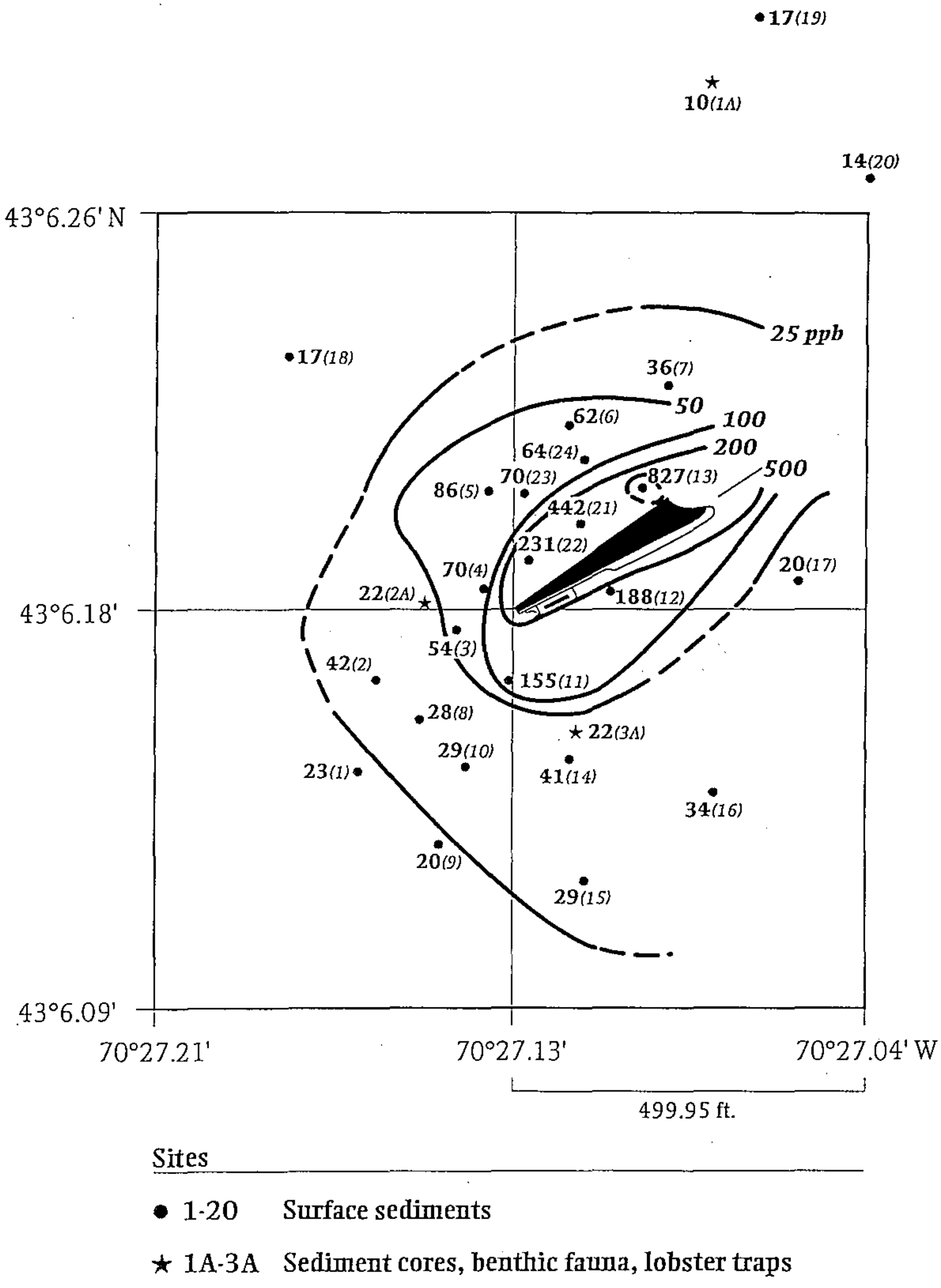


Figure 1. Mercury concentration gradients around the Empire Knight. Numbers in bold identify surface sediment samples, numbers in parentheses identifiy sediment core or biota samples.

If the mercury accumulated in sediment as a result of diffusion from hold #5, the patterns of the isopleths might be expected due to bathymetry and water circulation. The tidal ellipse at a nearby station has a north-south major axis and the mean (non-tidal) winter-time currents at 33 m depth flowed to the south-southwest at 4.6 centimeters (cm) second^{-1} (Vermersch et al. 1979). (These are the only site-specific current data available, and give a general approximation of oceanographic conditions in the area). Tidal and storm-generated currents could be much higher. Bottom currents are constrained on the east by a low ridge. Bottom sediments near the wreck have a low clay-silt concentration (Crecelius 1994), suggesting that some winnowing of these sediments occurs.

Estimated mass of mercury in sediment

To calculate the mass of mercury in surface sediment outside the wreck, we used the isopleths from Figure 1 and assumed a uniform depth for mercury contamination of 5 cm. (Five cm was chosen as a conservative estimate, taken from the core data showing mercury concentrations at depth.) The area of each isopleth (between concentration lines) was then calculated, and these areas summed to give a total mass of approximately 2.3 kg. This represents only 0.03 percent of the total estimated quantity of mercury in the cargo, indicating that only a very small amount of mercury has adsorbed to sediment near the ship over the last 50 years. Though the largest potential source of mercury at the *Empire Knight* site is clearly the elemental mercury shipped in hold #5, other sources of mercury that would be typically found on a ship of the age of the *Empire Knight* include paint, alloys, and navigational or weather instruments.

Sediment core samples

Core samples provided a profile of the sediment at depth. Twelve core samples were collected, sectioned, and analyzed by depth. The first two core samples were sectioned into 1-cm layers, to a depth of 5 cm. Since these results showed that sediments from 1 to 5 cm were fairly homogeneous, for later samples, sections encompassed 5-cm layers (1 to 5 cm, 5 to 10 cm, etc.; Table 6). Core analyses indicate a fairly well-mixed sediment, though mercury levels generally decreased with depth. Since the cores were not age-dated, we do not know at what rate sedimentation occurred.

Table 6. Mercury concentrations in core sediment samples collected at the *Empire Knight* from 1991-93.

Station	Depth (cm)	Total Mercury ng/g dry weight (ppb)	Date Sampled
2A	0-1	47	Sep 91
	1-2	47	
	2-3	65	
	3-4	40	
	4-5	43	
6B	0-1	20	Sep 91
	1-2	16	
	2-3	18	
	3-4	15	
	4-5	12	
1A	0-5	10	Aug-Sep 93
	5-10	<5.6	
	10-15	7	
	15-20	<5.6	
	20-25	<5.6	
	25-30	<5.6	
	30-35	<5.6	
2A	0-5	22	Aug-Sep 93
	5-10	18	
	10-15	<5.6	
	15-20	6.2	
	20-25	<5.6	
	25-30	<5.6	
	30-35	<5.6	
3A	0-5	22	Aug-Sep 93
	5-10	7	
	10-15	<5.6	
	15-20	5.6	
	20-25	<5.6	
5A	0-1	478	Oct 93
	0-1	486	
	1-5	161	
	5-10	107	
6A	0-1	1660	Oct 93
	1-5	1610	
	5-10	1240	
7A	0-1	1900	Oct 93
	1-5	947	
	5-10	363	
8A	0-1	1150	Oct 93
	1-5	2040	
	5-10	95	
9A	0-1	113	Oct 93
	1-5	112	
	5-10	78	
10A	0-1	765	Oct 93
	1-5	481	
	5-10	140	
11A	0-1	60	Oct 93
	1-5	64	
	5-10	66	

Two core samples were analyzed for methylmercury in the 1- to 5-cm layer. Core 6A contained 5.0 ppb methylmercury (dry weight) and core 8 contained less than 1.0 ppb methylmercury (dry weight). Since these two cores had high total mercury values in the 1- to 5-cm layer,(1660 ppb for 6A and 1150 ppb for 8A), the percentage of the total represented by methylmercury is quite small.

Special Samples Taken from Hold #5

Black sediment from hold #5

Divers observed quantities of a black sediment inside hold #5 and it was postulated that this might contain a sulfide compound of mercury. Two samples of this sediment were collected and analyzed. Results indicate that the black material is primarily iron sulfide and is probably the product of ship hull corrosion. The samples contained about 8 to 10 percent iron, with smaller amounts of lead and tin. Large quantities of these metals occur in solder that was used in many of the containers on the ship. The black sediment contained only about 2 to 3 parts per million (ppm) mercury wet weight) which may well be the concentration that mercury is found in such sources as ship steel and solder materials.

