

## The inorganic chemistry of peat from the Maunachira channel-swamp system, Okavango Delta, Botswana

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**Abstract**—The Okavango Delta is a large (18000 km<sup>2</sup>), low gradient (1:3600), alluvial fan situated in the semi-arid Kalahari basin of northern Botswana. Seasonal floodwaters from tropical Angola disperse on the fan creating both perennial (6000 km<sup>2</sup>) and seasonal (7000 to 12000 km<sup>2</sup>) swamps. Ninety-five percent of this water is lost annually by evapotranspiration. Organic rich sediment (peat) is a major sediment of the perennial swamps. Peat formation commences during senescence of the plants, when certain nutrients are recycled while others are lost by rainwater leaching. Further changes in chemistry occur during subaqueous decay of the plants which involve both gains and losses of constituents. Decaying plants trap detrital mineral matter which becomes an integral part of the peat. The main sources and forms of inorganic matter in the peat are: allochthonous kaolinite (40%) and quartz (20%) and both allochthonous and autochthonous phytolithic silica (30%). Several inorganic components (Fe, K, P, Na, Ca and Mg) which make up the remaining 10% are associated with the organic fraction. Ion exchange plays only a minor part in their uptake and it seems that these metals are taken up during bacterial activity in the peat. The weight proportion of inorganic matter (ash) decreases downstream, mainly due to a decrease in allochthonous mineral matter. Volume percentage also decreases but is low throughout, generally less than five percent. This study has revealed that the low-quantity allochthonous mineral matter is the main reason for the long-term survival of this ecosystem. Uptake of soluble ions by the peat is important in off-setting evaporative concentration of metals.

### INTRODUCTION

THE 18000 km<sup>2</sup> Okavango Delta of northern Botswana (Fig. 1) represents the terminal depository of a large drainage system located in tropical, central Angola. The delta is situated within the semi-arid Kalahari desert, but discharge at the apex is sufficiently large and gradients within the delta sufficiently low to cause extensive inundation and hence permanent swamp formation, creating a unique ecosystem. Fine-grained organic-rich detritus is a principal sediment type accumulating in the delta (MCCARTHY *et al.*, 1988b). This is mainly the byproduct of biomass production, but many processes appear to contribute to its formation. A detailed chemical and mineralogical study was undertaken in order to characterize the inorganic chemistry of these sediments and to examine the mechanisms whereby they incorporate inorganic material. This knowledge is essential to understanding the ultimate causes for the continued survival of the wetland in this essentially endorheic basin, the controls on the chemistry of the sediments, and the function of the organic-rich material in this dynamic ecosystem. The results may have bearing on the chemistry of coal.

CASAGRANDE and ERCHULL (1976, 1977) have discussed the complex interrelationships which are responsible for the inorganic chemistry of peats in the Okefenokee swamps. In the case of the Okavango sediments, these variables are equally complex. The contribution of plant material to the chemistry of these sediments will depend on the species contribution as well as the contribution of different plant organs to each species. The composition of the water is also likely to play a role, indirectly via its effect on plant chemistry and directly by ion exchange interaction with the sediment. Detrital material of mineral and plant origin will also contribute to the chemistry of the sediment. The relative contribution of each of these processes will vary from place to place in the swamps, depending on local conditions.

Because of this diversity of process, a variety of techniques were applied in this study including chemical and mineralogical analysis of the sediment and of plants collected over a large area, decomposition experiments and ion exchange studies.

### THE OKAVANGO DELTA

The delta is situated within active grabens defined by north westerly and north easterly striking fault sets (HUTCHINS *et al.*, 1976). Although referred to as a delta because of the classic "birds foot" arrangement of its distributaries, the system is more akin to an alluvial fan, having a gently sloping, conical surface with gradients of the order of 1:3600 (UNDP, 1977; WILSON and DINCER, 1976).

In the upper "panhandle" region of the delta (Fig. 1), the Okavango River is confined in a relatively narrow graben, but at its southern end the river divides into several distributaries which define the actual delta. These channels are typically less than 25 meters wide and are insufficient to accommodate the discharge of the Okavango River. Consequently, extensive areas flanking the channel systems are inundated with water producing swamps, permanently in the upper reaches (6000 km<sup>2</sup>) and seasonally in the lower reaches (7000 to 12000 km<sup>2</sup>). The average depth of the water in the permanently flooded region is about 1.5 m (UNDP, 1977). Seasonal water level fluctuations in the panhandle are of the order of 2 m, but reduce to about 0.2 m in the perennial swamps and rise to about 1.5 m in the lower, seasonal parts of the delta (UNDP, 1977). The perennially flooded swamp areas support a productive plant community consisting dominantly of *Cyperus papyrus* L. in the upper reaches and *Miscanthus junceum* (Stapf.) Stapf. in the lower reaches. *Thelypteris interrupta* (Willd.) K. Iwats. is locally important (SMITH, 1976). In the permanent swamps, the vegetation grows on a low-density, organic-rich sediment substrate, which extends up to and actually forms the margins of the channels, where it is stabilized by vegetation (MCCARTHY *et al.*, 1988a). Water levels usually slope away from the channels through the flanking vegetation (WILSON and DINCER, 1976; MCCARTHY *et al.*, 1988a) resulting in continual loss of water from the channels as surface flow through the vegetation and probably also as subsurface flow through the permeable sediment. The perennial swamps are dotted with islands ranging in size from individual anthills a few square meters in area to large island chains several kilometers long. These support a variety of large trees (SMITH, 1976). Also present

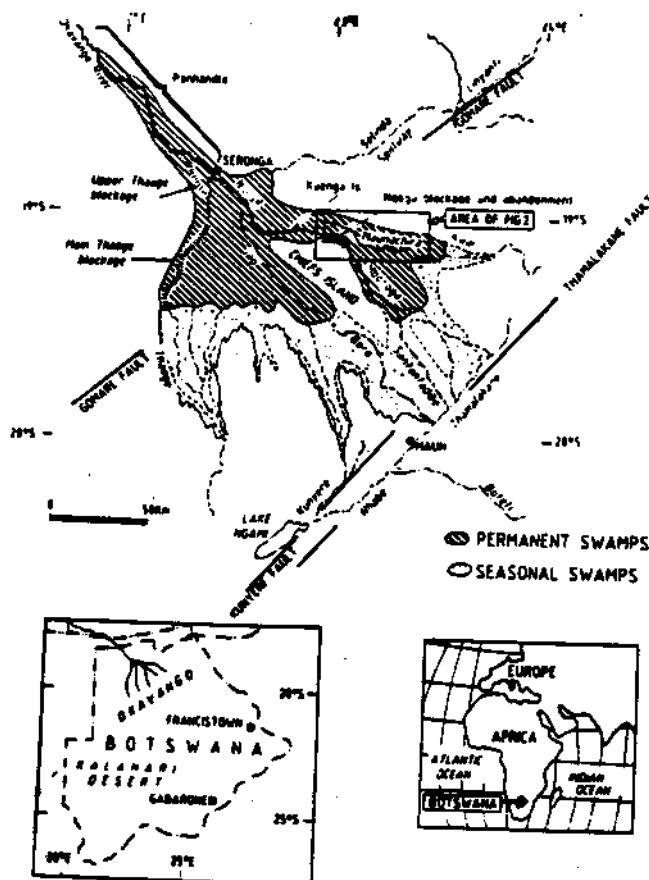


FIG. 1. Locality map.

are open water bodies, some in excess of a square kilometer in area, referred to as *madiba* (singular, *lediba*).

Aggradation within the channel systems results in blockage by plant debris and abandonment, causing changes in the distribution of water (WILSON, 1973; SHAW, 1984; MCCARTHY *et al.*, 1986a). Fire is an important process in the perennial swamps, as in other swamp areas (e.g. Okefenokee; CYPERT, 1961; COHEN, 1974). Surface fires burn off accumulated dead plant material approximately every third year and destroy all subaerially exposed plant material but do not affect the submerged organs. However, following abandonment of a channel, the flanking organic-rich sediment may desiccate and burn, leaving dry land (MCCARTHY *et al.*, 1986a, 1987; ELLERY *et al.*, 1989).

