An empirical model for describing the influence of water content and concentration of sulfamethoxazole (antibiotic) in soil on the total net CO₂ efflux

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Abstract: The aim of the study was to describe the impact of the soil water content and sulfamethoxazole, SUL, (antibiotic) concentration in soil on the net CO₂ efflux. Soil samples were taken from topsoils of a Haplic Fluvisol and Haplic Chernozem. Soil samples were packed into the steel cylinders. The net CO₂ efflux was measured from these soil columns after application of fresh water or SUL solution at different soil water contents. The experiments were carried out in dark at 20°C. The trends in the net CO₂ efflux varied for different treatments. While initially high values for water treatment exponentially decreased in time, values for solution treatment increased during the first 250–650 minutes and then decreased. The total net CO₂ effluxes measured for 20 hours related to the soil water content followed the second order polynomial functions. The maximal values were measured for the soil water content of 0.15 cm³ cm⁻³ (Haplic Fluvisol with water or solution, Haplic Chernozem with solution) and 0.11 cm³ cm⁻³ (Haplic Chernozem with water). The ratios between values measured for solution and water at the same soil water contents exponentially increased with increasing SUL concentration in soils. This proved the increasing stimulative influence of SUL on soil microbial activity.

Keywords: Repacked soil columns; Antibiotics; Soil respiration; CO₂ emission; Birch effect; CO₂ efflux stimulation.

INTRODUCTION

Emission of CO₂ from various sources into the atmosphere is one of the factors affecting the climate change. Vegetation and soils are important carbon pools. Soil can store a large amount of carbon. However, due to management practices soil can become also a significant source of CO₂ in the atmosphere (Bahn et al., 2010; Kuzyakov, 2006). A CO₂ efflux from the soil surface is influenced by many abiotic and biotic factors including soil temperature, soil water content, organic carbon content, composition and activity of microbial community, etc. (Balogh et al., 2011; Buchmann, 2000; Davidson and Janssens, 2006; Davidson et al., 1998; Fér et al., 2014, 2018a; Zhong et al., 2016). The microbial activity and consequently CO₂ emission can be influenced by many amendments including contaminants that can occur in the soils environment. Recently, treated wastewater is used for irrigation due to a water scarcity. Sewage sludge or farm biosolids are used as fertilizers. Nowadays, with the development of instruments and measurement accuracy, it has been found that these sources include variety of micropollutants including the human and veterinary pharmaceuticals that can contaminate soils and plants (Charuau et al., 2019; Golovko et al., 2016; Ivanová et al., 2018; Klement et al., 2020; Kodešová et al., 2019a, b; Velicchi and Zambello, 2015). Depending on compounds and soil properties, pharmaceuticals can be strongly sorbed in the soils environment or can be highly mobile and can contaminate ground water (e.g., Fér et al., 2018b; Klement et al., 2018; Kočárek et al., 2016; Kodešová et al., 2015; Schaffer and Licha, 2015; Schmidová et al., 2020). On one hand, their dissipation from soils is mostly driven by microbial conditions (e.g., Al-Khazray et al., 2018; Biel-Maeso et al., 2019; Hurtado et al., 2017; Kodešová et al., 2016, 2020; Shen et al., 2018; Srinivasan and Sarmah, 2014; Zhang et al., 2017). On the other hand, pharmaceuticals and particularly

antibiotics can strongly affect a microbial structure and activity (i.e., also CO₂ efflux). Antibiotics can either inhibit the activity of microorganisms and consequently reduce degradation of compounds or the activity and degradation of compounds can be enhanced due to an interaction among compounds in soil solution (Caraccilo et al., 2015; Chen and Xie, 2018; Frková et al., 2020; Grenni et al., 2018; Thelusmond et al., 2019; Zhi et al., 2019).

