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Evaluation of toxicity of the pesticides, chlorpyrifos and arsenic, in the presence of compost humic substances in aqueous systems

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Abstract

An improved understanding of pesticide toxicity in natural systems can have important consequences for pesticide management and remediation strategies for contaminated areas. The interaction between humic substances extracted from compost natural organic matter and both organic and inorganic pesticides was evaluated for its effect on the toxicity of pesticides in the aqueous phase. The toxicity of contaminants was measured using the Microtox® toxicological bioassay. Solutions containing concentrations ranging from 2 to 42 mg C/l of humic substance extracted from a South Texas compost were added to concentrations of the organic pesticide, chlorpyrifos, and toxicity reduction ranging from 50 to 100% was demonstrated. Different concentrations of arsenic ranging from 0.5 to 5 mg/l were also associated with three different concentrations of humic substances and the arsenic toxicity was consistently reduced by a factor of 100%. These results demonstrate a significant relationship between humic substance interactions with organic and inorganic pesticides, and pesticide toxicity in natural systems, and may also suggest a mechanism for pesticide toxicity reduction in natural waters through compost humic addition for contaminated groundwaters and surface waters.

Keywords: Pesticides; Toxicity; Humic substances; Arsenic; Chlorpyrifos

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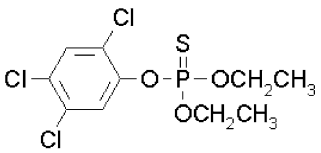
1. Introduction

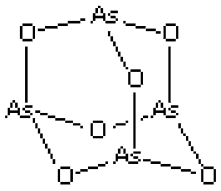
Pesticide usage in the world today has been growing at a significant rate in great efforts to increase crop yields in many countries. While the application of these compounds can protect crop production in the agriculture operations and help control infestations in residential areas, their persistence in the environment and their presence in surface water runoff and groundwater is a concern for community water supplies and recreational water bodies. It has been shown in the past that natural organic matter, which is commonly found in groundwaters and surface waters, can bind many organic and inorganic compounds [1,2].

The organic pesticide, chlorpyrifos (Fig. 1a), introduced in 1965, is one of the most widely used chemical organophosphate insecticides in the market today [3]. It is a broad-spectrum insecticide, which is used to kill a wide variety of insects by disrupting their nervous system. It is not only effective in controlling a variety of insects, including cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice but also suitable for use on grain, cotton, field, fruit, nut, vegetable crops and domestic lawns and ornamental plants [4]. About 40 million kg of chlorpyrifos is manufactured per year and it is an active ingredient in about 800 products in the US [5]. During the mid-1990s, 9–12 million lb (4–5.5 million kg) were used annually in non-agricultural situations in over 17% of households [6]. Agricultural usage estimates vary even more with annual application somewhere between 10 and 21 million lb (4.5–10 million kg). Some studies have shown chlorpyrifos, as a neurotoxicant, can cause brain damage in fetal rats when pregnant rats are given the compound [5]. Recently, the Environmental Protection Agency (EPA) and the manufacturers of chlorpyrifos have agreed to eliminate nearly all-household applications of the insecticide, but agriculture use continues.

Arsenic is a ubiquitous element that exists in a variety of oxidation states in nature, including -3, 0, $+3$, and $+5$ [7]. There exist concerns about the potential teratogenicity and developmental toxicity of inorganic arsenic. The predominant uses of arsenic in the US are in the manufacture of pesticides (including wood preservatives), dessicants, glass, alloys,



(a)



(b)

Fig. 1. The chemical structure of: (a) chlorpyrifos; (b) arsenic trioxide.

electronic components (semiconductors), pigments, and pharmaceuticals [8,9]. Acute exposures to large doses of inorganic arsenic may be fatal. In addition, inorganic arsenic has been classified as a known human carcinogen [10]. Although not commonly used as a pesticide, its high toxicity and persistence from past usage and usage as a dessicant for cotton crops, caused this compound to be selected as an inorganic pesticide for this study. Fig. 1b shows a structural diagram of arsenic (+3 oxidation state) in a stable form as arsenic trioxide.

