Science of the Total Environment 957 (2024) 177514

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Advancing the analysis of volatile selenium species in high-humidity and low-volatility paddy systems: A novel approach for speciation and quantification

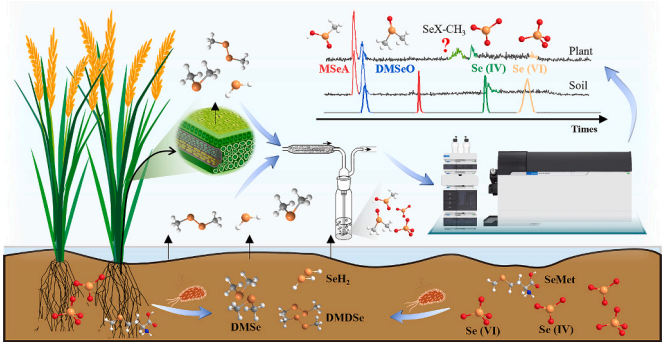
Xuefeng Yang [a,b], Kang Mao [a], Chuanyu Chang [a], Guopei Huang [a], Shuxun Shao [c], Hua Zhang [a,*]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

HIGHLIGHTS

- Novel method to capture volatile Se in high-humidity and low-concentration paddy.
- Detection limits of 1.2 pg and 1.4 pg for DMSe and DMDSe were achieved.
- DMDSe was identified as the primary volatile Se form in soil and rice plants.
- A potential plant-based volatile organic Se species was discovered.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Christopher Rensing

Keywords:
Volatile selenium
Speciation
Preconcentration
HPLC-ICPMS
Paddy systems

ABSTRACT

Selenium (Se) volatilization represents a crucial component of the Se biogeochemical cycle in paddy systems. However, current existing methodologies for capturing volatile Se (VOSe) in high-humidity and low-volatility paddy systems are insufficient. This study developed an innovative approach to capture and quantify VOSe from soil and rice plants, such as DMSe (dimethylselenide) and DMDSe (dimethyldiselenide). Initially, the efficacy of preconcentration was enhanced by optimizing the sampling apparatus, which significantly reduced water vapour by 43.5 % and increased the Se concentration by 37.7 % within 6 h sampling. Subsequently, HPLC–ICPMS analysis refinements included the screening and optimizing chromatographic columns and mobile phases, achieving absolute detection limits of 1.2 pg and 1.4 pg for DMSe and DMDSe, respectively. For validation, VOSe were quantified in the paddy systems, with DMSe and DMDSe volatilized rates from soil measured at 16.55±9.94 $ng{\cdot}m^{-2}{\cdot}h^{-1}$ and 124.49±120.34 $ng{\cdot}m^{-2}{\cdot}h^{-1}$, and from rice plants at 38.38±29.85 $ng{\cdot}m^{-2}{\cdot}h^{-1}$ and 72.54±94.66 $ng{\cdot}m^{-2}{\cdot}h^{-1}$, respectively. Additionally, volatile H_2Se and potential plant-based volatile organic Se species were found. This represents the first accurate and sensitive method for the in-situ capture of trace VOSe in high-humidity, low-volatility paddy systems, providing invaluable insights into the biogeochemical processes of Se volatilization.

* Corresponding author.
E-mail address: zhanghua@mail.gyig.ac.cn (H. Zhang).

https://doi.org/10.1016/j.scitotenv.2024.177514
Received 18 August 2024; Received in revised form 18 October 2024; Accepted 9 November 2024
Available online 15 November 2024

1. Introduction

Selenium (Se), an essential dietary trace element, is biogeochemically cycled as various species in the environment, impacting human and animal health (Tan et al., 2016; Wen and Carignan, 2007; Winkel et al., 2012). Annually, terrestrial ecosystems release an average of 19.7 Gg gaseous volatile Se (VOSe) into the atmosphere (Feinberg et al., 2020). Despite atmospheric deposition more than 12.9Gg to the soil, approximately 7 $Gg{\cdot}yr^{-1}$ Se is transferred from land to the ocean via the atmosphere (Feinberg et al., 2020). Se in soils is the primary factor determining the Se concentration in crops, which is a crucial source of Se intake for humans (Combs, 2001). This implies that the release of VOSe can decrease soil Se concentrations and therefore Se levels in crop food and dietary intake (Blazina et al., 2014; Feinberg et al., 2021; Feinberg et al., 2020; Vriens et al., 2014b).

Rice plants, which serve as a fundamental staple crop for Se intake for more than half of the global population (Fukagawa and Ziska, 2019), covert inorganic Se species (selenite (Se[IV]) and selenate (Se[VI])) to selenoaminoacids(e.g., SeMet (selenocysteine) and MeSeCys (methyl selenocysteine)) and thus to volatile dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) (Kushwaha et al., 2022; Sun et al., 2010). Similarly, soil microbes in paddy systems mediate the formation of DMSe and DMDSe (Chasteen and Bentley, 2003), yet the types and quantities often vary (Heine and Borduas-Dedekind, 2023; Zhang and Frankenberger, 1999). DMSe and DMDSe have been identified as major components of VOSe (Chasteen and Bentley, 2003; Kushwaha et al., 2022; Quang Toan et al., 2019). However, it remains ambiguous whether their release by soil microbes and rice in paddy systems results in decreased Se in soil and rice. While VOSe in paddy systems can be indirectly assessed using a Se volatilization model (Feinberg et al., 2020), this method entails considerable uncertainty and only estimates the total VOSe. Nevertheless, it is imperative to note that the volatilization rate is intricately linked to the speciation of VOSe (Zhang and Frankenberger, 2000). DMSe has a significantly lower vapour pressure (0.38 kPa) and a faster volatilization rate than DMDSe (32 kPa) (Karlson et al., 1994). Therefore, there is a strong need to accurately assess the speciation, sources, and fluxes of VOSe to comprehensively evaluate the biogeochemical cycle of Se in paddy systems.

However, accurately quantifying the speciation and concentrations of VOSe in paddy systems initially requires an appropriate preconcentration method, which is a considerable challenge. DMSe and DMDSe have been extracted from plants (Dietz et al., 2003; Duan et al., 2009; Meija et al., 2002), water (Pecheyran et al., 1998), and urine (Bueno and Pannier, 2009) using headspace solid-phase microextraction (HS-SPME) (Dietz et al., 2003; Duan et al., 2009; Meija et al., 2002) and purge and cryogenic trapping (PT-CT) (Feldmann, 1997; Pecheyran et al., 1998) for preconcentration. While complicated pretreatment for HP-SPME and pressurized gases (e.g., He) for PT-CT is highly impractical for analysing VOSe in paddy systems. Activated carbon, which has high-efficiency adsorption and portable deployment, is widely used to quantify VOSe in soil (Biggar and Jayaweera, 1993; Zhang and Frankenberger, 1999; Zhang et al., 1999), plants (Banuelos et al., 2005; Biggar and Jayaweera, 1993; Lin et al., 1999), and the atmosphere (Haygarth et al., 1994). But the strong adsorption of activated carbon makes desorption and speciation analysis challenging. Another method for the preconcentration of VOSe species involves using strong oxidizing solutions (Winkel et al., 2010; Zhang and Frankenberger, 2000). For example, DMSe and DMDSe can be converted into stable dimethylselenosulfoxide (DMSeO) and methylseleninic acid (MSeA) respectively by HNO_3 oxidization (Winkel et al., 2010), and this method has been used to quantify DMSe and DMDSe from wetland (Vriens et al., 2014a, 2014b) and Antarctic soils (Ye et al., 2021). However, HNO_3 absorbs water vapour, increasing volume and decreasing concentration, which reduces the accuracy and stability of speciation and quantification, particularly in high-humidity paddy systems. Consequently, methods for preconcentrating VOSe in high-humidity and low-volatility paddy system fields are lacking.

In addition, the analytical method following preconcentration is another critical process for accurately identifying VOSe speciation. Gas chromatography (GC) (Le Bras et al., 2023) and high-performance liquid chromatography (HPLC) (Vriens et al., 2014a, 2014b; Ye et al., 2021) are the primary methods for separating Se species. HNO_3 trapping combined with HPLC can capture and identify VOSe more quickly (Vriens et al., 2014a, 2014b; Ye et al., 2021) than SPME (Dietz et al., 2003; Duan et al., 2009; Meija et al., 2002) and PT-CT (Feldmann, 1997; Pecheyran et al., 1998) combined with GC. Furthermore, inductively coupled plasma mass spectrometry (ICPMS) has high sensitivity and low detection limits and is more suitable for analysing samples that contain low concentrations than atomic absorption spectroscopy (AAS) (Martens and Suarez, 1999), atomic emission detector (AED) (Campillo et al., 2007) and atomic fluorescence spectroscopy (AFS) (Pecheyran et al., 1998). Accordingly, HNO_3 preconcentration followed by HPLC–ICPMS detection is a potential method for analysing VOSe (Vriens et al., 2014a, 2014b; Ye et al., 2021). However, the strongly acidic of HNO_3 affects sample separation using chromatographic columns(Vriens et al., 2014a; Ye et al., 2021), which are generally suitable for pH range of 1–14. Previous studies have detected the DMSeO and MSeA in HNO_3 though direct dilution, but these methods do not address the influence of salinity and acidity in samples. Therefore, screening and optimizing suitable chromatographic columns and mobile phases to decrease the influence of salinity and acidity is crucial for obtaining qualitative and quantitative results of VOSe from high-humidity and low-volatility paddy systems.

