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REDISTRIBUTION OF TRACE ELEMENTS UPON THE WEATHERING OF VOLCANIC ASH SOILS IN COSTA RICA

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**CENTRO AGRONOMICO TROPICAL DE
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GANADERIA DE COSTA RICA (MAG)**

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Summary

Redistribution of trace elements upon weathering over Al/Fe-humuscomplexes and amorphous minerals was studied in a sequence of soils derived from andesitic ash on the Turrialba volcano in Costa Rica. All profiles are located on the northern slope where the mean annual precipitation reaches up to 8000 mm (Nieuwenhuyse, not published). The profiles were described, and both undisturbed core samples and field moist samples were taken. A part of the samples was analyzed, the analyses done include selective dissolution and total chemical analysis with XRFS.

Dry bulkdensities increase from 0.25-0.40 g/cm^3 in the profiles at lower altitudes to 0.90-1.40 g/cm^3 in the profiles at higher altitudes. At the same time moisture contents decrease from about 300% in the profiles with low altitudes to about 90% in the profiles with high altitudes. There is a large difference between the measured CEC and the derived effective CEC. The measured CEC is too high due to adsorption of Mg^{2+} along with SO_4^{2-} by amorphous minerals. Total C contents reach up to 20%. The top of each profile, except of profile T3, is pure non-allophanic, while the bottom is pure allophanic.

With two sets of graphs the interaction between trace elements and organic matter and allophane was studied. Zr was used as reference. The first set shows the contents of trace elements versus the organic matter content. To exclude the diluting effect of organic matter a second set was prepared showing the interaction between trace elements and allophane. Both sets show that the profiles are devided into two groups (T1, T2 and T3 versus T4-T8) and that important processes in the partitioning of trace elements are physical and chemical weathering.

This approach, together with the other results, has led to the following conclusions. CEC determination using $MgSO_4$ gives CEC values which are too high. Soils at lower altitudes (640-950 m) show more progressive weathering than soils at higher altitudes. Co, Cu, Ga, La, Pb, V and Zn form complexes with organic matter. Cr, Co and V are bound to allophane. Since V is bound to organic matter and allophane, V would be of limited use as a reference element. The present study is based on bulk data only, therefore further research is neccesary.

Contents

Appendixes

1 Introduction

Costa Rica is part of a volcanic chain that covers Central America and which is part of the Circum Pacific Fire Ring. More than 200 volcanic centres have been recognized in Costa Rica (Alvarado, 1993). One of these centres is the Turrialba volcano, where the samples used in this research were taken. The Turrialba is a stratovolcano, which has alternating layers of lava and pyroclastic material such as volcanic ash.

Volcanic ash consists for the greater part of volcanic glass and thus weathers rapidly. During weathering amorphous clay minerals can be formed, the most important being allophane and imogolite. At the same time humus can form complexes with aluminium- and iron-ions. Andesitic ash has a high content of trace elements which are partly set free upon weathering. After liberation the trace elements are either transferred to humuscomplexes and/or amorphous clay minerals or are leached out to the groundwater.

The aim of this student research is to study the redistribution of trace elements over Al/Fe-humuscomplexes, amorphous clay minerals and crystalline minerals upon the weathering of volcanic ash soils in a sequence on the Turrialba volcano in Costa Rica. I studied the trace elements Ba, Co, Cr, Cu, Ga, La, Nb, Ni, Pb, Rb, Sr, V, Zn and Zr. Information on the partioning of trace elements gives more insight in the development of natural background levels of trace elements in soils. This is of interest because of the increased attention for soil pollution. Unfortunately, because of lack of time, I could not analyse all samples. Also there was not enough time to perform all the originally planned analyses. However, it seems that there is enough information to draw some conclusions about the partioning of trace elements. This report is an attempt to draw those conclusions.

2 Background information

2.1 Volcanic ash soils

Volcanic ash soils, also called Andosols, are relatively young soils that developed in pyroclastic material and whose colloidal fraction is dominated by short-range-order minerals and/or Al-humuscomplexes (ICOMAND, 1988). Usually the parent material is volcanic ash, but it can also be tuff, pumice, cinders, lahars and other volcanic ejecta. Andosols possess very distinctive properties which determine the chemical characteristics. The most important characteristics being high content of soil organic matter, variable and pH-dependent ion exchange capacity and the presence of active aluminium and iron. Active aluminium and iron occur as paracrystalline aluminosilicates, interlayer Al-ions in layersilicates, Al/Fe-humuscomplexes, exchangeable Al^{3+} and ferrihydrite. Other properties are low bulkdensity, thixotropy, strong affinity for phosphate ions, strong reaction with fluoride under the liberation of hydroxyl ions, difficult dispersion, high water content and irreversible drying. (Mizota and Van Reeuwijk, 1989; Nanzyo *et al.*, 1993; Inoue, 1986).

A weathering sequence for minerals in volcanic soils is according to Raiesi Gahrooee (1994): volcanic glass + feldspar $\rightarrow$ allophane $\rightarrow$ halloysite $\rightarrow$ metahalloysite $\rightarrow$ gibbsite. A parameter estimating the weathering status of a soil is the activity ratio, Fe_o/Fe_d, in which Fe_o stands for the oxalate extractable Fe and Fe_d stands for the dithionite-citrate extractable Fe. Fe_o/Fe_d is an index for the degree of crystallinity or "age" of iron oxides. Values for (young) andosols are usually higher than 0.75, whereas for older soils the values are much lower (Mizota and Van Reeuwijk, 1989). Important parameters that influence weathering are temperature, rainfall regime, texture and vegetation. The rate of chemical weathering of tephras increases with increasing temperature and leaching (Shoji *et al.*, 1993; Walraven, 1994), grasses tend to foster andosolisation whereas forest promotes podzolisation (Arai *et al.*, 1986; Mizota and Van Reeuwijk, 1989; Shoji *et al.*,1993). There can be an admixture of accessory or accidental minerals and of minerals from eolian dusts (Shoji *et al.*, 1993).

Andosol formation is essentially the weathering of parent material in the presence of organic matter. Initial weathering is probably strongly influenced by sulphuric and hydrochloric acid produced by dissolution of volcanic gases in water. This results in an extensive liberation of elements and reprecipitation of silica (Raiesi Gahrooee and Buurman (a), not published) Al- and Fe-ions that are released during weathering are complexed with organic matter forming Al/Fe-humuscomplexes. There is a strong accumulation of organic matter in the topsoil. This is because these complexes are protected against bio-degradation by the toxicity of aluminium and by the inaccessibility of the organo-metallic complexes to enzymes (Mizota and Van Reeuwijk, 1989; Inoue, 1989). In addition to this Al/Fe-complexes are immobile owing to their high metal/organic ratio, caused by the rapid weathering yielding much Al and Fe (Mizota and Van Reeuwijk, 1989). Al not tied up in humuscomplexes reacts with Si to form amorphous clay minerals, predominantly allophane and imogolite and, under certain circumstances, halloysite. According to Dahlgren *et al.* (1993) allophane and imogolite can be found in soils where the $(Al_p+Fe_p)/C_p$ ratio exceeds 0.1, where Al_p, Fe_p and C_p stand for pyrophosphate extractable Al, Fe and C. A value of 0.1 for $(Al_p+Fe_p)/C_p$, represents the saturation of humus with Al- and Fe-ions. Fe that is not complexed by organic matter can form ferrihydrite, excess Si can precipitate in the form of opaline silica.

The soil pH is of great importance in the formation of amorphous clay minerals. The formation of allophane/imogolite is favoured by pH values of 5-7, whereas lower pH values favour the formation of metal-humuscomplexes. Because the environment in which the soil formation takes place changes constantly, andosols usually have a binary composition, the soils contain both Al/Fe-humuscomplexes and allophane/imogolite. A good parameter estimating the binary composition of a soil is the binary ratio, Al_p/Al_o, where Al_p stands for the pyrophosphate extractable Al and Al_o stands for the oxalate extractable Al. The binary ratio ranges from 0 for true allophanic soils to 1 for true non-allophanic soils (Mizota and Van Reeuwijk, 1989; Nanzyo *et al.*, 1993).

There is an abundance of trace elements in andesitic ash. Upon weathering these elements are repartioned over the soil constituents. Some expectations about the behaviour of trace elements can be formulated. Monovalent ions like Rb^+ and some divalent ions, for example Ba^{2+}, behave similar to Na^+ and K^+. Like Na^+ and K^+ they can be adsorbed by clay and by organic matter. Similarly to Ca^{2+} and Mg^{2+}, Ba^{2+} and Sr^{2+} do not form strong complexes with organic matter. Other divalent and trivalent elements do, for example Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and La^{3+}. Ions that have similar sizes to Al, Mg or Si can substitute these in the lattice of layer silicates and probably also in the allophane and imogolite structure. V, Ga, Ti, Ni, Zn and Cr are known to substitute for Si. Ti, P, Ni, Co and Zn occur in appreciable amounts in allophane. (Aller *et al.*, 1989; Raiesi Gahrooee and Buurman (b), not published). According to Nanzyo *et al.* (a) (1993) especially Pb and Cu, and to a lesser extent Zn, accumulate in allophane. However Cu, Pb and P are bound to the surface rather than substituting for ions in the lattice.

2.2 Setting

Costa Rica is located in the southern part of Central America between Panama and Nicaragua. The western boundary of the country is formed by the Pacific Ocean, the eastern boundary is formed by the Caribbean Sea. Volcanism in Costa Rica is generated by subduction of the Cocos and Nazca plates underneath the Caribbean plate (Nieuwenhuyse, not published). This caused the uplift of a mountain range that crosses over the country. More than 200 volcanic centres have been recognized in Costa Rica, most of them are located in this mountain range (Alvarado, 1993).

During fieldwork in Costa Rica profiles were described and samples were taken on the Turrialba and the Rincón de la Vieja volcanoes and to the west of the Arenal volcano. nearby the Arenal lake. Figure 2.1 (p5) shows the location of the volcanoes.

In this study only the profiles described and the samples taken on the Turrialba volcano are used. Therefore only the profile sites located on the Turrialba are treated. The last recorded activity of the Turrialba was in 1864-1866 (Alvarado, 1993). The climate in the Caribbean is hot and humid throughout the year, with a mean annual temperature of 25 to 27 °C and with a relative air humidity reaching daily values of 85 to 90% (Nieuwenhuyse, not published). Climate in the central mountainous regions varies greatly at short distances, temperatures on the eastern slopes decrease with altitude with about 0.52 °C every 100 m (Nieuwenhuyse, not published). On the caribbean side the rainfall increases with altitude at the transition lowland-central mountain ranges, high orographic rainfall occurs on the lower and middle (north)eastern slopes of the mountains, with mean annual values reaching up to 8000 mm (Nieuwenhuyse, not published).

Profiles were described and samples were taken at the caribbean side of the Turrialba volcano, from an altitude of 640 m to an altitude of 3160 m, with intervals of about 500 m. After describing a profile, two or three undisturbed core samples and one moist sample were taken from each horizon. The locations of the sample sites, T1 through T8. are shown in Figure 2.2 (p6). Short profile descriptions can be found in Appendix 1.

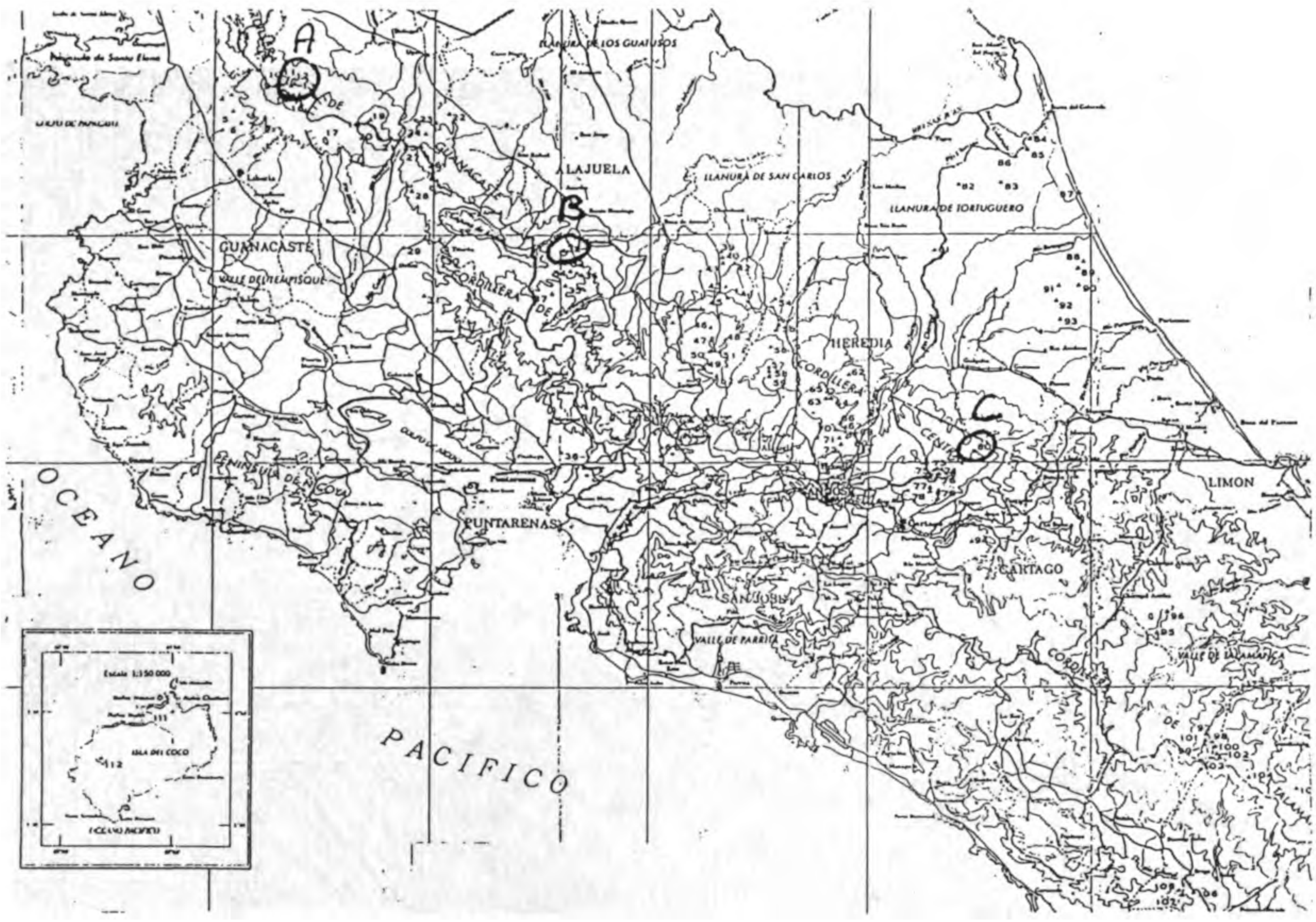


Fig. 2.1 Volcanoes of Costa Rica. Rincón de la Vieja (A), Arenal (B) and Turrialba (C). From Aparatos volcanicos de Costa Rica. Observatorio vulcanologico y sismologico de Costa Rica, Universidad National, 1987.

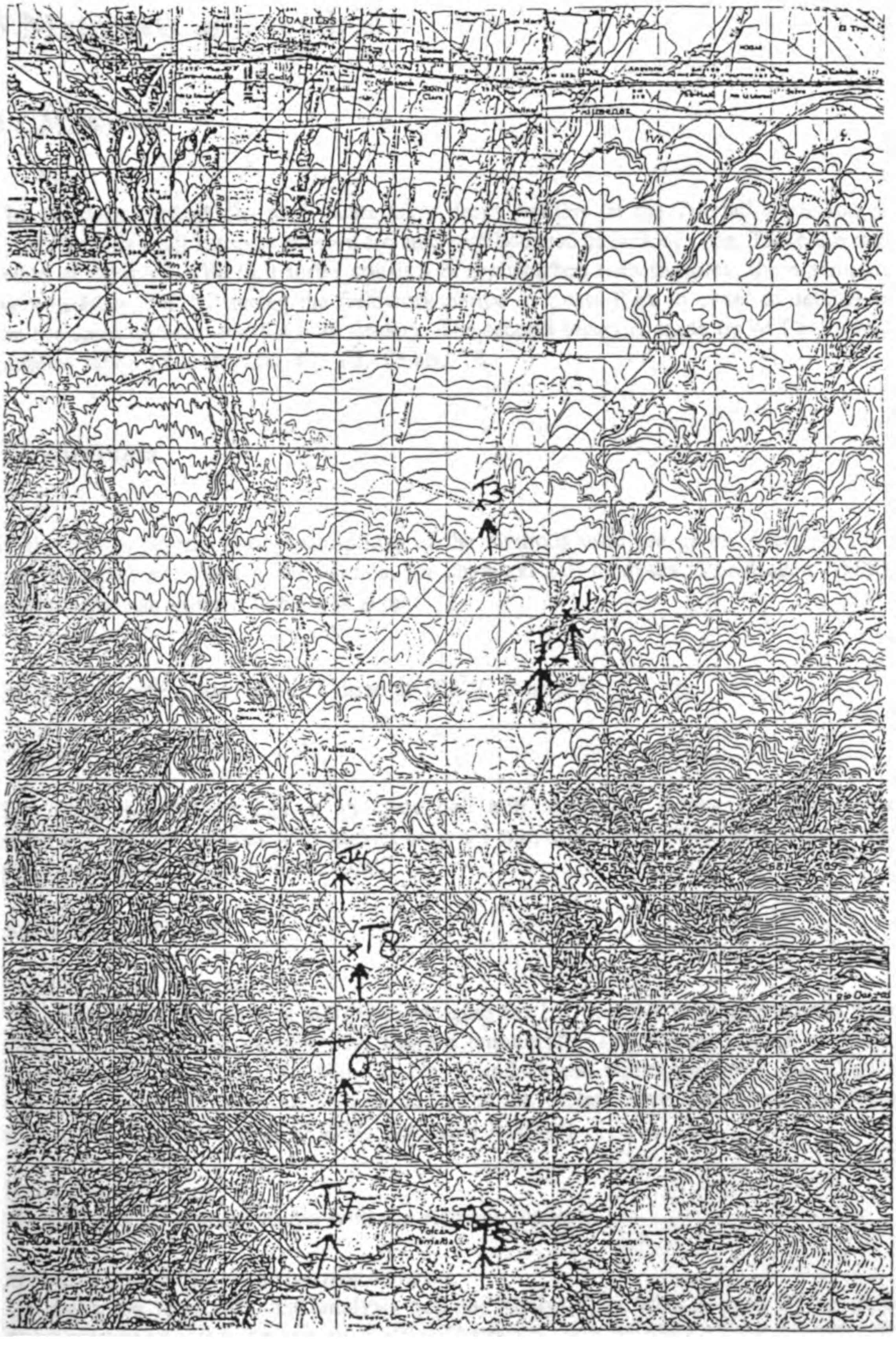


Figure 2.2 Locations of the sample sites T1 through T8. On part of a map of Costa Rica from Instituto Geografica Nacional, San José, Costa Rica.

