# Effects of nano-SiO$_2$ on the adsorption of chiral metalaxyl to agricultural soils ☆

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## ABSTRACT

The application of nanotechnology in agriculture, pesticide delivery and other related fields increases the occurrence of engineered nanoparticles (ENPs) in soil. Since ENPs have larger surface areas and normally a high adsorption capacity for organic pollutants, they are thought to influence the transport of pesticides in soils and thereafter influence the uptake and transformation of pesticides. The adsorption pattern of racemic-metalaxyl on agricultural soils including kinetics and isotherms changed in the presence of nano-SiO$_2$. The adsorption of racemic-metalaxyl on agricultural soil was not enantioselective, in either the presence or the absence of SiO$_2$. The adsorption of racemic-metalaxyl on SiO$_2$ decreased to some extent in soil-SiO$_2$ mixture, and the absolute decrease was dependent on soil properties. The decreased adsorption of metalaxyl on SiO$_2$ in soil-SiO$_2$ mixture arose from the competitive adsorption of soil-dissolved organic matter and the different dispersion and aggregation behaviors of SiO$_2$ in the presence of soil. Interactions between SiO$_2$ and soil particles also contributed to the decreased adsorption of metalaxyl on SiO$_2$, and the interactions were analyzed by extended Derjaguin—Landau—Verwey—Overbeek theory. The results showed that the presence of nano-particles in soils could decrease the mobility of pesticides in soils and that this effect varied with different soil compositions.

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## 1. Introduction

Large amounts of a range of pesticides have been applied agriculturally to reduce the undesirable effects of pests; among these, chiral pesticides account for more than a quarter of all pesticides currently in use (Garrison, 2006; Ulrich et al., 2012). Because of the high cost of chiral separation of enantiomers and the lack of concern about enantioselective effects, most chiral pesticides are used as racemates (Kasprzyk-Hordern, 2010; Lewis et al., 1999). Although the physicochemical properties of different enantiomers are comparable and no enantioselective difference in chemical transformation has been observed, enantioselectivity has a significant impact on pharmacodynamics, pharmacokinetics, environmental fate, and ecological effects. Enantioselective degradation of chiral pesticides in various environmental media has been reported (Celis et al., 2013; Chen and Liu, 2009; Liu et al., 2005; Maillard et al., 2016), and it has been suggested that enantioselective transformations occurred mostly in microorganisms or enzyme-dominated biotransformations (Müller and Kohler, 2004; Ribeiro et al., 2013).

Adsorption/desorption is a key process controlling transport, biodegradation, and bioavailability (Alonso et al., 2015; Guo et al., 2000; Sims et al., 1991). For chiral pesticides, enantioselective adsorption to soil, sediments, or aquatic components would govern the amount of enantiomers available for enantioselective degradation and bioavailability (Celis et al., 2013; Garrison, 2006). A large body of work has focused on enantioselective degradation; however, investigations into adsorption of chiral pesticides onto soils are limited, and the process was not fully understood. It has been reported that adsorption of metalaxyl is influenced by soil pH, soil organic matter (SOM) content, the ratio of enantiomers, and other factors (Celis et al., 2015; Fernandes et al., 2003; Gondar et al., 2013). For example, a dependence of metalaxyl adsorption to soils on soil pH values lower than 5.0 has been reported, while no relationship was found for pH values higher than 5.0, and negative charges distributed on SOM surfaces could also influence the adsorption of metalaxyl (Gondar et al., 2013). The adsorption of chiral metalaxyl on soil from non-racemic solutions is enantioselective, while nonenantioselective adsorption has been reported from racemic solutions (Celis et al., 2015). Sorption-desorption

isotherms have indicated that the sorption of metalaxyl enantiomers on unamended and on olive-mill waste (OMW)-amended soil (2% w/w) is nonenantioselective (Gámiz et al., 2013). Although the adsorption quantities of metalaxyl enantiomers on soil were mostly unchanged in the presence of OMW, adsorption appeared to increase in the presence of biochar prepared from OMW (Gamiz et al., 2016).

Various ENPs have entered agricultural soils after increasing application in modern agriculture (Kookana et al., 2014), food technology (Das et al., 2009), soil remediation (Gardea-Torresdey et al., 2014), and the addition of biosolid to agricultural soils (Peralta-Videa et al., 2011). It has been reported that >97% of SiO$_2$ nanoparticles were incorporated into sludge biomass with initial concentration between 10 ppb and 10 ppm (Grass et al., 2014), which suggested that SiO$_2$ can enter soil in biosolid amended process (Yang et al., 2014). Because of their potential detrimental effects on the terrestrial environment, ENPs have been categorized as an emerging pollutant (Westerhoff, 2009). Recently, researches have been undertaken into ENP transport in soils (Darlington et al., 2009), the uptake and accumulation of ENPs by terrestrial plants (Deng et al., 2014; Zahra et al., 2015), the effects of ENPs on soil microbial community compositions and activities, and the influence of ENPs on the uptake and transport of co-existent pollutants including pesticides and metal ions (Deng et al., 2014; Dinesh et al., 2012; Jin et al., 2014; Liang et al., 2016; Oloumi et al., 2014). For example, it has been showed the presence of TiO$_2$ or SiO$_2$ enhanced both chemical and biological degradation of racemic-metalaxyl (*rac*-metalaxyl) in agricultural soils (Liang et al., 2016). It has also been reported that the accumulation of *p,p'*-DDE in whole *Glycine max* L. plants was reduced by 34% and 40% after exposure to nano-Ag at concentrations of 500 and 2000 mg/L, respectively (De la Torre-Roche et al., 2013). Notably, the effects of ENPs on the bioaccumulation of organic pesticides and ENPs themselves by plants in soils were quite different from those generated in hydroponic experiments (Deng et al., 2014). These results suggested that the properties of ENPs changed to some extent after introduction into the soil environment. Since the adsorption of organic pollutants on ENPs is usually substantial, it is reasonable to assume that the adsorption of organic pollutants will be increased by the presence of ENPs in soils. However, the interactions within soil, ENPs, chiral pesticides and the subsequent influence on the enantioselective adsorption of chiral pesticides have not been well explored. Therefore, it is worthwhile investigating the effects of ENPs on the sorption of chiral pesticides to soils.

