



# Phosphine in soils, sludges, biogases and atmospheric implications—a review

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## Abstract

This is a review of previously published and unpublished results of research into the occurrence of phosphine (PH<sub>3</sub>) in the environment in the form of matrix bound phosphine in soils, aquatic sediments and sludges (range ng kg<sup>-1</sup> to μg kg<sup>-1</sup>), free phosphine in formed biogases (range ng m<sup>-3</sup> to μg m<sup>-3</sup>) and in the atmosphere (range pg m<sup>-3</sup> to ng m<sup>-3</sup>).

The reviewed data support the hypothesis of the existence of a small gaseous link in the phosphorus cycle, which could become important over the long term.

Matrix-bound phosphine in soils can be interpreted as a stationary state concentration of phosphine between production and consumption. This phosphine turnover within the soil may be important even if the stationary state concentration (matrix-bound phosphine) is small. Under such circumstances, a slow migration process of phosphine in the interstitial gas sphere of soils is possible. Such a process would influence the balance of phosphorus in agricultural and wetland soil.

The detection of easily oxidizable phosphine as a ubiquitous trace gas in the atmosphere can be interpreted as the residue of an important turnover of phosphine between widely distributed emission sources and sinks such as soils and sediments. The atmosphere can carry gaseous phosphorus to remote places.

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## 1. Introduction

Phosphine (PH<sub>3</sub>), a volatile and toxic molecule containing phosphorus in the oxidation state 3, is produced by humans for industrial application and as a pesticide. It is also contained in several waste media (WHO, 1988).

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Regarding its natural occurrence, phosphine is only common in the methane and hydrogen atmosphere of the gas planets (Prinn and Lewis, 1975). Phosphine is rare in the earth's environment because it is easily oxidized by air (WHO, 1988), and is difficult to produce. New analytical developments made it possible to detect small amounts of phosphine in soil, sludge and biogases in the environment (Devai et al., 1984, 1988; Devai and DeLaune, 1995; Eismann et al., 1997; Gassmann and Glindemann, 1993; Gassmann and Schorn, 1993; Gassmann, 1994; Glindemann and Bergmann, 1995; Glindemann et al., 1996a; Han et al., 2000; Iverson, 1968; Liu et al., 1999). Tsubota (1959) found not phosphine but phosphites as reduced phosphorus compounds in a Japanese paddy field. Phosphine was even found to be a worldwide trace component in the earth's atmosphere (Gassmann and Glindemann, 1996; Glindemann et al., 1996a).

Several independent reports claim that phosphine can be produced by biochemical processes in the laboratory (Cao et al., 2000; Devai et al., 1984, 1988; Eismann et al., 1997; Gassmann and Glindemann, 1993; Iverson, 1968; Jenkins et al., 2000). Most of these results have been summarized in a review (Roels and Verstraete, 2001). Therefore, biochemical processes (such as the bacterial reduction of phosphates or natural organophosphorus compounds) would support a gaseous link to the phosphorus cycle in the environment.

This is contrary to the common assumption that in contrast to carbon, nitrogen, sulphur, oxygen, and some other elements, phosphorus can only cycle in different non-volatile forms of phosphates and phosphonates (Graham and Duce, 1979; Bolin and Cook, 1983). It is unquestionable that the finding of phosphine is a scientific curiosity. Phosphine is also connected with the ignition of swamp lights (*Ignis Fatuus*), spontaneous human combustion (SHC), the phosphorescence of graves and fire-breathing dragons (Emsley, 2000).

An important question is whether phosphine gas is an important component of the geochemical cycling of phosphorus in the environment. One of the more practical questions is whether phosphine is a significant pool of phosphorus nutrient in agricultural farmland, where total P can be very high (eutrophication), or in highland wetlands, where P can be limiting for the biosphere.

We present here a review of published and previously unpublished numbers on the occurrence of

phosphine in soils (the source or sink), in developed gases (the possible emission medium) and in the atmosphere (the carrier of phosphine).

## 2. Definitions and generalized reviewed methods

Free phosphine is the concentration of phosphine, which is spontaneously free measurable in gas samples such as biogas or air. Its unit is mass phosphine-phosphorus per  $\text{m}^3$ , and it is measured using gas chromatography.

