

Environmental Risk Assessment of Polyhexamethyleneguanidine Phosphate by Soil Adsorption/Desorption Coefficient

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ABSTRACT: This study was performed to determine the adsorption-desorption characteristics of polyhexamethyleneguanidine phosphate in three different soil types of textural classification. Adsorption and desorption studies is important for prediction their fate and generating essential information on the mobility of chemicals and their distribution in the soil, water and air of our biosphere. The detection limit of the test substance quantified by a spectroscopic method using Eosin indicator was 0.25 $\mu\text{g/mL}$. The reproducibility of analytical method was confirmed by the preliminary test. The concentrations of polyhexamethyleneguanidine phosphate in aqueous solution were 1.36 ± 0.09 , 2.45 ± 0.01 , and 4.25 ± 0.05 $\mu\text{g/mL}$ by a spectroscopic method using Eosin indicator. The adsorption percents of polyhexamethyleneguanidine phosphate in soil were greater than 95.2% for all three test soils. The desorption percents from the adsorbed soil were less than 4.5, 4.7 and 4.7%. Therefore, the adsorption coefficients (K) were greater than 110, 111 and 116. The adsorption coefficient calculated as a function of the organic carbon content (Koc) of the test soils were greater than 9,181, 11,100, and 8,942, respectively. Therefore, the test substance, polyhexamethyleneguanidine phosphate could be concluded as medium or high adsorption (>25%) and poorly desorption (<75%) in soil media. Therefore, this chemical is likely to be retained in soil media and may not pose a risk in the aquatic environment.

Key Words: adsorption, desorption, polyhexamethyleneguanidine phosphate, adsorption coefficient

INTRODUCTION

Polyhexamethyleneguanidine phosphate (PHMG-P), poly(imino-carbonimidoyl-imino-1,6-hexanediy) phosphate, is used as a microbial additive in plastics, fabric softeners, paints, swimming pools and papers and for sanitation in food processing plants and cooling towers.¹⁾ Due to its low LC₅₀ (0.23 mg/L at 96 hours) for Red Killifish (*Oryzias latipes*)²⁾, PHMG-P can be classified as very toxic compound to fish. The Predicted Environmental Concentration (PEC)/ a Predicted No Effects

Concentration (PNEC) ratio for the aquatic environment, assuming nationwide use, is 56 on the report of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) in Australia. This value is significantly greater than 1, indicating an immediate concern to the aquatic compartment¹⁾.

The fate of chemicals and their behavior in soil is influenced by several factors including adsorption, desorption and decomposition. The adsorption of chemicals to soils is an important process affecting the interactions between chemical and soil in the our environment. In addition, adsorption and desorption are involved in determining the chemicals movement and leaching potential through the soil profile, their bio-availability by microorganism, and persistence³⁾. There

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are many studies of adsorption and desorption of pesticides including imazosulfuron⁴, simazine⁵, flufenacet⁶, and atrazine⁷. As a consequence of cationic character, PHMG-P is expected to have a high affinity for organic matter in soil. However, no information for adsorption and desorption of PHMG-P has been reported.

The objective of this study was to determine the adsorption coefficient of PHMG-P from adsorption and desorption percent and to evaluate the hazard to the aquatic environment considering soil adsorption and desorption characteristics when the PHMG-P is used.

MATERIALS AND METHOD

Chemicals

Polyhexamethyleneguanidine phosphate, poly (iminocarbonimidoylimino-1, 6-hexanediy), phosphate was provided by SK Chemicals Co., LTD. and had a purity of 98%. All solvents and reagents used were analytical grade.

Soils

The test soils used in the adsorption/desorption test were collected from three different soil sites in Daejeon, Korea. These soils had a pH's between 4

and 8, an organic carbon content between 0.6 and 3.5% (Table 1). The soils were collected from the horizon A (upper 20 cm), air-dried, and passed through a 2 mm sieve.

