Short communication

Airborne mercury pollution from a large oil spill accident on the west coast of Korea

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ABSTRACT

Atmospheric mercury pollution was recognized after a large oil spill on the west coast of Korea on 7 December 2007. In this study, the concentrations of gaseous elemental mercury (GEM: Hg^0) in air were measured both shortly after the oil spill ($\sim$100 h) and 1 month after the accident near the accident site. When the Hg concentration levels were compared between two seashore sites and two parallel sites offshore, the values tend to decrease further offshore. The unusual rise in Hg concentration levels observed on the seashore area shortly after the accident (mean of 16.4 ± 9.85 ng m^{-3}) dropped dramatically after 1 month with active cleanup activities (2.99 ± 1.40 ng m^{-3}). Because of the connection between crude oil and Hg (one of the major impurities), the unusual rise in the atmospheric Hg after the oil spill can be explained by the active evasion of Hg from the spilled crude oil. Although Hg levels determined a few days after the accident did not exceed the reference exposure limits (REL) proposed by several agencies, the early build-up of elemental mercury level due to the oil spill might have exerted certain impacts on the surrounding environments.

1. Introduction

Mercury and its compounds are included in the Title III listing of hazardous air pollutants (HAP) by US EPA due to their potential impact on human health [1]. As a result, they are subject to standards and regulations such as clean air mercury rule issued in 2005 [2]. In the atmosphere, Hg speciation is dominated by three environmentally relevant forms: gaseous elemental mercury (GEM: Hg^0), reactive gaseous mercury (RGM), and total particulate mercury (TPM) [3]. These different forms of mercury have different characteristics in terms of transport, deposition, and influence on ecosystems [4]. If accumulated in human body, mercury can affect the nervous system, cardiovascular system, digestive tract, and kidneys as well as the physical development, especially young children [5].

On 7 December 2007 (at 7.30 am), an oil spill occurred nearly 8 km from Mallipo Beach (Tae An area) in South Korea. An oil tanker (the Hebei Spirit) carrying 232,582 tons (about 1,462,896 barrel) of crude oil was hit by a vessel that was transporting a crane [6]. The accident was the worst oil spill in Korea, as 12,388 tons of crude oil spilled into the sea. About 490,000 people consisting of coast guard officers, soldiers, residents, and volunteers collaborated to clean up the spill site. Many workers involved in the early stages of the cleanup operation complained of several symptoms such as headaches, nausea, dizziness, and eye irritation [7]. A number of mercury species are known to exist in crude oil, while the elemental mercury is typically the major component along with traceable quantities of dialkylmercury (i.e, RGM) [8]. In light of the complex chemical properties of crude oil, a large number of airborne pollutants including Hg were likely released into the surrounding atmosphere, especially in the early phase of the accident.

In order to assess the immediate impact of this accident on air quality in the surrounding environment, an instantaneous field campaign was conducted to measure a number of airborne pollutants including heavy metal species, polycyclic aromatic hydrocarbons (PAHs), and odorous compounds. In this work, we report our measurements of Hg concentration levels in air that were conducted two times: (1) within 100 h and (2) 1 month after the accident.

2. Materials and methods

2.1. Sampling

In order to measure the status of Hg pollution near the oil spill site, field measurements were undertaken during the early and late

Table 1
A brief description of air sampling for the Tae An oil spill study

Sampling campaign	Order	Sample ID[a]	Sample collection time	Wind velocity (m s^{-1})	Temperature (°C)	Relative humidity (%)
[A] First phase (11 December 2007)	1	A-1	14:23	5.3	11	53
	2	A-2	14:28	5.3	11	53
	3	A-3	14:45	4.65	10	60
	4	A-4	14:50	4.65	10	60
	5	A-5	15:15	5.7	11	59
	6	A-6	15:20	5.7	11	59
	7	B-1	14:28	4.2	11	55
	8	B-2	14:33	4.2	11	55
	9	B-3	15:08	4.7	9	62
	10	B-4	15:13	4.7	9	62
	11	B-5	15:35	5.3	10	65
	12	B-6	15:40	5.3	10	65
	13	C-1	16:10	2.5	11	54
	14	C-2	16:15	2.5	11	54
	15	D-1	16:30	1.3	9	58
	16	D-2	16:35	1.3	9	58
[B] Second phase (9 January 2008)	1	A-1b	10:10	3.5	6	35
	2	A-2b	10:15	3.5	6	35
	3	A-3b	10:40	3.6	6	42
	4	A-4b	10:45	3.6	6	42
	5	A-5b	11:10	3.6	6	42
	6	A-6b	11:15	3.6	6	42
	7	B-1b	10:15	3.8	6	36
	8	B-2b	10:20	3.8	6	36
	9	B-3b	10:45	2.1	7	45
	10	B-4b	10:50	2.1	7	45
	11	B-5b	11:15	3.9	6	42
	12	B-6b	11:20	3.9	6	42
	13	C-1b	11:47	0.9	6	40
	14	C-2b	11:52	0.9	6	40
	15	D-1b	11:32	1.5	6	40
	16	D-2b	11:37	1.5	6	40