Matrix-bound phosphine is the concentration of phosphine in soils, sediments, sludges and other condensed media. Its unit is mass phosphine-phosphorus per kg soil, etc., and it is measured similarly to the analysis of phosphine residue in grain (Nowicki, 1978) fumigated with phosphides or phosphine (anaerobic digestion of the soil with a strong mineral acid ( $\text{H}_2\text{SO}_4$ , HCl) or alkaline solution (NaOH) and subsequent quantification of phosphine in the reaction gas). More details of the methods can be found in the references. This chemical digestion can hydrolyze non-volatile phosphides into phosphine gas. It can also, however, liberate phosphine from a form in which it is adsorbed in the matrix (therefore the name matrix phosphine) into phosphine gas. Therefore, matrix-bound phosphine is a function of the applied digestion method, and does not necessarily refer to the pre-existence of phosphine gas in the matrix, because it could be in the form of solid phosphides. Phosphides, on the other hand, can hydrolyze in biological aquatic media (Glindemann et al., 1998) to form free phosphine gas.

## 3. Reviewed results and discussion

In soils, the concentration of phosphine is in the range  $\text{ng kg}^{-1}$  to  $\mu\text{g kg}^{-1}$  (Table 1). This is very low compared with their phosphate content, which is generally much higher.

Eismann et al. (1997) simulated phosphine production and consumption by soil samples in the laboratory, showing that biological metabolites such as sulfide, glucose, formate, and pyrogallol can accelerate the release of phosphine from the soil. Generally, however, the consumption of phosphine by soil is faster than

Table 1  
Matrix-bound phosphine in aquatic sediments, soils, stone minerals, and animal/human waste which is placed on soils as fertilizer

Sample matrix	Location	Independent samples ( <i>n</i> )	Phosphine (ng kg <sup>-1</sup> )		Digesting agent	References
			Average	Range		
Water, bottom, fresh	Hamburg harbour	10 locations	60	0–387		
Sediment, surface	Hamburg harbour	10 locations	99	43–201		
Sediment, subsurface	Hamburg harbour	10 locations	216	93–753	10% NaOH	Gassmann (1994)
Water, bottom, salty	German bight	18 locations	8	0–28		
Sediment, surface	German bight	18 locations	770	158–1923		
Sediment, subsurface	German bight	18 locations	853	81–2217		
Sediment, surface	Hamburg harbour	10 locations	24	0.2–56.1	10% NaOH	Gassmann and Schorn (1993)
Soil, industrial area	Germany	2 locations	60845	18440–103250	1N H <sub>2</sub> SO <sub>4</sub>	Eismann et al. (1997)
Soil, rural area	Germany	5 locations	4476	840–17050		
Sediment, fresh	Elster river, Germany	26 (4 locations, 5 seasons)	227	4–1140		Glindemann (not published)
Sediment, landfilled over 1 year	Elster river, Germany	5 (1 location, 5 depths)	137	110–165		
Sediment, landfilled, after 4 weeks of full scale acidic leaching	Elster river, Germany	5 (1 location, 5 depths)	20	10–30	1N NaOH	
Soil of virgin tropical forest	Mahé, Seychelles	3 (1 location, 3 depths)	3	1–5		
Sewage sludge, raw	Germany	3 plants	97	65–135		
Sewage sludge, digested	Germany	2 plants	118	85–150		
Dewatered sludge	Germany	3 plants	85	10–220		
Manure, cattle	Germany, 1 plant	24 (4 seasons, 6 stages)	802	9.53–9021	1N H <sub>2</sub> SO <sub>4</sub>	
Manure, swine	Germany, 2 plants	36 (4 seasons, 11 stages)	1626	16–11550		
Stone minerals	Mineral collection	11 minerals	1818	11–6672	1N HCl	
Soil of paddy field, flooded	Beijing, China	4 (1 location, 4 depths)	9	2–13	1N H <sub>2</sub> SO <sub>4</sub>	Liu et al. (1999)
Sediment of water reservoir	Beijing, China	4 (1 location, 4 depths)	3	2–4		
Soil of paddy field, drainage after tilling	Beijing, China	11 (1 location, 11 depths)	2	0–7	1N H <sub>2</sub> SO <sub>4</sub>	Han et al. (2000)
Soil of paddy field, drainage before harvest	Beijing, China	10 (1 location, 10 depths)	3	0–11		
Manure, cattle	Germany	1	14	14	10% NaOH	Gassmann and Glindemann (1993)
Manure, swine	Germany	1	964	964		
Sewage sludge, before incubation	USA	11 locations	74	8–204	10% NaOH	Devai et al. (1999)
Sewage sludge, after 7 days of incubation	USA	11 locations	545	111–2053	10% NaOH	Devai et al. (1999)

