

BACKGROUND VALUES OF 32 ELEMENTS IN DUTCH TOPSOILS, DETERMINED WITH
NON-DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The ranges of background values of 32 elements in Dutch topsoils (0-10 cm) are presented. For this purpose soil samples were collected in 28 nature reserves. The samples were analysed by means of neutron activation. Considerable differences in element concentrations may occur between the sampled areas. For the majority of the analysed elements a significant linear relationship exists between background values and clay contents. For part of the elements studied, the ranges of background values are in agreement with ranges reported for soils in other countries, but for certain elements distinct differences are observed. The concentrations of some elements in clay soils exceed proposed maximally tolerable concentrations for farming land. With the performed analysis a good insight could be obtained into the background values of many elements in soils. For the elements Cd, Cu, Hg, Ni and Pb another analytical procedure should be used.

INTRODUCTION

During the last years a growing concern about soil contamination has developed in The Netherlands as well as in other industrialized countries. Contamination of the topsoil with inorganic substances is one of the problems in this respect. For judging the degree of contamination of the soil at a certain location, information should be available on the natural element concentrations in the soil at that location. However, the original element concentrations in the soil have been raised by diffuse atmospheric immission of inorganic pollutants and by application of manure, sewage sludge etc. The concept "background value" can be defined as the sum of the natural concentration and the concentration that should be ascribed to the diffuse pollution just mentioned.

Non-destructive neutron activation analysis is applied to various research projects in which large series of soil or sediment samples are involved. As an example we mention a series of studies of environmental problems associated with the large quantities of trace elements bound to sediments moving through the Dutch rivers, estuaries and coastal waters (De Bruin 1983).

The purpose of this paper is to report ranges of background values of a number of elements in mineral soils in The Netherlands, in relation to general soil characteristics.

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MATERIALS AND METHODS

General information on soils

Soil samples have been collected in 28 nature reserves distributed over the whole country (Fig. 1). Most of the sampled soils have developed in aeolian sediments with a sandy or loamy texture. A minority of them has developed in alluvial sediments, both river clay and sea clay. The main type of clay mineral in Dutch soils is illite. The textural classes of the sampled soils are indicated in figure 1. The sediments are of Pleistocene or Holocene age. In The Netherlands hardly any rock formation occurs at the surface of the earth's crust.

Sampling

For several reasons (direct contact, plant nutrition, soil ecology) knowledge of background values in the upper layer of the soils was considered as most important. Therefore, the layer 0-10 cm of the mineral soil was sampled. This depth commonly corresponds with the depth of the A1-horizon.

In each of the sampled reserves 3 rectangular plots of 10 m x 12 m at a distance of 50 to 100 m were selected. In each rectangle 42 soil samples were collected in a systematic grid system of 6 x 7 sampling points. From each rectangle the 42 samples were united to 1 composite sample, resulting in 3 composite samples per nature reserve. This method of sampling was chosen to diminish the influence of local anomalies. The sampling was carried out between autumn 1979 and spring 1981.

Pretreatment

The soil samples were dried at 35°C during 48 hours. Clods were crushed with a wooden mortar or with a Retsch mechanical stone breaker. The soil was sieved with a 2 mm nylon sieve.

General characteristics

A part of the minus 2 mm fraction was used to determine the particle size distribution and the organic carbon content according to standard methods.

Neutron activation analysis

Another part of the minus 2 mm fraction was homogenized by milling with a Retsch mechanical agate mortar during 20 min. From the homogenized material 200 mg portions were packed into polyethylene containers. For the determination of elements using short-lived isotopes an irradiation of 7 sec was carried out, immediately followed by a measurement of γ -ray spectra. For the determination of elements using long-lived isotopes an irradiation of 1 h was carried out, followed by measurements of γ -ray spectra after 4 and 10 days. In both cases the thermal neutron flux was about 10^{13} n/cm². sec. The γ -ray spectra were converted into element concentrations using computer based data handling and analysis. For detailed information on neutron activation analysis one is referred to De Bruin and Korthoven (1972). The samples have been analysed singularly. Standards with known element concentrations have been analysed regularly together with the samples under consideration. The reported concentrations are the

