

The quality of sulphur selected fractions in soil from Nature reserve Žitavský Luh

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The aim of our work is to determine selected fractions of sulphur, and organic carbon in soil samples from the nature reserve Žitavský Luh. We compared characteristics in samples from different soil types during years 2010–2012. From soil types there are Mollic Fluvisol, Eutric Fluvisol and Histi-Umbric Gleysol in the wetland. The quantity of sulphate sulphur was an interval from 61.65 mg kg⁻¹ (Eutric Fluvisol, depth 0.00–0.15 m) to 352.15 mg kg⁻¹ (Histi-Umbric Gleysol, depth to 0.10 m). The interval measured values of chloride – soluble sulphur quantity was from 39.03 mg kg⁻¹ (Eutric Fluvisol, depth to 0.45 m) to 303.30 mg kg⁻¹ (Histi-Umbric Gleysol, depth to 0.15 m). The average quantity of heat-soluble sulphur (277.40 mg kg⁻¹, depth to 0.15 m) was the largest in Histi-Umbric Gleysol and the smallest in the soil type Eutric Fluvisol (46.58 mg kg⁻¹, depth to 0.15 m). The quantity of organic carbon in soil was highest in the A-horizons. The highest value of organic carbon in the soil type was in Histi-Umbric Gleysol (72.10 g kg⁻¹; in 0.00–0.10 m). The environment protection and ecological measures oriented to decrease of discharged sulphur compounds caused the fall of the supply of sulphur. The deficit of sulphur is one of the limiting factors for vegetal production.

Keywords: soil type, fractions of sulphur, sulphur dynamics, Nature reserve Žitavský Luh

1. Introduction

The soil has many functions in environment. It is one of the elemental components which are one of the most important parts of environment. Chemical changes in soil composition have contributed largely to the knowledge of natural edaphic systems and their corresponding modification after the intrusion of agronomic management (Aguilera et al., 2002). The wetlands are interesting not only economic view but, they have very important role in composition of forest and plant communities, as well. They are characterized by specific position, climate and soil conditions.

Lowland wetlands are obviously situated in valleys that are supplied by streams and other water sources. The fluvial layers are different chemical and physical nature and mechanical composition. Their current status cannot be considered satisfactory. Agricultural and industrial revolution, the growing population are all factors that influenced the increased use of natural resources, which resulted in environmental degradation (Lacko-Bartošová et al., 2005). Recession brew can be traced across the sub-central lowland for decades (Mezera, 1958). The soil as one of the fundamental components of the environment also serves many functions here (Zaujec, 1998; Hreško et al., 2008; Vollmannová et al., 2002). The nature and properties of soil bases was depend on soil moisture,

level of groundwater, as well as the nature and properties of wetland parent material.

Although these factors are reflected in the development of plant communities and forest cover. For several decades, there is a technical adjustment to the rivers in these areas, except there is no Žitavský Luh. By adjusting the watercourse of the river Žitava prevent flooding in this area and acquire additional land for growing crops.

In order to maximize yields of crops grown affects the essential characteristic of the soil-fertility. The origin and development of soil influences formation of its elementary attribute-fertility (Hanes et al., 1997). Fertility is the result of complex action of physical, chemical, and biological attributes and different processes in soil. The type of soil, soil class and depth of soil, soil structure, content of available nutrients, accessible water and soil temperature regime, pH, quantity and quality of soil organic matter, biological activity directly influence it. The quality and quantity of humus in soil is a basic index of its fertility" (Spychaj-Fabisiak et al., 2003). The quality humus is the conclusive assumption for stable soil fertility but it is not its guarantee, because for example, compression of soil, absence of nutrients and other factors may decrease the productive ability (Hanes, 1998). The missing nutrients in soil are filled-up by fertilisation,

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for example we increase the intensity of mineralisation of sulphur organic fractions in soil.