Humic substances (HS), the major refractory fraction of soil organic matter, are mixtures; and their chemical composition is still not well understood [11]. Humic substances are typically the major component of organic matter in compost, soils and natural waters. In boreal forest lakes, they originate from decaying plant material in coniferous forest soils or peat lands in the catchment areas and are transported to the lakes via surface runoff [12]. Metals and other cations may become complexed by HS. Chelation by neighboring carboxyl and phenolic groups is generally considered to be the major mode of metal complexation [13]. They have been classified into three fractions based on water "solubility": (1) humin is the fraction not soluble in water at any pH value; (2) humic acid (HA) is not soluble under acidic conditions (pH <2) but becomes soluble at higher pH; (3) and fulvic acid (FA) is soluble at all pH conditions [11]. Dissolved humic substances (DHS) are essentially a mixture of humic and fulvic acids of different molecular weights [13]. Natural organic matter can act as a partition medium for toxicants [1,14,15]. In aqueous solution, the soil sorption of low-polarity organic solutes usually occurs mainly by attachment to dissolved organic matter, unless the soil organic matter content is very low [16]. Humic substances have been known to reduce heavy metal toxicity by binding the metal [2].

Assessment of exposure of living organisms to toxic chemicals in water bodies requires information on the concentration that is available to those species. However, the approach to exposure assessment commonly relies not on the level that is biologically available, but rather on the total concentration [17]. In this research, the toxicity of chlorpyrifos and arsenic in the presence of a humic substance extracted from a South Texas compost was evaluated. The objective of this study was to evaluate the effect of compost humic substance (CHS) association on the toxicity of organic and inorganic pesticides, and determine the differences in toxicity response. The results may demonstrate a difference between reported compound toxicity and actual toxicity in some natural systems, and may also suggest a benign method of toxicity reduction through humic or compost addition for contaminated water bodies.

2. Methodology

2.1. Materials and methodology

The humic substance in this study was extracted using the procedures recommended by International Humic Substance Society (IHSS) under basic conditions [16]. The extracted compost humic substance was contacted with solutions containing dissolved concentrations of the pesticide of interest. The Microtox® bioassay was used to assess the toxicity of the

solutions with and without the humic substances. From these data, an assessment was made of the relative toxicity of chlorpyrifos and arsenic acid in the absence and presence of the CHS.

Experiments were also conducted to measure the amount of unbound chlorpyrifos and correlate that value to toxicity measurements. CHS in solution was added to the aqueous solutions containing the contaminants, chlorpyrifos and arsenic acid. After reaching equilibrium, the high molecular weight CHS molecules have interacted with chlorpyrifos and arsenic. UV-Vis spectroscopy measurements at 254 nm for experimental solutions were monitored to establish that equilibrium was reached in a few seconds, and observed over time to demonstrate no loss of absorbance due to particle aggregation and precipitation. The UV-Vis spectra were obtained using an SLM-AMINCO 3000 UV-Vis scanning spectrophotometer.

Some samples were subjected to additional analyses to measure the unbound fraction of pesticide remaining in solution. Upon acidification, the CHS was precipitated in a complex with the bound contaminant. The centrifuge was used to separate the dissolved and complexed contaminant. The supernatant was decanted and aqueous phase contaminant concentration measured. The results of this evaluation were used to establish the extent of interaction between the organic pesticide and the humic substance.

