Aluminum Dialkyl Phosphinate Flame Retardants and Their Hydrolysates: Analytical Method and Occurrence in Soil and Sediment Samples from a Manufacturing Site

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Supporting Information

ABSTRACT: Aluminum dialkyl phosphinates (ADPs) are emerging phosphorus flame retardants due to their superior characteristics, but their analytical method, and occurrence and fate in environments have never been reported. For the first time, we developed a method for the analysis of trace ADPs and their hydrolysates (dialkyl phosphinic acids, DPAs), and studied their occurrences and fates in soils and sediments. We found that ADPs are hardly dissolved in water and organic solvents, but are dissolved and hydrolyzed to DPAs in 30 mM $\text{NH}_3 \cdot \text{H}_2\text{O}$, thus both ADPs and DPAs can be determined by liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) in the form of DPAs. ADPs and DPAs in soil and sediment samples were determined by (i) extracting both ADPs and DPAs with 75 mM $\text{NH}_3 \cdot \text{H}_2\text{O}$, and selectively extract DPAs only with formic acid–water–methanol (5:5:90, v/v/v); (ii) quantifying the total content of ADPs and DPAs, and DPAs by LC-MS/MS analysis of the DPA contents in the former and the latter extract, respectively; and (iii) calculating ADPs from the content difference between the former and the latter extracts. The limit of quantifications (LOQs) of the proposed method were 0.9–1.0 $\mu\text{g}/\text{kg}$, and the mean recoveries ranged from 69.0% to 112.4% with relative standard deviations $\leq 21\%$ ($n = 6$). In soil and sediment samples around a manufacturing plant, ADPs and DPAs were detected in surface soils in the ranges of 3.9–1279.3 and 1.0–448.6 $\mu\text{g}/\text{kg}$, respectively. While ADPs were found in all the samples of the soil and sediment cores from the drain outlet and the waste residue treatment site at levels ranging from 30.8 to 4628.0 $\mu\text{g}/\text{kg}$, DPAs were found in more than 90% of these samples with concentrations in the range of 1.1–374.6 $\mu\text{g}/\text{kg}$. The occurrences of ADPs and DPAs are not in correlation with the total organic carbon, whereas the occurrences of DPAs are highly correlated with the sample pH. Our study also suggests that the DPAs in the samples sourced from the hydrolysis of ADPs. The high hydrolysis degrees of ADPs (up to 49.6%) suggest that once released into the environment, ADPs are likely to coexist with their hydrolysates. Thus, to evaluate the environmental safety of ADPs, the environmental behavior and toxicity of both ADPs and DPAs should be considered.

INTRODUCTION

The production and use of brominated flame retardants (BFRs) have been gradually phased out in the United States (U.S.) and European Union (EU) due to their persistence, bioaccumulation, and toxicity to animals and humans.^{1–5} Currently, many new flame retardants were developed as substitutes for BFRs.^{6,7} Aluminum dialkyl phosphinates (ADPs, aluminum salts of phosphinic acid having alkyl and/or aryl substitutes) is one class of the most promising compounds with superior characteristics like strong flame retardant activity of its own and the synergism to combine with some nitrogen containing organic substances. The excellent heat stability, improved mechanical and electrical property, and low smoke during

combustion of ADP-containing composites make ADPs a class of potential flame retardants in the electricity and electronic industry.⁸ Although no information is available on the production volumes, ADPs have already been produced in many countries including Germany,^{9–12} U.S.,^{13,14} and China^{15–17} in recent years.

With their production and wide application, ADPs will inevitably be introduced into environments. However, a very

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Table 1. Mass Spectrometry Conditions for the Analysis of the Target Compounds

Compound	Abbreviation	Structure	Transitions ^a	Collision energy (eV)	Tube lens
Aluminum methylethyl phosphinate	AMEP		<u>107.2</u> > <u>63.4</u>	29	-73
			107.2 > 78.3	17	-73
Methylethylphosphinic acid	MEPA		<u>107.2</u> > <u>63.4</u>	29	-73
			107.2 > 78.3	17	-73
Aluminum diethyl phosphinate	ADEP		<u>121.2</u> > <u>63.4</u>	40	-73
			121.2 > 92.3	17	-73
Diethylphosphinic acid	DEPA		<u>121.2</u> > <u>63.4</u>	40	-73
			121.2 > 92.3	17	-73
Aluminum methylcyclohexyl phosphinate	AMHP		<u>161.1</u> > <u>63.4</u>	43	-92
			161.1 > 78.3	24	-92
Methylcyclohexyl phosphinic acid	MHPA		<u>161.1</u> > <u>63.4</u>	43	-92
			161.1 > 78.3	24	-92

