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Heavy metals and VOCs contamination of urban groundwaters in Seoul, Korea

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Abstract

We measured the concentrations of heavy metals and VOCs in groundwaters (N=38) in Seoul. The comparison of our data with U.S. Environmental Protection Agency's Maximum Contaminant Levels for Drinking Water and with the Korean Drinking Water Standards shows that most of the metals except for Fe and Mn do not exceed the levels. However, the concentrations of most heavy metals (esp., Zn, Cu, Cr, Ni) tend to increase in residential and industrialized areas. The examination of the metal speciation using Anodic Stripping Voltammetry (ASV) and TOC analyzer indicates that large amounts of Zn occur as labile metal fraction, whereas Cu occurs as non-labile forms at many sites, possibly due to its tendency to be adsorbed onto inorganic colloidal particles to form electroinactive species in groundwater. The most frequently existed VOCs in Seoul groundwaters are trichloroethylene and tetrachloroethylene, especially in agricultural, industrial, and high traffic areas.

Key words: heavy metals, VOCs, urban groundwater, Seoul

1. Introduction

The contamination of urban groundwaters in densely populated metropolitan area such as Seoul is an important environmental issue and is affected by very compositive sources. Heavy metals and VOCs in urban areas are important ambient pollutants because of their detrimental effects on human health, and are originated from diverse point and non-point sources. Major sources of heavy metal pollution include the storage of hazardous materials and wastes, atmospheric precipitates such as aerosol, and fine particles which is associated with vehicle exhaust. The sources of VOCs in urban area contain vehicle exhaust, gasoline evaporation, emission of organic solvents from factory, oil leakage due to accident, and fertilizer (Kourtidis et al., 1999; Lee et al., 2001).

Many researches related to heavy metals contamination have been carried out in Korea. However, the study on heavy metals and VOCs contamination in urban groundwaters is scarce. Due to a rapid economic growth since early 1960s, Seoul has serious environmental problems because of an intense urbanization and industrialization. In the end of 2001, the number of registered vehicles in Seoul is over 2.55×10^6. More than two million vehicles consumes extraordinary amount of oil ($>8 \times 10^7$ barrels annually). Residential and road areas also result in the emission of domestic sewage (about 1.5×10^4 tons/day), automobile pollutants, de-icing chemicals and so on. Precipitation through city parks and gardens, roads, and impermeable roofs may recharge those anthropogenic pollutants into urban groundwaters (Barrett et al., 1999). Therefore, this study aims to investigate the distribution and occurrence of heavy metals and VOCs and the speciation (complexation) of heavy metals in urban groundwaters of Seoul.

2. Methods

Field campaigns for this study have been done for 38 monitoring sites in September 2001. Based on land-use characteristics, the sampling sites were classified into five areas: less-contaminated, residential, agricultural, traffic, and industrialized. The concentrations of heavy metals were analyzed by ICP-MS (Perkin-Elmer SCIEX ELAN 6000). In order to determine the concentrations of electrochemically labile fraction of Cu, Pb, and Zn, the filtered and non-acidified water samples were also analyzed by ASV (Chemtronics TEA-3000). The DOC concentrations were analyzed for filtered samples using the combustion/non-dispersive infrared gas analysis method by Total Organic Carbon Analyzer (TOC-5000A). The samples were also analyzed for forty kinds of VOC using gas chromatography (HP 5890) directly

Table 1. Heavy metals concentrations of urban groundwaters in Seoul.