[a] Site information from sample ID: A (longitude = 126°8′39″, latitude = 36°47′0″: seashore site first), B (longitude = 126°8′45″, latitude = 36°47′8″: seashore site second), C (longitude = 126°84′4″, latitude = 36°46′52″: one block distance apart from site A), and D (longitude = 126°8′52″, latitude = 36°47′3″: one block distance apart from site B).

stage of oil spill cleanup process. The collection and analysis of Hg in this study are confined to gaseous elemental form of mercury. Hence, GEM (or Hg^0) is hereafter referred to as Hg, unless specified otherwise. Our first sampling campaign started on the afternoon of 11 December 2008 which was within 100 h of the accident. A brief description on the sampling campaign, i.e., schedule, site description, and other meteorological conditions are shown in Table 1. Initially, two seashore sites (named A and B) which are positioned parallel to seashore with 200 m distance between each other were selected to collect the air samples affected most significantly by the oil spill (Fig. 1: latitude (36°47′0″ and 36°47′8″N) and longitude (126°8′40″ and 126°8′47″E)). Six samples were collected from both A and B sites at the same interval over a period of 1 h. These samples were then named A1 through A6 and B1 through B6. In addition, two parallel sites which is at one block distance from the two seashore sites of A and B were selected and referred to as C and D, respectively; both C and D sites are toward an offshore direction near a residential area. For the analysis of several pollutants including GEM, samples were collected in 10-L Tedlar bags (SKC Corp., USA) through a vacuum sampler (ACEN Co. Ltd., Korea). These Tedlar bags were immediately put into black packets to avoid exposure to light and analyzed in the lab.

The second sampling campaign was conducted on 9 January 2008 which was 33 days after the accident. All samples were collected according to the procedures employed in our first study. A total of six replicate samples were collected at the two seashore sites (A and B) at 20 min intervals along with those for the parallel sites C and D. In this second field trip, we also conducted instant monitoring of the Hg level using a continuous Hg analyzer (Lumex RA-915$^+$, Russia) [9].

2.2. Analysis

2.2.1. Gold amalgam method with cold vapor atomic absorption spectrometry

The analysis of Hg was made by the gold amalgam method with cold vapor atomic absorption spectrometry. The preconcentration of Hg was accomplished by transferring Hg samples contained in Tedlar bag sampler to the Au–amalgam tube (or trap) using a mini-pump (MP-∑ 300, SIBATA, Japan). The flows of the pump were checked each time before starting the experiment and were maintained at 500 ml min^{-1} for each sample. Each sample collected by the Au trap was desorbed thermally and detected at a wavelength of 253.7 nm by a nondispersive double beam, flameless atomic absorption system using a mercury analyzer (WA-4, Nippon Instrument Co., Japan). The absolute detection limit of our Hg analyzer is ca. 2 pg of Hg. The precision of our Hg measurement averaged ~1%, if evaluated in terms of relative standard error (R.S.E. = mean × 100/S.E.) for five replicate injection data of vapor-phase standards. Details on the analytical performances of our instrumental setup for Hg analysis by the combined application of Tedlar bag sampling and Au–amalgam method has been described elsewhere [10]. For the statistical analyses, differences in spatial (or temporal) distribution of Hg were then evaluated by a Student's t-test through a comparison of concentration data for sites A and B (e.g., A1–A6 and B1–B6) or for sites C and D (e.g., C1–C2 and D1–D2) in each experimental phase (refer to Table 1 for details).

