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Role of sulphate in affecting soil availability of exogenous selenate (SeO_4^{2-}) under different statuses of soil microbial activity

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Abstract: We investigated sulphate application, different statuses of soil microbial activity and their joint effects as variables associated with changes in potentially plant-available selenium (Se_{ppa}) and soil Se fractionation during the course of an incubation study. The time-resolved behaviour of added selenate (400 µg Se/kg as Na_2SeO_4) in two agricultural soils was elucidated by means of single extraction (50 mmol/L $NH_4H_2PO_4$), sequential extraction procedure (SEP) and chemical speciation analysis in phosphate extracts. The decrease in phosphate-extractable Se, a consequence of soil aging, was inhibited by sulphate (by 34% and 29% in Chernozem and Cambisol, respectively) and by gamma-irradiation (by 46% and 20% in Chernozem and Cambisol, respectively) after 72 days of incubation as compared to the control treatments. Glucose amendment dramatically decreased Se_{ppa} only in the Chernozem. After 1 year, the initial soil treatment with respect to inhibited or stimulated microbially-mediated processes substantially controlled the distribution pattern of exogenous Se as observed using the SEP. Application of sulphur fertilisers and sources of labile organic matter is thus an essential agronomic practice to correct unfavourable amounts of Se_{ppa}.

Keywords: micronutrient; soil extraction; immobilisation; bioreduction; anion competition; sterilisation

Human health issues in both seleniferous and selenium (Se)-deficient areas are primarily related to the amount of Se available in the soil (Fordyce 2013). Selenate (SeO_4^{2-}) represents a chemical species for effective crop biofortification with Se (Hawkesford and Zhao 2007, Ducsay et al. 2016); on the other hand, it poses a risk due to its high mobility in the soil environment, especially under oxidising and alkaline pH conditions (Nakamaru and Altansuvd 2014). Once exogenous SeO_4^{2-} emerges in a soil (fertilisation or contamination event), its redox stability depends on the soil pH, redox potential (Eh), microbial activity, and microbial community structure (Fellowes et al. 2013, Nakamaru and Altansuvd 2014). The conversion of SeO_4^{2-} to selenite (SeO_4^{2-}), elemental Se (Se^0) or even selenide (Se^{2-}) is an integral part of soil aging and decreases the bioavailability of Se in soil (Li et al. 2016). Several weeks up to months after SeO_4^{2-} input into soil, SeO_4^{2-} can still be detected in various extracts as the predominant Se species (Keskinen et al. 2010, Fellowes et al. 2013, Wang et al. 2019). Moreover, it may last up to several decades, until the exogenous Se merges into the native distribution in soil (Wang et al. 2017). It has been well documented that sulphate oxyanion and organic matter sources may interfere with SeO_4^{2-} behaviour in soil in both a microbial-driven (Aguilar-Barajas et al. 2011, Fellowes et al. 2013, Wang et al. 2019) and an abiotic manner (Goh and Lim 2004, Favorito et al. 2018, Praus et al. 2019b). Thus, it is essential to explore the impacts of agronomic practices on the fate of exogenous SeO_4^{2-} and potentially plant-available selenium (Se_{ppa}) in particular soils.

Against this background, the objective of the present study is to elucidate the effects of added sulphate and labile organic matter on temporal changes in the

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availability of exogenous SeO_4^{2-} in soil. We designed an incubation experiment on two arable soils to address the following hypotheses: (i) distinct statuses of soil microbial activity largely control the stabilisation of exogenous Se in soil aging processes; (ii) sulphate inhibits SeO_4^{2-} from entering unavailable Se reserves in soil; (iii) both labile organic matter and sulphate amendments significantly alter the Se chemical fractionation in soil.

