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Phosphine in various matrixes

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Abstract: Matrix-bound phosphine was determined in the Jiaozhou Bay coastal sediment, in prawn-pond bottom soil, in the eutrophic lake Wulongtan, in the sewage sludge and in paddy soil as well. Results showed that matrix-bound phosphine levels in freshwater and coastal sediment, as well as in sewage sludge, are significantly higher than that in paddy soil. The correlation between matrix bound phosphine concentrations and organic phosphorus contents in sediment samples is discussed.

Keywords: phosphine concentration; sediment; paddy soils; sewage sludge

Introduction

Phosphorus in its reduced form (phosphine, PH_3), like carbon, nitrogen and sulfur, has been recognized as a ubiquitous gaseous constituent of the atmosphere. Devai *et al*. (1988) first succeeded in identifying phosphine in the emissions from sewage plants. Glindemann and his collaborators, improving analytical techniques for ambient phosphine, have detected phosphine from various anaerobic emission sources, such as marsh, landfill sites, sewage sludge, paddy field, and animal manure etc. (Glindemann, 1996a; Gassmann, 1996; Liu, 1999). The formation of phosphine was found to be closely relative to the activities of microorganisms (Devai, 1988; 1995; Glindemann, 1995; Liu, 1999; Han, 2000). Emismann *et al*. (Emismann, 1997) found soil and sediment can absorb phosphine, so the amount of phosphine emitted to the atmosphere is only a small fraction of phosphine retained in soil or sediment in the matrix-bound form. Matrix-bound phosphine was detected in freshwater/coastal sediment, animal slurry and paddy soil(Gassmann, 1993; 1994; Glindemann, 1995; Liu, 1999; Han, 2000). Since China is facing serious eutrophication problems, it is of interest to make a survey on matrix-bound phosphine in eutrophic freshwater and eutrophic coastal sediments, using the same analytical procedure.

1 Experimental

Two sediment core samples (10 – 20 and 70 – 80 cm, respectively) were taken from coastal water (Jiaozhou Bay, Qingdao, water depth 5 m), a freshwater sediment sample was taken from a eutrophic lake(Wulong, Nanjing, water depth 1 m). A sample of blackish water sediment was taken from a prawn pond (in the coastal area of Qingdao City, water depth 0.5 m). The sampling sites are shown in Fig. 1. For comparison, samples of sewage sludge (0 – 20 cm) and paddy soil (0 – 10 cm) were taken from the Beijing Municipal Wastewater Treatment Plant and the paddy field in the suburb of Beijing after rice harvest. All the analyses were completed as soon as the samples were brought back to the laboratory.

The concentrations of matrix-bound phosphine in the samples were determined according to the procedure described elsewhere(Glindemann, 1995; Han, 2000). One gram of each core segment was digested with 5 ml 0.5 mol/L H_2SO_4 for 5 minutes at 100℃ under a nitrogen atmosphere. The liberated phosphine was purged with 50 ml pure nitrogen out of the reaction vessel into a 50 ml disposable polypropylene-syringe, from which it was directly transferred into the gas-chromatographic injection port after drying and cryo-trapping. Gas samples in syringes were at first allowed to pass through a drying tube containing the MERCK 101567 drying agent (Merck KGaA, 64271 Darmstadt, Germany) for the removal of H_2O, CO_2 and H_2S. The phosphine in the gas samples was then enriched in two successively connected capillary cryo-traps kept at

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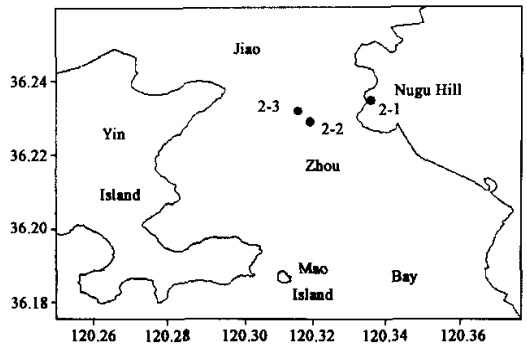

Fig. 1 Schematic illustration of the sampling sites

– 110℃ and was then led into the GC injection port from the capillary traps through a 6-port valve. A HP-5890 gas chromatograph was equipped with a capillary column(cross-linked 5 % Ph Me Silicone, 25 m × 0.2mm × 0.33 μm film thickness, Hewlett Packard) and a thermo-ionic nitrogen-phosphorus-detector (NPD). About 10—100 ml of sample gas were cryo-trapped to reach a detection limit for phosphine of 0.1 ng/m^3. Every sample was measured at least twice with a maximum deviation of about 20%. A certified standard phosphine gas (675 ppm phosphine in nitrogen v/v) was used for calibration. Both standard gas samples and the actual samples followed the same procedure, namely, passing through the drying tube and cryo-traps, then entering the capillary column to the detector.

