

## **Report for 2002WA12B: Facilitated Transport of Pesticides by Organic Colloids**

- Water Resources Research Institute Reports:
  - Flury, Markus, Claudio O. Stockle, and Richelle Allen-King, 2003, Facilitated Transport of Pesticides by Organic Colloids, State of Washington Water Research Center, Washington State University, Pullman, Washington, State of Washington Water Research Center Report WRR-13, 25 pp.

Report Follows

## **Problem and Research Objectives**

The presence of pesticide in ground water is of great concern for groundwater quality. National monitoring programs have found pesticides in shallow and confined aquifers. For instance, the National Water Quality Assessment (NAQWA) reported that 48.4% of the 2,485 wells sampled in the United States contained evidence of pesticides. Atrazine is the most common pesticide reported in groundwater in the United States and Europe. This pesticide is widely used in both agricultural and industrial land for the control of weeds.

There are several studies that link the presence of colloids with the enhancement of pesticide mobility, under both laboratory and field conditions. In addition, there is direct evidence that the presence of colloids enhances the movement of atrazine. But due to the large amount of different colloids, the current information allows only general conclusions that cannot be used in the assessment of the overall movement of pesticides.

One kind of colloid that is particularly important is natural and artificial organic matter that possesses great affinity with pesticides. As the use of wastewater irrigation increases and addition of organic amendments to agricultural soil becomes more and more popular, it becomes necessary to establish the conditions under which the interaction of organic colloids and pesticides pose a threat for the groundwater.

The objectives of the present research are to:

- Elucidate the mechanism of mobilization and transport of organic colloids.
- Investigate the transport of atrazine as facilitated by various well-characterized organic colloids.
- Develop a conceptual model for colloid-facilitated transport.

## **Methodology**

The study was done with 4 different types of porous media: silica sand, iron-coated silica sand, clay-mineral-coated silica sand, and humic-material-coated silica sand. Procedures were worked out to coat the silica sand with the different materials and to characterize the coated sands. Column transport experiments were carried out to characterize column packings and stability of the coatings on the sand. No experiments with atrazine have been carried out to date, but will be conducted in summer 2003.

### *Silica Sand*

Silica sand (J. T. Baker) was sieved and cleaned with citrate-dithionite to remove iron and treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter.

### *Iron Oxide*

Ferrihydrite was synthesized with a methodology proposed by Schwertmann and Cornell (2000)<sup>1</sup>. Briefly, 2000 ml of warm water (75°C) was added to 20 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O.

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<sup>1</sup> Schwertmann, U. and Cornell, R. M. 2000. Iron oxide in the laboratory. Wiley-VCH 2<sup>nd</sup> edition, 181 p.

The mixture was stirred and put back in the oven for 10 to 12 minutes and cooled down in ice (0.5 to 1<sup>0</sup> C). The material was then dialyzed until the EC of the water reached a value less than 5  $\mu$ S/m.

Extensive tests were carried out to evaluate the ferrihydrite concentrations and the pH at which a homogeneous and extensive coating of the sand was obtained. The coating on the silica sand was done with a modification of the methodology developed by Scheidegger et al. (1993)<sup>2</sup>. Briefly, the procedure was done in a 50 ml polyethylene tube, initial pH was 6.5; after 24 hours the pH was increased to 7.0 for 24 hours and finally to 7.5 for 24 for hours. The pH modification was done with fresh 0.001 M NaOH. Vigorous stirring ensured uniformity of the pH in the solution. The uniformity and extend of the coating was evaluated with SEM.

### *Humic Material*

Coating of humic material over the sand surface was done following the methodology developed by Kopal et al. (1997)<sup>3</sup> and Yang and Koopal (1999)<sup>4</sup>. The procedure consists in a modification of the sand surface to aminopropil silica and the coating of the humic material over the sand.

First, the humic material was purified. Ten grams of Aldrich humic acid were dissolved in NaOH at pH 11, stirred overnight and centrifuged to remove precipitated undissolved material. Then the supernatant was brought to pH 2 with 1 M HCl, stirred for 24 h and centrifuged at 12,100g in a Beckman centrifuge. The precipitate was rinsed with 0.01 M HCl several times to convert the humic acid to its proton form.

