Nucleophilic Radical Substitution Reaction of Triazine Herbicides with Polysulfides

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Triazine herbicides are among the most widely used herbicides in the United States. Many triazine compounds are relatively stable under natural conditions and have become prominent contaminants in hydrologic systems. It was previously reported that chloro-*s*-triazine compounds were rapidly dechlorinated in water by polysulfides, and the reaction was assumed to be aromatic nucleophilic substitution (S_NAr). In this study, we evaluated the effect of free radical inhibitors on the reaction rate of polysulfides with herbicides atrazine, simazine, and cyanazine. The reaction was significantly inhibited by radical scavengers oxygen and 1,4-benzoquinone, suggesting involvement of free radicals in the reaction. Spectral analysis of the reaction mixture using electron spin resonance showed that after the reaction, the free radical concentration in polysulfide solution substantially decreased. These evidences indicate that radical sulfur anions may also be involved in the reaction, likely via a free radical substitution reaction ($S_{RN}1$) mechanism. Amendment of sodium tetrasulfide significantly reduced the leaching of atrazine or simazine from packed sand columns. Therefore, polysulfide salts may be potentially used to remove residues of triazine herbicides in environmental media.

KEYWORDS: Chloro-*s*-triazine herbicides; $S_{RN}1$ reaction; polysulfides; dechlorination; remediation

INTRODUCTION

Halogenated organic compounds (HOCs) have been heavily used as solvents, degreasing agents, and pesticides. Many of these compounds are recalcitrant to degradation in the environment, and a great effort is being made to prevent further pollution and to decontaminate environmental media that are already polluted from previous uses (*1*). Currently, however, there are few safe and effective decontamination methods for these chemicals. Chemical treatments based on oxidation reactions and physical means are often nonselective and may damage the target environmental systems. Therefore, it is necessary to identify new selective approaches to decontaminating these compounds in environmental media (*2*).

An important group of HOCs, the triazine herbicides, have been widely used on a great number of important crops in the United States over the last several decades. Because of their widespread use as well as their relatively high mobility in the soil−water phases, triazine herbicides and their metabolites have been frequently detected in U.S. hydrological systems (*3*). In a recently published study, triazine herbicides and other azine analogues were found to be dechlorinated by polysulfides (S_n^{2-}) (*4*). The reaction was suggested to be nucleophilic aromatic substitution (S_NAr), in which the chlorine was replaced by a sulfur dianion. The S_NAr mechanism was deduced from the second-order nature of the reaction, the products formed, and reactivity trends (*4*).

Here, we propose that an alternative mechanism for the reaction may be radical nucleophilic substitution, or $S_{RN}1$. It is well-known that radical anions $^\bullet S_3^-$ and $^\bullet S_4^-$ are the most reducible chemical species in polysulfides (*5*, *6*). For instance, in the cyclic voltammetry test, $^\bullet S_3^-$ and $^\bullet S_4^-$ reduction peaks were observed at all temperatures and all scan rates (*5*). Recently, Rossi et al. (*7*) reviewed the nucleophilic substitution reactions by the electron transfer (ET) pathway. For heteroaromatic compounds, competition between an ET process and a S_NAr process can occur mainly when more than one heteroatom is present. Genesty et al. (*8*) also reported that the reaction between S_4^{2-} and 3-bromoquinoline in the presence of a redox mediator had led to a mixture of products resulting from $S_{RN}1$. However, in Lippa et al. (*4*), the potential role of radical sulfur anions in the substation reaction of triazines was neglected and no effort was made to measure changes of free radical levels during the reaction. The first objective of this study was therefore to further explore the reaction mechanisms between polysulfides and three chloro-*s*-triazine herbicides, atrazine [2-chloro-4-(ethylamino)-6-iso-propyl-amino-*s*-triazine], cyanazine {2-[4-chloro-6-(ethylamino)-*s*-triazin-2-yl)amino]-2-methylpropionitrile}, and simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine]. The reaction between nucleophiles and triazine herbicides was previously studied to understand its potential significance in natural attenuation of these pesticides in reduced environments such as marine or salt marsh systems (*4*). Given the great efficiency of this reaction, it is likely that this reaction may be valuable as a remediation strategy for decontaminating pesticide residues in soil or aquifer phases. The second objective was therefore to evaluate the feasibility of using the polysulfide-induced dechlorination reaction for decontaminating herbicide residues in solid media.

