

Chemical Compositions in Rainwater at Hiroshima Prefecture, Japan

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(Received Feb. 6, 2002)

Abstract : From May 1999 to July 2000, concentration of 17 metals (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, Zn), 4 ions (NH_4^+ , Cl^- , NO_3^- , SO_4^{2-}) and pH in rainwater were investigated. The volume-weighted mean concentrations (VWM) of NO_3^- and SO_4^{2-} were 16.0 and 17.0 $\mu\text{mol L}^{-1}$. The average pH was 4.53, which ranged from 3.83 to 6.06. The characteristic variations of these species were investigated in terms of the source of these species by principal component analysis (PCA) and interelement correlation coefficients. The elements were classified into three categories: anthropogenic source (Cd, Cu, Fe, Ni, Pb, V, Zn, NH_4^+ , NO_3^- , SO_4^{2-} and H^+), soil and crust dust (Al, Ba, Ca, Fe, Mn) and sea salts (Mg, Na, Cl).

In addition, we compared the concentrations in rainwater, which were taken on the same day in three sites (Higashi-Hiroshima, an urban-facing area and a mountain-facing area of Mt. Gokurakuji) in order to examine the regional effect against the concentrations in them. At the urban-facing area of Mt. Gokurakuji, the concentrations of chemical compositions were higher than other areas.

Key words : rainwater, chemical composition, regional effect and Higashi-Hiroshima.

1. Introduction

Acidification of rainwater and other atmospheric aqueous forms arises mainly from the atmospheric oxidation of sulfur and nitrogen. It is well recognized that trace metals present in atmospheric waters play an important role in aqueous phase oxidation of these acid rain precursors, such as Fe, Mn and Cu. Both Fe and Mn can catalyze the oxidation of S (IV) by oxygen, and together they have a synergistic effect.¹⁻⁴ Trace metals work not only micronutrients to marine organisms

(eg. Fe⁵) but also toxic material to human health according to bioaccumulation after deposition (eg. Pb and Cu etc). These metals are deposited on the surface of water or land by dry fallout and wet deposition. In wet deposition, aerosols and gases are dissolved or suspended in precipitation: rain, hail, fog and mist. Dry deposition of particles occurs by direct impaction and gravitational setting on land or water surfaces.⁶

Monitoring of the concentrations of chemical species in the atmosphere provides important information about the sources and the enabled flux amount of them. In particular, it is very important information for studying acid precipitation and related environmental problems in fast economic growing regions such as the East Asian

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region. The region's fast growing economy, based on heavy industry has led to increased usage of fossil fuels, resulting in increased emission of chemical species such as heavy metals, SO₂ and NO_x. A large amount of atmospheric pollutants from the Asian Continent may be transported to the Pacific Ocean by meteorological phenomena. Several studies have examined major ions, but only few study for trace metals in wet deposition collected in the East Asian region.⁷⁻⁹

In this paper, we report on the concentration of 17 metals (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, Zn), 4 ions (NH₄⁺, Cl⁻, NO₃⁻, SO₄²⁻) and pH in rainwater collected in Higashi-Hiroshima, Japan for 14 months (May, 1999 - July, 2000). The purpose of this study was to investigate their characteristic variations in terms of the source of atmospheric elements by principal component analysis (PCA) and used interelement correlation coefficients. In addition, we compared the concentrations in rainwater, which were taken on the same day in three sites that were Higashi-Hiroshima (semi-rural area), an urban-facing area (urban area) and a mountain-facing area (rural area) of Mt. Kokurakuji in order to examine the regional effect against the concentrations in rainwater.

2. Experimental section

2.1 Reagents

Fe working solutions were prepared by diluting a commercial AAS standard solution (1000 mgL⁻¹, Wako chemical. Co.) and them of other metals were used ICP-MS standard solution (100 mgL⁻¹, SPEX). HNO₃ and H₂O₂ were purchased from Tama chemical. Co. (pure 100 series). Other reagents were super special grade (Katayama Chemicals) and N, N-dimethyl-p-phenylene diamine dichloride (Wako chemical. Co.) used without further purification.