To assess microbial conditions a basal respiration (i.e., CO₂ accumulation rates) (Molaei et al., 2017) or substrate induce respiration can be measured using a small amount of a disturbed soil sample (Anderson and Domsch, 1985). CO₂ accumulation rates can be also measured during the degradation experiment (OECD, 2002). However, information about an actual influence of a certain antibiotic on a CO₂ emission from the surface of a larger soil samples is limited. To our knowledge, there is no study evaluating the coupled impact of antibiotic (in our case SUL) concentration in soil and soil water content on the net efflux of CO₂ from the soil. Therefore, the goals of our study were a) to evaluate the effect of increasing soil water contents on the soil CO₂ efflux from approximately one-kilogram soil samples packed in steel cylinders; b) to evaluate the impact of the increasing soil water content and concentration of SUL in soils on the soil CO₂ efflux; and c) to propose an empirical model how to describe the influence of water content and concentration of SUL in soil on CO₂ efflux.

MATERIALS AND METHODS

Sulfamethoxazole

The pharmaceutically active ingredient SUL (Table 1), which is very often used in human and in veterinary medicine, was chosen for this study. SUL is a sulfonamide bacteriostatic antibiotic that is mostly used in combination with trimethoprim,

Table 1. Sulfamethoxazole properties (<https://www.drugbank.ca/>) and the average parameters K_F and n of the Freundlich sorption isotherm ($s = K_F c^{1/n}$, where s is the concentration sorbed onto the soil particles and c is the concentration in soil water) and average dissipation half-life DT_{50} measured on 11 topsoils by Kodešová et al. (2015, 2016).

CAS	Molecular structure	MW (g mol ⁻¹)	Solubility (mg L ⁻¹)	Log Kow
723-46-6		253.28	610	0.89
pKa	K_F (cm ³ /n μg ^{1-1/n} g ⁻¹)	n	DT ₅₀ (days)	
pKa ₁ = 1.7 (basic) pKa ₂ = 5.6 (acidic)	2.22±1.68	1.65	7.84±3.2	

Table 2. Basic soil properties: the average values and standard deviation of electric conductivity measured in water (EC_{H2O}) and ethanol (EC_{ET}), active soil reaction (pH_{H2O}), potential soil reaction (pH_{KCl}), oxidizable organic carbon content (C_{ox}), particle density (ρ_s), bulk density (ρ_D), total soil porosity (P) and sand, silt and clay content (%) for the Haplic Fluvisol (A) and the Haplic Chernozem (B).

	EC _{H2O} (μS cm ⁻¹)	EC _{ET} (μS cm ⁻¹)	pH _{H2O} (–)		pH _{KCl} (–)	C _{ox} (%)
A	100.1±1.2	2.7±0.10	7.06±0.02		5.88±0.05	1.62±0.01
B	119.1±0.4	3.5±0.2	8.16±0.03		7.21±0.01	1.79±0.01
	ρ _s (g cm ⁻³)	ρ _D (g cm ⁻³)	P (%)	Sand (%)	Silt (%)	Clay (%)
A	2.58±0.01	1.43±0.06	46.2±0.02	69.0	19.2	11.8
B	2.52±0.01	1.39±0.05	47.4±0.02	5.4	58.1	36.5

which is an antifolate antibacterial agent. SUL is highly mobile in the soil-water environment, because its sorption on soil constituents is low (i.e., low Freundlich K_F coefficients in Table 1). Its stability in soils is also relatively low (i.e., low dissipation half-life, DT_{50} in Table 1). Its dissipation in soils is mainly due to biodegradation under aerobic conditions and can be significantly affected by its initial concentration in soils (Shen et al., 2018; Srinivasan and Sarmah, 2014). This means that there is a strong interaction between SUL and microbial community that should largely affect CO₂ effluxes from soils. SUL was purchased from BDL Czech Republic Ltd. (Turnov, Czech Republic), and has 98% analytical grade purity. Compound (2 mg) was dissolved in fresh water (2 L). The actual concentrations in the applied solution were analyzed using the normal injection LC-MS/MS method, described by Golovko et al. (2016). The intended concentration was 0.1 μg mL⁻¹ and measured concentration was 0.097 μg mL⁻¹.