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MATERIALS AND METHODS

Chemicals. Standards of atrazine, cyanazine, and simazine (the chemical purity of each compound was >98%) were obtained from Chem Service (West Chester, PA). Sodium tetrasulfide crystals (99%) were purchased from Great Western Inorganics (Arvada, CO). Crystals of sodium tetrasulfide were purified by rinsing with deoxygenated toluene to remove excess elemental sulfur that might have formed during storage and were then dried under nitrogen. Borate buffer (pH 9.5) was obtained from VWR (West Chester, PA). Polysulfide solutions were prepared by dissolving purified sodium tetrasulfide crystals in borate buffer. The reagent 1,4-benzoquinone (99%) used in the free radical inhibition experiment was obtained from Aldrich (Milwaukee, WI).

Kinetics Experiments. A series of kinetics experiments were conducted in tetrasulfide-borate solution with and without free radical inhibitors to understand the role of free radicals in the reaction between the triazine herbicides and the polysulfides. Because tetrasulfide was expected to be present in borate solution as multiple sulfur dianions, including S_2^{2-}, S_3^{2-}, and S_4^{2-} (5), polysulfide concentrations were expressed as the nominal concentration of tetrasulfide in this study. The reaction kinetics between polysulfides and atrazine, simazine, or cyanazine was first determined without free radical inhibitor but at varying tetrasulfide concentrations. A stock solution of sodium tetrasulfide was prepared in borate buffer at 400 mM. The herbicide stock solution was prepared at 100 μM in water (atrazine and cyanazine) or 1:1 (v/v) water−methanol (simazine). The reaction was initiated by mixing stock solutions of the herbicide and sodium tetrasulfide in 25 mL of borate buffer in 40 mL serum bottles. The initial herbicide concentration was 20 μM, and the initial polysulfide concentrations were 0, 1, 2, 5, 10, 20, and 30 mM. All treatments were performed in triplicate. All sample bottles were closed with Teflon-lined rubber septa and aluminum caps and then incubated at room temperature (21 ± 1 °C). After equilibration for 0.5, 1.0, 1.5, 2.0, 2.75, 3.5, 5.0, 6.75, 9.0, or 23.0 h, a 0.5 mL aliquot (three replicates) was withdrawn from the reaction mixture using a 1.0 mL syringe and transferred to a 2 mL autosampler vial. The samples were kept in a freezer at −21 °C until analysis by high-pressure liquid chromatography (HPLC).

Reaction kinetics was further determined in the presence of a nitrogen headspace and after the addition of 1,4-benzoquinone to understand the role of free radicals in the reaction. To eliminate oxygen from the reaction system, a stream of nitrogen was bubbled through the sodium tetrasulfide solution in the serum bottle for 30 min before herbicide addition. A treatment without nitrogen purge was used as the control. The initial herbicide concentration was 20 μM, and the initial polysulfide concentration was 10 mM. The spiked samples were kept at room temperature, and aliquots were removed for analysis of the remaining herbicide concentration at different time intervals. For the experiment with 1,4-benzoquinone, the reaction mixture was prepared in a collapsible plastic glovebox (Fisher) filled with nitrogen. Different amounts of the 1,4-benzoquinone stock solution (10 mM in acetone) were added into borate buffer to arrive at initial concentrations of 120, 240, and 360 μM. The initial polysulfide concentration was 20 mM, and the initial herbicide concentration was 20 μM. A control treatment without 1,4-benzoquinone amendment was similarly prepared. The samples were equilibrated at room temperature, and aliquots of the reaction mixture were removed for analysis after different time intervals following the initiation of the reaction.

To analyze atrazine, simazine, or cyanazine in the reaction media, a 30 μL aliquot of the aqueous sample was injected into an Agilent-1100 series HPLC. Herbicides were eluted on a 250 mm × 4.0 mm (i.d.) reverse phase column (Hypersil ODS, 5 μm, Agilent, Wilmington, DE) and detected using a variable multiwavelength UV detector at 230 ± 10 nm for all compounds. The mobile phase was made of acetonitrile and water that was acidified to pH 3 with phosphoric acid. The percentage of acetonitrile was 60% for atrazine, 55% for cyanazine, and 50% for simazine. The flow rate of the mobile phase was 0.9 mL min^{-1}, and the temperature of the column was maintained at 35 °C. The concentration of herbicide was calculated by external calibration with standards.

