



Pesticide adsorption in relation to soil properties and soil type distribution in regional scale

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ABSTRACT

Study was focused on the evaluation of pesticide adsorption in soils, as one of the parameters, which are necessary to know when assessing possible groundwater contamination caused by pesticides commonly used in agriculture. Batch sorption tests were performed for 11 selected pesticides and 13 representative soils. The Freundlich equations were used to describe adsorption isotherms. Multiple-linear regressions were used to predict the Freundlich adsorption coefficients from measured soil properties. Resulting functions and a soil map of the Czech Republic were used to generate maps of the coefficient distribution. The multiple linear regressions showed that the K_F coefficient depended on: (a) combination of OM (organic matter content), pH_{KCl} and CEC (cation exchange capacity), or OM, SCS (sorption complex saturation) and salinity (terbutylazine), (b) combination of OM and pH_{KCl} , or OM, SCS and salinity (prometryne), (c) combination of OM and pH_{KCl} , or OM and ρ_z (metribuzin), (d) combination of OM, CEC and clay content, or clay content, CEC and salinity (hexazinone), (e) combination of OM and pH_{KCl} , or OM and SCS (metolachlor), (f) OM or combination of OM and CaCO_3 (chlorotoluron), (g) OM (azoxystrobin), (h) combination of OM and pH_{KCl} (trifluralin), (i) combination of OM and clay content (fipronil), (j) combination of OM and pH_{KCl} , or OM, pH_{KCl} and CaCO_3 (thiacloprid), (k) combination of OM, pH_{KCl} and CEC, or sand content, pH_{KCl} and salinity (chlormequat chloride).

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1. Introduction

Groundwater contamination caused by pesticides used in agriculture is an environmental problem worldwide. Groundwater contamination depends on many factors and conditions. Groundwater vulnerability maps, which may be constructed using the DRASTIC methodology [1], assume soil texture, hydrological conditions, hydrogeological settings and climatic conditions and does not account for the properties of a contaminant. One factor is a soil cover and specific pesticide adsorption in soils. It was documented in many studies that sorption processes of organic compounds depend on the sorbent physicochemical properties as pH, cation exchange capacity, ionic strength, surface area, etc. [2]. The organic matter content is usually suggested to have a greatest effect on the pesticide adsorption in natural soils. Pesticide partition (distribution) coefficient (K_D) is usually calculated (based on the positive

Abbreviations: BCS, basic cation saturation; CEC, cation exchange capacity; EA, exchangeable acidity; GUS, groundwater ubiquity score; HA, hydrolytic acidity; OC, organic carbon content; OM, organic matter content; SCS, sorption complex saturation.

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correlation between the organic carbon content and the K_D coefficient) assuming the organic carbon fraction in soil and the organic carbon partition coefficient (K_{OC}) [3]. However, also other factors may play an important role. Richter et al. [4] summarized various equations relating the K_D coefficient to organic carbon (OC) and pH. Either linear or nonlinear equation for the K_D value and OC was presented. The multiple linear regression between the K_D value and OC, pH, and OC multiplied by pH was also introduced. In addition, a nonlinear relationship between the K_D value and OC with the pH impact (pH as the exponent in the exponential function) was shown. Kozák and Vacek [5,6] assumed even more soil properties and proposed a pedotransfer rule for the prediction of the K_D coefficients for atrazine. They used a multiple linear regression to evaluate relationship between the K_D coefficients and the organic matter content (OM), pH, clay content and cation exchange capacity (CEC). Different sorption behavior of acidic and basic pesticides with respect to soil properties was documented by Kah and Brown [7]. pH impact depends on pesticide acidity ($\text{p}K_a$) and base ($\text{p}K_b$) constants [8]. The multiple linear regression between the log K_D value and log OC and log D (the lipophilicity profile of the pesticides) was applied by Villaverde et al. [9]. Rodriguez-Rubio et al. [10] showed that the larger content of calcium carbonate increased 2,4-D sorption.

Eleven pesticides were examined in our study: terbutylazine, prometryne, metribuzin, hexazinone, metolachlor, chlorotoluron, trifluralin, azoxystrobin, fipronil, thiacloprid and chlormequat chloride.

Terbutylazine sorption was studied previously by Dousset et al. [11], Meyer-Windel et al. [12], Singh et al. [13], and Finocchiaro et al. [14]. Dousset et al. [11] found that the adsorption in clay soils was not related to clay or OC, but to the degree of humification of the organic matter. A non-linear equation was used by Meyer-Windel et al. [12] to describe relationship between K_F and OC. The K_F coefficient was higher for soils with higher OC [13]. Finocchiaro et al. [14] showed that the K_D coefficient was significantly correlated with OC and amorphous iron oxides.

Prometryne sorption was measured by Yang et al. [15] and Oliver et al. [16]. Yang et al. [15] showed that the K_F coefficient had a good correlation with OM for 6 soils. Oliver et al. [16] found that the relationship between K_D and OC was not significant, but the relationship between derived K_{OC} and pH was significant.

Metribuzin sorption was examined by Garcia-Valcarcel et al. [17], Daniel et al. [18], and Kah and Brown [7]. Metribuzin adsorption in 18 soil of Central Spain did not show any correlation with studied soil properties [17]. The K_F was related positively to OM [18]. Adsorption was negatively correlated with soil pH and positively correlated with OC [7].

Hexazinone sorption was investigated by Donati et al. [19] and Calderon et al. [20]. Very low values of K_D and K_{OC} were measured for 6 soils [19]. Higher K_F values were measured in soil with higher OM [20].

Metolachlor sorption was measured by Wang et al. [21], Singh et al. [13], Liu et al. [22], Weber et al. [23], Vryzas et al. [24] and Si et al. [25]. Wang et al. [21] showed good correlation between the K_F coefficient and the OM. The K_F coefficient was higher for soils with higher OC [13]. Liu et al. [22] presented that the K_F coefficient increased with OC. The K_D coefficient for soil humic acid was greater than on clay. Weber et al. [23] presented that the retention of metolachlor was positively influenced by OM and clay content. Principal component and multiple regression analyses showed K_F dependence on OC in the plough layers and on the clay content and pH in the subsurface horizons [24]. Si et al. [25] showed the K_D dependence on OM.

Chlorotoluron sorption was studied by Meyer-Windel et al. [12], Gao et al. [26], Hiller et al. [27], Kodešová et al. [28,29]. A linear relationship between the Freundlich adsorption coefficient (K_F) and organic carbon (OC) was proved by Meyer-Windel et al. [12]. Adsorption increases with increasing N content [26]. The K_F values positively correlated with OC [27]. The K_F values were higher in soil horizons with higher OC [28,29].

Trifluralin sorption was examined by Tavares and Rezende [30] and Cooke et al. [31]. The herbicide adsorption increased with increasing OM [30]. Trifluralin exhibited strong partitioning to the soil solid phase and low desorption potential [31].

Azoxystrobin adsorption increased in the compost-amended soils [32].

Fipronil sorption was investigated by Bobe et al. [33], and Masutti and Mermut [34]. The K_F coefficient increased with the increasing OM [33]. The K_F values for two tropical soils showed that the presence of higher amount of poorly crystalline Fe-oxhydroxides increased fipronil adsorption [34]. Thiacloprid sorption was investigated using 22 soils [35]. Sorption was not significantly related with soil characteristics, namely OC, clay content, and pH. Correlation with OC was obtained for some separated land uses.

Chlormequat chloride adsorption decreased in the presence of heavy metals [36].

