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PHOSPHINE IN THE LOWER TERRESTRIAL TROPOSPHERE**

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Gaseous phosphine (phosphane, PH_3) was found from September 1994 to September 1995 in both rural and urban air from Germany, Argentina, Israel, Namibia, Tunisia and the Seychelles for the first time. The maximum value of 157 ng/m^3 phosphine was detected in German urban air in Berlin. In Germany the PH_3 concentrations at night (about 1 ng/m^3) were 10 times higher than during daytime. The findings show that phosphine is an atmospheric carrier of phosphorus in its global biogeochemical cycles.

Under oxidizing conditions, the natural state of phosphorus P on earth is predominantly non-volatile phosphate. Reductive chemical [1] and microbial [2-8] compartments on earth are potential emitters of phosphine. Previously, however, ambient phosphine has only been detected in the workplace atmosphere or the immediate vicinity of punctual fumigation and industrial sources [9] where analysing health hazards has been a matter of concern. Phosphine has never been investigated as a fast gaseous atmospheric carrier of the fertilizer P or as a component of atmospheric chemistry. Phosphine is oxidized in air to soluble phosphate [1,10]. Lewis et al. [11] found a summer maximum peak of soluble phosphate in Colorado rain water and speculated that it is associated with the pre-existence of an atmospheric volatile phosphorus compound. This raises the question of whether phosphine is a widespread trace component in the earth's atmosphere.

Phosphine in air 1 m above both a rural and an urban area was detected for the first time on the evening of September 21, 1994. Between 7.05 and 8.35 pm, the distribution of its concentration was measured at 13 sampling locations spread over a rural area of about 200 km^2 , the centre of this area being 15 km east of Leipzig (Table 1). The average concentration of $2,030 \text{ pg/m}^3$ was about half the value of $4,630 \text{ pg/m}^3$ from Leipzig itself (6 locations spread over a 20 km^2 central area of the city, sampled between 10.50 and 11.25 pm). Subsequent exploratory measurements of phosphine in rural and urban air from several German towns and locations around the world produced positive results wherever they were carried out (Table 1).

A long-term study at a standard sampling location in Leipzig (a garden near the eastern periphery of the city) from September 1994 to July 1995 (Fig. 1) resulted in two summer maximum trends and a continuously recurring large difference between the levels of phosphine in atmospheric air at night and during the day. The average level of measurements carried out on 77 days was 850 pg/m^3 phosphine at 7 am (representative for the night) and 120 pg/m^3 at 1 pm (representative for the daytime). Correlation of the data with the wind direction indicated that phosphine came from all directions. During measurements at shorter intervals over a few days, about 3 hours after sunset the concentration reached a high not systematically different from the value at 7 am. About 4 hours after sunrise the concentration began to decrease and reached a low from about 11 am to sunset. In order to ascertain the existence of phosphine at different heights, synchronous measurements were carried out on 8 days at 7 am on the university tower in the center of Leipzig (height 120 m - average 480 pg/m^3), beside the tower (1 m - 660 pg/m^3) and at the standard sampling location (1 m - 820 pg/m^3).

The results from very different sampling locations (Table 1) provide evidence that phosphine is a globally widespread component in the lower terrestrial troposphere. Concentrations above urbane areas were significantly higher than above rural areas, indicating emission by concentrated human activities.

The night-time/daytime difference of phosphine concentration (Fig. 1) supports the hypothesis of phosphine fluxing permanently from terra into the atmosphere. PH_3 can dissipate over a wide area and accumulate at night because it is not autoxidizable. However hydroxyl-radicals induced by UV from daylight cause its cleavage ($\text{PH}_3 \rightarrow \text{H}\cdot + \cdot\text{PH}_2$) and oxidation [4,5], making the permanent phosphine flux into the atmosphere appear in different concentrations during the day and at night-time. The "stationary state" concentration observable could be the residue of dissipation and (during daytime) incomplete oxidation.