MATERIAL AND METHODS

Soils and soil analysis. Two arable soils, a Chernozem (silty loam) and a Cambisol (sandy loam), were collected from the topsoil (0–20 cm) at experimental stations in Prague-Suchdol and Humpolec, respectively, both in the Czech Republic. The soils were air-dried in an oven at 35°C and passed through a 2-mm sieve. Following the soil pretreatment, 6 kg of each soil were obtained for soil characterisation and the incubation experiment. Soil pH_{H_2O} at a solid:liquid ratio of 1:5 (*w*/*w*) was 8.1 and 5.6 for Chernozem and Cambisol, respectively. The other chemical characteristics were as follows: $Se_{aqua\ regia}$ 347 and 219 µg/kg; $Fe_{ammonium\ oxalate}$ 1617 and 4461 mg/kg; $Al_{ammonium\ oxalate}$ 1372 and 1814 mg/kg; C_{H_2O} 62 and 102 mg/kg; S_{H_2O} 15 and 22 mg/kg; $P_{Mehlich\ 3}$ 96 and 89 mg/kg, in Chernozem and Cambisol, respectively. The description of the methods employed and additional physicochemical properties of the soils can be found in Praus et al. (2019a, In Press).

Incubation experiment. The thoroughly homogenised soil samples were weighed into 18 polyethylene vessels (per soil type) in an amount equivalent to 150 g dry weight (DW). As indicated in Table 1, six of the vessels (per soil type) were exposed to 27 kGy of γ-irradiation (cobalt-60). Individual aqueous solutions of K_2SO_4, KH_2PO_4, $(NH_4)_2SO_4$, glucose and Na_2SeO_4 were prepared and mixed in a manner that the spraying of these solutions provided the soil treatments described in Table 1. Soil moisture was set to 55% of water-holding capacity by the addition of high-purity water (HPW). Sealed vessels, in triplicate per treatment, were incubated at 23 ± 2°C under light/dark (8 h/16 h) cycles for 10 weeks. To maintain aerobic or semi-aerobic conditions, gas exchange between the vessel interior and the ambient atmosphere was allowed once a week. Irradiated treatments were strictly manipulated in a laminar flow box using a flame-sterilised stainless-steel spoon. After 1.5, 8.5, 24 and 72 days of incubation, ~15 g of moist soil were withdrawn from each vessel for the determination of the parameters of interest.

Soil analysis over a 10-week incubation period. Four grams of each treatment were weighed into a 50-mL polypropylene centrifuge tube and shaken with 24 mL of 50 mmol/L $NH_4H_2PO_4$ (without pH adjustment) on a reciprocating shaker (200 rpm) for 2 h. The soil suspensions were then centrifuged (7000 × g) for 10 min and filtered (KA-5 paper; particle capture of ≥ 3 µm, Papírna Perštejn, Perštejn, Czech Republic). The selenium concentration in 5-fold diluted (HPW) filtrates was measured using inductively-coupled plasma mass spectrometry (ICPMS; Agilent 7700x, Agilent Technologies Inc., Santa Clara, USA), operated in helium mode. Quality control for the determination of Se was performed by analysing a standard reference material (SRM 1640a, Trace Elements in Natural Water, NIST). Selected 50 mmol/L phosphate extracts sampled during the 1st and the 4th campaign were subjected to inorganic Se speciation analysis conducted on the same day as the extraction. First, an aliquot of the extract was filtered (0.20 µm, NYLON) and 2.5-fold diluted (HPW); 1 mL of the filtrate was pipetted into a 1.5-mL glass vial for Se speciation analysis. The concentration of total Se in the remaining filtrate was measured by ICPMS. Anion exchange high-performance liquid chromatography (AE-HPLC), coupled to ICPMS via a PEEK capillary tubing, was used for Se speciation. Standard solutions of 0.5, 2, 5, 20, 50 and 100 µg/L Se of both selenate (Se^{VI}) and selenite (Se^{IV}) were prepared by dissolution and dilution of Na_2SeO_4 (Sigma-Aldrich, Steinheim, Germany) and Na_2SeO_3 (Fluka, Neu-Ulm, Germany) with HPW. The chromatography system (Agilent 1260, Agilent Technologies Inc., Santa Clara, USA) was equipped with an analytical

Table 1. Supply of elements to individual treatments of the incubation experiment

Treatment (n = 3)	Se (µg/kg)	S	P	C	N
		(mg/kg)			
Control	400	–	–	–	–
S_{100}	400	100	–	–	–
$S_{50}P_{50}$	400	50	50	–	–
$S_{50}P_{50}C_{440}N_{44}$	400	50	50	440	44
γ-control	400	–	–	–	–
γ-S_{100}	400	100	–	–	–

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column Hamilton PRP-X100 (150 mm × 4.6 mm, 10 µm; Hamilton Company, Reno, USA), which was isocratically eluted (1.00 mL/min) by an aqueous mobile phase (pH 8.5) containing 25 mmol/L $(NH_4)_2HPO_4$ (Supriatin et al. 2015). The sample injection volume was 100 µL, and the column was heated to 30°C. Soil pH_{H2O} and DW were monitored throughout the incubation period.

