

## **Japan-wide stream chemistry monitoring (JWSM) 2003**

Eiichi KONOHIRA, Akemi ITAYA, Nagoya University  
Takashi WAKAMATSU, Central Research Institute of Electric Power Industry  
Junko SHINDO, National Institute for Agro-Environmental Sciences  
and  
Takahito YOSHIOKA, Research Institute for Humanity and Nature

### **1. Outline of JWSM 2003**

To understand the formation processes of stream water chemistry, we conducted systematic stream water sampling and chemical analyses as the Japan-Wide Stream Monitoring (JWSM) 2003. Stream water chemistry of forested areas in Japan has been monitored in previous studies. But these studies covered a limited region in Japan, and even though the monitoring sites covered more areas in Japan, sampling density was not sufficient. JWSM covered all over Japan except Chiba and Okinawa prefecture where we could not find suitable sampling sites.

Totally, 1278 samples from headwater streams were collected in the summer season of 2003 (1st July - 11th October). Samples were collected only once during the period. All catchments were covered by forest and completely free from human activities, such as houses, paddy fields and croplands. Catchment areas were variable depending on sites ranging from less than 1km<sup>2</sup> to more than 100km<sup>2</sup>, with 5.3km<sup>2</sup> as the average. As stream samples were collected at different climate conditions, we tried to take samples in ordinary flow conditions and did not take them during or just after rainfall to avoid direct influence of the rainfall on the stream water chemistry. Samples were collected in clean polycarbonate bottles after being rinsed 3 times by the sample. Collected samples were kept under refrigeration and sent to a laboratory by a transport company (Yamato transport Ltd). Samples were filtrated usually within 24 hours after sampling with a Whatman GF/F filter at the laboratory. Electric conductivity and pH were measured immediately after the filtration. Major anions and cations were measured by ion chromatography. Dissolved Inorganic Phosphate (DIP) concentrations were measured by molybdenum-blue method. Some samples showed much higher concentrations than other samples due to the contribution of hot spring water from volcanic areas. The extreme values of each ion were judged by the Smirnov test ( $p < 0.01$ ) and samples containing extreme values were omitted. 36 out of 1278 samples were omitted by the Smirnov test, meaning that 1242 data were used in this analysis.

Results of Nitrate (NO<sub>3</sub><sup>-</sup>) and DIP, which are major nutrient in water will be discussed in this report. Japanese average concentration of NO<sub>3</sub><sup>-</sup> and DIP was 26.1μM and 0.29μM, respectively. Natural stream contain significant amount of NO<sub>3</sub><sup>-</sup>, and N/P ratio was 90 in mol basis showing that streams are rich in nitrogen compare with phosphorous. JWSM 2003 also showed Japanese average value of major dissolved ions, indicating back ground level of water quality (Table1, Table2)

### **2. Regional distribution of NO<sub>3</sub><sup>-</sup> and its controlling factors**

Figure 1 shows the distribution of NO<sub>3</sub><sup>-</sup> concentrations in each site. Streams in northern part of

Japan (Hokkaido and Tohoku region) usually showed very low  $\text{NO}_3^-$  concentrations. Forest ecosystems in low temperature retained nitrate within the ecosystems and did not release  $\text{NO}_3^-$  to streams. Higher concentrations were found around Metropolis of Tokyo and also along with Seto Inland Sea. These areas were located in middle of Japan, and no features in climate conditions could be found in these areas. On the other hand, these areas were very close to big cities include Tokyo, Osaka, Okayama, Hiroshima and Fukuoka, suggesting human impacts highly contributed to stream  $\text{NO}_3^-$  concentrations. These streams are free from direct influence of human activities, such as houses, paddy fields and croplands. Only indirect influences of nitrogen pollution by way of atmosphere could explain higher  $\text{NO}_3^-$  concentrations around big cities.

Figure 2 shows relationship between stream  $\text{NO}_3^-$  concentration and atmospheric N deposition rate to the catchments. Significant correlation was found between them, confirming that atmospheric N deposition rate was a main factor to decide  $\text{NO}_3^-$  level in Japanese stream waters. Since correlation coefficient between stream  $\text{NO}_3^-$  concentration and atmospheric N deposition rate was low (Figure 2), other factors (climate, geology and vegetation) might contribute to  $\text{NO}_3^-$  level in Japanese stream waters. Application of multiple regression analysis showed that catchment slope, catchment direction, annual precipitation, annual mean temperature and atmospheric nitrogen deposition rate were significant parameters for stream  $\text{NO}_3^-$ . Relative importance among these parameters was analyzed by normalized coefficient of them. Normalized coefficients were 0.501(atmospheric nitrogen deposition), -0.275 (annual precipitation, negative correlation), 0.250 (annual mean temperature), 0.142 (catchment slope) and -0.081 (catchment direction).