^aQuantitative ion transitions are underlined.

recent study showed that aluminum salts of diethylphosphinic (ADEP) affected the sublethal life cycle parameters of *daphnid* for chronic exposure, such as cumulative reproductive output and population growth rate.¹⁸ In addition, our preliminary study indicated that aluminum salts of methylethylphosphinic (AMEP), methylcyclohexyl phosphinic acid (AMHP) and ADEP showed mild hepatotoxicity and reproduction toxicity to male BALB/c mice. Unfortunately, the environmental behaviors of ADPs are far from known. This partly is because ADPs are new compounds with no analytical methods for their determination in environmental matrixes at trace levels. ADEP in the test solutions was determined by ICP-AES through determining phosphorus,¹⁸ but it is infeasible to measure ADPs in environmental matrixes because of the ingenerate of phosphorus in environment.

It was estimated that the log_{K_{OW}} of ADEP was −0.44,¹⁹ and the water solubility given by National Industrial Chemicals Notification and Assessment Scheme (NICNAS) was less than 1 mg/L,²⁰ suggesting that ADPs are both hydrophobic and

oleophobic. Therefore, we speculated that soils and sediments are one of the main pools of ADPs in the environment. In addition, it is well-known that the levels of pollutants in soils and sediments could provide information about environmental contamination of an area in long periods of time,²¹ and could be helpful for understanding the persistence of organic chemicals in the environment, which is fundamental to assess their potential hazard to humans and wildlife.²² Thus, it is of great importance to study the occurrence and distribution of ADPs in soils and sediments. Besides, from the structures of ADPs (Table 1), it is speculated that hydrolysis is a major transformation route for ADPs. Therefore, determining the hydrolysates of ADPs (dialkyl phosphinic acids, DPAs) is of helpful for understanding the transformation of ADPs.

In this work, as standards of DPAs are not commercially available, we first synthesized and characterized three DPAs, namely methylethylphosphinic acid (MEPA), diethylphosphinic acid (DEPA) and methylcyclohexyl phosphinic acid (MHPA). Then, a sensitive method that allows for the

determination of AMEP, ADEP and AMHP and their corresponding hydrolysates MEPA, DEPA, and MHPA at trace levels in soils and sediments was developed. Finally, the occurrence and distribution of these ADPs and their hydrolysates in soils and sediments around a manufacturing plant were studied. To the best of our knowledge, this is the first report on the analysis and behavior of ADPs and their hydrolysates in the environment.

MATERIAL AND METHODS

Chemicals. HPLC grade methanol, acetonitrile, ethanol, *n*-hexane, acetone, ethyl acetate, and dichloromethane were supplied by Fisher Scientific (Fair Lawn, NJ). Formic acid (99% purity) was from Acros Organics (Morris Plains, NJ). Nitric acid (65%) was obtained from Merck (Darmstadt, Germany). Ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$, 15 M) and hydrogen peroxide (30%, w/v) were from Sinopharm Chemical Reagent Co. (Beijing, China). Ultrapure water was obtained from a Milli-Q ultrapure water system (Millipore, Bedford, MA). AMEP, ADEP, and AMHP with purity >95% were provided by Jiangnan University (Hubei province, China).

Individual stock solutions of ADPs (100 mg/L) and DPAs (1000 mg/L) were prepared by dissolving an appropriate amount of each substance in 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ and methanol, respectively, for storage. Mixtures of working standards were prepared weekly by combining the stock solution and diluting with 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$. The stock and working solutions were stored at 4 °C.

