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Sulphur status in agricultural soils determined using the Mehlich 3 method

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ABSTRACT

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Several sets of soil samples were chosen to demonstrate the applicability of the Mehlich 3 extractant for the determination of sulphur (S) in soils. Archived samples from 139 basal soil monitoring plots (BSMS) sampled in 1995 and 2013, samples from eleven long-term field trials sampled in 1981 and 2017, 1167 soil samples from the areas vulnerable to S losses and 720 samples from the non-vulnerable areas sampled in 2010 were chosen for the experiments. Mehlich 3 clearly showed a statistically highly significant decrease in the soil S content caused by reduction of SO_2 emissions in the long-term field experiments from 33 mg/kg in 1981 to 8 mg/kg in 2017 for the median of the untreated controls. Similar results were obtained for BSMS samples, where an average decrease from 26 mg/kg in 1995 to 17 mg/kg in 2013 was found. Mehlich 3 also showed that more than 52% of samples from the areas vulnerable to S losses were in a very low content category in contrast to only 3% of soils from the other areas. Mehlich 3 clearly proved the capacity to distinguish changes in the content of soil S in all studied cases.

Keywords: long-term sulphur changes; criteria for Mehlich 3 extractable sulphur; soil testing; multielement method

Soil testing in the Czech Republic substantially changed in 1991 when a set of traditional individual extractants (Egner P, Schachtschabel K, Schachtschabel Mg) that had been used for 30 years was abandoned and a new system using a multielement universal soil extractant (Jones 1990) started to be used. At first, it was Mehlich 2 extractant (Mehlich 1978) and several years later the system was slightly modified by using Mehlich 3 extractant (Mehlich 1984, Zbíral and Němec 2000). These changes of the soil testing scheme opened the way for an effective adoption of inductively coupled plasma optical emission spectroscopy (ICP-OES) which is a fast multielement technique with a wide linear concentration range and an adequate sensitivity for all elements from micronutrients to macronutrients extracted by Mehlich 3 (Zbíral 2000). Nowadays, the ICP-OES instruments are commonly used in soil testing laboratories and therefore these laboratories can take full advantage of the multielement potential of Mehlich 3 extractant.

Mehlich 3 is a suitable method for a large-scale soil testing, where high sample throughput is demanded. This extractant has been used in Central Institute for Supervising and Testing in Agriculture laboratories for more than 20 years for the determination of phosphorus (P), potassium (K), magnesium (Mg) and calcium (Ca). The determination of available soil micronutrients (zinc, copper, iron, manganese and boron) in this extractant has started recently (Zbíral 2016a). ICP-OES can also simultaneously determine sulphur (S) in Mehlich 3 extracts but the determination of S was not included in the soil testing scheme because there was more than adequate input of this element from the coal burning power plants and no S deficiencies were anticipated. The political consequences after 1989 resulted in clean air acts and desulphurization of the emissions, all of which led to a decrease of atmospheric S depositions (Haneklaus et al. 2002). SO_2 emissions in the Czech Republic (CR) were reduced by more than

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90% from 1990 to 2006. The European Environment Agency reported a decrease of 74% between 1990 and 2011 for EU member states (EEA 2015). This situation can only be welcomed but there is one drawback – S is becoming a nutrient that should be taken into account, mainly from the point of view of S fertilizing. The problem is even more critical because the area of crops with high S demand (especially oilseed rape) has risen. Haneklaus et al. (2002) reported that during the 1990's macroscopic S deficiency became the most widespread nutrient disorder in the northern Europe. Sources of soil S, its transformation, mobilization and immobilization, retention and movement, is a very complex issue discussed in detail e.g. by Edwards (1998), Haneklaus et al. (2002), Mitchell and Alewell (2008), Scherer (2009). One very important fact is that a shortage of the S supply also lowers the utilization of nitrogen (N) and results in a deterioration of crop quality (Carciochi et al. 2017). Haneklaus et al. (2002) reported that on average each kg of S shortage causes 15 kg of N to be lost in the environment.