Preparation of aqueous solution

0.01 M calcium chloride (CaCl₂) solution was prepared by dissolving 1.11 g of calcium chloride (CaCl₂) in distilled water and made up to 1 L.

Analytical methods

To prepare the pH 3.6 glycine buffer, 50 mL of 0.1 M glycine solution were added to 2.5 mL of 0.2 M Hydrochloric acid and made up to 100 mL with distilled water. Standard solutions were prepared at 0, 0.2, 0.4, 0.6, 2, 4, 6, 10 and 20 µg/mL concentrations. For the quantification, 10 mL of sample solution, 10 mL of glycine buffer (pH 3.6) and 1.0 mL of 0.05% Eosin were added in a 20 mL vial and mixed with vortex. The vial left for 5~10 min at room temperature and was analyzed at 549 nm by UV/Vis spectrophotometer.

Experimental methods

To determine the method detection limit, 30 g of the test soil was added to 250 mL centrifuge bottle and

Table 1. Physicochemical properties of test soils

Test soil	I	II	III
Soil order	Entisols	Entisols	Inceptisols
Soil series	NamGae	IpSeok	SaChon
Classification	Sandy Loam	Loamy Sand	Loam
Location	Daejeon	Daejeon	Daejeon
Horizon	A (0~20 cm)	A (0~20 cm)	A (0~20 cm)
% Sand	56.6	80.4	40.7
% Silt	29.9	13.4	40.3
% Clay	13.5	6.2	19.0
% Organic matter:	2.1	1.7	2.3
% Organic carbon	1.2	1.0	1.3
pH (1:1 H ₂ O)	5.4	5.9	5.2
Cation Exchange Capacity (MEQ/100 g)	8.2	6.3	10.6
Extractable cations (MEQ/100 g)			
Ca	2.9	1.9	3.0
Mg	0.5	0.3	0.6
Na	0.3	0.2	0.2
K	0.3	0.2	0.2
H	4.2	3.7	3.7

was reequilibrated with twice its weight of water. This reequilibration was carried out for 24 hours at room temperature by recipro shaker (200 rpm). The method detection limit (MDL) test⁸⁾ was performed in seven replicates using one soil type, sandy loam. One hundred and fifty mL of the aqueous solution (0.01 M CaCl₂) was added and agitated for 16 hours in the incubator at room temperature (24 ± 1°C) by recipro shaker (200 rpm). The centrifuge bottles were tightly closed during the agitation to avoid volatility losses. The aqueous solution was separated by centrifugation for 10 min at 3500 rpm, and the test substance was added to form a solution of 0.2 µg/mL. The solution was analyzed by spectroscopic method using Eosin indicator as described above.

For the preliminary test, reequilibration, agitation and centrifugation were performed following the same procedure as described above. The preliminary test was performed in triplicate using one soil type, sandy loam. The test substance was added to form a solution of 1, 2, and 4 µg/mL. The solution was analyzed by spectroscopic method using Eosin indicator as described above.

For the screening test, adsorption, the solution of test substances was prepared in 0.01 M CaCl₂ at a level of 5 µg/mL. The adsorption step was performed in duplicate at the single concentration using three types of soil. Blanks included each of the three soils with only 0.01 M CaCl₂ solution (no test chemical) and a single control of the test substance solution with no soil. Thirty g of the soil was added to the test solution and agitation was begun immediately. Agitation condition was the same as described above. After agitation, this suspension was centrifuged to obtain a clear solution. Centrifugation condition was the same as described above. The volume of clear aqueous solution was measured and analysed immediately the concentration of the parent compound by spectroscopic method using Eosin indicator. The volume of the supernatant was recorded for subsequent correction of desorption data.

For the screening test, desorption, to each solid phase was added a volume of 0.01 M CaCl₂ solution and this mixture was agitated for 16 hours. It is then centrifuged and the supernatant was retained for analysis. The whole desorption procedure was repeated with same volume of fresh 0.01 M CaCl₂ solution.