Synthesis and Characterization of DPAs. DPAs were synthesized using ADPs by solid-phase extraction (SPE). Briefly, individual ADPs (10 mg) were dissolved in 20 mL of 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$, respectively. The respective solutions were loading on the mixed-mode anionic-exchanger (MAX) cartridges (500 mg, 6 mL; Waters, Mildford, MA), which were conditioned with 6 mL methanol and 6 mL water prior to use. After sample loading, the MAX cartridges were washed by 1 mL of 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ and 1 mL methanol successively. Then the analytes were eluted by 5 mL of 2% (v/v) formic acid in methanol. The elutions were evaporated to near dryness by gentle nitrogen stream under 40 °C, and finally freeze-dried in a lyophilization apparatus (Heraeus-Christ, Germany). The synthesized DPAs were characterized with nuclear magnetic resonance (NMR, Bruker ARX 400, Karlsruhe, Germany). The ^1H NMR spectra of DPAs were recorded on 400 MHz spectrometers in D_2O at ambient temperatures.

Dissolution of ADPs in Various Solvents. Water and various organic solvents like methanol, ethanol, acetone, acetonitrile, and *n*-hexane were tested for dissolving ADPs. In addition, aqueous solutions adjusted to pH 2.8, 5.3, 6.8, 8.8, and 11.2 with $\text{NH}_3\cdot\text{H}_2\text{O}$ and formic acid were also used to test the solubility of ADPs at different pH values. Specifically, 10 mg of the target ADP was, respectively, mixed with 20 mL of the test solvent or solution mentioned above. After sonication for 2 h, the mixture was centrifuged at 10 000 rpm for 10 min and then filtered through a 0.22 μm filter. Since preliminary experiment indicated that ADPs showed the highest solubility in 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ (pH 11.2), all the filtrates were diluted by 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ and analyzed by ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). To further study the solubility of ADPs at pH 11.2, a mixture of 20 mL 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ and 10 mg AMHP (the most insoluble one among the studied ADPs) were sonicated for 2 h and centrifuged at 10 000 rpm for 10 min. The supernatant and

precipitate were digested using a CEM Mars 5 Xpress (Matthews, NC) with a microwave-assisted digestion procedure modified from the U.S. EPA method 3052 (see details in the Supporting Information (SI)), respectively. The Al content in the two digestion solutions was measured by inductively coupled plasma mass spectrometry (ICPMS, Agilent 7700 Agilent Technologies, Santa Clara, CA) with Al standard solutions prepared by diluting a certified reference material (10 mg/L Al, Environmental Calibration Standard, UL ISO 9001, Agilent Technologies) with 5% (v/v) HNO_3 .

Sample Collection and Pretreatment. All soil and sediment samples were collected around a manufacturing plant (30°48'45.08"N, 113°45'39.91"E) in Wuhan, Hubei province in central China (SI, Figure S1) in June and July, 2013. The plant suspended production at the end of 2011 for scale up in another place, and some new factories for other products were built around it since then. This prohibited us to sample around it in a large scale in the horizontal direction. We collected soil samples at the top 0–10 cm surface layer with a stainless steel scoop. Samples 1–8 were located 10 and 50 m north, northeast, northwest and west of the plant, respectively. As industrial wastewater in the production plant was discharged into Yunshui River through a concrete drainage channel, surface sediments (3–5 cm deep, samples 9–12) located at 0 m, 30 m, 100 and 600 m downstream of the plant outlet, respectively, were collected with a grab sampler (Wildco Ekman Grab, 152 × 152 × 152 mm, Buffalo, NY). To overcome inhomogeneity, at each site five separate soil samples were collected and mixed thoroughly to obtain one composite sample. Moreover, 4 soil and sediment cores (A, B, C and D) were collected using an in-house built steel gravity tube (120 cm long and 12 cm i.d.) and the cores were sliced at 5 cm intervals onboard. Sediment core A located at the drain outlet of the plant, soil cores B and C located in the place where waste residues were treated, and soil core D located about 50 cm north of B and C where no waste residue was discharged. Cores A and B were collected in June, 2013 with a depth of 45 and 50 cm, respectively. Cores C and D were collected a month later with the same depth of 120 cm. All the soil and sediment samples were immediately packed in polyethylene bags and freeze-dried once transported back to the laboratory.

The freeze-dried solids were grinded to particles smaller than 100-mesh and stored in brown glass bottles at 4 °C until analysis. The total organic carbon (TOC) of soil and sediment samples was measured using a Solids TOC Analyzer (O.I. Analytical). A separate aliquot of sample was mixed with ultrapure water (1:5 by dry weight) and the pH value was measured using a pH meter.²³ Each sample was measured triplicate for both TOC and pH.