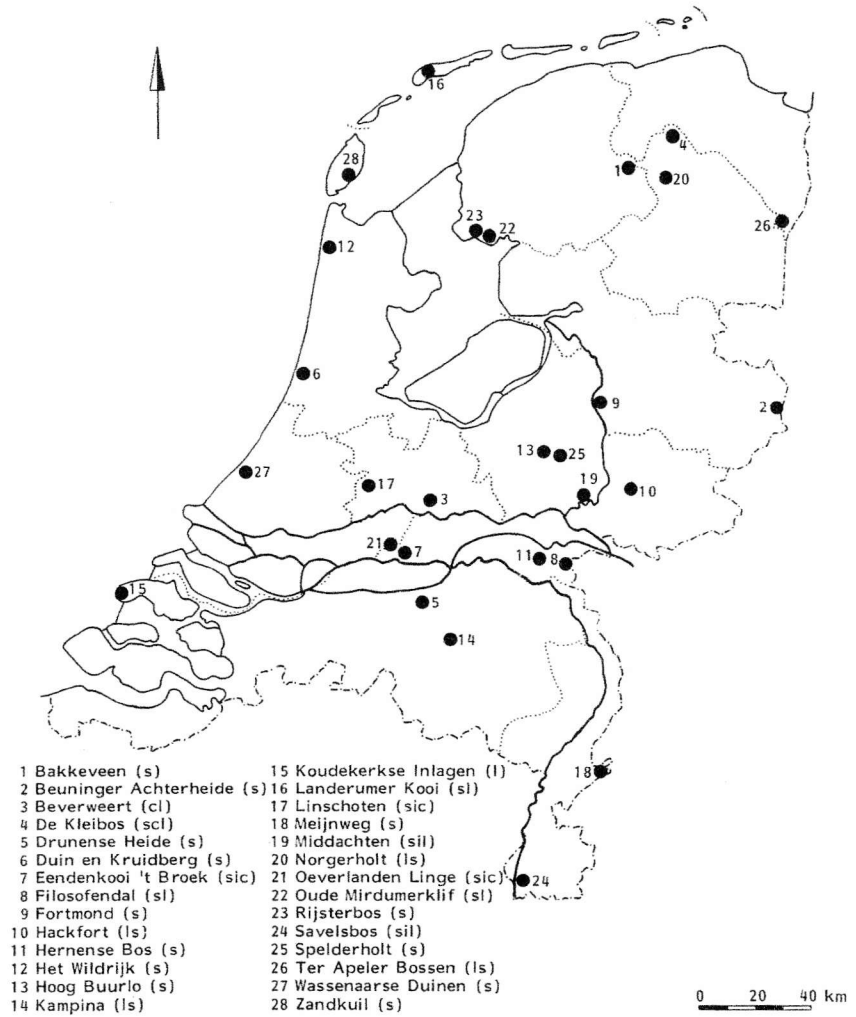


Figure 1. Location, names and soil textural classes of sampled sites. Textural class names according to Soil Survey Staff (1951). (s=sand, ls=loamy sand, l=loam, cl=clay loam, sil=silt loam, sl=sandy loam, scl= sandy clay loam, sic=silty clay).

arithmetical means of the 3 composite samples per nature reserve and are based on dry weight (105°C).

RESULTS AND DISCUSSION

Ranges of background values

In figure 2 the ranges of background values are presented. A striking feature of this figure is its vertical extent, with a spread in concentrations of 8 orders of magnitude.

