The Content of Selenium and Its Chemical Form in Rain Water and Aerosol in Tokyo

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Abstract

Selenium content and its chemical form in rain water and aerosol in Tokyo was studied during the period from June 1975 through the end of 1977. Analysis of selenium was carried out by fluorometric method. The content of total selenium in rain water ranged from 5 ng l^{-1} to 118 ng l^{-1} with an average value of 69 ng l^{-1} . Most of selenium in rain water was in tetravalent state which occupied 0.5 to 0.9 in the total. And the rest of selenium in rain water was present in particulate forms.

On the other hand, the content of selenium in aerosol in Tokyo ranged from 1.7 ng m^{-3} to 4.2 ng m^{-3} with an average of 3.0 ng m^{-3} . It was found that the chemical form in a water soluble part of selenium in aerosol is tetravalent ion, and its ratio to total is 0.5 to 0.6.

1. Introduction

Selenium is one of the sulfur group elements, but the occurrence and behavior of selenium in the environment is much different from sulfur (Bertine and Goldberg, 1971; Weiss, *et al.*, 1971). Up to now, many studies on sulfur in the atmosphere and rain-fall have been done. However only few studies on selenium (Rancitelli *et al.*, 1970; Hashimoto *et al.*, 1971) have been published, because of the difficulty of the method of determination of minor quantity of selenium in water and in the air. Recently the present authors developed a new method of analysis of selenium in the environmental substances (Sugimura and Suzuki, 1977). Using this method the present authors carried out the analysis of selenium in different chemical forms in rain water and aerosol in Tokyo collected during the period from June 1975 to December 1977. In this paper, the results of observations are presented with some discussions.

2. Sampling and a method of analysis

Sampling of rain water, snow melt and aerosol

in Tokyo was done during the period from June 1975 to the end of 1977.

Sampling was done at each rain and snow-fall by using rain pot made of polyvinyl chloride with 1 m^2 which was installed in the test field in front of the laboratory (Geochemical Laboratory, Koenji-kita, Suginami, Tokyo). The sampling of aerosol was carried out by using a high volume sampler with a glass fiber filter. Usually, rain water of 5 liter and the air of 200 m^3 were used for the analysis.

Immediately after sampling water, suspended matter was filtered through a filter paper. The determination of selenium in rain water and aerosol was carried out by the fluorometric method using Se(IV)-DAN complex dissolved in cyclohexane media. Intensity of fluorescence of Se(IV)-DAN complex extracted into a cyclohexane was measured at a wavelength of 520 nm with the exciting radiation of the wavelength of 375 nm. Se(IV) is separated by the adsorption on the synthetic resin. Se(VI) and total Se were coprecipitated with tellurium. The detailed explanations of analytical procedures are described in another paper (Sugimura and Suzuki, 1977). In this paper, only a brief explanation on the analytical method are given.

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The total selenium (suspended + dissolved) were coprecipitated with tellurium in the presence of hydrazine sulfate as a reducing agent. The precipitate was dissolved in conc. HNO_3 and evaporated nearly to dryness and the residue was dissolved again in 6M HCl and boiled for three minutes. Selenium coprecipitated with tellurium was also converted finally to Se(IV) -DAN complex.

The separation of Se(IV) and Se(VI) in rain water was done by the adsorption method of Se(IV) -DDTC complex on the XAD-2 resin. Se(IV) adsorbed on the XAD-2 resin was eluted by mixed solution of HNO_3 and HClO_4 and the effluent was evaporated nearly to dryness on a hot plate. The residue was analyzed with the same method as used for the total selenium.

Se(VI) which was not adsorbed on the XAD-2 resin and remained in the effluent was treated in the same way as in the case of the total selenium.

The residue on a filter paper was dissolved in nitric acid and the solution was evaporated nearly to dryness on a hot plate. The residue was analyzed with the same method as used for the total selenium.

The aerosol samples were dissolved in nitric acid on a hot plate and the solution was evaporated nearly to dryness and the residue was treated with HF solution, which was analyzed with the same method as used for the total selenium.

It was confirmed that the standard deviation of the analytical results is below 10%.

3. Results and discussions

The results of analyses of selenium (Total Se, Se(IV) and Se(VI)) in rain water and suspended matter are summarized in Table 1.

3.1 The content and deposition of total selenium in rain water

As seen in Table 1, the content of total selenium in rain water ranged from 5 ng l^{-1} to 118 ng l^{-1} with an average of 69 ng l^{-1} .

No regular change was observed on the content of total selenium in rain water throughout a year. As seen in Fig. 1, there is an inverse correlation between the content of total selenium in rain water and an amount of rainfall.