2 Results and discussion

The contents of the total phosphorus and organic phosphorus in the samples were determined according to the procedures described in the Analysis Methods of Soil Chemistry (1983).

The results are shown in Table 1 and Table 2.

Table 1 Levels of matrix-bound phospine in various types of sediments

Types of sediment	Sampling location	Sampling date	Core depth, cm	Matrix-bound PH_3 level, Mean ± *SD*	Total P, mg/kg dry	Organic P, mg/kg dry	Reference
Prawn pond sediment	On the coastline of Jiaozhou Bay, China	Sep.18, 2000	7—8	78 ± 30 ng/kg dry (n = 5) (1.0 ± 0.4 nmol/L, wet)	489	70	This work
Coastal sediment	Jiaozhou Bay, China (2)	Sep.18, 2000	10—20	60 ± 35 ng/kg dry (n = 5) (0.9 ± 0.5 nmol/L, wet)	358	25	This work
Coastal sediment	Jiaozhou Bay, China (3)	Sep. 18, 2000	70—80	271 ± 28 ng/kg dry (n = 5) (3.8 ± 0.4 nmol/L, wet)	547	20	This work
Freshwater lake sediment	Wulongtan in Nanjing, China	Sep.19, 2000	0—20	335 ± 85 ng/kg dry (n = 5) (3.1 ± 0.8 nmol/L, wet)	2080	172	This work
Freshwater river sediment	River Elbe in Hamburg Harbour, Germany	Aug.5—Sep.9, 1992	0—2 2—5	1.4—6.5 nmol/L, wet 3.0—24.3 nmol/L, wet	—	—	Gassmann, 1994
Oceanic sediment	North Sea (Bight), Germany	Nov. 16—Dec.11, 1992	0—2	5.1—62.1 × 10^{-3} nmol/L, wet			Gassmann, 1994
			2—5	0.4—71.6 × 10^{-3} nmol/L, wet	—	—	

Table 2 Levels of matrix-bound phosphine in sewage sludge and paddy soil

	Sampling location	Matrix-bound PH_3, Mean ± *SD*, ng/kg dry	Total P, mg/kg dry	Organic P, mg/kg dry	Reference
Sewage sludge	Beijing Sewage Plant	314 ± 16 (n = 3)	13500	4773	This work
Paddy soil (drainage)	Beijing suburb	10.4 ± 3.9 (n = 6)	960	147	This work
Paddy soil (flooding)	Beijing suburb	13 (n = 3)	—	—	Liu , 1999

The levels of matrix-bound phosphine in the coastal sediments in Jiaozhou Bay are 0.9 and 3.8 nmol/L wet weight, respectively(Table 1). The concentration of matrix-bound phosphine in the sediment from prawn pond (1.0 nmol/L wet

weight) was at the same level as that in the 20 cm segment of the coastal sediment core. The concentration of matrix-bound phosphine was higher in the 80 cm segment of sediment core. Similar levels were reported by Gassmann(Gassmann, 1994) in the 0—2 cm and 2—5 cm segments of the sediment cores from Hamburg Harbour and from North Sea(Bight), whereas higher phosphine concentrations were reported in deeper layers. This might be explained by the migration of phosphine from the surface sediment layer into water.

Only limited data are available on the phosphine levels in different types of sediments in the world. The levels of matrix-bound phosphine in Jiaozhou Bay area are of the same order of magnitude as those in the Hamburg Harbour Area (Gassmann, 1994), and are significantly higher than those from North Sea in Germany. Table 1 also gives the matrix-bound phosphine concentrations in a prawn pond near Jiaozhou Bay, as well as in the freshwater sediment from the eutrophic lake Wulongtan. The highest level of matrix-bound phosphine detected so far (335 ± 85 ng/kg dry weight) was found in the sediment of this lake with heavy phosphorus load. The high levels of matrix-bound phosphine in these sediments could be attributed to the high organic phosphorus content in the sediments (Devai, 1995).

Similar high concentration of matrix-bound phosphine (314 ± 16 ng/kg dry weight) was observed for sewage sludge, in which the organic phosphorus content was the highest (Table 2). The phosphine concentration in a paddy soil after harvest was listed in the table too. The matrix-bound phosphine level in paddy soil is the lowest among all samples collected. We attribute the lower concentration of matrix-bound phosphine in paddy soil to the lower anaerobic condition than those sediments and sludge.

3 Conclusions

In view that China is the world's leading producer of farmed fish, accounting for 61% of total farmed fish(Brown, 1998), the flux of phosphine in eutrophic water bodies should not be overlooked. An occasional disturbance of coastal sediments and a subsequent sudden release of matrix-bound phosphine from coastal sediments might stimulate red tide, which is dangerous to aquaculture in a similar way as heavy metals(Stigliani, 1991). Further research work is necessary to elucidate such a time-bomb mechanism.

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