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Composition of marsh gases in the central and eastern United States

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Abstract—Summer samples of marsh gases in Minnesota (fresh-water), Louisiana, and Delaware (fresh-water and brackish-water) yielded 50–85% methane, 3–52% "excess nitrogen", 4–15% carbon dioxide, and small amounts or traces of hydrogen, carbon monoxide, propane, hydrogen sulfide, and C_4–C_7 hydrocarbons. These types of gas flows were found to decrease drastically in winter periods of sampling, and large amounts of "air" accumulate in some marsh and lake sediments. Carbon dioxide decreases in the winter samples, but carbon monoxide and hydrogen sulfide showed relative increases. Ethane is present in several, and butane in one, sample from Minnesota in the fall. There is a drop in "excess nitrogen" (non-air N_2) in the winter as compared to summer samples.

Specimens of marsh plants were placed in culture flasks with mud from each collecting locality and allowed to culture for several months. In composition, the cultured gases are predominantly methane, carbon dioxide, and "excess nitrogen". Hydrogen, ethane, propane, and hydrogen sulfide are minor components. Carbon monoxide was not detected, in contrast to marsh gases. *Phragmites* from industrially polluted Delaware Bay evolved many additional hydrocarbons in culture. pH and Eh were monitored for *Typha* in culture; pH remained near 7 and Eh near −100 mV after stabilization.

Carbohydrate analyses of marsh plants indicate xylans exceed cellulose as a major source of methane in these samples; mannose, galactose, and arabinose are also important potential contributors.

Delta carbon-13 values of methane from marsh gases sampled are more negative than those from laboratory-cultured source plants, whereas delta deuterium values of methane from marsh gases are less negative than those of cultured source plants.

INTRODUCTION

THIS paper presents results of studies on the environment, origin, and composition of marsh gases from Minnesota and Delaware in supplement to results provided in an earlier paper (SWAIN *et al.*, 1977). In that paper results were given of field sampling and laboratory analyses of marsh gases from natural and cultured samples from Louisiana, Minnesota and Delaware. The present paper concerns samples collected in late fall 1974 and winter 1975, together with a discussion of laboratory cultured samples. A similar seasonal study of marsh gas is that of KING and WIEBE (1978).

MARSH GASES FROM NEAR MARSH SURFACE

The variation in composition of marsh gas collected just beneath the marsh surface by means of a large inverted glass funnel is shown in Tables 1 and 2 for fall and winter Minnesota localities. As determined from earlier studies (SWAIN *et al.*, 1977) and the present one, the methane values are low in early summer, increase during late summer and early fall and decrease to low or negligible amounts in late fall and winter after freeze-up. The presence of large amounts of trapped air in the bog sediments during the winter is notable (Table 2). It is not known whether this represents atmospheric air or a biologic mixture of O_2 and N_2. Argon was not recorded in the analyses. The pH values in the sediments are weakly acid and Eh values range from slightly negative to slightly positive, although the Eh at the Mille Lacs, Minnesota locality was more strongly positive at the time of sampling.

The methane contents of surface fresh- and salt-water marsh samples from Louisiana (SWAIN *et al.*, 1977) in late summer were not greatly different than those of the freshwater Minnesota samples at the same time of the year. As noted previously a relationship to pH, Eh, tidal action or lack of it, and nature of source material and substrate, is shown by the methane values in the marshes studied (SWAIN, 1972, 1975; SWAIN *et al.*, 1975, 1977).

MARSH GASES FROM BELOW THE MARSH SURFACE

The variation in methane flow obtained by inserting 3-in-dia. glass tubes into the marsh sediment, evacuating the tube, and monitoring the flow on a seasonal basis has been reported previously for Minnesota and Delaware marshes (SWAIN, 1972, 1975; SWAIN *et al.*, 1975, 1977). Such flows were found to vary by about one order of magnitude during the summer and fall, and in the present study, to decrease to negligible amounts (Tables 1 and 2).

