

PHOSPHINE IN THE URBAN AIR OF BEIJING AND ITS POSSIBLE SOURCES

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Abstract. Both as an air pollutant and as a gaseous component of the local phosphorus cycle, phosphine (PH₃) was found in the urban air of Beijing. Other possible sources, like paddy fields and water reservoirs, were selected for testing the hypothesis of the biological phosphine formation. Phosphine in the urban air of Beijing was measured in different seasons. In the summertime phosphine levels typically peak in the early morning and then decline towards noon. The maximum concentration at 6.00 am was 65 ng m⁻³ whilst that at noon was 11 ng m⁻³. In spring and in wintertime, the phosphine levels in the urban air of Beijing were lowest. A first screening revealed phosphine also in gas and in sediment samples from a paddy field near Beijing, the Beijing Shisanling water reservoir, and the refuse tips Changping of Beijing as well as in the ambient air adjacent to these sampling sites. The maximum phosphine concentrations in these gas samples were 41 (marsh gas, paddy field), 135 (marsh gas, reservoir), 1062 (landfillgas) ng m⁻³, and in the ambient air samples 146 (air, paddy field), 166 (air, reservoir), and 71 (air, refuse tips) ng m⁻³. In sediment samples, the highest matrix-bound phosphine levels were 13 (paddy field), and 3.9 (reservoir) ng kg⁻¹. These comparatively high concentrations of the readily oxidizable phosphine in air indicate hitherto unknown but important phosphorus emission sources, which might reduce the biomass growth in Chinese fields and forests by a general phosphorus limitation. Phosphine is also a constituent of the air pollution in China. However, more work has to be done to evaluate the different sources of atmospheric phosphine.

Keywords: atmosphere, environmental analysis, phosphine, paddy field, refuse tips, reservoir

1. Introduction

Phosphine as an industrial product has been widely investigated for its toxic effects on living organisms (Al Hakkak, 1988; Garry *et al.*, 1989; World Health Organization, 1988; Duma *et al.*, 1977; Bakheit *et al.*, 1985; Nakakita, 1987; Leitao *et al.*, 1987; Eismann *et al.*, 1997). However, as a natural product and as a pollutant from unknown sources, our knowledge is restricted to 'matrix-bound' phosphine contained in anaerobic sediments, sludges and soils (Gassmann and Glindemann, 1993; Gassmann, 1994; Eismann *et al.*, 1997) and to volatile phosphine in biogas



from communal waste digestion (Devai *et al.*, 1988; Glindemann *et al.*, 1996b) and from animal manure (Glindemann and Bergmann, 1995), in marsh gas (Glindemann *et al.*, 1996b; Devai and Delaune, 1995), and in landfill gas from refuse tips (Glindemann *et al.*, 1996b). A mechanism for the formation of phosphine in biogas by hydrolysis of iron phosphide was proposed by Glindemann *et al.* (1998). Phosphine is oxidized in air to soluble phosphate (Gmelin Handbook, 1993). Lewis *et al.* (1985) found a summer maximum peak of soluble phosphate in Colorado rain water and speculated that it is the oxidation product of an atmospheric gaseous carrier of phosphorus.

In China, it has never been investigated whether phosphine contributes to the air contamination. Moreover, China as a predominantly agricultural country with large areas of paddy field, and numerous eutrophic lakes and reservoirs, should be a favourite place of studying the natural volatile phosphorus emissions. A further challenge to start the phosphine measurements in China is to finish the previous and innovative but unsuccessful attempts (due to the lack of modern analytical equipments, especially gaschromatography) of Tsubota (1959), who first tried to investigate the phosphine problem in Japanese paddy fields.

2. Definitions, Materials and Methods, Sampling Sites

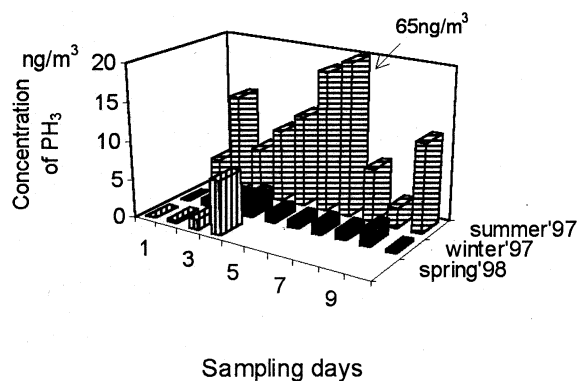
Marsh gas is a product of bioconversion processes in anaerobic sediments. It was sampled by a funnel placed directly upon the sediment.