possible production. Therefore, the concentration of phosphine did not increase with time in the analysed soil samples. “Matrix-bound” phosphine, however, can always be found in soil and sludge samples. Therefore,

matrix phosphine in biological samples may be a stationary state concentration of phosphine between production and consumption. Even if this phosphine turnover were important, only a small residue of

Table 2  
Free phosphine in gas products of the biosphere

Sample	Location	Independent samples ( <i>n</i> )	Phosphine, range (ng m <sup>-3</sup> )	References
Biogas from sediments of sewage plants and shallow lakes	Hungary	11	11600000–382000000	Devai et al. (1988)
Landfill gas	Germany, 1994–1995	36 (1 plant, 4 seasons)	0–17731	Glindemann et al. (1996b)
Composting gas, municipal waste		14 (2 plants, 2 seasons)	22–341	
Composting gas, cattle manure biosolids		3 (seasons)	0–55	
Composting gas, swine manure biosolids		4 (seasons)	31–1015	
Interstitial gas, stored sewage sludge, limed		8 (2 plants)	833–23233	
Interstitial gas, stored sewage sludge, unlimed		3 (1 plant)	9–29	
Biogas of sewage plant		16 (4 plants, 4 seasons)	0–6167	
Marsh gas of Elster river		6 (3 locations, 2 seasons)	0–4	
Biogas of cattle manure		4 (seasons)	0–13	
Putrefaction gas of cattle manure storage		3 (seasons)	123–238	
Biogas, swine manure digestion		4 (seasons)	0–1623	
Putrefaction gas, swine manure storage		14 (2 plants, 4 seasons)	51–8995	
Biogas, putrefaction gas, 3 swine and cattle farming plants	Germany, 1996	50 (3 plants, 4 seasons)	2–47000	Glindemann (unpublished)
Landfill gas	Beijing, China	11 (wells)	32–1062	Liu et al. (1999)
Marsh gas, paddy field	Beijing, China	4	26–41	
Marsh gas, water reservoir	Beijing, China	4	44–135	
Monoseptic bacterial culture headspace	UK	12 (bacterial strains)	0–76000	Jenkins et al. (2000)
Faeces mixed bacterial culture headspace	UK	6	36000–720000	
Flatus gas of human colon, 2 males, meat rich diet	UK	4	0–40000	Chughtai et al. (1998)
Headspace in sewage sludge inoculated media	Switzerland	2	113–125	Rutishauser and Bachofen (1999)

Table 3  
Emission flux of phosphine from the biosphere

Origin	Location	Emission ( $\text{ng m}^{-2} \text{h}^{-1}$ )	References	Number of samples ( <i>n</i> )
Soil of brackish marsh	Louisiana, USA	0.42–3	Devai and DeLaune (1995)	2
Louisiana salt marsh		0.91–6.52	Devai and DeLaune (1995)	2
Soil of paddy field	Beijing, China	–13 to +22	Han et al. (2000)	144
Intertidal mud flat area	North Sea, German bight	4500	Gassmann (2001, personal communication)	

Table 4  
Phosphine in the atmosphere at locations around the world (height 1 m above ground, sampled at night between 10 p.m. and 6 a.m., unless otherwise indicated)

