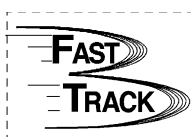




PERGAMON



Atmospheric Environment 37 (2003) 2429–2433

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

Phosphine gas in the upper troposphere

Dietmar Glindemann^{a,b,*}, Marc Edwards^a, Peter Kusch^c

^a Virginia Polytechnic Institute and State University, 418 Durham Hall (0246), Blacksburg, VA 24061, USA

^b Institute of Animal Hygiene and Veterinary Public Health, University of Leipzig, Semmelweisstr. 4, Leipzig D-04103, Germany

^c Centre for Environmental Research Leipzig-Halle Ltd., Permoser Str. 15, Leipzig D-04318, Germany

Received 30 September 2002; accepted 12 March 2003

Abstract

The gas phosphine (PH₃) is a part of an atmospheric link of the phosphorus cycle on earth. Phosphine was reported elsewhere to be found worldwide in remote air samples in the lower troposphere in the low ng/m³ range during the night, when oxidation is inhibited. But much less phosphine (pg/m³ range) was found during daylight around noon in this reactive contaminated atmosphere.

Here we found for the first time gaseous phosphine in remote air samples (0.39–2.45 ng/m³, 16 locations) in the high troposphere above the North-Atlantic in November 1995 during daylight around noontime. The maximum concentration was measured at the highest altitude of 12,500 m. No night measurements could be conducted to compare day and night values.

The finding of the reactive phosphine under the sunlight in the high troposphere far from possible terrestrial sources is strange.

A model experiment shows that phosphine could possibly survive the daylight much longer at high altitudes because of a lack of UV-induced oxidants in the clean and dry air. Additional model experiments indicate that phosphine can easier sustain its mobile gaseous state in the atmosphere compared to gases like hydrogen sulfide and ammonia which stick easier to aerosol and are subject to faster washout and return to Earth's surface.

However, the ultimate fate of phosphine is the oxidation to form phosphoric acid as a low pH agent and as possible condensation nuclei for clouds at very high altitudes.

The potent sources and atmospheric chemistry which allow phosphine to accumulate in the upper troposphere are still to be discovered.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: 7803-51-2; Atmosphere; Phosphorus cycle; Phosphate; Gas chromatography

1. Introduction

It was thought that phosphorus can cycle in the atmosphere only as phosphate bound to aerosols such as plant pollen, dust and sea spray (Graham and Duce, 1979; Pierrou, 1979). The fallout of phosphorus has been

estimated to be in the range 3.6–9.2 Tg P/yr for terrestrial ecosystems, giving a total fallout from the atmosphere of 6.3–12.8 Tg P/yr (Pierrou, 1979).

However, Lewis et al. (1985) found a summer maximum peak of soluble phosphate in continental rain water and ruled out leaching of aerosol phosphorus from plant pollen or from other aerosols. They anticipated a terrestrial source and flux of a volatile phosphorus compound into the atmosphere which is oxidized in air to return back to earth as a significant flux of phosphate, 10 times higher than the flux of plant pollen phosphorus. Phosphine (PH₃) could be a candidate explaining this phenomenon.

*Corresponding author. Virginia Polytechnic Institute and State University, 418 Durham Hall (0246), Blacksburg, VA 24061, USA.

E-mail address: dglinde@aol.com (D. Glindemann).

URL: <http://www.glindemann.net>.

Phosphine is a toxic gas and important chemical reagent (Gmelin, 1993). It is an amphoteric chemical which hydrolyzes only with concentrated acids or bases. The water solubility of phosphine at room temperature is low (partition coefficient gas/water about 5).