Study sites, soil sampling and basic soil properties

The study was performed on the soil samples collected from two experimental research stations of the Czech University of Life Sciences Prague in the Czech Republic. The research station A is in Prague-Troja, (50.122°N, 14.399°E) and B is in Prague-Suchdol (50.128°N, 14.374°E). The soil type in the area of the Prague-Troja research station was defined as the Haplic Fluvisol developed on sediments of river Vltava and soil type in Prague-Suchdol was described as the Haplic Chernozem on loess (WRB, 2015). The soil samples (10 kg of disturbed soil from each location) were taken in March 2018 from the depth of 0–8 cm of the bare soils at 3 spots and transported within one day to the laboratory. Parts of the grab soil samples, which were next used to determine basic soil properties, were air-dried

and sieved through a 2-mm mesh. The basic chemical and physical properties (Table 2) were determined using standardized laboratory techniques: active soil reaction (pH_{H2O}) and potential soil reaction (pH_{KCl}) (ISO 10390, 2005), salinity (EC) (Rhoades, 1996), oxidizable organic carbon content (C_{ox}) (Skjemstad and Baldock, 2008), particle size distribution (Gee and Or, 2002) and particle density (ρ_s) (Flint and Flint, 2002). Additional information about soil properties of studied soils were published by Pavlů et al. (2021) for A location and by Kodešová et al. (2015, 2016, 2019a, b, 2020) and Klement et al. (2020) for B location.

Parts of soil samples intended for the laboratory measurement of the net CO₂ and water (H₂O) effluxes from soils were also air-dried. The soil was homogenised and aggregates with a diameter of larger than 1 cm were extracted using a 10-mm mesh. This treatment of the material preserved the natural aggregation of the soil and at the same time it was possible to pack the material into the 665 cm³ steel cylinders so that the bulk density of the naturally consolidated soil was achieved. The bulk densities and porosities of the naturally consolidated soils (Table 2) were measured on the 100 cm³ undisturbed soil cores (Dane and Topp, 2002), which were taken in four replicates on the both experimental plots.

Experimental setup for measuring net CO₂ and H₂O effluxes from the soil sample surface

Two experiments were performed for each soil. The first set of experiments (A1 and B1) was carried out with fresh water and the second set of experiments was carried out with SUL solution (SUL dissolved in fresh water). The experiment for each soil and treatment lasted 6 days. At the beginning of each experiment the air-dried soil (989 and 855 g for A and B, re-

spectively) was packed into the 665 cm³ steel cylinder (diameter of 11 cm and height of 7 cm) and then the net CO₂ and net H₂O effluxes were measured in one minute interval for 20 hours using the LCI-SD portable photosynthesis system with a Soil Respiration Chamber (that is described below). Next, the soil was spread into the tray, wetted using the sprayer, mixed and packed back into the cylinder, and measurements of the net CO₂ and net H₂O efflux were repeated again for 20 hours. This procedure was recurred several times as long as it was possible to treat the soil without destroying its structure. Five wetting steps were set for both soils. The intended volumetric soil water (θ) contents for A samples were 0.02 (air-dried soils), 0.06, 0.11, 0.15, 0.19 and 0.24 cm³ cm⁻³, and for B samples were 0.02 (air-dried soils), 0.07, 0.11, 0.14, 0.17 and 0.21 cm³ cm⁻³. The actual volumetric soil water content was checked gravimetrically.

The net CO₂ and net H₂O efflux were measured using the LCI-SD portable photosynthesis system with a Soil Respiration Chamber, according to Instruction Manual to Soil Respiration Hood V2 (ADC BioScientific, 2011). Two main components of soil respiration were measured: the net CO₂ efflux (NCER) and the net H₂O efflux (W_{flux}). Soil CO₂ emission (net molar flow of CO₂ in/out of the soil (p mol s⁻¹) is characterized as

$$C = u(-\Delta c) \quad (1)$$

where u is molar air flow in mol s⁻¹; Δc is the difference in CO₂ concentration through the soil chamber, (μ mol mol⁻¹)

$$\Delta c = C_{ref} - C_{an} \quad (2)$$

where C_{ref} is the CO₂ flowing into the soil chamber (μ mol mol⁻¹), C_{an} is CO₂ flowing out from the soil chamber (μ mol mol⁻¹).

The net CO₂ efflux (C_e per unit area) symbol $NCER$ (μ mol s⁻¹ m⁻²) is described as:

$$NCER = u_s(-\Delta c) \quad (3)$$

where u_s is the molar flow of air per square metre of soil, mol m⁻² s⁻¹; Δc is the difference in CO₂ concentration through soil hood, μ mol mol⁻¹.

