



# The abiotic degradation of methyl parathion in anoxic sulfur-containing system mediated by natural organic matter



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## HIGHLIGHTS

- NOM significant enhanced the abiotic degradation of methyl parathion in sulfide solution.
- Methyl parathion reductive transformation mediated by NOM was specific to sulfide rather than other sulfur species.
- Removal efficiency of methyl parathion related remarkably with NOM concentration and pH value.
- Both the nitro group reduction and hydrolysis ( $S_N@C$ ) were acknowledged to be two transformation mechanisms.

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## ABSTRACT

Although the kinetics and transformation of methyl parathion have been investigated extensively, its abiotic degradation mechanism in anoxic sulfur-containing groundwater system is still not clear. In this work, the abiotic degradation of methyl parathion in anoxic sulfur-containing system mediated by natural organic matter (NOM) was investigated in batch experiments. It was found that the removal of methyl parathion (up to 80.7%) was greatly improved in sulfide containing NOM compared to those in sulfide alone (with 15.5%) and in NOM alone (almost negligible). Various sulfur species presented significant differences in behaviors methyl parathion degradation, but followed by the pseudo-first-order model well. No facilitated degradation of methyl parathion was observed in sulfite ( $SO_3^{2-}$ ) or thiosulfate ( $S_2O_3^{2-}$ ) containing NOM such as anthraquinone. Although elemental sulfur ( $S^0$ ) and cysteine could further improve the degradation rate of methyl parathion, their impacts was very limited. The removal efficiency of methyl parathion in anoxic sulfur-containing system were related remarkably with NOM concentration and solution pH. Based on the transformation products identified by gas chromatography-mass spectrometer (GC/MS) and liquid chromatography high resolution mass spectrometer (LC/HRMS), both the nitro group reduction and hydrolysis ( $S_N@C$ ) processes by sulfide ( $HS^-$ ) were further proved to be two predominant reaction mechanisms for the abiotic degradation of methyl parathion in anoxic sulfur-containing system. The results of this study help to understand the natural attenuation of methyl parathion under anoxic sulfide-containing groundwater system mediated by NOM.

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## 1. Introduction

As well known, organophosphorus pesticides (e.g., methyl parathion) that can perturb pest's function of nervous system have been used extensively in agricultural practice as an alternative to organochlorine pesticides banned completely in worldwide (Curl et al., 2002). Due to its relatively low hydrophobicity, residues of methyl parathion could be mobilized via various processes such

as leaching and surface water groundwater interactions under the prevailing anoxic conditions in the subsurface (Jurado et al., 2012). Additionally, their half lives of more than several months may cause environmental health problems via bioaccumulation in the food chain which have become a major concern worldwide (Lartiges and Garrigues, 1995). Efforts have been made to unravel its actual fate and transport under anoxic sediment conditions (Navarro-Ortega et al., 2010).

To date, studies on the abiotic degradation of methyl parathion have focused on the effects of minerals (Janos et al., 2014; Seger and Maciel, 2006), reduced sulfur (Wu et al., 2006), and divalent metal ions (Smolen and Stone, 1997). Their catalytic hydrolysis involved in

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electrophilic and nucleophilic substitutions was commonly found to be the predominant transformation pathway controlling its fate in the environment (Liu et al., 2015; Wu et al., 2006). Moreover, oxidation dissipation by manganese dioxide ( $\alpha$ -MnO<sub>2</sub>), in which the thiophosphate functionality (P=S) was oxidated to its corresponding oxon form (P=O), was demonstrated to be another major attenuation mechanism in our recent study (Liao et al., 2016).

The reduced sulfide (HS<sup>-</sup>) produced by biological reduction of sulfate that occurs widely not only in marine sediment pore waters (Rickard and Luther, 2007) but in inland groundwater (Li et al., 2014; Zeng et al., 2012) in areas such as Jiangnan plain, one of China's major grain production regions (Gan et al., 2014). HS<sup>-</sup> behaves as potent nucleophilics to enhance remarkably methyl parathion hydrolysis involved in the bimolecular substitution reaction (S<sub>N</sub>@C) (Wu et al., 2006). Meanwhile, dissolved natural organic matter (NOM) containing substantial redox active functionalities (such as quinone) had played an important role in modulating the biogeochemical behaviors of contaminants under reductive species-prevailing conditions (Fe<sup>2+</sup> and HS<sup>-</sup>), which been ascribed primarily to its ability of serving as electron transfer mediators (Zhang et al., 2014; Dunnivant and Schwarzenbach, 1992). In addition, other inorganic sulfur species including elemental sulfur, sulfite, thiosulfate and polysulfide were also formed concurrently via redox reactions between sulfide and NOM in anoxic sediment environments (Yu et al., 2015; Heitmann and Blodau, 2006), which acted as nucleophiles to further facilitate pollutants degradation (Schwarzenbach et al., 2003). For example, the rapidly dehalogenation of fumigants and herbicides via bimolecular substitution reactions by thiosulfate or sulfite was found previously (Bian et al., 2009; Wang et al., 2000). The elemental sulfur could also be transformed to polysulfides (S<sub>n</sub><sup>2-</sup>) through redox reaction with sulfide (Heitmann and Blodau, 2006), which possessed higher nucleophilic capacity than sulfide to intensify methyl parathion hydrolysis (Wu et al., 2006). Notably, organic sulfur compounds generated abundantly by means of the Michael addition reaction between sulfides and NOM were also demonstrated to be potent reductants to promote the reductive transformation of pollutants (Doong and Chiang, 2005; Vairavamurthy and Mopper, 1987). Although the reductive transformation of methyl parathion had been validated in previous studies, including in anoxic sulfur-containing soil systems (Adhya et al., 1981) and in sulfide containing commercial humic acids (HAs) (Guo and Jans, 2006), the mechanism for NOM-mediated enhanced degradation of methyl parathion with the presence of various reduced sulfur species has not been fully understood.