Spectroscopic Analysis. To understand the role of free radicals in the reaction, spectroscopic analysis was performed using the reaction

Table 1. Pseudo First-Order Rate Coefficient k_{obs} (h^{-1}) for the Disappearance of Selected *s*-Triazine Herbicides (20 μM) in Sodium Polysulfide Solutions at 21 °C

initial polysulfide concentration	atrazine	cyanazine	simazine
water (control)	<0.0002	<0.0002	<0.0002
1 mM	0.003 ± 0.001	0.004 ± 0.001	0.005 ± 0.001
2 mM	0.009 ± 0.001	0.010 ± 0.002	0.008 ± 0.003
5 mM	0.029 ± 0.002	0.030 ± 0.004	0.027 ± 0.003
10 mM	0.061 ± 0.003	0.064 ± 0.005	0.059 ± 0.004
20 mM	0.147 ± 0.013	0.149 ± 0.027	0.138 ± 0.038
30 mM	0.216 ± 0.015	0.233 ± 0.034	0.210 ± 0.027

mixture by electron spin resonance (ESR) spectrometry. ESR analysis was carried out to evaluate the relative content of free radicals in sodium tetrasulfide solution in ambient air, in nitrogen, after the addition of 1,4-benzoquinone and after the reaction with the triazine herbicides. The initial sodium polysulfide concentration was 50 mM, the initial benzoquinone concentration was 360 μM, and the initial herbicide concentration was 200 μM. The samples were equilibrated for 24 h before analysis. Samples for ESR spectroscopy were produced by placing 0.2 mL of sample solution in a 3 mm (o.d.) × 17.7 cm (length) quartz tube, which was inserted into the resonator cavity. For analysis, aliquots of samples were scanned by an ESR spectrometer EMX ER077 (Bruker, Ettlingen, Germany) equipped with the Bruker WINEPR version 4.22 software. The samples were analyzed in the X-band (∼9.33 GHz) frequency range with a TE 102 cavity. All analyses were run with a 4 G modulation amplitude at 100 kHz modulation frequency with 8 mW of microwave power (9).

Column Leaching Experiment. A leaching experiment was conducted using packed sand columns to demonstrate the potential usefulness of polysulfide amendment for decontaminating triazine herbicides in a solid media. The experiment was carried out with atrazine and simazine. The sand (90 mesh, P. W. Gillibrand, Simi Valley, CA) was packed into PVC cylinders 48 cm (length) by 5 cm (i.d.) at a bulk density of 1.40 g cm^{-3}, and the packed columns were sealed at both ends with prefabricated caps with a brass inlet and outlet. The packed columns were saturated with water, and a pulse of 20 mL of acetone−water solution (1:9, v/v) containing 1.6 mg of atrazine or simazine was injected into the column from the top end. In one treatment, 20 mL of solution containing 80 mg of sodium tetrasulfide was injected into the column from the top end, and in another treatment, 20 mL of water was similarly injected. The columns were kept at room temperature for 7 days, and then, water was applied to the top end of the column at 1.0 mL min^{-1}. The leachate was collected from the bottom end using a Bio-RAD model 2110 fraction collector (Bio-RAD, Richmond, CA). The collected leachate samples were analyzed for atrazine and simazine by HPLC under the conditions given above.