Ground water is an important source of drinking water in the Czech Republic. Our study is a part of a project, which is focused

on the assessment of the risk of the selected pesticide leaching into the groundwater within the entire region of the Czech Republic. First of all, results of the project will be used to optimize a national groundwater quality monitoring system, which is operated by the Czech Hydrometeorological Institute [37]. In addition, they may help to improve pesticide management within the areas with an increased pesticide leaching potential. In order to construct the specific groundwater vulnerability maps for selected pesticides based on the modified DRASTIC methodology, the maps of the K_F coefficients within the region of the Czech Republic were produced, which are presented here. The goals of this study were: (1) to select representative soils of the Czech Republic and determination of soil physical and chemical properties; (2) to measure adsorption isotherms of selected pesticides; (3) to determine pedotransfer rules for estimating sorption coefficients from the measured soil properties; (4) to apply the pedotransfer rules, the soil map of the Czech Republic [38] and the Czech soil information system PUGIS [39] for estimating the adsorption coefficients of pesticides for soils of the Czech Republic.

2. Materials and methods

2.1. Soil chemical and physical properties

Thirteen representative soils (11 samples from humic horizons of various soil types and 2 substrates) of the Czech Republic (Table 1) were selected to study a pesticide adsorption in soils. Soils were selected based on the soil map of the Czech Republic [38], and the Czech soil information system PUGIS [39] to cover a large variability of soil properties, which may influence pesticides adsorption in soils. 20 kg of dry soil was collected from each location. The soil samples were dried, ground and sieved through the 2-mm sieve. The basic chemical and physical soil properties (Table 1) were obtained using standard laboratory procedures under constant laboratory temperature of 20 °C: the soil $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} [40], the exchangeable acidity (EA) [41], the cation exchange capacity (CEC) [42], the soil hydrolytic acidity (HA) [43], the basic cation saturation (BCS) (difference between CEC and HA), the sorption complex saturation (SCS) (percentage of BCS in CEC), the total organic carbon content (TC) [44], the organic matter content (OM) (TC multiplied by 1.724), the CaCO_3 content [45], the soil salinity [46], the particle density (ρ_s) [47], and the particle size distribution (fractions of clay, silt and sand) [48]. Measured properties of the representative soils of the Czech Republic in Table 1 show wide variability.

2.2. Pesticide adsorption isotherms

Pesticides (Table 2) were selected based on the following properties: water solubility (S), soil half-life (DT_{50}) and sorption coefficient K_{OC} . The GUS (groundwater ubiquity score) index [50] was also used to assess a leaching potential:

$$\text{GUS} = \log \text{DT}_{50}(4 - \log K_{OC}) \quad (1)$$

Pesticide of low to very higher mobility (GUS index), and moderate and large solubility were selected. In addition one pesticide (trifluralin) of very low mobility was studied. Pesticide selection was made to cover pesticides of various functions, which have been the most frequently applied in the Czech Republic. The pesticide stability was also assumed to minimize experimental errors due to pesticide degradation.

The adsorption isotherms were measured using a standard batch equilibrium method. 10 g of air dried, ground and sieved (the 2-mm sieve) soil were placed into the 50 cm³ glass bottle. 20 cm³ of solution of a known pesticide concentration were added into the glass bottle. Bottle was shaken for 24 h using the shaking apparatus at 20 °C. Five (three) initial pesticide concentrations and

Table 1
Basic chemical and physical soil properties pH_{KCl} , $\text{pH}_{\text{H}_2\text{O}}$, exchangeable acidity (EA), cation exchange capacity (CEC) hydrolytic acidity (HA), basic cation saturation (BCS), sorption complex saturation (SCS), OM (organic matter content), CaCO_3 content, salinity, bulk density (ρ_s), sand, silt and clay content.

Soil type	Location	Parent material	pH_{KCl}	$\text{pH}_{\text{H}_2\text{O}}$	EA (mmol + kg ⁻¹)	CEC (mmol + kg ⁻¹)	HA (mmol + kg ⁻¹)	BCS (mmol + kg ⁻¹)	SCS (%)
Stagnic Chernozem Siltic	Milčice	Marlite	7.43	8.06	0.88	403.8	2.76	401.04	99.3
Haplic Chernozem	Ivanovice na Hané	Loess	6.28	7.07	0.99	271.3	8.58	262.73	96.8
Haplic Chernozem	Praha Suchdol	Loess	7.21	7.69	0.72	263.8	4.20	259.60	98.4
Chernozem Arenic	Velké Chvalovice	Gravelly sand	6.94	7.44	0.78	141.3	3.76	137.54	97.3
Greyic Phaeozem	Čáslav	Loess	6.53	6.90	0.55	297.5	8.71	288.79	97.1
Haplic Luvisol	Hněvčeves	Loess	5.63	6.33	0.95	240.0	10.98	229.02	95.4
Haplic Cambisol	Humpolec	Orthogneiss	4.37	4.81	2.08	260.0	23.49	236.51	91.0
Haplic Cambisol	Předbořice	Syenite	5.03	5.82	1.55	228.8	21.18	207.63	90.7
Haplic Cambisol	Jince	Quartzite	4.99	5.30	1.84	236.3	18.46	217.84	92.2
Dystric Cambisol	Vysoké nad Jizerou	Paragneiss	4.79	5.33	2.15	284.2	32.11	252.09	88.7
Arenosol Epieutric	Semice	Sand	5.74	6.23	0.57	91.3	7.88	83.43	91.4
Loess	Praha Suchdol		7.40	8.14	0.99	241.3	3.02	238.28	98.7
Sand	Písková Lhota		8.11	8.61	0.55	56.3	1.71	54.59	97.0

Soil type	Location	Parent material	OM (%)	CaCO_3 (%)	Salinity ($\mu\text{S cm}^{-1}$)	ρ_s (g cm ⁻³)	Sand (%)	Silt (%)	Clay (%)
Stagnic Chernozem Siltic	Milčice	Marlite	5.03	28.01	71.3	2.23	29.5	54.6	15.8
Haplic Chernozem	Ivanovice na Hané	Loess	3.05	0	56.1	2.48	13.2	75.5	11.4
Haplic Chernozem	Praha Suchdol	Loess	3.47	7.80	43.7	2.52	24.4	56.3	19.3
Chernozem Arenic	Velké Chvalovice	Gravelly sand	1.59	2.50	41.8	2.56	73.6	20	6.4
Greyic Phaeozem	Čáslav	Loess	2.33	0.10	26.1	2.51	9.5	77.1	13.4
Haplic Luvisol	Hněvčeves	Loess	1.78	0	32.9	2.43	9.6	76.5	13.9
Haplic Cambisol	Humpolec	Orthogneiss	2.82	0	157.8	2.39	55.4	34.7	9.9
Haplic Cambisol	Předbořice	Syenite	2.95	0.20	8	2.77	59	36.2	4.8
Haplic Cambisol	Jince	Quartzite	2.78	0	16.2	2.75	35.9	43.7	20.3
Dystric Cambisol	Vysoké nad Jizerou	Paragneiss	3.99	0.24	9.6	2.64	25.3	57.8	16.9
Arenosol Epieutric	Semice	Sand	1.14	0.16	48.2	2.52	83.7	12.8	3.5
Loess	Praha Suchdol		0.76	11.60	7.7	2.53	23.7	51.8	24.5
Sand	Písková Lhota		0.04	1.03	4.6	2.83	93.7	3	3.3