Methane flows from below-surface samples in Louisiana marshes in late summer 1974 showed that saltwater localities had markedly lower values than freshwater localities for reasons discussed earlier (SWAIN *et al.*, 1977).

Table 1. Analyses of marsh gases from Minnesota; samples collected fall, 1974
All are "funnel samples"; mol. % on air free basis

Location	Hydrogen	Methane	Propane	CO	CO_2	N_2	H_2S	Others	pH	Eh
Fish Lake, Minnesota (Typha latifolia)	0.05	55.32	0	0	3.75	39.97	0		5.1	+110
Anderson Pond, Minnesota (Typha latifolia)	0.09	81.18	0.02	0	8.87	9.53	0		5.9	+20
Cedar Creek Bog Lake, Minnesota (Decodon verticillatus)	0.06	77.4	0	0	3.20	18.79	0	ethane-trace	5.9	0
Mille Lacs Lake No. 1, Minnesota (Typha latifolia)	0.06	66.87	tr.	0	4.17	28.13	0		6.1	+212
Mille Lacs Lake No. 2, Minnesota (Typha latifolia)	0.07	76.40	0	0	4.45	18.33	0	ethane-trace *n*-butane-trace		
Mille Lacs Lake No. 3, Minnesota (Typha latifolia)	0.08	81.53	0.03	0	9.68	8.18	0	ethane-trace		

COMPOSITION OF MARSH GASES

Mass spectral analyses of marsh gases from Minnesota and Louisiana were discussed previously (SWAIN *et al.*, 1977). Some additional analyses from Minnesota and Delaware are presented here (Tables 1–3). Ethane is present in several Minnesota samples, collected in the fall, not noted previously, and butane is apparently present in one sample. Carbon monoxide, which had previously been noted in the Minnesota and Louisiana samples, was not detected in the fall samples from Minnesota (Table 1), although it is present in the winter samples (Table 2). Carbon monoxide also occurs in several of the Delaware marsh gas samples.

Carbon dioxide forms a very small percent of the marsh gases in the Minnesota winter samples, whereas it is an important component in the summer and early fall samples. The striking decrease in methane in the winter samples was already mentioned, and there is also a major drop in the "excess nitrogen" in the winter as compared to the summer samples.

Carbon monoxide and, to a lesser extent, hydrogen sulfide appear to be the only authigenic components that generally increase relative to the other gases

Table 2. Composition of marsh gas samples from Minnesota, winter, 1975; values in parentheses are on an air-free basis

Locality	Plant and sediment type and date sampled	Air %	Non-air N_2%	H_2	CH_4	C_2H_6	C_3H_8	CO	CO_2	H_2S
Cedar Creek Bog 8 ft of depth	*Decodon* peat 01.23.75	99.5	0.19	0	0	0	0	0.10	0.08	0
Cedar Creek Bog 9 ft of depth	*Decodon* peat 01.23.75	99.7	0.08	0	0	0.02	0.02	0.13	0.04	0
Cedar Creek Bog 10 ft of depth	*Decodon* peat 01.23.75	99.5	0.18	0.14	0	0	0	0.11	0.05	0.01
Cedar Creek Bog 10 ft of depth	*Decodon* peat 01.18.75	99.7	0	0	0	0	0	0.14	0.04	0.01
Cedar Creek Bog Top of peat	*Decodon* peat 01.23.75	93.2	5.38	0	0.65	0.01	0	0.11	0.59	0.01
Cedar Creek Bog Top of peat	*Decodon* peat 01.23.75	91.1	6.53	1.56	trace	0	0.01	0.10	0.70	0
Cedar Creek Bog Top of peat	*Decodon* peat 01.23.75	92	6.03	0	1.25	0	0	0.08	0.64	0.01
Lake Johanna Depth of water, 40 ft	Copropel 01.25.75	95.8	3.87	0	0.06 (1.42)	0	0	0.11 (2.60)	0.15 (3.53)	0
Anderson Farm Pond	*Typha* peat 03.2.75	3.5	14.6	tr	76.85 (79.6)	0	0	0	4.9 (5.1)	0
Cedar Creek Bog Top of peat	*Decodon* peat 03.21.75	19	28.7	tr.	51.2 (63.2)	0	0.2	0	1.08 (1.3)	0