There were several studies focused on the choice of the most suitable extractant for plant available sulphur. Matula (1999) compared several multinutrient soil tests (Mehlich 2, Mehlich 3, KVK-UF, 0.01 mol/L $CaCl_2$, 1:5 water extract and saturated soil paste resin capsule extraction) and its suitability for S bioavailability in short-term (21 days) vegetative trials. He did not find a relationship between the S content in Mehlich 2, Mehlich 3 and 0.01 mol/L $CaCl_2$ and S in the dry matter of shoots, which can be attributed probably to the short term of the trials dealing only with the immediately available sulphur. Esmel et al. (2010) reported no predictability for Mehlich 3, water and 0.025 mol/L KCl extraction for tomato plant tissue. Rao and Sharma (1997) compared Mehlich 3 and four other extractants (monocalcium phosphate, monocalcium phosphate + acetic acid, Morgan reagent and calcium chloride). They found that Mehlich 3 – extractable S correlated with the results of other extractants but only Mehlich 3 significantly correlated with S uptake by tea crops. Ostatek-Boczynski and Lee-Steere (2012) studied the possibility of using Mehlich 3 also for determination of S and other nutrients and micronutrients. They found a very good correlation with the calcium phosphate extractant and concluded that Mehlich 3 extractant is a suitable diagnostic tool to assess nutrient status of soils in sugarcane growing areas. The relationships between several extraction methods (water extraction, Mehlich 3 and *aqua regia*) were studied on 147 soil samples collected from basal soil monitoring plots (BSMS) (Zbíral 1999). In comparison with water extracts, Mehlich 3 extracted 1.26 times higher and *aqua regia* 20 times higher S amounts. A statistically highly significant linear relationship was found between water extraction and Mehlich 3 extraction (R^2 = 0.62). Kowalenko et al. (2014) studied in detail five extractants including Mehlich 3 for different soils and different sampling depths. The authors emphasized the influence of the subsurface S for some soils.

The main goal of our study was to evaluate the possibility of Mehlich 3 extractant for determination of S status in agriculture soils. The second goal was to assess the long-term changes in soil S content before and after the decline of S aerial deposition using the Mehlich 3 method.

MATERIAL AND METHODS

Soil samples were obtained from three different sources: basal soil monitoring system (sampling years 1995 and 2013), long-term field trials (sampling 1981 and 2017) and samples taken from the regular soil testing (2010 sampling campaign). All soil samples were air-dried and a fraction under 2 mm diameter was used for analysis. All samples were analysed under the same analytical conditions in one laboratory to minimize differences from the analytical measurements. Chemicals were of analytical purity grade. Sulphur in Mehlich 3 soil extract was determined simultaneously with the other elements using ICP-OES Spectroblue (Spectro GmbH., Kleve, Germany) by the method 30074.1 (Zbíral 2016b) at the emission line 182.034 nm.

The first estimate of the criteria (Table 1) was used to evaluate the results according to their dis-

Table 1. Proposal of criteria for Mehlich 3 extractable sulphur (S)

S (mg/kg)	Category
< 10	very low
11–20	low
21–30	suitable
31–40	good
> 40	high

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tribution into five concentration categories. The criteria given here are only a working proposal.

Calculations of descriptive statistics and frequency analyses were performed in Excel 2016 (Microsoft, Redmond, USA). NCSS Statistical Software (NCSS, LLC, Kaysville, USA) was used for determination of the significance of differences between the observed periods by Kruskal-Wallis' one-way ANOVA. Testing of the significance of the differences between the selected factors was done using a two-way ANOVA, general linear model (GLM).

RESULTS AND DISCUSSION

Case 1 – Basal soil monitoring system. Samples were collected from the monitoring plots defined as rectangles of 25 × 40 m. 139 topsoil samples from arable land sampled in 1995 and repeatedly in 2013 were analysed.

The network of the monitoring plots in BSMS was described by Sáňka et al. (1998). Selection of the monitoring plots respected the scale and ratio of soil types occurring in the CR. The BSMS plots were treated according to the landowners' needs and therefore the results from this system give a relatively good estimate of the status and changes on the agricultural land in the CR. The comparison of the distribution of the results into the individual categories in 1995 and 2013 is given in Figure 1. It can be seen that in 1995 about 22% samples were in very low and low categories but in 2013 the percentage in these categories rose nearly to 70% and the average decrease of available S was from 26 mg/kg in 1995 to 17 mg/kg in 2013. ANOVA (general linear model) clearly showed that time was the main source of statistically highly significant difference between the two sample sets ($P \leq 0.000002$).

