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Abstract
The degree of the emission of the mutagenic phosphane from animal slurry have become an issue of hygiene which so far has not been investigated. This work clearly detects spontaneously emitted free phosphane from animal slurry for the first time and correlates the degree of its emission with different disposal technologies. The subjects of the investigations are the simple storage process and processes involving biogas plants for the digestion both of pig and cattle slurry. Pig slurry generates about one magnitude more phosphane than cattle slurry. The maximum concentration detected in putrefaction gas was 14621 ppt(v/v). Putrefaction gas samples from fresh fecal slurry in primary (mediary storage) tanks followed by storage basins and sedimenters contains the highest concentrations. The mainly methanogenic biogas process generates the smallest concentrations but the highest fluxes of phosphane. Fluxes and concentrations in open basins are significantly higher during summer than in winter. The correlation of phosphane and dimethyldisulfide concentrations indicates that primary lytic processes play a role in the liberation of phosphane. Individual samples of the imission in air give a maximum value of 35 ppt. By comparison, measurements of phosphane in Hungarian digester gas from municipal sewage treatment show that maximum concentrations could be some orders of magnitude higher. Therefore the data base for phosphane from animal slurry must in future be expanded. The results of analysis so far achieved cannot be interpreted from either a human or veterinary medical viewpoint.

Introduction:
Animal slurry can cause acute and chronic intoxications, often attributed to hydrogen sulfide or ammonia. Phosphane has so far not been taken into consideration as another cause. Phosphane (hydrogen phosphorus, PH_3) is highly toxic (7, with 200 ref. about of toxicity, analytics and fate). Phosphane has in air a half-life of between 5 and 28 hours and can thus accumulate in work atmosphere. Phosphane concentrations above 100 ppm(v/v) have an acute disordering effect on the metabolism; at above 400 ppm(v/v) phosphane causes acute asphyxia and sudden death. Subtoxic doses have a cumulative effect. The following chronically toxic effects in animal experiments have been described: retardation of the cell-dividing cycle of the spleen in rodents, the impact on the liver-enzyme activity of chickens, chromosome aberrations in the ovaries of hamsters, and changes in DNA synthesis in mouse tissue. ALAVANJA et al. (1) found an increase of malignous lymphatic neoplasms (PMR 202, PCMR 218) and an increased risk of lymphocytic and reticulocytic sarcoma (PCMR 191) among workers handling phosphane in grain fumigation. GARRY et al (4) describe the genotoxicity of phosphane at merely the level of some nanograms of phosphane per litre of human lymphocyte suspension (chromosome aberrations like acentric, dicentric and quadriradial rings, stable chromosome rearrangements such as translocations and inversions). The actual toxic effect is attributed to the oxidation product of phosphane monohydroxy-dihydro-phosphane ($HOPH_2$). The bacterial formation of phosphane in putrefying media has been controversially discussed for about one century. RUDAKOV (6) describes soil bacteria capable of producing phosphane. DEVAY et al (2) found up to 450 ppm (v/v) phosphane in putrefaction gas, which would be fatal when inhaled. Some other authors failed to find such phenomena. GASSMANN and GLINDEMANN (5) cultivated a mixing culture of fecal flora under sulfate reducing conditions. After alcaline digestion of the biomass, matrix-bounded phosphane was liberated. Furthermore they found

phosphane after alkaline digestion of faeces and slurry. The degree of the emission of the toxic and mutagenic phosphane from animal slurry have become an issue of hygiene which so far has not been investigated (2). The present work observes whether free phosphane is emitted from slurry spontaneously and how this emission depends on the type and process stages of treatment technology. The biogas plants investigated are the largest (pig slurry) and one of the most modern (cattle slurry) in Europe. Toxicological investigations are not subject of this work.

Material and methods:

Types of gas samples, methods of their obtainment:

Biogas (digester gas, fermentation gas) is the product of regulated methanogenesis in closed anaerobic digestion tanks or fermenters. It flows 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 has to be accumulated in swimming funnels prior to mixing with air and flows into sample bags as result of the hydrostatic pressure of the liquid replaced in the funnel. Polluted air around emission sources is mainly working atmosphere which is pressured by pumps into sample bags. Such air samples are of limited use because of the uncontrollable influences of atmospheric motions. Accumulated air is an artificial air sample simulating a high accumulation of phosphane in the air above an emission source (basin) under a low layer of atmospheric inversion. The sampling funnel of about 0,2 m^2 containing 10 litres of clean air was placed upon the surface of the bassin for 10 minutes.

