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Precipitation Chemistry and Corrosion of Metal Plates

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ABSTRACT

From April 1991 to March 1992, precipitation samples were collected in Nara City and eight other sites in Nara Prefecture. Carbon steel plates were exposed to the open air outdoors in eleven sites in the prefecture. Precipitation chemistry was assessed in terms of ionic composition and concentration. The corrosion of sample plates was also observed in relation to precipitation chemistry as well as major air pollutants.

Precipitation samples were subjected to elaborate analytical measurements in order to determine commonly measured inorganic ions. Individually, the following chemical species in precipitation were determined in some samples: organic acids, aldehydes, hydrogen peroxide and dissolved sulfur dioxide. The annual mean of rainfall and pH, electric conductivity and concentrations of major ions in acid rain samples in Nara City site were as follows: rainfall; 113.0 mm/month, pH; 4.61, electric conductivity; 25.3 μS/cm, H^+; 24.5 μeq/l, SO_4^{2-}; 63.1 μeq/l, NO_3^-; 25.6 μeq/l, Cl^-; 35.5 μeq/l, Na^+; 16.1 μeq/l, NH_4^+; 24.4 μeq/l, K^+; 2.3 μeq/l, Ca^{2+}; 37.9 μeq/l, Mg^{2+}; 7.4 μeq/l, nss(non sea salt)-SO_4^{2-}; 59.1 μeq/l and nss-Ca^{2+}; 37.3 μeq/l.

A set of two samples of metal plate was used: one was exposed directly to both precipitation and air pollutants (Type A), and the other only to air pollutants containing sea salt (Type B). The corrosion rate of the Type A sample exceeded that of Type B: 2.2 and 1.2 mg/cm^2/month for Types A and B, respectively for a set of samples in the Nara City sites. An X-ray diffraction study of the sample plates exposed to the precipitation and air pollutants containing sea salt showed that the corrosive products of α-, β-, γ-FeOOH and Fe_3O_4 were formed on these plates. These findings suggest that precipitation plays an important role in producing metal corrosion as well as air pollutants.

(Key words: Precipitation chemistry, Corrosion of metal plates, Acid rain, Japan, Hydrogem peroxide, Organic acid, Aldehydes)

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1. INTRODUCTION

Acid rain has been recognized in North Europe, the East of North America and the Far East of Asia with Japan as center and most recently in the South-West of China. Acid rain has caused damage to forests and lakes in North Europe and North America, and such environmental pollution has become an international problem on a global scale on account of its long-range-transport. In Japan acid rain is recognized in almost all areas, but fortunately as much damage to the ecosystem as that caused in North Europe and North America has not been suffered (Publication by Japan Environment Agency (JEA)). However, in future, damage to the ecosystem, cultural heritage, buildings and materials etc. caused from acid rain is to be suspected. Accordingly, an investigation of acid rain was carried out to grasp the real state of affairs in the Nara Prefecture. This paper presents the information gained so far.

2. SAMPLING AND ANALYSIS

Location of sampling sites

Nara Prefecture covering an area of 3692 km^2 has a population of about one and a half million people. Nara City, ancient city and the seat of the prefectural government, was the oldest capital from 710 to 794 A.D. in Japan. The city is located in an inland basin area about 45 km away from the coastline and about 50 km away from Osaka, the second largest urban area in Japan.

Acid deposition

Investigations on acid deposition were performed at 9 points in Nara Prefecture (Figure 1), from Apr., 1991 to Mar., 1992.

Sampling, analysis and management of precision of data-sets of acid deposition were performed according to the manual of JEA.

The sampling of acid deposition was carried out with a filtering collection sampler which has a collecting face with a diameter of 20 cm. Whole rain water samples were collected every week (52 times in the year for sampling No. 1-7 and 12 times in Jun., Jul. and Oct. for sampling No. 8-9). Yet in Nara City, wet/dry separating sampler was carried out, and wet depositions were collected every week (52 times in the year), while dry depositions were collected every month (12 times in the year).

Items of analysis were pH, electric conductivity (E.C.), SO_4^{2-}, NO_3^- , Cl^-, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}, the pH was measured by the glass electrode method, E.C. by the electric conductivity meter method and anions and cations were measured by ion chromatography (IC).

Management of precision of data-sets was performed by both the ion balance and E.C. comparison methods.

Organic acids and aldehydes in rain water

Investigations on organic acids and aldehydes in rain water had been performed earlier in Nara City from Jun., 1985 to May, 1986. Rain water samples were collected with every rainfall for a year. The analysis of organic acids of rain water samples was performed by

