

Molecular weights of humic acids in podzol and ferrallitic soils of the savannas of French Guyana and their evolution related to soil moisture

J. F. TURENNE

*Office de la Recherche Scientifique et Technique Outre-Mer,
Centre ORSTOM de Cayenne, Cayenne*

Different molecular weight fractions of humic acids from A_1 horizons of ferrallitic and podzol soils have been separated by means of gel filtration, after extraction with 0.1 N sodium pyrophosphate. Soil sampling was related to seasonal changes in climatic periods (drying, dry, rewetting, saturation). Results are compared to those of electrophoretic analysis. Among the fractions, some are permanent in the soil extract and others appear or disappear according to the climatic variations. A fraction with a molecular weight of 3000 seems to be one of the characteristics of dynamic phases in humus changes in podzol soils and can be related to soil moisture at the time of sampling.

INTRODUCTION

The Old Coastal Plain of French Guyana is a narrow belt of about 1500 km² parallel to the coast, bounded in the north by the Young Coastal Plain (mangrove and subcoastal swamps), and in the south by the Precambrian Guyana shield. Two main kinds of soil are to be found in these savannas, these being podzols and podzolic (USDA; spodosols) and ferrallitic (USDA; plinthic or ochric tropudult).

The climate of this area is equatorial with two dry seasons more or less accentuated during the year. There is also extreme variability of rainfall and the existence of an ecological dry season with less than 30 mm of monthly rainfall.

From the calculation of evapotranspiration (*ETP*) according to Penman's formula (albedo, 0.25) using data from the meteorological station of Kourou we can define for the period 1969-70 certain important climatic events, starting from the time when the increasing rainfall, R , equals half the *ETP* ($R = 0.5 ETP$) and the humid period begins. This continues until the *ETP* becomes higher than the rainfall. From this point, the post-humid season is established, and then the dry season follows. The pre-humid season goes from the point when $R = 0.5 ETP$, to the point when $R = ETP$.

In these savannas two vegetation groups are well defined in relation to the soils. These are: (a) high grass savanna with *Schizachyrium* and *Trachypogon* on ferrallitic soils; and (b) low savanna with *Rhynchospora barbata* and *Bulbostylis lanata* on podzolic soils.

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In a former study it was shown that from an identical material (clay and sorted fine sand) the differentiation between podzolic and ferrallitic soils can be related to the percentage of humic acids which are immobile under electrophoresis and the behaviour of these acids during the rainy season. These acids occur in smaller quantities in A_0 and A_1 horizons of podzols and podzolic soils under savanna or forest than in the corresponding horizons of ferrallitic soils. This evolution is very much influenced by the ecological conditions; the ground water table varies much more in podzolic soils and remains in the upper horizon for a longer part of the year.

In all cases during the rainy season, the electrophoretically mobile part of the humic acids increases in A_0 – A_1 horizons, from 55.4 to 61.2 per cent for ferrallitic soils and from 62.2 to 70.5 per cent for podzols.

Also, there is a positive correlation between immobile humic acids and the fine fraction (clay + fine sand, 0–2 μm) only during the rainy season which shows that decreases in the immobile humic acid fraction can be directly related to the progressive disappearance of clay in the upper horizons of podzols.

A study of seasonal evolution shows that there is a relation between the post-humid, dry, and prehumid periods and the variation of both the quantity and composition of organic matter (sodium pyrophosphate non-extractable fraction, immobile humic acids, mobile humic acids and fulvic acids). The size of the different fractions varies according to the season.

In the post-humid period there is a significant decrease of fulvic acids, a decrease of mobile humic acids and, when drying is accentuated a decrease in the immobile humic acids appears accompanied by a significant increase of the non-extracted fraction, 'humin'. This can be seen as early as July/August for ferrallitic soils and in September for podzols where mineralization phenomena, being much more accentuated in July/August, lead to a diminution of the non-extractable fraction. An increase of total carbon (10.8 per cent to 12 per cent and 13.6 per cent) is connected with this variation.

In the prehumic period there is a significant decrease in the non-extracted fraction and a significant increase of electrophoretically mobile humic acids and fulvic acids. A decrease in carbon, 13.3 per cent to 11.5 per cent, for ferrallitic soils and 7.48 per cent to 6.37 per cent for podzols, follows these changes. During polymerization or depolymerization phases there is a strong possibility of movement between the different fractions of the organic matter.