Porewater from these black sediment samples was also analyzed and contained no soluble mercury (< 0.1 ppb; Crecelius 1993).

Cargo scrape samples

Scrape samples were collected to address concerns about possible mercury contamination in encrusted material covering large items of cargo inside hold #5, such as locomotive parts. Since some cargo needed to be moved from the wreck onto the seafloor to allow access into hold # 5, these cargo were sampled by scraping an area of encrusted material from the cargo's surface. The six scrape samples were composed of silt, mud, and biota and were analyzed for total and elemental mercury (Table 7). Total mercury concentrations (dry weight) were high compared with sediment or biota samples with values ranging from over 7,000 ppb to 61,000 ppb dry weight. However, these concentrations represent a small total mass of mercury. These values are not altogether surprising, given the proximity of the cargo to the bulk of the mercury. Elemental mercury makes up a very small portion of the total mercury in these samples (Table 7); therefore, the mercury on the cargo is likely in an inorganic form.

Mercury Pathways in Seawater

Chemical and physical processes

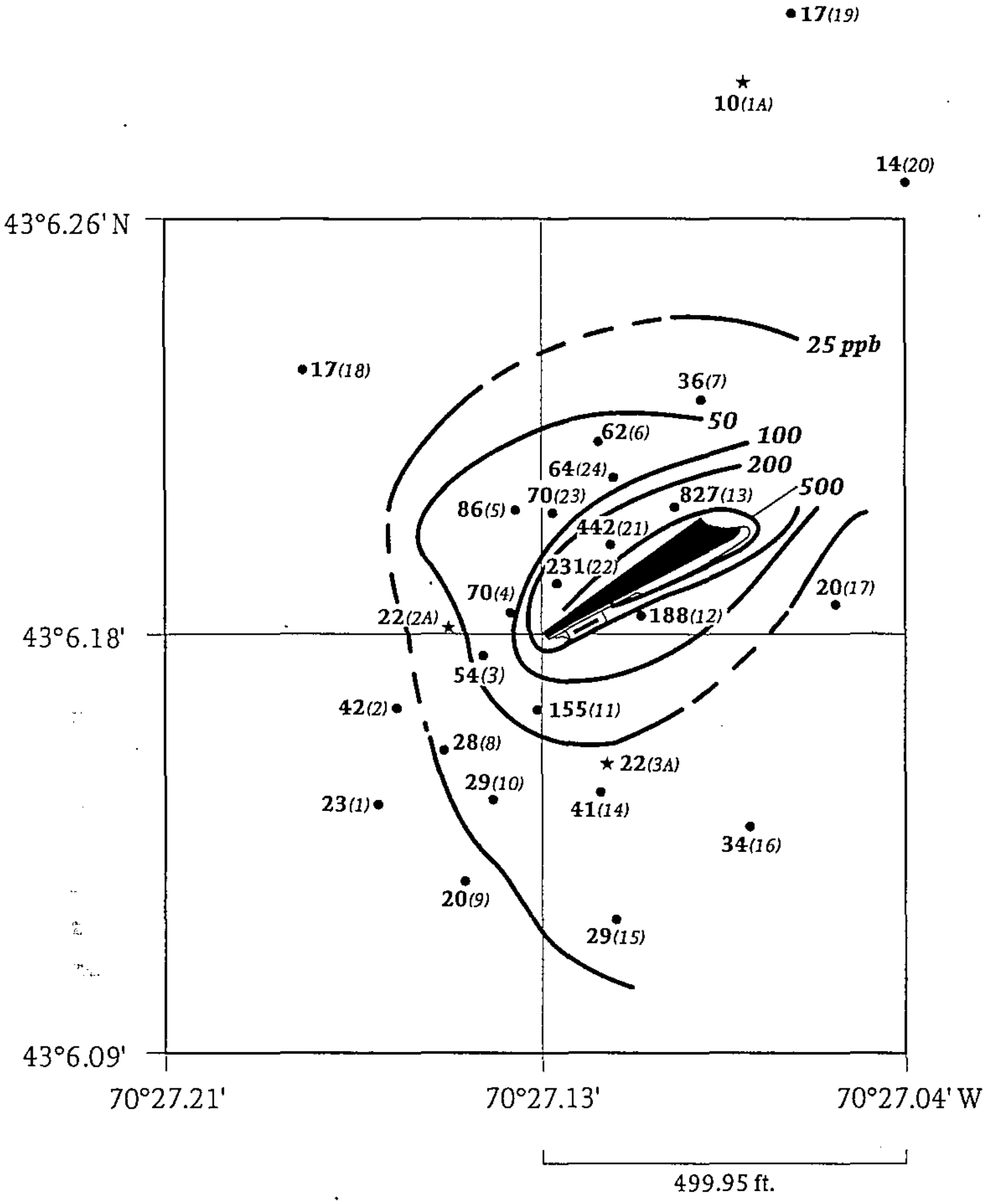
After release in seawater, elemental mercury may dissolve, disperse, and/or oxidize to form other mercury compounds (Figure 2). Although the rates of all these processes are slow, dissolution, which transports elemental mercury into the water column, is the main environmental fate pathway in seawater. Elemental mercury that is dissolved in seawater will eventually volatilize to the atmosphere. Dissolved elemental mercury can also attach to particles and precipitate back to the seafloor. Elemental mercury can also physically disperse through the action of currents or gravity.

Elemental mercury can also be oxidized to form other dissolved or particulate mercury compounds such as mercuric and mercurous salts. This oxidation process proceeds very slowly and is a less important fate pathway than dissolution. The mercuric form of mercury can be methylated by bacteria if the mercuric ions are not bound to other molecules. Methylation is thus severely restricted in seawater environments by both the limited availability of free mercuric ions and the presence of methylating bacteria. Both the availability of mercuric ions and the presence of methylating bacteria are affected by environmental conditions such as oxygen, organic matter, and temperature (Compeau and Bartha 1984). Methylation is greatest under anoxic conditions and organic matter is needed to stimulate growth of the appropriate bacteria. Therefore, methylation is not a pathway of primary concern at most marine sites with elemental mercury. (For more detailed descriptions of the physical chemistry of mercury and on the three specific pathways discussed below, see Spencer and Voigt 1968, Compeau and Bartha 1984, Toribara et al. 1979, and Beckvar et al. 1994, Appendix A.)

Table 7. Scrape samples from *Empire Knight* cargo analyzed for total and elemental mercury.

Scrape Sample	Total Mercury ppb dry weight	Elemental Mercury ppb dry weight
1	*14,200	0.5
2	7,410	0.3
3	61,200	0.3
4	5,100	2.0
5	11,500	0.8
6	2,210	11

* mean of 2 replicates



Sites

●	1-20	Surface sediments
★	1A-3A	Sediment cores, benthic fauna, lobster traps

Figure 2
Mercury concentration gradient around *Empire Knight*

Empire Knight pathways

As can be seen in Figure 1, sediment contamination around the *Empire Knight* decreases with distance from the ship, with highest levels of mercury located within 15 m (50 ft) of the wreck. These patterns imply that some mercury was somehow transported from the hold to the sediments outside. Our next step was to investigate which chemical pathways could be responsible for this transport, and project the potential impact of these pathways in the future. To assist the NOAA team evaluate the chemical fate of mercury at the *Empire Knight*, a chemist specializing in the geochemistry of mercury, Dr. Robert Mason, was hired to independently evaluate the mercury pathways at the site. Dr. Mason's complete report is included in Appendix A.

Three main potential pathways for mercury at the *Empire Knight* (dissolution, physical dispersion, and oxidation) are discussed below:

Dissolution

As would be expected at a marine site with elemental mercury, the *Empire Knight* data supports dissolution as the main pathway by which mercury is transported from hold #5. According to Dr. Mason,

> "Mercury is being lost from the site primarily by dissolution of elemental mercury, with gas evasion to the atmosphere being the route of final loss... As the solubility of elemental mercury is low, diffusion through the boundary layer surrounding each exposed mercury 'globule' is likely to be the limiting factor on dissolution rate."