Sulphur is a major inorganic element, essential for the entire biological kingdom because of its incorporation into amino acids, proteins, enzymes, vitamins, and other biomolecules (Castellano and Dick, 1991; Jedlovská and Feszterová, 2004; Johnson, 1984; Komarnisky, Christopherson and Basu, 2003). Unlike humans and monogastric animals, plants can use inorganic sulphur and synthesize sulphur-containing amino acids such as methionine and cysteine (Baker, 1977). In the last decades, sulphur has become a frequent limiting nutrient deserving closer examination (Amelung et al., 1998; Dail and Fitzgerald, 1999; Eriksen, 1997b, 1997a; Chowdhury et al., 2000; Sorensen, 1981; Tabatabai and Bremner, 1972; Wander and Traina, 1996; Zhou, He and Lin, 1999). Correspondingly at present, scientists investigate more often S-cycling, S-requirement in plants and S-depletion from soil pools (Chapman, 1997; Miller and Donahue, 1990; Sharma and Swarup, 1996; Stevenson, 1986). It is important to monitor the selected fraction of sulphur in the soil and not just in terms of impact on the quality of production and income, but also in terms of environmental protection (Kalocsai, 2002; Ložek, 2004).

The aim of our work was to determine selected fractions of sulphur (sulphur sulphate, chloride-soluble sulphur, heat-soluble sulphur), organic carbon and the ratio between them. We compared chemical characteristics in samples from different types, which were taken from the soils close to nature reserve Žitavský Luh in different depths, during three years (2010–2012).

2. Material and methods

Nature reserve Žitavský Luh serves as habitat of many rare species of flora and fauna. It is located in southern Slovakia

(N 48° 11'; E 18° 18'), 20 km south-east in the direction of the city of Nitra, at an altitude of 132 to 133 meters above sea level. It is a protected area, declared in 1980 area of 74.69 hectares. This area is important in growth of wetland ecosystem types.

Žitavský Luh is situated in the middle Žitava river alluvial plain, between the municipality Maňa and the district border Nové Zámky – Nitra (Figure 1). It is located to the area of Hronská hilly county. The soil conditions of Žitavský Luh are influenced by soil water which comes from the precipitation and ground water (Hreško et al., 2006). High soil water level influences on the physical, chemical and biological reactions and processes (Zaujec et al., 2005).

Žitavský Luh has climatographical lowland climate, with mild temperatures. The alluvial plane Žitava's January average temperature is from -4.14 °C (2010) to +0.88 °C (2012). The July average temperature is from 25.07 °C (2010) to 22.77 °C (2011), with annual precipitation from 860 mm (2010) to 450 mm (2012). The number of sunshine days is over 50 per year. The snowy season is not longer than 90 days (Lengyel, 2004).

The soil samples were collected after the sunny weather in the southern part Žitavský Luh from 3 pits from different soil types: Mollic Fluvisol (a distance of 5 m from the agricultural soil and 50 m of the artificial wall for water reservoirs), Eutric Fluvisol (agricultural unused soil in 70 m distance from water source), Histi-Umbric Gleysol (withdrawn after release and drying of water reservoirs in the summer months). The soil samples were taken from similar depths in 2010–2012 years. All chemical analyses were made in duplicate. Values are mean of two replicates. Soils were classified according to the World Reference Base for Soil Resources (WRB, 2006). The soil samples were collected from the pits from selected horizons. After collection they were air-dried at



Figure 1 The monitoring region – Žitavský Luh

laboratory temperature, homogenized and sieved over a sieve with mesh 0.25 mm.

We determined following chemical analysis:

- Soil pH, active pH (1 : 2.5 – soil and distilled water) and pH in KCl (1 : 2.5 – soil : water, 1 mol dm⁻³ KCl) – potentiometrically.
- Sulphate sulphur (SS), chloride soluble sulphur (CISS), and heat soluble sulphur (HSS) were measured by the Williams and Steinbergs method especially used for this type of soils (Williams and Steinbergs, 1958).
- The content of the total organic carbon was determined by the Tyurin method in modification of Nikitin (Dziadowiec and Gonet, 1999).