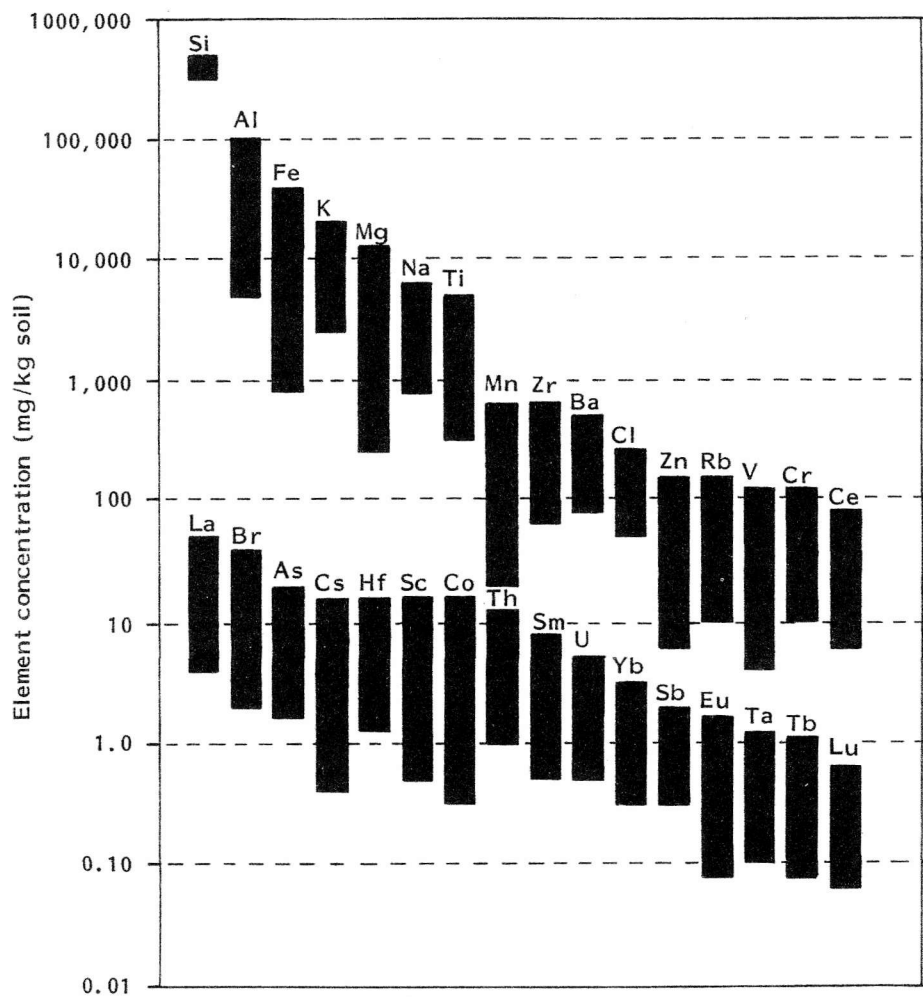


Figure 2. Ranges of background values of 32 elements in Dutch topsoils.

The concentrations of Si, Al, Fe, K, Mg and Na are the highest. This group of elements including O and Ca is commonly referred to as major elements. These eight elements make up 99.3 weight per cent of the earth's crust (Taylor 1964).

The remaining elements are called minor or trace elements. A part of these elements (e.g. As, Co, Cr, Sb, V and Zn) often plays a role in problems of contaminated soil.

With the outlined procedure about 30 elements are determined in the standard procedure. With other procedures or with preconcentration, additional elements such as Cd, Cu, Hg, Ni, which also often play a role in problems of soil contamination, can be determined. For the element Pb another method of analysis has to be used.

Background values in relation to general soil characteristics

The relation of element concentrations to clay contents and organic matter contents has been examined.

For the majority of the analysed elements a significant linear correlation exists between background values and clay contents (Table 1). The increase of element concentrations with clay content may be ascribed to high element concentrations in minerals in the clay fraction in comparison with

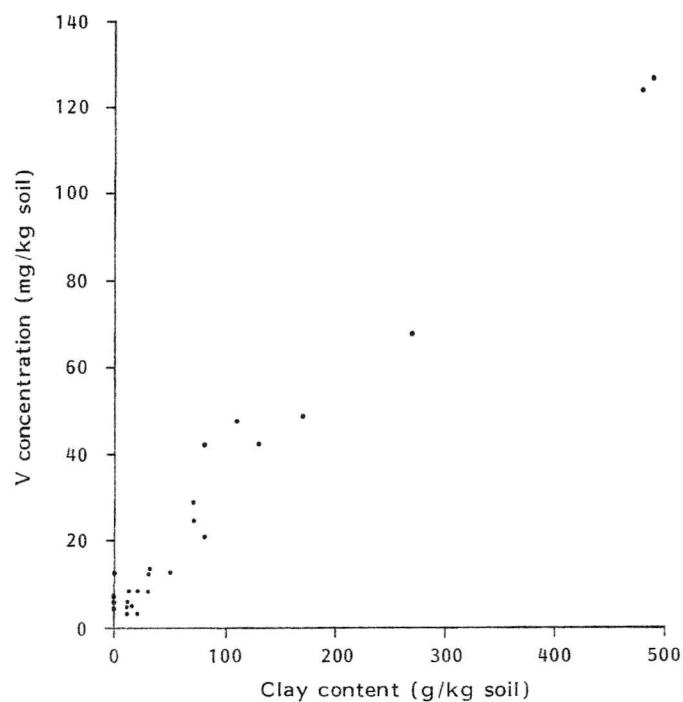


Figure 3. Relation between clay contents and vanadium background values in Dutch topsoils.