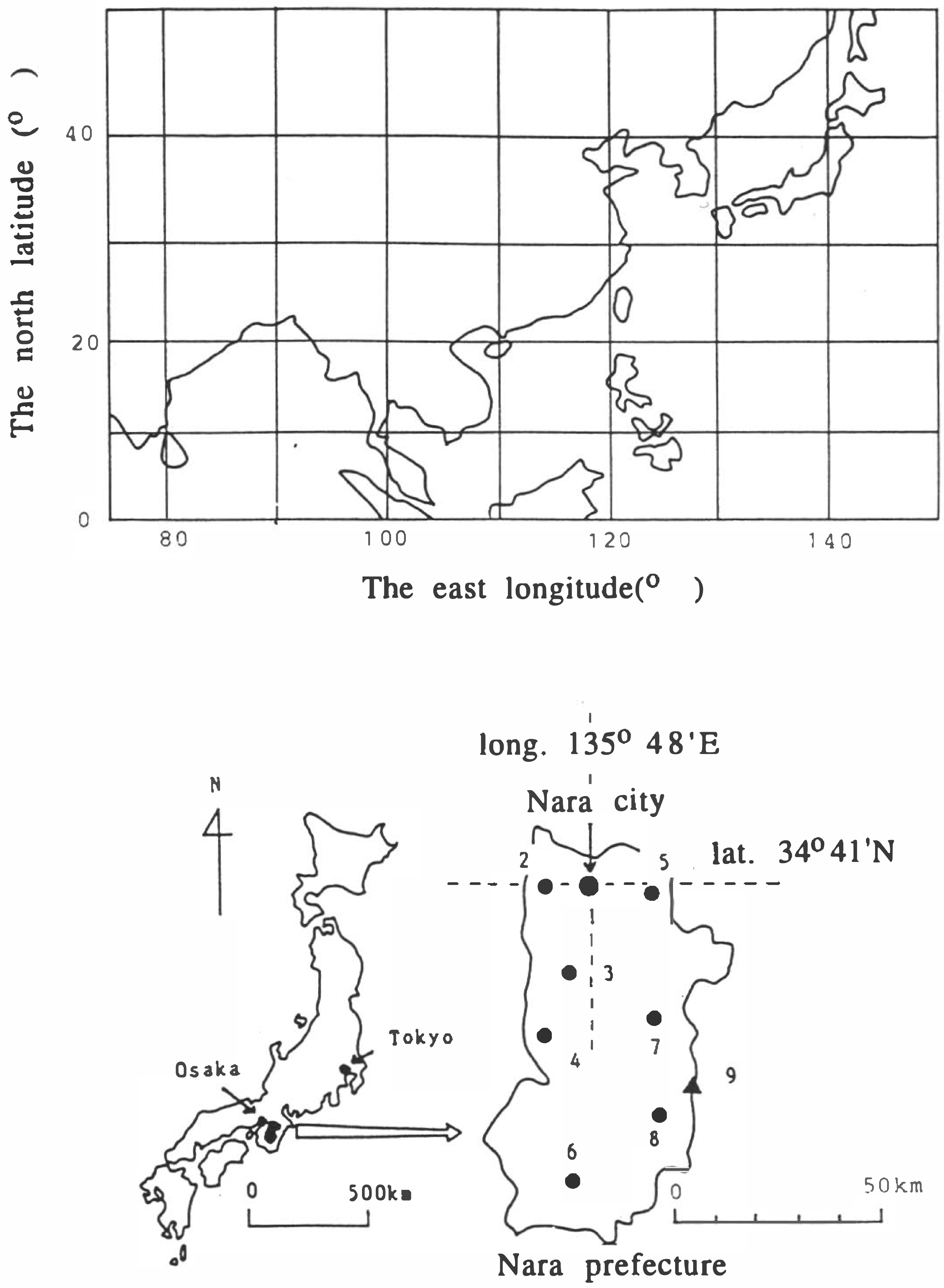


Fig. 1. Location and code number of the sampling sites in Nara prefecture.

both the ICE (ion chromatography exclusion) and IC (ion chromatography) methods, while that of the aldehydes was performed by the HPLC (high performance liquid chromatography) method.

Hydrogen peroxide and dissolved SO_2 in rain water

Investigations on hydrogen peroxide and dissolved SO_2 in rain water were performed in Nara City in the summer (Jun. and Jul., 1990) and winter (Dec., 1990 and Jan., 1991) seasons when rain water samples were collected at every rainfall. The analysis of the hydrogen peroxide of rain water samples was performed by the spectrofluorometric method using enzymes, and that of dissolved SO_2 was performed by a modified IC method.

Corrosion of Metal Plates

Investigations on corrosion of metal (carbon steel) plates were performed at 11 places in Nara Prefecture from Apr., 1991 to Jul., 1992 using air and total exposures. The analysis was performed by the gravimetric method as well as the thin film X-ray diffraction method.

3. RESULTS AND DISCUSSION

3.1 Acid Deposition

The average annual rainfall, pH, E.C. and the concentrations of ions in acid rain measured in Nara Prefecture are shown in Table 1. The average annual pH at 7 points in Nara Prefecture are 4.55-4.85, showing a tendency to be low in the winter season. The average annual SO_4^{2-} and NO_3^- concentrations in rain water were 63.1-30.2 μeq/l and 26.3-10.2 μeq/l, respectively, with a tendency for both to be high in the winter season. The average composition of anions in rain water was in the order of high to low: SO_4^{2-} (48%)>Cl^-(30%)>NO_3^-(21%), and the concentration of SO_4^{2-} was about twice that of NO_3^-. That of cations was NH_4^+(27%)>Ca^{2+}(24%), H^+(23%)>Na^+(17%)>Mg^{2+}(7%)> K^+(3%). Anionic and cationic components were well balanced in rain water to become electrically neutral. The average concentrations of nss (non sea salt)-SO_4^{2-} and Ca^{2+} were 41.8 μeq/l and 20.0 μeq/l, respectively, and the rate of nss-SO_4^{2-} and nss-Ca^{2+} to SO_4^{2-} and Ca^{2+} were 92% and 98%, respectively, because Nara Prefecture is an inland area about 45 km away from coast line. The average ratio of Cl^- to Na^+ concentration was 2.0. It is well known that Cl^- and Na^+ originate in sea salt, but in an inland area such as Nara Prefecture, the contribution of sea salt was expected to be small or minimal. Thus Cl^- produced from the combustion of plastic goods containing Cl^-, such as vinyl chloride, in many kinds of incinerators or large incinerator plants is considered to be the main source of Cl^- in this inland area. It is expected that sea salt and Cl^- produced from artificial activities dissolved into rain water causing the ratio of Cl^- to Na^+ to be higher than that of sea salt.

The average annual dry and wet deposition in Nara City is presented in Table 2. The wet deposition for all components except Ca^{2+} was higher than the dry deposition, and for SO_4^{2-} and NO_3^-, the wet deposition was 5 times that of the dry deposition. Table 3 shows the trends of pH and ion concentrations of acid rain in Nara City, which have been almost constant for the past 10 years. In fact, these values are nearly the average values in Japan.