The perennial swamps can be viewed as a layer of water-saturated, organic-rich sediment resting on a sand substratum and supporting a blanket of vegetation on its upper surface. Channels, islands and *madiba* make up a very small proportion of the total area of the system. Channels are, however, important in that they act as conduits for the dispersal of the seasonal flood waters, for the supply of water to compensate for evapotranspiration losses from the swamps, for the supply of nutrients to sustain plant growth, and for the dispersal of sediment brought into the delta by the Okavango River.

### THE STUDY AREA

The area chosen for this study lies in the remote northeastern portion of the delta along the Maunachira channel (Figs. 1 and 2). The age of the Maunachira channel system is not known, but this area probably experienced inundation in the mid-nineteenth century (MCCARTHY *et al.*, 1988b). Initially, the Maunachira channel had no direct connection to the Okavango-Nqoga channel system but was supplied by water seepage through the swamp. The lower reaches of the Nqoga channel began to block in the 1920s, and these blockages proceeded progressively further upstream (WILSON, 1973). A cross-link between the still-active section of the Nqoga and Maunachira

channel (Cross-cut channel, Fig. 2) began to develop and was established by the 1950s. It was only with the development of a link that the Maunachira channel system became directly connected to the Okavango River. A further link was established in 1972 when a channel was cut linking the head of the Maunachira with the Nqoga channel.

The samples used in this study were collected along the Maunachira channel, the Cross-cut channel, the still-active lower Nqoga channel and in excavations along the abandoned Nqoga channel (Fig. 2).

## MATERIALS AND METHODS

### Samples

A variety of materials was sampled in the perennial swamps, including living and senescent plants and organic rich sediments (Fig. 2). For logistical reasons, sediment samples were collected near channels and hence the results of this study apply particularly to the important near-channel environment. At one locality core samples were taken at varying distances from the Maunachira channel to examine lateral compositional changes (Fig. 2). The peat samples collected in swamp areas were obtained using an 8 cm diameter peat corer (WRIGHT *et al.*, 1984). For convenience, the organic rich sediment will be referred to as peat, irrespective of its inorganic content. The terms "plant ash" and "peat ash" as used here refer to the residue left after complete oxidation (by burning at 700°C) of carbonaceous material of plants and peat, respectively. The latter includes mineral matter as well as metals associated with the organic fraction of the peat.

### Analytical methods

Samples were dried to constant mass at 110°C and then pulverized in a swing mill. Weighed aliquots were ashed at 700°C and percent ash determined gravimetrically. The ash samples were analysed by X-ray fluorescence spectrometry using the method of NORRISH & HUTTON (1969). Analytical precision is as stated by MCCARTHY (1976). Carbon, hydrogen and nitrogen were determined using an analyser by the National Chemical Research Laboratory of the Council for Scientific and Industrial Research. Quoted values are accurate to better than 0.3 percent.

### Mineralogical studies of peat

The mineralogy of the samples was investigated using standard powder X-ray diffraction techniques after removal of the organic fraction using hydrogen peroxide treatment. This was augmented by conventional light microscopy.

### Determination of quartz content of peat

A sample of pure quartz sand from the Okavango Delta was crushed in an agate pestle and mortar and then dispersed in acetone. After two minutes, the supernatant liquid, which included suspended quartz, was decanted and evaporated to recover the quartz.

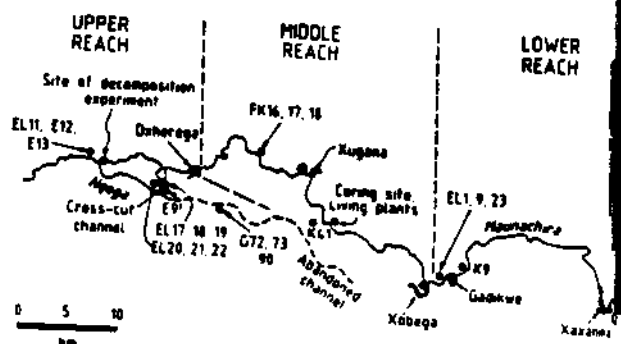


FIG. 2. Sample locations within the study area.

grainsize distribution of this material was similar to that of quartz in the peat, as judged by microscopic examination. Aliquots of an individual pulverized peat sample were spiked with known quantities of the fine quartz. The intensities of the 1011 reflections ( $\text{Cu K}_\alpha$  radiation) were measured. The quartz content in the original peat sample was determined by the method of addition from these data, which then served as a calibration for the remaining samples. Three separate mounts were made for each sample and results averaged. Replicate determination of one sample indicated a precision of 14 percent for the method.

#### Measurement of ion exchange properties

A large quantity of peat was homogenized to a slurry in a food blender, and excess water was removed by vacuum filtration. Fifty gram aliquots of the resulting material were placed in plastic bottles and, to separate samples, 5 ml of potassium chloride solution, or 5 ml of calcium chloride solution, or 5 ml of distilled water or 5 ml hydrochloric acid (3 molar) was added. Several different concentrations of KCl and  $\text{CaCl}_2$  were used (see Fig. 3 for final concentrations in the samples). The slurries were agitated for three days at room temperature ( $20^\circ\text{C}$ ), whereafter the aqueous phase was removed by vacuum filtration and analysed by atomic absorption spectrophotometry. The quantity of peat in each of the test samples was determined gravimetrically after drying to constant mass at  $110^\circ\text{C}$ . The concentration of absorbed metal in the peat was calculated from mass balance considerations.

#### Decomposition studies

A quantity of living and senescent *C. papyrus* stalks was harvested, cut into short lengths and respectively mixed to form composite samples. A number of plastic mesh bags (2 mm apertures) were filled with either living or senescent stalk material (about 0.15 kg dry weight in each bag). The bags were submerged in a papyrus sudd in a channel at a water depth of about 50 cm and the sudd was closed over the bags so that they were in darkness. Bags were withdrawn after two months and four and one-half months, dried, weighed and the contents crushed for analysis.

## RESULTS

#### Composition of plant material

To establish the possible contribution of plant material to peat chemistry, living plants representing the major species

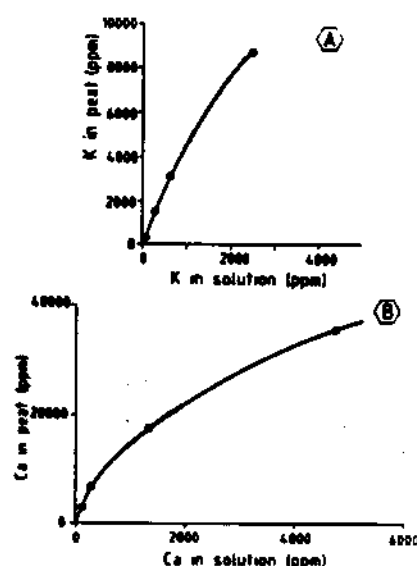


FIG. 3. Plots of concentration of dissolved metals against metal content of equilibrium peat: (a) potassium; (b) calcium.

TABLE 1  
Analysis of plant material

	PL2	PL3	PL1	PL8	PL4	PL5	PL4
H	-	1.06	0.63	0.75	0.93	0.78	1.32
C	-	40.44	41.86	39.77	41.73	42.38	40.56
H	-	5.50	5.32	4.78	5.18	5.20	5.15
Ash	12.28	9.24	7.67	1.95	5.12	5.94	12.60
O*	-	43.80	44.69	52.70	47.06	45.74	40.17
Ash composition							
$\text{SiO}_2$	81.48	83.84	74.20	63.10	75.18	43.04	66.51
$\text{TiO}_2$	0.25	0.01	0.01	0.18	0.02	0.31	0.05
$\text{Al}_2\text{O}_3$	3.02	0.14	0.32	1.89	0.62	2.89	0.20
$\text{Fe}_2\text{O}_3$	3.69	0.12	0.09	1.31	0.19	2.30	0.18
MnO	0.60	0.26	0.35	1.23	0.38	2.86	0.23
HgO	1.54	1.75	2.23	2.71	1.55	7.07	4.83
CaO	3.01	3.21	3.96	4.72	4.01	11.96	13.50
$\text{Na}_2\text{O}$	0.44	0.42	7.59	3.45	3.22	0.50	0.25
$\text{K}_2\text{O}$	3.56	6.64	6.67	17.11	10.41	23.41	10.50
$\text{P}_2\text{O}_5$	0.25	0.94	0.60	1.66	0.76	1.44	0.97
TOTAL	97.84	97.33	98.01	97.38	96.33	95.79	97.22
O/C	-	1.08	1.07	1.33	1.13	1.08	0.99
C/N	-	7.35	7.83	8.32	8.06	8.15	7.88
C/H	-	38.15	66.13	53.09	44.87	54.33	26.68
C/SiO <sub>2</sub>	-	5.22	7.32	32.32	10.84	16.58	4.84

