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The photochemical reactions of iron species in rain and snow in Higashi-Hiroshima, Japan

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Abstract : This paper describes the concentrations of total dissolved iron (tFe) and Fe^{2+} in rainwater and snow, the relationship of Fe species with other metals and ions in bulk rainwater, and the Fe^{2+} generation mechanism in aqueous samples in rainwater of time series collection. Volume weight mean concentrations of tFe and Fe^{2+} were 3.22 and 1.25 μgL^{-1} in bulk rainwater, and 50.1 and 43.5 μgL^{-1} in snow, respectively. Fe^{2+} was significant fraction to the tFe, accounted for 3.25-93.4% of the tFe in rainwater and 87% in snow. We also investigated temporal variations of tFe, Fe^{2+}, other metals and ions in rainwater of time series collection during rain event. Although the concentration range of tFe was different from those of other species, a decreasing trend of tFe from the beginning of the rain event was similar with other species. However, though Fe^{2+} did not show such a decreasing trend, Fe^{2+}/tFe was in good correlation with solar radiation. From the results of multiple linear regression analysis and thermodynamic calculations (Mineql+), Fe^{2+} in our samples may be generated from photochemical reduction of Fe^{3+} species (such as $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and Fe-oxalate) at daytime.

Key words : *iron species, rainwater, snow, photochemical reduction*

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1. Introduction

The dissolved Fe species (Fe^{2+}, Fe^{3+},and $Fe(OH)^{2+}$etc) are one of the most important metal species in environmental samples, because they are present at concentrations at least an order of magnitude higher than those of other metals. On the basis of laboratory studies and field measurements, they rapidly react with many of the oxidants and reductants in natural waters and atmospheric water droplets, and the reactivity depends upon the oxidation states.[1-5] Therefore, Fe speciation in atmospheric waters is important because the different forms have different chemical reactivities. They have been implicated as a host of important redox reactions occurring in troposphere, including interconversion of S(IV) to S(VI), and the generation of hydrogen peroxide and OH radicals in cloudwater.[6-9] There have been several reports on the concentrations of Fe^{2+} and Fe^{3+} in fog and cloud water in which included micromolar ranges of Fe. Erel et al.[8] reported Fe^{2+} concentrations of 300 - 5000 nM and Fe^{2+}/total dissolved Fe (tFe) ratios of 0.17 - 0.55 in fog and

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cloudwater. Behra and Sigg[10] found 20 - 90% of tFe in fog samples collected at Zurich were soluble Fe^{2+} over pH 3-7 ranges. Since tFe and Fe^{2+} are nanomolar level in rainwater, there have been a few reports[11, 12] especially none for temporal variation of Fe^{2+} and ratio of Fe^{2+}, and Fe^{3+} (or tFe) in rainwater. Moreover, there have been no reports on the concentrations of Fe^{2+} and tFe in rain and snow at Japan and Asia until now.

The aim of this work is to determine the concentration of tFe and Fe^{2+} in rainwater and snow, and to measure temporal variation of the concentration of Fe species, other metals, and anions as a function of time during rain events as well as to elucidate the sources of Fe species, and to present a model calculation using analytical data.

2. Experimental section

2.1. Sampling

Rainwater and snow samples were collected with polyethylene (PE) bottles equipped with Teflon-coated PE funnels (all acid-cleaned) on the roof of the Higashi Hiroshima campus building of Hiroshima University at Higashi-Hiroshima, Japan. Bulk rainwater samples (n=13) were collected during Apr.-Jul. and time series collection during rain event (n=17) took place during Feb.-Mar. 2000. The samplers were set up just before precipitation events. The sample bottles were shielded from sunlight with aluminum foil in order to prevent reduction of Fe^{3+} by sunlight. Snow sample was collected at Feb. 9, 2000 and allowed to melt in a refrigerator (<4 ℃, about 2 hours).

2. 2. Reagents

Fe^{3+} working solutions were prepared by diluting a commercial atomic absorption spectrometer standard solution (Wako chemical Co.) containing 1000 mgL^{-1} of Fe^{3+}. Fe^{2+} stock solution was prepared by dissociating of $Fe(NH_4)_2(SO_4)_2 6H_2O$ (Wako chemical Co.) into 0.01M hydrochloric acid. Working solution of Fe^{2+} was prepared by diluting the stock solution with pre-acidified Milli-Q water (MQW, pH=3.0 HCl) with 40 mM Ferrozine (FZ, 3-(2-pyridyl)-5,6-diphenyl-1, 2, 4-triazine-p, p-disulfonic acid) and then adjusted pH 6-7 by 0.1M NaOH.