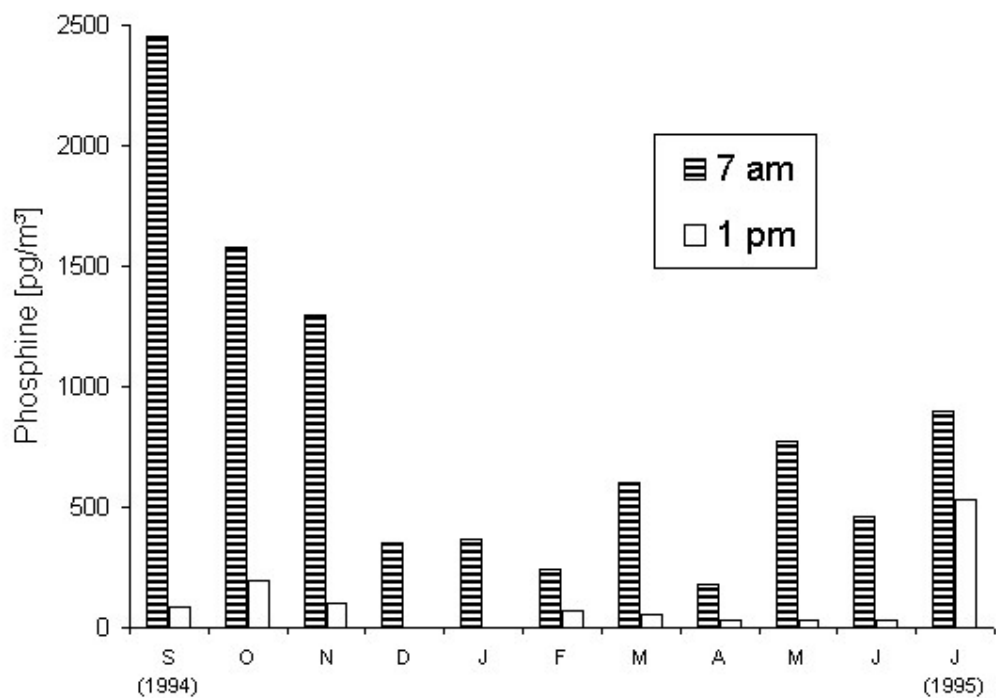
Interpreting the 7 am concentration as the residue of homogeneous dissipation into large aliquots of the atmosphere allows the size of the phosphine flux required to accumulate 850 pg/m^3 equally distributed in 1 km^3 of the lower troposphere to be estimated at 0.850 g/km^3 per night or $310 \text{ g/(km}^3\cdot\text{yr)}$. However phosphine ought also to flux from terra by daylight, even if the measured residue of this flux expressed as a daytime value of concentration is negligible (Fig. 1) and dissipation is rather short-ranged. Therefore a source flux of $620 \text{ g/(km}^3\cdot\text{yr)}$ phosphine seems more realistic. Extending this model from 1 km^3 to the air volume of the boundary layer (1 km height)

above Germany indicates that 221 Mg/yr phosphine flux into the atmosphere and are precipitated as phosphate after oxidation somewhere. This small contribution of atmospheric phosphine to the phosphorus cycle could be not insignificant for areas where P limits the biomass stock [12]. Another approach to estimate the turnover of phosphine is to balance the source processes that would cause the atmosphere to accumulate phosphine in measurable quantities. The conditions for phosphate reduction are more frequently fulfilled than might be assumed. For example we found 10^5 pg/m³ phosphine stochastically present in waste gas from lignite power plants. After looking at the phosphorus industry, investigations should therefore also target other possible environmental biospheric and geospheric sources, as well as human activities where phosphine is released "inadvertently".

Table 1

Phosphine in the atmosphere at locations around the world (height 1 m, at night)

Sampling location	Sampling time	(n)	Phosphine [$\mu\text{g}/\text{m}^3$]	
			Average	Range
Germany, urban location in Berlin	Sept. 18, 1995	2	157050	135380 - 178700
Germany, urban area in Leipzig	Sept. 21, 1994	6	4630	3930 - 5900
Germany, rural area east of Leipzig	Sept. 21, 1994	13	2030	1110 - 3420
Germany, urban area in Hamburg	Oct. 5, 1994	5	2030	650 - 4490
Germany, rural area west of Stuttgart	Oct. 13, 1994	6	1520	490 - 3060
Germany, urban location in Leipzig (see Fig.)	Sep.t 94 - July 95	77	850	0 - 8880
Argentina, urban area in Buenos Aires	April 11, 1995	5	620	320 - 1200
Tunisia, rural location near Hammamet	March 23, 1995	6	510	0 - 1150
Seychelles, Mahé	April 1995	13	280	0 - 410
Israel, rural area, Ein Bokek and Rishon Lezion	Jan. 19+22, 1995	4	130	0 - 300
Namibia, rural area	March 1995	5	40	0 - 280



Legend to Figure 1

Fig. 1. Phosphine in urban air: long-term study of 7 am and 1 pm levels, 1994-1995.

Gas chromatography was used with PLOT column 25m x 0.53mm x 10 μm Al₂O₃/Na₂SO₄ and optimized NPD on HP 5890. Injection was performed through solid NaOH on porous support filled in a 50mm x 4 mm tube into "sample in" of a 6-port vent to remove CO₂, H₂S and H₂O. Phosphine was separated from the matrix (air, C₁-C₂) by a capillary cryotrap (-110°C) filled with Porapack Q in the line of the sample loop of the vent, and cryofocussed in a similar smaller pre-column trap prior to the run. The detection limit of phosphine from a 500ml air sample was 5 $\mu\text{g}/\text{m}^3$ with a peak width of 0.7 sec. The standard deviation of the method was 10%. The data base comprises about 300 atmospheric samples taken on 77 days (2 samples each at 7 am and at 1 pm). The standard sampling place was a garden east of Leipzig at a height of 1 m. The standard deviations of the actual fluctuations between the measuring dates had the same order of magnitude as the averages.

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