Fractionation of soil Se using sequential extraction. After the last sampling in week 10, five soil treatments in triplicate (per soil type) were allowed to age for another 52 weeks. In addition to the treatment described above, the soils were moistened twice to avoid dryness. We used a slightly modified sequential extraction procedure (SEP) proposed by Wright et al. (2003) and tested by Keskinen et al. (2009) to estimate soil biogeochemical fractions with which exogenous Se was associated at the end of the incubation. Soil aliquots (~2.5 g) were successively extracted with 10 mL of the following solutions: (i) 100 mmol/L KCl for 1 h (soluble Se); (ii) 100 mmol/L $(NH_4)_2HPO_4$ at pH 8.0 for 2 h (adsorbed Se); (iii) 100 mmol/L NaOH for 3 h (organically associated Se); (iv) 100 mmol/L Na_2SO_3 at pH 7 for 4 h (elemental Se); (v) *aqua regia* at 180°C for 18 min (residual Se). During the first four steps, the suspensions were shaken on a tube rotator (30 rpm, 23 ± 2°C) and subsequently centrifuged (2680 × g for 10 min) and filtered (KA-5 paper). Soil samples were rinsed with 10 mL of 100 mmol/L KCl between individual steps, and the rinse was added to the extract of the preceding step. Oven-dried (35°C) reweighed soil residues arising from step four were exposed to *aqua regia* microwave-assisted digestion (Discover SP-D, CEM Corp., Matthews, USA). All supernatants were diluted up to 20-fold (HPW) and analysed for Se by ICPMS. Native (non-incubated) soils were also subjected to the same SEP for comparison.

Statistical analysis. The statistical significance of differences between Se_{ppa} determined in a given treatment at $t_{1.5d}$ and the referential Se_{ppa} estimated for t_0 in a given soil was tested using a one-sample *t*-test. The statistical significance of differences in Se_{ppa} (i) among soil treatments at a given sampling time and (ii) among soils of a given treatment sampled at $t_{1.5}$–t_{72d} were evaluated by a one-way analysis of variance (ANOVA), followed by Holm-Sidak's multiple comparison post-hoc test. The *P*-values < 0.05 were considered significant. All statistical analyses were executed using SigmaPlot 11.0 (Systat Software, Inc., San Jose, USA).

RESULTS AND DISCUSSION

Soil extraction using phosphate anions is useful in monitoring changes in the potentially plant-available selenium reserves (Keskinen et al. 2010). The estimated Se_{ppa} immediately after SeO_4^{2-} input into both experimental soils (at time t_0) is depicted by horizontal dashed lines in Figure 1 (the sum of Se_{KCl} and Se_{PO4} from native soils (Table 2), plus the addition of 400 µg/kg Se in the form of SeO_4^{2-}). In both soils, Se_{ppa} recovered at $t_{1.5d}$ did not significantly differ from the estimated Se_{ppa} at t_0. In general, Se_{ppa} decreased progressively with incubation time, regardless of soil type and treatment (Figure 1). The reduction in Se_{ppa} in acidic Cambisol became significant in a shorter time as compared to Chernozem. Interestingly, comparing only the percentage of decline in Se_{ppa} between t_0 and t_{72d} in both soils brought unexpectedly consistent results; the declines were 30–31% for control treatments, 20–21% for S_{100} and 26% for $S_{50}P_{50}$. When the same comparison was performed for treatments where microbial activity had been induced/suppressed, the declines for Chernozem and Cambisol were different (77% and 38% for $S_{50}P_{50}C_{440}N_{44}$, 17% and 24% for the γ-control, respectively). Sulphate addition to γ-irradiated soils smoothed out the differences in Se_{ppa} between both soils. The results of the one-way ANOVA executed on extraction data collected from individual soil treatments at the same sampling time are not shown because the differences among treatments were predominantly insignificant. Nevertheless, there were some noteworthy relationships between soil treatment and Se_{ppa}. Firstly, sulphate addition (S_{100}) suppressed the conversion of exogenous Se to an unavailable soil reserve in both soils (Figure 1), namely by up to 48 µg Se/kg in Cambisol (t_{24d}) and up to 45 µg Se/kg in Chernozem (t_{72d}) as compared to the corresponding control treatments. Combined amendment ($S_{50}P_{50}$) followed the effect of sulphate (S_{100}), but at a lower intensity. Easily available sources of C and N ($S_{50}P_{50}C_{440}N_{44}$) to soil microorganisms decreased Se_{ppa} dramatically only in the Chernozem, as early as at $t_{8.5d}$. On the contrary, γ-rays (γ-control) decreased irreversible Se immobilisation by up to 62 µg Se/kg in Chernozem (t_{72d}) and by up to 38 µg Se/kg in Cambisol (t_{24d}) as compared to non-irradiated controls. The addition of sulphate to γ-irradiated soil (γ-S_{100}) did not intensify the effect of γ-rays. Table 3 depicts the proportional distribution of SeO_4^{2-} and SeO_3^{2-} in 50 mmol/L $NH_4H_2PO_4$ soil extracts from the incuba-