2.2.2. On site monitoring of Hg by a continuous Hg analyzer (Lumex RA-915$^+$)

The on-line monitoring of Hg data in air was made shortly using an RA-915$^+$ Hg analyzer (Lumex, St. Petersburg, Russia) during the
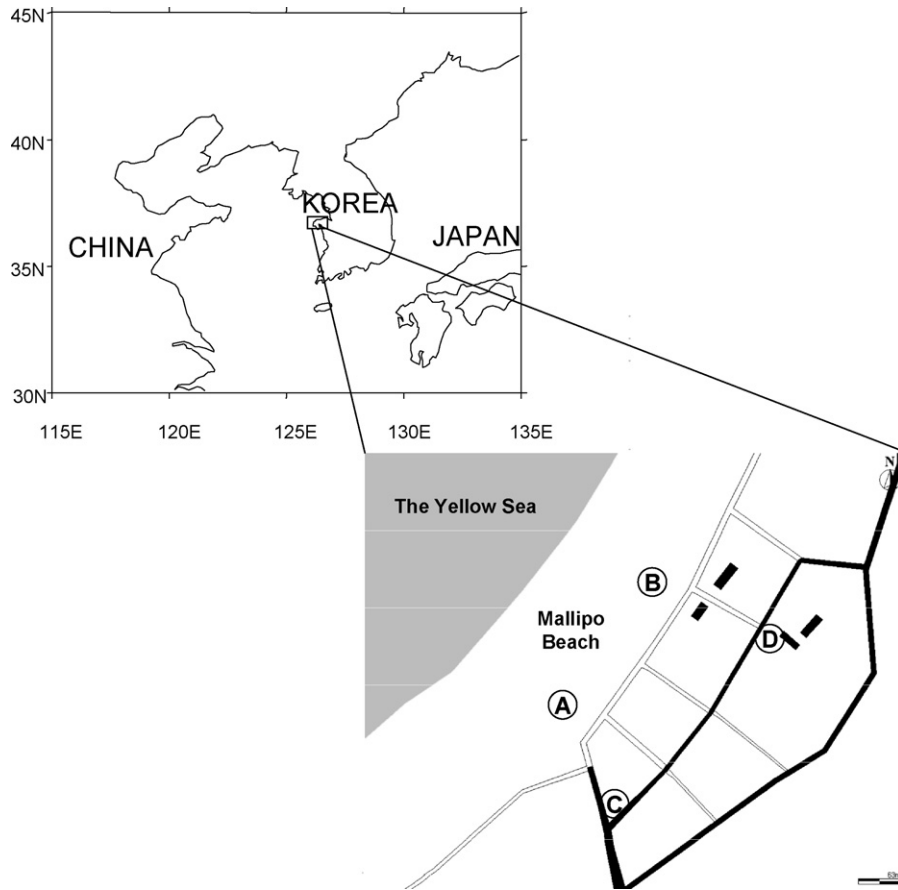
Fig. 1. A map of the sampling sites affected by the oil spill (Mallipo beach at the Tae An county, Republic of Korea): two near seashore sites of A and B and two reference sites of C and D.

second sampling trip. The operation of the RA-915^{+} is based on differential Zeeman atomic absorption spectrometry using a high-frequency modulation of light polarization (ZAAS-HFM). The Hg analyzing system was operated to monitor Hg concentrations at 5-s intervals for 1 h (between 11.05 am and 12.05 pm) at a seashore location (near site A). The monitoring of Hg was made only from one site due to the limited availability of electricity. According to our inter-comparative study between different analytical approaches for Hg, we were able to confirm that the results obtained by Lumex analyzer exhibited a very strong correlation with those of standard CVAAS method (by WA-4) ($r = 0.94$, $P = 6.66E{-}16$, and $N = 26$) [9].