It is thought that phosphine reacts with ozone only slowly. The rate constant of phosphine oxidation by atomic oxygen is about $5 \times 10^{-11} \text{ cm}^3/\text{s}$ (Nava and Stief, 1989). Direct atmospheric photolysis is not possible in the low troposphere where the low spectral limit of light is 300 nm. The rate constant of atmospheric oxidation of phosphine by OH[·] radicals is $1.4 \times 10^{-11} \text{ cm}^3/\text{s}$. For a given average OH[·] radical concentration of 5×10^5 molecules/cm³ in the low troposphere, the average atmospheric half-life is 28 h. Much higher OH[·] radical concentration during sunshine can reduce the half-life down to 5 h. The final product of the reaction of phosphine with the hydroxyl radical is the phosphate ion, which falls to earth, to carry on the global phosphorus biogeochemical cycle (Frank and Rippen, 1987).

Over the past decade, numerous anthropogenic and environmental emission sources of phosphine have been identified (WHO, 1988; Devai et al., 1988; Gassmann and Glindemann, 1993; Gassmann, 1994; Devai and Delaune, 1995; Glindemann et al., 1996a, 1998; Eismann et al., 1997; Liu et al., 1999). Biological phosphine formation by selected microbial strains was published by Jenkins et al. (2000), see also the review of Roels and Verstraete (2001). These emission sources could produce enough phosphine to be a trace component throughout the Earth's atmosphere influencing the biogeochemical cycles of phosphorus and the atmospheric chemistry of phosphorus.

Previously, phosphine was only recognized as a significant trace component of the atmosphere of the giant gas planets (Prinn and Lewis, 1975), causing the visible red structures on Jupiter by photolysis and formation of elemental phosphorus in the high atmosphere.

On earth, the fumigation of food with phosphine (Frank and Rippen, 1987; Pratt, 1999) was found to produce measurable atmospheric concentrations of 1000 ng/m³ downwind and 100 m apart from the silo.

By using a more sensitive analytical method (detection limit of 50 pg/m³), atmospheric phosphine was found worldwide in the Earth's lower troposphere (Glindemann et al., 1996b; Gassmann et al., 1996; Liu et al., 1999; Han et al., 2000) at a height of 1–300 m at an order of concentration of 1000 pg/m³ in remote air and peaks of 100,000 pg/m³ in air in populated areas. These samples were taken during the night, when oxidation is inhibited. But less phosphine (pg/m³ range) was found during daylight around noon in this reactive contaminated atmosphere.

Here, we present the discovery of atmospheric phosphine in the remote high troposphere during daylight.

2. Method

Air samples were taken by a research plane FALCON 20 E during flight D-CMET North-Atlantic, 24–25 November 1995 (D.L.R. Flugabteilung Oberpfaffenhofen) between Canada and the Azores (see Table 1). The samples were sucked from the outside through stainless-steel tubing and were stored in Tedlar sampling bags

Table 1
Phosphine in remote North-Atlantic air at high altitudes in samples obtained during Flight