Preparation of Spiked Samples. To spike ADPs into the samples, into a 2 L polytetrafluoroethylene jar were added 5.0 mg each of the ADPs (as powders) and the blank soil sample (1000 g, also as powder), and then homogenized on a rotary shaker for 48 h. To prepare the DPA spiked sample, into the powdered blank soil sample (0.5 g) was added 2.5 μg each of the DPA standard solutions prepared in methanol and mixed thoroughly. These spiked samples were stored in brown glass bottles at 4 °C for evaluating the extraction recovery under different extraction conditions.

Extraction of Analytes. Aliquots (0.5 g) of soil and sediment samples were weighed and transferred into a 15 mL polypropylene centrifuge tube in duplicate. One was treated by 2.5 mL aqueous solution of 75 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ to extract both

ADPs and their hydrolysates DAPs, and another one was treated by 2.5 mL formic acid–water–methanol (5:5:90, v/v/v) to extract the DPAs only. After vortex-mixed for 1 min, the mixtures were then sonicated for 30 min and centrifuged at 10 000 rpm for 10 min at 4 °C. The supernatants were loading on the MAX cartridges. The elutions were evaporated to complete dryness by gentle stream of nitrogen under 40 °C and finally made up to 1.0 mL with 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ for UPLC-MS/MS analysis.

UPLC-MS/MS Determination. Liquid chromatography (LC) separation was undertaken using a Waters Acquity UPLC (Waters, Mildford, MA) separation module equipped with a BEH C_{18} column (2.1 mm $\times$ 100 mm; particle size, 1.7 μm , Waters, Mildford, MA). The mobile phase was a mixture of 15 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ in ultrapure water (A) and methanol (B) with a flow rate of 0.2 mL/min under gradient conditions: 5% B held for 1 min in the initiation, and increased linearly from 5% to 70% in 4 min, then increased to 100% in 0.1 min and held for 1.5 min, and finally returned to the initial composition in 0.10 min. The column was equilibrated for 3 min before the next injection. The injection volume was 10 μL and the column oven was set at 45 °C.

A TSQ Quantum Access (Thermo Fisher Scientific, San Jose, CA) triple quadrupole mass spectrometer was interfaced to the LC system. The electrospray ionization (ESI) was operated in the negative ion mode, and the best conditions were set as follow: spray voltage 3000 V, and capillary temperature 300 °C. Nitrogen was used as the sheath gas (35 units) and aux gas (15 units). Argon was used as the collision gas at a pressure of 0.2 Pa.

Method Validation. Since ADPs and DPAs were extracted with different solutions, the analytical method was validated under three extraction cases: (i) DPA spiked soil samples extracted with 75 mM $\text{NH}_3\cdot\text{H}_2\text{O}$; (ii) ADP spiked soil samples extracted with 75 mM $\text{NH}_3\cdot\text{H}_2\text{O}$; and (iii) DPA spiked soil samples extracted with formic acid–water–methanol (5:5:90, v/v/v). In addition, since isotope labeled standards are unavailable for the target compounds, three types of standard calibration curves were prepared for the method assessment in the three cases mentioned above: (i) neat standard curves plotted by using water with 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ -dissolved standard solutions from 1.0 to 1000.0 $\mu\text{g/L}$; (ii) matrix-matched standard curves plotted by using standards spiked in extracts of blank samples before UPLC-MS/MS analysis; and (iii) matrix-fortified standard curves plotted by using extracts of blank samples spiked before pretreatment.

Recoveries and precisions were determined by analyzing soil samples spiked at three levels in six replicates in the three cases mentioned above. Recoveries were calculated by comparing the peak areas of blank samples spiked before pretreatment to the counterparts spiked before UPLC-MS/MS analysis. The precisions, expressed as percent relative standard deviations (RSD, %), were determined using six replicates of spiked soil samples. The limit of quantification (LOQ) and the limit of detection (LOD) represent the lowest spiked concentration that can yield a signal-to-noise ratio (S/N) greater than 10 and 3 in the selected production chromatogram, respectively. The matrix effect was evaluated according to the strategy proposed by Matuszewski et al.,²⁴ that is, the ratio between the slope of matrix-matched standard curve and the slope of standard solution curve was subtracted and multiplied by 100 to obtain the percentage.