3. Results and discussion

3.1. The status of Hg pollution at the seashore area

The results of our first field study showed a significant rise in atmospheric mercury on the seashore area a few days after oil spill. In the first study, the mean concentrations of Hg at two seashore sites (A and B) averaged 16.4 ± 9.85 ng m^{-3} which are much higher than those measured from a block away distance (C and D sites), i.e., 9.52 ± 3.15 ng m^{-3} (Fig. 2). Although the C and D sites showed low Hg values relative to the seashore sites of A and B, their Hg levels were still significantly high relative to the levels commonly found in other coastal areas of Korea (e.g., about 3 ng m^{-3} [11]). When the results of each individual site were compared, there was a pattern of spatial gradient with the decreasing concentration across site A (20.4 ± 11.9 ng m^{-3}) > B (12.5 ± 5.89 ng m^{-3}) > C (11.7 ± 2.94 ng m^{-3}) > D (7.34 ± 1.54 ng m^{-3}). In light of the similar
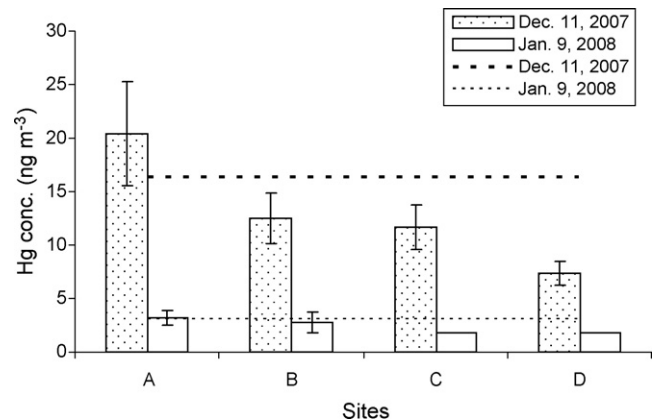
Fig. 2. A comparison of the mean mercury concentration levels between short after and 1 month after the oil spillage accident. Dotted lines represent the mean concentrations derived from the two seashore sites (A and B).

nature of the study sites, a spatial variation in Hg concentration level between sites (i.e., A vs. B and C vs. D) can be ascribed to such factors as a development of spatial concentration gradient due to distance differences from sources. In addition, the short-term variabilities of the Hg may also have to be considered, as its distribution may be affected by such factors as short-term changes in micrometeorological conditions (e.g., wind direction) at the time of sampling [12,13].

To examine the possible effect of oil clean up activities on the observed Hg concentration levels, the second sampling study was

Table 2
Comparison of Hg concentration levels for the two sampling campaigns (in ng m^{-3})

| Sites	First campaign (11 December 2007)			Second campaign (9 January 2008)			Results of a t-statistics	
	Mean	S.D.	N	Mean	S.D.	N	t	p
A	20.4	11.9	6	3.20	1.28	6	3.52E+00	0.0055
B	12.5	5.89	6	2.78	1.77	6	3.87E+00	0.0031
C	11.7	2.94	2	1.78	0.03	2	4.77E+00	0.0412
D	7.34	1.54	2	1.76	0	2	5.12E+00	0.0360
A and B	16.4	9.85	12	2.99	1.40	12	4.67E+00	0.0001
C and D	9.52	3.15	4	1.77	0.03	4	4.15E+00	0.0027

conducted 1 month after the accident. The mean Hg values between the two periods are illustrated for all four sites in Fig. 2. The results of the second field study showed a significant drop (about five times) in Hg concentration levels in the area. Comparison of the overall mean Hg levels (derived for two seashore sites A and B) between two study periods showed a significant decrease from 16.4 ± 9.85 (first, $N = 12$) to 2.99 ± 1.40 ng m^{-3} (second, $N = 12$). When the results of the individual sites were compared for the second campaign, the mean values of A and B (2.99 ± 1.40 ng m^{-3}) were still higher than those of offshore sites C and D (i.e., 1.77 ± 0.03 ng m^{-3}). In comparison, the Hg concentrations measured instantly by the Lumex analyzer in the second field trip averaged as 3.64 ± 0.97 ng m^{-3} (a range of 0.16–7.42 ng m^{-3}, $N = 590$) (Fig. 3).

When the results of the two periods are compared, the differences in Hg concentration levels were significant statistically (Table 2). Knowing that the Hg levels in the second campaign resumed the normal regional concentration levels in the area [11], the unusual rise in the atmospheric Hg after a few days of the oil spillage accident can be explained by the active evasion of Hg from oil spills. In addition, the notable drop in the observed Hg concentrations during the second campaign may be ascribable to the natural dilution effect through time which was accompanied after broad clean up activities at the accident site. According to a report by a joint United Nations–European Commission Assessment Team on 27 December 2007, the prospects for rehabilitation were optimistic due to the quick and effective action of the Korean authorities and cleanup volunteers [14].