2.2. Humic substance extraction

A number of methods for the extraction of humic substances from soil using sodium hydroxide solution have been published. These methods are generally successful and yield comparable results. The IHSS method has been determined to be an acceptable method for the extraction of humic substances from soils [16]. This method was implemented in the Environmental Laboratory, Texas A&M University at Kingsville, to extract the humic substances from South Texas compost. The compost used was obtained from samples collected at the landfill at Brownsville, TX. Briefly, four 250 ml glass centrifuge bottles were filled with 20 g of compost sample; to each bottle 200 ml of distilled (DI) water was added; the pH of the soil suspension was adjusted in the range 1–2 using 1 M HCl, the glass bottles were sealed and put into a shaker for 1 h. After shaking the samples were centrifuged at $6555 \times g$ for 30 min and the supernatant decanted. The material was neutralized to pH 7 using 1 M NaOH. Two hundred milliliters of 0.1 M NaOH was added under a nitrogen gas stream to re-suspend the material and the bottles were immediately sealed. The bottles were shaken for 12 h and later centrifuged at $6555 \times g$ for 1 h. The supernatants were decanted and acidified to pH 1 using 6 M HCl and allowed to stand for 2 h. The bottles were again centrifuged at $6555 \times g$ for 30 min. A minimum amount of 0.1 M KOH was used to dissolve humic substances fraction under the nitrogen gas. The solution was again centrifuged for 30 min and the supernatant was decanted. The final two steps were repeated three times. After decanting the supernatant, the solid phase at the bottom was assumed to be humic substance including both humic and some fulvic acid. Finally, the solid humic substances were obtained by air-drying the CHS solution at room temperature in a fume hood. A humic quality of 42% total organic carbon by weight was obtained as measured with a Shimadzu T-5000 total organic carbon analyzer.

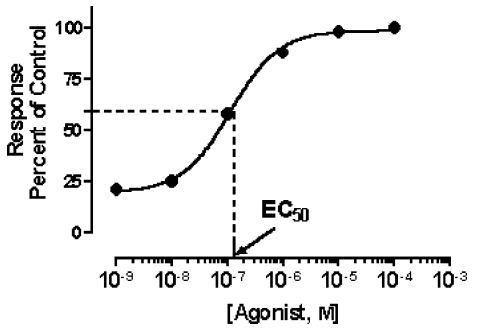


Fig. 2. Schematic showing definition of EC_{50} (Microbics Corporation, 1992).

2.3. Toxicological bioassay by Microtox®

The toxicity of contaminants in this research was measured using the Microtox® toxicological bioassay. Microtox® measured the decrease in respiration, and subsequent light output, of a luminescent bacterium *Vibrio fischeri* as the toxic response. The Microtox® test is a simple, reliable test for screening microorganism toxicity. The test measures the fraction of luminescent bacteria that die in the test and the number of bacteria involved is measured in millions. Microtox® testing is a rapid, cost-effective tool in assessing toxicity of effluents, sediments, leachates, soils, sludges, groundwaters and surface waters. The EC_{50} of the Microtox® analysis is the sample concentration that reduces the reagent light output by 50%. Fig. 2 is a theoretical graph depicting the operational determination of EC_{50} for a particular sample.

In developing an aquatic microorganism as a bioindicator, baseline data about the toxicity of this particular microorganism is needed [18]. Therefore, the determination and development of applicability of a bioindicator organism through toxicity testing also allows one to determine "safe" or tolerable levels of toxicants for those species in aquatic ecosystems [18]. In this study, the safe level was defined as that level when the EC_{50} of toxicity analysis was greater than 100% when using the Microtox® method. With this method there are several orders of magnitude fewer species than in conventional biological assays, and hence the Microtox® test should give better statistically reliable results. The EC_{50} curve was established for the different diluent concentrations and the baseline of the pesticide sample. The effect measured by the Microtox® toxicological bioassay, light loss, is related to the rate of biological activity, and is measured at both 5 and 15 min of sample exposure time. Under normal conditions, with Microtox® microorganisms in good condition, the test with a 100 mg/l phenol solution will produce an EC_{50} between 25 and 35% in both 5 and 15 min analysis [19]. The results of the phenol standard test can be offered as evidence that system and operations are operating normally. In this research, the Microtox® experimental protocol and materials were evaluated with a standard phenol test experiment and the EC_{50} was determined to be 27% for 5 min and 28% for 15 min of analysis, which is well within the manufacturers recommended range. Fig. 3 is an example dose–response curve as