FZ and 1-octanesulfonic acid sodium salt were purchased from Sigma. Hydrogen peroxide was the TAMAPURE-AA100 grade purchased from Tama chemicals Co.. HPLC grade MeOH was used, and hydrochloric acid (35%), acetic acid (99.7%), ammonium water (25%) and other reagents were of super special grade (Katayama Chemicals). N, N-dimethyl-p-phenylene diamine dichloride (Wako chemical. Co.) was used without further purification.

2.3. Sample Analysis

2.3.1. Fe^{2+} analysis

Fe^{2+} was determined by modification of the FZ-HPLC method reported by Zhung et al.[11] FZ formed a very stable complex with Fe^{2+} (3:1) with stability constant of 3.7×10^{15} (= $[Fe(FZ)_3^{2+}]/[Fe^{2+}][FZ]_3$). The complex, $Fe(FZ)_3^{2+}$ could be separated from the other compounds in sample (including the excess amount of FZ) by HPLC. In order to make the complex of $Fe(FZ)_3^{2+}$ ($\geq$ 99%) in solution, more than 30 mM FZ was required. If FZ was not over 30 mM, formed complex would be broken up. For the $Fe(FZ)_3^{2+}$ measurement, 0.04 mL of 1 mM FZ was mixed with 0.96 mL of the sample in small polypropylene microcentrifuge tube, and 5 minutes were allowed to form the stable $Fe(FZ)_3^{2+}$ complex. The formed complex was analyzed by HPLC equipped with A 25-cm-long×4.6-mm ID SUPELCOSIL LC-18 reversed phase column and 100 mL sample loop. The column temperature was 20±1 ℃. The mobile phase consisted of 1.050 g NaCl, 0.030 g 1-octanesulfonic acid sodium salt, 170 mL spectral grade MeOH, and 830 mL MQW (>18.2 MΩ). Mobile phase was purged with Ar gas for 20 minutes, and the flow rate was 0.9 $mLmin^{-1}$. The absorbance at 295 nm was monitored by a Shimadzu SPD10A detector. When the Fe^{2+} concentration was lower than 1.7 μgL^{-1}, 50-100 mL filtered rainwater was pre-concentrated with a Sep-pak cartridge. The standard deviation for sample with 1.1 μgL^{-1} of Fe^{2+} was 5.0%

(n=6), implying the detection limit of 0.17 μgL^{-1}. *Fig.* 1 and 2 showed the calibration curve and typical chromatograms. The rainwater samples were analyzed within 30 minutes after sample collection.

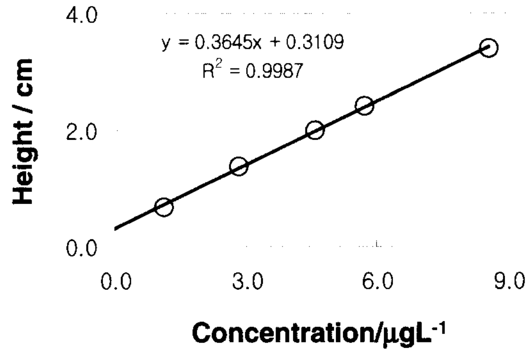

Fig. 1. The calibration curve for different Fe^{2+} concentrations at optimum conditions.

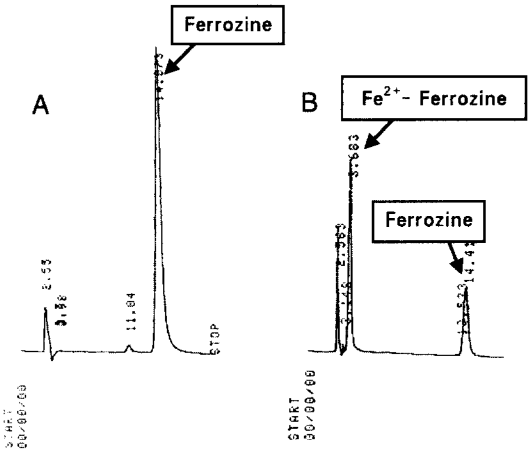

Fig. 2. The chromatograms of ferrozine and Fe^{2+}-Ferrozine complex. (A) blank (only ferrozine) (B) 8.5 μgL^{-1} Fe^{2+} and ferrozine complex.

