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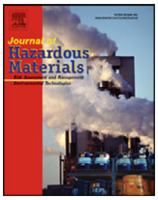

Biotransformation of chlorpyrifos in riparian wetlands in agricultural watersheds: Implications for wetland management

M. Ekrem Karpuzcu[a,c,*], David L. Sedlak[a], William T. Stringfellow[b,c]

[a] Department of Civil and Environmental Engineering, University of California Berkeley, Berkeley, CA 94720-1710, United States
[b] Ecological Engineering Research Program, School of Engineering & Computer Science, University of the Pacific, 3601 Pacific Avenue, Stockton, CA 95211, United States
[c] Earth Sciences Division, Geochemistry Department, Lawrence Berkeley National Laboratory, MS 70A-3317, Berkeley, CA 94720, United States

HIGHLIGHTS

- Chlorpyrifos biotransformation rates vary spatially and temporally in sediments.
- Phosphotriesterase enzyme activity is correlated with chlorpyrifos biodegradation.
- Hydroperiod differences affect the biotransformation rates.
- Wet-dry cycling is proposed as a wetland management strategy.

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ABSTRACT

Biodegradation of the organophosphate insecticide chlorpyrifos (O,O-diethyl O-(3,5,6-trichloropyridin-2-yl) phosphorothioate) in sediments from wetlands and agricultural drains in San Joaquin Valley, CA was investigated. Sediments were collected monthly, spiked with chlorpyrifos, and rates of chlorpyrifos degradation were measured using a standardized aerobic biodegradation assay. Phosphoesterase enzyme activities were measured and phosphotriesterase activity was related to observed biodegradation kinetics. First-order biodegradation rates varied between 0.02 and 0.69 day^{-1}, after accounting for abiotic losses. The average rate of abiotic chlorpyrifos hydrolysis was 0.02 d^{-1} at pH 7.2 and 30 °C. Sediments from the site exhibiting the highest chlorpyrifos degradation capacity were incubated under anaerobic conditions to assess the effect of redox conditions on degradation rates. Half-lives were 5 and 92 days under aerobic and anaerobic conditions, respectively. There was a consistent decrease in observed biodegradation rates at one site due to permanently flooded conditions prevailing during one sampling year. These results suggest that wetland management strategies such as allowing a wet-dry cycle could enhance degradation rates. There was significant correlation between phosphotriesterase (PTE) activity and the chlorpyrifos biotransformation rates, with this relationship varying among sites. PTE activities may be useful as an indicator of biodegradation potential with reference to the previously established site-specific correlations.

1. Introduction

Agricultural pesticides are indispensable in modern agriculture and are required to maintain high levels of production, but they can have adverse effects on aquatic ecosystems [1]. Due to the extremely long persistence and toxicity of organochlorine insecticides, more biodegradable and environmentally less problematic insecticides have been sought to replace them. The use of organophosphate insecticides has been growing as an alternative, as they were more biodegradable and were regarded biologically more efficient [2]. Organophosphate insecticides rank among the most widely used insecticides in the United States and are used extensively worldwide. Over 500 million kg of pesticides are used each year in the United States, of which approximately 18 million kg consist of organophosphate insecticides [3].

An important pathway for unintentional introduction of these compounds into aquatic ecosystems is surface runoff from treated fields. Runoff from irrigation and precipitation mobilize and transport dissolved and particle-associated pesticides into adjacent water bodies, where they may impact non-target aquatic invertebrates and fish [4]. Organophosphate insecticides are ubiquitous in streams and surface waters draining agricultural and

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* Corresponding author at: Department of Civil and Environmental Engineering, University of California Berkeley, Berkeley, CA 94720-1710, United States.
Tel.: +1 510 637 9705.
E-mail address: ekarpuzcu@berkeley.edu (M.E. Karpuzcu).

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urban areas in the US. In the San Joaquin Valley of California, four counties are ranked in the top ten nationally for both agricultural production and pesticide use [5,6]. Section 303(d) of the Federal Clean Water Act requires that states develop a list of water bodies that do not meet water quality standards, establish priority rankings for waters on the list, and develop action plans, called Total Maximum Daily Loads (TMDL), to improve water quality. The San Joaquin River and its tributaries are on the California 303(d) list for impairment by organophosphate insecticides chlorpyrifos and diazinon and chlorinated insecticides [7].

The organophosphate chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2 pyridylphosphorothioate) was commonly used for both household and agricultural applications until it was banned for household use by the USEPA in 2000 [8]. Its use in Europe is also subject to special regulations. The European Union (EU) Water Framework Directive lists chlorpyrifos among 33 priority substances, for which Environmental Quality Standards (EQS) are required [9]. Chlorpyrifos is still one of the most widely used insecticides in agriculture and each year, an estimated 8–10 million kg of chlorpyrifos are applied in the US [3]. In 2010, approximately 583,000 kg of chlorpyrifos (active ingredient) was applied in California [6]. Pulses of chlorpyrifos have been reported in the San Joaquin and Sacramento Rivers in California [10–12].

Chlorpyrifos has moderate volatility (Henry's Law Constant, 4.2 Pa m^3 mol^{-1}, vapor pressure 2.5 mPa), limiting partitioning to the gas phase [13]. It has limited solubility in water (reported as approximately 1.3 mg/L) and a moderately high log octanol–water partition coefficient (i.e., log K_{ow} 4.96) [13–15]. As a hydrophobic compound, chlorpyrifos partitions from water to surfaces. In riparian wetlands, chlorpyrifos partitions to soil and plant surfaces followed by biodegradation [15].