3.2 Organic Acids in Rain Water

An application of the ion chromatography exclusion (the ICE-method) to the determination of carboxylic acid concentration in rain water was examined (Matsumoto, 1988). It was found that the ICE-method was suitable for the rapid and simultaneous determination of five carboxylic acids: formic, acetic, propionic, succinic and glutaric acids. But, as the ICE-method was unsuitable for the determination of oxalic acid and malonic acid due to poor separation, these acids were determined by regular ion chromatography. The carboxylic acids in rain water were completely decomposed for several days at room temperature, but, these were stable for three months or more when the samples were spiked with $CHCl_3$ or $HgCl_2$. The method established in this study was applied to the analysis of rain water collected in Nara City for a year. The annual mean concentration of carboxylic acids were as follows: 0.181 μg/ml for formic acid, 0.112 for acetic acid, 0.004 for propionic acid, 0.018 for oxalic acid, 0.007 for malonic acid, 0.010 for succinic acid and 0.005 for glutaric acid (Table 4). The monthly variations in the concentration of formic and acetic acids in rain water were high in summer and low in winter (Figure 2). The annual mean percentage of concentration of hydrogen-ion concentration yield from the carboxylic acids to the hydrogen-ion concentration in rain water was established to be 3.89% for formic acid, 0.59% for acetic acid and 4.94% for all carboxylic acids (Table 4).

Table 1. Annual average of rainfall, pH, E. C. and ion concentrations of acid ain at each sampling places.

														nss-[1]	
	Sampling	Rainfall	pH	E.C.	H^+	SO_4^{2-}	NO_3^-	Cl^-	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Ca^{2+}
No.	places	(mm/month)		(μS/cm)						(μeq/ℓ)					
1	Nara[2]	113.0	4.61	25.3	24.5	63.1	25.6	35.5	16.1	24.4	2.3	37.9	7.4	59.1	37.3
2	Ikoma[3]	124.4	4.55	24.1	28.2	52.5	26.3	36.1	16.5	29.9	2.0	25.0	5.8	48.4	24.4
3	Kashiwara[4]	105.1	4.66	21.5	21.9	48.7	21.1	25.7	11.3	28.3	3.6	19.0	4.9	45.9	18.6
4	Gojo[5]	145.6	4.83	18.2	14.8	38.3	16.8	29.9	16.1	20.5	4.3	16.5	4.9	34.3	15.9
5	Yamazoe[6]	157.2	4.63	22.8	23.4	51.8	24.8	33.0	18.3	28.3	2.3	21.0	6.6	47.2	29.3
6	Totsukawa[7]	249.5	4.85	15.4	14.1	30.2	10.2	20.9	13.9	12.7	3.3	12.5	9.1	26.7	12.0
7	Higashi[8]	118.9	4.76	16.1	17.4	33.3	15.2	19.2	9.6	17.2	1.8	10.5	3.3	30.9	10.1
8	Kamikita[9]	279.4	5.02	9.0	9.5	23.1	7.3	11.3	6.5	12.2	2.8	5.0	2.5	21.5	4.8
9	Mt. Ohdai[10]	323.5	5.14	6.8	7.2	15.6	5.0	5.1	3.5	10.5	1.3	3.0	1.6	14.7	2.9
	Avg.[11]	144.8	4.70	20.5	20.0	45.4	20.0	28.5	14.4	23.3	2.8	20.5	5.8	41.8	20.0

1) nss-: non sea salt- 2) Nara city 3) Ikoma city 4) Kashiwara city 5) Gojo city 6) Yamazoe villa

7) Totsukawa village 8) Higashiyoshino village 9) Kamikitayama village 10) Mt. Ohdaigahara

11) Avg.(Average) was calculated by values gained from sampling No.(1-7)

Table 2. Wet and dry deposition of components in Nara City.

	H^+	SO_4^{2-}	NO_3^-	Cl^-	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	nss-[1] SO_4^{2-}	nss-[1] Ca^{2+}	ΣA[2]	ΣC[3]	Σ(A+C)[4]
	(meq/m²/month)													
Wet	2.9	5.22	2.33	2.59	0.97	3.92	0.17	1.07	0.49	4.98	1.03	10.14	9.52	19.66
Dry	0.0	0.98	0.51	1.11	0.46	0.19	0.09	1.77	0.35	0.86	1.75	2.60	2.86	5.46
Σ(wet+Dry)[5]	2.9	6.19	2.84	3.70	1.43	4.11	0.26	2.84	0.85	6.55	2.79	12.73	12.39	25.12
Wet/Σ(Wet+Dry)(%)	100.0	84.2	82.0	70.1	68.0	95.3	65.3	37.7	58.3	76.0	40.0	80.0	76.8	78.3

1) nss-: non sea salt- 2) Sum of anions 3) Sum of cations 4) Sum of anions and cations

5) Sum of wet and dry depositions

Table 3. Trend of rainfall, pH, E. C. and ion concentrations of acid rain in Nara City.

Period	Rainfall (mm/month)	pH	E.C. (μS/cm)	H^+	SO_4^{2-}	NO_3^-	Cl^-	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	nss-[1] SO_4^{2-}	nss-[1] Ca^{2+}
				(μeq/ℓ)										
1981 Apr.-1982 Mar.		4.75	23.7	17.8	56.8	19.5	32.2	15.2	20.0	2.3			53.0	
1982 Nov.-1983 Oct.		4.67	22.4	21.4	41.2	30.0	42.6	38.3	23.8	4.1	27.9	9.1	31.6	26.4
1988 Apr.-1989 Mar.	113.6	4.6	19	25.1	39.6	15.0	20.0	15.2	15.5	2.3	23.0	6.6	35.8	22.4
1991 Apr.-1992 Mar.	113.0	4.61	25.3	24.5	63.1	25.6	35.5	16.1	24.4	2.3	37.9	7.4	59.1	37.3
Avg.[2]	113.3	4.66	22.6	22.2	50.2	22.5	32.6	21.2	20.9	2.8	29.6	7.7	44.9	28.7

1) nss-: non sea salt- 2) Average

Table 4. Concentration (μg /ml) of carboxylic acids and aldehydes in rainwater in Nara City. And percentage (%) of contribution of hydrogen-ion concentration yield from carboxylic acids to the hydrogen-ion concentration in rainwater.