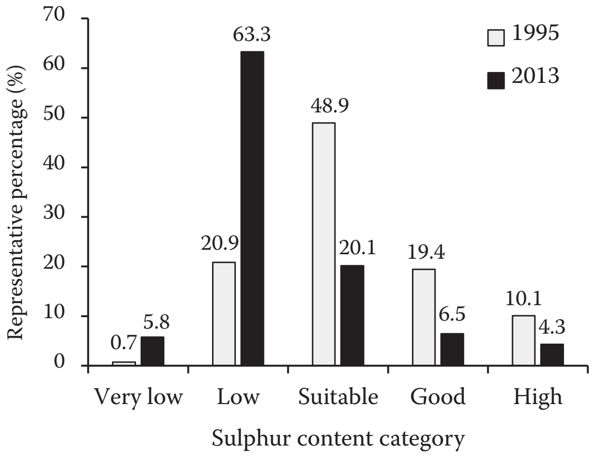

Figure 1. Percentage of distribution of sulphur into categories for soils from the basal soil monitoring system sampled in 1995 and in 2013

Case 2 – Long-term field trials. Archived samples from eleven experimental sites representing different soil and climatic conditions of the CR sampled in 1981 and 2017 were compared. Soil sampling was carried out from topsoil at the depth of 0–30 cm after harvest. The experiments have a randomized design, five fertilization treatments were chosen for the investigation: control (zero treatment); farmyard manure only (FYM); nitrogen, phosphorus, potassium low (level 1); medium

Table 2. Long-term field experiments. Aggregated results from all experimental sites for two sampling years and five fertilizing combinations. Contents of Mehlich 3 extractable sulphur (S) (mg/kg)

Fertilizing	Year	Mean	Minimum	Lower quartile	Median	Upper quartile	Maximum
Control	1981	33.1	22.4	24.3	28.1	38.2	72.4
	2017	8.3	5.5	6.0	8.2	11.0	12.2
FYM	1981	33.5	21.6	25.2	29.5	35.5	65.6
	2017	8.2	4.2	5.0	5.4	13.9	16.9
N1P1K1	1981	49.5	24.6	25.5	34.6	39.0	197.0
	2017	28.9	4.7	10.0	27.2	51.0	65.1
N2P2K2	1981	42.6	24.6	26.0	28.2	40.0	130.0
	2017	40.1	6.9	12.9	43.6	68.8	82.9
N3P3K3	1981	50.0	25.8	27.8	29.2	45.2	191.0
	2017	62.8	6.8	11.7	60.4	108.0	175.0

Control – zero treatment; FYM – farmyard manure only; N1P1K1 – nitrogen (N), phosphorus (P), potassium (K) low (level 1); N2P2K2 – N, P, K medium (level 2); N3P3K3 – N, P, K high (level 3)

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Table 3. Changes in the Mehlich 3 extractable sulphur (S) (mg/kg). Results from individual sites of the long-term field trials, control treatments

Site/Year	CHT	HOR	HRA	JAR	LIP	PJA	STV	UHO	VYS	VER	ZAT
1981	72.4	23.2	32.3	25.7	30.1	28.1	26.1	22.4	38.2	24.3	41.6
2017	8.8	11.0	8.3	11.6	5.7	12.2	7.1	6.5	8.2	5.5	6.0

CHT – Chrastava; HOR – Horažďovice; HRA – Hradec nad Svitavou; JAR – Jaroměřice; LIP – Lípa; PJA – Pusté Jakartice; STV – Staňkov; UHO – Uherský Ostroh; VYS – Vysoká; VER – Věrovany; ZAT – Žatec

(level 2); and high (level 3). Each of the five treatments had six replications. One part of nitrogen applied in spring was in the form of ammonium sulphate. Detailed description of the long-term trials is given in Klement et al. (2012).

The differences between the sampling years were statistically highly significant for the control and FYM application ($P \leq 0.000001$). For the remaining combinations with a regular ammonium sulphate application, the differences were not statistically significant but it can be estimated from Table 2 that for level 1, fertilization of the S content is decreasing, for level 2 fertilization S is in balance and for level 3 the content of Mehlich 3 – extractable S is increasing. The contents of S in the control and FYM were only 8 mg/kg in 2017 – it was about 25% of the S contents in 1981. The biggest differences in Mehlich 3 extractable S for control were observed in Chrastava (from 73 to 9 mg/kg) and in Žatec (from 42 to 6 mg/kg) (Table 3). These experimental sites are located in the vicinity of several coal burning power plants in the CR and in the former German Democratic Republic where there were enormous aerial depositions of S in the past.

