

C-1.1.2 Development of Screening and Analysis Method for Precipitation Data Sets

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Abstract

Three approaches were made for data evaluation and source estimation of acid deposition. 1) A normal distribution theory was applied for formulating the basis for ion balance screening. Experimentally determined parameters in the formula enabled us to predict the probable ranges for ion balance, 2) Probable errors associated pH measurement with glass-electrode was evaluated on the basis of both theory and experiments, and 3) SLS method was modified to precipitation chemistry data analysis. This method was further applied to datasets for two sites on Japan Sea coast, Iwamizawa and Yoshinotani to predict the numbers of main sources and their chemical compositions, which will provide a very useful tool for source analysis without any information on source chemistry.

Key Words: Ion Balance, Precision, pH, sources, sulfate, Japan Sea

1. Introduction

Data quality evaluation is indispensable in the analysis of precipitation chemistry data because its quality directly affects the validity of conclusion of the research. The quality of the data is usually evaluated in terms of ion balance¹⁾. However, the acceptable limits were not set through theoretical discussions but empirical practices²⁾. Some mathematical theory should be applied to this evaluation method.

Hydrogen ion concentration is determined with pH measurements which could be highly problematic for precipitation waters. This precision should be evaluated both theoretically and experimentally.

Source prediction is an important analysis in the study of acid deposition, but commonly employed analysis methods including elementary mass balance method require some information on source chemistry. SLS method is capable of

4. Self-Consistent Least-Mean Square (SLS) Method for Source Estimation

Without any source information, the SLS method enables the number of sources, their chemical composition as well as relative contributions. A schematic explanation for this method is given in case of assumed three sources (Fig. 3). Concentrations of a component at sources A, B, and C (C_A , C_B , C_C) are first assumed. With these values and precipitation chemistry data, relative contribution of each source, F_A , F_B , F_C are then computed. This iteration is conducted until C's and F's are significantly converged.

This newly modified method was applied to datasets for sites on Japan Sea coast²⁾, Iwamizawa and Yoshinotani. The result is shown in Table 3. Iwamizawa site was interpreted to be affected by three sources whose chemical components were 1) sulfate and nitrate salts of calcium and ammonium, 2) seasalt, and 3) partially neutralized acids. Similar results were obtained for Yoshinotani (Table 3).

These findings are consistent with proposals by Tsurumi et al.⁴⁾ and Satake et al.⁵⁾ that some fraction of sulfate were in the form of calcium sulfate. Present result suggests that this compound could be deposited over a wide range of Japan Sea coastal area. Hara et al.^{6, 7)} suggested that sulfate deposition intensity increased in winter along this coastal area. The present result supports their results.

References

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predicting the number of sources and their chemical composition without any source information. A method derived from the SLS for precipitation chemistry data analysis will be applicable to many datasets available in Japan²⁾.

In this study, ion balance was theoretically discussed with some experimentally determined parameters, errors associated with pH measurements were evaluated with theory and experimentation, and further, the SLS method was modified for precipitation chemistry data analysis and applied to available datasets for Japan Sea coast.

2. Model for Ion-Balance Screening

A measured value for an ionic species, i , obeys the normal distribution, $N(\mu_i, \sigma_i^2)$ on the basis of error theory, which further suggests ion balances, $R1(=C/A)$ and $R2(=\Lambda_{calc}/\Lambda_{meas})$ obey normal distributions. The mean and standard deviation in the normal distributions will be obtained from the means and standard deviations of individual component ions: $\mu_R = \mu_C/\mu_A$, $\sigma_R^2 = (\mu_C/\mu_A)^2 \times (\sigma_C^2/\mu_C^2 + \sigma_A^2/\mu_A^2)$.

The standard deviation for cation sum, C and anion sum, A were the sums of each standard deviation for each component, which was estimated from standard deviation in reproducibility experimentation of ten precipitation samples. The means and standard deviations were shown in Table 1. From these parameters, probability functions for $R1$ and $R2$ are eventually obtained. Both $R1$ and $R2$ probability functions for a sample are illustrated in Fig. 1. The $R1$ and $R2$ values were well in the conventional acceptable range, 0.80-1.20, but the standard deviations considerably. For the precipitation samples in Table 1, $R1$ and $R2$ were illustrated as ellipses with standard deviations in Fig. 2. In these ways, the $R1$ and $R2$ values will be quantitatively discussed. The standard deviations were well smaller than the ion balance difference from unity. This strongly suggests that random errors do not significantly affect the ion balance, and that systematic errors should be reviewed in such cases.