Sample preparation: All gas samples were transported in Tedlar sampling bags. Hydrogen sulfide and carbon dioxide were removed prior to analysis by alkaline washing with the lime Drägersorb 400 (DRÄGER AG, Lübeck, Germany).

Trace analysis of phosphane by gas chromatography: The HP 5890 II gas chromatograph was equipped with a thermionic nitrogen phosphorus detector (NPD). Simultaneous flame photometric detection (FPD) in phosphoric modus served in selected cases to verify the identity of phosphane. Moreover the identity of phosphane was proved by comparing the retention time on columns Poraplot U, S and Plot Al_2O_3/Na_2SO_4. The standard column Poraplot Q (Chrompack) was 10 m long with 0.32 µm ID. The gas samples of mostly 5 - 50 ml were cryo-trapped to remove the matrix methane or air and to focus the phosphane peak. The detection limit was 0.1 ppt(v/v) for 50 ml samples and 0.01 for 500ml. Concentration was estimated by comparison with a standard. Each sample was measured twice with a maximum deviation of about 20%. Concentration of dimethyl disulfide (DMDS) by gas chromatography: The HP 5890 II gaschromatograph was equipped with flame photometric detection in sulfuric modus. The 100 µl gas samples were injected by a syringe without focusing. The detection limit was 0.1 ppm(v/v). Hydrid-value: This summary effect of easily oxidizable basic and neutral hydrides (phosphane, arsane etc.) was measured with an electrochemical hydride sensor PAC PH3 (DRÄGER AG, Lübeck). The minimum display value is nominally 0,01 ppm(v/v).

Characterization of plants observed:

A) Cattle slurry and biogas processing: A flow of 100 m^3/d fresh slurry after short storage in an open primary tank (gas sample in the table described as "putrefaction gas, primary tank") is digested in two serial closed anaerobic fermenters (biogas, fermenter 1 and 2). The biogas of both fermenters (mixed biogas before refining) i cleaned (mixed biogas after refining) prior to usage for energy generation. The digested slurry is separated with a centrifuge into a solid and a liquid phase. The solid undergoes anaerobic rotting in storage piles (interstitial gas).

B) Pig slurry and biogas processing: A flow of 200 m^3/d fresh slurry after sedimentation (putrefaction gas, sedimenter 1) and centrifugation of the solid phase (interstitial gas, solid phase, fresh) with a centrifuge is digested in an 8,000 m^3 closed anaerobic fermenter (biogas, fermenter 1). After sedimentation (putrefaction gas, sedimenter 2) The digested slurry is stored for a long time in an open basin (putrefaction gas, basin 8). The liquid phase of sedimenter 2 is additionally digested in a closed aerobic fermenter (process air). The solid phase from the centrifuge undergoes anaerobic rotting (interstitial gas, solid phase, rotting) in storage piles.

C) Pig slurry and simple storage processing: A flow of 40 m^3/d fresh slurry is stored in an open primary tank (putrefaction gas) and then in an open storage basin (putrefaction gas). The surface of the primary tank is covered with a floating layer of porous clay (tank 1) or straw (tank 2). D) is similar to C) but without floating layer.

Experimental results:

Table 1 contains the concentrations and fluxes of phosphane from anaerobic emission sources. The flux of phosphane from open tanks is the quotient of the daily accumulated gas volume and the funnel area

multiplied by the whole area of the tank and the concentration of phosphane. The flux of phosphane from fermenters is the volume of biogas produced daily multiplied by the concentration of phosphane. Table 2 contains the concentration of phosphane imission into the work atmosphere near the emission sources.
Table 3 compares the concentrations of phosphane in primary tanks and storage basins of two plants with simple storage processing over a time interval from May to July 1994, correlated with the concentration of dimethyl disulfide and hydride value. The variation of floating layers takes place inside the sampling funnel.