Landfill gas from refuse tips is also mainly a product of anaerobic processes. It was taken as triplicate samples by disposable 50 mL plastic syringes from 11 passively degassing manifolds drilled down to 4 m depth.

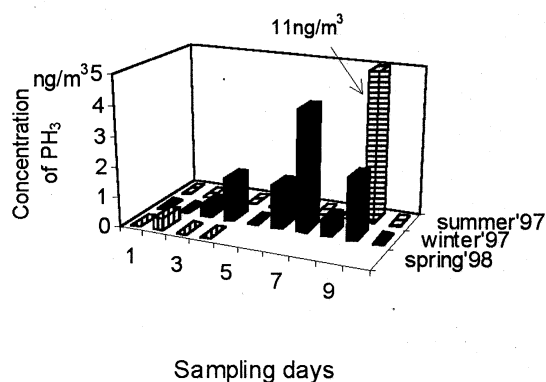
Matrix-bound phosphine is defined as phosphine liberated from sediment or other condensed matters by an acidic or alkaline digestion procedure. This treatment released phosphine from such different as adsorbed phosphine, metalphosphine-complexes, in inorganic phosphides. We used a preparative procedure very similar to that applied by food chemists determining the phosphine residues of fumigated cereals by digesting the sample in sulfuric acid (Nowicki, 1978).

2.1. SAMPLING SITES

Urban air was sampled in the center of the Chinese capital Beijing. They were taken in summer and winter 1997 on 10 successive days from the 9th to the 18th of July, and from the 19th to the 28th of december. In spring 1998, other urban air samples were collected on 4 successive days from the 23th to the 26th of March. Marsh gas samples from a paddy field and a water reservoir were taken 30 and 50 km, respectively, off the center of Beijing, and the landfill gas sampling site was 35 km away Beijing. The refuse tip for landfill gas sampling was dissected by 11 drill-holes, which had a mean distance of about 50 m from each other.



a) 6:00AM



b) 12:00AM

Figure 1. Phosphine concentration (ng m^{-3}) in urban air of the center of Beijing early in the (a) morning and at (b) noon (note the different phosphine concentration scales) in summer and winter 1997, and in spring 1998.

2.2. SAMPLE PREPARATION OF MATRIX-BOUND PHOSPHINE

Triplicate core sediment samples were taken from different depth at paddy fields, or reservoirs. One gram sediment was digested with 5 mL 1 N H₂SO₄ for 5 min at 100 °C under an anoxic nitrogen atmosphere. The liberated volatile phosphine was purged with 50 mL nitrogen out of the reaction vessel into a 50 mL disposable syringe from which it was directly transferred into the gas chromatographic injection port.

TABLE I
Air sampling days in 1997 and in 1998 in the center of Beijing

	Number of sampling days				
	1	2	3	4	5
Summer 1997	July 9	July 10	July 11	July 12	July 13
Winter 1997	Dec. 19	Dec. 20	Dec. 21	Dec. 22	Dec. 23
Spring 1998	March 23	March 24	March 25	March 26	
	Number sampling days				
	6	7	8	9	10
Summer 1997	July 14	July 15	July 16	July 17	July 18
Winter 1997	Dec. 24	Dec. 25	Dec. 26	Dec. 27	Dec. 28
Spring 1988					

2.3. SAMPLE PREPARATION FOR PHOSPHINE IN AIR SAMPLES

The air samples were taken and transported in Tedlar sampling bags, or were directly sucked into 50 mL disposable polypropylene-syringes, from which the samples were introduced into the injection port of the gas chromatograph. There, the gas sample passed an adsorptive trap filled with solid NaOH (removes H₂S, CO₂ and H₂O, but is indifferent to PH₃), after which it was cryotrapped.

2.4. SEPARATION AND DETECTION OF PHOSPHINE

A gas chromatograph HP 5890 A equipped with a PLOT Al₂O₃/Na₂SO₄ column (Chrompack) and a thermionic nitrogen-phosphorus-detector (NPD) was used for all of the phosphine determinations. Between 10 to 100 mL of gas sample were cryotrapped to reach a detection limit for phosphine of 0.1 ng m⁻³. A certified technical phosphine gas standard (1000 ppm (v/v) phosphine in nitrogen) served for quantification (for details see Glindemann *et al.*, 1996a).

