

A study on selenium quantification using ICP-MS with oxygen reactive gas in soil of Korea

Hyun-Young Kim^{1,2}, Young-Kyu Hong¹, Jin-Wook Kim¹, and Sung-Chul Kim¹,★

¹Department of Bio-Environmental Chemistry, Chungnam National University, Daejeon 34134, Korea

²SAP Analysis and Evaluation Corp., Daejeon 34016, Korea

(Received April 25, 2024; Revised May 16, 2024; Accepted May 20, 2024)

Abstract: This study evaluates a method for quantifying selenium (Se) concentration in soil using inductively coupled plasma mass spectrometry (ICP-MS), with oxygen as a reaction gas. This approach addresses the challenge of detecting low levels of Se in complex soil matrices and aims to effectively minimize interference problems typically associated with argon plasma in traditional ICP-MS analyses. The analytical method utilizes conditions optimized for minimizing spectral interference and were validated by linearity, accuracy, precision, limit of detection (LOD), and limit of quantification (LOQ). The method demonstrated good linearity, high accuracy (90–97 %), and remarkable sensitivity, achieving detection and quantification limits of 0.15 µg/kg and 0.44 µg/kg, respectively. Developed analysis method for Se in soil was applied to field samples in the different regions of South Korea and Se concentration ranged from 0.11 to 0.52 mg/kg. Correlation analysis between Se concentration and soil properties showed that Se concentration was significantly correlated with cation exchange capacity (CEC) and available phosphorus among other soil properties.

Key words: selenium, oxygen, reaction gas, soil, correlation

1. Introduction

Selenium (Se) is an essential micronutrient for human health, participating in numerous physiological processes and providing anti-aging and anti-cancer benefits.^{1,2} Recent studies have demonstrated that Se is effective for patients with COVID-19.^{3,4} However, the threshold of beneficial and toxic levels of Se is a narrow concentration range, and exceeding recommended intakes can induce adverse effects. The Korean dietary guidelines specify a daily Se consumption of 60 µg

for adults, with a maximum permissible limit of 400 µg.⁵ It is important to note that the Se content in the human body is highly dependent on dietary intake, and crops represent a significant source of daily Se intake.⁶ Given that Se is present in soil as selenate (Se⁶⁺) and selenite (Se⁴⁺) and can be transferred to crops,⁷ the Se content of cultivated soil can influence the Se concentration in crops.⁸

Different levels of Se concentration in soil and crop can have significant implications for local public health.^{9,10} Areas with low Se concentrations in soil

★ Corresponding author

Phone : +82-(0)42-821-6737 Fax : +82-(0)42-821-6731

E-mail : sckim@cnu.ac.kr

This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

may exhibit higher incidences of Se deficiency, which can affect thyroid function and immune response, potentially increasing susceptibility to diseases.^{11,12} Conversely, areas with excessively high levels of Se may expose the population to risks of selenosis.¹³ These disparities highlight the need to assess how agricultural practices and soil properties influence Se content in arable soil. Intercropping, the use of Se-rich fertilizers and irrigation techniques, can affect the level of Se in both soil and crops.¹⁴⁻¹⁶ Additionally, environmental factors such as precipitation, soil pH, cation exchange capacity (CEC), and the presence of competing ions can significantly impact the availability of Se for plant uptake.¹⁷⁻¹⁹ As a result, there can be significant variation in Se levels in crops, even within the same region.

The variability in Se content is also affected by the type of bedrock underlying the soil.^{20,21} Soils derived from igneous rocks, such as granite, generally exhibit lower Se concentrations than those derived from sedimentary rocks.^{22,23} For instance, on Hainan Island in China where the soils predominantly composed of granite (an igneous rock) have an average Se concentration of 0.56 mg/kg,²⁴ whereas the Daba Mountain region, with its shale-dominant sedimentary composition, reports a significantly higher average Se content of 5.70 mg/kg.²⁵

However, in South Korea, while active research is being conducted on the distribution of heavy metals such as lead, cadmium, and zinc in agricultural soils, studies focusing on Se remain scarce, and no standard analytical methods have been established. Additionally, granite and granitic gneiss, which are abundant and typical bedrock in South Korea, are known for their generally low Se concentrations.^{26,27} Considering these conditions, more precise and accurate analytical method for Se quantification is necessitates to determine the Se content in soil.

