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Imidacloprid adsorption by soils treated with humic substances under different pH and temperature conditions

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The mobility of a pesticide in soil is determined by the extent and strength of sorption, which is influenced by either the existing soil humus or exogenous humic substances. Exogenous humic acids (HAs) were added to soil to enhance the amount of soil organic carbon (SOC) by 2.5, 5.0 and 10.0 g kg^{-1}. Imidacloprid sorption of the treated soils was studied at three pH levels (4.5, 6.0 and 7.5) and two temperatures (15 and 25°C). Soil imidacloprid adsorption was related to pH and the type and quantity of added HAs. Humic acid (HA) and fulvic acid (FA) derived from peat had different effects on adsorption of imidacloprid. When soil solution pH was 6, the amount of adsorbed imidacloprid was enhanced with increasing exogenous HA. On the contrary, the amount of adsorbed imidacloprid decreased with increasing quantity of exogenous FA. Adsorption of imidacloprid in the FA treatment at 5.0 and 10.0 g kg^{-1} was lower than the controls (untreated soil or treatment with HAs at 0 g kg^{-1}) when the soil solution pH was 6.0. However adsorption of imidacloprid in the HA treatment was higher than the controls. Imidacloprid adsorption was usually higher under lower pH and/or lower temperature at same condition. Imidacloprid sorption fitted the Freundlich isotherm, indicating that exogenous humic substances influenced adsorption of imidacloprid, which in turn was affected by environmental conditions such as pH and temperature. Thus, exogenous HA can be used to control the mobility of soil pesticide under appropriate conditions to decrease pesticide pollution diffusion and probably increase effectiveness of pesticides.

Key words: Imidacloprid, soil adsorption, humic acid, fulvic acid.

INTRODUCTION

Progressive increase of production and application of chemicals for agriculture as well as for plant protection and animal health has converted the problem of environmental pollution into national and international issues (Capel et al., 1995; Torrents et al., 1997).

Sorption is one of the most important factors that affects the fate of pesticides in the soil and determines their distribution in the soil/water environment, which is widely used to describe the process of a pesticide partitioning between water solution and soil (Gawlik et al., 1997). Sorption also determines availability of pesticides in the soil solution that governs the amount of pesticide that is available for uptake by plants and the effectiveness of pesticides (Walker, 2000). It is reported that adsorption is one of the most important processes which controls all other processes such as their movement, persistence and degradation and determines the fate of pesticides in soil systems (Baer and Calvet, 1999)

It is well known that soil organic matter (SOM) properties affect the sorption of organic molecules (Ahmad et al., 2009). pH of soil can also affect sorption of organic molecules by influencing ionization of the organic molecule as well as affecting accessibility of different organic

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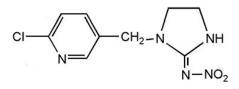
Figure 1. Structure of Imidacloprid.

matter functional groups (Khan, 1978). Therefore the relationship between SOM and pesticides is of major interest. Although several studies have shown an increase in sorption of pesticide with increasing amount of SOM (Mallawatantri and Mulla, 1992; Conzalez and Ukrainczyk, 1996; Bekbolet et al., 1999), little is known about the effects of SOM composition. Humic substances are the dominant organic components in soils (Stevenson, 1994) and generally comprise more than 70% of SOM. Sorption of pesticides to humic substances associated with soil or the aquifer solid phase usually inhibits their transport (Sensi et al., 1994). On the other hand, binding to dissolve humic substances will facilitate desorption from the solid phase and thereby enhance pollutant transport (Rebhun et al., 1996; Spark and Swift, 2002). There is little information on the sorption of pesticides in soils associated with exogenous humic substances. It is necessary to study pesticide sorption of soils treated by humic substances to obtain the theoretical foundation for the use of humic substances to control soil pesticide mobility, reduce the diffusion of pesticide in soils and enhance the effectiveness of pesticides.

