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Geochemistry of Holocene clays of the Rhine and Meuse rivers in the central-eastern Netherlands

A.L. Hakstege,[1] S.B. Kroonenberg[1] & H. Van Wijck[2]
[1] *Department of Soil Science and Geology, Agricultural University, P.O. Box 37, 6700 AA Wageningen, The Netherlands*
[2] *Technical Centre for Ceramic Industries, P.O. Box 40, 6994 ZG De Steeg, The Netherlands*

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Abstract

Major and minor element geochemical analysis of Holocene clays from five borings in the Rhine and Meuse floodplains shows that Rhine deposits have less SiO_2, MnO, Nb and Zr and more CaO, MgO, Na_2O, P_2O_5, Rb and Sr than Meuse deposits. Geochemical differences between old and young floodplain clays of the Rhine are due to different granulometry and depositional regime. Multivariate statistics show that more than 70% of variance in the deposits is related to provenance and sorting during transport and deposition. Pb and Zn concentrations are correlated with organic matter content, and vegetation horizons in old floodplain deposits are naturally enriched in these heavy metals. Pb and Zn, therefore, are potential paleoclimatic indicators. Increased contents of Pb, Zn, Cr, Ba and V in young floodplain sediments dating from the last century are due to industrial pollution.

Introduction

The chemical composition of fluvial deposits reflects provenance, sedimentary transport and deposition, as well as postdepositional diagenesis and soil formation. In recent sediments, moreover, the influence of man is appreciable. Climatic oscillations can profoundly change the impact of these factors. Not only discharge may change, but also vegetation cover, rates and type of soil formation in the provenance area, the ratio bed load/suspended load, sedimentation rates and postdepositional processes. All these changes are likely to be reflected in the chemical composition of fluvial deposits. Chemostratigraphy in Pleistocene fluvial sediments in the Netherlands has already supplied many new data on past fluvial dynamics (Moura & Kroonenberg 1990, Schout & Kroonenberg 1990). (Sub)recent sediments have been studied geochemically by several authors, including De Groot & Salomons (1985), Japenga et al. (1990), Van der Weijden & Middelburg (1989) and Winkels & Van Diem (1991), but surprisingly little information is available on the geochemistry of Holocene deposits.

In this paper the results of a geochemical survey of five borings in the Holocene floodplains of Rhine and Meuse in the Netherlands are reported. Two different sedimentary environments are distinguished here: old floodplains and recent floodplains. The formation of the old floodplains started after the climatic shift at the Pleistocene-Holocene transition, resulting in the formation of meandering river systems with channel, bank and floodbasin deposits on top of sandy Late Pleistocene braided river deposits (Miedema 1987, Verbraeck 1984). Deposition in the old floodplains ended after the con-

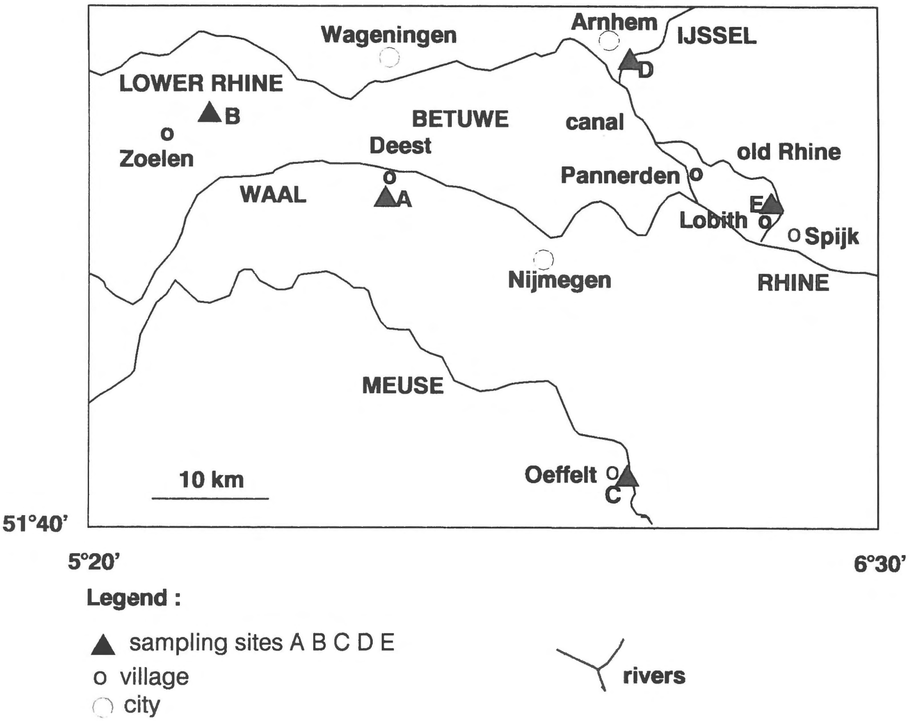

Fig. 1. Sample location map.

struction of dikes in the Early Middle Ages. The recent floodplains started to form between the dikes, and sedimentation actually continues until the present day.

Two sampling sites are situated in old floodplain clays: (A) Deest, south of the river Waal and (B) Zoelen, between the rivers Rhine and Waal. The other three are located in the recent floodplains of the rivers Meuse (C, Oeffelt), Rhine-IJssel (D, Arnhem) and Rhine (E, Lobith) (Fig. 1.).

Old floodplain clays

In the old floodplains, only floodbasin deposits were investigated. Basin clays between the Rhine and Waal increase in thickness from 0.5–4 metre in the east to 5–6.5 metre in the west (Verbraeck 1984). They were formed from the Atlanticum (±6000 BP) until the construction of dikes around 1300 AD prevented further sedimentation. Age-markers in basin clays are dark grey, heavily textured vegetation horizons, which indicate periods of non-deposition or very low sedimentation rates. In a detailed soil survey in the Betuwe area (Havinga 1969, Havinga & Op 't Hof 1983), four vegetation horizons could be distinguished within 2.20 metre depth. They occur on top of successive clay beds and separate sedimentation phases. Two vegetation horizons are usually well developed and represent soil surfaces in the Middle Bronze Age (±3700 BP) and Roman era (±1900 BP), based on archaeological evidence (Havinga 1969).