Because the soil is a complex environmental matrix, precise and sensitive techniques are required for accurate determination of Se content. Several methods have been employed for this purpose, such as hydride generation-atomic absorption spectrometry (HG-AAS),²⁸ atomic fluorescence spectrometry (AFS),²⁹

and inductively coupled plasma atomic emission spectroscopy (ICP-AES).³⁰ Although these methods are widely used for measuring Se in soils, still there is an incompetence to measure low levels of Se content in soil due to their high quantification limits.^{31,32} Inductively coupled plasma mass spectrometry (ICP-MS) is a highly sensitive and rapid technique that is particularly effective for detecting and quantifying multiple trace elements, including Se.^{33,34} Nevertheless, despite its high sensitivity, the commonly used plasma gas, argon (Ar), can introduce spectral interferences that may impair quantitative measurements.³⁵⁻³⁷ Collision/reaction cells (CRC) are widely utilized in ICP-MS to minimize argon-based interferences and enhance the measurement of trace amounts of Se.^{38,39} However, using hydrogen as a reaction gas in CRC can lead to reactions with bromine in the sample, producing polyatomic ions such as BrH^+ and SeH^+ , which complicates the accurate determination of Se.⁴⁰⁻⁴²

The main purpose of this study is to evaluate oxygen (O_2) as the reaction gas in ICP-MS for quantifying low concentrations of Se in soil and monitoring Se levels in arable soil in South Korea.

2. Experimental

2.1. Reagents and instruments

Nitric acid (HNO_3) and hydrochloric acid (HCl), utilized for cleaning vessels and preparing samples, were acquired from CHEMITOP (Jincheon, Korea). The selenium (Se) stock solution (1,000 $\mu\text{g/mL}$) was purchased from AccuStandard (New Haven, CT, USA). Rhodium (Rh) purchased from Sigma-Aldrich (St. Louis, MO, USA) was selected as the internal standard due to its uncommon abundance in soil and its frequent use in the quantification of rare elements.^{37,43} The Se content in the soil was determined with an inductively coupled plasma mass spectrometer (ICP-MS, NexION 1000, PerkinElmer, Waltham, MA, USA), using oxygen and argon gases of ultra-high purity (99.999 %) and a certified reference material (LGC6145, Bosung Science, South Korea) was used for accuracy evaluation.

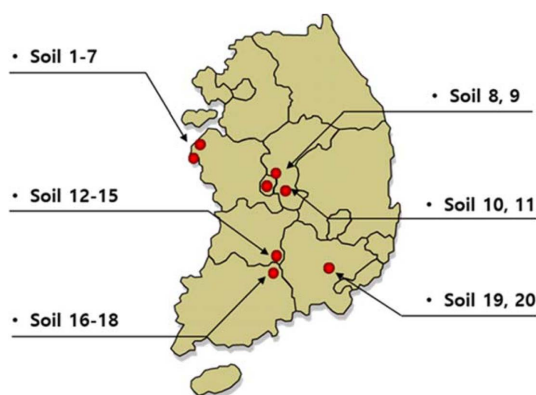


Fig. 1. Sampling locations for monitoring of selenium in soil.

2.2. Soil sampling and analysis methods

Samples were collected from different areas of a domestic agricultural field in South Korea (Fig. 1). Soil samples were obtained using hand auger at depths of 0–15 cm after the removal of surface debris. Five subsoil samples from each site were combined into a single sample and thoroughly mixed to achieve homogenization. The samples were air-dried at 20 °C for soil analysis and then passed through a 2 mm sieve to measure soil properties.

Soil pH and electrical conductivity (EC) were measured using a pH meter (Orion Star™ A111, Thermo Fisher Scientific, Waltham, MA, USA) and an EC meter (SevenCompact™ Conductivity Meter S230, Mettler Toledo, Columbus, OH, USA), respectively, after thoroughly mixing 5 g of soil with 25 mL of deionized water at 150 rpm in a 50 mL flask for 30 min. The Walkley-Black⁴⁴ and Bray No. 1 method with a UV-Vis spectrophotometer (UVmini-1240, Shimadzu, Kyoto, Japan) were used to determine the soil organic matter (SOM) and available phosphate (Av. P). Cation exchange capacity (CEC) was analyzed using a 1 M NH₄OAc extraction method. Total Se in soil was extracted by aqua regia. Specifically, 3 g of soil sample was placed into a 250 mL beaker, and 21 mL of HCl and 7 mL of HNO₃ were added. The beaker was covered with a watch glass and heated at 200 °C for one hour. After cooling to room temperature, DI water was added to bring the final volume to 400 mL. The entire extracted sample was filtered

using a 0.45 μm hydrophilic membrane filter for instrumental analysis.

