IC/93/334
INTERNAL REPORT
Limited Distribution

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

SORPTION OF WATER VAPOUR
BY THE Na^+-EXCHANGED CLAY-SIZED FRACTIONS
OF SOME TROPICAL SOIL SAMPLES

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MIRAMARE – TRIESTE

September 1993

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ABSTRACT

Water vapour sorption isotherms at 299K for the Na^+-exchanged clay-sized ($\leq 2\mu m$ e.s.d.) fraction of two sets of samples taken at three different depths from a tropical soil profile have been studied. One set of samples was treated (with H_2O_2) for the removal of much of the organic matter (OM); the other set (of the same samples) was not so treated. The isotherms obtained were all of type II and analyses by the BET method yielded values for the Specific Surface Areas (SSA) and for the average energy of adsorption of the first layer of adsorbate (E_a). OM content and SSA for the untreated samples were found to decrease with depth. Whereas removal of organic matter made negligible difference to the SSA of the top/surface soil, the same treatment produced a significant increase in the SSA of the samples taken from the middle and from the lower depths in the profile; the resulting increase was more pronounced for the subsoil. It has been deduced from these results that OM in the surface soil was less involved with the inorganic soil colloids than that in the subsoil. The increase in surface area which resulted from the removal of OM from the subsoil was most probably due to disaggregation. Values of E_a obtained show that for all the samples the adsorption of water vapour became more energetic after the oxidative removal of organic matter; the resulting ΔE_a also increased with depth. This suggests that in the dry state, the "cleaned" surface of the inorganic soil colloids was more energetic than the "organic-matter-coated surface". These data provide strong support for the deduction that OM in the subsoil was in a more "combined" state than that in the surface soil.

1 INTRODUCTION

The devastating effects of droughts in the Sahel regions of West and Central Africa are vivid demonstrations of the importance of water to growing plants and to the fauna, including humans, that live off these plants. Soil water, the source of most of the plant's requirement for water, provides a medium in which nutrients are dissolved and transported to the roots of plants. It is also an active agent in the genesis of the soil.

In Sierra Leone, where a dry season of six months alternates with a wet season of roughly equal duration, the amount of water in the soil during the dry season will depend on the tenacity of the binding of water to the soil components, and this in turn will depend on the nature of the soil and on the temperature of the soil environment. During drought conditions the amount of water in the soil can decrease to molecular levels, and such will have severe influence on the soil microbial population, and on their abilities to transform animal and vegetable litter into humus, and to release mineral nutrients from humifying and humified substances.

This paper proposes to examine the interactions between water at the molecular level and the colloidal fractions from selected samples from a tropical soil profile.

2 EXPERIMENTAL

2.1 Materials

The tropical soil samples used were taken from Province F shown in the Soil Map of Sierra Leone, and were provided by the Director of the Rice Research Station at Rokupr in the North-West of the country. Soils in Province F are formed from the weathering of igneous and metamorphic rocks (Odell *et al.* 1974).

Soil samples were taken from three depths (0–20, 20–40, and 40–60 cm) in each of several profiles in order to obtain data representative of soils in an area of $6km^2$ around the village of Morcosa, which was then a targeted area for intensive agricultural activity. The region has a mean annual temperature of 305K and an annual rainfall of the order of 300 cm. The rainy season (May to October) is followed by a dry season of six months. Some information about the samples studied is given in Table 1.

Sample	Depth (cm) in profile	Treated for organic matter removal
M_1B	0–20	NO
M_1A	0–20	YES
M_2B	20–40	NO
M_2A	20–40	YES
M_3B	40–60	NO
M_3A	40–60	YES

Table 1: Description of Samples Used.

2.2 Methods

2.2.1 Isolation of Soil Clay Fractions.

Adsorption studies were carried out on the clay-sized fractions ($\leq 2\mu m$ equivalent spherical diameter, or e.s.d.) from the soil samples. The clays were isolated by suspending the $\leq 2mm$ soil particles (obtained by dry sieving) in distilled water, and then homogenizing the samples by first using an electrically operated mixer, and then ultrasonicating the suspension (130 Watts for 10 minutes). The homogenized suspensions were then transferred to tall cylindrical glass vessels, and the soil particles were allowed to settle under gravity. On the basis of Stoke's equation, which allows calculations of sedimentation times for particles of different e.s.d. values, volumes of the suspensions containing particles of clay dimensions (i.e. $\leq 2\mu m$) were siphoned from the cylinders to depths of 10cm after 8 hours at 20^oC (or to the same depth after 7 hours and 7 minutes at 25^oC) (Day, 1965). A continous flow method described Oladimeji (1976) was also used to isolate the clays.

