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Gallium, Indium, and Arsenic Pollution of Groundwater from a Semiconductor Manufacturing Area of Taiwan

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Gallium arsenide (GaAs) and indium arsenide (InAs) are widely used semiconductor materials (Singh et al. 2001). Semiconductor manufacturing of gallium arsenide and indium arsenide devices includes four main operations: (1) ingot growing, (2) wafer processing, (3) epitaxy, and (4) device fabrication (Van Zant, 2000). GaAs and InAs can be toxic in animals and humans. And acute and chronic toxicity to the lung, reproductive organs, and kidney have been associated with exposure (Chepesiuk 1999). A single dosage of 100 mg/kg of GaAs and InAs resulted in acute pulmonary inflammation and pneumocyte hyperplasia after 14 days (Tanaka 1996; Webb et al. 1986). Chronic exposure (2-year observation period) to lower doses (<1 mg/L) of GaAs and InAs produced systemic toxicity and definite pulmonary lesions (Ohyama 1988). In addition, testicular toxicity was observed and tumor occurrence increased significantly in mice when GaAs and InAs were injected intraperitioneally (Omura et al. 2000). There is also evidence of renal toxicity. CD rats exposed to GaAs developed mitochondrial swelling of renal proximal tubule cells and dose-dependent inhibition of δ-aminolevulinic acid dehydratase (ALAD) in the blood, kidney and liver (Goering et al. 1988; Conner et al. 1995). In an aqueous environment, Ga, In and As are inorganic ions. Gallium and indium ion in water can cause immune system diseases and reduced blood leukocyte count (Betoulle et al. 2002; Burns et al. 1991).

Arsenic has been classified by International Agency for Research in Cancer (IARC) as a Group I carcinogen; that is to say, it is a documented human carcinogen. Much of the information gathered linking arsenic to cancer has been obtained through studies of human exposure via drinking water (Smith et al. 1992). Bladder, liver, lung, and kidney cancers have been linked to the consumption of drinking water containing elevated levels of arsenic (Chen et al. 1985 and 1992; Smith et al. 1992; Tanaka et al. 1996). The Environmental Protection Agency (EPA) of Taiwan has recommended that arsenic levels in drinking water not exceed 10 μg/L (EPA, Taiwan 1997). Arsenic has been well documented as one of the major risk factors for blackfoot disease. Blackfoot disease (once endemic to the southern coast of Taiwan) is attributed to intake of groundwater contaminated with arsenic from pesticides (Chen et al. 1985 and 1992).

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In Taiwan, Taiwan's economic development history is well known. The Hsinchu Science-Based Industrial Park (HSIP), in particular, has played a decisive role in the development of Taiwan's economy. It was established in 1980 to manufacture "high-tech" commodities. Currently about 350 companies in HSIP manufacture integrated circuits (ICs), computers and peripheral devices, telecommunication devices, optoelectronics, biotechnology products, and precision machinery (Chen and Huang 2004). Industrial parks like the HSIP have been recognized as an effective way of promoting technology development, urban renewal, and economic growth.

Gallium, indium, and arsenic are widely used semiconductor manufacturing elements, and doubt has been expressed that groundwater is contaminated via industrial effluents. Contaminated water may be a health risk to people living nearby. However, data obtained from monitoring gallium, indium, and arsenic in groundwater has been insufficient to demonstrate this risk. Monitoring gallium, indium, and arsenic levels in groundwater may provide a good database for future studies of the health risks of groundwater pollution or of environmental strategies for groundwater pollution control. The aim of the present study is to determine the amounts of gallium, indium, and arsenic in groundwater near the HSIP, Taiwan.

MATERIALS AND METHODS

At sites in and around the Hsinchu Science-Based Industrial Park (HSIP), located in Hsinchu, Taiwan (the northwestern part of Taiwan), we measured gallium, indium, and arsenic levels in groundwater and the geographical variations in these levels, and determined the statistical significance of differences in target metal concentrations between different sampling districts. The levels obtained in this investigation were compared with previously published values (Kiriyama and Kuroda 1988) and limits recommended for drinking water (EPA, Taiwan 1997).