3. Results

The level of phosphine in the urban air of Beijing's city center and corresponding sampling days are shown in Figure 1 (Table I contains the dates according to the number of sampling days).

In all morning samples of urban air in summertime 1997 and spring 1998 phosphine could be detected. During most of the days, the early morning phos-

TABLE II

Phosphine concentrations in urban air of Beijing and in biogases emitted from a paddy field, a water reservoir and refuse tips as well as in the ambient air adjacent to these places (30 to 50 km off the city of Beijing) at different daytimes and seasons

Sampling site	Phosphine (ng m^{-3})			n ^a
	Maximum	Minmium	Mean value	
<i>Urban air, 6:00 AM</i>				
Summer, 1997	65	2.6	15	3 × 10
Winter, 1997	2.7	0	1.2	3 × 10
Spring, 1998	7	0	2.2	3 × 4
<i>Urban air, 12:00 PM</i>				
Summer, 1997	11	0	1	3 × 10
Winter, 1997	2	0	0.57	3 × 10
Spring, 1998	0.4	0	0.1	3 × 4
<i>Biogases and air adjacent the biogas sources (summer, 1997, noon)</i>				
Marsh gas, paddy field	41	26	31	3
Adjacent air, paddy field	146	127	137	3
March gas, reservoir	135	44	90	3
Adjacent air, reservoir	166	50	98	3
Landfill gas from refuse tips	1062	32	400	11
Adjacent air, refuse tips	71	1	14	11

^a Numbers of the samples.

phine level surmounts the phosphine level at noon which is sometimes below the detection limit (also shown in Table II in detail).

Only one summer sample at noon (17th July, 1997) contained more phosphine (11.0 ng m^{-3}) than the corresponding morning value (2.6 ng m^{-3}). On this exceptional day the sky was overcast and the temperature was the lowest compared to the other summer sampling days. In contrast to the summer sampling days where phosphine is rare at noon, phosphine could be detected in six winter noon samples, generally at the same level as the winter morning samples.

The maximum value of phosphine in landfill gas (1062 ng m^{-3}), is more than 16 times above the maximum value in urban air (65 ng m^{-3}). The levels in ambient air adjacent to and around the biogas sources (between 71 and 166 ng m^{-3}) still exceed the values in air of the city of Beijing. However, in these latter cases, we have to mention, that during the sampling time the sky was cloudy and the temperature was relatively low. Nevertheless, it was very surprising, that the air around and adjacent to the paddy field and the water reservoir contained more phosphine than

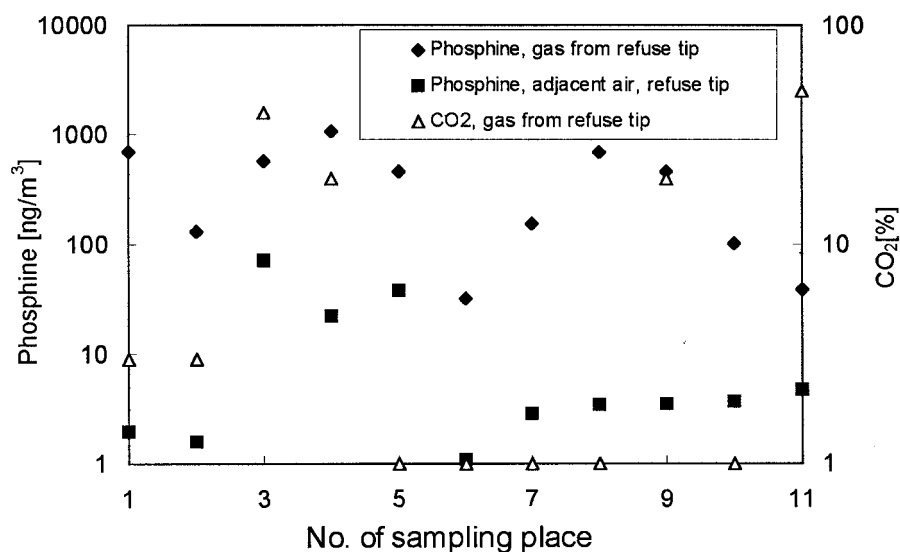


Figure 2. Comparison of the PH_3 and CO_2 content in landfill gas from 11 drill-holes of a refuse tip with the PH_3 content in ambient air around this sampling place.

the biogases directly taken from the sediments.