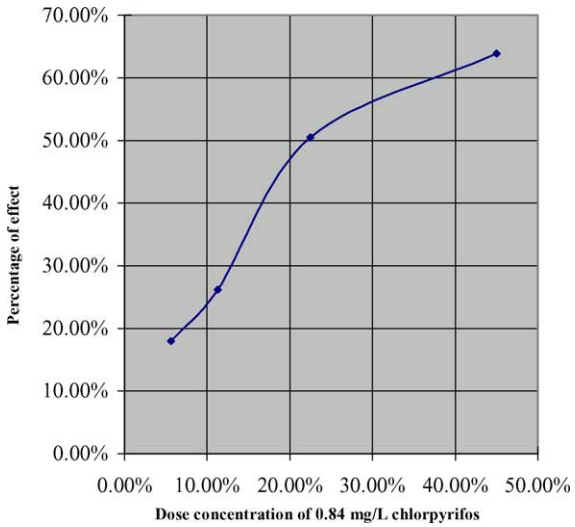


Fig. 3. An example dose–response curve of 0.84 mg/l chlorpyrifos as measured with Microtox® in this study (5 min analysis).

determined for a solution of 0.84 mg/l chlorpyrifos using the Microtox® approach for the 5 min analysis.

2.4. Experimental protocols

An aqueous stock solution of 0.84 mg/l chlorpyrifos was prepared with DI water and a certified Dursban® solution. The baseline toxicity for this chlorpyrifos concentration was obtained from EC_{50} evaluations by the Microtox® method. Three different concentrations of 0.5, 1 and 5 mg/l arsenic stock solutions were also prepared with deionized water from a 1000 mg/l Fisher Scientific AA standard arsenic(III) solution. The baseline toxicity for three arsenic acid samples was obtained as EC_{50} by Microtox® method. A stock solution of 168 mg C/l CHS in DI water was used in the experiments to add to 100 ml of total sample volume to formulate the 2.1, 4.2 and 42 mg C/l of CHS solutions for use in experiments. Chlorpyrifos standards for GC/MS analyses were also prepared from the stock for calibration. A Perkin-Elmer Autosystem Gas Chromatograph Q-Mass model 910 GC/MS was used to measure chlorpyrifos concentrations in the dissolved phase after interaction with CHS.

A typical experiment consisted of the addition of the addition of chlorpyrifos stock solution to an acid washed 250 ml Erlenmeyer flask followed by the addition of sufficient CHS stock solution to achieve the desired CHS concentrations. The solutions were mixed on a shaker table for approximately 30 min and the samples were prepared for Microtox® testing. All experiments were replicated at least three times and the mean values for EC_{50} and standard deviation reported. ANOVA analyses were performed on toxicity results for significance testing.

Table 1
Baseline toxicity measurements to establish the safety of compost humic substance and the toxicity of chlorpyrifos after 15 min of analysis

Concentration of CHS (mg C/l)	The value presented as EC_{50} by Microtox® method
2.1	Safe level EC_{50} >100%
4.2	Safe level EC_{50} >100%
42	Safe level EC_{50} >100%

Table 2
The toxicity of chlorpyrifos in solution without compost humic substance as EC_{50} using the Microtox® method

Concentration of chlorpyrifos (mg/l)	Toxicity for 5 min analysis (EC_{50}, %)	Toxicity for 15 min analysis (EC_{50}, %)
0.84	25.06 ± 1.20	31.57 ± 1.51

3. Results and discussion

3.1. Baseline toxicity evaluations of compost humic substance

Three different concentrations of CHS were used to evaluate its baseline effect on toxicity for Microtox® organisms. The baseline toxicity of CHS was determined to be negligible as evidenced by the results in Table 1, which indicates that the apparent toxicity of CHS at the concentration levels used in this study was not significant.

The EC_{50} values for the baseline chlorpyrifos solution used in the study are presented in Table 2. The results showed that the baseline toxicity of chlorpyrifos to the microorganisms is high even at such a low concentration (0.84 mg/l).