PL2: *M. juncea* roots and rhizomes;

PL1: *C. papyrus* stems;

PL4: *C. papyrus* umbel;

PL4: *T. interrupta* leaves

PL3: *M. juncea* leaves;

PL8: *C. papyrus* roots & rhizomes;

PL5: *T. interrupta* roots

\* oxygen by difference

in the permanent swamps were collected and analysed. Results are presented in Table 1. The ash content is uniformly low. The organic fraction consists predominantly of carbon and oxygen with the oxygen to carbon weight ratio varying between 0.99 and 1.33, close to the value for carbohydrate (1.33). The carbon/hydrogen ratio varies between 7.3 and 8.3 and is somewhat greater than the carbohydrate ratio of approximately 6. The carbon/nitrogen ratio is very variable, and different parts of the same plant have quite different C/N ratios.

The chemical composition of the ash is variable both between species and between different parts of the same plant. The dominant constituent of the ash of all species examined is  $\text{SiO}_2$ , which occurs in the plants as phytoliths (ANDREJKO and COHEN, 1984a). The abundance of silica in leaves and stems tends to be slightly higher than in roots and rhizomes. Alumina and iron tend to be higher in roots and rhizomes than stems which may reflect contamination, although GAUDET (1977), who also noted iron enrichment in papyrus rhizomes, considered this to be metabolic. The alumina content in all parts of the plants is nevertheless low, indicating active exclusion of this component by the plants. Magnesium, calcium and potassium are important constituents of all species, and the potassium content may reach fairly high abundances in papyrus and *T. interrupta*. Sodium is concentrated in papyrus, but its abundance in other species is low.

The compositions of ash from the same parts of a given plant species from different localities may vary widely: for example, in Table 1 the ash of a sample of papyrus stems contained 6.67 wt%  $\text{K}_2\text{O}$  (sample PL1), while another sample

TABLE 2  
Analysis of fresh and decomposing papyrus

	EL2	EL14	EL22	EL6	EL15	EL23
N	0.68	0.70	0.83	0.35	0.41	0.30
C	42.92	44.08	42.67	41.03	43.01	43.42
H	5.78	5.81	5.40	5.38	5.70	5.40
Ash	5.84	5.46	8.80	8.38	7.15	6.06
O <sup>a</sup>	44.74	43.95	42.10	44.06	42.85	44.52
Ash composition						
SiO <sub>2</sub>	64.92	66.75	70.20	75.93	85.07	80.42
TiO <sub>2</sub>	0.0	0.11	0.32	0.02	0.06	0.21
Al <sub>2</sub> O <sub>3</sub>	0.35	1.84	5.82	0.50	1.40	3.96
Fe <sub>2</sub> O <sub>3</sub>	0.74	1.58	6.31	0.46	1.53	5.18
MnO	0.39	0.34	0.57	0.51	0.54	0.34
MgO	1.40	2.67	0.54	0.52	0.76	0.61
CaO	5.28	14.00	4.91	4.97	0.50	6.81
Na <sub>2</sub> O	7.94	3.39	0.45	8.93	0.42	0.35
K <sub>2</sub> O	16.19	5.96	1.54	7.13	1.19	1.01
P <sub>2</sub> O <sub>5</sub>	1.93	2.03	0.91	0.20	0.32	0.42
TOTAL	99.14	98.68	99.70	99.74	99.79	99.31
% of initial						
mass	100%	88%	62%	100%	94%	76%
O/C	2.04	1.00	0.99	1.05	0.98	1.03
C/H	7.43	7.59	7.82	7.78	7.58	7.92
C/N	63.12	62.97	51.41	119.5	106.9	86.84
C/SiO <sub>2</sub>	11.24	12.09	6.20	6.57	7.20	8.88

<sup>a</sup> Oxygen by difference

collected at a different locality contained 16.19 percent (Table 2, EL2). This phenomenon has previously been recorded by GAUDET (1975), who reported that the between-site variation is greater than that between different parts of the same papyrus plant from a single locality. The causes of this variability were not investigated in this study.

#### Chemical changes in plant material during decomposition

Dead plant material will experience rapid decay on submersion, and numerous studies have been carried out to investigate this phenomenon, particularly as it concerns nutrient recycling (e.g., HOWARD-WILLIAMS and HOWARD-WILLIAMS, 1978). In the case of papyrus, which is the dominant species in the study area, it has been shown that chemical changes occur initially during senescence and further changes occur during subaqueous decomposition (GAUDET, 1977). To investigate these changes under field conditions in the Okavango Swamps, decomposition experiments were carried out on both living and senescent papyrus stalks. Analytical data are listed in Table 2.

Papyrus has evolved a nutrient conservation strategy whereby essential nutrients (especially N and P) are translocated from senescing culms to be reutilized in new growing culms (GAUDET, 1977). The effects of this can be seen by comparing analyses EL2 and EL6 (Table 2). The C/N ratio of the senescent stalks is approximately twice that in living material. In contrast, the O/C and C/H ratios do not differ markedly. In the ash, there is a large difference in the P<sub>2</sub>O<sub>5</sub> content. GAUDET (1977) also reported major loss of certain

metals, notably Na and K, due to rainwater leaching from senescent papyrus stalks. Such losses, particularly in the case of K<sub>2</sub>O, are also evident on comparing senescent and living stalk compositions (EL6 and EL2), respectively.

Decomposition of previously living and senescent stalks is associated with further chemical changes (GAUDET, 1977, and Table 2). The C/N ratio of both falls, probably reflecting bacterial activity in the decomposing material. The O/C and C/H ratios do not, however, exhibit systematic changes nor is there any systematic change in ash content in spite of major mass loss (Table 2). It seems that C, H and O and inorganic ash components are lost in more or less the same relative abundances during decomposition. The products of this decay most probably include both soluble and insoluble organic and inorganic compounds. In contrast, there is a net gain in N in the decaying material, which is greater in the case of the senescent stalks.

Certain important changes occur in the ash chemistry during decomposition. Alkalis are strongly leached, sodium to very low levels, while potassium seems to stabilize around 1 to 2 weight percent. In the case of previously living material, P<sub>2</sub>O<sub>5</sub> is initially gained, then leached, while in contrast, P<sub>2</sub>O<sub>5</sub> is actually absorbed by the senescent material during decomposition. Other changes of note are an apparent absorption of calcium and magnesium during initial decomposition as well as an increase in alumina, the latter probably reflecting entrapment of detrital particulates by the stalks during the experiment. Iron abundance also increases, and a good positive correlation exists between iron and alumina contents of the ash (Fig. 4). Living plant material exhibits the same relationship (Fig. 4). As will be discussed later, this relationship does not hold for the peats (Fig. 4), which are enriched in alumina relative to iron. This suggests that the mechanisms of concentration of alumina and iron during decomposition are different, alumina being physically trapped as clay particles, while iron is fixed by some chemical means, although some physical entrapment of colloidal iron hydroxides may

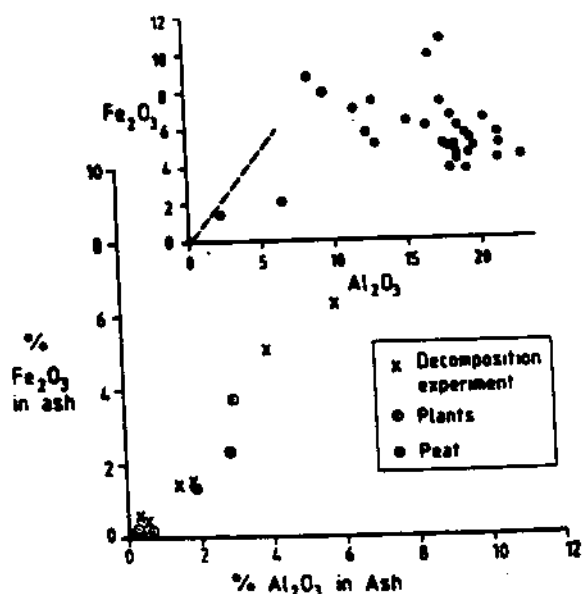


FIG. 4. The relationship between total iron (as Fe<sub>2</sub>O<sub>3</sub>) and Al<sub>2</sub>O<sub>3</sub> in peat and plant ash.