Here, we developed a sensitive and accurate method for both the speciation and quantification of volatile DMSe and DMDSe from soil and rice using in situ moisture removal capture and ion exchange chromatography (IEC)–HPLC–ICPMS analysis. Initially, this method optimized outdoor capture devices, reducing moisture interference while ensuring the efficient capture of VOSe. Subsequently, the separation effects of PRP-X100 and PAX-500 in different mobile phases have been studied, achieving 15 min separations of different VOSe in 0.5 $mol{\cdot}L^{-1}$ NH_4NO_3 matrix samples. Finally, we captured and measured VOSe in a high-humidity and low-volatility soil–rice system from Enshi of China, known as the "Se Capital of the World," and identified another potential plant-based volatile organic Se, demonstrating the accuracy and applicability of this method for analysing VOSe in paddy systems.

2. Materials and methods

2.1. Chemicals

DMSe ($(CH_3)_2Se$, 99 %) and DMDSe ($(CH_3)_2Se_2$, 99 %) are commercially available from Alfa Aesar and are diluted 1000 times in methanol to prepare a working solution, following the method described by Winkel et al. (2010). Standard substances, such as selenite (Se[IV], 99 %), selenate (Se[VI], 99 %), and methylseleninic acid (MSeA, 95 %), for trapping products verification were purchased from Sigma–Aldrich. Chromatographically pure ammonium nitrate (NH_4NO_3), ammonium acetate (NH_4Ac), ammonium citrate ($C_6H_8O_7{\cdot}NH_4$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), aqueous ammonia ($NO_3{\cdot}H_2O$), acetic acid (CH_3COOH), and methanol (CH_3OH) for the mobile phases were also purchased from Sigma–Aldrich. All other reagents used were of analytical grade or higher purity, were diluted with 18.2 MΩ high-purity deionized water, and were generated using Milli-Q.

2.2. Indoor preconcentration experiments

The preconcentration efficiencies of DMSe and DMDSe were studied using the preconcentration apparatuses shown in Fig. 1a and b. Specifically, the flowmeter, Teflon T-junction, and three 25 mL brown borosilicate gas-washing bottles (containing 10 mL HNO_3, twice-distilled, 69.5 %) were sequentially connected using platinum-cured silicone tubing. Following a 20 min purge of the preconcentration system with

50 mL·min^{-1} N_2, 10 μL of diluted DMSe and DMDSe working solutions were injected via a micro gas chromatography syringe. HNO_3 was used to oxidize the VOSe compounds DMSe and DMDSe into specific forms, DMSeO and MSeA, respectively (Winkel et al., 2010). And DMSeO and MSeA can be directly used for qualitative and quantitative analysis by HPLC-ICPMS. This preconcentration system exemplifies ideal laboratory conditions. However, in field preconcentration experiments, water vapour, along with VOSe, enters the preconcentration system, increasing the volume of the trapping solution to >10 mL (see Section 3.1 for details). To minimize the influence of water vapour, a gas-washing bottle (containing 10–15 mL ultrapure water) was positioned ahead of the Teflon T- junction to simulate water vapour volatilization, and a drying tube (filled with soda lime,2–5 mm, Sigma-Aldrich) was installed before the trapping bottle to remove water vapour, thus reducing its interference with the trapping of VOSe.

2.3. Field preconcentration experiment

The VOSe released from the paddy soil was trapped, as shown in Fig. 1c. The sampling flux box (transparent polypropylene box, 47 L, 0.3 m^2), drying system, indoor preconcentration system, and vacuum pump (60 L·h^{-1}, KNF) (Vriens et al., 2014a) were connected by Teflon tubing in the paddy fields at three regions (high-Se: soil = 19.76 ppm, middle-Se: soil = 4.45 ppm and low-Se: soil = 0.53 ppm) of Enshi, China. To balance the atmospheric pressure and determine the atmospheric Se background, the other end of the flux box was connected to the outside using an activated carbon tube (0.6 g, ThermoFisher), which was used for Se capture in a previous study (Banuelos et al., 2005; Schilling and Wilcke, 2011; Zhang et al., 1999).

The preconcentration scheme for VOSe from rice was similar to that used in paddy fields (Scheme 1). Rice potted in well-mixed Se-rich natural soil from three regions mentioned above was enclosed within a hermetically sealed acrylic tube, and a similar gas pipeline system was used to preconcentrate Se volatilized from the rice metabolism, as shown in Fig. 1d. To determine the soil background, two similar thriving rice potted plants were selected. One potted plant was used directly for trapping volatile Se from rice, while the other had its aboveground parts cut off at the water surface level, leaving the rest of the plant to simultaneously capture Se for background deduction. Supporting information is provided in Text S1. The drying system was replaced every 6 h, and the trapping solution was changed every 12 h (Section 3.1). The trapping solution (HNO_3) from the brown bottle was transferred to 20 mL precleaned brown glass vials.

2.4. Analysis of total gaseous Se and speciation

To mitigate the influence of Ar^2 (m/z = 76, 78 and 80), total Se (m/z = 78 and 80) was quantified by ICPMS with an instrument (Agilent Technologies 8900, USA) equipped with an oxygen collision cell after 10 predilutions of the trapping solution. The mass values detected for the analytical element Se and the internal standard element Ge were 94 (m/z = 78 + 16) and 88 (m/z = 72 + 16), respectively (Text S2). Se speciation analysis initially involved the addition of 1 mL of the trapping solution (HNO_3) and $NH_3{\cdot}H_2O$ in an ice water bath to form a 0.5 mol·L^{-1} NH_4NO_3 salinity system with a pH of 7.5, which ensured chromatographic column separation efficiency without the use of a strong acid. Subsequently, an HPLC instrument (Agilent Technologies 1100, USA) was used, with the mobile phase eluting at a flow rate of 1 mL min^{-1} and an injection volume of 100 μL. And the sample was injected into anion exchange PRP-X100 (Hamilton, 4.6×250 mm, 5 μm) and PAX-500 (Thermo Scientific, 4×250 mm, 8.5 μm) columns. The eluate was mixed with the internal standard Ge through a T-junction before entering the ICPMS for analysis. The speciation was identified by matching retention times and quantified by peak integration using MassHunter Workstation (Agilent Technologies, USA) software. Unknown Se speciation was analysed by a Q Exactive instrument (Thermo

