The Use of Scattered Radiation in X-Ray Fluorescence Analysis of Soil and Plant Materials

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THE USE OF SCATTERED
RADIATION IN X-RAY FLUORESCENCE ANALYSIS
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by

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The isolated atom model of X-ray scatter was used to develop a new analytical strategy for internal standardisation in X-ray fluorescence spectrometry. The method which was applicable to both geological and biological materials, defined quantitatively, by how much and within what limitations, various calibration techniques could improve analyses, for particular elements in specific materials.

The analytical strategy was based on a modified peak-to-background ratio equation, where the background intensity was raised by an exponent T. The variable T, combined as special cases, all existing analytical strategies which used scattered X-rays and the simple linear calibration where $T = 0$. Variation in T was evaluated using extensive computer processing of matrix data for typical soil and plant materials. It was found that values of T varied with analyte, scatter wavelength, type of scatter, and the matrix component contributing to mass absorption error.

The procedure developed to select the optimum calibration strategy, for any combination of mass absorption errors in soil and plant analysis, showed:

(i) how much each interfering component contributed to both initial and final analyte error,
(ii) which value of T, for various scatter wavelengths and types of scatter, gave optimum reduction in analyte error,

and,

(iii) if any improvement over the various strategies commonly used, could be achieved.

Consequent limitations of some analytical methods which have been proposed in the literature were discussed.

Extremely variable matrices were specially prepared to test the method for zinc and zirconium analysis. The improvement in quality of matrix compensation was as predicted from theory. Values of T were tabulated for analysis of various groups of elements in soil and plant materials and situations were described where successful calibration using scattered radiation was most unlikely.

The methods developed were among those used to analyse soils and metalliferous sewage sludge in an experimental programme designed to establish for local conditions

(i) maximum permissible sewage sludge application rates and,

(ii) the effect of sludge application on pasture production and quality.

Although the digested sludge contained useful amounts of plant and animal nutrients, metal content was too high to permit its indiscriminate use as a soil additive. The metal contents were not high enough however to prohibit the judicious utilisation of the sludge within prescribed limits.

Highly significant results from both glasshouse and field trials showed that chromium contamination of sludge could decrease pasture production. It appeared that chromium may have blocked plant uptake of nutrient cations. With the sludge chromium concentration at about 0.5%, and the total sludge application at the recommended level of 250 t/ha, no deleterious effects were likely, provided a good supply of nutrient cations was maintained in the soil.

Zinc was found to be the limiting contaminant in herbage, and copper concentrations were near the upper safety limits. Potassium deficiency was probably a greater pastoral constraint than was metal toxicity. No other elements were found in herbage, in concentrations likely to be injurious to animal health, or restrictive to plant yield.

Preface

This thesis is in two parts, which, although written separately, are the results of concurrent research. The first involves the application of physics and computer mathematics to spectrochemical analysis by X-ray fluorescence. The methods developed are used in the second part, which presents the findings of a research programme into the disposal on pasture of a metalliferous sewage sludge. This aspect of the study was partly funded by the Christchurch Drainage Board and the second part of this thesis incorporates much of the report presented to the Board. The separate volume, "Tables of Mass Absorption Errors and Background Corrections for Soil and Plant Analysis by X-ray Fluorescence", accompanying this study, incorporates user instructions and is therefore self contained. The overall conclusions are summarised in the last chapter but specific conclusions and more detailed discussions are given, in context, at the end of each relevant section.

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PART 1

Theoretical Evaluation of the Ability of Scattered Radiation to Correct for Mass Absorption Errors

CHAPTER 1

X-RAY FLUORESCENCE SPECTROMETRY

1.1 INTRODUCTION

X-ray fluorescence is a widely used, non-destructive, instrumental method of chemical analysis. When irriadiated by an energetic source of X-rays, elements within the sample absorb some of the radiation and re-emit X-rays of a longer wavelength. Elemental concentrations are related to the measured intensity of re-emitted characteristic radiation. This extremely rapid technique is applicable to a wide range of elements and samples.

Detection limits however, may barely reach the level of minor constituents in many common materials and analyses are subject to many instrumental and interference uncertainties. Although simple in concept, X-ray spectrometric installations have become expensive and complex. The recent additions of automation and electronic data processing have revitalised the technique and ensured the survival of this very useful method of multi-elemental chemical analysis.

The motivation behind the first part of this study is the development of improved methods for trace element analysis of powdered soil and plant material; particularly methods which combine better accuracy with minimum analysis time. The general principles of X-ray spectra, X-ray production and detection, electronic instrumentation, sample preparation and general analytical techniques have been extensively reviewed elsewhere (Jenkins and De Vries, 1970; Carr-Brion and Payne, 1970; Muller, 1972; Bertin, 1978). This investivation concentrates on problems of interelemental absorption-enhancement effects and internal-standardisation methods using scattered X-rays.

The main problems which beset quantitative X-ray spectrochemical analyses involve the nature of the specimen matrix. Matrix effects arise from the elemental composition of the remainder of the sample (termed absorption-enhancement effects for the particular analyte under consideration) and from the physical features of the specimen (surface texture, particle size and heterogeneity). Physical matrix effects can be largely eliminated by appropriate specimen preparation and presentation techniques while absorption-enhancement effects dictate the particular analytical strategy used. Chemical absorption-enhancement and physical matrix effects, can both vary from being negligible to making nonsence of experimental results. A myriad of methods and techniques for sepcific elements in most materials have been developed to eliminate, circumvent or correct for, matrix effects.

Most of the general analytical methods developed to reduce absorption-enhancement effects have been applied to soil and plant tissue analysis. Such complex materials have frequently required a combination of techniques to reduce all sources of error to within acceptable limits. Variations of the dilution/fusion/heavy absorber/ mathematical correction method of Norrish and Hutton (1969) for geological samples have found wide application (Fabbi, 1972; Harvey et al., 1973; Haukka and Thomas, 1977; Parker, 1978).

Matrix similarity between plant specimens has in some cases led to success with simple calibration standardisation (Jenkins and Hurley, 1966; Mudroch and Mudroch, 1977). Low absorber dilution techniques (Evans, 1970) and thin film methods of sample preparation (Fields and Furkert, 1971) have increased accuracy. Hutton and Norrish (1977) used corrections for mass absorption of the plant sample while Norrish and Hutton (1977) extended their matrix correction method developed for geological specimens (Norrish and Hutton, 1969) to analysis of highly variable plant materials.

X-ray spectrometric analysis is largely a calibration method involving either conversion of intensity data to analytical concentration via calibration curves or derivation of mathematical relationships obtained from measurements on standards. Mathematical correction methods, particularly those involving influence coefficients or absorption corrections, usually involve complex calculations, data storage and the use of automated computer-controlled spectrometers.

Methods using variable take-off angle (Ebel, 1969) and fundamental parameters (Criss and Birks, 1968) involve extensive use of tabulated constants. Such methods, although theoretically attractive, have had only limited success when applied to complex systems (Muller, 1978; Keith and Loomis, 1978; Palme and Jagoutz, 1977).

1.2 SCOPE OF THE INVESTIGATION

The method investigated in Part I of this study to compensate for matrix effects is internal-standardisation using the intensity of primary X-rays scattered by the specimen. The use of scattered X-rays (Andermann and Kemp, 1958) may give complete or substantial correction for many instrumental and sample sources of error.

An additional advantage is that not all elements that contribute significantly to variations in absorption by the sample must be measured. Methods using scattered X-rays have been developed for a wide variety of materials.

Scattered X-rays may be used either directly, as in peak to background ratio techniques, or to estimate mass absorption coefficient corrections. Their use is especially applicable to trace element analysis in low atomic number matrices where the scattered intensity is high and can be measured precisely with short counting times. Individual elements may be determined without reference to the others, sample preparation is minimal and no additions need be made to samples. As with any technique, approximations and limitations also exist. Scattered X-rays are relatively ineffectual in correcting for secondary fluorescence excited by the shorter wavelength spectral lines of other matrix elements. Fortunately such enhancement is significant only in specific cases (Franzini *et al.*, 1976b).

The utilisation of scattered radiation methods has been largely empirical. Selection of scattering wavelength, type of scattered radiation and the particular correction technique used, has usually involved trial and error. Taylor and Andermann (1969, 1971) and Bertin (1978) have suggested that the various approaches still need a complete unifying theoretical justification based upon physical principles. One intention of this investigation is to examine the application to soil and plant analysis, of those X-ray spectrometric techniques that use scattered X-rays.

Isolated atom X-ray scattering theory, applied in a form suitable to geological and biological analyses has been used to develop theoretical correction techniques whose effectiveness is able to be tested. The immediate aim of the study is to establish not only if a technique can improve results for particular elements in specific materials but by how much and within what limitations.

CHAPTER 2

SCATTERED X-RAYS

2.1 HISTORICAL INTRODUCTION

The linear absorption coefficient of a material is defined from basic X-ray theory, as the reduction in intensity per unit distance traversed. This coefficient, μ^* (see[1] below) is the sum of a photoelectric absorption coefficient τ and a linear scattering coefficient σ. Photons which deviate or scatter from their collinear path through the absorber can be characterised according to whether the collision is elastic (Rayleigh scattering) or inelastic (Compton scattering).

Inelastic scatter, involving a collision with a loosely bound electron, results in a slight decrease in photon energy with a corresponding increase in wavelength. The recoil electron carries away the energy difference in the form of kenetic energy. As no phase relationship can exist between an incident and inelastically scattered photon, Compton scattering is termed incoherent. (Note that not all incoherent scatter is necessarily inelastic.) Incoherent scatter predominates when photon energy greatly exceeds the orbital electron binding energy.

Rayleigh scatter results from elastic mechanical collision between a photon and an atom as a whole. This coherent scatter predominates when the binding and photon energies are of the same order of magnitude.

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[1] Nomenclature in this study follows that of the International Union of Pure and Applied Chemistry, (1977). An exception is the use of the terms mass absorption μ, and linear absorption μ^*, where this study follows the traditional X-ray spectrometric usage instead of the Commission V.4 recommendation of linear attenuation μ, and mass attenuation μ/ρ .

In X-ray fluorescence spectrometry, scatter of the primary X-ray beam by the specimen, results in the presence of both continuous spectrum and X-ray tube target lines in the secondary spectrum. Often regarded as a nuisance, this background of primary radiation can give some information about matrix properties of the sample. Analyte fluorescent intensity is also affected in a similar way by matrix properties.

The technique of using scattered radiation as an internal standard to compensate for matrix effects was first described in detail by Andermann and Kemp (1958), who demonstrated, empirically, the effectiveness of the peak-background ratio in correcting for a variety of instrumental, operational and specimen errors. They recalled in a qualitative way, the basic theoretical photon intensity scattered by an atom as given by the classical calculations of Compton and Allison (1935). By considering the scattering of an incident wave by a group of Z electrons around a nucleus, Compton and Allison (1935) gave the coherent and incoherent fractions of the total scattered intensity (I_s) as:

$$S = I_s/Z.I_e = Z.f^2 + (1 - f^2) \qquad (1)$$

where the scattering factor S was the ratio of the actual scattering to that which would occur if each electron acted independently; I_e the free electron (Thomson) scattering intensity; and f the atomic scattering factor.

Using various approximations, Andermann and Kemp (1958) showed qualitatively, that a line-to-scattering ratio was less sensitive to varying Z (i.e. changing matrix composition) than line intensity alone. From equation (1), $I_s \mathrel{\tilde{\propto}} Z^{(1\text{ to }2)}$. Considering attenuation in traversing the sample, the observed scattered intensity I_0, was given by,

$$I_0 \mathrel{\tilde{\propto}} I_s\,\mu^{-1} \mathrel{\tilde{\propto}} Z^{(1\text{ to }2)}.\mu^{-1} \qquad (2)$$

where the absorption coefficient (mass or linear), could be substituted by,

$$\mu \overset{\sim}{\propto} Z^{3} \qquad (3)$$

Analyte fluorescent intensity (I_i) could also be approximated by the simple relationship,

$$I_i \overset{\sim}{\propto} \mu^{-1} \overset{\sim}{\propto} Z^{-3} \qquad (4)$$

Hence $\quad I_i/I_0 \overset{\sim}{\propto} Z^{-(1\text{ to }2)} \qquad (5)$

which was less dependent on Z than I_i alone.

Compton incoherent scattering of a primary X-ray tube target line has been used extensively as a measure of mass absorption coefficient. Simple integration of attenuated primary and secondary X-ray beams, gives the total analyte fluorescent intensity per unit area for an infinitely thick sample as

$$I_i = k.C.\mu^{-1} \qquad (6)$$

where $\quad C$ = analyte concentration

μ = mass absorption coefficient

k = constant, determined by;

(i) instrumental design and efficiency

(ii) fluorescent yield

(iii) sample matrix

Equation (6) also assumes several relationships involving spectral distributions and attenuation as described by Norrish and Chappell (1967).

It follows from equation (6), that quantitative analyses must directly or indirectly make allowance for variation in mass absorption coefficient of the samples. Reynolds (1963, 1967) reasoned that since, (from equation 6)

$$C \overset{\sim}{\propto} I_i.\mu$$

and $\quad C \overset{\sim}{\propto} I_i/I_0$ (Andermann and Kemp, 1958)

then $\quad \mu \overset{\sim}{\propto} I_0^{-1} \qquad (7)$

There are many extensions to or refinements of this method where mass absorption coefficients are linearly calibrated against the Compton scattered portion of various X-ray tube spectral lines (Walker, 1973; Delong and McCullough, 1973; Leake and Peachey, 1973; Wilband, 1975; Nesbitt et al., 1976; Kieser and Mulligan, 1979).

Franzini et al. (1976a) showed that the relationship between Ag Kα Compton scattered intensity and mass absorption coefficient was logarithmic rather than linear, while Leoni and Saitta (1977) used the function to calculate absorption coefficients. Coherent scattering was used by Steel (1973) and Murata (1976) to correct for interfering contamination of scattered background peaks of tube target elements.

In spite of the observation by Reynolds (1963) that coherently scattered tube target lines were unsuitable as internal standards, such scattering has been used successfully by Cullen (1962), Vos (1972) and Childs and Furkert (1974). A general background combination of both coherent and inco herent scattering has been used successfully by Clark and Mitchell (1973), Williams (1975) and Feather and Willis (1976).

Opinions vary widely as to optimum method of selecting prospective internal standards or of measuring absorption coefficients. As pointed out by Taylor and Andermann (1971), there is no basis in the explanation of peak/scatter ratios, for the inclusion or exclusion of any particular wavelength or type of scattered radiation. The many successful variations using scattered radiation have often been the result of a convenient or pragmatic selection of wavelength and scattering type. Usually no argument is put forward to justify a particular selection on theoretical grounds.

2.2 INTENSITY DERIVATIONS

The total absorption coefficient of an element is given by,

$$\mu^* = \tau + \sigma \quad (\mathrm{cm}^{-1}) \tag{8}$$

The true or fluorescent photoelectric absorption coefficient τ, corresponds to the X-ray photon disappearing completely and the absorbed radiation being used for ejection of a lower-level electron from the atom. The total linear scattering coefficient σ, corresponds to the deflection of the X-ray photon from its original direction of propagation by collision with either an electron or atom as a whole.

The coefficients μ^*, τ, and σ, are measures of the fraction of energy absorbed per cm^3. By dividing each coefficient by the density of the element ρ, the "mass" coefficient μ, is obtained. This corresponds to absorption by a screen of such thickness that it contains unit mass per cm^2. The corresponding coefficients per atom are obtained by dividing the mass coefficient by the number of atoms/g, given by N_0/A, where N_0 is Avogadro's number and A is the atomic weight.

i.e., $$\mu_a^* = \tau_a + \sigma_a \ (\mathrm{cm}^{-1}) \tag{9}$$

This atomic coefficient may be expressed as,

$$\mu_a^* = k.Z^m.\lambda^n + \sigma_a(Z,\lambda) \tag{10}$$

where k, m and n are constants within wavelength ranges not containing an absorption edge. Typical values for photoelectric absorption are (International Tables for X-ray Crystallography, 1962),

$$\lambda < \lambda_k; \ \tau_a = 2.64 \times 10^{-26} \ Z^{3.94}\lambda^3 \tag{11a}$$

$$\lambda_k < \lambda < \lambda_L; \ \tau_a = 8.52 \times 10^{-28} \ Z^{4.30}\lambda^3 \tag{11b}$$

(wavelength λ, in $\mathring{A}$)

The atomic scattering coefficient (σ_a) discussed previously, is the sum of the Compton scattering and the Rayleigh scattering. Coherent scatter, resulting from mechanical collision between a photon and an atom as a whole, increases approximately with Z^2 (equation 1). However since photoelectric absorption increases more rapidly ($f(Z)^4$, equation 11), coherent scattering becomes less important for shorter wavelengths and for atoms of higher Z. Incoherent scatter, arising from an inelastic collision between a photon and a comparatively loosely-bound electron is roughly proportional to Z (equation 1) and changes more slowly with wavelength than either the photoelectric or coherent components. Hence the ratio of incoherent to coherent radiation scattered by a given element increases with photon energy and decreases with increasing atomic number (Taylor and Andermann, 1969).

The assumption made in equation (3) that $\mu = f(Z^3)$, i.e., $\mu_a = f(Z)^4$; holds only if $\tau_a >> \sigma_a$. Total attenuation (equation 9), involves both scatter and true photoelectric absorption but only the latter is a function of Z^4. The total absorption coefficient measured for a primary beam increases with increasing wavelength but the ratio of total scattered to photoelectric absorption decreases with increasing wavelength. For example, using an X-ray wavelength of 0.41 Å and C as absorber, it can be calculated that the ratio of σ_a/τ_a is 4:1. If the wavelength is increased to 1.24 Å the total absorption ($\sigma_a + \tau_a$) increases about 9-fold but the ratio falls to 1:6. For Cu as absorber, the comparable ratios are 1:24 and 1:170 for 0.41 Å and 1.24 Å respectively. The total absorption increases 20-fold at the longer wavelength (International Tables for Crystallography, 1962). Thus the approximation, $\tau_a >> \sigma_a$ becomes more inaccurate with decreasing atomic number of the matrix and decreasing analyte wavelength. Analytical methods based on Andermann and Kemp (1958), (equation 5), and Reynolds (1963), (equation 7), incorporate the above approximation.

The theoretical intensity of radiation scattered by a group of electrons can be derived using quantum mechanics. The total intensity scattered by a free atom where each electron has its own probability distribution, is given as, (International Tables for X-Ray Crystallography (1962),

$$I_s = I_e(F^2 + R(Z - F')) \tag{12}$$

where I_e is the free electron (Thomson) scattering intensity,
F is the atomic structure factor for coherent scattering,
$R(Z - F')$ is the incoherent intensity function, with
R the Breit-Dirac recoil factor, given by,
$R = (v'/v)^3$ where v and v' are the frequencies of the incident and incoherently scattered X-rays respectively. The difference between equation (12) above and equation (1) given by Compton (1935) is that Compton's equation assumes that each electron in the atom has the same probability of occurring at a given position as every other electron. Equation (12) also takes into account forbidden electronic transitions to occupied states and the recoil velocity of an electron after collision. Atomic structure factors and incoherent intensity functions for equation (12) are tabulated for a range of elements and wavelengths (Tables for X-ray Crystallography, 1962, 1974).

From the basic formulae for derivation of fluorescent X-ray intensities given by Sherman (1955) and the scattered radiation formulae of Compton (1935), Kalman and Heller (1962) developed a rigorous theoretical expression relating the ratio of peak intensity to that scattered at a chosen nearby wavelength, with the concentration of a minor matrix element. By making a series of simplifying assumptions, and using empirically measured constants, they successfully applied the technique to several trace elements in silicate based matrices. Champion *et al*. (1966) used a different set of simplying assumptions, to derive "sample scatter factors". These factors were used as peak to background ratio corrections for matrix effects in aqueous solutions.

Although the theoretical bases of both Kalman and Heller (1962) and Champion et al. (1966) were quite general, the particular applications developed were rather specific. The present study uses a similar type of theoretical derivation, which is applicable generally and can be easily tested for suitability in any particular application.

2.2.1 Fluorescent Radiation

The intensity of fluorescence of an elementary slab of sample from a monochromatic source is given by the expression

$$I_i = w_\lambda . J_\lambda . C_i . \mu_{i\lambda}^* . dl \qquad (13)$$

where I = Intensity of radiation measured as a rate of flow of photons,

i = analyte,

C = concentration as weight fraction,

J = Incident intensity,

λ = wavelength,

dl = slab thickness,

$\mu_{i\lambda}^*$ = linear absorption coefficient of analyte $_i$ at wavelength λ, and

w_λ = a ratio related to fluorescent efficiency.

The intensity at the surface of a specimen from a polychromatic source can be derived by summation over wavelength and specimen depth, to obtain

$$I_i = C_i \int_{\lambda_o}^{\lambda_E} J_\lambda . w_\lambda \mu_{i\lambda}^{*} \int_{o}^{L} e^{-l(\mu_{M\lambda}^{*}\sec\phi + \mu_{Mi}^{*}\sec\psi)} dl . d\lambda \qquad (14)$$

where l = sample thickness from the surface,

L = "infinite thickness", such that $e^{-l}(\mu_{M\lambda}^{*}\sec\phi + \mu_{Mi}^{*}\sec\psi) << 1.0$,

λ_o = minimum wavelength from source,

λ_E = absorption edge for element i,

$\mu_{M\lambda}^{*}$ = matrix linear absorption coefficient, at wavelength λ,

μ_{Mi}^{*} = matrix linear absorption coefficient at λ_i, and

ϕ and ψ = angles of incidence and exit (from normal to sample surface).

Implicit in this derivation are the following assumptions:

(i) Absence of secondary fluorescence, and
(ii) Perfect homogeneity.

The radiation detected from an infinitely thick sample, is then given by:

$$I_i = k_1 . C_i \int_{\lambda_o}^{\lambda_E} \frac{J_\lambda . w_\lambda . \mu_{i\lambda}^{*} . dl}{\mu_{M\lambda}\sec\phi + \mu_{Mi}\sec\psi} \qquad (15)$$

where μ = mass absorption coefficient = μ^{*}/ρ, and

k_1 = a constant incorporating various instrumental details.

Following application of the mean value theorem of integral calculus, $\bar{\lambda}$ exists for a given primary spectral distribution such that $\lambda_0 < \bar{\lambda} < \lambda_E$ (Kalman and Heller, 1962). The exact value of $\bar{\lambda}$ is determined by the dependence of μ upon matrix composition and wavelength. Champion *et al*. (1966) verified experimentally the consistency of $\bar{\lambda}$ for a W spectrum. They showed that a high degree of reliance could be placed on subsequent simplifying assumptions which were likely to be encountered in biological and geological samples. Equation (15) may thus be simplified to:

$$I_i = \frac{k_2 . C_i}{\mu_{M\bar{\lambda}} \sec\phi + \mu_{Mi} \sec\psi} \qquad (16)$$

where k_2 incorporates k_1, the fluorescent efficiency $w_{\bar{\lambda}}$ (for a given element $\mu_{i\bar{\lambda}}$), and the primary spectral distribution $J_{\bar{\lambda}}$ (Kalman and Heller, 1962).

For materials that do not have a major absorption edge between $\bar{\lambda}$ and λ_i, absorption coefficients are linearly related by equation (11a). Since geometric factors are constant in a spectrograph, then equation (16) may be simplified to obtain the common analytical calibration relationship:

$$I_i = \frac{K . C_i}{\mu_{Mi}} \qquad (17)$$

2.2.2 Background Scatter

The ratio corresponding to w_λ in equation (13) but related to the scattering efficiency by a free atom, is given from equation (12),

$$I/I_e = F^2 + I_c$$

where I_c is the incoherent (Compton) intensity function. The scattered intensity per unit area of an elementary slab, at wavelength λ, for all atoms of element i can then be given by:

$$I_{o\lambda} = \frac{\rho . C_i . N_o}{A_i} \left(F_i^2 + (I_c)_i\right)_{i\lambda} . J_\lambda . dl \qquad (18)$$

where N_0 = Avogadro's number (atoms/mole), and
A = Atomic weight (g/mole).

By summation over all elements and integration over the sample thickness as before, the measured intensity at a given λ for n elements at the surface of an infinitely thick sample can be reduced to:

$$I_{o\lambda} = \frac{k_3 . J_\lambda \sum^{n} (C_i . F_i{}^2 / A_i)}{\mu_{m\lambda} \, (\sec\phi + \sec\psi)} + \frac{k_3 . J_{(\lambda - \delta\lambda)} \sum^{n} (C_i . (I_c)_i / A_i)}{\mu_{M(\lambda-\delta\lambda)} \sec\phi + \mu_{M\lambda} \sec\psi} \qquad (19)$$

where k_3 is a constant incorporating instrumental details
and $\delta\lambda = (1 - \cos(\phi + \psi)).h/m.c$

where h is Plank's constant, m the rest mass of an electron and c the velocity of light. The first and second terms of equation (19) are respectively the coherently scattered background intensity and the incoherently scattered contribution, originally of a slightly shorter wavelength.

Assumptions implicit in the derivation of equation (19) are as follows.

(i) The angles ϕ and ψ are such that the contribution of diffracted radiation is at most very weak (compared with that of the diffusely scattered radiation) and may be neglected.

(ii) Any crystallites are largely disordered and scatter as amorphous units.

(iii) If the matrix consists of several components, individual constants are additive to obtain an average value for the matrix as a whole. There is no simple solution to the obvious problems that

(a) wave functions of chemically bound outer electrons must be modified with respect to those of free atoms, and

(b) chemical bonding results in forbidden states for recoil electrons, resulting in a slight reduction of intensity of the Compton effect (Lonsdale, 1962).

As geometric factors are constant in a spectrometer, the Compton wavelength shift is small with $\delta\lambda \approx 0.02$ to 0.03 Å. In the absence of a major absorption edge, $\mu_\lambda \approx \mu_{(\lambda-\delta\lambda)}$.

Equation (19) may thus be reduced to:

$$I_{o\lambda} = \frac{k_4(J_\lambda \sum^{n}(C_i.F_i^2/A_i) + J_{(\lambda-\delta\lambda)}\sum^{n}(C_i.(I_c)_i/A_i)}{\mu_\lambda} \qquad (20)$$

Further simplifications may be made for specific cases by noting:

(i) for scattering of X-ray tube continuous spectrum, $J_\lambda \approx J_{(\lambda-\delta\lambda)}$, and both terms contribute to the intensity,
(ii) for an incoherent scattered tube line, $J_{(\lambda-\delta\lambda)} >> J_\lambda$, and the second term predominates, and
(iii) for coherent scattering of a tube line, $J_\lambda >> J_{(\lambda-\delta\lambda)}$, and the first term predominates.

In practice not all background radiation monitored by the detector originates from scatter of primary radiation by the sample. The analysing crystal and chambers surrounding the sample and crystal may contribute minor amounts of background radiation and it is usually not possible to adjust for these small contributions in a normal analytical procedure. Electronic noise may also increase background counting rates but allowance can easily be made for this source of error.

2.3 ANALYTICAL THEORY

The following formulation is proposed as a further means of investigating the theoretical implications of peak-background correction techniques. Both peak and scattered intensity can be expressed as functions, f' and f" respectively, of the sample matrix. Hence it should be possible to derive another function of f' and f", that for a given analyte concentration, is invariant with matrix composition.

i.e. $f(I_i, I_0) = f(f'(Z), f''(Z)) = k$

Recalling the approximations made by Andermann and Kemp (1958) in the derivation of their method, it can be noted from equation (10), (11) and (17) that,

$$I_i \overset{\sim}{\propto} Z^{-3}$$

and from equations (1), (2) and (12) that,

$$I_0 \overset{\sim}{\propto} Z^{-(1 \text{ to } 2)}$$

The arrangement suggested cancels out the effect of Z as follows,

$$\frac{I_i}{(I_0)^T} = \frac{Z^{-3}}{(Z^{-(1 \text{ to } 2)})^T} = k \qquad (21)$$

where the exponent T is a constant for as wide a matrix variation as the above approximate proportionalities allow.

If I_i is relabelled as P (net "peak" intensity) and, I_0 as B ("background" intensity), to avoid proliferation of subscripts, then equation (21) becomes,

$$\frac{P}{B^T} = k \qquad (22)$$

If two matrices, a and b, with identical analyte concentration are considered, then the fractional variations in denominator and numerator are equal when,

$$(P_b/P_a)/(B_b/B_a)^T = 1 \qquad (23)$$

Using equation (17), $P_b/P_a = \mu_a/\mu_b$ (24)

where μ is the mass absorption coefficient of the matrix at the analyte wavelength. Equation (20) may be simplified to

$$B_M = k.S_M/\mu$$

where S_M is a constant for a particular matrix (M), calculated for the appropriate set of instrumental variables and tabulated constants. In this study S is termed the "scatter efficiency" coefficient, and is proportional to the matrix scatter efficiency per unit mass. Hence, $B_b/B_a = (S_b/\mu'_b) X (\mu'_a/S_a)$ (25)
where μ' is the mass absorption coefficient of the matrix at the wavelength of scattered radiation.

Solving equations (23), (24) and (25) yields,

$$T = \log (\mu_a/\mu_b)/\log(\mu'_a.S_b/\mu'_b.S_a) \quad (26)$$

Hence, for any two matrices and scatter wavelength, a unique value of T can be found, such that $P/B^T = k$ for constant analyte concentration. Assumptions implicit in equation (26) are those of equations (17) and (20);

(i) absence of secondary fluorescence,
(ii) perfect sample homogeneity,
(iii) analyte wavelength less than a major absorption edge within the sample,
(iv) negligible diffraction phenomena,
(v) component scattering intensities additive, and unaffected by chemical bonding.

Several special cases of equation (22) are already in general use in X-ray spectrometry.

(a) $T = 0$, (i.e. $B^T = 1$) is the common analytical method using a simple spectrometric calibration curve of net peak intensity plotted against concentration. The limited effectiveness of such a curve in compensating for specimen errors is well known. Successful calibration is achieved only if standards and samples have very similar matrix properties.

(b) $T = 1$ is essentially the peak to background ratio method originally described by Andermann and Kemp (1958), which has been widely used to provide complete or substantial corrections for a variety of instrumental and sample errors.

(c) The analytical methods based on Reynold's (1963) use of the ratio of a scattered tube line as an internal standard, are equivalent to the special case of $T = 1$ and letting $J_\lambda = 0$ in equation (20).

The present study attempts to provide a unifying basis for peak-background calibration methods incorporating the above special cases. Inherent in such an investigation is the evaluation of variation in T and the choice of wavelength and type of scattered radiation upon which T may be dependent. From the rough approximations for Z, in equation (21), it is seen that for full effectiveness, values of T should range from about 1.0 (incoherent scattering alone) to about 2.0 (coherent scattering alone), with a value of T for general combined background of somewhere between 1.0 and 2.0.

A possible analytical program to investigate the values of T is as follows.

(a) In a given reference matrix, find the value of T for a given concentration of interfering component.

(b) Compare the values of T over a range in concentration of the component.

(c) Compare the values of T for a variety of interfering components and concentration ranges.

(d) Determine the wavelength dependence of T for each interfering component.

(e) Compare values using total background with those using either coherent or incoherent scattering only.

(f) Extend the reference matrix to cover the range of sample materials likely to be encountered in biological and geological samples.

The computation workload, involving considerable shuffling of data is possible only by computer. At the same time the computer may calculate the magnitude of peak error originating from variations in mass absorption. Knowing this range of possible improvement, a decision can then be made as to which corrections are worthwhile. By comparing values of T for exact compensation in each case, it may be possible to optimise corrections for multiple interferences and specify the range of matrix variation, over which these corrections are valid. If such a calibration procedure can be found for a particular situation; then, because of the simplicity of the correcting function, little information is required about the composition of the sample. Each element can be measured in isolation and no additional measurements would be necessary.

The main application of this study is the rapid trace elemental analysis of soil and plant material, where for most elements of interest, the wavelength of the analyte is less than a major absorption edge within the sample. Powdered samples are preferred as dilution of the sample using fusion/matrix addition techniques has the disadvantage of decreasing sensitivity and increasing sample preparation time. As most minor element studies are not concerned with a complete major elemental composition of the sample, those methods requiring complete knowledge of the matrix involve much unnecessary work. Since, to reduce counting errors, minor elemental analyses require that similar amounts of time are needed at the background and peak positions, the scattered radiation at the peak position is already measured accurately, These advantages make the investigation of further improvements in peak-background ratio techniques an attractive proposition.

CHAPTER 3

COMPUTATION OF THEORETICAL CORRECTIONS

3.1 CHOICE OF VARIABLES

3.1.1 Physical Constants

Evaluation of constant exponents (T) from equation (20) involves the use of tabulated values of mass-absorption coefficients, atomic scattering factors and Compton scattering intensities. The scattering constants used in this study are essentially those found in "International Tables for X-ray Crystallography", (1962). These tables are prefaced by detailed discussion of their method of calculation and accuracy. When ratios of matrix properties are considered, systematic errors should theoretically cancel. Provided such a set of tables constitutes a consistent set of data, then for the purposes of this study any systematic errors in tabulated values should have a negligible effect on the conclusions.

Published values of mass-absorption coefficients show considerable variation particularly at longer wavelengths. The wide range of coefficients for Al, collated from published tables and formulae by Short and Tabock (1975), illustrates the significant disagreement between sources and the difficulty in selecting coefficients with confidence. The absorption coefficients used by the computer programs in this study were based on those published by Jenkins and De Vries (1970), which although a consistent set, needed to be amended slightly where disagreement with other sources was significant. The tables of Thinh and Leroux (1979), are a more recent attempt to provide a single comprehensive source of mass-absorption coefficients.

The published values for the various constants used in the computer programs were plotted on large sheets (0.5 m X 0.75 m) of graph paper. Discontinuities and occasional printing errors became obvious and new data points could be added easily and the curves amended. Usually two such sheets were sufficient to cover the necessary range of each parameter. This procedure simplified interpolation between published data points and the averaging of data that was inconsistent.

3.1.2 Matrices

A reference matrix for both soil and plant material was selected by considering the major elements affecting absorption and scattering. This choice of a typical elemental composition was the starting point for considering variation in the matrix. The elements and concentrations chosen for a base matrix are listed in the computer tables in Appendix 2, and p40. Six major interfering fractions within each basic matrix were selected. For each interfering fraction, five levels of addition were chosen to cover the extreme variations likely to be encountered in an analytical situation.

The interfering elements selected for soil mineral material were Na, Si, Al, Ca and Fe. Preliminary investigations showed the effect of K addition to be similar to Ca and Mg to Na for the analytes of interest and the range of natural variation found in soil. As explained later, the computer printout, when abbreviated to a minimum, fitted six interfering fractions per page of "type B" tables. This restriction forced the limited selection as made above. For soil samples, the increments were specified as being in the oxide form to simplify isomorphous substitutions and to ensure the correct amount of associated oxygen was being considered. The approximate ranges in concentration of each fraction considered for soil samples were as follows:

(i) Na_2O, 0.6% to 7%
(ii) SiO_2, 33% to 75%
(iii) Al_2O_3, 10% to 33%
(iv) CaO, 0.7% to 11%
(v) Fe_2O_3, 3.6% to 13%
(vi) Organic material
0% to 50%.

As each interfering fraction was varied individually, the range of sample composition considered varied according to the rate of addition of the other fractions. The ranges listed above should cover the composition of most soils.

The inclusion of the organic fraction of the soil is an important consideration in this study. The mass-absorption coefficients for elements most likely to be found in soil organic material are much smaller than the coefficients for many elements found in typical soil mineral matter. The errors resulting from a large variation in the ratio of these two groups of elements are reasonably substantial for most analytes. Brown and Kanaris-Sotiriou (1969) suggested that the mass absorption coefficient of a soil for S radiation could be regarded as the sum of an organic and a mineral fraction. Extreme variations in the composition of soil mineral material produced less than 4% error in S values, compared with about 1.0% error for each percent of organic material added (Livingstone, 1973). Similar results were obtained for S (Bergseth and Kristiansen, 1978) and P (Bergseth and Kristiansen, 1979). Organic-rich soils were analysed for a variety of elements by Leake and Peachey (1973) using a background ratio method. Bergseth (1975) also reported a similar method for Zn in soils that contained highly variable amounts of organic material.

Variation in the effective composition of an organic fraction also introduces error into the analysis of predominately mineral soil material, but this secondary variation is much less than that caused by changes in the proportion of organic matter. Structural water and hydroxyls have rather similar absorption characteristics to organic matter, particularly when compared with mineral material. A good estimation of the combined effect of all low absorption fractions may be based on loss in weight on ignition (Brown and Kanaris-Sotiriou, 1969; Livingstone, 1973).

The six major interferences chosen for plant material were, C, N, Mg, K, Ca and mineral soil contamination. Levels of addition to the reference matrix in each case were 1% increments up to a total of 5%, except for C which was varied in 2% increments up to a total of 10%. These ranges would cover the composition of most types of plant material. Preliminary investigation showed that the scattering and absorption effects of Na in plant material were similar to Mg, and those of Si to soil contamination. The range of natural variation of S and P in organic material is limited and, although they have large elemental parameters, concentrations are small and overall effects relatively constant. Soil mineral material is included, because dust is an important contaminant in many agricultural trials particularly those involving species such as grasses where the basal leaf structure acts as a trap (Anderson _et al._, 1973; Whitton and Wells, 1978).

The choice of (i) reference matrix, (ii) composition of an interfering component, (iii) range in concentration of an interfering component, and (iv) the number of interfering components, can easily be modified or specified to suit any particular situation. A major factor influencing the particular selection in this study was the volume of input and output data that could readily be processed and presented in a compact form. In attempting to make this study generally applicable, the choice of variables is intended to establish trends and eliminate quickly those situations where further investigations are unwarranted.

3.1.3 Wavelengths

Scattering and mass-absorption parameters are wavelength dependent and correction procedures are dependent on the wavelengths of both the analyte and scattered radiation. Analyte wavelength is fixed, but scattered radiation can be monitored over a wide spectrum. An important wavelength of scatter to be considered is the background below the analyte peak. In practice this background is measured either side of the analyte peak and interpolated to the peak position to obtain net peak intensity. If the background intensity curve is flat, measurement at one side of the peak is often considered sufficiently accurate. Scattered lines from the metal anode of the X-ray tube are also important wavelength positions to be investigated. Tube target wavelengths considered for the commonly used X-ray tubes were,

(1) Ag $K\alpha$, $\lambda = 0.561$ Å
(2) Mo $K\alpha$, $\lambda = 0.710$ Å
(3) Au $L\alpha$, $\lambda = 1.278$ Å
(4) W $L\alpha$, $\lambda = 1.476$ Å
(5) Cr $K\alpha$, $\lambda = 2.291$ Å

Including the analyte wavelength, a total of six wavelength positions were evaluated for each of the previous matrix types and interfering components. These wavelengths cover a range sufficient to estimate trends in correction techniques commonly used. Computations at other wavelengths are readily available because the basic matrix data corresponding to any other analyte wavelength are evaluated when the background position of that analyte is considered. However each additional wavelength processed would increase computer printout by over 500 pages when all analytes and other variables were considered.

3.1.4 Analytes

The values of T calculated from equation (26) should have simple values between 1.0 and 2.0 provided the wavelength of the analyte is less than a major absorption edge within the sample. The first major absorption edge in soil, is that of Fe with those elements heavier than Co satisfying the above condition. For plant material, the heaviest element affecting the simple relationships between concentration and peak and scattered intensities is likely to be either K or Ca. However there are many reports of successful analytical techniques for lighter elements below a major absorption edge. Crossing an absorption edge must alter a correction technique but as light elements such as P and S are of particular interest in many studies, such elements are included to ascertain the effectiveness of past assumptions such as $T = 0$ or $T = 1$.

The theoretical corrections proposed in this study can be extended to cover most elements of interest in X-ray fluorescent analysis of whole soil and plant material. Such an investigation is beneficial even if only to show that a certain technique cannot hope to succeed. By evaluating the magnitude of error in each case it is also possible to define the limits of applicability of a correction.

In this study, some elements not normally of interest, and some usually present in amounts below detection limits were included to provide a continuous series. As the investigation proceeded, the bank of computer data and programs increased to include more elements and variables. The final result was an exhaustive set of tables for 20 elements, namely P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Zr, Mo and Pb.

3.2 COMPUTER ANALYSIS

Considering all variables, the final task design for the computer analysis was to cycle through the following steps.

1.	Reference matrices (soil and plant material)	2
2.	Analytes (as listed above)	20
3.	Scattering wavelengths (analyte plus 5 tube lines)	6
4.	Interfering components (as listed above)	6
5.	Levels of interference (combinations of 5 steps)	15
6.	Types of scattering (Compton, Rayleigh and total)	3
7.	For each combination of (1) to (5), calculate the fractional (%) variation in analyte intensity.	
8.	For each combination of (1) to (6), calculate the fractional (%) variation in background scatter.	
9.	For each corresponding combination of (7) and (8), calculate the value of T.	

For each combination of analyte and matrix, a deck of cards was built up comprising;

(i) header cards specifying matrix, interfering component with concentrations, and analyte wavelength,
(ii) parameter cards, one for each element in both reference matrix and interfering component, and

(iii) coded work flow cards indicating new interfering component, different scatter wavelength, or recycling for another analyte.

Each parameter card for a particular analyte and element contained the following information specified at the wavelength of the analyte.

(i) Analyte, matrix and interference identification.
(ii) Element identification and atomic weight.
(iii) Mass-absorption coefficient.
(iv) Rayleigh atomic scattering factor.
(v) Compton-scattering Intensity.
(vi) Matrix fraction of element.

For computations at other than the analyte wavelength, the program substituted the appropriate mass-absorption coefficients and scattering parameters obtained from a similar deck of cards prepared for each scattering wavelength. Altogether about 2000 cards were used and about 65000 values of T were generated.

Each set of approximately 100 results from the combination of steps 5, 6, 7, 8, and 9 was arranged to fit two pages of printout. This printout also contained, for the particular element and wavelength, a copy of the specific data used for the matrix and interfering fraction under consideration. These sets of full data and printout are referred to as Type A tables. Examples of the two pages of output for some of the 1440 combinations of element-matrix-wavelength-interference are found in Appendix 2.

It was impracticable to line print all possible combinations of Type A tables (2880 pages). Instead, about one-sixth of the combinations was printed to provide a hard copy of all basic data used for each combination of element-matrix-interference but at the analyte background wavelength only. Further examples for each new wavelength were printed to ensure the correct substitutions were taking place. The remainder were retained on disk file and consulted by V.D.U. where necessary and eventually discarded. Output of Type A tables was necessary to check that correct specifications, data and workflow logic were being followed. The program itself checks for other error conditions: such as, sample constituents not adding to 100%, or data missing, and warns accordingly. However the ever-present human element in reading input data from graphs, verifying punched data and examining printouts for obvious mistakes may result in some, hopefully minor, undetected errors.

Type B tables are abbreviated versions of Type A tables. Each Type B table is a summary of results covering 12 pages of Type A tables. Type B tables contain no initial specifications or data and give results for five simple increments only in level of interfering component. The advantage of Type B tables is that results for six interfering components for a particular element-matrix-wavelength combination fit on one page for easy reference. The volume of tables, "Mass Absorption Errors and Background Corrections for Plant and Soil Analysis by X-ray Fluorescence", forming part of this study, consists of approximately 240 pages of Type B tables.

Several Fortran programs, used to generate tables of absorption errors and background corrections were developed over a number of years. These were amalgamated into a single comprehensive program as the need to provide overall trends of absorption and scattering characteristics became apparent. The program listed in Appendix 1 is the version used to generate the tables forming part of this study. Had the magnitude of the final task been envisaged initially, some aspects of program logic could have been streamlined. However, once a set of data cards started to grow, it was uneconomical to alter the overall method of computer analysis. Probably the most important change would have been to make more use of software programing to generate specifications and parameters rather than rely on key-punched data.

The mini computer used to produce the final sets of tables was a PDP11/40 incorporating 124k core and hard disk storage. Tables required for reproduction were printed directly from disk files using a Qume printer.

Details of card formats and card deck organisation can be ascertained by examination of the appropriate Fortran statements in the program listed as Appendix 1.

3.3 INTERPRETATION OF TABULATED RESULTS

3.3.1 Description of Tables

The layout of Type A tables follows the sequence of computation. Listed first are the data and derived parameters for both sample and interfering fraction. The six examples of Type A tables given in Appendix 2 show the data for the reference soil and plant matrix and each tube line. A different element and interfering fraction was chosen for each example. Results of computations are listed in a triangular matrix form according to amount of interfering fraction added and increased base level.

The error in analyte intensity (termed "peak enhancement"), from variation in absorption, increases with amount added and also varies across the table according to reference content. The pattern of errors follows that expected from simple combination of two components with different absorption coefficients. The errors are given as percentage deviation and may be either positive or negative depending on the relative values of absorption coefficients. The intensity ratio is obtained by adding 100% to each error. Besides showing which elements or fractions cause the most error, peak enhancement tables are very useful in deciding weightings given to values of T.

The variation in scattered intensity, (termed "background" enhancement), is at the wavelength specified previously in the printout. The variations are expressed as percentage deviations from the intensity obtained for the basic matrix. The "exponent value" T, for each combination of peak and background enhancement is calculated according to equation 26. The tables of background enhancement and exponent value T are then repeated for each of the Compton and Rayleigh components of the total scatter, considered separately.

The accompanying volume of Type B tables is prefaced by user instructions and an explanation of the abbreviations used. Although showing only the first column of each matrix of Type A tables, Type B tables contain enough information to ascertain the applicability and specific corrections for each analysis.

3.3.2 Matrix Scatter Efficiency

Sample scattering efficiencies at analyte wavelength of Compton and Rayleigh components for typical soil and plant material are shown in Figure 3-1. To present the results effectively, the x-axis is plotted as analyte atomic number rather than Kα wavelength. In an X-ray analytical sense, atomic number is as useful as wavelength and the two variables are easily interchanged with scale adjustment. The curves are plotted as "Compton only" (lower) and "Compton + Rayleigh" (upper), with the result that the upper line represents total scattering efficiency, and intervals in the y-direction represent Compton and Rayleigh components respectively.

Features to note from Figure 3-1 are;

(i) the decrease in Compton component with decreasing atomic number.

(ii) the much larger increase in Rayleigh component with decreasing atomic number.

(iii) the higher ratio of Compton:Rayleigh scatter for plant material compared with soil.

(iv) the small contribution of Compton scatter to the total scatter, except possibly at very short wavelengths (high atomic number).

Sample absorption is the more important factor in determining scatter intensities. Figures 3-2 and 3-3 show respectively, variation with analyte of mass absorption coefficient and total scattered intensity. At longer wavelengths (smaller Z) the intensity of scattered radiation from both soil and plant samples, decreases to a few percent of intensities at shorter wavelengths. Decreased X-ray tube output and geometrical factors in detection, place further limitations on the use of scattered X-rays at longer wavelength.