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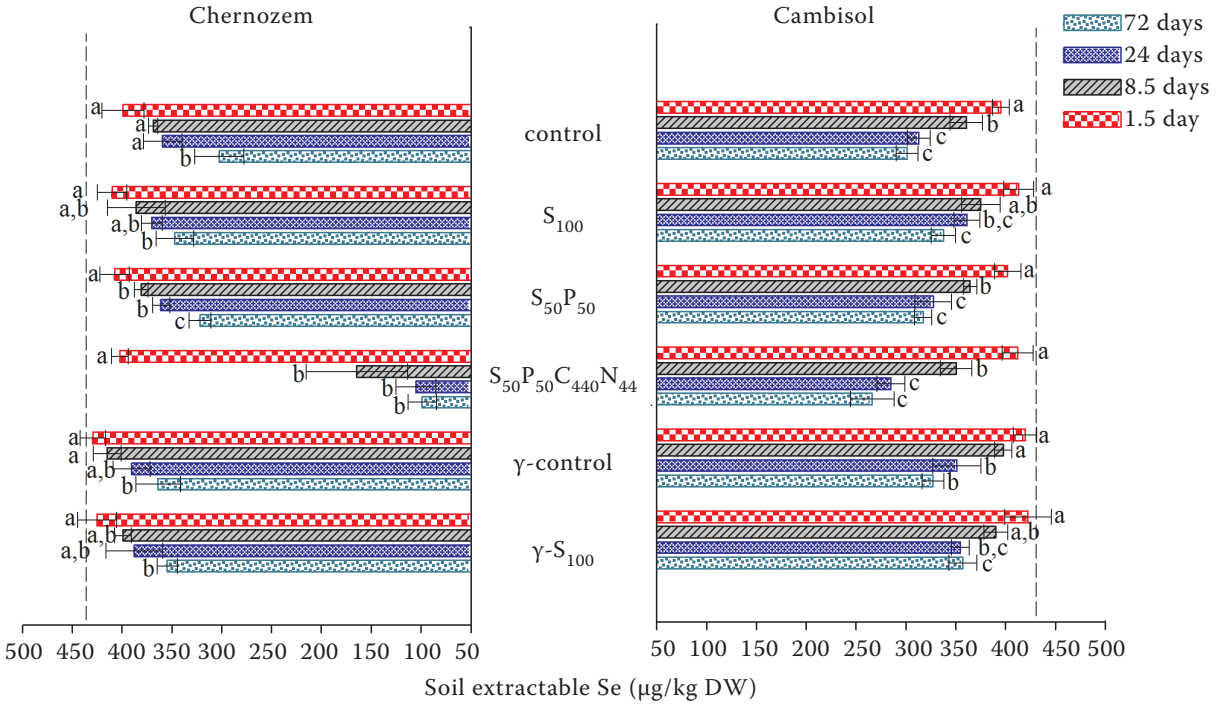