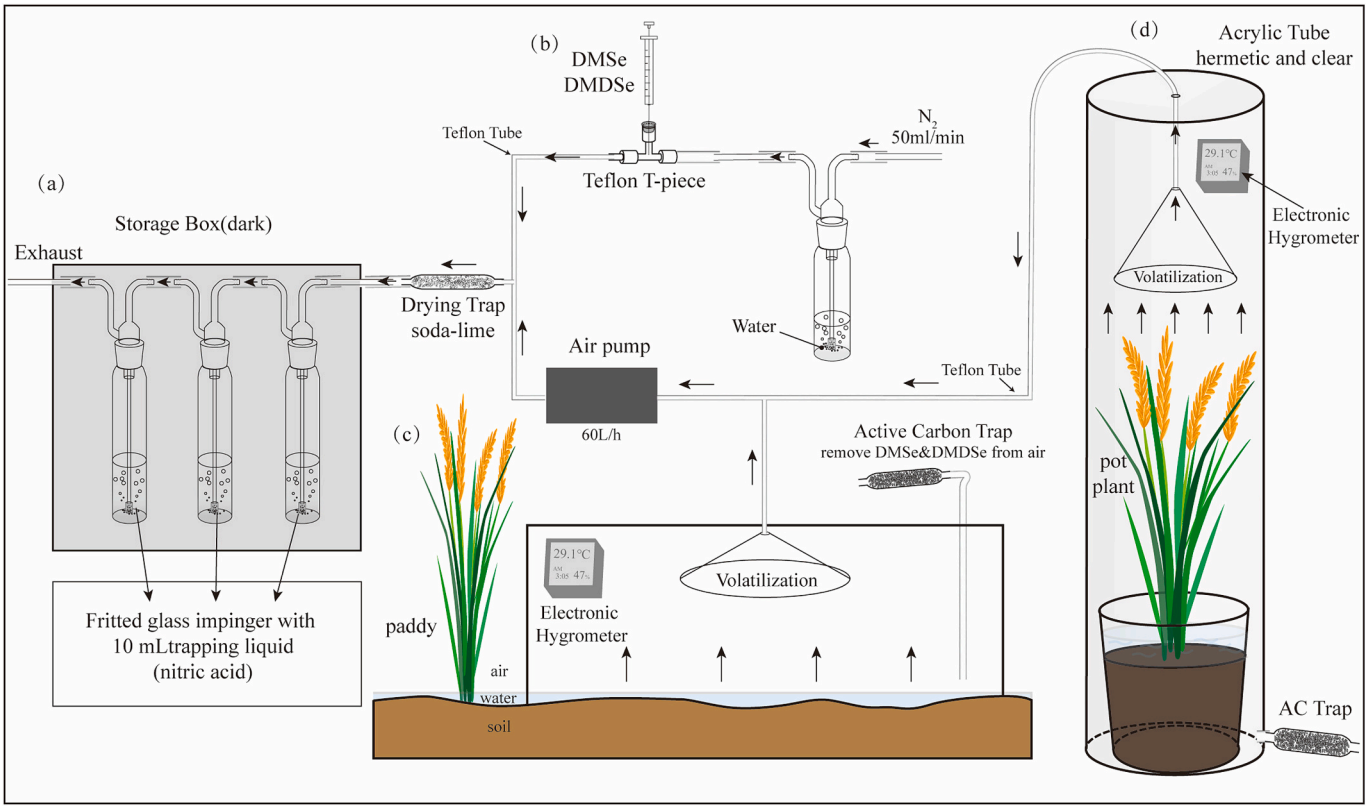
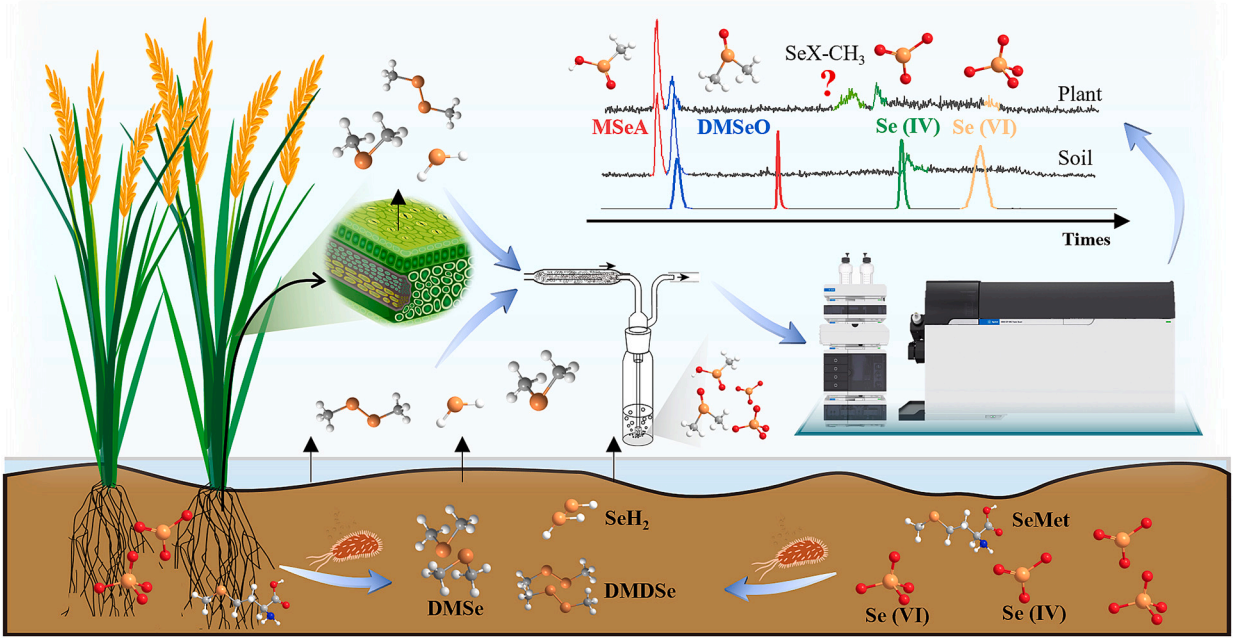


Fig. 1. VOSe preconcentration device for environmental soil–rice systems. (a) Three 25 mL brown borosilicate gas-washing bottles (containing 10 mL HNO_3); (b) indoor simulated VOSe volatilization; (c) field paddy soil VOSe preconcentration device; (d) rice VOSe preconcentration device.



Scheme 1. Preconcentration coupled with HPLC-ICPMS to analysis VOSe from paddy systems.

Fisher Scientific, USA). Isocratic elution was performed at a flow rate of 1 mL·min^{-1} with 10 mM ammonium acetate (pH 7.5) and 1 % methanol as the mobile phases and PAX-500 as the chromatographic column. Additional information is provided in Table S1.

All the above experiments were conducted in triplicate to express the uncertainty and errors that is associated with the analysis. Sample pollution was strictly controlled during the collection, pretreatment, and analytical processes. The glassware used for capture and storage was heated at 480 °C for 3 h after being thoroughly cleaned, and the other containers were rinsed with ultrapure water three times before use and completely dried. After collection, the samples were transferred quickly and sealed in three-layer self-sealing bags.

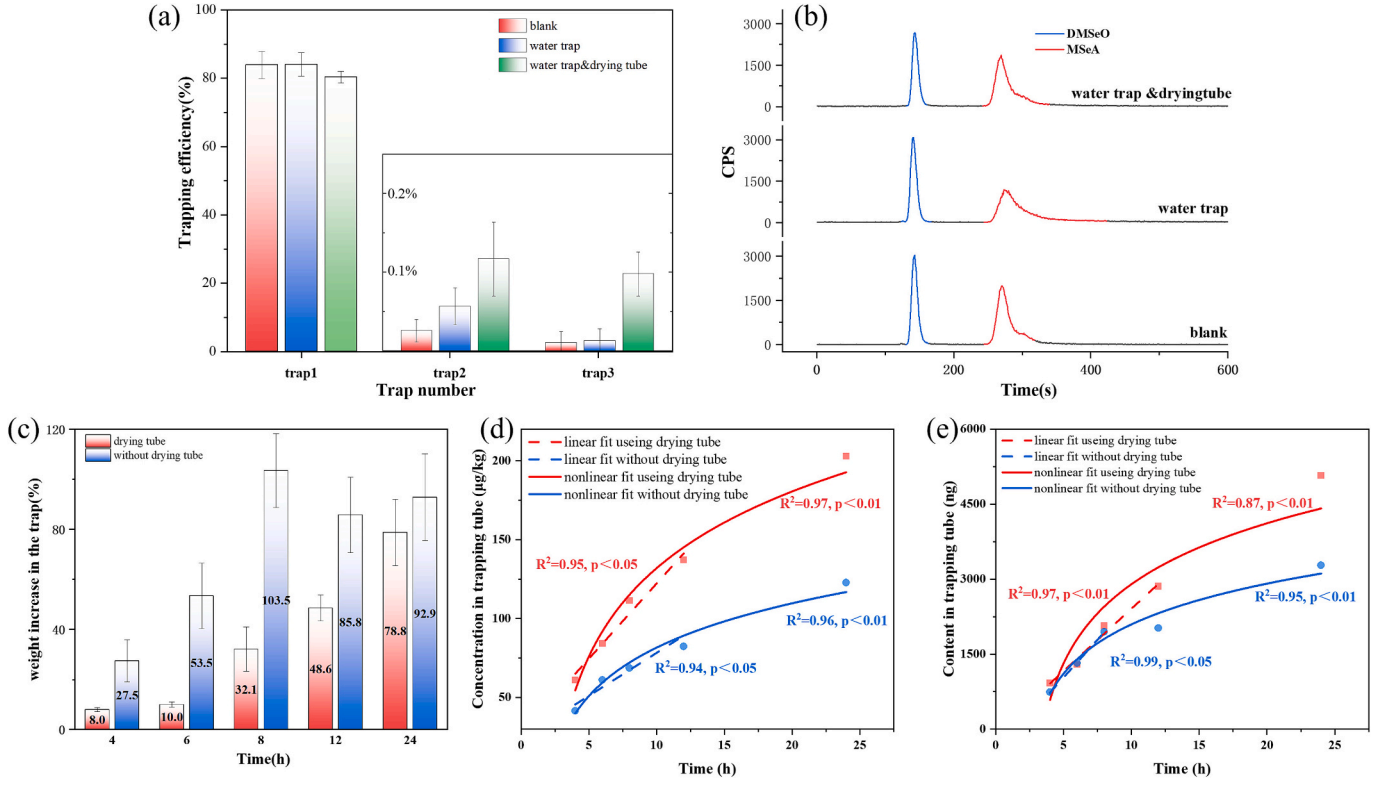


Fig. 2. Preconcentration efficiencies of DMSe and DMDSe with different methods (a) and corresponding chromatograms (b); impact of the drying system on field paddy capture (c); effect of the field capture drying system on the Se concentration (d) and content (e).