3 Materials and methods

3.1 Materials

The samples used in this study were taken from profiles on the Turrialba volcano in Costa Rica. Not all samples taken were analysed because of lack of time. There are two series of samples. The first series consists of undisturbed core samples, these samples were dried at 105 °C during the fieldwork period in Costa Rica in order to determine the moisture content and the bulk density. The second series is made up of field moist samples taken from profiles T1, T2, T3 and T8.

3.2 Methods

In the following text short descriptions of the methods used are given. More detailed protocols can be found in the Manual for chemical soil analyses (Van Lagen, 1993), except when an other reference is given.

3.2.1 Undisturbed core samples dried at 105 °C (series I)

Pretreatment

The samples were crushed in an agate ball mill, thereafter stones and roots were removed and the samples were sieved over a 1 mm sieve. A part of each sample was pulverised using the Sialon Micromill.

Analytical techniques

Total chemical analysis
The samples were ignited at 900 °C to measure the L.O.I. After that glass tablets were made by melting the sample with lithium tetraborate. The concentrations of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P) and minor elements (Ba, Co, Cr, Cu, Ga, La, Nb, Pb, Rb, Sr, V, Zn and Zr) in the tablets were determined by X-ray Fluorescence Spectrometry (XRFS). (protocol Kuijper).

Total C and N
Total C and N were measured with the element analyzer.

Moisture content of the pulverised samples
For both the total chemical analysis and the analysis for total C and N the dried pulverised material is the reference state. Therefore, after grinding of the samples, the moisture content was determined again by drying the samples at 105 °C.

3.2.2 Field moist samples (series II)

Pretreatment

Field moist samples were used for chemical analysis because of irreversible changes that take place during drying in soils containing allophane. In order to homogenize the samples roots and stones were removed from the soil samples, thereafter the samples were homogenized with a mixer and sieved over a 2 mm sieve. It was necessary to add some extra water (about 30 ml) to the samples, otherwise the mixer could not be used.

Analytical techniques

Moisture content
The moisture content was determined by drying the samples at 105 °C, because the reference state for the following chemical data is the dried material. Since the moisture content of the moist material may change with time, the moisture content was measured three times with intervals of about one month.

pH
The pH-H_2O was determined in a water suspension prepared of moist material, in a dry-soil/solution ratio of 1:5 after 2 hours shaking.

The pH-KCl was measured in the same way using a 1 M KCl solution instead of water.

The pH-NaF was measured in a suspension of 1 g soil in 50 ml 1 M NaF after 2 minutes shaking (Van Reeuwijk, 1992).

P-retention
By Blakemore's procedure. The samples were treated with a 1000 mg P/l KH_2PO_4 solution of pH=4.6. After shaking overnight the remaining P in this solution was measured colorimetrically.

CEC and exchangeable bases
The exchangeable bases were removed by leaching with 0.1 M $BaCl_2$. In the leachate the concentrations of Ca and Mg were measured by Atomic Adsorption Spectrometry (A.A.S.), the concentrations of Na and K were determined by Atomic Emission Spectrometry (A.E.S.). Thereafter the soil solution was brought to an ionic strength of 0.01 M with 0.0025 M $BaCl_2$. Then the Ba at the exchange complex was removed with 0.02 M $MgSO_4$, the remaining Mg in solution was measured using the A.A.S.

Exchangeable Al
The samples were extracted with 1 M KCl. In the extracts Al was measured colorimetrically using an auto analyzer.

Dithionite-citrate, oxalate and pyrophosphate extractions
To determine the "free" Al and Fe the soil was extracted with a 17% citrate/1.7% dithionite buffer in a dry-soil/solution ratio of 1:60. After shaking overnight Al and Fe

in the extracts were measured with the A.A.S.

The "amorphous" Al, Fe and Si were extracted in an acid oxalate solution with a dry-soil/solution ratio of 1:100. The solution was shaken for four hours in the dark, after that the elements were measured by A.A.S. Hoe vaak? 2x (vragen aan Frans)

In order to measure the organically bound Al and Fe, and C from these complexes the samples were extracted with a sodium pyrophosphate solution of pH>9 in a dry-soil/solution ratio of 1:100. After shaking overnight Al and Fe in the extracts were measured using the A.A.S., the extracted C was measured using the element analyzer.

Particle-size distribution
The particle-size distribution was determined with a Laser particle-sizer. This was done without pretreatment of the moist sample.

4 Results and discussion

The analytical results are given in appendices 2, 3, 4, 5, 6 and 7. Appendix 2 contains the results of the measurements for particle-size distribution. In appendix 3 bulk densities and mass losses upon drying can be found. Appendix 4 contains the general soil data, appendix 5 total C and total N and appendix 6 the selective dissolution data. The results of total chemical analysis can be found in appendix 7.

4.1 Physical analysis

Particle-size analysis is done on field moist samples from profiles T1, T2, T3 and T8 (series II). Bulkdensities and moisture contents are determined on all undisturbed core samples (series I).

4.1.1 Particle-size analysis

Particle-size analysis is done without pretreatment of the samples. In figure 4.1 the the 50-percentile values of the particle-sizes is set out against the altitude. The top of each profile is given the right altitude, while the depth within the profile is exaggerated. For example, the Ah2 of profile T3 is positioned at 6.31 and the Bw at 5.85.

A 50-percentile particle-size means that 50 volume percent of the sample consists of particles having a smaller particle-size. For most samples the 50-percentile is smaller than 63 µm. Exceptions are samples 11, 12, 39, 40, 42, 43 and 46. Samples 39, 40, 42, 43 and 46 are taken from profile T8 which is located at a higher altitude, thus closer to the crater, and may therefore have larger particle-sizes. The samples from this profile with a 50-percentile particle-size smaller than 63 µm are taken from horizons that are thixotropic (appendix 1).

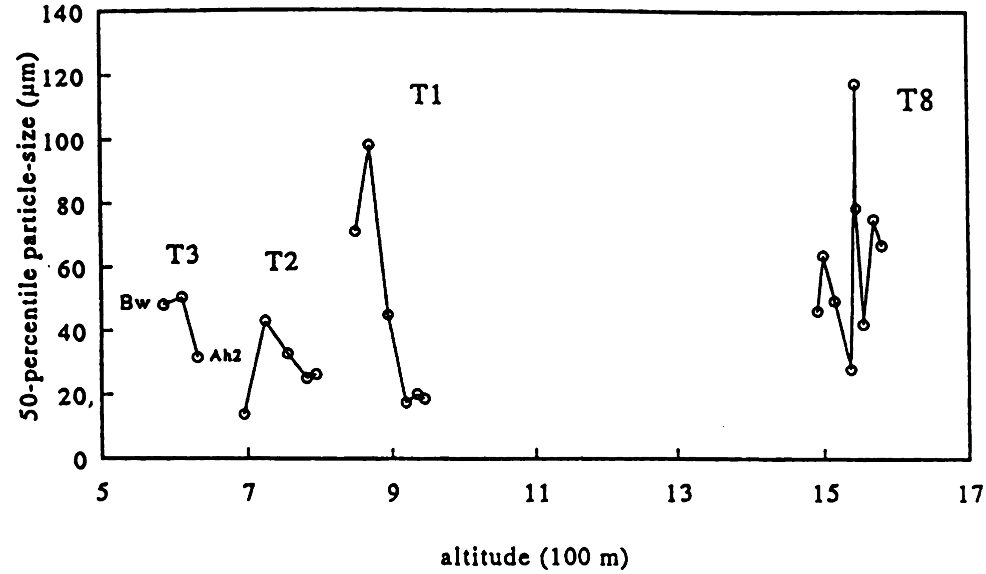


Figure 4.1 50-Percentile values of the particle-sizes against altitude.

4.1.2 Dry bulk density and moisture content

A low dry bulk density and a high moisture content are associated with the predominance of non- and paracrystalline constituents in the clay fraction or with the predominance of soil organic matter. The bulk density of the fraction < 2 mm, measured at pF=2, becomes less than 0.9 g/cm^3 (andic soil property requirement (Mizota and Van Reeuwijk, 1989)) when the allophane content is greater than about 5% (Nanzyo *et al.* (b), 1993). Non-allophanic andosols meet this requirement when the content of soil organic matter is greater than about 3% (Nanzyo *et al.* (b), 1993).

In this study dry bulk densities were determined, this was done on the complete samples. Figure 4.2 shows that the dry bulk density decreases with increasing altitude. Dry bulk densities in the profiles with low altitudes are very low, about 0.25-0.40 g/cm^3, suggesting a high amount of noncrystalline clays and/or soil organic matter. Since bulk densities in profiles T1, T2, and T3 decrease with increasing depth, they probably have a high content of amorphous clay minerals in the lower horizons. The samples from profiles T6 and T7 have higher bulk densities than the other samples.

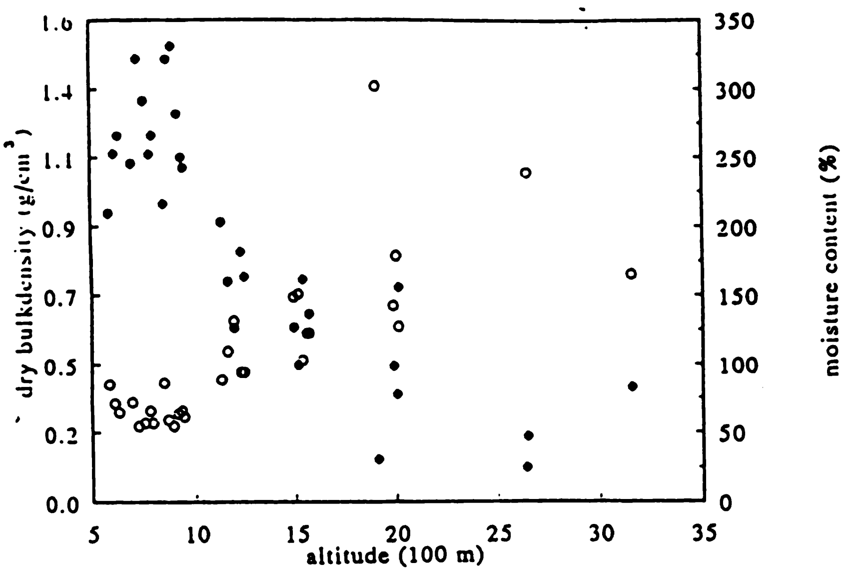


Figure 4.2 Dry bulk density and moisture content against altitude. ○: dry bulk density; ●: moisture content.

Figure 4.2 also shows that moisture contents decrease with increasing altitude. The determined moisture contents are very high, values as high as 300% have been found for samples from profiles at low altitude. At high altitudes moisture contents are lower, but still exceed 90%. High moisture contents and low bulk densities were expected especially for profiles T1, T2 and T3 (lower altitudes), because they are thixotropic throughout the profile. Of the profiles at higher altitudes T6, T7 and T8 have some horizons that are thixotropic, while T4 and T5 are non-thixotropic throughout the profile (appendix 1).

After grinding the loss on drying at 105 °C was determined again. Figure 4.3 shows that the ground samples still contain some water. Figure 4.3 also shows that the amount of retained water increases when original water content increases, this water lost is held by amorphous clay minerals in very small pores within aggregates.

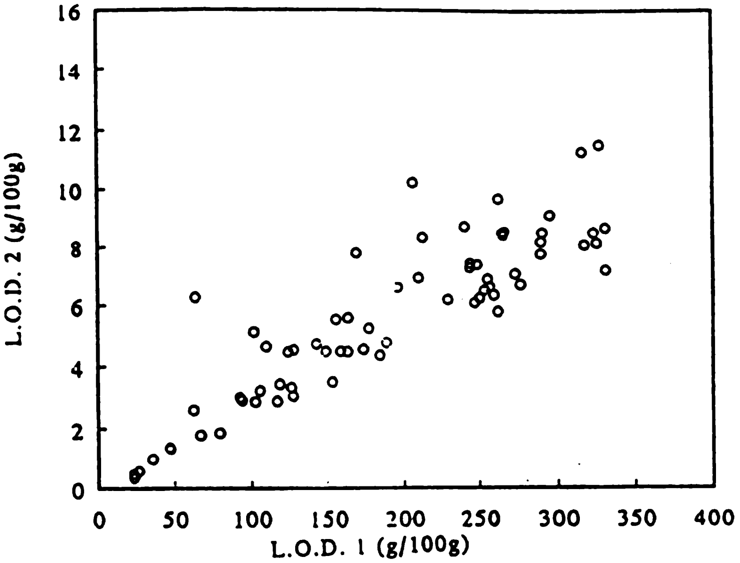


Figure 4.3 The first loss on drying (L.O.D. 1) versus the second loss on drying (L.O.D. 2).

4.2 Chemical analysis

Chemical analysis was done on samples from profiles T1, T2, T3 and T8 (series II). Analysis for total C and total N was done on all samples from series I and on some from series II, namely on samples 23, 23a, 39, 42, 43 and 46.

4.2.1 Moisture content

Moisture contents were determined for the pretreated samples of series II, this was done because the used reference state for the chemical data is the dried material. Determination of the moisture content was necessary, because during pretreatment of the samples from series II some extra water was added. Since the moisture content may vary with time, the moisture content was determined three times with intervals of about one month. Figure 4.4 shows that there was little change in the moisture contents with time.

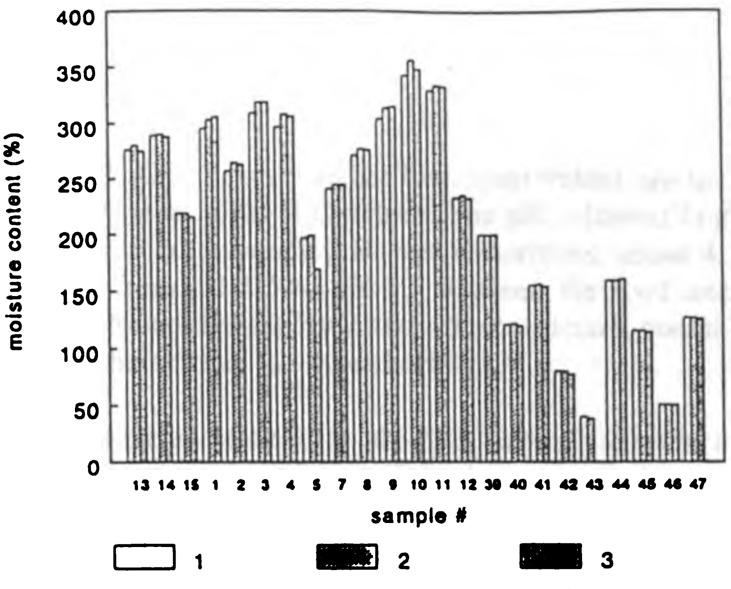


Figure 4.4 Comparison of different moisture contents. For each sample the moisture content was determined three times, with intervals of about one month.

4.2.2 Total C and total N

Both total C and total N decrease with depth within the profile. Values for total C are high, values as high as 20% have been measured. Total N varies from 0 to 1.7%. The relation between total C and total N can be seen in Figure 4.5. The slope of the regression line is the C/N quotient, which equals 12 (r^2 = 0.93) and which falls within the range of C/N ratios most occurring in andosols (12-16) (Arai *et al.*, 1986). Sample 24 has a relatively high C/N quotient, it originates from the Ah1 of profile T5, which has abundant roots. Sample 39 from the Ah1 of profile T8 has a relative low C/N quotient, possibly due to a measurement error resulting in an N value which is too low.