It has been reported that nano-SiO$_2$ could be used as a fertilizer to enhance seed germination and stimulate antioxidant system of crops (Ranjan et al., 2016), and could also be used for pesticide delivery (Nuruzzaman et al., 2016), which would increase the opportunity for SiO$_2$ entering terrestrial system. Therefore, nano-SiO$_2$ was chosen as ENP proxy in the present study. The first objective of this study is to reveal the extent to which the adsorption of chiral metalaxyl on soil is influenced by the presence of SiO$_2$. The second objective is to quantify the adsorption changes of *rac*-metalaxyl on SiO$_2$ nanoparticles after it entering the soil and to reveal the pathway through which such change occurs. This work should help to reveal the influence of ENPs on the transport and transformation of metalaxyl in the terrestrial environment.

## 2. Experiments and methods

### 2.1. Chemicals and soil samples

#### 2.1.1. Chemicals

Racemic-metalaxyl (*rac*-metalaxyl, 98%) was purchased from Aladdin (Shanghai, China) and nano-SiO$_2$ (Degussa Aerosil A380;

average surface area: 380 m$^2$/g; particle size: 7 nm) was purchased from Degussa AG (Marl, Germany). All organic solvents (HPLC grade) and other chemicals were of the highest commercially available purity. A stock solution of *rac*-metalaxyl (400 mg/L) and other solutions were prepared using ultrapure water (resistivity > 18.2 MΩ cm).

#### 2.1.2. Soil samples

Three different soil samples were collected from Wuhan (S1), Chongqing (S2) and Qianjiang (S3) along the Yangtze River (China) at a depth of 10 cm. The soils were air-dried, gently crushed, sieved (2 mm), and stored at room temperature. Pre-experiments showed that there was no metalaxyl in these soil samples. Soil properties analysis was completed according to the procedure that described in Pansu and Gautheyrou (2006). Clay minerals quantification was performed based on the area of the corresponding peaks from X-ray diffraction spectra. The characteristics of soil samples are listed in Table 1.

#### 2.1.3. Soil samples with low organic matter (S1-LOM)

The organic carbon in soil S1 was partially removed by hydrogen peroxide (H$_2$O$_2$) oxidation (Pansu and Gautheyrou, 2006). Specifically, 10 g of soil samples were added to 100 mL of H$_2$O$_2$ solution (1%), the dispersion was left in contact for one hour, and then it was heated at 60 °C. 30% H$_2$O$_2$ was added slowly until effervescence stopped and then the sample was maintained for another 5 h. Surplus H$_2$O$_2$ was removed by boiling the solution at 105 °C. The dispersion was stirred with a glass rod to suspend the sample during the whole process. The dried sample was sieved (2 mm) and stored at room temperature and used as S1-LOM. The final organic carbon content in the S1-LOM sample was 0.5%.

#### 2.1.4. Soil extraction solutions

Soil samples were added to ultrapure water at different soil/water ratios (1 g/20 mL, 1 g/10 mL, 1 g/5 mL, and 1 g/2.5 mL) and then the suspensions were shaken for 6 h (250 rpm, 25 °C). The extraction solutions were separated by centrifugation (4000 rpm, 10 min) followed by filtration using a glass microfiber filter (Whatman, pore diameter = 0.7 μm). Unless otherwise stated, soil extraction solution was obtained at a soil/water ratio of 1 g/5 mL. Physicochemical properties of soil extraction solutions are listed in Table S1 (Supporting Information).

### 2.2. Adsorption of rac-metalaxyl on soils in the presence or absence of SiO$_2$

#### 2.2.1. Adsorption kinetics

The adsorption kinetics of *rac*-metalaxyl was investigated in soil, SiO$_2$, and soil-SiO$_2$ mixture. Soil samples weighing 8 g were first added to a 100-mL Erlenmeyer flask, followed by the addition of 40 mL of a 4.5 mg/L *rac*-metalaxyl aqueous solution. The dispersion was then shaken using a reciprocal shaker at 250 rpm at a temperature of 25 °C in the dark. Aliquots (2 mL) were pipetted from this sole flask at different time intervals (0, 2, 5, 10, 15, 20, 30,

**Table 1**
Physicochemical properties and clay mineralogy of the soil samples.

| Soils | pH | CEC cmol/kg | OC% | soil texture | | | clay mineralogy[a] | | |
|-------|-----|------|------|------------|----------|----------|--------|--------|--------|
| | | | | Sand (%) | Silt (%) | Clay (%) | V (%) | I (%) | K (%) |
| S1 | 7.0 | 11.8 | 0.95 | 10.0 | 64.6 | 25.4 | 6.0 | 74.0 | 20.0 |
| S2 | 5.8 | 2.9 | 1.23 | 24.0 | 54.0 | 22.0 | 14.3 | 52.6 | 33.1 |
| S3 | 8.0 | 12.0 | 0.75 | 60.3 | 30.5 | 9.2 | 27.8 | 55.6 | 16.5 |

[a] V, I and K represents vermiculite, illite and kaolinite, respectively.