The trends shown in Figures 3-1, 3-2 and 3-3 are those to be

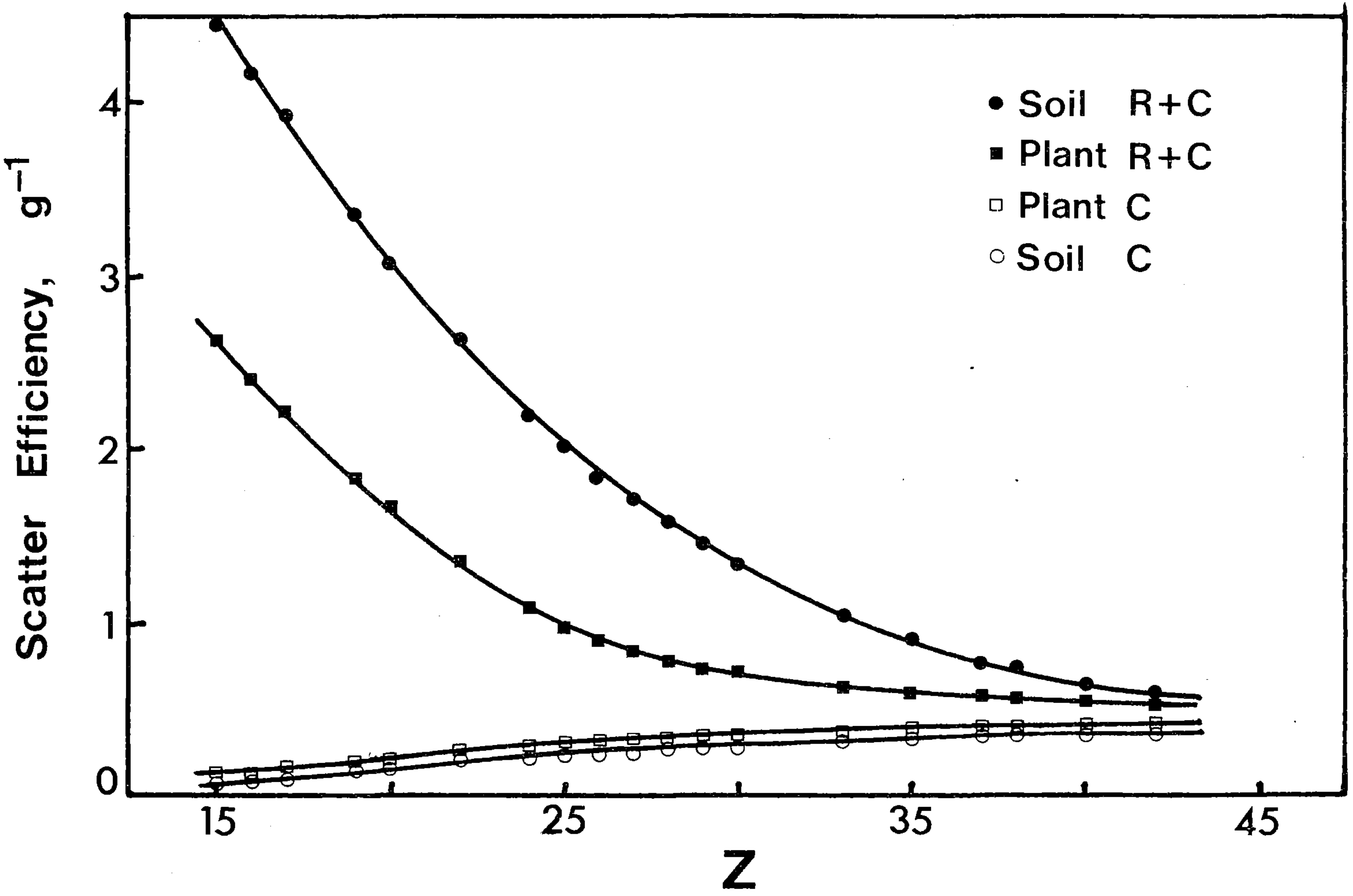

Figure 3-1. Compton and Rayleigh + Compton scatter efficiency at analyte wavelength for typical soil and plant material.

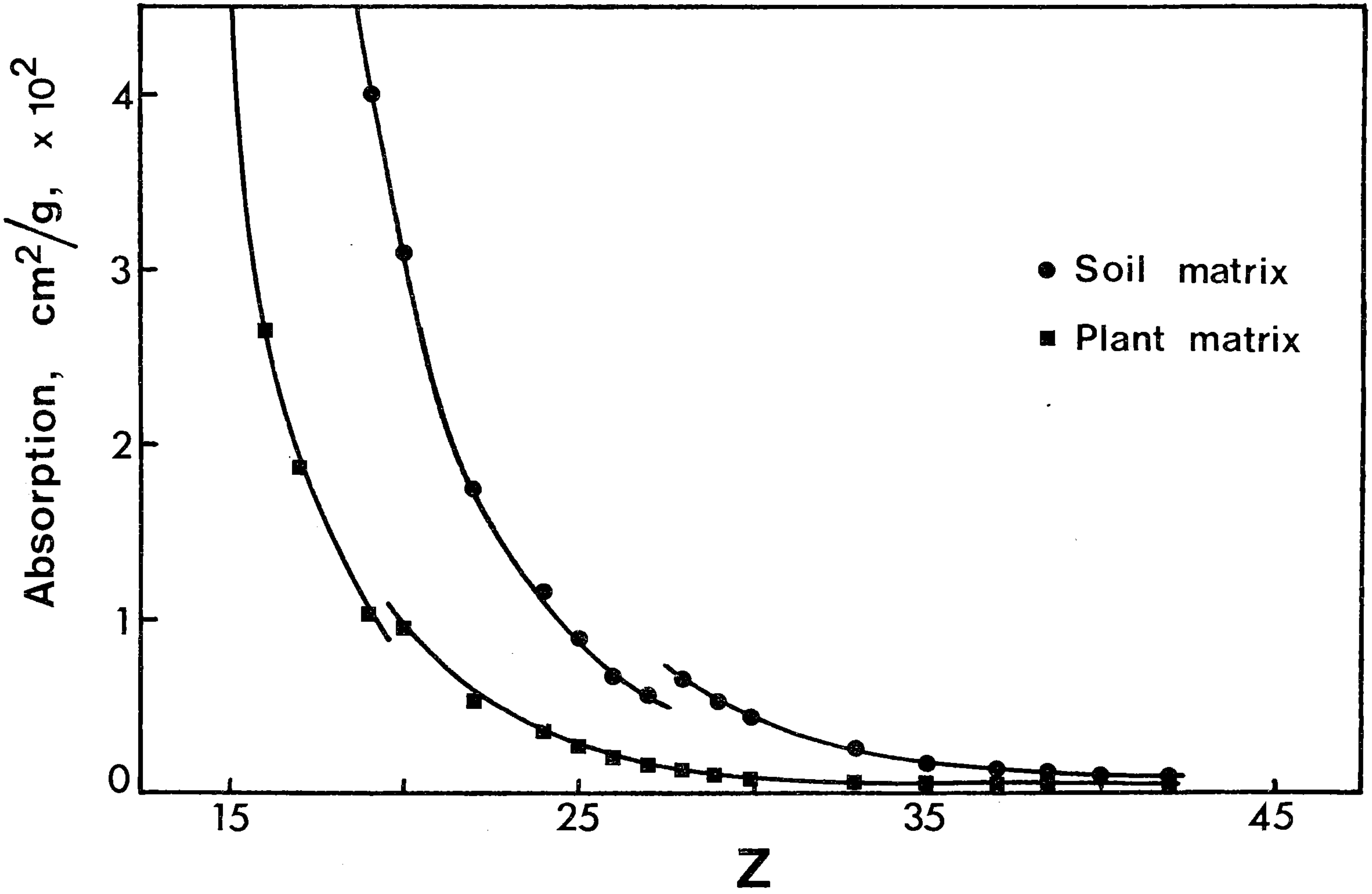

Figure 3-2. Mass absorption coefficient of typical soil and plant material at analyte K_α line.

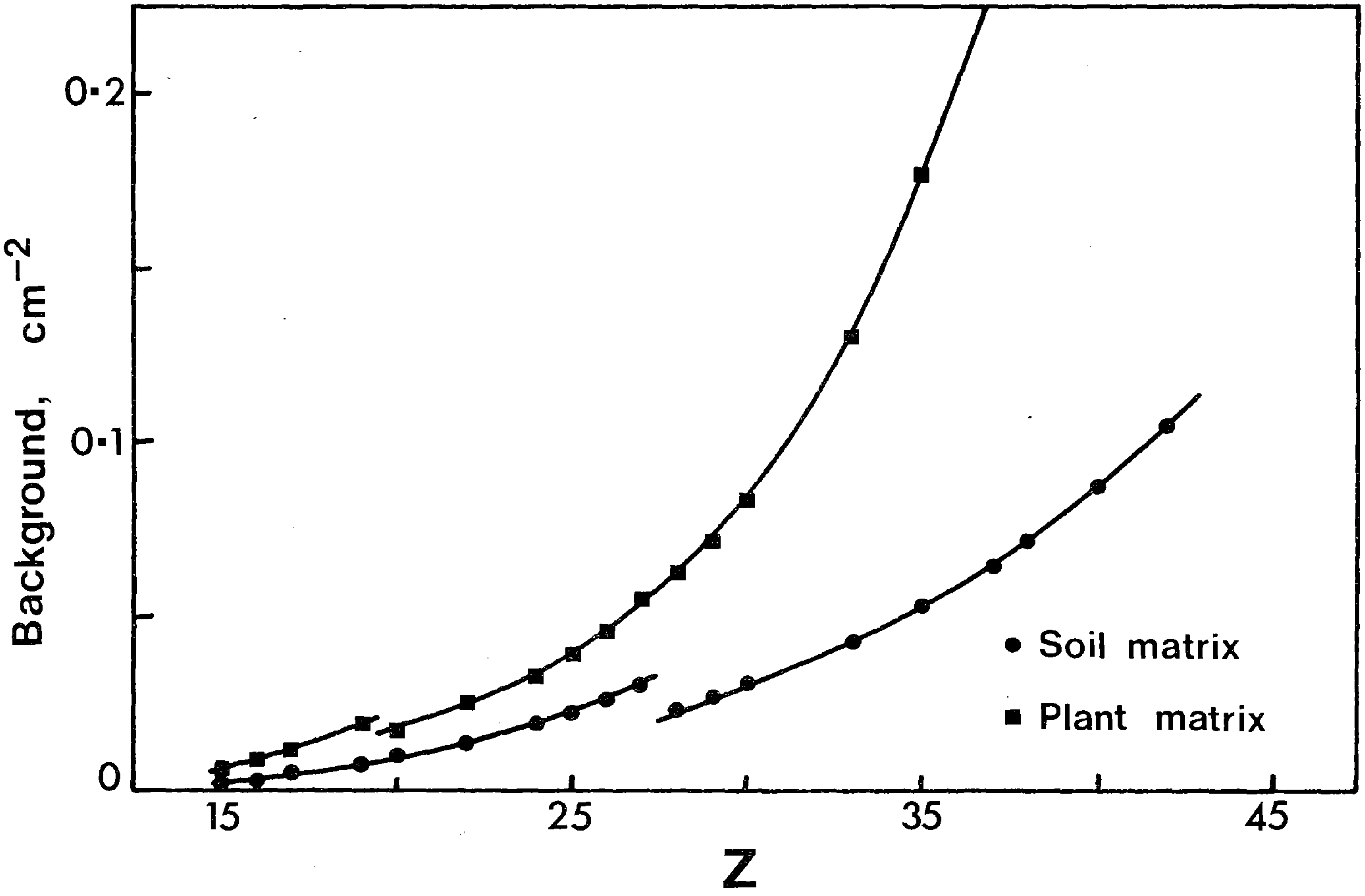

Figure 3-3. Total background scatter observed at analyte wavelength for typical soil and plant material.

expected from the well established principles of X-ray spectrometry. The purpose in presenting the summary of data for typical soil and plant material is to provide an easy pictorial reference for comparing specific applications.

3.3.3 T Values

If corresponding peak and background enhancements from tables are expressed as a ratio by adding 100 to each value, then it may be checked that the background ratio raised to the power of T gives the peak ratio. The sign of T depends mathematically on the signs of the two deviations. In most cases both are either negative or positive, making T positive, which is the ideal theoretical situation.

Values of T, for a particular analyte and interfering component, vary slightly depending on concentration of the interfering component. This variation is a consequence of the simple linear combination of the respective mass-absorption and scatter coefficients. In most cases this variation is negligible compared with the overall range of T between interfering components. Although such small variations are precise, the input absorption and scatter data may not be sufficiently accurate. The additional uncertainty introduced into an overall correction by neglecting such minor variations is probably well covered by the inherent inaccuracy of the input data. Unfortunately computers also round numbers according to decimal places and not to significant figures. In general, care must be exercised not to place too much importance on computational precision of T values, when results are possibly subject to systematic errors from input data.

Examples of variation in values of T with interfering fraction for soil and plant material respectively are shown in Figures 3-4 and 3-5. The x-axis is again plotted as atomic number. The wavelength of scatter is that of the analyte Kα line and total scatter is considered. From the data in the attached tables, a pair of similar figures can be prepared for such of Compton, Rayleigh and total scatter corrections for each scattering wavelength. Alternatively, variation in T with scatter wavelength may be plotted as in Figure 3-6 for the particular case of Cu in plant material.

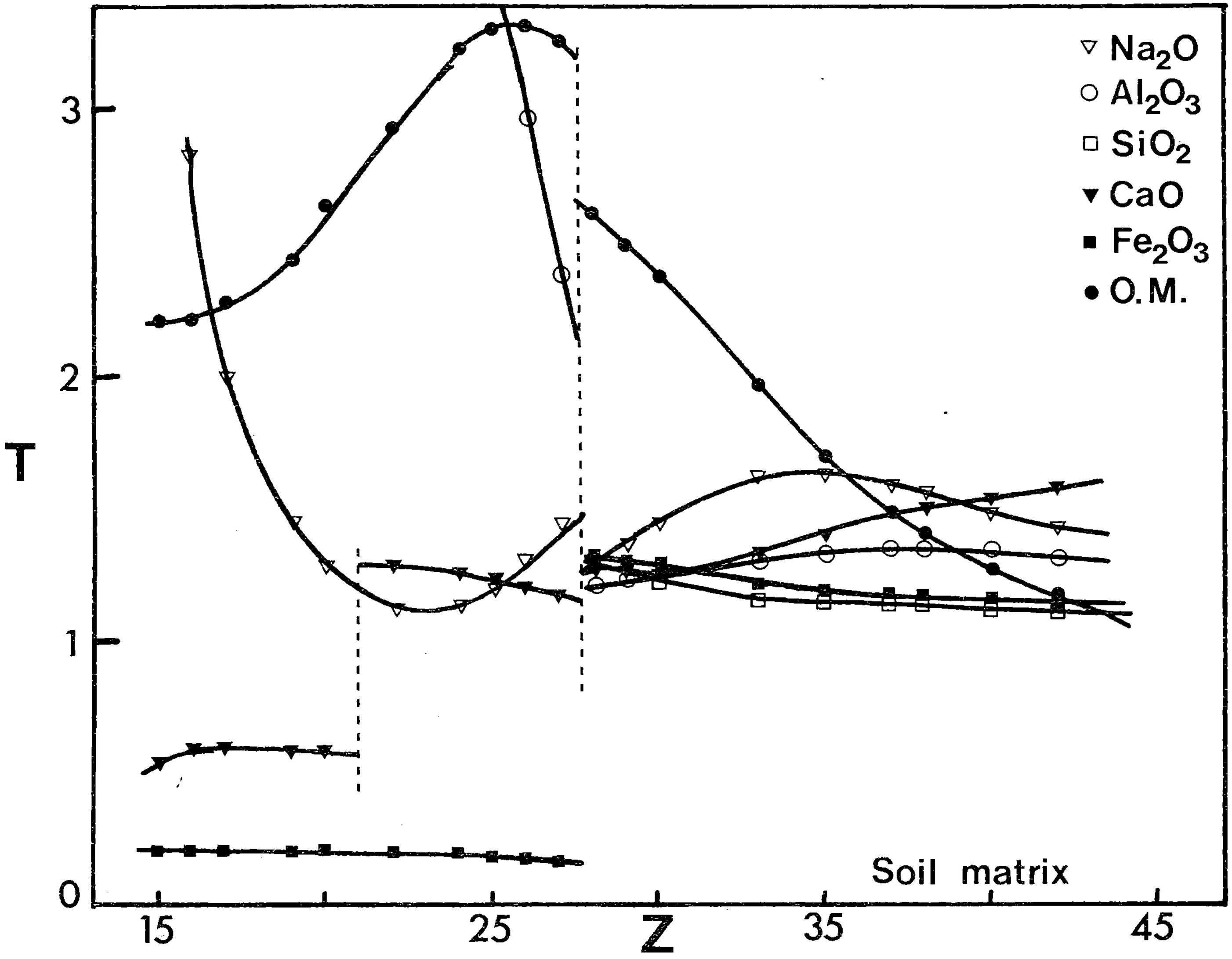

Figure 3-4. Variation in T with analyte for various interfering components in typical soil material.

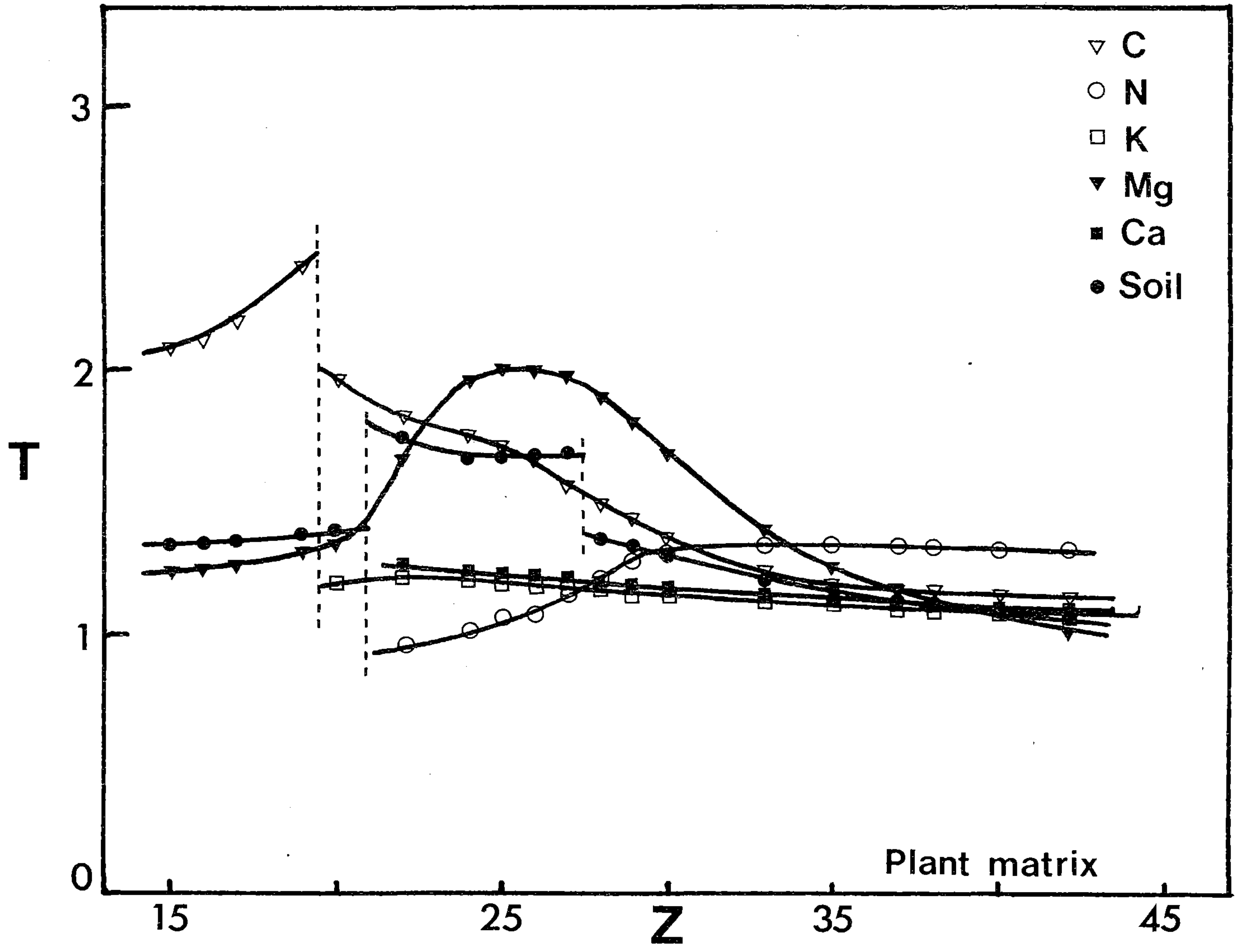

Figure 3-5. Variation in T with analyte for various interfering components in typical plant material.

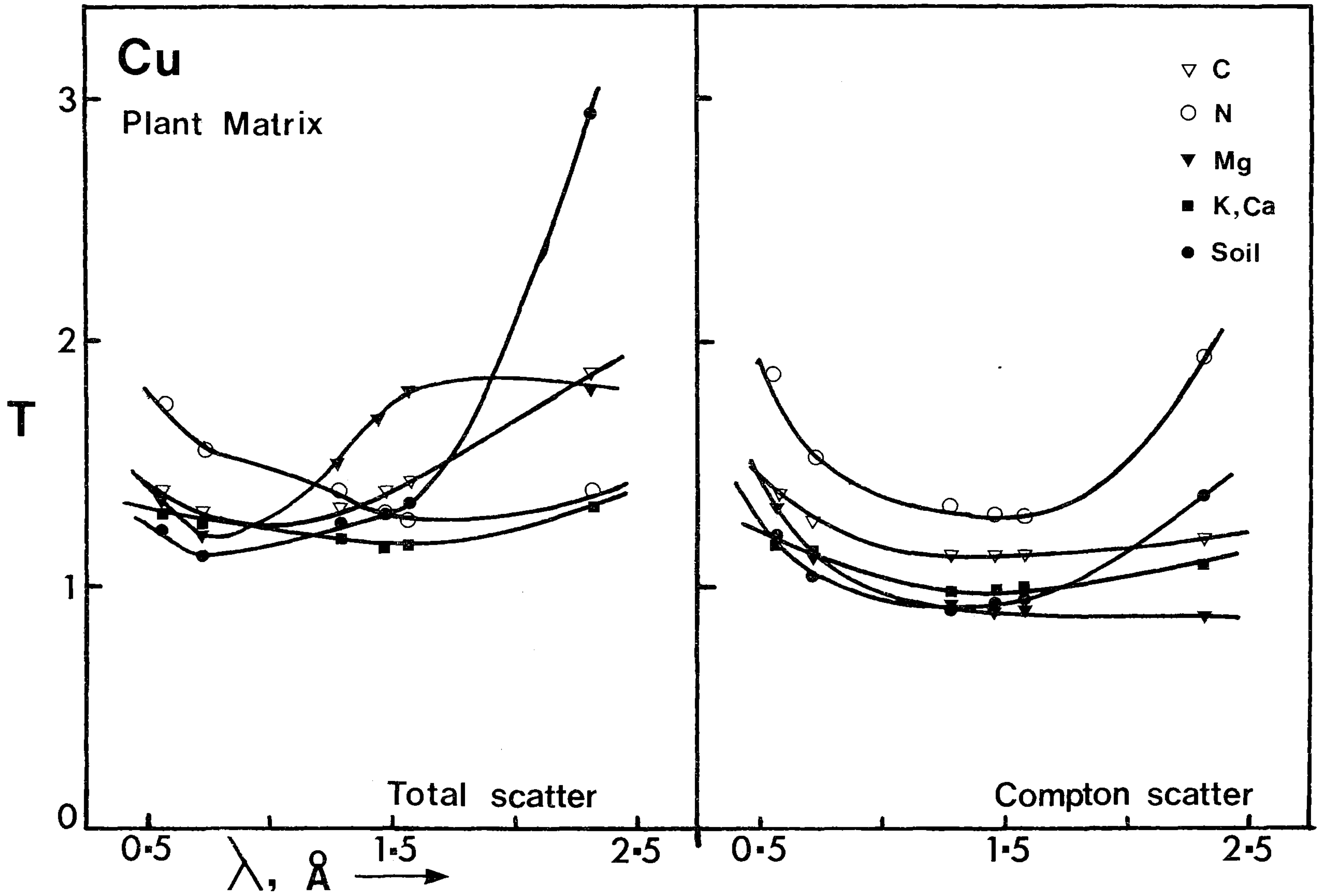

Figure 3-6. Variation in T with scatter wavelength for various interfering components in the analysis of typical plant material for copper.

Above the major absorption edge in each matrix, T values generally fall in the theoretical range of T = 1 to T = 2. For Compton scattering of tube lines, $T \approx 1$ for most interfering components, a result not unexpected considering the many successful calibrations relating μ^{-1} with Compton scattering. As expected, T values become erratic for lighter analytes with much of the variation caused by change in absorption. Mathematically, the magnitude of T becomes very small when peak deviation is small, but as there is little peak error anyway, these small T values are often relatively unimportant. When a T value is very large, the implication is that a background correction is ineffectual and hence, the actual use of a lesser value of T only partially corrects the error. It is thus evident that any system of combining T values for multiple corrections must also include a weighting factor dependent on the seriousness of the peak enhancement error.

3.4 PROCEDURE FOR OPTIMISATION OF CALIBRATION STRATEGY

Each exponent value (T) corresponds to the addition of a specified fraction of interfering component to a reference matrix. Individual values of T for specific matrices are sometimes abnormally large or small, or as in a few rare cases, even negative. A system of weighting must cater for these abnormalities and show clearly an optimum solution for minimising errors. It must also be kept in mind that a T value, is after all, only a mathematically derived number, representing exact coincidence of two separate phenomena. Deviation from each precise value of T, may or may not reintroduce significant error, depending on the specific matrices involved.

For a constant analyte concentration the value of T has been calculated from mass absorption coefficients and X-ray scattering theory, so that,

$$\frac{\text{Net Peak Intensity}}{(\text{Background})^{T}} \quad \text{is constant.}$$

When analyte concentration is linearly related to the above function, the calibration is compensated for absorption error, introduced by the specified fraction, if present in sample matrices.

The elemental compositions of the reference matrices from which all interference deviations have been considered are listed as follows.

Typical Plant Material Reference Matrix

	(%)
H	4.0
C	59.0
N	5.0
O	29.0
Mg	0.3
P	0.3
S	0.3
K	1.5
Ca	0.6

Typical Soil Material Reference Matrix

	(%)
O	49.0
Na	1.5
Mg	1.0
Al	10.0
Si	31.0
K	1.0
Ca	1.0
Ti	0.5
Fe	5.0

Each value of T compensates exactly for only one source of peak error. The appropriate functions of background, which in turn are dependent on wavelength and type of scatter must be combined for multiple compensations. The system used for combining T values for multiple absorption error corrections considers the magnitude of each peak error with variation in T. The various possibilities are represented by the lines in Figure 3-7 and any particular analytical situation involves the use of one or more such lines. The weighting system described here is simple in application and does not require extensive plotting of data or computations. The method is basically a diagramatic use of key information from Type B tables. The stepwise procedure to arrive at an optimum calibration strategy is as follows. (See 4·2 and 4·3 for examples).

(1) Estimate the approximate range of variation expected in each interfering component likely to be encountered in the samples to be analysed by the procedure. Compare

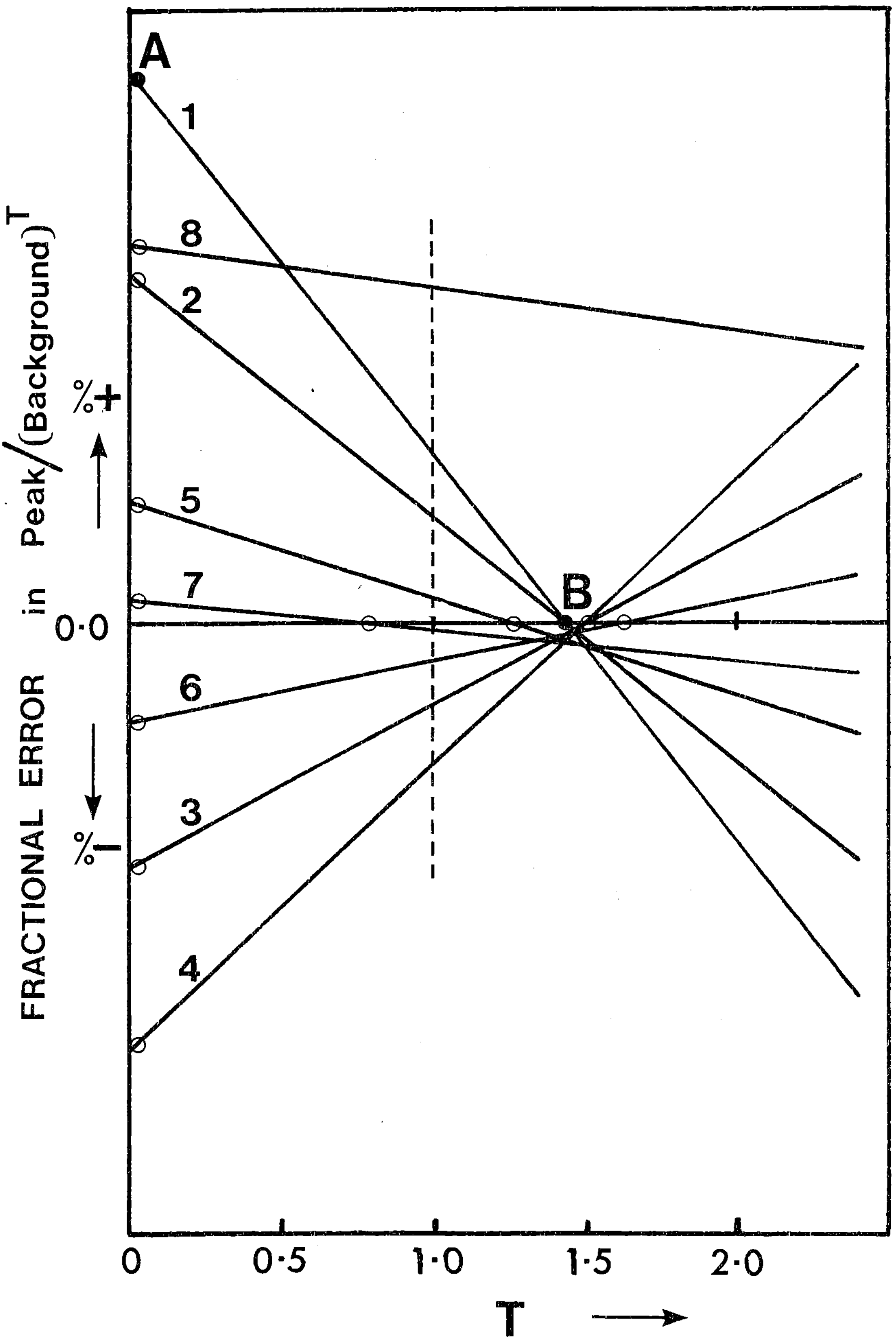

Figure 3-7. Examples of procedure for optimisation of calibration strategy (see text for explanation).

each amount with that in the "reference" matrix above. Determine a maximum deviation (either positive or negative) to cover the range of variation from the reference. This value is termed the "amount added" and although usually positive, in practice it may be negative for impoverished samples. The effect on procedure of a negative "amount added", is to change the signs of the "increase" values in the table leaving the sign of T unaltered.

(2) Rank the interfering components in terms of "peak increase" error, corresponding to each "amount added" in the appropriate table.

(3) For a particular wavelength of scatter, read from the table each corresponding value of T for the type of scatter (total background, Compton or Rayleigh). If a decision has not been made as to which wavelength or type of scatter to consider, repeat this and remaining steps for various combinations to ascertain any difference between choices.

(4) Draw axes similar to those shown in Figure 3-7. Mark the peak increase for the major interfering component as the y axis intercept (point A). The corresponding T value is plotted as x axis intercept (point B). Line AB represents the approximate error in analyte concentration as a function of T. Lines 1 and 2 may represent differing amounts of the same interfering component but in practice only the maximum level expected is drawn. Point B varies only slightly with amount added as explained in 3.3.3. If the peak error is negative, lines such as 3 and 4 have a positive slope.

(5) Draw a line for maximum amount of each interfering component (e.g. 5, 6, 7, and 8). Ideally, when all values of T are similar, the plot assumes a star shape. The residual analyte error at any value of T is repre-

sented by the algebraic sum of the vertical distances from that point on the T axis.

(6) Choose the optimum value of T to minimise the sum of the vertical distances for the particular maximum levels of interference plotted. The required calibration function is then,

$$\text{Concentration} \propto \frac{\text{Net Peak Intensity}}{(\text{Background})^{T}}$$

From a "star" diagram such as Figure 3-7 it is immediately obvious:

(i) how much each interfering component contributes to both initial and final analyte error.

(ii) which value of T gives optimum reduction in analyte error, and,

(iii) whether any improvement over the strategies commonly used can be achieved.

NOTES

(a) If T = 0 is chosen (i.e. the y axis), the vertical intervals represent the error in analyte peak intensity resulting from the simple traditional "counting rate versus concentration" calibration strategy.

(b) If T = 1 is chosen, the vertical intervals represent the residual error for the common "Peak/Background ratio versus concentration" strategy.

(c) If the T values plotted are those for a Compton scattered tube line, then a choice of T = 1 is the standard "absorption correction using scattered tube line" method. From the values of T in the tables, the likelihood of one of the above special cases being an optimum choice is very improbable.

(d) For small values of T (e.g. line 7), overall error is relatively unaffected when the y axis intercept is also small. If necessary, a more detailed check can be made, as described in (f) below, for those situations where extrapolation may increase the error.

(e) For extra large values of T (e.g. line 8), any background ratio exponentiation method is effective only to the extent that the line drawn falls below the horizontal. No harm is done by applying a correction based on T values for the other interferences but a completely separate strategy is needed to eliminate the residual error for such interferences.

(f) Strictly speaking, the line AB plotted in Figure 3-7 is an approximation for a slightly curved function passing through A and B. As curvature is always concave in the positive y direction, the straight line approximation results in a slight overestimation of error for lines with a negative gradient, and vice versa for lines with a positive gradient. The difference is never more than a few percent of maximum error at mid point and is usually negligible. If necessary, intermediate points for any value of T can be obtained using an exponential function on a hand calculator and peak and scatter ratios from the tables. Accurate plots for Zn and Zr in Figures 4-1 and 4-5, illustrate the small magnitude of error resulting from a straight line approximation.

Considering (i) the variation in values for T shown in Figures 3-4 and 3-5 for total scatter only, at analyte wavelength only, and (ii) the variation in T with wavelength for total and Compton scatter shown for Cu as an example in Figure 3-6, then it can be appreciated that tables such as the attached volume are invaluable in the investigation of any calibration strategy.

An analytical strategy related to using a T value has been found in literature for the specific case of Zn analysis in plant material (Bergseth, 1975). The degree of agreement is most satisfactory. Bergseth (1975), in analysing peats for Zn, found experimentally that a modified peak to background ratio $I_{Zn}/I_{0}^{1.17}$ was independent of matrix for soils with organic matter contents in the range 30% to 90%.

Hutton and Norrish (1977), while experimentally determining background intensity from mass absorption coefficients, found also, that for Zn in plant material, $u \propto I_0^{-1.16}$. The major contributors to variation in mass absorption of plant materials are K (12% per 1%K) and Ca (14% per 1%Ca). The corresponding T values for Zn (Z = 30) in plant material for K and Ca (Figure 3.5) are 1.17 and 1.16 respectively. Most other T values for Zn are also in the range 1.2 to 1.3, although the effect on absorption of other components is rather less.

In commercial simultaneous multichannel X-ray spectrometers, the output is greatly reduced if, for every peak position, two additional channels are needed for measurement of background intensity on either side of the peak. An additional benefit of the data contained in the attached volume of tables is that they can be used to predict background intensity from known or measured absorption coefficients. The tables may be used directly to calculate the "k" constants which were defined and determined experimentally in the method of Hutton and Norrish (1977). Relationships between Compton scatter of a tube line and total background at other wavelengths can also be derived directly from the tables.

The reports cited above are the only references found to date, with similar methods, or data supporting the analytical strategy proposed in this study. In contrast, there are a host of publications that indirectly assume T = 0 or T = 1. Included are all calibration-standard methods where, T = 0 and analyte line intensity from the sample is compared with that from standards having the same form as the sample. According to Bertin (1978), it is probable that over half of all analyses performed fall into this category. Methods using scattered X-rays, either background ratio or scattered target-line ratio assume T = 1. Only those methods that approach reduction of absorption-enhancement effects by sample addition or dilution, thin film or mathematical methods avoid making such indirect assumptions. These later methods are generally not suited to analysis of minor constituents in a matrix. Application of a T value technique to existing successful calibrations must extend the range of matrix, over which errors remain negligible.

CHAPTER 4

TESTS USING EXTREME MATRIX ERRORS

4.1 SPECTROMETRIC METHODS

4.1.1 Standards

Synthetic standards with a wide variation in absorption properties were prepared to test the ability of the calibration procedures to correct for extreme matrix errors. The particle size, analyte distribution, and other matrix properties of artificial standards may vary widely, particularly when compared with naturally occuring samples. However, such variations are ideal for testing calibration procedures. Chemically analysed natural standards were less suitable because of (a) limited range of variation in matrix properties for X-ray purposes, (b) tedious or less accurate analytical techniques for some of the elements of interest, (c) introduction of systematic errors when using chemical techniques on different types of sample, and (d) insufficient or inaccurately known amounts in readily available International standards. Artificial standards have an accurately known amount of the required analyte at a concentration where counting errors can be avoided.

Pure SiO_2 as ground quartz (65%), Al_2O_3 (19%), Fe_2O_3 (7%), $CaCO_3$ (4%) and MgO (5%) were mixed to produce a reference matrix with approximately the same mass absorption coefficient as typical soil mineral material. A silt loam topsoil was also used as a reference matrix. Analytes Zn and Zr were chosen as examples because of their relative abundance in natural systems, their importance in agricultural and soil research and the ease of their measurement using X.R.F. Neighbouring elements in the periodic table with similar analytical properties are also important. Each constituent making up a reference matrix was initially checked where applicable for content of Zn and Zr using the standard spectrochemical technique of known additions. Where necessary a correction was also made for Sr which has an interfering line with Zr (Stern, 1976; Smith et al., 1974). Known amounts of $ZnSO_4$ or ZrO_2 were added to the reference matrices, with thorough mixing being ensured by using a wet paste and dry grinding in a Tema mill, (WC_2 lined).

The reference standards were then amended with large amounts of interfering components their maximum levels being as follows:

50/50 mix wheat straw and lucerne	50%
SiO_2	40%
Al_2O_3	30%
Fe_2O_3	20%
Synthetic "O.M." (40% cellulose, 10% urea, 50% benzoic acid)	40%

Such additions produce very large errors due to absorption-enhancement effects. The intention was to ascertain how well the theoretical corrections would compensate for such extreme interferences.

The X-ray fluorescence installation used was a manual Philips 1540 all-vacuum spectrometer, equipped with 2kW, Cr and W tubes and standard manual counting equipment. The operating conditions and ancilliary procedures used were those standard to X-ray spectrometric analysis.

4.1.2 Data Processing

A computer program was developed to process the X-ray counting data and calculate calibration equations in terms of various peak-background ratio functions. Considerable care was taken in the program to include and combine every statistical error, including the monitoring of a reference sample with very high analyte intensity to evaluate machine drift. For error in compound quantities, the standard errors were combined using general partial derivative equations for dependent or independent variables. Of particular interest was the derivation of standard error in the gradient and intercept of the regression lines and the calculation of residuals. These parameters reflected the scatter of data points around the line and gave a picture of the residual random errors in the whole analytical procedure.

The linear regression subroutine weighted each pair of data according to the standard error in the dependent variable. In X-ray spectrometric calibrations, chemically determined analyte content is usually assumed to be the independent variable (Mitchell, 1968), but with precise X-ray counting, the inaccuracy or imprecision of chemically determined contents may also limit the analysis. Usually there is no justification for assuming either variable to have the greater error and hence a regression of "x on y" is as valid as a regression of "y on x". The program developed performed both regressions and produced two calibration lines, the, usually slight, difference between them depending on the scatter of the data. The choice of which line to take as final calibration line was resolved by selecting the bisector.

Back-substitution of the original counting data into the final calibration line provided a comparison between specified chemical and X-ray implied concentrations. The form of this comparison was to express the difference between the two values as the number of calculated standard errors separating the two concentrations. From mean value theorem considerations, the calculated error is a reasonable estimation of the error probability in the calculated concentration, if the difference values form a normal distribution with mean zero and standard deviation unity.

The two computer programs used are listed in Fortran in Appendix 3. The first program (HXSTD) processes data from standards to produce a calibration equation. The required value of T is specified in the header and may be left blank (T = 0) for a standard counting rate versus concentration calibration. The second program (HXRAY) uses a calibration equation derived from a previous execution of HXSTD to calculate concentrations in unknown samples. Although developed on a PDP 11/40 minicomputer, these programs could easily be adapted to an on-line microprocessor system with a high level language.

4.2 ZIRCONIUM ANALYSIS

The error in zirconium concentration for interfering components in a typical soil matrix is shown in Figure 4-1. The diagram is drawn

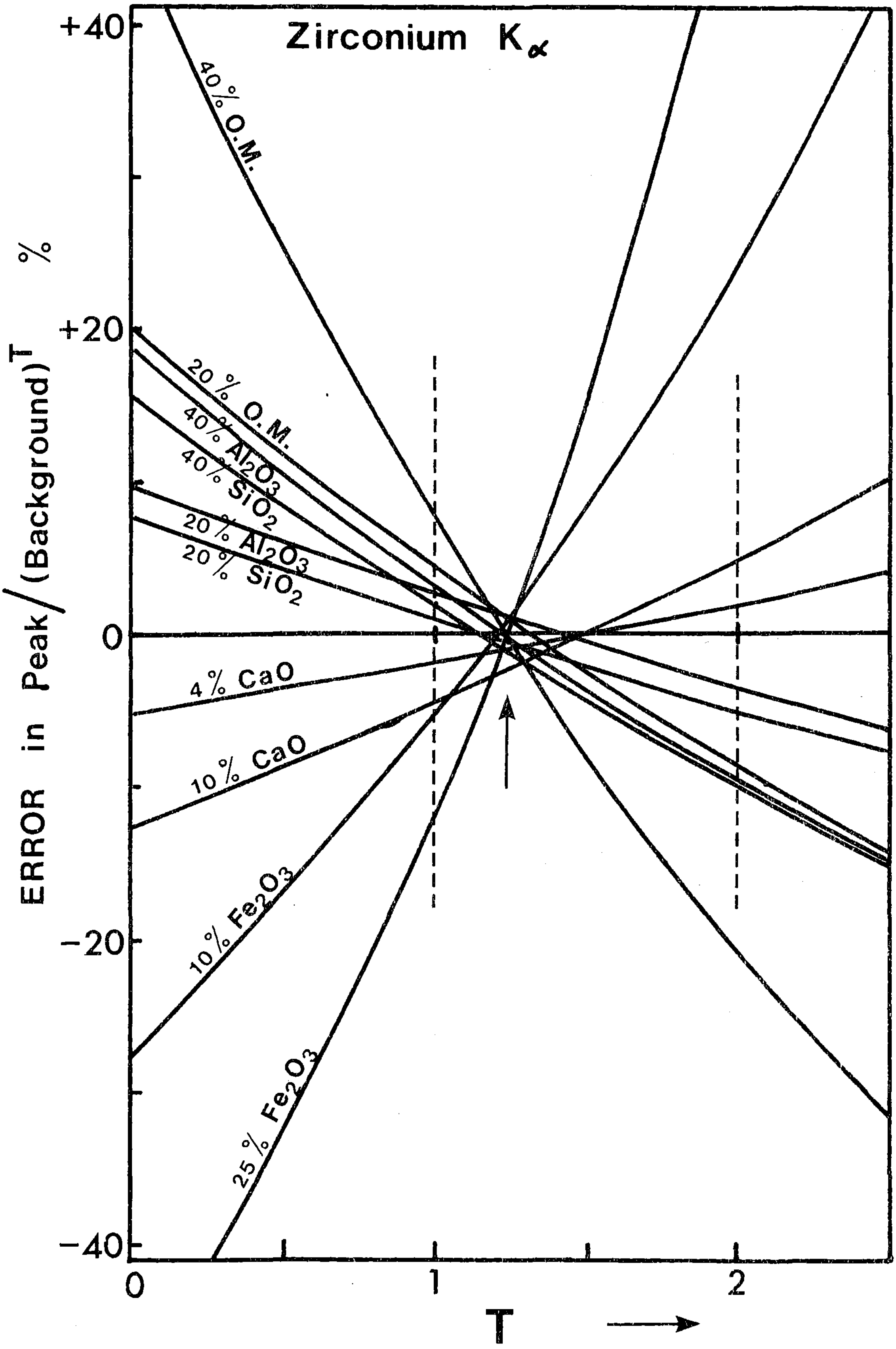

Figure 4-1. Error in zirconium analysis for various interfering components in a typical soil matrix.

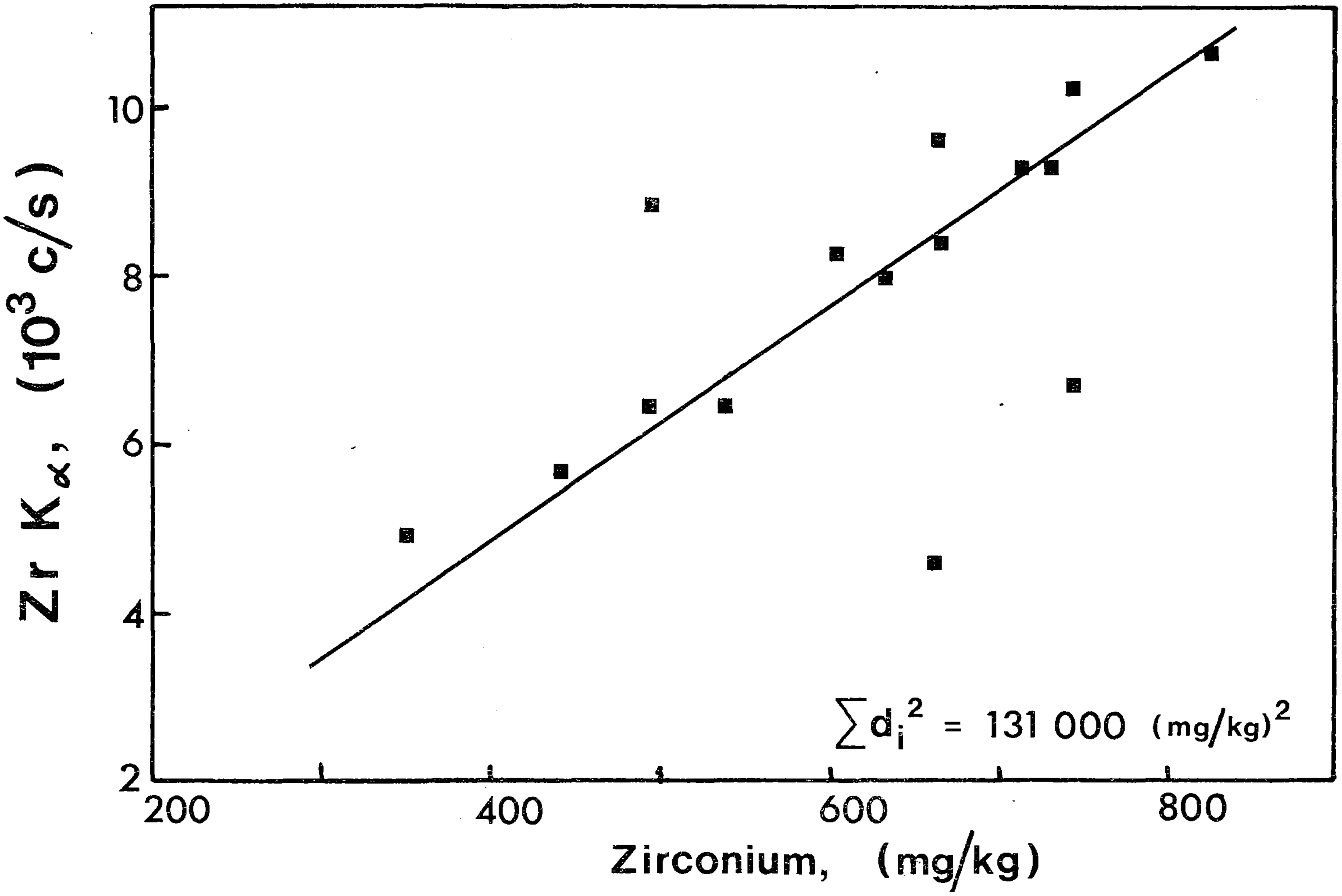

Figure 4-2. Uncorrected calibration line using net peak intensity for zirconium standards.