Imidacloprid   [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine] (Figure 1), is a systemic insecticide with a novel mode of action introduced to the market with the commercial names Admire, Gaucho or Confidor. The solubility of imidacloprid is 0.51 g/l in water (20°C). Imidacloprid is effective for controlling aphids, whiteflies, thrips, scales, psyllids, plant bugs and various other harmful pest species, including resistant strains. This pesticide is used as seed-dressing, soil treatment and foliar treatment in different crops (Bai et al, 1991; Liu et al., 1995; Tomlin, 1999). Since the imidacloprid has been extensively used in agricultural areas and drawn attention as a promising insecticide (Heijbrock and Huijbregts, 1995; McTier, et al., 2003), so the transport, retention and transformation are more and more of a public concern.

The aim of the present work was to obtain information on the role of exogenous humic substances on the capacity of a soil to adsorb imidacloprid. We have investigated the sorption of imidacloprid on a soil treated with humic substances under different pH and temperature conditions.

MATERIALS AND METHODS

Soil and chemicals

Samples of the 0 - 20 cm layer of an agricultural soil (Ferralsols by

UN WRB taxonomy) were collected from Tiantai City, Zhejiang Province, southeast China. The samples were air-dried and passed through a 1 mm sieve, which has the following composition and characteristic: pH (measured in distilled water) 7.1, organic matter 10.0 g kg^{-1}, sand (> 0.01 mm) 71.2% and clay (< 0.01 mm) 28.8%, and cation-exchange capacity 9.49 cmol kg^{-1}.

Imidacloprid (purity 99%) was supplied by Bayer (Germany). A stock standard solution was prepared by dissolving 10.1 mg of imidacloprid in 100 ml of 0.01 M CaCl$_2$ solution and stored at 4°C. All solvents were filtered through a 0.45 μm Millipore membrane filters before injection.

HAs extraction

Relatively pure HA and FA were extracted from a peat from Heilongjiang province, northeast China, according to the procedures recommended (Swift, 1996) by the International Humic Substances Society with one modification: after passing through an XAD-8 resin column, the FA solution was passed through XAD-2 resin. A Perkin Elmer CHN S/O Series II 2400 Element Analyzer was used to measure HAs. HAs was ashed by incineration at 750°C for 5 h after drying to constant weight at 105°C, then calculated by differences.

The elemental composition (% by weight) of the HA was 55.03 C, 5.74 H, 3.35 N and 1.0 ash. The corresponding values for the FA were 43.52 C, 4.54 H, 1.74 N and 4.1 ash.

HA and FA addition to soil

Three weights (0.125, 0.250 and 0.500 g) of HAs (HA or FA) were dissolved in 50 ml of deionized water, mixed well with 50.0 g soils and air-dried for about 10 days at room temperature, then passed through a 1 mm sieve. Addition of HAs increased the soil organic carbon content of the samples by 2.5, 5.0 and 10.0 g kg^{-1}, respectively.

Adsorption studies

Individual adsorption experiments were conducted in triplicate for the purpose of reproducibility and reliability. 0.01 M CaCl$_2$ water solution as background solution was adjusted by adding the least amount of 0.1 M NaOH and 0.1 M HCl that background solution pH was 4.5, 6.0, 7.5. 50 mg l^{-1} NaN$_3$ was added to each reactor as a biocide to prevent any microbial activity during the sorption studies. Soil samples (2.00 g) was weighted into each flask and placed with 10 ml of 0.01 M CaCl$_2$ solution. The imidacloprid concentration in the solutions were 1.0 and 5.0 mg l^{-1}. Samples were equilibrated for 16 h in the dark on an oscillating shaker (180 rpm) at room temperature (25°C). Imidacloprid volatilization and degradation were found to be negligible during the experimental procedure by blank experiment.