RESULTS AND DISCUSSION

Effect of Free Radical Inhibitors on Reaction Kinetics. The reaction of atrazine, cyanazine, and simazine with polysulfides was followed under different conditions to understand the role of free radicals in the reaction. The reaction rates were first measured between polysulfides and herbicides at different initial tetrasulfide concentrations under ambient conditions (room temperature and ambient air headspace). The disappearance of the herbicide parent compound over time was fitted to a first-order decay model to estimate the rate coefficient k_{obs} (**Table 1**). The fit was generally good, with the correlation coefficient $r^2 \geq 0.95$. In untreated water, all chloro-*s*-triazine herbicides were found to be stable with no noticeable degradation over 72 h. However, the disappearance of all chloro-*s*-triazine herbicides was accelerated in the sodium tetrasulfide solution, and the rate of disappearance was proportional to the initial polysulfide concentration, as shown in **Figure 1** for atrazine. At an initial polysulfide concentration of 10 mM, the
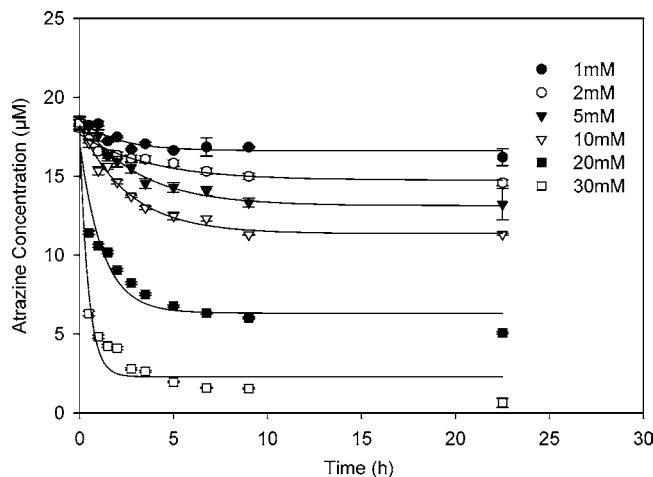
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Figure 1. Dissipation of atrazine (20 μM) in sodium tetrasulfide solutions at room temperature (21 $\pm$ 1 °C). Legends indicate the initial sodium tetrasulfide concentrations used. Symbols are measured data points, and curves are fitted lines by using a simplified second-order kinetics model as defined in eq 1.

$T_{1/2}$ of *s*-triazine herbicides was reduced to <12 h. When the initial polysulfide concentration was increased to 30 mM, the $T_{1/2}$ values of atrazine, cyanazine, and simazine decreased to ~3 h. Under these conditions, polysulfides enhanced the dissipation of each herbicide by several orders of magnitude.

Because $S_{RN}1$ is a second-order reaction as an S_N2 reaction (*10*), the reaction between the polysulfides and the triazine herbicides may be characterized using second-order kinetics (*2*). When the initial herbicide concentration C_0 is much smaller than the initial polysulfide concentration X_0, the kinetics can be approximated by the following first-order model:

$$C_t = C_0 \, e^{-\mu X_0 t} \tag{1}$$

where μ is the second-order rate coefficient (M^{-1} s^{-1}), t is the elapsed time, and C_t is herbicide concentration at time t. The second-order rate coefficient μ was estimated through regression by fitting the measured data to eq 1. The mean μ values were 1.98×10^{-3} ($r^2 = 0.99$), 1.90×10^{-3} ($r^2 = 0.99$), and 2.14×10^{-3} M^{-1} s^{-1} ($r^2 = 0.99$) for atrazine, simazine, and cyanazine, respectively. These values were in general agreement with observations by Lippa and Roberts (*4*), who reported a μ value of 6.90×10^{-3} M^{-1} s^{-1} for cyanazine and 5.64×10^{-3} M^{-1} s^{-1} for atrazine at a temperature (25 °C) slightly higher than that used in this study (21 °C).

The effect of molecular oxygen and benzoquinone, two common radical inhibitors, was evaluated in the reaction between sodium tetrasulfide and herbicides (*11*, *12*). When oxygen was removed from the reaction media after purging with nitrogen, the reaction rate between polysulfides and each herbicide increased significantly ($\alpha = 0.05$; **Table 2**). For instance, the estimated k_{obs} for atrazine in nitrogen (0.214 h^{-1}) was more than two times greater than that in air (0.061 h^{-1}). A similar enhancement was observed also for cyanazine and simazine after nitrogen purge. These results suggest that molecular oxygen in the ambient air may have scavenged free radicals in the polysulfide solution, thus reducing the reaction rate. The reaction was inhibited after the addition of another free radical inhibitor, 1,4-benzoquinone, and the inhibition became more pronounced at higher benzoquinone concentrations (**Table 2**). Under the test conditions, the addition of benzoquinone at 360 μM reduced the reaction by >50%. The overall