three replicates of each concentration were applied for each soil. Solutions were prepared using common pesticide products (except for hexazinone) to obtain approximately the same concentrations ($c_{\text{ini}} = 1, 2, 5, 10$ and $25 \mu\text{g cm}^{-3}$) for almost all studied pesticides (active substances in the pesticide products). Accordingly lower concentrations were prepared for pesticides with lower water solubility: fipronil, ($c_{\text{ini}} = 0.2, 0.5, 1, 1.5$ and $2 \mu\text{g cm}^{-3}$), azoxystrobin and terbuthylazine, ($c_{\text{ini}} = 1, 2, 4, 6$ and $10 \mu\text{g cm}^{-3}$), and trifluralin ($0.1, 0.2$ and $0.3 \mu\text{g cm}^{-3}$). Pesticides were dissolved in the 0.02 M CaCl_2 solution. After shaking, the analyzed soil suspension was placed into the centrifuge tube and centrifuged for 30 min at 12,000 rotations per minute. The actual initial ($c_{\text{ini},a}$) and final equilibrium pesticide concentrations (c_{eq}) in solutes ($\mu\text{g cm}^{-3}$) of terbuthylazine, prometryne, metribuzin, hexazinone, metolachlor, chlorotoluron, azoxystrobin, fipronil and thiacloprid were measured using the HPLC technique (Dionex; USA). The chlormequat chloride concentration was measured using the following chromatographic system (HPLC/MS technique): Ultimate 3000 RS (Dionex; USA), with mass spectrometry detector 3200 QTRAP (Applied Biosystems; USA). Gas Chromatography-Electron Capture Detection (GC-ECD) (Hewlett-Packard, USA) technique was used for determination of trifluralin concentration in the aqueous phase.

The pesticide concentration adsorbed on soil particles (s) was expressed as the amount of solute per mass unit ($\mu\text{g g}^{-1}$) using the following equation:

$$s = 2(c_{\text{ini},a} - c_{\text{eq}}) \quad (2)$$

Data points of the adsorption isotherms were given by the final pesticide concentration $c = c_{\text{eq}}$ [ML^{-3}] and s [MM^{-1}]. The Freundlich equation was used to fit data points of the adsorption isotherms:

$$s = K_F c^{1/n} \quad (3)$$

where K_F [$\text{L}^{3/n} \text{M}^{1-1/n} \text{M}^{-1}$] and n [-] are empirical coefficients. If $n = 1$, K_F (the Freundlich adsorption coefficient) is defined as the distribution coefficient K_D [$\text{L}^3 \text{M}^{-1}$]. Linear transformation of equation and laboratory data [3] and the least square method were applied to compute the unknown empirical coefficients. In addition the average n coefficient for each pesticide was calculated and the Freundlich equation with the fixed average n value was used to fit again experimental data points (linearly related $c^{1/n}$ and s values) and to obtain the K_F values using the least square method.

2.3. Pedotransfer rules for the K_F coefficient prediction

First of all the simple regression was used to relate the K_F coefficients and various soil properties. Then the multiple linear regressions were used to define pedotransfer rules for the prediction of the K_F coefficient (for the fixed n value) from the other measured physical and chemical soil properties. Kozák and Vacek [5,6] proposed estimation of the distribution coefficients K_D using the following multiple linear regression equation:

$$Y = b_0 + b_1 \text{OM}[\%] + b_2 \text{pH}_{\text{KCl}} + b_3 \text{CEC}[\text{mmol} + \text{kg}^{-1}] + b_4 \text{clay}[\%] \quad (4)$$

where Y is the unknown distribution coefficient K_D , and b_0, b_1, b_2, b_3 and b_4 are regression coefficients that represent correlation with organic matter content (OM), pH_{KCl} , cation exchange capacity (CEC) and clay content. Therefore the relationship between the K_F ($=Y$) parameter and the organic matter content, pH_{KCl} , cation exchange capacity and clay content (Table 1) was studied for each pesticide. Then the variables of low significance were eliminated from the regression analysis to get new equations for the K_F coefficients predictions. Finally, all measured physical and chemical properties (Table 1) were included in the regression analysis to improve predictions of the K_F values.

Next the regressions between the K_F coefficients of various pesticides were also evaluated. Multiple linear regressions were

Table 2
Pesticide water solubility, sorption coefficient K_{OC} , soil half-life and groundwater ubiquity score (GUS).

Pesticide	Chemical group ^a	Pesticide type	Product	Pesticide content in product	Water solubility ^a ($\mu\text{g cm}^{-3}$)	K_{OC} ^a ($\text{cm}^3 \text{g}^{-1}$)	Half-life ^a (days)	GUS ^a	pK_a	Specification ^a
Terbutylazine	Triazine	Herbicide, Microbiocide, Algicide	Click 500 SC	500 g 1000 cm ⁻³	6.6	219	76.7	3.13	2.0	Base
Prometryne	Triazine	Herbicide	Gesagard 80	800 g 1000 g ⁻¹	33	400	41	2.25	4.1	Base
Metribuzin	Triazinone	Herbicide	Sencor 70 WG	700 g 1000 g ⁻¹	1165	38	11.5	2.57	1.0	Base
Hexazinone	Triazinone	Herbicide	Standard	1000 g 1000 g ⁻¹	33,000	54	105	4.58	2.2	Base
Metolachlor	Chloroacetamide	Herbicide	Dual Gold 960 EC	960 g 1000 cm ⁻³	530	200	90	3.32	NA	No dissociation
Chlorotoluron	Urea	Herbicide	Syncuran 80 DP	800 g 1000 g ⁻¹	74	205	45	2.79	NA	No dissociation
Trifluralin	Dinitroamine	Herbicide	Treflan 48 EC	480 g 1000 cm ⁻³	0.221	8765	181	0.13	NA	No dissociation
Azoxystrobin	Strobilurin	Fungicide	Heritage	500 g 1000 g ⁻¹	6.7	423	70	2.53	NA	No dissociation
Fipronil	Phenylpyrazole	Insecticide	Regent 800 WG	800 g 1000 g ⁻¹	3.78	577	142	2.67	NA	No dissociation
Thiacloprid	Neonicotinoid	Insecticide, Molluscicide	Calypto 480 SC	480 g 1000 cm ⁻³	184	615	15.5	1.44	NA	No dissociation
Chloromequat chloride	Quaternary Ammonium	Plant growth regulator	Stabilan	581 g 1000 cm ⁻³	886,000	168	10	1.77	NA	Complete dissociation

NA—not applicable.

^a FOOTPRINT [49].

used again to express pedotransfer rules for the K_F coefficient (for different pesticides) predictions from soil (Table 1) and pesticide (Table 2) properties. In addition the K_D value (calculated from the pesticide organic carbon distribution coefficient, K_{OC} , and fraction of organic carbon in each soil) was included into analysis:

$$K_D = \frac{\text{OM}(\%)}{1.724 * 100} K_{OC} \quad (5)$$

2.4. The K_F coefficient maps

Resulting pedotransfer rules, the soil map of the Czech Republic [38] and the Czech soil information system PUGIS [39] were applied for estimating the K_F parameters of soils of the Czech Republic. The PUGIS database did not contain all data measured in this study and utilized for improved predictions. Therefore the maps of the K_F parameters calculated using the most significant properties from OM, pH_{KCl} , CEC, clay are shown here. Maps of the soil properties within the area of the Czech Republic are shown in Fig. 1.