2.3. Method validation

To evaluate the accuracy, precision, and other validation parameters of the developed analytical method, the standard addition method was employed. It was assumed that each soil sample contained Se, and a predetermined concentration of a standard Se solution was added to each sample. The linearity of the method was evaluated by constructing calibration curves at five concentration levels (1, 5, 10, 20, and 40 μg/L). The accuracy and precision were determined through a recovery test at two Se concentration levels (0.33 and 3.33 mg/kg). Following the addition of the Se standard solution to each sample, the observed results were compared with both the measured and expected concentrations. The recovery test was conducted in triplicate, and the relative standard deviation (RSD) was calculated to assess precision. To establish the limit of detection (LOD) and limit of quantitation (LOQ) for ICP-MS, soil samples were spiked with the lowest concentration from the linear calibration plot and analyzed seven times. Subsequently, LOD and LOQ were derived from the standard deviation of these measurements.

2.4. Statistical analysis method

Statistical analyses were performed using the Statistical Package for Social Science (SPSS) version 26.0 (2021, SPSS Inc., Chicago, IL, USA) and all experiments were performed in triplicate and expressed as mean value and standard deviation.

3. Results and Discussion

3.1. Optimizing ICP-MS condition

Selenium (Se) has six isotopes and the selection of an appropriate isotope for the soil is important for the accuracy of the analysis (Table 1).^{45,46} As shown in Table 1, isotope ⁷⁶Se and ⁷⁸Se have low linearity (less than 0.95) and ⁷⁴Se have a lowest abundance among six isotopes. ⁸⁰Se has the highest abundance and good linearity among the Se isotopes, but the

Table 1. Information of Se isotope-specific interferences with Ar₂

Isotope	Atomic mass (m/z)	Abundance (%)	Interferences	Resolution required [†]	Coefficient of determination (R ²)
⁷⁴ Se	73.9225	0.89	³⁶ Ar, ³⁸ Ar	-	0.9809
⁷⁶ Se	75.9192	9.37	³⁶ Ar, ⁴⁰ Ar	-	0.9224
⁷⁷ Se	76.9199	7.63	-	-	0.9999
⁷⁸ Se	77.9172	23.77	³⁸ Ar, ⁴⁰ Ar	9,970	0.9414
⁸⁰ Se	79.9165	49.61	⁴⁰ Ar, ⁴⁰ Ar	9,521	0.9988
⁸² Se	81.9167	8.73	-	10,891	0.9993

[†]Reference from S. D'Illio *et al.* (2011)

lower required resolution compared to ⁷⁸Se and ⁸²Se can lead to increased interference in the separation (Table 1). Sonia D'Illio *et al.* reported that oxygen gas is useful to avoid interference of argon gas for Se analysis and also doesn't require high resolution instrument such as ICP-SFMS (inductively coupled plasma sector field mass spectrometry).⁴⁷ For these reasons, the isotope selected for this study was ⁸²Se, as it exhibited good linearity in the calibration curve and did not interfere with the Ar gas.

In order to avoid interference of Ar gas in Se analysis, oxygen (O₂), ammonia (NH₃), methane (CH₄), and nitrous oxide (N₂O) as a reaction gas were employed in the previous studies.^{48,49} These varied reaction gases can provide interference reduction, improved detection limit, and reduced on-peak background levels. Among those reaction gases, ammonia is not preferred to analyze Se in soil due to endothermic reaction between Se and NH₃. In case of CH₄, when the sample contains high concentration of Ca, CH₄ can interfere with Ar gas.

In addition, N₂O is also inadequate to analyze Se because of disproportion of N₂O and instability of NO in high pressure. Meanwhile, the high ionization potential of O₂ (12.07 eV) prevents the formation of exothermic oxidation channels for most cations, enabling accurate measurement of low Se concentrations in soil.⁴⁷ For this reason, O₂ was adapted for a reaction gas to measure Se with the flow rate varied from 0.1 to 0.5 mL/min to determine the optimal conditions for Se analysis in soil. The optimal ICP-MS conditions obtained in this experiment are summarized in Table 2.

Table 2. Optimized operating conditions for ICP-MS for Se measurement in soil

Parameter	Value
ICP-MS	
RF power	1600 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	0.98 – 1.02 L/min
DRC	
O ₂ reaction gas flow	0.3 mL/min
Quadrupole rod offset	-10 V
Rejection parameter q (RPq)	0.8

3.2. Quality analysis and quality control (QA/QC) for Se analysis in soil

To evaluate the accuracy and precision of the analytical process using the standard addition method (SAM), soil samples with a known concentration (0.16 ± 0.01 mg/kg) were spiked with two Se concentrations (Table 3). The result from the recovery test showed that recoveries of 91.6 % for the low (0.33 mg/kg) and 97.1 % for the high (3.33 mg/kg) concentration levels were achieved in the spiked soil samples. The precision expressed as RSD in two concentration levels were 1.35 % and 1.43 %, respectively. In addition, the accuracy was re-evaluated using soil CRM (Table 3) containing Se certified value of 1.81 mg/kg, with a level of confidence of approximately 95 % and an uncertainty of 0.13 mg/kg. The test resulted in a recovery of 93.3 % and an RSD of 0.65 %.

