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Scientific paper

SULPHUR CYCLING BETWEEN TERRESTRIAL AGROECOSYSTEM AND ATMOSPHERE*

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Central gas station of the natural gas borehole system Podravina is located near the village Molve. It delivers more than a quarter of total energy used in Croatia to its consumers. Over the years, adapting technology to increasingly demanding and rigorous standards in environmental protection has become paramount. Yet, despite all the industry has undertaken to address the risk of harmful substances entering the food chain, a multidisciplinary research team of independent scientists monitors the content of specific substances in all components of the ecosystem.

This paper presents measurements of total sulphur contents in soil surface [(0 to 3) cm] and subsurface [(3 to 8) cm] layers (study period: autumn 2006 - spring 2010) and in plants (study period: spring 2000 - spring 2010), and the concentration of gaseous sulphur compounds in the air. Concentrations of hydrogen sulphide (H_2S) and mercaptans (RSH) were measured from the summer of 2002 until the autumn of 2010, while concentrations of sulphur dioxide (SO_2) were measured from the spring of 2008 until the autumn of 2010. The paper also shows total annual atmospheric sulphur ($S\text{-}SO_4$) deposition at Bilogora measuring station (study period: 2001 - 2010). Average monthly concentrations of H_2S in air varied between 0.2 μg m^{-3} and 2.0 μg m^{-3}, RSH between 0.1 μg m^{-3} and 24.5 μg m^{-3}, and SO_2 between 0.4 μg m^{-3} and 2.8 μg m^{-3} depending on the location and the season of sampling.

Mean values of total sulphur in soil and in *Plantago lanceolata* plant ranged between 610 mg kg^{-1} and 1,599 mg kg^{-1} and between 3,614 mg kg^{-1} and 4,342 mg kg^{-1}, respectively, depending on the soil type, location, and sampling depth. Average values of total sulphur mass ratio for all examined single soil samples (n=80) were 1,080 mg kg^{-1} for both studied layers, and 4,108 mg kg^{-1} for all analysed plant samples (n=85). Average total annual atmospheric sulphur deposition at Bilogora measuring station was 6.3 kg of $S\text{-}SO_4$ per hectar.

KEY WORDS: *air, deposition, H_2S, mercaptans,* Plantago lanceolata*, SO_2, soil, total sulphur*

The northern part of the Pannonian plain in Croatia is a traditional agricultural region [Western Pannonian region according to Bašić et al. (1)] rich in natural gas. The coexistence of agriculture and energy is clearly essential to stakeholders. Central gas station (CGS) of the natural gas borehole system Podravina is located near the village Molve. Natural gas is not a pure product. When gas is extracted from a field under the supercritical conditions (high pressure and temperature) it may contain harmful and corrosive components such as CO_2, H_2S, RHS, Hg^0 etc. In CGS,

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natural gas is collected, treated, purified, and distributed to consumers. For the past 21 years, the scientists within a multidisciplinary research team have monitored its influence on air, water, soil, plants, forests, animals (wild and domestic), as well as humans. Since 1991, the Institute for Medical Research and Occupational Health, Zagreb (Environmental Hygiene Unit) has been in charge of the environment and air quality monitoring on carefully selected representative locations in CGS, while the soil and plant quality monitoring has been the task of the Faculty of Agriculture, University of Zagreb (Department of General Agronomy).

In the past, all pollutants from different industrial sources were emitted in the atmosphere. As landowners became more aware of the ecological and health problems, they insisted on some improvements. As a result, some technological processes were modified, such as the installation of two mercury (Hg) absorbers using active carbon impregnated with sulphur, LO-CAT unit (H_2S oxidation in elementary S), and RTO unit (oxidation of reduced sulphur compounds to SO_2). Despite all the measures that were taken to protect the environment and local public health, it was still necessary to establish a quality multidisciplinary monitoring programme since only independently collected scientific data could provide relevant information for conclusions and possible solutions for the environment protection.

Sulphur is a biogeoelement in agroecosystem and a macronutrient for plants, as well as a constituent of certain essential amino acids, vitamins, enzymes, and aromatic oils. Sulphur deficient plants tend to have low sugar but high nitrate content in their sap and leaf chlorosis, which can cause lower yield and lower plant quality (2, 3). But high concentrations of S in soil or air can be toxic to plants, animals, and humans (4-6). The three major natural sources of sulphur that can be available for plant uptake are (1) organic matter; (2) soil minerals; and (3) sulphur gases in the atmosphere (7).