3. Results and discussion

3.1. Pesticide adsorption isotherms

Resulting parameters K_F and n of the Freundlich adsorption equations are not shown here. The K_F coefficient is commonly used to assess pesticide sorption in various soils (the large K_F value indicates large pesticide sorption). However, fitting the same experimental data the K_F value depends on the n coefficient (the lower K_F values are obtained for lower n values, e.g. higher $1/n$ values). The relatively similar n values for various soils were obtained only for metolachlor. Therefore the average n coefficient for each pesticide was used to fit the experimental data points again and to obtain the K_F values, which may be used to assess impact of soil properties on the pesticide adsorption on soil particles (Table 3). The K_F values for various pesticides and different soils show, that there is no general trend of pesticide sorption in soils, which can be applied for all pesticides. It is evident that the largest adsorption (the largest K_F value) was observed either in soil sample from Stagnic Chernozem Siltic (the soil with the largest organic matter content) or in Dystric Cambisol and Haplic Cambisol on syenite (higher OM and low pH). The lowest pesticide adsorption (the lowest K_F value) was measured either in sand or loess (as expected due to very low OM content). Considerably different behavior was examined for chlormequat chloride.

3.2. Pedotransfer rules for the K_F coefficient prediction

The statistical correlation between the K_F coefficients and soil properties is shown in Table 4. The highest correlation between the K_F coefficients and organic matter content (OM) (compared to the correlations between the K_F value and other properties) was obtained for terbuthylazine, metribuzin, metolachlor, chlorotoluron, azoxystrobin, fipronil and thiacloprid. The highest correlation between the K_F coefficients and hydrolytic acidity (HA) was found for prometryne and trifluralin. Almost no correlation of the K_F coefficients and soil properties was observed for hexazinone. The K_F value was only negatively correlated with clay content. The highest correlation between the K_F coefficients and basic cation saturation (BCS) was found for chlormequat chloride.

Assuming the general suggestion that OM mostly affects the pesticide sorption in soils, it is evident that the satisfactory correlation between the K_F coefficient and OM was found for all nonionic pesticides. In the case of the two basic pesticides of moderate solubility and moderate K_{OC} value, the better correlation between the K_F coef-

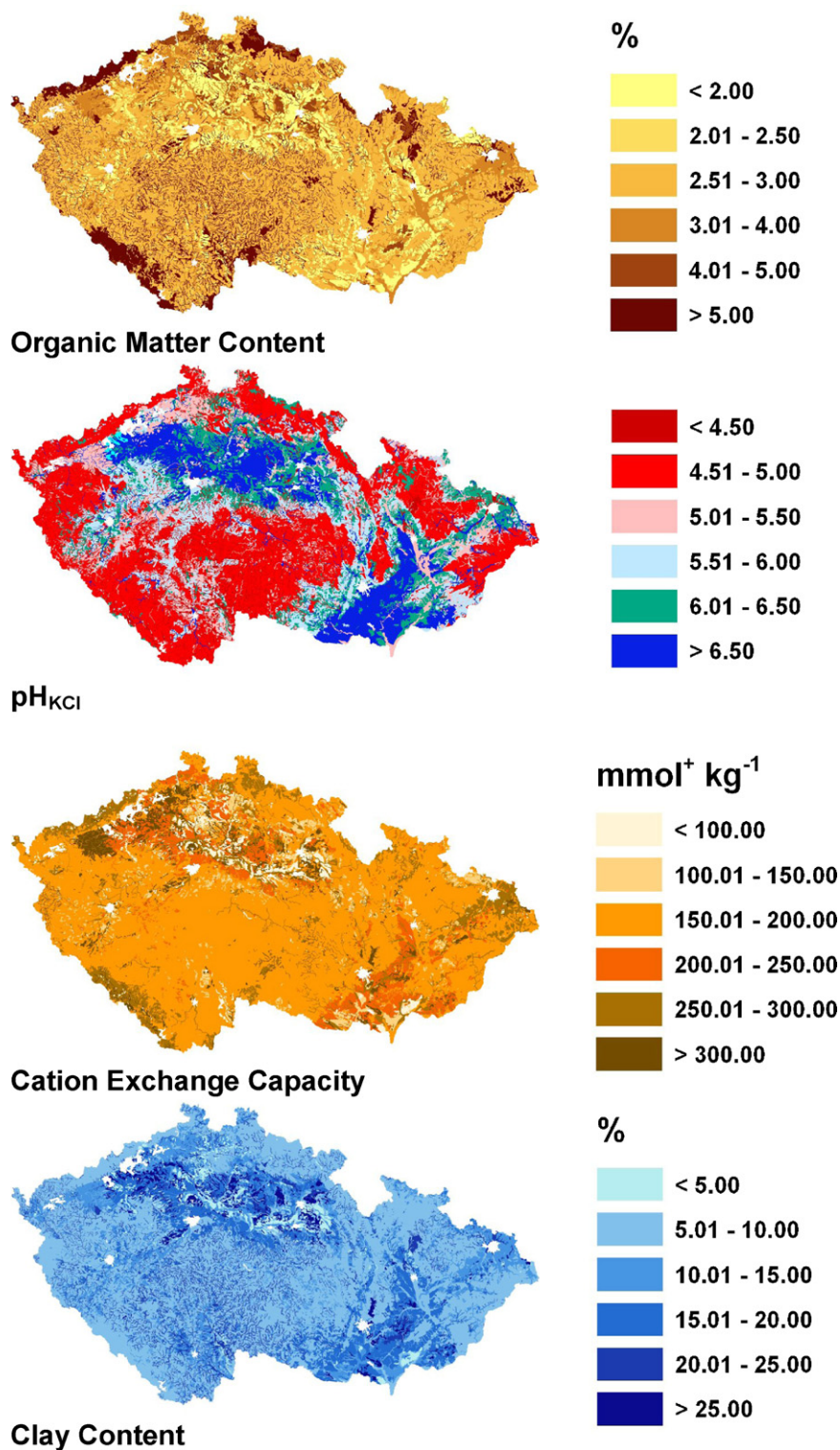


Fig. 1. Organic matter content, OM (%), pH_{KCl} (–), cation exchange capacity, CEC (mmol⁺ kg⁻¹), and clay content (%) in soils of the Czech Republic.

efficient and OM was obtained for terbutylazine ($pK_a = 2$) compared to prometryne ($pK_a = 4.1$). According Hornsby et al. [8], while the basic pesticides of $pK_b > 11$ (e.g. $pK_a < 3$) should behave like non-ionic compounds except at extremely acid conditions, the basic pesticides of pK_b between 4 and 11 (e.g. $3 < pK_a < 10$) are sensitive to pH under normal soil pH range (5–8). Since soil pH was even lower than 5, adsorption of both pesticides was affected by soil pH (negative correlation between K_F and pH). Adsorption of weak base increases with decreasing pH until a maximum is achieved

and decreases thereafter. The pH corresponding to the adsorption maximum is sometimes close to the pK_a of the molecule [51]. Adsorption of some weak bases (triazines) decreases with increasing pH due to the effect of pH on protonation of the molecule [51]. The pH impact was greater for pesticide with pK_a between 3 and 10 as would be expected. Moderate (metribuzine $pK_a = 1$) or no (hexazinone $pK_a = 2.2$) correlation was observed for basic pesticides of large solubility and low K_{OC} value. Despite the low pK_a value a negative correlation with pH was obtained for metribuzine.

Table 3
Coefficients K_F ($\text{cm}^3/\text{h} \mu\text{g}^{1-1/n} \text{g}^{-1}$) of the Freundlich adsorption isotherms obtained for the average n parameter for each pesticide.