Table 1. Linear correlation coefficients for the relation between background values and clay contents in Dutch topsoils.
 *** significant at $p < 0.001$; ** idem at $p < 0.01$; * idem at $p < 0.05$.

element	correlation coefficient	number of observations	significance
Al	0.98	26	***
As	0.86	28	***
Ba	0.86	28	***
Br	0.27	28	
Ce	0.94	28	***
Cl	0.52	21	*
Co	0.96	28	***
Cr	0.94	28	***
Cs	0.98	28	***
Eu	0.97	28	***
Fe	0.93	28	***
Hf	0.06	28	
K	0.80	27	***
La	0.96	28	***
Lu	0.87	28	***
Mg	0.96	24	***
Mn	0.81	26	***
Na	0.49	28	**
Rb	0.96	28	***
Sb	0.69	28	***
Sc	0.99	28	***
Si	0.23	25	
Sm	0.95	28	***
Ta	0.87	27	***
Tb	0.94	28	***
Th	0.95	28	***
Ti	0.83	26	***
U	0.93	27	***
V	0.99	26	***
Yb	0.88	28	***
Zn	0.87	28	***
Zr	0.13	27	

concentrations in the loam and sand fraction and to adsorption of elements at the surface of clay minerals. As an example the relation between clay contents and the concentrations of the element V has been visualised (Fig. 3). Also in other countries, e.g. Sweden (Andersson 1977), Austria (Aichberger 1980) and Canada (McKeague & Wolynetz 1980) such correlations have been found for a number of elements. However the correlation coefficients are systematically higher for the Dutch situation. This should be ascribed to the phenomenon that soils in The Netherlands have been developed from mineralogically rather uniform sediments, in contrast to soils in the other countries which have generally been developed from different types of hard rock.

The elements Zr and Hf do not occur in common minerals but in specific minerals, usually zircon. The highest concentrations of these elements have been found in sandy and loamy soil, which can easily be explained by the high resistance against weathering of zircon.

In Table 2 the ranges of background values are given, grouped to textural classes. The contents of Co, Cs, Sc, Sm, Tb, U and V systematically increase in the series sand - loam - clay. For the elements Al, Ba, Ce, Cr, Eu, La, Lu, Mg, Mn, Rb, Ta, Th, Ti and Yb some overlap can be noticed in concentrations between the textural classes; nevertheless, a clear increase in concentrations can be observed in the series mentioned.

Table 2. Ranges of background values of elements (mg/kg soil) in Dutch topsoils, grouped to soil textural classes (sand: sand and loamy sand; loam: loam, silt loam, sandy loam and sandy clay loam; clay: silty clay).

* contents refer to less than 3 composite samples per nature reserve.

** no data available.

element	sand	loam	clay
Al	4,740 - 24,600	23,300 - 55,400	88,200*- 90,900
As	1.4 - 18	5.1 - 13	19 - 21
Ba	80*- 266	168 - 416	466 - 525
Br	2.0 - 18	5.7 - 42	14 - 16
Ce	5.9 - 25	22 - 57	69 - 81
Cl	52 - 194	121 - 246	**
Co	0.30 - 2.0	2.4 - 10	14 - 16
Cr	11 - 43	33 - 75	99 - 117
Cs	0.38*- 2.0	2.1 - 9.0	13 - 17
Eu	0.08 - 0.41	0.36 - 1.2	1.3 - 1.7
Fe	760 - 20,000	7,860 - 23,000	33,300 - 39,000
Hf	1.3 - 16	3.5 - 16	5.0 - 6.2
K	2,760 - 11,900	8,620*- 18,400	14,600*- 21,800
La	3.6 - 14	13 - 32	39 - 49
Lu	0.06 - 0.20	0.17 - 0.49	0.48 - 0.58
Mg	249*- 2,510	1,640 - 8,030	11,800 - 13,800*
Mn	19 - 187	115 - 534	470 - 651*
Na	771 - 5,400	3,080 - 6,630	4,860 - 5,140
Rb	8.9 - 45	43 - 108	117 - 152
Sb	0.30 - 1.8	0.51*- 2.2	1.5 - 2.2
Sc	0.53 - 2.6	3.0 - 9.2	12 - 16
Si	329,000 - 478,000	331,000 - 453,000	**
Sm	0.50 - 2.0	2.0 - 5.4	6.1 - 8.2
Ta	0.10*- 0.40	0.30 - 0.96	0.95 - 1.2
Tb	0.08*- 0.19	0.25 - 0.70	0.81 - 0.92
Th	1.1 - 3.9	3.3 - 9.0	11 - 13
Ti	322 - 1,770	1,390 - 4,470	4,440*- 4,850
U	0.47*- 1.2	1.4 - 2.6	2.9 - 5.4
V	4.1 - 21	25 - 68	124*- 126
Yb	0.29 - 1.1	1.0 - 2.7	2.5 - 3.2
Zn	6.4*- 43	28* - 150	135 - 153
Zr	58*- 633	126 - 619	212*- 280

For a number of elements a significant linear correlation exists between background values and organic matter contents (Table 3). This correlation is strongest for the elements Br and Cl. Also in Norwegian forest soils significant linear correlations were found between organic matter and halogens (Lag & Steinnes 1976). There are indications that halogens are concentrated in the humus layer of the soil (Lag & Steinnes 1976), but the binding mechanism is still unknown.