3. Results and discussion

3.1. Preconcentration method

3.1.1. Construction and evaluation of preconcentration

Se preconcentration experiments utilizing a capture device configured for indoor experimentation revealed a capture efficiency for DMSe and DMDSe mixture of 83.9 ± 4.0 % in first trap and <1 % in second and third trap (Fig. 2a), which is similar to previous studies by Winkel et al. (2010) and Ye et al. (2021). However, this ideal indoor simulation was unsuitable for outdoor environments characterized by high humidity and low Se concentrations, with an 85.8 % of the weights increase in trapping solution observed after 12 h of continuous sampling in paddy fields (Fig. 2c). To reduce water vapour interference, simulations of water vapour volatilization and removal in the laboratory yielded preconcentration efficiencies for DMSe and DMDSe mix solution of 84.0 ±3.5 % and 80.4±1.7 %, respectively (Fig. 2a). Trace amounts of water vapour accompanying Se in the capture solution did not significantly impact the Se preconcentration efficiency ($p > 0.05$) (Fig. 2b). Although the excessively long piping and drying system reduced the DMDSe and DMSe capture efficiency by 4 %, this reduction was significantly less than the interference caused by water vapour on VOSe preconcentration.

Compared to the indoor conditions, the decrease in water vapour caused by the drying system was better demonstrated in the field environment, with only an 8.0 % weight increase of trapping solution over 4 h, which was significantly lower than the 27.5 % increase for direct capture. Moreover, the diminished absorption of water vapour led to a 46.7 % increase in trapping solution concentration, facilitating the acquisition of more precise environmental data. It's noted that when the capture time exceeded 8 h, the volume of the solution began to increase rapidly (Fig. 2c), which means that the absorption of water vapour by this desiccant was limited. Hence, it is recommended to replace the drying tube every 4–6 h.

3.1.2. Time and efficiency of preconcentration

Fig. 2d and e illustrate the variation in Se preconcentration efficiency with time in paddy fields. Both the Se concentration and content exhibited a linear relationship with time ($p < 0.05$) within the first 12 h of preconcentration, whereas prolonged sampling led to a logarithmic curve in the preconcentration efficiency ($p < 0.01$). Because the drying system cannot completely prevent the absorption of water vapour, an extended preconcentration time will cause it to be ineffective, as evidenced by 78.8 % and 92.8 % increases in the weights of the two types of trapping solutions after 24 h (Fig. 2c). Additionally, the contents measured by both methods showed no significant differences within the first 6 h ($p>0.05$). This observation might be because within a certain concentration range, HNO_3 can effectively retain VOSe, suggesting that acid dilution within 50 % by water vapour does not significantly impact the content of VOSe. However, employing a drying system can significantly reduce moisture absorption, enhancing the capture efficiency and sample concentration, particularly within the 4–6 h range, where the concentration increased by 46.7 % and 37.7 %, respectively. Over a 12 h sampling period, the weight increase was maintained within 30 % by changing the drying system every 6 h. Thus, this method achieves higher preconcentration efficiency and requires less time to obtain higher concentration samples within 6–12 h, which is much less than that previously reported (24 h) (Vriens et al., 2014a, 2014b; Ye et al., 2021). Overall, this method can enrich VOSe in different environmental media based on validation in actual field environments. When sampling in high-humidity environments, it is recommended to use a drying system and collect samples over 12 h.

3.2. IEC–HPLC–ICPMS method

3.2.1. Prevention of interferences from matrices

In this work, Hamilton PRP-X100 and Thermo PAX-500 columns were utilized to separate various Se species. The PRP-X100 column was able to effectively separate DMSeO and MSeA in the four mobile phases NH_4NO_3, NH_4Ac, $C_6H_8O_7{\cdot}NH_4$, and $NH_4H_2PO_4$, with retention times ranging from 118 to 129 s for DMSeO and 158–235 s for MSeA, respectively (Fig. 3, a_3-d_3). Among them, NH_4NO_3 and $NH_4H_2PO_4$ demonstrated superior peak shapes and longer separation intervals compared to the other solvents. Similarly, the PAX-500 column was able to separate MSeA and DMSeO effectively using the same four mobile phases, with retention times of 108–112 s for MSeA and 133–136 s for DMSeO, respectively (Fig. 3, e_3-f_3). Since PRP-X100 and PAX-500 are anion exchange columns, the MSeA and DMSeO retention effects should be similar. However, the retention behaviours of MSeA and DMSeO were notably opposite.

Because of the neutralization dilution, we speculated that the sample matrix significantly influences the separation of MSeA and DMSeO. In fact, three signal peaks were found in the MSeA and DMSeO trapping solutions separated by Q Exactive full scan PAX-500, occurring at 109 s, 135 s, and 307 s. Here, the peak at 135 s corresponds to DMSeO (m/z 128.949), while those at 109 s and 307 s represent MSeA (m/z 126.9656) (Fig. S2, Text S3). This is because the NH_4NO_3 in the sample matrix directly elutes MSeA. However, the presence of NH_4NO_3 in the MSeA matrix is inevitable, as the HNO_3 trapping solution requires neutralization and dilution before analysis. Similarly, previous study have reported that matrix effects lead to peak shifts when different species of Se can be separated by direct 50-fold dilution in HNO_3 (Vriens et al., 2014a). Although the matrix interference can be reduced by increasing the dilution, a higher concentration of Se in the initial solution is needed. Therefore, it is necessary to further optimize the matrix effect to reduce its interference with sample separation.

3.2.2. Optimization of the column and mobile phase

Matrix effects are eliminated by purifying the sample and optimizing the analytical method. Although the sample can be purified by adsorption and desorption (Karasiński et al., 2024), the additional experimental process will increase the uncertainty. This study uniformly diluted all the samples 30 times to a 0.5 mol·L^{-1} NH_4NO_3 matrix to mitigate interference from the solvent effect. Fig. 3 illustrates the separation effects of NH_4NO_3, NH_4Ac, $C_6H_8O_7{\cdot}NH_4$, and $NH_4H_2PO_4$ for various Se species using PRP-X100 and PAX-500 columns. Within the PRP-X100 column, MSeA and DMSeO coeluted when directly eluted by NH_4Ac and NH_4NO_3, with retention times of 113–117 s (Fig. 3, b_2 and c_2). In addition to DMSe and DMDSe, H_2Se present in the environment can be oxidized to Se[IV] or Se[VI] by HNO_3 (Vriens et al., 2014a, 2014b). Although $C_6H_8O_7{\cdot}NH_4$ effectively separates DMSeO (129 s) and MSeA (158 s), it also directly elutes Se[IV], causing the overlap of MSeA and Se[IV] at 158 s (Fig. 3, a_2). In the PRP-X100 column, $NH_4H_2PO_4$ proved to be the optimal mobile phase for the separation of DMSeO (150 s), MSeA (263 s), and Se[IV] (400 s) from 0.5 mol·L^{-1} NH_4NO_3 matrix samples (Fig. 3d), but also for the separation of Se[VI] (Fig. S3 and Text S4).