Discussion of results:
Anaerobic emission sources: (table 1) pig slurry generates higher concentrations and fluxes of phosphane than cattle slurry. The concentration in biogas is much lower than in putrefaction gas from the storage and sedimenting stages. The flux in biogas is much higher than in putrefaction gas from the same plant. In the case of pig slurry, the concentration of phosphane in putrefaction gas from simple storage processing is generally higher than in putrefaction gas from stages in plants with biogas processing. The (absolute) fluxes of phosphane in table 1 divided by the flux of slurry would give specific fluxes in µg phosphane per day and m^3 slurry. The quotient of specific fluxes of biogas processing and simple processing would be lower than the quotient of absolute fluxes. The emission of phosphane decreases from summer to winter, corresponding to the expectations of a microbial cause. This decline is more markedly expressed by fluxes than by concentrations.
Imission into the working atmosphere (table 2): The maximum concentration of phosphane was 35,3 ppt(v/v) in process air from an aerobic digester for anaerobic digested slurry in plant B. The other values are relatively low because the biogas (the main source) is burned before imission into the atmosphere.
Comparison of putrefaction gas from primary and storage tanks for pig slurry and the correlation of phosphane with dimethyl disulfide (DMDS) and hydride-value (table 3): The concentration of phosphane in the plants with storage technology is comparably high in primary tanks . During sampling in plant C, the influence of odor-minimizing floating layers of porous clay or straw inside the sampling funnel on the concentration of phosphane was tested. DMDS is generated during the putrefying lysis of microorganisms and a correlation with phosphane (comparison of averages) indicates a relation between the lysis of fecal bacteria and liberated phosphane. DMDS was not detected in biogas which contains lower concentrations of phosphane. The hydride value correlated with phosphane could be interpreted as indicating the presence of other interesting neutral or basic easily oxidizable hydrides.
Basis for simple technological strategies to reduce the emission of phosphane: The emission of phosphane from slurry can be reduced by biogas processing where the phosphane is burned before imission into the atmosphere. Simple open storage processing is more problematic than biogas processing. Fresh fecal matter which contains matrix-bounded phosphane (5) should not come into long-term contact with sedimented old active sludge in open tanks; alternatively, this old sludge should not be allowed to accumulate.
The concentrations and fluxes of free phosphane from animal slurry were much lower than expected after the remarkable results of others studying municipal sewage processing (3). In order to achieve a conclusive assessment of the problem of phosphane from slurry, we will extend our investigations, to a higher number of samples and toxic trace components. Other future work will be related to the causes and the manipulation of this phosphane. The results of analysis so far achieved cannot be interpreted from either human or veterinary medical viewpoint.

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table 1
Concentration and flux of phosphane in gas samples from anaerobic stages of animal slurry processing. Seasonal trend from spring 1994 to winter 1994/95

sample	concentration phosphane / ppt/v/v)				flux phosphane / (µg/d)			
	spring	summer	autumn	winter	spring	summer	autumn	winter
plant A: cattle slurry and biogas processing (100 m³/d slurry)								
biogas, fermenter 1	13	3	**0.3**	10	44	10	1	34
biogas, fermenter 2	5		**0**	9	17	0	0	30
mixed biogas, before refining		4	**0.4**	0		27	3	0
mixed biogas, after refining	158	2	**1**	0	1068	14	7	0
putrefaction gas, primary tank (50 m2)		140	**123**	238		1	0	0
interstitial gas, solid phase, fresh (20 m2)		0	**18**	0		0	0	0
interstitial gas, solid phase, rotting (100 m2)		0	**5**	55		0	0	0
sum (independent fluxes)						14	7	0
plant B: pig slurry and biogas processing (200 m³/d slurry)								
biogas, fermenter 1	95	197	**81**	212	209	433	178	466
putrefaction gas, sedimenter 1 (70 m²)		1623	**77**	370		10	0	1
putrefaction gas, sedimenter 2 (70 m²)	438	1797	**49**	1945	7	44	1	13
putrefaction gas, basin 8 (3000 m²)	70	371	**76**	156	31	266	26	20
interstitial gas, solid phase, fresh (10 m²)		32	**21**	52		0	0	0
interstitial gas, solid phase, rotting (150 m²)	555	1015	**31**	57	5	11	0	0
process air, aerobic fermenter	15	35	**27**	6	1497	3583	2788	607
sum (independent fluxes)						4347	2993	1108
plant C: pig slurry and simple storage processing (40 m³/d slurry)								
putrefaction gas, primary tank (100 m²)	5085	8995	**359**	1685	29	51	3	5
putrefaction gas, storage basin (1500 m²)		1827	**51**	548		309	10	17
sum (independent fluxes)						359	13	22

