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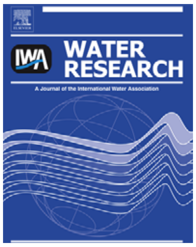

Dechlorination of chloroacetanilide herbicides by plant growth regulator sodium bisulfite

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ABSTRACT

Chloroacetanilide herbicides are frequently detected in groundwater and surface waters, and pose high risks to aquatic biota. In this study, sodium bisulfite ($NaHSO_3$), a plant growth regulator used in China, was used to remove three chloroacetanilide herbicides including alachlor, acetochlor and S-metolachlor. These herbicides were rapidly dechlorinated by $NaHSO_3$ in neutral conditions. The dechlorination was accelerated with increasing pH, temperature and $NaHSO_3$ concentrations. Kinetic analysis and mass spectrum identification revealed that the reaction followed S_N2 nucleophilic substitution, in which the chlorine was replaced by the reactive specie sulfite. Alachlor and its isomer acetochlor had similar reaction rates, whereas they were more readily transformed than S-metolachlor that had larger steric hindrance and weaker electrophilicity. The transformation products were chloroacetanilide ethane sulfonic acids (ESAs), which were also encountered as major metabolites of these herbicides in natural environment via common metabolic pathways and were less toxic to green algae compared to the parent herbicides. These results indicate that $NaHSO_3$ can accelerate transformation of chloroacetanilide herbicides to the less toxic transformation products by nucleophilic substitution and dechlorination in aquatic environment. $NaHSO_3$ can be potentially used for the removal of chloroacetanilide herbicides from wastewater effluent, spill sites and accidental discharge.

1. Introduction

Chloroacetanilide herbicides are among the most commonly used pesticides in agriculture for pre-emergence control of annual grasses and broadleaf weeds in corn, soybeans, and many other crops. About 15,900 metric tons of acetochlor was used in the United States in 2001, followed by 10,900 metric tons of S-metolachlor and 4100 metric tons of alachlor (Kiely et al., 2004). The consumption of acetochlor is more than 10,000 metric tons every year in China (Ye, 2003). Due to the prevalent use of these herbicides and their relatively high solubility in water, the herbicides and their degradation products have been frequently detected in groundwater and surface waters (Kolpin et al., 1996; Boyd, 2000; Cerejeira et al., 2003; Xue et al., 2005; Hildebrandt et al., 2008).

Alachlor and acetochlor are characterized as class B2 human carcinogens by the U. S. Environmental Protection Agency, whereas metolachlor is viewed as a class C human carcinogen (USEPA, 1995, 1998, 2006). Chloroacetanilide herbicides have moderate to high chronic toxicity to aquatic

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vertebrates and invertebrates, high toxicity to aquatic plants (USEPA, 1998) and some green algae (Junghans et al., 2003; Cai et al., 2007). The concentrations reported in surface waters could result in extensive adverse effects on aquatic plants (USEPA, 1998). Therefore, the removal of these pesticides' contaminations from wastewater effluent and the environment is of great importance.

Chloroacetanilide herbicides can be attenuated naturally in the soil–water system. The ethane sulfonic acid (ESA) and oxanilic acid derivatives of alachlor, acetochlor and metolachlor have been frequently detected as the major transformation products of chloroacetanilide herbicides in water at higher levels than those of their parent compounds (Kalkhoff et al., 1998; Kolpin et al., 2000; Spalding et al., 2003). However, the transformation may be very slow under the relatively dilute or nutrient-limited conditions such as some groundwater and river water (Larson et al., 1995; Potter and Carpenter, 1995). Recently, it has been reported that some sulfur compounds could rapidly transform chloroacetanilide herbicides to less toxic products (Gan et al., 2002; Loch et al., 2002; Zheng et al., 2004b). This provides a new strategy for the remediation of chloroacetanilide-contaminated aqueous environments.

Sodium bisulfite ($NaHSO_3$) is used as a plant growth regulator in China (Zhang and Peng, 1984; Wang et al., 2000a,b). Given that $NaHSO_3$ is an agrochemical with low toxicity, using $NaHSO_3$ as the remediation reagent of chloroacetanilide herbicide contamination would have minimal impact on the agricultural system and the environment. The specific objectives of this study were to (i) determine reaction rates of three chloroacetanilide herbicides (alachlor, acetochlor and S-metolachlor) with sodium bisulfite in water, (ii) explore reaction mechanisms by evaluating reaction kinetics and activation parameters, identifying transformation products, and using hybrid density functional theory (DFT) calculation, and (iii) investigate the changes of toxicity of transformation products following the degradation of the parent herbicides.