Acids & aldehydes	Concentration			Percentage of contribution		
	Range	Mean[1]	S.D.[2]	Range	Mean	S.D.
Formic acid	0.034～0.664	0.181	0.119	0.87～10.3	3.89	2.48
Acetic acid	0.018～0.484	0.112	0.094	0.04～3.81	0.59	0.71
Propionic acid	n.d.[3]～0.028	0.004	0.005	0.0 ～0.20	0.02	0.04
Oxalic acid	n.d. ～0.076	0.018	0.015	0.0 ～0.72	0.27	0.20
Malonic acid	n.d. ～0.024	0.007	0.007	0.0 ～0.45	0.09	0.11
Succinic acid	n.d. ～0.081	0.010	0.014	0.0 ～0.27	0.05	0.06
Glutaric acid	n.d. ～0.026	0.005	0.005	0.0 ～0.21	0.03	0.03
HCHO	0.048～1.103	0.262	0.192			
CH_3CHO	0.020～0.473	0.146	0.128			
C_2H_5CHO	0.005～0.063	0.021	0.021			
C_3H_7CHO[4]	n.d. ～0.06	0.01	0.02			
C_6H_5CHO	n.d. ～0.15	0.01	0.03			

1) Sample number:49 2) Standard deviation 3) not detected

4) Sum of n- and iso-C_3H_7CHO concentrations

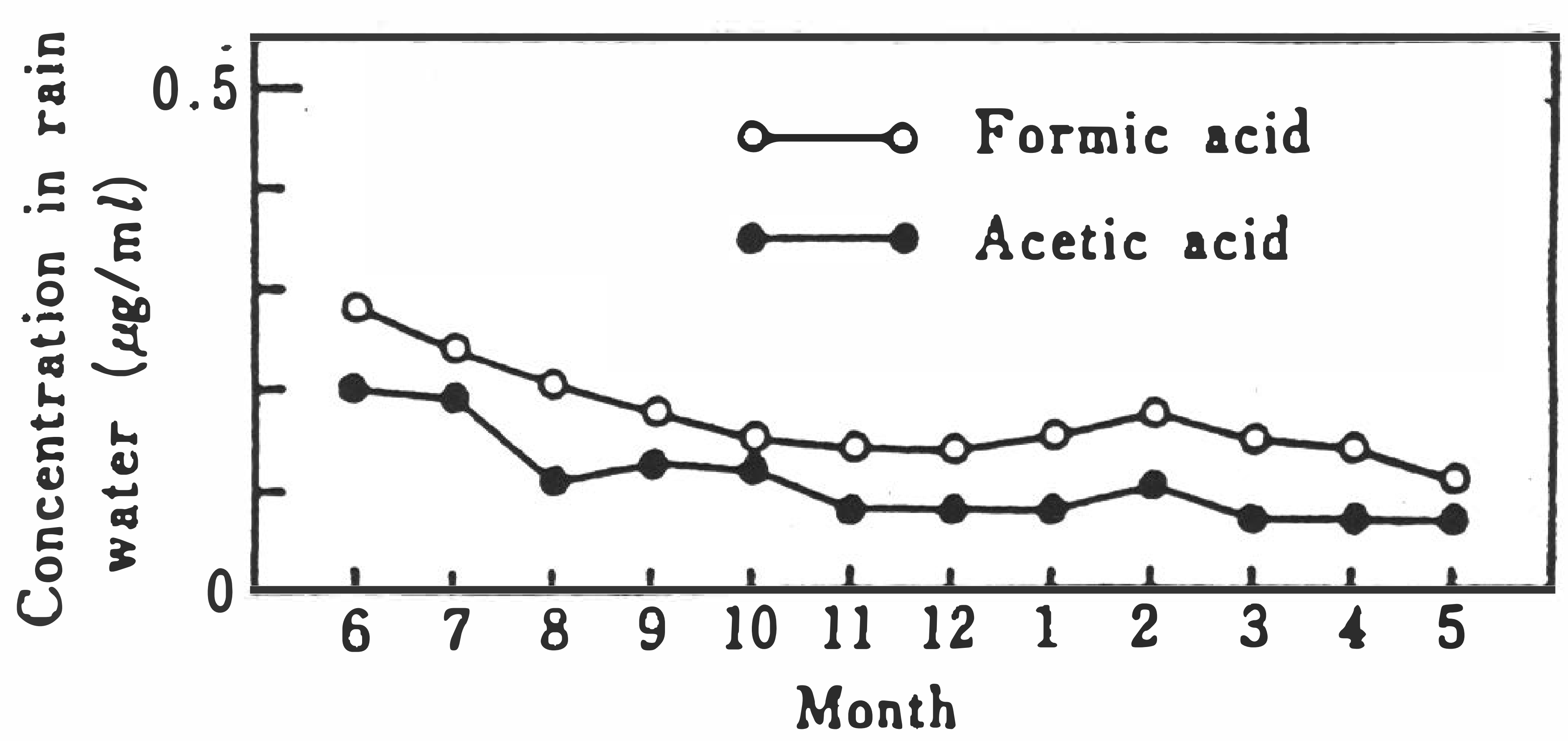


Fig. 2. Monthly variations of concentration of formic acid and acetic acid in rain water collected in Nara City in a period from June, 1985 to May, 1986.

3.3 Aldehydes in Rain Water

It is commonly said that the origins of aldehydes in the atmosphere are mainly the primary production by an imcomplete combustion of fossil fuels and a secondary production by a light chemical reaction. Since such aldehydes are easily absorbed in rain water due to their high water solubility and since they have irritants, these compounds cannot be ignored in research on precipitation chemistry due to the effects they cause on the ecosystem, especially human body. Also formaldehydes are the most abundant aldehyde compound in the atmosphere, and few others have been detected in rain water. Good field data needed as input to physico-chemical models in order to completely understand the role of aldehydes in the chemistry of rain water.