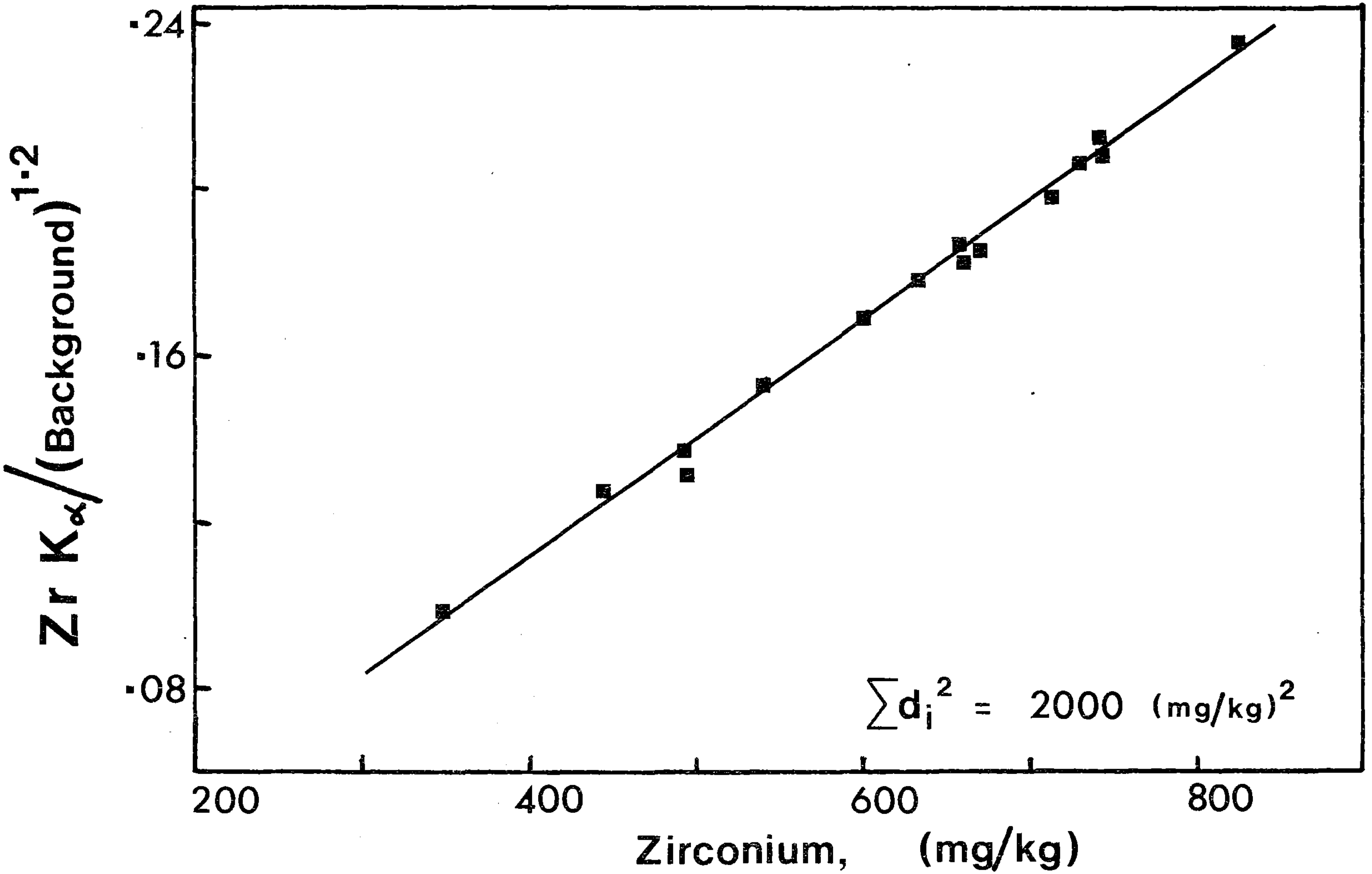

Figure 4-3. Corrected calibration line using modified peak to background ratio for zirconium standards.

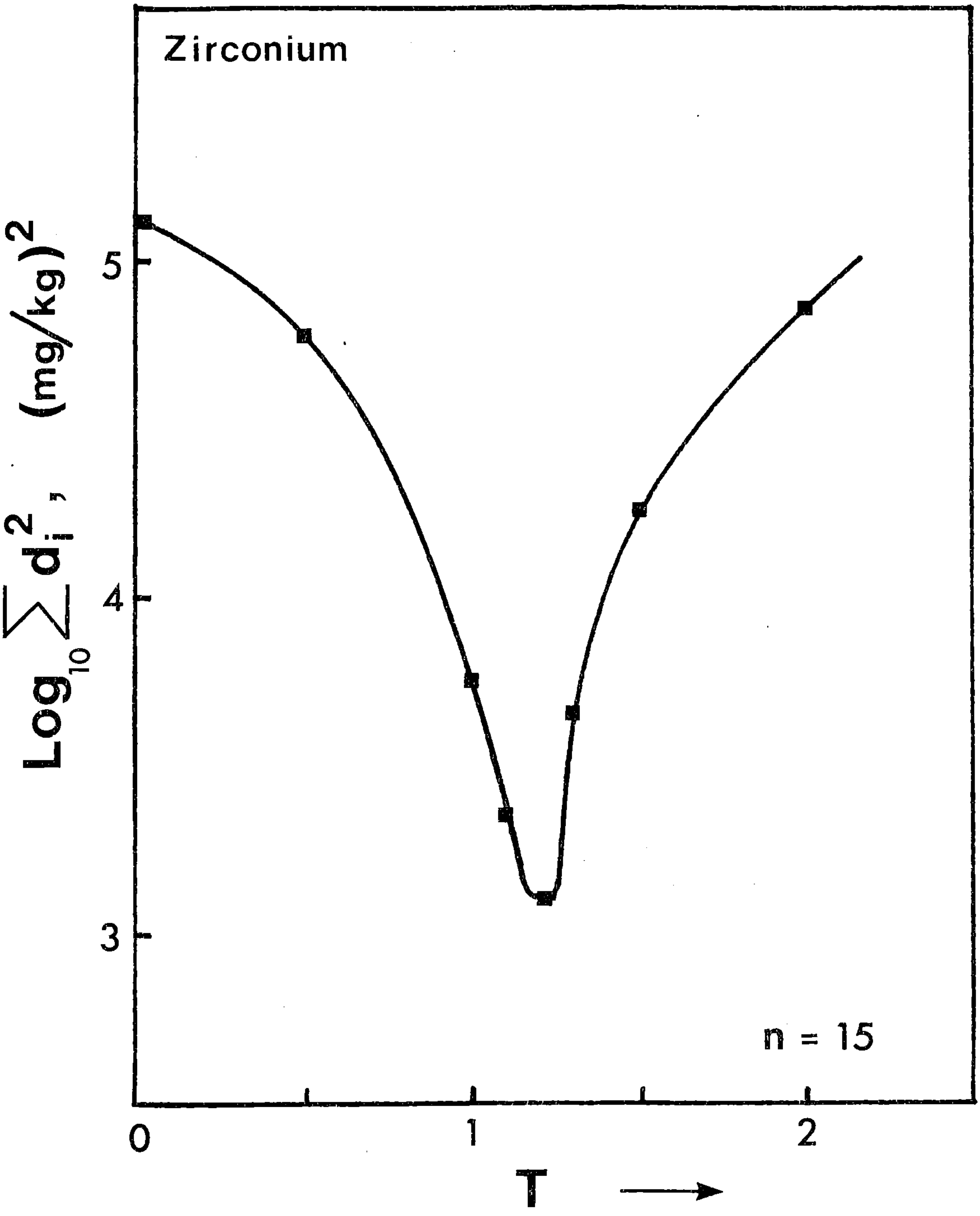

Figure 4-4. Variation in sum of residuals squared for calibration lines with T for zirconium standards.

according to the procedure outlined in section 3.4 for Figure 3-7. Intercepts on the vertical axis indicate the large errors resulting from variation in mass absorption as individual components are added to the matrix. The errors decrease with increasing T up to approximately T = 1.2 and then increase for higher values of T, (not including CaO).

Figure 4-2 is the resultant calibration graph for 15 synthetic Zr standards, prepared as outlined in the previous section. As expected from the extremely diverse nature of the samples, the simple peak intensity versus concentration calibration strategy (T = 0), is not satisfactory. The sum of residuals squared is 131,000 $(mg/kg)^2$ with individual errors of up to 100%.

The same counting data was then reprocessed using a peak to background ratio with T = 1.2. The resultant calibration graph is plotted as Figure 4-3. The vast improvement is indicated by a sum of residuals squared of 2000 $(mg/kg)^2$. The calibration procedure using the same data was repeated several times with different values of T. The sum of residuals squared for each calibration line is plotted on a log scale against T in Figure 4-4. As predicted from theory the fit is best when T = 1.2. Considering that these particular sample matrices were altered by additions of up to 20% wheat straw and lucerne, 40% "synthetic O.M.", 40% ground quartz, 30% Al_2O_3, and 20% Fe_2O_3, the resultant final calibration was most satisfactory.

4.3 ZINC ANALYSIS

Figure 4-5 shows the error in Zn concentration for various interfering components in a typical soil matrix. The line for "organic material" has a much greater T axis intercept than for the other components. If the value of T = 1.3, which is the optimum for the other components, is chosen, then only about 60% of the error from organic material is eliminated.

The calibration graphs for 15 synthetic Zn standards, before and after applying the peak to background ratio corrections are shown in Figures 4-6 and 4-7 respectively. The improvement in fit with sum

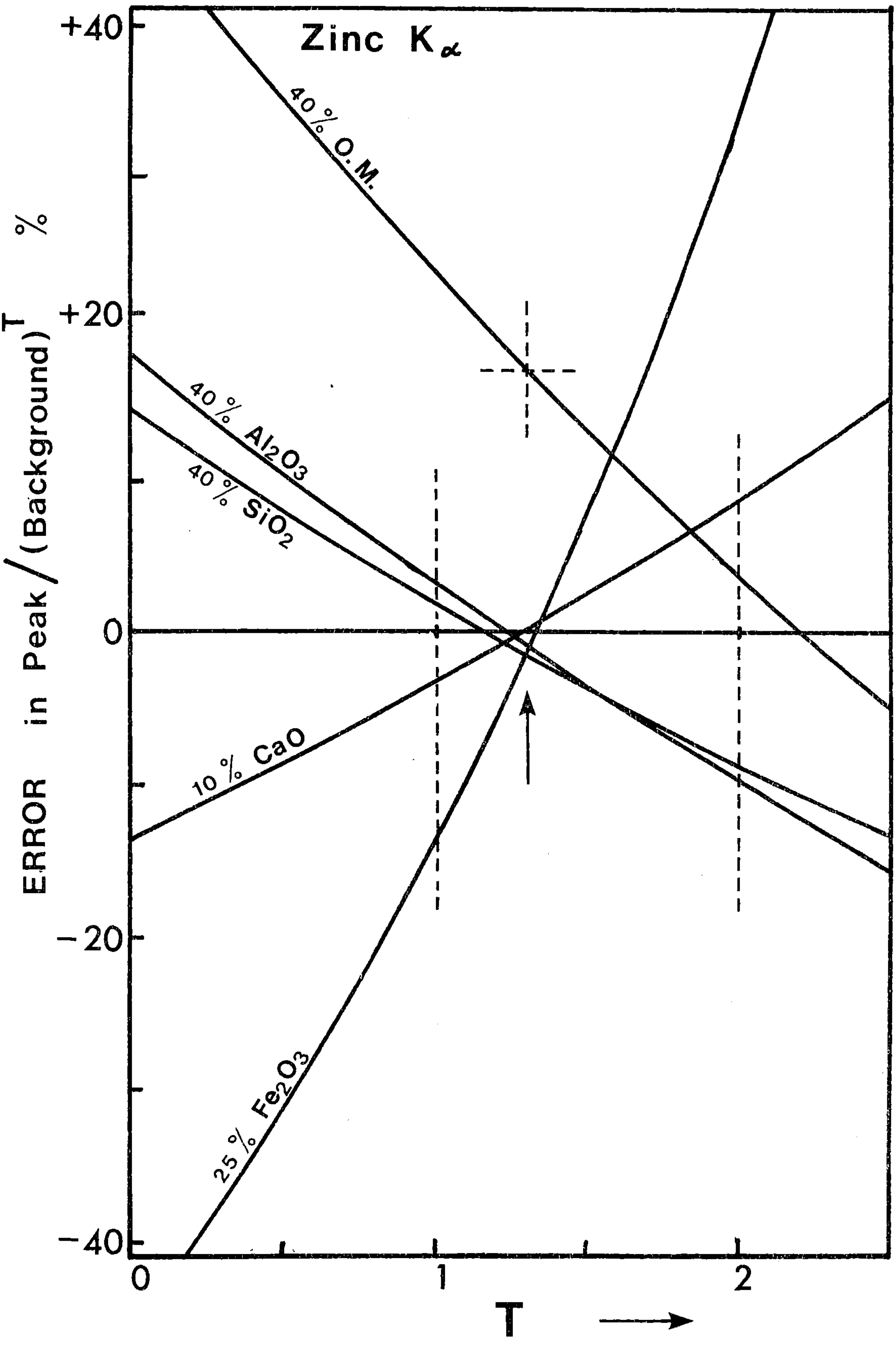

Figure 4-5. Error in zinc analysis for various interfering components in a typical soil matrix.

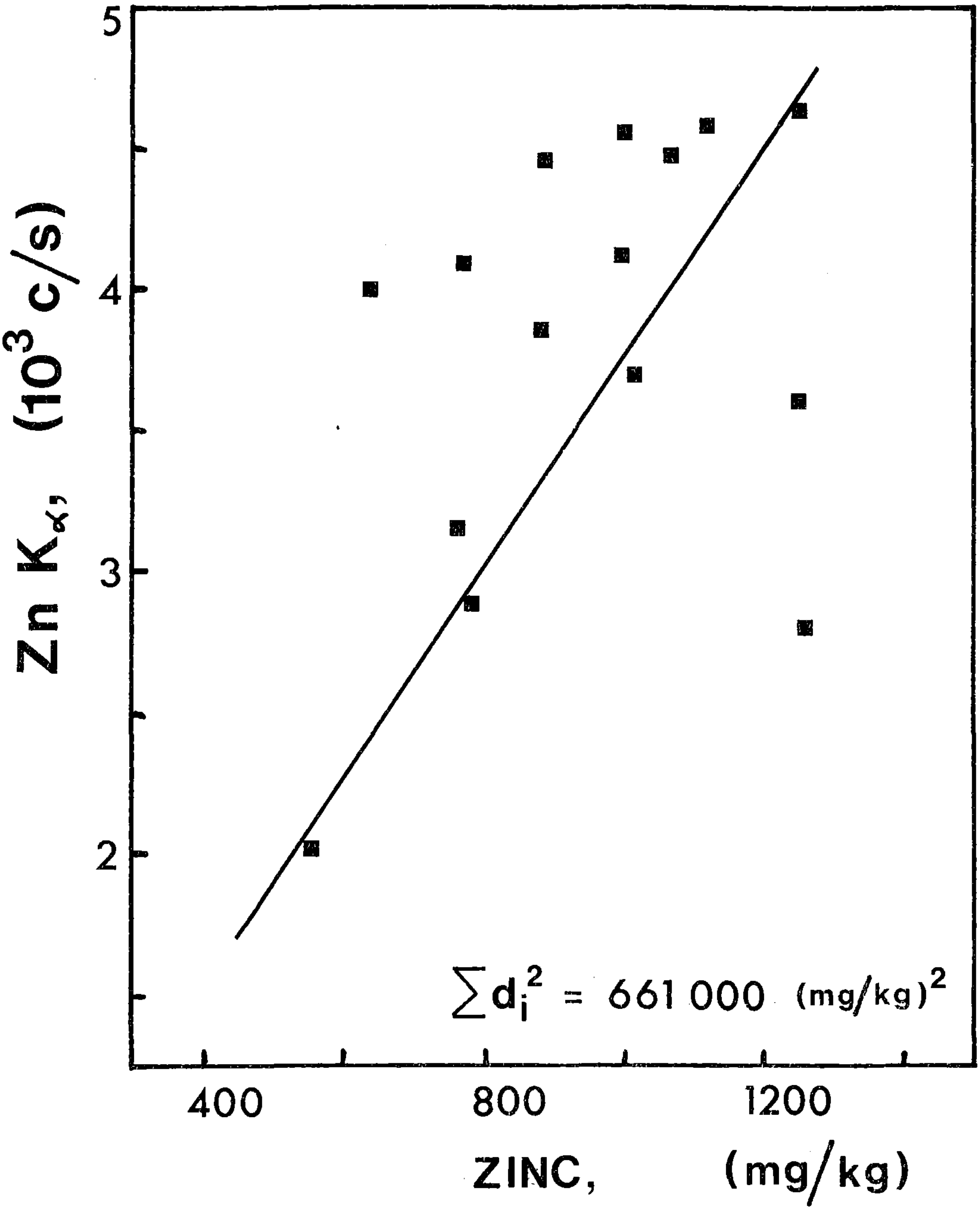

Figure 4-6. Uncorrected calibration line using net peak intensity for zinc standards.

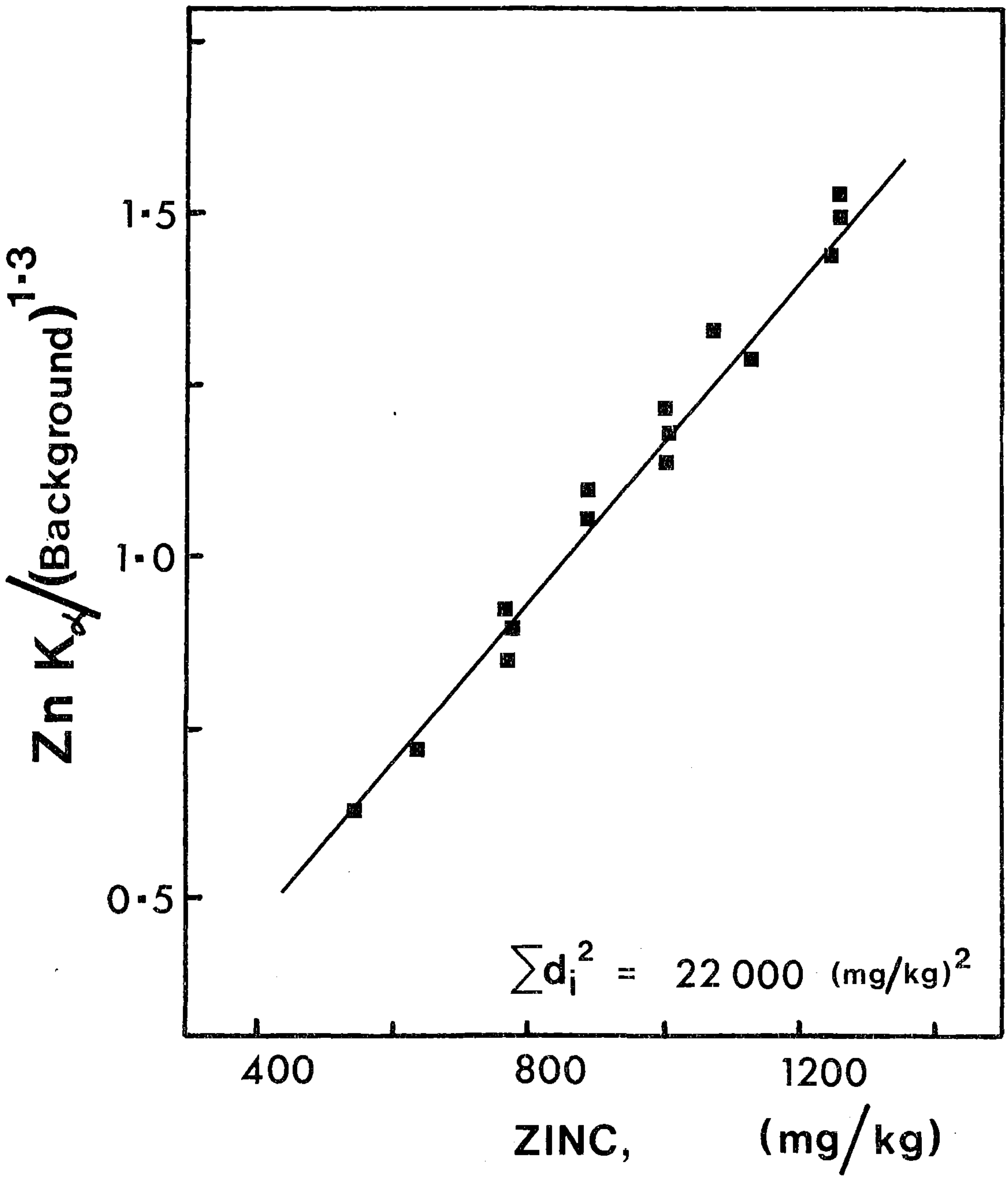

Figure 4-7. Corrected calibration line using modified peak to background ratio for zinc standards.

of residuals squared decreasing from 660,000 to 22,000 $(mg/kg)^2$ is quite satisfactory. The Zn standards which were based mostly on additions to natural soil, had matrix additions of up to 50% wheat straw and lucerne, 40% ground quartz, 30% Al_2O_3, and 20% Fe_2O_3.

4.4 ADDITIONAL CORRECTIONS USING IGNITION LOSS

As explained in section 3-4, if a particular interfering component has a greater T value than that chosen for calibration, then only a fraction of the error resulting from that component is eliminated. In soil samples the T values for organic material (Figure 3-4) are consistently above those for other interfering components. If the actual amount of organic material in a soil sample is known, then a separate correction can be applied to eliminate the remainder of the error. The simplest measure of organic material in soil is loss on ignition at 550°C. An additional advantage of a loss on ignition determination is that structural water and hydroxyls, not removed by oven drying, have been expelled from many clay minerals at this temperature. As reviewed in section 3.1.2, the combined effect of all such low absorption components may be estimated from loss on ignition. Similarly for plant matrices, high absorption components may be estimated by ash content.

Compensation for organic material has been achieved using a set of experimentally derived constants and graphs (Bergseth and Kristiansen, 1978, 1979). However a simpler method based on that of Brown and Kanaris-Sotiriou (1969), was described by the author (Livingstone, 1973) for soil analyses of S, and can be readily adapted to other elements. The measured net peak intensity (I), and hence analyte concentration is modified according to the equation,

$$I' = I(1 - k(\%O.M.))$$

It is easily shown that $k = (\mu_m - \mu_o)/\mu_m \cdot 10^{-2}$

where μ_m = mass absorption coefficient of reference (mineral) matrix

μ_o = mass absorption coefficient of interfering (organic material) component.

%O.M. is estimated by % loss on ignition.

Mass absorption coefficients for various matrices and analyte wavelength are easily calculated and most are directly available for typical examples in the attached volume of tables.

From a plot of T versus analyte error (e.g. Figure 4-5), the proportion of error (d), still present at a less than optimum value of T, is easily measured using the appropriate vertical intervals. The value of k actually used is then reduced by the same proportion to obtain, $k' = d(\mu_m - \mu_o)/\mu_m \, .10^{-2}$. The following Table 4-1, gives examples of d and k' at recommended values of T for typical soil analytes above the Fe absorption edge. The wavelength of scatter is that of the analyte.

TABLE 4-1: CONSTANTS USED FOR CORRECTING PEAK INTENSITY FROM SOIL MATRICES RICH IN ORGANIC MATERIAL

	T	d	k'
Ni	1.32	0.50	0.0040
Cu	1.30	0.45	0.0036
Zn	1.28	0.40	0.0032
As	1.22	0.33	0.0026
Br	1.21	0.25	0.0020
Rb	1.20	0.16	0.0012
Sr	1.20	0.12	0.0009
Zr	1.19	0.02	0.0001

4.4.1 Zinc in Organic Rich Soil Matrices

Two sets of twelve Zn standards were prepared to test the "loss on ignition" correction for its ability to eliminate residual errors in situations where T values provide incomplete compensation for organic material in soil. One set had mineral interfering components of quartz, Al_2O_3 and Fe_2O_3 while the other had organic material additions of up to 50% wheat straw and lucerne.

Figure 4-8 shows the sums of residuals squared of the cali-

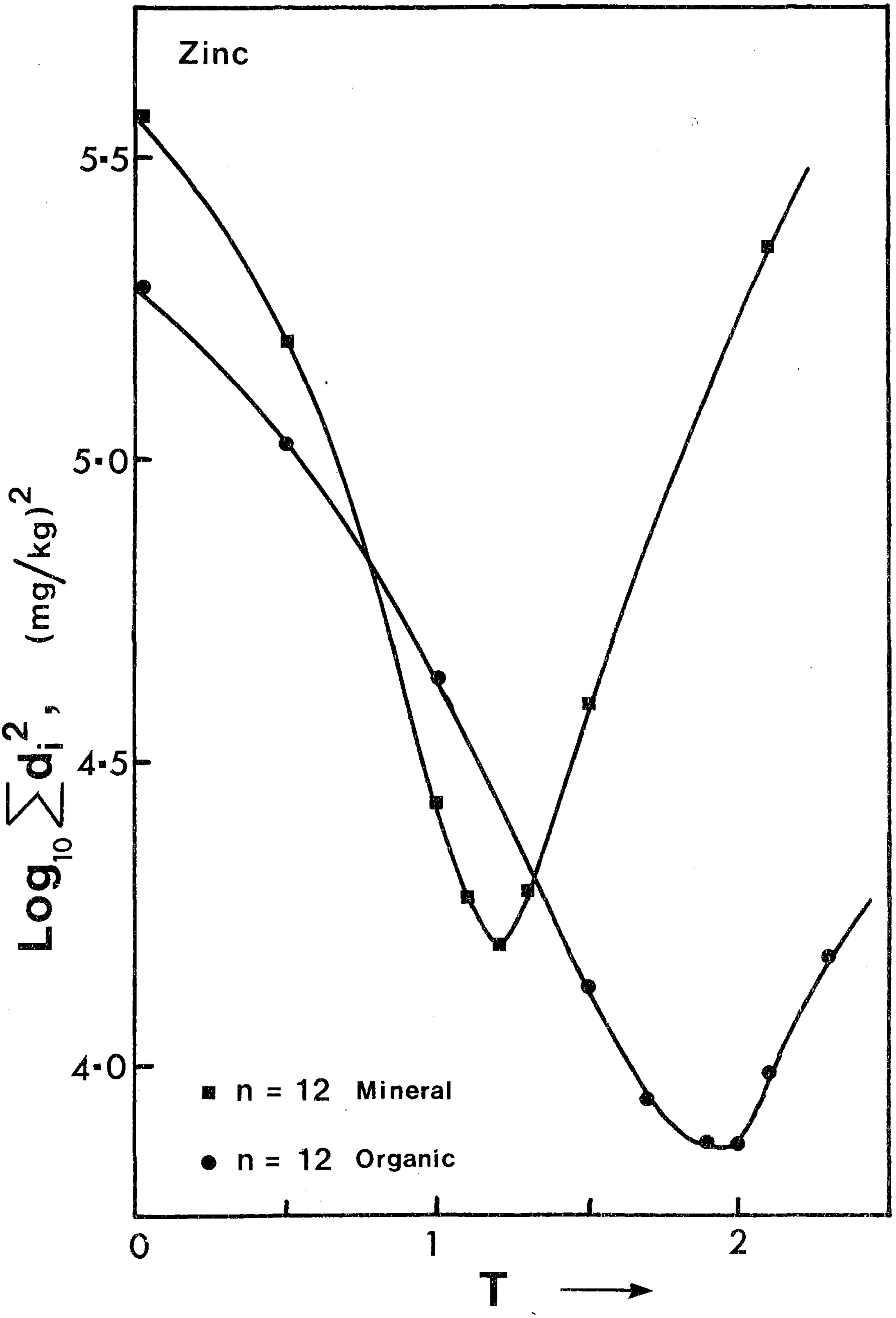

Figure 4-8. Variation in fit of calibration lines with T for zinc standards with either mineral or organic interfering components.

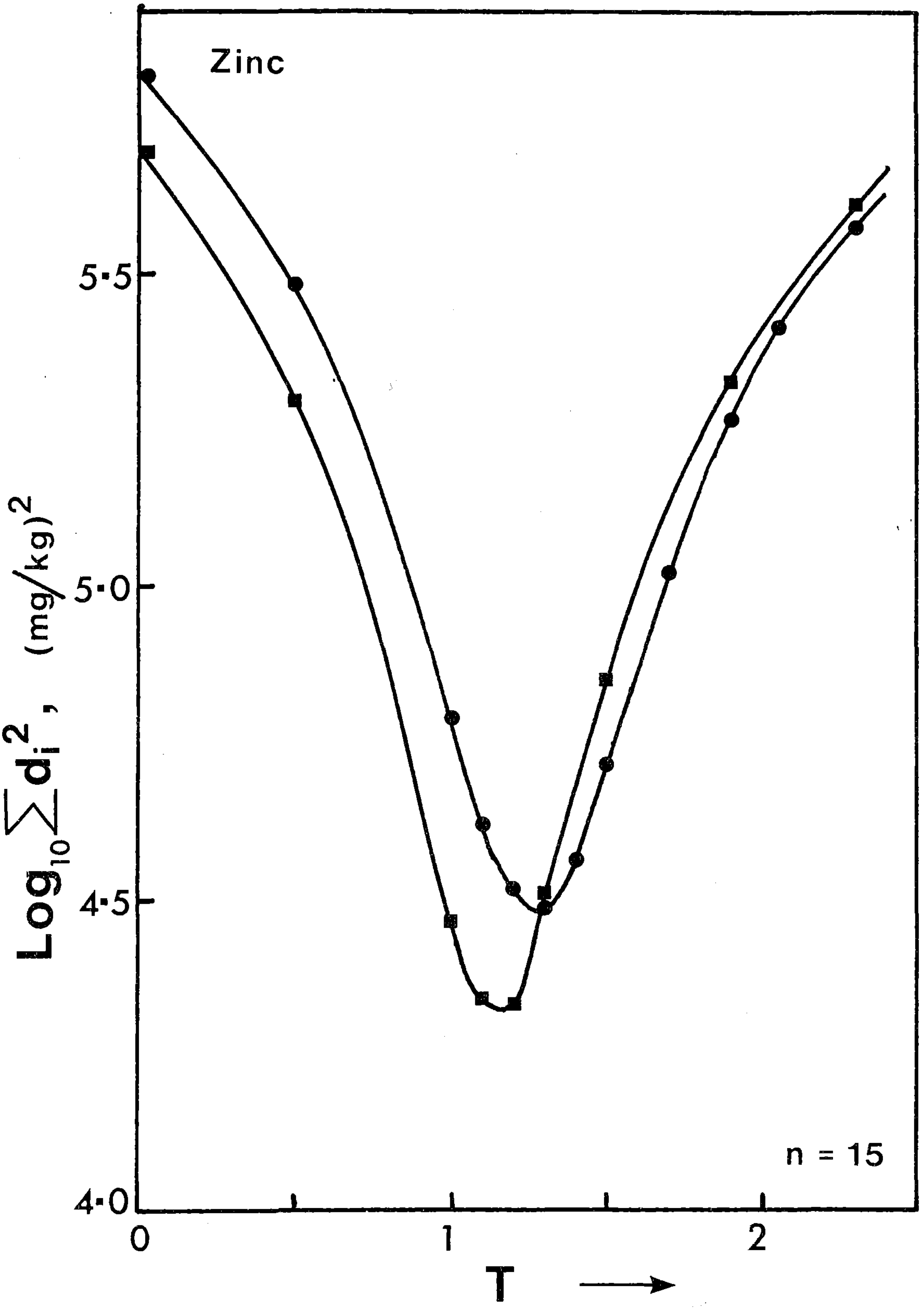

Figure 4-9. Variation in fit of calibration lines with T for zinc standards with ■ and without ● extra correction using loss on ignition.

bration lines for each set of standards plotted on a log scale against T. The experimental optimum values of T correspond well with the theoretical T values of 1.25 and 2.0 for the appropriate high levels of interference of mineral and organic components respectively.

Figure 4-9 shows the effect on calibration errors of the additional "loss on ignition" correction in Table 4-1. The 15 standards used were those shown in Figures 4-6 and 4-7. Without the loss on ignition correction, the optimum value of T = 1.4 lies between the optimum values for mineral and organic interferences alone. The minimum value in the residuals squared, corresponds to the minimisation of vertical intervals in Figure 4-5 while taking all lines into account. Using the loss on ignition correction, the optimum value of T shifts to a lower value corresponding to that for the mineral interferences alone. The improvement in fit with the correction illustrates the effect of minimisation of vertical intervals in Figure 5-4 whilst being able to ignore the "organic line".

A similar correction procedure to eliminate residual error could be developed for soil contamination, as measured by ash content, in predominantly plant matrices. Although the effect of soil on sample absorption is relatively large, the T values for soil in plant matrices do not differ greatly from other interfering components, making any additional correction largely unnecessary.

4.5 RECOMMENDED STRATEGIES FOR PLANT AND SOIL ANALYSIS

Detailed information on the likelihood of successful peak to background calibration is found in the attached volume of tables which, together with the optimising procedure as previously described, should be consulted for the matrix variation in question. The combinations of matrix composition, scatter type, scatter wavelength and interfering components are too many to attempt even a summary. Instead, a few broad observations are outlined for various groups of analytes using some examples of T values given in Tables 4-2 and 4-3.

As a general conclusion, it may be noted that reported calibration methods relating reciprocal of mass absorption coefficient with a Compton scattered tube line are basically sound. Most interfering components have corresponding T values of approximately unity but some special cases, particularly involving lighter elements such as organic material in soil, or nitrogen rich fractions in plant material, require other values of T for complete correction. For analytes below a major absorption edge, a Compton scattered line is often less satisfactory than some other strategy.

Conclusions such as that of Feather and Willis (1976) that, "Background intensity at any position is linearly related to the reciprocal of the mass absorption coefficient for any wavelength between (major element) absorption edges", are shown to be invalid. In this study, values of T for total scatter are not near unity, even under the most favourable conditions. It should be noted that the analytical procedure of Feather and Willis (1976) differed from the commonly used peak-to-background ratio method. Their procedure used a "residual background" (R), which was assumed to be composed of electronic noise and non-sample scatter. This was then subtracted from the "measured background" (B) to obtain "true background", i.e.

$$(B - R) = K_1/\mu.$$

By comparing the above equation with a simplified verson of equation (20) (for a specific matrix and analyte), as used in this study and by others (Champion _et_ _al_., 1966; Franzini _et_ _al_., 1976a), i.e.

$$B = k_2.S/\mu$$

the residual background of Feather and Willis (1976), is shown to be,

$$R = B(1 - k_3/S).$$

The residual background R, is thus a function of both sample scatter and the scatter coefficient of their "blank" samples. This subtraction of an experimentally measured portion of background for each particular analyte, in addition to correcting for any possible non-sample scatter and noise, also scaled the sample scatter in such a manner as to force their linear calibration to hold true. A similar assumption by Williams (1976) also neglects any variation in scatter coefficient between standard and sample matrices. The basis of her method was that "the mass absorption ratio of sample to standard is inversely proportional to the ratio of the background scatter".

It is evident from the tables of T values, that reported calibration methods which have attempted to relate the reciprocal of mass absorption coefficient with either a Rayleigh scattered tube line or a combination of background scatter, are approximations which work over relatively small variations in sample matrix only. To be more widely successful, these methods, involving some component of Rayleigh scatter, need modification using a combination of T values as previously described.

In their theoretical calculations, Taylor and Andermann (1971) used an isolated atom model of X-ray scattering, similar to that used in this study. Their calculations showed that the quality of matrix compensation was independent of the scattered wavelength used as the internal standard, but attempts to verify this independence experimentally, failed. They found superior compensation at shorter wavelengths, or by using Compton scatter alone. They concluded that since their theoretical calculations indicated an absence of wavelength dependence, the isolated atom model was only partially valid and suggested that additional mechanisms such as diffraction effects would have to be considered.

In this study, a considerable variation in T with wavelength was found when using a similar isolated atom model. Mass absorption coefficients and scatter intensities are both related indirectly to wavelength in different ways. At shorter wavelengths, measured mass absorption coefficients also include a true photoelectric absorption component which is not part of the scatter process. The wavelength trends in the calculated T values in this study support the trends found experimentally by Taylor and Andermann (1971). Since their theoretical calculations did not agree with their own experimental results, whereas the exhaustive calculations of this study definitely show wavelength dependence, it must be concluded that the physical constants or methods used for their calculations were insensitive.

4.5.1 Elements in Soil with $Z > 27$.

Elements with $Z > 27$ are above the Fe absorption edge with straightforward values of T as seen from Figure 3-4 and Table 4-2a. The described procedure for selecting T and additional correction for organic material if necessary, gives successful calibration. The values listed in Table 4-1 for total scatter at the analyte wavelength are those used by the author for regular analysis of mineral soils and soils amended with sewage sludge with loss on ignition values of up to 40%. Other elements such as Pb with L spectra lines above the Fe absorption edge may also be analysed successfully. The Pb line used by the author has been included in the attached volume of tables.

From Table 4-2a it is clear that Cr target lines are useless in correcting for mass absorption errors, with no ability whatsoever to correct for Fe and Si interferences in particular. It may also be seen that the ability of a Compton scattered tube line to correct for lighter organic material interference increases with decreasing wavelength. However, this trend must be offset against a slightly adverse movement of the Compton T values for Si and Fe at shorter wavelengths.

4.5.2 Elements in Soil with $Z < 27$.

The analytes of interest are most likely P, S. Cl, Ti, Cr and Mn. From Table 4-2b, the T values for Si and Al interference although erratic, are relatively unimportant because of the small absorption errors introduced at these wavelengths.

For Ti, Cr and Mn, the two interferences needing close attention are Ca (including K which has a similar effect) and Fe and it is impossible to correct for both at the same time. The small T value for Fe is particularly critical when considering scatter at the analyte line. The large negative Compton T value for Cr tube scatter makes an ideal calibration possible but the Compton line is difficult to separate out in practice. If either Fe or Ca is relatively invariant in the sample matrices, then full compensation can be made for the

Table 4-2a. EXAMPLES OF T VALUES FOR ANALYSIS OF ELEMENTS Z > 27 IN SOIL MATERIAL

ANALYTE	PEAK ERROR (% per +1%)	T VALUE						
			Compton Tube Line			Rayleigh Tube Line		
		K Line	Cr 2.29A	Au 1.28A	Ag 0.56A	Cr 2.29A	Au 1.28A	Ag 0.56A
COPPER	Z = 29							
Na	0.70	1.38	2.38	0.99	0.97	1.87	1.78	2.39
Al	0.74	1.24	3.15	0.99	0.98	8.77	1.47	2.51
Si	0.66	1.26	5.06	0.90	0.87	-4.11	1.22	2.08
Ca	-2.11	1.27	0.71	0.94	1.02	0.94	1.38	10.9
Fe	-4.64	1.29	120.	0.92	0.89	-2.74	1.31	1.92
O.M.	0.87	2.50	0.76	0.79	0.91	6.19	6.29	2.38
ZINC	Z = 30							
Na	0.72	1.45	2.42	1.00	0.98	1.90	1.81	2.43
Al	0.74	1.28	3.12	0.98	0.97	8.70	1.45	2.49
Si	0.68	1.22	5.14	0.91	0.89	-4.18	1.23	2.11
Ca	-2.17	1.26	0.73	0.96	1.05	0.96	1.41	11.2
Fe	-4.67	1.27	121.	0.92	0.90	-2.76	1.32	1.94
O.M.	0.87	2.39	0.76	0.79	0.91	6.19	6.28	2.38
STRONTIUM	Z = 38							
Na	0.73	1.59	2.49	1.03	1.01	1.95	1.86	2.50
Al	0.77	1.34	3.31	1.05	1.03	9.24	1.55	2.64
Si	0.72	1.14	5.42	0.96	0.93	-4.40	1.30	2.23
Ca	-2.04	1.50	0.68	0.90	0.98	0.90	1.32	10.5
Fe	-4.97	1.18	129.	0.98	0.95	-2.94	1.41	2.06
O.M.	0.86	1.40	0.76	0.78	0.91	6.15	6.24	2.36
ZIRCONIUM	Z = 40							
Na	0.73	1.51	2.47	1.02	1.00	1.94	1.85	2.48
Al	0.77	1.35	3.32	1.05	1.03	9.26	1.55	2.65
Si	0.72	1.14	5.50	0.97	0.95	-4.47	1.32	2.26
Ca	-2.04	1.53	0.69	0.91	0.98	0.90	1.32	10.5
Fe	-5.03	1.17	130.	0.99	0.97	-2.98	1.42	2.09
O.M.	0.86	1.28	0.75	0.78	0.90	6.11	6.20	2.35

Table 4-2b. EXAMPLES OF T VALUES FOR ANALYSIS OF ELEMENTS $Z < 27$ IN SOIL MATERIAL

ANALYTE	PEAK ERROR (% per +1%)	T VALUE						
			Compton Tube Line			Rayleigh Tube Line		
		K Line	Cr 2.29A	Au 1.28A	Ag 0.56A	Cr 2.29A	Au 1.28A	Ag 0.56A
SULPHUR	Z = 16							
Na	0.23	2.82	0.81	0.33	0.33	0.63	0.60	0.81
Al	0.04	-0.16	0.12	0.04	0.04	0.34	0.06	0.10
Si	-0.15	0.51	-1.11	-0.20	-0.19	0.90	-0.27	-0.46
Ca	0.80	0.59	-0.26	-0.35	-0.38	-0.35	-0.51	-4.04
Fe	0.26	0.18	-6.33	-0.05	-0.05	0.15	-0.07	-0.10
O.M.	0.81	2.21	0.72	0.74	0.86	5.80	5.89	2.23
POTASSIUM	Z = 19							
Na	0.30	1.45	1.03	0.43	0.42	0.81	0.77	1.03
Al	0.06	-0.35	0.22	0.07	0.07	0.61	0.10	0.17
Si	-0.15	0.48	-1.18	-0.21	-0.20	0.96	-0.28	-0.48
Ca	0.82	0.57	-0.26	-0.35	-0.38	-0.35	-0.51	-4.02
Fe	0.24	0.16	-5.89	-0.05	-0.04	0.13	-0.06	-0.09
O.M.	0.82	2.42	0.72	0.75	0.86	5.86	5.95	2.25
MANGANESE	Z = 25							
Na	0.41	1.21	1.37	0.57	0.55	1.07	1.02	1.37
Al	0.23	2.98	0.99	0.31	0.31	2.77	0.46	0.79
Si	0.09	-0.81	0.63	0.11	0.11	-0.51	0.15	0.26
Ca	-3.03	1.22	1.03	1.36	1.47	1.36	1.99	15.8
Fe	0.26	0.17	-6.55	-0.05	-0.05	0.15	-0.07	-0.10
O.M.	0.78	3.35	0.69	0.71	0.82	5.56	5.65	2.13
IRON	Z = 26							
Na	0.38	1.31	1.30	0.54	0.53	1.03	0.97	1.30
Al	0.26	2.34	1.08	0.34	0.34	3.00	0.50	0.86
Si	0.09	-1.05	0.69	0.12	0.12	-0.56	0.17	0.28
Ca	-3.15	1.20	1.07	1.42	1.53	1.41	2.07	16.4
Fe	0.26	0.17	-6.48	-0.05	-0.05	0.15	-0.07	-0.10
O.M.	0.78	3.34	0.69	0.71	0.83	5.59	5.68	2.15

other using total scatter at analyte wavelength. Depending on the expected ranges of concentration in Ca and Fe, a choice of T is possible between about 0.2 and 1.2. Any choice of T within this range only partially corrects for organic material and an additional correction is needed for full compensation.

Changes in mineral composition of the soil have only minor effects on matrix absorption for P, S and Cl. Consideration of variations in Ca and Fe which have the most influence on matrix absorption indicates a possible slight improvement with T approximately 0.2 for total scatter at analyte wavelength. Organic material has a major effect on absorption which may be eliminated with a large T = 2.1 provided Ca and Fe are invariant. Otherwise the effect of organic material can be eliminated using solely the additional loss on ignition correction, with a value of k = 0.0074.

In general, it is evident that scattered tube lines, either above or below the Fe absorption edge cannot correct for a combination of interferences for soil analytes below the Fe edge. Hence, such methods proposed by Vos (1972) and Childs and Furkert (1974) can at best be successful over a relatively small variation in sample matrix.

4.5.3 Elements in Plant Material with Z > 21

For those elements with wavelengths above the Ca and K absorption edges, the application of the optimising procedure should give good calibration with T values (Figures 3-5 and 3-6, Table 4-3a) in the range 1.0 to 1.3. For Ni, Cu and Zn, excellent results have been achieved using T = 1.17 for total scatter at analyte background.

From Table 4-3a it can be seen that for light elements, (e.g. Mn), there is generally no clear-cut choice between wavelengths or between types of scatter and hence each application needs separate calibration. As atomic number increases to Zn, the T values for total scatter are more uniform than for the Compton and Rayleigh components separately, particularly for total background at the shortest wavelengths (not shown in Table 4-3a). For still higher atomic number analytes (e.g. Sr), and shorter wavelength, uniformity in T values

Table 4-3a. EXAMPLES OF T VALUES FOR ANALYSIS OF ELEMENTS Z > 21 IN PLANT MATERIAL

ANALYTE	PEAK ERROR (% per +1%)	T VALUE						
			Compton Tube Line			Rayleigh Tube Line		
		K Line	Cr 2.29A	Au 1.28A	Ag 0.56A	Cr 2.29A	Au 1.28A	Ag 0.56A
MANGANESE	Z = 25							
C	0.54	1.71	1.10	1.07	1.26	2.23	1.70	1.68
N	0.26	1.07	1.81	1.25	1.74	1.13	1.36	1.23
Mg	-2.82	1.99	0.89	0.94	1.35	3.28	9.41	1.74
K	-11.0	1.22	0.97	0.94	1.13	1.36	1.50	1.79
Ca	-13.0	1.22	1.00	0.89	1.11	1.39	1.31	1.71
Soil	-2.50	1.69	0.90	0.63	0.78	2.30	1.41	1.07
NICKEL	Z = 28							
C	0.58	1.47	1.17	1.14	1.35	2.38	1.82	1.79
N	0.27	1.19	1.92	1.33	1.85	1.20	1.45	1.31
Mg	-2.77	1.91	0.87	0.92	1.32	3.22	9.22	1.71
K	-11.8	1.19	1.05	1.01	1.21	1.46	1.62	1.93
Ca	-13.9	1.18	1.08	0.96	1.20	1.50	1.41	1.85
Soil	-3.85	1.34	1.39	0.97	1.21	3.57	2.18	1.65
ZINC	Z = 30							
C	0.57	1.35	1.17	1.14	1.34	2.37	1.81	1.78
N	0.28	1.34	1.96	1.36	1.89	1.23	1.48	1.34
Mg	-2.74	1.68	0.86	0.91	1.31	3.19	9.13	1.69
K	-12.0	1.17	1.06	1.02	1.23	1.47	1.63	1.95
Ca	-14.2	1.16	1.11	0,98	1.22	1.53	1.45	1.89
Soil	-3.79	1.30	1.37	0.96	1.19	3.51	2.14	1.63
STRONTIUM	Z = 38							
C	0.52	1.14	1.07	1.04	1.23	2.17	1.66	1.63
N	0.27	1.32	1.90	1.32	1.82	1.19	1.43	1.30
Mg	-2.50	1.10	0.79	0.83	1.20	2.91	8.33	1.54
K	-11.5	1.11	1.01	0.98	1.18	1.42	1.57	1.87
Ca	-13.4	1.10	1.04	0.92	1.15	1.44	1.36	1.78
Soil	-3.68	1.09	1.33	0.93	1.16	3.41	2.08	1.58

Table 4-3b. EXAMPLES OF T VALUES FOR ANALYSIS OF ELEMENTS $Z < 21$ IN PLANT MATERIAL

ANALYTE	PEAK ERROR (% per +1%)	T VALUE						
			Compton Tube Line			Rayleigh Tube Line		
		K Line	Cr 2.29A	Au 1.28A	Ag 0.56A	Cr 2.29A	Au 1.28A	Ag 0.56A
PHOSPHORUS	Z = 15							
C	0.31	2.09	0.64	0.62	0.74	1.30	0.99	0.98
N	-0.11	1.98	-0.78	-0.54	-0.75	-0.49	-0.59	-0.53
Mg	-3.74	1.23	1.18	1.25	1.80	4.38	12.5	2.32
K	-0.55	-0.49	0.05	0.04	0.05	0.06	0.07	0.08
Ca	-0.77	-0.60	0.06	0.05	0.06	0.08	0.07	0.10
Soil	-2.80	1.33	1.00	0.70	0.88	2.58	1.57	1.20
SULPHUR	Z = 16							
C	0.33	2.09	0.69	0.67	0.79	1.40	1.06	1.05
N	-0.09	2.30	-0.61	-0.42	-0.58	-0.38	-0.46	-0.41
Mg	-3.85	1.23	1.22	1.29	1.85	4.51	12.91	2.39
K	-0.60	-0.54	0.05	0.05	0.06	0.07	0.08	0.09
Ca	-0.80	-0.77	0.06	0.05	0.06	0.08	0.08	0.10
Soil	-2.91	1.32	1.05	0.73	0.91	2.69	1.64	1.24
POTASSIUM	Z = 19							
C	0.37	2.37	0.77	0.75	0.89	1.56	1.19	1.18
N	-0.06	-11.3	-0.41	-0.28	-0.39	-0.26	-0.31	-0.28
Mg	-3.88	1.31	1.23	1.30	1.86	4.53	13.00	2.41
K	-0.66	-0.52	0.06	0.05	0.06	0.08	0.09	0.10
Ca	-0.89	-0.75	0.07	0.06	0.07	0.09	0.09	0.11
Soil	-3.01	1.37	1.08	0.76	0.94	2.78	1.70	1.29
CALCIUM	Z = 20							
C	0.50	1.87	1.02	0.99	1.17	2.06	1.57	1.55
N	0.14	0.73	0.98	0.68	0.94	0.61	0.74	0.67
Mg	-3.18	1.45	1.00	1.06	1.52	3.71	10.6	1.97
K	-11.0	1.12	0.97	0.94	1.12	1.35	1.50	1.79
Ca	-0.65	-0.43	0.05	0.04	0.05	0.07	0.06	0.08
Soil	-2.56	1.50	0.92	0.64	0.80	2.35	1.44	1.09

gives several options for excellent calibration.