Second, the silica sand surface was modified with 3-aminopropyl-dimethyl-methoxysilane (Silar Laboratory). Sixty grams of clean sand was added to 2% (w/w) of the 3-aminopropyl-dimethyl-methoxysilane in toluene solution for 1 h, using a CaCl<sub>2</sub> guard tube to exclude CO<sub>2</sub>. The modified sand was then transferred to a vacuum oven and cured at 150<sup>0</sup>C for 20 h.

300 ml of the purified humic acid was mixed with 60 g of aminopropyl sand and stirred for two hours at room temperature. Then the sand was separated form the humic acid solution and cleaned with deionized water until the supernatant was colorless.

### *Column Experiments*

The experiments were carried out under water-saturated conditions. The columns were pre-wetted from the bottom with the same solution that was used in the experiment. The reason for this was to avoid air entrapment in the column. The solutions used in the column studies were prepared to mimic the ion composition in soil pore water, and had

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<sup>2</sup> Scheidegger, A., Borkovec, M. and Sticher H. 1993. Coating of silica sand with goethite: preparation and analytical identification. *Geoderma*, 58:43-65.

<sup>3</sup> Kopal, L. K., Yang, Y., Minnaard, A. J., Theunissen, P. L. M., Van Riemsdijk, V. H. 1997 Chemical immobilization of humic acid on silica. *Colloids Surf. Physicochem. Eng. Aspects*. 141:385-395.

<sup>4</sup> Yang, Y and Koopal, L. Immobilization of humic acids and binding of nitrophenol to immobilized humics. *Colloids Surf. Physicochem. Eng. Aspects* .151:201-212

ionic strength of 15.4 mmol/L. The characteristic of the pore water solution of the Palouse soil was obtained from the National Soil Database ([www.statlab.iastate.edu/soils/nsdaf/](http://www.statlab.iastate.edu/soils/nsdaf/)). Sodium nitrate was used as a conservative tracer to monitor the column properties. Nitrate was measured with a UV/VIS spectrophotometer at 220 nm (Hewlett Packard, model 8452A).

Column studies were carried out to evaluate the potential mobility of the different organic colloids fraction obtained in the previous phase of the research. The mobility of Atrazine will be studied in the presence and absence of the different organic colloids fractions. These experiments with Atrazine will be conducted in summer 2003.

#### *Conceptual Model for Colloid-facilitated Transport*

A conceptual model for colloid-facilitated pesticide transport was developed. The model was based on literature findings and hypothesized mechanisms of pesticide-organic matter-porous material interactions.

### **Principal Findings and Significance**

#### *Ferrihydrite Synthesis and Coating*

The synthesis of ferrihydrite produced 6-L ferrihydrite as verified XRD measurement. Ferrihydrite concentration in solution after the dialysis was 192 mg/100 ml. This value was closely correlated with expectations based on stoichiometric calculations.

Extensive experiments were done to characterize the coating. At pH 7.8 a large amount of ferrihydrite was coated (143 mg Fe/g sand) but SEM analysis showed that the coating was irregular and with large particle size (Figure 1a) and at pH 5 the amount of iron coated was very low (1.99 mg Fe/g sand). Therefore a different approach was chosen to coat the sand; the pH was changed gradually over three days starting at pH 6.5 and increased in 0.5 pH units until reaching a pH 7.5 at the third day. This methodology is referred as a three-day coating (Figure 1b). With this methodology the coating was more uniform. Currently, we are determining the surface area of the coated sands using gas absorption techniques.

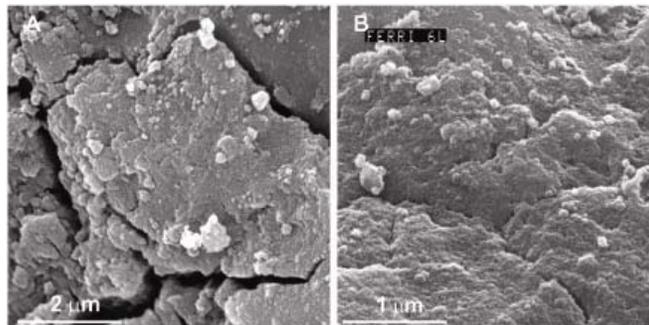


Figure 1. Ferrihydrite-coated sand surface. (a) coated at pH 7.8 (b) 3-day procedure

A second experiment, conducted with a different initial ferrihydrite concentration and a 10 mM NaNO<sub>3</sub> background showed that the uniformity and the amount of coating is concentration dependent (Table 1). We found that the amount of ferrihydrite coated over the sand was higher than reported by Scheidegger et al. (1993)<sup>5</sup> and Lo and Chen (1997)<sup>6</sup> and similar to that reported by Benjamin et al. (1996).