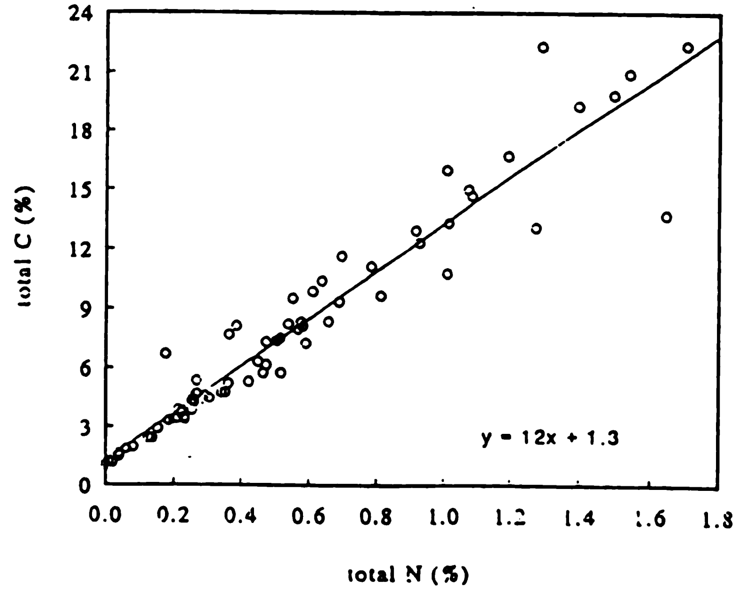


Figure 4.5 Total C against total N, r^2 of the regression line equals 0.93.

4.2.3 Soil acidity

Measured pH-H_2O values are rather low, most values are lower than 6. There appears to be a general trend in pH-H_2O values. The pH is lowest in the A-horizons, about 4-5, and higher in the corresponding B- and C-horizons, about 4.5-6.5. In profile T1 there is a transition from pH 6.5 to pH 5.3 between the Bw1 and the Bw2. Buurman and Meijer (1995) found that the Bw2 has a finer structure, contains more sexquioxides and is further weathered than the other horizons.

pH-KCl shows the same trend as pH-H_2O, lowest values in the A-horizons and higher values in the corresponding B- and C-horizons. In the A-horizons the pH-KCl is often higher than the pH-H_2O. For the horizons at greater depth the differences between pH-H_2O and pH-KCl are very small, and for many samples less than zero. This indicates a low humus content, low extractable Al and the presence of para-crystalline aluminosilicates in those horizons (Nanzyo *et al.* (a), 1993).

4.2.4 Fluoride reaction and phosphate retention

Although pH-NaF is not used anymore as a parameter for soil classification, it can still be used as an additional characteristic for andosols. All samples show a strong reaction with fluoride. An exception is the Ah1 of profile T8 that doesn't react as strongly as the other samples, it has a pH-NaF of 9.1 (one of the criteria for andosols was a pH-NaF > 9.4 (Mizota and Van Reeuwijk, 1989)). Thus in this sample no allophane is expected. this is also shown by the amount of Si extracted with acid oxalate, which is zero.

Phosphate retention, also a reaction caused by active Fe and Al, largely follows the same pattern as pH-NaF. All samples except for samples from the Ah1, 3CB and ash of profile T8, have a phosphate retention higher than 85% (criterium for andosols (Mizota and Van Reeuwijk, 1989)).

4.2.5 Exchangeable Al, exchangeable bases and CEC

Aluminium ions extracted by a 1 M KCl solution represent the exchangeable Al retained by the exchange complex. Extracted amounts are all very low, about 0-0.2 cmol(+)/kg. The A-horizons of profiles T1, T2 and T8 have somewhat higher extractable Al, about 1-7.4 cmol(+)/kg.

CEC is very high, values as high as 30 cmol(+)/kg have been found. These values are too high for andosols. The high CEC can be explained by adsorption of sulphate on amorphous minerals. If sulphate is adsorbed, magnesium is adsorbed also and the measured CEC is too high. In contradiction to the high CEC, the effective CEC (here sum of exchangeable bases and exchangeable Al) is very low, about 0.1-10.5 cmol(+)/kg. Since in a perhumid climate all the bases are leached out to the groundwater, a low contribution of exchangeable bases to the CEC is expected.

In figure 4.6 the difference between the CEC and the effective CEC is set out against the amount of silica extracted with acid oxalate. The difference increases with increasing Si_o, this means that the difference insreases with increasing allophane content, so the high CEC is probably caused by sulphate adsorption on allophane.

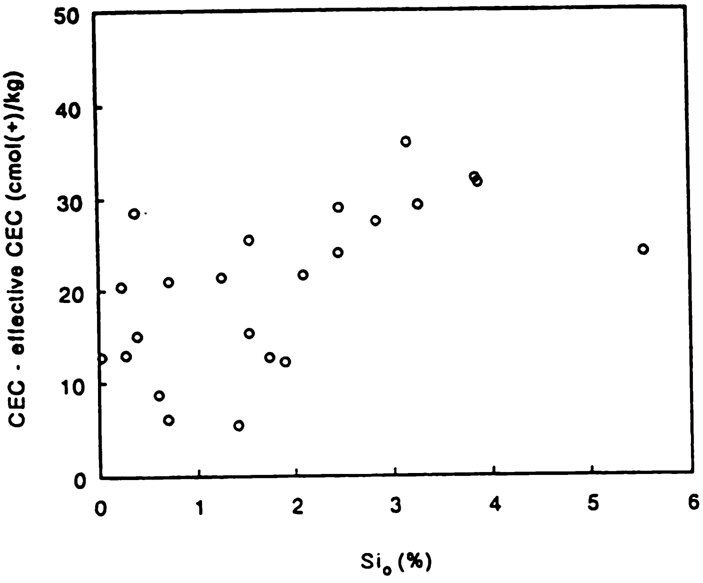


Figure 4.6 Difference between CEC and effective CEC against Si_o.

4.2.6 Selective dissolution data

Amounts of C in organic complexes, determined by extraction with pyrophosphate, are high. They vary from about 2 to about 10%. The C_p for samples containing ash is lower, about 0.5%. The relation between organically bound Al and Fe, the C from these complexes and the total C content can be seen in figure 4.7. As expected Al_p, Fe_p and C_p increase when total C increases.

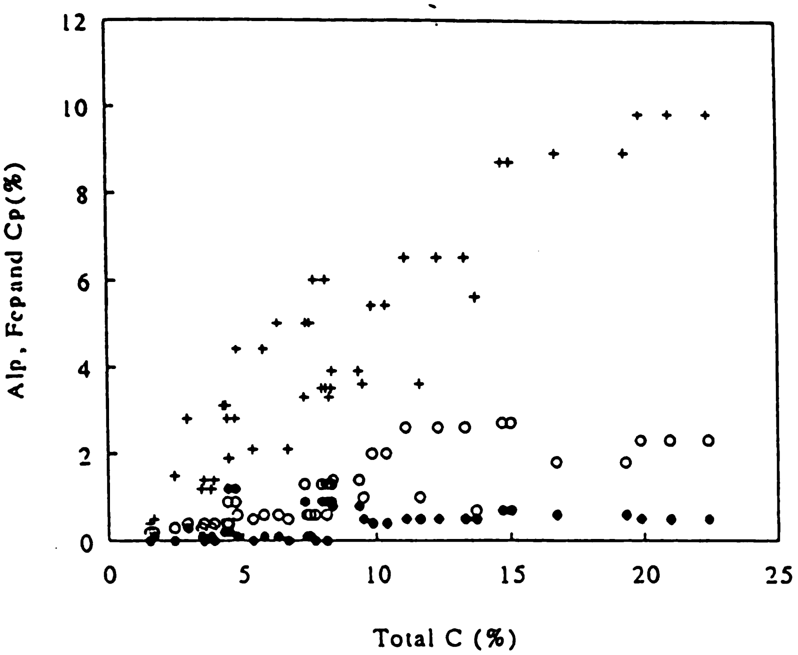


Figure 4.7 Al_p, Fe_p and C_p versus the content of organic matter. O: Al_p; ●: Fe_p; +: C_p.

According to the findings in literature the ferrihydrite content can be estimated using the equation (Mizota and Van Reeuwijk, 1989; Dahlgren *et al.*, 1993; Childs *et al.*, 1991):

$$\%\ ferrihydrite = \%Fe_0 * 1.7$$

According to Parfitt and Childs (1988), Fe_0 is often a good measure of the quantity of ferrihydrite in a soil. The work of Childs *et al.* (1991) supports the statement that Fe_0 is useful in indicating and estimating the amount of ferrihydrite in soils. However, Childs *et al.* (1991) removed organic matter from the sample before they determined the oxalate extractable iron. Because the Fe-components extracted with acid oxalate include humus-Fe, I corrected Fe_0 for the amount of Fe present in Fe-humuscomplexes using:

$$\%\ ferrihydrite = (\%Fe_o - \%Fe_p) * 1.7$$

There are no trends visible in the contents of ferrihydrite calculated in this study. Profile T8, however, has lower ferrihydrite contents than the other profiles, this can be the result of less weathering.

A parameter that can be used to estimate the crystallinity of iron oxides is the activity ratio, Fe_o/Fe_d, where Fe_0 stands for the oxalate extractable Fe and Fe_d stands for the dithionite-citrate extractable Fe. Values for (young) andosols are usually high (>0.75), for older soils the values are much lower (Mizota and Van Reeuwijk, 1989). Values found in this research are, with a few exceptions, higher than 0.5, and often higher than 0.8.

The binary ratio, Al_p/Al_0, gives information about the composition of the colloidal fraction (Mizota and Van Reeuwijk, 1989). In this ratio Al_p is the amount of Al extractable with pyrophosphate, and Al_0 is the amount of Al extractable with acid oxalate. Figure 4.8 shows the binary ratios. As expected there appears to be a general trend that Al_p/Al_0 is highest in the A-horizons and decreases in the corresponding B- and C-horizons. Many horizons seem to have a nearly pure-end-member composition, they are either pure allophanic ($Al_p/Al_0=0$) or pure non-allophanic ($Al_p/Al_0=1$). All horizons of profile T3 are allophanic. The Ah1 horizons of profiles T1, T2 and T8 are non-allophanic and the B- and C-horizons of these profiles are allophanic. A few horizons have a binary ratio between 0.2 and 0.8, for these horizons a designation as either allophanic or non-allophanic would be inaccurate. These horizons are the Ah2 of profile T1, Ah2 and AB of profile T2 and Ah2 and Bw1 of profile T8.

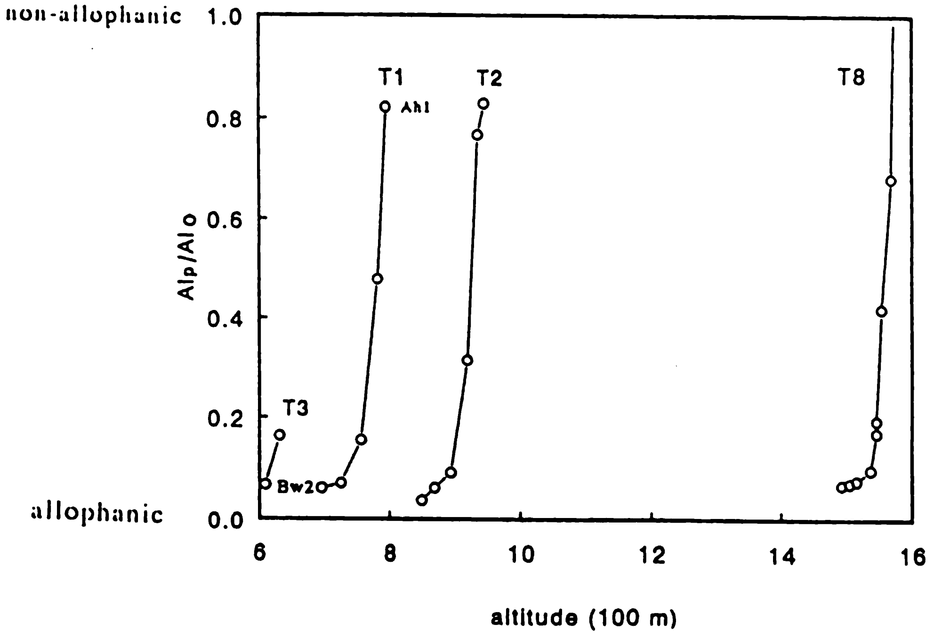


Figure 4.11 Binary ratio against altitude.

Contents of allophane are calculated in two ways. Parfitt and Wilson (1985) give a method to estimate the allophane content in soils. The contribution of imogolite to the amount of para-crystalline alumino-silicates is considered to be relatively small, so that the calculated allophane content would represent the amounts of both allophane and imogolite. Parfitt and Wilson approached the relationship between the Al/Si-ratio of allophane and the Si-content of allophane using the equation:

$$y = -5x + 23.4$$

in which:

y = %Si in allophane

$x = (Al_o - Al_p)/Si_o$

The allophane content can then be calculated using:

$$\% \, allophane = \frac{100}{y} * \%Si_o$$

The content of allophane and imogolite is also estimated in another way, using the equation (Nanzyo *et al.*, 1993):

$$\% \, allophane + imogolite = 7.1 * \%Si_o$$

Figure 4.9 shows, for the samples used in this study, the relation between the two ways in which the allophane/imogolite content is calculated.

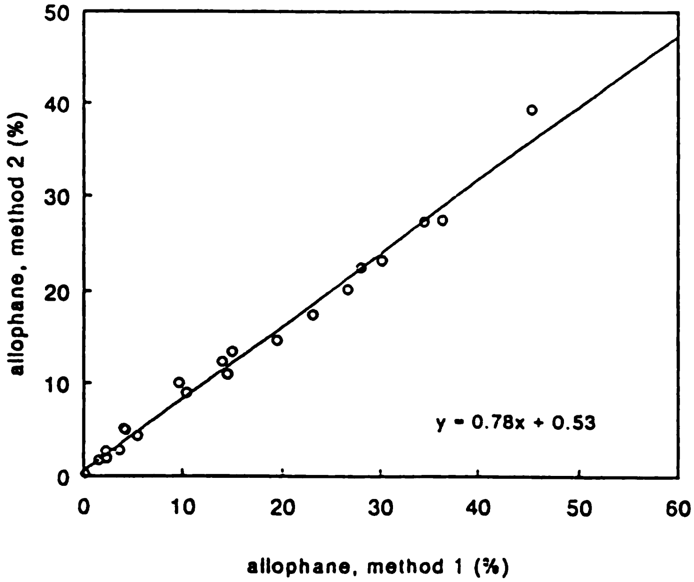


Figure 4.9 Allophane content calculated according to Parfitt and Wilson (1985) (method 1), compared to the allophane content calculated according to Nanzyo *et al.* (1993) (method 2).

Allophane contents calculated according to Parfitt and Wilson are higher than allophane contents calculated according to Nanzyo *et al.*. Meijer (1995) estimated the allophane contents through analysis of the physical data and of the X-ray Fluorescence Spectrometry (XRFS) data. The allophane contents estimated by Meijer are higher than both the allophane content calculated according to Parfitt and Wilson and the allophane content calculated according to Nanzyo *et al.*. Therefore I assumed that the method according to Parfitt and Wilson gives the best approximation of the allophane content.

All profiles have high allophane contents in the B and C horizons, profile T1 and T3 also in the Ah2 horizon. Profile T8 has lower allophane contents than the other profiles. The highest allophane contents are found in the B and C horizons of profile T2.

The Al/Si atomic ratio for allophane is calculated by $(Al_o-Al_p)/Si_o$. Al/Si-ratios for allophane found in this research vary from 1.1 to 3.3. Thus many values that do not lie within the range of allophane (1.0-2.5) are found. For different reasons, all determined Al/Si-ratios are used for the calculation of allophane contents:

> - Figure 4.10 (p20) shows the Al/Si ratio in the oxalate extract compared to the Al/Si-ratio calculated from XRFS data, values for samples with a high allophane content are represented by black dots. If the allophane contents would be higher than calculated from the selective dissolution data, they could either follow the line trough point A and approach 2.5, or they could follow the line trough point B and approach 3. A maximum Al/Si ratio of 2.5 is expected from the crystallography of allophane.
>
> - Figure 4.10 also shows that high Al/Si ratios are found for samples that have a high content of allophane. These samples are taken from horizons that are very thixotropic (appendix 1). However, some of these very thixotropic horizons contain gibbsite, which is also extracted by acid oxalate and causes the calculated allophane content to be too high.
>
> - The calculated allophane contents are underestimates because the acid oxalate extraction is incomplete. If an Al/Si ratio of 1.0-2.5 instead of an Al/Si ratio of 1.0-3.3 would be used for the estimation of allophane contents, the calculated contents would be even lower.
>
> - If a maximum Al/Si ratio of 2.5 instead of a maximum Al/Si ratio of 3.3 would be used for the calculation of amounts of allophane, discontinuities would be introduced in the trends that are looked at.

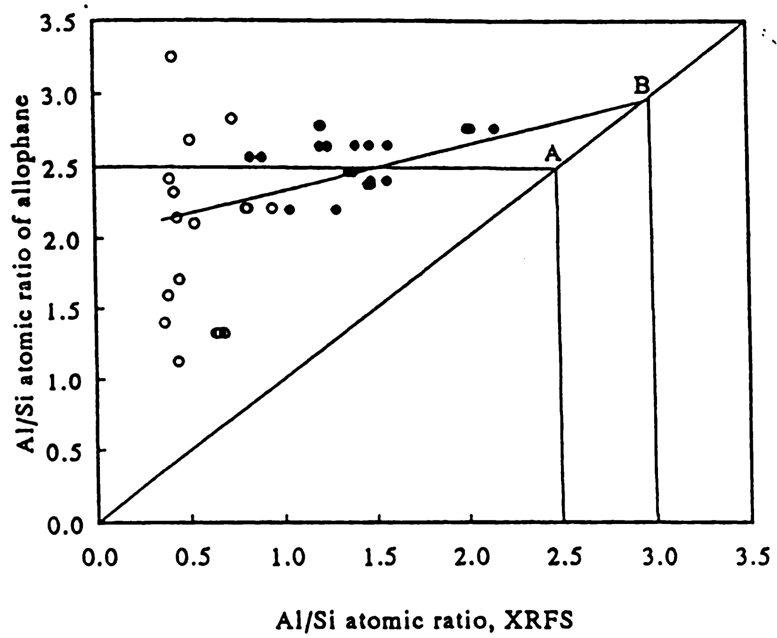


Figure 4.10 Comparison of the Al/Si atomic ratio of allophane with the Al/Si atomic ratio calculated from XRFS data. O: samples with ≤ 20% allophane; ●: samples with > 20% allophane.