Hsinchu City was divided into three administrative divisions including the Science-based Industrial Park (a 625-acre semiconductor manufacturing site located at east of Hsinchu City), the North District, and Hsiangshan District (the control district far away from HSIP). Totally, 90 samples were analyzed in this study. A total of 30 samples were collected from each of three districts. Samples were collected during August of 2004 using a previously described ultra-clean sampling technique (Stetzenbach et al. 1994), with modifications. Groundwater samples from the 10-m depth water-layer were collected in 125-ml PFA-Teflon bottles which were previously soaked in 20% nitric acid, followed by 20% hydrochloric acid, and rinsed with de-ionized water (>18.2 MΩ). Groundwater was collected after the well was flushed with at least 3 well volumes and after pH, temperature, and conductivity were stabilized. Samples were collected with a 0.45-μm groundwater filter (Gelman Science, Ann Arbor, MI, USA). The filters were placed directly on the pump outlet tubing, and water was allowed to pass through the filter for at least one min prior to collection. The water was pumped from the source using a peristaltic device equipped with acid-washed Teflon tubing. After sampling, samples were sealed in polyethylene bag and transported on ice to the laboratory. The samples were placed in a laminar flow hood and preserved by adding concentrated nitric acid to obtain a 0.02% solution. All samples were stored at 4 ℃ and analyzed within 24 hr of collection. Approximately 25 ml of groundwater sample was digested with 25 ml of nitric acid in a microwave digestion bomb (MD2000, CEM Corporation, Matthews, North Carolina, USA). Samples were analyzed by inductively coupled mass spectrometry method (Hall et al. 1996; Matschat et al. 1997). All samples were analyzed three times using a Perkin-Elmer Elan 5000 Inductively Coupled Mass Spectrometer (ICP-MS). The operating conditions were as follows: 1) Carrier gas (argon, 99.999%): 0.8 L/min; 2) plasma gas (argon, 99.999%): 13 L/min; 3) auxiliary gas (argon, 99.999%): 0.8 L/min; 4) pump rate: 1.5 ml/min; and 5) power: 1055 KW.

All chemicals used were of analytical-reagent grade. Aqueous stock solution (1000 mg/L) of Ga(III) and In (III) were prepared using $Ga(SO_4)_3$ and $In(SO_4)_3$ (Fluka Chemie AG, Basel, Switzerland). As(V) stock solution containing 1000 mg/L As was prepared by dissolving sodium arsenate (Na_2HAsO_4; ACS reagent) (Sigma, St. Louis, MO, USA) in 1% (v/v) HCl solution, diluted from 12 M HCl (Optima; Fisher, Pittsburgh, PA,USA). As(III) stock solution containing 1000 mg/L As was prepared by dissolving sodium m-arsenite ($NaAsO_2$) (Sigma, 96.7% purity) in 1% (v/v) HCl solution. Calibration curves were plotted from concentrations (0.002 to 10 μg/L) of Ga(III), In (III), As(III), and As(V) standards. The recovery yields of trace metals were 93%, 95%, 97%, and 98% for Ga(III), In (III), As(III) and As(V), respectively. The detection limits of trace metals were < 5 ng/L. Arsenic concentrations reported in this study include the concentration of As(III) and As(V).

To test for significant differences between district means (including the Science-based Industrial Park, North District, Hsiangshan District means), analysis of variance (F) and Kruskal-Wallis test were performed. Statistical analyses were conducted using $SPSS/PC^+$ (SPSS, Inc., Chicago, IL, USA). All tests were regarded as significant when $p< 0.05$.

RESULTS AND DISCUSSION

Our results could provide a database with which to gauge potential health risk or develop environmental strategy for controlling groundwater metal pollutants contributed by semiconductor industrial effluent.

Box-plots of target metal concentrations in HSIP, the North District, Hsiangshan District (the control) are given in Figure 1. In HSIP, metal concentrations in well water samples were 7.91-41.39, 0.95-20.05, 9.45-105.45 μg/L for Ga, In, As, respectively, and averaged 19.34, 9.25, and 34.19 μg/L, respectively. Their presence in decreasing order of concentration was arsenic > gallium > indium, and the concentration of arsenic was about 1.8 and 3.7 times that of gallium and indium, respectively. This decreasing order was also apparent in the North District and Hsiangshan District. A reasonable explanation is that the rate of arsenic compound use is higher than that of gallium or indium compounds. These results agreed with those of Chepesiuk (1999), Van Zant (2000), and Yuan (2004) who ranked semiconductor materials (in decreasing order of usage) as follows: As > Ga > In. The results demonstrated the arsenic is the major metal pollutant produced during semiconductor manufacturing processes. Concentrations were compared between groundwater sites in or near Hsinchu City to look for significant between-site differences. The results showed that mean levels of arsenic, gallium, and indium were significantly higher concentration in HSIP ($p<0.05$) than in the North District or Hsiangshan District (the control), suggesting gallium, indium, and arsenic (widely used in semiconductor manufacturing) were introduced into groundwater via industrial effluents. Differences in three metal levels between the North District and Hsiangshan District were not statistically significant ($p>0.05$), indicating that these contaminants had not spread to the control areas. Nevertheless, monitoring the groundwater concentrations of these metals should continue in these areas.