In the contribution we are presenting the average values from analysis, and analysis were performed in triplicate. The obtained data were analysed using the Statgraphics Centurion XVI (Statpoint Technologies, Inc., USA). A multifactor ANOVA model was used for individual treatment comparisons at $p \leq 0.05$. We would like to contribute to closer understanding of land cover areas with analysing the values of selected chemical characteristics during the monitored years.

3. Results and discussion

Sulphur content in soil depends on soil type, the particle-size distribution and depth of sampling (Tabatabai, 2005). We determined wide range of measured contents of selected sulphur fractions in soil (Table 1). Sulphur content in soil was statistical significant to the soil type and the depth.

Sulphate sulphur content (SS) was in interval from 61.65 mg kg⁻¹ (Eutric Fluvisol, depth 0.00–0.15 m) to 352.15 mg kg⁻¹ (Histi-Umbric Gleysol, depth 0.00–0.10 m). The average value of sulphate sulphur content was approximately equal in Mollic Fluvisol (215.00 mg kg⁻¹)

and in Histi-Umbric Gleysol (216.70 mg kg⁻¹). We observed the differences in the A-horizons between selected soil types (between Mollic Fluvisol and Eutric Fluvisol, and between Eutric Fluvisol and Histi-Umbric Gleysol). It is interesting, that the concentration in Mollic Fluvisol and in Histi-Umbric Gleysol is comparable despite that the soil samples came from different depths. In the case of studied chemical characteristic was concentration in Mollic Fluvisol and Histi-Umbric Gleysol equal (Table 1). A thickness of A-horizons were different, therefore we recalculated the sulphate sulphur content to bulk density of soils. The content of SS decreased in the following order: Mollic Fluvisol (0.081 kg m⁻²) > Histi-Umbric Gleysol (0.051 kg m⁻²) > Eutric Fluvisol (0.013 kg m⁻²). In cases of Mollic and Eutric Fluvisols, the higher content of sulphate sulphur was in subsoil.

These results are consisted with those reported by several authors (Fecenko and Bališ, 2003; <http://www.spectrumanalytic.com>, 2014; Whitehead, 1964), that the content of sulphate sulphur is accumulated in these layers. Soluble sulphates (SO₄²⁻) seldom accumulate in the plow layer because they are leached into the B-horizon. Dynamics of sulphates (SO₄²⁻) in the soil is similar as the dynamics of nitrates. Sulphates are moving similarly as the nitrates (Fecenko, 2003). Soluble sulphates as a part of precipitations are infiltrated in the soil during the winter, when they are easily leached or percolated down especially in lower horizons (Fecenko, 2003).

The results showed that the quantity of sulphate sulphur in the soil can affect the depth of the soil sampling, year, and soil pH (Zimny et al., 1988). Much of this sulphate probably comes from past application of fertilizers that contain sulphur (<http://www.soil.ncsu.edu>, 2014). It confirmed our results as well (Table 1).

Table 1 The selected sulphur fraction – sulphate sulphur (SS)

Horizon	Depth in m	Min. value in mg kg ⁻¹	Max. value in mg kg ⁻¹	Average value in mg kg ⁻¹	Standard deviation	Average in soil type in mg kg ⁻¹
Mollic Fluvisol						
Amc	0.00 – 0.35	129.63	202.02	159.22	31.00	215.00
A/CGo	0.35 – 0.65	216.29	280.50	243.60	27.08	
CGo	> 0.65	231.04	250.00	242.04	9.48	
Eutric Fluvisol						
Akp	0.00 – 0.15	31.30	92.03	61.65	24.76	98.48
C	0.15 – 0.45	68.39	167.00	126.20	49.31	
C/Go	> 0.45	74.51	123.80	109.58	24.94	
Histi-Umbric Gleysol						
Ao	0.00 – 0.10	287.06	454.19	352.15	73.58	216.70
Gor	0.10 – 0.30	89.12	174.01	125.71	30.01	
Gr	> 0.30	136.97	190.88	172.55	0.54	