RESULTS AND DISCUSSION

Hydrolysate Identification and Standard Solution Preparation.

The synthesized DPAs were characterized by NMR, and results showed that the purity were >90% for MHPA, and >95% for both MEPA and DEPA (SI Figures S2–S4). UPLC-MS/MS was further used for identification and to obtain detailed mass spectra for DPAs. Full scans under negative mode for each compound were acquired by direct infusion of each standard solution (1 mg/L), prepared in 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$, at a flow rate of 5 $\mu\text{L/min}$ with the range 35.0–500.0 (m/z). For MEPA identification, the full-scan spectrum showed a peak at m/z 106, corresponding to the molecular weight of MEPA $[\text{M-H}]^-$. The collision induced dissociation (CID) spectrum showed major product ions at m/z 77 and 63 (SI Figure S5), which are consistent with alkyl cleavages and the losses of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$, respectively. Similar characteristics of mass spectra were observed for DEPA and MHPA (SI Figure S5).

To analyze with UPLC-MS/MS, the target compounds must be prepared in solutions. It was found that all the three ADPs were poorly soluble in water and various organic solvents including methanol, ethanol, acetone, acetonitrile and *n*-hexane. Insoluble substances were also observed in aqueous solutions with different pH values except for pH 11.2. Since the highest solubility of ADPs was observed at pH 11.2, the solubility values of ADPs at different pH were normalized to that at pH 11.2 and shown in Figure 1. All the ADPs exhibited strongly pH

Figure 1. Effects of pH on the solubilities of ADPs. Aliquots of 10 mg each of analyte were added into 20 mL aqueous solutions of different pHs adjusted with $\text{NH}_3\cdot\text{H}_2\text{O}$ and formic acid. The resulting mixture was sonicated for 2 h, centrifuged at 10 000 rpm for 10 min, filtered through 0.22 μm filters, and the ADPs in the filtrate were determined by UPLC-MS/MS. Each point represents the mean values for three replicates.

dependent solubility with minimum one at pH 6.8. The dramatically increased solubility at lower and higher pH values might be attributed to the hydrolysis of ADPs to form DPAs or diacylphosphinic anion. This speculation was confirmed by the identical mass spectrum of ADPs and their corresponding DPAs. Table 1 lists the characteristic ions and collision energy for each compound during selected reaction monitoring (SRM) acquisition. In addition, the solubility showed an order of $\text{AMEP} > \text{ADEP} > \text{AMHP}$, which agreed to the increased hydrophobicity of their hydrolysates. To evaluate the dissolution degree of ADPs in 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ (pH 11.2), 10.2 mg AMHP (containing 0.54 mg Al according to the

Figure 2. Recoveries of ADPs and DPAs determined using different extractants. A, C: blank soil powders (0.5 g) were spiked with 2.5 µg each of the DPAs in solutions, and extracted with different concentrations of $\text{NH}_3\cdot\text{H}_2\text{O}$ (A) or mixtures of different proportions of methanol, water and formic acid (C); B, D: blank soil powders (1000 g) were spiked with 5.0 mg each of the ADPs as solid powders, and extracted with different concentrations of $\text{NH}_3\cdot\text{H}_2\text{O}$ (B) or mixtures of different proportions of methanol, water and formic acid (D). Each bar represents the mean values $\pm$ standard deviation for six replicates, and MeOH and FA represent methanol and formic acid, respectively.

Table 2. Analytical Performance of the UPLC-MS/MS Method for Soil Samples

extraction solvent	compound	linear range ($\mu\text{g/kg}$) ^a	R ^{2a}	LOQ ($\mu\text{g/kg}$) ^a	slope of standard curve			matrix effect ^b (%)
					neat	matrix-matched	matrix-fortified	
75 mM NH ₃ ·H ₂ O	MEPA	0.92–921.7	0.9972	0.92	1530.3	1004.6	735.2	34.3
	DEPA	0.93–930.7	0.9939	0.93	3990.6	3434.7	2862.0	13.9
	MHPA	0.95–947.1	0.9999	0.95	5578.9	5211.2	4271.2	6.6
	AMEP	1.0–1000.0	0.9963	1.0	1530.3	984.3	693.8	35.7
	ADEP	1.0–1000.0	0.9918	1.0	3990.6	3587.6	2744.5	10.1
	AMHP	1.0–1000.0	0.9975	1.0	5578.9	5289.1	4197.8	5.2
	Formic acid–water–methanol (5:5:90, v/v/v)							
	MEPA	0.92–921.7	0.9933	0.92	1530.3	827.3	515.4	45.9
	DEPA	0.93–930.7	0.9942	0.93	3990.6	4163.8	3010.4	−4.3
	MHPA	0.95–947.1	0.9964	0.95	5578.9	5839.2	4029.1	−4.7