### 3. Regional distribution of DIP and its controlling factors

DIP concentrations were distributed following log-normal distribution, and medium value was  $6.6\mu\text{g/L}$ . Streams showing low concentrations (less than  $4.0\mu\text{g/L}$ ) occupy 28% of all streams. On the other hand, 89 streams exceeded  $20\mu\text{g/L}$ , occupying 7% of all streams. Streams in higher concentrations of DIP were found in northern part of Ibaraki pref., Saitama pref., West part of Tokyo Metropolis, Hokuriku district and East part of Chugoku district between Ishikawa pref. and Tottori pref., mountainous are in Shikoku and Kyushu district, and northern part of Saga pref. (Figure 3). Streams in lower concentrations were found in central part of Hokkaido, Chubu and Tokai district and west part of Chugoku district (Figure 3).

DIP concentrations in stream waters were different significantly by geology, and higher in the order of igneous rocks, metamorphic rocks, sedimentary rocks. Among sedimentary rocks, Higher concentrations were found in Palaeozoic, compared with in Cenozoic and Mesozoic. Among igneous rocks, intermediate or basic rocks (eg., andesite) were higher in DIP concentrations than acid rocks (eg., rhyolite, granite). These streams DIP differences agreed with phosphorous content in geologies of the catchments reported in previous studies. In relation to other substances, DIP concentrations positively correlated with  $\text{SiO}_2$  concentrations except for Mesozoic and Palaeozoic sedimentary rocks. These facts that DIP concentrations related to geology and  $\text{SiO}_2$  suggests that phosphorous contents of bedrocks and weathering processes are major factors controlling DIP concentration in streams.

#### 4. Change in Japanese stream water chemistry in recent 50 years

The JWSM 2003 was the first opportunity to demonstrate stream water chemistry on a Japanese national scale. But about 50 years ago (1943-1958), Kobayashi (1971) reported river water chemistry on a Japanese national scale. He mainly observed major rivers having a large catchment area and many of the observation points were located down streams comparing with the JWSM 2003. Although sampling locations were different, these two observations were conducted to understand background level of river water chemistry. Moreover, observation results by Kobayashi (1971) included some direct influences by human activities, but the observed period (1943-1958) was before economic and industrial development in Japan after 1960. River water chemistry might be free from human influences in many substances, and it was close to stream water chemistry at that time. We assumed that we could detect change in Japanese stream water chemistry in recent 50 years by these data sets. As mentioned above, sampling locations were different in two data sets and average values of prefectures were used for comparison (Figure 4).

Figure 4 shows that pH decreased and  $\text{HCO}_3^-$  increased in recent 50 years. Other anions and cations usually decreased except for N compounds,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . These results suggests that stream water chemistry changed in recent 50 years and that forest environments controlling stream water chemistry might have been changed in this period. Reasons and mechanisms which generated these changes are not clear in this study, but clear increase in  $\text{NO}_3^-$  concentration in recent 50 years supports that atmospheric N deposition would be a main factor to control  $\text{NO}_3^-$  level in 2003. Increase of atmospheric N deposition in recent 50 years could explain increase of  $\text{NO}_3^-$  concentration in stream water in this period.

#### References

- Kobayashi, J. (1971), Health diagnosis of water, Iwanami shinsho No.777, pp. 207, Iwanami shoten, Tokyo. (in Japanese)
- Shindo J., E. Konohira, T. Yoshioka, K. Okamoto and H. Kawashima (2005), Nationwide estimation of nitrogen load and nitrogen concentration in natural catchments, Environmental science 18 (4) : 455-464 (in Japanese with English summary)