The LOD and LOQ were determined by spiking soil samples with the lowest concentration (1 µg/kg) from the linear calibration curve and analyzing them

Table 3. Accuracy and precision of the developed method

SAM Spike levels	Amount added (mg/kg)	Amount recovered (mg/kg)	Accuracy (Recovery, %)	Precision (RSD, %)
Low	0.33	0.31 ± 0.01	91.6 ± 1.2	1.35
High	3.33	3.24 ± 0.05	97.1 ± 1.4	1.43
CRM	Certified value (mg/kg)	Amount recovered (mg/kg)	Accuracy (Recovery, %)	Precision (RSD, %)
LGC6145	1.81 ± 0.13	1.69 ± 0.01	93.3 ± 0.6	0.65

Table 4. Limit of detection (LOD) and limit of quantification (LOQ)

Equipment	LOD (µg/kg)	LOQ (µg/kg)
ICP-MS	0.15	0.44
ICP-AES	6.89	20.88

seven times. Additionally, to compare these values with another instrumental method, LOD and LOQ were also calculated using an ICP-AES instrument (iCAP 7000 Series, Thermo Fisher Scientific) and are presented in Table 4. The LOD and LOQ for the ICP-MS method were established at 0.15 µg/kg and 0.44 µg/kg, respectively. In contrast, the LOD and LOQ values for ICP-AES were found to be 6.89 µg/kg and 20.88 µg/kg. This comparison demonstrates that the LOD and LOQ for ICP-MS are significantly lower than those for ICP-AES, indicating superior sensitivity of the ICP-MS method.

3.3. Method utilization concentration of selenium in field samples

A comprehensive Se analysis using ICP-MS was conducted on a total of 20 topsoil (0–15 cm) samples collected from diverse regions across South Korea. The results are presented in Table 5 as the mean and standard deviation (mean ± SD), obtained from three replicate experiments. The results for Se concentration in arable soil samples were determined to range from 0.11 to 0.52 mg/kg. The Se content of the soils analyzed in this study is similar but tends to be lower. This is likely due to the influence of various physicochemical and environmental parameters such as organic-mineral binding, accumulation, transport, and bioavailability of Se in the soil, in addition to the

Table 5. Selenium concentration in field samples analyzed using developed analytical method

Sample name	Concentration (mg/kg)	Sample name	Concentration (mg/kg)
Soil 1	0.49 ± 0.023	Soil 11	0.35 ± 0.026
Soil 2	0.23 ± 0.002	Soil 12	0.11 ± 0.008
Soil 3	0.14 ± 0.006	Soil 13	0.17 ± 0.006
Soil 4	0.16 ± 0.009	Soil 14	0.15 ± 0.015
Soil 5	0.11 ± 0.009	Soil 15	0.15 ± 0.006
Soil 6	0.43 ± 0.015	Soil 16	0.13 ± 0.023
Soil 7	0.28 ± 0.008	Soil 17	0.15 ± 0.023
Soil 8	0.21 ± 0.004	Soil 18	0.52 ± 0.023
Soil 9	0.30 ± 0.053	Soil 19	0.30 ± 0.004
Soil 10	0.52 ± 0.030	Soil 20	0.19 ± 0.013

geology of the soil.^{50,51}

Previous studies have demonstrated that the Se content of granite-bearing soils ranges from 0.15 to 1.01 mg/kg.⁵² This result agrees with our study that the sampling sites were in area where was characterized by igneous rocks known as predominantly comprised of granite-bearing material and showed low Se concentrations.^{53,54}

3.4. Relationships between Se content in samples and physicochemical properties

The correlation between Se content and soil physicochemical properties is presented in Table 6. Chemical forms of selenate (SeO₄²⁻) and selenite (SeO₃²⁻) are the primary forms of Se in typical agricultural soils, both of which possess anionic properties.⁵⁵ Among the physicochemical properties, significant correlation was obtained for CEC, Av. P and Cu, while pH, EC, SOM, Ni, Zn, Pb, As and Hg showed no significant correlations. Concentration of Se exhibited a positive correlation with CEC, Av. P, and Cu at 0.56 ($p < 0.05$),

Table 6. Correlation of physicochemical properties of soils related to Se concentration (n= 20)

Variables	pH	EC	CEC	Av. P	SOM	Cu	Ni	Zn	Pb	As	Hg
Se	0.08	0.15	0.56*	0.61**	0.39	0.47	0.12	0.39	-0.08	-0.05	0.30

*Correlation are significant at $p < 0.05$; **Correlation are significant at $p < 0.01$.

