Pergamon

PII: S0045-6535(96)00226-3

Chemosphere, Vol. 33, No. 5, pp. 913–920, 1996

0045-6535/96 $15.00 + 0.00

Volatile Organic Compounds in Water near Petrochemical Factories in Taiwan

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(Received in USA 26 February 1996; accepted 29 May 1996)

Abstract

Water samples were analyzed for volatile organic compounds (VOCs) from various locations in and around Taiwan's Ho-Chin River. High concentrations of 1,2-dichloroethane and benzene were detected near a petrochemical plant's waste water outlet.

Introduction

Since 1985, Taiwan's petrochemical industry has grown vastly generating approximately one-third of Taiwan's total industrial profits and employing over 1.5 million people.[1] The petrochemical industry's manufacturing processes are complex and involve many different types of raw materials. Waste water from petrochemical factories generally contains many volatile organic compounds (VOCs) including benzene, toluene, and halogenated aromatics.[2,3] VOCs are easily vaporized and biodegraded under aerobic conditions.[4] VOCs have become ubiquitous in the environment,[5-7] being found in underground water, tap water, spring water, mountain water, waste water, soil, air and spoiled food. There may be a transfer of VOCs from one source to another, as well. Contact with VOCs can harm bodily systems including respiratory, hematopoietic, hepatic and renal.[8] Furthermore, VOCs such as benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorobenzene, hexachlorobutadiene,

tetrachloroethene, trichloroethene and vinyl chloride are all either known or suspected carcinogens.[9]

With the exception of one tap water company in Taipei, there are currently no standards for allowable VOC levels in drinking water. The government has set 0.15 mg/L as the allowable level for halomethane in drinking water. In 1995, the United States E.P.A. evaluated the levels of 27 VOCs in drinking water and set goals for future maximum allowable levels.[10] In the future, more compounds will be added to this list. Currently, in Taiwan, there is very little baseline data on petrochemical factory outputs of VOCs. No research had been done on possible contamination of underground water sources and other waterways.

The hypothesis is that VOCs from petrochemical factory waste water may contaminate underground water sources, eventually contaminating drinking water and may then be released into the air exacerbating an already serious problem with VOC air pollution. The authors hope this study will serve as a reference and stimulate discussion within the Taiwan government and lead to a comprehensive approach for testing and controlling the levels of VOCs in both waste water and sources of drinking water.

Experimental

Chemicals

Twenty-four purgable compounds were purchased from Supelco Inc. (Supelco, Bellefonte, Pa., U.S.A.). Bromochloromethane, 1,4-difluorobenzene and chlorobenzene-d5 were obtained from Supelco Inc. for use as internal standards. Surrogate standards 1,2-dichloroethane-d4, toluene-d8 and p-bromofluorobenzene were purchased from Supelco Inc.

Water Sampling and analytical methods

Sampling: Waste-water samples were retrieved from five locations along the Ho-Chin River, in Kaohsiung, and also near petrochemical plants. Samples were also taken from tap water and underground water in residential areas near the Ho-Chin River. Figure 1 presents a map of sampling sites with the positions of the petrochemical plants. Tap water samples were collected after allowing the tap water to flow for three minutes. Samples were collected in a 30 mL brown bottle containing 30 mg ascorbic acid, each bottle was filled completely, sealed with paraffin and stored at 4 °C. VOC concentrations were determined within three days.

Collection: Ho-Chin River samples include two from an industrial area, two from a residential area, and one from a site near where the river empties in to the Taiwan Straits. Ho-Chin River samples were collected following the same method described above.