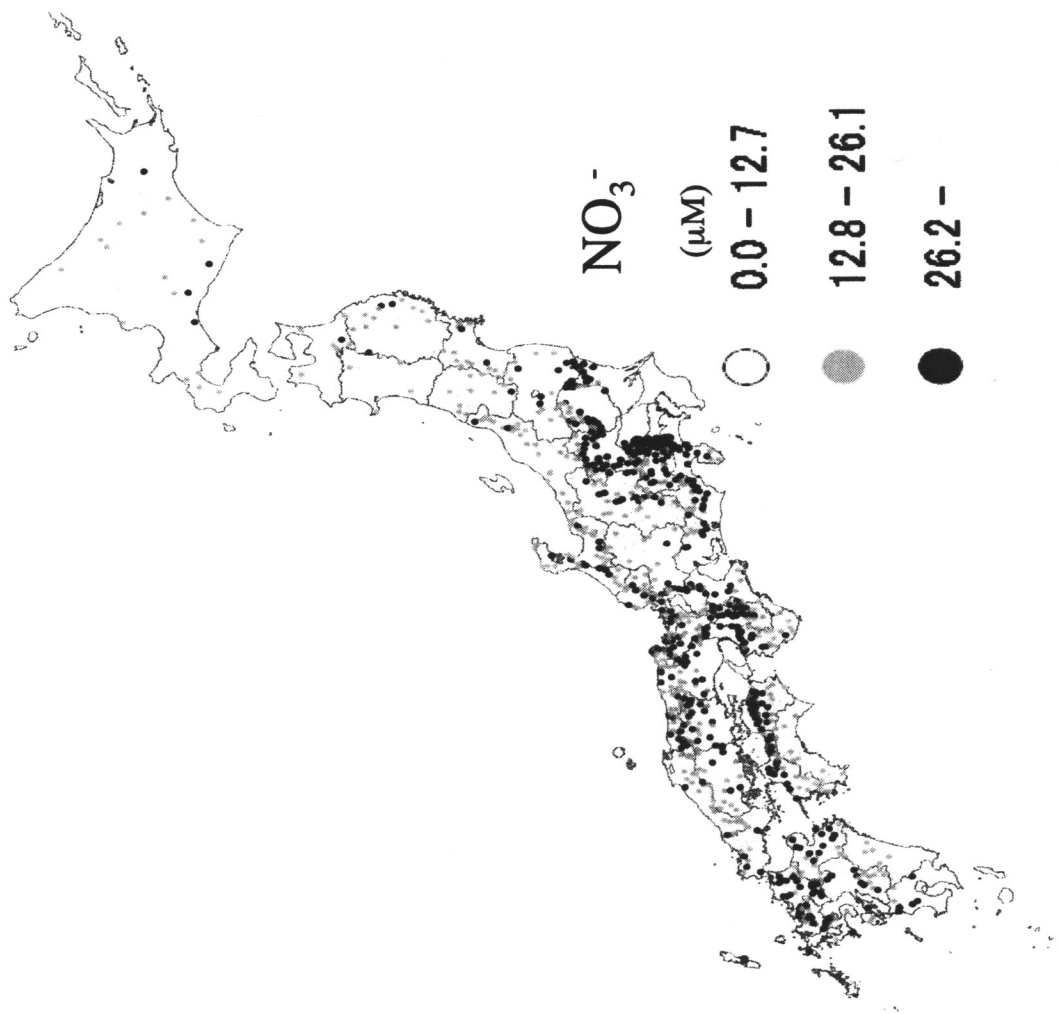


Fig.1 Distribution of NO<sub>3</sub><sup>-</sup> concentrations in natural streams