According to Deloch (8), natural total sulphur content range is different in grasses (corn 1,700 mg kg^{-1} of dry matter (DM), barley 1,800 mg kg^{-1} of DM), legumes (bean 2,400 mg kg^{-1} of DM, soybean 3,200 mg kg^{-1} of DM) and cruciferae (rape 10,000 mg kg^{-1} of DM, radicchio 17,000 of DM). Some authors have studied the influence of atmospheric sulphur (SO_2 and H_2S) from different anthropogenic sources, mostly power plants, on soil and the uptake in some plant species. Reimann et al. (9) measured total sulphur concentrations in some plants from different catchments in northern Europe and one location near the nickel smelter and refinery. They found the median S concentration of 965 mg kg^{-1} in moss; 990 mg kg^{-1} in conifers; 1,490 mg kg^{-1} in shrubs; and 1,900 mg kg^{-1} in deciduous trees with significantly higher concentrations observed on a polluted location. In a field study conducted in the vicinity of two thermal power plants in India, Agrawal et al. (10) noted a high correlation between the emission from power plants and elemental concentrations of sulphur in the leaves of evergreen and deciduous plants (significantly higher concentrations on polluted than on unpolluted sites). Fidalgo-Hijano et al. (11) obtained the following results in a study conducted in the city of Madrid on different plants as bioindicators of sulphur emission: a higher accumulation of sulphur was found in vegetable species located near highways and dense traffic roads and near the areas with high population density. The minimal accumulation of SO_2 was registered in winter and spring seasons (from January to April) due to the end of vegetative growth, while maximal values were recorded during the summer season (from June to September), due to stomatal opening. Regarding sulphur in agroecosystem, our team has already studied sulphur behaviour in central Croatia through field experiments on an unpolluted site and has published data related to sulphur wheat grain uptake depending on the fertilisation (12) and S-SO_4 losses from soil with drainage water (13).

The goal of this paper is to study sulphur cycling between terrestrial agroecosystem and atmosphere and to present the results of measurements of total sulphur content in soils, total sulphur content in plants, concentration of gaseous sulphur compounds (H_2S, RSH, SO_2) in air, and annual atmospheric sulphur (S-SO_4) deposition measured during the monitoring that was carried out over several years in the vicinity of CGS Molve.

MATERIAL AND METHODS

Samples of air, soil, and plants were collected at four locations in the vicinity of boreholes Molve 9 (M9), Molve 10 (M10), Molve 11 (M11), and Molve 12 (M12). Geographic locations of sampling sites in the area of CGS Molve were described and summarised in our previous study (14) regarding arsenic in soil and air measured in the surroundings of CGS Molve.

Air sampling and analysis

Measurements of H_2S, RSH, and SO_2 concentrations in air were done twice a year, in a 30-day period during the warmer season (summer time) and a 30-day period during the colder season (winter or early spring or late autumn). Samples of H_2S and RSH were collected during 24 hours by forcing the air to the filter paper Whatman No. 41 impregnated with mercury(II) chloride with the addition of urea as an antioxidant (H_2S) and mercury(II) acetate with the addition of acetic acid (RSH). Analysis of H_2S was carried out spectrophotometrically by molybdenum blue method (15, 16). Mercaptans were also determined spectrophotometrically after adding *N,N*-dimethyl-p-phenylenediamine hydrochloride and Reissner reagens (17). Samples of SO_2 were collected by forcing air through the absorption solution of hydrogen peroxide (18) and the resulting concentration of sulfate ions was determined by ion chromatography (19). The analysis was performed on Dionex DX 120 chromatograph equipped with suppressed conductivity detection, Dionex AS14 analytical column, and AG14 guard column. The eluent was 3.5 mmol L^{-1} Na_2CO_3/ 1 mmol L^{-1} $NaHCO_3$ solution.

This paper presents average monthly mass concentrations of gaseous sulphur compounds (H_2S, RSH, and SO_2) in air during the study period of summer 2002 - autumn 2010 (H_2S and RSH) and during the study period of autumn 2008 - autumn 2010 (SO_2). Generally, the measured concentrations were very low, and sometimes even below the limit of detection of the used method.