4.5.4 Elements in Plant Material with $Z < 21$.

Analyte wavelength for elements with $Z < 21$ is below the Ca and K absorption edges and together with Mg, matrix variation in these elements upsets calibration. Below the absorption edges, background scatter is increasing faster than absorption and T values become negative or erratic. In general the optimisation procedure shows that a peak to background ratio at analyte wavelength is often worse than a "normal" calibration assuming $T = 0$. There may even be a case in some situations for using a negative T value, i.e. relating analyte concentration directly to scatter, rather than as a function of reciprocal background.

For P, and S, a slight improvement in calibration may be possible using the shortest scatter wavelength available instead of $T = 0$. For K and Ca in plant material, it is seen from Table 4-3b that T values for the major interferences fall in the range 1.1 to 1.5 for scatter at analyte wavelength, indicating a possible calibration strategy. Compton lines appear less satisfactory and self absorption also upsets calibration. The interesting case of N interference in K analysis illustrates a situation where a large negative T value has no effect on calibration when the peak error due to N is small.

For all analytes in plant material, below the K and Ca absorption edges, there appears to be no calibration strategy which completely removes the error for highly variable samples.

"Note that Cl was not one of the six interfering elements considered in choice of plant matrix variation. (See S 3.1.2 first and last paragraphs). Cl variation may have a large effect on Ca and K, similiar to the 11% per +1% for K in Ca analysis and Cl should be considered in situations where its variation is significant."

PART 2

Disposal on Pasture of Christchurch Sewage Sludge

CHAPTER 5

DISPOSAL OF SLUDGE

5.1 GENERAL INTRODUCTION

Disposal of sewage sludge on agricultural land is basically a problem of balance between the cumulative effects of sludge-borne heavy metals and plant nutrient supply from organic material. In the last decade, the ever increasing attention focused on environmental issues has produced a flood of literature devoted to sewage sludge disposal. Some reports have more of an emotive than scientific impact while others do not distinguish clearly between the two opposing aspects of sludge disposal.

Many early studies were tentative investigations which have been subsequently reviewed and quoted many times. Consequently there has been a tendency for tentative suggestions to become accepted as fact, with cautions in interpretation being overlooked. In the printing rush, information has sometimes been published which is not scientifically complete. As some of these reports are liable to be quoted to a particular end, care must be exercised not to give weight to information which is inconclusive.

Excellent research publications and reviews on the use of sewage sludge and the effects of heavy metals on land are available. Aspects of particular interest to the question of disposal of Christchurch Drainage Board sludge are referenced as fully as possible. No attempt is made here to review the whole general field of metalliferous sewage sludge disposal. The review by Leeper (1978), an authority in this area of study, has condensed the literature and previous reviews to basics and presented all the general aspects important to agriculture.

5.2 DESCRIPTION OF SOIL AND SLUDGE

The majority of the Drainage Board soils which are suitable for sludge disposal are classified as Kairaki sand (N.Z. Soil Bureau, 1967, 1974). This sand dune soil is freely to rapidly draining and only recently stabilised. The soil is weakly developed with little or no topsoil. Motukarara loam, mostly sandy, is found in a few slow-draining interdune hollows and Motukarara silt loam occurs along the estuarine edges. Conversion of the dune soils into flat pasture has buried most of the interdune hollows and left paddocks of flattened freely draining material. Over the years variable quantities of both dried and liquid sludge have been deposited on the surface of these paddocks or worked in, to form a stable topsoil. For the young, weakly-developed Motukarara silt loam, permanent lowering of the water table by draining and elimination of estuarine-induced salinity, has provided a reasonable soil suitable for grazing, particularly in summer. Sludge disposal on the flat, slowly-draining silt loam has been and still is, limited to small amounts of liquid sludge in summer.

Samples of the sandy dune material and sludge from the drying beds were analysed to provide data for comparison with other reports and to characterise the materials used in subsequent trials. The results given in the following tables are for, (i) four sand samples each comprising about ten "grab" subsamples bulked from a particular truckload of sand, and (ii) six dried sludge samples each bulked from a particular drying bed. The sand samples were chosen to represent the range of visual variation between truckloads. Differences were confined to slight colouration due to moisture content and minor amounts of organic products from the dune surface. Variation between the sludge samples was probably due to settling and decomposition within the holding lagoons. Each lagoon collected sludge for many weeks before it was emptied, either directly onto pasture or into a drying bed comprising a shallow pit moulded in sand.

Table 5-1 lists properties of the sand and sludge, determined using the methods described in Section 6.3. Standard errors for the measurement replicates are given in brackets. In the case of derived quantities, the standard errors are combined using the appropriate

TABLE 5-1: SOME PROPERTIES OF KAIRAKI SAND AND CHRISTCHURCH DIGESTED SEWAGE SLUDGE

Property	Sand	Sludge
Loss on Ignition (%)	1.38 (0.03)	54.5 (2.0)
Bulk density (t/m^3)	1.37 (0.07)	0.39 (0.02)
pH (H_2O)	6.43 (0.09)	6.60 (0.05)
(0.01 M $CaCl_2$)	5.54 (0.11)	6.44 (0.04)
Mineral Material		
Coarse sand	30%	4%
Fine sand	68%	17%
Silt	<2%	35%
Clay		44%
Soluble (me/kg)		
K	-	13.1 (1.4)
Na	-	23.6 (2.6)
Mg	-	36.4 (3.3)
Ca	-	245 (27)
C.E.C. pH 7, (me/kg)	34 (1)	440 (30)
Ca as carbonate (me/kg)	-	311 (16)
Exchangeable (me/kg)		
K	1.5 (0.1)	2.9 (0.2)
Na	3.4 (0.2)	4.5 (1.4)
Mg	4.0 (0.1)	18.1 (2.1)
Ca*	14.2 (0.6)	400 (50)
Zn	0.08 (0.04)	0.30 (0.04)
Cu	<0.01	0.32 (0.04)
Cr	<0.04	<0.15
Total Exchangeable Bases (me/kg)	23.1 (1.0)	420 (60)

*Determined by leaching with NaOAc pH 8.8 to get exchangeable + soluble Ca (640 ± 40 me/kg), then subsequently leached with NH_4OAc pH 7 to get carbonate Ca.

formula.

The loss on ignition (organic matter content), bulk density, mechanical analysis, pH and cation exchange capacity (CEC) values are within the ranges normally found. An objective in sludge disposal is to maintain the soil pH in the range 6.5 to 7.0. Hence the question of whether to measure CEC at other than pH 7, is not important, unless base saturation is required at original field pH. The generally low levels of exchangeable bases and CEC in the sand are typical of such a low fertility soil. However K is less than half and Na over twice the levels expected in such a sand. This probably reflects the influence of wind borne Na from the nearby sea.

Soluble salts in the dried sludge were high. This was expected considering the rapid initial decomposition of the organic sludge material with precipitation of salts from solution as the pore water dries. The high level of free Ca as carbonate, ensures that the saturation of Ca on exchange sites approaches 100%. The other exchangeable cations were present at low levels. Exchangeable K was very low and the exchangeable Na was possibly maintained from the high initial Na content of raw sewage. The process of separation of sludge from suspension tends to leave the more mobile monovalent K and Na in the discharged liquid, to the detriment of the plant nutrient quality of the sludge. In the presence of excess Ca, any K, Na or Mg released by decomposition of organic material, has difficulty in competing for exchange sites. As the sludge ages, the released cations tend to remain in soil solution and are subject to leaching. The low levels of exchangeable K found in the sludge are expected to have a deleterious effect on pasture quality, as commented on later.

Total metal concentrations in the sand material and sludge, determined by X-ray fluorescence spectrometry, are given in Table 5-2. Complete scans were taken of the samples to check the levels of all elements present. Only those metals present in abnormal quantities or likely to be important are reported in detail. Although not necessarily of interest, every detectable element has been reported elsewhere by Whitton and Wells (1978) for a similar sludge. Typical means and ranges (brackets) of metals in various groups of sludges are

TABLE 5-2: MAJOR METAL CONCENTRATIONS IN KAIRAKI SAND AND CHRISTCHURCH DIGESTED SEWAGE SLUDGE

	Sand	Sludge
	mg/kg	
Ni	29 (4)	142 (4)
Cu	53 (5)	595 (5)
Zn	62 (6)	2080 (40)
Cr	20 (4)	4780 (160)
Pb	17 (4)	359 (9)
Cd	<2	2 - 4

TABLE 5-3: MEAN AND RANGE OF METAL CONTENTS FOR TYPICAL SLUDGES

	N.Z.*	U.K.**	U.S.A.***
		mg/kg	
Ni	130	510	371
	(12-350)	(20-5300)	(12-2800)
Cu	460	970	1024
	(310-720)	(200-8000)	(84-10400)
Zn	1000	4100	3315
	(700-1200)	(700-49000)	(72-16400)
Cr	340	980	2013
	(66-850)	(40-8800)	(22-30000)
Pb	300	820	1380
	(95-610)	(120-3000)	(80-26000)
Cd	4	<200	74
	(2.5-4.5)	(<60-1500)	(2-1100)

*Mean of 3 from Quin and Syers (1978)
Whitton and Wells (1978)
Wells and Whitton (1976)
**Mean of 42 from Berrow and Webber (1972)
***Mean of 57 from Page (1974)

given in Table 5-3. Note that for New Zealand, the sample number of three is considerably less than that of the others (42 and 57).

Compared with the New Zealand sludges (Table 5-3), Christchurch Drainage Board sludge (Table 5-2), has a higher Zn level and a considerably higher Cr level. Otherwise metal contents are typical of those reported for sludges of a predominantly domestic origin. When compared with U.K. and U.S.A. sludges (Table 5-3) which have a large industrial component, most metal levels in Christchurch sludge are at the lower end of the range. The exceptions for Christchurch sludge are
(i) a modest amount of Zn, and
(ii) a Cr content some 3.5 times greater than the overseas average.
From a metal toxicity viewpoint, Cr is not usually considered a hazard, particularly when other metals are present in much higher amounts.

5.3 FIELD SURVEY OF SLUDGED SOIL

An initial field survey was undertaken to determine the extent of sludge-induced properties in the sandy soils. Analysis of metal contaminants was carried out for 10 sites, core sampled at 10 cm intervals to a depth of 1.0 m. Three cores were included from unsludged, undisturbed sites. Several cores were taken from sites with a history of extremely heavy sludge application. Tables of total elemental analysis by X-ray fluorescence spectrometry and other properties are listed in Appendix 4. The data emphasise the extent to which soil properties have been influenced by sludge application. These analyses provide a basis for estimating composition and amounts of sludge applied previously and indicate whether any further application is allowable.

Loss on ignition values (Appendix 4) were used to estimate the amount of sludge previously applied. Unsludged natural sites (cores 1, 2 and 3) showed a buildup of organic material since dune stabilisation, of about 15% in the top 10 cm and about 6% in the 10 - 20 cm layer. It was assumed that this natural organic material was thoroughly mixed or buried when the dunes were bulldozed into flat paddocks. In estimating original sludge content the following assumptions were required:
(i) organic material is measured by loss on ignition;

(ii) organic to mineral ratio of deposited sludges has remained constant;

(iii) organic to mineral ratio of sludge does not alter after deposition;

(iv) buildup of new organic material in the topsoil since original sludging is negligible.

Factors (iii) and (iv) may counteract each other as significant amounts of organic material must have decomposed, and built up particularly in surface layers. Natural topsoil organic material decomposes at about 1.5% p.a. Using the above assumptions and a present sludge organic concentration of 54%, the approximation was derived that; "original sludge content" = 1.8 x "loss on ignition".

Qualitative observations from data in Appendix 4, using the above relationship, included the following.

1. Very high levels of sludge application have occurred in the past. Some deeper layers, where decomposition is less likely, gave estimates of over 50% (30 - 50 cm core 4 and 40 - 50 cm core 5). Application rates varied widely down profiles with organic rich zones sometimes separated by a sandy layer (20 - 30 cm layers in cores 5 and 8 and the 50 - 60 cm layer in core 4). Each core was sampled down to pure sand material.

2. Zinc has moved down the profile resulting in enhanced zinc concentrations in more sandy layers underlying highly sludged layers (20 - 30 cm layer in core 5 and layers 20 - 30 and 50 - 60 in core 8). Zinc mobility appears to be limited to the layer below the high sludge layer. Williams et al. (1980) found that, where a sludge with a high metal content was applied to soil, increased metal availibility and metal movement in the soil were predominately limited to a depth of 10 cm below the area of sludge incorporation. They used a soil with loam texture but it appears that a similar trend occurs in sandy material.

3. Mobility of Cu, Ni, Pb and Cr can be estimated in a similar manner. Chromium appears to be the least mobile with the other metals falling between Cr and Zn. This order is similar to that reported by Dijkshoorn et al. (1979) and Williams et al. (1980).

4. Estimated Zn concentrations in the original sludge, calculated for deeper layers, were mostly between 2,300 and 3,000 mg/kg plus any losses from the system. It would therefore appear that previous Zn

levels were a little higher than the present 2,000 mg/kg.

5. Estimated Cr concentrations in the original sludge had a maximum of about 0.5% in top layers (cores 6, 7 and 8) where maximum decomposition, and hence concentrating effect, was most likely. Other deeper concentrations were often about 0.3% Cr. As present Cr concentration in sludge is around 0.5%, recent sludge may have a slightly increased Cr content.

6. Metal concentrations and the relative proportions of metals, vary widely between layers. Original Cu estimates for several layers exceeded 1,000 mg/kg, compared with a present concentration of about 600 mg/kg. Previous Ni and Pb concentrations agreed with recent sludge (140 mg/kg and 600 mg/kg respectively), but with occasional estimates reaching 2 - 3 times present values.

7. The pH values for all cores were below 6.5, the minimum required for safe disposal of metalliferous sludge. Ameliorative action is necessary, as outlined in the recommendations of Chapter 6.

8. Cation exchange capacities (CEC) reflect the low natural CEC for sand material. CEC does not increase with estimated sludge content to the extent expected from the use of fresh sludge. This trend possibly results from the increased residual nature of organic material as sludge matures.

Quantitative relationships describing the above qualitative observations can be evaluated statistically but, at this stage, the workload is not justified by immediate benefits.

The original objectives of the research proposal were to use glasshouse and field trials to establish sludge application rates and the effect of sludge on pasture production and quality. As investigations proceeded, some aspects were found to be unnecessary in the light of other published reports, while other aspects needed greater attention. The investigation of chromium in particular was not envisaged initially,

CHAPTER 6

SLUDGE INFLUENCE ON PASTURE

6.1 SLUDGE ON SOIL

Sewage sludge can be an excellent fertiliser on crops or pasture. However most reports concerning the beneficial use of large amounts of sewage sludge involve sludges with low metal content. Early reports of trials such as those by Vlamis and Williams (1961) or Coker (1966) emphasised the value of nutrients contained in sludge. Yield increases were usually attributed to N and P in the sludge.

In the past decade, no report on the use of sewage sludge has been complete without an adequate appraisal of the potential metal contamination (Purves, 1972). Many reports have concentrated solely on the availability and uptake of sludge-borne metals used on agricultural land (Haan, 1975; Dowdy and Larson, 1975b; Kelling et al. 1977a, 1977b, 1977c). Guidelines for the permissible levels of toxic metals in sewage sludge were suggested by Chumley (1971) and Chaney (1973). The fate and effects of various elements was reviewed by Page (1974). Adverse effects of sludge-borne metals on a variety of crops were reported by Dowdy and Larson (1975a, 1975b), Williams (1975) and Cunningham et al. (1975a). Tarbox and Outram (1975) gave some similar data for pasture.

Reports such as those by Patterson (1971) and Spotswood and Raymer (1973) emphasised the cumulative effects of metals when the same area of land was used continually for sludge disposal. The eventual decay of organic material complexed with metals, increased their availability in the soil. More recently, Wollan and Beckett (1979), Williams, et al. (1980) and Schauer et al. (1980), investigated the interactions of sludge-borne heavy metals with soil and the distribution of metals through the soil profile. Their results showed that extractability and movement were predominantly limited to the zone of sludge application.

Reports by Wells and Whitton (1970), and Quin and Syers (1978) on the use of sewage effluent on pasture in New Zealand showed only beneficial effects from the use of sludge containing very low levels of sludge-borne metals. Using New Zealand sludge of low to modest metal content, lucerne yields in pot trials were substantially increased (Wells and Whitton, 1976; Whitton and Wells, 1978). No excessive accumulation of metals in herbage was observed.

A main objective of the present study was to evaluate the acceptable level of sludge-borne metals applied to the soil. Relationships between yield, metal composition of the herbage and food chain effects were considered. The nutrient status of sludge was not a prime consideration because in a disposal situation, nutrient status does not represent a major constraint. It is of interest to note that elements, such as Cu and Zn, that are called "trace elements" or "micro-nutrients" or "fertilisers" in soil, are referred to as "heavy metals" or "contaminants" or "toxic" in sewage sludge applied to the soil.

Examination of cause and effect can result in ambiguity in use of the words "toxic" and "toxicity". The toxicity of a particular element, to say a plant is defined as some injurious or deleterious effect. This toxic effect, often a decrease in plant growth, is caused by an excess amount of the element. However the cause of the stunted growth may be considered as either a build up of the element in the plant tissue itself or a high concentration in the source of supply to the plant, or maybe both. On the other hand, the injurious effect or toxicity, may also include a build up of the element in the tissue. A typical toxic metal pathway sludge-soil-solution-root-tops-animal, contains some transitions which involve deleterious effects and other which do not. When processes are grouped together, care must be taken when referring to accumulation of a toxic element to ensure separation of cause and effect.

Hence the apparent ambiguity when referring to say "a toxic level of Zn in grass". Such a statement can mean either, the grass itself is stunted through an oversupply of Zn, or that the grass is quite healthy but that an animal eating the grass may be affected by the excess Zn.

According to Chaney (1973) the elements in sludge that are a potential hazard to the food chain by plant accumulation; are Zn, Cu and Cd. Entry into the food chain depends on translocation of the absorbed metal from the root to the edible portions above the soil. Zn, Ni and Cd are easily translocated to plant tops, particularly in acid soils. Dijkshoorn _et al_. (1968) in reviewing,
(i) removal from the soil by plant uptake (Kelling _et al_. 1977c),
(ii) plant and soil concentration ratios (Hara and Sonoda, 1979), and
(iii) relative translocations (Pettersson, 1976); concluded that in general the relative uptakes by the shoots of plants declined in the order; Zn > Ni > Cd > Pb > Cu > Cr. The uptakes declined because of a parallel decrease in the rate at which the metals were translocated from the roots to the tops.

Cadmium is one of several metals that have come under suspicion in recent years as possible environmental contaminants that might be harmful to human health. Chaney (1973) suggested a formula that ensured Cd, in a food crop grown on a sludge treated soil, was not a potential food-chain hazard. He recommended that the Cd content of sludge be reduced to 0.5% or less than that of the Zn content. Cadmium levels in Christchurch Drainage Board sludge are less than 4 mg/kg and with a Zn level of over 2,000 mg/kg,Cd content is certainly well below the consequent maximum recommendation of 10 mg/kg. Residues of Cd from phosphatic fertilisers or roadside accumulation from attrition of rubber tyres are greater potential hazards than the small amount of Cd at present in Christchurch sludge.

Lead is well recognised as having deleterious effects on animal life and hence is an environmental hazard. Lead has little effect on plant growth and is especially excluded from some parts of the plant (Dijkshoorn _et al_. 1979). The lack of Pb accumulation from sludge appears to be related to the presence of high amounts of phosphate in sludge (Chaney, 1973).

Christchurch sludge has a present Pb concentration of about 350 mg/kg and even with massive application rates, this source would not contribute significantly to environmental totals. Formulae for limiting the use of metalliferous sewage sludge do not encorporate Pb and maximum herbage levels of Pb in sludge trials are generally only a few mg/kg (Dowdy and Larsen, 1975b; Whitton and Wells, 1978; Dijkshoorn et al. 1979). Such levels are insignificant compared with pollution from automative exhausts and Pb concentrations in pasture species of 500 to 1,000 mg/kg, found for example adjacent to the Auckland Motorway (Ward et al. 1978; Brooks, 1979).

Mercury does not appear to be the food-chain accumulator in agriculture, that it is in the oceans (Chaney, 1973; Rogers, 1976; Bloom, 1979). In addition, Hg was not detectable (< 1 mg/kg) in Christchurch sludge. Nickel presents no threat to the food chain, because being readily translocatable, the plant is severely injured first (Chaney, 1973).

Copper may be translocated in quantities high enough to be toxic to animals, but usually harms the plant in the process (Chaney, 1973).

A more detailed discussion, particularly for elements Zn, Cu and Cr, can be found with the results of the various trials.

6.2 HEAVY METALS IN SLUDGE

The first formula for limiting the use of metalliferous sludge was outlined by Chumbley (1971). His recommendation, in a U.K. Agricultural Department Advisory Service (A.D.A.S.) report, was based on the work subsequently published by Webber (1972).

From experience gained in advisory work and from the results of pot experiments, they suggested that in a soil, Cu was twice as toxic and Ni was eight times as toxic as the same amount of Zn. The maximum permitted level of metal application to topsoil, was given as the addition of 250 mg/kg "zinc equivalent" (i.e. mg/kg Zn + 2 mg/kg Cu + 8 mg/kg Ni). The pH of the soil had to be at least 6.5.

This recommendation did not take into account any other important soil property. Williams (1975), who was also involved in the work, subsequently noted, that the formula weightings were tentatively based on soluble metal content of the soils in which the crops were grown.

There is general agreement (Cunningham et al. 1975a) that since the mobility of nearly all toxic metals is greatest in acid soils, liming to at least pH 6.5 is necessary to reduce the possibility of metal toxicity in plants.

The well known recommendation of Chaney (1973) was to limit metal additions on agricultural soils to the same "zinc equivalent" levels not exceeding 5% of the CEC of the untreated soil (at pH greater than 6.5).

The translation of 250 mg/kg equivalent into degrees of saturation of CEC results in a soil with a CEC of about 160 me/kg having 5% saturation of heavy metals without damage (at pH 6.5).

As noted by Keeney et al. (1975) and Leeper (1978), it is easy to find examples where the 5% CEC formula for maximum application rate is far too cautious. Indeed the Environmental Protection Agency (E.P.A.) suggested a limit of 10% of the CEC, (Keeney et al. 1975; Cunningham et al. 1975a; Leeper, 1978), although the actual recommendation did not appear in any of the well known references examined, (EPA 625/1-75-006, EPA 670/2-74-005). The EPA guideline altered the definition of "zinc equivalent" to (mg/kg Zn + 2 mg/kg Cu + 4 mg/kg Ni), (Keeney et al. 1975; Cunningham et al. 1975a).

The validity of these simple criteria has been criticised (Leeper, 1978; Whitton and Wells, 1978). Keeney et al. (1975) noted that this interim guide was based on the hypothesis that CEC was related to soil factors which control metal availability. No experimental evidence was then available to support or refute the empirical equation. Many other factors were involved and the guideline must remain subject to revision. For instance Cunningham et al. (1975a) noted that Cu, Zn and Ni interact to enhance their toxic effects, but also indicated that with the crops studied, the relative toxicities of Zn:Cu:Ni were 1:2:1.

A sludge application rate based on limiting the heavy metal additions to 10% of the soil CEC can be calculated as follows.

Metal concentration = $EW.CEC.10^{-1}$ (mg/kg)
where EW(Zn) = 32
and CEC has units of (me/kg).

Amount metal = 32.y.d.CEC (kg/ha)
where d = soil depth (m)
y = soil bulk density (t/m^3)

Amount of sludge = $32.y.d.CEC.10^3/S$ (t/ha)
where S is the weighted sum of the sludge concentrations of Ni, Cu, and Zn in (mg/kg).

Example: Christchurch sludge, where

S = 3840 mg/kg
CEC = 34 me/kg (Kairaki sand)
y = 1.37 t/m^3 "
d = 0.20 m

has an application rate of 77 t/ha.

This application rate of 77 t/ha corresponds to a 3% w/w addition of sludge (oven dry) mixed to 20 cm.

The "10% CEC" guideline was basically formulated for highly metalliferous sludges and soils with a high CEC. However when considering application of sludge on sandy soils with a very low natural CEC, then the CEC of the mix depends primarily on the usually much higher CEC of the added sludge. Both the organic material and clay fraction of the mineral material (approximately 50% and 20% respectively for Christchurch sludge) contribute to sludge CEC. If, as in the case of the local sludge, the metal content is modest, then the sludge by itself constitutes a "soil" whose metal content is not greatly in excess of the recommended levels.

Relating the guideline to CEC, allows for the "soaking up" of the metal cations as they are released on decay of organic material complexed with the metals (Spotswood and Raymer, 1973). However, the build up of additional organic material in a sandy soil, from plant growth induced by the sludge nutrients must be balanced against this process. The clay content of sludge also contributes to the sludge CEC and is not subject to breakdown as is the organic material. The CEC of the added clay persists and supplements the original soil CEC. However, the residual nature of sludge clay and organic material does not contribute the usual quota of exchangeable sites expected of such components in a normal soil material. Christchurch sludge has a CEC of 440 me/kg whereas if the usual rule-of-thumb formula for normal soil is applied (Helling et al. 1964), where,

$$\text{CEC (me/kg)} = 5\ (\%\ \text{clay}) + 20\ (\%\ \text{OM})$$

then this sludge should have a CEC of over 1,000 me/kg.

From the preceeding discussion it would seem reasonable to recalculate the application rate using a combined CEC of sand and sludge. Assuming that the combined CEC is linear with the relative weight fractions of the components and by letting the sludge application rate x, be a function of 10% of the CEC, then, as before,

$$x\ (\text{t/ha}) = k.\text{CEC}$$
$$\text{where}\ k = (32.y.d.10^3)/S$$

If the cation exchange capacities of sludge and sand are CEC' and CEC" respectively, then

$$x/k = \left(\frac{10^4.y.d}{10^4.y.d + x}\right).\text{CEC}'' + \left(\frac{x}{10^4.y.d + x}\right).\text{CEC}'$$

$$\text{and}\quad x^2 + x(10^4.y.d - k.\text{CEC}') - k.10^4.y.d.\text{CEC}'' = 0.$$

Solving this quadratic equation for Christchurch sludge, with values as before and including,

$$\text{CEC}'\ (\text{sludge}) = 440\ \text{me/kg}$$

results in an ammended application rate of 115 t/ha. This is a 50% increase over the previously "recommended" rate.

Consideration of the following points;

(i) the uncertainty in relating loadings to CEC alone,

(ii) the tentative nature of the original 10% limit,

(iii) that the guideline was formulated for soils used for food crops and not for more resistant pasture species,
(iv) the uncertainty in calculating the CEC in unusual cases such as low metal content, low soil CEC, and high clay content in the sludge,
(v) the uncertainty in the definition of "Zinc equivalent", and
(vi) reports where heavier applications appear non-detrimental,

shows there is no simple method of testing whether a particularly heavy application rate is safe other than by direct experiment.

6.3 SLUDGE POT TRIAL, MATERIALS AND METHODS

A glasshouse pot trial was set up to evaulate application rates of Christchurch Drainage Board sludge when mixed with the sandy dune soil from the Board's farm. The properties of the sludge and sand base used were described in section 5.2.

Sludge-sand mixtures weighing about 1.3 kg in 12 cm x 12 cm plastic pots were leached to eliminate soluble salts (conductivity of 1:5 v/v suspension was generally reduced to below 0.008 S/m). Following pH and titration curve measurements the mixtures were treated with $Ca(OH)_2$ to bring the pH within the range 6.6 to 6.9. No fertiliser was added. After eight weeks each pot (with drip tray) was planted with either five perennial ryegrass *(Lolium perenne)* or five white clover *(Trifolium repens* L.*)* seedlings. The few seedlings which died were replaced a week later. The levels of sludge used were 0%, 4%, 7.7%, 15%, 31% and 62% w/w (oven dry), with each treatment having four replicates. Plants were harvested above 1 cm at 14 weeks and again at 20 weeks by which stage some pots were becoming root bound. The pots were emptied and soils sieved and retained for analysis.

Measurements of pH, CEC and exchangeable cations were taken

(i) at planting,
(ii) just prior to second harvest (pH only) and
(iii) when pots were emptied.

Methods for measurement of pH, titration curves, CEC and exchangeable cations followed the general methods described by N.Z. Soil Bureau staff (1972). Herbage cations (K, Na, Mg and Ca) were determined by Atomic Absorption following ignition of a 0.1 g sample of oven dry material, digestion with 5 ml 2M HCl, and dilution to 100 ml. Trace metal determinations followed a similiar proceedure using 5 g plant material, 10 ml 2M HCl and diluting to 50 ml. Duplicate determinations were preformed on bulked treatment replicates.

Differences commented on in this report were "significant" at $p<0.05$ or "highly significant" at $p<0.01$, unless otherwise indicated.

All concentrations and weights given in this report are expressed on an oven dry (110 ^{o}C) basis unless otherwise indicated.

6.4 RESULTS AND DISCUSSION

6.4.1. Herbage Yields

Total herbage yields (two harvests) for ryegrass and clover are shown in Figure 6-1 with pH and yield data in Appendix 6. The vertical bars show the standard errors of the four replicates. In general, yields increased spectacularly with sludge treatment with no adverse effects apparent visually. Simple analysis of variance showed significant increases in yield of ryegrass up to the addition of 15% sludge. Clover replicates were prone to large variations and beyond the 4% sludge treatment differences were not significant. A possible exception was the decrease in yield at the highest treatment level of 60% sludge.

The increases in yield for both ryegrass and white clover emphasise the beneficial fertiliser aspects of sewage sludge application on the low fertility sand material. Coker (1966a, 1966b), compared pasture responses from sewage sludge nutrients with equivalent inorganic fertilisers, and showed there was little difference in yield or nutrient content of the pasture. He found that distribution of

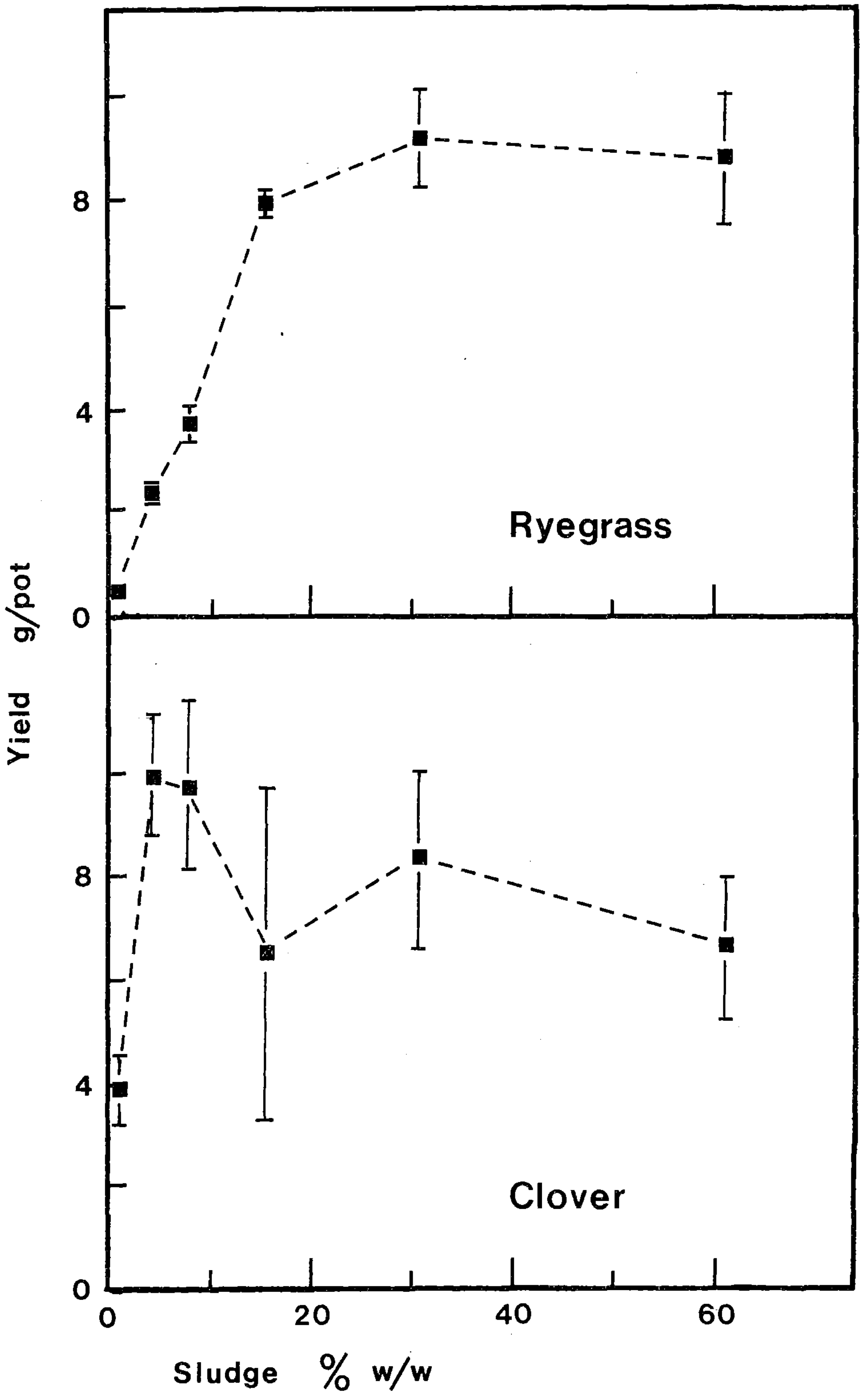

Figure 6-1. Yields of ryegrass and clover in the sludge pot trial.

pasture species with sludge application was much the same as that expected from literature reports on fertiliser response.

6.4.2. Cation Uptake

Herbage concentrations of Na, K, Ca and Mg are shown in Figure 6-2. Potassium levels are below those generally accepted (M.A.F., 1978) as sufficient for healthy growth (dotted line). Other reports have shown (Coker, 1966b; Williams, 1975; Kelling et al. 1977a) that the amount of K in dried sludge is not sufficient to provide for the full requirements of grass and can limit yields.

McNaught (1970) defined a "critical level" as the minimum concentration of nutrient in plant tissue for maximum yield. The values of K for New Zealand conditions are given as 2.0% to 2.5% for ryegrass and 1.8% to 2.3% for white clover. Herbage K levels in this trial are below these levels. The usual relationship between cations in pasture plants, is that a decreased K concentration leads to increases in the Na, Mg and Ca contents. This inverse relationship between Na and K is particularly evident in the ryegrass results and to a lesser extent in clover. Since K is invariably present in amounts well in excess of animal needs (Smith and Middleton, 1978), dietary deficiency of K in ruminants is most unlikely although plant tissue K levels may be sufficiently low to reduce yield.

The associated levels of Na and Mg in ryegrass and clover when K levels are deficient are listed by M.A.F. (1979). Trial levels of associated Na, for K in the deficient range (0.3% to 1.7% K), were found to be within the specified ranges of 0.3% to 0.6% Na (clover) and 0.3% to 1.0% Na (ryegrass). Such elevated levels for Na are an indication of K deficiency. Similarly the elevated trial levels for associated Mg, when K is deficient were within the ranges 0.25% to 0.30% Mg (clover) and 0.23% to 0.35% Mg (ryegrass). Calcium contents are quite high but such values are to be expected considering the high amounts of Ca originally present in the sludge and the $Ca(OH)_2$ applied to raise pH.

The CEC's and exchangeable (including soluble) bases for the

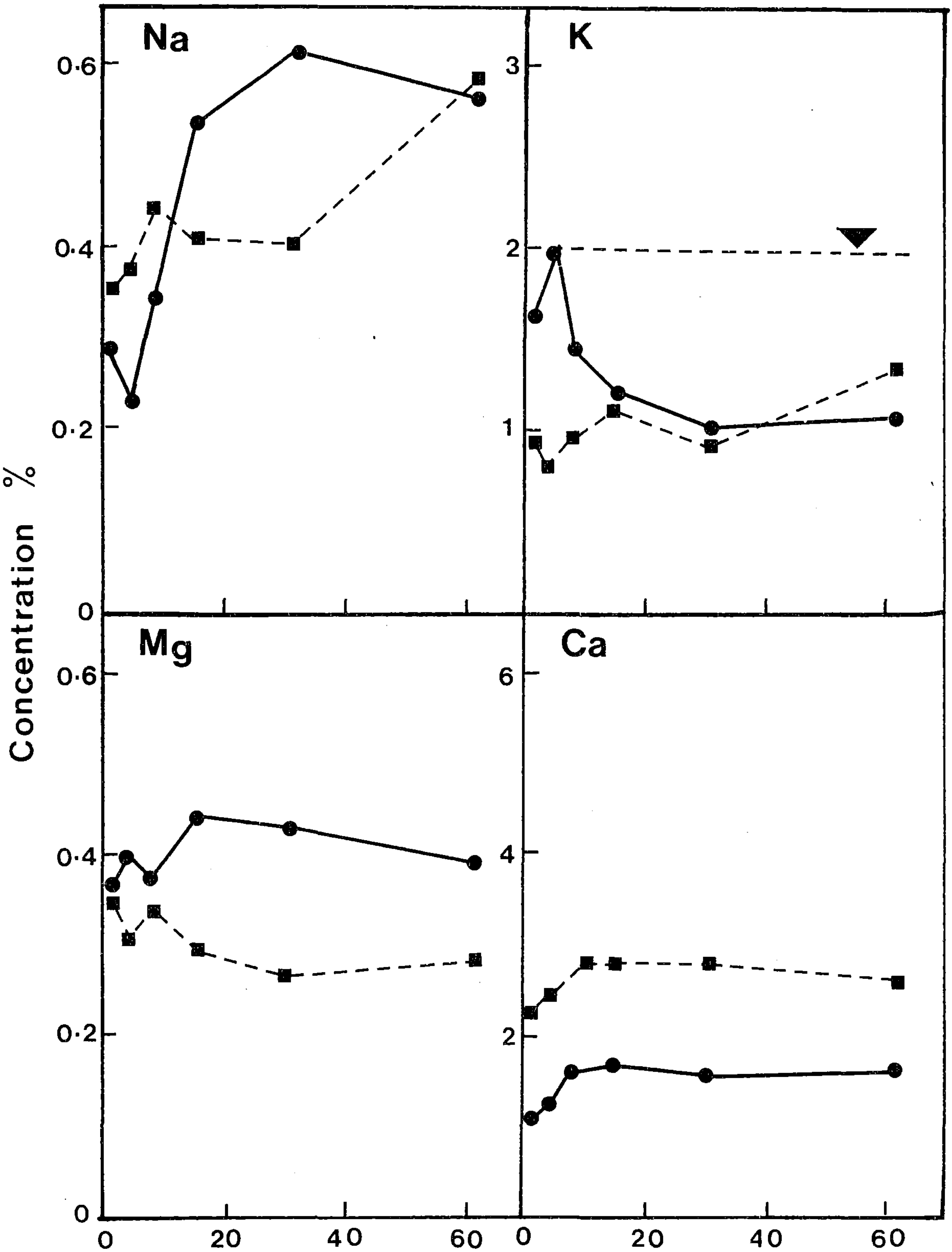

Figure 6-2. Effect of sludge on uptake of Na, K, Mg and Ca in ryegrass (●–●) and clover (■–■). ▼ concentrations below dotted 2% line are deficient (M.A.F., 1978).

TABLE 6-1: EXCHANGEABLE BASES IN SLUDGE POT TRIAL SOILS

Sludge % (w/w)	CEC	Na	K	Ca	Mg
	me/kg				
	Initial Values at Planting				
0	24	0.2	1.7	11	3.7
4	44	3.0	3.6	45	7.8
8	60	1.7	2.7	48	7.8
15	94	5.0	4.4	120	9.3
31	160	10	7.6	220	16
62	280	19	12.5	370	24
	After Harvests				
0	29	0.8	0.7	19	1.1
4	42	0.7	1.2	28	1.5
8	62	0.8	1.0	55	1.1
15	96	1.0	1.0	88	1.1
31	180	2.5	1.4	181	1.8
62	300	3.8	2.0	294	3.2

Values are the means for ryegrass and clover, each with duplicate determinations of four replicates bulked.

pot soils at planting and after harvest are shown in Table 6-1. The initial values of CEC are approximately those expected from a linear combination of the known CEC's of sand and sludge. The CEC's did not alter significantly during the trial. Comparison with basic levels in the sludge (Table 5-1) indicates that although previously leached, the pot values of available Na, K and Mg still include some soluble salts. This is possibly due to their release by mineralisation of organic sludge material during the eight weeks between leaching and planting. The exchangeable Ca figures besides including Ca in solution, also include Ca as carbonate. Considering the initial leaching which lowered the pH of the pots and subsequent addition of $Ca(OH)_2$ which raised the pH to within 6.5 to 7.0 (see Appendix 6), the only significance of a final Ca content is that soil cations are still dominated by Ca.

After harvest, all levels of Na, K and Mg were somewhat depleted and Ca still dominated the exchange sites. The high rate of utilisation of the limited supply of Na, K and Mg is emphasised in Table 6-2. This shows the ratio of cations accounted for in uptake to the tops, compared, for ryegrass, with the initial exchangeable amounts in the pot. Occasional overflowing of pot drip trays may also account for some minor losses from the system.

TABLE 6-2: RATIO OF UPTAKE OF CATIONS IN RYEGRASS TOPS, TO INITIAL EXCHANGEABLE PLUS SOLUBLE CATIONS IN THE POT

Sludge (w/w)	Na	K	Mg
		%	
0%	20	7	3
4%	53	27	8
7.7%	25	42	12
15%	33	51	28
31%	23	30	21
62%	16	28	18

The level (15% sludge) at which maximum amount of cations were taken up, corresponds to the maximum yield (Figure 6-1). As the utilization rate is not constant, other factors must also be involved. Before the yield maximum, the limiting factor is possibly N and P (Kelling _et al_. 1977a), with metal toxicity effects after.

6.4.3. Heavy Metals

Herbage trace element concentrations of interest are shown in Figures 6-3 and 6-4. With the possible exception of Zn at high sludge treatments, levels are generally within a safe range (M.A.F., 1978).

Toxic metal studies of plant tissue have shown the root to be a better indicator organ than most other parts. Since the root prevents much of the toxic metal from reaching the plant tops, metal analysis of roots is probably the most direct method available to demonstrate toxic levels of metal. Effects such as leaf chlorosis caused by Zn, Cu or Ni can actually be attributed to decreased Fe transport by roots (Chaney, 1973). Recently Dijkshoorn _et al_. (1979) noted that the sequence of metals arranged in decreasing relative toxicity (Zn, > Ni, > Cd, > Cu, > Cr) paralleled the order of decreasing relative uptake and translocation to tops. This sequence was also that of increasing retention in the roots. The quicker build up of metal in the roots was presumably associated with a downwards shift in the plant, of the sites first injured. Dijkshoorn _et al_. (1979) concluded that, for a given metal-plant combination, the degree of partitioning of the metal between roots and tops was sufficiently characteristic to warrant the use of the more practicable tops analysis as an index to phytotoxic plant content.

In general, it is not possible to diagnose heavy metal toxicity from the observation of crop symptoms (Webber, 1972), although it appears that this is how such conclusions are sometimes reached. To test any particular factor all other variables must be held constant, either literally as in a single factor experiment or by the use of statistical methods, such as multiple regression, when several factors are varied. An alternative method is to relate the desired single

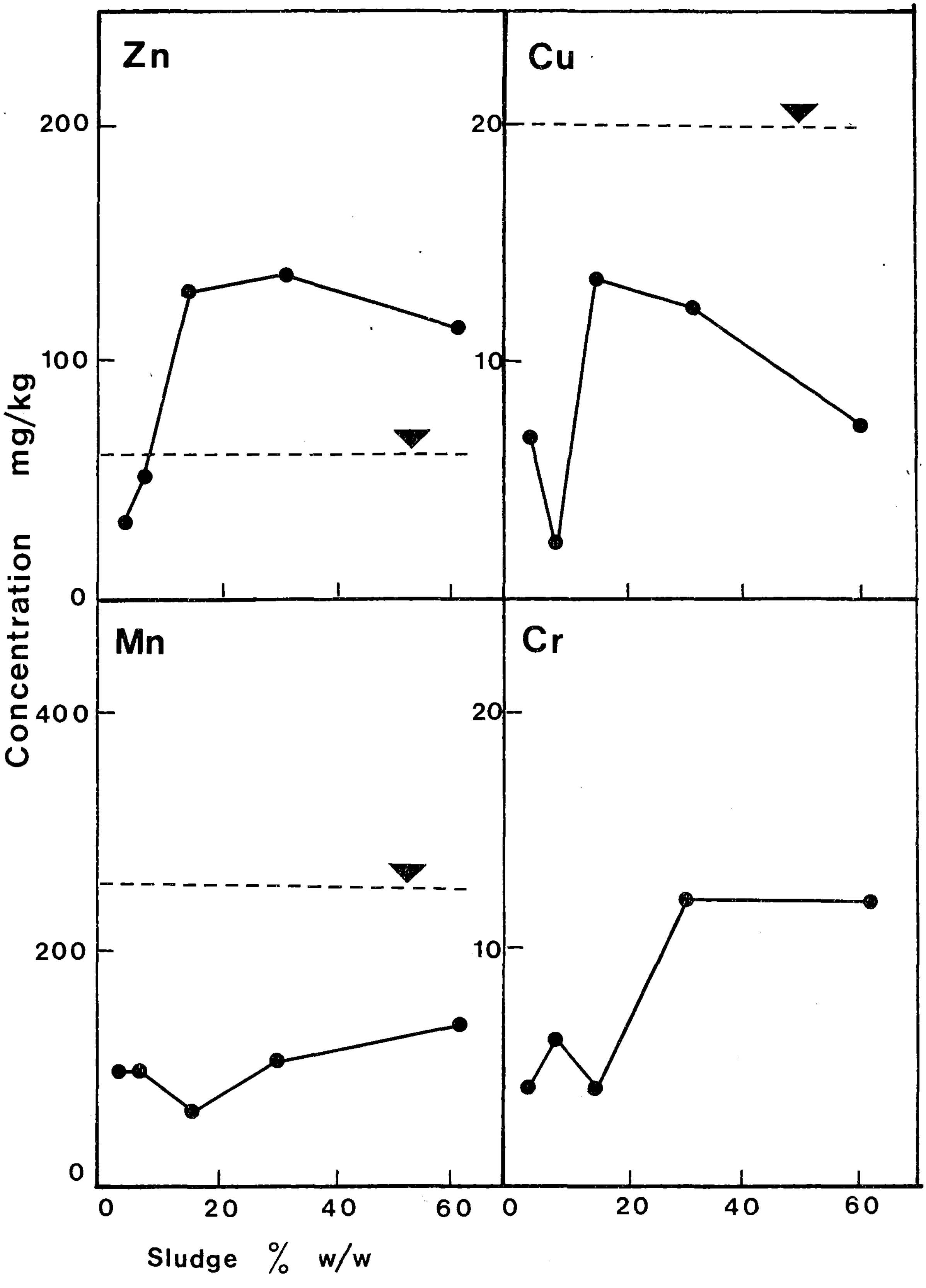

Figure 6-3. Effect of sludge on uptake of Zn, Cu, Mn and Cr in ryegrass.

▼ concentrations above the dotted lines are potentially toxic (M.A.F., 1978).