Soil type	Location	Terbutylazine $n = 1.21$	R^2	Prometryne $n = 1.17$	R^2	Metribuzin $n = 1.31$	R^2	Hexazinone $n = 1.64$	R^2	Metolachlor $n = 1.06$	R^2	Chlorotoluron $n = 1.20$	R^2
Stagnic Chernozem Siltic	Milčice	4.78	0.896	6.51	0.998	1.31	0.993	0.74	0.957	4.12	0.995	11.89	0.998
Haplic Chernozem	Ivanovice na Hané	3.12	0.931	4.14	0.998	0.90	0.991	1.05	0.823	2.51	0.994	4.07	0.998
Haplic Chernozem	Praha Suchdol	3.53	0.960	4.27	0.998	1.03	0.991	0.31	0.979	2.72	0.995	4.64	0.995
Chernozem Arenic	Velké Chvalovice	2.51	0.996	2.54	0.998	0.42	0.984	0.69	0.899	1.38	0.994	2.17	0.996
Greyic Phaeozem	Čáslav	2.95	0.956	3.67	0.999	0.78	0.992	0.74	0.940	1.94	0.936	3.34	0.994
Haplic Luvisol	Hněvčeves	2.91	0.996	3.88	0.999	0.64	0.973	0.76	0.944	1.90	0.976	2.71	0.998
Haplic Cambisol	Humpolec	3.47	0.934	5.78	0.992	0.81	0.997	0.40	0.895	3.49	0.984	3.73	0.994
Haplic Cambisol	Předbořice	4.79	0.924	8.03	0.999	2.52	0.890	1.33	0.953	3.37	0.995	4.41	0.998
Haplic Cambisol	Jince	3.97	0.930	6.92	0.999	1.96	0.892	0.15	0.920	2.88	0.998	3.91	0.998
Dystric Cambisol	Vysoké nad Jizerou	6.35	0.938	11.38	0.999	1.55	0.993	0.59	0.859	6.10	0.984	7.50	0.996
Arenosol Epieutric	Semice	2.70	0.965	3.87	0.994	0.36	0.900	0.64	0.675	2.43	0.981	2.19	0.992
Loess	Praha Suchdol	0.91	0.948	1.08	0.996	0.17	0.895	0.44	0.896	0.77	0.962	0.85	0.909
Sand	Písková Lhota	1.21	0.973	1.20	0.973	0.09	0.932	0.78	0.457	0.30	0.948	0.46	0.954

Soil type	Location	Trifluralin $n = 1$	R^2	Azoxystrobin $n = 1$	R^2	Fipronil $n = 1.54$	R^2	Thiacloprid $n = 1.30$	R^2	Chlormequat chloride $n = 1$	R^2
Stagnic Chernozem Siltic	Milčice	–	–	18.50	0.967	10.60	0.599	9.96	0.993	9.88	0.994
Haplic Chernozem	Ivanovice na Hané	413.12	0.757	10.36	0.898	6.31	0.661	6.74	0.991	10.51	0.991
Haplic Chernozem	Praha Suchdol	423.98	0.741	11.51	0.929	4.97	0.426	8.25	0.985	8.96	0.998
Chernozem Arenic	Velké Chvalovice	263.91	0.830	6.05	0.928	3.92	0.707	3.28	0.977	4.49	0.951
Greyic Phaeozem	Čáslav	345.13	0.915	7.00	0.909	5.87	0.754	4.76	0.971	7.15	0.988
Haplic Luvisol	Hněvčeves	356.24	0.829	11.55	0.985	3.99	0.607	4.20	0.994	7.07	0.988
Haplic Cambisol	Humpolec	641.52	0.854	9.09	0.951	5.54	0.593	4.52	0.993	6.50	0.880
Haplic Cambisol	Předbořice	537.54	0.900	10.71	0.949	6.63	0.583	5.44	0.989	4.12	0.997
Haplic Cambisol	Jince	709.42	0.778	8.75	0.954	5.64	0.397	4.56	0.992	5.30	0.998
Dystric Cambisol	Vysoké nad Jizerou	743.30	0.810	16.17	0.970	8.23	0.615	8.45	0.989	4.31	0.998
Arenosol Epieutric	Semice	338.11	0.910	4.92	0.967	4.92	0.717	2.33	0.995	2.20	0.990
Loess	Praha Suchdol	179.72	0.812	7.35	0.967	2.38	0.524	1.15	0.979	9.80	0.997
Sand	Písková Lhota	126.98	0.758	2.36	0.973	2.30	0.585	0.25	0.933	2.21	0.999

Table 4
Statistical correlations between the K_F coefficients and soil properties: pH_{KCl} , $\text{pH}_{\text{H}_2\text{O}}$, exchangeable acidity (EA), cation exchange capacity (CEC) hydrolytic acidity (HA), basic cation saturation (BCS), sorption complex saturation (SCS), OM (organic matter content), CaCO_3 content, salinity, bulk density (ρ_z), sand, silt and clay content.

	pH_{KCl}	$\text{pH}_{\text{H}_2\text{O}}$	EA	CEC	HA	BCS	SCS	OM	CaCO_3	Salinity	ρ_z	Sand	Silt	Clay
Terbutylazine	-0.584*	-0.574*	0.627*	0.560*	0.717**	0.493	-0.553*	0.855***	0.079	0.083	0.078	-0.267	0.287	0.111
Prometryne	-0.695**	-0.684**	0.763**	0.474	0.842***	0.392	-0.700**	0.750**	-0.037	0.043	0.055	-0.212	0.217	0.125
Metribuzin	-0.560*	-0.539	0.609*	0.451	0.627*	0.392	-0.494	0.667*	-0.014	-0.125	0.242	-0.210	0.215	0.122
Hexazinone	0.117	0.195	-0.246	-0.142	-0.070	-0.137	0.006	-0.081	-0.112	-0.232	0.186	0.192	-0.047	-0.641*
Metolachlor	-0.608*	-0.597*	0.683**	0.574*	0.746**	0.504	-0.587*	0.836***	0.119	0.222	-0.198	-0.271	0.272	0.178
Chlorotoluron	-0.118	-0.105	0.287	0.774**	0.243	0.762**	-0.036	0.925***	0.632*	0.224	-0.481	-0.352	0.347	0.257
Trifluralin	-0.873***	-0.889***	0.877***	0.550	0.907***	0.461	-0.775**	0.834**	-0.416	0.265	0.036	-0.256	0.238	0.233
Azoxystrobin	-0.234	-0.191	0.409	0.840***	0.359	0.816***	-0.076	0.901***	0.528	0.152	-0.487	-0.580*	0.565*	0.448
Fipronil	-0.292	-0.278	0.348	0.734**	0.377	0.706**	-0.209	0.918***	0.444	0.238	-0.409	-0.322	0.350	0.118
Thiacloprid	-0.191	-0.175	0.290	0.798**	0.296	0.780**	-0.032	0.972***	0.415	0.217	-0.439	-0.536	0.547	0.329
Chlormequat chloride	0.297	0.297	-0.094	0.747**	-0.284	0.791**	0.595*	0.433	0.539	0.245	-0.646*	-0.776**	0.738**	0.663*

* $p < 0.05$.** $p < 0.01$.*** $p < 0.001$.

No correlation with pH was obtained for hexazinone (as also mentioned above). The reasons were probably the very low pesticide adsorption ability and a small K_F values variability. Poor correlation between the K_F coefficient and OM was obtained for chlormequat chloride (ionic compound of complete dissociation). Adsorption increased with increasing sorbent surface capacity, which is typical for totally soluble compounds.