2.2 Instruments

An ICP/MS (Perkin Elmer-Sciex, Elan 5000) was used for analyzing heavy metals (Al, Ba, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Sr, V, Zn) as described by Takeda⁹ in

detail. The concentration of Na, Ca, Mg and K were determined by ICP-AES (Perkin Elmer, Optima 3000) equipped with an ultrasonic nebulizer (Cetec, U-5000AT). The analytical parameters for ICP/MS and ICP-AES were summarized in Table 1. The FIA system was used for analyzing dissolved Fe as described by Kim.^{10,11} Ion chromatography (Dionex, DX 500 series) was used for analyzing ions (NH₄⁺, Cl⁻, NO₃⁻, SO₄²⁻).

Table 1. The parameters for ICP/MS and ICP-AES measurements

Parameters	ICP/MS	ICP-AES
Plasma		
RF power	1000 W	1300 W
Plasma Ar gas flow rate	15 mLmin ⁻¹	15 mLmin ⁻¹
Auxiliary Ar gas flow rate	0.8 mLmin ⁻¹	0.5 mLmin ⁻¹
Nebulizer Ar gas flow rate	0.83-0.85 mLmin ⁻¹	0.8 mLmin ⁻¹
Mass Spectrometer		
Dwell time	2000 ms	-
Scanning mode	Peak Hop	-
Spectral peak processing	Integrated	-
Point/pectral peak	5	-
Number of replicates	5	-
Sample uptake rate	1.25 mLmin ⁻¹	1.5 mLmin ⁻¹

2.3 Sampling

Samples were collected manually using Teflon-coated polyethylene (PE) funnels with an opening diameter 24 cm (or 30 cm) and PE sample bottles screwed into the funnels neck. They were set just before a precipitation event, then immediately transported to the laboratory (class 100) after event. After weighting of sample bottle, sample was divided into two: one was for pH measurements and the other was filtered with a 0.45 μm PTFE membrane filter (Millipore, Omnipore). The filtered sample was used for the analysis of 17 metals and 4 ions.

Samples were taken on the roof of the Higashi-Hiroshima campus building of Hiroshima University at Higashi - Hiroshima, which has a population of about 120,000 and is located 35 km east of Hiroshima. On the same day that rain samples were collected at Hiroshima University, addition rain samples were also collected on the southern slope

(urban-facing area) and northern slope (mountain-facing area) of Mt. Gokurakuji in Hatsukaichi, is located 20 km west of the Hiroshima (Fig. 1).

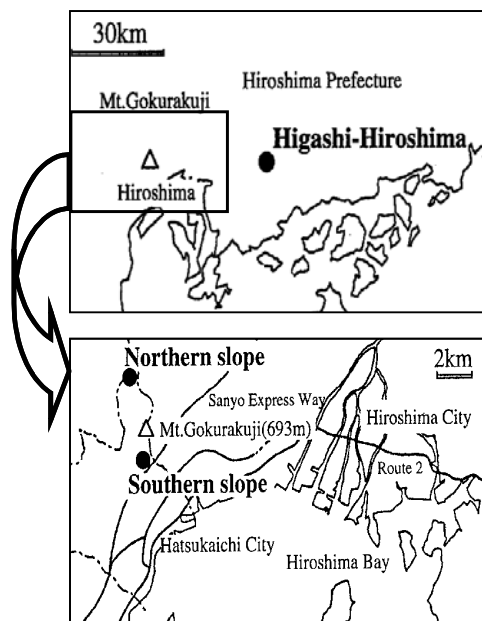


Fig. 1. Sampling site of rainwater.