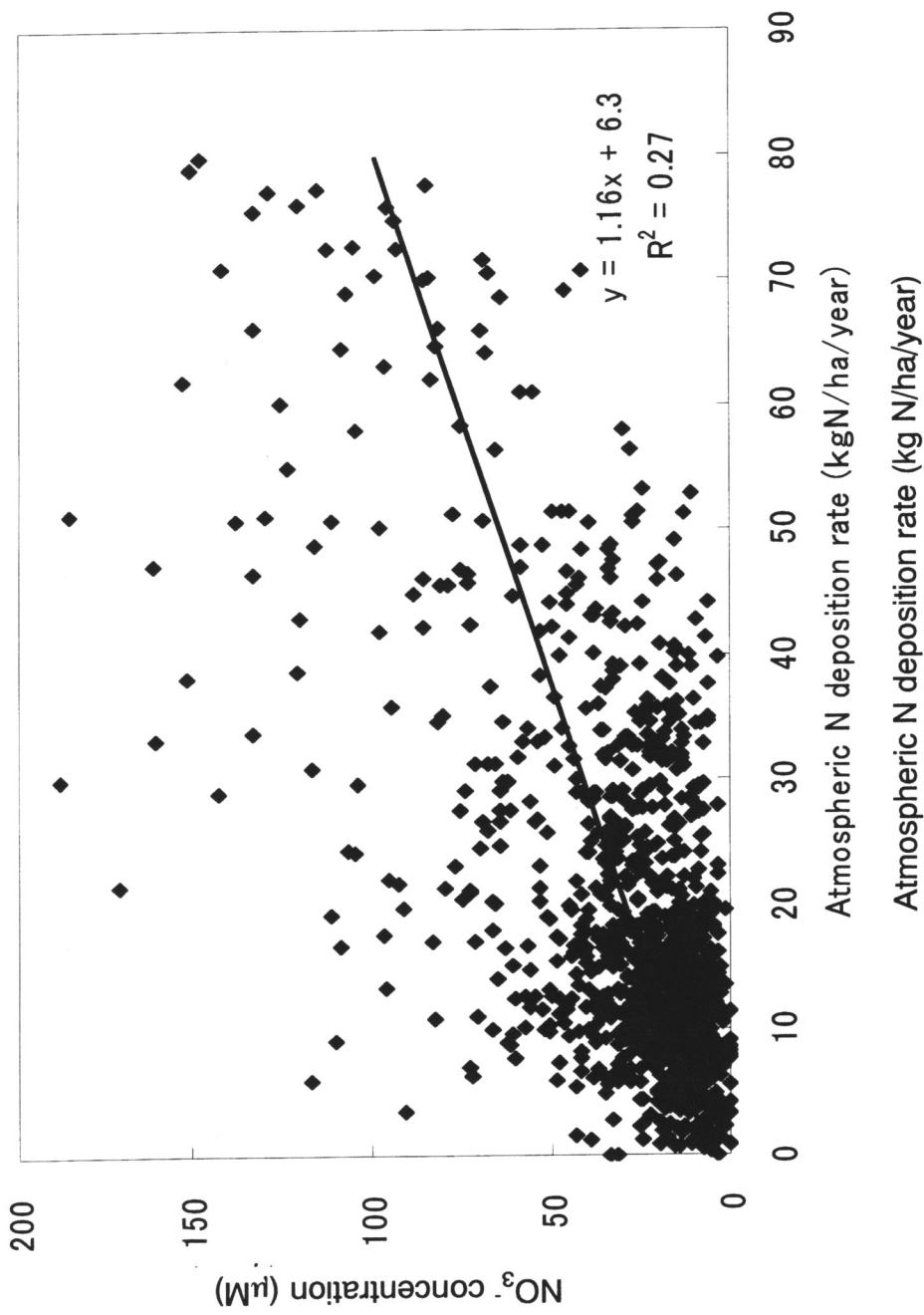


Fig.2 Relationship between atmospheric N deposition rates (Shindo et al, 2005) and stream NO<sub>3</sub><sup>-</sup> concentrations.