Table 2 The values of soil pH

Horizon	pH _{H₂O}	pH _{KCl}	pH _{H₂O}	pH _{KCl}	pH _{H₂O}	pH _{KCl}
	Mollic Fluvisol		Eutric Fluvisol		Histi-Umbric Gleysol	
Amc	7.90	7.10	6.30	4.81	6.01	5.42
A/CGo	7.99	7.20	7.18	5.62	7.04	6.59
CGo	8.25	7.35	7.48	6.55	8.05	6.75

Table 3 The selected sulphur fraction – chloride-soluble sulphur (CISS)

Horizont	Depth in m	Min. value in mg kg ⁻¹	Max. value in mg kg ⁻¹	Average value in mg kg ⁻¹	Standard deviation	Average in soil type in mg kg ⁻¹
Mollic Fluvisol						
Amc	0.00–0.35	232.43	298.00	268.24	27.11	206.00
A/CGo	0.35–0.65	151.00	258.30	197.10	45.09	
CGo	>0.65	125.00	182.69	152.20	23.66	
Eutric Fluvisol						
Akp	0.00–0.15	23.81	59.13	42.90	42.90	74.48
C	0.15–0.45	24.18	57.12	39.03	39.03	
C/Go	>0.45	106.28	202.65	141.51	141.51	
Histi-Umbric Gleysol						
Ao	0.00–0.10	162.51	423.58	303.30	107.56	266.96
Gor	0.10–0.30	194.18	349.59	266.56	46.85	
Gr	>0.30	180.05	302.05	231.03	45.53	

The soil pH was determined (Hrivňáková, et al., 2011). The values are summarized in Table 2.

The content of chloride-soluble sulphur (CISS) was in interval from 39.03 mg kg⁻¹ (depth 0.15–0.45 m) to 303.30 mg kg⁻¹ (depth 0.00–0.15 m). In Mollic Fluvisol and Histi-Umbric Gleysol was determined the decrease trend of chloride-soluble sulphur (Table 3).

In opposite, the value of content chloride-soluble sulphur was growing with depth in Eutric Fluvisol (depth 0.00–0.15 m, 42.9 mg kg⁻¹, depth > 0.45 m; 141.51 mg kg⁻¹). It can be connected with heigher level of groundwater and its changes in mentioned soil profiles. The different values of chloride-soluble sulphur were observed from point of view thicknesses of horizons. In A horizons of mentioned soils the contents of chloride-soluble sulphur were in Mollic Fluvisol 0.136 kg m⁻², in Histi-Umbric Gleysol 0.044 kg m⁻² and in Eutric Fluvisol 0.009 kg m⁻². The leaching can affect on these values in addition to weather conditions and absorption of sulphur plants (Scott et al., 2014).

The average quantity of heat-soluble sulphur (HSS) was the highest in Histi-Umbric Gleysol (277.40 mg kg⁻¹, depth 0.10–0.30 m) and the lowest in the soil type Eutric Fluvisol (46.58 mg kg⁻¹, depth 0.00–0.15 m). The soil type of Histi-Umbric Gleysol was analyzed the highest content of heat-soluble sulphur 423.58 mg kg⁻¹ (depth 0.10–0.30 m).

Changes in the content of heat-soluble sulphur can be affected from migration, content of organic matter and soil reaction. Achievements values of heat-soluble sulphur are summarized in Table 4.

The processes of mineralization and resynthesis of organic sulphur fractions are sweeping in the soil (Whitehed, 1964). Resynthesis of sulphur organic fractions in soil requires presence of organic acceptors (Ketterings et al., 2012). If the organic acceptors absent, the mineralization is predominate over sulphur organic fractions resynthesis. The content of sulphate sulphur in soil is increasing (Vaněk et al., 2003). The quantity of acceptable (sulphate) sulphur is unevenly changing in the different soil types depending on soil depth. Dynamic changes of selected fractions of sulphur quantity can be found throughout the soil profile there is a change in the sulphur content (sulphate sulphur, chloride-soluble sulphur, heat-soluble sulphur) and is therefore not possible to conclude that would be universally valid. The soils contain less sulphur than 1000 mg kg⁻¹ identified by lots of authors as the sulphurous poor (Trocme, 1970).