Soil and plant sampling and analysis

Soil and plant samples were collected twice a year, in spring and autumn, on four locations in the vicinity of the above mentioned boreholes. Surface [(3 to 8) cm] and subsurface soil samples [(3 to 8) cm] were taken with a Holland probe and a knife following the Protocols of soil sampling (20). Plant samples were also collected with a knife. Ribwort Plantain (*Plantago lanceolata* L.) plant (leaves and stems) was gathered as an indicator. In the borehole M9 area, soil and plant samples were collected for two different types of soil (locations M9 and M9 hill). All examined locations included five soil types, dominant in respect of their texture and moisture regime: according to Croatian classification (21) they are classified as: M9 and M12: Eugley, M9 hill: Distric Regosols, M10: Stagnic Luvisols and M11: Gleysols or According to the World Reference Base (WRB) for soil resources (22): M9: Gleysol vertic dystric and M9 hill: Regosol acric, M12: Gleysol vertic, M10: Stagnosol luvic and M11: Gleysols clayic. According to their texture, two of them belong to heavy clay soils (M9 and M12), two to silt loam soil (M10 and M11), and one to light sandy soils (M9 hill).

Soil samples were air-dried, ground, sieved (< 2 mm) and homogenised according to the ISO Protocol (23). Plant samples were first dried in the oven at 105 °C until a constant mass was reached, and were then ground and homogenised.

Analyses of *Plantago laceolata* samples and soil samples on total sulphur content were done by elementary analyser Vario Macro CHNS, Elementar, Deutschland, 2006 following the ISO Protocol (24).

Accuracy and precision were controlled by Reference Material (RM: ISE and IPE, Wepal) and by repeating the same sample measurements, respectively. Accuracy and precision limits were determined within the standards and were acceptable.

This paper presents measurements of total sulphur mass ratio in soil, in surface and subsurface layers (study period: autumn 2006 - spring 2010), as well as in plants (study period: spring 2000 - spring 2010).

The paper also shows total annual atmospheric sulphur (S-SO_4) deposition at Bilogora measuring station (study period: 2001 - 2010) (25).

RESULTS AND DISCUSSION

Sulphur components in air

Monthly average mass concentrations of H_2S for each measuring period measured in CGS surroundings are presented in Figure 1. Monthly average concentrations of H_2S in air varied between 0.2 μg m^{-3} (spring 2006) and 2.0 μg m^{-3} (summer 2002), and the maximal daily value (6.6 μg m^{-3}) was measured during the summer of 2009. According to Croatian legislation, in particular the Regulation on Limit Values of Pollutants in Air (26), the limit values (LVs) for H_2S in air are 2 μg m^{-3} (for an average time of one year) and 5 μg m^{-3} (for a 24-hour collecting period, but LVs may not be exceeded more than seven times during a calendar year). The results cannot be compared with the LV (for one year) because we performed measurements only 60 days per year which is only 17 % of all data; however, they could be indicative. During the examination period, the measured values (average daily concentrations) exceeded LV (5 µg m^{-3}) three times in 2002, and once in 2004, 2009, and 2010.

Monthly average mass concentrations of RSH for each examination period measured in CGS surroundings are presented in Figure 2. These varied between 0.1 µg m^{-3} (winter 2006) and 24.5 µg m^{-3} (summer 2005), and the maximal daily value measured was 89.2 µg m^{-3}. According to national legislation (26), LVs for RSH in air are 1 µg m^{-3} (for an average time of one year) and 3 µg m^{-3} (for a 24-hour collecting period, but LVs may not be exceeded more than seven times during a calendar year). As we can see in Figure 2, in the period from 2002 until 2006, mass concentrations of RSH were frequently higher than 3 µg m^{-3} while in the period from 2007 until 2010, the limit value of 3 µg m^{-3} was not exceeded. In the period from 2002 until 2006, there were a number of days with daily concentrations of RSH higher than 3 µg m^{-3}. There were months when only one day per month exceeded the LV (at M9, M10, and M12 in summer 2002 and at M12 in summer 2005), but there were also months where all 30 daily measured values were higher than 3 µg m^{-3} (at M11 in summer 2004 and at M10 in summer 2005). In 2007, a system for burning waste gases was built in CGS Molve (RTO unit - oxidation of reduced sulphur components to SO_2), which is a probable reason for such a decrease in the RSH content in air.