In comparison to PRP-X100, the 0.5 mol·L^{-1} NH_4NO_3 matrix in PAX-500 directly retained MSeA and DMSeO without peak repetition at 108 s and 135 s, respectively. However, $C_6H_8O_7{\cdot}NH_4$, NH_4Ac and $NH_4H_2PO_4$ also eluted Se[IV] (106 s) and Se[VI] (103 s–112 s), resulting in direct overlap of MSeA, Se[IV] and Se[VI] in the 103 s–112 s region (Fig. 3, e-g). Fortunately, NH_4NO_3 eluted MSeA, DMSeO, Se[IV] and Se[VI] at 109 s, 135 s, 545 s, and 691 s, respectively (Fig. 3h). Although some Se [IV] (29.6± 3.2 %) and Se[VI] (<1 %) peaks drifted to 110 s, this drift was stable, which did not impede qualitative and quantitative analyses of Se species. Thus, the NH_4NO_3 matrix influences Se species separation, but selecting appropriate chromatographic columns and mobile phases can markedly enhance the separation effect and efficiency. In addition,

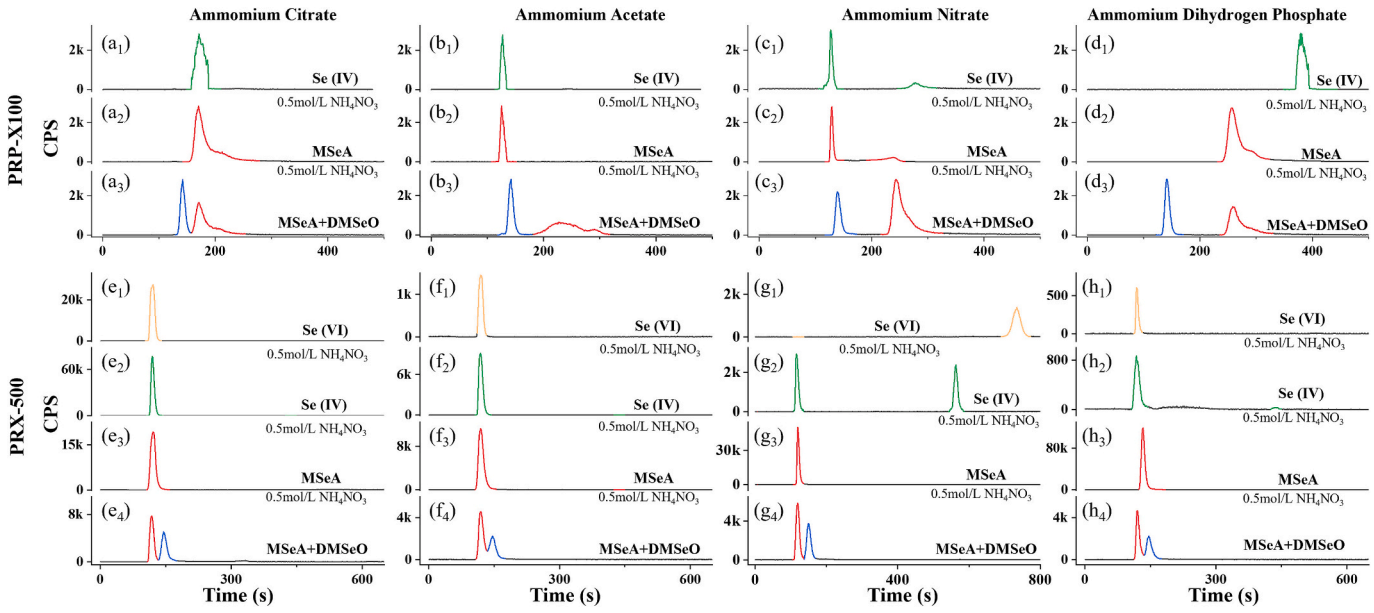


Fig. 3. Separation of Se species in various mobile phases using PRP-X100 and PAX-500 columns. For PRP-X100: (a) $C_6H_8O_7{\cdot}NH_4$, (b) NH_4Ac, (c) NH_4NO_3, (d) $NH_4H_2PO_4$; for PAX-500: (e) $C_6H_8O_7{\cdot}NH_4$, (f) NH_4Ac, (g) NH_4NO_3, (h) $NH_4H_2PO_4$.

the neutralization method directly solves the problem of sample acidity, which prevents damage to the column from HNO_3, and the dilution ratio is 20 times lower than that of previous studies (Vriens et al., 2014a). Comprehensively, the PRP-X100 column with $NH_4H_2PO_4$ and the PAX-500 column with NH_4NO_3 in this study represent two Se species separation methods suitable for analysing trace high-salt samples.

3.2.3. Evaluation of limit detection

The detection limits for PRP-X100 and PAX-500 are detailed in Table 1, along with comparisons with detection limits from other methods to further substantiate the viability and precision of the previously mentioned methods. All substances within the range of 0.2–20 ppb (RPR-X100) and 0.05–20 ppb (PAX-500) exhibited excellent linearity, with correlation coefficients exceeding 0.99 (Fig. S4). The absolute detection limits (ADLs) of DMSeO, MSeA, Se[IV], and Se[VI] with

Table 1
ADLs and MDLs of VOSe species determined by different methods.

Preconc. method	Analysis method	Species	ADLs [a] (pg)	MDLs [a,b,c] ($ng{\cdot}L^{-1}$)	Sample	Ref
HS-SPME	GC-AED	DMSe	190	25	Water	Campillo et al., 2007
		DMDSe	50	7.0		
		Se(IV)	20	3.0		
	GC-ICPMS	DMSe	–	700	Plant	Dietz et al., 2003
		DMDSe		900		
		DMSe	–	7		Meija et al., 2002
		DMDSe		1		
		DMSe	–	33		Duan et al., 2009
		DMDSe		7.1		
	GC–MS	DMSe	–	65	Water soil and biological	Ghasemi et al., 2011
		DMDSe		57		
		DMSe		0.54 ng	Microbial	Moreno-Martin et al., 2021
		DMDSe		0.42 ng		
	GC-ICPMS	DMSe	0.13	–	Normal urine	Bueno and Pannier, 2009
		DMDSe	0.26			
	GC-ICPMS	DMSe	–	1.0	Water	Amouroux et al., 1998
		DMDSe		2.8		
PT-LT		Total Se	66	0.033 $pg{\cdot}L^{-1}$	Air	Feldmann, 1997
	GC-AFS	DMSe	4	4.4 $pg{\cdot}L^{-1}$	Water	Pecheyran et al., 1998
		DMDSe	4.5	6.9 $pg{\cdot}L^{-1}$		
Tenax TA adsorption	TD-GC-ICPMS	DMSe	$9*10^{-3}$	0.4 $pg{\cdot}L^{-1}$	Air	Le Bras et al., 2023
		DMDSe	$8*10^{-3}$	0.2 $pg{\cdot}L^{-1}$		
Static chamber	HPLC–ICPMS/MS	DMSeO	4.6	2.4 $pg{\cdot}L^{-1}$	Soil	Vriens et al., 2014a
		MSeA	3.4	2.4 $pg{\cdot}L^{-1}$		
		DMSeO	1.2 (12 $pg{\cdot}g^{-1}$)	8.3 $pg{\cdot}L^{-1}$	Soil and plant	This study
		MSeA	1.4 (14 $pg{\cdot}g^{-1}$)	9.7 $pg{\cdot}L^{-1}$		
		Se(IV)	1.1 (11 $pg{\cdot}g^{-1}$)	7.6 $pg{\cdot}L^{-1}$		
		Se(VI)	0.7 (7 $pg{\cdot}g^{-1}$)	4.9 $pg{\cdot}L^{-1}$		

Note: a, MDLs = ADLs* Dilution Multiple/Recovery rate/preconcentration volume.
b, Preconcentration volume is 720 L of captured air volume within 12 h.
c, Here, $pg{\cdot}L^{-1}$ was the unit of MDLs for convenience in comparison with other methods. In practical applications, $ng{\cdot}m^{-2}{\cdot}h^{-1}$ was the unit. Text S5.

the PAX-500 column were 1.2 pg, 1.4 pg, 1.1 pg, and 0.7 pg, respectively. Correspondingly, the ADLs for DMSeO, MSeA and Se[IV] with the RPR-X100 column were 15.0 pg, 15.0 pg, and 14.2 pg, respectively. The determination of ADLs is significantly influenced by instrument sensitivity and the signal-to-noise ratio. In this research, ADLs = (3σ-b)/a, (σ, a and b were the standard deviation, intercept and slope respectively).

Compared with ADLs, method detection limits (MDLs) are true indicators for assessing method efficacy. In this study, the MDLs of PAX-500 were 8.3 pg·L^{-1} (DMSe), 9.7 pg·L^{-1} (DMDSe), 7.6 pg·L^{-1} (Se[IV]), and 4.9 pg·L^{-1} (Se[VI]). Here, DMSe and DMDSe were pre-oxidized species of DMSeO and MSeA. The MDLs was generally lower than those previously reported by other methods. Despite the fact that two methods, low-temperature enrichment and material capture, can achieve relatively low MDLs (0.033 pg·L^{-1} to 0.4 pg·L^{-1}) (Feldmann, 1997; Le Bras et al., 2023), but low-temperature enrichment only reports total Se in air (Feldmann, 1997), and material capture requires laboratory equipment modifications for thermal desorption (Le Bras et al., 2023). In contrast, our method can enrich VOSe from soil and plants in paddy environments and achieve lower MDLs through simple dilution, representing an effective approach for pg-level environmental Se analysis. Additionally, while the MDLs of RPR-X100, 10.4 pg·L^{-1} (DMSeO), 10.4 pg·L^{-1} (MSeA), and 9.9 pg·L^{-1} (Se[IV]), were higher than the PAX-500 column, the former is sufficient for paddy systems analyses of VOSe (Fig. S3) and is widespread availability in laboratories further supports its potential for broad application.