Theoretical calculations on the rate of dissolution produce varied estimates, depending on the assumptions made about the size of the mercury globules. Based on several different assumptions, Mason calculates a half-life of 60 to 60,000 years for the remaining mercury at the *Empire Knight* (calculations are shown in Appendix A).

In addition to the size and distribution of the remaining mercury, advection of water from outside the hull is another factor that could impact the dissolution rate. As it appears that most or all of the mercury is still contained in the hold of the sunken ship, mixing could be extremely restricted between mercury-contaminated water and uncontaminated seawater. Currently, dissolution inside the hold appears to be occurring at a very slow rate, based on the low measurement of mercury in porewater (< 0.1 ppb) collected from inside the hold.

Physical dispersion

During the break up and sinking of the *Empire Knight*, vials could have been breached and elemental mercury may have been lost to the sediments surrounding the ship. This could have caused a patchy distribution of mercury in the sediment data. Elemental mercury beads up because of its very high surface tension and forms droplets. However, the low total amounts of mercury calculated in sediment indicates that little mercury has been lost through this pathway (Figure 1).

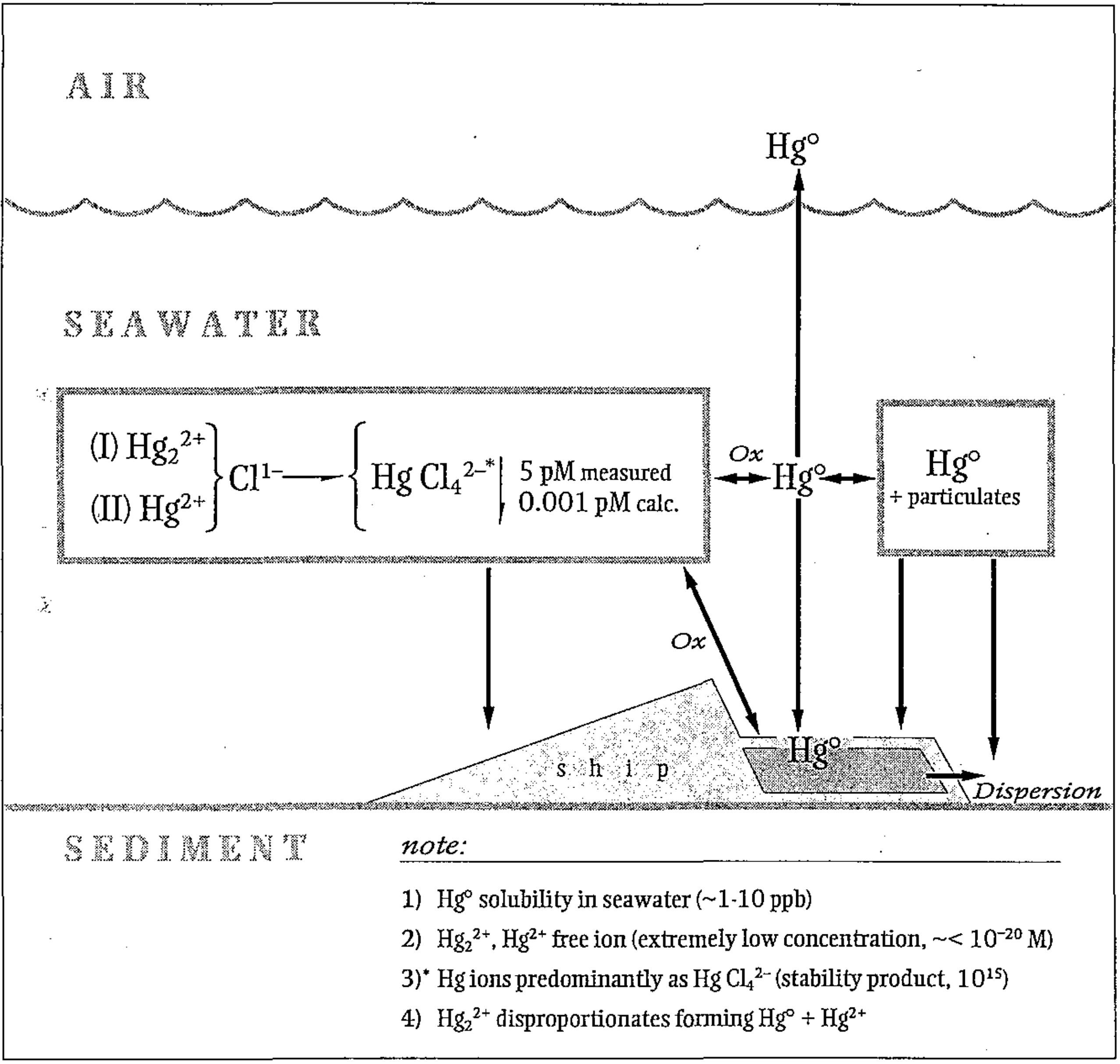
As vials corroded over time, mercury would also have been released, but would likely have flowed to the lower portions of the hold, or through cracks and crevices to the bottom of the ship. Exploratory activities in recent years by salvagers and the 1993 sampling and removal operation may have contributed to physical dispersion.

Oxidation

The oxidation pathway is of special interest to this risk assessment because of the concern about the potential for methylation of mercury ion (Hg II) formed from the oxidation of elemental mercury (Hg^0). Elemental mercury cannot be methylated; therefore, if no pathway exists for oxidation of mercury, methylation cannot occur. If elemental mercury is oxidized to Hg II, the potential for methylation depends on a number of environmental conditions, which may not exist in the hold of the ship (Compeau and Bartha 1984).

Elemental mercury can form two stable oxidation states (+1 (Hg I) and +2 (Hg II)). The +1 state (Hg I) appears to disproportionately form the +2 state (Hg II) and transform back into elemental mercury (Figure 2). The most stable form of Hg II is its chlorides in seawater. Oxidation could occur if oxidizing agents (such as peroxides) were present, either in cargo or seawater. Since no oxidizing agents were listed in the cargo manifest and ambient seawater concentrations of natural oxidizers are low, little of the elemental mercury could be oxidized. Reduction of Hg II to elemental mercury is the primary sink for ionic mercury in seawater: much of the elemental mercury that is oxidized will likely be reduced back to elemental mercury (Mason 1994). This elemental mercury will eventually be lost to the atmosphere. Mason (1994) estimates that about 3 percent of the initial elemental mercury could have been oxidized at an approximate rate of 1.6×10^{-6} per day, compared to a much higher rate of *reduction* of approximately 10^{-2} to 10^{-3} per day. Mason concludes that very little oxidation of elemental mercury has occurred at the *Empire Knight*.

Inorganic Mercury Pathways



note:

1) Hg° solubility in seawater (~1-10 ppb)
2) Hg_2^{2+}, Hg^{2+} free ion (extremely low concentration, ~< 10^{-20} M)
3)* Hg ions predominantly as $Hg\,Cl_4^{2-}$ (stability product, 10^{15})
4) Hg_2^{2+} disproportionates forming $Hg^{\circ} + Hg^{2+}$

Figure 2. Diagram of inorganic mercury pathways at the *Empire Knight* site

The Potential for Methylation

As discussed above, elemental mercury cannot be methylated, based on its physical chemistry (Spencer and Voigt 1968, Toribara et al. 1979, Compeau and Bartha 1984). Elemental mercury must first be oxidized (transformed to the bivalent form Hg II) before methylation is possible. Conditions at the *Empire Knight* site make it unlikely that mercury is oxidizing at anything more than a very low net rate and, therefore, little ionic mercury is produced. The amount of ionic mercury available for methylation is further limited by other physical processes that compete for the ionic mercury. Both uptake by particulates and reduction back to elemental mercury compete with methylation to make the ionic mercury unavailable for methylation. Therefore, only a small fraction of the ionic mercury is available for methylation.

The rate of methylation will be controlled by both the availability of Hg II and the population of methylating microbes. In addition, specific conditions must exist to sustain and promote the growth of these bacteria. While the presence of organic matter and low oxygen conditions will promote growth of the bacteria, these conditions will not increase the rate of elemental mercury oxidation (formation of ionic mercury). The system is still limited by a lack of Hg II for methylation.