| Location | Date | Local time (24h) | Position Long. (W) | Position Lat. (N) | Altitude (m) | Phosphine (pg/m ³) (N.d. = not detected) | | | |
|----------------------------|------|------------------|--------------------|-------------------|--------------|--|------|------|------|
| | | | | | | Average | 1 | 2 | 3 |
| Flight Bangor—St. Johns | 24 | 12.00 | 56°14.5 | N46°21 | 10,058 | 230 | 250 | 220 | 230 |
| Flight Bangor—St. Johns | 24 | 12.26 | 57°22 | 47°03 | 10,058 | 200 | 280 | 290 | 280 |
| Canada, St. Jones, Airport | 25 | 09.48 | 52°43 | 47°33 | 1 | 40 | N.d. | 60 | 60 |
| Canada, St. Jones, Airport | 25 | 09.53 | 52°43 | 47°33 | 1 | 10 | N.d. | 30 | N.d. |
| Flight North-Atlantic | 25 | 11.11 | 45°29.5 | 44°47.8 | 12,497 | 2450 | 2480 | 2420 | 3850 |
| Flight North-Atlantic | 25 | 11.46 | 41°58 | 43°41 | 12,497 | 2110 | 2090 | 2090 | 2150 |
| Flight North-Atlantic | 25 | 12.02 | 40°14 | 43°07 | 12,497 | 1260 | 1710 | 1650 | 410 |
| Flight North-Atlantic | 25 | 12.29 | 37°50.7 | 42°13.5 | 12,497 | 770 | 830 | 830 | 660 |
| Flight North-Atlantic | 25 | 12.58 | 34°54.1 | 41°04 | 12,497 | 1610 | 1650 | 1600 | 1600 |
| Flight North-Atlantic | 25 | 13.14 | 33°33 | 40°30 | 12,497 | 570 | 550 | 550 | 610 |
| Flight North-Atlantic | 25 | 13.28 | 32°39.8 | 40°06 | 12,497 | 590 | 550 | 610 | 610 |
| Flight North-Atlantic | 25 | 13.43 | 31°13.4 | 39°30 | 12,497 | 680 | 720 | 660 | 660 |
| Flight North-Atlantic | 25 | 13.47 | 30°14.5 | 39°08 | 12,497 | 610 | 500 | 550 | 770 |
| Flight North-Atlantic | 25 | 14.05 | 29°30 | 38°52 | 12,497 | 390 | 390 | 390 | 390 |
| Azores, Punto D, Airport | 27 | 09.06 | 37°44 | 25°42 | 1 | 140 | 140 | 150 | 120 |
| Azores, Punto D, Airport | 27 | 09.14 | 37°44 | 25°42 | 1 | 0 | N.d. | N.d. | N.d. |

with polypropylene vents (from SKC, USA). The bags were stored and shipped in an air-tight barrel with charcoal pellets which produced a phosphine-free storage atmosphere. Two control sample bags, which were filled before the experiment with phosphine-free air and shipped in the barrel, did not contain phosphine after the trip to Leipzig–America–Leipzig. The air samples were shipped to our laboratory in Leipzig and measured by gas chromatography as described earlier (Glindemann et al., 1996b). The detection limit of the method was 30 pg/m^3 . The stability of these samples after 5 days of shipping was tested. We stored standards of phosphine (between 500 and 5000 pg/m^3) in Tedlar bags stored in a dark barrel and found that the concentration declined by 50% over 5 days. This effect was not corrected for the field samples. Therefore, we suspect the presented values (Table 1) are probably about 50% too low.

In another model experiment, the gas phase chemical reactivity of phosphine with possible atmospheric absorbents like water droplets and organic aerosol was tested and compared to reduced sulfur species and ammonia. Gas standards (100 ml) of 10 ppmv of phosphine (PH_3), a mixture of each 10 ppmv of hydrogen sulfide (H_2S), methylsulfide (methanethiol, MS) and dimethylsulfide ($\text{CH}_3\text{-S-CH}_3$, DMS) and 100 ppmv ammonia (NH_3), balance nitrogen, were mixed with 900 ml clean air (gas chromatography grade) in a Tedlar gas sample bag and stored for 24 h in the dark. Three bags were prepared for each compound. One bag contained air, but two bags contained additionally either 1 ml of water (simulating water droplets) or 1 ml of hexane (simulating organic aerosol). The gas in each bag was analyzed by injection of $100 \mu\text{l}$ gas into a gas chromatograph-mass-spectrometer (Hewlett Packard GC 5890 II, MSD 5970 B, Column No. 19091J-419, Carrier gas flow: 2 ml/min). The peaks of ion 34 (PH_3), 34 (H_2S), 17 (NH_3), 47 (methanethiol) and 62 (dimethylsulfide) were used to quantify the concentration of the analytes.