Biodegradation is a major factor determining the fate of organophosphate insecticides in the environment [16]. Organophosphate insecticides contain three phosphoester linkages (i.e., phosphotriesters). The organophosphate insecticide biotransformation pathways by most bacteria have been shown to be similar, with phosphotriesterase, also called organophosphate hydrolase, catalyzing the first degradation step, hydrolysis of P-O-alkyl and P-O-aryl bonds (Fig. 1) [2,17]. Studies have suggested that the utilization of chlorpyrifos as a source of phosphorus depends on the presence of both phosphomonoesterase and phosphodiesterase activity which are necessary to release inorganic P for uptake and ethanol for utilization as a carbon source by microorganisms [18]. Thus, all three types of phosphoesterase enzymes would be required for complete mineralization of chlorpyrifos. The most prominent of the heterocyclic metabolites from chlorpyrifos degradation in soils is 3,5,6-trichloro-2-pyridinol (TCP), the phosphotriesterase product. Other heterocyclic products have been identified, including chlorpyrifos oxon (*O*,*O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphate), desethyl chlorpyrifos (*O*-ethyl *O*-3,5,6-trichloro-2-pyridyl phosphate), and TMP (3,5,6-trichloro-2 methoxypyridine); however, TCP has been consistently found at comparatively higher concentrations than other heterocyclic metabolites [19].

Natural treatment systems, such as treatment wetlands and vegetated ditches, have been proposed as structural best management practices (BMPs) for the control of pesticides in agricultural landscapes [10,20–27]. Natural treatment systems have been shown to remove chlorpyrifos from agricultural runoff [1,10,24,26]. Previous studies have mostly focused on sorption of chlorpyrifos to wetland sediments and soils with removal efficiency assessed by measuring inlet and outlet concentrations in water samples. However, it is also important to know the fate of the chlorpyrifos within the wetland system. In the long term, particle-associated insecticides stored in sediments can be transported via runoff and other processes where they could impact downstream surface water systems. Therefore, it is important to quantify the ultimate fate and transformation rate of chlorpyrifos within the system before reaching conclusions on how effective a natural treatment system is with respect to contaminant attenuation. Although transformation of chlorpyrifos in field soils has been extensively studied [28–34], data on chlorpyrifos transformation in wetland sediments is scarce. There has been only one study investigating chlorpyrifos degradation in sediments from a constructed wetland [35], while a couple of studies have been done with sediments from urban streams and nursery recycling ponds [36,37].

The main purpose of this study was to investigate factors controlling biodegradation of the organophosphate insecticide chlorpyrifos in sediment deposits from agricultural drains and wetlands receiving agricultural return flows. In addition, phosphoesterase enzyme activities were measured to assess the potential for predicting transformation rates. With this information, it should be possible to better manage treatment wetlands for enhanced organophosphate insecticide removal.

2. Materials and methods

2.1. Field sites

Four field sites, Hospital Creek (coordinates 37.61056/−121.22861), Ingram Creek (37.60028/−121.22417), Ramona Lake (37.47558/−121.06992) and the San Joaquin River National Wildlife Refuge (SJRNWR, 37.63138/−121.20442) were selected for inclusion in this study (Fig. 2). The sites were chosen based on their diverse levels of riparian function and the availability of pesticide monitoring data. All sites are located in Stanislaus County, CA on the west side of the San Joaquin River within a predominately agricultural watershed. The Hospital Creek and Ingram Creek sites represent typical agricultural drains in the study region and have drainage areas of 9.5 km^2 and 29 km^2 respectively [38]. Ramona Lake is a permanent wetland originally constructed to retain irrigation drainage as part of a catfish-farming operation in the mid-1960s. It has become silted and is now predominantly a marsh ecosystem. It is occasionally utilized for storage of irrigation drainage by local growers. Ramona Lake receives drainage from 20.23 km^2 of farmland and has a surface area of approximately 81,000 m^2 with an average depth of 0.6 m. Dominant vegetation at Ramona Lake consists of tule (*Schoenoplectus acutus*) and cattail (*Typha latifolia*) [39]. The SJRNWR study site is a 270,010 m^2, riparian wetland with an average depth of approximately 0.6 m and a drainage area of 38.45 km^2. Dominant vegetation at the SJRNWR include native willows (*Salix exigua* and *Salix goodingii*), annual fireweed (*Epilobium brachycarpum*), and bermuda grass (*Cynodon dactylon*) [39]. It is former farmland that is being restored to a managed riparian wetland by the U.S. Fish and Wildlife Service (USFWS).

2.2. Sample collection

Monthly samples were collected from field sites. Approximately 500 g of wet surface sediments were collected from each field site using a stainless steel shovel and wide mouth Mason jars. The shovel was washed with detergent (Alconox Inc.) and rinsed at least three times thoroughly with deionized water before each use. Sampling equipment was also rinsed in site water prior to taking any samples. Samples were immediately placed in a cooler with ice and transported to the laboratory on the same day. Upon arrival in the lab, samples were homogenized using an aluminum spoon and split in two halves. One part was kept at 4 °C until analysis and the other part was frozen at −20 °C. An aliquot of the refrigerated sample was air dried and stored at room temperature for the