Under anoxic conditions, ionic mercury can become strongly complexed with sulfide and hence be unavailable for methylation. Demethylation will also occur, converting methylmercury back to either ionic or elemental mercury by microbial organisms. Mason therefore concludes that only very limited methylmercury could be produced from the *Empire Knight.*

ECOLOGICAL RECEPTOR AND ENDPOINT CHARACTERIZATION

From our exposure assessment, we determined that most of the mercury contamination was in the immediate vicinity of the wreck and that mercury remained, in large part, in a stable and largely unreactive form. The remaining task in assessing ecological risk was to determine the impact of this mercury on the ecological community. Were biological organisms living near the *Empire Knight* acting as "receptors" by accumulating mercury, and was mercury being magnified through the food web? To answer these questions, we chose to sample organisms from different trophic levels: various species of benthic invertebrates representing low trophic levels with direct access to mercury inside the wreck and in the sediment; lobsters and crab, also benthic invertebrates but more mobile with scavenging and predatory feeding habits; and predatory fish, representing a potential endpoint for biomagnification. Samples from these groups of organisms provided an overall assessment of bioavailability of the impacts to the marine ecosystem around the site that may be occurring or could be expected to occur.

Special sampling of commercial species destined for human consumption was also conducted to address the original concerns about possible risks to local fisheries expressed by the states of Maine and New Hampshire. Because mercury is ubiquitous in the marine system, we were also interested in tracing any mercury contamination measured in mobile species (such as fish or lobster) to the *Empire Knight* specifically. Samples were collected to answer the following questions:

- ☐ Have benthic invertebrates living on or near the wreck been contaminated by mercury? If so, do patterns of contamination in species resemble those in the sediment?
- ☐ Is there evidence of biomagnification of mercury in predatory species?
- ☐ Do commercial fish species near the site exceed the U.S. Food and Drug Administration screening level for mercury?

Benthic Invertebrates

Benthic invertebrates were sampled at the *Empire Knight* during two periods in the fall of 1993. The objective of the first sampling in August-September was to provide an overview of the potential mercury contamination in invertebrates living on the seafloor around the wreck. In October 1993, a second set of samples targeted organisms living on or in the wreck itself, including hold #5, where the mercury was stored.

Initial characterization of biota

In August and September 1993 a variety of invertebrate species were collected from the same station locations used for sediment and core samples. Species sampled included lobster, snail, scallop, clam, hermit crab, anemone, starfish, brittle star, urchin, bristle worms, mussel, and rock crab (Table 8). The same species were not found at each station, making it difficult to compare directly between stations. (Rates of mercury uptake can vary greatly by species, so caution must be used when pooling samples or comparing between species (Beckvar et al. 1994).) All samples were analyzed for total mercury.

Total mercury concentrations in these invertebrates varied, but were generally lower than what would have been expected from a site with such a large potential source of mercury. The lowest values were measured in an urchin (< 0.004 ppm wet weight) located at station 3A (See Figure 1 for station locations). In contrast, the highest two measured values were a snail at 3.3 ppm and a bristle worm at 18.0 ppm (both wet weight). (The bristle worm was collected from hold #5 where the mercury was stored and was located inside a broken mercury vial. Because of the sampling procedure used for the earliest samples, it is not known if the mercury measured in the worm had actually been incorporated into the tissue of the worm.) Setting aside these highest values, but still including samples from very mobile species such as lobster, the majority of the samples fall below 0.25 ppm. These values, though indicative of an elevation over background, are much lower than values that have been found at other sites with mercury contamination (Langston 1986, Evans and Engel 1994). Overall, the highest values of mercury contamination were from locations close to or on the ship.

Characterization of biota in hold #5 and vicinity

Since several of the samples collected near the wreck in August and September showed high levels of mercury contamination, a second set of invertebrate samples was collected in October, to better characterize patterns of mercury contamination on the wreck and in particular, inside hold #5. Inside hold #5, 53 invertebrate specimens were collected and 26 specimens were collected from the seafloor at distances at least 15.2 m from the hatch cover of hold #5. (Exact sample locations were not recorded for the seafloor samples.) The October biological samples were analyzed for total and methylmercury to address questions about potential methylation at the *Empire Knight.*

Table 8. Mercury concentrations in invertebrates sampled from locations around the *Empire Knight* in August - September 1993.

Species Group	Tissue Analyzed	Total Mercury ppm wet weight range	mean	Sample Size	Stations Sampled
lobster	muscle	0.051 - 0.37	0.190	10	1A
crab	muscle	0.076 - 0.16	0.104	4	3A
clam & scallop	soft tissue	0.046 - 0.18	0.118	4	3A, 13-2, 17-2
urchin	soft tissue	<0.004 - 0.018	0.013	6	2A, 3A, 13-2
starfish	cross-section	0.021 - 0.23	0.062	11	1A, 2A, 3A, 11-2, 13-2, 19-2
Individual Samples					
snail	muscle	3.3		1	13-2
brittle star	cross section	0.92		1	3A
anemone	soft tissue	0.035		1	3A
worm	whole	0.025		1	8-1
mussel	soft tissue	0.055		1	hull
bristle worm	whole	18.0		1	hold 5

Tables 9 and 10 show the tissue concentrations for total and methylmercury (wet weight) in invertebrate species sampled. Data are averaged by species group for all samples from hold #5 (Table 9), and for all seafloor samples (Table 10). Several overall patterns are noticeable in both groups: methylmercury concentrations are much lower than total mercury concentrations (from 1 to 3 orders of magnitude lower) and all methylmercury concentrations are less than 0.025 ppm. However, some distinct differences between the two areas can also be seen.

Table 9. Total and methylmercury measured in invertebrates sampled from hold #5 inside the *Empire Knight* in October 1993.

Species Group	Total Mercury ppm wet weight mean	Methyl Mercury ppm wet weight mean	Sample Size
urchin	2.676*	0.0014	9 **
starfish	0.756*	0.0093	10**
crab	0.714*	0.0010	8
mussel	0.214	0.0078	10
scallop	0.174	0.0216	4
anemone	0.071	0.0032	10

* mean is strongly influenced by 1 or more high values
** not all samples analyzed for methylmercury

Table 10. Total and methyl mercury measured in invertebrates sampled from the seafloor around the *Empire Knight* in October 1993.

Species Group	Total Mercury ppm wet weight mean	Methyl Mercury ppm wet weight mean	Sample Size
lobster*	0.260	0.2300	1
starfish	0.239	0.0250	5
scallop	0.224	0.0172	1
urchin	0.173	0.0092	6
mussel	0.080	0.0043	5
crab*	0.060	0.0255	4
anemone	0.027	0.0042	5

* muscle tissue only

Organisms living in hold #5 have higher total mercury concentrations overall than organisms living on the seafloor. The highest mean values for samples from hold #5 (urchins, starfish, and crab) reflect several extremely high values from the data set. When an extremely high number is averaged with numbers that are much lower, the mean is strongly influenced by the extreme value, and the mean is inflated. Two urchins from hold #5 had total mercury concentrations of 19.6 ppm and 2.58 ppm. Thus the mean value for total mercury in urchins (2.68 ppm) is high because of these extreme values, even though all other urchins collected in hold #5 had mercury concentrations well below 1 ppm. Likewise, crab and starfish samples contained individual specimens with high values: for crab, the two highest values were 1.4 ppm and 2.6 ppm (total mercury), while one starfish was measured at 5.9 ppm total mercury. However, looking at the complete set of data from hold #5, including the extremely high values, only the urchins show an average concentration greater than 1 ppm total mercury.

Lobster contamination

Several lobsters were collected in traps located near the wreck at station 1A. Lobsters are of special interest because of their importance for local fisheries. Lobsters are also predators, and thus represent a potential accumulator of mercury from contaminated food sources. As such, we would expect mercury in lobster to be in the upper range among biological samples. However, since lobsters are mobile, ranging up to hundreds of kilometers (MacKenzie and Moring 1985), they will accumulate contaminants from many locations and many sources. Therefore, the contamination levels measured represent each individual's lifetime exposure, much of it likely originating from sources other than the *Empire Knight*. As an example of other sources of mercury in the New England aquatic environment, the city of Boston (combined Deer/Nut Island Boston Treatment plant) under its primary treatment scenario, discharged 0.14 metric tons of mercury per year into Massachusetts Bay through sewage outfalls (NOAA 1993).

Values for total mercury in lobster muscle at the *Empire Knight* ranged from 0.048 to 0.39 ppm wet weight. No samples measured greater than 1 ppm, the FDA screening level. In addition, these values fall well within the range that can be found in lobsters sampled from other locations in the region (Table 11).