The relations between the K_F values for various pesticides and soil properties described using the multiple linear regressions, assuming the Kozák and Vacek [5,6] relationship (after eliminating the independent variables of low significance) are shown in Table 5. It is evident that the worst correlations (R^2 value) and the lowest significance (p value) of the independent variables were obtained for metribuzin and hexazinone. A slightly better correlation and the higher variable significance were obtained for chlormequat chloride. The R^2 value and p value for other pesticide indicated relatively good relationship between the K_F values and applied soil properties. Resulting equations showed that the K_F values for chlorotoluron and azoxystrobin appeared to be dependent solely on organic matter content (positive relationship with OM). The relationship between the K_F values and OM (positive relationship) and pH_{KCl} (negative relationship) was found for prometryne, metribuzin, metolachlor and trifluralin. The K_F value for terbutylazine was positively related with OM, negatively with pH_{KCl} and CEC. The K_F value for thiacloprid was positively related with OM and pH_{KCl} . The positive and negative relationship between the K_F value and OM and clay content, respectively, was found for fipronil. The K_F value for hexazinone was positively related with CEC, negatively with OM and clay content. The K_F value for chlormequat chloride was positively related with pH_{KCl} and CEC, negatively with OM.

Improved correlation between the K_F values and extended set of variables is presented for some pesticides in Table 6. The correlations between the K_F values and soil properties in Table 4 were

assumed when processing multiple linear regressions. The K_F values for terbutylazine and prometryne were positively related with OM and negatively with sorption complex saturation (SCS) and salinity (Table 6). Such relationships were obtained despite of that the second best correlation (Table 4) was found between the K_F values and HA. Better correlations (using the multiple regression analysis) were obtained between the K_F values and combination of OM and SCS ($R^2 = 0.9315, 0.9349$) than K_F and combination of OM and HA ($R^2 = 0.9029, 0.9180$) for terbutylazine and prometryne, respectively. The negative relationship of K_F with SCS and positive with OM was found also for metolachlor. Also in this case, the better correlation was obtained between K_F and combination of OM and SCS ($R^2 = 0.9334$) then between K_F and combination OM and HA ($R^2 = 0.9047$). The K_F value for metribuzin was positively related with OM and soil particle density. The higher R^2 (0.7893) was obtained, when OM and ρ_z were applied then R^2 (0.6029) for OM and HA. The equation for the chlorotoluron and thiacloprid K_F values predictions includes (compared to equation in Table 5) also the CaCO_3 content (positive and negative relationship, respectively). CEC and BCS were not statistically significant in both cases. As expected, the K_F values of hexazinone were positively related with CEC and negatively with clay content and salinity. Impact of OM was not significant. The equation for the K_F value prediction for chlormequat chloride was also very different compared to the equation in Table 5. The K_F value was positively related with pH_{KCl} and salinity, and negatively with sand content (e.g. positively to increased soil particle surface due to presence of clay and silt particles). No improved relationships were obtained for trifluralin, azoxystrobin and fipronil.

Correlations between the K_F values for all pesticides are presented in Table 7. Trifluralin was excluded from analysis due to the high K_F values. Close correlation was found mainly between prometryne, terbutylazine and metolachlor, which was also documented

Table 5
Pedotransfer rules for the prediction of the K_F coefficients ($\text{cm}^{3/n} \mu\text{g}^{1-1/n} \text{g}^{-1}$) from the other physical and chemical soil properties—organic matter content (OM), pH_{KCl} , cation exchange capacity (CEC) and clay content (assumed by Kozák and Vacek [5,6]), which were statistically significant at the 90% or higher confidence level.

Pesticide	Regression equations	R^2	p
Terbutylazine	$K_F = 4.36 + 1.16 \text{ OM} (\%) - 0.38 \text{ pH}_{\text{KCl}} - 0.0064 \text{ CEC} (\text{mmol} + \text{kg}^{-1})$	0.893	0.0001
Prometryne	$K_F = 9.51 + 1.24 \text{ OM} (\%) - 1.24 \text{ pH}_{\text{KCl}}$	0.804	0.0003
Metribuzin	$K_F = 1.74 + 0.28 \text{ OM} (\%) - 0.24 \text{ pH}_{\text{KCl}}$	0.588	0.0118
Hexazinone	$K_F = 0.83 - 0.119 \text{ OM} (\%) + 0.0033 \text{ CEC} (\text{mmol} + \text{kg}^{-1}) - 0.050 \text{ clay} (\%)$	0.576	0.0441
Metolachlor	$K_F = 3.76 + 0.79 \text{ OM} (\%) - 0.50 \text{ pH}_{\text{KCl}}$	0.837	0.0001
Chlorotoluron	$K_F = -0.91 + 2.01 \text{ OM} (\%)$	0.856	0.0000
Trifluralin	$K_F = 839.7 + 80.6 \text{ OM} (\%) - 97.9 \text{ pH}_{\text{KCl}}$	0.904	0.0000
Azoxystrobin	$K_F = 2.51 + 2.89 \text{ OM} (\%)$	0.812	0.0001
Fipronil	$K_F = 2.40 + 1.62 \text{ OM} (\%) - 0.070 \text{ clay} (\%)$	0.883	0.0000
Thiacloprid	$K_F = -1.92 + 2.11 \text{ OM} (\%) + 0.273 \text{ pH}_{\text{KCl}}$	0.957	0.0000
Chlormequat Chloride	$K_F = -4.168 - 0.957 \text{ OM} (\%) + 0.693 \text{ pH}_{\text{KCl}} + 0.037 \text{ CEC} (\text{mmol} + \text{kg}^{-1})$	0.752	0.0044

Table 6

Pedotransfer rules for the prediction of the K_F coefficients ($\text{cm}^{3/n} \mu\text{g}^{1-1/n} \text{g}^{-1}$) from the other physical and chemical soil properties. The statistically significant properties at the 90% or higher confidence level: organic matter content (OM), pH_{KCl} , cation exchange capacity (CEC), particle density (ρ_p), sorption complex saturation (SCS), CaCO_3 content and salinity.

Pesticide	Regression equations	R^2	p
Terbutylazine	$K_F = 5.00 + 1.21 \text{ OM} (\%) - 0.46 \text{ pH}_{\text{KCl}} - 0.0095 \text{ salinity} (\mu\text{S cm}^{-1}) - 0.0060 \text{ CEC} (\text{mmol} + \text{kg}^{-1})$ $K_F = 19.15 + 0.92 \text{ OM} (\%) - 0.19 \text{ SCS} (\%) - 0.0075 \text{ salinity} (\mu\text{S cm}^{-1})$	0.956 0.972	0.0000 0.0000
Prometryne	$K_F = 48.77 + 1.54 \text{ OM} (\%) - 0.50 \text{ SCS} (\%) - 0.0159 \text{ salinity} (\mu\text{S cm}^{-1})$	0.983	0.0000
Metribuzin	$K_F = -7.41 + 0.49 \text{ OM} (\%) + 2.81 \rho_p (\text{g cm}^{-3})$	0.789	0.0004
Hexazinone	$K_F = 0.95 - 0.054 \text{ clay} (\%) + 0.0025 \text{ CEC} - 0.0044 \text{ salinity} (\mu\text{S cm}^{-1})$	0.772	0.0030
Metolachlor	$K_F = 19.91 + 0.85 \text{ OM} (\%) - 0.20 \text{ SCS} (\%)$	0.933	0.0000
Chlorotoluron	$K_F = -0.68 + 1.74 \text{ OM} (\%) + 0.11 \text{ CaCO}_3 (\%)$	0.924	0.0000
Thiacloprid	$K_F = -4.57 + 2.39 \text{ OM} (\%) + 0.636 \text{ pH}_{\text{KCl}} - 0.075 \text{ CaCO}_3 (\%)$	0.973	0.0000
Chlormequat Chloride	$K_F = 1.81 - 0.083 \text{ Sand} (\%) + 1.100 \text{ pH}_{\text{KCl}} + 0.0289 \text{ salinity} (\mu\text{S cm}^{-1})$	0.869	0.0003

Table 7

Correlation matrix between the K_F coefficients of different pesticides.