3.3. Trace VOSe in the paddy systems

3.3.1. Quantitative and qualitative analysis VOSe

Using the developed method, VOSe was collected from soil and plants in three regions of Enshi, known as the "Selenium Capital of the World" (Fig. 1). Comprehensively, the concentrations of various Se forms released from the soil were 16.55±9.94 ng·m^{-2}·h^{-1} DMSe and 124.49±120.34 ng·m^{-2}·h^{-1} DMDSe. In contrast, the plants released 38.38±29.85 ng·m^{-2}·h^{-1} DMSe and 72.54±94.66 ng·m^{-2}·h^{-1} DMDSe, both exceeding the method detection limits (Fig. 4b). Among them, DMSe and DMDSe released from soil were 15.31±1.93 ng·m^{-2}·h^{-1} and 168.26±23.29 ng·m^{-2}·h^{-1} in high-Se region, 25.83±11.44 ng·m^{-2}·h^{-1} and 194.96±151.56 ng·m^{-2}·h^{-1} in middle-Se region, 8.51±3.12 ng·m^{-2}·h^{-1} and 10.25±2.34 ng·m^{-2}·h^{-1} in low-Se region. Correspondingly, DMSe and DMDSe released from plants were 93.00±3.51 ng·m^{-2}·h^{-1} and 246.58±21.11 ng·m^{-2}·h^{-1} in high-Se region, 28.37 ±3.24 ng·m^{-2}·h^{-1} and 25.65±20.93 ng·m^{-2}·h^{-1} in middle-Se region, 15.31±1.33 ng·m^{-2}·h^{-1} and 19.02±3.04 ng·m^{-2}·h^{-1} in low-Se region. This shows that the developed method can be applied to environments with different soil Se concentrations. Additionally, small quantities of Se[IV] and Se[VI] were found in the trapping solution from both soil and plant Se volatilization (Fig. 4). The concentrations of Se[IV] and Se[VI] in soil trapping solution were 0.55 ±0.28 ng·g^{-1} and 0.94 ±0.58 ng·g^{-1}, and that Se[IV] and Se[VI] in plants trapping solution were 0.24± 0.06 ng·g^{-1} and 0.14±0.04 ng·g^{-1}. Given the use of ADL and MDL calculation methods with higher confidence and detection limits, some Se[IV] and Se[VI] concentrations were below the detection limit. However, the contents of Se[IV] and Se[VI] could still be quantitatively analysed.

Furthermore, a potential plant-derived volatile organic Se component was found (Fig. 4a). Previous studies have indicated that soil and seawater may release minor amounts of DMSeS, alongside DMSe and DMDSe (Le Bras et al., 2023). However, the order of reactivity for oxidation reactions is Se—Se (172 kJ·mol^{-1}) > Se-S > S-S (240 kJ·mol^{-1}) (Shao et al., 2018; Xu et al., 2013), making DMSeS more predisposed to forming MSeA (Vriens et al., 2014a, 2014b). Thus, this substance may not be DMSeS. Additionally, the elution time for this compound was 506 s, positioned between MSeA and Se[IV]. This positioning leads to the hypothesis that the substance could be an organic molecule exhibiting properties similar to inorganic Se. Because substances bearing organic functional groups are eluted before inorganic salts in ion-exchange chromatography columns. This discovery suggested that the potential plant-derived volatile organic Se component might represent a third type of volatile organic Se. Such findings are supported by research on *Brassica juncea* (Meija et al., 2002), which has shown that plants can release other VOSe components, thus challenging the traditional understanding that plant metabolism primarily focuses on producing DMSe and DMDSe. This insight contributes to establishing a new physiological and biochemical selenium cycle within plants.

3.3.2. Possible mechanisms for VOSe from different sources

Previous studies have shown that DMSe is the primary VOSe released from soil, water, plants and other media (Bueno and Pannier, 2009; Meija et al., 2002; Vriens et al., 2015). In contrast, in this study, volatile DMDSe significantly exceeded DMSe in paddy soil, which was in accordance with previous findings on wetland soil and marine volatilization (Campillo et al., 2007; Vriens et al., 2014a, 2014b). Generally,

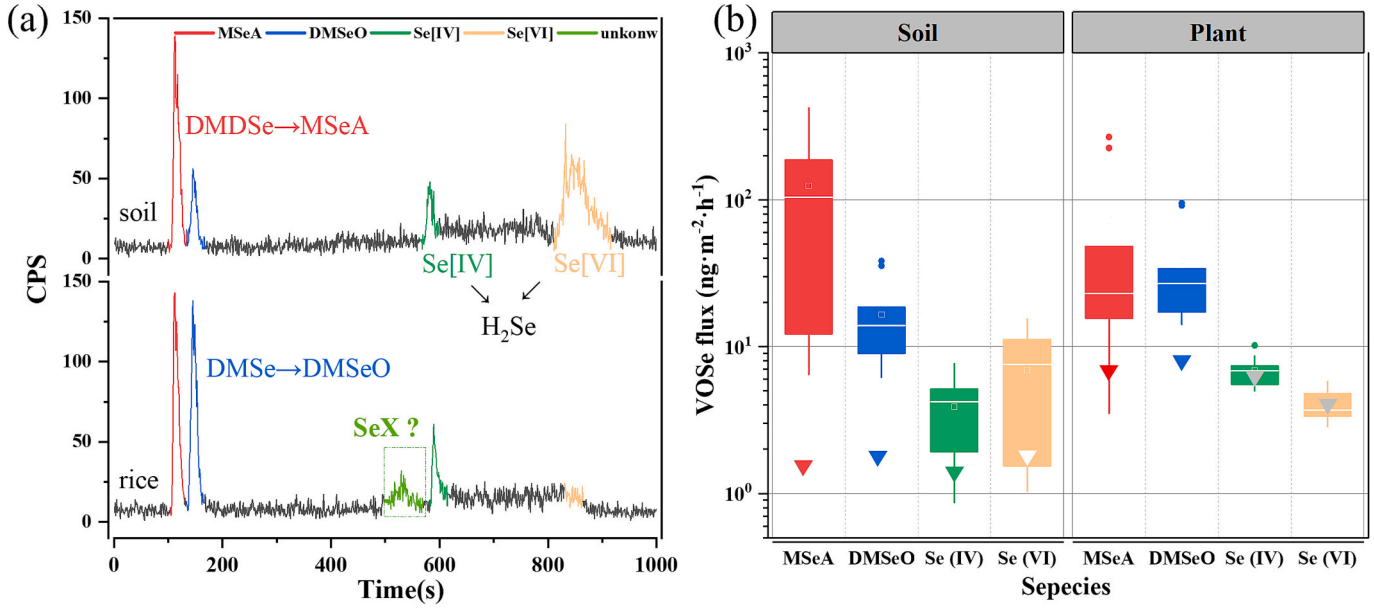


Fig. 4. (a) VOSe species from soil and plants by PAX-500; (b) release flux of different Se species; triangles indicate MDLs (Text.S5).

DMSe is more volatile than DMDSe due to its higher vapour pressure (32 kPa compared to 0.38 kPa for DMDSe) (Karlson et al., 1994), and it is less readily absorbed by soil and water (Zhang et al., 1999). However, the volatilization of DMSe is also influenced by soil and water, with only 4.3–16.8 % of DMSe released into the air from moist soil (Zhang et al., 1999). Recent studies suggest that DMDSe, with its longer half-life (Heine and Borduas-Dedekind, 2023), may exhibit a longer volatility duration. Additionally, soil microbes mediate the formation of DMSe and DMDSe through methylation, but different microbes produce different methylation products; for instance, *Staphylococcus aureus* can specifically produce DMDSe (Moreno-Martin et al., 2021). It is hypothesized that the microbial community in paddy fields primarily consists of microbes that produce DMDSe. Furthermore, Se[IV] and Se[VI] are likely oxidation products of H_2Se. Although current research on volatile H_2Se in microbes is limited, Se^{2-} is widely recognized as an essential product of Se metabolism (Kushwaha et al., 2022). Recent studies have also shown that H_2Se, like H_2S (Liu et al., 2021), is an important intracellular signalling molecule produced via the mediation of selenoamides and cysteine (Kang et al., 2022).