3. Results and discussion

The concentration of phosphine (upper troposphere, three measurements of each sample and average) in Table 1 is correlated with the altitude, the geographic coordinates, and the local time of each sample. Fig. 1 shows the graphic correlation between altitude, coordinates and concentration. The air samples taken between 11.46 am and 2.05 pm local time at an altitude of 12500 m contained between 0.39 and 2.45 ng/m^3 phosphine. This was more than the concentration at sealevel (0.03 ng/m^3 in St. Jones, Canada and 0.07 ng/m^3 in Ponto Delgado, Azores). No night samples could be

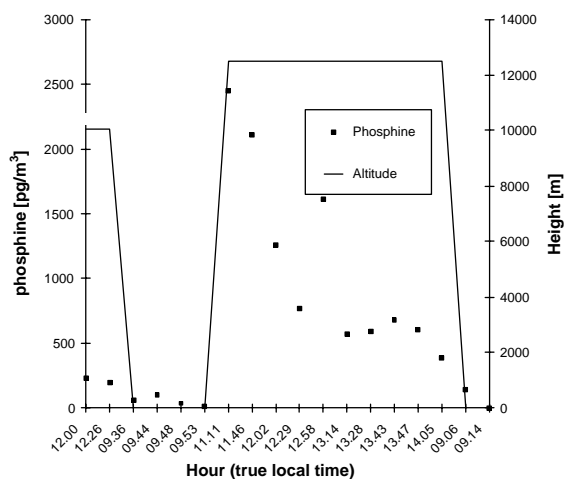


Fig. 1. Phosphine in remote North-Atlantic air in dependence of altitude and true local time.

taken to compare day and night values. Also, we had no capacity to repeat these measurements.

The finding of the reactive phosphine at 10 km altitude around noontime under the influence of high UV-radiation needs explanations.

The chemical stability experiment (Table 2) shows that phosphine compared to ammonia and reduced sulfur compounds is the only gas that can survive a combination of air, liquid water (representing atmospheric water droplets) and hexane (representing organic atmospheric aerosol). Ammonia, H_2S and methanethiol as trace compounds are “sticky” gases” which are highly water soluble and can undergo adsorption at acidic or basic sites of the used bags. Dimethylsulfide is not water soluble, but it is soluble in hexane.

This simple model experiment indicates that phosphine could be a very mobile trace gas in the atmosphere, which is much less attracted by water droplets or organic aerosol than are H_2S , methanethiol, and dimethylsulfide.

In yet another experiment, we tested the stability of phosphine in very clean and dry air (gas chromatography grade purity) in 11 Tedlar bags (can be penetrated by UV) under the influence of UV radiation, by storing the bags in a 200 L compartment with enclosed UV lamp (useful for biological laboratory sterilization). Surprisingly, we did not find a significant additional decline of phosphine compared to the other bags without UV light. This additional experiment explains that the presence of oxygen and even of UV light is not enough to produce a fast complete autoxidation of phosphine in air within hours or a day.

In summary, our results support the hypothesis that phosphine has a longer lifetime at high altitudes even in presence of higher UV radiation.

Table 2

Stability of phosphine and other trace gases in contact with air, water, and hexane in a Tedlar bag (after 24 h of storage, theoretical initial concentration 1 ppmv (NH_3 10 ppmv), average of two samples, detection limit 0.1 ppmv)

| | Concentration/ppmv (N.d. = not detected) | | | | |
|-----------------------|--|----------------------|---------------|--------------|-----------------|
| | PH_3 | H_2S | NH_3 | Methanethiol | Dimethylsulfide |
| Initial concentration | 1 | 1 | 10 | 1 | 1 |
| Dry air | 0.8 | 0.4 | 3 | 0.7 | 0.9 |
| Air + 1 ml water | 0.7 | N.d. | N.d. | N.d. | 0.8 |
| Air + 1 ml hexane | 0.4 | N.d. | 3 | N.d. | N.d. |

Another problem is to quantify the source processes that would cause the atmosphere to accumulate phosphine in measurable quantities at high altitudes. The sources which have to be discussed (publication in preparation) are industries (including inadvertent phosphide and phosphine generation by a combination of high temperature and chemical reduction of phosphate, for example in metallurgy), the biosphere, geochemistry, cosmic phosphide-containing fallout (Friel and Goldstein, 1976), and atmospheric lightning chemistry.

