Baseline concentration of Cd, Co, Cr, Cu, Pb, Ni and Zn in surface soils of South Africa

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THE AIM OF THIS STUDY WAS TO DRAW up baseline concentrations for several environmentally important trace elements in South African soils. A major inventory of some 4500 soil profiles has been compiled in South Africa over the past three decades and information on chemical composition can now readily be generated for the country as a whole. Selected soil samples from surface horizons were analysed by inductively coupled plasma–mass spectrometry for total (nitric acid-extractable; EPA method 3050) and available (NH_4EDTA-extractable) fractions of Cd, Co, Cr, Cu, Ni, Pb and Zn. A baseline concentration range (defined as 95% of the expected range of background concentrations) was calculated for each element from geometric means and standard deviations after the data set was normalized by log 10 transformation. These supposedly natural, baseline values were used to revise South African guidelines and to set the total investigation level and the total maximum threshold level in each case as follows: Cd 2 and 3; Co 20 and 50; Cr 80 and 350; Cu 100 and 120; Ni 50 and 150; Pb 56 and 100; and Zn 185 and 200 mg kg^{-1}, respectively. Four-fifths of all soils were found to be Zn-deficient, one-third Cu-deficient and one-fifth Co-deficient.

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Introduction

Although cases of trace element deficiency and toxicity have been documented in many parts of South Africa,[1] no comprehensive description of trace element concentration has yet been attempted for the country as a whole. The Natural Resources Land Type mapping project, begun in the mid-1970s, has provided a collection of samples from soil profiles selected to represent the main soil forms in each land type and therefore to provide representative coverage of most of the soils of South Africa. Archived samples numbering in the thousands have now been analysed for a variety of trace elements, in terms of both available and total concentrations.

Defining background concentrations for trace elements and heavy metals in soils is essential for recognition and management of pollution as well as defiencies for plants and humans. The concept of a background concentration is intended to convey some idea of the natural range in concentration that can be expected prior to contamination through human activity. This depicts an ideal situation that no longer exist in most countries, therefore baseline concentrations, defined as 95% of the expected range of background concentrations, are used to give an indication of the trace element content of an uncontaminated soil.[2] Only by deciding on a natural range is it possible both to assess the likelihood of contamination and to develop guidelines for maximum threshold levels of trace elements in soils. Such guidelines are now available for a number of countries.[5,6] Conspicuously, they differ, meaning that, at least at a national level, specific guidelines should be developed that accommodate geochemical eccentricity. In countries where detailed information has been collected, it is often argued that baseline concentrations should even be developed for particular soil types, some being quite different from others.[2] Two sets of guidelines for maximum metal and inorganic content in soils have been formulated for South African soils: the first in 1991,[7] and a proposed revision in 1997.[8] Both relate to soil contamination from the disposal of sewage sludge, but since they provide the only criteria for soils in South Africa, they have been applied in a wider context.