0.61 ($p < 0.01$), and 0.47 ($p < 0.05$), respectively. While phosphorus has been demonstrated to facilitate Se extraction, its correlation may be influenced by the availability of crops across different species.^{56,57} Cu exhibited a significant positive correlation in this study, in contrast to prior results which suggested a non-significant negative correlation.⁵⁸ Numerous factors can influence this correlation, including soil type, the mineral content available to plants, sampling depth, the type and content of oxides, as well as potentially low selenium concentrations.⁵⁹⁻⁶¹

The physicochemical properties that were not found to be significant in this study include pH, which exhibited a weak negative correlation, increasing in significance with the subsoil layer.⁶² The anionic nature of Se in soil is typically anticipated to exhibit a negative correlation with pH. However, in this study, topsoil samples were collected and analyzed, leading to the conclusion that varied research outcomes may have resulted from the influence of factors exhibiting stronger correlations than pH. To clarify the correlation between Se and pH, it is necessary to consider various factors such as the mobility of Se in the soil in accordance with pH, and the adsorption of Se in the soil due to aluminum and iron oxides.^{63,64} Regarding the correlation with SOM, previous studies have indicated that Se is bound to 67–86% colloidalized organic matter in soil, thus suggesting an anticipated positive correlation between organic matter and Se.⁶⁵

4. Conclusions

This research developed and validated a method using oxygen as a reactive gas in ICP-MS for the effective quantification of selenium (Se) in soil samples. The isotope of Se to be analyzed was selected as ⁸²Se, and the method demonstrated good sensitivity

and accuracy, with low detection and quantification limits that facilitate the assessment of Se at trace levels. When applied to agricultural field samples, the concentration of total Se was found to be in the range from 0.11 to 0.52 mg/kg, which is similar to previous studies with granite as the underlying bedrock. An investigation of correlations with soil physicochemical properties was conducted and found significant positive correlations were found in CEC, Av. P, and Cu. However, due to the lack of studies on Se and variables, it will be important to consider soil characteristics and the physiological characteristics of the crops grown to understand the relationship between Se and variables according to specific agricultural soils. This study confirms the utility of the method for accurate monitoring of Se in agricultural soils, contributing to better dietary management and public health policies regarding Se exposure.

Acknowledgements

The authors would like to thank Department of Bio-Environmental Chemistry, Chungnam National University and SAP Analysis and Evaluation Corp. for their interest and support.

References

1. M. P. Rayman, *The Lancet*, **356**(9225), 233-241 (2000). [https://doi.org/10.1016/S0140-6736\(00\)02490-9](https://doi.org/10.1016/S0140-6736(00)02490-9)
2. M. Navarro-Alarcon and C. Cabrera-Vique, *Sci. Total Environ.*, **400**(1-3), 115-141 (2008). <https://doi.org/10.1016/j.scitotenv.2008.06.024>
3. J. Zhang, E. W. Taylor, K. Bennett, R. Saad, and M. P. Rayman, *Am. J. Clin. Nutr.*, **111**(6), 1297-1299 (2020). <https://doi.org/10.1093/ajcn/nqaa095>
4. L. Pecoraro, L. Martini, C. Salvottini, L. Dalle Carbonare, G. Piacentini, and A. Pietrobelli, *Child Adolescent Obes.*,