We found, for example for the first time phosphine in stack gas of a powerplant burning fossil browncoal (using the same method as for air, 13 samples taken within 1 h, highly fluctuating concentrations, average = 9250 pg/m^3 , s.d. = 14,860, min = <30, max = 44,120). However, no phosphine was detected in stack gas of two powerplants burning natural gas and oil. We know it is difficult to imagine how phosphine could be formed in the burners and should survive to be emitted as such. We explain this finding by chemical reduction of phosphate impurities in the glowing coal and the escape of phosphine under temporarily chemically reductive conditions and turbulent flames.

Out of control underground coal mine fires in North China which cause smoke emission visible even from space (Ottl et al., 2002) could provide this phosphine-forming mechanism and explain why atmospheric phosphine is high in the Beijing region. Another more fancy possibility to explain tropospheric phosphine could be incomplete oxidation of phosphine used to improve the efficiency of air plane jet engines (Twarowski, 1995).

Another possibility is the formation of phosphine by atmospheric lightning chemistry (unpublished results, lightning method see Glindemann et al., 1999). We acquired spark discharge experiments in our laboratory to simulate lightning and revealed the reduction of phosphate to phosphine in presence of organic matter as reductive chemical. Similarly, phosphate-containing organic matter (soil, plants, pollen, dust) struck by lightning could form a plasma with local phosphate-reducing conditions forming phosphine.

4. Summary

There are indications that phosphine exists in two vertical atmospheric regions with quite different atmospheric chemistry:

- In the lower troposphere, phosphine is observable at night in the 1 ng ng/m^3 range, with peaks of 100 ng/m^3 in populated areas. During the day under the influence of UV-induced oxidants, the concentration is much lower in the pg/m^3 range (Glindemann et al., 1996b, Liu et al., 1999).
- In the upper troposphere, above an altitude of 10 km, the concentration of phosphine is in the 1 ng/m^3 range even around noontime (this publication).
- Phosphine could be a very mobile gaseous phosphorus species which can rise up very high in the atmosphere without major “wash out” compared to other more water soluble and “sticky” gases like reduced sulfur gases which could be adsorbed by water droplets and organic aerosol.
- More field experiments, including comparison of day and night samples are necessary to verify the existence of phosphine (PH_3) vertically throughout the atmosphere (high troposphere, stratosphere).
- It is of interest to balance the potent source processes that would cause the atmosphere to accumulate phosphine in measurable quantities.
- Phosphine could be a vector of oxy-acids of phosphorus, important as condensation nuclei for clouds in the high troposphere and stratosphere.

Acknowledgements

German Aerospace Center (DLR, sampling). Centre for Environmental Research Leipzig-Halle Ltd. (joint project 08/95). Partially supported, by NSF (grant no. BES-0201849). Opinions expressed are those of the authors and not necessarily those of the Foundation.