4.3 Total chemical analysis

Total chemical analysis is done on all samples from series I and on some from series II, namely on samples 23, 23a, 39, 42, 43 and 46.

4.3.1 Introduction

In this paragraph I will look at the interaction between trace elements and organic matter and allophane. This is done using the trace element contents measured with XRFS and the calculated amounts of organic matter and allophane from the previous paragraph. Also, it is assumed that all profiles have developed in the same parent material. Analysis of the contents of major elements by Meijer (1995) show that this is a reasonable assumption.

Analysis of the XRFS data also shows that Zr is the most suitable reference element, Zr is immobile and shows no scatter due to interactions. Both physical and chemical weathering affect the isovolumetric Zr content of the soil. Physical weathering is the loss of mineral matter through erosion. In this case, there is no chemical breakdown of minerals and all elements are lost to the same extend (sorting of minerals not considered). Chemical weathering does involve the breakdown of minerals. Mobile elements are leached out to the ground water and the soil becomes enriched in both immobile elements as Zr and mobile elements that are bound in secondary minerals. Both processes are depicted in figure 4.11 using Zr as a reference element. The dots on the x-axis represent samples from horizons with only physical weathering, Zr is lost from the parent material in the same amount as other elements. Deviations from the x-axis are the result of chemical weathering (and sorting), in this case there is an enrichment of Zr due to the loss of other elements. Figure 4.11 shows that the profiles at lower altitudes (T1, T2 and T3; open circles) are more chemically weathered than the profiles at higher altitudes (T4-T8; closed circles). Explanations for this feature may be higher temperatures, higher precipitation values and/or less deposition of fresh ash at lower altitudes. Also sorting due to solifluction may play a role.

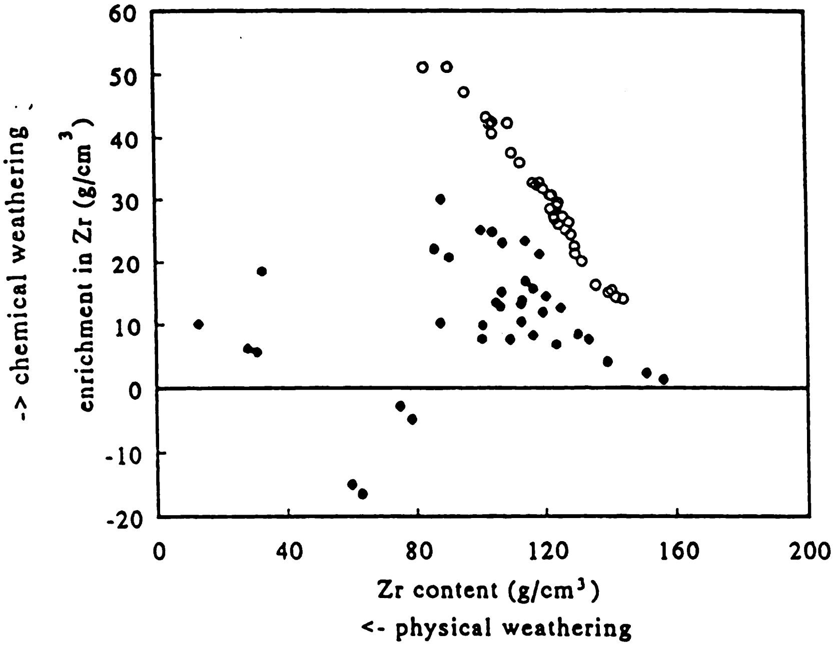
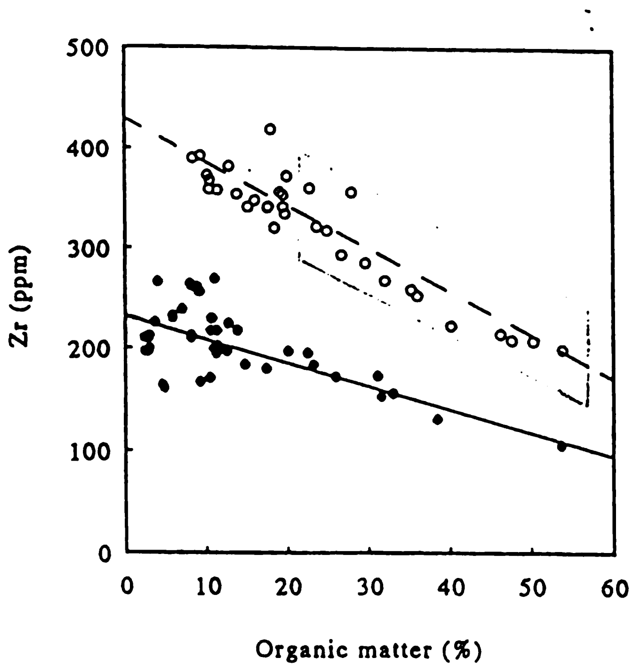


Figure 4.11 Physical weathering versus chemical weathering, using Zr as reference element. O: samples from profiles T1, T2 and T3; ●: samples from profiles T4-T8.

4.3.2 Interaction between trace elements and organic matter

Figure 4.12 shows the relation between the Zr content and the organic matter content. A few trends can be seen from this figure. Firstly, the profiles fall apart into two groups. Samples from profiles at lower altitudes (T1, T2 and T3; open circles) have higher Zr contents than the samples from profiles at higher altitudes (T4-T8; closed circles), owing to an enrichment of Zr due to chemical weathering. Secondly, the Zr content decreases when the amount of organic matter increases. This is due to dilution of the mineral matter by organic matter. The scatter of the black dots (samples from profiles T4-T8) may be caused by variations in the parent material. Because Zr is inert, interaction between other trace elements and organic matter can be seen through deviations from the pattern for Zr.



k ≈ 1

Figure 4.12 Relation between the Zr content and the organic matter content. O: samples from profiles T1. T2 and T3; ●: samples from profile T4-T8.

The contents of Ba, Co, Cr, Cu, Ga, La, Nb, Ni, Pb, Rb, Sr, V and Zn are also plotted against the organic matter content, the plots can be seen in figure 4.13. The lines in these figures show how the pattern would be if there would be no interaction between the trace elements and organic matter. Deviations from this pattern indicate either leaching out of the profile (The dots lie below the lines) or complexation with organic matter (the dots lie above the lines). Figures 4.13f and 4.13g for La and Nb have a lot of scatter. The contents of both La and Nb are close to the detection limit causing errors. In addition to this, the sialon mill, which is used for grinding of the samples, causes impurities of Yttrium in the samples, which disturbs the measurement of Nb (Kuijper, 1995).

As can be seen from figure 4.13a Ba is an element that is easily mobilized. The concentrations of Ba in the samples from profiles T1, T2 and T3 are lower than the concentrations of Ba in the samples from the other profiles. The closed circles follow the same pattern as for Zr, here Ba is still present in primary minerals, upon weathering Ba is mobilized. Ba in the upper horizons from profiles at lower altitudes (open circles) is also little mobilized.

Co is example of a trace element that is complexed by organic matter. Figure 4.13b shows the relation between the Co-content and the organic matter content. The Co contents in the samples from profiles at high altitude (black dots) have a pattern that is somewhat similar to the pattern for Zr. However, since the Co content is close to the detection limit, it is not visible if the Co content decreases with increasing organic matter content. The Co contents in samples from profiles at higher altitudes (open dots) clearly increase when the content of organic matter increases, showing that Co is bound to organic matter.

As can be seen from figure 4.13, Co, Cu, Ga, La, Pb, V and Zn are bound to organic matter. Trace elements that show no interaction with organic matter are Ba, Cr, Nb, Ni, Rb and Sr. In literature many different findings are reported. Raiesi Gahrooee and Buurman (b) (in press) found that Co, Cr, Cu, Ni, Pb, Zn and Zr are bound to organic matter. Walraven (1995) found that Cr, Cu, Rb and Zr are bound to organic matter. According to Aller *et al.* (1989) Co, Cu, Ni, Rb, Sr and Zn are complexed by organic matter. Davies (1980) reports that Cu and Zn are fixed by organic matter and Nicholas *et al.* (1974) report the same for Cu. Abd-Elfattah and Wada (1981) found that Pb, Cu, Zn and Co are adsorbed by humus, but that humus is not a strong adsorbent for heavy metal cations. These findings correspond to the results of the present study, except for Cr, Ni, Rb, Sr and Zr. Since Zr is the reference element in this study, it is assumed that Zr does not show interaction with organic matter.

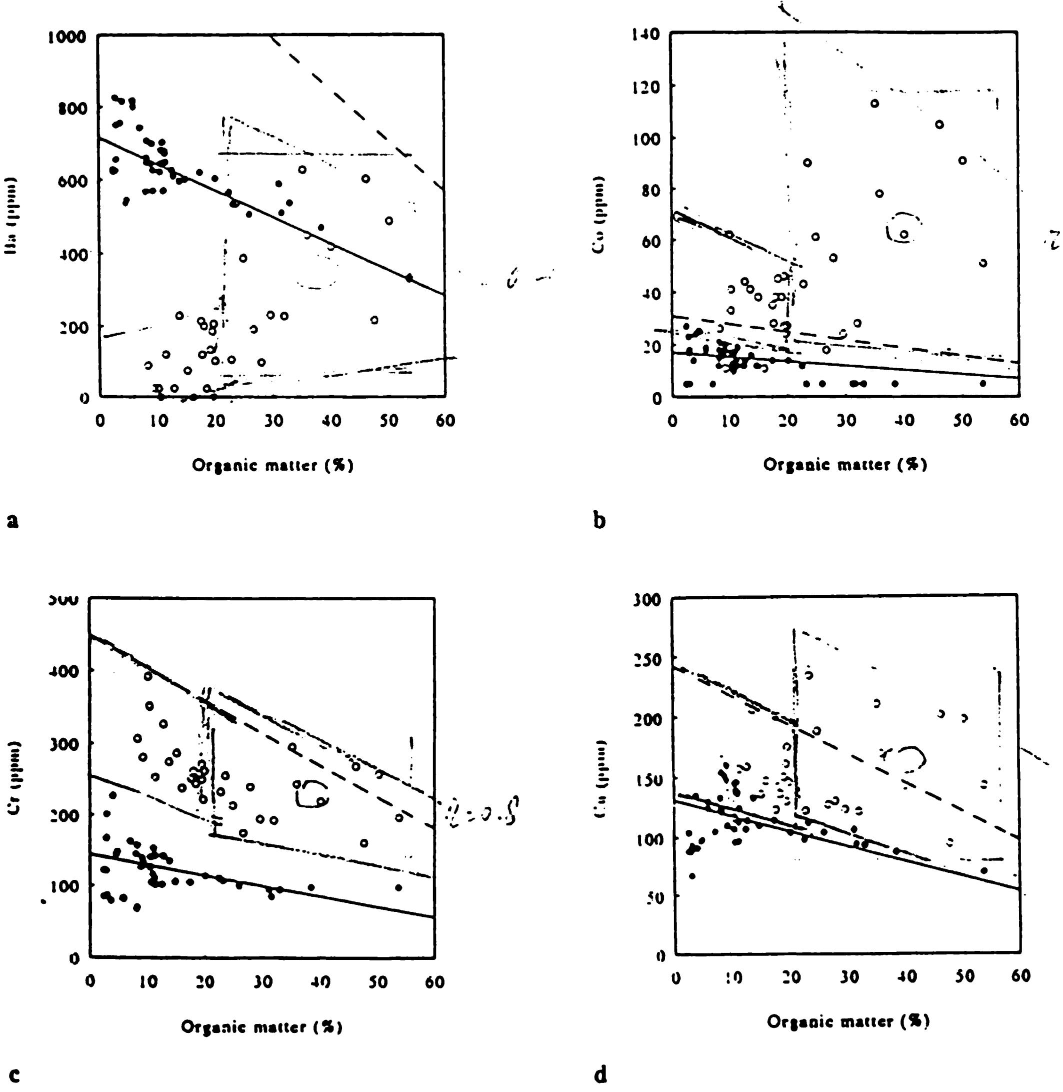


Figure 4.13 a-d Relations between the contents of trace elements and the organic matter content. (a) Ba: (b) Co: (c) Cr: (d) Cu. O: samples from profiles T1, T2 and T3: ●: samples from profiles T4-T8.

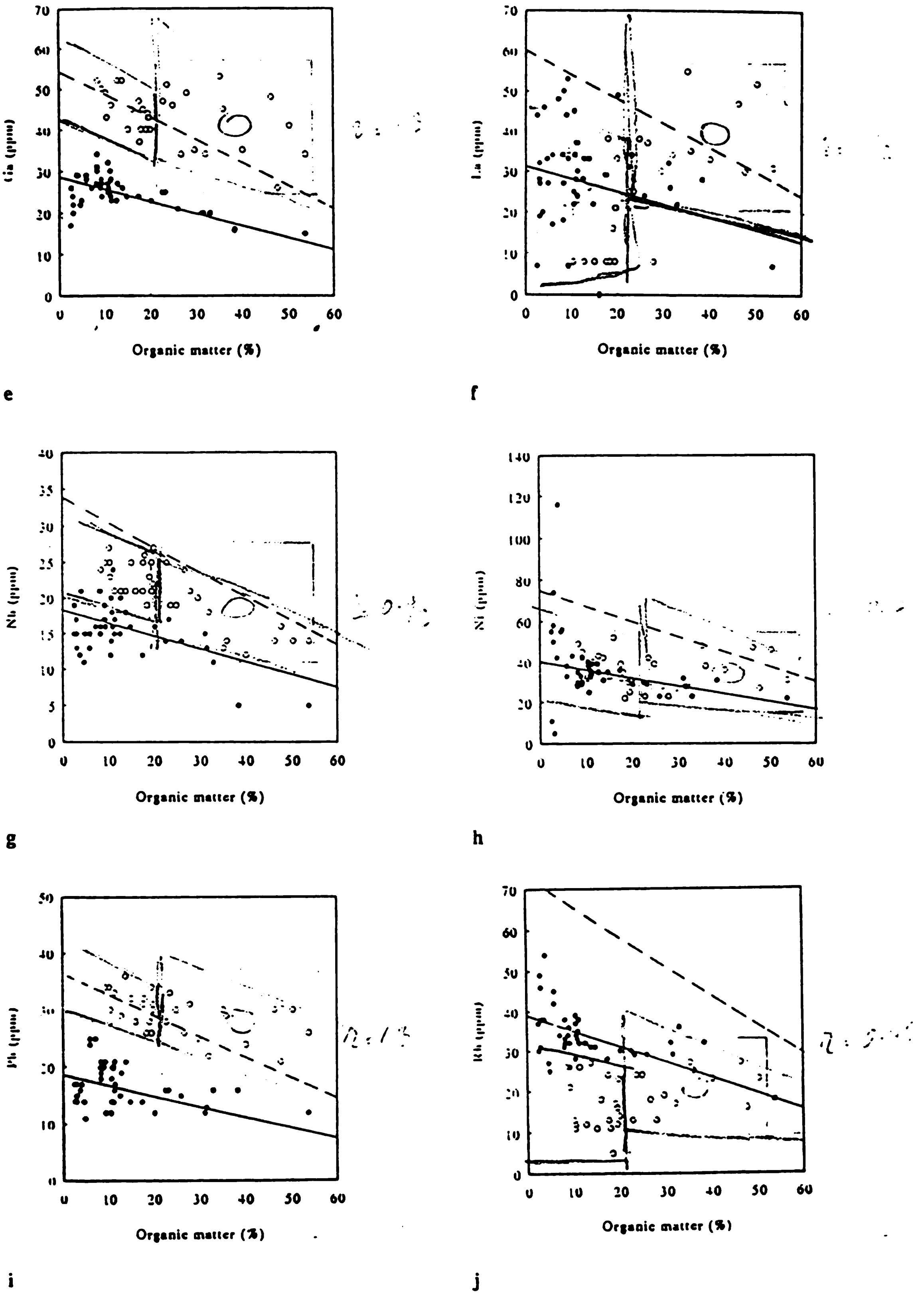


Figure 4.13 e-j Relations between the contents of trace elements and the organic matter content. (e) Ga: (f) La; (g) Nb; (h) Ni; (i) Pb; (j) Rb. O: samples from profiles T1, T2 and T3; ●: samples from profiles T4-T8.

