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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 (~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 $16.4 \pm 9.85\ ng\ m^{-3}$) dropped dramatically after 1 month with active cleanup activities ($2.99 \pm 1.40\ ng\ m^{-3}$). 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

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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-$\sum$ 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