Sorption, Degradation and Leaching of the Phenoxyacid Herbicide MCPA in Two Agricultural Soils

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Abstract

MCPA is the phenoxyacid herbicide widely used for weed control in cereals in Slovakia. However, little is known on the processes governing the environmental fate of MCPA in soils from Slovakia. Laboratory experiments were performed to evaluate the sorption, desorption, degradation, and leaching behavior of MCPA in two agricultural soils with high sand content and different soil organic carbon content. The extent of MCPA sorption was higher in chernitsa than that in regosol, in accordance with the higher organic carbon content of the former soil than the latter. MCPA was readily desorbed from soils with 10 mmol l^{-1} CaCl$_2$ solution with the desorption rate ranging from 44.5 to 77.5% of the sorbed MCPA. The half-life values showed that the degradation of MCPA was fast in chernitsa ($t_{1/2}$ = 2.2 days) and almost six times faster than in regosol ($t_{1/2}$ = 11.7 days). Leaching tests, performed in manually packed soil columns, indicated that MCPA was more mobile in regosol than in chernitsa with 16.44% of the applied MCPA recovered in the leachates of regosol, and 1.12% found in the leachates of chernitsa. Thus, differences in the leaching behavior of MCPA coincided well with the results of the batch sorption and degradation experiments.

Keywords: pesticide, mobility, persistence, desorption

Introduction

Herbicides are used worldwide for weed control in modern production agriculture. Direct application of herbicides into the soils may often lead to groundwater contamination by their leaching. There are many reports confirming the occurrence of herbicides, including phenoxyacids such as MCPA and 2,4-D in groundwaters underlying the agricultural soils [1, 2]. Sorption, desorption and degradation are major processes influencing the potential for herbicides to be leached from the soil into the groundwater [3].

These processes control the mass of a herbicide in soil solution which is available for vertical transport through a soil profile. Sorption-desorption processes of herbicides in soils are related both to the texture and properties of the soils and to the chemical structure of the herbicides [4, 5]. Many factors may influence degradation of herbicides in soils, including the soil organic carbon content, soil moisture and temperature, type and size of soil microbial population as well as the physico-chemical properties of the herbicide [6]. Understanding sorption, degradation and leaching of herbicides in soils is essential in predicting their fate in the environment and possible health impacts on living organisms, including human beings.

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Table 1. Physico-chemical properties of soils.

Soil type	Locality	%			Texture	pH_{H_2O}	OC[1] (g kg^{-1})	Clay mineralogy
		Clay	Silt	Sand				
Chernitsa	Stupava	11.0	15.0	74.0	sandy loam	7.96	11.9	Ill > Chl[2]
Regosol	Lozorno	0.6	13.9	85.5	sandy	5.76	4.8	Ill > Chl

[1]OC – total organic carbon content;
[2]Ill – illite, Chl – chlorite.

The phenoxyacid herbicide MCPA (4-chloro-2-methylphenoxyacetic acid) is used to post-emergence control of annual and perennial broad-leaved weeds, mostly in cereals [7]. MCPA is commonly used in production of crops in Slovakia due to its high selectivity. Although MCPA is only a moderately toxic herbicide compared to triazine herbicides, monitoring its residues in water and soil is crucial because it can influence the nervous system upon adsorption through the skin and its prolonged inhalation can cause dizzines, burning in the chest and coughing [8]. Several authors have found that MCPA is degraded in soil within 1 to 16 weeks by microbial degradation via 4-chloro-2-methylphenol to ultimately harmless form [8-10]. Soil organic carbon content, soil pH and Fe and Al oxyhydroxides appear to be a predominant factors influencing retention of phenoxyacid herbicides in soils [11-14]. In general, MCPA is weakly retained in soils and migrates easily through soil columns [15, 16].

The soils from the Zahorie area in western Slovakia differ from the other soils of Slovakia in their pedogenesis since they are formed on non-carbonate aeolian sands. In many parts of the Zahorie area, light, sandy soils with relatively low organic matter content are utilized for cereal production. Therefore, it may be expected that highly soluble herbicides such as MCPA used in cereal fields of western Slovakia will have an increased potential for leaching into the subsoil layers and potentially into the groundwater. Taking this into account, the main objectives of this study were to determine the sorption-desorption, degradation, and leaching behavior of MCPA within the top layer (0-20 cm) in two sandy soils collected from fields of the Zahorie area situated in western Slovakia. To better assess the leaching risk of soil-applied MCPA in agricultural fields of the Zahorie area, it is necessary to describe quantitatively in the first step its environmental fate processes in soils.