Table 3. Analyses of marsh gases from Delaware: mol. % on air free basis: F. funnel sample: T. tube sample: fall. 1974 and winter. 1975

Location	Hydrogen	Methane	Propane	CO	CO_2	N_2	H_2S	Others
Dragon Creek. Del. (F) 09.16.74	trace	27.2	0.5	1.0	6.5	64.7	0	0
Dragon Creek. Del. (T) 09.16 to 09.23 74	0	19.3	0.2	1.2	10.2	69.2	0	0
Dragon Creek. Del. (F) 09.23.74	0	40.0	0	0.5	7.0	52.5	0	0
Dragon Creek. Del. (F) 09.30.74	0	37.6	0	1.4	8.0	53.0	0	0
Port Penn. Del. (F) 09.16.74	0.03	36.3	0.02	0	5.8	57.9	0	0
Fleming Landing. Del. (F) 02.28.75	trace	65.2	0	0	4.7	30.1	tr.	0

during the winter. Hydrogen shows a similar, but less consistent increase.

GASES EVOLVED FROM LABORATORY CULTURES

As described in previous reports, specimens of marsh plants were placed in culture flasks with mud from each collecting locality and allowed to culture for several months (SWAIN, 1975; SWAIN *et al.*, 1977). Results supplemental to those reported previously are shown in Table 4.

Most cultures (under the helium or nitrogen atmosphere) showed an initial low period of methane generation followed by a rise in rate of generation to a peak 4–6 weeks after the culture started, then a gradual decline for several weeks. In composition the cultured gases are predominantly methane, carbon dioxide, and "excess nitrogen". Hydrogen, ethane, propane, and hydrogen sulfide are minor components. In contrast to the marsh gas samples, carbon monoxide was not detected. Emanations from a cultured sample of *Phragmites* from highly contaminated Delaware Bay yielded a large variety of organic compounds (Table 5).

pH and Eh were monitored in a culture of *Typha latifolia* for 2 months. pH remained in the range 7–7.1 and Eh ranged between −80 and −120 mV during the period.

Table 4. Composition of gases from cultured plant samples; mol. % on air-free basis

Species and location Date culture began	Date sampled	H_2	CH_4	C_2H_6	C_3H_8	CO	CO_2	N_2	H_2S
Decodon verticillatus	11.04.74	tr.	38.0	tr.	0.03	0	32.90	28.47	0
Cedar Cr. Bog,	12.04.74	tr.	28.28	tr.	0.02	0	38 48	46.77*	0
Minn.	01.30.75	0.04	45.4	0	0	0	34.6	19.9	0
07.08.74	02.18.75	0	15.3	0	0	0	27.6	56.8	0
	04.17.75	0	0	0	0	0	0	0	0
Typha latifolia	11.04.74	tr.	34.50	0	tr.	0	39.19	25.70	0
Anderson Pond.	12.04.74	tr.	23.60	0	tr.	0	26.80	49.18*	0
Minn.	01.30.75	0.03	44.9	0	0	0	42.1	13.0	0
07.08.74	02.18.75	0	45.4	0	tr.	0	46.4	8.0	0
	04.17.75	0	46.4	0	0	0	46.4	7.2	0
Eichornia crassipes	11.04.74	0.04	26.72	tr.	tr.	0	34.14	38.43	0
L. Guillaume. La.	12.04.74	0.33	22.40	tr.	tr.	0	28.63	48.4*	0
09 02.74	01.30.75	0.03	41.5	0	0	0	36.2	22.3	0
	02.18.75	0	41.4	0	0	0	39.4	19.2	0
	04 17.75	0	0	0	0	0	0	0	0
Amaranthus australia	11.04.74	0 03	32.75	0	0.03	0	37.04	29.14	0.29
(=Acnida	12.04 74	tr.	30.89	0	tr.	0	34.93	33.17*	0 27
cuspidata)	01.30.75	0 04	54.9	0.01	0.01	0	35.3	9.5	0.18
Calcasieu R.. La	02.18.75	0	53.8	0	0	0	37 4	8.7	0
09.02.74	04.17.75	0	0	0	0	0	0	0	0
Alternanthera	11.04.74	0	1.84	0	tr.	0	51.07	46.4	0.10
philoxeroides	12 04.74	0	1.44	0	0.02	0	39.78	58 26*	0 08
Sabine WL area.	01.30.75	0.02	49.4	0.02	0.02	0	38 4	12 0	0
La.	02.18.75	0	48.5	tr.	0	0	41.4	10 0	0
09.02.74	04.17.75	tr.	43.0	tr.	tr	0	30 0	27.0	0