The following sites in the old floodplains were investigated:

(A) Deest (Fig. 3): In this boring old floodbasin clays with two vegetation horizons at depths of 110–130 cm and 150–170 cm are found, which we suppose to be formed in Roman and Middle Bronze times. This is corroborated by pollen-analytical research and C14-dating by Teunissen (1990). Sedimentation of basin clay started ± 5000 BP. Radiocarbon dating at depths of 150 and 165 cm, corresponding with the top and bottom of the deeper vegetation horizon, yields respective ages of 3140 ± 55 BP and 3660 ± 55 BP and confirms the Middle Bronze Age.

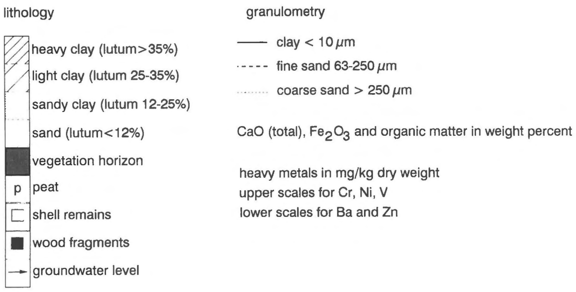

Fig. 2. Legend of drill hole sections (Figs 3–7), showing lithology, granulometry and contents of CaO, organic matter, Fe oxide and heavy metals.

(B) Zoelen (Fig. 4): This basin clay was deposited just west of an ancient channel (±8000–3700 BP) and consists of old floodbasin deposits on top of bank deposits between 150 and 190 cm depth and again floodbasin deposits (Verbraeck 1984). A vegetation horizon from the Roman era at a depth of ±90 cm near Zoelen is described by Havinga & Op 't Hof (1983), but was not observed in our section. In the area near Zoelen at least six different meandering river systems could be distinguished using palynological analyses and radiocarbon dating (Hofstede et al. 1989). The average accumulation per year is estimated at 0.75 mm in the backswamp and at 0.24 mm on the riverbanks (Hofstede et al. 1989).

Recent floodplain clays

These are mainly sandy clays with layers of fine sand. The recent floodplain sediments were formed as pointbar, bank and channel-fill deposits. Their thickness is extremely variable: from less than one metre up to more than ten metres. Deforestation upstream starting in the Early Middle Ages caused a substantial increase of the sediment load, and influenced especially the silt content. Around 1300 AD dikes were built, narrowing the river channels. With the construction of groynes the course of the rivers became even more confined. Estimates for the present sedimentation rate in the floodplains of the lower Rhine are 0.1–0.7 mm/year; just

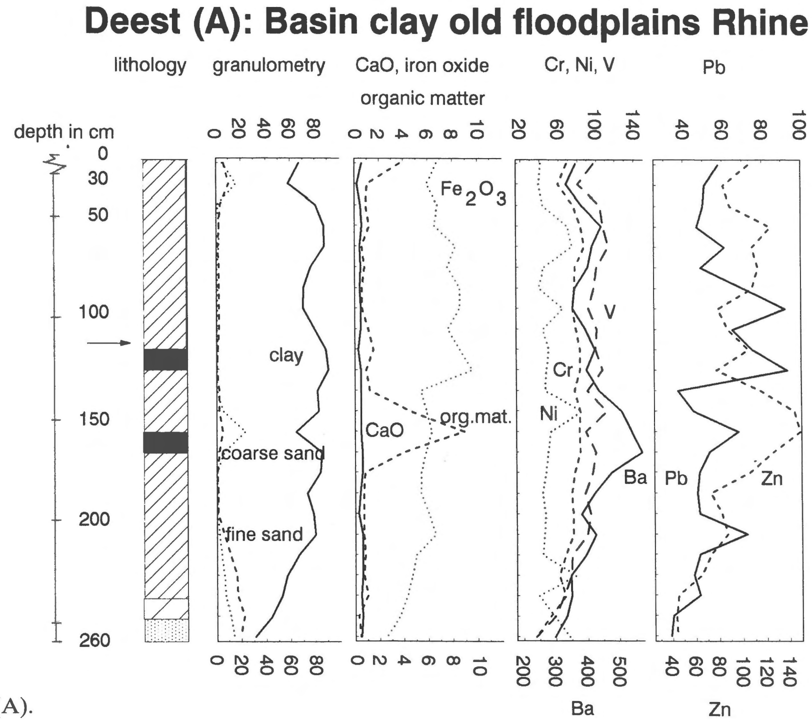

Fig. 3. Section Deest (A).

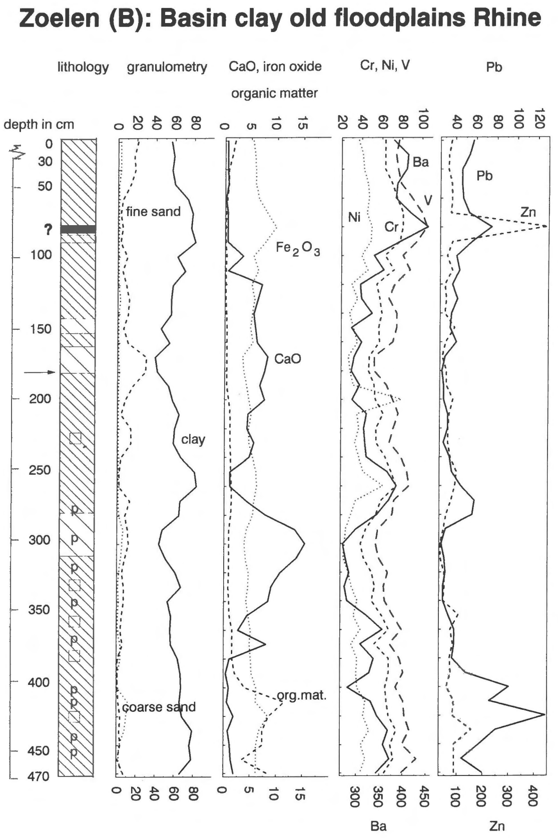
Zoelen (B): Basin clay old floodplains Rhine

Fig. 4. Section Zoelen (B).

after the construction of dikes the sedimentation rate was higher: 0.7–22 mm/year (Middelkoop & Van der Perk 1991). Another estimate of 1–5 mm per year is based on the recent sediment supply (Japenga et al. 1990). In our sections (Figs 5, 6), recent sediments deposited in the floodplain between the dikes cannot be distinguished with certainty from the underlying deposits formed in the natural landscape, though the observed increase in clay content from one metre depth upwards might reflect the construction of dikes. Because of poor preservation of pollen and other organic material in this oxidized environment, age data are scarce. The following borings are from the recent floodplains:

(C): Oeffelt (Fig. 5): The top of the succession consists of recent river floodplain deposits of the Meuse. Below ±170 cm depth the clays become more sandy and may be of Pleistocene age (Stiboka 1976, Miedema 1987). The recent channel of the Meuse dates from the Subatlanticum and was mainly formed in the period 250–500 AD (Verbraeck 1984). The rather low dikes in this area were constructed recently (around 1941) and hardly affected the sedimentation regime.