2.2.2 Removal of Organic Matter from the Clay.

Isolated clay-sized samples (ca. 10g in $50cm^3$ of distilled water, to which $10cm^3$ of 30% H_2O_2 was added) were gently heated on a hot plate or sand bath. This procedure will not remove all of the organic matter, but it is considered to interfer least with the iron oxides in the clay-sized components (Kunze, 1965).

2.2.3 Determinations of Organic Matter Contents.

Total organic matter was determined by the Walkley-Black method (Allison, 1965) in which samples were treated with a mixture of $0.5M K_2Cr_2O_7$ and concd. H_2SO_4. Excess dichromate was titrated against 0.5M ammonium ferrous sulphate, using 'ferroin' as an indicator.

Humified organic matter was determined by first extracting the samples exhaustively with 0.1M aqueous sodium pyrophosphate, followed by further extraction (exhaustive) with 0.5M aqueous NaOH. Estimates of the amounts of organic matter present in the extracts were made from measurements of absorbance at 400nm. Standard curves were obtained using dry humic substances isolated from the same soils. This procedure does not, of course, take account of the humin fraction associated with the clay-sized components. The organic matter contents of the extracts were also measured using the Walkley-Black method, as described.

Non-humified organic materials (the light fraction) were floated in carbon tetrachloride (specific gravity = 1.59). The humified organic matter, which invariably was associated with the denser inorganic soil fraction, sank in this "heavy liquid". The non-humified floating, light fraction was then removed, dried, and weighed (Ford and Greenland, 1968).

2.2.4 Determination of the Free Iron Oxide Contents.

Free iron oxides were extracted from clay-sized samples (ca. 2g) using a solution composed of a mixture of 0.3M sodium citrate ($40cm^3$) and 1M $NaHCO_3$ ($5cm^3$) to which was added solid sodium dithionite (1g). The mixture was heated (to not more than $80^{\circ}C$) for 15 minutes, with occasional stirring. This extraction process was repeated twice for each sample. Iron in the extracts was first oxidised to the Fe^{3+} state by adding H_2O_2, and then reduced to Fe^{2+} by dropwise addition of $SnCl_2$. When reduction was complete, and excess $SnCl_2$ was removed, the Fe^{2+} concentration was determined by titrating this solution against 0.005M $K_2Cr_2O_7$, using N-phenylanthranillic acid as indicator (Olson, 1965).

2.2.5 Measurement of Some Physico-Chemical Properties.

Cation-exchange capacity (CEC) was measured at pH4 using ^{22}Na as index cation (Yormah, 1981).

Mineralogical investigations used XRD, DTA-TGA, and IR procedures.

Specific surface areas of the soil clay samples were measured by the BET method, using water vapour as the sorptive (or sorbing species), and Na^+-exchanged clay-sized fractions as sorbents. An all-glass Macbain-Bakr type apparatus (consisting of a thin glass sample-holder, containing 20-40 mg of sample attached to the end of a previously callibrated helical spring capable of responding to small weight changes caused by the sorption of water vapour) was used for the sorption studies. The apparatus was housed in a thermostated fume cupboard where weight and pressure measurements could be made at different temperatures (accurate to $\pm0.05^{\circ}C$). Weight changes were measured to an accuracy of 0.005 mg g^{-1} of sorbent, using a cathetometer to record the extension of the helical spring (see Hayes et al., 1984).

3   RESULTS

Data from XRD, DTA-TGA, and IR analyses indicated that kaolinite was the principal clay mineral in all the samples studied, and there was evidence too for goethite and gibbsite in these samples. Georgia (Na^+-exchanged) kaolinite (from the Oneal pit) was included among the samples for comparisons of the different interactions with water vapour. It is well known that the (hydr)oxide and organic matter associations with soil clays alters the surface properties of these clays in comparison with those of the "pure" parent minerals.