- Higashi-Hiroshima (Semi-rural area)
- Northern slope (Mountain facing area)
- Southern slope (Urban facing area)

Sampling bottles were cleaned as follows: (1) they were placed into 2% Extran solution (Merck, Extran MA-01) for at least 24 hours, (2) leached with 1 M HCl for least 24 hours, (3) filled 0.5 M HNO₃, and left for 5 days, (4) rinsed with Milli-Q water (MQW, <18 M Ω), filled with MQW, then allowed to stand for 3 days, (5) finally rinsed with MQW and dried. Another plasticware was placed into 2% Extran solution for at least 24 hours and leached 1 M HCl or HNO₃ for least 48 hours and rinsed with MQW.

3. Results and discussion

3.1 Chemical composition of precipitation

68 rainwaters were sampled from May 1999 to July

2000 at Higashi-Hiroshima with the exception of over 50 mm per one event that have a pouring rain such as Typhoon. All precipitation volume was 1156 mm during sampling period. To check on the quality of the analysis, the rate of anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na, Ca, Mg, K, H⁺ and NH₄⁺) were calculated.¹² The average of cation/anion ratio (ion balance) was 1.063 with a range 0.889-1.324 (Fig. 2A).

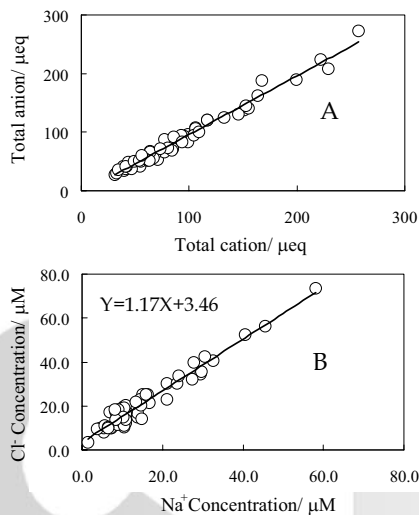


Fig. 2. Relationship between ion balance between total anion and cation(A) and Na⁺ and Cl⁻ concentrations(B).

The high value of ion balance seems to be due to the unmeasured organic acids such as oxalic acid, formic acid and acetic acid in rainwater.¹³ Miyake reported the presence of them at Higashi-Hiroshima.¹⁴ The precipitation volume weighted mean concentrations (VWM) and these ranges for 17 metals, 4 ions and pH were summarized in Table 2. VWM of most elements were higher than previous report, but pH was similar to previous report.⁹ It could anticipate that increased NO₃⁻ and SO₄²⁻ were neutralized by high concentration of NH₄⁺. Fig. 2B showed the relationship of Na⁺ and Cl⁻ in rainwater. Though the ratio of Cl⁻/Na⁺ in rainwater was similar to them in seawater (Cl⁻/Na⁺ = 1.16), surplus Cl⁻ was measured in this study. The increment of elements could associate with increment of gaseous or particulate

emission from fossil fuel combustion and industrial active than them at previous study.⁹

Table 2. Precipitation volume weight mean(VWM), ranges and median of chemical species in rainwater at Higashi-Hiroshima(n=68, May 1999-July 2000)

Elements	VWM	Range		Median	Previous report ⁹
		Min.	Max.		
unit: μgL^{-1}					
Precipitation	1156 mm				
pH	4.53 ^a	3.83	6.06	4.45	4.55 ^a
Al	6.07	1.08	38.5	7.21	6.06
Ba	0.68	0.08	3.60	0.83	0.37
Ca	68.4	2.17	522	71.7	94.5
Cd	0.44	0.06	3.04	0.42	0.06
Cr	0.49	0.03	2.62	0.27	-
Cu	2.16	0.12	12.6	1.36	0.62
Fe	2.47	0.29	22.2	3.91	-
K	78.9	5.76	588	72.4	28.1
Mg	42.3	9.27	188	46.5	25.8
Mn	2.72	0.15	18.2	3.08	1.64
Mo	0.16	0.07	0.89	0.11	-
Na	276	24.8	1330	340	154
Ni	0.45	0.03	3.08	0.36	0.26
Pb	4.35	0.05	40.9	4.57	1.24
Sr	0.43	0.08	1.99	0.51	0.13
V	0.49	0.05	3.03	0.32	0.23
Zn	10.6	0.84	46.9	12.0	4.77
*Cl	15.6	3.50	45.1	17.8	10.4
*NO ₃ ⁻	16.0	2.80	90.6	18.9	14.8
*NH ₄ ⁺	17.0	5.20	71.3	19.9	14.7
*SO ₄ ²⁻	17.0	6.71	94.1	18.2	12.0
nss-Ca	62.5	1.63	495	66.8	85.7
*nss-SO ₄ ²⁻	16.8	5.04	70.8	19.7	14.3