Only at the refuse tip sampling area (the conditions are such as we would have expected it) does the phosphine content of the gas emissions (up to 1062 ng m^{-3}) from the drill-holes greatly exceed the phosphine content of the ambient air (up to 71 ng m^{-3}). As is also visible in Figure 2 the phosphine content in the ambient air rises and falls according to the phosphine content of gases inside the drill-holes (see Figure 2).

The results of the 'matrix-bound' phosphine measurements are given in Table III. Here, the surface sediments of the paddy field contained three times more matrix-bound phosphine (up to 12.58 ng kg^{-1}) than sediments from the water reservoir (up to 3.92 ng kg^{-1}) at the same depth. With increasing depth (up to 40 cm), however, the phosphine contents of the sediments of both sampling sites decreases to a low and almost identical level of about 2 ng kg^{-1} .

4. Discussion and Conclusions

The results from this first phosphine screening in China show unexpected high phosphine values in the morning urban air of the city of Beijing. The values are 4 to 15 times higher than found in the city of Leipzig, (Glindemann *et al.*, 1996a). While the general trend – the decline of the phosphine content from morning to noon – is the same in both cities, we do not know what the sources for phosphine are. We consider phosphine as an urban air pollutant formed by industrial (in waste gases) or environmental (in marsh gas, landfill gas, biogas) emission sources.

TABLE III

Matrix-bound phosphine in the sediment samples of paddy field and the water reservoir (ng kg⁻¹)

Depth (cm)	Phosphine (ng kg ⁻¹)	
	Paddy field	Reservoir
0–10	12.58	3.8
10–20	10.6	3.92
20–30	12.01	1.89
30–40	1.7	2.06

Another big difference between Beijing (China) and Leipzig (Germany) is seen in the phosphine content in marsh gas (135 vs 4 ng m⁻³) and in the air around the marsh gas source (166 vs 1 ng m⁻³). The long-term concentration in Leipzig air is 1 ng m⁻³ (Glindemann *et al.*, 1996a).

The biogas inside the drill-holes of the refuse tips contained the highest phosphine concentration (1066 ng m⁻³) measured in China. However, in contrast to the air around the marsh gas sources, the air adjacent to the refuse tips contained almost less phosphine (71 ng m⁻³) than landfill gas and more phosphine than the summertime-air in Beijing on a cloudy day (65 ng m⁻³).

As the marsh gas sources (paddy field and water reservoir) continuously emit phosphine to the atmosphere, their sediment layers should reflect these emissions by showing a certain concentration of matrix-bound phosphine. In fact, all surface sediment layers contain phosphine. There is more in the upper layer and less in the lowest one, whereby the paddy field sediments contain much more matrix-bound phosphine than the water reservoir sediments. This strong difference between the two sediments might be accounted for the bigger amount of plant debris accumulated on the paddy field sediment surface layer than onto water reservoir surface layer.

The phosphine measurements in urban air at different times and seasons clearly indicate an important influence of temperature and daylight on the phosphine formation and oxidation in air. The higher the temperature the more phosphine will be formed. The less the daylight intensity is, the more phosphine will survive oxidative attack mediated by the solar UV-radiation, which transforms phosphine back to phosphate. In Beijing, obviously, more phosphine will be formed and more phosphine will survive compared to Leipzig, Germany. Because all atmospheric phosphine finally will be converted to water-soluble phosphate, which reaches the Chinese soil via rain, nobody can say, at the moment, whether this generally higher phosphine formation has toxic effects on living organisms, or negative influences on the extent of the national crop harvest, or positive distributing effects on the

even dissemination of phosphorus all over the country. As the redistribution of phosphorus via phosphine works also as an additional phosphorus fertilizer all over the country, where areas with rich phosphorus sources are losing their surplus and less benign areas are gaining to a certain extent additional phosphorus, the investigation of the still hypothetical phosphate reduction deserves more scientific attention. Our investigations, which we made so far, reveal the reality of phosphine as the volatile component of the biogeochemical phosphorus cycle. However, its local and global impact onto the phosphorus cycle remains a task which should be accomplished within the near future.

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