Sampling location	Sampling time	Number of samples ( <i>n</i> )	Phosphine [ $\text{pg m}^{-3}$ ]		Source
			Average	Range	
Germany, urban location in Berlin	18 September 1995	2 locations	157050	135380–178700	
Germany, urban area in Leipzig	21 September 1994	6 locations	4630	3930–5900	
Germany, rural area east of Leipzig	21 September 1994	13 locations	2030	1110–3420	
Germany, urban area in Hamburg	5 October 1994	5 locations	2030	650–4490	
Germany, rural area west of Stuttgart	13 October 1994	6 locations	1520	490–3060	
Germany, Leipzig, 120 m, top of university tower	September 1994–July 1995	8 days	480	0–980	Glindemann et al. (1996)
Germany, urban location in Leipzig	September 1994–July 1995	77 days	850	0–8880	
Germany, urban location in Leipzig, 12 a.m.	September 1994–July 1995	77 days	116	0–1720	
Argentina, urban area in Buenos Aires	11 April 1995	5 locations	620	320–1200	
Tunisia, rural location near Hammamet	23 March 1995	6 locations	510	0–1150	
Seychelles, Mahé	April 1995	13 locations	280	0–410	
Israel, rural area, Ein Bokek and Rishon Lezion	19, 22 January 1995	4 locations	130	0–300	
Namibia, rural area	March 1995	5 locations	40	0–280	
High altitude 12,500 m, trans North Atlantic flight with research airplane	24–25 November 1995	12 locations/heights	956	200–2450	Glindemann (unpublished)
Germany, marine air, North Sea	Summer 1996	9 locations	250	41–855	Gassmann (1994)
China, Beijing, urban residential area	Summer 1997	10 days	14890	2600–64800	Liu et al. (1999)
China, Beijing, urban residential area	Winter 1997	10 days	1230	0–2700	
China, Beijing, urban residential area, 12 a.m.	Summer 1997	10 days	1100	0–11000	
China, Beijing, urban residential area, 12 a.m.	Winter 1997	10 days	970	0–4000	
Beijing, tower, high altitude, 0 to 300 m above ground	25 March 1998	7 heights	1414	1100–2300	
China, near Beijing, paddy field (adjacent air), 12 a.m.	25 June 1997	3 locations	137290	127220–145860	

Table 4 (Continued)

Sampling location	Sampling time	Number of samples ( <i>n</i> )	Phosphine [ $\mu\text{g m}^{-3}$ ]		Source
			Average	Range	
China, near Beijing, water reservoir (adjacent air), 12 a.m.	25 June 1997	4 locations	97970	50120–166280	
China, Beijing, urban landfill site (adjacent air), 12 a.m.	27 June 1997	11 locations	14020	1080–71000	
China, Beijing, paddy field (adjacent air)	25 June 1999–28 September 1999	4 days	42000	2500–100000	Han et al. (2000)
China, Beijing, paddy field (adjacent air), 12 a.m.	25 June 1999–28 September 1999	4 days	4500	1000–7000	

this turnover could be observed as matrix-bound phosphine.

Under such circumstances, a slow migration process of phosphine in the interstitial gas sphere of soils is possible. Such a process would influence the balance of phosphorus in agricultural and wetland soils. To our knowledge, no experiments have ever been undertaken to document phosphine migration in soil.

In biogases, the concentrations of phosphine is in the range  $\text{ng m}^{-3}$  to  $\mu\text{g m}^{-3}$  (Table 2). No other form of volatile phosphorus has been reported or detected in biogases. Devai et al. (1988) found exceptionally high values, but the number of measurements performed was relatively small.

The number of measured fluxes of phosphine (Table 3) is almost insufficient to draw any conclusions. The biogas concentrations in Table 1 can be taken to estimate flux because the quantity of biogas flux can be estimated for sites such as swamps and biogas digesters.

In atmospheric air, the concentration of phosphine is in the range  $\text{pg m}^{-3}$  to  $\text{ng m}^{-3}$  (Table 4). The reported concentration of phosphine in China is significantly higher near paddy fields than in urban residential areas. Phosphine has been measured in the atmosphere at altitudes of 120, 300 and 12,500 m.

The data of phosphine in atmospheric air in Table 4 indicate important sources and a flux of phosphine, which accumulates in the night atmosphere and decreases until noon of the following day through oxidation (oxidation mechanism by solar radiation and OH radicals see Frank and Rippen, 1987; WHO, 1988). This could explain the finding of soluble phosphate in rain water (Lewis et al., 1985). Over the long term this flux could be important for the long-range transport of phosphorus to remote places.

Compared to the large number of studies on the occurrence of phosphates, the historical data presented in this review on phosphine are still insufficient to draw final conclusions. Nevertheless, the numbers presented can be used to draw a preliminary picture. The reviewed data support the hypothesis of the existence of a small gaseous link to the phosphorus cycle. This gaseous phosphorus cycling including the migration of phosphine within different soil compartments and the exchange of phosphorus between soil and the atmosphere could become important over the long term.

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