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Solubility of Cyanide in Contaminated Soils

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ABSTRACT

At more than 200 sites in the Netherlands, the soil is contaminated with cyanide as a result of industrial activities. The mobility of cyanide, which mainly occurs in the form of iron cyanide complexes [$Fe(CN)_6^{3-}$ + $Fe(CN)_6^{4-}$], plays an important role in predicting the possible hazards for the environment and human health. Cyanide mobility was investigated by assessing data on cyanide concentrations in groundwater at contaminated sites, and by examination of three contaminated soils. High cyanide concentrations were found in the groundwater at sites with alkaline soils (pH ca. 7.5), whereas much lower concentrations were found in the groundwater with acidic soils (pH ca. 4). This agreed with the assumption that the behavior of cyanide in these contaminated soils is largely governed by the solubility of Prussian blue [$Fe_4(Fe(CN)_6)_3(s)$], which is relatively insoluble under acidic conditions. In the acidic soils, the concentrations in the soil water appeared to be close to equilibrium with Prussian blue. In alkaline soils this precipitate is extremely soluble. The presence of this material here was possibly the result of slow dissolution kinetics. Precipitation of Prussian blue in acidic soils does not prevent dissolved iron cyanide concentrations from exceeding Dutch soil quality standards.

CYANIDE HAS BEEN called one of nature's most toxic substances (Fuller, 1984). However, its toxicity strongly depends on the chemical form in which it is present. The free form [HCN(aq) + CN^-] is extremely toxic whereas iron cyanide complexes [$Fe(CN)_6^{3-}$ + $Fe(CN)_6^{4-}$] are considered to be relatively harmless. Cyanide is often found as a soil contaminant at industrial sites, especially on the sites of former gasworks and of electroplating industries (Alesii and Fuller, 1976). On the sites of former gasworks, of which there are 234 in the Netherlands, cyanide was mainly discharged onto the soil surface in solid waste material. These wastes contained complexed cyanide as a solid phase, most likely Prussian blue, a precipitate of iron and iron cyanide [$Fe_4(Fe(CN)_6)_3(s)$]. Leaching of this material after disposal results in contamination of the soil and groundwater with complexed cyanide. This complexed cyanide is not thermodynamically stable in soil solutions, and tends to decompose to free cyanide. However, decomposition proceeds extremely slowly in the dark; the half-life of complexed cyanide varies from years to hundreds of years, depending on pH and redox potential (Meeussen et al., 1992a). Because of this slow decomposition, the complexed form can persist in soils. However, exposure to daylight dramatically increases the decomposition rate of these iron cyanide complexes. Complete decomposition then occurs within hours or days, depending on light intensity (Meeussen et al., 1989, 1992a). Therefore, complexed cyanide cannot be regarded as a completely safe form of cyanide. The possible risks for negative effects on human health and the environment are strongly influenced by the physicochemical behavior of cyanide in soils. Insight in this behavior and how it is affected by soil parameters like pH and pe enables better evaluation of those risks.

The behavior of contaminants in soils is largely governed by the interaction between the dissolved contaminant and soil solid phases. In the case of soil contamination with cyanide in the form of iron cyanide complexes, this interaction is probably dominated by precipitation of Prussian blue (Meeussen et al., 1990). This precipitate is often considered to be insoluble, but in fact its solubility strongly depends on the pH and redox potential of the soil solution. As will be discussed later, Prussian blue is only slightly soluble at pH 4, but very soluble at pH 7.

In the Netherlands, soils with a pH of about 7 and acidic soils with a pH of about 4 are common. The more alkaline pH values are found in soils in the lower areas of the country, which are primarily calcareous clay soils formed by sea and river sedimentation. The more acidic pH levels are found in sandy soils in the higher parts of the country. The difference in pH between those soil types is expected to cause a rather large difference in solubility of Prussian blue and hence also a large difference in mobility of cyanide between those soil types.

The main objective of this study was to investigate the solubility of cyanide in the field as influenced by pH and redox potential, and to verify if the observed solubility is governed by equilibrium with Prussian blue and the calculated solubility of this precipitate.

We studied this solubility in field situations by evaluating available data on cyanide concentrations measured in groundwater at contaminated sites, and by determining the distribution of cyanide in soil profiles at three contaminated sites with different pH levels.