Site characteristics		Dissolved constituents(㎍/l)										
		Fe	Mn	Co	Ni	As	Se	Cr	Pb	Zn	Cd	Cu
Less-contaminated	range	33.9-249.9	0.1-3.3	0.02-0.2	n.d.-3.0	1.3-4.7	0.5-3.9	n.d.-0.4	n.d.-0.1	7.2-23.3	0.01-0.03	n.d.-9.3
(n=6)	mean	101.4	1.5	0.1	1.2	2.7	1.1	0.3	0.1	16.4	0.0	3.8
Residential	range	178.8-259.4	0.3-722.4	0.2-2.5	0.2-4.0	3.1-4.5	1.2-2.7	n.d.-6.3	n.d.-1.0	17.3-298.9	0.03-0.07	2.6-3212.6
(n=6)	mean	208.0	123.1	0.6	1.6	3.7	2.0	2.9	0.4	94.1	0.1	469.6
Agricultural	range	25.0-197.5	0.3-32.7	0.02-0.5	n.d.-7.9	1.4-4.0	0.4-1.8	n.d.-2.0	n.d.-0.4	11.0-935.1	0.01-0.05	3.4-160.1
(n=5)	mean	106.9	10.8	0.2	2.4	2.6	1.1	2.0	0.3	245.0	0.0	47.8
Traffic	range	33.0-354.8	0.7-148.4	0.00-0.5	n.d.-4.2	2.3-4.7	0.5-21.3	n.d.-6.1	0.02-0.6	2.70-392.7	0.01-0.05	0.6-26.7
(n=13)	mean	212.5	28.4	0.2	1.6	3.5	3.0	2.9	0.2	75.4	0.0	7.2
Industrialized	range	134.3-5521.6	0.4-1432.1	0.1-1.5	1.2-21.1	2.6-6.1	1.0-3.0	1.0-13.5	0.1-23.5	14.2-294.3	0.02-0.34	0.6-117.5
(n=8)	mean	883.0	236.6	0.6	5.3	4.1	1.8	5.7	3.1	93.0	0.1	28.5
Standards	EPA[1)]	300	50			50	50	100	15	5000	5	1300
	Korea[2)]	300	300			50	10	50	50	1000	10	1000

1) U.S. EPA's Maximum Contaminant Levels (MCLs) for drinking water (U.S. EPA, 2001)

2) Korean Drinking Water Standard (MOE, 2002)

n.d. = not detected (below the detection limit)

interfaced with a HP5970 mass selective detector (MSD). For the extraction and concentration of water samples, Tekmar LSC 3000 sample concentrator and ALS 2016 were used.

3. Results and Discussion

3.1. Heavy metals

Heavy metals transported from catchments to urban groundwaters is originated from several sources, including agriculture and other types of land-use, natural weathering of rocks and soils, emissions from anthropogenic activities, and atmospheric deposition from local and/or regional sources (Lindstrom et al., 2001). In order to investigate the characteristics of heavy metal concentrations in relation to local land-use and to study the complexation of heavy metals with DOC, we analyzed the heavy metal concentrations by ICP-MS and ASV. Most of the heavy metals examined, except for Fe and Mn, did not exceed the contamination

Table 2 . The concentrations of Zn and Cu in groundwaters in Seoul. as analyzed by ICP-MS (for total concentrations) and ASV (for labile concentrations)

Sample No.	Site characteristics	Zn ICPMS	Zn ASV	labile (%)	Cu ICPMS	Cu ASV	labile (%)
DB-2	Less-contaminated	10	8	84	5	<1	
KB-2	(n=6)	13	4	32	11	6	55
KB-3		22	16	72	8	<1	
SCH-2		23	10	43	14	2	14
KA-2		<1.5	8		5	<1	
CR-6		23	22	94	11	<1	
JR-1	Residential	45	30	67	10	<1	
JR-4	(n=6)	17	4	23	48.0	18	38
KA-1		18	6	34	8	<1	
YC-1		24	14	59	8	<1	
NW-3		96	32	33	11	<1	
NW-4		160	47	29	36	20	56
KS-1	Agricultural	168	40	24	30	22	73
KS-4	(n=5)	935	260	28	21.0	6	29
KS-6		11	0.05	0.5	204	102	50
SCH-3		70	38	54	8	2	25
SCHO-6		40	0.05	0.1	52.0	44	85
CR-1	Traffic	28	22	78	11	<1	
CR-2	(n=13)	30	20	67	11	<1	
CR-3		26	4	15	37	30	81
CR-8		10	6	58	9	8	89
CR-9		77	12	16	18	6	33
JR-2		299	86	29	4106	1540	38
JG-6		173	148	85	8	<1	
JG-7		393	238	61	6	<1	
JG-8		46	32	69	10	<1	
JG-9		28	24	87	6	<1	
JG-10		52	48	92	6	2	33
JG-12		10	4	40	6	<1	
JG-13		38	16	42	29	<1	
GR-2	Industrialized	61	0.05	0.1	150.0	108	72
GR-3	(n=8)	86	0.05	0.1	118.0	90	76
GR-6		33	22	68	11	<1	
GR-7		294	189	64	7	<1	
GR-9		112	44	39	8	<1	
KCH-2		119	74	62	11	<1	
YP-2		14	10	70	7	<1	
YP-3		24	0.05	0.2	6	<1	