Monthly average mass concentrations of SO_2 for each measuring period observed in air in CGS surroundings are presented in Figure 3. These were very low and ranged between 0.4 µg m^{-3} (at M11, in summer 2005) and 2.8 µg m^{-3} (at M10, in summer 2010) depending on the location and the season of sampling, while the maximal daily value (9.3 µg m^{-3}) was measured during the autumn of 2009. According

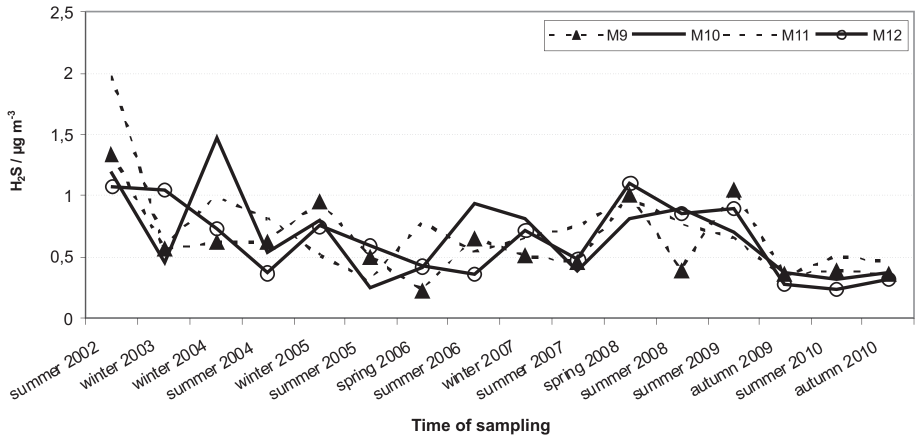

Figure 1 *Average monthly concentration of H_2S measured in air in central gas station (CGS) surroundings*

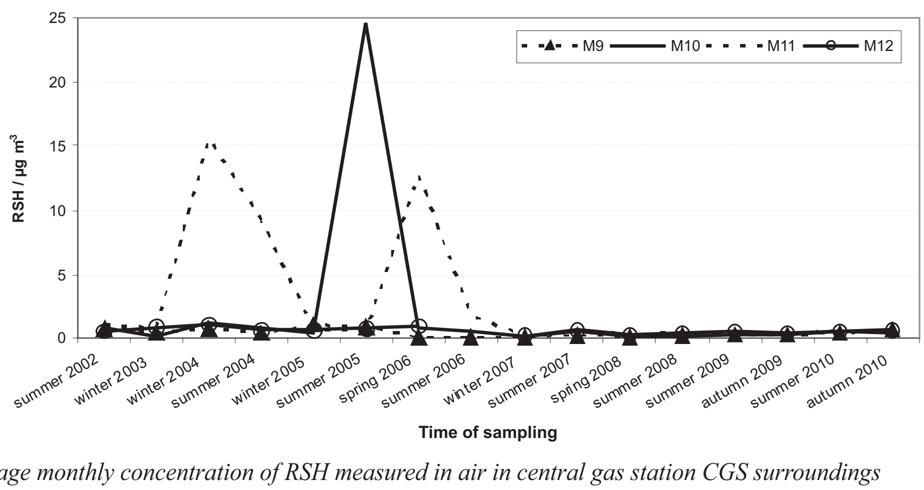

Figure 2 *Average monthly concentration of RSH measured in air in central gas station CGS surroundings*

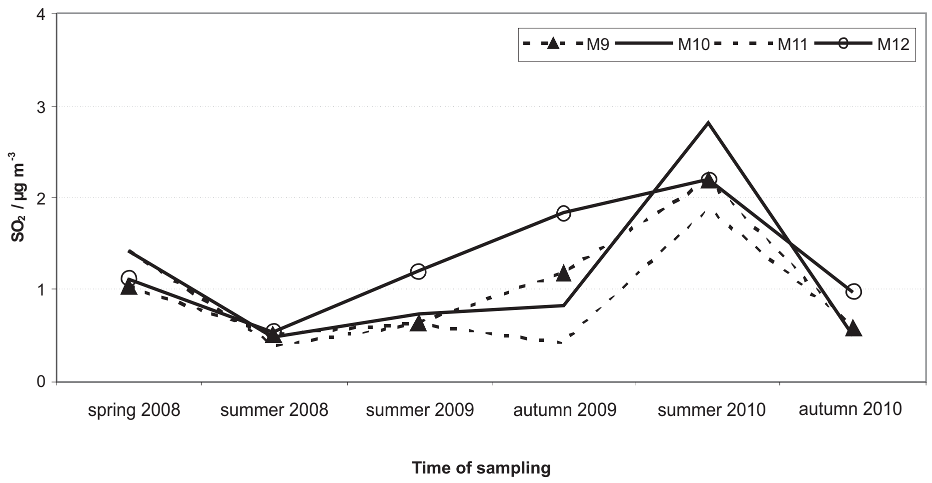

Figure 3 *Average monthly concentration of SO_2 measured in air in central gas station (CGS) surroundings*