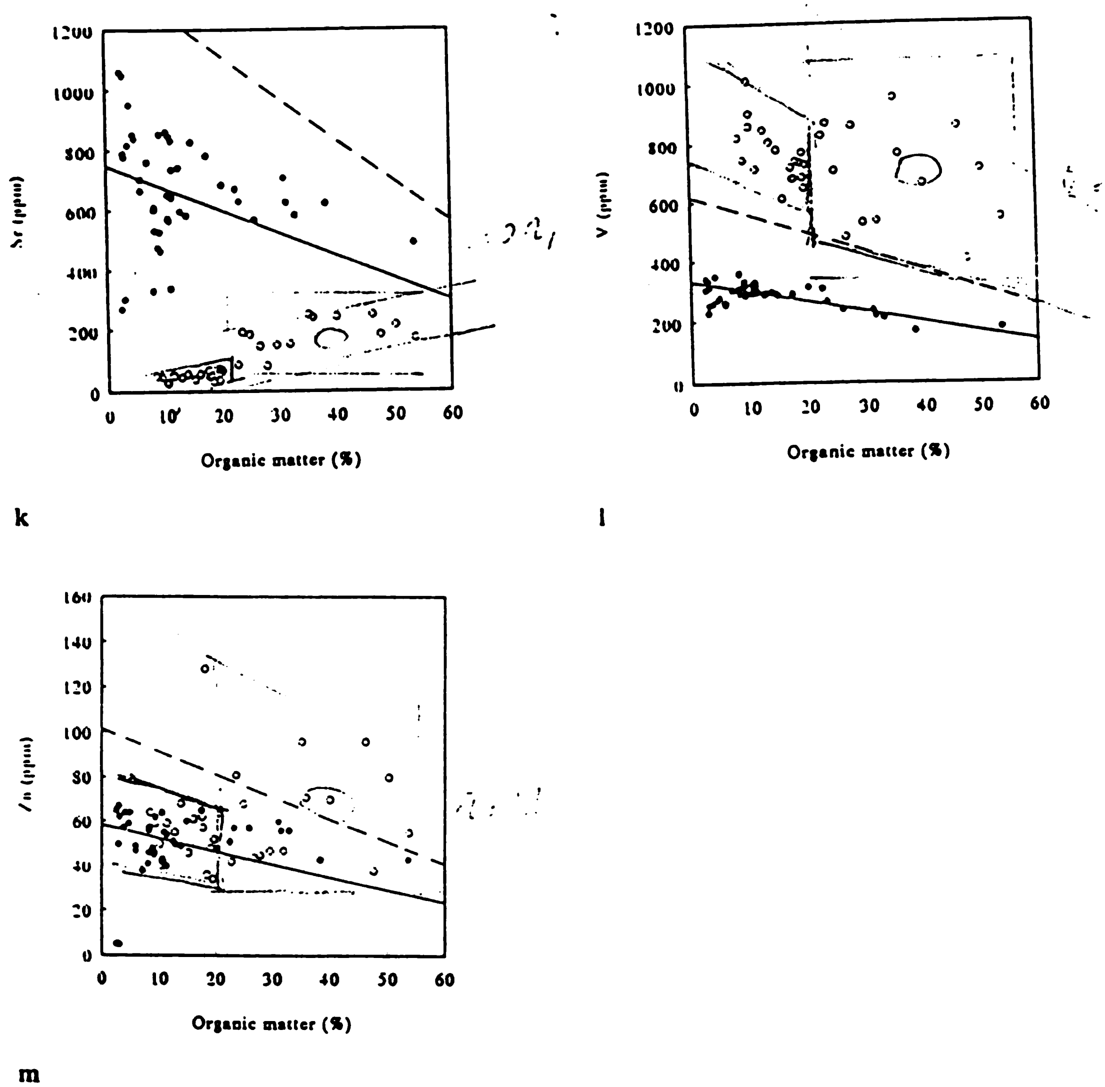


Figure 4.13 k-m Relations between the contents of trace elements and the organic matter content. (k) Sr; (l) V; (m) Zn. O: samples from profiles T1, T2 and T3; ●: samples from profiles T4-T8.

4.3.3 Interaction between trace elements and allophane

Because dilution by organic matter seems to be trivial, graphs of trace element contents against allophane were prepared also. The relation between the Zr content and the allophane content is shown in figure 4.14. Here the diluting effect of organic matter is compressed to the left side of the diagram. Also the profiles are not separated into two groups because at the left side of the diagram higher dilution by organic matter is compensated by higher weathering for the lower altitude profiles. The scatter of the black dots in figure 4.14 is less than the scatter of the black dots in figure 4.12. This is because the allophane content of profiles T4 trough T7 was not determined. Figure 4.14 shows that the Zr content increases with increasing allophane content. This is because the soil is enriched in Zr as a result of chemical weathering. Again interactions between other trace elements and allophane can be spotted through deviations from the pattern for Zr.

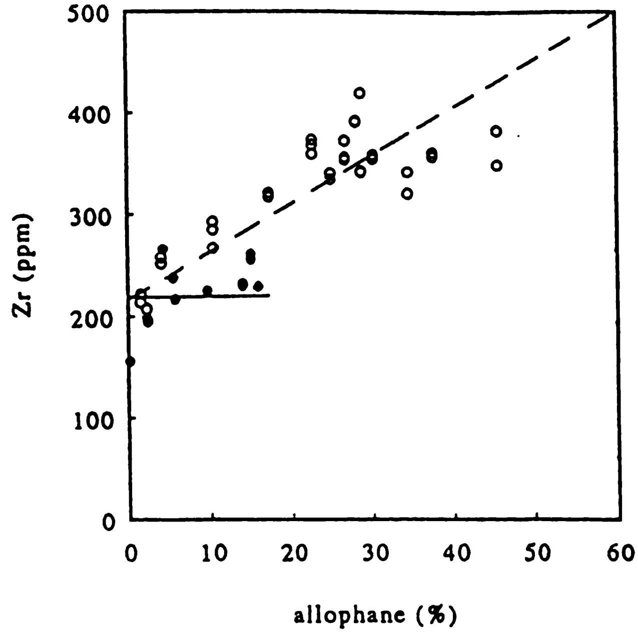


Figure 4.14 Relation between the Zr content and the allophane content. O: samples from profiles T1, T2 and T3; ●: samples from profile T8.

The relation between the contents of the other trace elements and the allophane content is shown in figure 4.15. The lines in the graphs show how the pattern would be if there were no interaction between the trace elements and allophane. The concentrations will be lower if an element is mobile, and higher if an element is bound to allophane. As can been seen from figure 4.15a, Ba has a pattern completely different from the pattern for Zr. While the Zr content increases with increasing allophane content, the Ba content decreases with increasing allophane content. Here again it is shown that Ba is a mobile element, Ba has no interaction with allophane. In contradiction to the Ba content, the V content increases when the allophane content increases. It does so more than the Zr content (the open dots lie above the dotted line) and therefore V must be bound to allophane.

Figure 4.15 shows that Cr, Co and V are bound to allophane. Ba, Cu, Ga, La, Nb, Ni, Pb, Rb, Sr and Zn do not interact with allophane. According to Walraven (1995) Zr, La, Ni, Sr, Rb and Zn are bound to allophane. Aller *et al.* (1989) report that Ni and Zn are fixed by allophane, Davies (1980) reports the same for Cu. Abd-Elfattah and Wada (1981) found that allophane has a high selectivity for Pb, Cu and Zn, and a lower selectivity for Co. Their data, however, this is based on data from Ca-saturated samples and cannot be compared to the data of this study. All these findings, except for Co, do not correspond to the results of the present study.

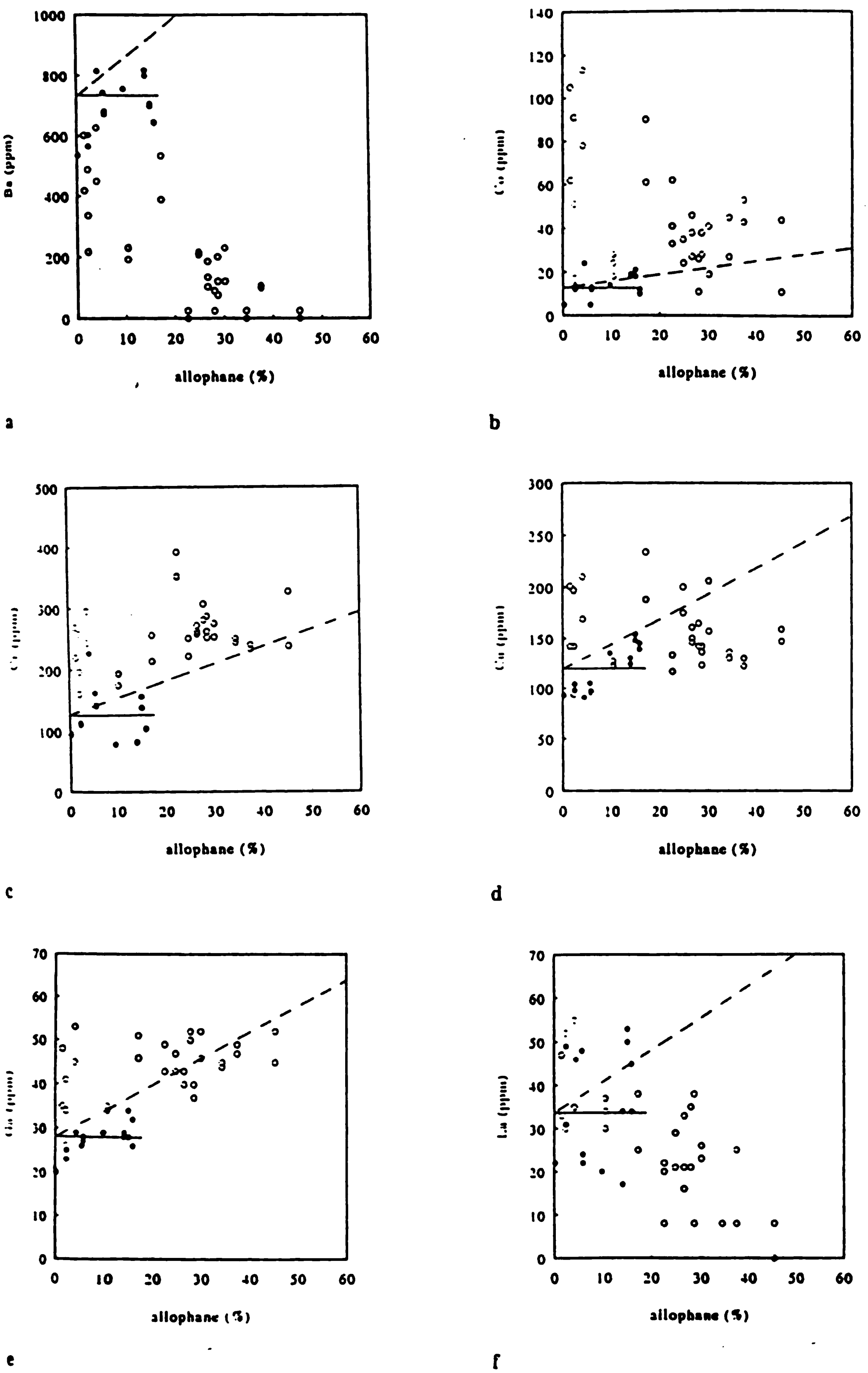


Figure 4.15 a-f Relations between the contents of trace elements and the allophane content. (a) Ba; (b) Co; (c) Cr; (d) Cu; (e) Ga; (f) La. O: samples from profiles T1, T2 and T3; ●: samples from profile T8.

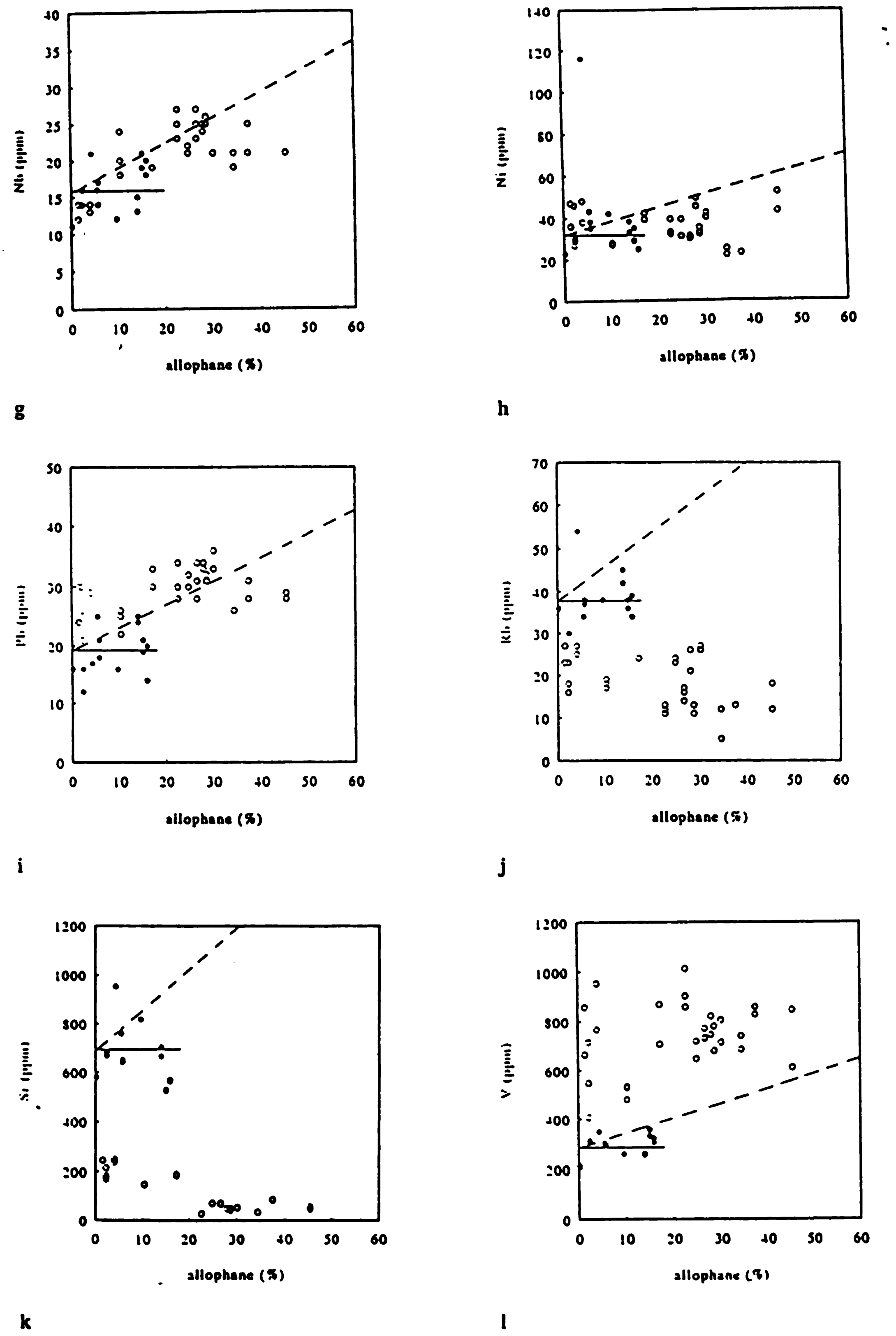
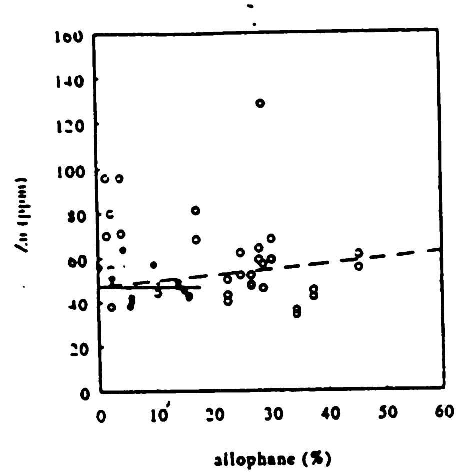


Figure 4.15 g-l Relations between the contents of trace elements and the allophane content. (g) Nb: (h) Ni: (i) Pb; (j) Rb: (k) Sr; (l) V. O: samples from profiles T1, T2 and T3; ●: samples from profile T5.



m

Figure 4.15 m Relations between the contents of trace elements and the allophane content. (m) Zn. O: samples from profiles T1, T2 and T3; ●: samples from profile T8.

4.3.4 Interaction between trace elements and ferrihydrite

Owing to its small paricle size and consequent high specific area (200-500 m^2/g) ferrihydrite is a highly reactive iron oxide. Even a small of ferrihydrite can strongly influence the sorptive properties of soils (Childs *et al.*, 1991). Therefore an attempt was made to look at the competition for trace elements between ferrihydrite and allophane by using a set of graphs where the element concentration was corrected for the amount of that element in ash and in organic matter by using:

$$trace\ element_{(corr)} = trace\ element - a*\frac{\%OM}{100} - b*\frac{\%ash}{100}$$

In which:

a = the amount of trace element in organic matter
b = the amount of trace element in ash
% OM = % organic matter
% ash = 100 - % organic matter - % allophane - % ferrihydrite

In order to correct for the amount of trace element in organic matter the first set of graphs must be used (figure 4.13), which are estimates. To correct for the amount of trace element in ash sample 23 (fresh ash) must be used, which is probably not representative for the whole set of samples. Also in order to estimate the amount of ash, the amounts of allophane and ferrihydrite must be used, while both are underestimates since the acid oxalate extraction is incomplete. Because in this way the number of errors accumulates, it was not possible to look at the competition for ferrihydrite and allophane for trace elements.

Some findings in literature can be reported. According to Raiesi Gahrooee and Buurman (in press) Ba, Co, Cr, Cu, Ni, Pb, Sr, Zn and Zr are fixed by the amorphous fraction. Walraven (1995) found that Co, Cu, Rb and Zn are bound to ferrihydrite. Aller *et al.*, report that Co, Cu, Zn, Sr and Ni can be found in iron-oxides, but also that Sr and Ni in solution can migrate over long distances. According to Davies (1980) iron oxide minerals are important hosts for trace elements like Co, Cr, V and Zn. Nicholas and Egan (1974) report that V can substitute for Fe, Ni, Cu and Zn. Abd-Elfattah and Wada (1981) found that, for Ca-saturated samples, iron oxides are very important adsorbents for Pb, Cu, Zn and Co.