- 4(1), 127-130 (2021). <https://doi.org/10.1080/2574254X.2021.1941706>
5. K. Choi and O. Lee, *J. Nutr. Health*, **55**(4), 430-440 (2022). <https://doi.org/10.4163/jnh.2022.55.4.430>
6. M. Xie, X. Sun, P. Li, X. Shen, and Y. Fang, *Compr. Rev. Food Sci. Food Saf.*, **20**(3), 2914-2940 (2021). <https://doi.org/10.1111/1541-4337.12748>
7. M. Wang, W. Yang, F. Zhou, Z. Du, M. Xue, T. Chen, and D. Liang, *Environ. Sci. Pollut. Res.*, **26**, 20475-20484 (2019). <https://doi.org/10.1007/s11356-019-04717-x>
8. J. Stroud, M. Broadley, I. Foot, S. Fairweather-Tait, D. Hart, R. Hurst, P. Knott, H. Mowat, K. Norman, and P. Scott, *Plant Soil*, **332**, 19-30 (2010). <https://doi.org/10.1007/s11104-009-0229-1>
9. G. Lopes, F. W. Ávila, and L. R. G. Guilherme, *Cienc. Agrotec.*, **41**, 605-615 (2017). <https://doi.org/10.1590/1413-70542017416000517>
10. H. Yang, X. Yang, Z. Ning, S. Y. Kwon, M.-L. Li, F. M. Tack, E. E. Kwon, J. Rinklebe, and R. Yin, *J. Hazard. Mater.*, **422**, 126876 (2022). <https://doi.org/10.1016/j.jhazmat.2021.126876>
11. L. Sher, *Med. Hypotheses*, **57**(4), 480-483 (2001). <https://doi.org/10.1054/mehy.2001.1369>
12. F. M. Fordyce, In 'Essentials of medical geology: Revised edition', 375-416, Springer (2012). https://doi.org/10.1007/978-94-007-4375-5_16
13. R. Loomba, T. Filippini, R. Chawla, R. Chaudhary, S. Cilloni, C. Datt, S. Singh, K. S. Dhillon, and M. Vinceti, *Sci. Total Environ.*, **716**, 135347 (2020). <https://doi.org/10.1016/j.scitotenv.2019.135347>
14. W. Tang, W. Tang, Y. Xie, X. Li, H. Li, L. Lin, Z. Huang, B. Sun, G. Sun, and L. Tu, *Int. J. Phytoremediation*, **25**(9), 1165-1172 (2023). <https://doi.org/10.1080/15226514.2022.2140779>
15. R. V. S. Lavu, G. Du Laing, T. Van De Wiele, V. L. Pratti, K. Willekens, B. Vandecasteele, and F. Tack, *J. Agric. Food Chem.*, **60**(44), 10930-10935 (2012). <https://doi.org/10.1021/jf302931z>
16. F.-J. Zhao, F. J. Lopez-Bellido, C. W. Gray, W. R. Whalley, L. J. Clark, and S. P. McGrath, *Sci. Total Environ.*, **372**(2-3), 433-439 (2007). <https://doi.org/10.1016/j.scitotenv.2006.09.028>
17. M. L. Galeas, L. H. Zhang, J. L. Freeman, M. Wegner, and E. A. Pilon-Smits, *New Phytol.*, **173**(3), 517-525 (2007). <https://doi.org/10.1111/j.1469-8137.2006.01943.x>
18. H. Renkema, A. Koopmans, L. Kersbergen, J. Kikkert, B. Hale, and E. Berkelaar, *Plant Soil*, **354**, 239-250 (2012). <https://doi.org/10.1007/s11104-011-1069-3>
19. J. L. Hopper and D. R. Parker, *Plant Soil*, **210**, 199-207 (1999). <https://doi.org/10.1023/A:1004639906245>
20. Y. Liu, X. Tian, R. Liu, S. Liu, and A. V. Zuza, *Catena*, **196**, 104926 (2021). <https://doi.org/10.1016/j.catena.2020.104926>
21. L. Hao, J. Zhang, S. Zhang, S. Ma, B. Li, J. Long, J. Fan, and K. Luo, *Environ. Geochem. Health*, **43**, 333-346 (2021). <https://doi.org/10.1007/s10653-020-00711-2>
22. F. Fordyce, O. Selinus, B. Alloway, J. Centeno, R. Finkelman, and R. Fuge. Springer Dordrecht, The Netherlands, (2013).
23. K. S. Dhillon and S. K. Dhillon, In 'Advances in Agronomy', **79**, 119-184, D. L. Sparks, Ed., (2003).
24. J. Gong, J. Yang, H. Wu, Y. Fu, J. Gao, S. Tang, and S. Ma, *Appl. Geochemistry*, **136**, 105147 (2022). <https://doi.org/10.1016/j.apgeochem.2021.105147>
25. Y. Li, W. Wang, K. Luo, and H. Li, *J. Environ. Sci.*, **20**(7), 859-864 (2008). [https://doi.org/10.1016/S1001-0742\(08\)62138-5](https://doi.org/10.1016/S1001-0742(08)62138-5)
26. N. Wells, *N. Z. J. Geol. Geophys.*, **10**(1), 198-208 (1967). <https://doi.org/10.1080/00288306.1967.10428190>
27. I. Caple, K. Andrewartha, S. Edwards, and C. Halpin, *Aust. Vet. J.*, **56**(4), 160-167 (1980). <https://doi.org/10.1111/j.1751-0813.1980.tb05669.x>
28. R. P. Matos, V. M. P. Lima, C. C. Windmüller, and C. C. Nascentes, *J. Geochem. Explor.*, **172**, 195-202 (2017). <https://doi.org/10.1016/j.gexplo.2016.11.001>
29. F. Wang and G. Zhang, *Appl. Spectrosc.*, **65**(3), 315-319 (2011). <https://doi.org/10.1366/10-0604>
30. National Institute of Environmental Research Notification, No. 2022-38 (2022.7.25), Republic of Korea.
31. N. Khan, I. S. Jeong, I. M. Hwang, J. S. Kim, S. H. Choi, E. Y. Nho, J. Y. Choi, B.-M. Kwak, J.-H. Ahn, T. Yoon, and K. S. Kim, *Food Chem.*, **141**(4), 3566-3570 (2013). <https://doi.org/10.1016/j.foodchem.2013.06.034>
32. J. Pinho, J. Canário, R. Cesário, and C. Vale, *Anal. Chim. Acta*, **551**(1), 207-212 (2005). <https://doi.org/10.1016/j.aca.2005.07.002>
33. C. Moor, T. Lymberopoulou, and V. J. Dietrich, *Mikrochim. Acta*, **136**, 123-128 (2001). <https://doi.org/10.1007/>