TABLE 4

Analyses of core samples from Maunachira

	CORE 1			CORE 2			CORE 3		
	1C(30)*	17(60)	1K(110)	2C(30)	2P(60)	2J(100)	3C(30)	3E(50)	3G(70)
Ash	33.23	18.14	54.83	14.03	16.39	24.03	12.68	21.39	14.56
Ash composition									
SiO <sub>2</sub>	73.83	72.43	72.13	68.10	61.79	64.86	67.42	75.20	67.40
TiO <sub>2</sub>	0.78	0.61	1.00	0.71	0.89	1.01	0.54	0.53	0.97
Al <sub>2</sub> O <sub>3</sub>	18.64	12.48	18.50	15.04	20.12	21.09	12.87	12.97	21.55
Fe <sub>2</sub> O <sub>3</sub>	9.94	5.83	5.90	6.27	6.33	5.71	7.44	4.95	5.07
MnO	0.12	0.14	0.06	0.16	0.13	0.10	0.10	0.14	0.06
MgO	0.69	1.00	0.69	1.17	1.10	1.09	1.16	0.87	0.95
CaO	2.20	5.86	1.53	6.74	5.62	4.74	7.06	3.96	3.45
Na <sub>2</sub> O	0.18	0.26	0.20	0.16	0.17	0.17	0.17	0.30	0.13
K <sub>2</sub> O	1.30	1.06	1.32	1.01	1.30	1.25	0.84	1.07	1.13
P <sub>2</sub> O <sub>5</sub>	0.33	0.48	0.14	0.63	0.46	0.33	0.80	0.39	0.35
TOTAL	101.02	100.15	99.48	99.99	97.90	100.33	98.39	100.40	101.05
Quartz	4.3	2.3	11.0	1.6	3.0	5.0	1.9	ND	3.4

\* Numbers in parentheses are depths in centimetres below surface

possible to apportion total SiO<sub>2</sub> determined by analysis (Tables 3 and 4) into plant silica, quartz and kaolinite. This was done by estimating the quartz content using X-ray diffraction and determining the contribution to total SiO<sub>2</sub> by kaolinite from the Al<sub>2</sub>O<sub>3</sub> content. The remaining SiO<sub>2</sub> was assumed to be of plant origin. Results are listed in Table 5. Petrographic examination of iron-rich samples also showed small concretions of iron oxide apparently bonded by organic material. These failed to produce an X-ray diffraction pattern, but after heating at 1000°C for several hours the main peaks of hematite were recorded, suggesting that the peats also contain amorphous iron oxides (BROWN, 1980).

The ash content of the peats (Table 3) is extremely variable, ranging between 6.3 and 73.8 weight percent. Although erratic, there is a general decrease in ash content downstream through the study area. To illustrate this, the area has been divided into upper, middle and lower reaches (Fig. 2), the boundaries being taken as the Dxheraga and Xobega madiba,

which serve as local base levels along the Nqoga-Maunachira channel system. The average ash content in the upper reach is 61.7 wt%, 30.8% in the middle reach and 14.3% in the lower reach.

Mineralogical breakdown of ash, based on the data in Table 5, indicates that in excess of 90 wt% of the average ash can be accounted for by just three constituents, namely quartz (15.8 ± 5.8%), kaolinite (45.1 ± 7.2%) and phyllosilic silica (32.2 ± 9.7%). It is notable that plant silica exceeds quartz. The relative proportions of phyllosilic silica, quartz and kaolinitic silica show no apparent systematic spatial variation through the study area (Fig. 6), although the data plotted in Fig. 6 indicate that the proportion of quartz to kaolinite

TABLE 5  
Contribution of detrital minerals and plants to the total SiO<sub>2</sub> of peat soil (expressed as weight percent of total ash)

Sample	Quartz	Kaolin	Plants	Total	Other plant
				SiO <sub>2</sub>	SiO <sub>2</sub>
KL11	23	21	28	74.40	-
KL15	9	27	31	67.78	-
PK17	22	25	21	69.59	1.11
KL18	13	21	37	72.04	-
KL19	14	19	39	73.39	-
G72	18	21	32	72.60	0.11
G73	18	23	29	70.97	0.11
G90	8	13	53	75.64	0.11
29	8	20	39	68.71	0.11
PK16	29	22	19	71.34	1.11
KL17	12	20	40	73.41	-
PK18	10	20	39	70.41	1.11
1C	12	19	41	73.85	-
1F	12	14	44	72.43	-
1E	20	21	30	72.15	-
2C	11	17	38	68.10	-
2P	18	23	19	61.79	-
2J	20	24	19	64.86	-
3C	14	15	37	67.42	-
3G	23	25	18	67.40	-
Mean	15	21	32	69.33	-
S.d.	5	3	9	4.85	-



FIG. 5. Photomicrograph of the insoluble residue after oxidation of the organic fraction of a peat sample. The scale bar represents 0.2 mm. The photomicrograph was taken under half-cross polarizers, and the quartz grains therefore appear white.

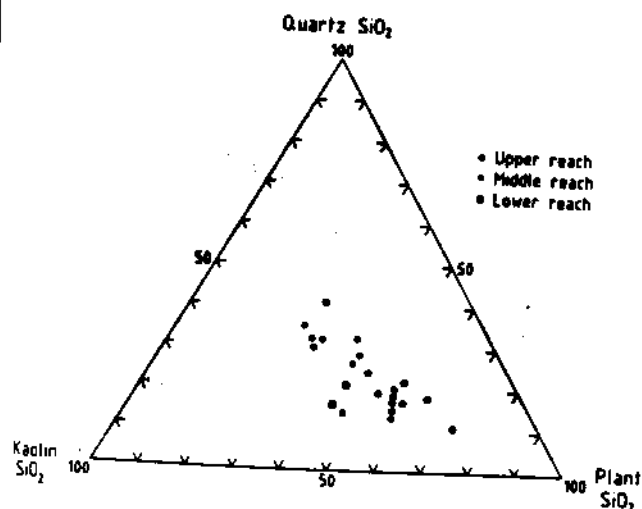


FIG. 6. Ternary diagram showing the relative proportions of kaolinitic silica, quartz and plant silica in peat.

silica is relatively constant, while the proportion of phytolithic silica tends to be more variable.

Three cores were taken at distances of 5 (core 1), 50 (core 2) and 100 meters (core 3) from the margin of the Maunachira channel (Fig. 2) using a coring tube. The cores were sampled at three depths, each sample being a 10 cm length of core. The results (Table 4) yield very few systematic variations. Similar, widely scattered results were obtained from core samples of peat in the Okefenokee Swamps by CASAGRANDE and ERCHULL (1976). Perhaps the only systematic features are a generally higher ash content in samples from the core nearest the channel and a higher  $\text{SiO}_2$  content in the ash of these samples. The similar alumina contents indicate that detrital kaolinite is distributed well beyond the immediate fringe of the channel as is detrital quartz (Table 4). It is likely that the decrease in ash content away from channels is far more rapid than that down channel, as indicated by sample K41 (Table 3) which was collected about 500 m from the channel; but the general inaccessibility of backswamp areas prevented sample collection to verify this.

Attempts to collect samples of the suspended load in the channels proved unsuccessful. As a compromise, a sample of sludge was collected from the rhizomatous zone in a papyrus stand on a channel fringe (sample E9, Table 3). It is probable that the bulk of this material was introduced during outflow from the adjacent channel and is thus representative of the suspended load in the upper reach of the study area. The composition of sample E9 is not significantly different from peat samples collected in the same general area (Table 3 and Fig. 2). This sample contained 68 wt% ash, almost half of which is plant-derived silica (Table 5). It is evident from this that a significant proportion of the suspended load is of plant derivation in mass terms and even more so in volume terms, as much consists of organic debris which has a very low density.