Similarly, plants produce volatile DMSe and DMDSe. However, the volatilization of Se, in the form of DMDSe and DMSe from plants, is considered essentially equivalent. It is generally believed that plants absorb tetravalent Se[IV], Se[VI] and organic Se from the soil, transporting these forms into their tissues (Natasha et al., 2018; Quang Toan et al., 2019). Due to selenium's chemical similarity to sulfur, this Se is converted into selenoamino acids such as selenomethionine (SeMet) and selenocysteine (SeCys). Plants subsequently convert SeMet and SeCys into DMSe and DMDSe, respectively (Natasha et al., 2018). Since the formation of DMSe and DMDSe in plants follows distinct pathways, the production of VOSe may be more dependent on the plant's inherent metabolic conversion efficiency (Wei et al., 2023). Additionally, the presence of Se [IV] and Se [VI] in the trapping solution suggests that plants may also generate H_2Se. While Se^{2-} is widely recognized as a key step in the biological Se metabolism that transforms inorganic selenium into organic selenium (Natasha et al., 2018), further investigation is required to determine whether H_2Se originates from this pathway.

Overall, both plants and microorganisms can produce VOSe, but the differences in metabolic processes and pathways lead to variations in the amount and forms of volatile selenium generated. More comprehensive biochemical studies are needed to fully understand the metabolic mechanisms of VOSe in microbes and plants, which could further elucidate the complex biogeochemical cycle of selenium.

4. Conclusion

This study combined in situ moisture removal with IEC–HPLC–ICPMS analysis to develop and validate a method for determining VOSe species in paddy soil–rice systems. The HNO_3 preconcentration method for capturing DMSe and DMDSe in the field proves to be both swift to deploy and cost-effective, thereby enhancing the analysis of VOSe in intricate environments. The collocation of RPR-X100 and PAX-500 columns at high salinity enables rapid separation of different species within 15 min, suggesting potential applicability in other high-salinity environments such as seawater. Furthermore, this method facilitated the first systematic analysis of VOSe species in paddy soil–rice system, revealing that plants and soil not only DMSe and DMDSe but also H_2Se and other VOSe species. Despite the low Se concentration hindering the qualitative identification of the third possible VOSe species in plants, it offers a promising direction for exploring the physiological metabolic pathways of Se. Moreover, this method has the potential to be applied in a wide range of natural environments, such as grasslands, lakes, and swamps, proving useful for accurately assessing the speciation, sources, and fluxes of VOSe. Comprehensively, this prospective work provides a practical approach for characterizing the environmental behaviour of VOSe in fields with high-humidity, low-volatility and difficult capture, contributing to a more comprehensive understanding of the biogeochemical cycle of Se in terrestrial ecosystems.

CRediT authorship contribution statement

Xuefeng Yang: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Kang Mao:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Chuanyu Chang:** Writing – review & editing, Writing – original draft. **Guopei Huang:** Writing – review & editing, Methodology. **Shuxun Shao:** Writing – review & editing. **Hua Zhang:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge the support from the National Natural Science Foundation of China (42377456), Youth Cross Team Project of CAS (JCTD-2021-17), Youth Innovation Promotion Association CAS (2023415), Qiankehe Platform Talents (GCC [2023] 046), Guizhou Provincial 2021 Science and Technology Subsidies (No. GZ2021SIG), Guizhou Provincial Major Scientific and Technological Program ([2024]013) and the Opening Funding of State Key Laboratory of Environmental Geochemistry (SKLEG2024222).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177514.

Data availability

Data will be made available on request.

References

Amouroux, D., Tessier, E., Pecheyran, C., Donard, O.F.X., 1998. Sampling and probing volatile metal(loid) species in natural waters by in-situ purge and cryogenic trapping followed by gas chromatography and inductively coupled plasma mass spectrometry (P-CT-GC-ICP/MS). Anal. Chim. Acta. 377 (2–3), 241–254. https://doi.org/10.1016/s0003-2670(98)00425-5.

Banuelos, G.S., Lin, Z.Q., Arroyo, I., Terry, N., 2005. Selenium volatilization in vegetated agricultural drainage sediment from the San Luis drain. Central California. Chemosphere 60 (9), 1203–1213. https://doi.org/10.1016/j.chemosphere.2005.02.033.

Biggar, J.W., Jayaweera, G.R., 1993. Measurement of selenium volatilization in the field. Soil Sci. 155 (1), 31–36. https://doi.org/10.1097/00010694-199301000-00005.

Blazina, T., Sun, Y., Voegelin, A., Lenz, M., Berg, M., Winkel, L.H.E., 2014. Terrestrial selenium distribution in China is potentially linked to monsoonal climate. Nat. Commun. 5. https://doi.org/10.1038/ncomms5717.

Bueno, M., Pannier, F., 2009. Quantitative analysis of volatile selenium metabolites in normal urine by headspace solid phase microextraction gas chromatography-inductively coupled plasma mass spectrometry. Talanta 78 (3), 759–763. https://doi.org/10.1016/j.talanta.2008.12.044.

Campillo, N., Penalver, R., Hernandez-Cordoba, M., Perez-Sirvent, C., Martinez-Sanchez, M.-J., 2007. Comparison of two derivatizing agents for the simultaneous determination of selenite and organoselenium species by gas chromatography and atomic emission detection after preconcentration using solid-phase microextraction. J. Chromatogr. A 1165 (1–2), 191–199. https://doi.org/10.1016/j.chroma.2007.07.064.

Chasteen, T.G., Bentley, R., 2003. Biomethylation of selenium and tellurium: microorganisms and plants. Chem. Rev. 103 (1), 1–25. https://doi.org/10.1021/cr010210+.

Combs, G.F., 2001. Selenium in global food systems. Br. J. Nutr. 85 (5), 517–547. https://doi.org/10.1079/BJN2000280.

Dietz, C., Perez-Corona, T., Madrid-Albarran, Y., Camara, C., 2003. SPME for on-line volatile organo-selenium speciation. J. Anal. At. Spectrom. 18 (5), 467–473. https://doi.org/10.1039/b211460g.

Duan, J., Li, X., Yu, C., Hu, B., 2009. Headspace stir bar sorptive extraction combined with GC-ICP-MS for the speciation of dimethylselenide and dimethyldiselenide in biological samples. J. Anal. At. Spectrom. 24 (3), 297–303. https://doi.org/10.1039/b813182a.

Feinberg, A., Stenke, A., Peter, T., Winkel, L.H.E., 2020. Constraining atmospheric selenium emissions using observations, global modeling, and Bayesian inference. Environ. Sci. Technol. 54 (12), 7146–7155. https://doi.org/10.1021/acs.est.0c01408.

Feinberg, A., Stenke, A., Peter, T., Hinckley, E.-L.S., Driscoll, C.T., Winkel, L.H.E., 2021. Reductions in the deposition of sulfur and selenium to agricultural soils pose risk of future nutrient deficiencies. Commun. Earth Environ. 2 (1). https://doi.org/10.1038/s43247-021-00172-0.

Feldmann, J., 1997. Summary of a calibration method for the deteremination of volatilemetal(loid) compounds in environmental gas samples by using gas chromatography–inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 12 (9), 1069–1076.

Fukagawa, N.K., Ziska, L.H., 2019. Rice: importance for global nutrition. J. Nutr. Sci. Vitaminol. (Tokyo) 65 (Supplement), S2–s3. https://doi.org/10.3177/jnsv.65.S2.

Ghasemi, E., Sillanpaa, M., Najafi, N.M., 2011. Headspace hollow fiber protected liquid-phase microextraction combined with gas chromatography-mass spectroscopy for speciation and determination of volatile organic compounds of selenium in environmental and biological samples. J. Chromatogr. A. 1218 (3), 380–386. https://doi.org/10.1016/j.chroma.2010.12.005.

Haygarth, P.M., Fowler, D., Sturup, S., Davison, B.M., Jones, K.C., 1994. Determination of gaseous and particulate selenium Over a rural grassland in the UK. Atmos. Environ. 28 (22), 3655–3663. https://doi.org/10.1016/1352-2310(94)00196-r.

Heine, P.A., Borduas-Dedekind, N., 2023. The ozonolysis of methylated selenide compounds in the atmosphere: isotopes, kinetics, products, and mechanisms. Environ. Sci. Technol. 57 (35), 13079–13087. https://doi.org/10.1021/acs.est.3c01586.

Kang, X., Huang, H., Jiang, C., Cheng, L., Sang, Y., Cai, X., Dong, Y., Sun, L., Wen, X., Xi, Z., Yi, L., 2022. Cysteine-activated small-molecule H_2Se donors inspired by synthetic H_2S donors. J. Am. Chem. Soc. 144 (9), 3957–3967. https://doi.org/10.1021/jacs.1c12006.