Table 1 list distribution and percentile of three trace metals, which were found in 90 wells of three districts. Arsenic was detected at concentrations exceeding the current limits in Taiwan for drinking water in 29 of the 30 well water samples collected from the industrial park. Percentile analysis of arsenic concentration revealed that levels in 96.7% of groundwater samples exceeded the limit (10 μg/L) and only 3.3% did not. Gallium concentrations exceeded 10 μg/L in 83.3% of groundwater samples and were 1-10 μg/L in about 17%. Gallium distributions were similar to those of arsenic, suggesting pollution. Indium concentrations were 0.05-10.0 μg/L in about 64% of samples.

The major range of Ga, In, and As concentrations in, respectively, about 93.3%, 100%, and 66.7% of samples from the North District was 0.01-1.00 μg/L. Overall, distribution of the groundwater metals concentrations in Hsiangshan District were all lower < 0.05 μg/L. Obviously, Ga, In, and As pollution of groundwater in the industrial park was significantly higher than in the other districts, suggesting semiconductor manufacturing polluted groundwater via industrial effluents.

The average arsenic concentration of groundwater was lower in the semiconductor industrial park (HSIP) in our study (34.19 μg/L) than in the endemic area of blackfoot disease in southern Taiwan (350-1100 μg/L) (Chen et al. 1985 and 1992), Nevada USA (1000 μg/L) (Warner et al. 1994), and Finland (980 μg/L) (Kurttio et al.,1998). However, the level exceeded the Environmental Protection Agency limit for arsenic (EPA, Taiwan 1997). Exposure to inorganic arsenic can elevate the risk of bladder, skin, and other cancers. The risk assessment forum has completed an assessment of the carcinogenicity risk associated with ingestion of inorganic arsenic (EPA USA, 1988). The multistage model was used to predict dose-specific cancer risk associated with ingestion of inorganic arsenic. Expressed as a single value, the cancer unit risk for drinking water is 5×10^{-5} per (μg/L). The risk of cancer mortality in Hsinchu residents in the semiconductor industrial park (HSIP) can be estimated from their consumption