The sorption isotherms (Figures 2 to 4) for all the soil clays, like that obtained for the Na^+-kaolinite (Figure 1), were of type II (Brunaeur, et al., 1938). This suggests that the adsorption process was physical, and that the sorbent was either non-porous, or more probably macroporous. Isotherms were analysed by the usual BET procedure (see Hayes et al., 1984). Analyses were restricted to the relative pressure (p/p_o) range 0.05 and 0.35, in which the BET theory is known to apply. The monolayer capacity, i.e. the amount of

vapour required to complete a monolayer (X_m), obtained from the BET plots was used to determine the specific surface area,(SSA), from the relation

$$S(m^2 g^{-1}) = X_m N A_m x 10^{-23} \qquad 1$$

where X_m is expressed in millimoles sorbate (or sorbed species) g^{-1} sorbent (or sorbing species), N is Avagadro's number, and A_m is the cross-sectional area (expressed as $\mathring{A}^2$) of the sorbate; $12.5\mathring{A}^2$ was used as the "effective" cross-sectional area of the water molecule (McClelan and Harnsberger, 1967; see also Greenland and Mott, 1978).

The BET C constant, which is exponentially related to the net energy of adsorption, $(E_a - L)$, was calculated from the relation

$$E_a - L = RTlnC \qquad 2$$

where E_a is the average energy of adsorption of the first layer of adsorbed molecules, and L is the latent heat of condensation of the adsorptive (i.e. the water vapour). The parameter E_a was therefore computed with the assumption that the "net energy of adsorption" (Brunaeur, et al., 1967) is unity. This assumption may not necessarily hold for the adsorption system studied here, but the values for E_a could be useful for comparing the energy involved in the interaction between the same adsorbate (i.e. the adsorbed water molecule) and several soil samples with differing surface properties.

Data for water vapour sorption by samples which were not treated for the removal of organic matter (OM) indicate that the sample from the surface soil (i.e. 0-20cm depth) had the highest specific surface area, and SSA values decreased with depth in the profile (Table 2).

Sample	Organic Matter Content (% of clay fraction)	Monolayer capacity (mmole g^{-1})	Relative Specific Surface Area m^2g^{-1}	C-constant	Energy of Adsorption (E_a) (kJ mol^{-1})
Kaolinite	—	0.39	29	36	- 52.9
M_1B	13.2	1.37	103	13	- 50.4
M_1A	2.1	1.36	102	21.6	- 51.6
M_2B	10.8	0.92	70	47	- 53.3
M_2A	3.1	1.81	89	82	- 54.9
M_3B	10.6	0.66	49	309	- 48.2
M_3A	4.0	1.07	80	176	- 56.8

Table 2.   Sorption Parameters

These results show that the removal of OM did not affect the surface area of the topsoil clays, but gave a moderate increase (27%) in that taken from the intermediate level (20-40 cm) in the profile. The surface area of the treated material from the subsoil sample (40-60 cm) was significantly greater (by 77%) than that from the untreated sample.

Values for E_a showed that removal of organic matter made little difference to the energy of adsorption of the colloids from the topsoil and from the intermediate depth. However, the energy of adsorption in the case of the materials from the subsoil increased after most of the OM had been removed.

4 DISCUSSION

4.1 Surface Area Measurements.

In the strict sense of BET terminology, a monolayer of water (and other polar species) is not adsorbed on the surfaces of heterogeneous adsorbents, such as clay minerals and soil clays containing polar groups and charge-neutralizing cations (Quirk, 1955). Such does not, however, invalidate measurements of specific surface areas (SSA) of such sorbents using water vapour and the BET approach, provided that it is understood that it is not the extent of the surface, per se, that is being measured, but rather the concentration of the surface polar groups which interact with water. In this sense the SSA becomes a measure of the water uptake, and it might be interpreted as a measure of the water holding-capacity of a soil as reflected in the concentration of surface polar groups which interact with water.