^aLinearity range, R^2 and LOQ were obtained from the matrix-fortified standard curves, which were used for quantitative determinations. ^bCalculated as $[1 - (\text{the slope of matrix-matched standard curves}/\text{the slope of neat standard curves})] \times 100\%$

molecular formula), the most insoluble one among the studied ADPs, was dissolved in 20 mL of 30 mM $\text{NH}_3\cdot\text{H}_2\text{O}$, and the Al content in the supernatant and precipitate were determined by ICPMS. Result showed that 0.52 mg and 0.02 mg Al were found in the supernatant and precipitate, respectively, indicating that $\geq 96\%$ AMHP was dissolved.

Optimization of the Sample Preparation Conditions. Since ADPs hydrolyzed to DPAs once dissolved, the contents of ADPs and DPAs in real samples cannot be distinguished by

UPLC-MS/MS, and the only way for respective quantification is to separate them in the extraction procedure. A reasonable approach is to seek a solvent that can extract both ADPs and DPAs, while another solvent that can extract only DPAs, thus ADPs can be obtained from their difference. To this end, a blank soil was spiked with 5 mg/kg each of the ADPs and DPAs, and then extracted with various solvents, mixed solvents, and aqueous solutions, respectively.

As ADPs are easily dissolved in alkaline solutions (Figure 1), solutions with 15, 30, and 75 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ were tested to extract both ADPs and DPAs. Figure 2A,B shows that by using 75 mM $\text{NH}_3\cdot\text{H}_2\text{O}$ as the extractant, the recoveries were nearly 100% for all the tested ADPs and DPAs. A variety of organic solvents such as methanol, acetonitrile, acetone, ethyl acetate and dichloromethane were tested, but none of them was able to extract DPAs except for methanol, which provided extraction efficiencies in the range of 5–10%. The mixture of formic acid–water–methanol (5:5:90, v/v/v) provided maximum extraction efficiencies for DPAs (77–82%) and minimum extraction efficiencies for ADPs (7–20%) (Figure 2C, D), thus was adopted to extract DPAs only in this study.

In order to minimize possible interference on the UPLC-MS/MS determination, the extract was cleaned up with a SPE step. MAX cartridge was selected for the SPE clean up considering the existence of phosphinic acid group in the target analytes. Results showed that this cartridge provided >90% recoveries for both ADPs and DPAs in the eluting step, whereas no ADPs and DPAs was lost in the loading and washing steps.

To enhance the method sensitivity, eluents from the SPE purification step was concentrated before injection into the UPLC-MS/MS system. Unfortunately, routine operation, that is, evaporating 5 mL of the 2% (v/v) formic acid in methanol spiked with 10 ng each of the analytes to near dryness under gentle stream of nitrogen, gave rise to great deviation (RSD > 70%, $n = 6$). We speculated that it was the residue of the nonvolatile formic acid that suppressed the analyte signals. Thus, we tried to evaporate 5 mL of 2% formic acid in methanol spiked with 10 ng of analytes to complete dryness. Result showed this modification did improve the repeatability (RSD < 9%). Under the above optimized conditions, the recoveries for ADPs and DPAs were all above 90% for the spiked soil samples.

Validation of the Analytical Method. Table 2 shows the analytical performance parameters such as linear range, LOQ, and the slope of standard curve of each analyte. The correlation coefficients (R^2) of the matrix-fortified calibration curves were all above 0.99, and the LOQs of the method were 0.9–1.0 $\mu\text{g}/\text{kg}$. The mean recoveries ranged from 69.0% to 112.4% with RSDs no more than 21% ($n = 6$, see SI Table S1). Matrix effect is another important parameter to evaluate the performance of LC-MS/MS interfaced with ESI.²⁵ All of the matrix effects were present as signal suppression at a level of <45.9%, which was acceptable for trace analysis (Table 2).