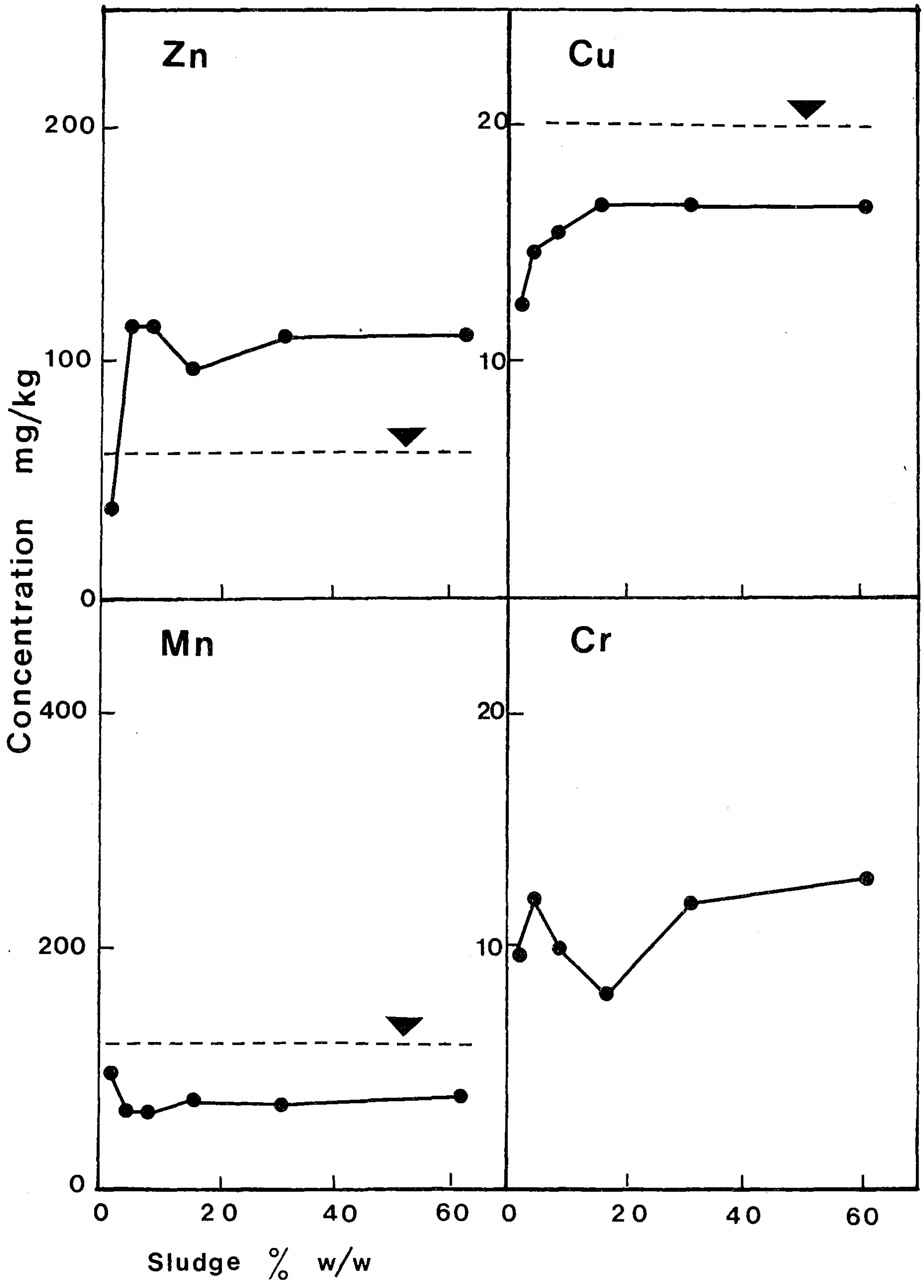

Figure 6-4. Effect of sludge on uptake of Zn, Cu, Mn and Cr in clover. ▼ concentrations above the dotted lines are potentially toxic (M.A.F., 1978).

factor to some other property of the system via a separate experiment. A relationship between plant symptom and for example, metal concentration in roots or tops, or extraction from soil solution, is derived for a particular metal in a single variable experiment. The related factor is then measured in the sludge trial.

As an example, Dijkshoorn et al. (1975) concluded that the upper limit of Zn in ryegrass tissue, as set by toxicity, is of the order of 700 - 1000 mg/kg. Ryegrass is a relatively tolerant species (Dijkshoorn et al. 1979). However, Wells and Whitton (1976) have claimed that, "high levels (up to 880 mg/kg) of zinc .... did not reduce yield, indicating that these levels were not toxic for lucerne". In their trial, Waitarere coastal yellow-brown dune sand was mixed with up to 100% sludge (Zinc equivalent 1950 mg/kg). However, the trial method of Wells and Whitton (1976) gave the only treatment variable as rate of sludge application. As sludge has a large number of active components, both nutrients and metals, an unaffected yield cannot be related to Zn levels, nor can it be concluded without additional information that Zn was not toxic because yield was not reduced.

Williams (1975) gives the results of a trial involving a high copper-contaminated sludge in which the rate of application was varied. He concluded that "A concentration of 80 mg/kg Cu in soil applied in sludge form resulted in a very large reduction in yield of leaves and roots". This conclusion may well be true but the reported experiment is not necessarily a demonstration of cause and effect of Cu. Similarly, Sykes (1974), and Tarbox and Outram (1974) do not differentiate clearly between application of a chromium-contaminated sludge and the individual effect of Cr. Webber (1972), in his original testing of metal toxicities of individual highly-contaminated sludges, was careful to note that, when interpretating the results, allowances must be made for the other factors.

6.4.3.1. Zinc

Zinc concentrations in the trial, of up to 135 mg/kg for ryegrass and 120 mg/kg for white clover were within the range of possible toxicity (M.A.F., 1978). The M.A.F. recommendation for pasture herbage (<60 mg/kg Zn) appears conservative compared with a wide variety of food crops: <200 mg/kg Zn (Allaway, 1968), <400 mg/kg Zn (Jones, 1972), and <300 mg/kg Zn (Cunningham et al. 1975a). Whitton and Wells (1978) considered their levels of <200 mg/kg Zn in lucerne and other food crops as generally not excessive. The sludge application rates on pasture of Quin and Syers (1978) were insufficient to produce appreciable increases in Zn concentration. The report of Tarbox and Outram (1974) involving the use of sludge on pasture is not easily understood because of their use of mg/l as Zn concentration units for solids.

Recent data on Zn levels in pasture species (Dijkshoorn et al 1979) showed yields of white clover and ryegrass were reduced by 50% at shoot concentrations of 500 mg/kg and 1000 mg/kg respectively. Yield reductions were less than 10% for approximately 150 mg/kg and 300 mg/kg for clover and ryegrass respectively. Soil pH which affects availability of Zn to the plant, did not alter the limiting shoot concentrations. Often surviving plants remained healthy in appearance with no symptoms other than a decrease in size. These concentrations were derived from special "uptake-yield" curves using extensive results from single-metal solutions, added to soil. As the amount of Zn taken up increased, with rising Zn concentration in the soil, the yield remained unchanged until the amount taken up reached a maximum. With further increase in soil Zn concentration, the amount taken up decreased slightly while the yield declined rapidly thereby concentrating the absorbed metal to still higher tissue concentrations until no plants remained. Such behaviour is not immediately obvious from "concentration-yield" curves. Ryegrass was slightly more tolerant to tissue Zn than white clover (and also plantain) but was distinctly more tolerant to soil Zn because relatively less soil Zn was translocated to the shoots in grass.

Zinc toxicity in animals is low, the more sensitive suffering if the diet contains more than 500 to 1000 mg/kg Zn (Underwood, 1971). Although the increasing use of Zn salts is becoming an accepted veterinary practice for grazing ruminants,Smith (1977, 1979) makes it clear that the difference between prophylactic and toxic dose rates is not great. Household Zn use is widespread in cosmetics and pharmaceuticals. Food crop plants that contain 1000 mg/kg Zn are usually severely injured. As yield is much reduced at Zn levels lower than those that injure the consumer, other factors tend to protect the food chain.

Assuming the most conservative recommendation of less than 60 mg/kg Zn in the herbage (M.A.F., 1978), then the sludge rate of 15% used in the pot trial for ryegrass and 5% for clover would appear to provide excessive amounts of Zn. As clover is not an important source of N in the presence of sludge and suffers in competition with ryegrass in such a situation (Coker, 1966a), an excess Zn level in clover could possibly be ignored when clover forms such a minor component (if any) of the sward. If soil pH is within the recommended range, as in this pot trial, then it can be concluded that a sludge application rate of 12% does not raise overall Zn values beyond a tolerable level.

Although not strictly comparable, translation of a 12% w/w sludge treatment in a pot trial to a field application rate, corresponds to an equivalent dose of about 250 t/ha or about four times the maximum E.P.A. recommendation. Keeney et al. (1975, quoting Hinesley, 1974) notes that evaluation of long term disposal sites in Europe and Australia and work at the University of Illinois, documented no toxicity in crops in which soils were overloaded by 4.5 to 6.4 times their calculated "zinc equivalent" values.

6.4.3.2. Copper

There is reasonably good agreement (Allaway, 1968; Jones, 1972; Chaney, 1973: Cunningham et al. 1975a; Kelling et al. 1977c) that Cu in herbage is potentially toxic to both plants and animals when concentrations are above the M.A.F. (1978) recommended maximum of 20 mg/kg. Inhibitive shoot Cu concentrations for 50% yield depression for clover and ryegrass, as given by Dijkshoorn et al. (1979), are 38 mg/kg and 18 mg/kg respectively. Although trial herbage levels for Cu were approaching these limits at the higher sludge application rates, analyses were generally within the M.A.F. (1978), "safe excess" range of 8 - 20 mg/kg. Underwood (1971) concluded that sheep were the most susceptable of all domestic livestock to Cu toxicosis and that cattle appeared to be less susceptable although experimental evidence was sometimes conflicting.

Complimentary or antagonistic interactions between elements may be more important in animal toxicity than a permissible intake level of a single potentially toxic element. This factor is particularly important in the case of Cu toxicity which can also depend on Zn, Mo, Ca and Fe dietary components (Underwood, 1971). Animals of high Cu status are less at risk from Cd or Zn poisoning than those on a barely adequate copper intake, because both Cd and Zn exert a direct antagonistic effect on Cu metabolism (Bremner, 1977; Underwood, 1979). It was concluded by Underwood (1979) that when a potentially toxic element interacts metabolically with others, there is no single safe, tolerable or permissible level of intake. A range of dietary levels is possible depending upon the chemical form and the ratio of that element to other elements. Bearing in mind the complexities of Cu interactions, the higher than normal Cu status of herbage found in the trial is probably not detrimental to animal health. However any increase in herbage Cu concentration must be avoided as the range between adequate nutrition and Cu toxicity is narrow.

6.4.3.3. Other Elements

Manganese results were included because of the mobility of this element into plant tops, particularly in acid soils. However the trial results were all in the safe range. This result contrasts with the usual agricultural concern over Mn and Cu deficiency, particularly at soil pH values exceeding 6.5. Chromium analyses are probably influenced by soil contamination, a problem considered later, and are of interest to the second pot trial. Nickel values in the herbage are not reported because of analytical variability in the results obtained. Considering the low sludge level of Ni when compared with the corresponding results for Zn and Cu, there is no likelihood of any deleterious effect from Ni (Page, 1974; Underwood, 1971). As discussed in Section 6.1, Cd, Hg and Pb, present no problem.

6.5 SLUDGE TRIAL CONCLUSIONS

The most important points to be noted from this sludge trial are as follows.

1. Yields increased by up to three fold for white clover and twenty fold for ryegrass on application of sludge. The increases were due to the higher nutrient status of the sludge as compared with the dune sand material.

2. Using the E.P.A. maximum sludge application rate of 3% w/w as a reference base, yield increases of up to three times the rate for clover and five times for ryegrass were observed. No subsequent decrease in yield was evident at 10 times the rate for clover and at least 20 times the rate for ryegrass.

3. These results were obtained with, and are conditional upon, the pH being adjusted to an acceptable level of 6.5 to 7.0.

4. Herbage analysis gave depressed K levels which indicated the high possibility that beneficial effects would result from supplementary additions.

5. Zinc was the only metal present in potentially toxic amounts in the herbage. Toxicity would occur only at very high rates of sludge application.

6. Provided pH is maintained correctly, the use of a sludge rate of 12% w/w should not raise Zn values beyond a tolerable level.

7. As Cu concentrations were nearing the region of possible toxicity, care must be taken not to further increase Cu content of sludge or herbage.

CHAPTER 7

SLUDGE CHROMIUM

7.1 TOXICITY OF CHROMIUM

Chromium which is widely distributed in nature, is not one of the metals usually considered as a hazard in sewage wastes. In the establishment of sludge application guidelines as described by Webber (1972) and recommended by Chumbley (1971), Cr was regarded as not toxic to plants unless present in very large amounts (over 500 mg/kg in the soil). Subsequent recommendations such as those of Chaney (1973), Baker and Chesnin (1975) and Keeney et al. (1975), considered Cr to be of low toxicity, and non-essential for plants. The concentration of Cr found in typical domestic sludge is such that very high sludge applications are required to produce Cr concentrations in soils that exceed those sometimes found naturally. Approximations of sludge enrichment of soils made by Page (1974) indicate that other trace elements such as Cd, Zn and Cu become limiting, relative to potentially hazardous concentrations, before Cr (and Ni) can present problems. However with Cr levels exceeding several thousand mg/kg in industrial sludges it was noted by Page (1974) that Cr may become a controlling factor in limiting the amount of sludge applied to soil.

The limited literature on the role of Cr in soils and in plant and animal nutrition has been well discussed by several authors. The distinction between trivalent Cr (cationic) and hexavalent Cr (anionic) has lost much of the importance attributed to it in earlier results, and attention is now focused on availability. As explained later it has now been found that trivalent Cr may oxidise readily to the hexavalent form under conditions prevalent in many field soils (Bartlett and James, 1979).

Some minor stimulatory effects of Cr salts on plant growth were collated by Mertz, (1969). On the basis of evidence then and possible indirect effects, Pratt (1966) concluded that reported stimulatory effects were generally small, erratic, and largely unverified. Extensive tests by Huffman and Allaway (1973a) established that Cr was not essential for higher plant growth, at a level of at least two orders of magnitude less than molybdenum, which is required in the smallest quantities of any known essential element. It has been shown however, that Cr is an essential nutrient for normal metabolism in man and some animals. Its primary effect appears to be involvement in the initial steps of glucose utilisation with Cr activity being closely tied to that of insulin (Mertz, 1969; Scott, 1972). No damage concerning humans and animals induced by excessive levels of Cr in soils or plant tissue have been reported so far (de Haan and Zwerman, 1976).

Chromium in its hexavalent form was particularly toxic to plants (Hunter and Vergnano, 1953; Pratt, 1966; Turner and Rust, 1971; Mortvedt and Giordano, 1975; Dijkshoorn et al. 1979), but only at very high levels to humans in direct contact with such chemicals (Sykes, 1975). Trivalent Cr has been considered the predominant form in the presence of organic material and at the pH values and redox potentials prevailing in most soils (Bartlett and Kimble, 1976a; de Haan and Zwerman, 1976; Cary et al. 1977b; Leeper, 1978). Nutrient solution studies by Huffman and Allaway (1973b) and Pettersson (1976) showed that for a variety of plants uptake and translocation of Cr and plant yield differed only slightly between trivalent and hexavalent Cr sources.

Using culture solutions of hexavalent Cr, Turner and Rust (1971) showed severe Cr toxicity in soybeans with solution concentrations as low as 0.5 mg/kg with the primary toxic effect at the root. Similar results were obtained by Hunter and Vergnano (1957) in oats, with low leaf concentrations of Cr and leaf symptoms being subsequent to root damage. Studies by Soane and Saunders (1959) using hexavalent Cr as an additive to sand caused severe stunting in corn at 10 mg/kg, but produced no specific symptoms. At 25 mg/kg they observed a particularly severe effect on the roots which were blackened and withered at the tips with a lack of root hairs. Using soils treated with hexavalent Cr, Mordvedt and Giordano (1975) found that very little corn growth resulted after application of Cr to the soil at a rate of 80 mg/kg. The narrow range of Cr concentrations found in the corn tops, of normal and retarded plants suggested that Cr was toxic to plant roots and that its translocation to plant top was very limited.

Using trivalent Cr mixed with soil in the same way, Mordvedt and Giordano (1975) found that although yields were not significantly affected at 80 mg/kg, they were reduced by 55% at 320 mg/kg. They suggested that trivalent Cr may have been fixed by the soil in forms which were less available than chromate to plants. Using sewage sludges with similar concentrations of Cr, mixed with soil, they found that neither plant growth nor Cr uptake was affected. They concluded that the availability of Cr to plants, when these wastes were applied to soil was quite low. Data taken from Dijkshoorn et al. (1979), who used trivalent Cr in soil in a study on metal uptake in pasture species (plantain, clover and ryegrass), showed that crop yields were decreased by about 50% at soil levels around 250 mg/kg Cr. Studies in toxicity of naturally occurring "serpentine" soils with high Cr levels indicate that their infertility may result from several factors and it is by no means certain that Cr is the only potentially toxic element involved (Soane and Saunder, 1959; Pratt, 1966; Anderson et al. 1973).

The concentrations of metals in sewage sludge are generally low unless there is specific industrial pollution. However, any metal must eventually prove toxic if available in high enough concentrations. Most reports involving the use of either domestic sludges with a relatively small quantity of metals or sludges with a high industrial component, have focused their attention on the problems of Zn, Cd, Cu and Ni. In comparison, any effects from Cr are negligible. Investigations of toxicity specific to Cr in soil-plant-animal interactions must therefore be limited to situations where Cr is available in large quantities in the soil, while other pollutants are present in only small quantities. The possible toxic effect of Cr is the limiting of optimum growth of the plant. As commented by Allaway (1968), Cr is one of the few essential elements for which no accumulation against a concentration gradient is evident at any point in the biological cycle from soil to plant to animal.

7.2 AVAILABILITY OF SOIL CHROMIUM

Concentration of Cr in soil solution and hence its availability to plants is extremely low. Anderson et al. (1973) found that even near the centre of a highly toxic area of serpentine soils containing 634 to 2100 mg/kg Cr, its concentration in solution was 0.02 µg/ml and that less than 5 mg/kg could be extracted by 2.5% acetic acid. Low Cr extractabilities from serpentine soils were found by Birrell and Wright (1945), while Lyon et al. (1968) separated less than 0.1% of the total soil Cr in 2.5% acetic acid. Leaching of 15 soils with high Cr contents (3% to 4% Cr_2O_3), with 1.0M ammonium acetate usually extracted less than 0.2 me/kg (Robinson et al. 1935). Any Cr that is released into soil solution would normally be sorbed very strongly by soil colloids (Lisk, 1972; Leeper, 1978). Mordvedt and Giordano (1975), although not giving the actual data, commented on the very low Cr extracted from their metal-amended sludges by 0.5 and 0.1M HCl and DPTA. The insolubility of Cr can be gauged by its average abundance in the lithosphere of 200 mg/kg (Baker and Chesnin, 1975) compared with its concentration in river water 0.00018 µg/ml and in sea water of 0.00005 µg/ml (Bowen, 1966).

While attemtping to increase Cr concentrations in food plants, Cary et al. (1977b) found the most consistent feature of their experiments was the pronounced tendency of soluble Cr added to soils to revert to forms that were unavailable to plants. In reviewing the soil chemistry of Cr, they concluded that the pH range of most arable soils favoured the formation of trivalent rather than hexavalent Cr. At pH 7 in a well-aerated soil the theoretical concentration of CrO_4^{2-} is found to be about equal to the concentration of $Cr(OH)_2^+$ (Bartlett and Kimble, 1976a, 1976b; Cary et al. 1977b). Although the concentration of hexavalent chromium was still extremely low, Cary et al. (1977b) concluded it may well have been this anion that was taken up by the plant. Other reports have noted (Patterson, 1971; Webber, 1972; Bloomfield and Pruden, 1975) that unlike most other metals, Cr was more toxic in soils with high pH values.

Insoluble Cr in soils appears to be in the form of hydrated oxides or hydroxides of trivalent Cr mixed with or isomorphically precipitated in iron oxides. Chromium readily forms chelates, some of which are extremely stable (Stevenson and Ardakani, 1972; Leeper, 1978). It was found by Bartlett and Kimble (1976a) that soil organic complexes of trivalent Cr were formed at low pH and appeared to remain stable and soluble even when soil pH was raised to levels where the Cr would be expected to precipitate out. In this context it has been noted that trivalent Cr is unique among many cations in that it is held so tenaciously by certain synthetic cation exchange resins that it can be removed only by ashing the resin (Lisk, 1972). Such behaviour would contribute to the low availability of soil Cr.

Recently Bartlett and James (1979) found that trivalent Cr oxidises readily to the hexavalent form under conditions prevalent in many field soils. In previous reports Bartlett and Kimble (1976a, 1976b) were unable to demonstrate oxidation at all, even under conditions of maximum aeration and high pH. When hexavalent Cr was added to soil, the presence of soil organic material brought about spontaneous reduction to trivalent Cr, even at pH above neutrality. Oxidation of Cr by soils was not discovered earlier because the importance ot studying fresh field soils rather than crushed, dried and stored samples, was not appreciated. Bartlett and James (1979) considered the explanation of the oxidation to be the presence in the soil of highly oxidised Mn which served as an electron acceptor in the reaction. They found plants were severely damaged by hexavalent Cr formed from trivalent Cr added to virtually any fresh moist soil sample. The hexavalent Cr had persisted for the five months up to publication date.

Liming a soil to lower the solubility of other metals such as Cd or Zn may increase the likelihood of Cr oxidation by allowing Mn to become oxidised. Such an effect of pH has been observed, as noted before. At high pH however, solubility of trivalent Cr may also be a factor limiting its oxidation rather than just the presence of oxidised Mn. Such findings may help to explain the variability of results in soil Cr studies and may also raise questions as to the availability of Cr in sewage sludge and the soil conditions favourable for its oxidation.

7.3 PLANT UPTAKE OF CHROMIUM

From a toxicity viewpoint, high levels of Cr in plant tissues are not injurious to animals consuming that plant, as Cr appears to be an essential animal nutrient. Studies on levels of Cr in plant tissues have focused on;

(i) its mobility within the plant,
(ii) the form in which it is available, and
(iii) the ratio of Cr to other elements.

No relationships have yet been found between Cr levels in plants and the soils upon which they are grown (Baker and Chesnin, 1975).

Reported levels of Cr in plant tissues vary widely. Anderson _et al_. (1973), concluded it was likely, that the Cr found in analysis of plant tops, in concentrations which could have been considered toxic was actually from soil material which their acid detergent washing procedure failed to remove. Although the plant material selected was free from obvious contamination and their washing procedure well described, microscopic examination showed the plant surfaces were still not completely free from adhering soil particles and that the problem of splash/dust contamination was as serious for Cr as it was known to be for Al. The values reported from two pot trials illustrate this point. Table 7-1A from Wells and Whitton (1976) is a regrouping of data showing total Cr values obtained from lucerne roots and tops in a trial on sludge/soil mixtures, where the roots were separated by water washing. The average tops/root concentration ratio was 0.04.

There were no obvious patterns between successive crops or with sludge/soil ratio but the results for roots tended to parallel those for Al and ash content. Table 7-1B of data, also for lucerne, from Whitton and Wells (1978), shows a reversed trend. The Cr tops/root concentration ratio was 3.4. In their discussion of soil contamination, Whitton and Wells (1978) derived average contamination

TABLE 7-1: PUBLISHED VALUES FOR CHROMIUM CONTENT OF LUCERNE

(A) Wells and Whitton, (1976),

Cr (mg/kg) Sludge	Cr (mg/kg) Soil	Tops	Roots
100	15	0.1 - 9.2	9.4 - 110
100	30	0.1 - 4.7	9.8 - 37
Average (n = 84)		1.44	
(n = 12)			33

(B) Whitton and Wells, (1978)

Cr (mg/kg) Sludge	Cr (mg/kg) Soil	Tops	Roots
850	220	9 - 26	2.7 - 4.5
850	20	11 - 42	2.3 - 19
850	130	7.8 - 32	0.46- 4.8
850	24	12 - 28	1.9 - 16
Average (n = 20)		18	5.3

values of 0.48% for the roots and 2.0% for the tops. Unless extreme care is taken in sample preparation, conclusions drawn from reputed Cr concentrations in plant tissue should be regarded as tentative.

Uptake of Cr by plant tissue and mobility of Cr within plant tissue is extremely low. Experiments with nutrient solutions as well as soil tests have shown that Cr is accumulated in the roots rather than in the shoots. Huffman and Allaway (1973b), Cary et al. (1977a) and Dijkshoorn et al. (1979) have reported shoot/root concentration ratios of from 0.1 to 0.004. Cary et al. (1977a) could not increase the translocation from roots to tops in a variety of plant species. They used ^{51}Cr in the form of organic acid complexes, trivalent cation and hexavalent anions added to soil, and increased trivalent concentration in nutrient solutions. From studies of translocation and uptake of CrO_4^{2-} in barley seedlings, Shewry and Peterson (1974) suggested that most of the Cr retained in the roots was present in soluble form in the vacuoles of root cells. Huffman and Allaway (1973b) found that, in fresh bean leaves, most of the supplied ^{51}Cr was present as a soluble, low-molecular-weight anionic complex not associated with any subcellular organelle. Plants that tended to accumulate Fe also accumulated Cr.

Dijkshoorn et al. (1979) endeavoured to relate toxicity with the shoot concentration of various metals (Zn, Ni, Cd, Pb, Cu, Cr), for the pasture species, plantain, white clover and ryegrass. Using chromium sulphate on a sandy soil it was found that of all the metals examined, Cr was the least tolerated in tissue with the lowest shoot concentrations. Chromium was tolerated at much higher levels in the soil because uptake by the shoot was disproportionally less. The inhibitive shoot concentrations of Cr for 50% yield depression were 4, 9 and 2.5 mg/kg respectively for plantain, clover and ryegrass. Chromium was more toxic in the shoots of grass than in clover, but less readily absorbed by grass, so that clover and grass were about equally sensitive to Cr in the soil. Corresponding Cr concentrations in the rather acid sandy soil were around 500 mg/kg. Although yield was reduced, the plants remained healthy in appearance with no symptoms other than reduced growth. Such low tissue levels, however, make diagnosis of Cr toxicity in herbage from field experiments difficult because of the possibility of dust contamination.

A study by Cunningham et al. (1975c), compared crop growth and metal uptake on soil treated with inorganic metal salts, with results obtained when a sewage sludge was amended with the metals before addition to the soil. Trivalent chromium acetate was used as the additive. Although this experiment was not designed to evaluate interactions between metals or the effects of individual metals, the higher Cr treatment produced the lowest yields. The inorganic metal treatment gave lower yields in all cases than the metal-amended sludge treatments which indicated that the metals were more available, and therefore more toxic, if present, in inorganic form. The Cr concentration in plant tissue was higher by a factor of four in the inorganic metal treatment than in the metal-amended sludge. In another trial with chromium acetate amended sludge, Cunningham _et al._ (1975b) found that increasing the concentration of Cr in the sludge (from 400 mg/kg to 1,400 mg/kg on a soil basis) approximately doubled the Cr concentration in plant tissue. More important however, it was noted that, by increasing the concentration of sludge Cr, plant tissue concentrations of Cu, Zn, Ni, Cd and Mn were significantly decreased. This reduction was possibly due to a blockage of absorption sites, interference with translocation of metals in the plant and/or a complexation of Cr and the other metals.

In the trials reported so far, herbage response to Cr has been related to its form and availability, with degree of toxicity decreasing in the order,

(i) hexavalent/trivalent in culture solution
(ii) hexavalent mixed with soil
(iii) trivalent mixed with soil
(iv) trivalent with sludge
(v) naturally present in sludge.

Chromium proves highly toxic to plant growth when it is available, but the uptake of Cr is very limited. The presence of Cr in the growing medium may also have a depressing effect on plant uptake of other cations. Excessive concentrations of Cr in plant tissue are both difficult to determine and inconsequential from the viewpoint of animal nutrition.

7.4 CHROMIUM IN SLUDGE

Levels of Cr in British sewage sludges (Berrow and Webber, 1972) ranged from 40 to 8,800 mg/kg. The highest concentrations were related to the use of Cr compounds in leather manufacture. In comparing trace element concentrations in sludges from several countries Page (1974) observed that most sludges had Cr contents ranging from 50 to 500 mg/kg, (median of 200 mg/kg). A few sludges had values greater than 1% with the extreme maximum being 3% to 4%.

Cationic Cr was presumed by Chumbley (1971), in his British Agricultural Department Advisory Service Recommendation, to be non toxic to plants unless present in very large amounts. The recommendation, which was based on the work reported by Webber (1972), defined a "large amount" of Cr as one exceeding 500 mg/kg Cr in the soil. Chaney (1973) does not list Cr in the table of limits for metal content of sludge, appropriate for land application. In most reports of sewage sludge trials this level has not been exceeded before the toxic effects of other metals become apparent. Table 4-2 sets out sludge Cr levels in some reported trials together with the zinc equivalent (as defined by the E.P.A.) of the other heavy metals.

Sludge application rates of Dowdy and Larson (1975) in trial 1 (Table 7-2) were so low that yields increased up to the maximum application rate of 30 t/ha. Tarbox and Outram (1975) in trial 2 used a high Cr sludge, firstly with a peat in which grass would not grow and secondly with a "topsoil". Grass yields increased with application of up to 100% sludge. Although the sludges in trials 1 and 2 both contained high levels of Cr and were similar to Christchurch sludge, there was no way one could observe any effect specific to Cr from such studies as the sludge application rate was varied, not the Cr content of the sludge.

The herbage yields found by Cunningham, Keeney and Ryan (1975a) using 4 sludges in trial 3, at first increased for low application rates (125 to 250 t/ha) but decreased thereafter for higher rates or subsequent crops. Yield decreases did not give any significant linear or partial regression coefficients with Cr. Sludge 3(b) was applied at a maximum rate of 5,300 mg/kg, which together with the lower Cr rates of the other sludges in the study and the high levels of other metals, would make statistical detection of Cr effects difficult in the presence of the other larger magnitude responses.

A further trial (4) by Cunningham, Ryan and Keeney (1975b) using metal-amended sludge to evaluate yield responses to considerably higher metal levels but used a low Cr sludge as a base. All metal

TABLE 7-2: CHROMIUM CONCENTRATIONS IN REPORTED SLUDGE TRIALS

Trial Reference	Sludge Cr	Sludge zinc equivalent**	Maximum soil Cr	Crop
	mg/kg			
1	4,600	2,100	200	barley
2	4,800	1,300	4,800	grass
3(a)	2,100	10,700	400	corn/rye
(b)	29,000	5,900	5,300	"
(c)	4,300	10,300	780	"
(d)	1,600	16,800	290	"
4	14,800 to 53,000	29,000 to 85,000	400 to 1,400	corn
5(a)	13,600	>14,000*	1,360	"
(b)	500	>2,100*	50	"
6	100	1,900	100	lucerne
7	850	3,500	850	lucerne & vegetables
8	66	1,800	-	pasture
9	4,800 to 27,000	3,800	200 to 5,000	pasture

* Zn only, no Cu or Ni values given

** (Zn + 2.Cu + 4.Ni)

References:

1. Dowdy and Larson (1975a)
2. Tarbox and Outram (1975)
3. Cunningham, Keeney and Ryan (1975a)
4. Cunningham, Ryan and Keeney (1975b)
5. Mordvedt and Giordano (1975)
6. Wells and Whitton (1976) (Levin sludge)
7. Whitton and Wells (1978) (Auckland sludge)
8. Quin and Syers (1978) (Templeton sludge)
9. Christchurch sludge (this study)

treatments gave marked yield decreases over the controls and yields decreased with each successive crop regardless of treatment. Regression analysis showed that Cr did not significantly affect yield. However, relative yields were increased significantly as the sludge Cr concentration increased indicating that Cr may have been inhibiting the uptake or translocation of the other metals, particularly in the case of high Zn levels. These conclusions were substantiated by tissue analysis which showed that with increasing sludge Cr, tissue concentrations of other metals decreased. Considering the immobility of Cr within plant tissue and noting that the ratios of Cr to other metals in this trial were still relatively low, then a blocking effect of high Cr on nutrient base cations would also be a possibility, particularly when toxic effects from high concentrations of other metals are absent.

No specific effects from sludge Cr were found by Mordvedt and Giordano (1975) for trial 5. In both sludges used, the concentrations of Zn alone exceeded those of Cr. The heavy metal contents of the New Zealand sludges used by Wells and Whitton (1976) and Quin and Syers (1978) in trials 6 and 8 were so low that no toxic effects could be expected. The Auckland Regional Authority sludge used by Whitton and Wells (1978) in trial 7 had a higher metal content, but by the standards of the previous industrial sludges there was no large component of Cr present and other metal concentrations were still low compared with high industrial component sludges.

Christchurch sludge on which this study is based is unusual in that, although the other metals are present in only modest amounts, the concentration of Cr, by itself, exceeds the zinc equivalent of the rest of the sludge. Hence this investigation is designed to measure the quality and quantity of pasture species at varying levels of Cr in the sludge disposed on the Kairaki dune material.

7.5 MATERIALS AND METHODS FOR THE Cr-AMENDED SLUDGE TRIAL

A second glasshouse trial to evaluate the effect of sludge Cr, used the same sludge (Tables 5-1 and 5-2) as in the previously described pot trial, amended by the addition of $CrCl_36H_2O$. An aqueous solution of the trivalent Cr salt was mixed with sludge to form a slurry which was then allowed to dry with occasional stirring over a period of several weeks. This redried sludge was mixed with sufficient unamended sludge to fill 64 plastic pots (with drip trays), each with 1.3 kg of a 4% w/w (oven dry) sludge-sand mixture. This was equivalent to a field application rate of 110 t/ha. The sludge Cr levels were increased by 0.33%, 0.97% and 2.23% (oven dry). These levels were substantially greater than would normally be encountered. This sludge/sand ratio had a zinc equivalent of about 17% of the sand CEC, or about 12% of the amended CEC as defined in Chapter 6.2. Each pot was leached over a period of four weeks to eliminate soluble salts (Cunningham et al., 1975a). Mixture pH values were then measured and titration curves against $Ca(OH)_2$ determined. Half the pots were then treated with $Ca(OH)_2$ to bring the pH within the range 6.5 to 6.9. Pots received no fertiliser treatment.

Planting of either five white clover or five ryegrass seedlings per pot was carried out eight weeks after mixing. Seedlings which died were replaced at weekly intervals for five weeks. Pots were harvested after 14 weeks and again at 20 weeks and then shifted out of the glasshouse as in the previous sludge trial. Measurements of pH were taken,

(i) on planting,
(ii) just prior to the second harvest and
(iii) when the pots were finally emptied.

Methods of analysis for herbage cations and trace metals were the same as for the previous sludge trial (Chapter 6.3) except that, with the poor yield for some treatments, there was insufficient plant sample for duplicate determinations and the consequent data as noted in tables of results should be treated with caution.

The glasshouse chromium trial consisted of three Cr levels plus an untreated control, treated and untreated pH, ryegrass and clover, each with four replicates (i.e. 64 pots). This method of using metal-amended sludge was similar to that used by Cunningham et al. (1975b), in establishing the effects of high rates of Cu, Cr, Ni and Zn in sludge. This was also the method used by Cunningham, et al. (1975c) for comparing the results of soil treated with inorganic salts with results obtained when sewage sludge was amended with metals before addition to the soil. As yields were higher for the sludge treatments than for the inorganic treatments they concluded that caution should be used when attempting to use results of applying inorganic salt treatment to soils when evaluating phytotoxicity and toxic metal uptake from soils amended with sewage sludge. The design of the pot trial reported here complies with these requirements. No other report to date has used chromium-amended sludge. The other report involving variation in Cr levels (Mortvedt and Giordano, 1975), compared inorganic salts on soils with sewage sludge.

7.6 RESULTS AND DISCUSSION

7.6.1 Herbage Yields

Total yields of ryegrass and clover after 20 weeks, are shown in Figure 7-1. Yield, pH and statistical data are listed in Appendix 7. The vertical bars shown in Figure 7-1 are the standard errors of the four replicates.

Yield decreased with increasing Cr treatment, the effect for ryegrass being somewhat less than for clover. Application of one way analysis of variance between Cr treatments and Duncan's multiple range test between mean differences, resulted in significant or highly significant differences in yield between all treatments except the first and second for ryegrass. Stepwise multilinear regressional analysis for the individual effects of pH and Cr gave highly significant multiple correlation coefficients (R = 0.91 and 0.66 respectively) for yield of clover and ryegrass.

Although the yield axis intercepts (14.3 ± 1.8 for clover and 3.1 ± 0.4 for ryegrass) are readily calculated, the temptation to assume a linear extrapolation to calculate yield depression from zero must be resisted. Absolute conclusions are limited to the range of

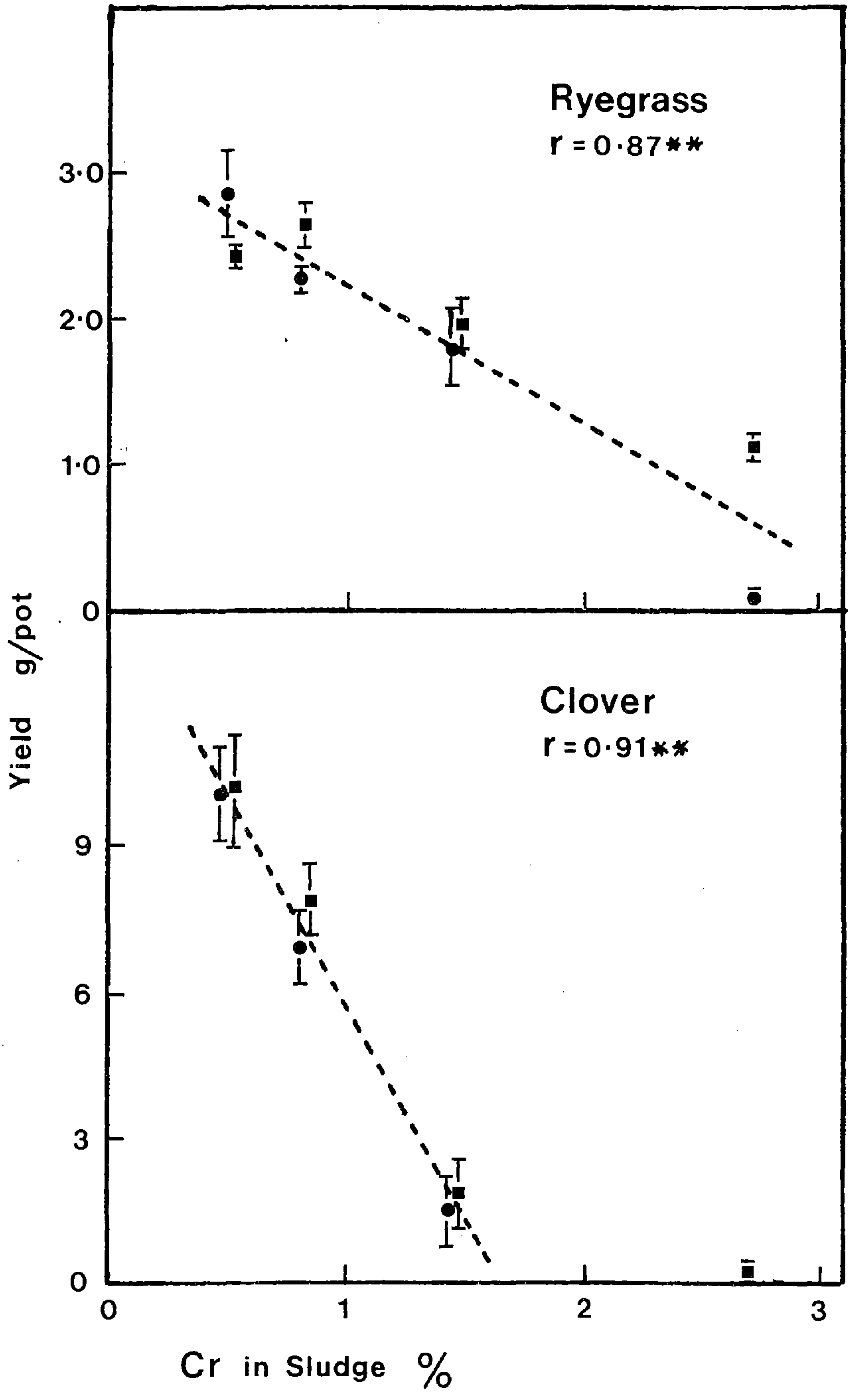

Figure 7-1. Yields of ryegrass and clover in the Cr-amended sludge pot trial at approximate pH 5.7 (●–●) and 6.8 (■–■).

values tested and without the availability of identical sludge containing no Cr there is no easy experimental method of proving enhancement of yield with Cr absent. Chromium is a non-essential element in plants and a threshold tolerance level may or may not exist. Because of the very low uptake of Cr such a threshold would be very hard to determine with any degree of certainty.

Seedling mortality increased dramatically with Cr treatment as shown in Figure 7-2. However a slight possibility exists that in the early stages of the trial the initial leaching to reduce salinity may have been incomplete and thus any subsequent overwatering could have enabled seedlings to survive better. Subsequent soil conductivity measurements (1:5 v/v suspension) were mostly below 0.008 S/m and salt accumulation toxicity is not expected until at least 0.02 S/m (for clover). Analysis of variance of percentage increase between harvests with Cr treatment (and hence possibly conductivity) was not significant, indicating that any effect due to decreasing conductivity was absent by harvest time. As initial conductivity measurements were not carried out implications that the mortality of the seedlings was due entirely to Cr toxicity must be treated with caution.

There was no significant improvement in fit for the pH variable for either ryegrass or clover. Patterson (1971) observed that Cr appeared to differ from other elements in that toxic effects were enhanced by raising the pH of the soil, and that in a field trial inhibition of growth was greatest at pH above 6.5. As noted in the review of soil chemistry of Cr in section 7.2, it is possible for both trivalent and hexavalent Cr to be present in soil.

The mechanism and chemical form in which extremely low concentrations of chromium become available to plants are not well defined.

Comparisons of the deleterious result of this trial, with other attempts to estimate the individual effect of Cr as the single variable in sludge, are limited to

(i) the original trial of Webber (1972),

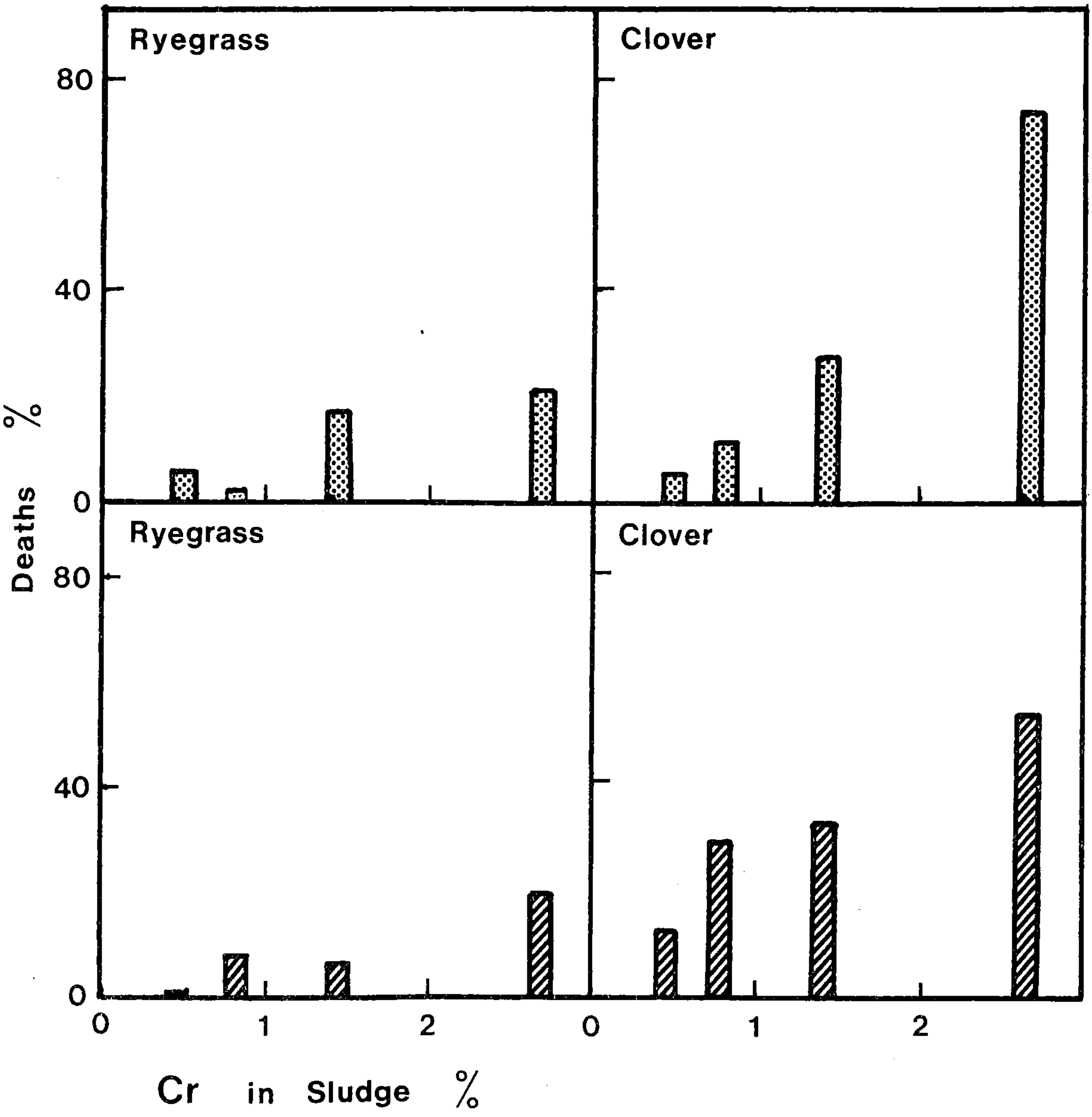

Figure 7-2. Seedling mortality from five replantings in the Cr-amended sludge pot trial at approximate pH 5.7 (░) and 6.8 (▨).

(ii) Mortvedt and Giordano (1975), and

(iii) Cunningham *et al*. (1975a, 1975b, 1975c).

Webber reported a field trial involving sludge adjusted to 4,400 and 8,800 mg/kg Cr. No data were given for the cropping soil used, and although it was noted that appropriate fertiliser dressings were applied, no further details were given. In the trial, the Cr/(Zinc equivalent) concentration ratio was about 3.2 in a "chromium-contaminated" sludge mixed with "uncontaminated" sludge of variable Zn content. The application rate used by Webber (1972) was 125 t/ha (which is about 5% by weight for a 20 cm depth of normal soil), such loadings are not sufficiently heavy to determine any detrimental effects from Cr with accuracy. Webber records that Cr gave either no response or at most a slight, but non-significant reduction in crop yields.

In a pot trial, Mortvedt and Giordano (1975) varied the application rate (maximum 10%) of a sludge containing 1.36% Cr which also contained 1.40% Zn, but they gave no data for other metals present. They compared the results with a non-contaminated sludge and with compost and showed that "concentrations of chromium in all three corn crops were not affected by waste application". They also noted that "the high chromium level in Sludge A resulted in a very high application rate (1,360 mg/kg Cr), yet neither plant growth nor chromium uptake was affected by application of this product", (avoiding the trap of attributing plant growth variation to application of high Cr). Although they correctly concluded "plant availability of chromium contained in these wastes applied to soil is quite low", this gave no information on the effect of the Cr in the wastes on plant yields. Details were given of considerable additional amounts of Mg, Ca, K, P, S and Mn fertiliser applied in the trial but none on the natural levels in the soil itself. Further experiments using solutions of trivalent and hexavalent Cr added to soil resulted in severe toxicity which indicated the much greater plant availability of inorganic Cr. Examination of their data shows that in situations where yields were reduced by inorganic Cr, tissue Cr levels were not significantly different from those in the sludge experiments, except at extreme toxicity where a breakthrough to the tops occurred.

The two sludges used by Mortvedt and Giordano (1975) both had Zn concentrations in excess of their Cr content. For soils at the same pH, they concluded that, although Zn contained in municipal wastes was available to crops, the plant uptake of Zn from the wastes was much lower than from equivalent rates of Zn applied as $ZnSO_4$. Using plant uptake and soil extraction data they found that the lower plant uptake of Zn was not accounted for entirely by any raising of pH by these wastes.

Cunningham et al. (1975b) found that relative crop yields were increased significantly in a highly metalliferous sludge as the Cr concentration increased, which indicated the Cr could be inhibiting the uptake or translocation of the other more toxic metals. They found significant decreases in plant tissue concentration of Cu, Zn, Ni, Cd and Mn with increasing sludge Cr concentration. Although it was not suggested by Mortvedt and Giordano (1975), such a blocking effect by Cr would explain the decreased Zn uptake that was observed. It would also explain why no plant growth variation was obtained by application of a sludge which, in addition to Cr, also contained very high levels of Zn. Cunningham et al. (1975c), used a technique of amending sludge with metal cations before treating the soil. They reported (Cunningham et al. 1975b), the trial that has involved the highest Cr content of sludge (1.48 to 5.30%). The sandy soil used had a CEC of 13 me/100 g and an exchangeable K level of 2.5 me/kg. No fertiliser was added although a fertilised control was included. The levels of the other metals applied were also extremely high (zinc equivalents of 29,000 to 85,000 mg/kg) but the sludge application rate was low (2.8% w/w or approximately 63 t/ha). All treatments initially gave marked yield decreases over the controls. Nutrient stress with continued cropping was indicated by subsequent yields decreasing further. From the relative increases in yield with increasing level of Cr, which was most pronounced in the case of the high Zn treatment, Cunningham et al. (1975b) suggested Cr was either blocking the uptake of Zn or affecting the translocation of Zn within the plant. This could have been either a physiological or a soil chemical process. These results are consistent with Zn being the most mobile and Cr the least mobile of all the metal cations within plant and soil (Dijkshoorn et al. 1979). Turner and Rust (1971) also reported that Cr in solution appeared to interfere with the plant uptake of a broad range of elements.