References

- Devai, I., Delaune, R.D., 1995. Evidence for phosphine production and emission from Louisiana and Florida marsh soils. *Organic Geochemistry* 23, 277–279.
- Devai, I., Felföldy, L., Wittner, I., Plósz, S., 1988. Detection of phosphine: new aspects of the phosphorus cycle in the hydrosphere. *Nature* 333, 343–345.
- Eismann, F., Glindemann, D., Bergmann, A., Kusch, P., 1997. Soils as a source and sink of phosphine. *Chemosphere* 35, 523–533.
- Frank, R., Rippen, G., 1987. Verhalten von phosphin in der atmosphäre. *Lebensmitteltechnik* 17, 409–411.
- Friel, J.J., Goldstein, J.I., 1976. An experimental study of phosphate reduction and phosphorus-bearing lunar metal particles. *Proceedings of the Seventh Lunar Science Conference*, pp. 791–806.
- Gassmann, G., 1994. Phosphine in the fluvial and marine hydrosphere. *Marine Chemistry* 45, 197–205.
- Gassmann, G., Glindemann, D., 1993. Phosphine in the biosphere. *Angewandte Chemie International Edition* 32, 761–763.
- Gassmann, G., Glindemann, D., van Beusekom, J., 1996. Offshore atmospheric phosphine. *Naturwissenschaften* 83, 129–131.
- Glindemann, D., Stottmeister, U., Bergmann, A., 1996a. Free phosphine from the anaerobic biosphere. *Environmental Science and Pollution Research* 3, 17–19.
- Glindemann, D., Bergmann, A., Stottmeister, U., Gassmann, G., 1996b. Phosphine in the lower terrestrial troposphere. *Naturwissenschaften* 83, 131–133.
- Glindemann, D., Eismann, F., Bergmann, A., Kusch, P., Stottmeister, U., 1998. Phosphine by bio-corrosion of phosphide-rich iron. *Environmental Science and Pollution Research* 5, 71–74.
- Glindemann, D., De Graaf, R.M., Schwartz, A.W., 1999. Chemical reduction of phosphate on the primitive earth. *Origins of Life and Evolution of the Biosphere* 29, 555–561.
- Gmelin Handbook of Inorganic and Organometallic Chemistry, 1993. Phosphorus, Supplement Vol. C1. Springer, Berlin.
- Graham, W.F., Duce, R.A., 1979. Atmospheric pathways of the phosphorus cycle. *Geochimica et Cosmochimica Acta* 43, 1195–1208.
- Han, S.H., Zhuang, Y.H., Liu, J.A., Glindemann, D., 2000. Phosphorus cycling through phosphine in paddy fields. *Science of the Total Environment* 258, 195–203.
- Jenkins, R.O., Morris, T.A., Craig, P.J., Ritchie, A.W., Ostah, N., 2000. Phosphine generation by mixed—and monoseptic—cultures of anaerobic bacteria. *Science of the Total Environment* 250, 73–81.
- Lewis Jr., W.M., Grant, M.C., Hamilton, S.K., 1985. Evidence that filterable phosphorus is a significant atmospheric link in the phosphorus cycle. *Oikos* 45, 428–432.
- Liu, J.A., Yahui, CHZ., Kusch, P., Eismann, F., Glindemann, D., 1999. Phosphine in the urban air of Beijing and its possible sources. *Water, Air, and Soil Pollution* 116, 597–604.
- Nava, D.F., Stief, L.J., 1989. Temperature study of oxygen atom and phosphine reaction rate: kinetic measurements and planetary atmospheric implications. *Journal of Physical Chemistry* 93, 4044–4047.
- Ottl, H., Roth, A., Voigt, S., Mehl, H., 2002. Spaceborne remote sensing for detection and impact assessment of coal fires in North China. *Acta Astronautica* 5, 569–578.
- Pierrou, U., 1979. The phosphorus cycle: quantitative aspects and the role of man. In: Trudinger, P.A., Swaine, D.J. (Eds.), *Biogeochemical Cycling of Mineral-Forming Elements. Studies in Environmental Science*, Vol. 3. Elsevier, Amsterdam.
- Pratt, S.J., 1999. Phosphine levels outside grain stores during Siroflo(r) fumigation. In: Jin, X., Liang, Q., Liang, Y.S., Tan, X.C., Guan, L.H. (Eds.), *Proceedings of the Seventh International Working Conference on Stored-Product Protection*, October 1998, Beijing, China, Sichuan Publishing House of Science and Technology. Chengdu, China, pp. 391–398.
- Prinn, R.G., Lewis, J.S., 1975. Phosphine on Jupiter and implications for the great red spot. *Science* 190, 274–276.
- Roels, J., Verstraete, W., 2001. Biological formation of volatile phosphorus compounds (a review). *Bioresource Technology* 79, 243–250.
- Twarowski, A., 1995. The effect of phosphorus chemistry on recombination losses in a supersonic nozzle. *Combustion and flame* 102, 55–63.
- WHO (World Health Organization), 1988. Phosphine and selected metal phosphides. *Environmental Health Criteria* 73, Geneva.