An application of HPLC to the determination of aldehyde concentration in rain water was examined (Matsumoto *et al.*, 1987). It was found that the following procedures were suitable for rapid and simultaneous determination of the five aldehydes, HCHO, CH_3CHO, C_2H_5CHO, C_3H_7CHO (*n*- and *iso*-) and C_6H_5CHO. First, a rain sample should be collected by a sampler into which 10 m*l* of 1000 μg/m*l* $HgCl_2$ solution is added in advance. To 1 m*l* of rain water sample, 200 μl of 1000 μg/m*l* 2, 4-dinitrophenylhydrazine (DNPH) and 20 μl of 5N H_3PO_4 solution are added, and the mixture is allowed to stand for 10 min to form DNPH derivatives of the aldehydes. Then, 50 μl of the sample solution is injected into a C18 column with an aqueous solution of CH_3CN (H_2O/CH_3CN:50/50, v/v). The present method gave an HCHO concentration in agreement with that determined by a conventional method (AHMT method), and definitely it provided better sensitivity: the detection limit for HCHO was 0.002 μg/m*l* in contrast to 0.05 μg/m*l* by the latter method. The reproducibility of the measurement was about 2.5% as expressed in terms of the relative standard deviation. The aldehydes in rain water were stable for four months when the sample was spiked with $HgCl_2$ or $CHCl_3$. The method established in this study was applied to the analysis of rain water collected in Nara City for a year. The annual mean concentrations of aldehydes were as follows: 0.262 μg/m*l* for HCHO, 0.146 for CH_3CHO, 0.021 for C_2H_5CHO, 0.01 for C_3H_7CHO and 0.01 for C_6H_5CHO (Table 4).

3.4 Hydrogen Peroxide and Dissolved SO_2 in Rain Water

It is well known that hydrogen peroxide (H_2O_2) is in existence as a gas phase in the atmosphere, and it is easily absorbed in rain water (Henry's constant: 10^5 mol/*l*·atm).

It performs an important role in changing dissolved SO_2 [S(IV)] into SO_4^{2-} [S(VI)] in rain water, and recently it has attracted a great deal of attention. Furthermore, recent investigations suggest that hydrogen peroxide itself might contribute to the ecosystem, especially plant and material damage. Therefore, measurements of H_2O_2 and S(IV) in rain water were undertaken.

The spectrofluorometric method making use of the enzymes, peroxidase and catalase, for the determination of H_2O_2 in rain water was examined and one procedure was found suitable (Matsumoto, 1992). To form the *p*-hydroxyphenylacetic acid (POPHA) dimer that had fluorescence with the addition of peroxidase from POPHA and H_2O_2 in the rain water, it was necessary to add 0.3 m*l* of 20 units/m*l* peroxidase solution to 10 m*l* of rain water sample containing 3000 ng/m*l* H_2O_2, and the reaction was completely performed for 1 minute. To remove the influence of organic peroxide interfering with the substance to measure H_2O_2, it was necessary to add 0.5 m*l* of 280 units/m*l* catalase solution to 10 m*l* of rain water sample containing 3000 ng/m*l* H_2O_2 to selectively decompose the H_2O_2 by catalase, and this reaction was left to perform for 1 minute.

For the determination of the S(IV) concentration in rain water, the method, that measured the difference between S(VI) and total S(VI) i.e. S(VI)+S(IV) concentrations in rain water by ion chromatography, was examined. All of the 5μg/m*l* S(IV) in 10 m*l* of rain water sample was converted into S(VI) by the addition of 0.1 m*l* of 30% H_2O_2 solution. It was found that the following procedures were suitable for the determination of the S(IV) in rain water. To measure the total S(VI) concentration, 0.1 m*l* of 30% H_2O_2 solution, excess H_2O_2, was added to 10 m*l* of rain water sample in order to convert S(IV) into S(VI), and then the total S(VI) concentration was determined to measure S(VI) concentration in this rain water sample by ion chromatography. In this way, the S(IV) concentration in rain water was determined to measure the difference between total S(VI) and S(VI) concentrations in rain water by ion chromatography, respectively. The rate of decomposition of H_2O_2 in rain water was less than 10% within 6 hours when 95 m*l* of the rain water sample was spiked with 5 m*l* of 1% triethanolamine (TEA) solution before rainfall and was kept at low temperature (4°C). The S(IV) in rain water was stable for more than 48 hours even at room temperature when the 95 m*l* of rain water was spiked with 5 m*l* of 1% TEA solution in a similar manner as above.

Concentrations of H_2O_2 in rain water were 983-39 ng/m*l* (mean 303 ng/m*l*) in the summer season and 29-2 ng/m*l* (mean 11 ng/m*l*) in the winter season; on the other hand, concentrations of S(IV) in rain water were 0.093-0.000 μg/m*l* (mean 0.022 μg/m*l*) in the summer season and 0.408-0.087 μg/m*l* (mean 0.268 μg/m*l*) in the winter season (Table 5).

3.5 Corrosion of Metal Plates

Studies on the corrosion of metal plates (carbon steel plates) were performed at 11 sampling places in Nara Prefecture for a year, and simultaneously, studies on acid rain and air pollution were performed (Matsumoto *et al.*, 1992). Two exposure methods of corrosion of metal plates were carried out: the total exposure (exposure outdoor) and air exposure (exposure in a ventilated shelter with a ventilation rate of 30%) methods. Total exposure was exposed directly to both precipitation and air pollutants, while air exposure was exposed only to air pollutants containing sea-salt. However, Nara Prefecture is about 50 km inland area from sea and the effect of sea-salt is very small.

The determination of corrosion of metal plates was performed by gravimetric analysis which measured the difference in weight between pre-exposure and post-exposure.

The average values of the amount of corrosion of metal plates at 11 sampling places were 182.3 mg/100 cm^2/30 day on total exposure and 88.1 mg/100cm^2/30day on air exposure, respectively (Table 6). It was recognized that the amount of corrosion of metal plates

Table 5. H_2O_2 and S(IV) concentrations in rain water[1] at Nara City in summer and winter seasons.