The humus quantity is an important parameter affecting the function of soil fertility. Fertility is the result of a complex interaction of physical, chemical and biological properties and various processes of soil (Hudec et al., 2012; Szombathová, Macák and Candráková, 2008).

Table 4 The selected sulphur fraction – heat-soluble sulphur (HSS)

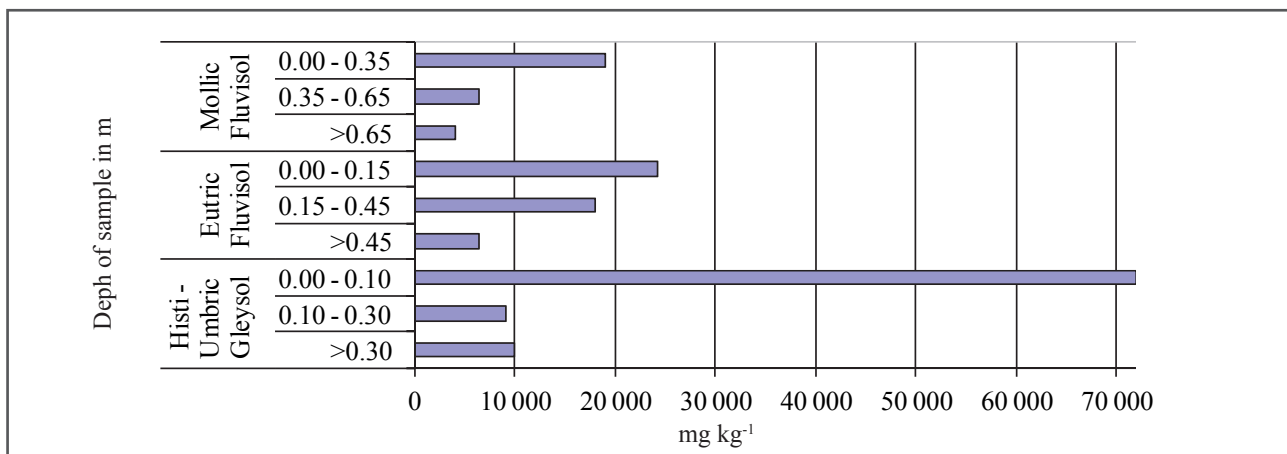
Horizon	Depth in m	Min. value in mg kg ⁻¹	Max. value in mg kg ⁻¹	Average value in mg kg ⁻¹	Standard deviation	Average in soil type in mg kg ⁻¹
Mollic Fluvisol						
Amc	0.00–0.35	170.00	422.00	270.62	108.95	259.12
A/CGo	0.35–0.65	205.92	298.00	260.74	39.59	
CGo	>0.65	204.15	290.12	246.00	35.13	
Eutric Fluvisol						
Akp	0.00 – 0.15	34.15	65.69	46.58	13.72	53.73
C	0.15 – 0.45	24.01	84.02	49.00	25.51	
C/Go	>0.45	29.89	106.96	65.61	31.71	
Histi-Umbric Gleysol						
Ao	0.00 – 0.10	143.39	249.43	183.74	46.85	178.10
Gor	0.10 – 0.30	221.61	323.60	277.40	18.67	
Gr	>0.30	49.19	111.13	73.17	25.97	

Immediately it affects soil type, soil sort, soil and topsoil depth, soil structure, nutrient content, water and thermal regime, pH, quantity and quality of soil organic matter, biological activity and the content of harmful compounds in the soil (Šimanský, 2012; Zaujec, 2000). The soil organic matter and its fractions are components of the soil, which can be changed (Sorensen, 1981).