Table 11. Mercury contamination in muscle tissue of American lobster, *Homarus americanus* collected near the *Empire Knight* compared with other locations in the region.

	Empire Knight ppm wet weight	Boston Harbor[1] ppm wet weight*	New York Bight[2] ppm wet weight	
muscle tissue	0.048 - 0.388	0.0028 - 0.347	New Jersey	0.080 - 0.310
			Dredge disposal	0.130 - 0.370
			New York Harbor	0.090 - 0.050
			Long Island Sound	0.090 - 0.360

[1]: MacDonald 1991

* dry weight converted to wet weight by multiplying by 1/4

[2]: Roberts et al. 1982

Methylmercury in Biota

The second set of biological samples from October 1993 was analyzed for methylmercury as well as for total mercury (Tables 9 and 10). Overall, methylmercury values are much lower than those for total mercury (by several orders of magnitude in many cases). The very low methylmercury values in biota confirm the conclusions reached in exposure assessment about the limited potential for methylation at the *Empire Knight*.

Since both invertebrates and fish preferentially take up methylmercury over inorganic forms of mercury (Fowler et al. 1978, Widom and Kendall 1979), if methylmercury were available at the *Empire Knight*, we would expect to see a high percentage of the total mercury tissue burden in biota as methylmercury. In contrast, methylmercury values from *Empire Knight* invertebrates are consistently low, while total mercury values vary considerably. The concentrations of methylmercury represent a low percentage of total mercury and do not correlate with the total mercury burdens in these animals. For example, urchins, the group with the highest mean for total mercury, has the second lowest mean for methylmercury.

This pattern is consistent with a low-level uptake of background levels of methylmercury, unrelated to sources of elemental mercury from the *Empire Knight*. These data reinforce the conclusions from the chemical pathways evaluation, that the main source of mercury to the organisms living in the hold is an inorganic form of mercury, and that methylmercury is an insignificant pathway for mercury uptake by biota at the *Empire Knight*.

Fish Sampling

Two otter trawl samples were collected in August and September near the wreck and tissue samples from flounder, cod, cunner, and sculpin were analyzed for total mercury (Table 12). Most of these fish are fairly wide-ranging (with the possible exception of sculpins) and thus would not be good indicators of very localized mercury uptake. However, if mercury concentrations in these fish were extremely high, it could indicate that bioaccumulation and biomagnification were occurring at the site. Results from the fish tissue analyses implied that biomagnification of mercury on a larger scale was not occurring at the *Empire Knight*. The levels of total mercury concentration for muscle tissue shown in Table 12 (using the mean of the six cunner samples) are all below 0.1 ppm wet weight, and therefore are more than one order of magnitude lower than the U.S. Food and Drug Administration screening level for methylmercury in fish tissue of 1 ppm (USFDA 1984). This interpretation can be viewed as conservative related to the *Empire Knight*, given that these fish may have been exposed to many other sources of mercury, including land-based inputs.

Table 12. Mercury concentrations in fish muscle tissue sampled from two trawls taken near the *Empire Knight* in August and September 1993.

Species Group	Total Mercury ppm wet weight		Sample Size
flounder	0.037		1
cod	0.092		1
sculpin	0.089		1
cunner	range 0.053 - 0.16	mean 0.084	6

FDA Seafood Study

Additional data on fish contamination were gathered through a cooperative survey conducted by the Maine Department of Marine Resources, NOAA, USCG, and the FDA. This study specifically targeted commercial fish species marketed locally for human consumption and used FDA screening methods to analyze for mercury contamination. Tissue samples were analyzed for methylmercury with results from all species measured falling well below the FDA limit of 1 ppm methylmercury. Therefore, the FDA district director concluded that no regulatory action was warranted based on these data (McDonnell 1994; see Appendix B).

RISK CHARACTERIZATION

The *Empire Knight* is an anomalous site in many ways. Although mercury is always a concern as a contaminant in the environment, the *Empire Knight* site is unique because of its deep-water marine environment and the fact that elemental mercury is the source contaminant. To determine whether mercury from the *Empire Knight* represented an environmental risk, we carefully evaluated chemical and biological pathways for mercury at the site. Though a large quantity of mercury likely still remains inside the hold, we see no evidence that this mercury is causing an adverse impact on the surrounding marine environment. Very localized contamination can be measured within the wreck and in the immediate vicinity, and elevated concentrations of mercury in sediments extend out to a maximum of 61 m (200 ft) from the ship.

The extent of the contamination in biota appears to be restricted to sessile or limited-mobility invertebrates living inside or near hold #5. The potential effects of this localized contamination have not been specifically evaluated in terms of possible toxicity to these organisms. No evidence of biomagnification was found in higher trophic level organisms, nor was there evidence that mercury from the wreck is a source to organisms living farther than 61 m from the wreck.

The question left unanswered is whether the remaining mercury could represent a risk to the marine environment in the future. To answer this question absolutely would require us to predict the future fate of the remaining mercury in the hold. Though it is impossible to give absolute assurances about future events, we can speculate based on the best available data. Dr. Mason summarizes his estimation of the environmental fate of the *Empire Knight* mercury, including future possibilities:

> "In summary, the mercury from the ship will continue to slowly dissolve into the water column with its eventual fate being volatilization to the atmosphere. A small increase in sediment concentration will result from the very slow oxidation of elemental mercury, although the extent of this can only be upper bounded at present. Based on estimates of dissolution rates it is likely that most of the mercury will be lost within a few hundred years, assuming a half-life for loss of 50-100 years. This mercury, being elemental, will not result in dramatic increases in the concentration of mercury in biota, especially with regard to methylmercury."
>
> "If there was a significant mixing event - a large storm, movement of the ship etc., this would lead to a redistribution of the mercury that could possibly enhance the rate of loss. There would likely be an increase in water column concentration at the time of maximum mixing but this concentration should not exceed the solubility limit of elemental mercury - 60 μg/L (ppb). In the long term, this mixing would have the likely outcome of increasing the dissolution rate thereby decreasing the time till all the mercury disappears. It is difficult to envisage any situation that would lead to an increased sustained environmental threat."

Based on this assessment, we would not expect substantial changes in ecological impact even if mercury were released more quickly (if the wreck, say, eventually broke apart or if hold #5 was disturbed in some other way). In these cases, the elemental mercury would be exposed to water circulation and dissolution rates would increase. However, as Mason points out, the dissolution rate is still limited by the solubility limit of mercury in seawater, and though short term increases in water concentrations of mercury might result, these would be diluted quickly.

The FDA sampling results and results from lobster sampling at the site show that seafood resources in the larger area around the *Empire Knight* site are not adversely affected by mercury from the wreck.

We feel confident in our conclusions, in the high quality of data collected at the site, and in the numerous experts who have participated in this assessment. Even so, we acknowledge that some people may feel uncomfortable with the idea of mercury remaining at the site for many hundreds of years. Based on the extensive information available to us, we do not foresee increased ecological risk from this site in the future.

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APPENDIX A

REPORT ON EMPIRE KNIGHT FATE AND EFFECTS OF MERCURY

by

Robert P. Mason

REPORT ON *EMPIRE KNIGHT*

FATE AND EFFECTS OF MERCURY

by

ROBERT P. MASON

SUMMARY

From an evaluation on the current available information on the processes controlling the biogeochemical cycling of mercury in marine waters, and after assessment of the data available on the concentration of mercury in sediments, scrape samples and biota, it is concluded that there is little long-term or immediate environmental risk posed by the elemental mercury remaining in the wreck of the *Empire Knight*. Mercury is being lost from the site primarily by dissolution of elemental mercury, with gas evasion to the atmosphere being the route of final loss. This input to the atmosphere will have a trivial impact on the global mercury cycle. Mass balance calculations suggest that a substantial fraction of the initial mercury remains on site and that it will take hundreds of years for all the mercury to be lost by dissolution. Finally, because of the perceived low risk, any remediation action should result from careful investigation of the available options as there is no need, based on the scientific evidence, for immediate mobilization toward removal of the remaining mercury.

