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SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF HEATED SOILS

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CHARACTERISTICS OF HEATED SOILS

SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF HEATED SOILS

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FIGURE LEGENDS:

- FIG. 1 Particle size distribution as a function of soil heating temperature.
- FIG. 2 Cation exchange capacity as a function of soil heating temperature.
- FIG. 3 Lime content as a function of soil heating temperature.
- FIG. 4 The pH as a function of soil heating temperature.
- FIG. 5 Organic carbon content as a function of soil heating temperature.
- FIG. 6 Water and NH_4OAc extractable Ca in relation to soil heating temperature.
- FIG. 7 Water and NH_4OAc extractable Sr in relation to soil heating temperature.
- FIG. 8 Water and NH_4OAc extractable Mg in relation to soil heating temperature.
- FIG. 9 Water and NH_4OAc extractable K in relation to soil heating temperature.
- FIG. 10 Water and NH_4OAc extractable Na in relation to soil heating temperature.
- FIG. 11 Electrical conductivity of saturation extracts of heated soils.

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The Chemical Rubber Co., Cleveland, Ohio.

TABLE I

Average percentage of total nitrogen in heated soils

Heating Temperature °C	S o i l				
	Hanford	Vina	Aiken	Soil No. 1SG	Soil No. 4FF
Control	0.049	0.130	0.130	0.108	0.016
100	0.048	0.131	0.125	0.108	0.016
200	0.047	0.130	0.125	0.103	0.015
300	0.027	0.081	0.076	0.081	0.010
400	0.013	0.043	0.028	0.049	0.008
500	0.002	0.008	0.008	0.005	0.002
600	**	**	**	*	**
800	*	**	**	*	**
1,000	*	*	*	*	*

* Not detectable; ** Trace.

TABLE 2

Solubility of reagent grade CaCO_3 and CaO in H_2O and in neutral normal NH_4OAc

Compound	Solubility in H_2O g./100 ml	Solubility in NH_4OAc g./100 ml
CaCO_3	0.00039	0.032
CaO	0.057	0.250

SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF HEATED SOILS

H. Nishita and R. M. Haug

It is known that the soil in the immediate vicinity of a nuclear detonation is exposed to heat ranging in temperature well above that causing fusion of geologic materials down to the ambient level. Our interest in heated soils stems from the fact that aside from the effect of ionizing radiation, one of the factors that needs to be known in assessing the growth response of plants in the immediate vicinity of a nuclear detonation is the effect of soil heating on the availability of the essential nutrient and nonessential elements to plants. Our previous paper (6) has discussed the growth and the elemental composition of bean plants grown in a soil that was exposed to different temperatures up to 1,000 ° C. Heating above 1,000 ° C caused the soil to become fused and unsuitable for plant growth. A brief review of the literature was also presented in the previous paper (6).

This paper gives several physical and chemical characteristics of five different soils after heating at various temperatures. The properties examined include particle size distribution, pH, cation exchange capacity, electrical conductivity, water and ammonium acetate extractable Na, K, Mg, Ca and Sr, and total N, lime and organic C contents.

MATERIALS AND METHODS

Five soils of widely different chemical and physical characteristics, which will be described in the text below, were used in this study. Soil No. 1SG was a saline-calcareous soil with montmorillonite as its pre-dominant clay mineral. Soil No. 4FF was a nonsaline, highly calcareous montmorillonitic soil. Hanford sandy loam and Aiken clay loam were slightly acidic soils with illite and kaolinite, respectively, as their predominant clay minerals. Vina loam was a slightly alkaline, montmorillonitic soil.

The heated soils were prepared by exposing the soils to various temperatures (100, 200, 300, 400, 500, 800 and 1,000 °C) for one hour in a temperature-calibrated muffle furnace. The soils were heated in Pt crucibles for treatments up to 600 °C. Alundum crucibles that were previously heat conditioned were used for the 800° and 1,000° treatments. As a precautionary measure against contamination from alundum, only that portion of the soil mass that was not in contact with the crucible during heating was taken for experimentation. To minimize the differential oxidation from the surface to bottom, which was observed previously (6), the thickness of the soil mass in the crucibles was always kept < 12 mm.