2.3.2. Other analyses and cleaning procedures

The FIA system, ICP-MS (Perkin-Elmer Elan 5000) and ICP-AES (Perkin-Elmer Optima 3000) were used for analyzing tFe and other metals, as described by Kim et al.[13,14] and Takeda et al.[15] Dionex ion chromatography (DX 500 series) was used for analyzing ions and organic acids.[16] The analytical parameters for ICP/MS, ICP-AES and ion chromatography were summarized in *Table* 1. All plastic wares were leached with 10% HNO_3 for 2 days, then with 24% HCl for another 2 days, and finally rinsed three times with MQW.

Table 1. The analytical parameters for ICP/MS, ICP-AES and Ion chromatograph

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 $mLmin^{-1}$
Ion chromatograph		
Column	IonPac AS 10	
Eluent/Flow rate	100 mM NaOH / 1 $mLmin^{-1}$	
Detector	Supressed Conductivity	
Sample volume	20 mL	

3. Results and discussion

3.1. tFe and Fe^{2+} in bulk rainwater and snow sample

The concentrations of tFe and Fe^{2+}, and the ratio of Fe^{2+}/tFe in samples, such as bulk rainwater (n=13, Apr. - Jul. 2000), snow, as well as the results of previous reports are summarized in *Table* 2. The Fe^{2+} concentration (VWM 1.25, 0.20 - 7.60 μgL^{-1}) was similar to those reported by Zhung et al. (about 30 - 120 nM)[11] and Kieber et al. (40 nM)[12]. The concentrations of Fe^{2+} and tFe were much lower than those observed in fog and cloudwater, in which both $Fe^{2+}$and tFe often occur in micromolar concentrations. The concentrations of Fe^{2+} in rainwater were relatively low because of the dilution of cloud droplets by rain out and wash out effects.

Table 2. The average iron concentration and the ratio of Fe^{2+} to tFe in environmental samples

Unit : $\mu g L^{-1}$

	Sample	Fe^{2+}	tFe	Ratio(%, Fe^{2+}/tFe)
This study	Rain water	1.25	3.22	3.25-93.4
	Snow	43.5	50.1	86.8
Our previous study[14]	Rain water		2.47	
P. Behra and L.Sigg[10]	Fog	1.12E+04	-	20 - 90
G. Zhung et. al.[11]	Rain water	1.68 - 6.70	5.59 - 16.8	25 - 53
	Snow	1.34 - 3.73	3.79 - 5.70	25 - 74
Kieber et. al.[12]	Rain water	2.23	14.4	60.0
S. M. Pehkonen et al.[18]	Atmosoheric water	16.8 - 279	-	-
D. M. McKnight et al.[19]	Stream(day time)	460	1400	32.9
	Stream(night time)	180	1400	12.9

In case of Fe, 1 $\mu g L^{-1}$ is 17.9 nM

Although the Fe^{2+} and tFe concentrations in rainwater varied greatly from one sample to another, Fe^{2+} was significant fraction of the tFe in the samples, accounted for 3.25 - 93.4% of the tFe. Zhung et al. found that the fraction of Fe^{2+} was 25 - 55%, and Kieber et al. reported averaged 60% of tFe in rain samples. The tFe and Fe^{2+} concentrations were 50.1 and 43.5 $\mu g L^{-1}$, respectively, and the ratio of Fe^{2+}/tFe was 87% in snow. The concentrations of Fe^{2+} and tFe were very higher than those reported by Zhung et al. (Fe^{2+}:24-67, tFe:68-102 $nmol kg^{-1}$). It is generally known that Korea and Japan have been affected by high pollutant aerosols and snow particles transported from Asian continent by strong northwest monsoons at winter. Takeda et al. mentioned that transported pollutant would be deposited in this study area at winter[15]. In spite of only one sample, the high concentration observed in sample may be associated with snow particles from the Asian continent by strong northwest monsoons.