The statistical analysis (one-way ANOVA) showed a statistically very significant difference between the tested periods in a single-factor model ($P \leq 0.00001$). Two-way ANOVA GLM confirmed that time was the main source of statistically very significant differences ($P \leq 0.000002$). Our results confirm the results of Balík et al. (2009) from the detailed study of the changes of S fractions for the soil samples from the same experimental sites between the years 1981 and 2007. The authors reported a decrease for all studied S fractions for the control and FYM. Changes of different soil sulphur forms under different fertilizing systems (Kulhánek et al. 2016) also showed that the biggest decrease was in the control treatment. From the results of both publications mentioned in this paragraph it is clear that the results estimated using the Mehlich 3 method follow the results of commonly used analytical methods used mainly for estimating of mineral S in soil.

Case 3 – Comparison of areas with different sulphur losses. Mehlich 3 extractable sulphur was determined in 720 soil samples representing all areas of the Czech Republic (set A) and in 1167 soil samples from the areas with sandy soils vulnerable to higher losses of this element (set B). Samples originated from the regular soil testing in 2010 sampling campaign. The results were evaluated according to the criteria in Table 1 and the frequency of the contents for the individual concentration levels is presented in Figure 2. For sample set B, 52% of samples had very low and 37% low level of Mehlich 3 extractable S. On the contrary for sample set A, it was only 3% and 36% of soils in these categories. The median for sample set A was 23 mg/kg and for sample set B only 9.8 mg/kg of Mehlich 3 extractable S.

From the presented cases it can be concluded that Mehlich 3 extractant proved its capability to reveal long-term changes in soil S content caused by the changes in aerial depositions and to determine areas vulnerable to S losses. Although

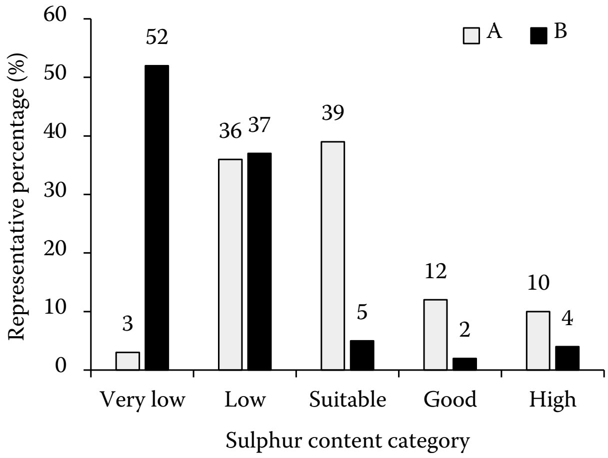

Figure 2. Percentage of distribution of sulphur into categories for soils from group A and B

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Mehlich 3 extractant was not always reported to be the best choice in comparison with the other extractants (Matula 1999, Esmel 2010, Ketterings et al. 2011) the results of our study clearly proved that Mehlich 3 extractant can be a valuable source of information about the S status in agricultural soils. But for a reliable fertilizer recommendation it is necessary to have also some information about subsoil S, local aerial deposition and possible access of plant roots to rich S groundwater or capillary ascending water (Haneklaus et al. 2002), as well as the data about relationships between Mehlich 3 results and S content in plants and its uptake. The first estimate of criteria for evaluation of the Mehlich 3 extractable S presented and used in this study can be taken only as a working draft and further adjustment for individual crops and for different soil and climatic conditions is necessary.

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REFERENCES

Balík J., Kulhánek M., Černý J., Száková J., Pavlíková D., Čermák P. (2009): Differences in soil sulfur fractions due to limitation of atmospheric deposition. Plant, Soil and Environment, 55: 344–352.

Carciochi W.D., Divito G.A., Fernández L.A., Echeverría H.E. (2017): Sulfur affects root growth and improves nitrogen recovery and internal efficiency in wheat. Journal of Plant Nutrition, 40: 1231–1242.

Edwards P.J. (1998): Sulfur Cycling, Retention, and Mobility in Soils: A Review. USDA General Technical Report NE – 250. Delaware, United States Department of Agriculture.