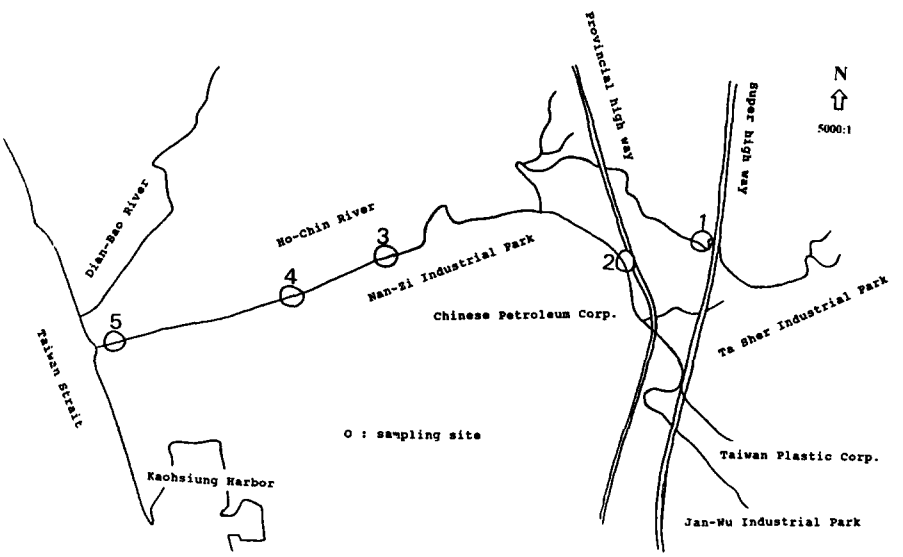

Fig 1. Sampling sites of VOCs in waster water among Ho-Chin River

VOC concentrations were determined using U.S. E.P.A. methods 524.2 and 624. Briefly, a 5 mL sample was injected into a "purge and trap" device (Tekmar LSC 3000, Cincinnati, Ohio, U.S.A.). Analytes were collected on ov-1 Tenax/silica gel/charcoal. A cryofocus was used to concentrate the VOCs. Purging was done at 35 °C for eleven minutes. Desorption was done at 180 °C for 5 minutes. Column cleaning was done at 200 °C for 10 minutes. The purge flow rate was 40 mL per min He(g).

VOCs were analyzed by gas chromatography-mass spectrometry (GC-MS, Perkin Elmer Q-Mass 910, Norwalk, CT, U.S.A.). Ionization mode was 70 eV with a mass range of 10-650 amu. The capillary column was DB-5 (30 m/0.25 mm/0.25 μm). Injection temperature: 200 °C. Initial column temperature: 35 °C (3 minutes). Temperature gradient: 4 °C/min. Final temperature: 100 °C.

Quality Control

With the exception of 1,1,2,2-tetrachloroethane with a purge efficiency of 88.7%, all other compounds had a purge efficiency of greater than 96.2%. With the exception of ethylbenzene with a trap efficiency of 21.8%, all other compounds had a trap efficiency above 84.5%. The relative standard deviations of two duplicates were 6.3% and 17.9%. The LODs of the VOC ranged from 0.02 to 1.48 μg/L.

Results and Discussion

Table 1 displays the results of an analysis of water samples taken from four different water purification plants, all serving the Kaohsiung metropolitan area. Samples were taken both before and after the purification process, which includes coagulation,

Table 1. VOC levels (μg/L) in water from five water purification plants in the Kaohsiung area

compounds	plant 1		plant 2		plant 3		plant 4	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1,2-dichloro-propane	4.70	2.63	ND	ND*	ND	ND	ND	ND
THMs		16.89	ND	9.63	ND	31.82	ND	44.41
chloroform	ND	5.81	ND	5.00	ND	16.54	ND	39.00
bromoform	ND	2.07	ND	ND	ND	ND	ND	ND
bromodichlor-methane	ND	5.92	ND	2.95	ND	12.19	ND	5.41
dibromochloro-methane	ND	3.09	ND	1.68	ND	3.09	ND	ND

(1): raw water, (2): purified water * ND: non-detectable

filtration, sedimentation and chlorination. Most of the raw water in these plants comes from the Kao-Pin River, with a small amount of additional water from underground sources. Both samples taken from Plant 1 was found to contain 1,2-dichloropropane. Samples from Plants 2 to 4 were found to be free of VOCs, both before and after the purification process. All but one of the water samples were found to contain halomethane after purification between 9.63 - 44.41 μg/mL. The legal allowable level for total halomethane in drinking water is 150 μg/mL. All samples tested were in compliance with this standard.

At Sites 1 and 2, underground water, tap water and filter water were tested for VOCs. Only underground water was tested at Sites 3 and 4. In Table 2, it can be seen that only the water from Site 1 contained VOCs. The tap water from this site contained 1,2-dichloropropane, toluene and ethylbenzene. However, at the same site, neither underground water nor filter water contained VOCs. Sites 3 and 4 were relatively far from the Ho-Chin River, but Sites 1 and 2 were relatively close, so there was concern that VOCs from the river had contaminated the underground water at these sites.