Table 2. Pseudo First-Order Rate Coefficient k_{obs} (h^{-1}) for the Disappearance of Selected *s*-Triazine Herbicides in Sodium Polysulfide Solutions under Ambient (Control Treatment), Nitrogen-Purged, and Benzoquinone-Amended Conditions

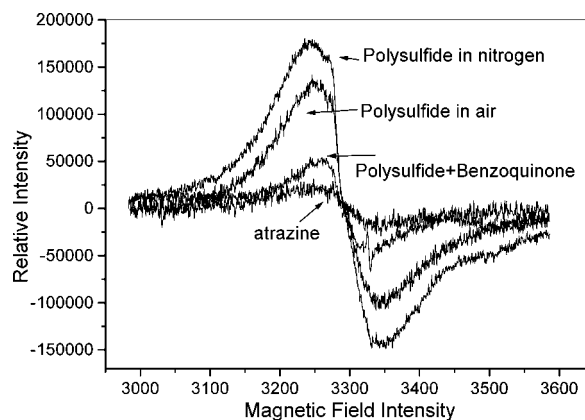| treatment	polysulfide (mM)	atrazine	cyanazine	simazine
control	10	0.061 ± 0.003	0.064 ± 0.005	0.059 ± 0.004
nitrogen purged	10	0.214 ± 0.024	0.224 ± 0.016	0.204 ± 0.009
control	20	0.147 ± 0.013	0.149 ± 0.027	0.138 ± 0.038
120 μM benzoquinone	20	0.124 ± 0.009	0.126 ± 0.013	0.123 ± 0.007
240 μM benzoquinone	20	0.106 ± 0.006	0.107 ± 0.0108	0.106 ± 0.004
360 μM benzoquinone	20	0.070 ± 0.004	0.075 ± 0.007	0.068 ± 0.005

Figure 2. ESR spectra of 50 mM sodium tetrasulfide solution following different treatments measured at 298 K. Legends indicate different treatments or conditions.

inhibitory influence of free radical scavengers suggests that free radicals may have contributed to the transformation reaction of *s*-triazine herbicides by polysulfides.

Changes in Free Radical Levels during Reaction. Analysis of changes in free radical concentrations in the polysulfide solution under the various experimental conditions provided additional evidence for the involvement of free radicals in the reaction. While there are a number of methods for the detection of free radicals, the most specific method is ESR (*13*). Typical ESR spectra are given in **Figure 2** for sodium tetrasulfide solution under ambient atmosphere, following nitrogen purge, after the addition of 1,4-benzoquinone and after the reaction with atrazine. The recorded ESR spectra of polysulfide solutions following various treatments were fitted to a Lorentzian line shape:

$$f(H) = \frac{32Y(H - H^0)(\Delta H_{pp})^{-1}}{\{3 + [2(H - H^0)(\Delta H_{pp})^{-1}]^2\}^2} \tag{2}$$

where H^0 is the center of the signal, ΔH_{pp} is the peak-to-peak line width, and Y is the maximum of the derivative of the signal. The fit between the experimental data and the $f(H)$ value was performed using a nonlinear least-squares method. The area A of the ESR signal was deduced from the parameters ΔH_{pp} and Y:

$$A = \sqrt{4/3} \pi Y (\Delta H_{pp})^2 \tag{3}$$

Table 3 gives the calculated results for the ESR spectra. It is evident that after reaction with the triazine herbicides, the ESR signal as area A for the reaction mixture significantly decreased. Under similar conditions, the addition of 1,4-benzuqionone also resulted in a much smaller response, while

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Table 3. Parameters of the ESR Absorption Signal in Sodium Tetrasulfide Borate Solution (pH 9.5) at 298 K Following Various Treatments

	Na_2S_4	atrazine–Na_2S_4	cyanazine–Na_2S_4	simazine–Na_2S_4
H^0 (G)	3309	3316	3319	3312
Y	1.38×10^5	1.53×10^4	1.52×10^4	1.46×10^4
ΔH_{pp} (G)	102.5	114.3	113.8	112.9
A ($\times 10^8$)	52.6 ($\pm$0.16)	7.3 ($\pm$0.09)	7.1 ($\pm$0.08)	6.8 ($\pm$0.07)

the purge with nitrogen resulted in a larger response, when compared to the reference sample that contained sodium tetrasulfide under an ambient atmosphere. These results suggest that after the substitution reaction the concentration of free radicals in the polysulfide solution decreased, and the effect was similar to that of free radical scavengers such as oxygen and 1,4-benzoquinone.