3. 2. Temporal variation of Fe^{2+} in rain event

Because rainwater contains many chemical species (oxidants, reductants and metals etc.), the relative concentrations of Fe^{2+} and Fe^{3+} could be determined by reaction rates of the simultaneously occurring oxidation and reduction processes. Fe^{2+} and organic acids (acetate, formate and oxalate) were immediately analyzed after the collection of rain samples in order to minimize reaction time of components as possible. *Table* 3 presents an example of the observed temporal variation of tFe, metals and ions during the rain event on Mar. 11 and 15 - 16, 2000. In general, the concentration of all the species was decreasing evidently in the course of meteorological events. They were affected by numerous factors that were precipitation volume, wind speed, pH and precipitation intensity. Luo[17] reported that rain intensity was the dominant factor for controlling wet-deposition flux. Although concentration range of tFe was different with other species, this decreasing trend was similar to other species from the beginning of the rain event. As the rain changed to sleet around 16:00, increased a little in the sample of 18:00 on Mar. 11, but the concentrations of them decreased from beginning of rain event on Mar. 15 - 16. However, Fe^{2+} and Fe^{2+}/tFe ratios were shown to have a different pattern with other chemical species (*Table* 4). The temporal variation of Fe^{2+}, tFe and solar radiation of the rain event at daytime and nighttime are shown at *Fig.* 3. The Fe^{2+}/tFe ratio continuously decreased from 76.5% to 6.0%, and their variation was larger during daytime rain event. On the other hand, Fe^{2+}/tFe ratio was low, and variation was small during nighttime rain event.

Table 3. The temporal variation of tFe and other species at rain event in Mar. 11 and 15-16, 2000

Sampling Time	tFe (μgL^{-1})	Mn (μgL^{-1})	Cu (μgL^{-1})	Cl$^-$ (μM)	NO^{3-} (μM)	SO$_4^{2-}$ (μM)	H_2O_2 (μM)	Acetate (μM)	Formate (μM)	Oxalate (μM)
March 11										
12:00	7.59	14.6	8.60	71.7	99.7	34.9	5.93	13.2	8.68	0.91
14:00	4.81	2.20	2.30	11.8	22.7	10.5	1.48	6.39	4.40	0.39
16:00	3.69	1.10	1.30	16.4	12.2	10.8	1.49	5.02	3.68	0.43
18:00	5.32	0.80	5.00	54.0	7.47	8.38	2.52	0.10	1.04	0.26
20:00	4.59	0.60	3.90	48.3	14.9	6.09	2.44	0.10	1.52	0.22
March 15-16										
23:00	14.5	4.25	3.10	23.9	73.1	39.3	0.07	10.6	14.7	0.57
0:00	4.57	0.69	0.84	19.3	17.0	8.25	0.05	4.55	4.96	0.19
2:00	3.55	0.69	0.88	11.2	15.3	8.70	0.04	5.28	2.65	0.27
4:00	3.16	0.24	1.10	3.08	7.86	4.72	0.31	3.40	2.07	0.16
6:00	2.09	0.17	1.80	13.0	7.27	4.36	0.11	8.43	1.57	0.20
8:00	0.79	0.41	0.95	5.41	14.6	10.3	0.25	2.73	2.18	0.48

Table 4. The concentratin of Fe^{2+} and tFe, and their ratio(Fe^{2+}/tFe) in time series collected rainwater(n=17) at Higashi-Hiroshima during Feb. - Mar. 2000

Date	Sampling Time	Deposition (mm)	pH	Fe^{2+} (μgL^{-1})	tFe (μgL^{-1})	Fe^{2+}/tFe (%)
Feb. 19	18:00	1.39	4.38	2.92	5.17	56.5
	20:00	2.68	4.56	0.89	3.35	26.6
Mar. 3	10:30	14.2	4.64	5.06	5.49	92.2
	12:30	1078	4.42	2.68	3.71	72.2
Mar.11	12:00	0.76	3.21	5.80	7.59	76.4
	14:00	2.16	3.44	3.07	4.81	63.8
	16:00	3.10	4.77	0.70	3.69	19.0
	18:00	2.94	4.90	0.69	5.32	13.0
	20:00	3.56	4.93	0.29	4.59	6.32
Mar. 15	23:00	2.45	4.01	1.33	14.5	9.17
	0:00	3.38	4.46	0.67	4.57	14.7
	2:00	8.04	4.64	0.40	3.55	11.3
	4:00	7.89	4.78	0.11	3.16	3.48
	6:00	10.8	4.81	0.11	2.09	5.26
	8:00	3.82	4.54	0.15	0.79	19.0
Mar.19	10:00	3.69	4.33	1.44	3.75	38.4
	12:00	7.34	4.45	1.24	1.75	70.9