Figure 1. Selenium (Se) extractable with 50 mmol/L $(NH_4)_2HPO_4$ from individual soil treatments at four different sampling times. Different letters indicate significant differences among Se extractabilities determined in a given soil and a given treatment at different sampling times. Vertical dashed lines represent an estimation of phosphate-extractable Se at t_0. DW – dry weight

tion experiment. The amounts of $Se^{(VI)}$ and $Se^{(IV)}$ extracted at $t_{1.5d}$, regardless of the soil treatment (n = 4), were 390 ± 11 µg/kg and 7 ± 0 µg/kg in Cambisol and 374 ± 15 µg/kg and 9 ± 2 µg/kg in Chernozem, respectively. These results imply a short-term stability of SeO_4^{2-} in both soils and an acceptable procedural

Table 2. Soil selenium (Se) fractions operationally defined by a sequential extraction procedure

Treatment (n = 3)	KCl-extractable	$(NH_4)_2HPO_4$-extractable	NaOH-extractable	Na_2SO_3-extractable	*Aqua regia*-extractable
	(µg/kg soil dry weight ± standard deviation)				
Chernozem					
Control	206 ± 12	68 ± 4	287 ± 18	16 ± 3	168 ± 18
S_{100}	271 ± 22	26 ± 2	216 ± 15	7 ± 1	182 ± 15
$S_{50}P_{50}C_{440}N_{44}$	20 ± 10	68 ± 7	289 ± 14	34 ± 2	172 ± 21
γ-control	333 ± 28	30 ± 2	206 ± 21	0 ± 0	162 ± 13
γ-S_{100}	293 ± 24	30 ± 3	182 ± 12	0 ± 0	166 ± 4
Native soil	11 ± 1	25 ± 0	157 ± 1	1 ± 1	162 ± 8
Cambisol					
Control	163 ± 19	73 ± 8	174 ± 10	12 ± 0	203 ± 12
S_{100}	209 ± 3	63 ± 2	177 ± 1	10 ± 1	145 ± 14
$S_{50}P_{50}C_{440}N_{44}$	134 ± 16	45 ± 0	195 ± 17	21 ± 4	193 ± 25
γ-control	293 ± 14	60 ± 8	168 ± 3	5 ± 1	144 ± 12
γ-S_{100}	299 ± 16	34 ± 5	142 ± 13	9 ± 1	130 ± 4
Native soil	5 ± 1	25 ± 1	137 ± 3	1 ± 1	57 ± 3

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Table 3. Distribution of $Se^{(IV)}$ and $Se^{(VI)}$ anions in phosphate soil extracts

Treatment (n = 3)		Incubation time (days)	$Se^{(IV)}$ selenite	$Se^{(VI)}$ selenate	Unidentified/lost
			(μg/kg soil DW ± SD)		
Chernozem	control	1.5	8.4 ± 0.5	369 ± 18	22
		72	14.6 ± 1.3	266 ± 15	21
	$S_{50}P_{50}$	1.5	7.3 ± 0.6	395 ± 27	4
		72	10.1 ± 0.5	277 ± 28	35
	$S_{50}P_{50}C_{440}N_{44}$	1.5	8.9 ± 0.9	363 ± 17	30
		72	57.1 ± 6.2	21 ± 5	21
	γ-control	1.5	11.7 ± 0.2	368 ± 29	50
		72	16.8 ± 1.0	285 ± 23	62
Cambisol	control	1.5	7.3 ± 0.6	384 ± 23	3
		72	12.0 ± 0.9	262 ± 26	27
	$S_{50}P_{50}$	1.5	7.6 ± 1.0	388 ± 14	6
		72	11.2 ± 1.1	270 ± 30	35
	$S_{50}P_{50}C_{440}N_{44}$	1.5	7.2 ± 0.6	381 ± 36	24
		72	10.2 ± 2.0	193 ± 21	63
	γ-control	1.5	6.7 ± 0.5	405 ± 38	8
		72	12.2 ± 0.5	272 ± 25	43