Reaction Mechanism. The above evaluation suggests that the reaction between polysulfides and triazine herbicides likely involved free radicals. A free radical chain reaction typically includes initiation, propagation, and termination steps (*14*). Oxygen or 1,4-benzoquinone can effectively scavenge free radicals, terminating the reaction chain (*15*). The polymerization reaction between sodium sulfide and chloroaromatic compounds was characterized in a previous study, where it was observed that if oxygen or hydroquinone was present, the reaction slowed (*16*). The authors interpreted the reaction as a $S_{RN}1$ reaction. Levillain et al. (*9*) studied S_n^{2-} by ESR spectroscopy and found that the signal of ESR significantly decreased with a decreasing $\bullet S_3^-$ concentration in the solution. Therefore, it may be speculated that $\bullet S_3^-$ is likely the most important free radical in polysulfides for the $S_{RN}1$ reaction with the triazine herbicides.

Many $S_{RN}1$ substitutions require an external stimulation involving the injection of a catalytic amount of electrons by dissolving metals in liquid ammonia or from an electrode (*17*). However, there are several examples where the reaction occurs without external stimulation, i.e., via the "thermal" $S_{RN}1$ mechanism (*18*). The reaction of triazine herbicides with polysulfides may occur through the thermal $S_{RN}1$ mechanism. In the initiation step, an ET from the S_n^{2-} may take place. This ET can follow a concerted dissociative step to directly afford a triazine radical and Cl^- (*19*). The triazine radical can react with the S_n^{2-} to give another intermediate radical (PhX$^{\bullet-}$), which by ET to the substrate forms the intermediates needed to continue the propagation cycle. PhX$^{\bullet-}$, a short-lived species, has been demonstrated to exist in $S_{RN}1$ processes by electrochemical investigation (*20*). On the whole, the process affords a nucleophilic substitution, in which a chlorine is replaced by a sulfur dianion. It must be noted that both $S_{RN}1$ and S_NAr obey the second-order kinetics and that both reactions lead to the formation of the same products. Therefore, analysis of reaction kinetics and products alone, as used in Lippa et al. (*4*), may not preclude the potential occurrence of $S_{RN}1$.

Although evidences presented above suggest a pathway from free radical reaction between polysulfides and triazine herbicides, S_NAr and $S_{RN}1$ may exist at the same time. Many of the features of the S_N/ET dichotomy have been analyzed, and the theoretical aspects have been reviewed (*21, 22*). In fact, because S_N and ET mechanisms both involve activation, which is associated with the single electron movement, they have a common link. Sometimes, the S_N reaction is even called "a single electron shift" mechanism, which means that the single ET occurs in a single step, which also involves the bond coupling between the nucleophile and the substrate, while in the ET mechanism, the single ET precedes the bond coupling
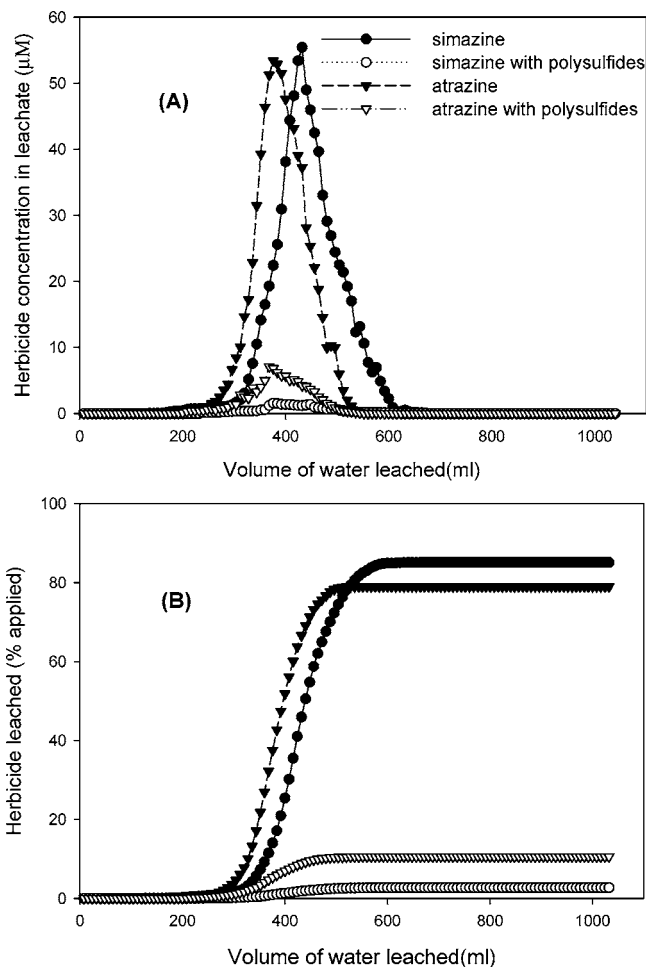
Figure 3. Effect of sodium tetrasulfide amendment on leaching of atrazine and simazine through sand columns. (**A**) Herbicide concentrations in leachate and (**B**) cumulative fractions of herbicide leached through the packed column.