MATERIALS AND METHODS

Soils:

Two sampling sites were selected, i.e. Combi savanna (podzols and ferrallitic soils) and Corossony savanna (podzols). Some of their physical and chemical properties are given in *Table 1*. Particle size analysis of the horizons shows a predominance of fine sands. The clay contents of ferrallitic soils are low and the leaching of clay is complete in podzol soils (*Table 1*). Both types of soils occur on the same material; the Corossony savanna samples are influenced by the presence of an old coastal ridge (coarse sands) not far from the sampling place.

Three A_1 horizon (0–8 cm) samples of each kind of soil were taken at intervals of about 30 days from each site. The first sampling was done on 29 July 1969, at the beginning of the dry season (post-humid period). The soil moisture of each sample was determined at the time of sampling.

Analyses

On the air-dried samples, carbon was measured by the Walkley-Black method and nitrogen by a modified Kjeldahl method. Humic acids were extracted with 0.1 *N* sodium pyrophosphate. Fulvic and humic acids were separated using 0.1 *N* H₂SO₄.

After dissolution in 1 *N* NaOH, humic acids were successively subjected to electrophoresis (7 V/cm) and separation on Sephadex gels. The gels used were: (a) Sephadex G25 with a fractionation range for peptides and globular protein with molecular weight (*MW*) of 1×10^3 to 5×10^3 and from 10^2 to 10^4 for dextrans; and (b) Sephadex G50 (fine) with a fractionation range for peptides and globular protein of *MW* 15×10^2 to 3×10^4 , and from 5×10^2 to 10^4 for dextrans.

In every case the eluant was distilled water. The Sephadex G25 F column has the following characteristics: inner diameter, 2.6 cm; length, 32 cm; gel height, 31 cm; and Sephadex G50: inner diameter, 2.5 cm; length, 45 cm; gel height, 32 cm. [Gel heights vary in G25 columns. These values are related to the series of samples from the podzolic soils.]

In the first fractionation on Sephadex G25, there were two peaks on the optical density curve (at 4200 Å) of the eluted fractions corresponding approximately to: (a) a fraction having a *MW* of 700; and (b) a fraction approximately equal to the upper limit of gel fractionation.

The fractions corresponding to this first peak contain humic compounds of a molecular weight higher than 800. The combined fractions were wetted with 0.1 *N* H₂SO₄ then dissolved in NaOH. This dissolved fraction was passed through Sephadex G50 F and the optical density of the eluted fractions was measured at 4200 Å.

In this latter operation, the qualitative study shows some definite molecular weights, which correspond to molecular structures found in the humic colloid studied. The determination of molecular weights was based on the elution volume; over a very wide range this volume is a linear function of the logarithm of the molecular weight.

The reference products used to determine the standard curve were: blue dextran (*MW* 2×10^6), yellow dextran (*MW* 2×10^4), cytochrome *c* (*MW* 13×10^3), and vitamin B₁₂ (*MW* = 1357).

With these points a straight line can be drawn which corresponded well with those given by Determann and Michel (in DETERMANN, 1969). The fact that solutions of aromatic substances containing hydroxyl and carboxyl groups have a longer elution time than would be expected from the size of their molecules was not taken into account. The qualitative results obtained are meaningful by themselves.

RESULTS

In this study only the dynamic phases of drying and rewetting periods are considered, the saturation phase (end of rainfall season) being different since this is the beginning of circulation of fulvic acids.

For the dynamic phases of drying, dry and rewetting periods, the soil moisture of the A₁ horizon is related to the difference (*R* - *ETP*) calculated for 10 days prior to the date of sampling. Variations in soil moisture are less marked in ferrallitic soils where the vegetation cover is thicker, the clay content higher and

Table 1. Some physical and chemical properties of the soils studied

Site	Soil moisture (%)	C (%)	N (%)	C/N	pH	Clay <0.2 μ m (%)	Silt <0.50 μ m (%)	Fine sand (%)	Coarse sand (%)
		Ferrallitic soil under high grass savanna							
Combi savanna	5.0	14.7	0.94	15.6	5.1	8.0	7.6	74.3	6.6
		Podzols under low savanna with <i>Rhynchospora</i>							
Combi savanna	8.4	5.3	0.38	13.9	5.9	1.2	11.5	84.6	0.5
Corossony savanna	9.6	8.3	0.56	15.2	5.3	1.5	5.0	43.3	27.0

the drainage better. For both kinds of soil, there are least three months of the surveyed period showing values less than six per cent which is very close to the wilting point (*Table 2*).