EEA (2015): Sulphur dioxide emissions. European Environment Agency, Copenhagen, Denmark. Available at: https://www.eea.europa.eu/data-and-maps/indicators/eea-32-sulphur-dioxide-so2-emissions-1/assessment-3#tab-related-briefings (accessed 04 Sep 2015)

Esmel C.E., Santos B.M., Rechcigl J.E., Toor G., Simonne E.H., Noling J.W. (2010): Searching for an ideal soil extractant for determining sulfur in sandy soils. Proceedings of the Florida State Horticultural Society, 123: 169–174.

Haneklaus S., Bloem E., Schnug E. (2002): Sulfur. In: Lal R. (ed.): Encyclopedia of Soil Science. New York, Marcel Dekker, Inc., 1282–1288.

Jones J.B.Jr. (1990): Universal soil extractants: Their composition and use. Communications in Soil Science and Plant Analysis, 21: 1091–1101.

Ketterings Q.M., Miyamoto C., Mathur R.R., Dietzel K., Gami S. (2011): A comparison of soil sulfur extraction methods. Soil Science Society of American Journal, 75: 1578–1583.

Klement V., Smatanová M., Trávník K. (2012): Fifty years of agrochemical testing of agricultural soils in the Czech Republic and forty years of long-term experiments in Central Institute for Supervising and Testing in Agriculture. Brno, Central Institute for Supervising and Testing in Agriculture.

Kulhánek M., Balík J., Černý J., Sedlář O., Vašák F. (2016): Evaluating of soil sulfur forms changes under different fertilizing systems during long-term field experiments. Plant, Soil and Environment, 62: 408–415.

Kowalenko C.G., Bittman S., Neilsen G.H., Kenney E., Hunt D.E., Nielsen D. (2014): Potential for improving sulfur tests on agricultural soils in contrasting ecoregions of British Columbia, Canada. Geoderma Regional, 1: 10–20.

Matula J. (1999): Use of multinutrient soil tests for sulphur determinations. Communications in Soil Science and Plant Analysis, 30: 1733–1746.

Mehlich A. (1978): New extractant for soil test evaluation of phosphorus, potassium, magnesium, calcium, sodium, manganese and zinc. Communications in Soil Science and Plant Analysis, 9: 477–492.

Mehlich A. (1984): Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Communications in Soil Science and Plant Analysis, 15: 1409–1416.

Mitchell M.J., Alewell C. (2008): Sulfur transformation and fluxes. In: Ward C. (ed): Encyclopedia of Soil Science. The Nertherlands, Springer, 757–764.

Ostatek-Boczynski Z.A., Lee-Steere P. (2012): Evaluation of Mehlich 3 as a universal nutrient extractant for Australian sugarcane soils. Communications in Soil Science and Plant Analysis, 43: 623–630.

Rao T.N., Sharma P.K. (1997): Evaluation of Mehlich III as an extractant for available soil sulfur. Communications in Soil Science and Plant Analysis, 28: 1033–1046.

Sáňka M., Chvátal V., Němec P. (1998): Basal soil monitoring and monitoring of atmospheric depositions. Procedures. Brno, Central Institute for Supervising and Testing in Agriculture. (In Czech)

Scherer H.W. (2009): Sulfur in soils. Journal of Plant Nutrition Soil Science, 172: 326–335.

Zbíral J. (1999): Comparison of some extracting methods for determination of sulphur in soils of the Czech Republic. Rostlinná Výroba, 45: 1–7.

Zbíral J. (2000): Analysis of Mehlich III soil extracts by ICP-AES. Rostlinná Výroba, 46: 141–146.

Zbíral J., Němec P. (2000): Data presentation, interpretation, and communication. Integrating of Mehlich 3 extractant into the Czech Soil Testing Scheme. Communications in Soil Science and Plant Analysis, 31: 2171–2182.

Zbíral J. (2016a): Determination of plant-available micronutrients by the Mehlich 3 soil extractant – A proposal of critical values. Plant, Soil and Environment, 62: 527–531.

Zbíral J. (ed) (2016b): Standard Working Procedures of the CISTA. Soil Analysis I. Method 30074.1. Brno, Central Institute for Supervising and Testing in Agriculture. (In Czech)

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