step (*22*). Because the S_N and ET mechanisms have a common link (*23*), it is possible that the reaction between polysulfides and triazine herbicides may occur simultaneously via the S_NAr and $S_{RN}1$ pathways.

Decontamination of Herbicide Residues in Sand. The rapid reaction and detoxification under varying environmental conditions makes the polysulfide-induced dechlorination reaction a versatile option for decontaminating these herbicides in environmental media. We tested the use of this approach for removing herbicide residues from sand as a simulation of sandy aquifer remediation. The amendment of polysulfides into the sand columns significantly reduced the herbicide concentrations in the leachate as well as the cumulative fraction of herbicide leached through the column (**Figure 3**). The peak concentrations of atrazine and simazine in the leachate were detected at 53.4 and 55.4 μM, respectively. In the polysulfide-amended columns, the maximum concentration was only 7.1 μM for atrazine and 1.6 μM for simazine. Cumulatively, about 79% of the spiked atrazine and 85% of the spiked simazine were recovered in the leachate in the nonamended columns. In contrast, only 7.1% of the spiked atrazine and 2.7% of the spiked simazine broke through the column after the amendment of sodium tetrasulfide. These preliminary observations suggest that the reaction may be used for removing herbicide residues in contaminated environmental media. Although not tested in this study, potential treatments may be also feasible for treating herbicide-containing wastewater from manufacturing processes or rinsing of pesticide

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containers, for decontaminating spills, and for cleaning up contaminated sites (e.g., at dealerships). However, more research is needed for further developing these applications. For instance, the role of oxygen needs to be better understood under field conditions as it lowers the reactivity of polysulfides, as demonstrated in this study. On the other hand, the use of polysulfides under reduced conditions may lead to the formation of undesirable byproducts such as hydrogen sulfide. The environment compatibility of this reaction should be also evaluated with consideration of the potential formation and adverse effects of various reduced sulfur species.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Coates, J.; Bruce, R.; Haddock, J. Anoxic bioremediation of hydrocarbons. *Nature* **1998**, *396*, 730−730.

(2) Gan, J.; Wang, Q.; Yates, S.; Koskinen, W.; Jury, W. Dechlorination of chloroacetanilide herbicides by thiosulfate salts. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5189−5194.

(3) Gustafson, D. L. *Pesticides in Drinking Water*; Van Nostrand Reinhold: New York, 1993.

(4) Lippa, K.; Roberts, A. Nucleophilic aromatic substitution reactions of chloroazines with bisulfide (HS^-) and polysulfides (Sn^{2-}). *Environ. Sci. Technol.* **2002**, *36*, 2008−2018.

(5) Gaillard, F.; Levillain, E.; Lelieur, J. Polysulfides in dimethylformamide: Only the radical anions S_3^- and S_4^- are reducible. *J. Electroanal. Chem.* **1997**, *432*, 129−138.