(D) Arnhem (Fig. 6): The location is in the recent floodplain of the IJssel river, near the bifurcation of the Rhine. The IJssel formed a distributary of the Rhine in the Subatlanticum (±3000 BP) and its later development was strongly influenced by man (Van de Meene 1977). Its deposits are mainly post-Roman. The lower part of the section shows many sandy intercalations which represent bank deposits.

(E) Lobith (Fig. 7): This location is situated in the floodplain of a former course of the Rhine, which was cut off by the construction of a canal near Pannerden in 1710. During heavy floods the area was still inundated until 1968, when the spill near Spijk was closed. These sandy clays were probably formed in post-Roman times (Stiboka 1975). Sedimentation changed with the enbankment around 1300 AD and practically ended after 1710 AD.

Materials and methods

Undisturbed clay samples (213 in total) were taken with a 3 cm diameter gouge in January and February 1991. At each of the five sampling locations, three holes, at distances of some tens of metres, were drilled until the Pleistocene sand was reached. One of these drill holes was sampled in detail at intervals of 10 cm, while the two others were sampled per lithological unit. The upper 30 cm of the sections in the topsoil was taken as one sample. The following characteristics were determined (see Table 1 for summary of results).

Granulometric composition is expressed in weight percentages of the fractions: clay (<10 μm), fine sand (63–250 μm) and coarse sand (>250 μm), determined by sedimentation and sieving analysis. The calculated rest fraction is silt (10–63 μm). In this paper the fraction <10 μm, normally used in the ceramic industry, is called the clay fraction, containing clay *sensu stricto* and fine silt. For fluvial clays a constant linear association of the clay fractions <10 μm and <2 μm (lutum) was demonstrated, which per-

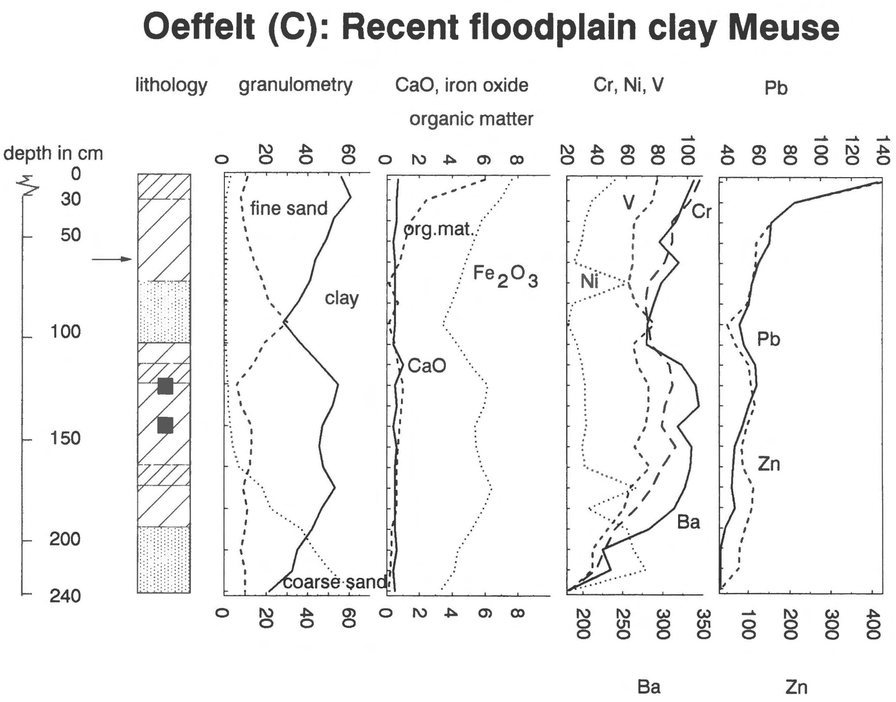

Fig. 5. Section Oeffelt (C).

mits conversion through division by 1.5 (Van der Zwan 1990).

Carbonate content was measured as CO_2 % and is expressed as $CaCO_3$ weight percentages. Specific surface area was measured by the method of equilibrium moisture content (Timmers 1990). Organic matter was determined by oxidation and is given in weight percentages.

Bulk chemical analysis was carried out on the 157 samples from the detailed surveys. The samples were dried, ground in a small tungsten carbide ball mill and ignited at 900° C to determine loss on ignition (LOI). One gram of the ignited sample was mixed with 4 grams lithium-tetraborate and fused for 15.5 minutes to a bead. Analyses on major and trace elements were carried out with X-ray fluorescence spectroscopy on a Philips XRF assembly. Results were calibrated using United States Geological Survey certified reference materials (Abbey 1980). Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P (expressed in weight percentages of oxides) were determined with a scandium tube, while Ba, Cr, Cu, Ga, La, Nb, Ni, Pb, Rb, Sr, V, Zn and Zr (expressed in mg/kg dry weight) were measured with a rhodium tube. Omitting loss of ignition, the major elements were recalculated to 100%. The results are compiled in Table 1. For some elements the analyzed values are below the detection limit (d.l.). This concerns all analyses for Co (d.l. 20mg/kg), nearly all for Cu (d.l. 10mg/kg), many for Ga (d.l. 10mg/kg) and few for La (d.l. 15mg/kg). These elements are excluded from statistical treatment.