The O/C and C/H ratios in the organic component of the peat (Table 3) are very similar to living vegetation, but the C/N ratios of peats are much lower. The trend of decreasing C/N ratio was noted in the decomposition experiment (Table 2), but the ratios in peat samples are much lower than attained

in decomposing vegetation. As most of the samples studied in this work come from below the surface, out of the zone of photosynthesis, this nitrogen enrichment must be the result of bacterial activity.

#### *Ion exchange properties of peat*

Peats are known to exhibit ion exchange properties (CASAGRANDE and ERCHULL, 1977; SZALAY, 1964), which may play an important role in shaping their inorganic chemistry. These properties were examined experimentally for potassium and calcium, representing mono- and divalent ions, using a composite peat sample from the coring site (Fig. 2). The results are expressed as concentrations in co-existing water and peat and are plotted in Fig. 3a and b. The results for Ca suggest that the Langmuir isotherm is obeyed by the peat, as has been found for other peats (SZALAY, 1964). The peat/water distribution coefficients calculated from these curves are 5 for K and 25 for Ca, indicating moderate ion exchange activity.

Experiments were also carried out on the peat composite to investigate the proportions of K and Ca which were labile in acid solution. A sample of peat was treated with 3 M HCl. After three days, only 4% of the K and 3% of the Ca had been leached.

#### *Water chemistry*

A limited number of analyses of swamp water are available for the Okavango Delta (HUTTON and DINCER, 1976). Compositions generally lie in the range shown in Table 6, although locally higher concentrations occur in groundwater-fed evaporation areas. In general, there is an increase in salinity from the Panhandle across the Delta due to evapotranspirational water losses (HUTTON and DINCER, 1976).

#### DISCUSSION

As a first approximation, peat can be regarded as a simple mixture of plant debris (mainly root material) and detrital mineral matter, and hence insight into sources of inorganic components can be obtained by seeking correlations between the concentrations of various constituents. In such an exercise, compositions of ash must be used rather than recalculated peat compositions, as spurious correlations can arise due to the diluting effect of the organic matter (Fig. 7b). Mineralogical examination has revealed that the inorganic detrital component in peat consists of quartz, kaolinite and phytolithic silica and therefore has a simple chemistry. In contrast, analysis of plants has shown that composition of plant ash

TABLE 6

Range of composition of swamp waters (after Hutton and Dincer, 1976)				
K	1	-	4	ppm
Na	2	-	7	ppm
Ca	5	-	12	ppm
Mg	1	-	3	ppm
$\text{HCO}_3^-$	20	-	80	ppm
$\text{SiO}_2$	13	-	35	ppm
TDS	30	-	150	ppm

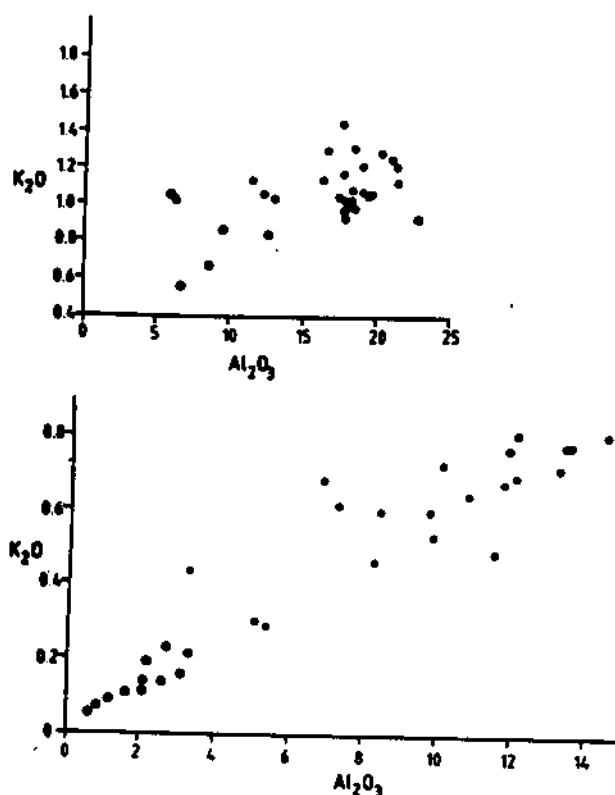


FIG. 7. a) Plot of  $K_2O$  against  $Al_2O_3$  abundance in peat ash. b) Plot of the same data as used in Fig. 7a, but expressed as weight percentage of unashed peat. The improved correlation arises from the diluting effect of organic matter, which extends the range of  $K_2O$  and  $Al_2O_3$  towards the origin of the graph.

is very variable and undergoes major changes during decomposition.

The simplest means of examining the relative contributions of the organic and inorganic end-members to the chemistry of the peat is by plotting the abundance of a component in the ash against the percentage ash. The expected relationships are shown in Fig. 8. Figure 8a illustrates the case where the content of component  $X$  in the detrital fraction is zero, while there is a finite amount of  $X$  in the plants. Plant material will have a finite amount of ash (typically around 5 weight percent). Mixtures of detrital material and plants on ashing will yield a curved mixing line as shown in Fig. 8a. Figure 8b illustrates the mixing model for a case where component  $Y$  is present in significant amounts in the detrital component but its abundance in plants is negligible. If an additional source of component  $X$  is present, compositions should plot above the mixing line, while leaching of  $X$  will result in compositions below the line (Fig. 8a). In the real world the organic end-member composition cannot be defined precisely, but such mixing models provide a useful conceptual framework in which to examine peat chemistry.

The abundance of  $P_2O_5$  in ash as a function of percentage ash is shown in Fig. 9a. The  $P_2O_5$  content increases with decreasing ash content, indicating that  $P_2O_5$  is associated with the organic component of the peat. Two reference mixing lines are included in the figure, both based on zero  $P_2O_5$  in the inorganic end-member and on the highest and lowest  $P_2O_5$  contents measured in plant material. Although broadly conforming with the model in Fig. 8a, most of the peat sam-

ples lie in the region of excess  $P_2O_5$ , indicating that an additional source of  $P_2O_5$  is likely. The plot of  $Al_2O_3$  in ash against ash content (Fig. 9b) conforms with the model outlined in Fig. 8b. The reference model in Fig. 9b is based on 25 weight percent  $Al_2O_3$  in the detrital end-member and zero  $Al_2O_3$  in the plant ash. The scatter of data points, especially at high  $Al_2O_3$  contents, probably reflects variations in the proportion of kaolinite in the mineral detritus in the peat. In Fig. 9c, the abundance of plant-derived silica in the ash is plotted against the ash content. The majority of samples lie in the field of silica enrichment, and there is no correlation with organic matter. This indicated a major additional source for plant silica. The plots of abundances of  $CaO$  and  $MgO$  in ash against ash content are shown in Figs. 9d and e, respectively. Both show characteristics of the mixing model described in Fig. 8a, but, like  $P_2O_5$  (Fig. 9a), additional sources of  $MgO$  and especially  $CaO$  in the peats seem likely.

There is a good positive correlation between  $P_2O_5$  and  $CaO$  contents of peat (Fig. 10a) which is not shared by plants. The ratio of  $CaO$  to  $P_2O_5$  of about 8 indicates that this relationship is not the result of the formation of an insoluble calcium phosphate mineral species and no such species was found. Rather, the  $CaO$ - $P_2O_5$  correlation suggests that the chemical environment in the peat leads to the fixation of both calcium and phosphorus.  $MgO$  and  $CaO$  are also positively correlated (Fig. 10b), and this relationship is different from that which exists in the plant material, also indicating chemical fixation of  $Mg$  by the peat.

Neither  $Na_2O$  nor  $K_2O$  abundances in peat conform to the mixing model (Fig. 11a, b). No alkali bearing mineral phase could be identified in the peats and it is likely that both mea-

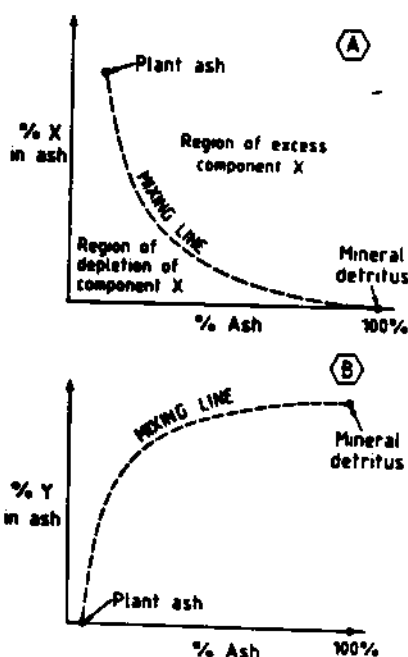


FIG. 8. Diagrammatic representation showing the expected relationship which would result from mixing of plant material with mineral detritus of allochthonous origin (kaolinite and quartz). The weight percentage of a component in the ash is plotted on the abscissa and the percentage ash in the sample is plotted on the ordinate. (A) illustrates the case where the plants are the major source of component  $X$ ; (B) illustrates the case where the detrital component is the dominant source of component  $Y$ .