(6) Leghie, P.; Lelieur, J.; Levillain, E. Comments on the mechanism of the electrochemical reduction of sulphur in dimethylformamide. *Electrochem. Commun.* **2002**, *4*, 406−411.

(7) Rossi, R.; Pierini, A.; Penenory, A. Nucleophilic substitution reactions by electron transfer. *Chem. Rev.* **2003**, *103*, 71−167.

(8) Genesty, M.; Degrand, C. Preparation of S_4^{2-} polysulfide from a sacrificial sulfur cathode and its use as a nucleophile in an electrochemically induced $S_{RN}1$ substitution reaction. *New J. Chem.* **1998**, *22*, 349−354.

(9) Levillain, E.; Leghie, P.; Gobeltz, N.; Lelieur, J. Identification of the S_4^- radical anion in solution. *New J. Chem.* **1997**, *21*, 335−341.

(10) Saveant, J. Electron transfer, bond breaking and bond formation. *Adv. Phys. Org. Chem.* **2000**, *35*, 117−192.

(11) Scamehorn, R.; Bunnett, J. Dark reactions of halobenzenes with pinacolone enolate ion−Evidence for a thermally induced aromatic srn1 reaction. *J. Org. Chem.* **1977**, *42*, 1449−1457.

(12) Shiraishi, Y.; Kojima, S.; Tomita, H.; Ohsuka, H.; Kawamura, T.; Toshima, N.; Hirai, H. Selective carboxylation of benzoic acid using cyclodextrin as mediator. *Polym. J.* **1996**, *28*, 619−626.

(13) Hanns, F. Structure of free radicals by ESR spectroscopy. In *Free Radicals*; Kochi, J., Eds.; Wiley Interscience: New York, 1973; Vol. 2, pp 435−491.

(14) Motherwell, W.; Crich D. *Free Radical Chain Reactions in Organic Synthesis*; Academic Press: San Diego, CA, 1992; pp 10−14.

(15) Michael, B.; Jerry, M. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley Publication: New York, 2001; pp 894−899.

(16) Annenkova, V.; Antonik, L.; Vakulskaia, T.; Voronkov, M. The interaction between sodium sulfide and chloroaromatic compounds in the *n*-methyl-2-pyrrolidone medium. *Doklady Akademii Nauk SSSR* **1986**, *286*, 1400−1403.

(17) Saveant, J. Mechanisms and reactivity in electron-transfer-induced aromatic nucleophilic-substitution−Recent advances. *Tetrahedron* **1994**, *50*, 10117−10165.

(18) Costentin, C.; Hapiot, P.; Medebielle, M.; Saveant, J. "Thermal" $S_{RN}1$ reactions: How do they work? Novel evidence that the driving force controls the transition between stepwise and concerted mechanisms in dissociative electron transfers. *J. Am. Chem. Soc.* **1999**, *121*, 4451−4460.

(19) Clarke, E.; Solouki, T.; Russell, D.; Martell, A.; Mcmanus, D. Transformation of polysulfidic sulfur to elemental sulfur in a chelated iron, hydrogen-sulfide oxidation. *Anal. Chim. Acta* **1994**, *299*, 97−111.

(20) Marquet, J.; Casado, F.; Cervera, M.; Espin, M.; Gallardo, I.; Mir, M.; Niat, M. Reductively activated polar nucleophilic aromatic-substitution−A new mechanism in aromatic chemistry. *Pure Appl. Chem.* **1995**, *67*, 703−710.

(21) Eberson, L.; Shaik, S. Electron-transfer reactions of radical-anions−Do they follow outer-sphere or inner-sphere mechanisms. *J. Am. Chem. Soc.* **1990**, *112*, 4484−4489.

(22) Shaik, S. The S_N2 and single electron-transfer concepts−A theoretical and experimental overview. *Acta Chem. Scand.* **1990**, *44*, 205−221.

(23) Tanaka, J.; Nojima, M.; Kusabayashi, S. Reaction of phenyl-substituted allyllithiums with tert-alkyl bromides−Remarkable difference in the alkylation regiochemistry between apolar process and the one involving single-electron transfer. *J. Am. Chem. Soc.* **1987**, *109*, 3391−3397.