The net H₂O flux (water flux) W_{flux} (mmol s⁻¹ m⁻²) is characterized as:

$$W_{flux} = \Delta e u_s / p \quad (4)$$

where u_s is the molar flow of air per square metre of soil, mol m⁻² s⁻¹; Δe is the differential water vapour concentration, m Bar; and p is the atmospheric pressure, mBar.

To avoid the influence of variable solar radiation (e.g., Fér et al., 2018a) and temperature (Schaufler et al., 2010; Yueste et al., 2007) on the measured values, the net CO₂ and net H₂O effluxes were measured in the dark and at 20°C in a growth chamber (KBF 240, Binder, Germany). The air humidity varied between 30 and 40%.

Next, the soil CO₂ efflux data was analyzed with the R software (R Development Core Team, 2015) to eliminate error measurements. This procedure, which was in detailed described by Fér et al. (2018a), includes the smoothing using the Savitzky-Golay filter to reduce the most urgent misleading records caused by the repeated disruption of the measurement conditions and the reconstruction of the potential unaffected course of the measurement by computing its continuum.

Data evaluation

Since the main aim of this study was the evaluation of the coupled impact of the antibiotic SUL and soil water content on the CO₂ emission from the soils, the analyses mainly focused on the net CO₂ efflux data. The initial, maximal and final values of the net CO₂ efflux were expressed for each treatment and related to the water content steps. The cumulative net CO₂ efflux and the total net CO₂ efflux for 20 hours were evaluated. The values of the total net CO₂ efflux for the water treatment were related to the soil water contents. To assess an influence of the SUL content in soils on the CO₂ emission, the ratios between the values of the total net CO₂ efflux for the SUL solution treatment were divided by the values of the total net CO₂ efflux for the water treatment only at the same soil water content. These ratios were next related to the SUL concentrations in soils expressed as follows:

$$s_i = \sum_{i=0}^N (V_i c) / m \quad (5)$$

where s_i is the concentration of SUL in soil (μ g g⁻¹), V_i is the volume of the applied solution (mL), c is the concentration of SUL in the solution (μ g mL⁻¹), m is the dry mass of the soil column (g), and N is the number of wetting steps.

The net H₂O efflux depended on the actual soil water content, but no influence of SUL on the net H₂O efflux was observed. This data is not further discussed in this paper.

RESULTS AND DISCUSSION

The trends of the net CO₂ effluxes for particular soil water contents considerably differed for different treatments (i.e., for fresh water and SUL solution). In the case of fresh water and A1 soil sample (Haplic Fluvisol), the initially high net CO₂ efflux exponentially decreased in time for all soil water contents (Fig 1a). The similar trends in the net CO₂ effluxes were observed for B1 soil samples (Haplic Chernozem) of soil water contents of 0.07 and 0.21 cm³ cm⁻³ (Fig 1c). For other soil water contents, the net CO₂ efflux initially increased (rise time varied between 250 and 300 min) and then declined. The range of the net CO₂ efflux was similar (0–2 μ mol s⁻¹ m⁻²) for both soil sample (A1 and B1). The very high soil respiration in the beginning after rewetting and then decrease in soil respiration is called the respiration pulse or the Birch effect (Birch, 1958), which was also find in our previous study where undisturbed soil samples were wetted by a capillary rise from the bottom of the soil samples (Fér et al., 2018a). The similar results were obtained by Iovieno and Bååth (2008), who demonstrated almost no respiration on the air-dried soil samples and exponential decrease of soil respiration after rewetting to 60% of water holding capacity (WHC). The exponential decrease in soil respiration was observed after rewetting (50% of WHC) soil samples after 4 days of air-drying by Meisner et al. (2013; 2015).

In the case of SUL solution, the net CO₂ effluxes measured on the A2 and B2 samples of soil water contents of 0.02 (A2 and B2), 0.06 (A2) and 0.07 (B2) cm³ cm⁻³ (Figure 1b and 1d) were similar to those measured for A1 and B1 samples of the same soil water contents (Figure 1a and 1c). This similarity can be explained by relatively low SUL amounts in soil samples (i.e., low concentrations of SUL in soils, expensed as weight of SUL per unit weight of dry soil) and thus likely a low influence on a microbial community. On the other hand, the trends in the

Fig. 1. Recorded net CO₂ effluxes (NCER) for 20 hours: (a) and (b) are A1 and A2 soil samples from the Haplic Fluvisol wetted with fresh water and SUL solution, respectively, and (c) and (d) are B1 and B2 soil samples from the Haplic Chernozem wetted with fresh water and SUL solution, respectively.