Using an average of 69 ng l^{-1} of total selenium in rain water, the annual deposition of total selenium was estimated to be about $110 \mu\text{g m}^{-2}$ assuming the annual amount of rainfall of 1,600

Fig. 1 The correlation between the content of total selenium in rain water and an amount of rainfall.

mm. The amount of annual deposition of total selenium in Tokyo (Koenji) is a little larger than the value given by Rancitelli *et al.*, (1970) in Quillayate, Wash., USA (about $70 \mu\text{g m}^{-2} \text{ y}^{-1}$) and is much larger than that in Greenland or Antarctica (1 to $3 \mu\text{g m}^{-2} \text{ y}^{-1}$; Weiss *et al.*, 1971).

3.2 The content of selenium in rain water in different chemical forms

As given in Table 1, among different chemical forms of selenium in rain water, the tetravalent selenium is dominant, which ranged from 5 ng l^{-1} to 104 ng l^{-1} with an average of 49 ng l^{-1} . On the other hand, the content of hexavalent selenium is less than 4 ng l^{-1} or even below a detection limit.

It is to be noticed that a content of selenium in suspended matter in rain water ranged from 6 ng l^{-1} to 38 ng l^{-1} with an average of 19 ng l^{-1} . In order to clarify the chemical form of selenium in suspended matter, the method used by Andren *et al.*, (1970) was used. It was found that selenium in suspended matter is dissolved in nitric acid, but it is not dissolved in hydrochloric acid. These result indicate that the chemical form of selenium in suspended matter may be in a metallic state.

On the basis of the above results, it is concluded that the chemical forms of selenium in rain water are tetravalent ions with a minute amount of hexavalent ions in a water phase and a metallic state in solid phase.

3.3 Correlation between the content of selenium and other several metallic elements

The correlation coefficient between content of selenium and other several metallic elements in

Table 1 The Content of Selenium in Rain Water in Tokyo

Date	Amount of rainfall (mm)	Total	Selenium Se (IV) (ng l ⁻¹)	Se (O)	Date	Amount of rainfall (mm)	Total	Selenium Se (IV) (ng l ⁻¹)	Se (O)
1975									
June 22	36.4	68			30	46.3	69	54	15
26	15.4	85			Sept. 3	23.5	71	44	25
July 5	88.0	31			8-9	30.3	55	50	14
6	33.0	57			20	30.0	57	41	14
21	30.7	70			27	27.2	50	38	10
Aug. 18	35.5	59			Oct. 20	16.8	79	56	23
23	16.5	95			24	24.0	71	41	28
Sept. 5	17.3	87			Nov. 11	19.5	85	57	27
24	59.2	38	22	15	14	19.8	82	55	25
29	33.4	57	41	14	Dec. 24	33.0	73	52	20
Oct. 3	16.5	79	68	10	1977				
5	90.0	21	12	8	Jan. 26-27	18.8	104	65	32
18	77.3	48	32	16	Feb. 10	12.0	112	72	36
Nov. 1	44.4	66	58	7	21	15.3	93	51	38
7	127.1	9	6		Mar. 17	28.2	84	57	24
15	66.4	37	20	15	23-24	38.1	67	43	20
19	29.7	81	68	11	27	15.5	74	51	20
23	25.1	73	54	16	30	83.0	28	10	15
Dec. 8	47.8	44	28	15	Apr. 7-9	44.5	45	21	20
1976					12-13	40.5	52	31	20
Feb. 5	43.8	54	27	26	18	5.2	114	82	27
22	22.1	83	73	7	27-28	5.9	112	91	19
29	33.0	72	50	21	May 4-5	15.4	96	63	30
Mar. 12	10.0	118	93	24	15	70.5	25	13	9
17	33.7	70	52	16	June 2-3	15.5	81	54	25
29	11.0	86			7	7.0	113	61	45
31	12.4	85			10	12.0	115	70	41
Apr. 6	49.0	55	34	18	17-19	75.0	31	21	10
13	26.3	67	51	15	23-27	81.5	20	10	8
20-22	13.8	98	83	14	July 1	3.5	111	104	7
23-24	19.0	91	78	13	7	30.0	64	41	20
30	34.8	48	40	7	11-12	35.3	51	40	9
May 2	29.2	55	42	13	16-17	15.5	72	46	24
16	30.5	56	45	11	Aug. 8-9	14.3	83	50	30
19	14.6	88	78	10	13-15	12.0	13	10	
25	56.0	40	23	16	22	8.0	91	56	34
June 5	30.0	67	41	25	Sept. 8	4.8	117	78	32
9	18.0	81	57	22	8-15	21.7	5	5	
15	22.2	64	50	12	18-19	38.0	43	27	12
24	56.3	38	27	10	26-27	13.0	87	52	35
July 3	12.3	87	70	16	29	11.9	104	81	20
10-12	67.0	42	35	6	Oct. 3-4	50.0	43	31	10
12-13	10.5	100	79	20	11	5.7	93	64	27
19-20	24.3	81	59	20	Nov. 4-5	7.8	102	71	30
Aug. 9	23.5	71	44	25	16-17	69.0	43	20	21
24-26	27.8	68	56	10	26-27	18.1	90	63	26
28	13.7	87	74	11	Dec. 17	43.6	52	37	12

rain water is shown in Table 2. The correlation coefficient between the content of selenium and that of copper, zinc and arsenic is higher, on the contrary, these between the content of

selenium and that of iron and aluminum is lower.