The results in Table 2 indicate significant differences in the modes of uptake of water vapour by the colloids in the surface soil and by those in the subsoil, as judged by the change in surface areas brought about by the H_2O_2 treatment of the samples. Removal of organic matter did not affect the surface area obtained for the surface soil colloids before and after treatment with the peroxide, but that treatment gave significant increases in the SSA for the samples taken deeper in the profile. These results indicate that the properties of the organic matter, and/or the nature and extents of its associations with the inorganic colloids in the subsurface soils are different from those in the surface soil.

In their considerations, Burford et al. (1964), divided soil organic matter into "free" (such as peat, unhumified and partially humified organic matter, and of course humified substances not in association with the inorganic soil components), and "combined" (or organic materials in naturally occurring clay-organic complexes) forms on the basis of the influences they have on surface area determinations using water vapour as adsorptive. In their view, the "free" organic matter will hold large amounts of the adsorbate (water) compared with other soil components, and its removal would therefore lead to a decrease of the measured surface area. On the other hand, removal of the "combined" organic matter would lead to disaggregation of the soil particles, and to an increase of the surface area available for adsorption. On the basis of such argument, it is reasonable to consider that the proportion of the total OM in intimate association with the inorganic colloids increased with depth in the profile, and treatment with H_2O_2 oxidized most of this organic matter and increased the separation of the clay particles, and also increased accessibility to sorption of water vapour. Considerations of the amounts of water vapour adsorbed by the colloids in the surface soil before and after removal of OM might suggest that the

organic matter there played an insignificant role in the uptake of water vapour. Dry humic substances are difficult to rewet because, during the process of drying, the polar groups associate towards the interior thus exposing to the exterior the hydrophobic moieties in the structures. Such hydrophobic surfaces will have little affinity for water vapour. On the other hand, it might be argued that removal of the organic matter from the surface soil also led to disaggregation, and to an increase in the contribution by the inorganic colloids to the surface area. This increase would compensate for losses arising from the destruction of the organic matter.

The SSA measured for the (untreated) topsoil colloids was significantly greater than that for the subsoil samples. That would suggest that the clays isolated from the topsoil were less well aggregated than those in the subsoil, had less of the organic matter associated with the inorganic colloids, and/or (but less likely) were more finely divided. No organic matter was removed (as light fraction) from the subsoil during the treatment with CCl_4, indicating that all of the organic matter present below the surface soil was associated with the inorganic soil components. The same treatment removed organic matter from samples from the surface soil, and of course that OM was not associated with the mineral components in the clay fraction. Also, extraction with sodium pyrophosphate and with sodium hydroxide removed least organic matter from the fractions from the surface (20, 24,and 27% of that in samples M_1B, M_2B, and M_3B, respectively) soil. Non-humified organic matter would not be removed by such treatments, nor would the so-called humin materials, which can be considered to be humified substances in intimate associations with the clays. The evidence which is available would suggest that the organic matter in the surface soil was less involved with the inorganic soil colloids than that in the subsoil.

4.2 Heats/Energies of Adsorption

The average energy of adsorption for the first layer of water molecules by the clay-sized samples (i.e. E_a), after removal of OM, increased with the depth at which the the samples were taken in the profile. It can be assumed that the energy of interaction between the water molecules and the soil clays is determined by the surface polar groups and by the charge-neutralizing Na^+ ions, because only weak van der Waals forces are involved in the adsorption of water at any siloxane surface that may be exposed. However, the Na^+-charge neutralizing cations may have only minor influences on water adsorption in the BET region of the isotherm (Keenan, et al., 1951). Martin (see van Olphen, 1975) considered that Na^+ ions donot become hydrated below a relative pressure of 0.075, and Farmer (1978) avers that under the conditions used here, the Na^+/OH_2 interaction is much weaker than the H_2O/H_2O interaction. Thus, it would be expected that, in the presence of organic matter, the initial uptake of water vapour will primarily involve interactions (such as hydrogen bonding) with the polar groups on the organic substances, and with the (hydr)oxide (especially those of iron and aluminium) surfaces.