Imidacloprid sorption-isotherm experiment

Individual adsorption experiments were conducted in triplicate to ensure reproducibility and reliability. Treated soils with a 10 g kg^{-1} increase in organic carbon and untreated controls were used. A series of imidacloprid concentrations of 0, 0.2, 0.5, 1.0, 2.5 and 5.0 mg l^{-1} were prepared. And the solution pH was adjusted by adding the minimum amount of 0.1 M NaOH or 0.1 M HCl. The pH of background solution was 6.0. The experiment temperatures were 15 and 25°C. Other procedures have been described previously.

In the blank experiments with the soil samples, imidacloprid was not detected in CaCl$_2$ water solution following the equilibration of the sample with background solution without addition of imidacloprid.

These materials did not interfere with the quantities of imidacloprid in solution in sorption experiments.

Imidacloprid analysis

After equilibrium, solution and solid phases were separated by centrifugation at 3,500 rpm for 10 min and then the equilibrium solution was filtered (0.45 μm). Concentrations of imidacloprid in equilibrium solution (Ce) were analyzed with HPLC fitted with BDS (250 × 4 mm I.D., 5 μm particle size) using acetonitrile-water (40:60) as the mobile phase at a flow rate of 1 ml min^{-1}. Chromatography column was performed at 40°C. Imidacloprid was detected at 270 nm and its retention time was 3.8 min.

Calculation of the amount of imidacloprid adsorbed

The amount of imidacloprid adsorbed (Q) was calculated by the following equation:

$$Q = (C_0-Ce)*V_0/m$$

where C_0 was the concentration of background solution, V_0 was the bulk of background solution, and m was the weight of dry soil.
All experiments were performed in triplicate and the mean values were taken.

RESULTS AND DISCUSSION

Effect of HA on imidacloprid adsorption

The adsorption of imidacloprid (the concentration of background solution were 0.5 and 5.0 mg l^{-1}, respectively) in the soils at 25°C and pH 6.0 is presented in Figures 2a and b. When the soil solution pH was 6.0, the amount of adsorbed imidacloprid was enhanced with increasing exogenous HA. Adsorption of imidacloprid in the HA treatment was higher than the controls. Imidacloprid is a medium molecular weight (255.7), neutral and polar organic molecule. It is easy to dissolve in polar organic matter and it is easier adsorbed by soil organic matter (Xuan et al., 2000). In the other hand, addition of exogenous HA to soils may increase the soil surface area, which provide additional hydrophobic sites and lead to increase in the amount of pesticide adsorption (Johnson et al., 1997; Guo et al., 1993). However, the amount of adsorbed imidacloprid decreased with increasing quantity of exogenous FA. Adsorption of imidacloprid in the FA treatment was lower than the controls. This could increase the mobility and leaching potential of imidacloprid.

The maximum adsorption and minimum adsorption were in the HA 10.0 g kg^{-1} treatment and FA 10.0 g kg^{-1} treatment, respectively, when the soil solution pH was 6.0. Figure 2c shows the sorption of imidacloprid on the HA treatment in pH 6.0 condition, where the amount of imidacloprid uptake by soil (Q) was plotted against the concentration of equilibrium solution (Ce). The results showed the effects of different amount of HA added in the order: 10.0 > 5.0 > 2.5 g kg^{-1}.

In this study, imidacloprid distribution in soil FA and HA

did not agree with other studies (Kohl and Rice, 1998), since the pesticide sorption was influenced by differences in the chemical nature of the organic carbon present in the soils (Oliver et al., 2005). Imidacloprid adsorption in a calcerous soil decreased with the addition of organic carbon (obtained from peat and tannic acid) (Flores-Cespedes et al., 2002), which perhaps contributes to the different organic compounds characteristics, the different sources of HAs and/or different characteristics of soil native and exogenous HAs.