recovery of SeO_4^{2-}. At t_{72d}, a consistent decline in extractable $Se^{(VI)}$ down to 272 ± 8 μg/kg (six treatments) was recorded in both soils where microbial activity had not been stimulated. This consistency in the occurrence of the main Se species with such a low standard deviation corroborates the identical availability of Se in both soils at t_{72d}, as mentioned above. The proportion of $Se^{(IV)}$ in soil extracts increased clearly between $t_{1.5d}$ and t_{72d} (Table 3). The most contrasting changes in Se speciation during soil aging were noticed in the $S_{50}P_{50}C_{440}N_{44}$ treatment, especially in the Chernozem, where $Se^{(VI)}$ decreased to 21 ± 5 μg/kg and $Se^{(IV)}$ increased to 57 ± 6 μg/kg. The differences observed in the time-dependent Se extraction pattern between γ-irradiated and non-irradiated control treatments (Figure 1) proved that soil microorganisms were involved in the immobilisation of SeO_4^{2-} in both soils. Similarly, Garcia-Sanchez et al. (2014) have reported a substantial microbial contribution to the kinetically controlled sorption of SeO_4^{2-} at non-sterile conditions as against autoclaved soil. Our γ-treated soils (27 kGy), by no means, could be considered free of surviving microorganisms. Blankinship et al. (2014) have decreased the count of colony-forming units (CFU) only from 10^7 to 10^4/g per day after exposure of the soil to γ-radiation (54 kGy). Thus, even in γ-irradiated soils, a biotic mechanism of SeO_4^{2-} immobilisation should not be omitted. Praus et al. (2019b) have investigated a fast abiotic sorption of SeO_4^{2-} in both soils under investigation in the present study and found no or a weak retention of SeO_4^{2-} where the difference between the soils was, in most cases, insignificant. Although both soils substantially differed in pH and oxalate-extractable Fe and Al (Material and methods), we did not observe contrasting values of Se_{ppa} acquired in their control treatments over 72 days of incubation (Figure 1). This finding might be explained by the extraction method used; phosphate may significantly release adsorbed Se oxyanions on soil particles (Keskinen et al. 2009). Thus, our Se_{ppa} data are probably insensitive to adsorbed Se. Neither soil pH fluctuation in a particular treatment over the course of incubation (≤ 0.3 pH unit, data not shown) or differences in pH among treatments at a given time (≤ 0.5 pH unit) are likely to be important influential factors. According to Figure 1, sulphate (S_{100}) interfered with slow irreversible abiotic retention and/or microbial immobilisation of Se during soil aging in both soils. The importance of the latter mechanism is emphasised by the fact that the Se_{ppa} in γ-control resembles that in S_{100}, indicating that a drop in viable microorganisms (γ-rays) as well as sulphate-selenate competition for transport into mi-

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crobial cells (Aguilar-Barajas et al. 2011) had the same consequence, preventing SeO_4^{2-} bioreduction. When assuming the enrichment of the phosphate extract in SeO_3^{2-} at the expense of SeO_4^{2-} in $S_{50}P_{50}C_{440}N_{44}$ in Chernozem (Table 3), we hypothesised that the addition of glucose helped to overcome a lack of electron donors and, along with a favourable soil pH (approx. 8), induced the pronounced bioreduction of SeO_4^{2-}, in which SeO_3^{2-} appears as an intermediate product. Moreover, a supportive role of decreasing soil Eh after oxygen depletion at conditions of boosted microbial activity should be mentioned. Fellowes et al. (2013) have observed a microbial-driven reduction of exogenous SeO_4^{2-} in a microcosm experiment even at oxic conditions when employing seleniferous soil. Selenite and elemental Se^0 phase were intermediate and final products of the reduction, respectively.