Materials and Methods

Herbicide

MCPA is a chlorinated phenoxyacid herbicide of molecular weight 200.6 g/mol and water solubility 273.9 mg l^{-1} at 25°C and pH=7. It has a disociation constant value of 3.07, therefore MCPA is mostly neutral at pHs < 3.07 and becomes negatively charged at pHs > 3.07. MCPA of purity > 99%, purchased from Dr Ehrenstorfer GmbH (Germany), was used in this study.

Soils

Two agricultural soils from the Zahorie area (western Slovakia) were selected for this study. The soils were sampled from the top 0- to 20-cm layer, air dried, and passed through a 2-mm sieve before their use in the experiments. Relevant physico-chemical properties and sampling locations of the soils are given in Table 1. The procedures followed for soil characterization are described in [13].

Sorption and Desorption Experiments

MCPA sorption-desorption in soils was obtained by the batch equilibration procedure using glass centrifuge tubes. Duplicate soil aliquots (2 g) were equilibrated with 10 ml of aqueous solutions of MCPA by rotating in an end-over-end shaker at 22±2°C for 24 h. Preliminary measurements on MCPA sorption kinetics have shown that sorption of MCPA in the soils reached equilibrium within 24 h since there were no significant differences in MCPA sorption between 24 h and longer equilibration periods. Five initial aqueous solutions with MCPA concentrations ranging from 1.66 to 56.6 mg l^{-1} were prepared from an aqueous solution containing 10 mmol l^{-1} $CaCl_2$ and 1 mmol l^{-1} NaN_3. After equilibration, the suspensions were centrifuged at 3,000 rpm for 15 min, and the supernatant solutions were removed using a glass pipette for subsequent analysis by reversed-phase high-performance liquid chromatography (HPLC) as described below. The amount of MCPA sorbed was calculated by the difference between the amount initially added and that remaining in equilibrium solution. The measurements with control samples containing only MCPA showed that there were no losses of MCPA due to adsorption onto the surface of the tubes, volatilization or microbial activity.

Desorption was measured immediately after sorption from the two equilibrium points of the sorption isotherms corresponding to the initial concentrations of 5.7 and 56.6 mg l^{-1}. After the removal of about 9 ml of the supernatant, an equal volume of 10 mmol l^{-1} $CaCl_2$ plus 1 mmol l^{-1} NaN_3 solution was added and the tube was rotated at 22±2°C for 24 h, then centrifuged and sampled as described above. All sorption and desorption experiments were conducted in duplicate.

MCPA sorption in soils was described by the Freundlich equation:

$$S = K_f C^n \qquad (1)$$

...where S is the amount of MCPA sorbed by the soil (mg kg^{-1}), C is the concentration of MCPA in solution at equilibrium (mg l^{-1}), K_f (mg^{1-n} l^n kg^{-1}) and n (unitless) are the empirical Freundlich constants, which can be calculated from the linear plot of log$S$ against log$C$. The constant K_f is the simple distribution coefficient K_d (l kg^{-1}) at $C = 1$ mg l^{-1} and n is a measurement of the intensity of sorption and reflects the degree to which sorption is a function of concentration.

Degradation Experiments

Two weeks before the start of the degradation experiment a set of 20 g portions for each soil was placed in the dark at 22±2°C and at soil moisture content of 15% by weight, in a batch covered with perforated aluminium foil. Then, MCPA in 10 mmol l^{-1} CaCl$_2$ solution (1 ml) was added to each 20 g portion of soil samples to give an initial concentration of ~10 mg MCPA kg^{-1} dry soil. The soils were allowed to equilibrate for 2 h and consequently thoroughly mixed. Wet soil samples were stored in the dark and soil moisture content was maintained at the initial level of 20% by weight. Incubation periods were 0, 1, 6, 8, 10, 15, 22, 30 and 40 days. Duplicate samples were taken at each time to measure remaining concentrations of MCPA in the soil. MCPA was extracted by shaking 0.5 g of duplicate soil samples dried by flowing air with 1 ml of acetonitrile-acetic acid solution (0.5% acetic acid) in a ratio of 50:50 (v/v) using an ultrasonic system for 2 h. After centrifuging at 10,000 rpm for 10 min., an aliquot of the extract was used for the analysis of MCPA concentration by HPLC. Extraction recoveries of this procedure were 86.4% and 78.8% for chernitsa and regosol, respectively, based on duplicates of freshly spiked samples.