- s006040170041
34. E. Vassileva, A. Becker, and J. Broekaert, *Anal. Chim. Acta*, **441**(1), 135-146 (2001). [https://doi.org/10.1016/S0003-2670\(01\)01089-3](https://doi.org/10.1016/S0003-2670(01)01089-3)
35. S. D'Ilio, N. Violante, C. Majorani, and F. Petrucci, *Anal. Chim. Acta*, **698**(1-2), 6-13 (2011). <https://doi.org/10.1016/j.aca.2011.04.052>
36. J. Machat, V. Otruba, and V. Kanicky, *J. Anal. At. Spectrom.*, **17**(9), 1096-1102 (2002). <https://doi.org/10.1039/B202167F>
37. H. Fujiwara, K. Kawabata, J. Suzuki, and O. Shikino, *J. Anal. At. Spectrom.*, **26**(12), 2528 (2011). <https://doi.org/10.1039/c1ja10191a>
38. A. S. Henn, F. S. Rondan, M. F. Mesko, P. A. Mello, M. Perez, J. Armstrong, L. A. Bullock, J. Pamell, J. Feldmann, and E. M. Flores, *Spectrochim. Acta B: At. Spectrosc.*, **143**, 48-54 (2018). <https://doi.org/10.1016/j.sab.2018.02.014>
39. J. Darrouzès, M. Bueno, G. Lespès, and M. Potin-Gautier, *J. Anal. At. Spectrom.*, **20**(2), 88-94 (2005). <https://doi.org/10.1039/B410142A>
40. L. Hinojosa Reyes, J. M. Marchante Gayón, J. I. García Alonso, and A. Sanz-Medel, *J. Anal. At. Spectrom.*, **18**(1), 11-16 (2003). <https://doi.org/10.1039/B209213A>
41. J. Rodríguez-Castrillón, L. H. Reyes, J. M. Marchante-Gayón, M. Moldovan, and J. I. García Alonso, *J. Anal. At. Spectrom.*, **23**(4), 579-582 (2008). <https://doi.org/10.1039/b716785g>
42. D. Schaumlöffel, K. Bierla, and R. Łobiński, *J. Anal. At. Spectrom.*, **22**(3), 318-321 (2007). <https://doi.org/10.1039/B611324A>
43. M. A. Bechlin, E. C. Ferreira, J. A. G. Neto, J. C. Ramos, and D. L. G. Borges, *J. Braz. Chem. Soc.*, **26**(9), 1879-1886 (2015). <https://doi.org/10.5935/0103-5053.20150165>
44. A. Walkley and I. A. Black, *Soil Sci.*, **37**(1), 29-38 (1934). <http://doi.org/10.1097/00010694-193401000-00003>
45. J. Darrouzès, M. Bueno, G. Lespès, M. Holeman, and M. Potin-Gautier, *Talanta*, **71**(5), 2080-2084 (2007). <https://doi.org/10.1016/j.talanta.2006.09.019>
46. C. A. Shand, M. Balsam, S. J. Hillier, G. Hudson, G. Newman, J. R. Arthur, and F. Nicol, *J. Sci. Food Agric.*, **90**(6), 972-980 (2010). <https://doi.org/10.1002/jsfa.3905>
47. S. D'Ilio, N. Violante, C. Majorani, and F. Petrucci, *Analytica Chimica Acta*, **698**(1-2), 6-13 (2011). <https://doi.org/10.1016/j.aca.2011.04.052>
48. B. L. Batista, J. L. Rodrigues, J. A. Nunes, V. C. de Oliveira Souza, and F. Barbosa, *Anal. Chim. Acta*, **639**(1), 13-18 (2009). <https://doi.org/10.1016/j.aca.2009.03.016>
49. Y. Wang and I. D. Brindle, *J. Anal. At. Spectrom.*, **26**(7), 1514-1520 (2011). <https://doi.org/10.1039/C0JA00210K>