The results of the present trial using very high levels of Cr amendment but no other metals, show a marked decrease in yield with increasing Cr content, a result not documented elsewhere for sludge-borne Cr. This trial used unfertilised soil of very low natural fertility compared with the highly fertile soils used by Mordvedt and Giordano (1975) and probably by Webber (1972). Fertility levels in the present trial were also several times lower than those used by Cunningham et al. (1975b). The concentrations of other metals present in Christchurch sludge were very low compared with the trials listed above. The Christchurch metal-amended sludge had a Cr/(Zinc equivalent) concentration ratio of over 7 compared with about 0.5 (Cunningham et al. 1975b) and less than 1.0 considering Zn only (Mordvedt and Giordano, 1975).

From the foregoing results and discussion it may be concluded that Cr in sludge causes a blockage of the absorption mechanism in plants and/or interference with translocation of all cations involved in plant physiology. Nutrient cations such as Ca, Mg and K may be included and not just the toxic metals. Chromium is a non-essential element in plants and it is the secondary nature of any Cr effect, combined with varying degrees of Cr availability, that has produced so many widely varying results. These may be grouped as follows.

(1) As levels of available Cr increase, plant growth decreases, with no other symptoms, including non-translocation of Cr to the tops (Hunter and Vergano, 1953; Soane and Saunders, 1959; Patterson, 1971; Turner and Rust, 1971; Mordvedt and Giordano, 1975; Dijkshoorn et al. 1979).

(2) At high levels of available Cr, sufficient to cause severe injury to the plant, mobility of Cr suddenly increases with a breakthrough into the tops (Hunter and Vergano, 1953; Mordvedt and Giordano, 1975; Cary et al., 1977a; Dijkshoorn et al., 1979).

(3) If a plant is not under nutrient stress and has a surplus of nutrient cations available, there is no

depression of yield in the presence of moderate amounts of Cr (Webber, 1972; Pettersson, 1976; Cunningham _et al._, 1975a). In some cases, indirect effects have resulted in yield increases (Pratt, 1966; Huffman and Allaway, 1973a; Cary _et al._, 1977b).

(4) When other toxic elements are present in large amounts blockage of them by Cr reduces toxic effects and even results in enhanced yields in some cases (Turner and Rust, 1971; Mordvedt and Giordano, 1975; Cunningham _et al._, 1975b).

In a situation in which no toxic metals are present but where there is considerable nutrient stress, it is possible to conclude that the effect of a high Cr content in sludge should be to decrease plant yield. Such an effect was observed in this study. One is thus faced with the opposing viewpoints that Cr is beneficial in sludge, if one wishes to suppress very high levels of toxic heavy metals from entering the plant, but is otherwise detrimental to optimum plant growth where supply of nutrient cations is limited.

7.6.2. Cations and Metal Uptake

Herbage concentrations of Na, K, Ca and Mg are illustrated in Figures 7-3 and 7-4. The data are listed in Appendix 7. Using the same general guidelines as before (M.A.F., 1978), K values were barely adequate (2% dotted line) for healthy growth. Elevated levels of associated Na, Ca and in particular Mg tended to support the expected response to K discussed in the previous sludge trial. The upward trend in K concentration in clover was probably a K depletion effect within the pot as at the higher Cr levels, herbage yields were very low.

Addition of Cr had an effect on CEC's and extractable (exchangeable at pH 7 plus soluble) cations of the pot soils after mixing, as shown in Table 7-3. As more trivalent Cr was added to the sludge, the CEC of the pot mixture decreased, indicating that some of the Cr became fixed on exchange sites in a non-exchangeable form. CEC's measured at the end of the trial averaged 4 me/kg lower than those

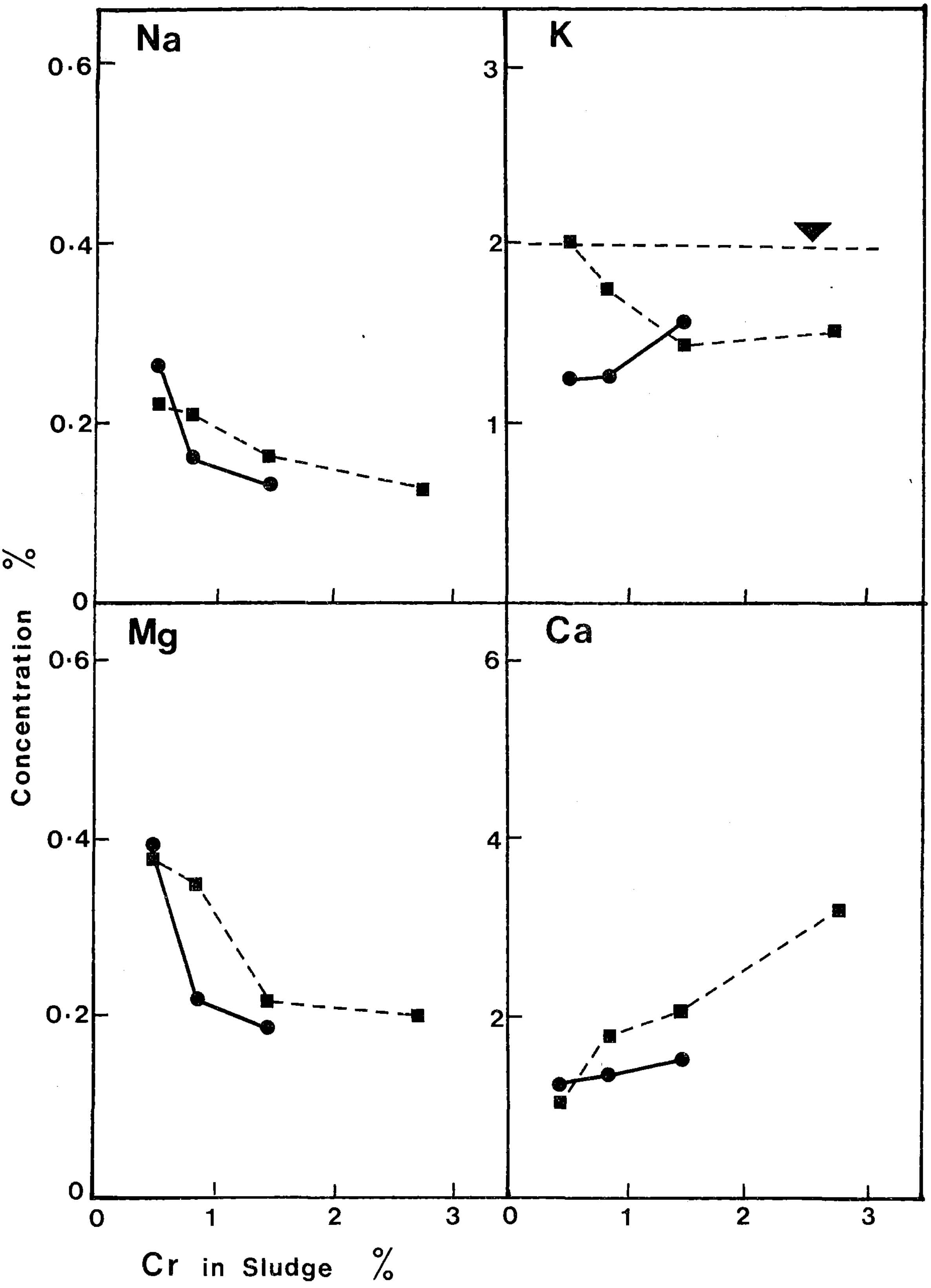

Figure 7-3. Effect of Cr-amended sludge on uptake of Na, K, Mg and Ca in ryegrass at pH 5.7 (●–●) and 6.8 (■–■).
▼ concentrations below dotted 2% line are deficient (M.A.F., 1978).

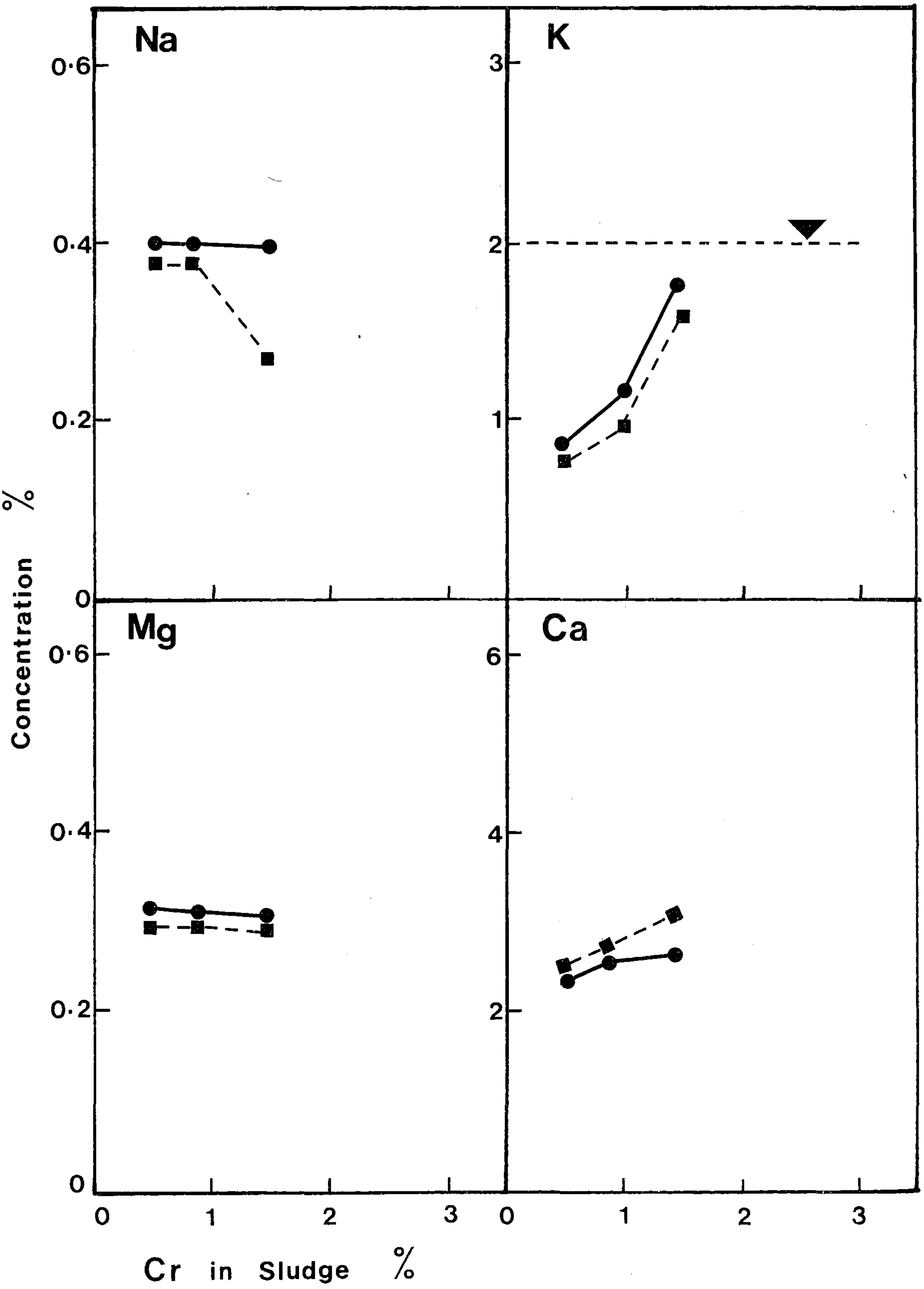

Figure 7-4. Effect of Cr-amended sludge on uptake of Na, K, Mg and Ca in clover at pH 5.5 (●–●) and 6.6 (■–■).
▼ concentrations below dotted 2% line are deficient (M.A.F., 1978).

TABLE 7-3. EFFECT OF ADDITIONAL CHROMIUM ON SOIL CEC AND EXTRACTABLE CATIONS

Cr added per pot mg/kg	CEC	Mg	Ca	K	Na	B.S. %
	me/kg					
0	44	6.3	36	3.1	2.1	108
130	42	6.6	60	2.3	1.6	169
390	36	6.9	55	2.8	0.8	182
890	36	9.6	80	3.1	1.4	263

given in Table 7-3. The loss of CEC is probably due to mineralisation of organic material but also indicates a non-reversibility of the fixing. The extractability of the monovalent cations, Na and K, did not alter significantly but that of the divalent cations Mg and Ca increased. The number of cations displaced was also greater than the number accounted for by decrease in CEC, shown by the increase in total extractable cations as a percentage of the CEC. This indicated that Cr also replaced fixed cations normally not exchangeable at pH 7 which were released into the soil solution.

The initial "release" of nutrient cations by Cr may account for some of the transitory, and often puzzling beneficial results of early trials, particularly those of field experiments rather than nutrient cultures (Huffman and Allaway, 1973a). Patterson (1971), for example, while applying Cr salt at 50 mg/kg 100 mg/kg and 500 mg/kg on a peat mixed with soil, noted that the effect of a single application of Cr at each rate was stimulatory to the crops, but after each annual application toxic effects became more marked.

Trace element concentrations of Zn, Cu, Mn and Cr are shown in Figures 7-5 and 7-6. The data are listed in Appendix 7. For both clover and ryegrass increasing the pH to approximately 6.8, was highly significant in reducing the Zn concentration to safer levels, again emphasising the importance of maintaining pH in the 6.5 to 7.0

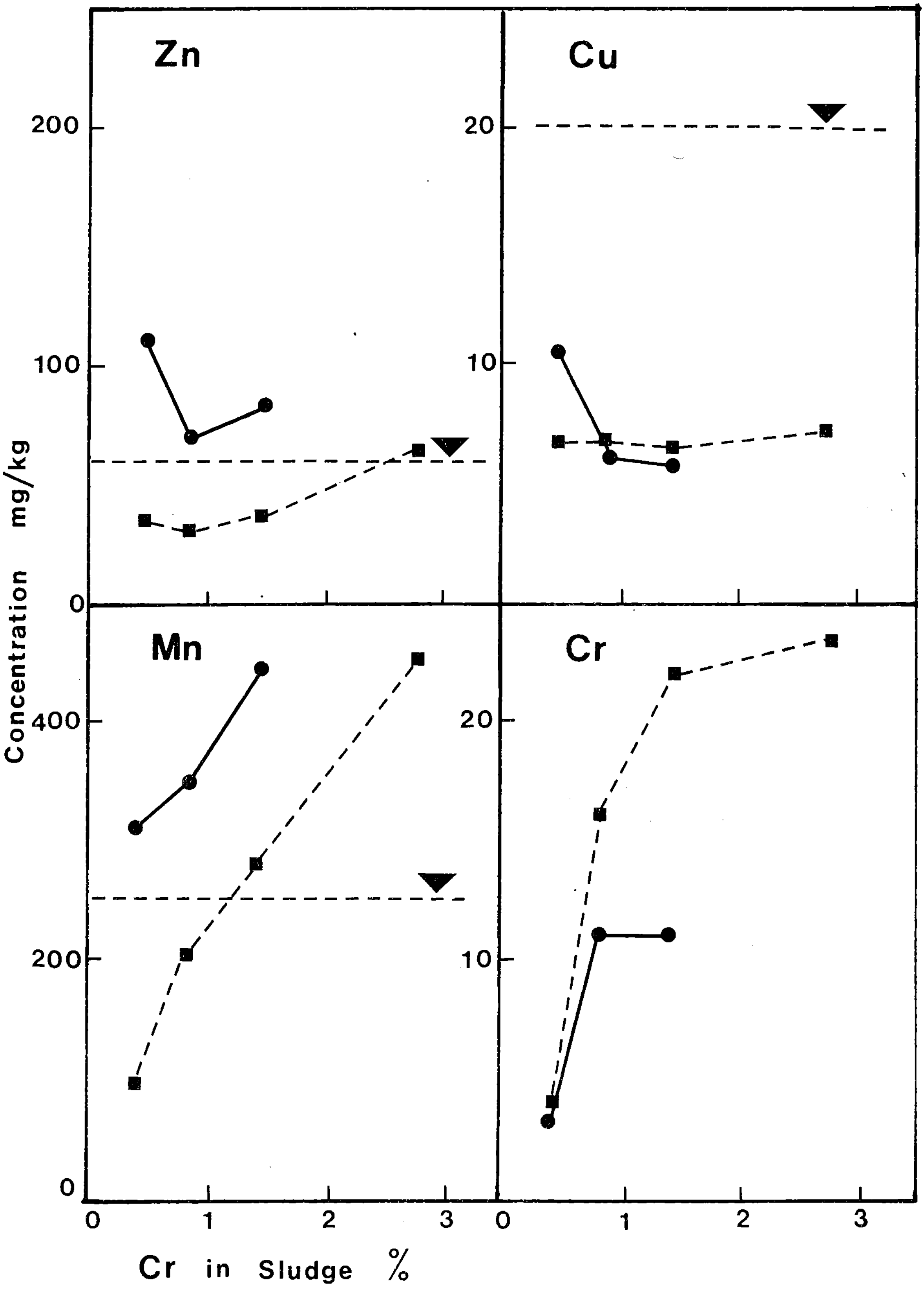

Figure 7-5. Effect of Cr-amended sludge on uptake of Zn, Cu, Mn and Cr in ryegrass at pH 5.7 (●—●) and 6.8 (■–■). ▼ concentrations above the dotted lines are potentially toxic (M.A.F., 1978).

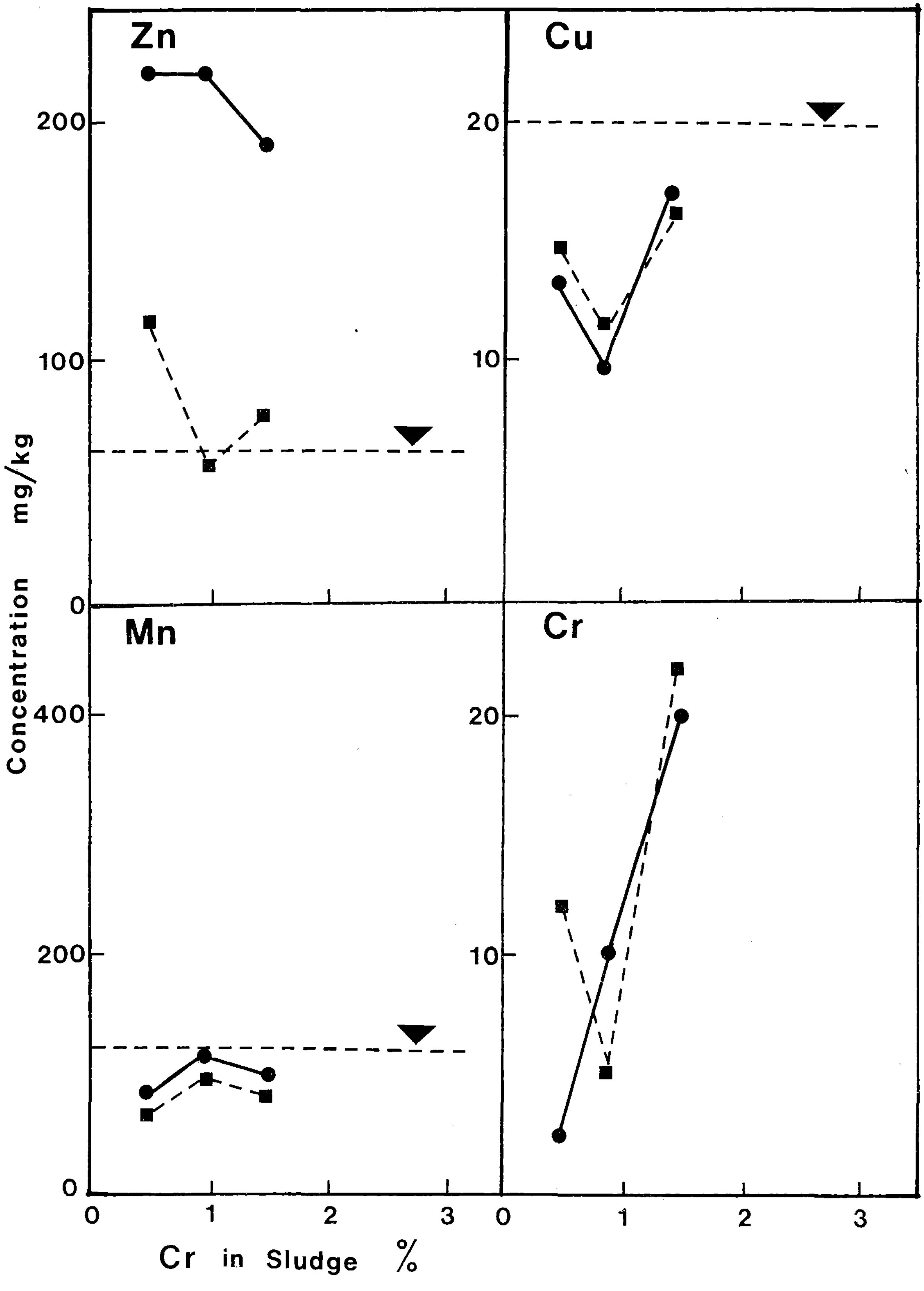

Figure 7-6. Effect of Cr-amended sludge on uptake of Zn, Cu, Mn and Cr in clover at pH 5.5 (●–●) and 6.6 (■–■).
▼ concentrations above the dotted lines are potentially toxic (M.A.F., 1978).

range. A similar result was obtained for Mn in ryegrass. The levels of the other elements were generally in the safe range, as discussed in the previous sludge trial. Chromium values tended to fluctuate, probably illustrating the contamination problems associated with its detection in plant tissue, rather than accurate trends in plant uptake. Most of the herbage Cr concentrations in this trial and in the previous sludge trial were above the 2.5 mg/kg (ryegrass) and 9 mg/kg (clover) values given by Dijkshoorn _et al_. (1979) for 50% yield reduction. As little Cr was added in the low sludge treatments significant dust/splash contamination is indicated. Although the data must be treated with caution, the generally increasing herbage concentration of Cr, with Cr treatment and with pH, are results consistent with preceding discussion. Whether this Cr is from contamination or uptake makes no difference to possible animal ingestion but simply provides more Cr for animal nutritional purposes.

7.6.3. Chromium from Tanning

As indicated by Berrow and Webber (1972), Page (1974) and Keeney _et al_. (1975), one of the main sources of Cr in sewage sludge is the tanning industry. The disposal of Cr in tanning wastes is not to be confused with the dereliction of land contaminated by waste from manufacture of Cr chemicals. Compared with the major smelter pollutions described by Breeze (1973) and Gemmell (1973), disposal of tannery wastes is a relatively minor problem.

The early report by Hamance and Taylor (1948) was designed to show that tannery chrome material was harmless, by simply growing a variety of plants in a high dosage plot and noting that no unusual symptoms were observed. With the release of the A.D.A.S. recommendations (Chumbley, 1971) naming a 500 mg/kg soil limit for toxicity for Cr, the British Leather Manufacturers Research Association (B.L.M.R.A.) reviewed the disposal of Cr wastes (Sykes, 1972) and reputed toxicity of Cr (Sykes, 1973). A similar study was carried out in New Zealand (Mason, 1976).

The Cr used in tanning is mostly in a trivalent form, and tanning industry reports place much emphasis on the lesser toxicity of trivalent as compared with hexavalent Cr, This apparent difference however, was related to the short term availability of Cr in the soil solution. Recent soil chemical and plant physiological studies have not been able to differentiate clearly between the two forms (Cary et al., 1977a, 1977b; Bartlett and James, 1979). Understandably, much emphasis was placed by Sykes (1972, 1973) on earlier reports citing beneficial results from Cr and he concluded that "chromium is unlikely to be harmful and may be beneficial when applied to agricultural land". Chromium is not an essential plant nutrient and any beneficial effects on plant growth have been shown by others to be either indirect or unverified (Pratt, 1966; Huffman and Allaway, 1973a).

Sykes (1972) states that "Published reports tend to be conflicting and the ones suggesting that chromium is highly toxic are based on work carried out under very artificial conditions". However such single variable experiments using "artificial" conditions are very necessary to avoid the type of experiment reported by Sykes (1974) which was desiged to "determine whether chromium derived from tannery wastes has any effect on crop yield". By varying sludge application rates, he concluded that "even at 1000 mg/kg chromium, ... the sewage sludge gave spectacular increases in yield." Such experiments, along with those of Tarbox and Outram (1975), who used a similar sludge with a high Cr content, cannot give any information as to the individual effect of Cr, when other components of the sludge are being incremented at the same time. The scale of the field experiment of Tarbox and Outram of four 0.84 m^2 plots would appear to be too small for them to be able to draw significant conclusions.

It is well known that Cr content of crops grown on Cr contaminated soil does not increase appreciably. It is also well known that ingested Cr is non-injurious to higher animals, and that Cr is very insoluble in soil. However reiteration of these facts by the tanning industry does not indicate the effects of trivalent Cr on plant growth. Lack of appreciation as to the significance or otherwise of data, leads to reports such as that of the New Zealand Leather and Shoe Research Association (1976), in which herbage analyses were given for sludge disposal sites, to support the view that, "tannery sludges can be safely applied to land, and vegetation can survive there, and that uptake of chromium by such plants is very low". Actually their levels of Cr (e.g. bulked grass and weeds, 20 - 33 mg/kg; "grass", 4.3 - 6.5 mg/kg) and those of Sykes (1974) (grass, 25 mg/kg wet weight), were very high compared with the critical value of 2.5 mg/kg for 50% yield reduction in ryegrass, given by Dijkshoorn et al. (1979).

Corning (1975), although rather critical of restraints on Cr sludges, did conclude that B.L.M.R.A. greenhouse tests agreed with the A.D.A.S. report (Chumbley, 1971), which gave a limit of 500 mg/kg in the soil, before deleterious effects on crop yields were evident. The literature reviewed in this report and the results of the Cr trial show that maximum supply of nutrient cations in the soil is also important in the neutralisation of Cr toxicity.

7.7 CONCLUSIONS FROM THE Cr-AMENDED SLUDGE TRIAL

The important points to be noted from the glasshouse trial using Cr-amended sludge and the previous discussion are as follows.

1. The glasshouse pot trial which used a low fertility sandy soil and Christchurch sludge amended with additional Cr, gave decreasing herbage yields of (81 ± 16)% for clover and (30 ± 16)% for ryegrass, per 1.0% Cr added to the sludge. These results were consistent with the interpretation that an effect of Cr on plants was a blocking of absorption and/or translocation both of nutrients and of toxic elements. In the present trial, where considerable nutrient stress was involved, a marked decrease in growth from Cr treatment was manifest.

2. Variations in pH from 5.5 to 6.9 did not have any significant effect on yield, but adjusting the pH to 6.9 was beneficial in that it significantly decreased the levels of Zn in plant tissue.

3. Addition of Cr decreased effective soil CEC and previously exchangeable and fixed cations were displaced into the soil solution.

4. The only effects detected from the use of Cr were decreased plant growth and lowered soil CEC. The disposal of waste containing Cr onto soils without causing deleterious effects on plant growth, involves the maintenance of soil fertility at levels sufficient to negate any adverse Cr effects.

CHAPTER 8

FIELD TRIAL

8.1 OBJECTIVES

The objectives of the field experiment were to establish relationships between;

(i) sludge application rate and pasture growth,
(ii) chromium content of the sludge and pasture growth, and
(iii) field responses compared with glasshouse results.

The requirements of such a study were;

(i) sufficient replication to reduce random variation,
(ii) large plot size,
(iii) several levels of each variable in the range where responses may be expected, and
(iv) all other trial factors invariant and as close as possible to naturally occuring conditions.

No reports of other field experiments using high chromium metal-amended sludge were found in the literature.

The limits of practicability for such a trial were three sludge levels (plus control), each with three metal-amended sludge Cr levels, each treatment having four (4.0 m^2) replicates.

8.2 MATERIALS AND METHODS

Dried sludge was metal amended using $Cr_2(OH)_2(SO_4)_2.Na_2SO_4.H_2O$. The method used to ensure complete metal amendment was to construct a box (3.0 m x 4.0 m x 0.5 m) with the bottom boards spaced 1 cm apart and completely lined with a single sheet of heavy duty (0.25 mm) black polythene to form a watertight container. This box was constructed inside another (3.5 m x 5.0 m x 0.1 m) shallow enclosure, similarly lined with polythene to form a watertight "drip tray". The chromium salt (75 kg) was mixed with dried sludge (2.5 m^3) while being passed through a soil shredder into the box which was then flooded with water. The amount of Cr salt to sludge used for this initial concentrate was determined from a prior laboratory test. It represented the maximum amount of Cr salt that could be added to an amount of sludge without becoming subject to subsequent leaching.

The concentrate in the box was allowed to air dry while being turned over several times during a period of several weeks. The polythene lining of the box was then removed and the contents leached three times with 2 - 3 m^3 water with drainage through the bottom cracks into the tray. The sludge was dried to field capacity and turned between each wetting. No colouration due to Cr salt was evident in the leachate and the conductivity of the final metal-amended sludge was 0.05 to 0.06 S/m. After final air drying, the metal-amended sludge concentrate was bagged and taken to the field site for further mixing with unamended sludge.

The field site was flattened Kairaki sand dunes as described in Chapter 5.2 and was close to a supply of water. Scant vegetation consisted of run-out lucerne pasture and weeds. It was assumed that the meagre soil development (mainly accumulation of organic material) would not significantly affect the properties of the new topsoil about to be placed over it. The site was divided into 48 of 2 m x 2 m plots, each permanently separated by a grid of (20 cm x 2.5 cm) untreated boards standing on edge. The plots were filled to the top of the boards with mixtures of fresh sand-dune material, shredded sludge and metal-amended sludge.

The new "topsoils" of known sludge, sand and chromium composition were randomly distributed throughout the area. A plan of the plots is given in Appendix 5.

The levels of the trial variables (oven dry basis) were as follows.

(i) Sludge rates: 195, 389, 584 t/ha,
(corresponding approximately to 9%, 22%, 46% w/w to a depth of 20 cm). (100% sludge = 780 t/ha to 20 cm).

(ii) Chromium in sludge; 0.48%, 0.79%, 1.09%.

The sludge rates used corresponded to shredded sludge applied at thicknesses of 5 cm, 10 cm and 15 cm. Allowance was made for approximately 15% sand incorporated upon removal from the drying bed. The control plots required a thin surface layer (0.5 cm) to stop wind drift of the sandy soil. The trial sludge rates which all correspond to the "plateau" region of the yield response curve gained from the previous glasshouse trial, would normally be considered "heavy to extreme".

The plots were autumn-sown with a ryegrass/clover mixture and were mown several times (clippings retained) to establish a sward. At no stage was natural rainfall not sufficient to provide adequate moisture. Conductivities measured for each plot on three bulked cores varied from 0.003 to 0.19 S/m. There was a slight tendency for the higher sludge treatments to have higher values but no consistent pattern for Cr treatment was observed. Conductivities in this range should not influence plant yield. Plots were close-mown, with the clippings removed and then harvested nine weeks later. A 1.0 m x 1.0 m x 20 cm frame was arbitrarily dropped somewhere near the centre of each plot and all herbage above 2.5 cm within the frame was cut with guarded handshears. The material removed was weighed, a 200 g sub-sample being retained for drying and analysis, and the remainder returned to the plot.

The trial area has been securely netting-fenced with the barb wires electrified, ensuring that the trial may be continued in future years.

8.3 RESULTS AND DISCUSSION

Variations between plots, particularly in pasture quality could be distinguished by visual examination. Clover survival to harvest was very poor. Weeds, particularly twitch, were more prominent in the higher chromium treatments and, to a lesser extent, in the high sludge treatments. The source of the twitch was either shredded sludge from around the edge of the drying beds, or more likely, from the original, now-buried surface. Assuming the latter, with roots extended below the new soil, then this surviving twitch increased the relative yields from those plots. If the work is to continue, spraying to eliminate twitch and re-establishment of a sward is desirable.

Field trial herbage yields are shown in Figure 8-1 with the data found in Appendix 8. Semi-quantitative results are included for ryegrass alone. Trends for Cr content of the sludge are shown in Figure 8-2. In the figures, the average value for each treatment is shown because diagramatic representation of trends is difficult when two variables are involved.

Stepwise multilinear regressional analysis for total herbage yield showed a significant decrease with soil Cr concentration ($R = 0.47$, $p = 0.02$) and with Cr and sludge concentrations together ($R = 0.55$, $p = 0.01$). The regression equation was

$$\text{Yield (t/ha)} = 2.25 + (0.0015 \pm 0.0016).\text{Sludge (t/ha)} - (2.9 \pm 1.7).\text{Cr (\%)}$$

From the equation it is seen that herbage yields increased slightly with increased Cr-free sludge application. Yields were significantly greater for all sludge rates than for the control. The increase in goodness of fit when sludge rate is included as a second variable is barely significant ($p = 0.06$); with less than 6% of the trial variation being explained by sludge application rate. This compared with 22% for Cr alone. These results were obtained in spite of the possible masking interference from twitch.

Results from pot and field trials were compared by reprocessing the field yield data using Cr content of the sludge and sludge application rate as the variables. Herbage yields showed a highly significant decrease with sludge Cr concentration ($R = 0.61$) with 37% of the trial variation being explained by Cr in the sludge. Total herbage yield in the field trial decreased at the rate of (41 ± 17)% per 1.0% Cr amended into the sludge. This compares with (81 ± 16)% for clover and (30 ±16)% for ryegrass in the pot trial, indicating reasonable agreement between the trials.

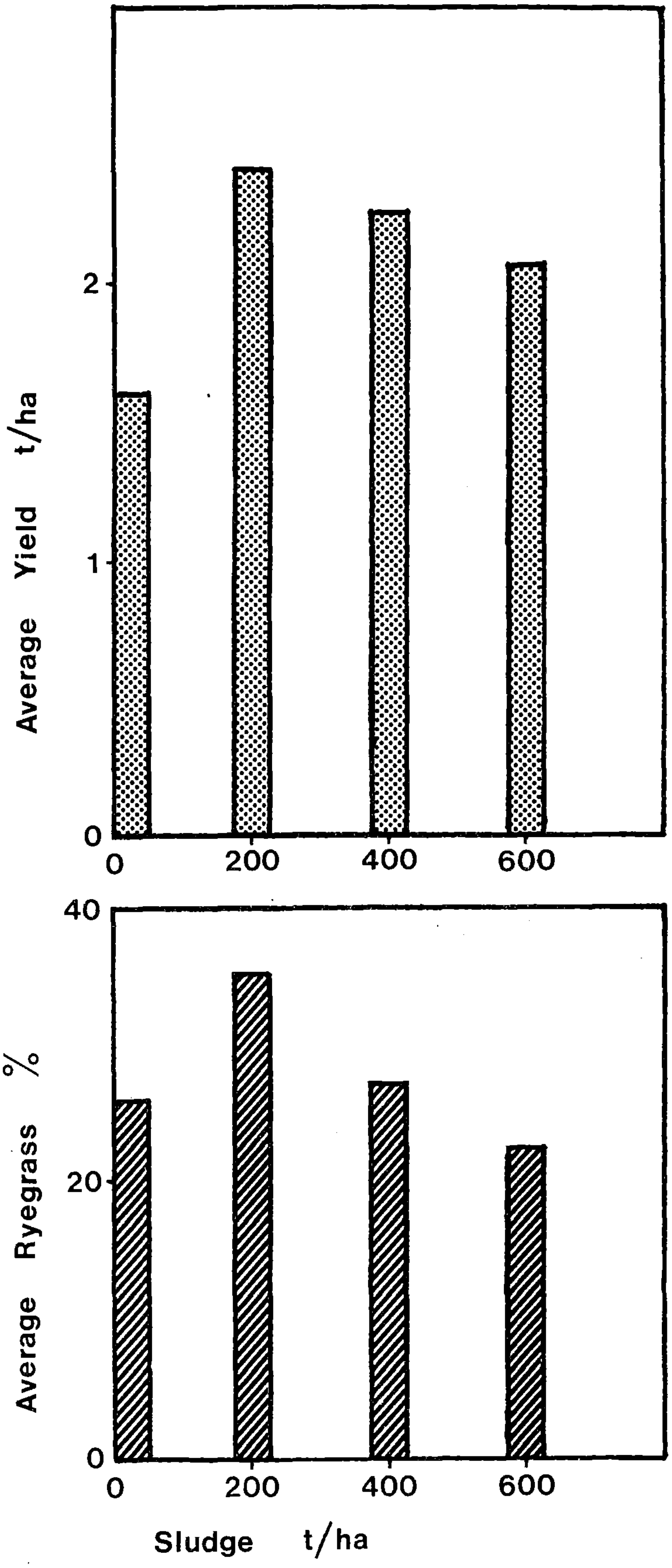

Figure 8-1. Effect of sludge application on field trial herbage yield.

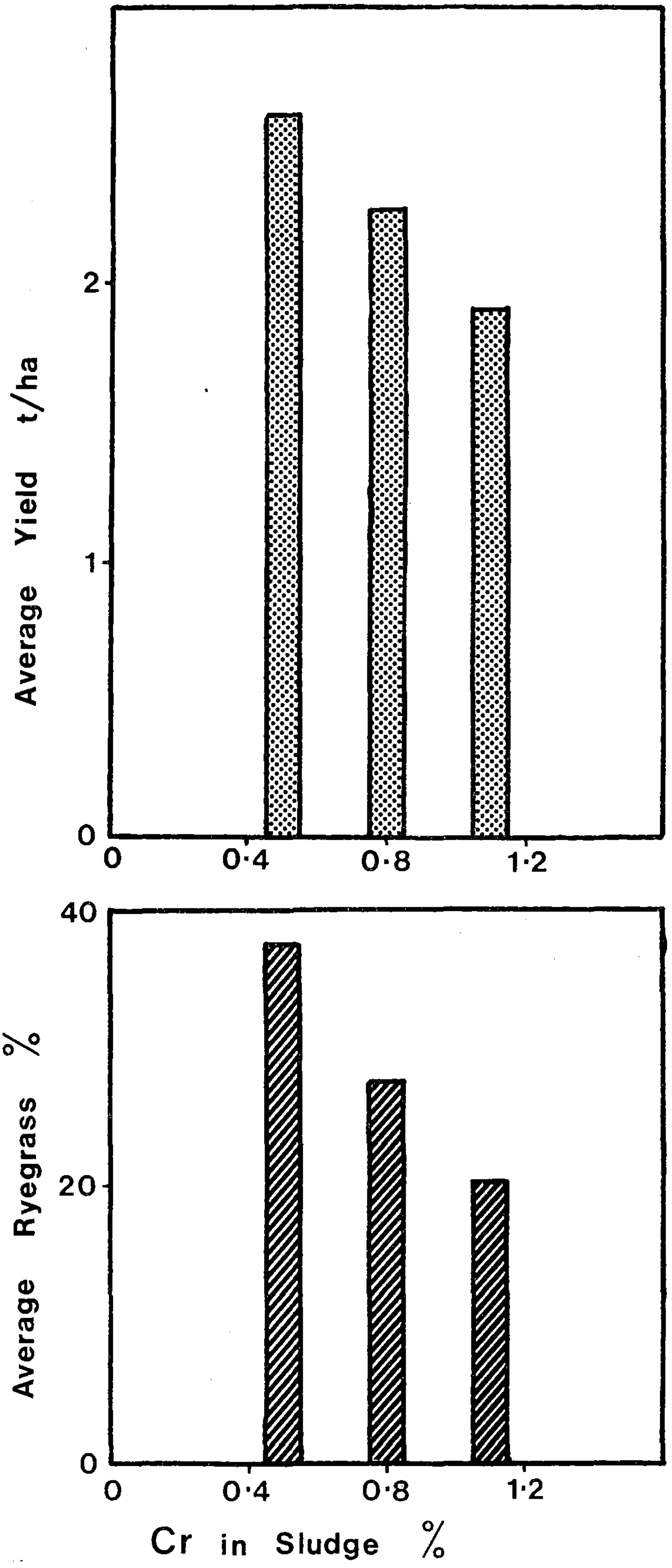

Figure 8-2. Effect of Cr in the sludge on field trial herbage yield.

The results shown in Figure 8-2 and Figure 7-1 for the effect of Cr on yield, show a definite trend which can be quantified with reasonable certainty. However, in order to measure these effects, the Cr application rates had to be enormous compared with those naturally present in Christchurch sludge. Table 8-1 gives maximum depression of yield, calculated on the basis of the field trial regression equation, that may be expected from varying application rates of typical Cr contaminated sludge.

Caution must be used in interpretation of extrapolated results below the limit of a trial treatment range. Although not normally acceptable, in this case toxicity from a non-essential element is considered. If a threshold tolerance concentration exists, then the actual effect will be less than that estimated. There is thus reasonable justification for concluding that values given for lower concentrations are the maximum possible effects. By making an assumption of linearity, the worst possible case has been allowed for. This is the only practical solution to the problem which arises when an identical sludge containing no Cr is not available.

TABLE 8-1: MAXIMUM POSSIBLE DEPRESSION OF YIELD FOR PASTURE SPECIES FROM CHROMIUM, CALCULATED FROM FIELD TRIAL RESULTS USING CHRISTCHURCH SLUDGE.

Sludge Rate t/ha	Maximum Yield Depression		
	% Cr in Sludge		
	0.05	0.5	2.5
60 (2%)	0.12%	1.2%	6.2%
250 (12%)	0.7%	7%	36%
420 (25%)	1.3%	13%	63%
800 (100%)	4.3%	43%	(>100%)?
See text for note on extrapolation beyond trial data levels.			

Inspection of the magnitude of yield depressions shows why a relatively small chromium toxicity has been difficult to detect in other trials. Webber (1972) used sludge containing 0.4% and 0.8% Cr at application rates of 125 t/ha with little response. For pasture species, a similar application rate (Table 8-1) gives a maximum yield depression of less than 5%. For the trial of Mortvedt and Giordano (1975), the maximum effect from the table corresponding to their application rate of about 200 t/ha of 1.36% Cr sludge, would be less than 15% depression. In their case, with greater amounts of zinc present, other effects also became important. In the trial by Cunningham _et al_. (1975b), application rates were 63 t/ha, which would have had equivalent maximum effects (Table 8-1) of less than 6% to 18%. However they showed that chromium was in fact beneficial in their situation, since extremely high levels of other metals completely dominated the yield depressions.

The maximum expected depression of pasture yield from 100% Christchurch sludge, containing about 0.5% Cr, is less than 43%. When this sludge is used at say 250 t/ha (the maximum rate recommended from zinc toxicity considerations), the maximum possible effect of Cr on yield is less than 7%. At 0.5% Cr in sludge at 250 t/ha, the soil concentration of Cr is about 600 mg/kg, which is near to the figure of 500 mg/kg below which, no Cr toxicity is to be expected, according to the field observations by Chumbley (1971).

8.4 FIELD TRIAL CONCLUSIONS

1. Field trial yields showed an increase in herbage yield with sludge applications, supporting the trends evident in the glasshouse trials. A slight increase was still evident at extremely high sludge application rates.

2. Field trial results, using varying rates of sludge and Cr treatments on low fertility soil, showed decreased herbage yield at the rate of (41 ± 17)% per 1.0% Cr amended into the sludge. Although caution regarding linear extrapolation below trial level still applies, it appear that 0.5% Cr in sludge applied

at 250 t/ha on Kairaki sand should, at worst, decrease pasture yield by less than 7%. At higher levels of applied Cr, the rapidly increasing detrimental effects on yield were ascertained with much greater reliability.

3. The field trial is designed to provide continuing information on long term effects of sludge on pasture yields and composition. Future results will show whether the existing trends are transient or persistent.

CHAPTER 9

GENERAL SUMMARY

The use, in X-ray fluorescence analysis, of primary radiation scattered by the specimen to overcome problems of interelemental absorption-enhancement effects was investigated. The various internal-standardisation methods used in soil and plant analyses were reviewed and the need for a unifying approach to selection of type of scattered radiation and scatter wavelength was discussed.

The isolated atom model of X-ray scatter was used to develop a new analytical strategy for internal standardisation in X-ray fluorescence analysis of geological and biological materials. The method defined quantitatively, by how much and with what limitations, a calibration technique could improve results for particular elements in specific materials.

The analytical strategy proposed is based on a modified, peak-to-background ratio equation, where the background intensity is raised by an exponent T. The use of a variable T in the equation, combines as special cases, all existing analytical strategies which use scattered X-rays, either as a general background or as a scattered tube line. The method also includes the special case of $T = 0$ which is the simple linear calibration of concentration vs net peak intensity.

Variation in values of T, needed for exact compensation for each source of mass absorption error, was evaluated using extensive computer processing of matrix data for typical soil and plant material. It was found that values of T varied with analyte, scatter wavelength, type of scatter, and the matrix component contributing to mass absorption error.

Extremely variable matrices were specially prepared to test the method for zinc and zirconium analysis. The improvement in quality of matrix compensation was as predicted from theory.

Some recommended strategies have been outlined for analysis of various groups of elements in soil and plant materials, including some situations where theory predicts that successful calibration, using particular scattered radiation, is most unlikely. The consequent limitations of some analytical methods which have been proposed in literature were discussed.

A volume of tables was prepared to assist in the selection of the optimum calibration strategy for any combination of mass absorption errors in soil and plant analysis. By using the described procedure, it is possible to show;

(i) how much each interfering component contributes to both initial and final analyte error,

(ii) which value of T for various scatter wavelengths and types of scatter, gives optimum reduction in analyte error and,

(iii) if any improvement over the various strategies commonly used, can be achieved.

The methods developed were among those used to analyse soils and metalliferous sewage sludge in an experimental program designed to establish permissible sewage sludge application rates, and the effect of sludge application on pasture production and quality. Although Christchurch sludge contained useful amounts of plant and animal nutrients, metal content was too high to permit its indiscriminate use as a soil additive. The metal concentrations were not high enough however to prohibit the judicious utilisation of the sludge within prescribed limits.

The maximum amount of sludge recommended for application to Kairaki sand, assuming the composition of sludge remains constant, is 250 t/ha. This recommendation is a compromise between the U.S. Environmental Protection Agency guidelines and experimental results obtained from the present field and pot trials. Once the above maximum quantity has been applied, no further sludge should be added for at least 30 years. A period of this duration is required to establish long-term losses from the soil-sludge system.

The above recommended level applies only if soil pH is maintained above 6.5. A programme for monitoring soil pH and of liming, when required, is essential to reduce the availability to plants of toxic metals applied.

Zinc was found to be the limiting contaminant in herbage. Any future increase in the sludge zinc concentration will decrease the maximum amount of sludge which may be applied. Although, within safe limits at present, herbage copper concentration may also become a limiting factor if sludge copper were to increase.

Application of potassium fertiliser is necessary to improve pasture quality and its use may also increase production. Potassium deficiency is probably a greater pastoral constraint, at present, than is metal toxicity.

Highly significant results from both glasshouse and field trials showed that chromium contamination of sludge could decrease pasture production. It appears that chromium may block plant uptake of nutrient cations. With the present sludge chromium concentration of about 0.5%, and total sludge application at the recommended level of 250 t/ha, no deleterious effects are likely, provided a good supply of nutrient cations is maintained in the soil. If sludge chromium concentration increases, pasture production would fall unless additional nutrient cations were also supplied.

No other elements were found in herbage, in concentrations likely to be injurious to animal health, or restrictive to plant yield.

ACKNOWLEDGEMENTS

I wish to thank all fellow Soil Science Department staff members for their comments and encouragement. Special thanks are due to Kay McKenzie (nee Ombler) and Linda Kilday for technical assistance in analytical and trial work.

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On a more personal note, I especially thank Dr. Alistair Campbell and Professor Roger Swift for their supervision, and in particular, for performing the onerous task of endlessly weeding out esoteric terminology and sentences of more than five lines. I must also thank Dr. Scott Black who had the pleasant misfortune to know a lot about practical agriculture and to occupy the office next to mine.

It is with sadness that I recall the valuable advice of Terry Ludecke, late Reader in the Department. His sudden death denied him the reward of seeing the results of the trials in which he took much interest.

My thanks are due to Beryl Bond for typing the script and all the greek symbols! I also wish to acknowledge the part of the New Zealand Lottery Distribution Committee in supplying funds to purchase X-ray equipment.