Organic matter

In both ferrallitic and podzol soils, organic matter (expressed as percentage of carbon) begins to show a slight decrease from the first post-humid period (*Table 2*). Then it increases again to reach a first maximum during the dry period for most of the samples; this maximum does not change or even slightly increases until the end of the dry season (ferrallitic soils).

During the pre-humid period, there is a clear decrease in the total amount of organic matter, from 13.8 per cent to 12.9 per cent for ferrallitic soils and from 9.2 per cent to 6.6 per cent or 5.5 to 4.1 per cent for podzols according to the rewetting rate (*Table 2*). A second maximum can be observed for all the samples at the end of the rainy season (June 1970).

Minima are to be observed at the beginning of the dry season, and in January (beginning of the wet season) when the savanna has just reached the soil moisture content which remains constant throughout the rainy season.

In all cases (TURENNE, 1972) the percentage total carbon is higher in ferrallitic soils (8 to 14 per cent) than in podzols (3 to 10 per cent).

Fulvic and humic acids

The amounts of fulvic and humic acids vary throughout the year but for the fulvic acid/humic acid ratio, values are lowest during the dry season; then gradually rise until January (rewetting). Afterwards they decrease when the surface is waterlogged owing to the mobilization of fulvic acids which drain away.

Immobile humic acids

The percentage of humic acids in the humic fraction increases with gradual drying but the percentage decreases when the drying period persists as a result of possible depolymerization caused by desiccation. Rewetting of the horizons results in a further decrease.

The study of humic acids fractionated by electrophoresis shows the direction of the evolution of organic matter; there is a maximum of immobile acids and a greater amount of the non-extracted 'humin' of organic matter when carbon is at a minimum. An increase of the carbon percentage is related to polymerization and the existence of polymeric fractions in the organic matter. These increases in carbon also correspond to periods when biological activity is likely to be reduced in the soil by desiccation or saturation.

Podzol and ferrallitic soils are clearly differentiated by the percentage of their immobile acids (*Table 2*).

Distribution of organic compounds at various periods of the year

Qualitative analysis shows that there are three permanent well defined fractions with molecular weights of (a) >30 000, (b) 1100 and (c) 700. They all appear when the amount of immobile humic acids is high, e.g., for sample No.17 in December for the ferrallitic soil, and No.19 in November and No.14 in September for the podzol (*Table 2*).

Variations in the amount of electrophoretically immobile humic acids, can be seen in the appearance of intermediate fractions at about 25 000 (e.g. sample No.20 in December and No.14 in October for the podzol) and a split of the 900–1300 fraction for a slight decrease of the immobile humic acids occurring after a maximum of polymerization.

Also a stretching of the *MW* 30 000 peak towards fractions smaller than 30 000, the stretching of the *MW* 1100 peak and the appearance of an intermediate fraction at about *MW* 3000 in podzol soils can be observed when there is a prolonged decrease in the amount of immobile acids. This fraction is accentuated in maximum rewetting and fractions higher than *MW* 30 000 disappear entirely after pronounced depolymerization. *Figure 1* shows, for Combi savanna, how this evolution appears on elution curves.

From *Table 2* the following can be distinguished: (i) changes corresponding to an increase of fractions <900 , $>25\ 000$ (polymerization, increase of the immobile humic acids) at the expense of the *MW* 3000 fraction (*MW* 2000 to 4000) in podzols (increase of the amount of total carbon); (ii) the opposite effect, e.g., an increase in the amount of immobile humic acids in August for the ferrallitic soil but a decrease of the total carbon is accompanied by a decrease of the 25 000 fraction and an increase of the fraction <900 . Afterwards, corresponding to the maximum total carbon the fraction with *MW* $>25\ 000$ increases and there is a decrease of the fraction <900 .