3. Precision of pH Measurement with Glass-Electrodes

The pH value determined with the glass-electrode is expressed theoretically as: $pH_G = -\log [H^+] - \log \gamma + F(E_s - E_{s,s})/(\kappa RT \ln 10)$. Application of Debye-Huckel and Henderson equations to this equation will provide estimates for theoretical errors due to the difference between standard solution and precipitation water samples. The error was suggested as high as 0.04 pH unit in most cases.

Errors associated with experimental determination were evaluated with electrodes of different types under various conditions. The results are shown in Table 2 with those by Midgley³⁾. Experimental errors were concluded to be 0.1. We recommend evaluation of electrode performance before the employment of a new electrode as well as periodical evaluation between experiments.

Table 1. Means and Standard Deviations

Sample Code	Concentration				Conductivity				
	pH	C	A	R ₁	σ ₁	Δ _{mean}	Δ _{oac}	R ₂	σ ₂
μeq L ⁻¹									
1	4.53	55.0	57.4	0.958	0.0230	13.6	16.2	1.197	0.0224
2	4.66	57.9	55.0	1.052	0.0323	11.9	14.1	1.187	0.0476
3	4.82	30.5	26.6	1.147	0.0401	16.8	8.28	0.493	0.0154
4	4.61	53.8	51.7	1.041	0.0883	12.0	14.41	1.201	0.0410
5	4.42	75.6	61.6	1.227	0.0688	15.5	20.31	1.310	0.0483
6	4.76	40.2	34.6	1.16	0.0246	9.48	10.10	1.065	0.0413
7	4.62	42.7	33.8	1.28	0.0333	9.22	12.12	1.314	0.0601
8	4.78	38.8	34.9	1.06	0.0287	7.87	9.70	1.23	0.0390
9	4.60	84.6	59.2	1.428	0.0194	2.27	17.34	7.637	0.493
10	4.63	42.5	32.3	1.32	0.0356	6.45	11.90	1.84	0.0543

Table 3. Estimated Sources and Chemical Compositions

Source	II	Na	K	NH ₄	Mg	Ca	Cl	NO ₃	SO ₄
Iwamizawa									
SI1	0.00	0.0	1.64	14.8	3.54	80.0	0.0	31.5	68.5
SI2	0.441	75.3	1.75	1.38	14.8	6.31	88.2	0.0	11.8
SI3	28.6	23.8	10.8	30.0	6.75	0.00	27.2	19.5	53.2
Yoshinotani									
SY1	0.00	9.55	0.00	0.00	10.8	79.7	0.00	53.4	46.6
SY2	0.00	13.7	6.88	68.0	3.05	8.44	18.2	17.0	64.8
SY3	3.77	0.00	47.0	2.99	0.466	45.8	7.11	0.0	92.9
SY4	93.3	6.74	0.00	0.00	0.00	0.00	0.00	32.0	68.0
SY5	0.00	77.0	1.52	0.00	18.8	2.76	88.3	0.0	11.7
(Seasalt)									
	0	77	2	0	18	3	90	0	9

Table 2. Characteristics of Glass Electrodes

No.	Type	Resistance kΩ	KCl Elusion Rate	Stirring Shift		Surge	Noise	Response κ		Bias	Junction Bias		
				pH	pH			static	dynamic			min	pH
This work													
1	Sleeve	6.7	1.7	-0.001	0	0.04	-0.2~0.04	0.004	0.007	7	0.993	-2.5	-0.006
2	Sleeve	7.6	220	+0.029	+0.031	0.14	-0.2~0	0.006	0.009	8	0.996	-2.5	0.058
3	Sleeve	5.0	4.7	-0.001	-0.002	0.025	-0.04~0.025	0.005	0.084	8	0.991	-2.8	0.090
4	Ceramic	7.0	0.32	-0.009	-0.009	0	0	0.003	0.003	13	0.985	-51.2	0.004
5	Ceramic	3.1	0.96	---	---	0	0	0.004	0.008	10	0.963	-53.3	0.044
6	Pin-hole	140	1.5x10 ⁻³	---	---	---	---	---	---	---	---	---	---
7	KCl-elusion	11	5.4(push)	+0.003	+0.001	0	0	0.003	0.014	0.5	0.992	-5.0	0.038
Midgley(1987)													
A	Sleeve	2.1~19	0.2~450									0.033~0.091	
B	Ceramic	0.3~150	<0.05~63									-0.14~0.117	
C	Capillary	30	3									0.008	
D	Pt-wire	0.9	58									0.005 <0.5	