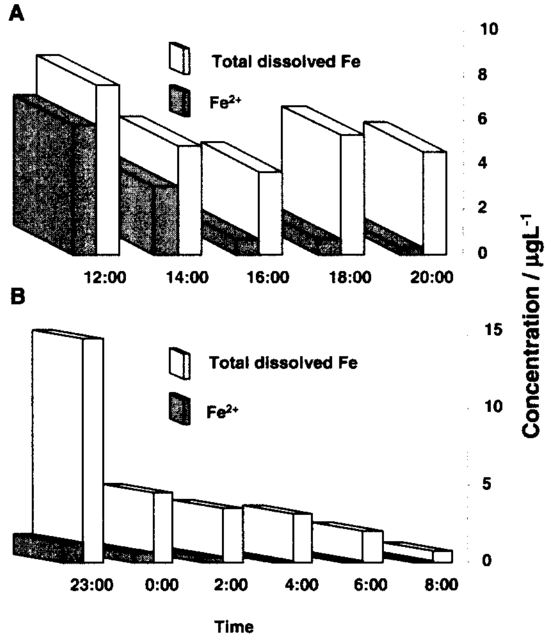

Fig. 3. The time series variation of Fe^{2+} and tFe at the rain event in Mar. 11(A) and 15-16(B), 2000.

3.3. Source of Fe species

It was very important to determine the source, speciation or precise form of occurrence, of iron in atmospheric waters because different forms of iron have different chemical and photochemical reactivity. Therefore, multiple linear regression analysis and thermodynamic calculations were carried out in order to reveal source and speciation form of dissolved iron in samples. *Table* 5 and 6 presented VWM, Min. and Max. concentrations of observed elements and inter-elements correlation coefficients among chemical components in bulk rainwater collected in April - July, 2000 (n=13). Although relatively few samples had been analyzed, the tFe presented same tendency, which showed significant correlation with not only crustal (soil) but also anthropogenic sources components[14], but Fe^{2+} did not show such a pattern. In addition, the tFe and Fe^{3+} (tFe minus Fe^{2+}) correlated positively with oxalate, whereas Fe^{2+} did not so. In order to confirm precise form of occurrence of Fe in the sample, thermodynamic calculations were carried out by Mineql+ (version 4.7, Schecher and McAvoy) that performs chemical equilibrium calculation in aqueous solution. This programme performs chemical equilibrium calculations using the Debye-Huckel equation for ionic strength corrections and the enthalpy change of reactions for temperature corrections of stability constants. The pH was fixed in the programme at the average of observed value at samples. The concentrations of Fe^{2+}, Fe^{3+} and other ions were used for the calculation in the program, which were the observed values in rain at Higashi-Hiroshima (*Table* 5).

Table 5. The volume-weighted mean, max and min concentrations of Fe^{2+}, tFe and other elements in rainwater samples (n=13) at Apr.- Jul. 2000

Unit : µgL^{-1}

Elements	VWM	Max	Min
Fe^{2+}	1.25	7.60	0.20
tFe	3.22	12.2	1.65
Al	6.39	22.4	3.91
Ba	0.78	2.43	0.34
Ca	96.6	397	28.0
Cu	1.76	4.30	0.62
K	120	460	10.2
Mg	52.5	125	25.8
Mn	3.10	11.7	1.23
Na	522	1222	248
Pb	5.24	20.2	0.78
V	0.75	1.61	0.25
Zn	12.4	28.7	5.31
$^{*}H^{-}$	28.7	79.4	18.6
$^{*}NH_4^{+}$	20.0	48.1	7.41
$^{*}Cl^{-}$	22.8	45.1	13.7
$^{*}NO^{3-}$	18.7	48.7	6.45
$^{**}SO4^{2-}$	20.3	53.9	9.57
*Acetate	2.99	9.68	1.37
*Formate	2.76	9.42	1.78
*Oxalate	0.93	2.99	0.19

Table 6. The correlation coefficients of Fe^{2+}, tFe and other elements in rainwater samples (n=13) at Apr. - Jul. 2000