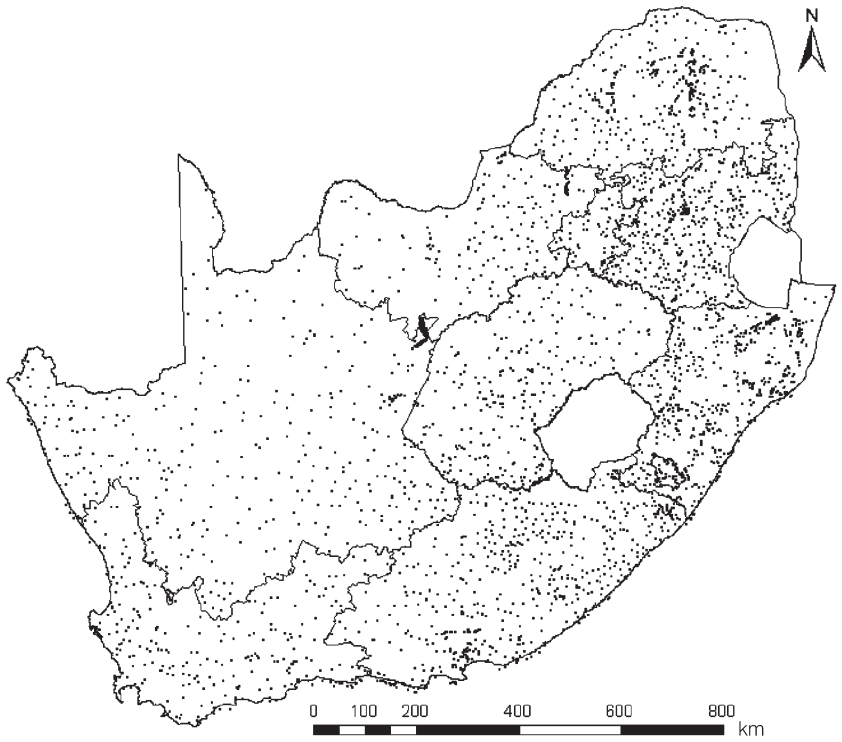

Fig. 1. Location of soil sampling sites in South Africa.

International criteria and the results of toxicological studies were employed to develop and revise these norms and some confusion remains as to which set is the most appropriate. Ultimately, the only appropriate set is one based on local data.

The objectives of this paper are to draw up a set of baseline concentrations for seven environmentally important trace elements based on detailed information that is now available, and to use this background as a basis for recommending maximum threshold levels for these elements in soils in South Africa. The information should also be useful for geographically assessing deficiencies of these same elements and for enhancing our geochemical understanding of the soil mantle.

Materials and methods

The distribution of sampling sites, numbering about 4500, is depicted in Fig. 1. The sites were selected to represent various soil patterns, terrain units and climate zones as described in the Land Type *Memoirs*.[9] A freshly dug soil profile was described and sampled at each site. For the trace element analyses, only topsoil samples, or the first diagnostic horizon, were used that may have had a thickness (in some cases) of 400 mm or more, although typically it would have been about 250 mm. Air-dried samples were gently crushed to pass a 2-mm screen prior to analysis. Most of the soil profiles (apart from about 700 sited later, in areas of scant sampling) are documented in detail in the national inventory of land types under custodianship of the ARC-Institute for Soil Climate and Water in Pretoria.

The US Environmental Protection Agency's acid digestion procedure (EPA method 3050)[10] was used to determine so-called 'total' or 'pseudo-total' element concentration in a randomly selected sub-set of soils amounting to about a third of the collection. In the case of metals, this method includes a fraction that is not readily available, but the technique does not dissolve silicates completely. An index of the readily bio-available fraction was estimated in all the soils by extraction with 0.2 M EDTA.[11] Seven trace metals considered to be of most interest in a South African context due to natural geological occurrences were analysed in the extracts by inductively coupled plasma–mass spectrometry (VG PlasmQuad II+). The method detection limits of these analytical procedures as well as the instrument detection limit are presented in Table 1.

The range, the mean and standard deviation (both arithmetic and geometric), and the median were used to summarize the data statistically. The baseline concentration range was calculated using the quotient and product of the geometric mean and the square of the geometric standard deviation, as recommended by

Table 1. Statistical summary of trace element analyses (available and total concentrations, mg kg ^{1}) in South African surface soils.

Element	MDL#	*N**	Median	Arithmetic mean	Arithmetic s.d.	Geometric mean	Geometric s.d.	Min.	Max.
Available (EDTA method)									
Cd	1.18	4441	0.01	0.02	0.05	1.02	1.07	nd	1.46
Cr	1.29	4351	0.10	0.16	0.28	1.15	1.15	nd	12.5
Ni	1.89	4441	1.02	2.39	5.47	2.35	2.04	nd	170
Pb	0.97	4441	2.12	3.32	4.38	3.33	1.89	0.02	109
Zn	3.22	4322	0.66	1.66	6.79	1.94	1.77	nd	210
Cu	5.33	4411	1.75	2.87	3.82	2.98	1.88	nd	67.3
Co	1.11	4321	1.99	3.63	4.79	3.20	2.24	nd	48.9
Total (EPA 3050 method)									
Cd	2.03	1391	0.001	0.10	0.32	1.30	1.45	nd	5.49
Cr	3.59	1391	46.3	71.9	92.8	45.4	2.79	nd	1329
Ni	35.6	1373	21.3	38.7	59.2	23.4	2.61	nd	906
Pb	3.91	1391	13.1	21.7	37.7	14.0	2.17	nd	532
Zn	10.08	1302	38.1	45.2	57.4	37.2	1.76	0.62	1647
Cu	6.76	1391	17.7	29.5	40.7	18.7	2.51	nd	789
Co	2.47	1302	8.44	18.0	30.5	10.2	2.59	nd	286