The content of total organic carbon in soil was the highest in the A-horizons and it decreased gradually with depth (Figure 2), except the Histi-Umbric Gleysol. The highest value of total organic carbon in the soil type was in Histi-Umbric Gleysol (A horizon has value of 72.10 g kg⁻¹ in a depth 0.00–0.10 m), which cause can be established by organic matter deposited during floods. The Histi-Umbric Gleysol was a sharp transition value of total organic carbon along the profile (72.10 g kg⁻¹ depth 0.00–0.10 m, 9.80 g kg⁻¹, depth 0.10–0.30 m; 11.5 g kg⁻¹, depth > 0.30 m). The humus quantity was decreasing with

depth in the soil profile of Mollic Fluvisol (19.50 g kg⁻¹, depth 0.00–0.35 m, 9.5 g kg⁻¹ depth 0.10–.30 m, 3.91 g kg⁻¹ depths > 0.65 m). Eutric Fluvisol had similar trend (Figure 2).

Sulphur has multifunctional role in the plant organism (Fecenko and Bálíš, 2003). Sulphur is essential for synthesis of certain amino acids in plants. It belongs to essential, irreplaceable nutrients for growing agricultural crops. In environment it is reliable to very important changes because of the variety of its chemical forms. The availability of sulphur for plants is also affected by immobilization and mineralization processes. Sulphur mineralization in the soil is typically attributed to either biological or biochemical processes (McGill and Cole, 1981). S mineralization is often rather related to initial S concentrations (Janzen and Kucey, 1988). Immobilization of sulphur is positively correlated with the ratio C : S in the substrate. Organic compounds are dominant and often form 90–95 % of total amount of the sulphur in