	Ace	For	Ox	Fe^{2+}	tFe	Fe^{3+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	K	Ca	Mg	Al	Cu	Mn	Zn	Pb
Ace	1.00	0.96	0.62	0.11	0.51	0.49	0.68	0.30	0.53	0.62	0.42	0.51	0.28	0.36	0.71	0.57	0.61	0.50
For		1.00	0.59	0.09	0.45	0.47	0.66	0.28	0.46	0.56	0.44	0.45	0.22	0.35	0.60	0.50	0.55	0.49
Ox			1.00	0.07	0.50	0.57	0.48	0.31	0.41	0.69	0.12	0.21	0.15	0.23	0.43	0.28	0.29	0.25
Fe^{2+}				1.00	0.57	0.00	0.10	0.04	0.09	0.17	0.31	0.34	0.24	0.40	0.03	0.47	0.09	0.04
tFe					1.00	0.38	0.36	0.37	0.30	0.55	0.54	0.60	0.59	0.61	0.27	0.82	0.25	0.16
Fe^{3+}						1.00	0.28	0.47	0.22	0.39	0.20	0.23	0.33	0.19	0.36	0.31	0.16	0.14
NH^{4+}							1.00	0.35	0.86	0.83	0.31	0.45	0.12	0.52	0.64	0.48	0.72	0.72
Cl^-								1.00	0.20	0.35	0.39	0.28	0.62	0.25	0.12	0.46	0.32	0.06
NO_3^-									1.00	0.77	0.22	0.40	0.05	0.55	0.57	0.40	0.62	0.73
SO_4^{2-}										1.00	0.28	0.50	0.14	0.51	0.68	0.51	0.72	0.57
K											1.00	0.71	0.48	0.63	0.10	0.84	0.25	0.09
Ca												1.00	0.33	0.70	0.31	0.82	0.43	0.27
Mg													1.00	0.26	0.07	0.63	0.09	0.00
Al														1.00	0.19	0.76	0.33	0.41
Cu															1.00	0.28	0.62	0.61
Mn																1.00	0.37	0.20
Zn																	1.00	0.64
Pb																		1.00

The calculation predicts Fe^{2+} occurred primarily as free metal cation in rain. In case of Fe^{3+}, $Fe(OH)^{2+}$ was 31%, $Fe(OH)^{2+}$ was 5% , and others were mostly Fe-oxalate, an iron complex with oxalate. By the results of two calculations, it is predicted that Fe-oxalate was a major form of Fe^{3+} species, and Fe^{2+} was not emitted from crustal and anthropogenic sources directly but generated by another process. The several mechanisms to generate Fe^{2+} in cloud, fog and surface water had been reported by previous studies. Graedel et al.[1], Zepp et al.[4] and Faust[9] have proposed that the photolysis of the aqueous $Fe(OH)^{2+}$ complex is a major source of OH radical in clouds and fog. Zuo and Hoigne[2], Faust and Zepp[3] and Hislop and Bolton[5] have also shown that the photolysis of Fe^{3+}-oxalate complexes is a major pathway for the formation of H_2O_2 in the atmospheric water. Because those samples contained high concentration of Fe and other chemicals at about micromolar level, it was not certain whether these mechanisms will be applied to rainwater samples containing nanomlar level Fe. In order to clarify the generation process of Fe^{2+} in rainwater, a plausible mechanism, such as photoreduction of Fe^{3+},was investigated in samples of the time series collection. As shown in *Fig.* 4, there was a good correlation between the ratio of Fe^{2+}/tFe and solar radiation when rainwater was collected. By the thermal dynamic calculation, Fe^{3+}-hydroxy and Fe^{3+}- oxalate complexes were predominant Fe^{3+} species in our samples. They were very sensitive photoreactive complexes as reported by some early reports. *Fig.* 5 and 6 presented the correlation of Fe^{2+}/tFe ratios, H_2O_2 and oxalate at nighttime and daytime. Although we had analyzed relatively few samples, they showed a linear trend at daytime, but did not so at nighttime. Zuo and Hoigne[2] had shown that H_2O_2 (up to approximately 28mM) could be generated upon photolysis of pH 4 solution containing oxalate (up to 250 mM, 250 times higher than our average conc.) and Fe^{3+} (up to 100 mM, 2500 times higher than our average conc.) under the laboratory conditions. In this experiment, the concentration of H_2O_2 was proportional to the concentration of Fe^{3+} and oxalate in the photolyzed solution, which agrees with the data presented in *Fig.* 6B.

