

Effect of the chemical forms of selenium on its volatilization from soils in Chinese low-selenium belt

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Abstract—Bio-availability of different forms of selenium and its rate of volatilization from soils in Chinese low-selenium belt were examined. Adding directly solutions of either inorganic or organic selenium compounds to soil could only slightly increase the rate of selenium volatilization from soil. Volatilization of selenium from soil was largely enhanced when certain nutritional solutions along with selenium compounds were added. Garlic water extract and seleno-amino acids, i.e., seleno-methionine and seleno-cysteine, were found more effective for their bio-availability to the volatilization process. Under laboratory simulating conditions, the volatilization rate of selenium from different types of soils in Chinese low-selenium belt was found in the range of 0.10–0.27 ng.kg⁻¹ soil.day⁻¹ over a 17 days period, generally followed by a decline with time of incubation.

Keywords: selenium; chemical forms; volatilization.

INTRODUCTION

The facts that there are areas of selenium deficiency, known as Chinese low-selenium belt, and the overlap of the belt with several diseases, such as Kaschin-Beck disease, Keshan disease and animal white muscle disease, make the research work on the biogeochemical cycling of the element meaningful. In the complex scheme of selenium cycling, contribution of volatilization process to the local selenium depletion and factors influencing this process are the major points to be considered. The evolution of volatile forms of selenium from soil is largely influenced by the soil chemical and physical conditions, such as bioavailability as function of the forms of selenium, temperature, soil moisture and microorganism activity. Chemical forms and soil nutritional condition were biochemically considered as two main parameters in controlling the volatilization loss of selenium from soil. Inorganic and organic selenium added directly to soil or present as plant and animal residues, may be converted to the volatile forms (Zieve, 1984; Doran, 1982). Previous work (Wang, 1989) had shown similar results to those reported by Zieve and Peterson (1981) on physical and chemical parameters, i.e., selenium volatilization

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being inhibited when temperature and soil humidity were too high or approaching to zero and when soil was steam sterilized.

Soils, plants, microorganisms and animals can all produce volatile forms of selenium (Cox, 1974; Lewis, 1966). Two different mechanisms were proposed to the selenium methylation; the non-enzymatic process (Reamer, 1980), in which hydrolyzed selenite are transformed into methylated forms by the replacement of hydrogen ions with positively charged methyl group, and the enzymatic process (Lewis, 1966), in which selenite or selenate was biologically transformed into seleno-amino acids and methylated forms are produced through the sequential incorporation of methyl group and then breakdown enzymatically to release volatile forms. In this paper, attempt has been made to quantitatively compare the bioavailabilities of different forms of selenium in volatilization process and to determine the volatilization rate of selenium from soils in Chinese low-selenium belt.

MATERIALS AND METHODS

Chemicals and instruments

Seleno-dl-methionine and seleno-cysteine were obtained from Sigma Chemical Company and selected as seleno-amino acids; 2-phenyl-1, 2-benzoisoselenazol 3 (2H)-on (Se-PZ-51, or Ebselen, a gift from FRG), as a bio-active compound; selenium-chondroitin sulfate, as a selenium-containing polysaccharide, was synthesized in this laboratory; and selenite and selenate were obtained from Beijing Chem. Co. Other chemicals used are analytical grade. Selenium determination was performed either in a Waters Model 210 HPLC unit equipped with a Shimadzu RF-535 fluorescent detector and a μ -porosil normal phase column, or in a Perkin-Elmer model 4000 atomic absorption spectrometer equipped with a model HGA-400 graphite furnace.

Procedures and selenium determination

Soil sample from Hebei Province was chosen for the experiments, soil samples were also collected from different provinces in Chinese low-selenium belt for simulating determination of volatilization rate of selenium. Soil samples were air dried at ambient temperature in laboratory.

The dried samples were ground and sieved, collecting particles smaller than 0.2mm for use. 50g of soil was put into a 1000 ml flask and humidified by using solutions prepared from different selenium compounds and nutrients to a humidity of 20%, at which the selenium volatilization was the most prevailed (Wang, 1989). The flask was then sealed and incubated at 27°C. After incubation, the flask was connected to nitrogen gas through the inlet tube and selenium evolved was collected from the outlet tube either to a 5 ml of nitric acid or to a absorption tube coated with palladium for selenium determination. Soil from Hebei Province was chosen for examining the influence of different chemical forms of selenium and nutrients addition on volatilization process.

Selenium determination was followed either by the HPLC-FID technique developed in this laboratory (Wang, 1989) after digestion in $\text{HClO}_3\text{-HNO}_3$ mixture and derivatization with 2,4-

diaminonaphthalene, or by improved hydride generation atomic absorption technique (Zhang, 1989).