nd, not detected, below instrument detection limit.
*All samples.
Method detection limits; instrument detection limits for all elements were 0.01–0.09 ppb.

Table 2. Ranges of concentration (mg kg ^{1}) of trace elements in selected regions and in South Africa (present study).

Element	Concentration ranges					
	USA[4]	Australia and New Zealand[5]	Florida[2]	Belgium[6]	South Africa total (EPA 3050)	South Africa available (EDTA)
Cd	0.04–0.8	0.04–2	0–0.33	0.02–5.3	0.62–2.74	0.89–1.17
Cr	–	0.5–110	0.89–80.7	1.17–119	5.82–353	0.87–4.52
Ni	4.1–56.8	2–400	1.7–48.5	0.3–23	3.43–159	0.57–9.78
Pb	4–23	<2–200	0.69–42.0	0.0–132	2.99–65.8	0.93–11.9
Zn	8–126	2–180	0.89–29.6	6.1–208	12.0–115	0.62–6.03
Cu	3.8–94.9	1–190	0.22–21.9	1.7–39	2.98–117	0.84–10.6
Co	–	2–170	–	0.03–7.7	1.51–68.5	0.64–16.1

[2]Chen *et al.* – EPA 3052 microwave digestion method.
[4]Holmgren *et al.* – nitric acid digestion of agricultural soils without anthropogenic contamination, 5th and 95th percentiles.
[5]Summers & Pech – nitric acid digestion of topsoil samples.
[6]Tack *et al.* – aqua regia digestion method.

Chen *et al.*,[2,3] including data below the instrument detection limit as suggested by Gilbert.[12] The baseline concentration range is a better reflection of variation than the range actually observed because it is freer of the distorting effect of outlier (anomalous) values. The upper limit of the baseline concentration range was set at the 97.5th percentile value of the population in order to minimize the influence of contamination (that is, to reflect natural concentrations more closely). The lower limit was set at the 2.5th percentile value in order to minimize problems that might be associated with analytical uncertainty near the lower limit of detection.

Results and discussion

The analytical data are summarized in Table 1. There is a close correspondence between the total median and geometric mean values for all elements except Cd, whereas the arithmetic means, related to the mean, reflect a marked skewness in the distribution of values. In the case of the EDTA method, the geometric means are higher than the corresponding median values but much the same as the arithmetic means (except for Cd and Cr). All metals besides Cd were about an order of magnitude more soluble by acid extraction (EPA 3050) than they were by EDTA extraction.

Baseline concentration ranges for the dataset are presented alongside similar data for other countries in Table 2. Generally, the upper limit of the total baseline range is high compared with US and Florida values, even though a stronger extraction method was used for Florida soils (EPA 3052), but is similar to those for Australia and New Zealand, which were also determined with a nitric acid digestion method.[5] Values for Cr, however, are conspicuously high compared to all the other countries and the total Ni concentration in South African soils WAs higher than that of the US, Florida and Belgium. However, the available (EDTA) concentration of both these elements was low. This is perhaps one example of how a regional geochemical anomaly makes it necessary to have locally established background levels before contamination can be assessed.

Table 3. Regional guidelines for maximum permissible trace element concentrations in agricultural soil (mg kg ^{1}).