Fig. 2. Initial (a), maximal (b) and final (c) values of the net CO₂ effluxes (NCER): A1 is the soil sample from the Haplic Fluvisol wetted with fresh water, A2 is the soil sample from the Haplic Fluvisol wetted with SUL solution, B1 is the soil sample from the Haplic Chernozem wetted with fresh water and B2 is the soil sample from the Haplic Chernozem wetted with SUL solution.

net CO₂ effluxes for higher soil water contents and therefore also higher SUL concentrations in both soil samples (A2 and B2) completely differed from those wetted with fresh water (A1 and B1). The net CO₂ efflux increased during the first 450 minutes for A2 and 250–650 minutes for B2 (when the maximal net CO₂ efflux was reached) and next decreased (Fig. 1b and 1d). The trends in the initial and maximal values of the net

CO₂ effluxes evaluated for particular soil samples were similar (Figure 2a and 2b). Values mostly initially increased with wetting and then declined. The final values of the net CO₂ effluxes for A1 and B1 also initially increased and then decreased with increasing wetting. However, in the case of A2 and B2, the final values initially increased and then values varied between (0.4–0.6 and 0.25–0.35 $\mu\text{mol s}^{-1} \text{m}^{-2}$, for A2 and B2, respectively).

The cumulative net CO₂ effluxes from the soil samples (Figure 3a and 3c) even better showed the effect of an increasing soil water content on the net CO₂ efflux. The total net CO₂ efflux (Figure 3a) increased up to the soil water content of 0.15 cm³ cm⁻³ (A1) and 0.11 cm³ cm⁻³ (B1) and then decreased. The results confirm the fact, that with an increasing soil water content the net CO₂ efflux is also increasing (Fér et al., 2018a; Moayano et al., 2018) due to improving conditions for aerobic microbes. During a further soil wetting, the soil pores are gradually filled with water, which aggravates conditions for aerobic microbes, and thus the flow of soil gas (i.e., also CO₂) is reduced (Fér et al., 2018a). Later on, the net CO₂ efflux is restricted even more due to anaerobic conditions that suppress the aerobic microbial activity (Moayano et al., 2012 or Xu et al., 2004). The similar soil water contents (0.09–0.17 cm³ cm⁻³) related to the highest net CO₂ efflux were presented in our previous study (Fér et al., 2018a), in which the net CO₂ efflux from the undisturbed soil samples collected from loess derived soils was measured using the same device. The higher soil water contents (0.20 and 0.18 cm³ cm⁻³) related to the highest net CO₂ efflux were documented by Yueste et al. (2007) and Jiang et al. (2015) for a Chromic Cambisol and Haplic Kastanozem, respectively. One of the reasons could be that a different equipment was used to measure the CO₂ efflux and/or both experiments were performed in the field conditions with undisturbed soils.

The cumulative net CO₂ effluxes from the soil samples wetted with SUL solution (Figure 3b and 3d) showed much steeper initial increases. The values of the total CO₂ effluxes from the soil samples wetted with SUL solution are considerably and slightly higher than those for samples wetted with fresh water (Figure 3a and 3c) for the Haplic Fluvisol and Haplic Chernozem, respectively. The reason of a higher influence of SUL on the net CO₂ effluxes from the Haplic Fluvisol than that from the

Haplic Chernozem could be a different influence of SUL on the soil microbial community. For instance, Frková et al. (2020) showed that SUL had a short-term stress effect on a microbial community in an Arenosol Epieutric (sandy soil that is the most similar to the Haplic Fluvisol) and the same Haplic Chernozem, which resulted in an increase in a basal respiration. This affect was more pronounced in the Arenosol Epieutric than in the Haplic Chernozem. However, the cumulative net CO₂ effluxes resulted from both treatments (Figure 4a) showed similar trends and the highest total net CO₂ efflux was measured at the 4th water content step for both soils (soil-water content of 0.15 cm³ cm⁻³ and 0.14 cm³ cm⁻³ respectively).