RESULTS AND DISCUSSION

Slight change of selenium volatilization from soil was observed when added with different forms of selenium, as shown in Table 1. No obvious difference could be traced among selenite, ebselen, and selenium polysaccharide. Addition of seleno-methionine increased significantly the selenium volatilization by 14 folds and only by 4 folds when added other compounds to the soil over a 12 days' experiment period when comparing with control group. These results meant that seleno-methionine could be noticed as the most bio-available form among selenium compounds tested in the experiment toward volatilization process in the soil. Increasing the concentration of selenite addition in the range of 0-1000 ng Se per 50 gram of soil resulted in no obvious effect on the selenium volatilization from the soil (Wang, 1989), suggesting that the non-enzymatic process was not chemodynamically correlated in this case.

Table 1 Influence of different selenium compounds on selenium volatilization from soil

Incubation time, day	Se evolved, ng Se/50g soil			
	1	2-3	4-7	8-12
Control	0.05	0.02	0.03	0.02
100 ng ebselen	0.10	0.13	0.09	0.05
100 ng selenite	0.11	0.16	0.14	0.13
100 ng Se-chs	0.15	0.10	0.08	0.10
100 ng Se-met	0.75	0.44	0.32	0.21

Se-chs=synthesized selenium-chondroitin sulfate

Se-met=seleno-methionine

Selenium determination by ETAAS Zhang, 1989

Soil from Hebei Province was used in the experiment

Addition of nutrients to soil sample had a significant effect on selenium volatilization from soil. In Table 2, three different nutrient solutions with sequential increase in selenium content were compared for their ability to stimulate the bioactivity of soil microorganism. It was interesting to notice that selenium released from the soil increased in the same manner as increasing of selenium content in the nutrient solutions. Since selenium in both peptonum, and beef extract is mainly bound to seleno-protein, this increasing could be, therefore, due to both the action of selenium in the nutrients, in forms of seleno-amino acids, and the increase in biological activity of microorganism through nutrient addition. In experiment solution D of Table 2, garlic water extract from Chinese high-selenium area was added instead of nutrient solution. This garlic water extract contained 14 percent of selenite and 85 percent of seleno-protein or peptides (Wang, 1988), and had hardly nutritional effect. Since no selenium evolved could be detected

under the same condition when only nutrient solution was incubated without soil, this increase in selenium volatilization in groups C and D suggested the equal importance of bioavailability of forms of selenium and bioactivity of soil organism in volatilization process. The selenium content in solution D was much more higher than in solution C while the volatilization of selenium from group C was higher than that from group D, this showed the importance of soil nutrient state in volatilization process. In both group C and D, high volatilization was continuously observed in the following days of the experimental period, indicating an accumulatively increased soil microbio-activity and a sufficient source of bio-available selenium for volatilization process existed.

Table 2 Influence of different nutrients and garlic water extract on selenium volatilization from soil

Incubation time, day	Se evolved, ng Se/50g soil			
	1	2	3	4
Nutrient A (0.15 μ g Se/L)	0.80	N.D.	N.D.	N.D.
Nutrient B (2.44 μ g Se/L)	2.60	1.50	0.20	N.D.
Nutrient C (18.3 μ g Se/L)	25.0	26.9	28.5	25.0
Solution D (134 μ g Se/L)	5.70	11.3	3.40	2.30

Data in parenthesis indicates selenium content in original nutrients solution or in garlic water extract.

A: 0.8% d-glucose

B: 0.6% peptonum-0.3% D-glucose-0.3% yeast

C: 6% peptonum-6% beef extract

D: rich-in-selenium garlic water extract

Selenium determination by DAN-HPLC

Table 3 shows the results of 4 days accumulative volatilization when added different forms of selenium (500 ng/50g soil) to the soil incubated under different nutrient conditions. In control experiment, only different nutrient solutions were added. Plus and minus in parentheses mean significant increase (+) or decrease (-) comparing with control group. It can be seen from the

Table 3 Influence of different forms on 4 days accumulative volatilization of selenium from soil incubated with different nutrients

Selenium addition: 10 μ g/kg soil

Conditions	Selenium evolved, ng/50g soil				
	Control	Selenite	Selenate	Se-met	Se-cys
Nutrient A	0.8	2.2(+)	1.2(+)	0.9	--
Nutrient B	4.3	1.7(-)	3.7(-)	12.8(+)	--
Nutrient C	105	103(-)	63(-)	143(+)	72(-)

Abbreviation see Table 1 and 2, Se-cys=seleno-cysteine.

Selenium determination by DAN-HPLC (Wang, 1989).

table that incubation with nutrient A had no obvious effect on selenium volatilization and that incubation with nutrients B and C had obvious effect on selenium volatilization.