Unit of precipitation : mm

*Unit : μmolL^{-1}

^a: Average value

3.2 To reveal the origin of elements

In generally, to reveal the origin of elements in environmental samples, some researchers carried out principal component analysis (PCA) and used interelement correlation coefficients.^{7,9,13} The PCA was performed on the whole data set to learn about the source characteristics that make up the sampled rainwater and about possible correlations between certain chemical species. The correlation matrix of the observed variables is examined to reduce the number of descriptive variables into a smaller set of

independent variables, the principal components in PCA. The PCA was carried out followed by varimax rotation to a set of orthogonal axes for 68 rain samples in which the concentrations for 17 elements and 5 ions (including H⁺ to calculate from pH) using the SPSS program (SPSS Inc.), and summarized result of at Table 3.

Table 3. Principal component analysis of rain samples at Higashi-Hiroshima

Elements	Rotated factor loading			
	Factor 1	Factor 2	Factor 3	Factor 4
Al	0.369	0.710	0.143	0.204
Ba	0.321	0.756	0.227	0.164
Ca	0.344	0.767	0.170	0.332
Cd	0.731	0.387	0.179	0.113
Cr	0.126	0.198	0.906	0.082
Cu	0.751	0.335	0.323	0.080
Fe	0.429	0.742	0.007	0.182
K	0.167	0.693	0.382	0.339
Mg	0.241	0.503	0.293	0.599
Mn	0.355	0.692	0.171	0.278
Mo	0.178	0.090	0.871	0.138
Na	0.252	0.395	0.265	0.772
Ni	0.281	0.302	0.752	0.138
Pb	0.775	0.236	0.102	0.239
Sr	0.421	0.744	0.256	0.111
V	0.789	0.256	0.279	0.158
Zn	0.765	0.384	0.292	- 0.001
H ⁺	0.739	0.215	- 0.026	0.282
NH ₄ ⁺	0.578	0.312	0.184	0.382
Cl ⁻	0.215	0.188	0.030	0.893
NO ₃ ⁻	0.541	0.506	0.195	0.412
SO ₄ ²⁻	0.752	0.479	0.154	0.317

The factor 1 group could be considered to be derived from anthropogenic sources, since Cd, Cu, Pb, V, Zn, H⁺, and SO₄²⁻ were major components in this group. They were emitted from combustion of fossil fuel and industrial waste. The factor 2 was consisted of Al, Ba, Ca, Mn and Fe, which originated from soil (crust) dust. Cr, Mo and Ni were involved in factor 3 group to anticipate another anthropogenic source group. They were used in metal industry such as harden steel, stainless steel. Especially, Mo was used in certain nickel-based alloys, which was heat-resistant and corrosion-resistant to chemical solutions. The factor 4 could be considered components of sea salts (Na, Mg, Cl).

Table 4. The inter-elements correlation coefficients in rain at Higashi-Hiroshima

	Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Mo	Pb	Sr	V	Zn	H ⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	
Al	1.00																						
Ba	0.70 **	1.00																					
Ca	0.72 **	0.86 **	1.00																				
Cd	0.56 **	0.48 **	0.52 **	1.00																			
Cr	0.15 **	0.25 **	0.29 **	0.46 **	1.00																		
Cu	0.52 **	0.44 **	0.48 **	0.85 **	0.42 **	1.00																	
Fe	0.79 **	0.72 **	0.72 **	0.56 **	0.23	0.51*	1.00																
K	0.63 **	0.83 **	0.90 **	0.48 **	0.31 *	0.39 **	0.71 **	1.00															
Mg	0.62 **	0.71 **	0.73 **	0.52 **	0.35 **	0.52 **	0.52 **	0.74 **	1.00														
Mn	0.86 **	0.80 **	0.85 **	0.56 **	0.23	0.53 **	0.82 **	0.74 **	0.68 **	1.00													
Na	0.46 **	0.58 **	0.68 **	0.54 **	0.45 **	0.44 **	0.68 **	0.68 **	0.74 **	0.55 **	1.00												
Ni	0.37 **	0.45 **	0.49 **	0.65 **	0.81 **	0.58 **	0.46 **	0.46 **	0.36 **	0.40 **	0.58 **	1.00											
Mo	0.56 *	0.31 **	0.34 **	0.48 **	0.80 **	0.44 **	0.33 **	0.33 **	0.36 **	0.23 **	0.31 **	0.81 **	1.00										
Pb	0.57 **	0.51 **	0.50 **	0.79 **	0.42 **	0.70 **	0.44 **	0.44 **	0.46 **	0.58 **	0.53 **	0.67 **	0.61 **	1.00									
Sr	0.69 **	0.87 **	0.91 **	0.63 **	0.35 **	0.55 **	0.83 **	0.83 **	0.68 **	0.80 **	0.59 **	0.51 **	0.36 **	0.59 **	1.00								
V	0.44 **	0.45 **	0.49 **	0.84 **	0.45 **	0.85 **	0.46 **	0.46 **	0.50 **	0.51 **	0.48 **	0.63 **	0.51 **	0.77 **	0.58 **	1.00							
Zn	0.59 **	0.55 **	0.55 **	0.85 **	0.48 **	0.80 **	0.52 **	0.52 **	0.50 **	0.64 **	0.54 **	0.71 **	0.56 **	0.83 **	0.63 **	0.86 **	1.00						
H ⁺	0.62 **	0.46 **	0.49 **	0.67 **	0.20 **	0.70 **	0.37 **	0.37 **	0.42 **	0.60 **	0.41 **	0.48 **	0.48 **	0.63 **	0.52 **	0.69 **	0.72 **	1.00					
NH ₄ ⁺	0.65 **	0.58 **	0.62 **	0.71 **	0.38	0.61 **	0.60 **	0.60 **	0.53 **	0.64 **	0.58 **	0.59 **	0.38 **	0.78 **	0.62 **	0.71 **	0.78 **	0.67 **	1.00				
Cl ⁻	0.32 **	0.40 **	0.46 **	0.31 **	0.11	0.22	0.55 **	0.55 **	0.60 **	0.34 **	0.80 **	0.18	0.16 **	*	0.39 **	0.25	0.25	0.31 *	0.39 **	1.00			
NO ₃ ⁻	0.70 **	0.64 **	0.72 **	0.70 **	0.42 **	0.66 **	0.65 **	0.65 **	0.64 **	0.69 **	0.65 **	0.61 **	0.48 **	0.65 **	0.71 **	0.71 **	0.77 **	0.78 **	0.85 **	0.40 **	1.00		
SO ₄ ²⁻	0.70 **	0.67 **	0.74 **	0.82 **	0.40 **	0.79 **	0.69 **	0.69 **	0.63 **	0.76 **	0.67 **	0.64 **	0.49 **	0.82 **	0.82 **	0.89 **	0.89 **	0.87 **	0.87 **	0.45 **	0.87 **	1.00	

** The significant level $p < 0.01$ * The significant level $p < 0.05$

We also computed interelement correlation coefficients of concentrations for 17 metals and 5 ions to confirm results of PCA (Table 4). The elements, which belong in the each group, appeared a high correlation. Ca was loaded at factor 2, but had high coefficients with NO_3^- ($r = 0.72$) and SO_4^{2-} ($r = 0.74$). These results revealed that NO_3^- and SO_4^{2-} were presented mostly as neutralized forms such as NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$, CaSO_4 and $\text{Ca}(\text{NO}_3)_2$ in the rain event.¹³

Because Fe have high reactivity in atmospheric aqueous system, we paid attention to emission source of them. They were involved in the factor 1 (0.429) and factor 2 (0.742) by PCA, and were significantly correlated with not only soil dust but also anthropogenic sources components. Therefore, it could anticipate that Fe was emitted from soil dust and anthropogenic sources in rainwater.