Effect of temperature

The sorption isotherms of imidacloprid in pH 6.0 conditions are presented in Figure 3, where the amount of imidacloprid uptake by soils (Q) is plotted against the equilibrium imidacloprid concentration (Ce). The results showed that adsorption capacities of the treated soils with increasing 10 g kg^{-1} organic carbon and 0 g kg^{-1} HAs treated soil (CK) are higher when experiment temperatures is 15°C than that is 25°C. The reason is that elevated temperature can enhance imidacloprid solubility (Kong et al., 2008) and the sorption process is an exothermic reaction mainly of physical type (Dios Cancela et al., 1992). Under greenhouse conditions, where the temperature is high, the amount of insecticide sorption would diminish, implying increased release into the environment (Fernandez-Bayo et al., 2007). In addition, increasing temperature can perhaps change 'characters of humic substances' such as adsorption to mineral and surface area that influences imidacloprid adsorption.

Amount of adsorbed imidacloprid is enhanced with increase of imidacloprid solution concentration over the range of concentrations (0.20 ~ 5.0 mg/l) studied in this experiment. This indicated that adsorption of imidacloprid on soil is not yet saturation, when imidacloprid concentration is 5.0 mg/l.

It is widely found that pesticide sorption isotherms are nonlinear and the isotherm nonlinearity depends largely on the properties of the soil or sediment and physicochemical characteristics of the pesticide (Yazgan et al., 2005; Li et al., 2003). The most commonly used model for quantifying pesticide sorption equilibrium for soils is the Freundlich model having the following form: $Q = K_f C_e^n$, where K_f and n are Freundlich model capacity factor and the isotherm linearity parameter, an indicator of site energy heterogeneity.

Table 1 shows the sorption of imidacloprid fit to the Freundlich isotherm and Freundlich isotherm parameters are presented. All isotherms were nonlinear, that is n < 1. The n values of imidacloprid ranged from 0.8935 to 0.9556. The n values of HA treatment are the lowest among three treatments that indicates soil treated by HA has more heterogeneous sorption sites. Perhaps soil treated by FA has many heterogeneous sorption sites too, but because in pH 6.0 condition more amount of FA absorbed soil minerals are dissolved and would then
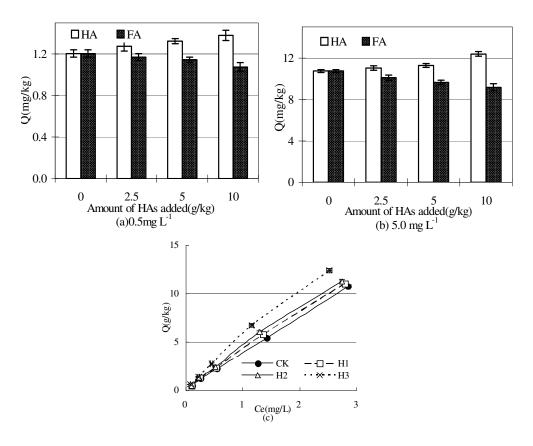
Figure 2. Adsorption of imidacloprid in differently treated soils (n = 3). H1, H2, and H3 were exogenous HA added to soil to enhance the amount of soil organic carbon (SOC) by 2.5, 5.0 and 10.0 g kg^{-1}, respectively.
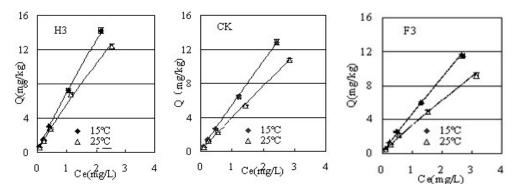

Figure 3. Sorption isotherms for imidacloprid on soils (n = 3). H3 and F3 refer to exogenous HA and FA added to soil to enhance the amount of soil organic carbon (SOC) by 10.0 g kg^{-1}, respectively.

Table 1. Freundlich constants and their coefficient for imidacloprid in soil.