Discussion and results

Differences between sampling sites

The analytical results (Table 1) show that within the Rhine system, old floodplain clays (locations A, B) are more clay-rich on average than young floodplain clays (D, E). This is reflected in higher average Al_2O_3, Rb, Ba, Cr, V contents and higher specific surfaces. Recent floodplain clays of the Meuse (Oeffelt, location C) have much higher SiO_2, MnO,

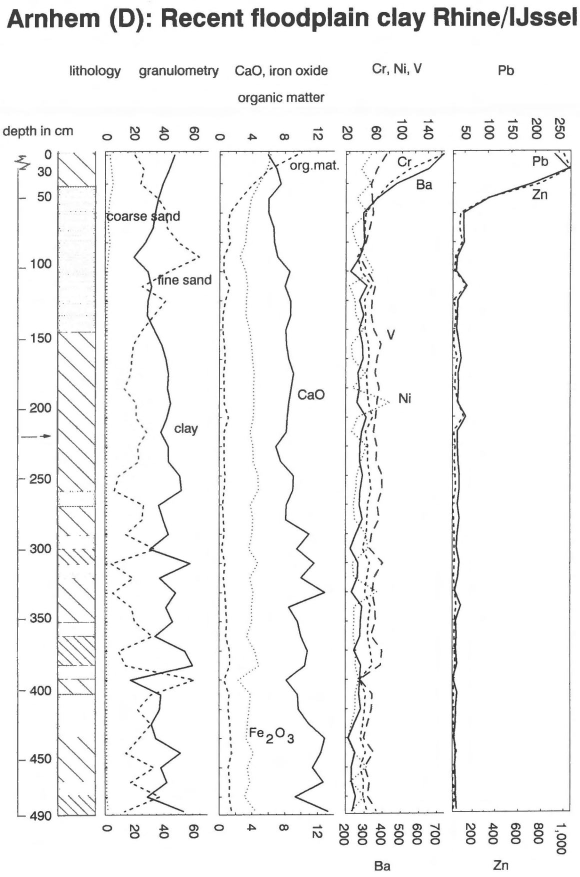

Fig. 6. Section Arnhem (D).

Nb and Zr and much less CaO, MgO, Na_2O, P_2O_5, Rb and Sr, than all Rhine deposits.

Compared with the average chemical composition of terrigenous shale (Taylor & McLennan 1985) the sampled clays contain more SiO_2 and less Al_2O_3, Na_2O and K_2O. For the trace elements most values are lower (Ba, Cr, Cu, Rb and V), with exception of Pb and Zn (Oeffelt, Arnhem). The clays of Deest are closest to this average shale composition.

Distribution of elements with depth

The distribution of elements with depth for each sample location is shown in Figs 2 to 7.

In the old floodplain of the Rhine (A, B), clay content is rather constant with depth until the contact with the underlying sands. The trace metals V, Ba and Cr follow this trend. Ca is low in profile A, but much more variable in profile B. At the vegetation horizons in profile A, peaks in the organic matter content coincide with high contents of Zn, Pb and Ba. A similar peak in the heavy metal concentrations is found in profile B at 90 cm depth, which may indicate a correlation with the vegetation horizon described by Havinga & Op 't Hof (1983), though no enrichment of organic matter is apparent from our data. Some of the deeper and more organic-rich peat occurrences in site B are also enriched in Pb and Zn. The distribution of Ni is different from the other heavy metals and not significantly correlated with any parameter.

In the recent floodplains of both Rhine and Meuse, grain size distribution with depth is much more variable, and Pb, Zn, V, Cr and Ba contents seem to vary with clay content except for the uppermost horizons. The conspicuous increase in Cr, Ba, Pb and Zn contents towards the surface in the recent floodplains of both Meuse (C) and Rhine (D) coincides with an increase in organic matter and is obviously caused by recent deposition of polluted sediment. The lack of this trend in the other locations (A, B and E) is in agreement with the assumption that sedimentation has ended there centuries ago.

Multivariate statistical analysis

Correlation matrix

In order to quantify the correlations suggested by the distribution of the elements per site and with depth, multivariate statistical analysis has been carried out. The correlation matrix for major elements, trace elements and grain size classes for the whole data set (not presented here because of its size), shows that the heavy metals V, Cr, Ba and Fe_2O_3 are correlated positively with clay content. Organic matter shows a good correlation with Pb, Ba, Zn and Cr. The total heavy metal content shows a positive linear relationship with the clay content, but less so with the organic matter content (Fig. 8). The highest correlation coefficients for V, Ba and Cr are with the specific surface area. The specific surface

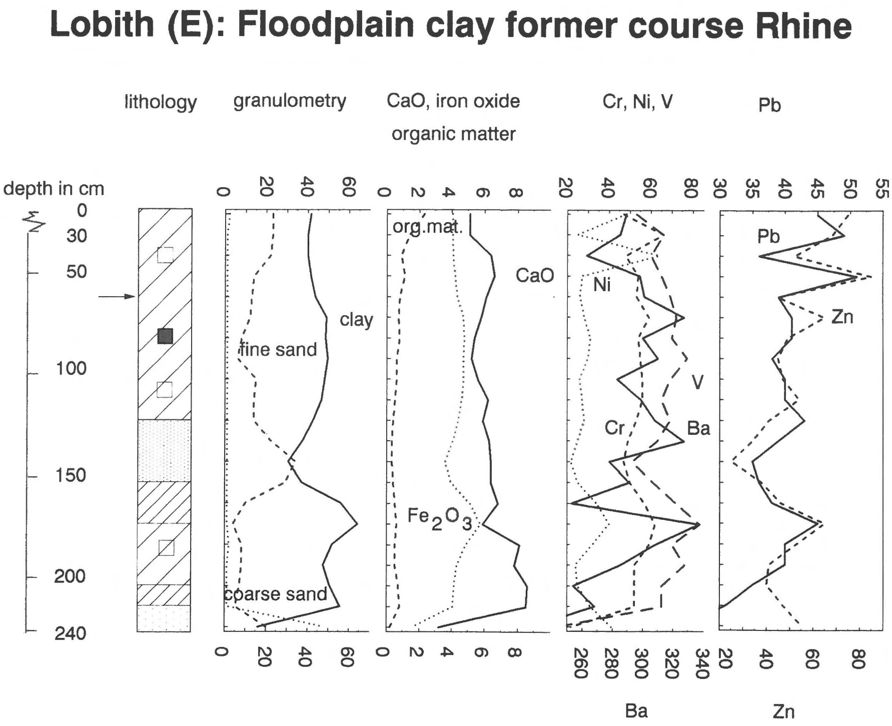

Fig. 7. Section Lobith (E).

area is clearly correlated with the clay fraction and to a lesser extent with Fe oxide and organic matter. Plots of specific surface area and Fe oxide against the total heavy metal content are similar to those for the clay fraction (Fig. 8) and are not presented here. P content is positively correlated with Pb, Zn, Cr and Fe_2O_3. Ni and MnO show overall low correlation coefficients.

The silt fraction is well correlated with Zr and Nb. The sand fractions and carbonate contents show very weak negative correlations with heavy metals.