to national legislation (26), LVs for SO_2 in air are 50 µg m^{-3} (for an average time of one year) and 125 µg m^{-3} (for a 24-hour collecting period, but LVs may not be exceeded more than seven times during a calendar year). During the study period, the LV (125 µg m^{-3}) was not exceeded. Considering the fact that the investigated area is relatively unpopulated, it is relevant to mention that national legislation (26) also prescribes LVs for the concentration of pollutants (SO_2 and NO_x) in air for the protection of ecosystem and vegetation. For SO_2, LV in air is 20 µg m^{-3} (for an average time of one calendar year and winter period), which is still high above the observed values in our study.

Sulphur in soil

Total sulphur mass ratio measured in surface [(0 to 8) cm] and subsurface [(3 to 8) cm] soil layers for each measuring period in CGS surroundings is shown in Figures 4 and 5, respectively.

According to Isaac and Kerber (27), normal concentration range of total S in soils is 500 mg kg^{-1} to 4,000 mg kg^{-1}. Total S in mineral soils may range from <20 mg kg^{-1} in sandy soils to >600 mg kg^{-1} in heavy texture soils. Organic soils may contain as much as 5,000 mg kg^{-1}. Moist soils, however, contain sulphur between 100 mg kg^{-1} and 500 mg kg^{-1} (28).

In a study conducted in the USA on Alberta soil samples (n=18), total sulphur content in different soil

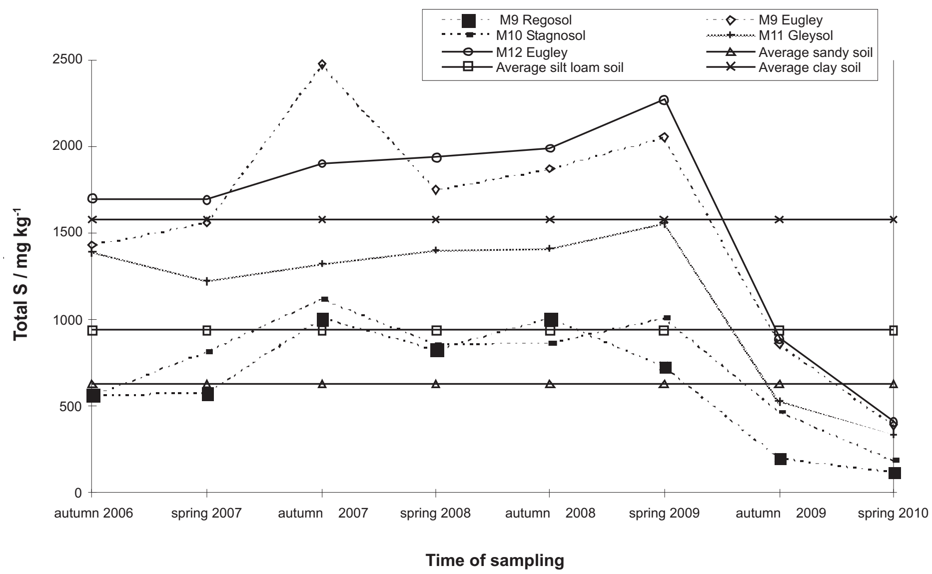

Figure 4 *Total sulphur mass ratio measured in surface soil layer [(0 to 3) cm] in central gas station (CGS) surroundings*