Table 3. Dissolved organic carbon (DOC) concentrations in groundwaters in Seoul

Sample No.	Site characteristics	DOC (ppm)
DB-2	Less-contaminated	0.51
KB-2	(n=6)	1.06
KB-3		0.35
SCH-2		0.87
KA-2		0.55
CR-6		1.22
JR-1	Residential	0.89
JR-4	(n=6)	1.52
KA-1		0.49
YC-1		0.59
NW-3		0.67
NW-4		0.61
KS-1	Agricultural	0.67
KS-4	(n=5)	0.71
KS-6		0.22
SCH-3		0.36
SCHO-6		0.60
CR-1	Traffic	0.75
CR-2	(n=13)	1.39
CR-3		0.78
CR-8		1.33
CR-9		0.75
JR-2		0.34
JG-6		1.52
JG-7		1.28
JG-8		1.24
JG-9		1.10
JG-10		1.54
JG-12		0.79
JG-13		1.82
GR-2	Industrialized	0.59
GR-3	(n=8)	0.95
GR-6		0.53
GR-7		0.39
GR-9		0.61
KCH-2		0.72
YP-2		0.48
YP-3		0.65

levels according to U.S. EPA's MCLs and Korean DWLs (Table 1). Comparison of the data from less-contaminated area with those from other areas, however, shows that some metals such as Zn, Cu, Cr, and Ni tend to be larger in amounts for residential and industrialized areas. This may indicate that heavy metal pollution is proceeding in groundwaters.

For the metals Cu, Pb, and Zn, the comparison of ICP-MS data with ASV data reflects that Cu and Pb tend to be existed mostly in electrochemically less available forms, whereas Zn occurs mostly in more available and mobile forms (Table 2). Such electrochemically non-labile forms (of Cu and Pb) may represent the adsorption onto inorganic colloidal particles. If considered the lower concentrations of inorganic anions for groundwaters in less-contaminated area, however, the presence of non-labile, organic complexes of Cu and Pb cannot be excluded. For the waters from agricultural area, where total anions were larger in amounts due to their derivation from fertilizer and manure, the role of organic complexation would be important, as indicated by the lower fraction of labile Zn. It is well known that DOC may form complexes with heavy metals even in low concentrations and thus plays an important role for controlling heavy metal speciation (Christensen et al., 1999). In groundwaters in Seoul, DOC is usually present in low concentrations (below 1.8 ㎎/ℓ; Table 3).

3.2. VOCs

For the 38 collected samples, data of VOCs are summarized in Table 4. Among the forty species analyzed, two species of alkyl benzenes (toluene, tert-Butylbenzene) and one species of ethers (MTBE), that are usually originated from automobile emissions, were detected but did not exceed the contamination levels (MCLs) in USA and Korea. Any relationship with local land use characteristics was not recognized. In the case of halogenated alkanes, twelve species (methylene chloride, chloroform, carbon tetrachloride, bromodichloromethane, dibromochloromethane, bromoform, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloroethane, 1,2-dichloropropane, 1,1,2-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane) were detected in small concentrations. Chloroform is usually emitted from wastewater treatment plants (Nikolaou et al., 2002) was detected in very small concentrations (<27.0 ppb) in all sites. Among the detected halogenated alkenes, i.e., cis-1,2-dichloroethylene, 1,1-dichloroethylene, trichloroethylene (TCE), tetrachloroethylene (PCE), contamination of TCE and PCE is recognizable in Seoul. In average concentration of TCE, the highest concentration was observed in industrial area (372.4 ppb), followed by agricultural (9.0 ppb), residential (4.4 ppb), traffic (1.5 ppb), and less-contaminated area (not detected). The mean concentrations of PCE also were higher in industrialized area (176.9 ppb) and traffic area (14.2 ppb); from the other areas, PCE was not detected. The comparison with MCLs shows that TCE in industrialized and agricultural areas are dangerous and should be monitored carefully. However, very wide variations of VOCs concentration within a specific areal type indicate that sources of most VOCs are very local and highly complicated.