Thus, batch experiments were carried out in this study to elucidate the transformation mechanisms of methyl parathion mediated by NOM (HAs extracted from field sediments and anthraquinone) in the presence of various reduced sulfur species both inorganic species (sulfide, sulfite, thiosulfate or elemental sulfur) and organic (cysteine). The results help to understand the natural attenuation of methyl parathion in anoxic sulfide-containing environments.

## 2. Materials and methods

### 2.1. Materials and chemicals

Methyl parathion (>99.6%) standard was purchased from Pesticide Research Institute (Shanghai, China). N, N-Dimethyl-1, 4-phenylenediamine sulfate (≥98.0%), N-hexane, dichloromethane (DCM) and methanol were HPLC grade and were obtained from ANPEL laboratory Technologies (Shanghai, China). Acetone was pesticide residue analysis grade and obtained from J.K. Baker (Phillipsburg, NJ). The commercial 4-nitrophenol (AR, 98%), sodium

sulfide nonahydrate (99.99%), sodium thiosulfate (99%), sodium sulfite (>98%), cysteine (>99%), sodium anthraquinone-2-sulfonate (97%) and tetrapropylammonium hydroxide (TPAOH) were obtained from Aladdin Industrial Inc. (Shanghai, China). Other chemical reagents used in the experiment were of analytical grade of high purity and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All of above reagents were used as received without further purification. Ultrapure water (18.2 MΩ cm resistivity) prepared from ultra-pure water system (Heal Force NW, China) was used in all experiments.

Five sediment samples were collected in September 2015 in our monitoring sites (Gan et al., 2014), where various organophosphorus and organochlorine pesticides have been utilized widely and occurred ubiquitously in water-soil environments (Wang et al., 2016; Zhou et al., 2011). The samples were from different geographic locations: 2 from river sediments labeled as TRS and DRS, 1 landfill sediment labeled as LS and the other 2 cropland sediments labeled as TS and CS. Sediment HAs were extracted according to the method described by Li et al. (2011). The more details were found in Fig. S1 (supporting information, SI).

### 2.2. Experiment methods

All glassware was soaked 4 h in KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> solution, rinsed several times with ultra-pure water and then dried at 180 °C prior to use. Batch experiments were conducted in 10-mL brown borosilicate glass bottles (CNW) capped with an alumina crimp and a PTFE-faced septa. All ultra-pure water with 80 °C was deoxygenated purged with ultrapure nitrogen (>99.999%) for 2 h prior to be transferred to the glovebox filled with ultrapure nitrogen gas (>99.999%). 0.01 M NaCl and 0.2‰ sodium azide was added into 0.05 M phosphate buffer (NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub>) to maintain ion strength and eliminate bacteria influence, respectively. All the stock solutions of chemicals were prepared using deoxygenated phosphate buffers (pH = 7) prior to experiment. The reaction solutions were mixed with pre-designed amount of phosphate buffer, sulfur species (sodium sulfide, sodium sulfite or sodium thiosulfate) and dissolved organic matter (sediment HAs or anthraquinone) solutions. In addition, a certain volume of deoxygenated HCl (1 M) was used to adjust pH value. All operations were carried out in the glovebox. The sealed bottles were pre-equilibrated at least 12 h in a thermostatic water bath (25 ± 0.5 °C). Subsequently, a certain volume of methyl parathion stock methanol solution was injected into the reaction solution to yield the initial concentration of 19.0 μM. After vigorous mixing, the samples were kept for later use in the water bath (25 ± 0.5 °C) in darkness. At pre-designed time intervals, the samples were taken out from the water bath and then aliquots were pipetted immediately into 2-mL vials for HPLC analysis. The effects of NOM concentrations and solution pH on methyl parathion degradation were also evaluated. All experiments were conducted in duplicate. Several control experiments under the same conditions, including sulfide alone, dissolved organic matter alone and pH buffer alone, were also conducted simultaneously.

To calculate the transformation products, aliquots (8 mL) were transferred into a separating funnel, followed by the addition of 0.5 mL HCl (1 M) to acidify the degradation products. Subsequently, the samples were extracted three times with 3 × 10 mL of DCM just prior to the analysis by gas chromatography-mass spectrometer (GC/MS) and liquid chromatography-high resolution mass spectrometer (LC/HRMS).

### 2.3. Chemical analysis

The residual contents of methyl parathion in samples were

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