* N_2 + He from atmosphere in culture flask.

Table 5. Composition of gases from cultured plant sample (*Phragmites communis*) from Port Penn, Delaware, on Delaware Bay; mass spectrometer analysis

Compound	Mol %*	Wt. %*
Hydrogen	0.02	
Methane	12.89	5.65
Ethylene	0.03	0.02
Ethane	0.03	0.03
Propane	0.09	0.11
Isobutane	0.09	0.14
n-Butane	0.07	0.11
Pentane	0.05	0.10
Isopentane	0.21	0.41
C_6H_{12}	0.07	0.16
C_6H_{14}	0.18	0.43
C_7H_{14}	0.04	0.10
C_7H_{16}	0.16	0.44
Benzene	0.01	0.02
Toluene	0.03	0.06
Argon	3.57	3.90
Oxygen	33.19	29.04
Carbon dioxide	49.26	59.26
* On nitrogen-free basis	99.99	99.98

VARIATIONS IN CARBOHYDRATE CONTENTS OF METHANE-PRODUCING PLANTS

Because of the importance of carbohydrates as source material for bacteriogenic methane, the total carbohydrate contents, free sugars, and polymeric sugars were analyzed in several plant species used in the culture experiments. Both fresh plant samples and those that had cultured with bacterial muds for varying lengths of time were analyzed. The total carbohydrate contents of the plants analyzed varied from 43 to 86% on a dry weight basis, and after culturing for 6 months the loss of carbohydrates ranged from as low as 21% (in *Distichlis spicata*) to as high as 83% (in *Typha latifolia*). The free sugar contents ranged from negligible to 4.9 mg/g in fresh plants and from 0.2 to 3.1 mg/g in samples cultured for 6 months. Glucose, galactose, mannose, arabinose, and xylose were variably represented among the free sugars, whereas ribose and rhamnose were not found in any of the samples. The abundance of mannose in several of the brackish water specimens was noted previously (SWAIN, 1971) and may have originated in yeasts and molds attached to the plants. Total carbohydrates were analyzed by a phenol–sulfuric acid method (DUBOIS *et al.*, 1956); free sugars were extracted with water and separated chromatographically.

The polymeric sugars in the plant samples were extracted with dilute sulfuric acid under reflux conditions and were separated chromatographically (Table 6). Xylose is the predominant sugar and galactose and arabinose are also major components. Glucose is an important although subordinate sugar in the polymeric components of these plants. A reconstruction of the possible polysaccharide suites in two fresh and decayed marsh plant species, based on data from Table 6 is shown in Table 7. Xylans predominate over other polysaccharides in both species. The carbohydrate analyses show that cellulose is subordinate to other sugars as plant components and probably also as sources of methane in these samples.