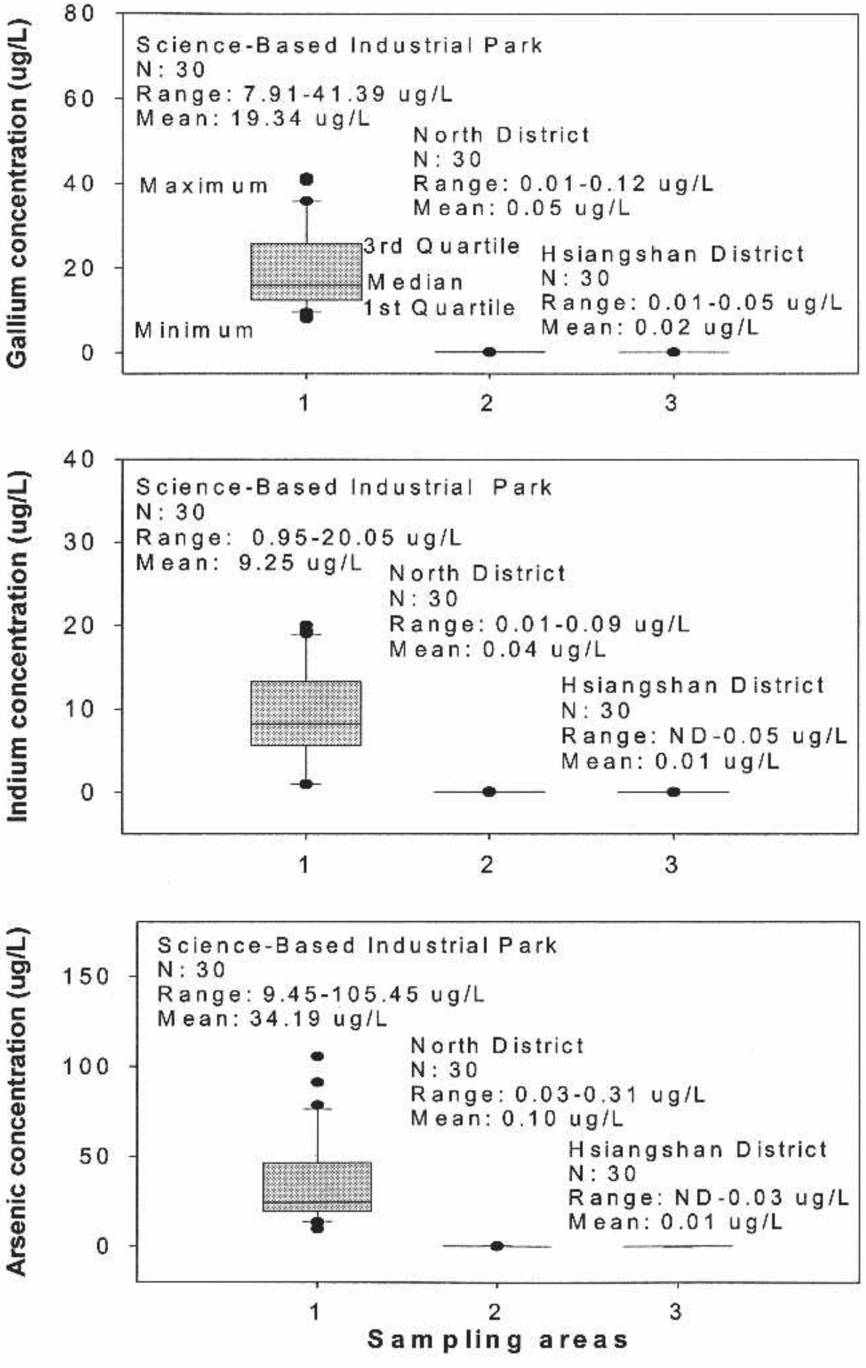

Figure 1. Box-plots of groundwater metal concentrations in sampling districts (Area 1: Science-Based Iindustrial Park, Area 2: North District, Area 3: Hsiangshan District; N: sample number).

Table 1. Distribution and percentile of groundwater metal concentrations in sampling districts.

Gallium levels (μg/L)	Science-Based Industrial Park		North District		Hsiangshan District	
	No. of Wells	Percentile (%)	No. of Wells	Percentile (%)	No. of Wells	Percentile (%)
< 0.01	0	0	0	0	0	0
0.01-0.05	0	0	15	50.0	30	100.0
0.051-1.00	0	0	13	43.3	0	0
1.01-10.00	5	16.7	2	6.7	0	0
>10	25	83.3	0	0	0	0
Indium levels (μg/L)	**Science-Based Industrial Park**		**North District**		**Hsiangshan District**	
	No. of Wells	Percentile (%)	No. of Wells	Percentile (%)	No. of Wells	Percentile (%)
< 0.01	0	0	0	0	2	6.7
0.01-0.05	0	0	21	70.0	28	93.3
0.051-1.00	4	13.3	9	30.0	0	0
1.01-10.00	15	50.0	0	0	0	0
>10	11	36.7	0	0	0	0
Arsenic levels (μg/L)	**Science-Based Industrial Park**		**North District**		**Hsiangshan District**	
	No. of Wells	Percentile (%)	No. of Wells	Percentile (%)	No. of Wells	Percentile (%)
< 0.01	0	0	0	0	4	13.3
0.01-0.05	0	0	6	20.0	26	86.7
0.051-1.00	0	0	14	46.7	0	0
1.01-10.00	1	3.3	10	33.3	0	0
>10	29	96.7	0	0	0	0

of arsenic, which was about 1.7×10^{-3}. The present study is first to monitor the gallium and indium levels in groundwater. Permissible levels of gallium and indium in groundwater have not been established. Groundwater levels of gallium were higher in the semiconductor industrial park (19.34 μg/L) than in Ikeda Lake, Japan (0.014 μg/L, lake-water) (Kiriyama and Kuroda 1988) or Hsiangshan District (0.02 μg/L). The difference demonstrates that groundwater has been contaminated via industrial effluents. Because they drink Ga and In contaminated groundwater, Hsinchu residents may be at increased risk for immune system diseases and for reduced blood leukocyte counts (Betoulle et al. 2002; Burns et al. 1991).

The groundwater levels of Ga, In, and As also indicate that the semiconductor industry in the region has affected this groundwater. Gallium, indium, and arsenic levels of groundwater of may be of great interest in the Hsinchu area springs because of the potential impact on lifespan and health. We suggest that wastewater treatment and management of high-tech semiconductor manufacturing be used to reduce Ga, In, As levels of industrial effluents. There are no criteria or standards for Ga, In. We should be further developed determination technique to monitor real-time and long-term pollution of Ga, In, As. The impact of long-term exposure to elevated levels of Ga, In, and As is still debatable and further study is clearly warranted. Finally, the data from this study can assist the EPA of Taiwan to develop a groundwater management strategy for protecting the public health.

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