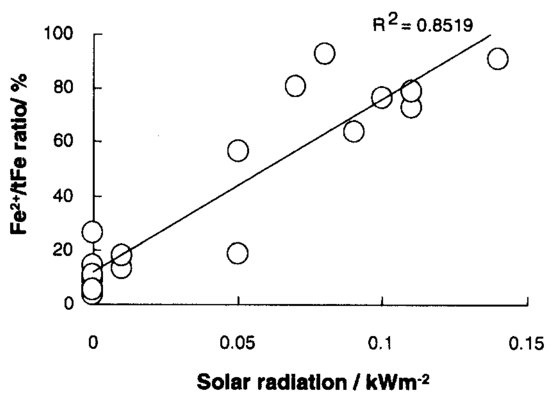

Fig. 4. The correlation between the ratio of Fe^{2+}/tFe in rainwater and solar radiation at the time when rain was collected. Solar radiation refer to HIRODAS that was meteorological observation system of Hiroshima University.

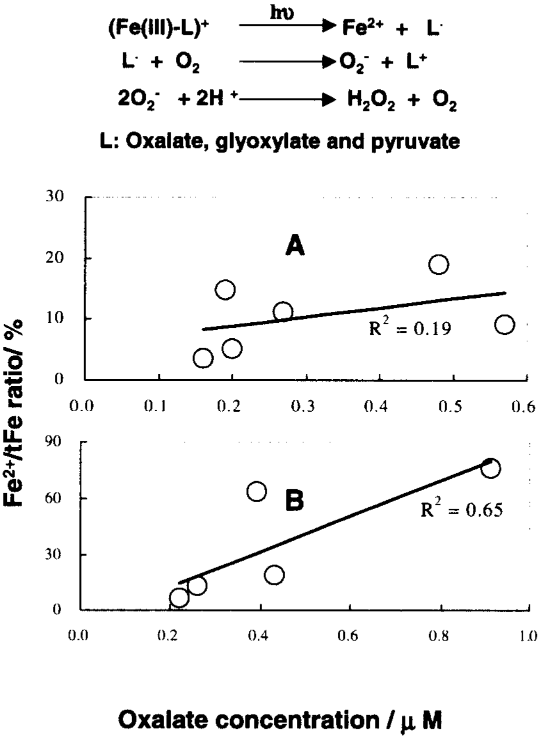

Fig. 5. The principal reaction and correlation between the ratio of Fe^{2+} and oxalate concentration at the night time (A) and day time (B) when rain water was collected.

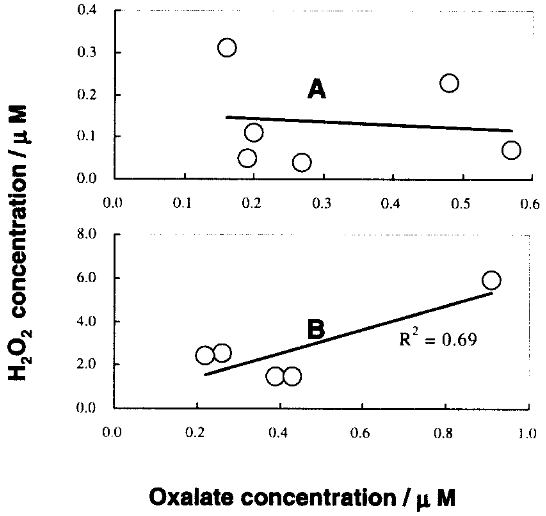

Fig. 6. The correlation between the H_2O_2 and oxalate concentration at the nighttime (A) and day time (B) when rain water was collected.

Though it needs more study, the results of this study imply that Fe^{2+} was generated by photochemical reduction of Fe^{3+} species ($Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and Fe-oxalate) at day time in our rain samples.

4. Conclusion

It was observed that the volume weighted mean concentrations of tFe and Fe^{2+} were 3.22 and 1.25 $\mu g\ L^{-1}$in the bulk rainwater and were 50.1 and 43.5 $\mu g L^{-1}$ in the snow, respectively. Fe^{2+} was in significant fraction of the tFe in all the samples, Fe^{2+} accounted for 3.25 - 93.4% of the tFe in rainwater samples, and was 87% in snow.

By the thermal dynamic calculation, Fe^{2+} occurred primarily as free metal cation, and Fe^{3+} was in various forms that were $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and Fe-oxalate in the samples. The result of inter-elements correlation coefficients indicates the possibility was low that Fe^{2+} was emitted from crustal and anthropogenic sources directly. The temporal variation of the concentration of tFe was similar to that of other inorganic species. The Fe^{2+}/tFe ratios during the daytime were significantly higher than those at nighttime in raining events. Fe^{2+} in rainwater samples may be generated by photochemical reduction of Fe^{3+} species ($Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and Fe-oxalate) at daytime.

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