MERCURY SOURCES, SINKS AND REACTIONS

The form of the mercury controls its fate and environmental effect. Assuming that at the time of sinking essentially all the mercury was in the elemental form, there are three possible pathways for the loss of mercury to the environment: dissolution, oxidation of elemental mercury and physical dispersion of the elemental mercury (Fig. 1). It is likely that some of the elemental mercury has been moved by atypical mixing events and is dispersed inhomogeneously around the wreck. If this has happened to any significant extent, then one would expect to find that some of the sediment samples collected will contain elevated levels of mercury. However, if the mercury is in the elemental form it is not bioavailable and "unreactive" (see below) and would therefore not constitute an environmental risk.

The most crucial fact in the estimation of the environmental risk is the rate of oxidation of elemental mercury to the more reactive and bioavailable ionic form - Hg(II) complexes. This is because the ionic mercury is taken up by microorganisms and is the form that is methylated. There is no evidence in the literature of methylation of elemental mercury. Further, if microbes are the principal methylators, then it is unlikely that elemental mercury, which does not bioaccumulate, would be methylated by these organisms. Ionic mercury is the precursor to methylmercury and to food chain accumulation of mercury (Fig. 1). Here we use the term ionic mercury to represent all the dissolved inorganic complexes (e.g. $HgCl_4^{2-}$, $HgCl_3^-$ and $HgCl_2$) and any labile (reactive) organic-mercury complexes. Because of the strong chloride complexation in seawater it is unlikely, based on thermodynamic calculations, that a significant fraction of the ionic mercury is bound to dissolved organic matter or to iron/manganese oxides. Thus, most of the Hg(II) is in the form of reactive chloride complexes.

This ionic mercury can suffer three major fates in the water column - reduction, particulate uptake and methylation. It has been shown in our laboratory studies, in our studies using natural waters and by the work of others, that phytoplankton and other microorganisms can reduce Hg(II) to elemental mercury and that this reduction rate typically proceeds at rates of 0.1 to 1% per day in ocean waters, depending on microbial activity and productivity. Often it seems that the reduction rate is limited by the rate of supply of ionic mercury. In the equatorial Pacific, for example, reduction and gas evasion is the primary sink for ionic mercury.

Abiotic reduction has also been demonstrated, although it occurs at a slower rate. Traces of reducing compounds are all that is required as the picomolar concentrations of mercury in natural waters make mercury less abundant than peroxide, for example. Thus, it is the tendency for Hg(II) to be reduced to elemental mercury rather than for elemental mercury to be oxidized in natural waters. This contradicts thermodynamic prediction but biotic mediation results in the predominance of the reduced forms of many other elements in surface waters.

As the reduction rate is relatively rapid (note that experimental results provide a net reduction rate), it would be difficult to measure the rate of oxidation but it is clearly less than the reduction rate i.e. less than 0.1% per day. Further, based on the distribution and mass balance of the various mercury compounds in the low oxygen waters of the equatorial Pacific, it was concluded that the rate of elemental mercury oxidation was extremely slow, considerably less than the estimated demethylation rates of 0.01-0.2% per day. From mass balance calculations, the rate was estimated at 0.01% per day. This result is consistent with the concentration data in sediments, for example (see below). It would be extremely difficult to design an experiment to measure such a low oxidation rate, considering the tendency for reduction, the low solubility of elemental mercury in water (around 60 μg/L) and its tendency to volatilize (saturation with respect to the atmosphere is 2 pg/L).

Based on current knowledge it is therefore reasonable to conclude that very little oxidation of the elemental mercury has occurred. Further, a large fraction of any ionic mercury formed is likely to be again reduced once in the water column. This is the primary sink for ionic mercury in surface waters. Any elemental mercury released into the water from the site would combine with the naturally formed elemental mercury and eventually will be lost to the atmosphere. As shown in Fig. 1, surface waters at 0.5 pM, are supersaturated with elemental mercury.

Mercury in living or dead suspended particles is a small fraction of the total e.g. less than 10% for the equatorial Pacific mixed layer. In Fig. 1, the pathway to methylation is shown as uptake and then methylation i.e. this assumes that biological methylation predominates and occurs within cells. While this has been shown for sulfate reducing bacteria, the mercury-methylating organisms receiving most scientific attention, this is not the only possible route. However, as methylation, particulate uptake (without methylation) and methylation compete for the available ionic mercury, and as methylation rates are at least as slow as reduction in oxic ocean waters, only a small fraction of the ionic mercury is methylated. This is true for methylation in the water column; for sediments, elemental mercury reduction is less. Here, availability of Hg(II) limits methylation in sediments. Under anoxic conditions, methylation is increased but anoxic conditions will not influence the rate of elemental mercury oxidation (see below). Again, using the equatorial Pacific as an example, about 7% is methylated under oxic conditions. In low oxygen regions, methylation would account for a larger fraction as reduction is less important in these regions. Higher anoxic conditions will result in a decrease as Hg(II) is made unavailable due to sulfide complexation. Further, this methylation rate does not include demethylation which will reconvert methylmercury to ionic mercury to elemental mercury - most microbes that demethylate mercury convert the methylmercury to elemental mercury rather than ionic mercury.

Overall, based on open ocean and estuarine studies it is reasonable to predict that about two-thirds of the ionic mercury is converted to elemental mercury, one-third is removed by particulate scavenging and sinking and about 10% of the particulate is methylmercury. Less than 5% of the water column mercury is methylmercury. Thus, one must conclude that the amount of methylmercury that could be derived from the elemental mercury of the *Empire Knight* is exceedingly small.

One concern is the influence of anoxia on the loss of mercury from the site. Thermodynamically, because of the strong formation constants of mercury-sulfide complexes, it is possible for the oxidation of elemental mercury to occur, if a suitable electron sink is available. Sulfate reduction is one possibility, especially as the formation of Hg-S complexes is required to shift the equilibrium sufficiently to be favorable. While this is thermodynamically possible, it is not a likely scenario. Further, as the intrinsic solubility of Hg in the presence of the solid HgS is around 1 nM, oxidation under anoxic conditions would not lead to a dramatic release of bioavailable mercury. If the loss of this mercury is limited by boundary layer diffusion mechanisms similar to that described below for elemental mercury, then the rate of loss would be 300 times less. While it is unlikely that anoxia will increase the rate of oxidation, there is no experimental evidence available to support this notion. However, the relative unavailability to organisms of sulfide-bound Hg, and its slow dissolution rate would lead to a minimal impact on the concentration of methylmercury in seafood.

In summary, it is evident, based on measured reactions for mercury reduction and methylation, and from considerations of the likely rate of mercury oxidation, that a very small fraction of the elemental mercury that was on the ship has been converted to ionic mercury. Of the small fraction that could have been oxidized, only a small part would have indeed been methylated. Thus, it is concluded that there has been very little environmental impact, considering increases in methylmercury in biota as the measure of this impact.

In light of this conclusion, the relatively low measured concentrations of elemental mercury in sediments and scrape samples suggest two possibilities: (1) analytical problems, which are addressed below and (2) that all this measured mercury represents a small fraction of the total and is indicative of the ionic mercury supply from (a) other parts of the ship (b) from oxidation of elemental mercury. Assuming, based on estimates of mercury in sediment, that mercury in sediments and other compartments (about 1% of the total) represents ionic mercury derived via oxidation and that about 30% of this oxidized mercury is deposited locally, one estimates that, at maximum, about 3% of the initial mercury has been oxidized. This represents an oxidation rate of 6×10^{-4} per year (1.6×10^{-6} per day) which is exceedingly small compared to the rate of reduction (around 0.1 to 1% per day; 10^{-2}-10^{-3} per day). Thus, even if the concerns over the analytical techniques prove to be unsubstantiated, the concentrations and speciation of the mercury in the sediment are not inconsistent with the interpretation of the pathways of mercury loss. If the analytical techniques are providing a representative picture of the speciation, the results suggest that little elemental mercury is being physically dispersed from the ship -assuming, of course, that the sediment sampling strategy would have located any "hotspots" of mercury, as would be expected of liquid mercury dispersed by physical dispersion processes.