3.2. Estimation of Hg emission due to oil spill and its implications

The Hg content in crude oil varies widely, while a significant proportion of Hg in oil is accounted for by its volatile components. This Hg content is found to be associated with many factors such as its geographical origin [15]. Although information concerning the Hg content of raw crude oil (at the spill incident) is unavailable, the quantity of the Hg evasion can be estimated roughly by utilizing the
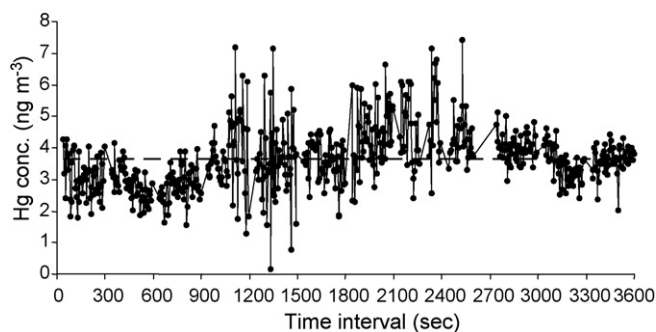
Fig. 3. An illustration of Hg concentration data measured near seashore area over an hour during the second campaign from 11.05 am on 9 January 2008. The dotted line shows the overall mean concentration (i.e., 3.64 ng m^{-3}).

Table 3
A summary of oil loss from the Hebei Spirit oil spill accident

Order	Company/location	Amount of oil loaded		Amount of oil released	
		Barrel	Tons	Barrel	Tons
1	Iranian heavy	471,193	74,914	33,323	5,298
2	Kuwait export	587,411	93,391	33,844	5,381
3	UAE upper Zakum	404,292	64,277	10,749	1,709
	Total	1,462,896	232,582	77,916	12,388

oil emission inventory data from the previous studies [7]; According to the analysis of crude oil samples collected from various locations on the globe, Hg content in oil varied from as little as 0.8 μg kg^{-1} (origin from middle east) to 220 μg kg^{-1} (Asian origin). Hence, the amount of Hg release due to this oil spill (12,388 tons as shown in Table 3) can theoretically fall in a broad range from as little as 9.91 to 2725 kg.

The emission rate of Hg from production and processing of oil and gas is about 10,000 kg per year in US according to US EPA [16]. In another report made by Maprani et al. [17], the total Hg evasion from 1 km area of Gossan Creek (a contaminated head water stream in Canada) was estimated at 6.4 kg per year. Because of the hazardous nature of Hg, the US EPA has issued a number of handling and cleanup guidelines for Hg spills indoors and at hazardous waste sites [18]. A cleanup of the mercury from sites contaminated by oils, radioactive, and organic materials is thus considered a challenging task due to mercury's volatile nature and diverse forms. If the reference exposure limits (REL) of elemental mercury (Hg^0) proposed by various agencies are concerned, the REL values fall in a relatively wide range of 80 ng m^{-3} [19], 90 ng m^{-3} [20], 200 ng m^{-3} [21], 300 ng m^{-3} [22], and 1000 ng m^{-3} [23]. The observed Hg concentration levels due to this oil spill accident are still moderately lower than all types of REL values. However, because of the hazardous nature, high bioaccumulation capacity, and long residence time (of elemental mercury) in the atmosphere, an instant increase in Hg exposure levels by such accident can still be critical from the human health and the environmental respects.

4. Concluding remarks

In this work, we reported the occurrence of atmospheric Hg pollution caused by a large oil spill on the west coast of Korea. Our initial study after a few days of the accident showed an unusual rise in Hg concentration levels (16.4 ± 9.85 ng m^{-3}) near the affected seashore area. As crude oil can contain a significant quantity of Hg, this rise was attributed to Hg evasion from the oil spill. However, Hg concentration levels exhibited a several-fold reduction following active cleanup at the site which took place for about 1 month period. The quantity of Hg released from this oil spill accident, if estimated based on previous inventories, can range from 9.91 to 2725 kg. Because of a low boiling point and rapid volatilization capacity, Hg can travel to deposit into various surface environments.

The evasion of Hg due to the oil spill accident may have contributed to a dramatic build-up of Hg levels immediately after the accident, allowing to gain a strong potential as sources of Hg re-emission for the surrounding environments.

Acknowledgements

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