table 2
Concentration of phosphane in air samples in the imission sphere of animal slurry processing. Seasonal trend from spring 1994 to winter 1994/95

sample	phosphane / ppt/v/v)			
	spring	summer	autumn	winter
plant A: cattle slurry and biogas processing (100 m³/d slurry)				
centrifuge shop, 2 m beyond centrifuge	0.0		**1.4**	0.3
centrifuge shop, near centrifuge	0.5		**1.7**	0.4
air on transporter of solid phase	1.3		**3.8**	0.0
accumulated air, primary tank		11.9	**10.8**	9.4
accumulated air, storage basin		0.9	**1.9**	0.7
plant B: pig slurry and biogas processing (200 m³/d slurry)				
process air, aerobic fermenter	14.8	35.3	**27.5**	6.0
process air, reservoir of aerobic fermenter		3.9	**1.7**	1.0
centrifuge shop, 1 m beside solid phase		0.1	**1.0**	0.0
centrifuge shop, near solid phase	0.2	4.8	**0.7**	0.0
30 cm above solid phase, rotting		10.2	**2.7**	0.3
150 cm above solid phase, rotting		2.8	**0.9**	0.0
near open aerobic digestion basin 7, west		0.0	**1.0**	0.2
near open aerobic digestion basin 7, east		0.2	**1.0**	0.2
near storage basin 8, north		0.1	**2.8**	0.0
1,5 m above storage basin 8		9.4	**0.8**	0.0
accumulated air, storage basin 8		12.9	**6.6**	6.3
sedimenter 2, 10 cm above surface	5.1		**3.3**	0.0
sedimenter 2, 100 cm above surface	1.4		**1.4**	0.0
sedimenter 2, outside, 1 m	0.4		**1.0**	0.0
windward of plant	0.0	0.0	**0.8**	0.0

table 3
Phosphane, dimethyl disulfide and hydrid value for putrification gas from simple storage processing of pig slurry

sampling place	date -1994	concentration PH_3 ppt(v/v)	DMDS ppm(v/v)	HYDRIDE ppm(v/v)
plant D				
primary tank	17. May	4930	0.0	0.0
	31. May	2884	0.0	0.0
	14. Jun	17	2.5	0.0
	28. Jun	612	0.0	0.2
	05. Jul	12023	0.4	0.2
	12. Jul	587	0.4	0.1
storage basin	17. May	151	0.0	0.0
("oligolysis", Cu-Ions	31. May	227	1.5	0.0
inhibit	28. Jun	504	1.1	0.2
generation of H_2S)	05. Jul	233	0.8	0.2
	12. Jul	123	1.3	0.2
plant C				
primary tank 1	25. May	3256	2.5	0.0
(without floating	01. Jun	1628	0.9	0.0
layer in sampling	15. Jun	742	10.2	0.3
funnel)	22. Jun	4727	5.7	0.9
primary tank 1	25. May	4930	13.7	
(10 cm porous clay	01. Jun	7349	2.5	
in funnel)	15. Jun	5212	53.1	1.2
	22. Jun	7636	25.0	0.1
primary tank 2	01. Jun	11349	2.8	0.0
(40 cm straw layer	06. Jul	14621	16.6	14.0
in funnel)				
primary tank 2	15. Jun	6212	14.0	2.8
(without layer)				
storage basin	29. Jun	888	0.5	0.1
(without layer)	06. Jul	487	16.5	0.4
	18. Jul	265	12.0	2.0
storage basin	29. Jun	828	1.5	0.1
(10 cm porous clay	06. Jul	1172	0.4	0.3
in funnel)	18. Jul	2536	0.4	0.3
statistical parameters for samples from primary tanks				
average		**5219**	**10.7**	**2.0**
maximum value		14621	53.1	14.0
standard deviation		4301	14.3	4.3
number of values		17	14.0	10.0
statistical parameters for samples from storage basins				
average		**674**	**3.6**	**0.4**
maximum value		2536	16.5	2.0
standard deviation		706	5.7	0.6
number of values		11	10.0	9.0