Date	H_2O_2 (ng/mℓ)			S(IV) (μg/mℓ)		
(year/month/day)	Max.	Min.	Avg.[2]	Max.	Min.	Avg.
90/ 6/ 1	304	48	105	0.081	0.000	0.031
90/ 6/ 5	983	243	497	0.063	0.000	0.018
90/ 6/15	803	105	310	0.042	0.000	0.025
90/ 6/27	364	44	156	0.059	0.000	0.027
90/ 6/28	382		382	0.000		0.000
90/ 6/29	414	39	255	0.051	0.000	0.020
90/ 7/ 3	217	85	151	0.093	0.000	0.040
90/ 7/12	836	187	564	0.031	0.000	0.015
90/12/11	22	3	9	0.267	0.087	0.113
90/12/15	13		13	0.301		0.301
90/12/18	21	8	15	0.387	0.176	0.244
90/12/21	29	3	11	0.391	0.215	0.298
91/ 1/12	8		8	0.215		0.215
91/ 1/17	2		2	0.408		0.408
91/ 1/21	27	2	15	0.400	0.168	0.307
91/ 1/25	17	9	12	0.317	0.209	0.254

1) rain water samples were collected each 1mm rainfall water until 5mm rainfall

2) Average

Table 6. Amount of corrosion of metal (carbon steel) plate by total and air exposure.

Sampling No.	Sampling place	Area[1]	Total exposure Avg.[9] (mg/100cm²/30day)	Total exposure Max. (mg/100cm²/30day)	Total exposure Min. (mg/100cm²/30day)	Total exposure Avg. of Area	Air exposure Avg. (mg/100cm²/30day)	Air exposure Max. (mg/100cm²/30day)	Air exposure Min. (mg/100cm²/30day)	Air exposure Avg. of Area
M-1(1)[2]	Nara City	Ci	221.2	366.6	77.2	(M-1～5) 227.2	115.6	193.3	47.6	(M-1～5) 144.9
M-2(2)	Ikoma City	Ci	191.5	320.0	57.3		129.1	249.8	14.2	
M-3(3)	Kashiwara City	Ci	182.4	230.7	117.3		104.0	168.3	31.6	
M-4	Ouji Town	Ci	204.7	327.8	68.2		135.6	222.4	43.0	
M-5	Mt. Ikoma	M.B.U.	336.0	624.6	168.0		249.1	486.2	38.5	
M-6(5)	Yamazoe Vil.[3]	R	209.3	390.8	79.8	(M-6～11) 145.0	75.0	142.4	37.5	(M-6～11) 40.8
M-7(6)	Totsukawa Vil.[4]	R	194.8	576.1	47.1		37.6	199.1	10.6	
M-8(7)	Higashi Vil.[5]	R	136.5	477.1	28.1		32.3	106.5	9.6	
M-9(8)	Kami Vil.[6]	R	136.4	307.1	65.8		41.2	235.9	6.4	
M-10	Shimo Vil.[7]	Cl	126.9	402.2	21.5		27.5	181.9	2.4	
M-11(9)	Mt. Ohdai[8]	M.C.	65.9	140.1	28.1		31.0	56.6	5.4	

1) Ci:City M.B.U.:Mountainous border of urban R:Rural Cl:Clean M.C.: Mountainous clean

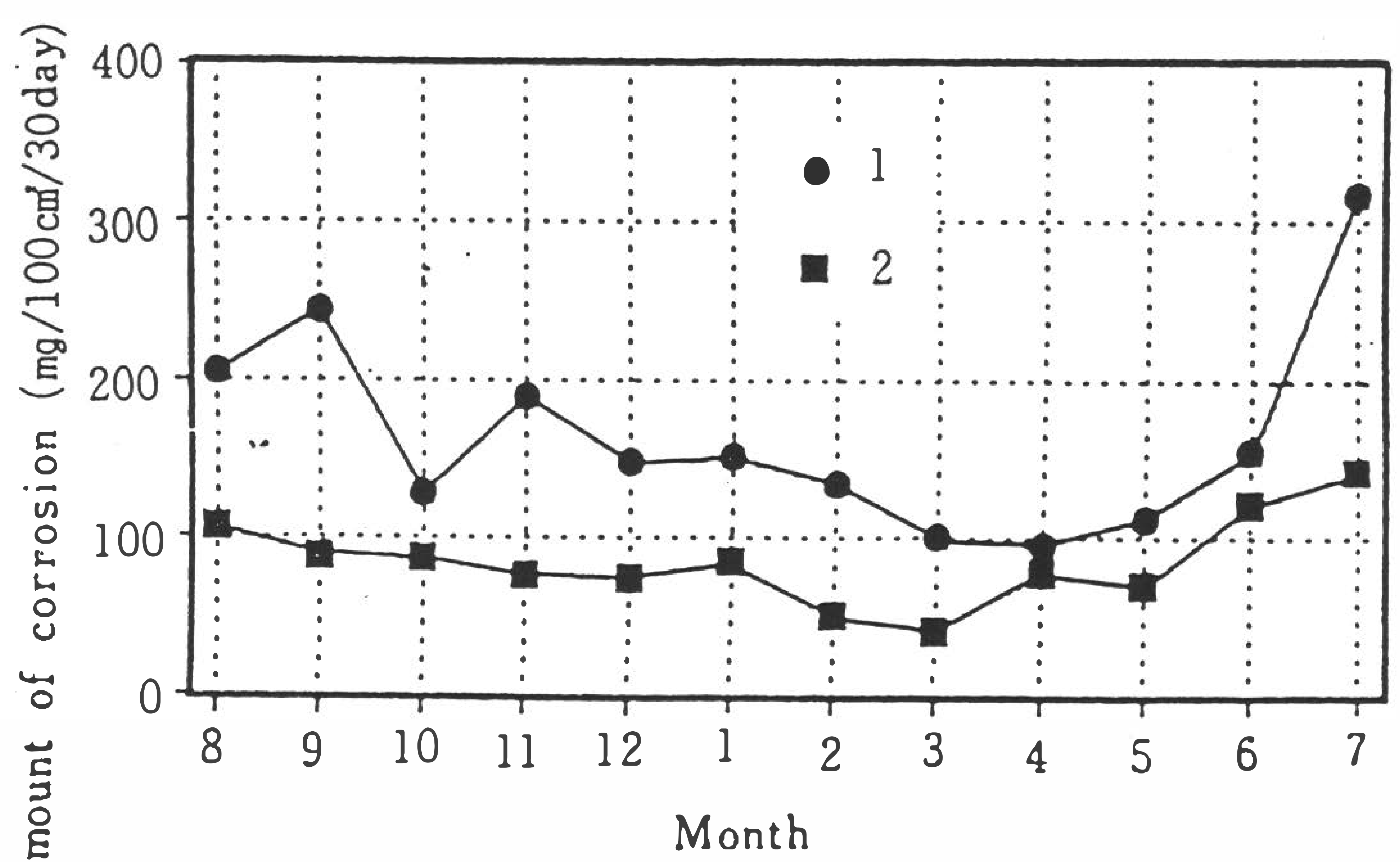
2) Numbers in parenthesis are numbers of sampling places of acid deposition