The higher energies for the adsorption of water vapour by the clay-sized materials after oxidation of the organic matter indicate that adsorption by the inorganic surfaces was more energetic than that by the organic surfaces. Treatment with H_2O_2 removed most of

the organic matter (for example, the inorganic matter content of M_1B was 86.8% prior to treatment with peroxide, and 97.9% after that treatment), and it is possible that, at least, some of the residual organic matter was composed of oxidation products (oxalic and other dicarboxylic and monocarboxylic acids). The "cleaned" adsorbing surfaces will be from kaolinite and (hydr)oxide species (mostly of iron, and some aluminium) in isolation or in association with with the clay mineral surfaces. (Hydr)oxides are known to interact strongly with water. In the case of iron (hydroxides) which were present in considerable abundance in this soil (18.6, 22.4, and 24.1 % respectively, in the clay-sized materials from samples M_1B, M_2B, and M_3B), the surface Fe ions complete their coordination shell of nearest neighbours through a hydrolytic reaction with water leading to hydroxylation of the surface. The hydroxylated surface then physically adsorbs additional water to a degree which will depend on the extent of the surface and on the type of parent oxide or hydroxide. It is considered, for example, that the first layer of physisorbed water is strongly bound to the surface of goethite and hematite (Schwartmann and Taylor, 1977), two widely occurring soil oxide minerals.

Only 16% of organic matter remained associated with the clay-sized fraction in the surface soil after the H_2O_2 treatment, whereas 28.7 and 37.7% of that associated with the clay fraction in the middle and lower depths, respectively, survived the oxidation process. That would indicate that protection provided for the organic matter by the inorganic colloids increased with depth, and inevitably this organic matter would have intimate contact with the inorganic colloids. Also the iron oxide content increased with depth, but it is not known to what extents the oxides/(hydr)oxides were free or combined with the clay minerals. Thus it might be considered that the higher energy of interaction of the water vapour with the clay-sized fraction of the surface soil before and after removal of organic matter might be attributed to greater availability of surface for adsorption. As organic matter was removed from the samples from the deeper levels of the profile, an increased "actively" sorbing surface was exposed, as evidenced by the greater magnitude of ΔE_a with increase in depth.

5   CONCLUSIONS

The surface soil contained the highest content of organic matter. A significant proportion of the organic matter in the surface soil was not humified, and could be removed by floatation in CCl_4. However, that organic matter was not associated with the clay-sized materials. It is clear that the humified organic matter in such soils is associated with the soil clays, and this organic matter is a major contributor to the cation exchange capacity (13.1, 11.9, and 12.9 meq per 100g of the 100-mesh fraction from samples M_1B, M_2B, and M_3B, respectively; at pH4) and to the general fertility of the soils. Much of the organic matter is not extracted in base, and is classified as humin. Although in the classical interpretations, humin is considered to be the least reactive of the soil humic substances, recent research has shown that it is similar in properties to humic and to fulvic acids (Hayes and Swift, 1990), and is protected through its intimate associations with the inorganic colloids (clays, oxides/hydroxides) from dissolution in aqueous solvents.

(It would appear that the polar groups are orientated inwards thereby exposing to the exterior a less reactive surface).

The data we have obtained indicate that increased and more energetic adsorbing surfaces are exposed when the organic matter is removed. This does not mean, however, that the soil will be a better medium for plant growth in the absence of organic matter. The increased surface areas of the clay-sized fractions when organic matter was removed from the M_2 and M_3 samples clearly indicate that the organic matter was involved in binding the inorganic particles.

The procedures used to measure the isotherms for the adsorption of water vapour do not give a true reflection of the capacity of the organic matter to hold water in the normal field soil environment. As indicated, humic substances when dried are very difficult to rewet (Hayes and Swift, 1990; Burchill et al., 1981) to an extent that they can assume the "spongy" or gel consistency characteristic of soil organic matter under field conditions. The adsorption isotherm measured only the binding of a monolayer of water and not the swelling capacity of the organic matter.

The organic matter at the surface of the tropical soil under study would be dried during the dry season and expose to the exterior its hydrophobic surface. At the advent of the rains the hydrophobic surface would aid runoff. The less well aggregated bare surface soils would then be more susceptible to erosion during the intense rainfall period (300 cm in six months).

Burning of slashed vegetation is part of the bush fallow farming method practised by many farmers in Africa. In Sierra Leone, burning is usaully carried out in March, the fifth and hottest month of the dry season. During this period the mean monthly temperature in the top 5cm of the soils in the region where the present samples were obtained is about $37^\circ C$ (at 15.00h). Thus the surface organic matter would be highly susceptible to combustion during this period.