Table 3. Linear correlation coefficients for the relation between background values and organic carbon contents in Dutch topsoils.
*** significant at $p < 0.001$; ** idem at $p < 0.01$; * idem at $p < 0.05$.

element	correlation coefficient	number of observations	significance
Al	0.16	26	
As	0.36	28	*
Ba	0.25	28	
Br	0.66	28	***
Ce	0.38	28	*
Cl	0.69	20	***
Co	0.35	28	
Cr	0.41	28	*
Cs	0.34	28	
Eu	0.34	28	
Fe	0.38	28	*
Hf	0.32	28	
K	0.34	27	
La	0.39	28	*
Lu	0.43	28	*
Mg	0.43	24	*
Mn	0.27	26	
Na	0.06	28	
Rb	0.29	28	
Sb	0.44	28	*
Sc	0.38	28	*
Si	0.56	25	**
Sm	0.37	28	*
Ta	0.42	27	*
Tb	0.36	28	*
Th	0.39	28	*
Ti	0.41	26	*
U	0.40	27	*
V	0.37	26	*
Yb	0.42	28	*
Zn	0.41	28	*
Zr	0.30	27	

Applications in studying soil pollution and air pollution

The reported ranges of background values can be used as reference data for the detection of polluted soils, merely by comparing concentrations. Rather constant ratios occur between many elements in the soils under consideration. Deviation of these ratios may also be used as an indication for contamination. In the field of air pollution these ratios can be used to calculate the soil contribution to the total concentration of a given element in aerosols. In a future paper we shall go into details concerning these ratios.

Comparison with background values in soils from other countries

The presented background values have a limited validity geographically. To illustrate this some data on background values in soils from five countries have been listed (Table 4). For a part of the elements the ranges of background values in different countries agree, like As and Zn in Belgian and Dutch soils, Cr in Canadian and Dutch soils and Co in Swedish and Dutch soils. However, for certain elements distinct differences are observed: relatively high maximal concentrations have been found for Sb in Dutch soils, for Cr and V in Belgian soils, for Co in Canadian soils and for Zn in Swedish soils. Differences in concentrations between soils from different countries can be explained by differences in parent material, in soil genesis and/or in the degree of contamination. Also the method of analysis can be important and especially the method of destruction. Therefore, a system of background values per country should be made.

Proposed maximal concentrations

Tietjen (1975) and Kloke (1979) listed the concentrations of several elements in the soil which they consider as maximally tolerable, based on the uptake of these elements in crops intended for human nutrition. Table 5 shows a part of their data. For the elements Cr and V the background values in some Dutch (clay) soils exceed the maximally tolerable concentrations

Table 4. Ranges of background values of some elements (mg/kg soil) in soils from several countries.

Data on Austrian soils from Aichberger (1980), on Belgian soils from De Temmerman et al. (1982), on Canadian soils from McKeague & Wolynetz (1980) and on Swedish soils from Andersson (1977).

: and **: see Table 2.

element	The Netherlands	Austria	Belgium	Canada	Sweden
As	1.4 - 21	**	0.4 - 25	**	**
Co	0.30 - 16	**	0.3 - 30	5 - 50	0.3 - 17
Cr	11 - 117	1.4 - 38	20 - 200	10 - 100	0.9 - 57
Sb	0.30 - 2.2	**	< 0.2 - 0.5	**	**
V	4.1 - 126	**	25 - 300	**	**
Zn	6.4* - 153	7 - 220	25 - 150	10 - 200	4.0 - 310

Table 5. Maximally tolerable concentrations of some elements (mg/kg soil) according to Tietjen (1975) and Kloke (1979).
 **: see Table 2.

element	maximally tolerable concentrations	
	Tietjen	Kloke
As	50	20
Co	50	50
Cr	100	100
Sb	**	5
V	**	50
Zn	300	300

proposed by Tietjen and Kloke. There is no motive, however, to assume that these clay soils are contaminated. So the conclusion that the proposed maximally tolerable concentrations are not valid for the Dutch situation without due consideration seems justified.

In view of the possible variation in background values for one element in different soils, it is advisable to make a differentiation in types of soil when tolerable concentrations of elements in soils have to be set. This would be desirable because of differences between different types of soil not only in background values but also in effects of a certain degree of contamination due to processes like cation and anion adsorption.

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