Principal component (factor) analysis

Principal component analysis was carried out using the SPSS PC+ package (Norusis 1986). A minimum number of factors, based on interrelationships among the variables, is chosen for an adequate and meaningful presentation of the data set. For the factor model to be appropriate, the variables should show at least one significant correlation with each other; thus Ni is left out. After several tests the model shown in Table 2 was selected as the most satisfactory. Five factors, each with eigenvalues more than one, were extracted from 24 variables representing 87.5% of the total variance. Each variable is expressed as a linear combination of these factors, called factor loading. The (absolute) value of a factor loading indicates the relative contribution of a variable to a factor. A negative factor loading implies an inverse relationship with the other variables in the factor, that show positive loadings. By Kaiser normalization and Varimax rotation on all variables the factor loadings are transformed for a better interpretation and presented as a rotated factor matrix (Table 2).

Clay content, Al_2O_3, TiO_2, Rb, K_2O, V, Cr, Ba and Fe (as Fe_2O_3) have high positive factor loadings in the first factor (1a). Fine sand and carbonates (CaO) have high negative loadings in this factor, indicating an inverse relationship with the clay fraction. In factor 2a, positive factor loadings are found for CaO, MgO, Sr and Na_2O, while negative contributions come from SiO_2 and coarse sand. Factor 3a is made up of heavy metals (Pb, Zn, Ba, Cr) combined with P_2O_5 and organic matter. Factor 4a is composed of loadings from the variables silt, Zr and Nb. The fifth factor (5a) deals with Mn, which shows a behaviour different from the other heavy metals.

As our interest is to gain insight in the natural variability, a second statistical treatment was carried out, omitting polluted samples in the topsoil of Arnhem (4 samples) and Oeffelt (2 samples). The results (Table 2), explaining 85.6% of the total variability, are similar for the factors: clay (1b), carbonates (2b) and silt (3b), but show a different distribution of heavy metals and phosphate. The explanation is that the observed combination of high concentrations of heavy metals (Pb, Zn, Ba, Cr) with phosphate and organic matter in topsoil (factor 3a) is mainly caused by pollution. Apparently the association of heavy metals with organic matter is much

Table 1. Arithmetic averages of major and trace element compositions and physical parameters per sample location. n= number of samples. Granulometric composition: c. sand= coarse sand (>250 μm), fine sand (63–250μm), silt (10–63μm) and clay (<10 μm). Coarse sand to organic matter in percent dry weight; silt calculated as rest fraction; specific surface area in m^2/g. Major elements: SiO_2 to P_2O_5 in weight percentages of the oxides and corrected for LOI. Trace elements: Ba to Zr in mg/kg dry weight. Standard deviation in parentheses, not indicated for values below detection limit (e.g. <10). Composition in column 'shale' is estimate of average terrigenous shale, excluding carbonate components (Taylor & McLennan, 1985)

location	shale	Deest (A)		Zoelen (B)		Oeffelt (C)		Arnhem (D)		Lobith (E)	
depth		2.60m		4.70m		2.40m		4.90m		2.40m	
n samples		24		45		21		46		21	
c. sand		4.6	(5.8)	2.4	(2.5)	12.4	(18.7)	1.4	(0.9)	3.3	(10.0)
fine sand		5.7	(6.4)	8.5	(6.7)	12.6	(5.4)	25.4	(13.2)	14.8	(8.1)
silt		17.5	(7.3)	26.8	(7.9)	30.9	(12.1)	33.9	(7.0)	37.3	(6.1)
clay <10 μm		72.3	(14.7)	62.3	(10.7)	44.0	(9.6)	39.3	(9.1)	44.6	(9.7)
$CaCO_3$ (%)		0.9	(0.2)	7.9	(7.1)	1.0	(0.2)	16.2	(3.4)	11.2	(2.2)
org. mat.		1.6	(1.9)	1.9	(2.6)	1.0	(1.2)	1.3	(1.6)	0.7	(0.4)
spec. surf.		161	(44)	125	(29)	96	(21)	72	(12)	84	(15)
SiO_2 (%)	62.8	69.40	(5.10)	67.70	(2.90)	78.80	(4.50)	69.30	(3.40)	70.80	(3.90)
TiO_2	1.0	0.86	(0.13)	0.76	(0.10)	0.77	(0.19)	0.61	(0.09)	0.73	(0.13)
Al_2O_3	18.9	16.90	(3.10)	14.60	(2.20)	11.0	(2.40)	10.60	(1.10)	11.50	(1.60)
Fe_2O_3	6.5	6.32	(1.66)	5.51	(1.23)	5.23	(1.09)	3.91	(0.71)	4.28	(0.77)
MnO	0.11	0.09	(0.07)	0.11	(0.08)	0.19	(0.06)	0.12	(0.03)	0.13	(0.05)
MgO	2.2	1.89	(0.39)	2.32	(0.39)	0.86	(0.20)	2.08	(0.31)	2.02	(0.32)
CaO	1.3	1.06	(0.37)	5.27	(4.40)	0.59	(0.21)	9.96	(2.29)	6.87	(1.85)
Na_2O	1.2	0.54	(0.13)	0.66	(0.11)	0.39	(0.19)	0.83	(0.09)	0.77	(0.08)
K_2O	3.7	2.86	(0.22)	2.84	(0.33)	2.08	(0.41)	2.52	(0.16)	2.71	(0.22)
P_2O_5	0.16	0.16	(0.09)	0.17	(0.03)	0.13	(0.05)	0.16	(0.07)	0.16	(0.03)
Ba (ppm)	650	405	(65)	335	(43)	301	(41)	294	(95)	290	(26)
Co	23	<20		<20		<20		<20		<20	
Cr	110	72	(12)	62	(10)	62	(15)	51	(21)	53	(8)
Cu	50	<10		<10		<10		<14		<10	
Ga	20	<16		<13		<11		<10		<11	
La	38	33	(8)	29	(6)	31	(8)	<22		<27	
Nb	19	18	(3)	18	(3)	26	(8)	19	(2)	19	(3)
Ni	55	52	(13)	39	(10)	39	(16)	35	(13)	31	(10)
Pb	20	56	(16)	46	(20)	56	(22)	51	(51)	39	(6)
Rb	160	132	(16)	120	(20)	90	(15)	87	(8)	96	(10)
Sr	200	111	(14)	141	(41)	69	(13)	204	(20)	164	(21)
V	150	89	(18)	76	(12)	76	(21)	57	(9)	65	(13)
Zn	85	93	(28)	78	(59)	116	(77)	114	(228)	51	(14)
Zr	210	197	(30)	207	(23)	368	(144)	242	(28)	262	(33)