The degradation data were fitted to the first-order rate equation:

$$C_t = C_0 \exp(-kt) \qquad (2)$$

...where C_t is the amount of MCPA remaining in the soil at a given time t (mg kg^{-1}), C_0 is the amount of MCPA in the soil at time zero (mg kg^{-1}), and k is the degradation rate constant (d^{-1}). The half-life $t_{1/2}$, which represents the time needed for 50% disappearance of the initial MCPA amount, was calculated from k with the equation:

$$t_{1/2} = \frac{\ln 2}{k} \qquad (3)$$

Leaching Experiments

For leaching experiments, air-dried soils were manually packed into glass columns measuring 17×2.5 cm (inside diameter). Two columns for each soil were used. A filter-paper and a 0.5 cm thick layer of acid-washed sand was placed in the bottom of the columns to prevent losses of soil and contamination of leachates with soil particles. The columns were packed to a height of approximately 15 cm with soil. The columns were saturated with 150 ml 10 mmol l^{-1} CaCl$_2$ solution and allowed to drain for 24 h before application of MCPA. Then, 2 mg MCPA dissolved in 1 ml HPLC-grade methanol were applied to the top of the columns. After application of the herbicide, the columns were leached with 50 ml d^{-1} of 10 mmol l^{-1} CaCl$_2$ aqueous solution for 15 days. Leachates from the columns were collected daily and analyzed by HPLC. At the end of the leaching experiments, soils were gently removed from the columns and subsequently cut in five fractions for extraction with acetonitrile and analysis by HPLC.

Analytical Procedure

MCPA was analyzed by a reversed-phase high-performance liquid chromatography (Hewlett-Packard model 1100) using a Lichrosphere-100 RP column (4.6× 125 mm, 5 μm) and a Hewlett-Packard 1046A fluorescence detector set at 232 nm. External solution standards were used to establish linear calibration curves for a fluorescence detector. The mobile phase was a mixture of acetonitrile and 0.03 mol l^{-1} acetic acid solution containing 5% acetonitrile at a ratio of 50:50 (v/v) at a flow rate of 1.0 ml min^{-1} (isocratic elution). The sample injection volume was 20 μl. The average uncertainty for the measured concentrations was about ±5% and the limit of quantification was 0.02 mg l^{-1}.

The sorption and degradation data were evaluated using GraphPad Prism version 4.00 for Windows (GraphPad Software, San Diego, California, USA).

Results

Sorption and Desorption

Sorption isotherms of MCPA in both soils are shown in Fig. 1. The sorption isotherms were adequately described by the linearized form of the Freundlich equation with a r^2 value greater than 0.93 being significant at the 0.001 probability level. The K_f values were 0.96 l kg^{-1} for chernitsa and 0.40 l kg^{-1} for regosol. The decrease in MCPA sorption was parallel with the decrease in total organic carbon content of the soils (Table 1). In general, the sorption isotherms for both soils were nonlinear as indicated by n values being lower than 1.

MCPA was readily desorbed from soils with 10 mmol l^{-1} CaCl$_2$ solution (Fig. 2). About 44.5 up to 77.5% of the sorbed MCPA was desorbed from soils in one desorption step. Thus, a large amount of MCPA may be leached through soil via mobile water.

Degradation

Degradation curves for MCPA in the two soils are illustrated in Fig. 3. According to Fig. 3, the half-life of MCPA calculated from the estimated degradation rate constant was

2.2 days for chernitsa and 11.7 days for regosol. Degradation of MCPA occurred significantly faster in chernitsa than in regosol, presumably reflecting differences in the microbial activity of these soils as a result of their different organic matter contents (Table 1). No MCPA could be detected in chernitsa after 40 days, whereas in regosol, 15% of the applied amount of MCPA remained after 40 days.