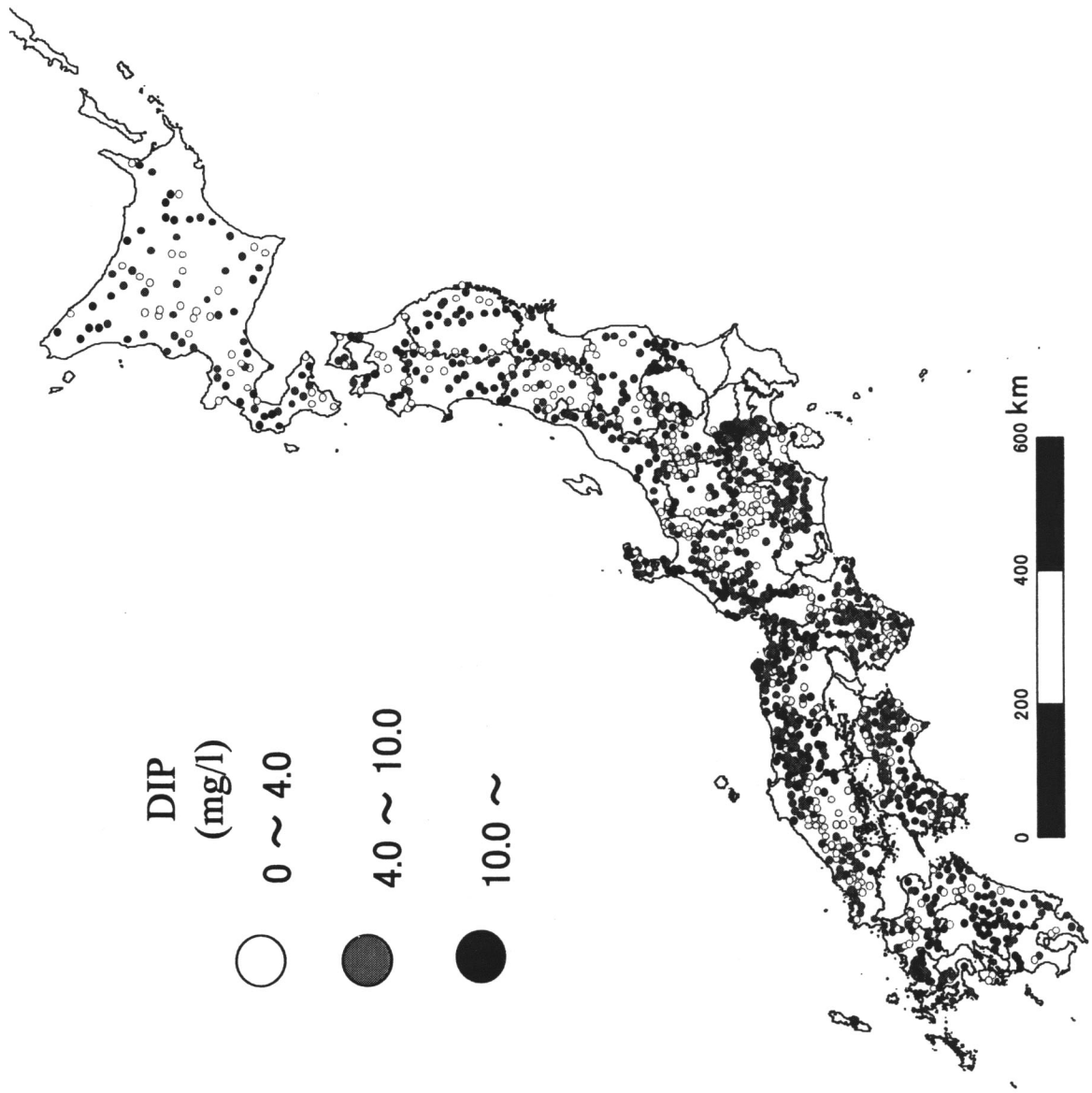


Fig.3 Distribution of DIP concentrations in natural streams

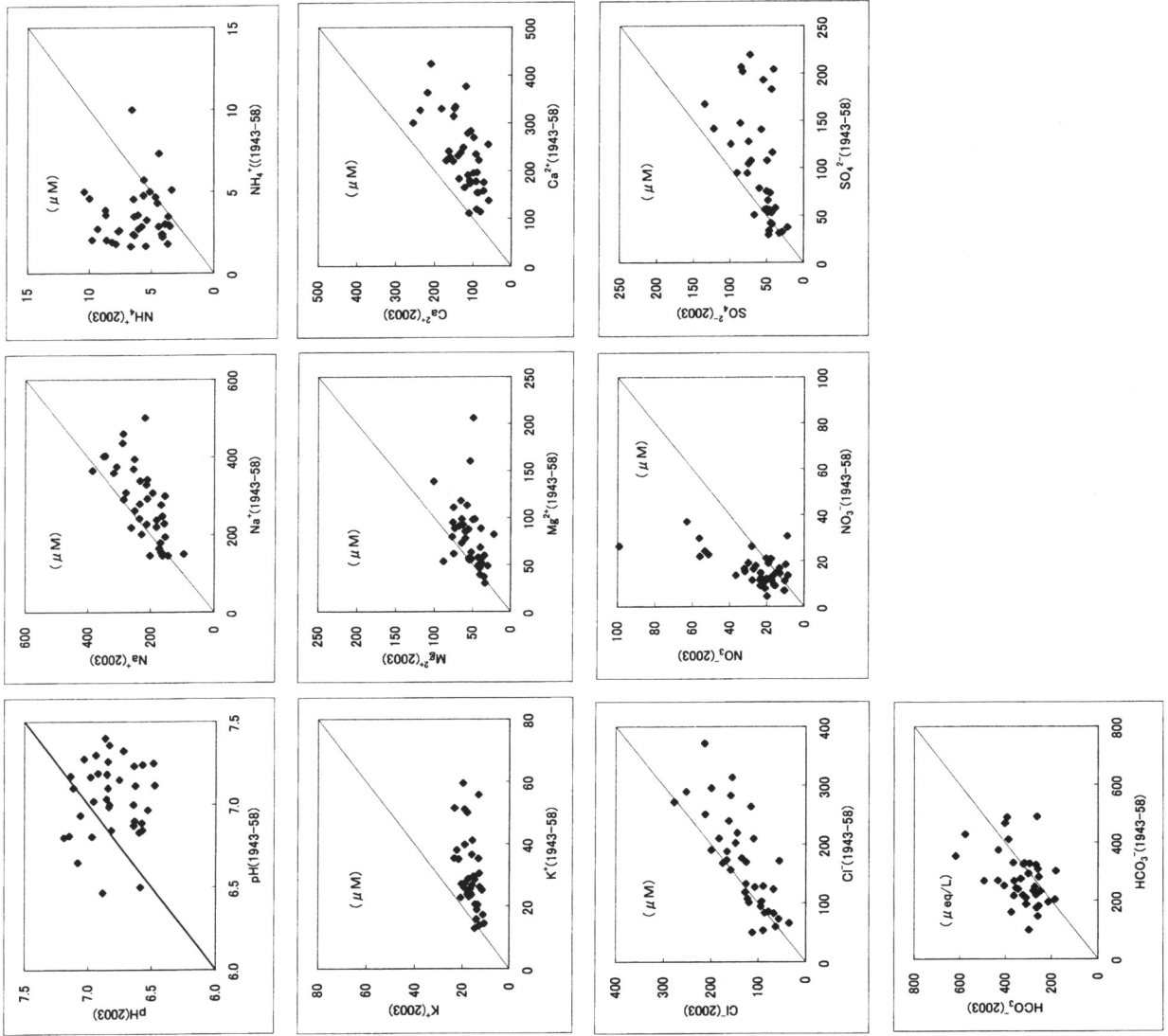


Fig.4 Relationships of Japanese stream water compositions between 1943-58 and 2003.

Table 1. EC, pH and anion concentrations averaged in each prefecture and those of all samples.