3) Yamazoe Village 4) Totsukawa Village 5) Higashiyoshino Village 6) Kamikitayamamura Village

7) Shimokitayama Village 8) Mt. Ohdaigahara 9) Average

in the city areas was greater than that in the rural areas on total and air exposure, and this increased in the summer season (Figure 3). The total/ air exposure ratios in rural areas were greater than those in city areas, and they did not change seasonally. In order to estimate the factors of corrosion of metal plates, a multiple regression analysis (MRA) was calculated by using the relation between the amount of corrosion of metal plates as subjective parameters and the acid rain, air pollution, meteorological factors as subordinate parameters. As a result of the MRA, the standard regression equation, whose coefficients of subjective parameters showed contribution rates, was as follows: amount of corrosion of metal plates (mg/100 cm^2/30 day)=0.26×[rain fall (mm)]+0.19×[H^+(μeq/ml)]+0.06×[SO_4^{2-}(μeq/ml)]-0.38×[NO_3^-(μeq/ml)]+ 0.31×[Cl^-(μeq/ml)]- 0.10×Na^+(μeq/ml)]-0.01×[NH_4^+(μeq/ml)]-0.04×[K^+(μeq/ml)]-0.09×[Ca^{2+}(μeq/ml)]+0.04×[Mg^{2+}(μeq/ml)] +0.34×[SO_2(ppb)]+0.09×[NO_2(ppb)]+0.10×[Cl^- (μg/100 cm^2/day)]+0.64×[Temperature(°C)]- 0.08×[Relative humidity(%)]+0.06×[wind velocity(m/s)], multiple correlation coefficient (R)=0.666, number of data sets (n)=75. The relationship between experimental values and MRA estimates are shown in Figure 4. In this equation, the parameters of large positive coefficients, such as rainfall, H^+, Cl^- (acid rain, air pollution), SO_2 and temperature, acted to increase amount of corrosion of metal plates. On the other hand, the parameters of large negative coefficients, such as NO_3^- and Na^+ in acid rain, acted to decrease or remove the amount of corrosion of metal plates. The factors contributing to the increase in the amount of corrosion of metal plates were in the following order: temperature>SO_2 >Cl^- (acid rain)>rain fall>H^+>Cl^- (air pollution). On the other hand, the factors contributing to the decrease in or removal of the amount of corrosion of metal plates were in the following order: NO_3^->Na^+. The parameters of either small positive or negative coefficients, such as SO_4^{2-}, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, NO_2, relative humidity and wind velocity, had little effect on the amount of corrosion of metal plates.

By the use of the thin film X-ray diffraction method, an identification of the corrosive compounds of metals, which was difficult under the conventional X-ray diffraction method, was tried (Matsumoto *et al.*, 1994).



1: Total exposure 2: Air exposure

Fig. 3. Monthly variation of the average amount of corrosion of metal plates by total and air exposure.