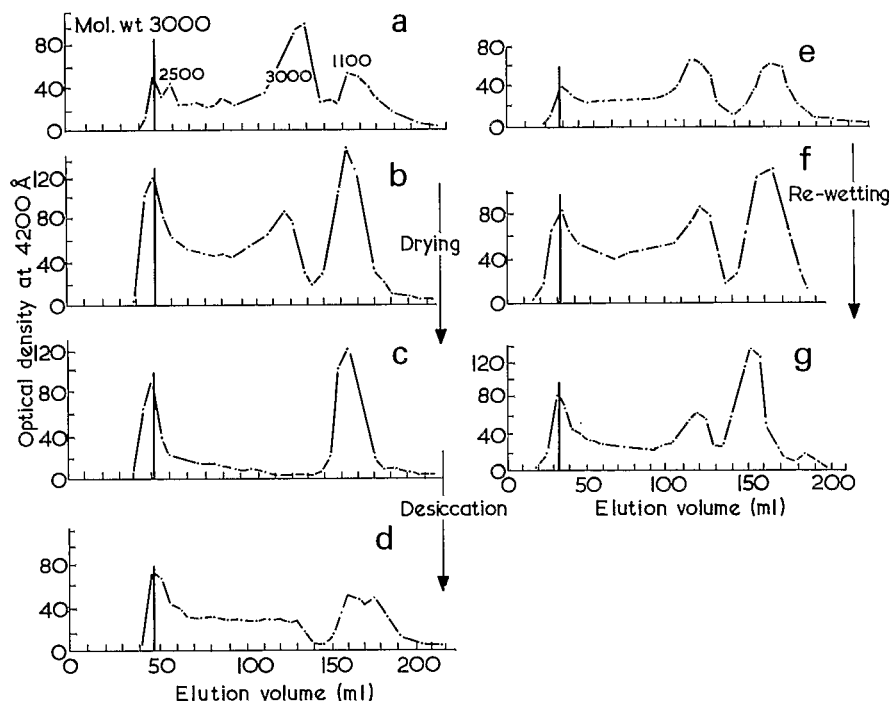


Figure 1. Gel-filtration; Humic acids elution curves for a podzol from Combi savanna during seasonal changes. (a) July, No.15; (b) August, No.15; (c) September, No.14; (d) October, No.14; (e) November, No.14; (f) December, No.14; (g) January, No.13

Table 2. Characteristics of samples used in Sephadex filtration

	<i>Jul</i>	<i>Aug</i>	<i>Sep</i>	<i>Oct</i>	<i>Nov</i>	<i>Dec</i>	<i>Jan</i>
	Corossony savanna: podzol						
Sample No.	20	20	20	20	19	20	20
Soil moisture (%)	18.7	10.7	2.5	3.0	5.5	11.4	23.5
Total carbon (%)	11.1	6.4	6.8	7.8	9.2	8.1	6.6
Total nitrogen (%)	0.77	0.38	0.49	0.56	0.77	0.53	0.52
C/N ratio	14.5	16.8	13.9	14.0	12.0	15.3	12.6
Fulvic acid (% C)	1.4	0.8	0.6	0.6	0.7	0.6	0.7
Humic acid (% C)	1.5	1.0	0.7	0.8	0.9	0.7	0.6
Extraction ratio	26.1	28.1	19.1	17.9	17.4	16.0	19.7
Non-extractable (%)	73.9	71.9	80.9	82.1	82.6	84.0	80.3
Immobile humic acids (%)	30.9	42.5	40.9	35.9	44.4	39.0	52.7
%							
of humic acids, according to							
molecular weight:							
<900	59.8	63.7	57.4	64.5	65.8	45.6	52.9
900-1300	2.3	3.1	6.3	2.7	2.9	8.5	5.1
1300-2000	4.5	1.0	8.4	0.6	0.0	5.9	1.4
2000-4000	10.5	6.3	2.2	3.5	2.9	4.2	11.5
4000-7500	6.8	5.5	5.2	5.8	5.1	3.5	10.7
7500-15000	5.9	4.9	7.1	6.1	6.0	5.4	10.4
15000-25000	4.6	4.7	8.4	6.1	5.6	10.9	4.3
>25000	9.0	10.0	5.1	10.8	11.7	16.6	4.3