Prefectures	n	EC (mS m <sup>-1</sup> )		pH		Cl <sup>-</sup> (μM)		NO <sub>3</sub> <sup>-</sup> (μM)		SO <sub>4</sub> <sup>2-</sup> (μM)		anion deficit (μ e)	
		average	SD	average	SD	average	SD	average	SD	average	SD	average	SD
Hokkaido	91	8.49	3.99	6.97	0.27	159	108	9.1	8.4	85.7	83.9	433	257
Aomori	28	8.50	3.05	6.59	0.36	278	122	9.9	8.6	82.7	53.3	310	189
Iwate	30	5.18	2.06	6.93	0.18	86.0	31.4	13.4	8.6	47.3	57.1	269	129
Miyagi	22	5.34	1.30	6.64	0.15	125	53.1	17.3	11.7	41.3	17.0	266	94.4
Akita	26	7.46	2.39	6.89	0.19	200	106	8.8	3.9	84.8	59.5	298	117
Yamagata	28	5.88	1.94	6.63	1.31	115	61.7	10.5	5.0	70.8	61.4	257	138
Fukushima	28	5.01	2.06	6.86	0.17	67.3	27.1	19.2	11.4	45.0	64.3	268	162
Ibaraki	11	7.48	2.55	6.85	0.12	109	37.1	51.4	35.0	57.5	35.1	393	162
Tochigi	29	5.80	2.23	6.68	0.31	44.5	21.1	29.3	14.9	75.2	66.1	285	212
Gunma	27	6.77	3.27	6.61	0.24	46.0	11.3	62.3	40.3	75.5	79.7	283	202
Saitama	19	10.54	3.79	7.24	0.20	52.0	20.9	102	35.4	97.5	66.0	609	221
Tokyo	13	7.85	1.89	6.83	0.17	55.8	19.5	99.1	37.0	72.8	22.3	401	171
Kanagawa	22	9.47	3.46	7.03	0.30	68.3	23.3	63.1	28.0	76.2	86.3	576	211
Niigata	39	6.70	4.12	7.15	0.26	145	87.1	16.3	6.2	74.5	122	279	198
Toyama	28	7.44	2.99	7.14	0.22	94.5	93.6	21.1	8.0	52.6	42.5	405	247
Ishikawa	25	8.10	2.39	6.84	0.20	253	120	15.4	10.6	54.7	53.7	344	134
Fukui	28	7.22	2.70	6.63	1.32	176	94.3	23.3	12.2	46.5	61.1	363	199
Yamanashi	30	7.95	3.99	6.84	0.24	32.5	14.1	34.1	22.7	79.1	84.8	431	191
Nagano	63	5.61	3.62	6.72	0.31	24.5	18.0	16.8	13.9	60.9	74.4	328	247
Gifu	30	3.97	2.76	6.75	0.30	35.2	22.4	13.0	8.6	21.7	15.8	255	235
Shizuoka	30	8.98	2.72	6.94	0.34	57.1	35.8	32.0	22.5	135	91.7	430	172
Aichi	19	4.35	2.14	7.19	0.30	63.3	24.1	20.2	12.7	29.1	15.1	260	174
Mie	22	6.38	3.03	7.06	0.22	92.4	30.4	23.1	16.8	51.2	27.1	332	245
Shiga	32	7.30	4.95	6.98	0.33	106	23.9	28.4	17.2	50.9	18.8	422	414
Kyoto	36	7.88	3.13	7.08	0.19	213	117	27.7	20.6	43.0	19.9	374	187
Osaka	20	11.06	5.98	7.12	0.22	163	59.2	53.4	33.5	98.9	68.8	619	424
Hyogo	28	7.13	2.81	6.82	0.28	155	72.1	28.2	11.8	49.3	23.7	353	250
Nara	25	6.88	3.70	6.70	0.25	81.9	36.1	41.7	36.7	54.5	38.9	392	281
Wakayama	31	7.32	3.40	6.57	0.23	119	51.3	21.0	12.2	90.1	46.2	312	219
Tottori	27	6.45	2.06	6.96	0.18	183	58.2	23.5	10.2	32.8	16.1	324	151
Shimane	26	6.03	1.81	6.53	0.18	214	64.2	15.6	6.6	43.1	22.3	185	80.7
Okayama	35	7.86	4.94	6.98	0.24	128	37.0	27.0	19.8	48.3	36.6	492	416
Hiroshima	28	5.20	3.68	6.64	0.33	125	36.9	20.3	15.3	45.9	46.0	216	245
Yamaguchi	21	5.34	1.80	6.48	0.21	166	65.6	17.8	11.0	47.2	13.8	181	95.5
Tokushima	29	7.02	2.20	6.64	0.14	112	80.9	19.9	15.6	66.8	44.7	361	164
Kagawa	16	8.82	1.83	6.87	0.23	167	41.9	56.1	23.6	122	28.8	321	173
Ehime	32	7.02	3.84	6.83	0.22	122	79.7	36.7	24.6	74.5	88.2	318	200
Kochi	34	5.55	1.89	6.72	0.18	89.3	41.8	10.7	5.0	44.5	16.2	296	176
Fukuoka	24	7.04	2.76	6.85	0.15	148	58.2	56.4	30.5	58.6	25.9	265	159
Saga	20	5.77	2.16	6.85	0.25	135	29.2	29.8	15.2	38.2	12.5	274	206
Nagasaki	6	6.52	2.57	6.49	0.27	200	112	25.8	23.5	42.2	18.4	260	116
Kumamoto	21	6.39	1.64	6.57	0.26	89.4	53.4	23.2	10.6	43.5	16.1	387	145
Oita	23	6.95	2.74	6.84	0.28	107	57.1	31.7	23.7	60.1	33.6	365	177
Miyazaki	27	5.40	1.72	6.60	0.22	78.0	31.4	10.6	4.9	49.6	24.6	249	159
Kagoshima	13	6.71	2.29	6.58	0.27	159	58.9	17.5	13.3	49.7	18.6	300	239
Japan	##	6.94	3.42	6.84	0.31	119	88.2	26.1	25.4	62.8	61.1	344	235



Table 2. Cation concentrations averaged in each prefecture and those of all samples.