The overall Se recovery of the SEP, calculated as the sum of Se extracted in five consecutive extraction steps (∑Se) from a particular treatment divided by its sub-total soil Se content increased by 400 µg/kg, was in the range of 78–100% for Chernozem and 95–108% for Cambisol. In Chernozem $S_{50}P_{50}C_{440}N_{44}$, the higher portion of Se unrecovered in the SEP may be attributed to Se biomethylation when the soil was amended with organic compounds (Zhang and Frankenberger 1999) at favourable pH conditions. Keskinen et al. (2010) have shown that chloride extraction represents a sensitive indicator of Se plant availability in soil. Consistently for both Se-fortified soils, the highest yields of Se_{KCl} (nearly 50% of ∑Se) were achieved in γ-irradiated treatments, being notably higher than those in the regular controls and slightly higher than those in the S_{100} treatments (Table 2). The lowest Se_{KCl} was acquired in $S_{50}P_{50}C_{440}N_{44}$ (3% of ∑Se in Chernozem). Incorporation of phosphate extraction after Se_{KCl} determination allows to distinguish ligand-exchangeable Se (specifically adsorbed Se oxyanions, mainly SeO_3^{2-}) from non-specifically adsorbed and soluble Se fractions. Several treatments, especially those of Cambisol, exceeded the Se_{PO_4} determined in corresponding native soils, implying that specific adsorption is a relevant mechanism for Se immobilisation. Interestingly, sulphate addition significantly decreased Se_{PO_4} only in the Chernozem. We believe this observation stems from the pronounced reduction of $Se^{(VI)}$ to $Se^{(IV)}$ in acidic Cambisol within 1 year of incubation; consequently, sulphate does not effectively compete with SeO_3^{2-} for soil sorption sites (Goh and Lim 2004). Selenium extractable with a hydroxide solution traditionally represents organically associated Se fractions in soil (Wright et al. 2003). We assume that Se_{NaOH} can be used as an index of $Se_{anorg} \rightarrow Se_{org}$ biotransformation in our study. From this point of view, the high values of Se_{NaOH} determined especially in the Chernozem (control and $S_{50}P_{50}C_{440}N_{44}$) indicate an extensive microbial-driven incorporation of exogenous Se into soil organic matter (SOM). Straightforwardly, sulphate amendment and γ-irradiation significantly decreased Se_{NaOH} in the Chernozem as compared to the control (Table 2). The selenium fraction recovered with Na_2SO_3 was low in all treatments and soils (max. 4–6% of ∑Se). We used the SEP refined by Wright et al. (2003), providing improved selectivity of sulphite towards elemental Se^0. The highest Se_{Na2SO3} were determined in $S_{50}P_{50}C_{440}N_{44}$ treatments, which offer a direct link between boosted microbial activity and the reduction of exogenous Se to the Se^0 phase. The most resistant fraction $Se_{aqua\ regia}$ may comprise recalcitrant Se_{org} and metal selenides. In the Chernozem, no treatment exhibited an increase in $Se_{aqua\ regia}$ after 1 year of soil aging, whereas in the Cambisol, this Se fraction more than doubled in the control and $S_{50}P_{50}C_{440}N_{44}$ treatments compared to un-selenised soil. A significant decrease in $Se_{aqua\ regia}$, induced by sulphate and γ-rays, in the Cambisol (Table 2) suggests that the recalcitrant Se might be of microbial origin. To resume the results of SEP, a significant portion of exogenous Se redistributed over the course of the incubation to the Se_{org} fraction in the alkaline Chernozem, whereas in the acidic Cambisol, it emerged in $Se_{aqua\ regia}$; this is in agreement with the findings of Wang et al. (2017). It should be kept in mind that the distribution pattern determined for Se, based on an SEP at a given time, might be highly sensitive to the amount of exogenous SeO_4^{2-} initially present, as Loffredo et al. (2011) have shown that this parameter largely controls the rate of SeO_4^{2-} stabilisation, especially in alkaline soil, where some $Se^{(VI)}$ bioreduction was assumed. Native Se in agricultural soils is frequently present in organic forms or associated with SOM (Keskinen et al. 2009, Supriatin et al. 2015). Accordingly, the role of soil microorganisms in the transformation of exogenous Se must be understood in much greater detail than is currently available in the literature. We recommend that Se availability to soil microbiota and the extent of specific microbial activity should be acknowledged as important soil variables controlling the fate of exogenous SeO_4^{2-} in soils under different agronomic treatments.

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REFERENCES

Aguilar-Barajas E., Díaz-Pérez C., Ramírez-Díaz M.I., Riveros-Rosas H., Cervantes C. (2011): Bacterial transport of sulfate, molybdate, and related oxyanions. Biometals, 24: 687–707.

Blankinship J.C., Becerra C.A., Schaeffer S.M., Schimel J.P. (2014): Separating cellular metabolism from exoenzyme activity in soil organic matter decomposition. Soil Biology and Biochemistry, 71: 68–75.