Table 2—continued

	<i>Jul</i>	<i>Aug</i>	<i>Sep</i>	<i>Oct</i>	<i>Nov</i>	<i>Dec</i>	<i>Jan</i>	<i>Feb</i>	<i>Mar</i>
Combi savanna: podzol									
Sample No.	15	15	14	14	14	14	13	13	14
Soil moisture (%)	22.9	17.9	5.7	0.2	4.9	7.7	23.3	27.6	25.9
Total carbon (%)	3.1	3.0	6.5	5.5	5.5	4.9	5.1	4.1	5.3
Total nitrogen (%)	0.31	0.31	0.45	0.38	0.45	0.38	0.49	0.38	0.42
C/N ratio	10	9.7	14.9	14.5	12.3	12.9	10.5	10.8	12.6
Fulvic acid (% C)	0.3	0.5	0.6	0.6	0.6	0.5	0.4	0.5	0.3
Humic acid (% C)	0.5	0.4	0.8	1.4	0.4	0.4	0.6	0.3	0.5
Extraction ratio	23.8	30.0	21.5	16.4	18.7	16.7	17.5	20.0	15.1
Non-extractable (%)	74.2	70.0	83.6	81.3	83.3	82.5	80.5	80.5	84.9
Immobile humic acid (%)	23.8	38	51	41	36	34	32.9	31.4	25
% of humic acids, according to molecular weight:									
<900	57.6	55.9	59.0	58.1	54.5	51.5	53.2	58.5	46.5
900–1 300	2.8	6.4	17	4.3	2.6	4.8	9.6	2.6	4.0
1 300–2 000	5.4	1.8	0.7	1.2	2.4	3.1	3.7	3.2	2.5
2 000–4 000	15.7	8.1		6.3	15.7	12.0	10.4	12.8	4.3
4 000–7 500	5.1	6.4	1.2	6.3	6.8	7.0	4.5	6.5	12.6
7 500–15 000	4.4	6.0	3.3	7.6	6.3	6.6	4.8	6.2	11.0
15 000–25 000	3.7	5.2	3.1	5.7	5.1	4.7	4.5	5.4	8.9
>25 000	5.1	10.6	15.1	10.5	8.5	10.2	9.3	4.8	11.3

Table 2—continued

	<i>Jul</i>	<i>Aug</i>	<i>Oct</i>	<i>Nov</i>	<i>Dec</i>	<i>Jan</i>	<i>Feb</i>	<i>Mar</i>
Combi savanna: ferrallitic soil								
Sample No.	16	17	16	16	17	17	16	18
Soil moisture (%)	17.8	6.1	0.8	0.9	5.7	17.7	26.6	20.3
Total carbon (%)	12.8	11.9	12.2	13.8	13.7	12.9	13.3	13.0
Total nitrogen (%)	0.77	0.84	0.84	0.98	0.91	0.80	0.80	0.73
C/N ratio	16.7	14.2	14.5	14.1	15.1	16.1	15.8	17.8
Fulvic acid (% C)	2.6	1.9	2.0	2.0	2.0	2.0	1.2	1.9
Humic acid (% C)	2.5	2.0	1.7	2.1	1.9	2.0	2.0	2.0
Extraction ratio	39.8	32.7	29.4	29.7	28.5	31.0	24.1	30.0
Non-extractable (%)	60.2	67.3	70.6	70.3	71.5	69.0	75.9	70.0
Immobile humic acids (%)	36.6	51.1	47.2	49.4	52.5	46.4	49.1	48.1
% of humic acids, according to molecular weight:								
<900	53.0	63.8	56.0	56.6	54.2	68.0	57.8	65.1
900–1 300	2.25	0.0	10.0	7.05	2.84	2.6	5.46	1.45
1 300–2 000	0.0	0.0	5.48	7.43	0.0	0.0	1.68	0.72
2 000–4 000	0.0	0.0	2.26	3.91	0.0	1.5	1.37	1.69
4 000–7 500	1.47	2.97	2.74	0.0	0.0	3.20	4.17	4.61
7 500–15 000	8.37	8.98	0.89	0.0	3.98	5.21	9.59	4.85
15 000–25 000	12.17	10.82	8.22	3.14	5.68	5.82	9.93	7.75
>25 000	22.18	13.20	13.70	21.60	33.05	13.09	9.59	13.56

During depolymerization (i.e. decrease of the immobile acids) there is a decrease of fraction $>25\ 000$ and an increase of the fraction <900 .

Relations between soil moisture, immobile humic acids and percentage of molecular fractions

(1) Between the amount of immobile humic acids (*IHA*) during electrophoresis (percentage of humic acids) and the fraction *MW* 2000–4000 for podzols:

$$F(2000-4000) = 0.617 IHA + 30.34$$

$$b \neq 0 \quad t = 3.955 (P < 0.01)$$

(2) Between soil moisture (*SM*) at the time of sampling and the fraction (*MW* 2000–4000) for podzols:

$$F(2000-4000) = 0.318 SM + 4.23$$

$$b \neq 0 \quad t = 2.61 (P < 0.05)$$

(3) Between the amount of immobile humic acids and the fraction *MW* 25 000 for podzols:

$$F(25\ 000) = 0.323 IHA - 1.82$$

$$t = 4.14 (P < 0.01)$$

For ferrallitic soils there are no correlations between immobile humic acids or soil moisture and the different molecular fractions, nevertheless we can distinguish a greater part of the fraction $>15\ 000$ according to soil moisture decreases or immobile humic acids increases.