ANALYTICAL PROCEDURES

The analytical procedures used by Battelle for the analysis of mercury in sediment, scrape samples and biota are well-tested, except for the procedure they used to estimate elemental mercury concentrations. According to Eric Crecelius, for sediment samples, the procedure involved adding a few grams of sediment to the normal sparging apparatus and bubbling for 15-20 minutes. Experiments done in this lab. with battery gels and other battery contents, show that while elemental mercury is released during bubbling, the time required to strip all the elemental mercury from solids is in the hours to days range. Nicolas Bloom, from Frontier Geosciences, found that it was difficult to completely recover dimethylmercury, which is volatile, spiked into sediments. He also assessed the time required for stripping to be on the order of a day. Further, the elemental mercury methods used by Battelle were not tested by doing spike additions, replicates or other typical quality control procedures. Thus, I am not confident that the method employed to estimate elemental mercury is providing a good estimate of concentration, and therefore caution using the results.

For the tissue sample, the elemental mercury concentration was estimated form the size of the initial peak on the chromatogram, which is where elemental mercury elutes. The retention time of this peak is typically determined by the void volume of the column i.e. any compound that is not retained by the column elutes at this time. Many compounds, such as water and volatile organic compounds, that are liquid at room temperature, are trapped on the carbon trap used for collection during the sparging step, and elute at this point in the chromatogram. If present in sufficient quantity, the compounds will condense within the analyzer and caused a scattering peak that registers as a signal because the excitation and fluorescence wavelengths are the same for atomic fluorescence measurement. Thus, it is quite possible for other compounds to give a false signal that seems to represent elemental mercury. Again, caution is required in interpreting this signal without some rigorous quality control.

As elemental mercury is unreactive i.e. it does not complex or react with tissue constituents, it should not accumulate in organisms as elemental mercury. Thus, it is difficult to envision how high elemental mercury concentration could be present except if they are present as a physical attachment to sand etc. within the shell of the respective organisms.

Finally, while high ppm concentrations have been found in a number of samples it is difficult to assess what fraction of the mercury is contained in these compartments i.e. the combined sediments and interior compartment inside the ship (e.g. scrape samples). An attempt should be made to estimate the order of this contamination i.e. is it a significant portion of the mercury within the hold or within the ship? It is probable that although these samples present high concentration, their overall contribution to the mass balance is minimal; i.e. 7×10^5 kg of 100 ppm sediment is equivalent to 1 % of the initial mercury load of the ship; similar to the estimate of mercury in the sediments.

RATE OF LOSS OF MERCURY FROM THE SITE

The primary route for loss of the elemental mercury is by dissolution. Any ionic mercury that was present on ship at the time of sinking would of rapidly dissolved and thus would have caused its impact 50 years ago. The sediment concentrations indicate that little mercury has been lost by physical dispersion. It is possible to estimate the dissolution rate into the water in two ways: experimentally and theoretically. Based on laboratory experiments, performed with a battery broken to allow dissolution of its elemental mercury containing contents (a comparable scenario would be elemental mercury mixed into sediments), the rate of loss of mercury was about 20 µg per g of mercury per day. If all the *Empire Knight* mercury was similarly dispersed in the hold, then the rate of loss would be about 150 g per day (8×10^{-3} per year) and half the mercury would be lost in about 90 years. Clearly, not all the mercury in the hold is as directly available for dissolution as that of a broken battery, and this estimate must be considered a maximum rate of loss.

As the solubility of elemental mercury is low, diffusion through the boundary layer surrounding each exposed mercury "globule" is likely to be the limiting factor on dissolution rate. The boundary layer would depend on the mixing regime in the vicinity of the mercury globule. The shape and size of the mercury globules influences the surface area. Considering 1 kg "blobs" of mercury (7,300 blobs for the cargo) with a surface area (A)/boundary layer (∂) ratio of about 200 cm (an median ratio derived from that found for spherical globules and that for a thin film), we estimate a rate of dissolution as:

$$R = D.(A/\partial)[Hg]$$

where D is the molecular diffusion coefficient of 3×10^{-5} cm^2 s^{-1}, A is the surface area, ∂ is the boundary layer thickness and [Hg] is the solubility concentration of elemental mercury, 60 µg/L. The water column elemental mercury concentration is negligible. Thus,

R = 0.2 g per day i.e. the mercury will remain for about three hundred thousand years (5 half-lives).

For 1 g blobs, R = 227 g per day (half-life 60 years; lifetime 300 years).

Both these estimates should be taken with caution. Until the nature and distribution of the remaining elemental mercury in the hold is known, accurate assessment is not possible. Clearly, a substantial fraction of the mercury remains (>50% of the original load).

IMPACT OF THE MERCURY

Taking, based on the above estimates, a reasonable input rate of around 100 g per day, what is the consequence. To reiterate, the influence of elemental mercury to organisms and to mercury concentrations in fish will be negligible. However, considering a venting area around the wreck of 100 m x 100 m the upward flux would be 0.01 g m^{-2} day^{-1}. At steady state, the gas exchange rate would match input, so:

$$0.01 \text{ g m}^{-2} \text{ day}^{-1} = K.[\text{Hg}]$$

where K is the piston velocity, 3 m day^{-1} used here, and [Hg] is the steady state mercury concentration. A value of 16 nM is obtained. This is substantially higher than the ambient water concentration of around 10 pM. However, if the loss rate was at the lower limit the water concentration would be 30 pM. Moreover, lateral mixing at a slow rate would substantially reduce the concentration. A current of 0.05 m s^{-1} (4.3×10^3 m day^{-1}) would totally swamp losses to the atmosphere, and would dilute the water concentration, for the 100 g per day scenario, to 10 x's background concentrations (10 pM elemental mercury). For less dissolution, the concentration would be lower. Knowledge of the currents and mixing in the region of the ship is required to further this calculation. These estimations however suggest that dissolution of elemental mercury from the ship could lead to locally higher elemental mercury concentrations in the water. As concluded above, this however represents little environmental impact on organisms, as reflected in the low concentrations of mercury found in organisms around the ship.

It is probable that a very small fraction of the mercury is oxidized and that this will continue with time. Considering that the ship has been on the seafloor for about 50 years i.e. about 10-20% of the expected lifetime of the mercury, one can put some bounds on the maximum amount of contamination likely overall. Using the estimates for mixing derived above, we estimate that the maximal possible input (i.e. assuming all mercury in sediment is derived from oxidation of elemental mercury) to be an increase in water concentration of about 1 pM in the immediate vicinity of the ship - about 20% of the average concentration (5 pM; Figure 1). Similarly, the sediments would be increased by a similar amount. This contamination, and any resultant increase in biotic concentration, will remain a small and a localized phenomenon. The influence of a continual very low input of ionic mercury on a biological organism will depend on its lifetime compared to that of the input, and to how much time it spends in the ship within its lifetime.

Finally, it is known that elemental mercury is oxidized in the atmosphere, especially in the presence of ozone, and that this oxidation of elemental mercury is one pathway by which mercury is incorporated into atmospheric deposition (particulate scavenging being the other principal pathway). Thus, it is probable that any elemental mercury from the ship that vents to the atmosphere will eventually be oxidized and deposited back to land or to water. Based on rates of oxidation and the atmospheric residence time of elemental mercury of one year, it is clear that the mercury will not be redeposited locally. Thus, how does the possible emissions to the atmosphere of elemental mercury compare with anthropogenic fluxes? Anthropogenic fluxes are estimated to be around 20 Mmol (10^6 moles) per year currently. A loss of 100 g per day is equivalent to 1.8×10^{-4} Mmol per year; clearly the input is small on a global scale. If all the *Empire Knight* mercury was volatilized in one year, this would be equivalent to 3.5×10^{-2} Mmol; 0.2% of one year's input of anthropogenic mercury. Clearly, the effect of the input to the atmosphere of elemental mercury from *Empire Knight* is very small compared to other sources of anthropogenic mercury to the atmosphere.

In summary, the mercury from the ship will continue to slowly dissolve into the water column with its eventual fate being volatilization to the atmosphere. A small increase in sediment concentration will result from the very slow oxidation of elemental mercury, although the extent of this can only be upper bounded at present. Based on estimates of dissolution rates it is likely that most of the mercury will be lost within a few hundred years, assuming a half-life for loss of 50-100 years. This mercury, being elemental, will not result in dramatic increases in the concentration of mercury in biota, especially with regard to methylmercury.

If there was a significant mixing event - a large storm, movement of the ship etc., this would lead to a redistribution of the mercury that could possibly enhance the rate of loss. There would likely be an increase in water column concentration at the time of maximum mixing but this concentration should not exceed the solubility limit of elemental mercury - 60 μg/L. In the long term, this mixing would have the likely outcome of increasing the dissolution rate thereby decreasing the time till all the mercury disappears. It is difficult to envisage any situation that would lead to an increased sustained environmental threat.