5 Conclusions

CEC determination using $MgSO_4$ is not suitable for andosols. Magnesium along with sulphate is adsorbed by amorphous minerals resulting in a CEC value which is too high.

Soils at lower altitudes (640-950 m) show more progressive weathering than soils at higher altitudes (1250-3160 m). The soils at low altitudes have higher allophane/imogolite contents and a higher content of the reference element Zr.

This study suggests that V is adsorbed by organic matter and allophane and thus would be of limited use as a reference element.

The approach used in this study leads to the conclusion that trace elements complexed by organic matter are Co, Cu, Ga, La, Pb, V and Zn. Co, Cr and V are bound to allophane. Because this conclusion is based on bulk data only, it is necessary to obtain additional information in order to verify this conclusion. The present study can be used as a starting point for further research.

6 Acknowledgements

It would have been impossible to present this report in its present form without the help of many people. First I'd like to thank my supervisor Ed Meijer for his commitment, help and advices. I'd also like to thank Peter Buurman, Toine Jongmans, André Nieuwenhuyse and again Ed Meijer for making the fieldwork in Costa Rica a very good and interesting experience from which I learned a lot. For help with my labwork I'm grateful to Bram Kuijper, Barend van Lagen and especially Eef Velthorst and Frans Lettink. And last, but not least, I want to thank my boyfriend Werner for his help and support.

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Appendix 1

Soil profile descriptions

Profile Turrialba 1

Location	N 10°07'25"; W 83°44'49"
Altitude	800 m
Exposition	N
Position	just below top, nearby steep slope
Slope	20%
Parent material	totally weathered andesitic ash, overlying andesitic lava
Vegetation	logged out rain forest
Precipitation	perudic, 6500-7000 mm/year
Drainage	well drained

O	-2-0 cm		roots and partly decomposed litter
Ah1	0-10 cm	1	5YR2.5/2; moist; silty clay loam; strong, very fine to fine, subangular blocky, locally fine granular; friable; thixotropic; very few, partially altered, sub rounded rock fragments; few, fine, medium and coarse roots; very fine to medium pores; few holes of large animals up to 10 cm in diameter; rainworm activity; gradual and smooth boundary to:
Ah2	10-27 cm	2	7.5YR3/2; moist; silty clay loam; weak, fine and very fine (sub)angular blocky; friable; thixotropic; very few, partially altered, andesitic rock fragments; rainworm activity; common, very fine to medium pores; gradual and smooth boundary to:
AB	27-60 cm	3	10YR3/4; moist; silty clay loam; structureless massive; friable; thixotropic; few, very fine to medium roots; common, very fine to medium pores;rainworm activity; aggrotubul of 2 mm in diameter; gradual and smooth boundary to:
Bw1	60-93 cm	4	10YR4/6; moist; silty clay loam; structureless massive; friable; thixotropic; common, very fine to medium pores; aggrotubul; rainworm activity; very few, very fine to medium roots; diffuse and smooth boundary to:
Bw2	93-120/150 cm	5	10YR5/8; moist; silty clay loam, occasionally sand grains; friable; slightly sticky, slightly plastic, thixotropic; very few and few, very fine and medium roots; few, very fine to medium pores; rainworm activity; few clay cutans; wavy, 2-5 cm, and clear boundary to:
B+2R	120/150+ cm	6	thixotropic; porous, partially weathered andesite, rich in feldspars, the outer part is soft.

Profile Turrialba 2

Location	N 10°06'53"; W83°45'02"
Altitude	950 m
Exposition	ZW
Physiography	mountainous area
Slope	5%
Precipitation	perudic, about 7000 mm/year
Parent material	andesitic ash
Land use	open tropical mountain forest
Drainage	well drained

O	-1-0 cm		living and partly decomposed roots and leaves.
Ah1	0-8 cm	7	5YR2.5/1; moist; silty clay loam; strong, fine granular and subangular blocky; friable; thixotropic; common, very fine to coarse roots; very few very fine pores; worm activity; gradual and smooth boundary to:
Ah2	8-20 cm	8	5YR2.5/2; moist; silty clay loam; moderate fine subangular blocky; friable; thixotropic; common, very fine to coarse roots; common. very fine to coarse pores; worm activity; gradual and smooth boundary to:
AB	20-40 cm	9	7.5YR3/4 and 7.5YR3/2; moist; silty clay loam; structureless massive; friable; thixotropic; few, fine to medium roots; common. very fine to medium pores; aggrotubul: diffuse and smooth boundary to:
Bw1	40-72 cm	10	7.5YR3/3; moist; silty clay loam; structureless massive; friable: thixotropic; few, very fine to fine roots; common, very fine to medium pores, locally filled with Ah material; diffuse and smooth boundary to:
2Bw2g	72-92 cm	11	10YR4/3; mottles: many, very fine to fine, distinct iron mottles and hypo coatings; few, fine to medium, faint greyish mottles 10YR4/2; silty clay loam; structureless massive; firm; thixotropic; common, very fine and fine pores; clear and smooth boundary to:
2Cg1	92+ cm	12	10YR5/2; moist; iron coatings on structure elements and along pores, 5YR5/8; locally pale yellow coatings; few, light and dark colored mineral grains; fresh, partially to totally altered mineral fragments up to 1 cm in diameter; weak coarse prismatic structure; firm; thixotropic: aggrotubuls.

Profile Turrialba 3

Location	N 10°08'34"; W 83°44'19"
Altitude	640 m
Exposition	N
Slope	all over 5%, local 100%
Precipitation	perudic
Parent material	vulcanic ash over andesitic lava
Land use	grassland
Drainage	well drained

Ah2	0-18 cm	10YR3/2; moist; silt loam; strong fine granular structure. moderate fine subangular blocky: friable; thixotropic; very few coarse gravel. andesitc. rounded, partially weathered; common fine roots: few very fine and fine pores; clear and smooth boundary to:

AB	18-45 cm	upper part 10YR4/4, lower part dominantly 10YR5/8, lower part with inclusions of upper part; silt loam; moist; weak (sub)angular blocky; friable; thixotropic; very few slightly weathered andesitic gravel; few fine roots; common very fine pores; aggrotubuls filled with Ah2 material; diffuse and smooth boundary to:
Bw	45-60/80 cm	10YR6/8; silt loam; structureless massive; friable; thixotropic; in the lower part of the horizon few slightly weathered andesitic rock fragments; common, very fine and fine roots; common, very fine and fine pores; abrupt and tonguing boundary to:
2R	80+ cm	thixotropic; andesitic rock fragments (boulders), strongly weathered, porous.

Profile Turrialba 4

Location	N 10°05'06"; W 83°47'55"
Altitude	1250 m
Exposition	N
Physiography	mountainous area
slope	5%
Parent material	andesitic ash, probably holocene
Vegetation	tropical mountain forest
Drainage	well drained

O	-2-0 cm	roots and partly decomposed litter.
Ah	0-17 cm 16	10YR2/1; many iron mottles and segregations around voids, 5YR5/8; silt loam; moderate fine (sub)angular blocky; friable; many, fine to coarse roots; few, fine to medium pores; clear and smooth boundary to:
Bw1	17-35 cm	10YR3/3; silt loam; weak, very fine subangular blocky; friable; common, very fine to coarse roots; common, very fine to medium pores; clear and smooth boundary to:
C1	35/39 cm	2.5YR3/0; loamy sand; single grain; discontinuous; abrupt and irregular boundary to:
2Bw1g	35/39-80 cm	10YR3/3; few, very fine iron mottles; silt loam; structureless massive; fresh mineral fragments of 2 mm in diameter; sand pockets, surrounded by iron; firm; few, fine to medium roots; common very fine pores; diffuse and smooth boundary to:
2BW2	80-108 cm	10YR3/2; few, very fine iron mottles, 5YR5/8; clay loam; structureless massive; fresh mineral grains; sand pockets, surrounded by iron; firm; few fine roots; few, very fine and fine pores; abrupt and smooth boundary to:
3Bw	108-130+	10YR4/3; locally iron segregates around burrows and roots, 5YR5/8; silty clay loam; structureless massive; few fresh mineral grains; few fresh ash inclusions smaller than 1 cm in diameter; friable; very few, very fine roots; common very fine pores.

Profile Turrialba 5

Location	N 10°01'12"; W 83°45'42"
Altitude	3160 m
Physiography	summit, surrounded by steep slopes
Slope	25%
Parent material	andesitic ash
Vegetation	ferns, grass
Drainage	slightly excessively drained

Ah1	0-4 cm	24	10YR2/1; moist; loamy sand; massive; friable; abundant, very fine to medium roots; pores not visible; abrupt and smooth boundary to:
AB	4-11 cm		10YR3/4; moist; loamy sand; up to 20% coarse, slightly altered, blocky fragments up to 1 cm in diameter; loose single grain; abundant very fine to medium roots; clear and smooth boundary to:
BC	11-30 cm		10YR5/4; on gravel surfaces common iron segregations, 5YR4/6; loamy sand; 50-70% coarse, slightly altered, hard, blocky fragments up to 1.5 cm in diameter; loose single grain; common fine to medium roots.
R	30+ cm		fine to gravelly volcanic ejecta; stratified; many iron segregates, 10YR6/8; many reduction mottles, 10YR5/1.

Profile Turrialba 6

Location	N 10°03'02"; W 83°46'57"
Altitude	2020 m
Exposition	N
Physiography	mountainous area
Slope	15-20%, slope processes
Parent material	andesitic ash
Vegetation	juncus/pasture trampled by cattle
Drainage	somewhat poorly, rapid runoff

Ah1	0-11 cm	27	7.5YR3/2; moist; loam; structureless massive; friable; abundant very fine roots; pores not visible; in the upper 20 cm rainworm activity; moderatly well drained; no surface rock outcrops; abrupt and smooth boundary to:
2Ah1	11-20/25 cm		5YR2.5/1; on the underlying horizon the presence of a hard iron band 2.5YR3/4; moist; loam; structureless massive; 2-20% fresh to completly altered, subrounded rock fragments; friable; many, fine to medium roots; common very fine pores; abrupt and wavy boundary to:
3Ah1	20/25-33 cm		5YR2.5/1; moist; structureless massive; less than 20% fresh and completly altered rock fragments; friable; common fine and medium roots; many fine pores; abrupt and wavy boundary to:
4C	33-49 cm		7.5YR2/0; moist; loamy sand; structureless massive; pockets of 3-10 mm in diameter, consisting of material of the underlying horizon; friable; the ash is non-thixotropic; common, very fine to medium roots, concentrated in the pockets; few fine pores; clear and wavy boundary to:
5Bw	49-69 cm		10YR3/3; irregular spots, 10 cm in diameter, locally layered appearance, 10YR5/1; presence of iron compounds, 10YR7/8; moist; loam/clay loam; structureless massive; friable; thixotropic; common, very fine to

		medium, randomly distributed roots; many fine pores; abrupt and wavy boundary;
6Ah	69-80 cm	5YR2.5/1; moist; structureless massive; less than 20% coarse, fresh to totally weathered fragments, up to 3 cm in diameter; friable; thixotropic; common very fine to medium roots; many very fine pores; clear and wavy boundary to:
6Bw	80-100 cm	structureless massive; 20-30% coarse, fresh to totally weathered fragments; friable; few, fine to medium roots; abrupt and smooth boundary to:
7C1	100+ cm	7.5YR2/0; iron bands, 5YR5/8; secondary material, 7.5YR5/8; sand; friable (appears to be hard in the field); 2-20% isotubuls, 12 mm in diameter, dominantly concentrated in the upper part of the horizon; stratified.

Profile Turrialba 7

Location	N 10°01'26"; W 83°47'06"
Altitude	2650 m
Physiography	just under the top of a 50% slope
Geology	exposure reveals at least 6 m of ash deposits
Land use	pasture with trees
Drainage	well drained

Ah1	0-4/10 cm	10YR3/1; many fine iron mottles around roots, 5YR5/8; sandy loam; friable; common, very fine to fine roots; common, very fine and fine pores; clear and wavy boundary to:
		thin iron pan
C1	4/10-10/20 cm	7.5YR2/0; sandy loam; massive; friable; thixotropic; common fine roots; common, very fine and fine pores; clear and wavy boundary to:
2C	10/20-14/24 cm	2.5YR4/2, with mixtures of over- and underlying horizons; common, medium distinct iron mottles, 7.5YR5/8; sandy loam; structureless; friable; thixotropic; common fine roots; common, very fine and fine pores; abrupt and wavy boundary to:
3Ah	14/24-44 cm	7.5YR3/2; loam; moderate fine, subangular blocky; friable; thixotropic; many, very fine and fine roots; many, very fine and fine pores; contains wedge of sandy ash, which looks like a mixture of C1 and 2C; abrupt and wavy boundary to:
		thin iron pan, 5YR5/8.
4C	44-87 cm	has an irregular structure of black sandy ash (7.5YR2/0) and loamy weathered ash (10YR6/2), both stratified, maybe due to slope processes.

Profile Turrialba 8

Location	N 10°04'09"; W83°47'01"
Altitude	1580 m
Physiography	northern slope of the Turrialba, on top of a small ridge
Slope	2-3%
Land use	pasture
Mean annual temperature	about 17-18 °C
Mean annual precipitation	about 7000 mm

Ah1	0-5 cm	10YR2/3; moist; loam; strong fine subangular blocky and fine crumb; very friable; not/slightly thixotropic (possibly thixotropy could not be felt due to a high amount of decaying roots and other organic matter); many fine roots; pores not visible; abrupt and smooth boundary to:
Ah2	5-12/15 cm	10YR2/1; common faint reddish mottles along root channels; moist; loam; weak medium angular blocky (probably due to compaction by cattle tramping); friable to firm; slightly thixotropic; many fine roots; many fine pores; abrupt and wavy boundary to:
		placic horizon, about 5 mm thick, 5YR5/8, continuous (at some places it looks like previous horizon grades more gradually into the following horizon and continuous under the placic horizon).
Bw1	12/15-29 cm	10YR3/4; moist; loam; weak subangular blocky; friable; thixotropic; many fine roots; abundant very fine pores and few common, fine and medium pores; abrupt and smooth boundary to:
2CB	29-30 cm	pumice layer, possibly deposited during an eruption about 2000 years ago; 10YR7/6, some more white colours; small pockets of ash (10YR2/1) occur at some places under this pumice layer.
3Bw1	30-49 cm	10YR3/4; moist; loam; weak subangular blocky; friable; thixotropic; common fine roots; abundant, very fine pores and few to common, fine and medium pores; clear and smooth boundary to:
3Bw2	49-67/70 cm	10YR3/3; moist; loam; massive with pores; slightly firm; thixotropic; common fine roots; abundant very fine pores and few to common medium pores; abrupt and broken boundary to:
3CB	67/70-69/73 cm	5YR4/3; moist; sandy loam; massive with some pores; firm; very thixotropic; few fine roots; few very fine pores; abrupt and broken boundary to:
4Bw	69/73-105+ cm	10YR3/4; moist; silt loam; weak subangular blocky to massive with pores; friable; thixotropic; few fine roots; many very fine pores and few, fine and medium pores.

NOTE: from 12/15 cm downward some coarse pores up to 1 cm in diameter occur throughout the profile.