3.4 The content of selenium in aerosol in Tokyo

The results of determination of content of selenium in aerosol in Tokyo was summarized

Table 2 The Correlation Coefficient between Content of Selenium and Other Several Metallic Elements in Rain Water in Tokyo

Precipitation	Fe	Al	Mn	Cu	V	Zn	As	Pb
0.95	0.62	0.64	0.83	0.87	0.77	0.89	0.89	0.69

Table 3 The Content of Total and a Water Soluble Part of Selenium in Aerosol in Tokyo (Koenji)

Date	Air volume	Selenium (ng m ⁻³)		
		Total	Water soluble	
1977				
Jan.	18	200	1.9	0.9
	21	220	2.3	1.1
	24	196	2.4	1.1
Feb.	8	210	2.8	1.4
	23	220	2.6	1.3
Mar.	8	224	3.0	1.6
	14	200	3.4	1.8
Apr.	12	220	3.7	1.9
	20	220	3.3	2.0
	22	220	4.0	2.4
May	10	220	4.2	2.6
	13	210	3.8	2.3
	17	200	3.6	2.1
June	5	220	3.2	1.9
	11	220	2.8	1.6
	21	210	3.3	1.8
July	3	220	3.0	1.8
	9	210	3.3	1.9
	20	210	2.7	1.6
Aug.	2	200	2.2	1.3
	16	224	1.7	0.9
Sept.	4	220	2.1	1.0
	22	220	3.6	1.9
Oct.	16	210	3.5	1.9
	30	210	3.2	1.6
Nov.	7	210	2.9	1.5
	11	220	2.4	1.2
	22	220	3.3	1.7
Dec.	1	210	2.1	1.0
	12	210	2.5	1.2
Average			3.0	1.6

in Table 3. As shown in Table 3, the content of total selenium ranged from 1.7 ng m⁻³ to 4.2 ng m⁻³ with an average of 3.0 ng m⁻³. No regular change was observed on the content of total selenium in aerosol throughout a year in the same trend as in the case of the total selenium in rain water. These values of selenium content in aerosol in Tokyo is close to that given by Rancitelli *et al.*, (1970) in New York City, N.Y. USA (5.7 ng m⁻³), but it is ten to fifty times higher than given by Duce *et al.*, (1971) to the air over the Atlantic Ocean.

A water soluble part of selenium in aerosol was eluted with rain water (pH 4 to 5) and was separated into Se(IV) and Se(VI) using XAD-DDTC method. As a result, it was found that the chemical form in a water soluble part of selenium in aerosol is tetravalent ion, and its ratio to total is 0.5 to 0.6. On the other hand, the chemical form of a water insoluble part of selenium in aerosol may be a metallic state, because selenium retained on a filter paper can be dissolved in nitric acid (Andren *et al.*, 1970).

3.5 The sources of selenium in the air

Main sources of selenium in urban atmosphere may be combustion products of fossil fuels. There is also another source of selenium containing in a soilly matter, however, it is estimated to be below 5% of the total, on the basis of the content of aluminum in rain water in Tokyo.

According to Andren *et al.*, (1970), the chemical form of selenium emitted to the atmosphere through combustion of fossil fuels is estimated to be Se(0) and SeO₂. The results of study by the present authors also support the view by Andren *et al.*, (1970).

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東京における降水・エアロゾル中のセレン含量と 化学形について

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1975年6月から1977年末までの期間に、東京（高円寺）において採取した降水とエアロゾル中のセレン含量とその化学形の研究を行なった。セレンの分析は、蛍光法を用いた。降水の全セレン含量は $5\sim 118\text{ ng l}^{-1}$ で、平均 69 ng l^{-1} を示した。降水中のセレンの大部分は4価の原子価をもち、その量は、全セレンの0.5~0.9を占める。残りのセレンは粒子状で存在することがわかった。また、東京におけるエアロゾル中のセレン含量は $1.7\sim 4.2\text{ ng m}^{-3}$ で、平均 3.0 ng m^{-3} であった。エアロゾルの水溶性部分に含まれるセレンの化学形は4価イオンであり、その割合は、全セレンに対し0.5から0.6であることが明らかとなった。