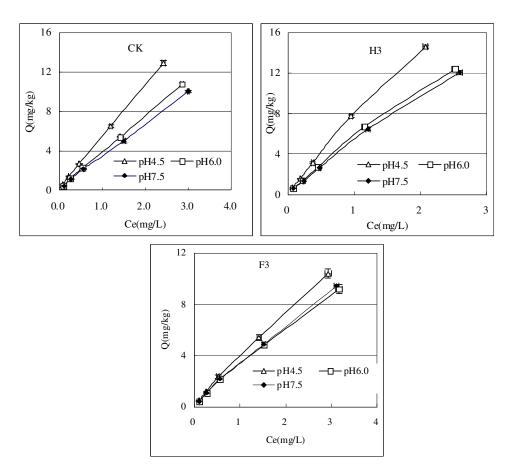| Treatment	15°C			25°C		
	K_f	N	R^2	K_f	n	R^2
10 g kg^{-1} HA (HA3)	6.944	0.9127	0.9987	5.5662	0.8935	0.9986
0 g kg^{-1} HA (CK)	5.4701	0.9556	0.9982	3.9837	0.9505	0.9979
10 g kg^{-1} FA (FA3)	4.6542	0.9483	0.9978	3.3129	0.9195	0.9975

Figure 4. Adsorption of imidacloprid under different pH conditions (n = 3).

increase imidacloprid solubility and decrease adsorption, then present the less sorption sites. Sorption coefficients (K_f) of imidacloprid ranged from 3.3129 to 6.944. It is apparent that K_f values of HA treatment is much larger than CK and FA treatments. This may be attributed to the adsorption capacities difference among three treatments. HA treatment has higher adsorption capacities than FA treatment and CK. Higher imidacloprid sorption in humic acid treatment may be due to the stronger affinity to the highly aromatic moieties.

The low Koc values determined for imidacloprid in the soils and its high water solubility suggest a high leaching potential (Fernandez-Bayo et al., 2007).There are many reports showing that sorption did not inhibit or even enhanced biodegradation of sorbed compounds (Ortega-Calvo et al., 1997), because sorbed compounds were still bioavailable, which decreased the pesticide diffusion and perhaps increased the effectiveness of pesticide. In addition, as carbon sources, exogenous humic substances can be used by microorganism and stimulate microbial activities, then increase the contaminants degradation and disappearance. So exogenous humic substances can be used to control soil pesticide mobility in appropriate condition, decreased pesticide pollution diffusion and increased pesticide disappearance.

Effect of pH

Adsorption of imidacloprid on the soil under different pH conditions is shown in Figure 4. Figure 4 shows that the adsorption capacities in all treatments were greatest when soil solution pH was 4.5 (low pH), irrespective of whether the soils were treated with HAs. Adsorption capacities decreased with increasing pH to an extent similar to that observed in other studies (Sheng et al., 2005). The effect of pH is probably due to the increased polarity of the humic material and the electrostatic interaction of cationic pesticide with soil particles at higher pH. High-selectivity sorption of organic cation by soils or minerals has been reported (Xu et al., 1997). A more polar humic substance would have a lower affinity for hydrophobic compounds. Schlautman and Morgan (1993) also suggested that the increase in the humic polarity altered its structure and therefore affected its capacity for hydrophobic interactions. At the same time there are other media, such as soil minerals and suspended grains in water and lower pH may increase the amount of humic substances (especially HA) adsorbed to these media (Laor et al., 1998). Adsorption of imidacloprid in the HA treatment was strong at low pH (Figure 4), in which imidacloprid adsorption was higher

than the control (0 g HAs kg^{-1}) at soil solution pH 4.5 and 6.0.

Conclusion

Soil imidacloprid adsorption was related to environment condition, types and amount of added HAs as follows: i) Humic acid (HA) and fulvic acid (FA) with the same sources had different effects on adsorption of imidacloprid, adsorption of the soil treated by HA is higher than FA in most condition. ii) Influence of humic substances on imidacloprid adsorption was affected by environmental condition such as pH and temperature. Adsorptions were higher in lower pH and/or lower temperature in most treatments. iii) The sorption of imidacloprid fitted to the Freundlich isotherm.

Exogenous humic substances influenced adsorption of imidacloprid, which was affected by environmental condition. Exogenous humic substances can be used to control soil pesticide mobility in appropriate condition and decrease pesticide pollution diffusion, thereby reducing the risk of leaching to groundwater aquifers.

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