Table 4. VOCs concentrations in groundwaters in Seoul

Site characteristics	(μg/l)	Alkyl benzenes		Ethers	Halogenated alkenes			
		toluene	tert-Butylbenzene	MTBE	cis-1, 2-Dichloroethylene	Trichloroethylene	Tetrachloroethylene	1, 1-Dichloroethylene
Less-contaminated (n=6)	range	0.2-0.5		2.9				
	mean	0.3		2.9				
Residential (n=6)	range	0.2-0.2	0.2	0.8-2.2	0.5	0.5-8.2		1.5
	mean	0.2	0.2	1.5	0.5	4.4		1.5
Agricultural (n=5)	range	0.2-0.3	0.2		0.6	5.4-11.5		8.5
	mean	0.2	0.2		0.6	9.0		8.5
Traffic (n=13)	range	0.1-0.2	0.2	0.6-5.5	0.7-20.3	0.3-3.2	3.4-35.4	0.5
	mean	0.2	0.2	2.0	5.8	1.5	14.2	0.5
Industrialized (n=8)	range	0.2-0.3	0.2	1.0-1.3	0.1-10.0	0.7-1429.9	0.7-353.0	0.8
	mean	0.3	0.2	1.1	5.0	372.4	176.9	0.8
Standards	EPA[1)]	1000		20-40	70	5	5	7
	Korea[2)]	700				30	10	30
detection limit		0.1	0.1	0.5	0.5	0.2	0.5	0.2

Site characteristics	(μg/l)	Halogenated alkanes						
		Methlyene chloride	Chloroform	Carbon tetrachloride	Bromodichloromethane	Dibromochlormethane	Bromoform	1, 1-Dichloroethane
Less-contaminated (n=6)	range	0.3-3.0	0.1-0.4					
	mean	1.5	0.3					
Residential (n=6)	range	0.7-2.7	0.3-6.1		0.5-1.4	1.1	0.6	1.4
	mean	1.6	4.0		0.8	1.1	0.6	1.4
Agricultural (n=5)	range	0.4-2.5	0.3-0.5					0.7-1.0
	mean	1.5	0.4					0.9
Traffic (n=13)	range	1.5-9.3	0.4-5.0	0.2	0.5-0.8			7.0
	mean	4.0	1.7	0.2	0.6			7.0
Industrialized (n=8)	range	1.6-4.0	0.1-27.0	0.2-2.0	0.1-0.6			0.3-10.4
	mean	2.5	8.5	0.8	0.5			3.1
Standards	EPA[1)]	5		5	0	60		
	Korea[2)]	20	80	2				
detection limit		0.2	0.1	0.1	0.1	0.5	0.2	0.2

Site characteristics	(μg/l)	Halogenated alkanes				
		1, 1, 1-Trichloroethane	1, 2-Dichloroethane	1, 2-Dichloropropane	1, 1, 2-Trichloroethane	1, 1, 2-Trichloro-1, 2, 2-trifluoroethane
Less-contaminated (n=6)	range					
	mean					
Residential (n=6)	range	0.1-2.0				
	mean	1.1				
Agricultural (n=5)	range	19.4-21.5	1.25			10.3
	mean	20.5	1.3			10.3
Traffic (n=13)	range	0.1-1.0				
	mean	0.4				
Industrialized (n=8)	range	0.6-115.1	0.3-8.0	1.4-5.1	0.7	
	mean	34.5	4.2	3.2	0.7	
Standards	EPA[1)]	200	5	5	5	
	Korea[2)]	100				
detection limit		0.1	0.1	0.2	0.2	0.1

1) U.S. EPA's Maximum Contaminant Levels (MCLs) for drinking water (U.S. EPA, 2001)

2) Korean Drinking Water Standard (MOE, 2002)

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