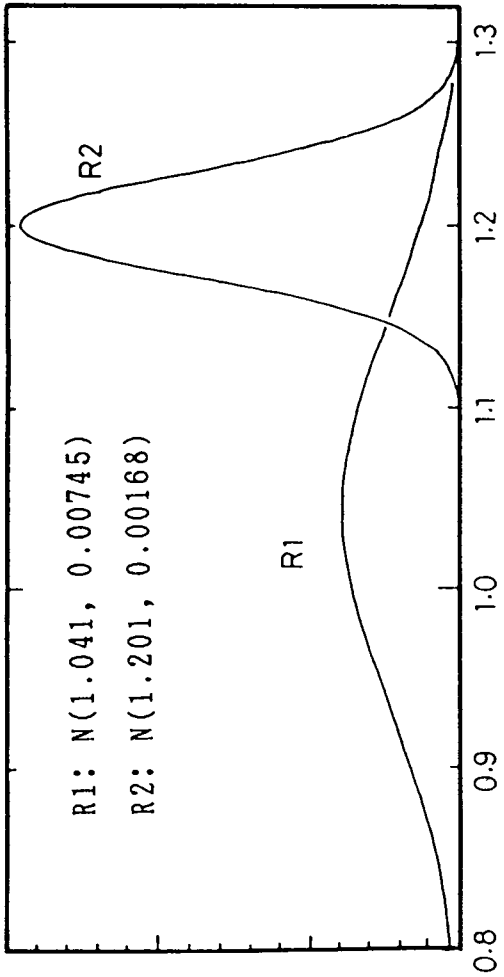


Fig. 1 Estimated Probability Functions for R1 and R2

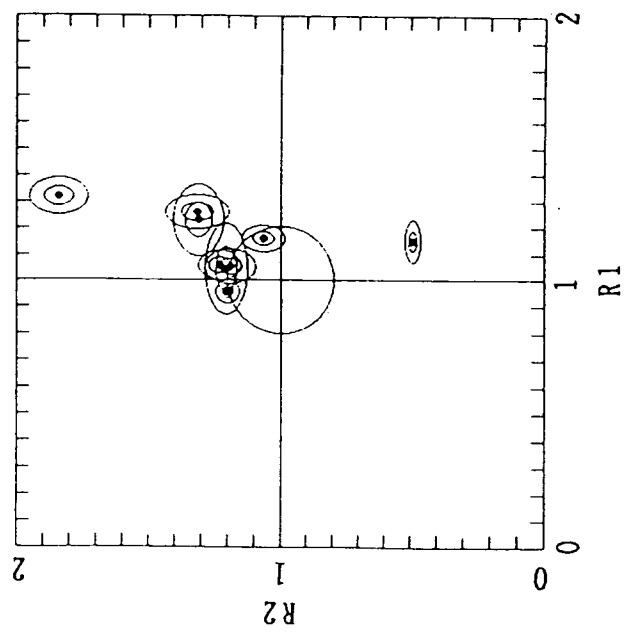


Fig. 2 R1 vs R2 with σ and 2σ

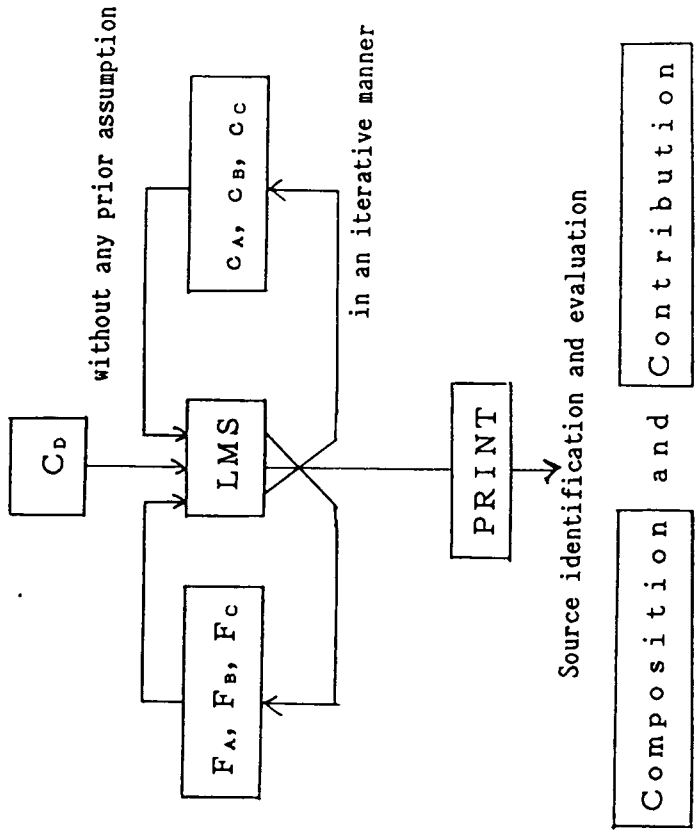


Fig. 3 Conceptual Diagram of SLS Method
 (LMS: least-mean squares)