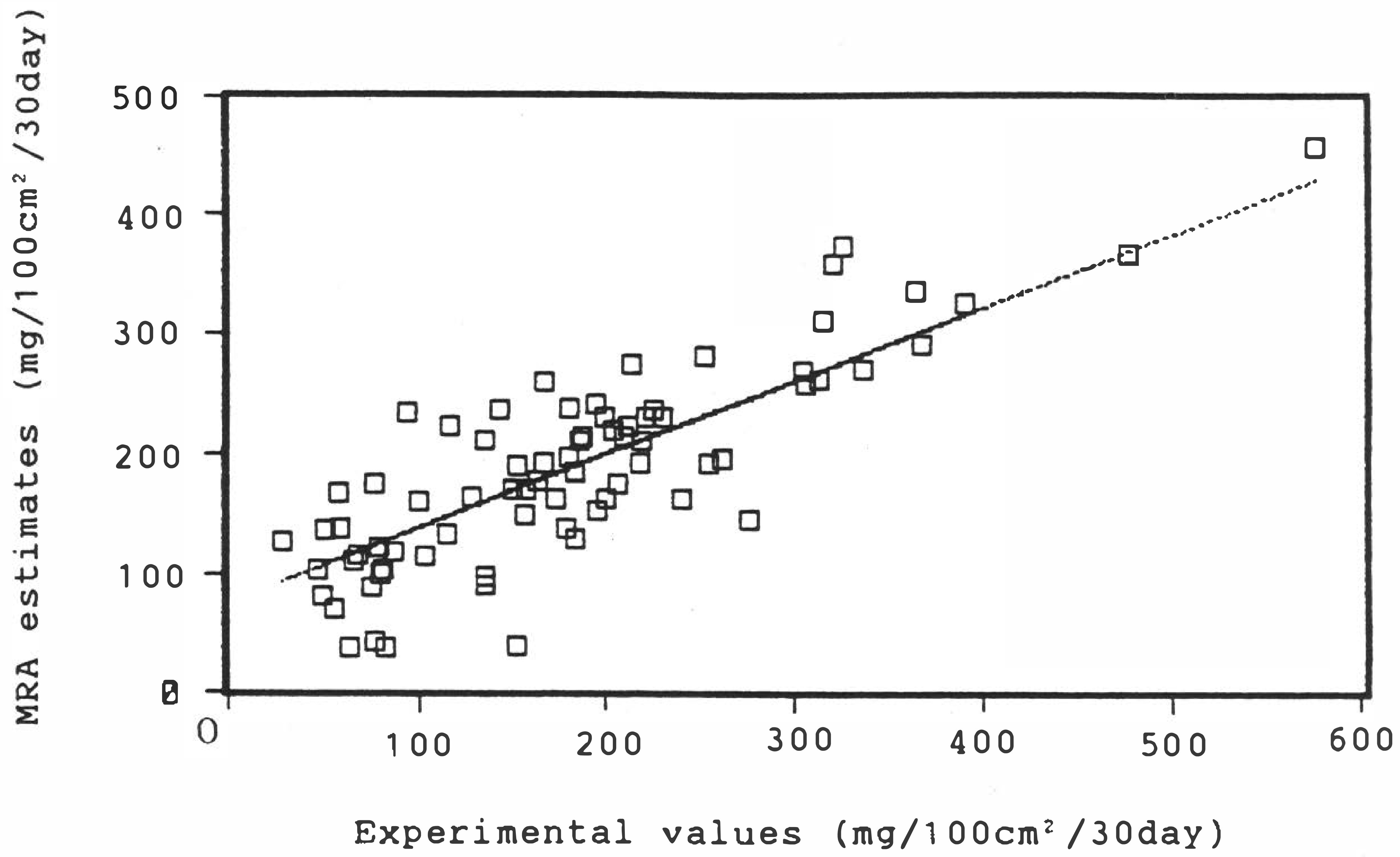


Fig. 4. Relationship between experimental values (amount of corrosion of metal plates by total exposure) and MRA estimates.

As a result, it was possible to obtain the diffraction pattern chart with good S/N ratios by directly attaching the metal plates to the sample holder and by using a monochromator. The crystal structure of corrosive compounds of metal plates exposed to 3 pieces of imitation acid rain each containing HCl, HNO_3 and H_2SO_4 were recognized to be α-FeOOH and γ-FeOOH by HNO_3 and H_2SO_4 and characteristic β-FeOOH and Fe_3O_4 including the above two compounds by HCl (Table 7). And concerning practical samples, the corrosive compounds of metal plates were mainly 4 kinds: α-FeOOH, β-FeOOH, γ-FeOOH and Fe_3O_4 in both the summer and winter seasons and by both total and air exposure in Nara City, commercial and residential district, and Totsukawa Village, clean and rural district. And while β-FeOOH and γ-FeOOH were mainly recognized in Nara City, γ-FeOOH was mainly recognized in Totsukawa Village (Table 8).

4. SUMMARY

The investigations of precipitation chemistry and corrosion of metal plates were carried out in Nara Prefecture. In consequence, acid rain and corrosion of metal plates caused by acid rain were recognized in this study. Since such acid rain and the damage caused by it are suspected to be on a very wide-range, it is necessary to conduct joint research on acid rain and its influences on the East of Asia.

Table 7. Identification of compounds of corrosion on carbon steel plates caused with dilute acid solution by thin film X-ray diffraction method.

Acid	Compounds (%)			
	α -FeOOH	β -FeOOH	γ -FeOOH	Fe_3O_4
HCl	9	48	29	15
HNO_3	33	0	67	0
H_2SO_4	28	0	72	0

Table 8. Identification of compounds of corrosion on carbon steel plates by thin film X-ray diffraction method.

	Total exposure				Air exposure			
	Summer		Winter		Summer		Winter	
Place	Compound	(%)	Compound	(%)	Compound	(%)	Compound	(%)
Nara City	α -FeOOH	13	α -FeOOH	7	α -FeOOH	26	α -FeOOH	28
	β -FeOOH	31	β -FeOOH	17	β -FeOOH	45	β -FeOOH	29
	γ -FeOOH	33	γ -FeOOH	61	γ -FeOOH	29	γ -FeOOH	43
	Fe_3O_4	23	Fe_3O_4	14	Fe_3O_4	0	Fe_3O_4	0
Totsukawa Village	α -FeOOH	7	α -FeOOH	6	α -FeOOH	8	α -FeOOH	0
	β -FeOOH	16	β -FeOOH	22	β -FeOOH	28	β -FeOOH	30
	γ -FeOOH	51	γ -FeOOH	60	γ -FeOOH	63	γ -FeOOH	70
	Fe_3O_4	26	Fe_3O_4	12	Fe_3O_4	0	Fe_3O_4	0

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REFERENECES

Matsumoto M., 1988: Determination and concentration of organic acids-carboxylic acids-in rain water by ion chromatography. *J. Japan Soc. Air Pollut.*, **23**, 64-71. (in Japanese)

Matsumoto M., Y. Nishikawa, K. Murano, and T. Fukuyama , 1987: Determination of aldehydes in rain water by HPLC. *BUNSEKI KAGAKU*, **36**, 179-183. (in Japanese)

Matsumoto M., 1992: Determination of hydrogen peroxide and dissolved SO_2 in rain water. *Ann. rep. Nara Prefect. Inst. Public Health*, **26**, 45-55. (in Japanese)

Matsumoto M., T. Tanaka, N. Ueda, and S. Tomita , 1992: Studies on corrosion of metal plates (carbon steel plates) by atmospheric environmental pollution containing acid rain. *J. Environ. Lab. Assoc.*, **17**, 170-177. (in Japanese)

Matsumoto M., and Y. Sato, 1994: Studies on the corrosion of metal plates (carbon steel plates) by atmospheric environmental pollution containing acid rain (II)-Identification of corrosive compounds of metal plates by the thin film X-ray diffraction method. *J. Environ. Lab. Assoc.*, **19**, 23-31.(in Japanese)