However, it is possible to set out for all ferrallitic samples an intermediate fraction, *F* (4000–15 000) (fraction about *MW* 7500) which correlates with soil moisture (*SM*):

$$F(4000-15\ 000) = 0.437 SM + 1.94$$

$$n = 11 (P < 0.01)$$

In ferrallitic soils as well as podzols a soil moisture variation involves a modification in the composition of the humic compounds.

Fractions having a molecular weight higher than 15 000 are more numerous in ferrallitic soils than in podzols.

DISCUSSION

The evolution of organic matter in the soil at different precise climatic periods shows two maxima at the end of the dry and wet seasons. An identical mechanism can be put forward for ferrallitic soils and podzols under savanna by studying the reaction of the organic matter to variations in environment.

The degree of polymerization is strongly influenced by climatic variations, but less by the instantaneous soil moisture value, regarded as a characteristic of the climatic situation of the horizon, than by the variations of this soil moisture. Here the composition of organic matter depends on the sample position in a succession of climatic events; this is illustrated by the practically identical composition of two samples: No.15 in August (drying up) and No.13 in January (rewetting) (Table 2).

In the first case we have a polymerization phase (drying up) whereas the other one is a beginning of depolymerization. The transient nature of polymerized and unpolymerized forms of organic matter must be expected under the climatic conditions of the Old Coastal Plain. However, it should be noted that the fraction having a molecular weight of 3000 is characteristic of humic fractions of the horizons of podzol soils, this fraction being absent from the corresponding horizons of ferrallitic soils. It is also a characteristic of the polymerization of organic matter and of the soil moisture conditions at least for the dynamic phases of drying, dry and rewetting.

BRUCKERT *et al.* (1971) have shown that this fraction appears in the drainage water (stream flow) of mor humus under beech and pine whereas it does not appear in the drainage water of mull humus under beech.

This fraction with a molecular weight of 3000 seems to have an extremely important role in the pedogenesis of podzolic soils and podzols. It seems to be related to horizon humidity. Correlations show it to be linked with the amount of electrophoretically immobile humic acids and with soil moisture; this is a characteristic of the dynamic phases of the organic matter evolution (depolymerization or polymerization) in the absence of clay minerals. In ferrallitic soils, these dynamics tend towards less fragmentation of organic molecules and more abundant fractions of high molecular weight.

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DISCUSSION

A. V. Downer:— Pyrophosphate has been observed to extract less organic carbon than NaOH and to remove more fulvic and less humic acids. This extractant would probably modify the fulvic/humic and the extractable C/non-extractable C ratios. Would you care to comment on this?

Author's reply:— 0.1 N sodium pyrophosphate is a moderate alkaline reagent and considering that the non-extractable/extractable ratios in these data vary between 60 and 85 per cent, it is certain that this reagent extracts only a small

part of the humus in organic matter. However, the results presented here show many significant differences, which allow us to think that this extraction can be useful for studying this evolution.

B. Dabin and C. Thomann (ORSTOM, Paris 1970, Initiations and Documents Techniques No.16) have shown that for soil with well decomposed organic matter changes in humus compounds with strong reagents as in the Tiurin method or with sodium pyrophosphate are not observed. Differences between these methods are only observed for soils with much non-decomposed organic matter and abundant prehumic products.

A. V. Downer:— Do you have any comment on the composition of the immobile humic acid fraction?

Author's reply:— I have not yet studied this composition, but from the literature they are probably quinones from oxidation of phenol groups.

N. Ahmad:— I have seen podzol soils in Guyana and Surinam; unfortunately I have not visited French Guyana as yet. However, your podzols appear to be much better developed, yet climatic and other factors in the same landscape as in Surinam and Guyana might be much the same. Do you have any comments on this?

Author's reply:— I have visited Surinam, but not Guyana. I have seen in Surinam well developed podzols in the Lelydorp landscape. The examples of podzols shown on the slide, are from Kouron savannas in French Guyana, and maybe the extreme conditions during periods of drying and wetting can lead to such development of horizons; such conditions being less accentuated under forests.

R. L. Jones:— Have you done functional group analysis on the MW 3000 fractions?

Author's reply:— Not yet.