	Terbutylazine	Prometryne	Metribuzin	Hexazinone	Metolachlor	Chlorotoluron	Azoxystrobin	Fipronil	Thiacloprid	Chlormequat Chloride
Terbutylazine	–	0.970***	0.799***	0.025	0.956***	0.789**	0.790	0.851***	0.817***	–0.027
Prometryne	0.970***	–	0.813***	–0.014	0.951***	0.679***	0.707**	0.760**	0.684**	–0.125
Metribuzin	0.799***	0.813***	–	0.130	0.661*	0.535	0.551	0.626*	0.579*	–0.024
Hexazinone	0.025	–0.014	0.130	–	–0.095	–0.005	–0.039	0.104	–0.037	–0.163
Metolachlor	0.956***	0.951***	0.661*	–0.095	–	0.785**	0.797**	0.837***	0.790**	0.028
Chlorotoluron	0.789**	0.679*	0.535	–0.005	0.785**	–	0.906***	0.954***	0.896***	0.344
Azoxystrobin	0.790**	0.707**	0.551	–0.039	0.797**	0.906***	–	0.831***	0.900***	0.479
Fipronil	0.851***	0.760**	0.626*	0.104	0.837***	0.954***	0.831***	–	0.869***	0.244
Thiacloprid	0.817***	0.684**	0.579*	–0.037	0.790**	0.896***	0.900***	0.869***	–	0.463
Chlormequat Chloride	–0.027	–0.125	–0.024	–0.163	0.028	0.344	0.479	0.244	0.463	–

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

above by the K_F values correlation with the same soil properties (Tables 5 and 6). Correlation was found also among chlorotoluron, azoxystrobin, fipronil and thiacloprid, which was also into some degree described by equations in Tables 5 and 6. Poor correlation of the metribuzin K_F values with the K_F values of other pesticides was observed. Hexazinone and chlormequat chloride did not correlate with any of the other pesticides.

More general equations predicting the K_F coefficients were investigated for several sets of pesticides. First, the sets of the pesticides, of which the K_F values closely correlated to each other, were explored: SET1 (terbutylazine, prometryne and metolachlor) and SET2 (chlortoluron, azoxystrobin, fipronil and thiacloprid). Second, all pesticides SET3 (excluding trifluralin and two differently behaving pesticides hexazinone and chlormequat chloride) were analyzed. All soil (Table 1) and pesticide (Table 2) properties (including the K_D value calculated using Eq. (5)) were assumed. Statistical analysis showed that only one pesticide property (the K_{OC} coefficient incorporated in the K_D value) was significant when estimating the K_F values. Results are shown in Table 8. Since a very good correlation was found between the K_F values in SET1 (Table 7), the very close relationships were found between the K_F values and either K_D , pH_{KCl} and CEC or K_D , SCS and salinity. The equations are

very similar to the equations in Tables 5 and 6. The K_F values depend on the n values. Therefore the n values were also included in the multiple linear regressions. The impact of the n values was less significant, probably because the n values in SET1 (1.21, 1.17 and 1.06 for terbutylazine, prometryne and metolachlor, respectively) varied less considerably than the n values in SET2 (1.2, 1.54, 1.30, and 1 for chlorotoluron, fipronil, thiacloprid and azoxystrobin, respectively). The K_D and n values significantly influenced regressions in SET2 and SET3. The CEC values were also statistically significant in SET2. The equation for SET3 documented that the K_F values mostly depended on the K_D values (e.g. on OM and K_{OC} as is usually suggested), but regression coefficient indicated weak correlation. In addition, the K_{OC} coefficient (Table 2) (and also the K_D coefficient) increased in different orders then the average pesticides adsorption (Table 3) in studied soils. Thus various soil properties (not only organic matter content) should be assumed when predicting pesticide adsorption behavior in various soils.

3.3. The K_F coefficient maps

Resulting maps of the K_F coefficients for selected pesticides are shown in Fig. 2. Resulting K_F values for all pesticides were

Table 8

Pedotransfer rules for the prediction of the K_F coefficients ($\text{cm}^{3/n} \mu\text{g}^{1-1/n} \text{g}^{-1}$) from the other physical and chemical soil properties. The statistically significant properties at the 90% or higher confidence level: $K_D = \text{OM } K_{OC} (1.724 \times 100)^{-1}$ (OM—organic matter content, K_{OC} —organic carbon distribution coefficient), pH_{KCl} , cation exchange capacity (CEC), sorption complex saturation (SCS), and salinity. SET1 (terbutylazine, prometryne and metolachlor), SET2 (chlortoluron, azoxystrobin, fipronil and thiacloprid), SET3 (terbutylazine, prometryne, metolachlor, chlorotoluron, azoxystrobin, fipronil, thiacloprid and metribuzin).

Pesticide	Regression equations	R^2	p
SET1	$K_F = 6.20 + 0.74 K_D (\text{cm}^3 \text{g}^{-1}) - 0.696 \text{ pH}_{\text{KCl}} - 0.0051 \text{ CEC} (\text{mmol} + \text{kg}^{-1})$	0.8274	0.0000
	$K_F = 2.64 + 0.72 K_D (\text{cm}^3 \text{g}^{-1}) - 0.705 \text{ pH}_{\text{KCl}} - 0.0046 \text{ CEC} (\text{mmol} + \text{kg}^{-1}) + 3.14n$	0.8352	0.0000
	$K_F = 29.28 + 0.69 K_D (\text{cm}^3 \text{g}^{-1}) - 0.295 \text{ SCS} (\%) - 0.0085 \text{ salinity} (\mu\text{S cm}^{-1})$	0.9087	0.0000
	$K_F = 25.49 + 0.67 K_D (\text{cm}^3 \text{g}^{-1}) - 0.296 \text{ SCS} (\%) - 0.0082 \text{ salinity} (\mu\text{S cm}^{-1}) + 3.43n$	0.9184	0.0000
SET2	$K_F = 12.35 + 0.50 K_D (\text{cm}^3 \text{g}^{-1}) + 0.0106 \text{ CEC} (\text{mmol} + \text{kg}^{-1}) - 9.58n$	0.6811	0.0000
SET3	$K_F = 10.82 + 0.71 K_D (\text{cm}^3 \text{g}^{-1}) - 7.94n$	0.6711	0.0000