3.2. The toxicity of chlorpyrifos after interaction with compost humic substance

Tables 3–5 list toxicity results for chlorpyrifos after interaction with three different concentrations of compost humic substance. The humic substance was very effective in

Table 3
The toxicity of chlorpyrifos after interaction with 2.1 mg C/l CHS presented as EC_{50} using the Microtox® method for 5 and 15 min of analysis

Concentration of chlorpyrifos (mg/l)	Toxicity for 5 min analysis (EC_{50}, %)	Toxicity for 15 min analysis (EC_{50}, %)
0.84	63.12 ± 3.02	72.01 ± 3.46

Table 4
The toxicity of chlorpyrifos with 4.2 mg C/l CHS presented as EC_{50} using the Microtox® method

Concentration of chlorpyrifos (mg/l)	Toxicity for 5 min analysis (EC_{50})	Toxicity for 15 min analysis (EC_{50})
0.84	Safe level EC_{50} >100%	Safe level EC_{50} >100%

Table 5
The toxicity of chlorpyrifos with 42 mg C/l CHS presented as EC_{50} using the Microtox® method

Concentration of chlorpyrifos (mg/l)	Toxicity for 5 min analysis (EC_{50}, %)	Toxicity for 15 min analysis (EC_{50}, %)
0.84	66.94 ± 3.21	78.92 ± 3.79

elevating the EC_{50} especially at a critical concentration of 4.2 mg C/l to completely safe levels (Table 4). Results showed a lower yet still significant toxicity change when the CHS was applied at lower (2.1 mg C/l, P-value $= 5.83 \times 10^{-5}$; Table 3) and higher (42 mg C/l, P-value $= 4.29 \times 10^{-5}$; Table 5) concentrations. Thus, the results show a significant change of toxicity of chlorpyrifos after its interaction with the humic material.

3.3. Comparing the toxicity of chlorpyrifos in the presence and absence of CHS

The toxicity reduction of chlorpyrifos in the presence of CHS was determined by comparing the toxicity with and without additions of CHS. When the toxicity was reduced to a safe level, the EC_{50}(after) was assumed to be 100%. The amount of toxicity reduction was defined as:

$$\text{toxicity reduction} = \frac{EC_{50}(\text{after}) - EC_{50}(\text{before})}{100\% - EC_{50}(\text{before})} \quad (1)$$

where EC_{50}(after) is the EC_{50} value of toxicity after interaction with CHS, and EC_{50}(before) the baseline EC_{50} value of toxicity.

Fig. 4 depicts the percent toxicity reduction by the three concentrations of CHS based on Eq. (1). The largest toxicity reduction occurred at a 4.2 mg/l CHS concentration for both the 5 and 15 min equilibrium times. Fig. 4 demonstrates that the percentage of the toxicity reduction were very similar after 5 and 15 min equilibrium times. This similarity is a strong indicator of accurate testing [19]. The trend in toxicity reduction for the humic–organic pesticide interaction does not appear to be linear.

It is possible that the toxicity reduction of chlorpyrifos interacted with 42 mg C/l CHS is not significantly greater than 4.2 mg C/l CHS because the interaction of a small amount of strongly adsorbing CHS may be largely responsible for most of the toxicity reduction. An excess concentration may potentially interfere with effective association between the toxicant and the humic substance.

The experiments between chlorpyrifos and CHS at a concentration of 42 mg C/l were repeated several times to verify the results and establish the confidence levels of the experimental results. Table 6 lists the toxicity results of replicate experiments of chlorpyrifos interacted with 42 mg C/l CHS. Data includes three measurements of toxicity of chlorpyrifos after interaction with CHS and the mean value for those three measurements.

The reproducibility for experiments is critically important for evaluating bioassay testing results. For these experiments, the standard error of the data was determined to be ±3.8% for the percent toxicity reduction of chlorpyrifos with 42 mg C/l CHS by 15 min Microtox® analysis.