The soils were prepared for analysis as follows. Twenty-five g. aliquots of air-dry soil were mixed with 50 ml. of double distilled water in Phillip's beakers and allowed to stand for about 14 hours with occasional mixing. The samples were then transferred to a Buchner funnel

(Whatman No. 42 filter paper) and leached with small aliquots of double distilled water until 500 ml. of leachates were collected. The ions in these leachates are called "water extractable ions" in this paper. Immediately following the water leaching, the samples were leached with neutral normal ammonium acetate (NH_4OAc) using small aliquots until 500 ml. of leachates were obtained. The ions in these leachates are designated as " NH_4OAc extractable ions". Alternatively, these ions may be considered as "exchangeable ions".

The extractable cations (Na, K, Mg, Ca and Sr) were determined by the use of an atomic absorption spectrophotometer (Perkin-Elmer Corp., Model 303). The cation exchange capacity determinations were made by distillation of adsorbed ammonia after extraction with acidified 10 per cent NaCl solution (7). The soil pH determinations were done on 1:1 suspensions using the glass electrode technique. The Allison method (1) was used to determine the organic and inorganic carbon. The saturation extracts of the soils were prepared according to Richards et al (8). The mechanical analysis was done by the piper method (5). The total N was determined with Coleman Model 29A Analyzer II using one g. aliquots of soil ground to pass through a 100-mesh screen. The operating parameters for the apparatus were essentially that prescribed by Keeney and Bremner (4).

RESULTS AND DISCUSSION

Figure 1 shows the particle-size distribution as a function of soil heating temperature. In general, the particle size distribution remained

unchanged until the heating temperature was in the 300° to 400° C range. Above this temperature range, the sand fraction in all soils, except soil No. 4FF, increased progressively with increasing temperature, while the silt and the clay fractions decreased. In soil No. 4FF, the sand fraction peaked at 800° C and then decreased. This decrease was compensated for by a large increase of the silt fraction. Otherwise, the silt fraction in all of the soils peaked at 400° C. The clay fraction always continued to decrease with increasing heating temperature above 300° C. The increased aggregation may be due to calcination in which iron oxides and aluminosilicates are involved (2).

The cation exchange capacity (CEC) generally decreased progressively with increasing temperature above 100° C (fig. 2). The CEC of two of the soils (Aiken c.l. and Vina l.) decreased rapidly above 200° C, while that of Hanford s.l. decreased more gradually. The effect shown by Aiken c.l. and Vina l. was due probably to their relatively high clay content. The aggregation of fine particles can cause a decrease of CEC. The aggregation of fine particles, however, is not the only factor contributing to the decrease of CEC. At the higher temperature levels, the dehydration of mineral crystal lattice and the resulting breakdown of the lattice structure can contribute to the CEC reduction also. In the lower temperature range in which the removal of crystal lattice water is minimal, simple drying of the colloidal particles may have had an influence. This is suggested by the fact that CEC started to decrease in the temperature range in which no apparent change of particle size distribution occurred. The two calcareous soils (No. 4FF and No. 1SG) differed from the non-calcareous soils in that the CEC decreased relatively slowly to around

600° C and then sharply above this temperature. This behavior of the calcareous soils appeared to be somewhat related to their lime contents (fig. 3). The lime content, particularly of soil No. 4FF, decreased sharply only after the temperature was raised above 600° C.

The pH of each soil decreased to a minimum at 200° C and then increased to higher values at higher temperatures (fig. 4). As discussed previously (6), the increase of pH may be due to the formation of oxides of several elements. Among the suggested reasons for the decrease are the oxidation of certain elements, the exposure of new surfaces, the dehydration of colloids and the resulting decrease of buffer action, and the increase of acid organic compounds.

The organic-C content of the soils generally changed only to a small extent for heating up to 200° C (fig. 5). It, however, decreased very rapidly with increasing temperature above 200° C and became nondetectable in the 600-800° C range. Since most of the soil N is in organic form, the total N was related to organic-C (table 1).