Calculation

The percent of the chemical adsorbed (A), the per-

cent of the adsorbed material which is desorbed (D), the percent of the adsorbed material which is not desorbed (R), the adsorption coefficient (K), and the adsorption coefficient calculated as a function of the organic carbon content of the soil (Koc) were calculated by following equations⁹⁾.

$$A(\%) = \frac{G - (C_e \cdot V_0)}{G} \times 100 = \frac{X}{G} \times 100$$

$$D(\%) = \frac{(C_1 - C_2) \cdot V - (V_0 - V) \cdot C_e}{X} \times 100$$

$$R(\%) = \frac{G - (C_e + C_1 + C_2) \cdot V}{X} \times 100$$

$$K = \frac{X/m}{C_e}$$

$$Koc = K \cdot \frac{100}{\% \text{ organic carbon}}$$

The measurable quantities required are:

- m : dry weight of soil employed (g)
- X : Quantity adsorbed (µg)
- C_e : concentration of substance remaining in solution (V) in the adsorption step (µg/mL)
- C₁ : concentration of substance in solution in the first wash (µg/mL)
- C₂ : concentration of substance in solution in the second wash (µg/mL)
- V₀ : original volume of solution employed (mL)
- V : volume of solution obtained after the adsorption step (mL)
- G : quantity of material recovered from the soilless control (µg)
- A : the percent of chemical adsorbed (%)
- D : the percent of adsorbed material which is desorbed (%)
- R : the percent of adsorbed material which is not desorbed (%)
- K : the adsorption coefficient
- Koc: the adsorption coefficient based on organic carbon content of the soil

RESULTS AND DISCUSSION

From the result of MDL test, the concentration of aqueous solution with test soil extract (blank) was 1.03 ± 0.12 µg/mL, and the concentration of test solution (soil solution with 0.2 µg/mL PHMG-P) was 1.21 ± 0.08 µg/mL. The concentration of PHMG-P was 0.18

$\pm 0.08 \mu\text{g/mL}$. Therefore, the MDL of PHMG-P was $0.25 \mu\text{g/mL}$, which is calculated from the equation of $\text{MDL} = T (n-1, 1-\alpha=0.99) \times S = 3.143 \times S$.

To assure applicability of the analytical method to the PHMG-P, preliminary test was performed. The results of PHMG-P concentration in aqueous solution with test soil extract were $1.36 \pm 0.09 \mu\text{g/mL}$, $2.45 \pm 0.01 \mu\text{g/mL}$, and $4.25 \pm 0.05 \mu\text{g/mL}$. So the reproducibility of the analytical method was confirmed by the preliminary test (Table 2).

The PHMG-P was not detected in equilibrium test solutions from the screening test by spectrophotometric analysis. So the MDL value, $0.25 \mu\text{g/mL}$ was applied to the concentration of equilibrium test solution of PHMG-P. The soil adsorption rate of PHMG-P calculated from the above concentration were greater than

95.2% for all three test soils (Table 3).

As seen in the adsorption experiment, PHMG-P was not detected in the test solution from the desorption experiment by spectrophotometric analysis. Therefore, the MDL value, $0.25 \mu\text{g/mL}$ was applied to the concentration of equilibrium test solution of PHMG-P for desorption rate calculation. The desorption rate of PHMG-P were less than 4.5, 4.7, and 4.7% for three test soils and the percent of adsorbed material which was not desorbed were greater than 95.5, 95.3, and 95.3% (Table 4).