**Figure 2** The content of total organic carbon in soil profiles

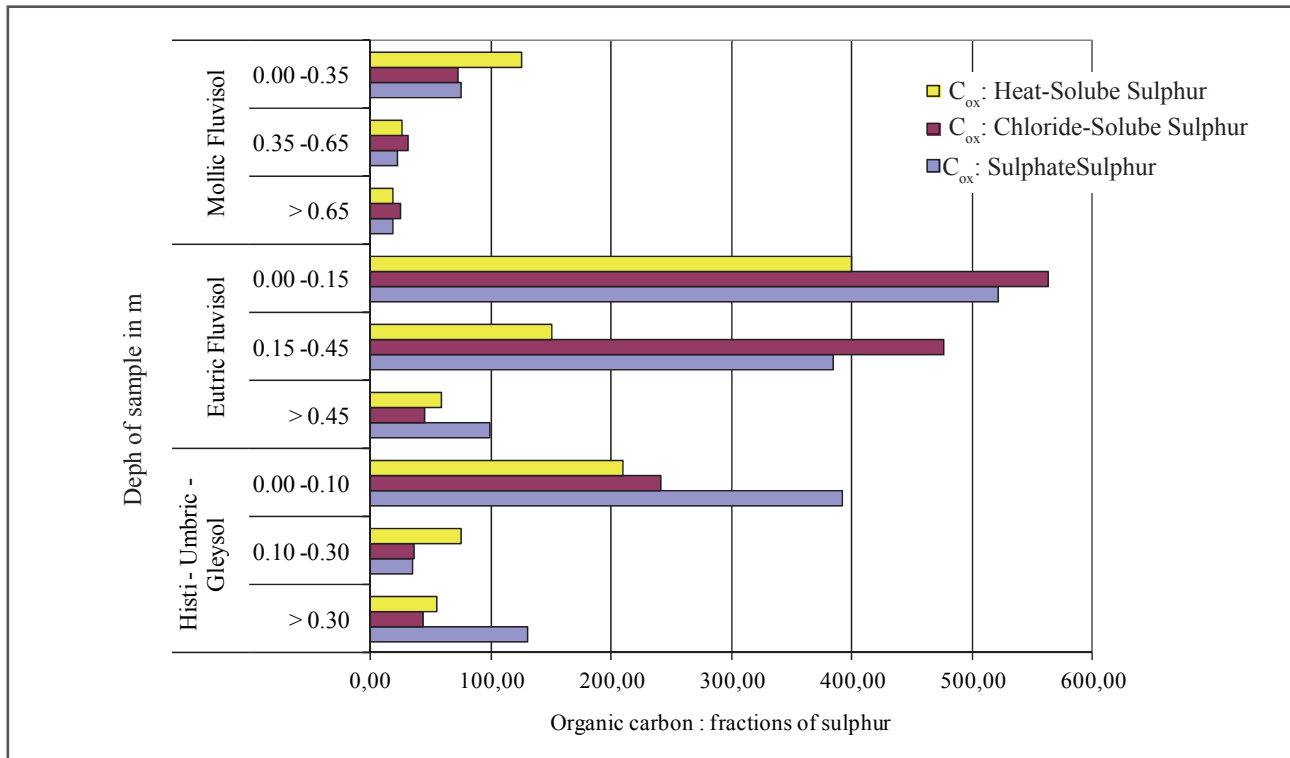


Figure 3 The carbon to sulphur ratio development of organic carbon and selected fractions of sulphur in soil

soil (Eriksen, 2009; Neptune et al., 1975; Solomon et al., 2001; Solomon et al., 2005 and Solomon et al., 2009; Tabatabai, 2005). Mineralization of organic sulphur compounds affects not only the composition of the substrate, but also the soil pH, temperature and moisture (Amelung, et al., 1998; KALI GbmH, 2013). Plant residues had a considerable effect on S mineralization (Blum et al., 2013). Predominant form of organic sulphur in most soils and there is a direct correlation between organic carbon and total sulphur concentration in the ratio of C : S equal to 108 : 1 (Stevenson, 1986). The inorganic compounds sulphate represents about 5 % sulphides and elemental sulphur does not exceed 3 % (Ložek, 2001; Schung, 2001).

The higher ratio the content of total organic carbon and selected sulphur fractions were analyzed in soil type Eutric Fluvisol (Figure 3, depth 0.00–0.15 m; C : SS = 515 : 1; C : CISS = 559 : 1; C:HSS = 402:1 C : SS = 515:1). The smallest ratio the content of total organic carbon and selected sulphur fraction were the soil type Mollic Fluvisol (Figure 3; depth >0.65 m; C : SS = 16 : 1; C : CISS = 26 : 1; C : HSS = 17 : 1). Despite the fact that plants absorb S mainly as sulphate, organic S (S directly bonded to C and ester S) pools are important sources of S to plants during their growing season (De Bona and Monteiro, 2010; Freney et al., 1975; Goh and Pamidi, 2003; McGill and Cole, 1981). The process of transformation of organic S to inorganic sulfate (mineralization) and the reverse process (incorporation of sulfate into soil organic

compounds or immobilization) play important roles in the cycling of S within the soil and are microbiologically mediated (Kertesz and Mirleau, 2004). With the high ratio C : S the immobilization of sulphur is increasing.

4. Conclusions

In Mollic Fluvisol the content of sulphate sulphur was increasing with depth but in chloride-soluble and heat-soluble sulphur fractions the content were decreasing. In Eutric Fluvisol the content of chloride-soluble sulphur and heat-soluble sulphur was increasing with depth. During the monitoring period the amount of sulphur fraction was changing and it depends on the differences in soil types and depths. In Histi-Umbric Gleysol the content of sulphate sulphur and chloride – soluble sulphur was decreasing with depths. On the one hand we can concluded that changes of the dynamic of the selected fractions sulphur content have a lot of varieties in the whole soil profile, on the other hand it is not possible to confirm the general validity. In the soil types Mollic Fluvisol and Histi-Umbric Gleysol there is to mobilization sulphate sulphur fraction. In Eutric Fluvisol, which is cultivated, there is immobilization, release the sulphate sulphur fraction from organic matter.

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