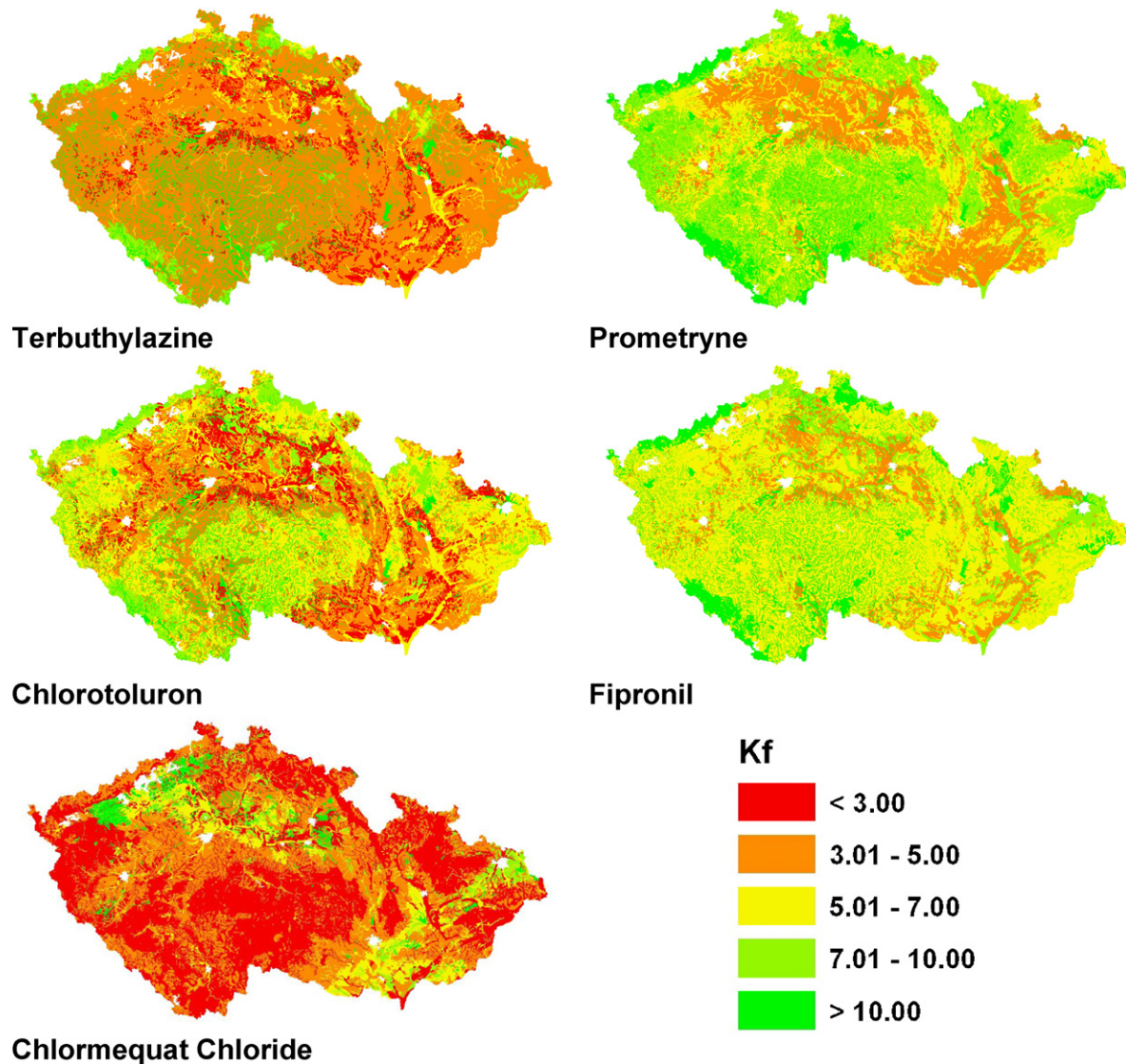


Fig. 2. The K_F coefficient of the Freundlich equation ($\text{cm}^3/n \mu\text{g}^{1-1/n} \text{g}^{-1}$) in soils of the Czech Republic.

influenced by OM (positively for terbutylazine, prometryne, chlorotoluron and fipronil and negatively for chlormequat chloride). While chlorotoluron adsorption parameters were calculated solely from the OM, the impact of other properties was variable for the other pesticides. The increasing pH_{KCl} and CEC values noticeably decreased terbutylazine sorption in soils with high OM. Similarly the increasing pH_{KCl} value evidently decreased prometryne sorption in soils with high OM. The impact of the clay content on the calculated K_F values seemed to be less important. On the other hand the K_F values of chlormequat chloride considerably increased with increasing CEC and pH_{KCl} values. Inclusion of other relevant soil properties (Table 6), which are not at present available in the PUGIS database, is required to increase reliability of the K_F coefficients distributions predictions.

4. Conclusions

Analysis in some degree verified previous findings, which were summarized in the introduction part. While relationships of high significance were obtained for basic pesticides of moderate solubility and moderate adsorption ability (terbutylazine and prometryne), relationships of the lowest significance were obtained for basic pesticides of large solubility and low adsorption

ability (metribuzin and hexazinone). Terbutylazine adsorption proved to correlate with OM. In addition, the multiple linear regressions showed that the K_F coefficient depended on combination either of OM, pH_{KCl} and CEC, or OM, SCS and salinity. The correlation between the K_F coefficients for prometryne and OM was less significant (as Oliver et al. [16]). However, the multiple linear regressions showed that the K_F coefficient depended on combination either of OM and pH_{KCl} , or OM, SCS and salinity. Results indicated that soil pH more impacted prometryne than terbutylazine adsorption due to $\text{p}K_a$ between 3 and 10 [8] (larger $\text{p}K_a$ than for terbutylazine), which is in agreement with findings of Wauchope et al. [52]. Similarly to findings of Garcia-Valcarcel et al. [17] a weak correlation was found between the K_F coefficient for metribuzin and studied soil properties. The multiple linear regressions showed that the R^2 values were slightly improved when including either OM and pH_{KCl} , or OM and ρ_z . No correlation was found between the K_F coefficient for hexazinone and OM on the contrary to Calderon et al. [20]. The K_F coefficient negatively correlated with clay content. Slightly better correlation was obtained using the multiple linear regressions and including either OM, CEC and clay content, or clay content, CEC and salinity. Large solubility and very low adsorption ability considerably impacted obtained results in these two cases.

Adsorption of nonionic pesticides closely correlated with OM, but in some cases various additional soil properties improved regressions, i.e. enhanced pesticide sorption. The K_F coefficient for metolachlor proved to correlate with OM. The multiple linear regressions showed that the K_F coefficient depended on combination either of OM and pH_{KCl} , or OM and SCS. The K_F coefficients for chlorotoluron and azoxystrobin proved to correlate with OM. In the case of chlorotoluron, the K_F coefficient relationship with the OM and CaCO_3 was documented. The K_F coefficient for trifluralin correlated with OM (as expected), but the best correlation with hydrolytic acidity was found. The relationship between the K_F coefficient, and OM and pH_{KCl} was obtained. The good correlation was observed between the K_F coefficient for fipronil and OM as expected. In addition the relationship between the K_F value, and OM and clay content was obtained. Good correlation was found between the K_F coefficient for thiacloprid and OM on the contrary to Oliver et al. [35]. The relationships between the K_F value, and either OM and pH_{KCl} , or OM, pH_{KCl} and CaCO_3 were also obtained.

Finally, poor correlation between the K_F coefficient and soil properties was found for chlormequat chloride (ionic compound of complete dissociation), probably due to total solubility and ionisation. The relationships between the K_F value and either OM, pH_{KCl} and CEC, or sand content, pH_{KCl} and salinity were explored.

Results showed, that there is no general equation, which may be used to predict the K_F values for various soils and pesticides. Very good regression between the K_F values and some soil properties and K_{OC} values (included in the theoretical K_D values) was found only for the set of 3 pesticides (terbutylazine, prometryne and metolachlor).

Resulting equations for predicting the K_F coefficients (pedotransfer rules) for particular pesticides were used to generate maps of the K_F values. Maps of the K_F coefficients distributions will be considered when evaluating pesticides groundwater vulnerability using modified DRASTIC methodology. Proposed pedotransfer rules may be also used to estimate pesticide sorption parameters, which are required for simulating water flow and contaminant transport in soils mathematically. Various mathematical models have been developed to predict potential pesticide leaching into the deeper layers and subsequently into the ground water. See for instance a review paper by Köhne et al. [53,54]. Measured data and proposed functions may be applied to solve particular problems in a local (soil profile or soil sample) scale or in regional and global scale [55,56]. Thus presented results may help solving particular problems not only within the Czech Republic, but also in regions with similar soil conditions.

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