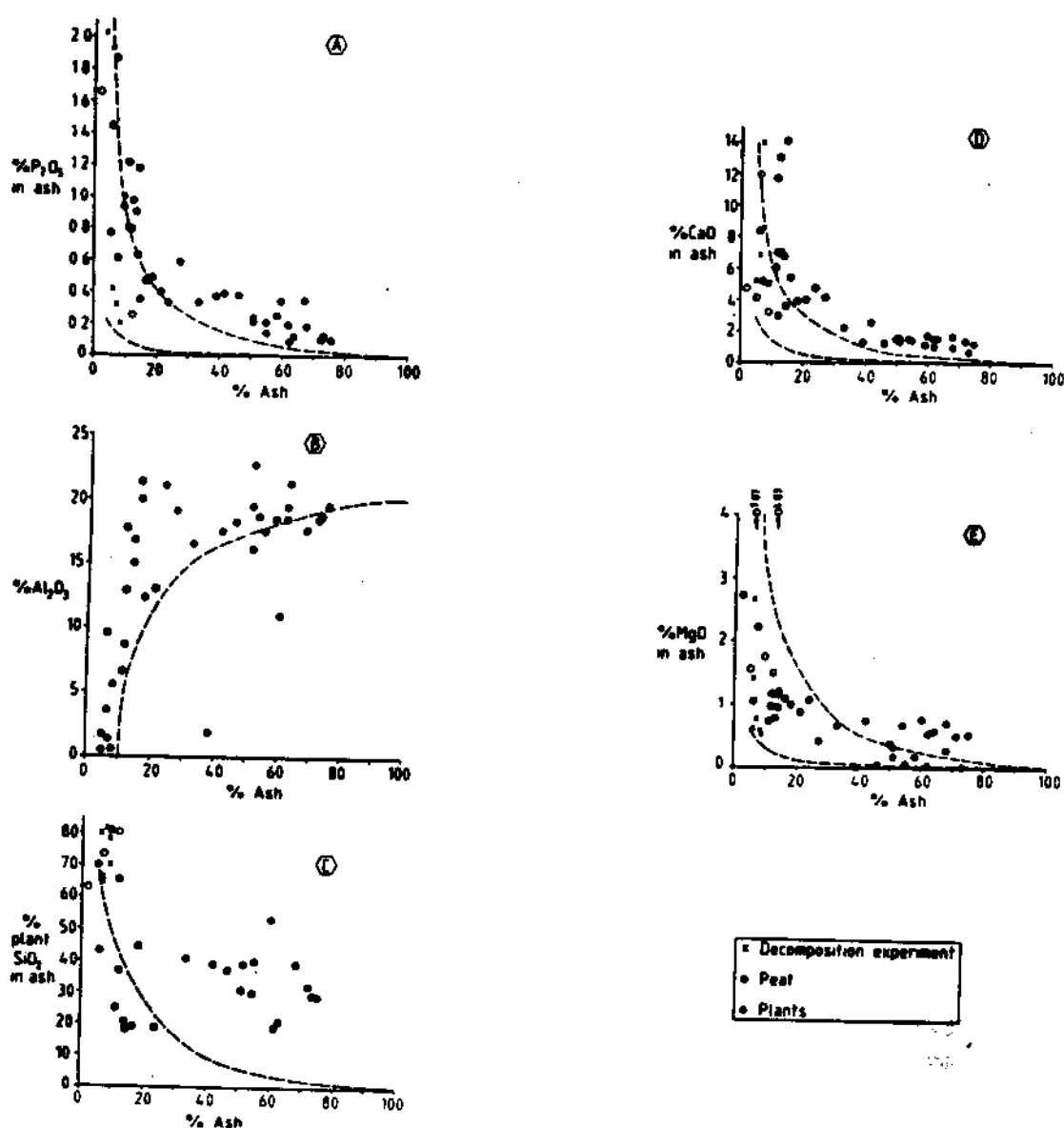


FIG. 9. Plots of the composition of ash as a function of the percentage ash for: (a)  $P_2O_5$ ; (b)  $Al_2O_3$ ; (c) plant silica; (d)  $CaO$ ; and (e)  $MgO$ . Broken lines are mixing lines. In cases where plant ash showed a wide range in composition, two mixing lines are shown representing upper and lower compositional limits.

are associated with the organic fraction of the peat. The abundances of  $Na_2O$  and  $K_2O$  are nevertheless independent of the amount of organic matter present. The decomposition experiment indicated that both are extremely labile in dead plant material and are rapidly leached. However, after prolonged decomposition, the abundances of these metals in the decaying plant material approach those of typical peat, which strongly favours  $K_2O$  over  $Na_2O$ . The potassium in peat is not, however, labile, even in acid solution.

WEAVER (1976) has noted that  $TiO_2$  is nearly always reported in analyses of kaolinite and has presented evidence that this  $TiO_2$  is present as a discrete surface-sorbed form. The abundances of  $TiO_2$  and  $Al_2O_3$  in the peats correlate well (Fig. 12), a consequence of this association. Ash samples of rhizomes of living plants as well as of decomposing papyrus stalks also lie on the same trend as the peat samples, further supporting the earlier inference that enhanced  $Al_2O_3$  contents in these materials is due to entrapment of detrital kaolinite.

The majority of the plant samples analysed have approximately equal amounts of  $Fe_2O_3$  and  $MnO$  (Table 3 and Fig. 13a). Similar results were obtained by GAUDET (1977) for papyrus. The decomposition experiments produced erratic results for  $MnO$  but showed a definite increase in  $Fe_2O_3$  content with time, in contradiction to the results of GAUDET (1977). A strong enrichment in iron is evident in the peat (Fig. 13a, c), and there is a weak, positive correlation between iron and manganese (Fig. 13a). The enrichment of iron relative to manganese may reflect differences in solubility under prevailing conditions (e.g. HEM, 1972) but is probably strongly influenced by the fact that the iron abundance of the water entering the swamp is about six times that of manganese (HUTTON and DINCER, 1976). The accumulation of iron in the peat is problematic. The precipitation of iron in peat bogs is apparently the result of oxidation barriers (STANTON, 1972). In the present instance, this cannot be the case. Channel margins are, if anything, reduction barriers, and both



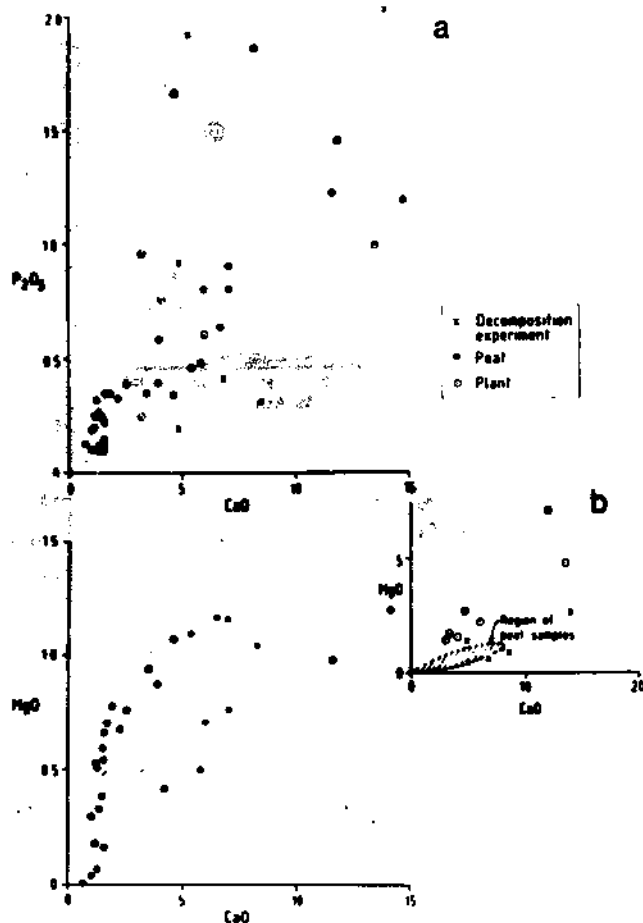


FIG. 10. a) Plot of  $P_2O_5$  content against CaO content of ash samples. b) Plot of MgO content against CaO content of ash samples.

iron and manganese are likely to be more soluble in the peats than in the more oxygenated waters of the open channelways (HEM, 1972). Accumulation of iron and manganese by inorganic processes is therefore difficult to understand.

