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Free phosphine from the anaerobic biosphere.
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ABSTRACT: The possible liberation of highly toxic and mutagenic phosphine from putrefying media raises the question of its significance as a problem of hygiene. Free phosphine was established by gas chromatography as a universal trace component in gas emitted from the anaerobic biosphere. Sources of phosphine include landfills, compost processing, sewage sludge, animal slurry and river sediments. We detected maximum concentrations in the order of 20 ppb(v/v).

INTRODUCTION: Phosphine PH_3, an input and output component of the chemical industry, metallurgy and fumigation, is known to be highly toxic. Therefore its use and emission requires special hygienic control (see 11 for an overview about aspects of toxicity, analysis, chemical sources and fate). The hygienic problem of phosphine has been under review since GARRY et al (5) and others (1) described the mutagenity of phosphine on humans, animals and plants. In particular, emissions from suspected microbial sources of phosphine must be taken into consideration; DEVAY et al (3) claimed to find up to 382 mg/m^3 (538 ppm (v/v)) phosphine in Hungarian digester gas, a concentration which could be fatal when inhaled. The capability of microorganisms to generate phosphine in putrefying media has long been the subject of controversially discussion (2,3,4,6-10). GASSMANN AND GLINDEMANN (4) developed a reproducible experiment to show the capability of a mixed faecal flora to produce matrix-bounded biogenic phosphine. They detected this "cryptic" phosphine after liberation by alkaline digestion in a variety of bio-sludges under laboratory conditions. However only free phosphine can be inhaled by humans in the environment. The possible liberation of highly toxic and mutagenic phosphine from putrefying media raises the question of its significance as a hygienic problem. The present work was carried out in order to produce a survey of the importance of sources suspected to spontaneously emit free phosphine anticipated to be biogenic. The investigations were carried out during different seasons of a year to register the impact of the climate. The expected results can be interpreted not so much causally but rather as phenomena, because the generation and liberation of phosphine is multicausal. We expected the highest concentrations in landfills,

compost processing, sewage, animal slurry and polluted river sediments, where the ancient anaerobic "microbial" capabilities encounter the anthropogenic enrichment of nutrients and can become a "human" problem for environmental investigation.

MATERIAL AND METHODS: (Details of the procedures are available from the authors)

Types of gas samples, principles of their obtainment: *Biogas (digester gas, fermentation gas)* is the product of regulated methanogenesis in closed anaerobic digesters. It flowed by means of its own overpressure into sampling bags. *Putrefaction gas* is the product of several unregulated, mainly anaerobic lysis and digestion processes in open sedimenters, tanks or basins. It had to be accumulated in floating funnels prior to mixing with air.

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It flowed through a tube from the top of the funnel into sample bags owing to the hydrostatic pressure of the suspension replaced by the gas in the funnel. *Landfill gas* is mainly a product of anaerobic processes in landfills. It had to be sampled by vacuum from a depth of several meters. *Interstitial gas* is a mixture of gaseous products and strong polluted deoxigenized air in the mainly anaerobic part of solid waste, for example in the composting process. It had to be sampled by vacuum pumps from a depth of about one metre. *Marsh gas* is chiefly a product of methanogenesis in aquatic sediments. It had to be sampled with flat funnels placed directly upon the sediment to avoid washing out the phosphine by bubbling through the water layer. Sample preparation: The gas samples were transported in Tedlar sampling bags. Bags for atmospheric samples had to be stored in containers free of phosphine. Hydrogen sulfide, carbon dioxide and water were removed prior to analysis using solid NaOH. Trace analysis of phosphine by gas chromatography: The HP 5890 II gas chromatograph was equipped with a thermionic nitrogen phosphorus detector (NPD). The standard column Poraplot Q (Chrompack) was 10 m long with an internal diameter of 0.32 µm. The gas samples (mostly 5 - 50 ml) were cryo-trapped to remove the matrix methane or air and to focus the phosphine peak. The detection limit was 0.1 ppt(v/v) for 50 ml samples and 0.01 ppt for 500ml. Concentration was estimated by comparison with a standard. Each sample was measured twice, with a maximum deviation of about 20%.

RESULTS: Table 1 contains the concentrations and fluxes of free phosphine in gas samples from the anaerobic biosphere. The maximum imission concentration of phosphine in the closed working atmosphere near the sources was 41 ppt (domestic sewage plant, sludge drying process, near centrifuge).

DISCUSSION: Spontaneously free phosphine is universally present in a variety of gases emitted from the biosphere. Landfills liberated the highest concentrations and fluxes. However, chemical source processes of phosphine via the hydrolysis of metal phosphides especially in landfills can not be excluded. Putrefaction processes in open basins also liberated high concentrations but low fluxes. The seasonal trend of the concentration and flux in gas from open putrefaction processes and landfill displays higher values in summer. The composting process (which is perceived as mainly aerobic), produced more phosphine in winter, which seems to be a result of the higher wetness of the medium as a condition for local anaerobiosis. Domestic sewage sludge liberates

phosphine immediately after stabilization with lime, which can be interpreted as analogous to the liberation of matrix-bounded phosphine by the process of alkaline digestion suggested by GASSMANN and GLINDEMANN (4). The German digester gas analyzed contained about 6 orders of magnitude less phosphine than the Hungarian samples from DEVAÝ (3). This could be caused by the efficient phosphate elimination procedure in the German sewage plants observed. Our future work will investigate both the biogenic and chemogenic mechanisms of the liberation of phosphine in the environmental biosphere.