Table 1. Ferrihydrite coating over silica sand as a function of initial ferrihydrite concentration in suspension.

Initial Ferrihydrite concentration (mg Fe/100 ml)	Fe coated on sand (mg Fe/g sand)			
	Rep 1	Rep 2	Rep 3	Mean
153.6	19.46	19.80	26.24	21.83
76.8	11.59	10.96	10.31	10.95
38.4	5.79	5.61	6.17	5.86
19.2	4.58	4.50	4.34	4.47

#### *Humic Material*

Humic material was successfully coated over the sand, but the main limitation was the low amount coated over the sand when we tried to coated monolayer of humic acid. The reason for this result can be related to the low silanol concentration on the sand surface (8  $\mu\text{mol}/\text{m}^2$ ). Because the sand has very low surface area (in order of 0.01  $\text{m}^2/\text{g}$ ) the number of silanol groups on the sand surface was low and therefore the amount of humic acid that can be coated is limited. To increase the amount of coating, we chose to coat multilayers of humic acids over the sand. The amount of humic material of the multilayer was pH dependent.

#### *Clay Material*

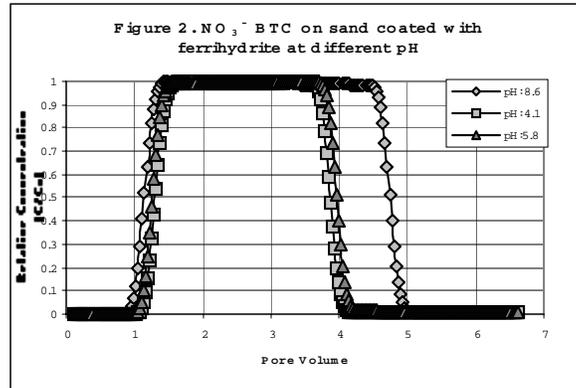
We found that clay coated sand methodology presented some stability problems; therefore, some preliminary experiments are under way to improve the stability under different pH conditions.

#### *Column Experiments*

Several column experiments with nitrate indicated that NO<sub>3</sub> in the ferrihydrite system did not behave as conservative tracer. At low pH the retardation of the breakthrough was more evident than at higher pH. It was surprising that even at pH 8.5 (higher than the point of zero charge of the ferrihydrite) it was still possible to observe retardation in the breakthrough of nitrate (Figure 2).

<sup>5</sup> Scheidegger, A., Borkovec, M. and Sticher H. 1993. Coating of silica sand with goethite: preparation and analytical identification. *Geoderma*, 58:43-65.

<sup>6</sup> Lo, S. and Chen, T. 1997. Adsorption of Se(IV) and Se(VI) on an iron coated sand from water. *Chemosphere* 35:919-930.



### Conceptual Model for Colloid-facilitated Transport

The conceptual model for colloid-facilitated atrazine transport was developed based on a literature review and is schematically depicted in Figure 3.

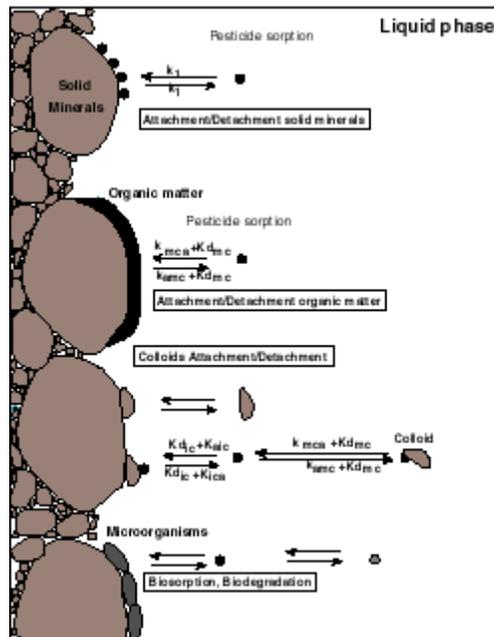


Figure 3. Conceptual model of colloid facilitated transport