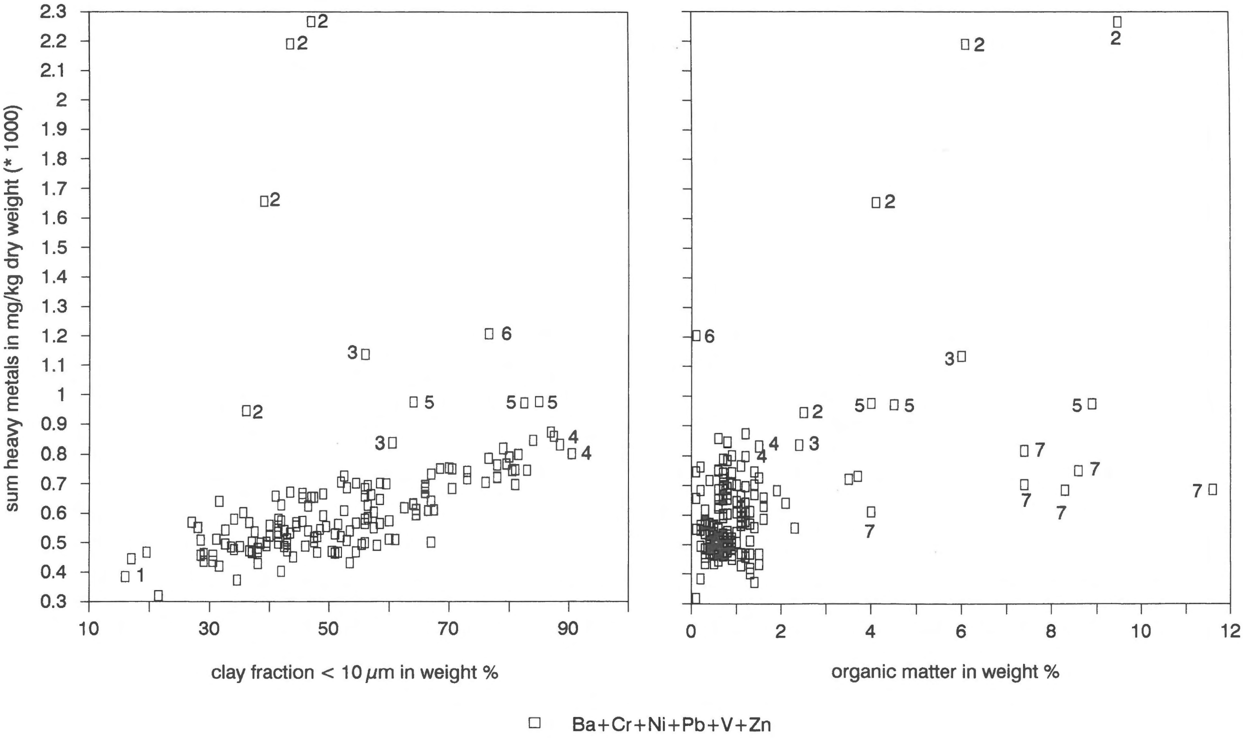

Fig. 8. Scatter plots of clay (<10 μm) and organic matter contents against the sum of heavy metal concentrations. Outliers are indicated as follows: 1) sand or sandy samples, 2) polluted topsoil (Arnhem), 3) polluted topsoil (Oeffelt), 4) shallower vegetation horion at Deest, 5) deeper vegetation horizon at Deest, 6) possible vegetation horizon at Zoelen, 7) peat intercalations at Zoelen.

less clear in the natural environment than in polluted sediments (except for Pb, factor 4b).

Factor scores

For each sample the relative contributions of the different factors, called factor scores, were calculated using the program FACTOR. Plots of factor scores for pairs of factors are useful for detecting outliers and clusters of samples. Factor scores for factor 1b (clay+ associated elements) and factor 2b (carbonates+ feldspars), are presented in Fig. 9. Clusters for Rhine (A, B, D, E) and Meuse (C) sediments are clearly separated because of factor 2b. Within the Rhine sediments, old (A, B) and recent (D, E) floodplain clays show different clusters due to factor 1b. A few samples from the old floodplain clays (B) fall within the cluster of the recent floodplain clays, because they were deposited as bank deposits. Two outliers represent vegetation horizons with high heavy metal contents. The Meuse samples show two different trends. The upper series represents samples deeper than 1.70 m, which contain more coarse sand (Fig. 5) and may be of Pleistocene age.

Causes of natural variability

Mineralogical composition

The association of well-correlated elements in specific factors can be translated to a large extent into mineralogical composition. High SiO_2 contents point to quartz, high Al_2O_3, K, Ba, Rb, V contents to clay minerals (and partly also alkali feldspars and micas), though from the present bulk geochemical data it cannot be established whether some of these elements occur within the crystal lattices of the clay minerals or in adsorbed form. Fe_2O_3 points to Fe-(hydr)oxides, CaO and Sr to carbonates, Na_2O to acid plagioclase feldspars, Zr and Nb to stable heavy minerals (zircon, rutile, sphene) (Van Meerten et al. 1988, Timmers 1990, Moura & Kroonenberg 1990). Granulometry is partly reflected in chemistry because of the preferent occurrence of minerals in specific grain size fractions: clay minerals in the finest fractions, heavy minerals, micas and feldspars in the silt and fine sand fractions, and quartz in all size fractions. This is the reason for the positive correlations of SiO_2 with coarse sand, Zr and Nb with silt, and a host of other elements with the clay fraction.

Variability in mineralogy is related to provenance of the sediments and to sorting processes during transport and deposition. The fact that the highest percentage of variance is found in factors related to these parameters (factors 1a/b, 2a/b, and 4a/3b) indicates that more than 70% of the natural variability of the chemical composition of Holocene fluvial sediments is due to geological processes.

