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Adsorption of methomyl on marine sediments

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Abstract

The adsorption behaviors of polar carbamate pesticide methomyl [$(CH_3S)(CH_3)C{=}N{-}O{-}(C{=}O){-}NH{-}CH_3$ or *S*-methyl-*N*-(methylcarbamoyloxy) thioacetimidate] on marine sediments treated by different methods were investigated. Ten hours were required for adsorption equilibrium of methomyl on sediments. The adsorption isotherms of methomyl on all sediments could be described by Freundlich equation very well. Adsorption of methomyl was completed mainly via the surface H-bond forces between function groups of organic constituents and methomyl molecules. In addition, microporosity action of clays and the van der Waals forces between clays and methomyl molecules might also play important roles in the adsorption of methomyl on sediments. Some external factors which could affect adsorption behaviors of methomyl were also investigated in the present study. Our results showed that the adsorption capacity of methomyl on the sediment decreased with increasing temperature and pH value. Moreover, the adsorption capacity of methomyl on the sediment appeared to be lower in natural seawater than in diluted seawater.

Keywords: Methomyl; Sediment; Adsorption; Freundlich; Seawater

1. Introduction

Agricultural and outdoor residential use of pesticides is a matter of environmental concern because these chemicals are recognized as a source of potential adverse environmental impact (nonpoint and point pollution) and their presence in seawater and sediments has grown considerably [1,2].

Methomyl, a broad spectrum carbamate insecticide, was widely used in China and many agricultural countries for crop protection [3]. Aqueous solutions of methomyl have been reported to decompose more rapidly on aeration, in sunlight, or in alkaline media [4]. The estimated aqueous half-life for the insecticide is 6 days in surface water and over 25 weeks in groundwater [4]. The hydrolysis half-lives of methomyl in solutions at pHs of 6.0, 7.0 and 8.0 were 54, 38, and 20 weeks, respectively. In pure water, the hydrolysis half-life has been estimated to be 262 days [5]. Methomyl has low persistence in the sediment environment, with a reported half-life of approximately 14 days [5]. Because of its high solubility in water and low affinity for sediment binding methomyl may have potential for groundwater and seawater contamination [5]. Recent investigations have shown that the soluble concentration of methomyl is higher in coastal waters than in offshore area, and nowadays, the concentration of methomyl in seawater presents a trend of increasing [6]. Because of the ubiquitous distribution in seawater as well as ecotoxicology of methomyl, it results in the pollution of marine environment, and has an unfavorable effect on marine organisms.

Adsorption equilibrium is an important parameter for assessing the fate, transport and toxicological impact of pollutants in the ecosystem [7]. In addition to affecting the mobility of pollutants, adsorption may directly influence the pathways and transformation rates of pollutants by surface associated chemical and microbial processes. In marine environment, suspended material is a major transport medium for pollutants [8,9]. Methomyl and other agrochemicals in seawater were adsorbed on the suspended particulate in the surface layer and settled to the bottom swiftly through less polluted seawater in the lower layer. Through liquid–solid interfacial adsorption and settling, pesticides could finally move into

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bottom sediments [10]. The adsorption capacity of suspended particulate for pesticides determined their final fate in marine environment [11]. Therefore, study on the sorption features of methomyl by marine sediments is of potential geochemical significance for further assessing the transport and fate of this compound in the ocean.

Numerous studies and reviews have examined sediment properties affecting the distribution of pesticides between soluble and adsorbed forms, in order to predict adsorption from the known properties of sediments. Sediment organic content [12–14] and sediment clay content [15,16] are specially important in non-polar pesticides adsorption because of their high surface areas and active adsorption sites. Hitherto, much effort has been directed toward understanding the sorption of a variety of hydrophobic compounds on marine sediments. Organic matter is recognized as the primary factor related to sorption of non-polar compounds and partitioning of these compounds into organic matter is considered to be the main mechanism for their sorption in sediment-water systems [17,18]. However, for polar compounds the partition mechanism of organic matter of sediment is not expected to be the same [11].

Up to date, there are still no reported studies on the adsorption of methomyl on marine sediments in seawater medium. The objectives of this study were to determine adsorption isotherms of methomyl on marine sediments, to examine different sorption properties of various types of sediments treated by different procedures, and to investigate the effects of sediment ingredients (e.g. organic carbon and clay) and environmental factor (e.g. medium, temperature and acidity) on the adsorption of methomyl. This aspect of research under seawater conditions will fill gaps in the literature. Meanwhile, the research will definitely provide valuable information for understanding more clearly the potential migration pattern of the pesticide in marine environment.

2. Experimental

2.1. Chemicals

The pure chemicals used in the experiments were purchased from Shanghai Chemical Reagent Co. and were used as received. Methomyl were got from Huayang Agrochemical Co. and had a purity greater than 98%. The insecticide is a crystalline solid of melting point 78–79 °C, v.p. 6.65 mPa at 25 °C, and water solubility of 57.9 g/l at 25 °C [4]. The standard solution was prepared by directly dissolving 0.8000 ± 0.0002 g methomyl into 100 ml seawater, and then diluting 25.00 ml of the solution with 475 ml seawater to make up a final methomyl concentration of 400 mg/l.

2.2. Seawater

Natural seawater (NSW) was collected from Jiaozhou Bay, China, filtered through 0.45 μm filter membranes, and irradiated with strong ultraviolet light to eliminate the effects of natural dissolved organic matter as far as possible [19]. The salinity and pH of the seawater were 33.4 and 8.03‰, respectively.

In order to study how the media influenced the sorption behavior of methomyl, two kinds of diluted seawater (DSW) were prepared from NSW and deionized water with the volume proportions of 2:1 (DSW1) and 1:1 (DSW2), respectively. The pH value of NSW is generally ∼8.00. In order to simulate natural situation as far as possible, the pH values of three kinds of media used in the study were all adjusted to 8.00 ± 0.03 with NaOAc solution and HOAc solution.

2.3. Sediment collection and treatment

Four sediment samples were collected from Jiaozhou Bay, Tanggu coastal sea, the South China Sea, and Yellow River Estuary, respectively. Sampling stations of sediments and their main physicochemical properties were given in Table 1. The sediment samples were treated according to the following three methods [19].

The quantities indicated below are per gram dry weight of the sediment samples.

A. No-treatment: sediment samples were only washed with distilled water, air-dried, and then ground. The part that could pass 150–250 mesh sieves was chosen as experimental material.
B. HCl-treatment: the sediment sample from (A) was mixed with 6 ml of distilled water and the pH of the suspension system was adjusted to 2.0 with HCl (1 M) solution. Immersion stirring was continued for 24 h. The system was washed by distilled water till the pH of the suspension system was 4.0. The samples were then filtered, air-dried, and ground to pass 150–250 mesh sieves. This treatment could remove the carbonate of sediment and the percentage of organic carbon content of sediment on dry weight basis increased accordingly.
C. H_2O_2-treatment: the sediment from (B) was added to 6 ml of 30% H_2O_2 and 3 ml of 0.02 M HNO_3 solution with

Table 1
Sampling stations of sediments and their organic carbon and clay contents (%)

Site	Location	Water depth (m)	Organic carbon (%)	Clay (%)
Jiaozhou Bay	36°08′N, 120°14′E	10	1.47	23
Tanggu Coastal Sea	38°58′N, 117°43′E	30	1.15	17
South China Sea	5°30′N, 113°30′E	2000	1.55	19
Yellow River Estuary	119°05′N, 37°54′E	5	1.62	30