Table 1: Phosphane in gas samples from the biosphere, seasonal trend 1994

Source	Type of gas sample	Phosphane / ppt (v/v)				Flow of phosphane / (µg/d)			
		Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Landfill									
Landfill in Wannsee, Berlin (48,000 m³/d landfill gas, area 0.65 km², mass 11 million t)									
Suction manifold B4/1	Landfill gas	960	2621	46	1548	41	111	2	65
Suction manifold B4/2	Landfill gas	247	8	0	13	0	0	0	0
Suction manifold B4/3	Landfill gas	1452	2111	14	3	0	0	0	0
Suction manifold B4/4	Landfill gas	106	474	1134	105	4	20	48	4
Suction manifold B4/5	Landfill gas	6468	1188	1082	5260	273	50	46	222
Suction manifold B4/6	Landfill gas	6340	17731	1034	2192	268	749	44	93
Main suction line PC01	Landfill gas		340		836		3831		9420
Main suction line PC02	Landfill gas		4255		627		47944		7065
Main suction line PC03	Landfill gas		3426		1315		38603		14817
Main suction line PC04	Landfill gas		1617		1000		18220		11268
Main suction line PC05	Landfill gas		3957		1616		44586		18208
Main suction line PC06	Landfill gas		3043		199		34287		2242
Waste disposal									
Composting plant, Berlin (4000 m³ composting piles)									
Gardening waste, fresh	Interstitial gas		3		71		0		0
Domestic biomass, premixed	Interstitial gas		24		85		1		5
Domestic biomass, composting	Interstitial gas		3		66		1		19
Domestic biomass, after composting	Interstitial gas		0		29		0		0
Composting plant, near Leipzig (700 m³ composting piles)									
Domestic biomass, premixed	Interstitial gas		23		341		0		5
Domestic biomass, composting	Interstitial gas		13		60		1		4
Domestic biomass, after composting	Interstitial gas		13		22		0		0
Sewage plant, Leipzig (150 m³/d solid phase from centrifugation of non digested sludge, stabilized with lime)									
Solid phase, immediately after addition of lime	Interstitial gas		9733	904	10849		685	64	764
Solid phase, 4 h after addition of lime	Interstitial gas		7801	5455	4055		549	384	286
Sewage plant, Berlin (120 m³/d solid phase from centrifugation of digested sludge, without lime)									
Solid phase, whithout lime	Interstitial gas		9	29	11		0	0	0
Sewage plant, Erfurt (72 m³/d solid phase from centrifugation of digested sludge, stabilized with lime)									
Solid phase, immediately after addition of lime	Interstitial gas			6889	23233			485	1636
Solid phase, 4 h after addition of lime	Interstitial gas			833	5257			59	370
Animal slurry technology, solid phase from centrifugation, composting pile									
Solid phase of pig slurry (30 t/d)	Interstitial gas	555	1015	31	57	5	11	0	0
Solid phase of cattle slurry (15 t/d)	Interstitial gas		0	5	55		0	0	0

Table 1 (continued): Phosphane in gas samples from the biosphere, seasonal trend 1994

Source	Type of gas sample	Phosphane / ppt (v/v)				Flow of phosphane / (µg/d)			
		Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Municipal sewage disposal									
Sewage plant, Berlin (anaerobic digestion of 1200 m³/d sewage sludge)									
Digester 1	Biogas	25	26	6	23	120	122	30	109
Digester 2	Biogas	23	31	9	5	107	145	42	24
Digester 3	Biogas	21	30	12	0	100	145	57	0
Sewage plant, Erfurt (anaerobic digestion of 850 m³/d sewage sludge)									
Digester 1	Biogas		94	64	55		531	362	310
Digester 2	Biogas	19	94	63	63	108	531	352	355
Mixed biogas after refining	Biogas	12	72	48	45	130	816	538	507
Open digestion basin, digester sludge	Putrefaction gas		33	16	33		20	3	2
Sewage plant, Leipzig (1000 m³/d sewage sludge, without anaerobic digestion)									
Sedimenter before centrifugation	Putrefaction gas		275	49	932		9	1	6
Sewage plant, Leipzig (100 m³/d sewage sludge)									
Emscher tank	Putrefaction gas		6167	29	4178		869	4	588
Natural aquatic sediments									
Basin of River Elster, Leipzig (270000 m², sediment layer of 1m)									
Fairground (50,000 m²)	Marsh gas		1		4		1		0
Landauer Bridge (50,000 m²)	Marsh gas		1		3		0		0
Landing stage BW (50,000 m²)	Marsh gas		2		4		2		0
Animal slurry technology									
Cattle slurry and biogas technology (100 m³/d slurry)									
Digester 1	Biogas	13	3	0	10	44	10	1	34
Open primary tank, feed slurry	Putrefaction gas		140	123	238		1	0	0
Pig slurry and biogas technology (200 m³/d slurry)									
Digester 1	Biogas	95	197	81	212	209	433	178	466
Sedimenter, feed slurry	Putrefaction gas		1623	77	370		10	0	1
Storage basin, digested slurry	Putrefaction gas	70	371	76	156	31	266	26	20
Pig slurry and simple storage processing (40 m³/d slurry)									
Open primary tank, feed slurry	Putrefaction gas	5085	8995	359	1685	29	51	3	5
Storage basin	Putrefaction gas		1827	51	548		309	10	17

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