Table 2. VOCs levels (μg/L) in several water samples

compounds	site 1			site 2			site 3	site 4
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(1)
1,2-dichloro-propane	ND	3.63	ND	ND	ND	ND	ND	ND
toluene	ND	1.85	ND	ND	ND	ND	ND	ND
ethlybenzene	ND	0.72	ND	ND	ND	ND	ND	ND
THMs	ND	17.38	2.57	ND	31.23	1.63	ND	ND
chloroform	ND	7.47	2.57	ND	26.40	1.63	ND	ND
bromoform	ND	ND	ND	ND	ND	ND	ND	ND
bromodichlor-methane	ND	7.28	ND	ND	4.83	ND	ND	ND
dibromochloro-methane	ND	2.63	ND	ND	ND	ND	ND	ND

(1): underground water, (2): tap water, (3): filter water

Tests prove that this has not happened. Furthermore, because the tap water contained VOCs but the filter water did not, the filtering system successfully removed VOCs. This is important because tap water in Taiwan is not potable. Water is either passed through a charcoal filter or boiled before drinking.

Table 3 displays the results from samples taken from the five sites along the Ho-Chin River. At Site 1, on a branch of the Ho-Chin River near an industrial area, 1,1,2-trichloroethane was detected, but other VOC levels were very low or not detected. At Site 2, along the main Ho-Chin River and downstream from a petrochemical plant, VOC levels were highest. This suggests that waste water is being dumped into the river. 1,2-dichloroethane and benzene were detected in relatively high concentrations. Low levels of many other VOCs were also detected. At Sites 3 and 4, further downstream, VOC levels gradually decreased. This may be the result of biodegradation and vaporization of VOCs. Also, river sediment may have absorbed some VOCs or river water may have diluted VOC concentrations.

Tests show VOC levels in the air have been linked to industrial and industrial/household waste-dumping sites.[11,12] Because the air in the Kaohsiung area is known to contain high levels of VOCs, this study hopes to show that the major source of the air pollution are waste-dumping sites. To emphasize the severity of Kaohsiung's air problem, a 1993 study[13] by Chan reported airborne VOC levels in Taipei is much lower than the levels in Kaohsiung. Chan shows that Taipei's air pollution comes mainly from motor vehicles. These levels are 3 to 8 times the current airborne VOC levels in Los Angeles, California, U.S.A. These VOCs come from petrochemical plant emissions, automobile emissions and as shown in this study, from waste-water VOC vaporization.

Table 3. VOC levels (μg/L) from water sampled from the Ho-Chin River

compounds	Site 1 (upstream)	Site 2 (downstream)	Site 3	Site 4	Site 5 (outlet)
ethylbenzene	0.86	1.61	3.84	ND	ND
1,2-Dichloro-ethane	ND	1698.00	1197.41	158.41	70.02
benzene	ND	258.59	158.76	0.73	2.09
trichloroethane	ND	5.11	10.15	2.05	ND
toluene	ND	7.42	5.19	ND	1.00
1,1,2-trichloro-ethane	419.69	21.43	18.52	4.69	1.38
tetrachloroethane	ND	4.16	4.88	1.75	ND
chlorobenzene	ND	1.60	1.65	ND	ND
chloroform	0.67	52.84	40.20	27.75	2.29
bromodichloro-methane	ND	1.57	ND	ND	ND

About 80% of Taiwan's petrochemical plants are located in the Kaohsiung area. Most of the plants have on-site waste-water treatment facilities, but do not effectively filter VOCs. Except for halomethane, Taiwan has no standards for allowable VOC concentrations in waste water or tap water. This study is the first to evaluate the impact of the petrochemical industry on the Ho-Chin

River. Previously, the government was concerned with inorganic pollutants and organic matter in waste-water, however, currently emphasis needs to be placed on the presence of VOCs. Neither raw water nor purified water in treatment plants was found to contain high concentrations of VOCs, except for total halomethane. Analysis of underground water yielded the same results. However, water samples from the Ho-Chin River were found to contain high concentrations of benzene, 1,2-dichlorethane and 1,1,2-trichloroethane.

Acknowledgements

This study was supported by a special grant from the National Science Council NSC 83-0421-B-039-020 Z
Craig E Mitchell served as a consultant during the study period

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