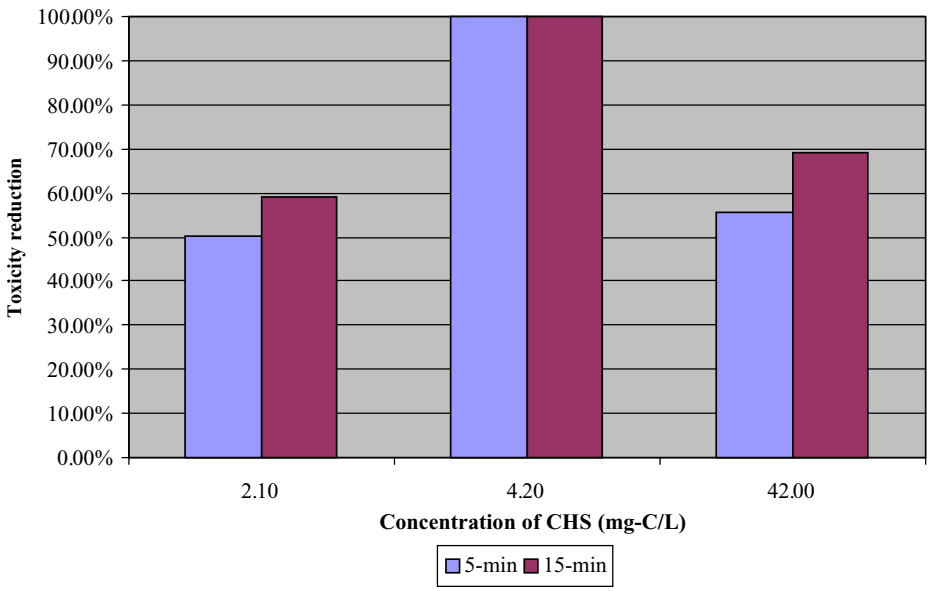


Fig. 4. The toxicity reduction of chlorpyrifos after interaction with three concentrations of compost humic substance.

3.4. The relationship between reduced unbound concentration and reduced toxicity

In order to measure the humic-bound chlorpyrifos concentration after the interaction, a separate experiment was completed. Upon addition to a solution containing the pesticide, CHS diffuses into the aqueous phase and interacts with chlorpyrifos. After reaching equilibrium, the high molecular weight CHS has completely interacted with chlorpyrifos. At low pH, humic substances are insoluble. After an adjustment to pH 2 with HCl, the CHS complexed with the bound pesticide was precipitated through centrifugation. The centrifuge, operated at $6555 \times g$ for 30 min, was used to separate the aqueous phase and complexed contaminant. The supernatant was decanted and the aqueous phase chlorpyrifos concentration measured with the Perkin-Elmer Autosystem Gas Chromatograph Q-Mass model 910 GC/MS. After the interaction of 0.84 mg/l chlorpyrifos with 4.2 mg

Table 6
An example of repeatability of toxicity of chlorpyrifos with 42 mg C/l CHS presented as EC_{50} by 15 min Microtox® analysis

Concentration of chlorpyrifos (mg/l)	EC_{50} toxicity of chlorpyrifos after interaction with 42 mg C/l CHS (%)			
	First test	Second test	Third test	Mean value
0.84	77.97	75.66	83.12	78.9

Standard error of the data is ±3.8%.

Table 7
The baseline toxicity of arsenic without interaction with compost humic substance as EC_{50} by Microtox® method

Concentration of arsenic (mg/l)	Toxicity for 5 min analysis (EC_{50}, %)	Toxicity for 15 min analysis (EC_{50}, %)
0.5	16.54	23.53
1	15.45	17.73
5	9	10.3

C/l CHS, the unbound aqueous phase concentration of chlorpyrifos had been reduced to 0.29 mg/l. Thus, a large amount of the pesticide chlorpyrifos was bound by CHS and it is probable that there is a relationship between extent of binding and toxicity reduction.

3.5. Toxicity evaluation for the inorganic pesticide arsenic with and without CHS

Table 7 shows the baseline toxicity of arsenic standard solutions at different concentrations. The toxicity for arsenic is very high as expected in selected concentrations for both 5 and 15 min Microtox® analysis.