SUGGESTIONS FOR FURTHER WORK

The major question that is unanswered is how much mercury is still within the ship. While this question relates directly to long-term fate and impact, knowledge of this would allow an assessment of the validity of the calculations and would provide some idea of the historical input that has occurred. Calculations suggest that enough mercury remains so that it should be easily located. Has been covered by sediment and coated with organic matter, making it less available for dissolution?

In the absence of attempting to quantify the remaining amount of mercury, efforts should then focus on obtaining better information on the mixing regime around the ship. What are the currents? How quiescent is it within the ship? If the loss rates approach the maximum estimates, then concentrations of elemental mercury in the water column should be elevated enough that they would exceed the natural variability found in natural water and would be relatively easily measured by scientists trained in the methods of measuring the low level speciation of mercury in water.

If the site is visited, then samples containing mercury (scrapes, sediment, liquid mercury, coated mercury "globules" etc.) should be collected in the mercury containing hold. These samples could be tested for the presence of elemental mercury and ionic mercury in the following manner. A few grams of samples is shaken for one hour with seawater (this seems to be enough time for equilibration) and the speciation and concentration in the water measured - elemental mercury and ionic (reactive) mercury. If there is any ionic mercury in the sample then is should dissolve immediately and the concentration will therefore depend on solid-dissolved distribution, which could be estimated from partition coefficient data. If all the mercury that is soluble is elemental, then the concentration should be around 60 μg/L, the solubility limit. Scenarios in between could be interpreted to assess the ratio of ionic to elemental mercury.

Otherwise, time and effort could be expended to develop a suitable protocol for the estimation of elemental mercury in sediments. This procedure could then be used to estimate the elemental mercury fraction in the sample.

APPENDIX B

ANALYTICAL RESULTS OF THE JOINT FDA, NOAA, MDNR, AND USCG FISH SURVEY

by

Edward J. McDonnel
District Director,
U.S. Food and Drug Administration

617-279-1675

February 17, 1994

William J. Brennan, Commissioner
Maine Department of Marine Resources
State House Station #21
Augusta, Maine 04333

Dear Commissioner Brennan:

Enclosed is a synopsis of the analytical results for the samples collected from the research vessel, Argo Maine, in October 1993. As you know, the samples were collected as part of a cooperative survey conducted by the Maine Department of Marine Resources, the National Oceanic and Atmospheric Administration, the National Marine Fisheries Service, the United States Coast Guard and the Food and Drug Administration (FDA) in response to potential mercury contamination in the vicinity of the sunken freight ship, Empire Knight. FDA's role in the survey focused on the collection and analysis of seafood samples harvested in the vicinity of the wreck site and evaluating the data to assess the potential health risks associated with the consumption of seafood from the area.

The samples were collected at three stations in close proximity to the wreck site. Samples were composited by species and area of harvest to provide a total of 34 samples. The samples were shipped to FDA's Buffalo District Laboratory for methyl mercury analysis. Sample results were forwarded to FDA's Office of Seafood where a review and assessment of the data was performed.

Because the samples exhibit a range of methyl mercury commonly encountered in the species collected and because they fall below FDA's action level of 1 ppm in seafood, we do not believe that follow-up regulatory action is warranted at this time. Please keep me informed of any additional samples of seafood that are collected at this site through your monitoring efforts. Also, I would greatly appreciate being apprised of any additional investigations and remedial actions you take at this site.

Please do not hesitate to contact my office if you need any further information or require assistance in future sample collections. My telephone number is 617-279-1726.

Sincerely,

Edward J. McDonnel
District Director

Enclosure

cc: Bruce Joule, Marine Resources Scientists, Maine DMR
John Lindsay, NOAA
Richard Roe, NMFS
Dr. Gregory Cramer, FDA, Office of Seafood
Willis I. Cobb, FDA, Augusta Resident Post
Captain David Pascoe, U.S. Coast Guard
BOS:EJM/ALS/kml 2/17/94

Samples harvested in the vicinity of the *Empire Knight* and analyzed for methylmercury contamination

Sample No.	Sample Weight (kg)	Species	ppm (µg/g)	Tow No.
94 -778-421	1.84	cod	none detected	1
94-778-422	2.84	winder flounder	none detected	1
94-778-423	0.11	redfish	none detected	1
94-778-424	0.45	ocean pout	0.200	1
94-778-425	1.78	white hake	0.048	1
94-778-426	9.42	monkfish	none detected	1
94-778-427	0.61	yellowtail flounder	none detected	1
94-778-429	1.5	lobster	0.037	1
94-778-429	1.70	silver hake	none detected	1
94-778-430	11.5	American plaice	none detected	1
94-778-431	11.5	small red hake	done detected	1
94-778-432	11.5	large red hake	none detected	1
94-778-433	1.22	silver hake	none detected	2
94-778-434	5.48	winter flounder	none detected	2
94-778-435	0.21	redfish	none detected	2
94-778-436	1.0	lobster	0.047	2
94-778-437	0.14	haddock	0.042	2
94-778-438	1.22	silver hake	none detected	2
94-778-439	8.04	monkfish	0.211	2
94-778-440	9.0	American plaice	0.035	2
94-778-441	1.07	yellowtail flounder	none detected	2
94-778-442	1.5	ocean pout	none detected	2
94-778-443	1.22	silver hake	0.043	2
94-778-444	6.5	cod	0.034	2
94-778-445	12.5	monkfish	0.036	3
94-778-446	0.63	haddock	0.040	3
94-778-447	19.0	red hake	0.036	3
94-778-448	10.5	American plaice	0.042	3
94-778-449	2.92	ocean pout	none detected	3
94-778-450	2.70	cod	0.043	3
94-778-451	4.95	winter flounder	0.040	3
94-778-452	8.5	haddock	0.042	3
94-778-453	0.85	yellowtail flounder	0.043	3
94-778-454	0.53	white hake	none detected	3

APPENDIX C

IDEAS FOR CONDUCTING AN ECOLOGICAL RISK ASSESSMENT AT THE EMPIRE KNIGHT BASED ON THE SUPERFUND MODEL

by

Mary Matta
Coastal Resources Coordination Branch
NOAA HAZMAT
7/22/94

Ideas for conducting an Ecological Risk Assessment at the *Empire Knight*, based on the Superfund model

Although this report is not a formal ecological risk assessment, much of the data collected by the Coast Guard may be useful in preparing an ecological risk assessment for the Empire Knight site. The first step in conducting a risk assessment is to formulate the potential problems at the site. The background information presented in this report can be used to create a conceptual model for the site that describes the likely fate of mercury at the wreck, pathways for mercury to reach biological organisms, and mechanisms of mercury toxicity.

Using the conceptual model, assessment endpoints are selected. These are expressions of the major concerns at the site. An assessment endpoint could be the health or reproduction of a particular species of concern, or a component of the ecosystem such as the health of the benthic community. At the Empire Knight, one assessment endpoint already identified is the accumulation of mercury in species consumed by humans. In some cases, the assessment endpoints can be measured directly. However, it is necessary to document that there is a pathway from the source of contamination to the assessment endpoint.

After assessment endpoints are selected, an evaluation of the potential for exposure to contaminants at the site is conducted. This evaluation includes measurements of concentrations of the contaminant along the pathway from the source to the species of concern. In the case of the Empire Knight, the Coast Guard has measured concentrations of mercury in sediment and organisms from low trophic levels (sessile organisms and benthic invertebrates).

An evaluation of the potential toxicity of the contaminants of concern (mercury) can include measuring actual effects of the contamination or predicting whether effects could occur using past studies or modeling. At the Empire Knight site, concentrations found in sediments and in low trophic level organisms could be compared to values from scientific literature associated with adverse effects. Concentrations of mercury measured to date in fish near the wreck do not pose any concern for human consumption. However, the fish sampled may not represent the "worst case" scenario since they may not spend much of their time at the wreck site.

Risk characterization combines the exposure and toxicity evaluations to determine the extent and magnitude of adverse effects or risk. The concentrations measured in sediment and organisms at the site are compared to concentrations known to cause adverse effects to determine the magnitude of potential risk. Any actual observations of adverse effects indicate that risk is present. The area over which effects would be expected should also be estimated. Risk characterization must include an assessment of the uncertainties involved at each step of the process.

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