Appendix 2

Particle-size distribution

		Horizon	Percentile particle sizes (µm) 10%	25%	50%	75%	90%
Turrialba 1 (T1):							
T-800m	1	Ah1	5	9	26	114	251
	2	Ah2	4	9	25	101	228
	3	AB	5	11	33	106	192
	4	Bw1	5	13	43	122	201
	5/6	Bw2	3	6	13	28	51
	5/6	Bw2	2	5	15	44	94
Turrialba 2 (T2):							
T-950m	7	Ah1	4	8	19	52	121
	8	Ah2	4	8	20	65	157
	9	AB	4	8	18	46	104
	10	Bw1	6	15	45	139	245
	11	2Bw2g	10	28	98	231	411
	12	2Cg1	6	19	71	177	336
Turrialba 3 (T3):							
T-640m	13	Ah2	5	10	32	113	201
	14	AB	7	16	50	122	196
	15	Bw	5	15	48	133	222
Turrialba 8 (T8):							
T-1580m	39	Ah1	9	22	67	184	381
	40	Ah2	7	18	75	204	422
	41	Bw1	6	13	42	117	234
	42	2CB	6	18	79	236	572
	43	/ash	9	31	118	278	494
	44	3Bw1	5	10	28	77	171
	45	3Bw2	6	15	50	136	235
	46	3CB	5	18	64	187	371
	47	4Bw	6	14	46	131	261

Appendix 3

Bulkdensities and mass losses upon drying

#	Horizon	dry bulk density (g/cc)	LOD1 g/100g	LOD2 g/100g
Turrialba 1 (T1):				
1a	Ah1	0.23	277	6.67
1b	Ah1	0.24	260	6.32
1c	Ah1	0.25	262	5.77
2a	Ah2	0.28	247	6.08
2b	Ah2	0.27	257	6.59
2c	Ah2	0.28	254	6.49
3a	AB	0.23	296	9.07
3b	AB	0.25	290	7.73
3c	AB	0.25	290	8.14
4a	Bw1	0.23	323	8.45
4b	Bw1	0.25	317	8.03
4c	Bw1	0.22	325	8.10
5/6a	Bw2	0.29	249	7.36
5/6b	Bw2	0.32	244	7.26
5/6c	Bw2	0.32	244	7.40
Turrialba 2 (T2):				
7a	Ah1	0.28	229	6.18
7b	Ah1	0.25	256	6.86
8a	Ah2	0.27	250	6.21
8b	Ah2	0.28	250	6.23
9a	AB	0.27	273	6.64
9b	AB	0.27	273	7.42
9c	AB	0.26	291	8.87
9d	AB	0.26	291	8.05
10a	Bw1	0.23	331	7.15
10b	Bw1	0.23	331	8.62
11a	2Bw2g	0.23	327	11.49
11b	2Bw2g	0.24	316	11.25
12a	2Cg1	0.30	263	9.66
12b	2Cg1	0.44	170	7.79
Turrialba 3 (T3):				
13a	Ah2	0.28	266	8.38
13b	Ah2	0.27	267	8.51
14a	AB	0.28	265	8.46
14b	AB	0.32	241	8.69
15a	Bw	0.35	213	8.32
15b	Bw	0.36	207	10.23
Turrialba 4 (T4):				
16a	Ah	0.40	178	5.24
16b	Ah	0.41	149	4.48
17a	Bw	0.39	189	4.77
17b	Bw	0.42	174	4.56
19a	2Bw1g	0.58	124	4.48
19b	2Bw1g	0.57	128	4.54
20a	2Bw2	0.46	164	5.58
20b	2Bw2	0.48	156	5.53
21a	3Bw	0.37	210	6.91
21b	3Bw	0.39	196	6.58
Turrialba 5 (T5):				
44a	Ah1	0.25	64	6.27
44b	Ah1	0.28	102	5.13
Turrialba 6 (T6):				
27a	Ah1	0.51	127	3.32
27b	Ah1	0.38	185	4.36
28a	2Ah1	0.71	63	2.60
28b	2Ah1	0.64	93	3.01
29a	3Ah1	0.51	103	2.87
29b	3Ah1	0.54	94	2.91
33a	7C1	1.48	26	0.60
33b	7C1	1.23	36	0.99
Turrialba 7 (T7):				
34a	Ah1	1.03	47	1.37
34b	Ah1	1.05	47	1.32
35a	C1	1.25	26	0.58
35b	C1	1.26	23	0.50
37a	3Ah	0.65	80	1.85
37b	3Ah	0.80	67	1.78
38a	4C; ash	1.33	24	0.38
38b	4C; ash	1.36	23	0.35
Turrialba 8 (T8):				
40a	Ah2	0.49	154	3.50
40b	Ah2	0.55	119	3.43
41a	Bw1	0.55	117	2.88
41b	Bw1	0.50	128	3.05
44a	3Bw1	0.46	159	4.49
44b	3Bw1	0.44	164	4.48
45a	3Bw2	0.69	93	3.00
45b	3Bw2	0.65	106	3.22
47a	4Bw	0.60	110	4.65
47b	4Bw	0.52	143	4.73

Appendix 4

General soil data

Profile Turrialba 1 (T1)

#	depth	horizon	pH				P-retention	CEC	exch Al	sum bases
	(cm)		H_2O	KCl	H_2O-KCl	NaF	(%)	(cmol(+)/kg)		
1	0-10	Ah1	3.9	4.2	-0.3	10.9	93.58	35.28	3.93	2.78
2	10-27	Ah2	6.3	4.4	1.9	11.7	95.25	23.28	1.04	0.88
3	27-60	AB	6.2	4.7	1.5	11.7	95.62	25.22	0.07	1.08
4	60-93	Bw1	6.5	4.9	1.6	11.6	95.52	27.59	0.04	0.04
5	93-120/150	Bw2	5.3	5.3	0.0	11.2	95.25	22.26	0.00	0.67

Profile Turrialba 2 (T2)

#	depth	horizon	pH				P-retention	CEC	exch Al	sum bases
	(cm)		H_2O	KCl	H_2O-KCl	NaF	(%)	(cmol(+)/kg)		
7	0-8	Ah1	4.2	4.1	0.1	10.5	95.38	30.44	7.39	2.64
8	8-20	Ah2	3.9	4.4	-0.5	11.5	95.15	28.72	5.81	1.99
9	20-40	AB	4.6	5.0	-0.4	11.7	95.43	26.89	0.37	1.01
10	40-72	Bw1	4.9	5.3	-0.4	11.8	95.52	32.70	0.10	0.94
11	72-92	2Bw2g	5.1	5.0	0.1	11.7	95.52	32.25	0.06	0.04
12	92+	2Cg1	5.0	5.3	-0.3	11.7	95.52	24.81	0.01	0.73

Profile Turrialba 3 (T3)

#	depth	horizon	pH				P-retention	CEC	exch Al	sum bases
	(cm)		H_2O	KCl	H_2O-KCl	NaF	(%)	(cmol(+)/kg)		
13	0-18	Ah2	4.7	4.9	-0.2	11.8	95.43	29.98	0.12	0.84
14	18-45	AB	5.1	5.1	0.0	11.7	95.43	30.27	0.17	0.83
15	45-60/80	Bw	4.7	6.2	-1.5	11.4	95.34	36.74	0.07	0.69

Profile Turrialba 8 (T8)

#	depth	horizon	pH				P-retention	CEC	exch Al	sum bases
	(cm)		H_2O	KCl	H_2O-KCl	NaF	(%)	(cmol(+)/kg)		
39	0-5	Ah1	3.9	4.3	-0.4	9.1	79.93	23.55	4.81	5.99
40	5-12/15	Ah2	5.3	4.7	0.6	10.9	92.29	17.41	1.44	3.01
41	12/15-29	Bw1	5.5	5.1	0.4	11.5	92.84	17.02	0.17	1.84
42	29-30	2CB	6.9	5.5	1.4	11.3	89.96	10.10	0.04	1.34
43	29-30	/ash	5.9	5.9	0.0	11.0	72.04	6.10	nd	nd
44	30-49	3Bw1	5.8	5.8	0.0	11.6	94.42	17.22	0.02	1.87
45	49-67/70	3Bw2	5.9	6.0	-0.1	11.5	93.03	12.68	0.01	-
46	67/70-69/73	3CB	5.9	6.0	-0.1	10.9	83.70	6.48	0.02	1.03
47	69/73-105+	4Bw	6.0	6.1	-0.1	11.4	93.49	13.91	0.01	1.70

nd: not done

-: error in measurement

Appendix 5

Total C and total N

Profile Turrialba 1 (T1)

#	horizon	total C (%)	total N (%)
1a	Ah1	22.41	1.71
1b	Ah1	19.87	1.49
1c	Ah1	20.96	1.54
2a	Ah2	11.13	0.78
2b	Ah2	13.35	1.01
2c	Ah2	12.35	0.93
3a	AB	8.33	0.58
3b	AB	7.97	0.57
3c	AB	8.14	0.58
4a	Bw1	7.40	0.51
4b	Bw1	7.53	0.51
4c	Bw1	6.33	0.45
5/6a	Bw2	4.34	0.26
5/6b	Bw2	4.37	0.25
5/6c	Bw2	4.25	0.26

Profile Turrialba 2 (T2)

#	horizon	total C (%)	total N (%)
7a	Ah1	16.74	1.19
7b	Ah1	19.31	1.40
8a	Ah2	15.01	1.07
8b	Ah2	14.70	1.08
9a	AB	10.39	0.64
9b	AB	9.86	0.61
10a	Bw1	11.65	0.69

Profile 2 (T2) continued

#	horizon	total C (%)	total N (%)
10b	Bw1	9.52	0.55
11a	2Bw2g	7.70	0.36
11b	2Bw2g	8.14	0.39
12a	2Cg1	5.36	0.27
12b	2Cg1	6.70	0.17

Profile Turrialba 3 (T3)

#	horizon	total C (%)	total N (%)
13a	Ah2	8.24	0.54
13b	Ah2	7.33	0.47
14a	AB	5.77	0.52
14b	AB	4.77	0.35
15a	Bw	3.51	0.23
15b	Bw	3.89	0.21

Turrialba 4 (T4)

#	horizon	total C (%)	total N (%)
16a	Ah	10.80	1.01
16b	Ah	9.66	0.81
17a	Bw	5.76	0.46
17b	Bw	5.32	0.42
19a	2Bw1g	3.41	0.20
19b	2Bw1g	3.39	0.23
20a	2Bw2	3.84	0.22
20b	2Bw2	3.71	0.22
21a	3Bw	3.34	0.18
21b	3Bw	4.62	0.29

Profile Turrialba 5 (T5)

#	horizon	total C (%)	total N (%)
24a	Ah1	22.34	1.29
24b	Ah1	16.01	1.01

Profile Turrialba 6 (T6)

#	horizon	total C (%)	total N (%)
27a	Ah1	12.96	0.91
27b	Ah1	13.14	1.27
28a	2Ah1	6.16	0.47
28b	2Ah1	7.26	0.59
29a	3Ah1	5.22	0.36
29b	3Ah1	4.75	0.34
33a	7C1	1.23	0.01
33b	7C1	1.18	0.02

Profile Turrialba 7 (T7)

#	horizon	total C (%)	total N (%)
34a	Ah1	3.86	0.25
34b	Ah1	4.36	0.25
35a	C1	1.98	0.08
35b	C1	1.90	0.06
37a	3Ah	4.55	0.26
37b	3Ah	4.69	0.27
38a	4C; ash	1.18	0.00
38b	4C; ash	1.02	0.00

Profile Turrialba 8 (T8)

	#	horizon	total C (%)	total N (%)
(102)	39	Ah1	13.75	1.65
103	40a	Ah2	9.36	0.69
	40b	Ah2	8.37	0.66
104	41a	Bw1	4.41	0.26
	41b	Bw1	4.70	0.27
(105)	42	2CB	2.92	0.15
(110)	43	/ash	1.67	0.04
106	44a	3Bw1	4.42	0.28
	44b	3Bw1	4.48	0.31
107	45a	3Bw2	2.43	0.12
	45b	3Bw2	2.43	0.13
(108)	46	3CB	1.51	0.04
109	47a	4Bw	3.43	0.21
	47b	4Bw	3.78	0.22

ash

#	horizon	total C (%)	total N (%)
23a		1.23	0.00
23b		1.00	0.00

Appendix 6

Selective dissolution data

Turrialba 1 (T1)

#	depth	horizon	acid oxalate (%)			pyrophosphate (%)			dithionite citrate (%)		Al/Si ratio[1]	binary ratio	allophane	activity ratio	ferrihy-drite
	(cm)		Al_o	Fe_o	Si_o	Al_p	Fe_p	C_p	Al_d	Fe_d		Al_p/Al_o	(%)	Fe_o/Fe_d	(%)
1	0-10	Ah1	2.8	2.6	0.4	2.3	0.5	9.8	2.4	3.3	1.3	0.8	2.3	0.8	3.7
2	10-27	Ah2	5.3	3.4	1.3	2.6	0.5	6.5	3.6	4.7	2.2	0.5	10.4	0.7	4.9
3	27-60	AB	8.1	4.0	2.5	1.3	0.9	3.5	3.2	6.0	2.8	0.2	26.7	0.7	5.3
4	60-93	Bw1	8.1	5.3	2.8	0.6	0.1	5.0	3.0	7.5	2.7	0.1	28.7	0.7	8.8
5/6	93-120/150	Bw2	6.2	4.7	2.1	0.4	0.2	3.1	2.6	6.1	2.8	0.1	22.7	0.9	7.7

[1]: $(Al_o-Al_p)/Si_p$

Turrialba 2 (T2)

#	depth	horizon	acid oxalate (%)			pyrophosphate (%)			dithionite citrate (%)		Al/Si ratio[1]	binary ratio	allopha-ne	activity ratio	ferrihy-drite
	(cm)		Al_o	Fe_o	Si_o	Al_p	Fe_p	C_p	Al_d	Fe_d		Al_p/Al_o	(%)	Fe_o/Fe_d	(%)
7	0-8	Ah1	2.2	3.2	0.2	1.8	0.6	8.9	1.6	3.6	1.6	0.8	1.6	0.9	4.4
8	8-20	Ah2	3.5	3.8	0.7	2.7	0.7	8.7	3.1	4.4	1.1	0.8	4.1	0.9	5.4
9	20-40	AB	6.4	3.9	1.6	2.0	0.4	5.4	3.5	4.9	2.8	0.3	17.3	0.8	6.0
10	40-72	Bw1	10.9	4.0	3.9	1.0	0.5	3.6	3.1	5.0	2.6	0.1	37.5	0.8	6.0
11	72-92	2Bw2g	9.8	2.4	3.8	0.6	0.0	6.0	2.5	4.4	2.4	0.1	34.5	0.6	4.1
12	92+	2Cg1	12.6	1.2	5.5	0.5	0.0	2.1	1.6	2.8	2.2	0.0	45.4	0.4	2.0

[1]: $(Al_o-Al_p)/Si_o$

Turrialba 3 (T3)

#	depth	horizon	acid oxalate (%)			pyrophosphate (%)			dithionite citrate (%)		Al/Si ratio[1]	binary ratio	allophane	activity ratio	ferrihy-drite
	(cm)		Al_o	Fe_o	Si_o	Al_p	Fe_p	C_p	Al_d	Fe_d		Al_p/Al_o	(%)	Fe_o/Fe_d	(%)
13	0-18	Ah2	7.8	3.1	2.5	1.3	0.9	3.3	2.9	4.7	2.6	0.2	24.9	0.7	3.7
14	18-45	AB	8.6	2.7	3.3	0.6	0.1	4.4	2.2	4.5	2.5	0.1	30.2	0.6	4.5
15	45-60/80	Bw	7.9	1.5	3.2	0.4	0.0	1.4	1.9	5.1	2.4	0.1	28.0	0.3	2.4

1: $(Al_o-Al_p)/Si_o$

Turrialba 8 (T8)

#	depth	horizon	acid oxalate (%)			pyrophosphate (%)			dithionite citrate (%)		Al/Si ratio[1]	binary ratio	allophane	activity ratio	ferrihy-drite
	(cm)		Al_o	Fe_o	Si_o	Al_p	Fe_p	C_p	Al_d	Fe_d		Al_p/Al_o	(%)	Fe_o/Fe_d	(%)
39	0-5	Ah1	0.6	0.6	0.0	0.7	0.5	5.6	0.7	0.9	-	-	0.2	0.6	0.1
40	5-12/15	Ah2	2.0	1.6	0.3	1.4	0.8	3.9	1.5	1.9	2.3	0.7	2.4	0.9	1.4
41	12/15-29	Bw1	2.2	2.4	0.4	0.9	1.2	2.8	1.3	2.5	3.3	0.4	5.7	1.0	2.0
42	29-30	2CB	1.8	1.9	0.6	0.4	0.3	2.8	0.8	2.8	2.4	0.2	5.5	0.7	2.9
43	29-30	/ash	1.2	1.0	0.7	0.2	0.1	0.5	0.3	0.9	1.4	0.2	4.3	1.1	1.6
44	30-49	3Bw1	4.6	2.4	1.5	0.4	0.2	1.9	1.1	2.2	2.7	0.1	15.9	1.1	3.7
45	49-67/70	3Bw2	4.0	1.8	1.7	0.3	0.0	1.5	0.8	1.6	2.1	0.1	14.0	1.1	3.0
46	67/70-69/73	3CB	2.6	1.1	1.4	0.2	0.0	0.4	0.3	0.9	1.7	0.1	9.6	1.2	1.9
47	69/73-105+	4Bw	4.3	2.1	1.9	0.3	0.1	1.2	0.9	2.1	2.1	0.1	15.0	1.0	3.4

1: $(Al_o-Al_p)/Si_o$

-: error

Appendix 7

Total chemical analysis

XRFS-data
(Based on dry weight at 105_C;2nd)