Because, even in the dry season, the relative humidity in the subsurface soils would be 95% or more, the organic matter would not be dried in the same way as that in the surface soil. The substantial amount of organic matter associated with the clay-sized fraction in the subsurface horizons would act as a reservoir for water (and nutrients) for plant roots in the dry season, and this organic matter could readily swell on the advent of the rains. Much of that organic matter is intimate association with the mineral colloids, and plays an important role in holding these particles together.

6   Acknowledgements

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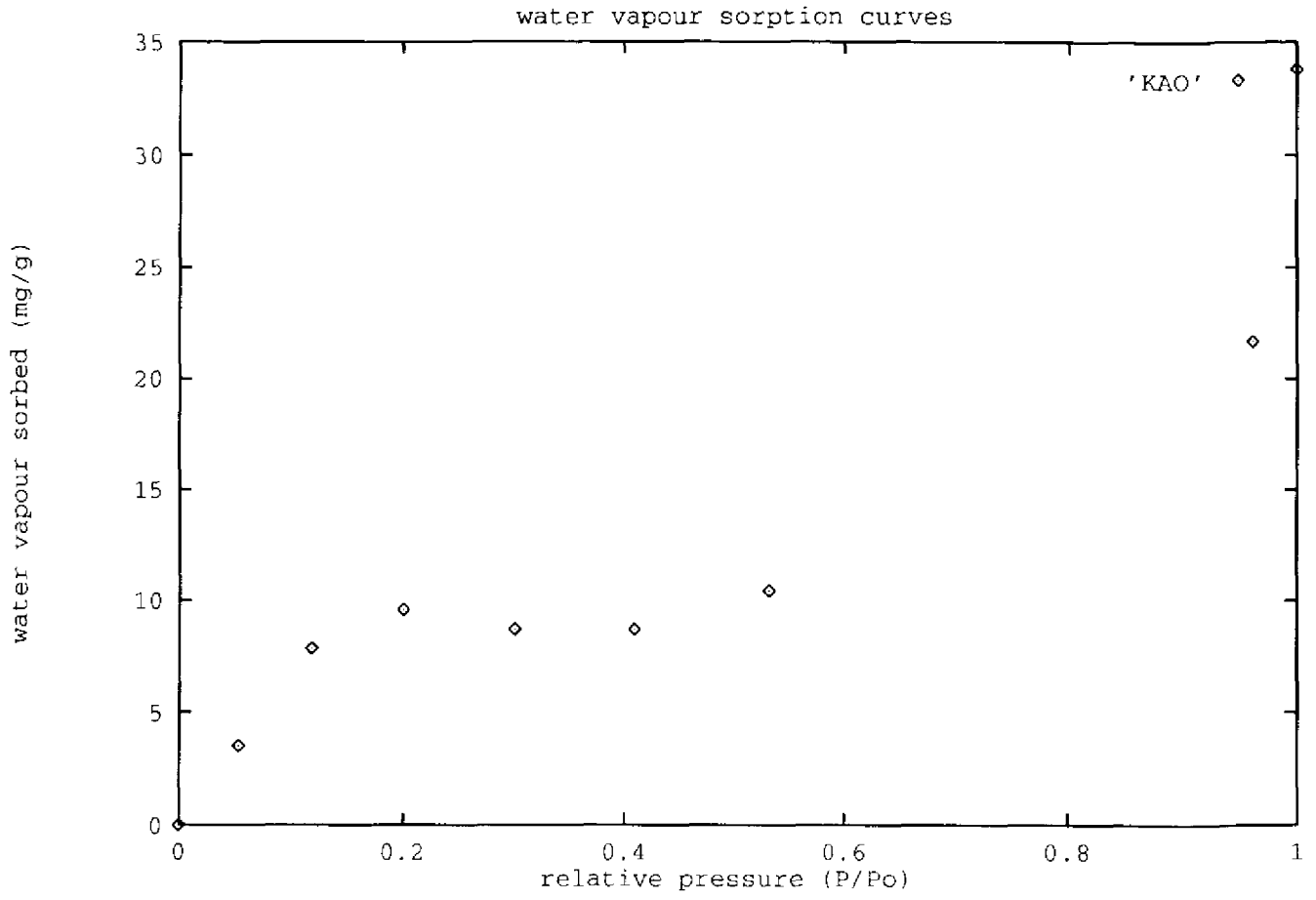