Mixing models indicate that plants may contribute significant proportions of several metals to the peat but this end-member is complex, as different plant parts have different compositions, and, furthermore, plant compositions change radically during decomposition. It is also evident that additional nondetrital sources are indicated for most metals. One possible source for some of the metals is from ion exchange between swamp water and peat, and, in fact, ion exchange activity was found in the experiments carried out as part of this work. However, several factors indicate that the excess metal contents of peat cannot be accounted for by ion exchange. Firstly, treatment of peat with 3 M HCl desorbed an insignificant proportion of potassium and calcium. Secondly, when expressed on a detrital-free, dry peat basis (Table 7), metal contents decrease downstream, whereas total dissolved solids in the water increases (HUTTON and DINCER, 1976). Finally, the content of potassium in the peat (detrital-free, dry peat basis) in the upper region of the study area is 1.28 wt% (as K), while the water in this region contains about 1.5 ppm K (HUTTON and DINCER, 1976), yielding a weight distribution coefficient of about 8500 in favour of peat. The distribution coefficient for Ca, calculated on the same basis,

is about 3300. These values are far in excess of the values determined in the ion exchange experiments, namely 5 and 25 for K and Ca, respectively. The peat is able to accumulate substantial quantities of metals, but clearly not in a form or to a degree compatible with normal ion exchange processes.

It is suggested that the additional source of several metals in the peat arises from bacterial activity (*e.g.* BEVERIDGE and MURRAY, 1976). Several factors support this suggestion. The C/N ratio of the peats is lower than that of living macrophytes and it has been shown that this ratio falls during decay of plant material (Table 2), while the O/C and C/H ratios do not change, indicating bacterial accumulation of nitrogen. The decomposition experiments indicate that during this decay, calcium, magnesium and phosphorus are also accumulated, especially by senescent plant material (Table 2), and the ratio of CaO to MgO in the decomposing material changes towards the value characteristic of peat (Fig. 10a, inset). Bacterial uptake would also account for the fact that the peat accumulates iron and manganese (*e.g.* ROBBINS *et al.*, 1988).

However, to place this in perspective, chemical and mineralogical evidence indicates that typically about 90% of the ash consists of quartz, kaolinite and phyllosilic silica, the last mentioned contributing about one-third of the ash. Hence, about 40% of the ash is of direct plant derivation.

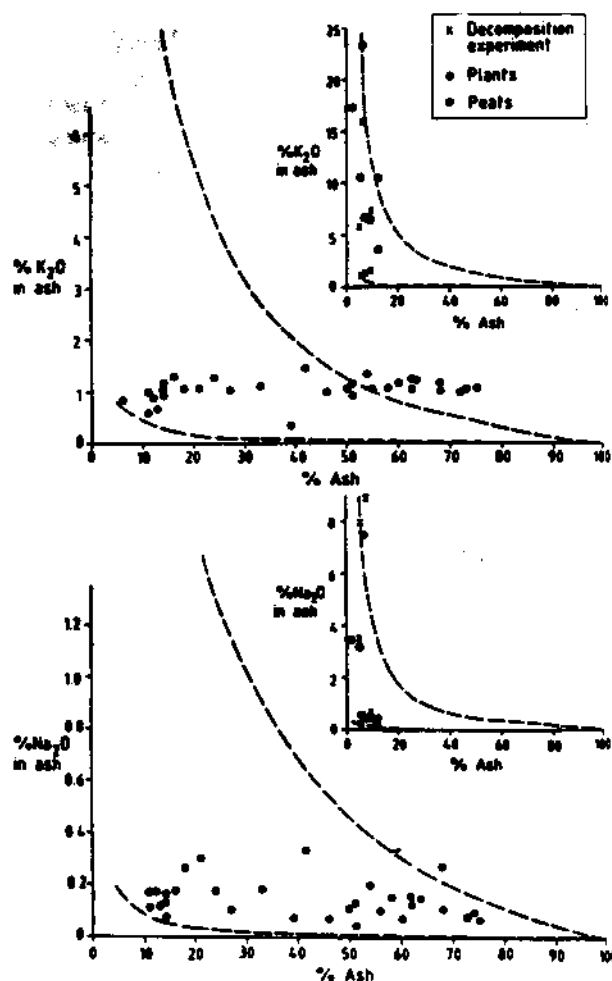


FIG. 11. Plot of (a)  $K_2O$  and (b)  $Na_2O$  in ash as a function of percentage ash. Broken lines represent mixing lines for extreme plant compositions.

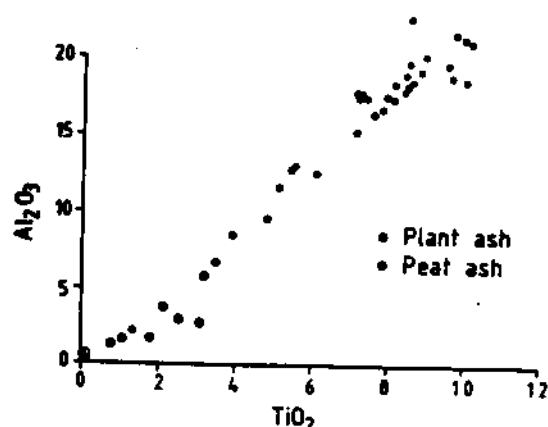


FIG. 12. Plot of  $\text{Al}_2\text{O}_3$  against  $\text{TiO}_2$  in peat and plant ash.

(phytoliths and absorbed metals); of the total peat, averaging 50% ash, some 76% by mass is of plant derivation. On a volume basis, it is estimated that about 98% of the material is of direct plant derivation.

Phytolithic silica is abundant in the peat. The mixing diagram (Fig. 9c) indicates that the quantity of phytolithic silica in the peats cannot be accounted for by the organic matter, and an additional source is indicated. Papyrus typically contains about 5% ash, some 70% of which is silica. Mean living biomass (almost entirely papyrus, with minor *T. interrupta*) in the area is  $2.2 \text{ kg m}^{-2}$ , and total turnover is  $4.4 \text{ kg m}^{-2} \text{ y}^{-1}$ . Thus, the biomass turnover will yield approximately  $150 \text{ g m}^{-2} \text{ y}^{-1}$  phytolithic silica. The concentration of dissolved silica in the swamp water is about 20 ppm (Table 6). If silica is passively taken into papyrus as a consequence of transpiration, the quantity of silica produced by the plants in one year would require the transpiration of some  $7500 \text{ l m}^{-2} \text{ y}^{-1}$ , equivalent to a transpiration rate of  $7500 \text{ mm y}^{-1}$ . However, hydrological models for the delta indicate a total evapotranspiration rate of  $1500 \text{ mm y}^{-1}$  (DINCER *et al.*, 1981). This disparity implies that silica must be actively taken up by papyrus, as has been shown for other sedges, and that silica in detrital quartz is being actively dissolved in order to meet the requirements of the plants.

Assuming an average peat thickness of 1.5 m, each square meter of surface is underlain by  $1.5 \text{ m}^3$  of peat with a dry mass of 150 kg, containing 24 kg of phytolithic silica. At the calculated production rate, this mass of silica would be generated in only 160 years. This generation time is comparable to the estimated lifetime of a channel system in this upper region of the delta (McCARTHY *et al.*, 1986a, 1988b). However, the peat also contains kaolinite in quantities comparable to the phytolithic silica content. As kaolinite is introduced as a detrital component, so too could phytolithic silica. This view is supported by the high phytolithic silica content of sludge sample E8 (Table 5). The phytolithic silica budget is thus complex, and hence abundance of plant silica would not show any simple relationship with ash content (Fig. 9c).