In order to classify the relationship between all chemical species and precipitation volume, we calculated log-log plots of concentration of all chemical species and

precipitation volume that showed a linear relationship. Table 5 summarized slope and correlation coefficients for 17 metals and 5 ions. The elements, which were emitted from soil dust, showed higher coefficient of slope and correlation than others did. It seemed that these elements were easily washed out at initial stage, and then concentration decreased gradually through precipitation events. Because they existed as coarse particles in the atmosphere, they were significantly affected by wash out. Cd and Pb showed high slope coefficient and low correlation coefficient. It could anticipate that the concentrations of Cd and Pb were effected not only from precipitation volume but also from other conditions such as pH.

3.3 Seasonal variations of elements

Seasonal variations in the monthly deposition and VWM were shown in Fig. 3 and 4. The monthly VWM of all elements were represented in general form: lower during May-September, and higher during December-February. However, high VWM of all elements were measured at August, 1999. Because temperature was higher over 30 °C, and humidity was higher also, a few day fell rain like squall at the tropics during short time at afternoon. The concentrations

Table 5. Slope and correlation coefficient of each elements between precipitation volume and concentration

Elements	slope coefficient	R
Al	- 0.54	0.49
Ba	- 0.52	0.35
Ca	- 0.80	0.42
Cd	- 0.53	0.26
Cr	- 0.16	0.04
Cu	- 0.35	0.11
Fe	- 0.71	0.41
K	- 0.70	0.33
Mg	- 0.43	0.36
Mn	- 0.52	0.41
Mo	- 0.15	0.07
Na	- 0.57	0.35
Ni	- 0.36	0.16
Pb	- 0.68	0.17
Sr	- 0.55	0.35
V	- 0.39	0.12
Zn	- 0.31	0.16
H ⁺	- 0.34	0.32
NH ₄ ⁺	- 0.37	0.37
Cl ⁻	- 0.34	0.31
NO ₃ ⁻	- 0.51	0.44
SO ₄ ²⁻	- 0.37	0.39

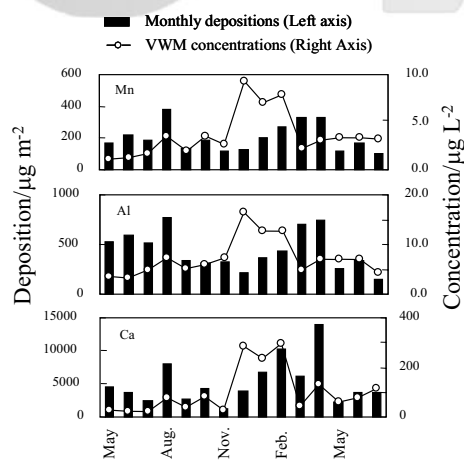


Fig. 3. Seasonal variations in the monthly deposition and VWM concentrations of Mn, Al and Ca.

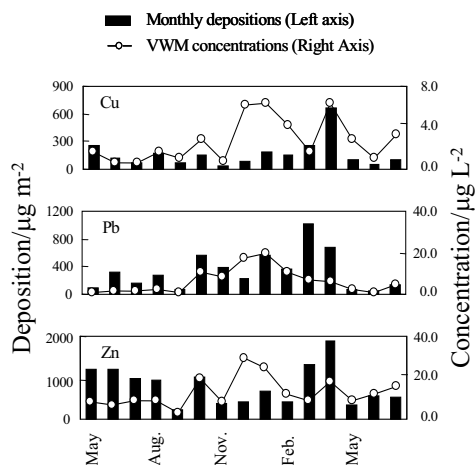


Fig. 4. Seasonal variations in the monthly deposition and VWM concentrations of Cu, Pb and Zn.