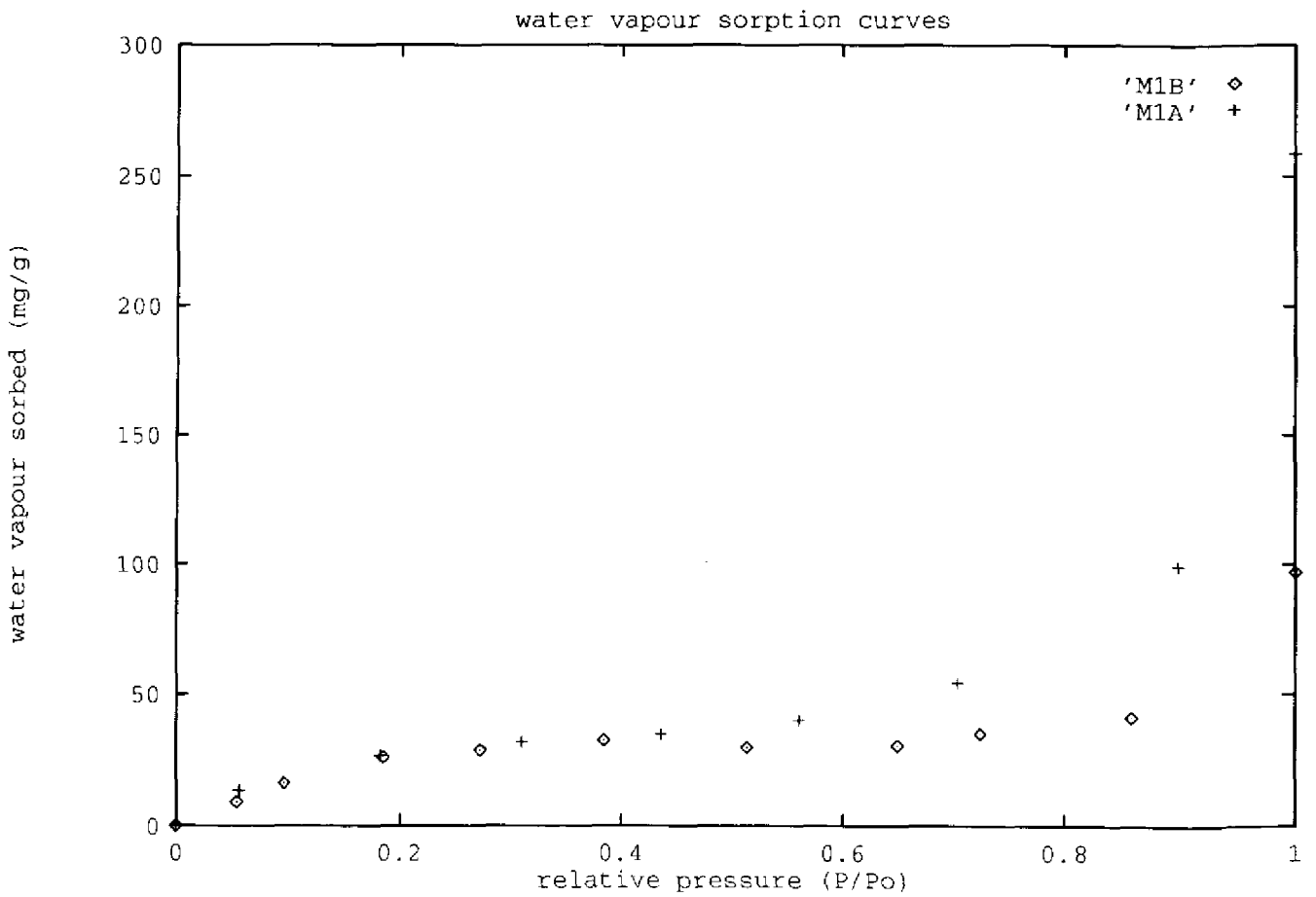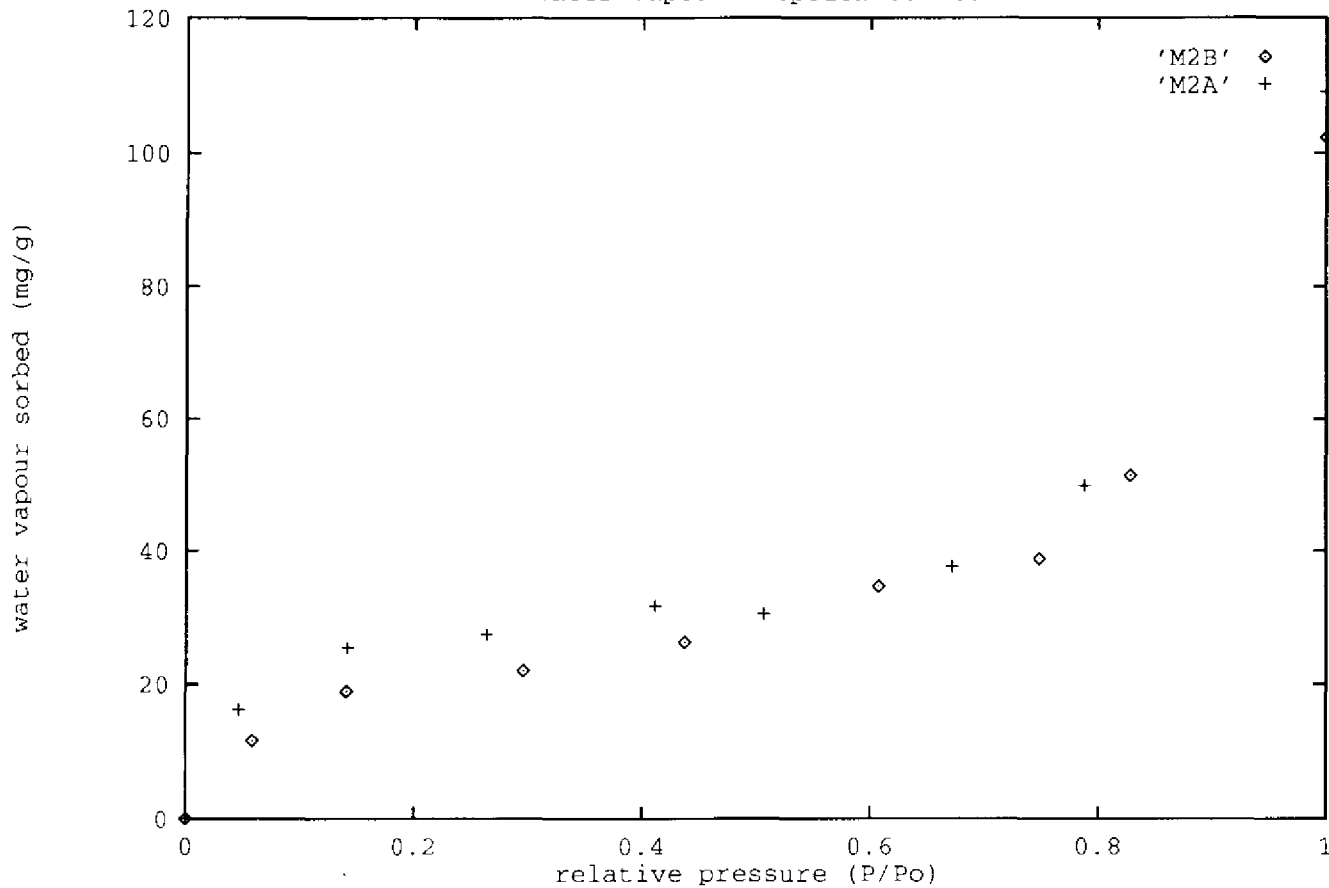
water vapour sorption curves

Fig.1

12

water vapour sorption curves

Fig.2

13

water vapour sorption curves

'M2B' ◇
'M2A' +

water vapour sorbed (mg/g)

relative pressure (P/Po)

Fig. 3

water vapour sorption curves

'M3B' ◇
'M3A' +

water vapour sorbed (mg/g)

relative pressure (P/Po)

Fig. 4