According to many studies, the binding of metals is one of the most important environmental qualities of humic substances [20]. All experiments interacting 2.1, 4.2 and 42 mg C/l CHS with arsenic at the concentrations listed in Table 7 reduced its toxicity to safe levels for both 5 and 15 min Microtox® analysis. The results suggest that CHS is very effective in binding arsenic even at 2.1 mg C/l concentrations which appears to be sufficient to reduce the Microtox® toxicity of even the very toxic 5 mg/l arsenic concentration.

3.6. A comparison of organic and inorganic pesticide toxicity reduction

It has been suggested that a binding interaction may reduce the toxicity of metals when interacted humic substances [21]. Non-linear adsorption interactions between humic substances and non-polar organic compounds have been observed by some investigators [22–25]. In this study, the differences between organic and inorganic pesticide toxicity reduction suggest different mechanisms of attachment and toxicity reduction.

From Fig. 4, it can be concluded that 4.2 mg C/l CHS was the most effective concentration in reducing the toxicity of the organic chlorpyrifos at several pesticide concentrations. The critical concentration of 4.2 mg C/l CHS was able to achieve 100% toxicity reduction at even the highest chlorpyrifos concentrations, while the higher concentration of 42 mg C/l CHS was apparently somewhat less effective. The causes for this apparent non-linear response are unknown. There may be some optimal binding critical concentration for the humic material and this pesticide. The interaction with a small amount of strongly adsorbing humic substance in the humic mixture may be responsible for the non-linear interaction of the non-polar compound with the humic substance [16]. At very high humic substance concentrations, binding effectiveness and toxicity reduction may be diminished for some portion of the humic material. Humic substance intra-molecular association at these high

concentrations may interfere with the toxicity reduction. Sorption linearity and hysteresis have been found to be dependent on SOM structure and composition [24]. Also, other humic–pesticide interaction studies have found that some pollutants are strongly bound or complexed with only some of the dissolved humic fractions which can associate and migrate independently [25]. Some humic fractions may have sites for pesticide association and deactivation which may be reduced or blocked in high concentrations of material. Even though we did not detect aggregation or precipitation of the humic material at the high concentrations, larger complexes or chains could present a case for less effective reactive surfaces.

For the experiments with the inorganic compound arsenic, CHS was effective in 100% toxicity reduction at all concentrations tested. No non-linear toxicity responses for the inorganic pesticide were measured at the concentrations tested.

These experiments suggest different types of toxicological responses for organic and inorganic pesticides after the interaction with humic substances. After the interaction of chlorpyrifos with 4.2 mg C/l CHS, the unbound aqueous phase concentration of chlorpyrifos had been significantly reduced as measured by GC/MS. This result demonstrates that the binding of chlorpyrifos by compost humic substance does occur but there may be a complex relationship between extent of interaction between the chlorpyrifos and humic substance, and toxicity reduction. The nature of this toxicity reduction and the mechanisms for reducing the bioavailability of the pesticide will require additional research, however, the results confirm the hypothesis that toxicity reduction can occur when compost humic substances interact with both chlorpyrifos and arsenic.

4. Conclusions

The specific objective of this study was to measure the toxicity of certain pesticides in the presence and absence of humic substances and evaluate the results. This study was also designed to compare the different interactions between organic and inorganic pesticides with the humic substance and the resulting toxicity behavior. Conclusions from the research include:

- The toxicity of chlorpyrifos was reduced by margins of 4.4–100% after interaction with compost humic substances at concentrations of 2.1–42 mg C/l. The data exhibited an apparent non-linear relationship between chlorpyrifos concentration and toxicity reduction depending on CHS concentrations.
- A reduction in the unbound fraction of chlorpyrifos was observed in experiments utilizing GC/MS analysis. These subsequent separation experiments demonstrated that a decrease in toxicity of the pesticides was probably associated with the interaction between the compost humic substance and the pesticide.
- Toxicity reductions of three different concentrations of arsenic that interacted with three different concentrations of compost humic substance all achieved 100% toxicity reduction. The large toxicity reduction implies highly effective binding between the toxicant and compost humic substance. Thus, arsenic demonstrates this high toxicity reduction even though it is a metalloid and not a true metal.