Occurrence of ADPs and DPAs in Soil and Sediments. Samples collected from surface soil around the plant and sediments along Yunshui River were analyzed by the proposed method. As shown in SI Table S2, AMEP and AMHP were detected in four of the eight soil samples with concentrations in the range of 5.1–692.1 $\mu\text{g}/\text{kg}$ and 3.9–1279.3 $\mu\text{g}/\text{kg}$, respectively. ADEP was detected in three of the eight soil samples at levels from 10.8 to 34.0 $\mu\text{g}/\text{kg}$. While in some samples were detected with ADPs but with no corresponding DPAs, there is no sample that with DPAs but with no corresponding ADPs, suggesting the DPAs in samples are hydrolyzed from ADPs. Based on the ADP and DPA concentration of each sample, it can be calculated that the values of ratio of DPA, defined as $\text{DPA}/(\text{ADP}+\text{DPA})$, were in the range of 0–27.7%, which can be regarded as the degrees of hydrolysis if assuming the DPAs were all hydrolyzed from the corresponding ADPs.

Among the sediment samples collected along the Yunshui River, only in the sediment of the drain outlet was detected AMEP (15.6 $\mu\text{g}/\text{kg}$), AMHP (202.8 $\mu\text{g}/\text{kg}$) and MHPA (95.9 $\mu\text{g}/\text{kg}$). No ADEP and DEPA was detected in the drain outlet. The possible reason for the significant lower concentrations of AMEP and ADEP could be attributed to their lower production than AMHP. Neither ADPs nor DPAs were found in sediments 30, 100, and 600 m downstream of the plant outlet, indicating their low mobility along with water flow.

For the sediment core collected from the drain outlet (core A), AMHP and MHPA were detected in all the slices with concentrations ranging from 30.8 to 739.6 $\mu\text{g}/\text{kg}$ and 1.1 to 332.5 $\mu\text{g}/\text{kg}$, respectively. However, AMEP was only detected in the surface layer at 15.6 $\mu\text{g}/\text{kg}$. For the two cores collected from the waste residue treatment site (cores B and C), ADPs were detected at ranges of 45.3–2854.8 $\mu\text{g}/\text{kg}$ (AMEP), 28.3–1795.1 $\mu\text{g}/\text{kg}$ (ADEP), and 1.7–524.4 $\mu\text{g}/\text{kg}$ (AMHP). In the samples with ADPs, over 90% were detected to contain their corresponding hydrolysates, with concentrations in the range of 2.4–206.6 $\mu\text{g}/\text{kg}$ (MEPA), 1.2–163.2 $\mu\text{g}/\text{kg}$ (DEPA) and 4.0–69.2 $\mu\text{g}/\text{kg}$ (MHPA), respectively. It is noteworthy that the concentrations of AMHP and MHPA were lower than the other two ADPs and their hydrolysates, which was on the contrary to that in the sediment core A. This is because the sediment core A was collected from the drain outlet that received the plant wastewater discharge containing high concentrations of AMHP, which is the main product of this plant. However, the two soil cores B and C were collected from the residues treatment site where more amounts of AMEP and ADEP than AMHP might be treated. No ADPs and DPAs were detected in core D that was collected nearby the waste residue treatment place, indicating their low horizontal transfer.

Distribution in Soil and Sediment Cores. Figure 3 shows the vertical distribution profiles of the ADPs and DPAs in soil and sediments. In the sediment core, the AMHP concentrations

Figure 3. Vertical concentration and pH profiles in sediment core A (A), soil core B (B), and soil core C (C). Core A was collected at the drain outlet of the plant in June, 2013; Core B and C were both located in the place where waste residues were treated, and were collected in June, 2013 and a month later, respectively. Each point represents the mean values $\pm$ standard deviation for three replicates.