Leaching

A very different picture of MCPA leaching was observed between the two soils used. Approximately only 1.12% of the MCPA applied to the columns with chernitsa were found in the leachates, while up to 16.44% were detected in the leachates of regosol (Fig. 4). At the end of the leaching experiments (i.e. after application of 750 ml of 10 mmol l^{-1} $CaCl_2$ solution within a 15-d period), MCPA was unevenly distributed in regosol and chernitsa and there

Fig. 3. Degradation curves of MCPA in soils. Data points and error bars represent means ± standard deviations of duplicate samples (N=2).
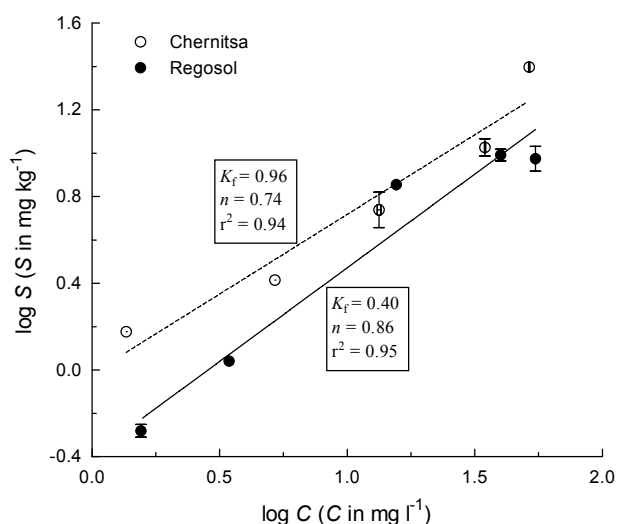

Fig. 1. Sorption isotherms of MCPA for soils. Data points and error bars represent means ± standard deviations of duplicate samples (N=2).

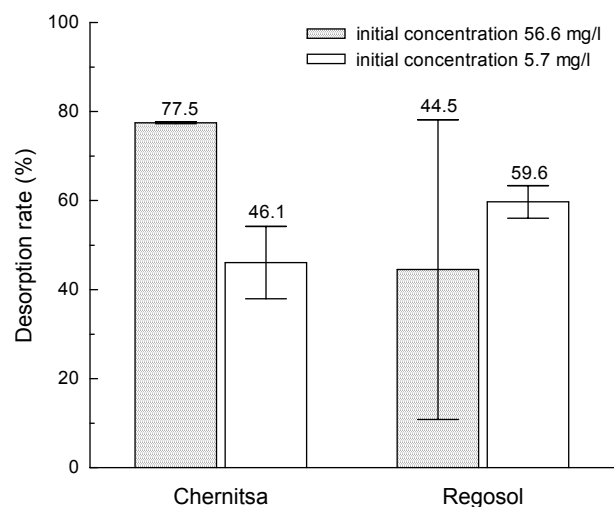Fig. 2. Percentages of MCPA desorbed from soils at the two initial concentrations. Data points and error bars indicate means ± standard deviations (N=2).
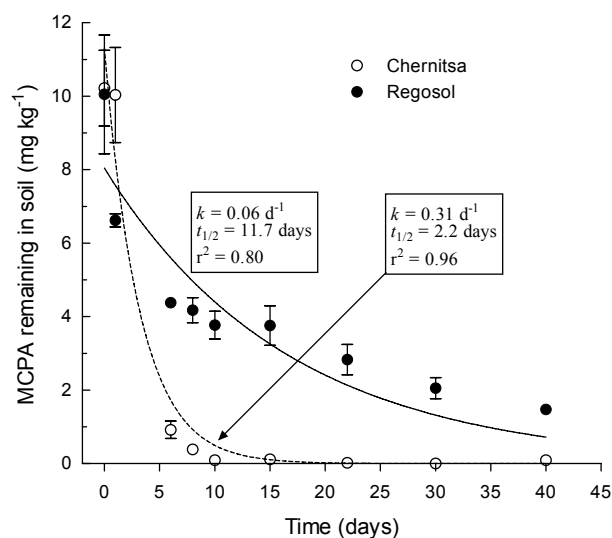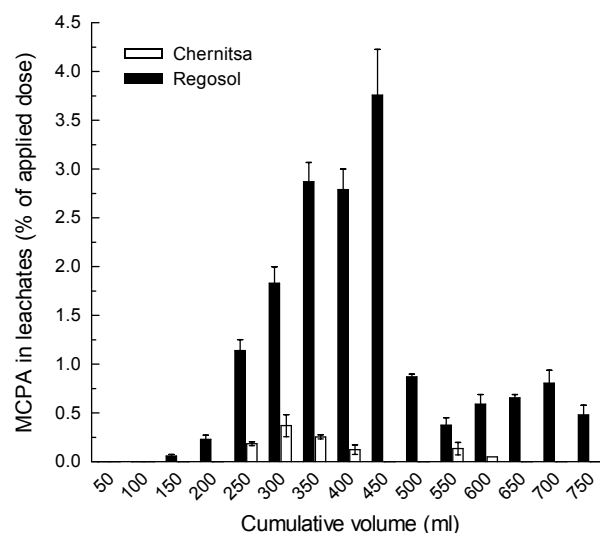