Ducsay L., Ložek O., Marček M., Varényiová M., Hozlár P., Lošák T. (2016): Possibility of selenium biofortification of winter wheat grain. Plant, Soil and Environment, 62: 379–383.

Favorito J.E., Eick M.J., Grossl P.R. (2018): Adsorption of selenite and selenate on ferrihydrite in the presence and absence of dissolved organic carbon. Journal of Environmental Quality, 47: 147–155.

Fellowes J.W., Pattrick R.A.D., Boothman C., Al Lawati W.M.M., van Dongen B.E., Charnock J.M., Lloyd J.R., Pearce C.I. (2013): Microbial selenium transformations in seleniferous soils. European Journal of Soil Science, 64: 629–638.

Fordyce F.M. (2013): Selenium deficiency and toxicity in the environment. In: Selinus O. (ed.): Essentials of Medical Geology. Revised 1st Edition. Dordrecht, Springer.

Garcia-Sanchez L., Loffredo N., Mounier S., Martin-Garin A., Coppin F. (2014): Kinetics of selenate sorption in soil as influenced by biotic and abiotic conditions: A stirred flow-through reactor study. Journal of Environmental Radioactivity, 138: 38–49.

Goh K.H., Lim T.T. (2004): Geochemistry of inorganic arsenic and selenium in a tropical soil: Effect of reaction time, pH, and competitive anions on arsenic and selenium adsorption. Chemosphere, 55: 849–859.

Hawkesford M.J., Zhao F.J. (2007): Strategies for increasing the selenium content of wheat. Journal of Cereal Science, 46: 282–292.

Keskinen R., Ekholm P., Yli-Halla M., Hartikainen H. (2009): Efficiency of different methods in extracting selenium from agricultural soils of Finland. Geoderma, 153: 87–93.

Keskinen R., Turakainen M., Hartikainen H. (2010): Plant availability of soil selenate additions and selenium distribution within wheat and ryegrass. Plant and Soil, 333: 301–313.

Li J., Peng Q., Liang D., Liang S., Chen J., Sun H., Li S., Lei P. (2016): Effects of aging on the fraction distribution and bioavailability of selenium in three different soils. Chemosphere, 144: 2351–2359.

Loffredo N., Mounier S., Thiry Y., Coppin F. (2011): Sorption of selenate on soils and pure phases: Kinetic parameters and stabilisation. Journal of Environmental Radioactivity, 102: 843–851.

Nakamaru Y.M., Altansuvd J. (2014): Speciation and bioavailability of selenium and antimony in non-flooded and wetland soils: A review. Chemosphere, 111: 366–371.

Praus L., Száková J., Steiner O., Goessler W. (2019a): Rapeseed (*Brassica napus* L.) biofortification with selenium: How do sulphate and phosphate influence the efficiency of selenate application into soil? Archives of Agronomy and Soil Science. doi: 10.1080/03650340.2019.1592163. (In Press)

Praus L., Száková J., Tremlová J. (2019b): Fast abiotic sorption of selenates (SeO_4^{2-}) in soils: Pitfalls of batch sorption data acquired by inductively coupled plasma quadrupole mass spectrometry (ICP-QMS). Archives of Agronomy and Soil Science, 65: 566–580.

Supriatin S., Weng L., Comans R.N. (2015): Selenium speciation and extractability in Dutch agricultural soils. Science of the Total Environment, 532: 368–382.

Wang D., Xue M.Y., Wang Y.K., Zhou D.Z., Tang L., Cao S.Y., Wei Y.H., Yang C., Liang D.L. (2019): Effects of straw amendment on selenium aging in soils: Mechanism and influential factors. Science of The Total Environment, 657: 871–881.

Wang D., Zhou F., Yang W., Peng Q., Man N., Liang D. (2017): Selenate redistribution during aging in different Chinese soils and the dominant influential factors. Chemosphere, 182: 284–292.

Wright M.T., Parker D.R., Amrhein C. (2003): Critical evaluation of the ability of sequential extraction procedures to quantify discrete forms of selenium in sediments and soils. Environmental Science and Technology, 37: 4709–4716.

Zhang Y.Q., Frankenberger W.T. (1999): Effects of soil moisture, depth, and organic amendments on selenium volatilization. Journal of Environmental Quality, 28: 1321–1326.

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