Provenance

The differences between Rhine and Meuse sediments of similar grain size are evidently related to primary mineralogical composition, and hence to source area. Why the Meuse sediments are richer in stable components like SiO_2, Zr and Nb than Rhine sediments is not clear, however. Clay beds in the recent floodplain of the Rhine are calcareous, in contrast with recent Meuse clays which have very low

Table 2. Rotated factor loadings analyses for two data sets of clay samples: a) all samples (except one sample from underlying sand at location E, n = 156) (left side of Table) b) all samples as under a) except polluted topsoil samples (n = 150) (right side of Table). Number of variables is 24. Factor loadings <[0.5] are omitted, except for Pb, Zn and P_2O_5. The five factors extracted represent respectively 87.5% (F1a–F5a) and 85.6% (F1b–F5b) of the total variance

Factor % variance	F1a 39.2	F2a 19.1	F3a 12.4	F4a 11.4	F5a 5.4	F1b 43.3	F2b 20.0	F3b 11.9	F4b 5.9	F5b 4.5
clay <10 µm	0.94					0.92				
$A1_2O_3$	0.92					0.91				
V	0.93					0.93				
TiO_2	0.91					0.92				
Rb	0.87					0.88				
Fe_2O_3	0.82					0.79				0.48
fine sand 63–250 µm	−0.81					−0.78				
K_2O	0.67					0.66				
MgO		0.86					0.87			
Sr		0.85					0.81			
SiO_2		−0.85					−0.85			
CaO	−0.55	0.79				−0.58	0.71			
Na_2O		0.61					0.66			
Pb			0.95			0.44			0.70	0.34
Zn			0.94			0.47			0.35	
P_2O_5			0.72				0.44			0.56
Ba	0.50		0.72			0.82				
Cr	0.62		0.71			0.92				
organic matter			0.63						0.68	
Zr				0.90				0.92		
Nb				0.87				0.89		
silt 10–63 µm				0.69				0.65		
coarse sand <250 µm		−0.63					−0.72	−0.56		
MnO					−0.69					0.70

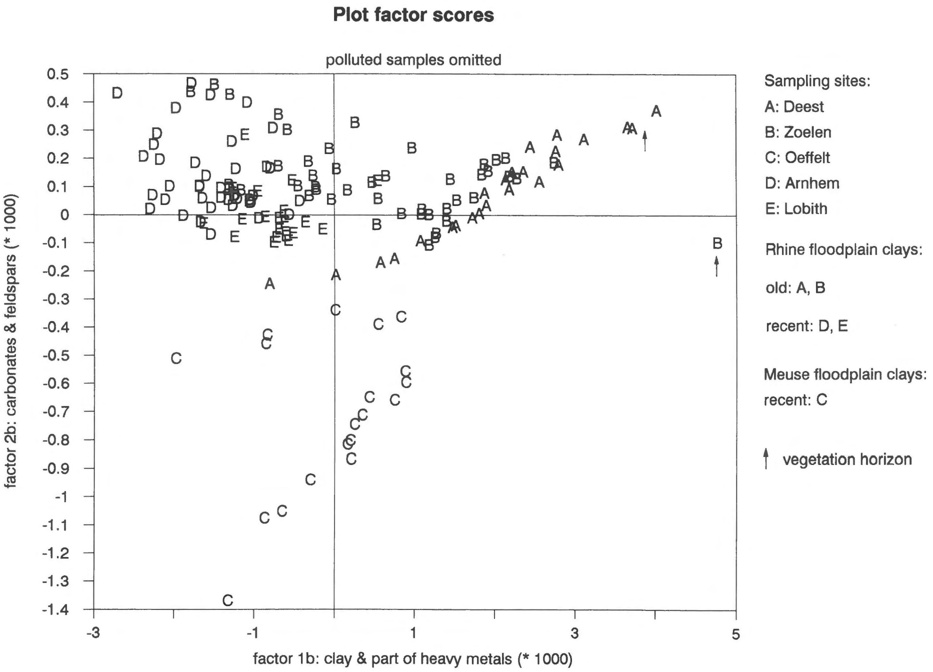

Fig. 9. Plot of the factor scores of factor 1b (clay+ part of heavy metals) against those of factor 2b (carbonates+ feldspars). Data labels (A–E) indicate sampling sites. Factors (5 in total) result from principal component analysis of the data set without the polluted topsoil samples.

calcium carbonate contents. This is attributed to admixture of acid waters from the Peel marshes to the Meuse waters further upstream (Stiboka 1976).

Transport and sedimentation

The differences between old and young Rhine floodplain sediments are due to the change in depositional regime caused by the construction of the dikes. In the old floodplain, there was a considerable spatial separation of different grain size fractions from natural levees to the basins. When sedimentation was restricted between the dikes, an overall coarsening of the sediment took place. Moreover, the increase of silt-rich sediment due to deforestation in the headwaters induced an absolute coarsening of the sediment load.

Carbonate content of the sediments is partly related to depositional environment (Havinga 1969). Sandy bank deposits, such as those intercalated in the clays at Zoelen (B), contain appreciable calcium carbonate. The old floodplain clays, however, show rather low contents of carbonates because of instantaneous decalcification during sedimentation in poorly drained, densely vegetated marshes rich in organic acids (Havinga 1969). Decalcification in the upper part of the clay layers in the recent floodplains is minimal.

Soil formation: redox conditions, organic matter and heavy metals

Redox conditions are different in old and recent floodplain clays. The old floodplain clays are waterlogged with only minor fluctuations in ground water level. Reducing conditions prevail from approximately one metre downwards, as shown by grey colours. Recent floodplain clays are generally well drained, with large seasonal fluctuations in groundwater level, and oxidized down to a depth of two metres or more, indicated by brown colours. Redox conditions of the soil affect the status of a number of metal ions, particularly for Fe and Mn, but also for Cr and Pb (Schmitt & Sticher 1991). The association of MnO, Fe_2O_3 and P_2O_5 in factor 5b might be related to redox processes, as indicated by its linkage with old floodplain clays, which were mainly formed in reducing conditions. No other elements seem to be influenced by redox processes, so that vertical mobility of heavy metals is probably very limited.

The behaviour of elements correlated with organic matter, and especially Pb and Zn, is more complex. Factor analysis including the polluted top samples from sites C and E shows good correlations between these metals (and P_2O_5, Ba and Cr as well) and organic matter content (Table 2, factor 3a), but when the polluted samples are omitted, only the correlation of Pb with organic matter is maintained (factor 4b), whereas Zn appears to have more affinity to clay.

This also appears from the vertical distribution profiles. In profile D, peaks in organic matter content coincide with peaks in Pb and Zn. In profile A, peaks of Pb and Zn coincide with the lower vegetation horizon, but the upper one is only high in Pb. In profile B a conspicuous peak of both elements occurs at a depth where no increase of organic matter had been detected, though in neighbouring borings made by Havinga & Op 't Hof (1983) a vegetation horizon was found at this depth.