were very high in them, which washed out regional pollutants. At April 2000, VWM of all elements were highest in measurements. It could explain the effect of Kosa phenomenon, which was yellow soil dust that was transported by strong westerly winds, and fell on Korea and western Japan during March-May. For monthly depositions, soil dust (crustal) elements showed similar pattern for all, but anthropogenic source elements represented for each others. The differences between the maximum and minimum values of anthropogenic source elements were smaller than those of soil dust elements, and they were deposited regularly throughout the year by rain event. It seemed that the depositions of anthropogenic elements were affected from regional sources such as traffic, industrial and domestic emissions also.

3.4 Regional effect against chemical concentrations in rainwater

Instantaneous collection of rain samples indicated that the concentrations of elements as a function of location were in order: urban-facing area of Mt. Gokurakuji > Higashi-Hiroshima > mountain-facing area of Mt. Gokurakuji (Table 6). Because the sampling site at urban-facing area of Mt. Gokurakuji is close to an urban area and

the Sanyo Expressway, the higher concentration may result from the emission of elements from automobiles, road dust and combustion of industrial and domestic waste. Our finding that chemical concentration in rainwater was higher in the urban area is consistent with the finding of Hoffmann.¹⁴

Table. 6. The VWM concentrations of elements in Mt.Gokurakuji and Higashi-Hiroshima (n = 6)

Site	Mt. Gokurakuji		Higashi-Hiroshima
	Mountaining Facing	Urban facing	
Precipitation	168	169	124
pH	4.42	4.36	4.38
Al	11.2	11.5	7.72
Ba	2.52	4.03	0.72
Ca	19.8	79.6	37.9
Cd	0.09	0.13	0.23
Cu	0.52	1.23	1.27
Fe	3.55	7.45	3.58
K	62.1	68.2	54.1
Mg	21.9	30.9	25.0
Mn	2.89	4.78	3.59
Na	104	140	117
Ni	0.24	0.47	0.19
Pb	4.93	5.38	6.46
V	0.53	1.26	0.62
Zn	6.96	22.6	10.1
*NH ₄ ⁺	29.5	49.2	33.8
*Cl ⁻	33.2	44.5	40.8
*NO ₃ ⁻	21.9	29.3	27.0
*SO ₄ ²⁻	15.7	25.3	16.9

Unit of precipitation : mm

* Unit : μmolL⁻¹

4. Conclusion

Monitoring and characteristic variations of chemical elements in rainwater were very important information for studying acid precipitation and related environmental problems in fast economic growing region such as East Asian region. The elements were classified into three categories by PCA and interelements coefficients: anthropogenic source (Cd, Cu, Fe, Ni, Pb, V, Zn, NH₄⁺, NO₃⁻, SO₄²⁻ and H⁺), soil and crust dust (Al, Ba,

Ca, Fe, Mn), and sea salts (Mg, Na, Cl). For soil dust (crustal) source elements, systemic seasonal variations were observed in volume-weighted mean concentration and depositions for all. However, anthropogenic source elements represented for each others because they were affected from regional sources such as traffic, industrial and domestic emissions. At urban-facing area of Mt. Gokurakuji, the concentrations of chemical species were higher than other areas in instantaneously collecting rainwater. Because the sampling site at urban-facing area of Mt. Gokurakuji was close to the Sanyo Expressway and an urban area, the higher concentration might result from the emission of elements from automobiles, road dust and combustion of industrial and domestic waste.

Acknowledgements

This work was partly supported by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Corporation (JST). We thank the following people for their assistance in this study: Mr. Masaaki Chiwa and Mr. Norichika Hashimoto (Hiroshima University, Japan) for sampling rainwater and Mr. Takayuki Miyake (Hiroshima University, Japan) and C. H. Jeong (KRD.CO.LTD) for data handling.

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