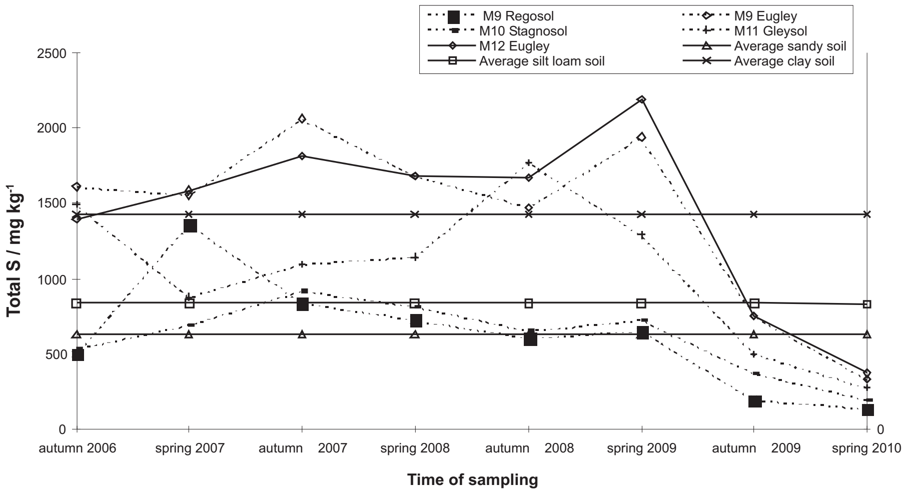

Figure 5 *Total sulphur mass ratio measured in subsurface soil layer [(0 to 3) cm] in central gas station (CGS) surroundings*

types in surface horizon were: up to 343 mg kg^{-1} in humic eluviated gleysol (lacustrine) in (0 to 10) cm; up to 869 mg kg^{-1} in orthic humic gleysol (lacustrine) in (0 to 12) cm; and up to 1,040 mg kg^{-1} in humic eluviated gleysol (till) in (0 to 3) cm (29).

In our case, mean values of total sulphur in soil ranged between 610 mg kg^{-1} observed on Stagnosol (M10) in subsurface horizon and 1,599 mg kg^{-1} measured on Eugley (M12) in surface horizon. For all examined periods, from autumn 2006 until spring 2010, single values of total sulphur in soil ranged between minimal 120 mg kg^{-1} measured on Regosol (M9 hill) in surface horizon in spring 2010 and maximal 2,470 mg kg^{-1} measured on Eugley (M 9) also in surface horizon in autumn 2007. Average values measured for sandy (n=8), silt loam (n=16), and clay (n=16) soils were in surface soil layer 631 mg kg^{-1}, 941 mg kg^{-1}, and 1,573 mg kg^{-1} and in subsurface soil layer 625 mg kg^{-1}, 832 mg kg^{-1}, and 1,426 mg kg^{-1}, respectively. Furthermore, the average values of all examined single samples (n=40) in surface and subsurface soil layers, were 1,132 mg kg^{-1} and 1,028 mg kg^{-1}, respectively. We observed a slightly lower mass ratio of total sulphur in deeper horizons (Figures 4 and 5) and an increasing trend of total S with a decrease in soil particle size (sandy < silt loam < clay).

Sulphur in plants

Total sulphur mass ratio recorded in Ribwort Plantain for each measuring period in CGS surroundings is shown in Figure 6.

According to Isaac and Johnson (30), normal concentration ranges of total S in plant tissue are between 500 mg kg^{-1} and 20,000 mg kg^{-1}.

Mean values of total sulphur in *Plantago lanceolata* ranged between 3,614 mg kg^{-1} measured in the plant grown on Stagnosol (M10) and 4,342 mg kg^{-1} measured in the plant grown on Eugley (M12).

Single values for all examined periods, from spring 2000 until spring 2010, for total sulphur in the plant were between minimal 1,910 mg kg^{-1} measured in the plant grown on Gleysol (M11) in spring 2000 and maximal 8,040 mg kg^{-1} measured in the plant grown on the same location and the same soil type on Gleysol (M 11) but in autumn 2008.

Average values observed in *Plantago lanceolata* grown on sandy (n=17), silt loam (n=34), and clay (n=34) soils where 4,184 mg kg^{-1}, 3,967 mg kg^{-1}, 4,212 mg kg^{-1}, respectively. Furthermore, the average values of total sulphur mass ratio for all examined single plant samples (n=85) were 4,108 mg kg^{-1} (Figure 6). As we already mentioned in the Introduction, according to Deloch (8), natural total sulphur content varies in different plants, depending on the plant species and cultivar; for example, in grasses like barley its content can be 1,800 mg kg^{-1} of DM, in legumes like soybean 3,200 mg kg^{-1} of DM and in cruciferae like rape as much as 10,000 mg kg^{-1} of DM (Figure 6). We observed an increasing trend in sulphur mass ratio in *Plantago lanceolata* over the years (from spring 2000 until spring 2010). The correlation was positive and ranged from medium to strong depending on the soil type, but we cannot connect this increase only and exclusively with the CGS Molve.