The water and the NH_4OAc extractable Ca, Sr, Mg, K and Na are shown in figures 6 through 10. In the figures, the numerical values of bar heights (usually above the shorter bars) are put in for convenience of comparison. The NH_4OAc extractable Ca in the noncalcareous soils (Hanford s.l., Aiken c.l. and Vina l.) decreased progressively with soil heating temperature above 100° C (fig. 6). At 1,000° C, it was only a small percentage of that for the control, i.e., Vina l., 1.52; Hanford s.l., 2.31; and Aiken c.l., 4.99 per cent. The water extractable Ca increased to a peak in the 300-400° C range and then decreased progressively with increasing temperature. From the results shown in figure 1, it may

be inferred that the decreasing Ca extractability above the 300-400° C range was due primarily to the aggregation of fine particles. In the calcareous soils (No. 1SG and No. 4FF), the NH_4OAc extractable Ca remained more or less constant to about 600° C and then increased drastically at 800° C. At 1,000° C it remained very high in soil No. 4FF, but decreased markedly in soil No. 1SG. The water extractable Ca in soil No. 1SG peaked at 600° C, while it increased drastically at temperatures above 600° C in soil No. 4FF. The difference between the two soils is probably accountable by the difference of their lime content. It will be noted in figure 3 that soil No. 4FF had very much higher lime content than soil No. 1SG.

It appears that the process of particle aggregation became ineffective in reducing Ca extractability when the lime content of a soil exceeded a certain level. The primary factor causing the marked increase of the extractability of Ca in calcareous soils at high temperatures probably was the conversion of CaCO_3 to CaO . This is supported by the fact that the lime content in the soils decreased sharply at temperatures above 600° C (fig. 3). Calcium carbonate begins to decompose into CO_2 at about 530° C under atmospheric pressure of 760 mm (10). Above 882° C, CaCO_3 is decomposed completely into the oxide. The solubility of CaO is much greater than CaCO_3 in both water and NH_4OAc (table 2). The greater solubility of these compounds in NH_4OAc may be explained as salt effect.

In general, the extractable Sr (fig. 7) behaved much like extractable Ca. This was expected since Sr reacts chemically somewhat like Ca.

In the noncalcareous soils, the NH_4OAc extractable Mg decreased with increasing temperature above 100° C, except at 600° C (fig. 8). Two of

the soils (Aiken c.l. and Vina 1.) showed a drastic increase at 600°C . The water extractable Mg showed two peaks -- one at 200°C and the other at 600°C . The peak at 200°C was much higher than at 600°C . In the calcareous soils, the NH_4OAc extractable Mg also increased sharply at 600°C , but the second peak of the water soluble Mg occurred at 500°C . In any case, all of the soils examined showed an increase of total extractable Mg at 600°C , indicating a more or less abrupt release of Mg around this temperature. It will be recalled that this enhanced Mg extractability at 600°C was reflected also in the increased Mg uptake by the plants grown in heated soils (6).

The soil component(s) causing the sharp increase of Mg extractability at 600°C has not been determined. Perhaps, one source might be the breakdown of the carbonates of Mg, particularly in the calcareous soils. The MgCO_3 occurs as the mineral magnesite. The natural, carbonate of Mg and Ca occurs as dolomite. These carbonates probably begin to decompose at lower temperature than CaCO_3 , which appeared to decomposed rapidly at about 800°C (fig. 6). According to Sidgwick (9), MgCO_3 is more readily dissociated by heat than any of the alkaline earth carbonates. Aside from the carbonate minerals, a number of minerals containing Mg in the crystal lattice or in the adsorbed form occur in soils. Among these are brucite, which is $\text{Mg}(\text{OH})_2$, and the alumino-silicates such as kaolinite, montmorillonite, illite, vermiculite, chlorite, etc. At sufficiently high temperatures, these minerals lose lattice OH water, resulting in the change or the breakdown of the crystal lattice structure. This in turn may render the Mg, if present, more readily extractable. In general, the temperature for the release of lattice OH water in alumino-silicate minerals occurs

in the range from about 300° to around 700° C (3). Dehydration of most minerals appear to be essentially complete around 800° C. The temperature for the peak loss of lattice OH water depends on the mineral. For example, the differential thermal curve for kaolinite show a sharp peak corresponding to the loss of lattice OH at 600° C, while that for halloysite occur at a somewhat lower temperature (3). In any case, Mg went through a soluble transition state(s) before being transformed into MgO, which is very insoluble (11).

