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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 (terbuthylazine), (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).

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 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 (pK_a) and base (pK_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.

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

Terbuthylazine 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-oxyhydroxides 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 pH_{H_2O} 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:

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

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 cm^3 glass bottle. 20 cm^3 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