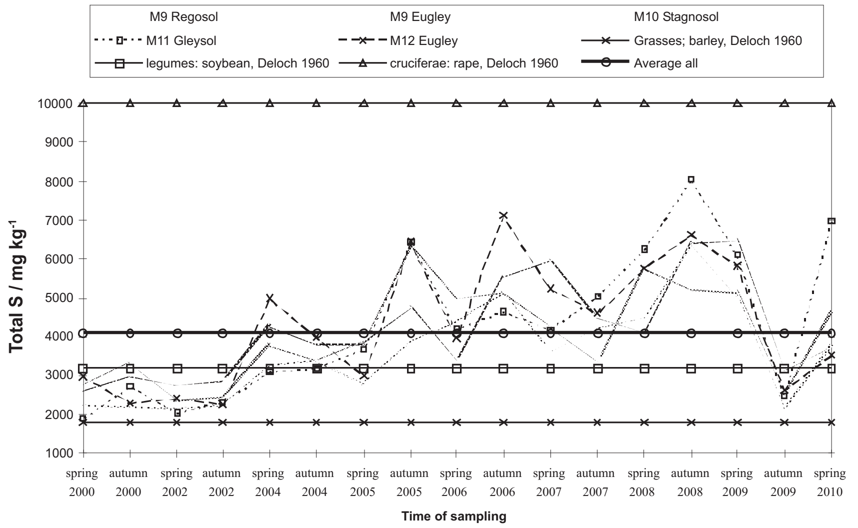

Figure 6 *Total sulphur mass ratio measured in Ribwort Plantain (*Plantago lanceolata*) in central gas station (CGS) surroundings*

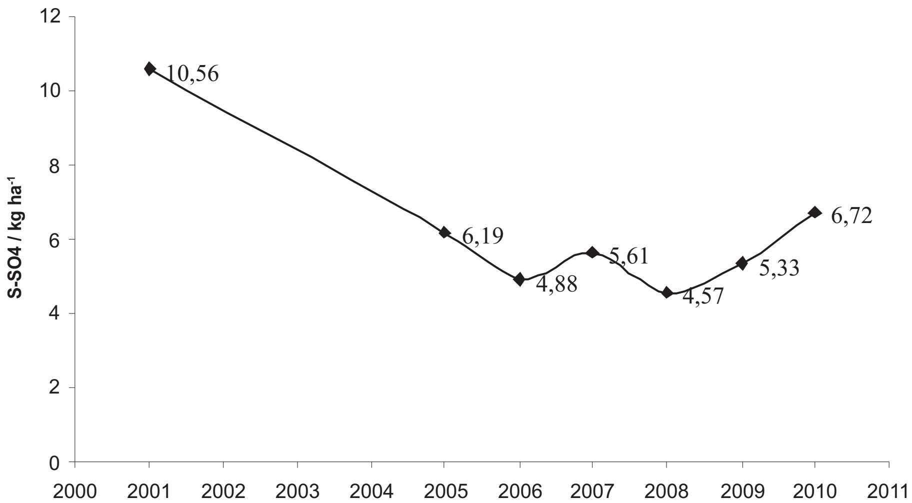

Figure 7 *Annual atmospheric total sulphur depositions at Bilogora measuring station; data from Central Bureau of Statistics RH, Statistical Yearbooks of Republic of Croatia (2001-2011), Meteorological and Hydrological Service*

Sulphur deposition and sulphur plant requirements

Annual atmospheric total sulphur deposition at Bilogora measuring station for the period 2001 through 2010 is presented in Figure 7 (25). This value ranged from 4.57 kg ha^{-1} (2008) up to 10.56 kg ha^{-1} (2001), the average deposition of S-SO_4 being 6.3 kg ha^{-1}. Nowadays in eastern North America, annual S deposition is more commonly below (8 to 10) kg ha^{-1}, due to the aplication of clean technology which is more energy efficient than the clasical industrial technology. The latter is still used in industrial China and India, where coal and oil burning cause as much as (50 to 75) kg ha^{-1} of sulphur fall level per year, while also in these countries, but in areas with no industry, deposition of S is generally as small as (1 to 5) kg ha^{-1} (7). The total S requirement in different crops depends on plant material production and crop species. Crops with high production of organic material, protein rich crops or cruciferae have a higher demand for S, for example 50 kg ha^{-1} for sugarbeet or cabbage. For this reason, they respond most sensitively to an inadequate S supply. Other crops have relatively low requirements for S, about 3 kg ha^{-1} for barley or wheat grain, for instance (5).