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LIST OF APPENDICES

APPENDIX 1

```
C     HXEXP DETERMINES THE BACKGROUND EXPONENT FOR P/B RATIOS
C     AW = ATOMIC WEIGHT
C     U = MASS ABSORPTIONS AT ANALYTE WAVELENGTH
C     UB= MASS ABSORPTIONS AT SCATTER WAVELENGTH
C     R = RALEIGH SCATTERING FACTOR
C     C = COMPTON SCATTERING FACTOR
C     P = PROPORTION PRESENT
C     Y AFTER EACH IS FOR INTERFERING FRACTION
C     T = TEMP STORAGE
C     NPC = PERCENTAGE INCREMENTS
C     WAVE = WAVELENGTH OF SCATTER
C     I = NUMBER OF ELEMENTS IN SAMPLE
C     J = NUMBER OF INTERFERING ELEMENTS
C     OUTPUT FILE 3 IS FULL PRINTOUT
C     OUTPUT FILE 4 IS CONDENSED PRINTOUT
C     ONE PAGE FILE 4 FROM 12 PAGES FILE 3
C
      INTEGER ZZ
      DIMENSION ELEM(15),Z(15),U(15),R(15),C(15),P(15),X(5,5),NUM(5)
      DIMENSION ZY(15),UY(15),RY(15),CY(15),PY(15),S(6),A(6),AB(6)
      DIMENSION UB(15),UBY(15),EN(5,5),UNDE(15),B(6),BACK(5,5)
      DIMENSION TR(15),TC(15),TRY(15),TCY(15),ID(15),HEAD(10),UNDER(10)
      DIMENSION NAME(15),OUTF(5),OUTG(5),OUTH(5),ROUT(5)
      DIMENSION POUT(5),QOUT(5),NOUTA(5),OUTB(5),OUTC(5),OUTD(5),OUTE(5)
      DIMENSION TUBE(2),IDEL(20),TDATA(20,3),NAMM(15)
      DATA ROUT/'(AE=','(AW=','(SW=','(SC=','(SR='/
      DATA X/25*0.0/,ZZ/'ZZ'/,OTH/'    '/,UP/'----'/
      CALL ASSIGN (2,'FOR005.DAT')
      CALL ASSIGN (3, 'LGLA.DAT')
      CALL ASSIGN (4, 'LGLB.DAT')
C
C     NTUBE=1 FOR ANALYTE BACKGROUND
C     NTUBE=2 FOR TUBE SCATTERED LINE
C
  106 READ(2,92)NTUBE,TUBE,WTUBE
   92 FORMAT(I1,51X,2A4,5X,F10.6)
      NT=0
      GO TO(39,94),NTUBE
   94 NT=NT+1
      READ(2,95)IDEL(NT),TDATA(NT,1),TDATA(NT,2),TDATA(NT,3)
   95 FORMAT(A2,28X,F10.5,F10.5,10X,F10.5)
      IF(IDEL(NT)-ZZ)94,96,94
   96 NT=NT-1
C
C     START NEW ANALYTE
C     READ ANALYTE HEADER CARD
C
   39 I=0
      NCNT=0
      READ(2,1)ELEM,WAVE,NCOMP,NRALE
    1 FORMAT(15A4,5X,F10.6,1X,I1,I1)
   13 I=I+1
C
C     READ SAMPLE DATA
C
      READ(2,3)NAME(I),Z(I),U(I),TR(I),TC(I),P(I),UB(I),ID(I)
    3 FORMAT(A2,8X,6(F10.5), 8X,A2)
      IF(NAME(I)-ZZ)13,5,13
    5 I=I-1
      GO TO(29,93),NTUBE
   93 DO 97 K=1,I
      DO 98 L=1,20
      IF(NAME(K)-IDEL(L))98,99,98
   98 CONTINUE
      WRITE(3,100)NAME(K)
  100 FORMAT('1FATAL ERROR, TUBE DATA MISSING FOR ',A2)
      GO TO 101
   99 TR(K)=TDATA(L,1)
      TC(K)=TDATA(L,2)
      UB(K)=TDATA(L,3)
   97 CONTINUE
      WAVE=WTUBE
      ELEM(14)=TUBE(1)
      ELEM(15)=TUBE(2)
C
```

```
C     START NEW INTERFERING FRACTION
C     READ INTERFERENCE HEADER CARD
C
   29 J=0
      NCNT=NCNT+1
      READ(2,67)HEAD,NPC
   67 FORMAT(10A4,20X,I2)
      DO 44 K = 1,15
      IF(ELEM(K)-OTH)45,46,45
   45 UNDE(K) = UP
      GO TO 44
   46 UNDE(K) = OTH
   44 CONTINUE
      DO 68 K=1,10
      IF(HEAD(K)-OTH)69,70,69
   69 UNDER(K)=UP
      GO TO 68
   70 UNDER(K)=OTH
   68 CONTINUE
      WRITE(3,8)ELEM,UNDE,HEAD,UNDER
    8 FORMAT('1',15A4,/,1X,15A4,/1X,10A4,/1X,10A4,/'0SAMPLE COMPOSITION'
     1,/1X,18('-'))
      WRITE(3,47)
   47 FORMAT(' ELEMENT  AW   ABSORP RAYLEIGH  COMPTON  PERCENT  SCAT.AB.
     1',/,)
      DO 4,K =1,I
    4 WRITE(3,7)NAME(K),Z(K),U(K),TR(K),TC(K),P(K),UB(K),ID(K)
    7 FORMAT(1X,A2,   6(F 9.1),2X,A2)
      TOT=0.0
      DO 84 K=1,I
   84 TOT=TOT+P(K)
      IF(TOT-100.2)85,85,86
   85 IF(TOT-99.8)86,91,91
   86 WRITE(3,87)TOT
   87 FORMAT(' WARNING, SAMPLE TOTAL = ',F6.2)
   91 NPCX=5*NPC
      WRITE(3,9)NPC,NPCX
    9 FORMAT('0INTERFERING FRACTION  (IN',I3,' % INCREMENTS TO',I4,
     1' %)',/' ',20('-'))
C
C     READ INTERFERENCE DATA
C
   14 J=J+1
      READ(2,3)NAMM(J),ZY(J),UY(J),TRY(J),TCY(J),PY(J),UBY(J),ID(J)
      IF(NAMM(J)-ZZ)14,11,14
   11 J=J-1
      GO TO(12,102),NTUBE
  102 DO 103 K=1,J
      DO 104 L=1,20
      IF(NAMM(K)-IDEL(L))104,105,104
  104 CONTINUE
      WRITE(3,100)NAMM(K)
      GO TO 101
  105 TRY(K)=TDATA(L,1)
      TCY(K)=TDATA(L,2)
      UBY(K)=TDATA(L,3)
  103 CONTINUE
   12 COIL=WAVE**3/(WAVE+0.0276)**3
      DO 10 K=1,J
   10 WRITE(3,7)NAMM(K),ZY(K),UY(K),TRY(K),TCY(K),PY(K),UBY(K),ID(K)
      DO 58 K=1,15
      R(K)=TR(K)
      C(K)=TC(K)
      RY(K)=TRY(K)
   58 CY(K)=TCY(K)
      NRUN=1
      TOT=0.0
      DO 88 K=1,J
   88 TOT=TOT+PY(K)
      IF(TOT-100.2)89,89,90
   89 IF(TOT-99.8)90,59,59
   90 WRITE(3,87)TOT
C
C     START NEW RUN
C     RUN = 1  FOR TOTAL SCATTER
C     RUN = 2 FOR COMPTON SCATTER ONLY
C     RUN = 3 FOR RAYLEIGH SCATTER ONLY
C     ABSN = ABSORPTION AT ANALYTE WAVELENGTH
C     ABSB = ABSORPTION AT SCATTER WAVELENGTH
C     SCAT = SCATTERING AT SCATTER WAVELENGTH
C     Y AFTER EACH IS FOR INTERFERING FRACTION
```

```
C
   59 ABSN=0.0
      ABSB=0.0
      SCAT=0.0
      DO 15 K=1,I
      ABSN=ABSN+0.01*P(K)*U(K)
      ABSB=ABSB+0.01*P(K)*UB(K)
   15 SCAT=SCAT+0.01*P(K)*((R(K)*R(K)+COIL*C(K))/Z(K))
      ABSNY=0.0
      ABSBY=0.0
      SCATY=0.0
      DO 17 K=1,J
      ABSNY=ABSNY+0.01*PY(K)*UY(K)
      ABSBY=ABSBY+0.01*PY(K)*UBY(K)
   17 SCATY=SCATY+0.01*PY(K)*((RY(K)*RY(K)+COIL*CY(K))/ZY(K))
      GO TO(60,61,61),NRUN
   60 WRITE(3,51)WAVE
   51 FORMAT('OWAVELENGTH OF SCATTERED BACKGROUND',' (A)', 6X,F10.3)
      WRITE(3,20)ABSN
   20 FORMAT(' SAMPLE ABSORPTION AT ANALYTE WAVELENGTH',6X,F7.1)
      WRITE(3,31)ABSB
   31 FORMAT(' SAMPLE ABSORPTION AT SCATTER WAVELENGTH',6X,F7.1)
      WRITE(3,22)ABSNY
   22 FORMAT(' INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH',F7.1)
      WRITE(3,32)ABSBY
   32 FORMAT(' INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH',F7.1)
   61 WRITE(3,16)SCAT
   16 FORMAT(' SAMPLE SCATTERING INTENSITY COEFFICIENT',6X,F8.2)
      WRITE(3,18)SCATY
   18 FORMAT(' INTERFERENCE SCATTERING INTENSITY COEFFICIENT',F8.2)
      ISAVE=I
      JSAVE=J
      DO 23 I=1,6
      S(I)=SCAT*(100+NPC-I*NPC)+SCATY*(I*NPC-NPC)
      AB(I)=ABSB*(100+NPC-I*NPC)+ABSBY*(I*NPC-NPC)
      B(I)=S(I)/AB(I)
   23 A(I)=ABSN*(100+NPC-I*NPC)+ABSNY*(I*NPC-NPC)
      DO 24 J=1,5
      DO 24 I=J,5
      RK=S(J)/S(I+1)
      RU=A(J)/A(I+1)
      RUB=AB(J)/AB(I+1)
      EN(I,J)=(A(J)-A(I+1))/A(I+1)*100.0
      BACK(I,J)=(B(I+1)-B(J))/B(J)*100.0
   24 X(I,J)=ALOG(RU)/ALOG(RUB/RK)
      DO 52,I=1,5
      K=6-I
      DO 52,J=1,K
      L=I+J-1
      EN(I,J)=EN(L,J)
      X(I,J)=X(L,J)
   52 BACK(I,J)=BACK(L,J)
      DO 30 I=1,5
   30 NUM(I)=NPC*(I-1)
      GO TO(37,55,55),NRUN
   37 WRITE(3,35)
   35 FORMAT('OPEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION',/' ',
     116('-'))
      WRITE(3,48)NUM
   48 FORMAT(' INCREMENTS',5(2X,'FROM ',I2,'%'),/15X,
     15(' -  '),' - % - ',5('  - '))
      DO 33 K=1,5
      LEVEL=K*NPC
      L=6-K
   33 WRITE(3,34)LEVEL,(EN(K,J),J=1,L)
   34 FORMAT('   +',I3,'%',3X,5(F10.2))
   55 WRITE(3,53)
   53 FORMAT('OBACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER',/' ',
     122('-'))
      WRITE(3,48)NUM
      DO 54,K=1,5
      LEVEL=K*NPC
      L=6-K
   54 WRITE(3,34)LEVEL,(BACK(K,J),J=1,L)
      WRITE(3,25)
   25 FORMAT('OEXPONENT VALUES',/' ---------------')
      WRITE(3,66)NUM
   66 FORMAT(' INCREMENTS',5(2X,'FROM ',I2,'%'),/3X)
```

```
      DO 26 K=1,5
      LEVEL=K*NPC
      NOUTA(K)=LEVEL
      L=6-K
   26 WRITE(3,27)LEVEL,(X(K,J),J=1,L)
   27 FORMAT('    +',I3,'%',3X,5(F10.3))
      J=JSAVE
      I=ISAVE
      GO TO(62,63,64),NRUN
C
C     STORE CONDENSED PRINTOUT DATA FROM RUN 1
C     INITIALISE FOR COMPTON-ONLY RUN 2
C
   62 POUT(1)=ABSN
      POUT(2)=ABSB
      POUT(3)=SCAT
      QOUT(1)=ABSNY
      QOUT(2)=ABSBY
      QOUT(3)=SCATY
      DO 71 K=1,5
      OUTB(K)=EN(K,1)
      OUTC(K)=BACK(K,1)
   71 OUTD(K)=X(K,1)
      NR=NCOMP+1
C
C     COMPTON SCATTERING ONLY, UNLESS 1 IN COL 77
C
      GO TO(36,63),NR
   36 DO 40 K=1,15
      C(K)=TC(K)
      CY(K)=TCY(K)
      R(K)=0.0
   40 RY(K)=0.0
      WRITE(3,65) ELEM,UNDE,HEAD,UNDER
   65 FORMAT('1',15A4,/,1X,15A4,  /1X,10A4,/1X,10A4)
      WRITE(3,42)
   42 FORMAT('0COMPTON SCATTERING ONLY',/' ',23('-'))
      NRUN=2
      GO TO 59
C
C     STORE CONDENSED PRINTOUT DATA FROM RUN 2
C     INITIALISE FOR RAYLEIGH-ONLY RUN 3
C
   63 POUT(4)=SCAT
      QOUT(4)=SCATY
      DO 72 K=1,5
      OUTE(K)=BACK(K,1)
   72 OUTF(K)=X(K,1)
      NC=NRALE+1
C
C     RALEIGH SCATTERING ONLY, UNLESS 1 IN COL 78
C
      GO TO(38,64),NC
   38 DO 41 K=1,15
      R(K)=TR(K)
      RY(K)=TRY(K)
      C(K)=0.0
   41 CY(K)=0.0
      WRITE(3,43)
   43 FORMAT('0RALEIGH SCATTERING ONLY',/' ',23('-'))
      NRUN=3
      GO TO 59
C
C     STORE CONDENSED PRINTOUT DATA FROM RUN 3
C
   64 POUT(5)=SCAT
      QOUT(5)=SCATY
      DO 73 K=1,5
      OUTG(K)=BACK(K,1)
   73 OUTH(K)=X(K,1)
C
C     PRINT OUTPUT FILE 4, CONDENSED DATA
C
      IF(NCNT-1)74,74,75
   74 WRITE(4,83)ELEM,WAVE,UNDE
   83 FORMAT('1',15A4,F7.3,' A',/1X,15A4)
      WRITE(4,76)POUT(1),POUT(2)
   76 FORMAT(2X,'(AE=',F7.2,')',/2X,'(AW=',F7.2,')')
```

```
      WRITE(4,77)POUT(3)
   77 FORMAT(2X,'(SW=',F7.2,')','    AMOUNT       PEAK    SCATTER   EXPONEN
     1T    COMPTON   EXPONENT   RAYLEIGH   EXPONENT')
      WRITE(4,78)POUT(4)
   78 FORMAT(2X,'(SC=',F7.2,')','     ADDED   INCREASE   INCREASE      VALU
     1E   INCREASE      VALUE   INCREASE      VALUE')
      WRITE(4,79)POUT(5)
   79 FORMAT(2X,'(SR=',F7.2,')',7X,'(%)',7X,'(%)',7X,'(%)',17X,'(%)',
     117X,'(%)')
   75 WRITE(4,80)HEAD
   80 FORMAT('0',10A4)
      DO 81 K=1,5
   81 WRITE(4,82)ROUT(K),QOUT(K),NOUTA(K),OUTB(K),OUTC(K),OUTD(K),OUTE(K
     1),OUTF(K),OUTG(K),OUTH(K)
   82 FORMAT(2X,A4,F7.2,')',I10,F10.2,3(F10.2,F10.3))
C
C     READ END CARD FOR RECYCLING
C     NPEAT = 1 REPEAT FOR NEW INTERFERENCE (LIMIT OF 6)
C     NPEAT = 2  REPEAT FOR NEW ANALYTE
C     NPEAT = 3  FINISH JOB AND EXIT
C     NPEAT = 4 START NEW JOB
C
      READ(2,49)NPEAT
   49 FORMAT(I1)
      GO TO(29,39,50,106),NPEAT
   50 WRITE(3,56)
   56 FORMAT('1')
      WRITE(4,56)
  101 CALL EXIT
      END
>
```

```
NICKEL IN PLANT MATERIAL                                      NI  LINE
------------------------                                      --------
VARIATION IN CARBON CONTENT
---------------------------

SAMPLE COMPOSITION
------------------
ELEMENT  AW    ABSORP RAYLEIGH   COMPTON   PERCENT   SCAT.AB.

H        1.0      0.4      0.1       1.0       4.0        0.4  NI
C       12.0      5.4      2.0       4.0      59.0        5.4  NI
N       14.0      9.1      2.5       4.8       5.0        9.1  NI
O       16.0     14.1      3.1       5.3      29.0       14.1  NI
MG      24.3     48.0      6.2       6.1       0.3       48.0  NI
P       31.0     90.0      7.6       7.3       0.3       90.0  NI
S       32.0    112.0      7.9       7.8       0.3      112.0  NI
K       39.1    180.0      9.1       9.4       1.5      180.0  NI
CA      40.1    214.0      9.7       9.7       0.6      214.0  NI

INTERFERING FRACTION  (IN  2 % INCREMENTS TO  10 %)
--------------------
C       12.0      5.4      2.0       4.0     100.0        5.4  NI

WAVELENGTH OF SCATTERED BACKGROUND (A)                 1.659
SAMPLE ABSORPTION AT ANALYTE WAVELENGTH               12.5
SAMPLE ABSORPTION AT SCATTER WAVELENGTH               12.5
INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH          5.4
INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH          5.4
SAMPLE SCATTERING INTENSITY COEFFICIENT                0.79
INTERFERENCE SCATTERING INTENSITY COEFFICIENT          0.64

PEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION
----------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%           1.15      1.16      1.17      1.19      1.20
  +  4%           2.32      2.35      2.38      2.41
  +  6%           3.52      3.57      3.61
  +  8%           4.75      4.81
  + 10%           6.02

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%           0.78      0.79      0.81      0.82      0.83
  +  4%           1.58      1.61      1.63      1.66
  +  6%           2.40      2.44      2.48
  +  8%           3.24      3.29
  + 10%           4.10

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%          1.465     1.460     1.454     1.449     1.444
  +  4%          1.462     1.457     1.452     1.446
  +  6%          1.459     1.454     1.449
  +  8%          1.457     1.451
  + 10%          1.454
```

```
NICKEL IN PLANT MATERIAL                                      NI  LINE
------------------------                                      --------
VARIATION IN CARBON CONTENT
---------------------------

COMPTON SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT              0.34
INTERFERENCE SCATTERING INTENSITY COEFFICIENT        0.32

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%           1.02      1.04      1.05      1.06      1.08
  +  4%           2.07      2.10      2.12      2.15
  +  6%           3.14      3.18      3.22
  +  8%           4.24      4.29
  + 10%           5.36

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%          1.121     1.120     1.119     1.117     1.116
  +  4%          1.121     1.119     1.118     1.116
  +  6%          1.120     1.119     1.117
  +  8%          1.119     1.118
  + 10%          1.119

RALEIGH SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT              0.45
INTERFERENCE SCATTERING INTENSITY COEFFICIENT        0.33

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%           0.60      0.61      0.62      0.63      0.64
  +  4%           1.21      1.24      1.26      1.28
  +  6%           1.84      1.88      1.91
  +  8%           2.49      2.53
  + 10%           3.15

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%          1.907     1.896     1.886     1.876     1.865
  +  4%          1.902     1.891     1.881     1.870
  +  6%          1.896     1.886     1.876
  +  8%          1.891     1.881
  + 10%          1.886
```

```
COPPER IN PLANT MATERIAL                                   CR  TUBE
------------------------                                   --------
VARIATION IN POTASSIUM CONTENT
--------------------------------

SAMPLE COMPOSITION
------------------
ELEMENT  AW    ABSORP RAYLEIGH  COMPTON  PERCENT  SCAT.AB.

H         1.0     0.4      0.3      0.9      4.0      0.5  CU
C        12.0     4.4      2.6      3.4     59.0     14.9  CU
N        14.0     7.4      3.4      3.9      5.0     25.3  CU
O        16.0    11.5      4.3      4.1     29.0     36.2  CU
MG       24.3    39.4      7.6      4.6      0.3    123.9  CU
P        31.0    73.0      8.7      5.9      0.3    228.5  CU
S        32.0    91.0      9.3      6.3      0.3    279.0  CU
K        39.1   149.0     11.3      7.3      1.5    425.0  CU
CA       40.1   178.0     12.1      7.7      0.6    490.0  CU

INTERFERING FRACTION  (IN  1 % INCREMENTS TO   5 %)
--------------------
K        39.1   149.0     11.3      7.3    100.0    425.0  CU

WAVELENGTH OF SCATTERED BACKGROUND (A)            2.291
SAMPLE ABSORPTION AT ANALYTE WAVELENGTH          10.3
SAMPLE ABSORPTION AT SCATTER WAVELENGTH          31.8
INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH   149.0
INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH   425.0
SAMPLE SCATTERING INTENSITY COEFFICIENT           1.09
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     3.45

PEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION
----------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%
                -  -     -    -  -    - % -     -    -  -    -  -
  +  1%        -11.91     -10.64      -9.62      -8.77      -8.07
  +  2%        -21.28     -19.23     -17.55     -16.13
  +  3%        -28.85     -26.32     -24.20
  +  4%        -35.09     -32.26
  +  5%        -40.33

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%
                -  -     -    -  -    - % -     -    -  -    -  -
  +  1%         -9.09      -8.01      -7.14      -6.41      -5.80
  +  2%        -16.37     -14.58     -13.09     -11.84
  +  3%        -22.34     -20.06     -18.14
  +  4%        -27.32     -24.70
  +  5%        -31.54

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%

  +  1%         1.331      1.347      1.366      1.385      1.406
  +  2%         1.338      1.356      1.375      1.395
  +  3%         1.346      1.365      1.384
  +  4%         1.354      1.373
  +  5%         1.363
```

```
COPPER IN PLANT MATERIAL                                   CR  TUBE
------------------------                                   --------
VARIATION IN POTASSIUM CONTENT
--------------------------------

COMPTON SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT            0.29
INTERFERENCE SCATTERING INTENSITY COEFFICIENT      0.18

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%
                -  -     -    -  -    - % -     -    -  -    -  -
  +  1%        -11.35     -10.26      -9.37      -8.63      -8.00
  +  2%        -20.45     -18.67     -17.19     -15.94
  +  3%        -27.91     -25.69     -23.82
  +  4%        -34.13     -31.64
  +  5%        -39.40

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%

  +  1%         1.052      1.039      1.027      1.018      1.009
  +  2%         1.046      1.033      1.023      1.013
  +  3%         1.040      1.029      1.018
  +  4%         1.035      1.024
  +  5%         1.031

RALEIGH SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT            0.80
INTERFERENCE SCATTERING INTENSITY COEFFICIENT      3.27

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%
                -  -     -    -  -    - % -     -    -  -    -  -
  +  1%         -8.27      -7.23      -6.38      -5.69      -5.11
  +  2%        -14.90     -13.15     -11.71     -10.50
  +  3%        -20.33     -18.09     -16.22
  +  4%        -24.86     -22.27
  +  5%        -28.70

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%   FROM  1%   FROM  2%   FROM  3%   FROM  4%

  +  1%         1.469      1.500      1.533      1.568      1.604
  +  2%         1.483      1.516      1.550      1.585
  +  3%         1.498      1.531      1.566
  +  4%         1.512      1.546
  +  5%         1.527
```

```
ZINC IN PLANT MATERIAL                                          AG  TUBE
------------------------                                        --------
VARIATION IN SOIL CONTAMINATION
--------------------------------

SAMPLE COMPOSITION
------------------
ELEMENT  AW    ABSORP RAYLEIGH  COMPTON  PERCENT  SCAT.AB.
H         1.0     0.4      0.0      1.0      4.0       0.4  ZN
C        12.0     3.7      0.9      5.6     59.0       0.4  ZN
N        14.0     6.1      1.1      6.3      5.0       0.6  ZN
O        16.0     9.4      1.2      7.2     29.0       0.7  ZN
MG       24.3    32.1      1.7     10.4      0.3       2.2  ZN
P        31.0    59.0      2.4     12.5      0.3       4.1  ZN
S        32.0    73.5      2.8     13.1      0.3       5.0  Z
K        39.1   122.5      4.0     15.0      1.5       8.3  ZN
CA       40.1   147.5      4.3     15.7      0.6      10.0  ZN

INTERFERING FRACTION  (IN  1 % INCREMENTS TO   5 %)
--------------------
O        16.0     9.4      1.2      7.2     49.0       0.7  ZN
NA       23.0    23.5      1.5      9.5      1.5       1.5  ZN
MG       24.3    32.1      1.7     10.4      1.0       2.2  ZN
AL       27.0    40.0      1.9     11.0     10.0       2.7  ZN
SI       28.1    50.3      2.1     11.8     31.0       3.3  ZN
K        39.1   122.5      4.0     15.0      1.0       8.3  ZN
CA       40.1   147.5      4.3     15.7      1.0      10.0  ZN
TI       47.9   168.0      5.0     16.7      0.5      12.0  ZN
FE       55.8   263.0      5.8     19.4      5.0      20.0  ZN

WAVELENGTH OF SCATTERED BACKGROUND (A)            0.561
SAMPLE ABSORPTION AT ANALYTE WAVELENGTH           8.4
SAMPLE ABSORPTION AT SCATTER WAVELENGTH           0.7
INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH    41.5
INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH     3.0
SAMPLE SCATTERING INTENSITY COEFFICIENT           0.50
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.52

PEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION
----------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%
                  -   -   -  -   -  - % -   -  -   -   -  -
  +  1%         -3.79     -3.65     -3.52     -3.40     -3.29
  +  2%         -7.30     -7.05     -6.81     -6.58
  +  3%        -10.57    -10.21     -9.87
  +  4%        -13.61    -13.17
  +  5%        -16.46

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%
                  -   -   -  -   -  - % -   -  -   -   -  -
  +  1%         -3.04     -2.95     -2.86     -2.78     -2.70
  +  2%         -5.91     -5.73     -5.57     -5.41
  +  3%         -8.60     -8.35     -8.12
  +  4%        -11.14    -10.83
  +  5%        -13.55

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%

  +  1%         1.250     1.242     1.234     1.227     1.221
  +  2%         1.246     1.238     1.231     1.224
  +  3%         1.242     1.235     1.228
  +  4%         1.239     1.231
  +  5%         1.235
```

```
ZINC IN PLANT MATERIAL                                          AG  TUBE
------------------------                                        --------
VARIATION IN SOIL CONTAMINATION
--------------------------------

COMPTON SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT           0.42
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.37

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%
                  -   -   -  -   -  - % -   -  -   -   -  -
  +  1%         -3.19     -3.10     -3.01     -2.93     -2.85
  +  2%         -6.19     -6.01     -5.85     -5.70
  +  3%         -9.01     -8.77     -8.53
  +  4%        -11.67    -11.37
  +  5%        -14.19

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%

  +  1%         1.192     1.183     1.174     1.165     1.157
  +  2%         1.188     1.178     1.170     1.161
  +  3%         1.183     1.174     1.166
  +  4%         1.179     1.170
  +  5%         1.175

RALEIGH SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT           0.09
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.15

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%
                  -   -   -  -   -  - % -   -  -   -   -  -
  +  1%         -2.35     -2.26     -2.18     -2.10     -2.03
  +  2%         -4.56     -4.39     -4.23     -4.09
  +  3%         -6.63     -6.40     -6.18
  +  4%         -8.60     -8.30
  +  5%        -10.45

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  1%  FROM  2%  FROM  3%  FROM  4%

  +  1%         1.626     1.627     1.629     1.631     1.633
  +  2%         1.627     1.628     1.630     1.632
  +  3%         1.627     1.629     1.631
  +  4%         1.628     1.630
  +  5%         1.629
```

```
RUBIDIUM IN SOIL                                              W L TUBE
----------------                                              --------
VARIATION IN ORGANIC MATERIAL
--------------------------------

SAMPLE COMPOSITION
------------------
ELEMENT  AW    ABSORP RAYLEIGH  COMPTON  PERCENT  SCAT.AB.

O       16.0     2.7      2.7      5.6     49.0     10.1  RB
NA      23.0     6.7      4.9      6.3      1.5     25.5  RB
MG      24.3     9.0      5.6      6.6      1.0     34.7  RB
AL      27.0    11.4      6.3      6.9     10.0     43.0  RB
SI      28.1    14.5      6.8      7.3     31.0     54.5  RB
K       39.1    34.7      8.5     10.0      1.0    132.0  RB
CA      40.1    41.5      9.0     10.4      1.0    159.0  RB
TI      47.9    50.7     10.0     10.0      0.5    180.0  RB
FE      55.8    80.0     12.7     11.3      5.0    283.0  RB

INTERFERING FRACTION  (IN 10 % INCREMENTS TO  50 %)
--------------------
H        1.0     0.4      0.1      1.0      4.0      0.4  RB
C       12.0     1.2      1.8      4.2     59.0      4.0  RB
N       14.0     1.8      2.2      5.0      5.0      6.6  RB
O       16.0     2.7      2.7      5.6     29.0     10.1  R
MG      24.3     9.0      5.6      6.6      0.3     34.7  RB
P       31.0    16.8      7.2      7.8      0.3     59.0  R
S       32.0    20.5      7.5      8.3      0.3     74.0  RB
K       39.1    34.7      8.5     10.0      1.5    132.0  RB
CA      40.1    41.5      9.0     10.4      0.6    159.0  R

WAVELENGTH OF SCATTERED BACKGROUND (A)          1.476
SAMPLE ABSORPTION AT ANALYTE WAVELENGTH        12.1
SAMPLE ABSORPTION AT SCATTER WAVELENGTH        44.8
INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH   2.5
INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH   9.0
SAMPLE SCATTERING INTENSITY COEFFICIENT         1.39
INTERFERENCE SCATTERING INTENSITY COEFFICIENT   0.72

PEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION
----------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%
                -  -    -   -  -   - % -    -   -  -   -  -
  + 10%          8.64      9.45     10.44     11.66     13.20
  + 20%         18.91     20.88     23.32     26.39
  + 30%         31.32     34.97     39.59
  + 40%         46.63     52.79
  + 50%         65.98

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%
                -  -    -   -  -   - % -    -   -  -   -  -
  + 10%          3.46      3.98      4.63      5.46      6.56
  + 20%          7.58      8.79     10.34     12.38
  + 30%         12.56     14.73     17.58
  + 40%         18.70     22.26
  + 50%         26.49

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%

  + 10%         2.436     2.315     2.194     2.073     1.952
  + 20%         2.372     2.250     2.129     2.007
  + 30%         2.304     2.182     2.060
  + 40%         2.232     2.109
  + 50%         2.157
```

```
RUBIDIUM IN SOIL                                              W L TUBE
----------------                                              --------
VARIATION IN ORGANIC MATERIAL
--------------------------------

COMPTON SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT           0.28
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.35

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%
                -  -    -   -  -   - % -    -   -  -   -  -
  + 10%         11.31     12.09     13.05     14.25     15.79
  + 20%         24.76     26.71     29.16     32.28
  + 30%         41.04     44.77     49.55
  + 40%         61.14     67.62
  + 50%         86.58

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%

  + 10%         0.773     0.792     0.810     0.828     0.846
  + 20%         0.783     0.801     0.819     0.837
  + 30%         0.792     0.811     0.829
  + 40%         0.802     0.821
  + 50%         0.812

RALEIGH SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT           1.10
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.37

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%
                -  -    -   -  -   - % -    -   -  -   -  -
  + 10%          1.43      1.68      2.00      2.42      2.99
  + 20%          3.14      3.72      4.47      5.49
  + 30%          5.21      6.23      7.60
  + 40%          7.75      9.41
  + 50%         10.98

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%  FROM 10%  FROM 20%  FROM 30%  FROM 40%

  + 10%         5.818     5.414     5.010     4.606     4.202
  + 20%         5.600     5.195     4.789     4.383
  + 30%         5.370     4.962     4.553
  + 40%         5.125     4.712
  + 50%         4.863
```

```
STRONTIUM IN SOIL                                         MO  TUBE
--------------------                                      --------
VARIATION IN IRON CONTENT (OXIDE)
------------------------------------

SAMPLE COMPOSITION
------------------
ELEMENT  AW    ABSORP RAYLEIGH  COMPTON  PERCENT  SCAT.AB.

O       16.0     2.3      1.4       6.8     49.0       1.3  SR
NA      23.0     5.7      2.0       9.1      1.5       3.2  SR
MG      24.3     7.7      2.2       9.7      1.0       4.2  SR
AL      27.0     9.6      2.6      10.4     10.0       5.2  SR
SI      28.1    12.3      3.0      10.9     31.0       6.6  SR
K       39.1    30.2      5.3      13.8      1.0      15.8  SR
CA      40.1    35.5      5.6      14.4      1.0      19.0  SR
TI      47.9    43.6      6.1      15.3      0.5      23.0  SR
FE      55.8    69.5      6.8      17.7      5.0      40.0  SR

INTERFERING FRACTION  (IN  2 % INCREMENTS TO  10 %)
--------------------
FE      55.8    69.5      6.8      17.7     70.0      40.0  SR
O       16.0     2.3      1.4       6.8     30.0       1.3  SR

WAVELENGTH OF SCATTERED BACKGROUND (A)           0.710
SAMPLE ABSORPTION AT ANALYTE WAVELENGTH         10.4
SAMPLE ABSORPTION AT SCATTER WAVELENGTH          5.8
INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH   49.3
INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH   28.4
SAMPLE SCATTERING INTENSITY COEFFICIENT          0.61
INTERFERENCE SCATTERING INTENSITY COEFFICIENT    0.94

PEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION
----------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        -6.96     -6.51     -6.11     -5.76     -5.44
  +  4%       -13.01    -12.22    -11.52    -10.89
  +  6%       -18.33    -17.27    -16.33
  +  8%       -23.03    -21.78
  + 10%       -27.22

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        -6.29     -5.80     -5.37     -5.00     -4.67
  +  4%       -11.72    -10.86    -10.10     -9.44
  +  6%       -16.46    -15.32    -14.30
  +  8%       -20.64    -19.27
  + 10%       -24.34

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        1.111     1.127     1.142     1.156     1.171
  +  4%        1.119     1.134     1.149     1.163
  +  6%        1.126     1.141     1.155
  +  8%        1.132     1.147
  + 10%        1.139
```

```
STRONTIUM IN SOIL                                         MO  TUBE
--------------------                                      --------
VARIATION IN IRON CONTENT (OXIDE)
------------------------------------

COMPTON SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT          0.36
INTERFERENCE SCATTERING INTENSITY COEFFICIENT    0.31

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        -7.51     -7.02     -6.59     -6.21     -5.88
  +  4%       -14.00    -13.15    -12.40    -11.73
  +  6%       -19.67    -18.55    -17.55
  +  8%       -24.66    -23.34
  + 10%       -29.09

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        0.924     0.924     0.925     0.924     0.924
  +  4%        0.924     0.924     0.924     0.924
  +  6%        0.924     0.924     0.924
  +  8%        0.924     0.924
  + 10%        0.924

RALEIGH SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT          0.25
INTERFERENCE SCATTERING INTENSITY COEFFICIENT    0.63

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        -4.56     -4.13     -3.76     -3.44     -3.16
  +  4%        -8.51     -7.74     -7.08     -6.50
  +  6%       -11.95    -10.92    -10.02
  +  8%       -14.98    -13.74
  + 10%       -17.67

EXPONENT VALUES
---------------
INCREMENTS  FROM  0%  FROM  2%  FROM  4%  FROM  6%  FROM  8%

  +  2%        1.545     1.594     1.644     1.692     1.741
  +  4%        1.568     1.618     1.667     1.716
  +  6%        1.591     1.640     1.690
  +  8%        1.613     1.662
  + 10%        1.634
```

```
ZIRCONIUM IN SOIL                                            AU  TUBE
-----------------                                            --------
VARIATION IN SILICON CONTENT (OXIDE)
------------------------------------

SAMPLE COMPOSITION
------------------
ELEMENT   AW    ABSORP RAYLEIGH  COMPTON  PERCENT  SCAT.AB.

O        16.0      1.7      2.3      5.9     49.0      6.6  ZR
NA       23.0      4.2      4.2      7.0      1.5     16.5  ZR
MG       24.3      5.7      4.9      7.3      1.0     23.0  ZR
AL       27.0      7.0      5.5      7.6     10.0     28.0  ZR
SI       28.1      8.9      6.1      8.0     31.0     35.0  ZR
K        39.1     22.1      7.7     10.8      1.0     83.0  ZR
CA       40.1     26.1      8.1     11.3      1.0    105.0  09
TI       47.9     32.0      9.0     11.2      0.5    122.0  ZR
FE       55.8     51.6     11.2     12.6      5.0    192.0  ZR

INTERFERING FRACTION  (IN  5 % INCREMENTS TO  25 %)
--------------------
SI       28.1      8.9      6.1      8.0     47.0     35.0  ZR
O        16.0      1.7      2.3      5.9     53.0      6.6  ZR

WAVELENGTH OF SCATTERED BACKGROUND (A)            1.278
SAMPLE ABSORPTION AT ANALYTE WAVELENGTH           7.7
SAMPLE ABSORPTION AT SCATTER WAVELENGTH          29.5
INTERFERENCE ABSORPTION AT ANALYTE WAVELENGTH     5.1
INTERFERENCE ABSORPTION AT SCATTER WAVELENGTH    19.9
SAMPLE SCATTERING INTENSITY COEFFICIENT           1.16
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     1.11

PEAK ENHANCEMENT, FROM VARIATION IN ABSORPTION
----------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%
                -  -    -   -  -    - % -   -   -  -   -   -
  +  5%          1.69      1.72      1.75      1.78      1.82
  + 10%          3.44      3.50      3.57      3.63
  + 15%          5.26      5.35      5.45
  + 20%          7.13      7.26
  + 25%          9.08

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%
                -  -    -   -  -    - % -   -   -  -   -   -
  +  5%          1.40      1.43      1.46      1.48      1.51
  + 10%          2.85      2.90      2.96      3.02
  + 15%          4.35      4.43      4.52
  + 20%          5.89      6.01
  + 25%          7.50

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%

  +  5%         1.207     1.205     1.202     1.200     1.198
  + 10%         1.206     1.203     1.201     1.199
  + 15%         1.204     1.202     1.200
  + 20%         1.203     1.201
  + 25%         1.202
```

```
ZIRCONIUM IN SOIL                                            AU  TUBE
-----------------                                            --------
VARIATION IN SILICON CONTENT (OXIDE)
------------------------------------

COMPTON SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT           0.30
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.31

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%
                -  -    -   -  -    - % -   -   -  -   -   -
  +  5%          1.74      1.77      1.80      1.83      1.86
  + 10%          3.54      3.60      3.66      3.72
  + 15%          5.41      5.49      5.58
  + 20%          7.33      7.45
  + 25%          9.33

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%

  +  5%         0.972     0.973     0.975     0.976     0.978
  + 10%         0.972     0.974     0.975     0.977
  + 15%         0.973     0.975     0.976
  + 20%         0.974     0.975
  + 25%         0.975

RALEIGH SCATTERING ONLY
-----------------------
SAMPLE SCATTERING INTENSITY COEFFICIENT           0.86
INTERFERENCE SCATTERING INTENSITY COEFFICIENT     0.80

BACKGROUND ENHANCEMENT, FROM VARIATION IN SCATTER
----------------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%
                -  -    -   -  -    - % -   -   -  -   -   -
  +  5%          1.28      1.31      1.33      1.36      1.39
  + 10%          2.60      2.66      2.71      2.77
  + 15%          3.97      4.05      4.14
  + 20%          5.39      5.50
  + 25%          6.85

EXPONENT VALUES
---------------
INCREMENTS   FROM  0%  FROM  5%  FROM 10%  FROM 15%  FROM 20%

  +  5%         1.320     1.316     1.312     1.308     1.304
  + 10%         1.318     1.314     1.310     1.306
  + 15%         1.316     1.312     1.308
  + 20%         1.313     1.310
  + 25%         1.311
```