It is of interest to examine metal budgets in the peat excluding phytolithic silica and those metals which are detritally introduced ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ). The average peat compositions for the various reaches of the study area have been recalculated on this basis and are listed in Table 7. In a 1.5

m column of swamp  $1 \text{ m}^2$  in area in the upper Maunachira area, the amount of metal in the living macrophytes is about 100 g while that in the peat is about 2900 g, and it is thus clear that the peat is a powerful accumulator of metals.

Peat is continually accumulating in the swamps at a rate which may locally cause aggradation up to of  $5 \text{ cm y}^{-1}$  (McCARTHY *et al.*, 1986a). The tendency of the peat to accumulate metals will have the effect of offsetting metal enrichment in the water which should occur given the very high evapotranspiration loss from the delta. For example, according to the hydrological model, each square meter of swamp loses  $1.5 \text{ m}^3$  of water per year by evapotranspiration. In the middle reach of the Maunachira channel system, this quantity of water contains about 9 g Ca, 7.5 g Na, 3.5 g K and 4 g Mg (based on the data of HUTTON and DINCER, 1976) which should accumulate in the residual water. However, suppose that one kilogram of peat accumulates per square meter per year in this area. This peat will incorporate 8.6 g Ca, 0.44 g

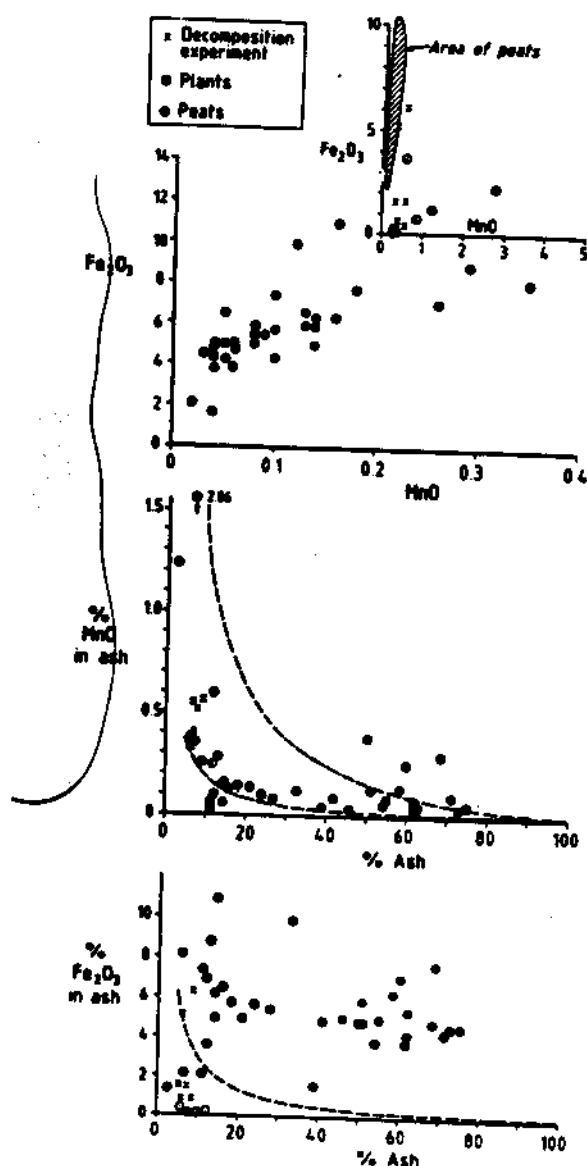


FIG. 13. Plots of (a) total iron (as  $\text{Fe}_2\text{O}_3$ ) against MnO in ash; (b) MnO in ash as a function of total ash; and (c)  $\text{Fe}_2\text{O}_3$  in ash as a function of total ash. Broken lines represent mixing lines.

TABLE 7  
Chemical compositions of peat ash and peat, recalculated  
excluding  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$

	Upper reach		Middle reach		Lower reach	
	Ash	Peat	Ash	Peat	Ash	Peat
$\text{Fe}_2\text{O}_3$	62.74	7.34	46.95	2.44	37.47	1.12
MnO	1.06	0.14	0.61	0.042	0.86	0.026
MgO	4.13	0.51	6.82	0.36	4.58	0.14
CaO	15.45	1.86	31.19	1.62	46.09	1.38
$\text{Na}_2\text{O}$	1.42	0.18	1.34	0.060	0.59	0.018
$\text{K}_2\text{O}$	12.62	1.52	9.50	0.49	4.53	0.14
$\text{P}_2\text{O}_5$	2.59	0.32	3.17	0.16	5.88	0.18
Organics	-	87.96	-	94.81	-	97.00
Total Ash	12.10		5.89		3.00	

Na, 3.0 g K and 1.6 g Mg (from Table 7) and will therefore remove most of the metals concentrated by evapotranspiration. The glaring exception is sodium, which accumulates as evaporitic salts (MCCARTHY *et al.*, 1986b). The peat therefore is important as a "de-ionizer" in this region of high evapotranspiration loss. GAUDET (1977) has recognized a similar role for papyrus swamp in the Sudd region of the White Nile.

### CONCLUSIONS

This study has revealed that the relationships between the inorganic chemistry of macrophytes and that of peat in the perennial swamps of the Okavango Delta is not a simple one. Chemical changes in the macrophytes commence at the onset of senescence as a result of nutrient recycling. Further changes occur due to leaching by rainwater. During subaqueous decay, major changes in inorganic chemistry occur, some components being lost, others gained, while major mass loss occurs. Organic and inorganic debris is released on a significant scale and becomes part of the potential suspended sediment load. While major changes in inorganic chemistry occur during decay, peat formation does not fractionate the C/H or C/O ratios. In contrast, peat formation results in a substantial decrease in the C/N ratio, probably reflecting bacterial activity. This decaying organic material combines with allochthonous detrital mineral matter in the form of quartz and kaolinite, and plant-derived silica to form peat. However, on a volume basis, the contribution of allochthonous mineral matter to the peats of the Okavango Delta is small, and we consider this to be the single most important reason for the existence of the delta in its present form. Had the proportion of allochthonous suspended load been significantly greater, rapid choking of the swamps would have occurred and the river system would have quickly prograded across the graben into the Kalahari desert.

While some 90 wt% of the peat ash can be accounted for by allochthonous detrital mineral matter and plant silica, the uptake of the remaining 10%, which includes Fe, Mg, Mn, Ca, Na, K and P, we believe is accounted for by bacterial activity. This uptake by the peat is a powerful agent for off-setting salt build-up which should occur in the swamp waters as a result of the severe evapotranspiration losses. Sodium,

however, is only weakly taken up by the peat and plants, and, accordingly, sodium salts dominate the evaporite deposits which occur in the delta.

Peat is a powerful collector of those inorganic components which are essential to living plants. In the normal evolution of the delta, channel systems ultimately become moribund and are abandoned. This leads to desiccation of the peat and its subsequent destruction by fire. Inorganic nutrients form part of the resultant ash and, through bioturbation by burrowing animals and insects, these enrich the otherwise sterile, sandy soils which characterize the delta (ELLERY *et al.*, 1988).

This study has important implications for the origin of low ash peats and coals in general. In order that a peat swamp might form at all requires an appropriate geomorphological setting in which perennial, laterally extensive, shallow flooding can occur. This setting must survive for a substantial period of time to allow sufficient time for significant peat accumulation. An essential requirement for long-term survival is a very low input of suspended inorganic detritus in the fluvial systems which drain into such a swamp. In the proximal reaches of such a swamp, ash content may be volumetrically small but large on a mass basis. Ash content will decline slowly and irregularly through the system, controlled by the distribution of channel systems. Filtration of allochthonous detritus in the proximal reaches is an important stage in the production of low ash peats. In the distal reaches, the proportion of allochthonous detritus is very low, and ash contents are accordingly also low. The composition of the ash changes significantly, and it appears that metal uptake in such regions is largely a function of bacterial activity. When bacterial activity declines to low levels, possibly in the most distal reaches of such a swamp or in the deeper peat, very low ash peats will result, which must be essential precursor to low ash coals.

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