2. Materials and methods

2.1. Chemicals

Technical grade alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide, 95.5%] and acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide, 95.2%] were purchased from Shandong Binnong Technology Co., Ltd. (Binzhou, China). S-metolachlor [S-2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(1-methoxypropan-2-yl)acetamide, 96%] was purchased from Syngenta (Suzhou) Crop Protection Co., Ltd. (Suzhou, China). All were used as received. $NaHSO_3$ and Na_2SO_3 were reagent grade.

Alachlor ESA (purity > 96.4%), acetochlor ESA (purity > 99.1%) and S-metolachlor ESA (purity > 96.9%) were prepared by the following procedures (Aga and Thurman, 2001) and used in acute toxicity assays. Briefly, the herbicides were refluxed with excess sodium sulfite in 10% ethanol/water (10/90, v/v) solution until the mixture became homogeneous. Following acidification with sulfuric acid, the products were extracted into methylene chloride. Then the methylene chloride was evaporated, and the reaction products were dissolved in hot ethanol. The hot ethanol mixture was filtered and allowed to stand undisturbed for recrystallization of the ESAs. The crystals obtained were washed several times with cold ethanol and identified as alachlor ESA, acetochlor ESA or S-metolachlor ESA by high-pressure liquid chromatography–mass spectroscopy (HPLC–MS).

2.2. Experimental systems

A series of experiments were conducted to understand the reaction kinetics between the herbicides and sodium bisulfite. In the first experiment, disappearance of herbicides was determined by HPLC in aqueous solutions containing sodium bisulfite at various concentrations. Sodium hydroxide was used to adjust 45 mL of sodium bisulfite solution to pH 7.3. After the solution was transferred to a 100 mL volumetric flask, 50 mL of phosphate buffer solutions (pH 7.3) was also added into the volumetric flask. Stock solutions of herbicides (20.0 mM) were prepared in methanol. To initiate the reaction, 1.0 mL of each herbicide solution was separately added into the volumetric flasks, and the volume was brought to the 100-mL mark with deionized water. The initial herbicide concentration was 0.2 mM. The initial $NaHSO_3$ concentration was 0, 5.0, 10.0, 20.0, 30.0 and 50.0 mM, respectively. The final concentration of total phosphate was 0.1 M. The flasks were immediately transferred to an incubator at $25 \pm 0.5\ ^{\circ}C$ under darkness. At intervals, 1.0-mL aliquots of solution were withdrawn from volumetric flasks and transferred to glass vials followed by HPLC analysis.

In the second experiment, the effect of pH values on the reaction rate of the herbicides was studied. The procedures were the same as those described in the first experiment to prepare and analyze the samples. The initial concentrations of herbicide and sodium bisulfite were set at 0.2 and 20.0 mM, respectively. The solution pH was 3.8, 6.1, 7.3 and 8.5, respectively. The control vials contained only herbicides in buffer solutions. All samples were incubated at $25 \pm 0.5\ ^{\circ}C$ in the dark.

Buffer solution at pH 3.8 was prepared by combining appropriate volumes of 0.2 M citric acid and 0.2 M sodium citrate. Solutions of pH 6.1 and 7.3 were prepared from 0.2 M phosphate buffer. Buffer solution at pH 8.5 was prepared from 0.2 M boric acid and 0.05 M sodium tetraborate. Sulfite ion concentrations were computed from the total sodium bisulfite concentration $[HSO_3^-]_T$ and measured pH values via ionization constants for sulfurous acid at 25 °C (Lide, 2002) that were corrected for ionic strength using activity coefficients $\gamma_{HSO_3^-}$ and $\gamma_{SO_3^{2-}}$ determined from the Davies approximation. Sulfite ion concentrations at other temperatures were computed using pKa values of temperature corrections performed with the Van't Hoff equation.

The effect of temperature on the reaction rate of the herbicides was also investigated. The procedures were the same as those described in the above experiment. The initial herbicide concentration was 0.2 mM. The initial sodium bisulfite concentration was 20.0 mM. The solution pH was 7.3. The samples were incubated at 15, 20, 25, 30, and 35 °C, respectively. Variation in temperature was less than 0.5 °C. The control experiments were conducted in the absence of sodium bisulfite at each temperature. All the experiments were carried out in triplicate.