CARBON AND HYDROGEN ISOTOPE ANALYSES

The average of $\delta^{13}C$ (PDB) analyses of the methane of 33 marsh gas samples was −52.7 ‰ as compared with an average of −45.7 ‰ for 13 cultures of plant specimens that were obtained from the same

Table 6. Carbohydrate analyses of fresh and cultured plant samples from marshes for marsh gases. Polymeric sugars, in percent of total acid extractable sugars

	Total sugars extracted (mg/g)	Locality	gal	glu	man	ara	xyl	rib	rha
1. Fresh samples									
Phragmites communis	35.4	Delaware Bay	8.0	11.3	8.0	26.1	44.8	0.8	1.0
Distichlis spicata	44.3	Delaware Bay	9.8	9.4	6.8	30.6	43.5	0	0
Typha latifolia	39.3	Minnesota, Fish Lake	23.6	8.5	3.7	27.9	36.3	0	0
Alternanthera philoxeroides	22.6	Louisiana, Sabine Wildlife area	18.2	15.9	0	29.5	34.1	0	2.3
Spartina patens	7.5	Louisiana, Sabine Wildlife area	22.2	15.0	4.3	22.2	31.6	2.2	2.5
Acidna cuspidata (= *Amaranthus australis*)	4.9	Louisiana, Calcasieu River	17.1	12.2	12.1	14.3	26.7	10.2	7.3
Eichornia crassipes	8.4	Louisiana, Guillaume Lake	16.8	14.6	6.1	31.7	23.2	3.0	4.6
2. Cultured samples									
Phragmites communis	36.4	Delaware Bay	22.5	16.1	7.9	14.4	39.1	0	0
Distichlis spicata	21.0	Delaware Bay	34.3	12.7	0	16.8	36.1	0	0
Typha latifolia	9.8	Minnesota, Fish Lake	9.3	18.4	8.1	25.7	38.0	0	0

Table 7. Comparison of polymeric sugars in fresh and decayed marsh plant specimens, calculated from monosaccharide analyses

Species	Calculated polymers in fresh plant		Calculated polymers in decayed plant	
Phragmites communis	1. Xylans (hemicellulose) (xyl (β 1–4) 45%) (ara (β 1–3) 26%)	71%	1. Xylans (xyl 39%) (ara 14%)	53%
	2. Cellulose (and Starch?) (glu (β 1–4) (β 1–4?))	11%	2. Cellulose? (glu)	11%
	3. Mannans (man (β 1–4))	10%	3. Mannans? (mn)	8%
	4. Pectic substances? (gal (β 1–4)) (may also include 1–3 and 1–5 ara)	8%	4. Pectic substances (gal)	23%
			5. Undet. glucans	5%
Distichlis spicata	1. Xylans	75%	1 Xylans (xyl 36%) (ara 17%)	53%
	2. Cellulose	9%	2. Cellulose?	9%
	3. Mannans	7%	3. Mannans	trace
	4. Pectic substances	10%	4. Pectic substances	13%
			5. Undet. glucans and galactans	24%

localities tested for marsh gas. δD (SMOW) analyses of methane from eight marsh gas samples showed an average of −239.9 ‰ as compared with an average of −334.1 ‰ for seven plant cultures from the same localities. Only two δD water analyses were obtained during this study: a fresh-water lake in Louisiana (−74 ‰) and a brackish water marsh, also in Louisiana (+25 ‰).

The observed values of δ^{13}C and δD are consistent with a bacterial origin of the methane (SCHOELL, 1980), although the cultured samples are exceptionally light in D. The relatively lighter values for ^{13}C of methane from marsh gases as compared to those from the plant cultures suggest that organisms other than macrophytes or a variety of intermediate metabolic products contributed importantly to methane generation in these samples. The explanation for the lighter D values in the methane from plant cultures than in the corresponding marsh gases is uncertain, but may be related to the fresher water of the culture sample environments than that of the marsh environments. The δD values of sea water are a little less negative than those for rainwater and ground water (SCHIEGEL and VOGEL, 1970) but the differences are small and may not be a factor in the variations observed here.

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