in the upper sections (173.0–739.6 $\mu\text{g}/\text{kg}$ at 0–20 cm depth) were significantly higher than that in the down sections (30.8–73.5 $\mu\text{g}/\text{kg}$ at 20–45 cm depth). Both the AMHP and MHPA concentrations peaked at depth of 10–15 cm, and showed significant negative relationship with depth ($p < 0.01$), except for the relatively lower concentration in the surface layers (0–10 cm). The low concentration in the top layer can be attributed to the washing by river water, and the stop of discharge as the plant stops production since the end of 2011. However, unlike the vertical distribution trends of ADPs and DPAs in core A, the concentrations of ADPs and DPAs in core B increased with the depth from 0 to 35 cm, and then almost kept constant with the depth further increased to 50 cm. To get the profiles at depth of >50 cm, a 120 cm deep soil core (core C) was collected at the same site of core B a month later. While the analyte profiles (except for AMHP) of core C in the depth of 15–50 cm agreed very well with that of core B, the analyte concentrations in the surface (0–15 cm deep) were elevated and showed a trend of decrease with the increase of depth. We speculate that a new discharge of ADPs occurred during the period between the two sampling time. This speculation was confirmed by the workers of the plant. With the increase of depth in the range of 30–120 cm, the concentration of AMHP decreased, whereas the AMEP and ADEP showed a concentration peak at 60 cm and 75 cm, respectively. The occurrence of the deepest peak at a depth order of ADEP > AMEP > AMHP implies the mobility of these compounds might have the same order, which remains for further study.

To understand the vertical distribution profiles of these compounds, the TOC and pH of these samples were also measured. Although ADPs was hydrophobic in nature, no correlationship was found between the TOC and ADP levels in all the three cores (data not shown). It is well-known that hydrophobic chemicals commonly showed positive correlation with the TOC contents in soil and sediment samples.¹⁹ However, ADPs showed special physicochemical characteristics that are neither hydrophilic nor lipophilic,²⁰ thus their contents are not in positive correlation with the TOC contents.

The occurrence of DAPs showed high correlation with the pH. As shown in Figure 3, the concentrations of DPAs increased with the decrease of pH ($p < 0.01$) in cores B and C. This agreed with the results shown in Figure 1, in which the dissolution (hydrolysis) of ADPs increased with the decline of pH for pH < 7. It is noteworthy that the pH of core C (3.6–5.7) was significantly lower than that of the nearby core D (5.4–7.6), where no ADPs and DPAs was detected, implying either the plant waste residue was treated with the addition of acids or the hydrolysis of ADPs decreased the pH of soil. In addition, core A showed a significantly negative correlation ($p < 0.01$) between depth and the ratio of MHPA, that is, ~35% in the surface layers (0–15 cm) in contrast to <11% in the lower layers. However, the depth was positively related to ratios of DPAs in the layers of 0–40 cm depth in core C, where pH was relatively constant. The reasons for the above phenomenon remain unknown and call for further research.

It should be emphasized that for all the three cores detected with ADPs and DPAs, the vertical profiles of DPAs agreed very well with that of the corresponding ADPs, again demonstrated that the DPAs in the samples sourced from the hydrolysis of ADPs. In addition, in all the three cores the hydrolysis degrees of AMHP (2.7–49.6%) were higher than that of AMEP (0.4–37.9%) and ADEP (0.6–29.3%). This is on the contrary to that in aqueous solutions, where AMHP shows lower hydrolysis

degree and thus solubility (Figure 1). This might be ascribed to the higher hydrophobicity of MHPA, which results in higher sorption to the organic matter and particles and therefore reduced freely dissolved concentration in pore water, and thus enhanced the hydrolysis of AMHP.^{26,27}

Environmental Implication. Our results demonstrated the occurrence of ADPs and their hydrolysates DPAs in soils and sediments after stop discharging from the manufacturing site for one year and a half, indicating that this emerging phosphorus flame retardants might be persistent in environments.²⁸ Furthermore, our study also suggested that the ADPs in soil and sediment samples could hydrolyzed to form DPAs, and both ADPs and DPAs showed low horizontal mobility and relatively higher vertical mobility in soil and sediments, indicating ADPs could contaminate the groundwater in the form of DPAs. The high hydrolysis degree of ADPs (up to 49.6%) suggests once released into the environment these compounds could coexisted with their hydrolysates. Thus, to assess the environmental safety of ADPs, the environmental behavior and toxicity of both ADPs and DPAs should be considered. Given currently there is very limited data on the toxicity of ADPs and no reports on the toxicity of DPAs, as well as the lack of information on the environmental transport and transformation of these compound, research on these issues are urgently needed.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional results are provided in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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