According to our previous studies and regarding sulphur in agroecosystem, we observed that the sulphur uptake in winter wheat grain increased on drained Stagnosol in central Croatia from 6.1 kg ha^{-1}

up to 16.9 kg ha^{-1} (12) and S-SO4 losses from soil with drainage water increased from 10.6 kg ha^{-1} to 15.2 kg ha^{-1} (13) depending on different nitrogen fertilisation doses that were applied.

Considering that sulphur is one of 17 plant nutrients (31) that are essential to the growth and development of all plants, it plays a key role in plant health. Losses (plant removal and leaching) and gains (precipitation) of sulphur in agroecosystem are usually in deficit, thus sulphur deficiencies can only be and usually are corrected by the application of an S fertiliser.

CONCLUSION

We have not observed elevated levels of sulphur compounds or its potential or mutual association with industrial activity for total sulphur in soil and total sulphur in the examined plant material Ribwort Plantain (*Plantago lanceolata* L.), but we have observed an increasing trend in sulphur mass ratio in *Plantago lanceolata* during the study period (from the spring of 2000 until the spring of 2010).

The concentrations of SO_2 and H_2S in air were generally low for the whole examined period.

Concentrations of RSH in air were relatively high by 2006 and often exceeded the limit daily value (LV=3 µg m^{-3}), but then ensued a period in which measured values were below the limit daily value. The most likely reason for this kind of RSH behaviour and abundance in air was the installation of the equipment for the incineration of waste gases (RTO units).

We definitely recommend further monitoring.

Acknowledgement

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Sažetak

KRUŽENJE SUMPORA IZMEĐU TERESTRIČKOG AGROEKOSUSTAVA I ATMOSFERE

Centralna plinska stanica plinskobušotinskog sustava Podravina nalazi se u Molvama, a potrošačima energije isporučuje više od četvrtine ukupne energije koja se troši u Hrvatskoj. Prilagodba tehnologije sve zahtjevnijim i strožim standardima zaštite okoliša tijekom godina bila je neupitna, no bez obzira na sve učinjeno od strane industrije, a s obzirom na rizik ulaska štetnih tvari u hranidbeni lanac, u okviru multidisciplinarnog istraživačkog tima nezavisni stručnjaci motre sadržaj potencijalno štetnih tvari i prate utjecaje na sve sastavnice ekosustava.

U ovom radu prikazane su vrijednosti ukupnog sumpora izmjerenog u tlu (u periodu od jeseni 2006. do proljeća 2010.) i u biljci (u periodu od proljeća 2000. do proljeća 2010.) te koncentracije plinovitih sumporovih spojeva u zraku. Koncentracije sumporovodika (H_2S) i merkaptana (RSH) mjerene su u razdoblju ljeto 2002-jesen 2010, dok su koncentracije sumporova(IV) oksida (SO_2) određivane u razdoblju proljeće 2008-jesen 2010. Prikazane su i godišnje vrijednosti ukupne atmosferske depozicije sumpora ($S\text{-}SO_4$) izmjerene na mjernoj stanici Bilogora (za period od 2001. do 2010.).

Srednje mjesečne koncentracije H_2S u zraku kretale su se između 0,2 μg m^{-3} i 2,0 μg m^{-3}, merkaptana između 0,1 μg m^{-3} i 24,5 μg m^{-3} te SO_2 između 0,4 μg m^{-3} i 2,8 μg m^{-3}, ovisno o lokaciji i sezoni uzorkovanja. Srednje vrijednosti ukupnog sumpora u tlu i u trpucu kretale su se redom od 610 mg kg^{-1} do 1 599 mg kg^{-1} te od 3 614 mg kg^{-1} do 4 342 mg kg^{-1}, ovisno o tipu tla, lokaciji i dubini uzorkovanja, dok su prosječne vrijednosti masenog udjela ukupnog sumpora, za cijeli period istraživanja, za tlo, iznosile 1 080 mg kg^{-1} (n = 80) za obje ispitivane dubine te 4 108 mg kg^{-1} za sve ispitivane uzorke trpuca (n = 85).

Prosječno godišnje ukupno atmosfersko taloženje sumpora na mjernoj stanici Bilogora iznosilo je 6,3 kg ha^{-1} $S\text{-}SO_4$.

KLJUČNE RIJEČI: *depozicija, H_2S, merkaptani,* Plantago lanceolata*, SO_2, tlo, ukupni sumpor, zrak*

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