Adding selenite and selenate to the soil incubated with nutrients B and C inhibited slightly the selenium volatilization, when comparing with control group. Addition of seleno-methionine could increase significantly selenium volatilization. Seleno-cystein inhibited also the process when incubated with nutrient C (Table 3). Results from Table 3 indicate a more bio-active component existed, in compared with selenite, selenate and seleno-cystein, in original nutrient C, and the volatilization process was even slightly interfered by these compounds. This active component seems to be seleno-methionine or its derivatives, of which a methylated positive charged ion (i.e., $(\text{CH}_3)_2\text{Se}^+\text{CH}_2\text{CH}_2\text{-CHNH}_2\text{COOH}$) had been detected in aqueous ethanol extracts of clover and ryegrass roots after growth with radioactive selenite (Peterson, 1962) and was thought to be directly related with selenium methylation process. More data was needed to explain the different behavior between seleno-methionine and seleno-cystein observed in this experiment.

The time course of volatilization, when adding different forms of selenium to the soil incubated with nutrient C, is shown in Fig.1, where it can be seen more clearly that the inhibitory effect of both selenate and seleno-cysteine occurred from the second day of incubation. Seleno-methionine, and partially seleno-cysteine, could be transformed to volatile form in the first day of incubation, suggesting that these two forms are directly bio-available to volatilization process. Selenite followed principally the same evolution pattern as control group, but evolved to a generally lower extent. Selenate and seleno-cysteine in later days inhibited the process. These observations supported the idea that the methylation of selenium in the soil of Chinese low-selenium belt be more likely governed by enzymatic process rather than non-enzymatic process. Since previous work showed no correlation between rate of selenium volatilization and selenium association forms in the soil (Wang, 1989), the authors assumed that the volatilization process in soils of Chinese low-selenium belt mainly consists of the decomposition of seleno-proteins of plant residue to release seleno-amino acids, especially seleno-methionine, followed by enzymatic breakdown of methylated seleno-amino acids after incorporation of methyl group derived from the soil solution.

Rate of selenium volatilization from different types of soils in Chinese low-selenium belt were simulated and the results was illustrated in Table 4. It could be noticed from the Table 4 that volatilization rate of selenium in these soils were in the range of 0.10-0.30 ng Se per kg soil per day, varying with the types of the soil. Lower volatilization rate, in case of yellow earth, was seemed to be due to weak bio-activity and, in case of meadow soils, due to the strong binding effect of selenium to humic acids depending on the content difference of soil organic matter.

A rough calculation could be made for comparing the flux of selenium in both volatilization and wet deposition process. For one hectare of land, the input from rainfall was estimated to be 0.5-3 g Se per year (Se concentration in inland rain water was determined to be in the range

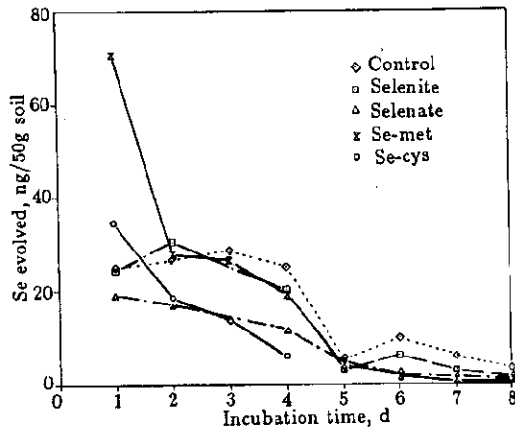


Fig. 1 Influence of different forms of selenium on volatilization from soil (Incubated with nutrient C, abbreviation see Table 1, 2 and 3)

of 0.1–0.6 mg/m³ (Zhu, 1988, annual rainfall 500mm), and output from volatilization process was estimated to be 0.08–0.2 g Se per year (average based on 200 days per year). Therefore, loss from volatilization was only one tenth of the input from rain water. This suggested that loss of selenium from the soils of Chinese low-selenium belt through volatilization could not be the essential pathway leading to the regional selenium depletion.

Table 4 Selenium volatilization rate from soils of Chinese low-selenium belt

Sampling site	Soil type	Soil Se content	Volatilization rate, ng/kg soil			
			1–3	3–8	8–17	Daily aver.
Heilongjiang	Meadow	39.7	0.6	0.8	0.8	0.13
Jilin	Meadow	60.5	0.6	1.0	0.4	0.12
Heilongjiang	Dark brown	190	1.6	1.2	0.4	0.19
Inner Mongolia	Castanozems	83.8	1.6	1.4	0.6	0.21
Shandong	Brown earth	67.5	2.0	1.8	0.8	0.27
Yunnan	Red earth	190	0.5	2.2	1.8	0.26
Gansu	Yellow earth	31.7	0.4	0.8	0.6	0.10
Gansu	Yellow earth	51.6	1.6	1.0	0.2	0.16

Condition: Temperature 25°C, Humidity: 20%

Selenium determination by ETAAS (Zhang, 1989)

Soil Se content in $\mu\text{g Se.kg}^{-1}$

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