50. J. Tolu, Y. Thiry, M. Bueno, C. Jolivet, M. Potin-Gautier, and I. Le Hécho, *Sci. Total Environ.*, **479-480**, 93-101 (2014). <https://doi.org/10.1016/j.scitotenv.2014.01.079>
51. Y. Xu, Y. Li, H. Li, L. Wang, X. Liao, J. Wang, and C. Kong, *Sci. Total Environ.*, **633**, 240-248 (2018). <https://doi.org/10.1016/j.scitotenv.2018.03.190>
52. J. Wu, *Geol. China*, **45**(6), 1167-1176 (2018). <https://doi.org/10.12029/gc20180607>
53. M. Imran, M. S. Akhtar, A. Mehmood, S. Rukh, A. Khan, C. Zhikun, and G. Mujtaba, *Arab. J. Geosci.*, **13**, 1-16 (2020). <https://doi.org/10.1007/s12517-020-06111-1>
54. M. Park, H.-T. Chon, and L. Marton, *J. Geochem. Explor.*, **107**(2), 161-168 (2010). <https://doi.org/10.1016/j.gexplo.2010.09.003>
55. F. Ali, Q. Peng, D. Wang, Z. Cui, J. Huang, D. Fu, and D. Liang, *Environ. Sci. Pollut. Res.*, **24**, 8315-8325 (2017). <https://doi.org/10.1007/s11356-017-8512-9>
56. J. E. Favorito, M. J. Eick, P. R. Grossl, and T. Z. Davis, *Plant Soil*, **418**(1), 541-555 (2017). <https://doi.org/10.1007/s11104-017-3299-5>
57. C. Zhao, J. Ren, C. Xue, and E. Lin, *Plant Soil*, **277**(1-2), 197-206 (2005). <https://doi.org/10.1007/s11104-005-7011-9>
58. M. B. Gabos, L. R. F. Alleoni, and C. A. Abreu, *J. Geochem. Explor.*, **145**, 35-39 (2014). <https://doi.org/10.1016/j.gexplo.2014.05.007>
59. J. L. Antanas Antanaitis, Sarunas Antanaitis, Gediminas Staugaitis, Pranas Viskelis, *J. Food Agric. Environ.*, **6**(1), 163-167 (2008). <https://doi.org/10.1234/4.2008.1100>
60. M. Wang and H. Chen, *Chemosphere*, **52**(3), 585-593 (2003). [https://doi.org/10.1016/S0045-6535\(03\)00240-6](https://doi.org/10.1016/S0045-6535(03)00240-6)
61. J. Yanai, S. Mizuhara, and H. Yamada, *Soil Sci. Plant Nutr.*, **61**(2), 312-318 (2015). <https://doi.org/10.1080/00380768.2014.997147>
62. H. Yamada, A. Kamada, M. Usuki, and J. Yanai, *Soil Sci. Plant Nutr.*, **55**(5), 616-622 (2009). <https://doi.org/10.1111/j.1747-0765.2009.00397.x>
63. L. H. E. Winkel, B. Vriens, G. D. Jones, L. S. Schneider, E. Pilon-Smits, and G. S. Bañuelos, *Nutrients*, **7**(6), 4199-4239 (2015). <https://doi.org/10.3390/nu7064199>

64. S. Goldberg, S. M. Lesch, and D. L. Suarez, *Geochim. Cosmochim. Acta*, **71**(23), 5750-5762 (2007). <https://doi.org/10.1016/j.gca.2007.04.036>
65. L. Weng, F. A. Vega, S. Supriatin, W. Bussink, and W. H. V. Riemsdijk, *Environ. Sci. Technol.*, **45**(1), 262-267 (2011). <https://doi.org/10.1021/es1016119>

Authors' Positions

Hyun-Young Kim : Graduate Student
Young-Kyu Hong : Postdoctoral Scholar
Jin-Wook Kim : Graduate Student
Sung-Chul Kim : Professor