Karasiński, J., Tetfejer, K., Radziński, P., Tupys, A., Gambin, A., Bulska, E., Halicz, L., 2024. Coprecipitation as a one-step se separation for determination of isotope ratios completed with revised uncertainty evaluation. Anal. Chem. 96 (9), 3763–3771. https://doi.org/10.1021/acs.analchem.3c04210.

Karlson, U., Frankenberger Jr., W.T., Spencer, W.F., 1994. Physicochemical properties of dimethyl selenide and dimethyl diselenide. J. Chem. Eng. Data 39 (3), 608–610. https://doi.org/10.1021/je00015a049.

Kushwaha, A., Goswami, L., Lee, J., Sonne, C., Brown, R.J.C., Kim, K.-H., 2022. Selenium in soil-microbe-plant systems: sources, distribution, toxicity, tolerance, and detoxification. Crit. Rev. Environ. Sci. Technol. 52 (13), 2383–2420. https://doi.org/10.1080/10643389.2021.1883187.

Le Bras, Z., Bouchet, S., Winkel, L.H.E., 2023. Sensitive and high-throughput analysis of volatile organic species of S, Se, Br, and I at trace levels in water and atmospheric samples by thermal desorption coupled to gas chromatography and inductively coupled plasma mass spectrometry. Anal. Chem. 95 (5), 2967–2974. https://doi.org/10.1021/acs.analchem.2c04751.

Lin, Z.Q., Hansen, D., Zayed, A., Terry, N., 1999. Biological selenium volatilization: method of measurement under field conditions. J. Environ. Qual. 28 (1), 309–315. https://doi.org/10.2134/jeq1999.00472425002800010038x.

Liu, H., Wang, J., Liu, J., Liu, T., Xue, S., 2021. Hydrogen sulfide (H_2S) signaling in plant development and stress responses. aBIOTECH 2 (1), 32.

Martens, D.A., Suarez, D.L., 1999. Transformations of volatile methylated selenium in soil. Soil Biol. Biochem. 31 (10), 1355–1361. https://doi.org/10.1016/s0038-0717(99)00044-9.

Meija, J., Montes-Bayón, M., Le Duc, D.L., Terry, N., Caruso, J.A., 2002. Simultaneous monitoring of volatile selenium and sulfur species from se accumulating plants (wild type and genetically modified) by GC/MS and GC/ICPMS using solid-phase microextraction for sample introduction. Anal. Chem. 74 (22), 5837–5844. https://doi.org/10.1021/ac020285t.

Moreno-Martin, G., Sanz-Landaluze, J., Eugenia Leon-Gonzalez, M., Madrid, Y., 2021. *In vivo* quantification of volatile organoselenium compounds released by bacteria exposed to selenium with HS-SPME-GC-MS. Effect of selenite and selenium nanoparticles. Talanta 224. https://doi.org/10.1016/j.talanta.2020.121907.

Natasha, Shahid, M., Niazi, N.K., Khalid, S., Murtaza, B., Bibi, I., Rashid, M.I., 2018. A critical review of selenium biogeochemical behavior in soil-plant system with an inference to human health. Environ. Pollut. 234, 915–934. https://doi.org/10.1016/j.envpol.2017.12.019.

Pecheyran, C., Amouroux, D., Donard, O.F.X., 1998. Field determination of volatile selenium species at ultra trace levels in environmental waters by on-line purging, cryofocusing and detection by atomic fluorescence spectroscopy. J. Anal. At. Spectrom. 13 (7), 615–621. https://doi.org/10.1039/a802246a.

Quang Toan, D., Wang, M., Thi Anh Thu, T., Zhou, F., Wang, D., Zhai, H., Peng, Q., Xue, M., Du, Z., Banuelos, G.S., Lin, Z.-Q., Liang, D., 2019. Bioavailability of selenium in soil-plant system and a regulatory approach. Crit. Rev. Environ. Sci. Technol. 49 (6), 443–517. https://doi.org/10.1080/10643389.2018.1550987.

Schilling, K., Wilcke, W., 2011. A method to quantitatively trap volatilized organoselenides for stable selenium isotope analysis. J. Environ. Qual. 40 (3), 1021–1027. https://doi.org/10.2134/jeq2010.0474.

Shao, D., Li, M., Wang, Z., Zheng, X., Lao, Y.-H., Chang, Z., Zhang, F., Lu, M., Yue, J., Hu, H., Yan, H., Chen, L., Dong, W.-f., Leong, K.W., 2018. Bioinspired diselenide-bridged mesoporous silica nanoparticles for dual-responsive protein delivery. Adv. Mater., 30(29). doi:https://doi.org/10.1002/adma.201801198.

Sun, G.-X., Liu, X., Williams, P.N., Zhu, Y.-G., 2010. Distribution and translocation of selenium from soil to grain and its speciation in paddy rice (Oryza sativa L.). Environ. Sci. Technol. 44 (17), 6706–6711. https://doi.org/10.1021/es101843x.

Tan, L.C., Nancharaiah, Y.V., van Hullebusch, E.D., Lens, P.N.L., 2016. Selenium: environmental significance, pollution, and biological treatment technologies. Biotechnol. Adv. 34 (5), 886–907. https://doi.org/10.1016/j.biotechadv.2016.05.005.

Vriens, B., Ammann, A.A., Hagendorfer, H., Lenz, M., Berg, M., Winkel, L.H.E., 2014a. Quantification of methylated selenium, sulfur, and arsenic in the environment. PLoS One 9 (7). https://doi.org/10.1371/journal.pone.0102906.

Vriens, B., Lenz, M., Charlet, L., Berg, M., Winkel, L.H.E., 2014b. Natural wetland emissions of methylated trace elements. Nat. Commun. 5. https://doi.org/10.1038/ncomms4035.

Vriens, B., Mathis, M., Winkel, L.H.E., Berg, M., 2015. Quantification of volatile-alkylated selenium and sulfur in complex aqueous media using solid-phase microextraction. J. Chromatogr. A 1407, 11–20. https://doi.org/10.1016/j.chroma.2015.06.054.

Wei, L., Liu, J., Hou, X., Chen, W., Feng, Y., Kong, W., Tang, Y., Zhong, C., Zhang, S., Wang, T., Zhao, G., Jiao, S., Jiang, G., 2023. Rice seedlings and microorganisms mediate biotransformation of Se in CdSe/ZnS quantum dots to volatile alkyl selenides. Environ. Sci. Technol. 57 (48), 20261–20271. https://doi.org/10.1021/acs.est.3c07094.

Wen, H., Carignan, J., 2007. Reviews on atmospheric selenium: emissions, speciation and fate. Atmos. Environ. 41 (34), 7151–7165. https://doi.org/10.1016/j.atmosenv.2007.07.035.

Winkel, L., Feldmann, J., Meharg, A.A., 2010. Quantitative and qualitative trapping of volatile methylated selenium species entrained through nitric acid. Environ. Sci. Technol. 44 (1), 382–387. https://doi.org/10.1021/es902345m.

Winkel, L.H.E., Johnson, C.A., Lenz, M., Grundl, T., Leupin, O.X., Amini, M., Charlet, L., 2012. Environmental selenium research: from microscopic processes to global understanding. Environ. Sci. Technol. 46 (2), 571–579. https://doi.org/10.1021/es203434d.

Xu, H.P., Cao, W., Zhang, X., 2013. Selenium-containing polymers: promising biomaterials for controlled release and enzyme mimics. Acc. Chem. Res. 46 (7), 1647–1658. https://doi.org/10.1021/ar4000339.

Ye, W., Yuan, L., Zhu, R., Yin, X., Bañuelos, G., 2021. Selenium volatilization from tundra soils in maritime Antarctica. Environ. Int. 146, 106189. https://doi.org/10.1016/j.envint.2020.106189.

Zhang, Y., Frankenberger, W.T., 2000. Formation of dimethylselenonium compounds in soil. Environ. Sci. Technol. 34 (5), 776–783. https://doi.org/10.1021/es990958y.

Zhang, Y.Q., Frankenberger, W.T., 1999. Effects of soil moisture, depth, and organic amendments on selenium volatilization. J. Environ. Qual. 28 (4), 1321–1326. https://doi.org/10.2134/jeq1999.00472425002800040037x.

Zhang, Y.Q., Frankenberger, W.T., Moore, J.N., 1999. Effect of soil moisture on dimethylselenide transport nod transformation to nonvolatile selenium. Environ. Sci. Technol. 33 (19), 3415–3420. https://doi.org/10.1021/es981136o.