#	Horizon	SiO2 (%)	TiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MnO (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	P2O5 (%)	L.O.I. (%)	SUM (%)
Turrialba 1 (T1):													
1a	Ah1	22.64	1.34	13.1	8.24	0.05	1.53	1.27	0.65	0.44	0.41	50.05	99.73
1b	Ah1	25.45	1.46	14.24	8.91	0.06	1.83	1.56	0.76	0.40	0.4	45.52	100.57
1c	Ah1	24.71	1.36	13.43	8.30	0.05	1.80	1.62	0.74	0.46	0.4	47.18	100.27
2a	Ah2	27.62	1.78	22.17	10.94	0.07	1.75	1.22	0.68	0.54	0.37	33.47	100.50
2b	Ah2	27.75	1.79	18.88	11.14	0.07	1.81	1.27	0.68	0.5	0.42	36.13	100.43
2c	Ah2	28.22	1.68	19.54	11.46	0.07	1.79	1.25	0.68	0.52	0.41	34.50	100.41
2d	Ah2	28.25	1.87	19.51	11.51	0.07	1.83	1.27	0.68	0.51	0.41	34.50	100.51
2e	Ah2	28.22	1.9	19.56	11.40	0.07	1.82	1.26	0.68	0.53	0.42	34.50	100.51
3a	AB	25.47	2.41	26.03	14.31	0.06	1.22	0.47	0.11	0.28	0.38	29.16	99.87
3b	AB	25.49	2.28	26.26	13.78	0.06	1.31	0.54	0.21	0.28	0.36	30.93	101.47
3c	AB	24.68	2.25	25.38	13.68	0.06	1.26	0.53	0.18	0.27	0.36	31.3	99.91
4a	Bw1	23.1	2.23	27.38	13.45	0.06	0.96	0.29	0.02	0.18	0.33	31.79	99.75
4b	Bw1	22.85	2.24	28.55	13.48	0.05	0.86	0.23	0	0.15	0.32	31.51	100.21
4c	Bw1	22.04	2.30	29.43	14.38	0.05	0.85	0.16	0	0.15	0.28	30.4	100.04
5/6a	Bw2	18.24	2.73	33.33	16.61	0.05	0.58	0.04	0	0.00	0.18	28.30	100.07
5/6b	Bw2	19.28	2.73	33.12	16.65	0.05	0.58	0.06	0	0.1	0.17	27.79	100.34
5/6a	Bw2	19.29	2.69	32.82	16.52	0.05	0.64	0.06	0	0.1	0.17	27.82	99.90
Turrialba 2 (T2):													
7a	Ah1	33.62	1.68	11.15	9.93	0.06	2.4	1.91	1.06	0.72	0.43	37.61	100.57
7b	Ah1	31.4	1.58	10.35	9.06	0.06	2.06	1.75	0.98	0.68	0.44	42.31	100.64
8a	Ah2	33.83	1.78	12.51	10.55	0.06	2.2	1.76	1.02	0.69	0.44	35.77	100.6
8b	Ah2	34.41	1.82	12.86	10.57	0.06	2.24	1.76	0.97	0.86	0.44	35.81	101.8
9a	AB	30.89	1.89	19.42	11.08	0.07	2.15	1.43	0.81	0.86	0.37	31.5	100.26
9b	AB	31.29	1.92	19.59	11.21	0.07	2.19	1.44	0.86	0.67	0.37	31.5	101.09
9c	AB	31.31	1.90	19.87	11.41	0.07	2.11	1.41	0.83	0.69	0.39	30.08	100.15
9d	AB	31.35	1.98	19.53	11.46	0.07	2.19	1.46	0.87	0.86	0.39	31.22	101.17
9e	AB	30.58	1.95	19.19	11.4	0.07	2.06	1.4	0.82	0.67	0.4	31.45	99.98
10a	Bw1	27.43	2.47	20.72	13.35	0.05	1.68	0.68	0.28	0.33	0.37	32.73	100.09
10b	Bw1	27.55	2.43	20.85	13.33	0.05	1.68	0.67	0.28	0.33	0.36	32.73	100.22
10c	Bw1	29.27	2.49	20.57	13.96	0.06	1.75	0.7	0.33	0.36	0.36	31	100.81
11a	2Bw2g	22.22	2.02	29.53	10.44	0.04	1.3	0.30	0	0.1	0.27	34.23	100.43
11b	2Bw2g	23.42	2.15	29.41	10.18	0.04	1.35	0.37	0	0.13	0.27	33.36	100.59
12a	2Cg1	27.8	2.32	30.4	9.15	0.04	1.93	0.95	0	0.17	0.23	28.66	101.27
12b	2Cg1	33.92	2.48	29.89	6.35	0.05	2.61	1.17	0	0.28	0.2	23.08	99.97
Turrialba 3 (T3):													
13a	Ah2	26.86	2.17	27.46	10.31	0.04	1.3	0.45	0.13	0.34	0.51	30.98	100.52
13b	Ah2	26.65	2.2	28.19	10.26	0.04	1.23	0.37	0.07	0.31	0.48	29.91	99.71
14a	AB	26.22	2.29	30.2	10.18	0.03	0.94	0.18	0	0.28	0.42	28.09	98.79
14b	AB	26.95	2.51	31.68	10.62	0.03	0.68	0.13	0.06	0.29	0.4	25.77	99.31
15a	Bw	26.83	2.69	33.26	10.65	0.03	0.67	0.04	0	0.27	0.23	24.34	98.94
15b	Bw	27.34	2.79	34.35	10.97	0.03	0.7	0.06	0	0.3	0.25	23.18	99.79
Turrialba 4 (T4):													
16a	Ah	39.74	1.16	15.78	5.38	0.06	2.57	4.04	2.37	1.17	0.65	27.42	100.38
16b	Ah	42.67	1.22	16.26	5.6	0.07	2.79	4.56	2.50	1.24	0.6	22.26	99.95
17a	Bw g	44.62	1.26	18.64	7.98	0.11	3.13	3.64	2.43	1.33	0.50	18.97	100.67
17b	Bw g	45.27	1.32	18.56	8.25	0.11	3.28	3.85	2.54	1.40	0.48	15.8	100.74
19a	2Bw1g	48.14	1.31	20.17	7.91	0.12	3.66	3.83	2.73	1.62	0.33	10.96	100.83
19b	2Bw1g	47.77	1.33	20.08	8.03	0.12	3.68	3.87	2.7	1.57	0.34	11.24	100.78
20a	2Bw2	44.46	1.37	21.06	8.30	0.12	3.37	3.54	2.53	1.39	0.41	14.17	100.83
20b	2Bw2	45.07	1.41	20.77	8.42	0.12	3.42	3.50	2.6	1.41	0.4	13.58	100.83
21a	3Bw	41.76	1.37	22.23	8.43	0.13	3.02	2.7	1.83	1.3	0.44	17.14	100.48
21b	3Bw	42.05	1.39	22.29	8.46	0.12	3.14	2.73	1.90	1.32	0.42	16.66	100.63
Turrialba 5 (T5):													
24a	Ah1	28.51	0.81	9.6	4.37	0.04	2.12	3.48	1.57	0.75	0.43	48.90	100.7
24b	Ah1	33.54	0.86	10.95	4.73	0.06	2.76	4.83	2.36	1.16	0.36	38.67	100.34
Turrialba 6 (T6):													
27a	Ah1	44.71	1.16	14.81	5.11	0.07	2.97	5.2	3.04	1.3	0.40	22.28	101.18
27b	Ah1	40.6	1.04	13.15	4.7	0.06	2.62	4.56	2.63	1.13	0.51	30.11	101.14
28a	2Ah1	48.57	1.35	16.46	5.82	0.06	3.52	6.36	3.37	1.29	0.44	13.79	101.06
28b	2Ah1	47.02	1.26	16.07	5.68	0.06	3.14	5.91	3.19	1.22	0.44	17.32	101.36
29a	3Ah1	48.90	1.36	16.54	7.6	0.13	3.86	5.5	3.32	1.31	0.43	12.64	101.72
29b	3Ah1	48.58	1.3	16.5	7.84	0.16	3.50	5.25	3.28	1.36	0.42	12.97	101.26
33a	7C1	55.91	1.18	16.01	7.72	0.12	8.46	6.55	3.79	1.78	0.3	2.02	101.88
33b	7C1	56.62	1.1	16.32	7.24	0.1	5.06	5.78	3.6	1.85	0.29	3.72	100.75
Turrialba 7 (T7):													
34a	Ah1	50.04	1.29	16.78	7.58	0.11	4.86	7.88	3.66	1.18	0.4	7.93	101.75
34b	Ah1	50.67	1.32	16.98	7.07	0.1	4.59	7.8	3.72	1.22	0.39	7.95	101.86
35a	C1	50.78	1.29	16.75	8.44	0.13	7.16	9.2	3.72	1.15	0.36	2.93	101.90
35b	C1	51.2	1.24	16.78	8.52	0.13	7.29	8.9	3.68	1.16	0.38	2.39	101.72
37a	3Ah	49.66	1.41	16.16	7.85	0.1	4.44	6.53	3.57	1.41	0.49	10.25	101.31
37b	3Ah	48.7	1.38	18.12	7.90	0.1	4.6	6.77	3.62	1.41	0.46	10.01	101.21
38a	4C; ash	52.52	1.53	17.27	8.45	0.13	6.44	8.58	4.06	1.36	0.48	0.95	101.83
38b	4C; ash	52.37	1.56	17.1	8.45	0.13	6.52	8.57	3.90	1.33	0.47	0.80	101.45
Turrialba 8 (T8):													
39	Ah1	39.25	0.96	12.2	4.73	0.07	2.44	4.1	2.47	1.2	0.58	32.86	100.86
40a	Ah2	44.13	1.37	15.80	6.19	0.07	2.86	4.76	2.75	1.22	0.43	21.32	101.02
40b	Ah2	44.64	1.30	16.11	6.4	0.07	2.68	4.94	2.81	1.22	0.43	20.51	101.44
41a	Bw1	48.58	1.22	17.79	7.69	0.06	3.48	3.97	2.87	1.47	0.31	12.53	100.82
41b	Bw1	49.05	1.28	17.52	7.91	0.06	3.5	4.03	2.66	1.49	0.33	13.12	101
42	2CB	51.37	1.31	17.53	7.87	0.07	3.45	3.64	2.41	1.5	0.34	10.1	99.65
43	/ash	52.3	1.49	16.37	8.02	0.11	6.83	6.56	3.81	1.78	0.46	3.43	101.21
44a	3Bw1	44.97	1.37	19.52	8.29	0.09	3.05	3.77	2.66	1.48	0.35	14.47	100.05
44b	3Bw1	45.78	1.36	19.91	8.33	0.09	3.11	3.71	2.62	1.45	0.34	14.97	101.88
45a	3Bw2	50.8	1.14	19	7.26	0.09	3.4	3.98	3	1.73	0.27	8.6	99.31
45b	3Bw2	51.92	1.16	18.31	7.37	0.09	3.38	3.6	2.84	1.74	0.25	9.03	100.77
46	3CB	52.04	1.14	18.86	7.43	0.11	4.42	5.52	3.72	1.62	0.27	5.15	101.34
47a	4Bw	45.75	1.47	20.56	8.7	0.1	3.69	3.91	2.62	1.37	0.28	12.90	101.51
47b	4Bw	45.38	1.41	20.56	8.53	0.1	3.46	3.86	2.67	1.43	0.27	13.19	100.9
Ash:													
23a	verso as t	75.44	1.53	7.24	2.43	0.04	1.56	1.75	1.15	1.08	0.28	7.54	100.09
23b		76.23	1.53	7	2.31	0.04	1.52	1.62	1.06	1.03	0.27	7.5	100.15

XRFS-data
(Based on dry weight at 105_C;2nd)

#	Horizon	Ba (ppm)	Ce (ppm)	Cr (ppm)	Cu (ppm)	Ga (ppm)	La (ppm)	Nb (ppm)	Ni (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)	Zr (ppm)
Turrialba 1 (T1):															
1a	Ah1	335	51	197	142	34	31	14	31	26	18	172	548	55	199
1b	Ah1	217	17	161	94	26	30	16	27	21	16	183	406	38	208
1c	Ah1	488	91	258	197	41	52	14	46	30	23	215	714	80	207
2a	Ah2	192	18	175	127	34	37	24	28	26	18	147	481	44	293
2b	Ah2	228	28	193	121	34	34	18	28	22	17	153	536	47	267
2c	Ah2	231	24	185	123	35	30	20	27	25	19	150	529	47	285
2d	Ah2	345	81	244	191	42	42	22	36	30	21	164	715	63	293
3a	AB	103	27	262	146	40	33	27	31	31	14	67	728	47	372
3b	AB	135	38	258	150	40	18	23	30	28	17	74	734	48	356
3c	AB	186	46	272	161	43	21	25	31	34	16	74	770	52	353
4a	Bw1	121	28	252	123	37	8	25	32	31	13	49	678	57	342
4b	Bw1	201	38	262	142	40	38	26	35	32	11	52	680	128	419
4c	Bw1	76	38	287	136	40	8	25	33	32	11	40	780	46	341
5/6a	Bw2	0	33	353	116	43	8	25	32	28	11	27	850	40	358
5/6b	Bw2	0	41	351	117	43	22	23	33	30	12	30	803	43	368
5/6c	Bw2	25	62	392	133	49	20	27	38	34	13	28	1012	50	373
Turrialba 2 (T2):															
7a	Ah1	418	62	220	142	35	33	12	36	24	23	243	664	70	222
7b	Ah1	602	105	268	201	48	47	14	47	30	27	249	858	96	214
8a	Ah2	449	78	244	169	45	35	14	38	29	25	240	766	71	252
8b	Ah2	627	113	298	210	53	55	13	48	30	27	250	953	96	258
9a	AB	387	61	214	168	46	38	19	30	30	24	184	706	68	317
9b	AB	219	17	163	131	34	17	19	31	28	20	186	520	51	309
9c	AB	534	90	256	234	51	25	19	42	33	24	192	869	81	321
9d	AB	251	18	169	138	37	36	21	29	27	18	163	546	47	304
10a	Bw1	99	53	240	130	49	8	21	23	31	13	84	859	45	356
10b	Bw1	107	43	233	122	47	25	25	23	28	13	88	828	42	360
11a	2Bw2g	25	45	244	136	45	8	19	22	26	5	34	740	36	320
11b	2Bw2g	0	27	250	130	44	8	21	25	26	12	37	684	34	341
12a	2Cg1	25	44	327	159	52	8	21	43	29	12	47	847	55	382
12b	2Cg1	0	11	238	147	45	0	21	52	28	18	57	611	61	348
Turrialba 3 (T3):															
13a	Ah2	207	24	222	175	43	21	22	31	30	23	75	647	52	334
13b	Ah2	215	35	251	200	47	29	21	39	32	24	69	718	62	340
14a	AB	229	41	275	206	52	25	21	42	36	27	57	806	68	354
14b	AB	121	19	253	157	46	23	21	40	33	26	52	713	59	358
15a	Bw	90	26	307	165	52	21	24	49	33	26	51	822	64	390
15b	Bw	25	11	281	142	50	35	25	45	34	21	49	745	59	392
Turrialba 4 (T4):															
16a	Ah	506	5	100	104	21	24	14	23	15	29	565	239	57	172
16b	Ah	533	5	107	112	25	34	17	29	16	29	526	254	57	184
17a	Bw	595	16	135	133	26	33	18	31	21	31	580	295	49	217
17b	Bw	610	14	142	114	27	33	20	35	19	32	594	290	50	224
19a	2Bw1g	560	18	70	121	30	18	18	30	18	33	609	290	57	212
19b	2Bw1g	648	15	68	123	31	27	15	28	21	32	600	292	58	210
20a	2Bw2	626	18	130	160	27	33	17	30	21	32	462	316	46	256
20b	2Bw2	645	16	127	151	26	44	17	33	20	34	473	317	48	261
21a	3Bw	567	12	145	133	27	34	21	29	20	31	331	305	41	264
21b	3Bw	570	14	153	137	30	37	24	33	20	35	338	315	40	259
Turrialba 5 (T5):															
24a	Ah1	329	5	98	70	15	7	5	22	12	18	487	180	43	108
24b	Ah1	470	5	98	87	18	28	5	31	16	32	520	169	43	131
Turrialba 6 (T6):															
27a	Ah1	588	5	95	108	20	32	15	32	12	32	704	236	60	173
27b	Ah1	510	5	85	94	20	26	13	28	13	29	623	219	56	153
28a	2Ah1	601	12	106	110	24	22	16	35	14	31	826	284	60	184
28b	2Ah1	620	14	105	114	24	29	12	36	14	28	780	287	65	180
29a	3Ah1	626	12	102	107.	23	28	15	39	15	32	741	287	51	167
29b	3Ah1	648	19	102	124	23	37	17	39	17	32	734	296	54	202
33a	7C1	751	18	201	67	22	27	13	74	17	46	779	253	62	200
33b	7C1	825	17	167	88	24	32	17	58	15	49	790	229	50	210
Turrialba 7 (T7):															
34a	Ah1	569	20	133	110	24	7	16	42	12	26	853	285	62	167
34b	Ah1	521	17	127	107	25	25	12	40	12	28	862	291	64	171
35a	C1	544	25	148	98	23	27	15	56	11	25	840	277	54	161
35b	C1	537	25	145	97	22	33	11	55	14	27	853	273	59	184
37a	3Ah	703	17	116	148	25	28	16	36	14	33	847	326	55	200
37b	3Ah	679	14	111	113	24	30	15	34	16	32	832	300	54	195
38a	4C; ash	625	23	121	91	24	28	17	50	14	31	1050	331	67	197
38b	4C; ash	623	27	122	104	26	44	19	55	14	30	1060	340	65	197
Turrialba 8 (T8):															
39	Ah1	536	5	95	93	20	22	11	23	16	36	580	213	56	156
40a	Ah2	565	12	111	98	25	31	14	30	16	30	668	306	51	195
40b	Ah2	603	14	114	104	23	49	16	29	12	30	682	312	48	197
41a	Bw1	681	13	141	96	27	22	14	38	18	37	651	296	42	217
41b	Bw1	672	12	143	97	28	24	17	35	21	38	642	294	40	217
42	2CB	743	5	163	105	25	48	16	43	25	34	760	302	38	238
43	/ash	815	24	227	91	29	46	21	116	17	54	853	348	64	266
44a	3Bw1	644	12	105	145	32	45	20	25	14	39	570	321	43	229
44b	3Bw1	648	10	104	139	26	34	18	25	20	34	564	306	42	229
45a	3Bw2	800	18	83	130	28	17	15	38	24	45	703	257	47	230
45b	3Bw2	817	19	82	124	29	34	13	33	25	42	645	260	49	232
46	3CB	756	14	79	135	29	20	12	42	16	38	818	258	57	225
47a	4Bw	707	21	157	154	34	50	21	35	19	38	530	356	46	261
47b	4Bw	690	18	139	148	28	53	19	29	21	36	526	330	45	256
Ash:															
23a		556	5	87	93	20	19	15	5	15	38	303	311	5	212
23b		629	5	85	88	17	7	15	11	17	37	271	304	5	210