Pb is considered immobile in soils and mainly fixed by organic matter (Alloway 1990), but Zn is reported to be relatively mobile at low pH (Schmitt & Sticher 1991). In the non-calcareous old floodbasin clays, where acidic conditions prevailed during sedimentation (Havinga 1969), Zn may therefore have been more mobile than Pb. In the calcareous younger floodplain deposits, Zn remains tied to organic matter.

Whether the increased Pb and Zn content of organic-rich layers originated by biological accumulation or by variations in primary supply in suspended sediment or water cannot be established from the present data. But as Havinga & Op 't Hof (1983) consider the widespread occurrence of vegetation horizons to be related to climatic change, the Pb and Zn contents of sediments could be valuable paleoclimatic indicators as well.

Pollution

Heavy metal pollution in Rhine and Meuse sediments

Since the beginning of this century, the Rhine has been contaminated with heavy metals due to intensive industrialization along its course. For all heavy metals, the contents in Rhine sediments increase up to 1955–1960, whereafter Pb and Zn are declining, later followed by Cr, Cu and Ni (De Groot & Salomons 1985). This decline is the result of an international programme for improvement of the quality of the Rhine water starting in the seventies (Ministerie V & W 1989). Studies on the pollution history of the Rhine were carried out in the lakes IJsselmeer and Ketelmeer, which are major sedimentation areas for the northern Rhine branch, the IJssel (Winkels & Van Diem 1991). Maximum concentrations for all studied metals were found between 1955 and 1975; Cd and Ni remained high until 1980. Later deposited sediments have rather low pollutant levels. A substantial decrease of heavy metal concentrations in recent sediments, between 1958 and 1981, was also observed by Japenga et al. (1990), who analyzed floodplain sediments of the Waal, sampled just after deposition. The trend of decreasing heavy metal pollution since the seventies is also demonstrated by a decrease in heavy metal loads of the rivers Rhine (Van der Weijden & Middelburg 1989) and Meuse (Ministerie V & W 1989, 1990a and 1990b). Part of the pollution in topsoils (Pb, Zn) originates from atmospheric deposition (Lexmond & Edelman 1987).

The sharp increase of heavy metal (Pb, Zn, Cr) contents in the upper 60 cm of profile D and their decrease (Pb, Zn) in the topmost horizon seem to reflect this history. Assuming that pollution started around 1900, an average sedimentation rate can be deduced of around 6 mm/year, which is slightly above the range of 1–5 mm/year obtained by Japenga et al. (1990).

The Meuse basin has been polluted with heavy metals for centuries, largely due to coal, lead and zinc mining. Metal mining activities have ceased since 1938, but the processing of metal ores continued until about 1950. Topsoil formed during the last

30 to 45 years in the valley of the Geul, a tributary of the Meuse, shows the highest metal concentrations (Leenaers 1989). This is also reflected in the higher Pb, Zn contents in the upper 40 cm of profile C.

Background levels

The average heavy metal contents of the soil parent material in a natural environment are generally called background levels. In the Netherlands, the upper limits of background values for heavy metals were established from their concentration in topsoil (0–10 cm) in natural environments and in cultivated soils (0–20 cm) in rural areas (Edelman 1984, Edelman & De Bruin 1986, Lexmond & Edelman 1987, Technische Commissie Bodembescherming 1990). Reference values for heavy metals in sediments and soils in the Netherlands are based on these limits (Ministerie VROM 1991a). This approach ignores possible contamination in topsoils and does not take into account the natural spatial and vertical variability of the chemical composition in soil and subsoil. More information on background values in the subsoil is needed to improve the system of reference values.

Because of strong correlations of heavy metal concentrations with clay and organic matter, reference values are defined for a standard soil composition of 25% clay and 10% organic matter content (Ministerie VROM 1991a). To make comparisons possible, we normalized our analytical results for trace metals on the standard soil composition (Van Wijck et al. 1992), using the correction formula applied by Winkels & Van Diem (1991) and Japenga et al. (1990). The normalized heavy metal concentrations with depth show the same trends as depicted in Figs 2 to 7. For Ba, all our normalized analytical results are above the reference value of 200 (Ministerie VROM 1990). This value is not based on published Ba contents in soils (Edelman 1984, Edelman & de Bruin 1986) and is in disagreement with the reference value of approximately 400 for the standard soil composition (Technische Commissie Bodembescherming 1990).

Pollution levels

The extent of pollution is measured in government sanitation surveys using a set of three values as quality criteria (Ministerie VROM 1990). The A value refers to the upper limit of current background levels and is, for heavy metals, taken as the reference value. For B value is a limit above which further investigation is necessary. The soils exceeding the C value, sanitation should be considered.

Most sampled clay beds are unpolluted (Van Wijck et al. 1992). Due to natural enrichment in the vegetation and peat horizons of basin clays in the old floodplains of the Rhine, the A values are in places exceeded for Zn, Pb and Ba. The polluted topsoils of the recent floodplains of the Rhine show Zn, Pb and Ba contents above the B value and those of the Meuse have Pb and Zn contents above the A value. Ni shows peaks above the A value in all deposits, especially in the clay bed of profile D near Arnhem.

Conclusions

More than 70% of the geochemical variability in the investigated fluvial sediments is determined by geological processes. Recent floodplain clays of the Meuse have more SiO_2, MnO, Nb and Zr and less CaO, MgO, Na_2O, P_2O_5, Rb and Sr than Rhine deposits, reflecting lithological differences in the source areas. Old floodplain clays in the Rhine system have more Al_2O_3, Rb, Ba, Cr, Ti and V than the young floodplain Rhine deposits because of less effective spatial grain size separation and hence coarser overall granulometry in the latter. Higher Ca (carbonate) and Sr contents in the latter are related to different pH and Eh conditions during accumulation.

Natural concentrations of Pb, and to a lesser extent of Zn, are related to organic matter accumulation in vegetation horizons and peat. These elements have potential as paleoclimatic indicators. Postdepositional mobility of metals appears to be very limited. Natural Pb and Zn concentrations in organic-rich deposits exceed the reference values

(A value) established by the government of the Netherlands.

Man-made heavy metal accumulation can be distinguished from natural ones on the basis of the good statistical correlations of Pb, Zn, Cr, and Ba with organic matter in the former. Pollution with these metals (3–5× background values, partly exceeding the B values) has been detected in the upper 40 cm in the recent Meuse floodplain clays and upper 60 cm in the recent Rhine floodplain clays. Heavy metal contents in most other fluvial clays do not exceed background values. Reference values for Ba should be reconsidered.

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