Element	South Africa 1991[7]	South Africa 1997[8]	Europe[13]	USA[14]	Australia & New Zealand[13]
Cd	2	2	1–3	20	3
Cr	80	80	–	1500	50
Ni	15	50	30–75	210	60
Pb	56	6.6	50–300	150	300
Zn	185	46.5	150–300	1400	200
Cu	100	6.6	50–140	750	60
Co	20	20	–	–	–

In Table 3 the two sets of guidelines published in South Africa for maximum permissible limits are compared with those used in other parts of the world. There is a wide discrepancy in levels of trace elements tolerated in agricultural soil in different countries. As indicated earlier, the South African guidelines were drafted based on a review of practices in other countries and do not take local circumstances (especially natural background concentrations) fully into account.

In formulating recommendations for an improved set of guidelines for maximum permissible limits, account needs to be taken of natural background levels as well as the degree to which current guidelines are unrealistic in the context of new local data (Table 4). The upper limit of the baseline concentration in Table 4 suggests that, except for Cr and Ni, the 1991 South African guidelines are fairly realistic whereas the more stringent 1997 guidelines are largely unrealistic (guideline values are well below the upper limit of the baseline concentration) and should be changed. New total investigation levels (TIL) above which further site investigations are recommended, and total maximum threshold levels (TMT) above which soils are considered to be contaminated, have been proposed in Table 4, which should better accommodate geochemical reality. In general, they have been adjusted to bring them into line with the maximum expected natural concentrations, while still protecting the soil environment. Chromium and Ni are the only elements with a TMT lower than the up-

Table 4. Derived statistics and recommended limits for total element concentrations (EPA 3050 method). The 97.5th percentile concentration is the maximum baseline value in Table 2.

Element	97.5th percentile cconentration (mg kg^{-1})	Samples > maximum permissible limit (%)		Total Investigation level (TIL) (mg kg^{-1})	Total maximum threshold level (TMT) (mg kg^{-1})
		1991	1997		
Cd	2.7	1	1	2	3
Cr	353	26	26	80	350
Ni	159	62	20	50	150
Pb	66	5	81	56	100
Zn	115	<1	32	185	200
Cu	117	3	85	100	120
Co	69	18	18	–	–

Table 5. Derived statistics for trace element deficiencies (NH_4EDTA method).

Element	Plant deficiency threshold[15] (mg kg^{-1})	Samples < deficiency threshold (%)
Zn	3	87
Cu	1	29
Co	0.5	21

per limit of the baseline concentration. Low thresholds were maintained mainly because applied Cr and Ni are in soluble forms and therefore the toxicity levels will be lower than when bound to the soil. Areas with trace element concentrations above these thresholds should be studied in detail to determine the environmental influence of the high trace element concentration. Ideally, the data need to be divided so as to represent major soil types, which would give a more refined basis for judging whether likely natural concentrations have been exceeded through contamination.

Three of the elements studied (Zn, Cu and Co) are important agricultural micronutrients and their sufficiency thresholds and the proportion of samples failing to meet this sufficiency in terms of extractability with EDTA is shown in Table 5. Four-fifths of all soils were Zn-deficient, one third was Cu-deficient and only one fifth was Co-deficient. These deficiency indications may be exaggerated as a result of the depth of sampling, which in most cases was greater than that normally used for assessing the fertility status of agricultural topsoils. Since nutrient status generally declines with depth, dilution with deeper, nutrient-poor soil may well have occurred. Nevertheless such statistics could be useful for prioritizing trace element studies in geomedicine, agriculture, forestry and wildlife management. Regional trends, including those linked to soil type and geology, will be included in follow-up studies.

Conclusions

On the basis of a countrywide survey of several trace elements in thousands of surface soils, we have determined baseline concentrations reflecting likely natural ranges. The proposed new TIL and TMT levels will be valuable in setting more realistic norms for environmental contamination that accommodate the geochemical peculiarities of the region, two examples being rather high Cr and Ni concentrations with low bio-availability.

This is the first quantitative report on the spatial extent and intensity of Zn, Cu and Co deficiency in South African soils. The database will be expanded in future communications to relate the distribution of elements to patterns of soil type and geology. This information should be of value not only in environmental pollution studies but also in health, agriculture, forestry and wildlife management.

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