Fig. 4. Distribution of MCPA in the leachates from soil columns. Data points and error bars are means ± standard deviations (N=2).

was a significant difference between the two soils concerning the depths in which MCPA was found (Fig. 5). The total amounts of MCPA extracted from the columns with chernitsa and regosol were 0.84% and 18.42% of the amount applied, respectively. In regosol, MCPA was found in all depth fractions, while only negligible amounts of MCPA were detected in the 0-3 cm and 6-9 cm fractions of chernitsa.

Discussion

Sorption and Desorption

The distribution coefficient values of MCPA obtained in this study are within the range of previously reported values of 0.01-1.94 $l kg^{-1}$ for soils with organic carbon contents

of 1-46 g kg^{-1} [13, 15, 17, 18]. The higher sorption of MCPA by chernitsa over regosol can be attributed to the higher organic carbon content of the former soil, which is consistent with previously reported positive correlations between sorption of acidic herbicides and soil organic carbon content [4, 12, 13]. Virtually the same K_{oc} values (K_{oc} = (K_f/ %OC) × 100) for both soils, 81 l kg^{-1} for chernitsa and 84 l kg^{-1} for regosol, also suggest that soil organic matter is the primary component responsible for MCPA sorption in these soils. Each soil had a low affinity for MCPA as indicated by the low K_f values and the corresponding K_{oc} values. MCPA, as well as other acidic herbicides, are predominantly present in an anionic form when soil pH is greater than 5. It is well-known that anionic forms of organic acids are generally weakly retained by most soils, since they are repelled by the predominantly negatively charged soil clay minerals or organic matter [19]. The slopes of isotherms ($n < 1$) indicated that the percentage of MCPA sorbed by soils decreased as the initial concentration of the herbicide increased. This might be explained by an increased difficulty to access the active sorption sites when herbicide concentrations are elevated. McCall et al. [20] used K_{oc} values to classify the mobility potential of pesticides through soil. Based on this classification and the measured K_{oc} values, MCPA would exhibit high mobility in both soils.

The high desorption rate of MCPA found in this study is a commonly observed phenomenon also for other acidic herbicides such as 2,4-D and bentazone, and in general it could be related to a weak interaction between acidic herbicides and soil components [4].
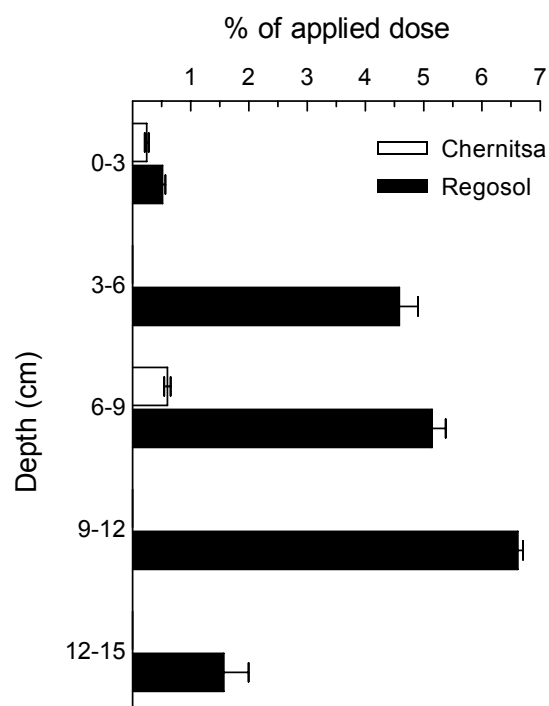
% of applied dose

Fig. 5. Percentage of applied MCPA remaining in different depths of manually packed soil columns at the end of the leaching experiment. Error bars represent standard deviations of the means (N=2).