This study suggests a potential mechanism for toxicity reduction involving organic pesticides through a binding interaction with humic substances. For inorganic pesticides, toxicity reduction for metalloid pesticides may operate similarly as for heavy metals when bound with humic substances. Pesticide toxicity in natural waters containing some humic substances may not be as high as measurements made in laboratory aqueous systems. This work also suggests an approach to inexpensively detoxify contaminated water resources for agricultural or municipal reuse and supports the potential benefits of toxicity reduction for application of compost products in some cases.

Additional research is needed to measure aqueous toxicity in the presence of humic substances with other organophosphate or organochloride pesticides. Further investigations will be needed to elucidate the mechanism of interaction between contamination and humic substances and determine its relationship to toxicity reduction. The apparent non-linear toxicity response for this organic pesticide after interaction with humic substances at varying concentrations suggests a complex relationship where several mechanisms for toxicity reduction may be operative.

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References

[1] C.T. Chiou, P.E. Porter, D.W. Schmedding, Environ. Sci. Technol. 17 (1983) 227.
[2] G.M. Gadd, A.J. Griffiths, Micro Ecol. 4 (1978) 303.
[3] W.J. Hayes, E.R. Laws, Handbook of Pesticide Toxicology, Academic Press, San Diego, 1990.
[4] Ambient Water Quality Criteria for Chlorpyrifos, Office of Water Regulations and Standards, US Environmental Protection Agency, 1986.
[5] B. Hileman, J. C&EN 78 (2000) 11.
[6] C. Cox, J. Pestic. Reform 14 (1994) 15.
[7] R.W. Boyle, I.R. Jonasson, J. Geochem. Explor. 2 (1973) 51–96.
[8] J.L.T. Waugh, Encyclopedia of Science and Technology, McGraw-Hill, New York, 1982.
[9] H.V. Aposhian, Rev. Biochem. Toxicol. 10 (1989) 99–265.
[10] IRIS Substance File: Arsenic, Inorganic, US Environmental Protection Agency, March 1997.
[11] G.R. Aiken, D.M. McKnight, R.L. Wershaw, P.L. MacCarthy, Humic Substances in Soil, Sediment and Water, Wiley, New York, 1985.
[12] M. Meili, Hydrobiologia 229 (1992) 23–41.
[13] W. Stumm, J.J. Morgan, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters, Wiley, New York, 1996.
[14] S.C. Wu, P.M. Gschwend, Water Resour. Res. 24 (1988) 1373–1383.
[15] R.P. Schwarzenbach, J. Westall, Stud. Environ. Sci. 17 (1981) 569–574.
[16] C.T. Chiou, D.E. Kile, D.W. Rutherford, Environ. Sci. Technol. 34 (2000) 1254.
[17] J. Tang, B.K. Robertson, M. Alexander, Environ. Sci. Technol. 33 (1999) 4346–4351.
[18] H.H. Alison, Black flies: bioindicator potential and toxic responses to chlorpyrifos and the microbial pesticide, Ph.D. dissertation, Clemson University, 1998.
[19] Manual for Operation of Microtox Systems, Microbics Corporation, 1992.

[20] S.E. Manahan, Environmental Chemistry, Lewis Publishers, Chelsea, MI, 2000.
[21] D.A. Hammer, Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Lewis Publishers, Chelsea, MI, 1989.
[22] S. Kleineidam, H. Rugner, B. Ligouis, P. Grathwohl, Sedimentary Geol. 129 (1999) 311–325.
[23] H. Rugner, S. Kleineidam, P. Grathwohl, Environ. Toxicol. Chem. 18 (1999) 1673–1678.
[24] G. Ding, J. Novak, S. Herbert, B. Xing, Chemosphere 48 (2002) 897–904.
[25] M. Pacheco, E. Pena-Mendez, J. Havel, Chemosphere 51 (2003) 95–108.