APPENDIX 3

```
C
C     PROGRAM HXSTD ANALYSES X-RAY FLUORESCENCE DATA
C     FROM SAMPLES OF KNOWN CONTENT TO FIND EQUATION
C     PARAMETERS TO APPLY TO UNKNOWN SAMPLES
C     S = CHEMICAL CONCENTRATION
C     R = PEAK COUNTRATE
C     E = ERROR PEAK COUNTRATE
C     L = IGNITION LOSS
C     B = BACKGROUND COUNTRATE
C     BE = ERROR BACKGROUND COUNTRATE
C     A = WORKING FILE
C     C = WORKING FILE
C     BETA = IGNITION LOSS FACTOR
C     T = BACKGROUND EXPONENT
C
      REAL L(40)
      REAL*8 CA,CB,GA,GB,GRAD,CEPT,EGA,ECA,EGB,ECB
      DIMENSION NAME(15,40),INAME(15),S(40),R(40),E(40),A(40)
      DIMENSION B(40),F(20),BE(40),HEAD(10),C(40)
      COMMON NUM
      CALL ASSIGN (3, 'ZR.DAT')
      CALL ASSIGN (2,'FOR005.DAT')
      STD=-1.0
      NUM=0
      NREF=0
C
C     READ HEADER CARD
C
      READ(2,60)HEAD,T,BETA,EB
   60 FORMAT(10A4,3(F10.5))
      BUF1=100.0*EB/(BETA+1.E-8)
      IF(BUF1)63,64,64
   63 BUF1=-BUF1
   64 WRITE(3,27)HEAD
   27 FORMAT('1X-RAY FLUORESCENCE    ',10A4,/,
     119('-'),/,
     2'0PROGRAM A    DETERMINATION OF EQUATION PARAMETERS',
     3/10('-'))
      WRITE(3,51)T,BETA,EB,BUF1
   51 FORMAT('0BACKGROUND EXPONENTIAL ',F12.5,/
     1'0IGNITION LOSS FACTOR ',F14.5,' + ',F7.5,' (',F5.2,
     2')',/)
      WRITE(3,70)
   70 FORMAT('0COUNTING DATA',23X,'PEAK      BACKGROUND',/,
     114('-'),23X,'----',6X,10('-'),/33X,
     2'COUNTS TIME  COUNTS TIME   P/B',/,33X,11('-'),2X,
     311('-'),'   ---')
C
C     READ COUNTING DATA ONE CARD AT A TIME
C
   24 READ(2,3)ICODE,PEAK,TIME,BACK,SEC,ORGAN,SULP,INAME
    3 FORMAT(I1,F9.0,F5.0,F10.0,F5.0,F10.1,F9.0,1X,15A2)
      SEC=SEC+1.E-2
      BACK=BACK+1.E-6
      GO TO(6,6,98),ICODE
C
C     CALCULATE COUNTRATE
C
    6 CP=PEAK/TIME
      CB=BACK/SEC
      CP=CP/(1.0-CP*2.E-6)
      CB=CB/(1.0-CB*2.E-6)
      COUNT=CP-CB
      FIG=(CP/CB)**0.5*SEC/TIME
      PLUS=(CP/TIME+CB/SEC)**0.5
      CBE=(BACK)**0.5/SEC
      GO TO(10,11),ICODE
C
C     DATA CARD IS REFERENCE CARD
C
   11 NBAT=0
      NREF=NREF+1
      IF(STD)12,12,13
   12 STD=COUNT
      NSEC=1
      WRITE(3,23)INAME,COUNT,NSEC
      GO TO 24
```

```
   13 FAC=COUNT/STD
      FACER=PLUS/STD
      PFAC=(COUNT-STD)/STD*100.0
      WRITE(3,16)PFAC
   16 FORMAT('0DRIFT FACTOR (PERCENT) ',F7.3)
      GO TO 24
C
C     DATA CARD IS SAMPLE CARD
C
   10 NBAT=NBAT+1
      NUM=NUM+1
      IF(NREF-2)34,35,35
   34 WRITE(3,36)
   36 FORMAT('0INITIAL REFERENCE CARD MISSING')
      GO TO 99
   35 IF(NBAT-3)20,20,21
   21 WRITE(3,22)
   22 FORMAT('0MORE THAN 4 SAMPLES PER BATCH')
      GO TO 99
   20 IF(NUM-40)30,30,32
   32 WRITE(3,33)
   33 FORMAT('0STORAGE LIMIT OF 40 SAMPLES')
      NUM=40
      GO TO 98
   30 PLUS=(PLUS/FAC*PLUS/FAC+(COUNT/FAC*FACER/FAC)**2)**0.5
      COUNT=COUNT/FAC
      DO 31 I=1,15
   31 NAME(I,NUM)=INAME(I)
      R(NUM)=COUNT
      E(NUM)=PLUS
      L(NUM)=ORGAN
      S(NUM)=SULP
      C(NUM)=1.0
      B(NUM)=CB
      BE(NUM)=CBE
      NTIME=IFIX(TIME)
      NSEC=IFIX(SEC)
      WRITE(3,23)INAME,PEAK,NTIME,BACK,NSEC,FIG
   23 FORMAT('0',15A2,F9.0,I4,F8.0,I4,3X,F4.2)
      GO TO 24
C
C     PRINT COUNTRATES
C
   98 WRITE(3,27)HEAD
      WRITE(3,71)
   71 FORMAT('0ANALYSIS DATA',19X,
     1'NET C/S          ERROR      CONC',/14('-'),19X,
     221('-'),'      ----')
      DO 72 I=1,NUM
      COUNT=R(I)
      PLUS=E(I)
      NSEC=IFIX(S(I))
      DEV=PLUS*100.0/COUNT
   72 WRITE(3,50)(NAME(J,I),J=1,15),COUNT,PLUS,DEV,NSEC
      IF(NUM-3)57,58,58
   57 WRITE(3,59)
   59 FORMAT('0INSUFFICIENT NUMBER OF SAMPLES')
      GO TO 99
   58 WRITE(3,1)
    1 FORMAT('0',/,'0REGRESSION ANALYSIS - NET C/S VS CONC',
     1/20('-'))
      CALL HXREG(C,R,S,GA,EGA,CA,ECA,1)
      EGG=EGA/GA/GA
      ECC=((ECA/GA)**2+(EGG*CA)**2)**0.5
      CALL HXREG(C,S,R,GB,EGB,CB,ECB,2)
      EG=(EGG+EGB)/2.0
      EC=(ECC+ECB)/2.0
      CALL HXBIS(GA,GB,CA,CB,GRAD,CEPT)
      DEV=100.0*EG/GRAD
      FIG=100.0*EC/CEPT
      IF(FIG)67,68,68
   67 FIG=-FIG
   68 WRITE(3,75)
      WRITE(3,76)GRAD,EG,DEV,CEPT,EC,FIG
C
C     PRINT BACKGROUND COUNTRATES
C
      WRITE(3,27)HEAD
      WRITE(3,53)
```

```
 53 FORMAT('OMATRIX DATA',19X,
     1'BACKGROUND C/S   ERROR       LOSS',/12('-'),19X,
     222('-'),'      ----')
      DO 52 I = 1,NUM
      COUNT=B(I)
      PLUS = BE(I)
      DEV = PLUS*100.0/COUNT
      ORGAN = L(I)
 52 WRITE(3,47)(NAME(J,I),J=1,15),COUNT,PLUS,DEV,ORGAN
 47 FORMAT('0',15A2,F8.2,' + ',F5.2,'(',F5.2,')',F8.1)
C
C     CORRECT USING LOSS ON IGNITION
C
      IF(BETA)55,54,55
 55 WRITE(3,27)HEAD
      WRITE(3,40)
 40 FORMAT('OCORRECTED FOR IGNITION LOSS',6X,
     1'CORRECTED C/S   ERROR    CONC',/28('-'), 6X,21('-'),
     2'    ----')
      DO 74 I=1,NUM
      NSEC=IFIX(S(I))
      A(I)=1.000+BETA*L(I)
      ER=((R(I)*L(I)*EB)**2+(E(I)*A(I))**2)**0.5
      R(I)=R(I)*A(I)
      ERROR=100.0*ER/R(I)
      E(I)=ER
 74 WRITE(3,50)(NAME(J,I),J=1,15),R(I),ER,ERROR,NSEC
 50 FORMAT('0',15A2,F8.2,' + ',F5.2,' (',F5.2,')',I8)
      WRITE(3,61)
 61 FORMAT('0',/,'OREGRESSION ANALYSIS - CORRECTED C/S VS',
     1' CONC',/20('-'))
      CALL HXREG(C,R,S,GA,EGA,CA,ECA,1)
      EGG=EGA/GA/GA
      ECC=((ECA/GA)**2+(EGG*CA)**2)**0.5
      CALL HXREG(C,S,R,GB,EGB,CB,ECB,2)
      EG=(EGG+EGB)/2.0
      EC=(ECC+ECB)/2.0
      CALL HXBIS(GA,GB,CA,CB,GRAD,CEPT)
      DEV=100.0*EG/GRAD
      FIG=100.0*EC/CEPT
      IF(FIG)65,66,66
 65 FIG=-FIG
 66 WRITE(3,75)
      WRITE(3,76)GRAD,EG,DEV,CEPT,EC,FIG
C
C     CORRECT USING BACKGROUND SCATTER
C
 54 IF(T)45,46,45
 45 WRITE(3,27)HEAD
      WRITE(3,44)
 44 FORMAT('OPEAK TO BACKGROUND RATIO',9X,
     1'RATIO',10X,'ERROR    CONC',/25('-'),9X,20('-'),
     2'    ----')
      DO 43 I = 1,NUM
      NSEC = IFIX(S(I))
      E(I)=((E(I)/B(I)**T)**2+(R(I)*BE(I)/B(I)**(T+1.0))**2)
      E(I)=E(I)**0.5
      R(I)=R(I)/B(I)**T
      ERROR=100.0*E(I)/R(I)
 43 WRITE(3,48)(NAME(J,I),J=1,15),R(I),E(I),ERROR,NSEC
 48 FORMAT('0',15A2,F8.4,' + ',F5.2,' (',F5.2,')',I7)
      WRITE(3,62)
 62 FORMAT('0',/,'OREGRESSION ANALYSIS - PEAK/BACKGROUND',
     1' RATIO',/20('-'))
      CALL HXREG(C,R,S,GA,EGA,CA,ECA,1)
      EGG=EGA/GA/GA
      ECC=((ECA/GA)**2+(EGG*CA)**2)**0.5
      CALL HXREG(C,S,R,GB,EGB,CB,ECB,2)
      EG=(EGG+EGB)/2.0
      EC=(ECC+ECB)/2.0
      CALL HXBIS(GA,GB,CA,CB,GRAD,CEPT)
      DEV=100.0*EG/GRAD
      FIG=100.0*EC/CEPT
      IF(FIG)77,78,78
 77 FIG=-FIG
 78 WRITE(3,75)
 75 FORMAT(/,/'OLINEAR COEFFICIENTS',/20('-'))
      WRITE(3,76)GRAD,EG,DEV,CEPT,EC,FIG
 76 FORMAT('OGRADIENT  (CONC/UNIT)',F10.3,' + ',F7.3,' (',
     1F5.2,')',/'OINTERCEPT (CONC)',F15.3,' + ',F7.3,' (',
     2F5.2,')')
```

```
C
C     BACK SUBSTITUTE PARAMETERS TO ORIGINAL DATA
C
   46 WRITE(3,27)HEAD
      WRITE(3,91)
   91 FORMAT('OCALCULATED VS CHEMICAL CONTENT',4X,
     1'COMPUTED CONC      CHEM  DIFF',/31('-'),4X,13('-'),
     25X,'----  ----')
      SUM=0.0
      DO 93 I=1,NUM
      SULP=GRAD*R(I)+CEPT
      ERROR=((E(I)*GRAD)**2+(R(I)*EG)**2+EC*EC)**0.5
      DEV=100.0*ERROR/SULP
      CORR=(SULP-S(I))/ERROR
      NSEC=IFIX(S(I))
      SUM=SUM+CORR
      B(I)=CORR
   93 WRITE(3,92)(NAME(J,I),J=1,15),SULP,ERROR,DEV,NSEC,CORR
   92 FORMAT('0',15A2,F7.1,' + ',F4.1,'(',F5.2,')',I5,F6.2)
      AVER=SUM/NUM
      SUM=0.0
      DO 94 I=1,NUM
   94 SUM=SUM+(AVER-B(I))**2
      SUM=(SUM/(NUM-1))**0.5
      WRITE(3,95)AVER,SUM
   95 FORMAT(/,/'OMEAN OF DIFFERENCES',F8.4,/,
     1'OSTANDARD DEVIATION',F9.4)
C
C     PRINT REFERENCE PARAMETERS
C
      BUF1=100.0*EB/(BETA+1.E-8)
      IF(BUF1)85,84,84
   85 BUF1=-BUF1
   84 WRITE(3,80)HEAD
   80 FORMAT('1STANDARD PARAMETERS',3X,10A4,/20('-'))
      WRITE(3,81)T,BETA,EB,BUF1
   81 FORMAT('OBACKGROUND EXPONENTIAL ',F12.5,/
     1'OIGNITION LOSS FACTOR ',F14.5,' + ',F7.5,'   (',F5.2,
     2')')
      CB=100.0*EG/GRAD
      CP=100.0*EC/CEPT
      IF(CP)82,83,83
   82 CP=-CP
   83 WRITE(3,4)GRAD,EG,CB,CEPT,EC,CP,STD
    4 FORMAT('OGRADIENT (CONC/UNIT)',F13.4,'   +',F8.4,
     1'   (',F5.2,')',/'OINTERCEPT (CONC)',F16.3,'    +',
     2F8.3,'   (',F5.2,')',/'OREFERENCE COUNTRATE',F12.2,/)
   99 CONTINUE
      CALL EXIT
      END
C
C
      SUBROUTINE HXBIS(GA,GB,CA,CB,GRAD,CEPT)
C
C     SUBROUTINE HXBIS BISECTS X ON Y AND Y ON X REGRESSIONS
C     TO OBTAIN GRADIENT AND INTERCEPT OF THE BISECTOR LINE.
C     GA AND CA ARE FOR Y TAKEN AS ACCURATE
C     GB AND CB ARE FOR X TAKEN AS ACCURATE
C     OUTPUT EQUATION Y = GRAD*X + CEPT
C     OUTPUT AS Y = CHEMICAL CONCENTRATION
C     OUTPUT AS X = COUNTRATE UNIT
C
      REAL*8 GA,GB,CA,CB,GRAD,CEPT,SA,SB,A,B,C
      COMMON NUM
      CA = -CA/GA
      GA = 1.0/GA
      SA=DSQRT(1.0+GA*GA)
      SB =DSQRT(1.0+GB*GB)
      P=1.0
    3 A = SA*GB-P*SB*GA
      B = SA-P*SB
      C = SA*CB-P*SB*CA
      GRAD = A/B
      CEPT = C/B
      IF(GRAD)1,2,2
    1 P=-1.0
      GO TO 3
    2 RETURN
      END
C
```

```
C
      SUBROUTINE HXREG(A,R,S,GRAD,EG,CEPT,EC,N)
C
C     SUBROUTINE HXREG PREFORMS A LINEAR REGRESSION OF R ON S
C     ACCORDING TO THE EQUATION  R = GRAD*S + CEPT  WHERE
C     ARRAY S IS CHEMICAL CONTENT TAKEN AS ACCURATE (X)
C     ARRAY R IS FLUORESCENCE COUNTRATE (Y)
C     ARRAY A IS WEIGHT ASSIGNED TO EACH PAIR OF (S,R)
C     N = 1, NORMAL PRINTOUT
C     N = 2, PRINTOUT HEADING REVERSED
C
      REAL*8 GRAD,CEPT,EG,EC,D,W,WX,WY,WXX,WXY,WDD
      REAL*8 DELTA,SUM,CORR,WYY
      DIMENSION A(1),R(1),S(1)
      COMMON NUM
      W=0.0
      WX=0.0
      WY=0.0
      WXX=0.0
      WXY=0.0
      WYY=0.0
      WDD=0.0
      DO 2 I=1,NUM
      W=W+A(I)
      WY=WY+A(I)*R(I)
      WX=WX+A(I)*S(I)
      WYY=WYY+A(I)*R(I)*R(I)
      WXY=WXY+A(I)*R(I)*S(I)
    2 WXX=WXX+S(I)*S(I)*A(I)
      DELTA=W*WXX-WX*WX
      GRAD=(W*WXY-WX*WY)/DELTA
      CEPT=(WY*WXX-WX*WXY)/DELTA
      DO 4 I=1,NUM
      D= GRAD*S(I)+CEPT-R(I)
    4 WDD=WDD+A(I)*D*D
      SUM=WDD
      WDD=WDD/(NUM-2)
      EG =(W*WDD/DELTA)**0.5
      EC =(WXX*WDD/DELTA)**0.5
      CORR=((WXX-WX*WX/W)*(WYY-WY*WY/W))**0.5
      CORR=(WXY-WX*WY/W)/CORR
      WX=EG*100.0/GRAD
      WY=EC*100.0/CEPT
      IF(WY)60,61,61
   60 WY=-WY
   61 GO TO(1,3),N
    1 WRITE(3,5)GRAD,EG,WX,CEPT,EC,WY,CORR,SUM
    5 FORMAT('0GRADIENT  (UNIT/CONC) ',F15.6,' + ',F11.6,' (',
     1F5.2,')',/'0INTERCEPT (UNIT)',F18.3,4X,'+',F9.3,4X,'(',
     2F5.2,')',/,'0CORRELATION COEFFICIENT ',F13.6,
     3/'0SUM OF RESIDUALS SQUARED',F13.1)
      GO TO 7
    3 WRITE(3,6)GRAD,EG,WX,CEPT,EC,WY,CORR,SUM
    6 FORMAT('0GRADIENT  (CONC/UNIT) ',F15.6,' + ',F11.6,' (',
     1F5.2,')',/'0INTERCEPT (CONC)',F18.3,4X,'+',F9.3,4X,'(',
     2F5.2,')',/,'0CORRELATION COEFFICIENT ',F13.6,
     3/'0SUM OF RESIDUALS SQUARED',F13.1)
    7 RETURN
      END
```

```
C      PROGRAM HXRAY CALCULATES UNKNOWN CONCENTRATIONS
C      FROM PARAMETERS ON TWO REFERENCE CARDS
C      FROM PREVIOUS EXECUTION OF HXSTD
C      R = PEAK COUNTRATE
C      E = ERROR PEAK COUNTRATE
C      L = IGNITION LOSS
C      B = BACKGROUND COUNTRATE
C      BE = ERROR BACKGROUND COUNTRATE
C      A = WORKING FILE
C      BETA = IGNITION LOSS FACTOR
C      T = BACKGROUND EXPONENT
C
       REAL L(80)
       DIMENSION NAME(15,80),INAME(15),R(80),E(80),F(20)
       DIMENSION B(80),BE(80),HEAD(10),PARA(10),A(80)
       CALL ASSIGN (2,'FTN5.DAT')
       CALL ASSIGN (3, 'FTN6.DAT',0,'NEW','CC')
       NUM=0
       NREF=0
       READ(2,60)HEAD
    60 FORMAT(10A4)
C
C      READ PARAMETERS FROM TWO REFERENCE C ARDS
C
       READ(2,66)PARA,T,BETA,EB,STD
    66 FORMAT(10A4,3(F10.5),F10.0)
       READ(2,67)GRAD,EG,CEPT,EC
    67 FORMAT(40X,4(F10.3))
       BUF1=100.0*EB/(BETA+1.E-8)
       IF(BUF1)65,64,64
    65 BUF1=-BUF1
    64 WRITE(3,27)HEAD
    27 FORMAT('1X-RAY FLUORESCENCE   ',10A4,/,
      119('-'),/,
      2'0PROGRAM B    EVALUATION OF UNKNOWN CONCENTRATIONS',
      3/10('-'))
       WRITE(3,1)PARA
     1 FORMAT('0PARAMETERS USED',3X,10A4,/16('-'))
       WRITE(3,51)T,BETA,EB,BUF1
    51 FORMAT('0BACKGROUND EXPONENTIAL ',F12.5,/
      1'0IGNITION LOSS FACTOR ',F14.5,' + ',F7.5,'   (',F5.2,
      2')')
       CB=100.0*EG/GRAD
       CP=100.0*EC/CEPT
       IF(CP)62,63,63
    62 CP=-CP
    63 WRITE(3,4)GRAD,EG,CB,CEPT,EC,CP,STD
     4 FORMAT('0GRADIENT (CONC/UNIT)',F13.4,'   +',F8.4,
      1'   (',F5.2,')',/'0INTERCEPT (CONC)',F16.3,'    +',
      2F8.3,'   (',F5.2,')',/'0REFERENCE COUNTRATE',F12.2,/)
       WRITE(3,70)
    70 FORMAT('0COUNTING DATA',23X,'PEAK      BACKGROUND',/,
      114('-'),23X,'----',6X,10('-'),/33X,
      2'COUNTS TIME  COUNTS TIME   P/B',/,33X,11('-'),2X,
      311('-'),'   ---')
       STD=-1.0
C
C      READ COUNTING DATA ONE CARD AT A TIME
C
    24 READ(2,3)ICODE,PEAK,TIME,BACK,SEC,ORGAN,SULP,INAME
     3 FORMAT(I1,F9.0,F5.0,F10.0,F5.0,F10.1,F9.0,1X,15A2)
       BACK=BACK+1.E-6
       SEC=SEC+1.E-2
       GO TO(6,6,98),ICODE
C
C      CALCULATE COUNTRATE
C
     6 CP=PEAK/TIME
       CB=BACK/SEC
       CP=CP/(1.0-CP*2.E-6)
       CB=CB/(1.0-CB*2.E-6)
       COUNT=CP-CB
       FIG=(CP/CB)**0.5*SEC/TIME
       PLUS=(CP/TIME+CB/SEC)**0.5
       CBE=(BACK)**0.5/SEC
       GO TO(10,11),ICODE
C
```

```
C     DATA CARD IS REFERENCE CARD
C
   11 NBAT=0
      NREF=NREF+1
      IF(STD)12,12,13
   12 STD=COUNT
      NSEC=1
      WRITE(3,23)INAME,COUNT,NSEC
      GO TO 24
   13 FAC=COUNT/STD
      FACER=PLUS/STD
      PFAC=(COUNT-STD)/STD*100.0
      WRITE(3,16)PFAC
   16 FORMAT('0DRIFT FACTOR (PERCENT) ',F7.3)
      GO TO 24
C
C     DATA CARD IS SAMPLE CARD
C
   10 NBAT=NBAT+1
      NUM=NUM+1
      IF(NREF-2)34,35,35
   34 WRITE(3,36)
   36 FORMAT('0INITIAL REFERENCE CARD MISSING')
      GO TO 99
   35 IF(NBAT-3)20,20,21
   21 WRITE(3,22)
   22 FORMAT('0MORE THAN 4 SAMPLES PER BATCH')
      GO TO 99
   20 IF(NUM-80)30,30,32
   32 WRITE(3,33)
   33 FORMAT('0STORAGE LIMIT OF 80 SAMPLES')
      NUM=80
      GO TO 98
   30 PLUS=(PLUS/FAC*PLUS/FAC+(COUNT/FAC*FACER/FAC)**2)**0.5
      COUNT=COUNT/FAC
      DO 31 I=1,15
   31 NAME(I,NUM)=INAME(I)
      R(NUM)=COUNT
      E(NUM)=PLUS
      L(NUM)=ORGAN
      B(NUM)=CB
      BE(NUM)=CBE
      NTIME=IFIX(TIME)
      NSEC=IFIX(SEC)
      WRITE(3,23)INAME,PEAK,NTIME,BACK,NSEC,FIG
   23 FORMAT('0',15A2,F9.0,I4,F8.0,I4,3X,F4.2)
      GO TO 24
C
C     PRINT COUNTRATES
C
   98 WRITE(3,27)HEAD
      WRITE(3,71)
   71 FORMAT('0ANALYSIS DATA',26X,
     1'NET C/S         ERROR',/14('-'),26X,
     221('-'))
      DO 72 I=1,NUM
      COUNT=R(I)
      PLUS=E(I)
      DEV=PLUS*100.0/COUNT
   72 WRITE(3,50)(NAME(J,I),J=1,15),COUNT,PLUS,DEV
C
C     PRINT BACKGROUND COUNTRATES
C
      WRITE(3,27)HEAD
      WRITE(3,53)
   53 FORMAT('0MATRIX DATA',19X,
     1'BACKGROUND C/S   ERROR      LOSS',/12('-'),19X,
     222('-'),'     ----')
      DO 52 I = 1,NUM
      COUNT=B(I)
      PLUS = BE(I)
      DEV = PLUS*100.0/COUNT
      ORGAN = L(I)
   52 WRITE(3,47)(NAME(J,I),J=1,15),COUNT,PLUS,DEV,ORGAN
   47 FORMAT('0',15A2,F8.2,' + ',F5.2,'(',F5.2,')',F8.1)
C
```

```
C     CORRECT USING LOSS ON IGNITION
C
      IF(BETA)55,54,55
   55 WRITE(3,27)HEAD
      WRITE(3,40)
   40 FORMAT('0CORRECTED FOR IGNITION LOSS',12X,
     1'CORRECTED C/S   ERROR',/28('-'), 12X,21('-'))
      DO 74 I=1,NUM
      A(I)=1.000+BETA*L(I)
      ER=((R(I)*L(I)*EB)**2+(E(I)*A(I))**2)**0.5
      R(I)=R(I)*A(I)
      ERROR=100.0*ER/R(I)
      E(I)=ER
   74 WRITE(3,50)(NAME(J,I),J=1,15),R(I),ER,ERROR
   50 FORMAT('0',15A2,F14.2,' + ',F5.2,' (',F5.2,')')
C
C     CORRECT USING BACKGROUND SCATTER
C
   54 IF(T)45,46,45
   45 WRITE(3,27)HEAD
      WRITE(3,44)
   44 FORMAT('0PEAK TO BACKGROUND RATIO',16X,
     1'RATIO',10X,'ERROR',/25('-'),16X,20('-'))
      DO 43 I = 1,NUM
      E(I)=((E(I)/B(I)**T)**2+(R(I)*BE(I)/B(I)**(T+1.0))
     1**2)**0.5
      R(I)=R(I)/B(I)**T
      ERROR=100.0*E(I)/R(I)
   43 WRITE(3,48)(NAME(J,I),J=1,15),R(I),E(I),ERROR
   48 FORMAT('0',15A2,F14.4,' + ',F5.2,' (',F5.2,')')
C
C     CALCULATE ELEMENT CONCENTRATIONS
C
   46 WRITE(3,27)HEAD
      WRITE(3,91)
   91 FORMAT('0CALCULATED ELEMENT CONTENT',11X,
     1'COMPUTED CONC   ERROR',/27('-'),11X,21('-'))
      DO 93 I=1,NUM
      SULP=GRAD*R(I)+CEPT
      ERROR=((E(I)*GRAD)**2+(R(I)*EG)**2+EC*EC)**0.5
      DEV=100.0*ERROR/SULP
   93 WRITE(3,92)(NAME(J,I),J=1,15),SULP,ERROR,DEV
   92 FORMAT('0',15A2,F12.1,' + ',F5.1,' (',F5.2,')')
   99 CONTINUE
      CALL EXIT
      END
C
```

```
X-RAY FLUORESCENCE   ZINC STANDARDS SYNTHETIC EX L.G.L.
------------------
PROGRAM A     DETERMINATION OF EQUATION PARAMETERS
---------
BACKGROUND EXPONENTIAL       1.27000
IGNITION LOSS FACTOR        -0.00320 + 0.00000 ( 0.00)

COUNTING DATA                            PEAK        BACKGROUND
-------------                            ----        ----------
                                     COUNTS TIME   COUNTS TIME    P/B
                                     -----------   -----------    ---
ZINC OXIDE STD NO 6                   26466.   1
DRIFT FACTOR (PERCENT)    0.562
SYNTHETIC BASE 1                      91570.  80   66239.  80    1.18
SOIL MATRIX 1                        160479.  80   68398.  80    1.53
SOIL MATRIX 2                        229754.  80   67590.  80    1.85
DRIFT FACTOR (PERCENT)    0.273
SOIL MATRIX 3                        300236.  80   67917.  80    2.11
SOIL MATRIX 4                        363005.  80   68168.  80    2.32
SYNTHETIC BASE 2                     437617.  80   67642.  80    2.56
DRIFT FACTOR (PERCENT)   -0.292
+20% QUARTZ                          393262.  80   69102.  80    2.40
+40% QUARTZ                          319300.  80   69895.  80    2.14
+15% ALUMINIUM OXIDE                 421446.  80   68646.  80    2.49
DRIFT FACTOR (PERCENT)    0.124
+30% ALUMINIUM OXIDE                 373633.  80   70919.  80    2.30
+10% IRON OXIDE                      337176.  80   51304.  80    2.57
+20% IRON OXIDE                      264452.  80   42158.  80    2.51
DRIFT FACTOR (PERCENT)   -0.461
+50% LUCERNE                         400053.  80   89515.  80    2.12
+40% SYNTHETIC O.M.                  404542.  80   84007.  80    2.20
+30% LUCERNE                         426407.  80   76703.  80    2.37
DRIFT FACTOR (PERCENT)   -0.355
+20% WHEAT STRAW                     431212.  80   73444.  80    2.43
+10% WHEAT STRAW                     428830.  80   70034.  80    2.49


ANALYSIS DATA                         NET C/S            ERROR       CONC
-------------                         ---------------------------    ----
SYNTHETIC BASE 1                      316.22 +  4.99 ( 1.58)          80
SOIL MATRIX 1                        1151.26 +  6.49 ( 0.56)         312
SOIL MATRIX 2                        2030.89 +  8.17 ( 0.40)         548
SOIL MATRIX 3                        2923.05 + 10.02 ( 0.34)         778
SOIL MATRIX 4                        3715.53 + 11.69 ( 0.31)        1010
SYNTHETIC BASE 2                     4671.12 + 13.73 ( 0.29)        1243
+20% QUARTZ                          4111.44 + 12.59 ( 0.31)         994
+40% QUARTZ                          3157.49 + 10.58 ( 0.34)         753
+15% ALUMINIUM OXIDE                 4477.82 + 13.38 ( 0.30)        1065
+30% ALUMINIUM OXIDE                 3821.77 + 11.96 ( 0.31)         884
+10% IRON OXIDE                      3604.03 + 11.23 ( 0.31)        1249
+20% IRON OXIDE                      2796.72 +  9.34 ( 0.33)        1255
+50% LUCERNE                         3948.07 + 12.51 ( 0.32)         636
+40% SYNTHETIC O.M.                  4075.06 + 12.71 ( 0.31)         769
+30% LUCERNE                         4447.51 + 13.41 ( 0.30)         882
+20% WHEAT STRAW                     4545.39 + 13.57 ( 0.30)        1004
+10% WHEAT STRAW                     4557.78 + 13.56 ( 0.30)        1127
```

```
MATRIX DATA                    BACKGROUND C/S   ERROR      LOSS
-----------                    ----------------------      ----

SYNTHETIC BASE 1                  829.26 +  3.22( 0.39)     0.0
SOIL MATRIX 1                     856.33 +  3.27( 0.38)     0.0
SOIL MATRIX 2                     846.20 +  3.25( 0.38)     0.0
SOIL MATRIX 3                     850.30 +  3.26( 0.38)     0.0
SOIL MATRIX 4                     853.45 +  3.26( 0.38)     0.0
SYNTHETIC BASE 2                  846.85 +  3.25( 0.38)     0.0
+20% QUARTZ                       865.16 +  3.29( 0.38)     0.0
+40% QUARTZ                       875.11 +  3.30( 0.38)     0.0
+15% ALUMINIUM OXIDE              859.44 +  3.27( 0.38)     0.0
+30% ALUMINIUM OXIDE              887.95 +  3.33( 0.37)     0.0
+10% IRON OXIDE                   642.04 +  2.83( 0.44)     0.0
+20% IRON OXIDE                   527.46 +  2.57( 0.49)     0.0
+50% LUCERNE                     1121.31 +  3.74( 0.33)    50.0
+40% SYNTHETIC O.M.              1052.17 +  3.62( 0.34)    40.0
+30% LUCERNE                      960.51 +  3.46( 0.36)    30.0
+20% WHEAT STRAW                  919.62 +  3.39( 0.37)    20.0
+10% WHEAT STRAW                  876.85 +  3.31( 0.38)    10.0


REGRESSION ANALYSIS - NET C/S VS CONC
-------------------

GRADIENT  (UNIT/CONC)         3.005127 +    0.615157 (20.47)
INTERCEPT (UNIT)            853.491    + 562.856     (65.95)
CORRELATION COEFFICIENT       0.783610
SUM OF RESIDUALS SQUARED    9719043.2
GRADIENT  (CONC/UNIT)         0.204332 +    0.041827 (20.47)
INTERCEPT (CONC)            156.822    + 152.327     (97.13)
CORRELATION COEFFICIENT       0.783610
SUM OF RESIDUALS SQUARED      660842.0

LINEAR COEFFICIENTS
-------------------

GRADIENT  (CONC/UNIT)      0.268 +   0.055 (20.55)
INTERCEPT (CONC)         -60.062 + 174.221 (*****)

CORRECTED FOR IGNITION LOSS      CORRECTED C/S   ERROR      CONC
---------------------------      -------------------        ----

SYNTHETIC BASE 1                  316.22 +  4.99 ( 1.58)     80
SOIL MATRIX 1                    1151.26 +  6.49 ( 0.56)    312
SOIL MATRIX 2                    2030.89 +  8.17 ( 0.40)    548
SOIL MATRIX 3                    2923.05 + 10.02 ( 0.34)    778
SOIL MATRIX 4                    3715.53 + 11.69 ( 0.31)   1010
SYNTHETIC BASE 2                 4671.12 + 13.73 ( 0.29)   1243
+20% QUARTZ                      4111.44 + 12.59 ( 0.31)    994
+40% QUARTZ                      3157.49 + 10.58 ( 0.34)    753
+15% ALUMINIUM OXIDE             4477.82 + 13.38 ( 0.30)   1065
+30% ALUMINIUM OXIDE             3821.77 + 11.96 ( 0.31)    884
+10% IRON OXIDE                  3604.03 + 11.23 ( 0.31)   1249
+20% IRON OXIDE                  2796.72 +  9.34 ( 0.33)   1255
+50% LUCERNE                     3316.38 + 10.51 ( 0.32)    636
+40% SYNTHETIC O.M.              3553.45 + 11.08 ( 0.31)    769
+30% LUCERNE                     4020.55 + 12.13 ( 0.30)    882
+20% WHEAT STRAW                 4254.49 + 12.71 ( 0.30)   1004
+10% WHEAT STRAW                 4411.94 + 13.13 ( 0.30)   1127
```

```
X-RAY FLUORESCENCE    ZINC STANDARDS SYNTHETIC EX L.G.L.
------------------
PROGRAM A     DETERMINATION OF EQUATION PARAMETERS
---------

REGRESSION ANALYSIS - CORRECTED C/S VS CONC
-------------------
GRADIENT   (UNIT/CONC)          3.060646 +    0.510675 (16.69)
INTERCEPT (UNIT)              687.197    +  467.256    (67.99)
CORRELATION COEFFICIENT         0.839893
SUM OF RESIDUALS SQUARED      6697924.7
GRADIENT   (CONC/UNIT)          0.230481 +    0.038456 (16.69)
INTERCEPT (CONC)               94.415    +  134.973    (*****)
CORRELATION COEFFICIENT         0.839893
SUM OF RESIDUALS SQUARED        504385.1

LINEAR COEFFICIENTS
-------------------
GRADIENT   (CONC/UNIT)       0.278 +   0.046 (16.72)
INTERCEPT (CONC)           -63.076 + 146.084 (*****)


PEAK TO BACKGROUND RATIO           RATIO           ERROR     CONC
------------------------          --------------------     ----
SYNTHETIC BASE 1                 0.0621 +  0.00 ( 1.63)     80
SOIL MATRIX 1                    0.2171 +  0.00 ( 0.68)    312
SOIL MATRIX 2                    0.3889 +  0.00 ( 0.56)    548
SOIL MATRIX 3                    0.5563 +  0.00 ( 0.51)    778
SOIL MATRIX 4                    0.7038 +  0.00 ( 0.50)   1010
SYNTHETIC BASE 2                 0.8935 +  0.00 ( 0.48)   1243
+20% QUARTZ                      0.7654 +  0.00 ( 0.49)    994
+40% QUARTZ                      0.5793 +  0.00 ( 0.50)    753
+15% ALUMINIUM OXIDE             0.8406 +  0.00 ( 0.48)   1065
+30% ALUMINIUM OXIDE             0.6884 +  0.00 ( 0.49)    884
+10% IRON OXIDE                  0.9799 +  0.01 ( 0.54)   1249
+20% IRON OXIDE                  0.9760 +  0.01 ( 0.59)   1255
+50% LUCERNE                     0.4441 +  0.00 ( 0.46)    636
+40% SYNTHETIC O.M.              0.5159 +  0.00 ( 0.46)    769
+30% LUCERNE                     0.6554 +  0.00 ( 0.47)    882
+20% WHEAT STRAW                 0.7329 +  0.00 ( 0.47)   1004
+10% WHEAT STRAW                 0.8074 +  0.00 ( 0.48)   1127

REGRESSION ANALYSIS - PEAK/BACKGROUND RATIO
-------------------
GRADIENT   (UNIT/CONC)          0.000770 +    0.000026 ( 3.33)
INTERCEPT (UNIT)               -0.025    +    0.023    (93.63)
CORRELATION COEFFICIENT         0.991786
SUM OF RESIDUALS SQUARED             0.0
GRADIENT   (CONC/UNIT)       1277.503068 +   42.540085 ( 3.33)
INTERCEPT (CONC)               46.049    +   29.003    (62.98)
CORRELATION COEFFICIENT         0.991786
SUM OF RESIDUALS SQUARED         28013.0

LINEAR COEFFICIENTS
-------------------
GRADIENT   (CONC/UNIT)  1288.040 +  42.894 ( 3.33)
INTERCEPT (CONC)           39.350 +  29.745 (75.59)
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X-RAY FLUORESCENCE   ZINC STANDARDS SYNTHETIC EX L.G.L.
------------------

PROGRAM A     DETERMINATION OF EQUATION PARAMETERS
---------

CALCULATED VS CHEMICAL CONTENT     COMPUTED CONC       CHEM  DIFF
------------------------------     -------------       ----  ----

SYNTHETIC BASE 1                  119.4 + 29.9(25.04)   80  1.32
SOIL MATRIX 1                     319.0 + 31.2( 9.79)  312  0.22
SOIL MATRIX 2                     540.2 + 34.2( 6.33)  548 -0.23
SOIL MATRIX 3                     755.8 + 38.3( 5.07)  778 -0.58
SOIL MATRIX 4                     945.8 + 42.6( 4.51) 1010 -1.51
SYNTHETIC BASE 2                 1190.2 + 48.8( 4.10) 1243 -1.08
+20% QUARTZ                      1025.2 + 44.6( 4.35)  994  0.70
+40% QUARTZ                       785.5 + 38.9( 4.96)  753  0.84
+15% ALUMINIUM OXIDE             1122.1 + 47.0( 4.19) 1065  1.21
+30% ALUMINIUM OXIDE              926.0 + 42.1( 4.55)  884  1.00
+10% IRON OXIDE                  1301.5 + 51.9( 3.99) 1249  1.01
+20% IRON OXIDE                  1296.5 + 51.9( 4.00) 1255  0.80
+50% LUCERNE                      611.4 + 35.4( 5.79)  636 -0.69
+40% SYNTHETIC O.M.               703.9 + 37.2( 5.29)  769 -1.75
+30% LUCERNE                      883.5 + 41.1( 4.65)  882  0.04
+20% WHEAT STRAW                  983.4 + 43.5( 4.42) 1004 -0.47
+10% WHEAT STRAW                 1079.4 + 45.9( 4.25) 1127 -1.04

MEAN OF DIFFERENCES -0.0123
STANDARD DEVIATION   0.9926



STANDARD PARAMETERS   ZINC STANDARDS SYNTHETIC EX L.G.L.
-------------------

BACKGROUND EXPONENTIAL       1.27000
IGNITION LOSS FACTOR       -0.00320 + 0.00000    ( 0.00)
GRADIENT (CONC/UNIT)     1288.0397   + 42.8939   ( 3.33)
INTERCEPT (CONC)           39.350    +  29.745   (75.59)
REFERENCE COUNTRATE     26465.87
>
```

Appendix 4. Soil survey data

CORE 1: PADDOCK 26, KAIRAKI SAND, UNDISTURBED TOESLOPE, UNSLUDGED

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P	CEC
			mg/kg								me/kg
0-10	17.7	5.5	13	35	160	19	55	114	1040	890	96
10-20	7.1	4.9	12	35	151	25	87	136	680	1050	51
20-30	4.0	5.1	14	36	132	20	66	143	420	980	39
30-40	2.4	5.2	13	23	101	21	42	139	210	620	26
40-50	1.3	5.4	12	38	83	17	19	122	150	540	15
50-60	1.6	5.7	12	31	86	23	27	129	160	490	14
60-70	1.7	5.8	12	35	80	26	18	119	200	430	14
70-80	1.3	6.4	14	34	85	21	11	118	200	430	13
80-90	1.2	6.9	13	34	70	23	19	118	140	350	11

CORE 2: PADDOCK 26, KAIRAKI SAND, UNDISTURBED, MIDSLOPE, UNSLUDGED

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P
			mg/kg							
0-10	15.0	5.3	13	35	76	21	33	134	1080	720
10-20	6.0	4.6	10	26	68	12	15	142	410	490
20-30	3.5	4.5	12	21	59	12	9	154	330	460
30-40	4.1	4.6	8	22	58	18	32	154	270	430
40-50	2.1	4.8	9	24	64	18	9	149	140	310
50-60	1.6	5.4	15	41	72	24	9	122	90	280
60-70	3.2	5.3	20	33	66	13	17	123	90	320
70-80	1.1	5.0	15	50	66	16	37	118	150	310
80-90	1.4	4.6	16	22	70	16	29	154	220	290

CORE 3: PADDOCK 26, KAIRAKI SAND, UNDISTURBED TOPSLOPE, UNSLUDGED

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P
			mg/kg							
0-10	15.0	6.1	14	22	75	27	44	135	920	580
10-20	5.4	5.8	16	19	75	23	42	143	370	480
20-30	4.1	5.6	14	30	60	19	19	130	180	400
30-40	1.9	6.0	10	27	70	26	20	124	100	370
40-50	1.5	5.9	15	34	73	21	30	126	100	370
50-60	1.5	6.3	16	33	72	14	39	135	90	340
60-70	1.3	6.4	11	39	66	14	22	120	70	270
70-80	1.2	6.0	14	33	64	16	22	126	50	290
80-90	1.3	5.9	12	23	70	22	30	134	60	250

CORE 4: PADDOCK 4, DUNE MATERIAL, SLIGHT HOLLOW, HEAVY DUMPINGS OF DRIED SLUDGE LEVELLED OVER

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P	CEC me/kg
			mg/kg								
0-10	20.7	6.0	44	170	620	610	165	122	1500	2800	78
10-20	10.0	6.0	54	193	730	710	188	137	2200	4400	55
20-30	17.3	5.9	83	350	980	240	310	118	2400	4500	126
30-40	31.8	5.8	124	560	1100	550	440	107	6700	5800	160
40-50	26.0	6.0	96	310	900	240	220	126	5000	3800	105
50-60	6.3	6.4	30	102	330	54	66	154	1200	1100	31
60-70	16.6	6.7	65	260	850	189	230	119	3400	3100	85
70-80	17.7	6.5	43	169	640	165	155	113	3500	2700	74
80-90	7.5	6.9	17	38	88	24	25	127	1600	570	44
90-100	1.5	7.0	12	35	61	27	12	130	250	340	14

CORE 5: PADDOCK 4, DUNE MATERIAL, SLIGHT RISE, HEAVY DUMPINGS OF DRIED SLUDGE LEVELLED OVER

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P
			mg/kg							
0- 10	15.1	6.7	72	360	840	1020	230	124	2300	4800
10- 20	9.7	6.3	64	240	610	380	22	121	2000	4000
20- 30	6.0	5.8	41	197	520	210	110	124	1500	2800
30- 40	33.1	5.6	97	440	1200	350	360	99	4500	4200
40- 50	14.3	5.0	46	168	600	91	120	112	4500	2400
50- 60	16.1	4.9	15	49	158	15	36	118	1700	670
60- 70	17.6	4.6	12	40	117	14	35	111	2300	800
70- 80	4.0	5.7	13	31	89	8	19	145	550	430
80- 90	1.6	6.1	13	25	64	19	21	151	280	330
90-100	1.3	5.9	14	30	66	21	12	151	280	330

CORE 6: PADDOCK 24, LEVELLED DUNE MATERIAL, DRY SLUDGED TO FORM TOPSOIL, 1973-74

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P	CEC me/kg
			mg/kg								
0-10	16.1	5.9	60	240	800	1400	210	124	2200	5000	67
10-20	18.0	5.7	63	250	800	1300	220	117	2200	4100	64
20-30	4.3	5.3	17	63	156	104	43	138	350	820	27
30-40	3.8	4.7	14	26	86	134	11	125	370	810	25
40-50	2.2	5.1	18	27	84	69	12	143	170	660	11
50-60	1.2	4.8	13	18	68	31	20	127	40	340	20
60-70	1.1	4.9	16	19	72	70	29	132	40	430	12
70-80	1.2	4.6	14	40	65	25	37	132	40	320	13
80-90	1.5	4.4	14	15	74	26	3	127	60	310	11

CORE 7: PADDOCK 24, LEVELLED DUNE MATERIAL DRY SLUDGED TO FORM TOPSOIL, 1973-74

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P
			mg/kg							
0-10	16.3	6.4	55	230	770	1500	160	119	2000	4600
10-20	10.7	6.3	46	166	530	820	123	116	1600	3700
20-30	2.0	6.1	14	28	78	28	38	133	80	450
30-40	1.7	4.7	19	14	74	17	29	132	70	330
40-50	1.2	4.5	15	11	73	25	13	145	60	330
50-60	0.9	4.5	17	14	67	27	30	154	60	380
60-70	0.9	4.6	11	18	73	20	21	133	60	320
70-80	1.0	4.5	13	17	69	25	21	137	50	330

CORE 8: PADDOCK 24, LEVELLED DUNE MATERIAL, DRY SLUDGED TO FORM TOPSOIL, 1973-74

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P
			mg/kg							
0-10	19.2	5.9	66	340	1100	1900	220	115	2400	5800
10-20	14.6	6.1	51	230	620	640	181	143	1400	3700
20-30	5.0	6.2	30	300	440	78	210	139	940	2300
30-40	8.5	6.0	38	250	460	91	193	127	1000	2100
40-50	12.0	5.8	34	290	460	72	220	132	740	2000
50-60	4.0	5.7	21	21	199	27	42	135	430	660
60-70	4.0	5.3	13	11	71	22	34	156	100	330
70-80	1.6	4.9	13	18	73	21	19	142	80	330
80-90	1.4	5.2	14	9	73	18	19	140	70	350

CORE 9: PADDOCK 20, LEVELLED DUNE MATERIAL, DRESSED WITH DRY SLUDGE, PRE 1970

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P
			mg/kg							
0- 10	14.5	6.4	60	220	590	230	310	137	1700	2600
10- 20	6.5	6.2	24	40	220	150	72	176	440	890
20- 30	1.2	5.9	16	0	124	41	19	220	50	430
30- 40	1.5	6.0	15	2	117	36	19	220	40	390
40- 50	1.2	5.5	15	4	111	41	34	220	100	400
50- 60	1.7	5.3	14	0	78	27	11	210	80	370
60- 70	1.6	5.6	13	2	81	29	20	165	60	340
70- 80	2.0	5.7	13	3	76	32	20	168	100	400
80- 90	1.6	5.4	12	14	73	26	20	171	60	310
90-100	1.3	5.5	13	0	68	25	45	155	40	340

CORE 10: PADDOCK 20, LEVELLED DUNE MATERIAL DRESSED WITH DRY SLUDGE, PRE 1970

Depth cm	% Ig Loss	pH	Ni	Cu	Zn	Cr	Pb	Zr	S	P	CEC me/kg
			mg/kg								
0- 10	19.1	5.4	65	300	500	270	280	127	1700	2900	136
10- 20	8.9	5.1	37	113	310	115	108	146	1000	1900	61
20- 30	1.7	5.6	17	10	141	30	19	159	70	430	13
30- 40	1.4	5.6	13	3	122	23	11	177	30	400	13
40- 50	1.4	5.6	15	11	124	23	11	164	30	350	
50- 60	1.5	5.5	15	4	125	26	27	153	70	330	12
60- 70	1.4	5.4	13	7	114	19	21	148	40	340	13
70- 80	1.5	5.1	16	12	113	29	29	145	60	380	10
80- 90	1.6	5.2	19	9	123	27	12	165	80	410	14
90-100	1.7	5.1	17	3	123	22	21	145	90	370	12

Appendix 5 Field Trial Site Plan

Sludge			
4	b	a	c
1	a	c	b
2	b	c	a
3	a	b	c
4	c	b	a
2	c	a	b
4	b	c	a
3	b	a	c
1	a	b	c
2	c	a	b
1	b	c	a
3	b	a	c
2	a	b	c
4	a	c	b
3	c	b	a
1	b	c	a

Road

Sludge (t/ha)	
1	15
2	200
3	390
4	590

Cr in sludge (%)	
a	0.5
b	0.8
c	1.1

Appendix 6-1. Herbage yields in the sludge pot trial

SLUDGE %(W/W)		RYEGRASS 14 wk	RYEGRASS 20 wk	CLOVER 14 wk	CLOVER 20 wk
		g/pot (110^oC)			
0	1	0.1	0.2	1.5	2.4
	2	0.3	0.3	0.6	1.9
	3	0.3	0.2	2.4	3.1
	4	0.2	0.3	2.1	2.0
8	1	3.1	1.1	3.4	6.6
	2	2.5	0.9	4.7	8.0
	3	1.9	1.0	3.0	3.7
	4	3.5	0.9	2.7	0.9
15	1	6.3	2.1	2.1	2.4
	2	6.4	2.0	0.7	0.7
	3	6.0	2.0	1.2	0.2
	4	5.4	1.8	6.2	6.5
31	1	7.5	2.4	6.0	5.6
	2	6.4	2.0	1.0	2.3
	3	7.7	2.9	3.3	4.7
	4	7.1	3.1	5.3	5.3
62	1	7.2	3.5	1.2	2.6
	2	5.1	1.2	1.4	0.3
	3	5.0	2.0	3.2	4.7
	4	8.3	3.1	2.9	5.5

Appendix 6-2. Mean pH of pots in the sludge trial

SLUDGE %(W/W)	PRE $Ca(OH)_2$ TREATMENT	PLANTING	17 wk	FINAL
	All pots		Ryegrass	
0	5.7	7.1	7.1	6.8
4	5.5	6.3	6.7	6.7
8	6.0	6.7	6.9	6.6
15	5.6	6.6	7.1	6.7
31	5.3	6.7	6.8	6.5
62	5.3	6.9	6.6	6.5
			Clover	
0			7.1	5.8
4			6.6	6.0
8			6.7	6.0
15			7.0	6.5
31			6.8	6.7
62			6.7	6.5

Appendix 6-3. Herbage concentrations of Na, K, Mg, Ca, Zn, Mn, Cu, Fe and Cr in the sludge pot trial

SLUDGE %(W/W)	Na	K	Mg	Ca	
Ryegrass	%(110°C)				
0	0.29	1.6	0.36	1.1	
4 *	0.22	2.0	0.39	1.3	
8	0.34	1.4	0.37	1.6	
15	0.54	1.2	0.44	1.7	
31	0.62	1.0	0.43	1.5	
62	0.57	1.1	0.39	1.6	
Clover					
0	0.35	1.0	0.35	2.3	
4 *	0.38	0.8	0.31	2.4	
8	0.44	0.9	0.33	2.8	
15	0.41	1.1	0.29	2.8	
31	0.40	1.0	0.26	2.8	
62	0.59	1.4	0.28	2.6	
	Zn	Mn	Cu	Fe	Cr
Ryegrass	mg/kg(110°C)				
0	-	-	-	-	-
4 *	32	97	7	60	4
8	52	92	2	170	6
15	130	62	14	150	4
31	130	104	12	170	12
62	110	133	8	160	12
Clover					
0	38	99	12	300	10
4 *	120	66	15	210	12
8	110	68	16	210	10
15	94	74	17	170	8
31	110	68	17	290	12
62	110	71	17	360	13

Values are the means of duplicate determinations of four replicates bulked.

* Values from the control of the Cr-amended sludge trial.

Appendix 7-1. Herbage yields for Cr-amended sludge pot trials (g/pot at 110°C)

Cr %		RYEGRASS 14 wk	RYEGRASS 20 wk	CLOVER 14 wk	CLOVER 20 wk
0.48	1	1.7	0.5	4.2	7.7
	2	2.5	0.5	4.2	6.4
	3	2.1	0.4	2.7	4.2
	4	3.0	0.7	5.4	5.4
	5	1.7	0.5	2.1	5.8
	6	1.6	0.9	5.0	6.2
	7	1.8	0.7	2.8	5.3
	8	1.9	0.6	6.1	6.8
0.81	1	1.8	0.7	1.0	3.5
	2	1.5	0.5	2.7	5.9
	3	1.6	0.8	1.8	5.5
	4	1.8	0.5	2.6	4.9
	5	1.9	0.8	3.4	4.6
	6	1.6	0.7	2.4	3.4
	7	2.0	0.8	3.3	5.9
	8	1.3	0.6	3.3	5.3
1.45	1	1.5	0.6	0.1	0.6
	2	1.2	0.5	0.5	3.2
	3	0.7	0.4	0.1	1.5
	4	1.7	0.7	0.1	0.1
	5	0.9	0.6	0.1	0.3
	6	1.7	0.7	1.1	2.6
	7	1.3	0.7	0.7	1.0
	8	1.4	0.6	0.4	1.2
2.71	1	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0
	3	0.0	0.0	0.0	0.0
	4	0.0	0.1	0.0	0.0
	5	0.8	0.4	0.1	0.2
	6	1.0	0.2	0.0	0.0
	7	0.5	0.4	0.0	0.2
	8	0.9	0.4	0.1	0.1

Appendix 7-2. Mean pH of pots in Cr-amended sludge trial

Cr %	ALL POTS MIXING	PLANTING	RYEGRASS 14 wk	RYEGRASS Final	CLOVER 14 wk	CLOVER Final
0.48	$Ca(OH)_2$ treated	6.3	6.7	6.7	6.6	6.0
0.81		7.1	6.9	6.8	6.9	6.0
1.45		6.8	7.1	7.1	6.9	6.3
2.71		6.4	6.3	7.0	6.7	7.1
0.48	5.5	not treated	6.7	6.5	6.5	5.6
0.81	5.3		6.8	6.6	7.0	5.7
1.45	4.4		6.5	6.4	6.9	5.1
2.71	3.5		5.1	5.3	5.0	5.4

Appendix 7-3. Herbage concentrations of Na, K, Mg, Ca, Zn, Mn, Cu, Fe and Cr in the Cr-amended sludge trial

Cr %	Na	K	Mg	Ca
Ryegrass	%(110°C)			
0.48	0.26	1.3	0.40	1.3
0.81	0.16	1.3	0.24	1.3
1.45	0.13	1.6	0.19	1.5
2.71	0.25*	2.0*	0.33*	3.7*
0.48	0.22	2.0	0.39	1.2
0.81	0.21	1.7	0.36	1.8
1.45	0.16	1.4	0.23	2.1
2.71	0.13	1.5	0.20	3.2
Clover				
0.48	0.40	0.9	0.32	2.4
0.81	0.39	1.2	0.32	2.6
1.45	0.39	1.8	0.31	2.5
2.71	-	-	-	-
0.48	0.38	0.8	0.31	2.4
0.81	0.39	1.0	0.30	2.7
1.45	0.27	1.6	0.29	3.1
2.71	0.39*	1.1*	0.42*	5.2*

	Zn	Mn	Cu	Fe	Cr
Ryegrass	mg/kg(110°C)				
0.48	107	310	10	370	3
0.81	68	350	6	(25)	11
1.45	79*	460*	6*	140*	11*
2.71	-	-	-	-	-
0.48	32	97	7	(55)	4
0.81	28	200	7	190	16
1.45	37	270	7	150	22
2.71	62*	460*	7*	160*	24*
Clover					
0.48	220	78	13	390	2
0.81	220	120	10	210	10
1.45	190*	100*	17*	280*	20*
2.71	-	-	-	-	-
0.48	120	66	15	210	12
0.81	55	95	12	210	5
1.45	75*	81	17*	220*	22*
2.71	-	-	-	-	-

The second set of four values in each group were CaOH$_2$ treated.

Values are the means of duplicate determination of four replicates bulked.

* Very low yield (or insufficient for duplicate determination)

Appendix 8.

Field trial Herbage Yield

Sludge	Yield					
	%Cr in Sludge					
	0.5		0.8		1.1	
t/ha	t/ha (110^{o})					
200	2.48	3.15	2.28	2.63	2.13	1.53
	2.90	2.94	2.67	1.59	1.73	2.33
390	2.06	2.29	2.67	2.28	1.72	1.94
	2.51	2.82	2.40	2.17	2.28	2.48
580	3.02	2.50	2.52	2.06	1.29	1.84
	2.13	2.03	2.55	1.60	1.45	2.17
0	1.11, 1.48, 1.55, 2.30 (Control)					

Field Estimation of Growth and Vigour of Ryegrass

Sludge	Fraction of Ground Cover					
	%Cr in Sludge					
	0.5		0.8		1.1	
t/ha	%(±5)					
200	50,	45	35,	30	35,	25
	50,	25	30,	40	25,	30
390	35,	30	25,	20	15,	10
	40,	40	30,	30	20,	25
580	25,	40	20,	25	10,	15
	40,	20	20,	20	25,	10
0	30, 35, 15, 25 (Control					