Degradation

Degradation of herbicides is affected by many factors involved in the interactions among microorganisms, chemical and soil components. It is also assumed that sorption, which controls herbicide concentrations in the soil solution, can limit herbicide degradation in soil by reducing its concentrations in the aqueous solution [21, 22]. Nevertheless, a significantly faster degradation of MCPA occurred in chernitsa compared with regosol (Fig. 3), although the MCPA sorption was higher in the former soil than in the latter (Fig. 1). Other factors, i.e. organic carbon content of the soils, could explain the observed difference in degradation rates of MCPA between chernitsa and regosol. Soil organic matter is an important source of nutrients, and the activity and size of soil microbial populations may be greater in soils with higher organic carbon contents [23, 24]. This may result in an increased rate of pesticide degradation. Therefore, the faster degradation of MCPA in chernitsa compared with regosol might be attributed to an increase in microbial activity due to the higher organic matter content of this topsoil. In general, degradation was an important process that reduced the concentration of MCPA in the soils, thus limiting its leaching potential.

The half-lives of MCPA for these two soils are similar to those reported in other studies ranging from 4 to 16 days [8, 10, 25].

Leaching

The leaching patterns of MCPA agree well with the results of the batch sorption and degradation experiments (Figs. 1 and 3). The higher mobility of MCPA in columns with regosol corresponded with the lower sorption measured in this soil (K_f=0.40 l kg^{-1}) and the higher persistence ($t_{1/2}$=11.7 days) compared with the higher sorption and fast degradation of MCPA in chernitsa (K_f=0.96 l kg^{-1} and $t_{1/2}$=2.2 days). The results indicate that MCPA may represent a contamination risk for groundwater when it is applied to sandy soils with relatively low organic matter content and high water permeability. This was pointed out by Socías-Viciana et al. [15] and Haberhauer et al. [16], who conducted short-term leaching experiments and reported the high MCPA leachability in sandy soils with 70-99% of the herbicide collected in the leachates.

The actual leaching behavior of MCPA in the two soils was compared with groundwater ubiquity score (GUS) values. GUS is commonly applied to evaluate pesticide leaching to groundwaters and it is calculated as:

$$GUS = \log t_{1/2} \times (4 - \log K_{oc}) \qquad (4)$$

The pesticides leaching to groundwater are those with GUS > 2.8. In contrast, the pesticides having GUS < 1.8 do not leach to groundwater and those having GUS = 1.8-2.8 are transitional [26]. The calculated GUS values are 0.72 and 2.22 for chernitsa and regosol, respectively. Based on the GUS values, MCPA in chernitsa could be classified as a

non-leacher, but MCPA in regosol would be a potential leacher, in accordance with the results of the column leaching experiments.

Conclusions

Laboratory experiments were performed to evaluate the sorption, desorption, degradation, and leaching behavior of the phenoxyacid herbicide MCPA in two agricultural soils with high sand content and different soil organic carbon content collected from fields of the Zahorie area in western Slovakia. Leaching tests, performed in manually packed soil columns, indicated that MCPA was more mobile in regosol than in chernitsa. Differences in the leaching behavior of MCPA coincided well with the results of the batch sorption and degradation experiments. MCPA was more sorbed by chernitsa than by regosol, likely due to the higher organic carbon content in chernitsa. Degradation rate of MCPA was higher in chernitsa compared with regosol. Overall, the extent of leaching of the phenoxyacid herbicide MCPA in two topsoils was controlled primarily by its degradation rate in these soils, and to a lesser extent by its sorption. Crop management practices that improve soil organic carbon content such as incorporation of green manure and crop residues in the soil would likely reduce MCPA leaching by increasing microbial activity, which accelerates MCPA degradation and increases MCPA sorption. These general data on the environmental behaviour of MCPA in agricultural soils are vital for preliminary assessment of the potential risk of groundwater contamination by this herbicide in western Slovakia.

Acknowledgements

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