The soil adsorption coefficient of PHMG-P calculated from the adsorption/desorption test results were greater than 110, 111, and 116 for the three types of soil, and the Koc values calculated as a function of the organic carbon content of the soils were greater than 9,181,

Table 2. Summary of preliminary test

Test substance	Polyhexamethyleneguanidine phosphate
Sample purity (%)	Higher than 98.0
Saturation concentration (g/L)	285
Description of a suitable analytical method	UV/Vis Spectrophotometer using Eosin indicator
Concentration of the test solution ($\mu\text{g/mL}$)	1, 2, 4
Analytical concentration of the test solution ($\mu\text{g/mL}$)	1.36 ± 0.09 2.45 ± 0.01 4.25 ± 0.05

Table 3. Screening test results of adsorption

Test soil	I		II		III	
Temperature ($^{\circ}\text{C}$)			24 \pm 1			
Ci ^{a)} ($\mu\text{g/mL}$)			5.0			
Ce ^{b)} ($\mu\text{g/mL}$)	ND ^{h)}	ND	ND	ND	ND	ND
X ^{c)} (μg)	738.2	738.2	738.2	738.2	738.2	738.2
m ^{d)} (g)	26.8		26.6		25.4	
X/m ($\mu\text{g/g}$)	27.5	27.5	27.8	27.8	29.1	29.1
G ^{e)} (μg)	775.7	775.7	775.7	775.7	775.7	775.7
V ^{f)} (mL)	140	141	144	145	144	144
A ^{g)} (%)	> 95.2	> 95.2	> 95.2	> 95.2	> 95.2	> 95.2

^{a)}Ci : initial concentration ($\mu\text{g/mL}$)

^{b)}Ce : concentration of substance remaining in solution (V) in the adsorption step ($\mu\text{g/mL}$)

^{c)}X : quantity adsorbed (μg)

^{d)}m : dry weight of soil employed (g)

^{e)}G : quantity of material recovered from the soiless control (μg)

^{f)}V : volume of solution obtained after the adsorption step (mL)

^{g)}A : the percent of chemical adsorbed (%)

^{h)}ND: not detected, < $0.25 \mu\text{g/mL}$

Table 4. Screening test results of desorption

Test Soil	I		II		III	
Temperature (°C)	24 ± 1					
C ^{a)} (µg/mL)	ND ^{d)}	ND	ND	ND	ND	ND
D ^{b)} (%)	< 4.4	< 4.5	< 4.7	< 4.7	< 4.7	< 4.7
R ^{c)} (%)	> 95.6	> 95.5	> 95.3	> 95.3	> 95.3	> 95.3

^{a)}C : concentration of substance in solution in the wash (µg/mL)

^{b)}D : the percent of adsorbed material which is desorbed (%)

^{c)}R : the percent of adsorbed material which is not desorbed (%)

^{d)}ND: not detected, < 0.25 µg/mL

Table 5. Summary of screening test

Test Soil	I	II	III
Temperature (°C)	24 ± 1		
A ^{a)} (%)	> 95.2	> 95.2	> 95.2
D ^{b)} (%)	< 4.5	< 4.7	< 4.7
R ^{c)} (%)	> 95.5	> 95.3	> 95.3
K ^{d)}	> 110	> 111	> 116
Koc ^{e)}	> 9,181	> 11,100	> 8,942

^{a)}A : the percent of chemical adsorbed (%)

^{b)}D : the percent of adsorbed material which is desorbed (%)

^{c)}R : the percent of adsorbed material which is not desorbed (%)

^{d)}K : the adsorption coefficient

^{e)}Koc: the adsorption coefficient based on organic carbon content of the soil

11,100, and 8,942, respectively (Table 5).

If little or no adsorption occurs (<25%), no further sorption tests are performed because the chemical will not be retained in soil media. If adsorption is moderate or high (>25%), a single desorption test is performed to establish whether or not this chemical is likely to be retained in soil media. If it is readily desorbed (>75%), no further sorption tests are required. If only poorly desorbed (<75%), the screening test is considered to be complete and the secondary or advanced phase in which an adsorption isotherm is determined and a mass balance established will be required^{9,10)}. In conclusion, PHMG-P could be adsorbed highly or in medium (>25%) and desorbed poorly (<75%) in soil media. Therefore, this chemical is considered to be retained in soil media. The calculated PEC/PNEC ratio using Koc values is 0.0063. On the basis of this PEC/PNEC ratio PHMG-P may not pose a risk to the environment¹⁾.

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