Calculated ratios between the total net CO₂ effluxes for samples wetted with SUL solution (A2 and B2) and fresh water (A1 and B1) exponentially increased with the increasing wetting (Figure 4b). This means that despite the soil water content largely controlled and at high values considerably restricted the net CO₂ efflux, the increasing SUL concentration in soils gradually increases the net CO₂ efflux.

The data points given by the water contents and the related total net CO₂ efflux for water treatments (A1 and B1) were fitted with the polynomial functions (Figure 4c). The intercepts of these two functions with x-axis were 0.0189 and 0.0183 cm³ cm⁻³ for A1 and B1, respectively, which can be assumed as bottom limits of the soil-water contents, for which and below these values no CO₂ efflux would be measured.

The data points given by the SUL concentrations in soils and ratios between the total net CO₂ effluxes for the samples wetted with SUL solution (A2 and B2) and fresh water (A1 and B1) were fitted with the exponential functions (Figure 4d). These equations expressed the impact of the SUL concentrations in soils under the setup experimental conditions. The calculated values of the ratios can be further considered as the multiplication coefficients with the help of which it would be

Fig. 3. Cumulative net soil CO₂ efflux (cum NCER) recorded for 20 hours: (a) and (b) are A1 and A2 soil samples from the Haplic Fluvisol wetted with fresh water and SUL solution, respectively, and (c) and (d) are B1 and B2 soil sample from the Haplic Chernozem wetted with fresh water and SUL solution, respectively.

Fig. 4. The total net CO₂ efflux (tot NCER) measured for 20 hours (a), the ratio between the total net CO₂ effluxes for the SUL solution treatment and the water treatment (b), the relationship between the total net CO₂ effluxes (tot NCER) and the soil water contents (c), the relationship between the ratio of total net CO₂ effluxes and the SUL concentrations in soils, which was calculated using Eq. 5 (d): A1 is the sample from the Haplic Fluvisol wetted with water, A2 is the soil sample from the Haplic Fluvisol wetted with SUL solution, B1 is the soil sample from the Haplic Chernozem wetted with water and B2 is the soil sample from the Haplic Chernozem wetted with SUL solution.

possible to predict the values of the total net CO₂ effluxes for certain SUL concentrations from the values of the total net CO₂ effluxes evaluated for the water treatment. However, at this moment results cannot be generalized for different solution concentrations. One of the reasons is that the SUL concentration in soil at each wetting step was calculated as a sum of volumes of solution that were cumulatively applied into soil multiplied by the SUL concentration in solution divided by the mass of soil, and no SUL dissipation in soil was assumed. The average dissipation half-life (Table 1) indicates a relatively high dissipation rate in soils. The first order kinetic equations and reaction constant derived from the DT₅₀ values could be used to calculate a possible decrease of SUL in each dose. Values in Table 1 were obtained at the same temperature (20°C) but at the optimal soil water contents that corresponded to the field water capacities. Dissipation of SUL under dry conditions would be much slower. In addition, there could be some SUL losses during the treatments. For a better definition of soil conditions, the actual SUL concentrations in soils should be determined at each wetting step. Another reason is that experiments were carried out with solution of one SUL concentration. Similar sets of experiments should be carried out with wider range of concentrations and a possibility to generalize this empirical model for variable soil water contents and actual concentrations in soils should be investigated.

CONCLUSION

Results of this study showed that under the established experimental conditions the relationships between the total net CO₂ effluxes from two soils recorded for 20 hours and the soil-water content could be approximately described using the second order polynomial functions. The antibiotic SUL considerably increased the net CO₂ efflux from soils. The values of the total net CO₂ efflux measured for the SUL solution treatment

were several times higher than those for the water treatment and this impact increased with the increasing SUL concentrations in soils. Further studies are needed to test the proposed empirical exponential model for estimating the multiplication coefficient from the SUL concentrations in soils for wider range of SUL concentrations in applied solutions. Nevertheless, results indicated a very progressive positive impact of SUL amount in soils on undesirable CO₂ emissions from the soil environment.

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