Prefectures	n	Na <sup>+</sup> (μM)		NH <sub>4</sub> <sup>+</sup> (μM)		K <sup>+</sup> (μM)		Mg <sup>2+</sup> (μM)		Ca <sup>2+</sup> (μM)	
		average	SD	average	SD	average	SD	average	SD	average	SD
Hokkaido	91	289	157	3.6	2.4	22.3	12.0	76.0	52.4	153	101
Aomori	28	386	147	4.1	3.0	19.1	9.8	76.8	51.7	100	57.0
Iwate	30	168	55.6	4.4	2.9	11.3	5.5	40.1	19.5	99.4	63.3
Miyagi	22	210	55.3	3.4	0.9	15.9	11.2	39.9	20.4	90.4	57.2
Akita	26	317	128	6.4	2.1	16.5	8.9	59.7	23.5	108	67.5
Yamagata	28	214	82.9	5.6	1.5	12.7	6.1	59.7	47.7	86.6	52.2
Fukushima	28	158	49.2	5.6	1.5	16.2	7.6	42.8	35.6	89.6	60.3
Ibaraki	11	219	61.9	6.5	1.7	18.0	6.0	65.8	34.4	147	71.3
Tochigi	29	148	55.8	5.5	1.7	14.9	11.4	44.4	26.0	126	70.1
Gunma	27	115	30.1	9.1	3.6	13.9	6.2	49.6	28.3	153	112
Saitama	19	143	67.5	6.8	4.0	13.1	3.4	80.0	42.0	317	150
Tokyo	13	156	42.5	5.1	1.9	13.2	2.3	53.5	17.4	210	78.2
Kanagawa	22	164	50.1	4.4	2.4	12.9	10.9	101	56.8	239	98.8
Niigata	39	211	86.9	5.4	1.5	18.9	10.8	62.9	42.2	114	121
Toyama	28	174	127	6.4	2.4	14.1	7.5	51.7	37.7	164	99.9
Ishikawa	25	350	147	6.4	2.1	20.5	9.8	64.4	29.6	108	75.0
Fukui	28	236	94.3	3.7	1.7	12.7	5.8	64.4	48.1	137	74.7
Yamanashi	30	129	49.1	6.7	4.5	17.2	15.7	68.2	41.8	183	101
Nagano	63	103	82.9	5.1	3.4	17.1	10.5	45.3	42.5	138	112
Gifu	30	97	22.4	6.1	3.1	13.4	6.0	22.1	21.3	93.2	114
Shizuoka	30	181	63.4	3.6	1.0	15.4	7.0	75.3	41.0	219	87.5
Aichi	19	146	63.5	4.7	1.7	17.6	10.2	35.0	34.5	81.8	57.4
Mie	22	170	48.4	5.4	2.3	17.9	14.0	38.6	22.0	140	122
Shiga	32	171	36.9	12.6	6.5	13.3	4.3	52.8	34.2	178	204
Kyoto	36	285	127	3.7	1.3	14.6	7.8	88.1	59.3	110	65.5
Osaka	20	345	166	4.5	1.3	23.4	12.6	73.5	48.6	257	188
Hyogo	28	251	84.0	4.2	2.0	16.1	8.4	55.3	47.4	126	90.7
Nara	25	167	66.8	8.4	3.5	14.1	10.6	49.2	47.0	169	119
Wakayama	31	262	117	3.9	1.6	17.2	7.4	52.1	25.0	123	89.7
Tottori	27	278	76.6	9.3	7.3	17.4	8.0	54.6	28.1	91.1	55.6
Shimane	26	287	75.9	9.8	4.0	15.2	4.2	34.8	18.9	59.7	35.8
Okayama	35	229	75.3	4.1	1.6	20.8	12.9	75.0	70.6	170	168
Hiroshima	28	213	57.1	6.0	4.4	19.4	10.3	34.0	48.9	73.4	108
Yamaguchi	21	250	89.3	8.6	3.6	16.6	5.2	30.4	15.8	61.8	38.1
Tokushima	29	202	128	8.1	4.5	14.8	8.3	40.2	21.0	161	89.3
Kagawa	16	307	51.5	7.5	1.6	23.4	7.6	43.0	23.1	183	84.0
Ehime	32	182	147	5.8	2.3	13.9	11.6	60.2	47.1	152	96.8
Kochi	34	163	65.6	7.8	3.0	10.8	3.7	37.2	21.2	115	85.8
Fukuoka	24	221	56.9	10.0	4.4	15.9	5.2	50.2	19.0	120	75.3
Saga	20	234	51.7	10.4	4.0	14.8	5.2	55.6	74.6	72.5	48.1
Nagasaki	6	254	80.9	8.7	3.2	21.7	11.9	57.5	26.4	85.4	69.8
Kumamoto	21	168	61.4	7.6	3.3	13.2	8.9	49.6	21.8	149	67.8
Oita	23	194	62.9	8.7	3.6	19.2	10.5	67.9	47.0	133	76.0
Miyazaki	27	155	46.5	6.6	3.3	11.8	7.0	39.2	27.0	92.6	63.9
Kagoshima	13	235	53.3	6.4	4.2	19.8	5.8	47.5	28.5	110	89.5
Japan	##	211	115	6.1	3.8	16.4	9.6	55.8	43.0	135	108