Potassium differed from the alkaline earth cations in that under several heat treatments of soil No. 1SG and Hanford s.l., the water extractable K was greater than the NH_4OAc extractable K (fig. 9). This effect in soil No. 1SG was probably due primarily to its saline nature. The cause of this effect in Hanford S.l. has not been determined. In general, the water soluble K in the noncalcareous soils reached a peak at 200° C, while it peaked at 300° or 400° C in the calcareous soils. The NH_4OAc extractable K in the noncalcareous soils decreased slowly, if at all, to 400° C and then sharply above this temperature. In the calcareous soils, it peaked at 500° C and then decreased at higher temperatures. The effect of heating on the extractability of K was delayed in the calcareous soils.

Sodium differed from the other cations examined in that the water extractable fraction was generally much greater than the NH_4OAc extractable fraction (fig. 10). In the three noncalcareous soils, the water extractable fraction generally increased to a maximum and then decreased to a minimum and increased again to a small extent at higher temperatures.

The maximum extractability occurred in the 200° to 300° C range and the minimum in the 500° to 600° C range. The NH_4OAc extractable Na in these soils peaked in the 300° to 400° C range. In the two calcareous soils, the water and the NH_4OAc extractable fractions increased to a maximum and then decreased progressively with increasing temperature without showing the tendency to increase again at the higher temperatures. The behavior of Na was not entirely unexpected, since it generally forms soluble compounds and has lower adsorption energy in the soil exchange complex than the other cations examined.

Figure 11 shows the electrical conductivity of the saturation extracts of the heated soils. This figure in effect summarizes the water extractability of all ions. It is evident that the greatest extractability of ions in the noncalcareous and the saline calcareous soil No. 1SG occurred at 200° C. In soil No. 4FF, it occurred at 300° C. Perhaps, noteworthy is the much lower but a definite peak at 600° C shown by the noncalcareous soils. This probably was due, at least in part, to the sharp increase of the water soluble Mg at about 600° C (fig. 8). The soil No. 4FF was unique in that its saturation extracts showed a marked increase of conductivity above 600° C. The results shown in figure 6 indicate that this was due primarily to the increase of water-extractable Ca. Water-extractable Sr also increased in the high temperature range (fig. 7.) but its absolute concentration was much less than that of Ca.

GENERAL DISCUSSION

A question on whether or not the elemental variation in a given species

could be used to estimate the temperature to which soils had been heated was considered. Among the elements analyzed, Ca appeared to provide the only possibility for this with the restriction that the soil must be calcareous. This is indicated by the general constancy of the NH_4OAc extractability of Ca to 600°C and then a drastic increase at 800°C shown by soils No. 1SG and No. 4FF in figure 6. A drastic increase of the extractable Ca in the heated soil compared to the control might be interpreted as due to the heating of the soil to at least 800°C .

In general, the results of this study show that soil heating at high temperatures can greatly affect the chemical and physical characteristic of soils. Thus, soil heating could be an important influencing factor on the elemental composition and the growth of plants growing in heated soils.

SUMMARY

The physical and chemical characteristics of five different heated soils were examined. The properties examined include particle size distribution, pH, cation exchange capacity, electrical conductivity, water and ammonium acetate extractable Na, K, Mg, Ca and Sr, and total N, lime and organic C contents.

FIG. 1 Particle size distribution as a function of soil heating temperature.

FIG. 2 Cation exchange capacity as a function of soil heating temperature.

FIG. 3 Lime content as a function of soil heating temperature.

FIG. 4 The pH as a function of soil heating temperature.

FIG. 5 Organic carbon content as a function of soil heating temperature.

FIG. 6 Water and NH_4OAc extractable Ca in relation to soil heating temperature.

FIG. 7 Water and NH_4OAc extractable Sr in relation to soil heating temperature.

FIG. 8 Water and NH_4OAc extractable Mg in relation to soil heating temperature.

FIG. 9 Water and NH_4OAc extractable K in relation to soil heating temperature.

FIG. 10 Water and NH_4OAc extractable Na in relation to soil heating temperature.

FIG. 11 Electrical conductivity of saturation extracts of heated soils.