MATERIALS AND METHODS

Calculation of Dissolved Iron Cyanide Concentrations in Equilibrium with Prussian Blue and Iron (Hydr)Oxide

The solubility of iron cyanide in equilibrium with Prussian blue as a function of pH and redox potential expressed as pe (pe = 16.95 Eh), was calculated with the computer program ECOSAT (Keizer et al., 1993). The chemical equilibria used as input for this program are listed in Table 1. The calculations were done at a total iron cyanide concentration ($Fe(CN)_6$) of 0.1 *M*, a total iron concentration of 1 *M* [total Fe = Fe − $Fe(CN)_6$], total Ca = 0.01 *M*, and an ionic strength of 0.03 *M*. The total amounts of iron and iron cyanide were not relevant, as long as precipitated iron hydroxide and precipitated Prussian blue was present. The amount of Ca and the ionic strength were chosen to represent conditions occurring in soil water. However, the results were not very sensitive for either of these parameters.

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Table 1. Equilibrium reactions and constants used in the speciation calculations.

Reaction	Log $K°$	Reference
Solid phases		
1. $Fe(OH)_3(s) + 3H^+ \rightleftarrows Fe3^+ + 3H_2O$	3.54	(Lindsay, 1979)
2. $Fe_3(OH)_8(s) + 8H^+ \rightleftarrows 3Fe^{3+} + e^- + 8\ H_2O$	4.63	(Lindsay, 1979)
3. $Fe_4(Fe(CN)_6)_3(s) \rightleftarrows 4Fe^{3+} + 3Fe(CN)_6^{3-} + 3e^-$	−84.5	(Meeussen et al., 1992b)
Iron hydroxo complexes		
4. $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	13.0	(Lindsay, 1979)
5. $Fe^{3+} + H_2O + e^- \rightleftarrows Fe(OH)^{2+} + H^+$	6.3	(Lindsay, 1979)
6. $Fe^{3+} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+$	−2.2	(Lindsay, 1979)
7. $Fe^{3+} + 2H_2O \rightleftarrows Fe(OH)_2^+ + 2H^+$	−5.7	(Lindsay, 1979)
8. $Fe^{3+} + 2H_2O + e^- \rightleftarrows Fe(OH)_2^0 + 2H^+$	−3.0	(Lindsay, 1979)
9. $Fe^{3+} + 3H_2O + e^- \rightleftarrows Fe(OH)_3^- + 3H^+$	−19.0	(Lindsay, 1979)
10. $Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3^0 + 3H^+$	−13.1	(Lindsay, 1979)
11. $Fe^{3+} + 4H_2O \rightleftarrows Fe(OH)_4^- + 4H^+$	−21.6	(Lindsay, 1979)
$Fe(CN)_6$ complexes		
12. $Fe(CN)_6^{3-} + e^- \rightleftarrows Fe(CN)_6^{4-}$	−6.0	(Beck, 1987)
13. $Fe(CN)_6^{3-} + e^- + H^+ \rightleftarrows HFe(CN)_6^{3-}$	10.4	(Beck, 1987)
14. $Fe(CN)_6^{3-} + e^- + 2H^+ \rightleftarrows H_2Fe(CN)_6^{2-}$	12.8	(Beck, 1987)
15. $Fe(CN)_6^{3-} + e^- + K^+ \rightleftarrows KFe(CN)_6^{3-}$	8.5	(Beck, 1987)
16. $Fe(CN)_6^{3-} + K^+ \rightleftarrows KFe(CN)_6^{2-}$	1.5	(Beck, 1987)
17. $Fe(CN)_6^{3-} + e^- + Ca^{2+} \rightleftarrows CaFe(CN)_6^{2-}$	10.1	(Beck, 1987)
18. $Fe(CN)_6^{3-} + Ca^{2+} \rightleftarrows CaFe(CN)_6^-$	2.6	(Beck, 1987)

Because of the very low decomposition rate of iron cyanide complexes in the dark, we assumed that these complexes did not decompose (Meeussen et al., 1992a). The calculations were done for pH values ranging from 3 to 8 and pe values ranging from −6 to 18.

Evaluation of Available Data

In the Netherlands, a large number of contaminated sites has been investigated for the presence of potentially hazardous substances. As a result, a lot of data are available on concentrations of cyanide present in soil and groundwater at former gasworks sites. Unfortunately, these data do not contain information about pH or pe levels. However, the geographical location and information on soil types enabled selection of two groups of six sites each, one group with a pH assumed to be below 5, and the other group with an assumed pH around 7.5.

The six acidic sites were located on the higher sandy soils in the province of Gelderland, and the six alkaline sites were located in the province of Zuid-Holland on calcareous clay soils. On each of these sites the groundwater had been sampled on 6 to 15 locations. In general, the distribution of cyanide in the soil at these sites was very heterogeneous. Part of the samples was virtually clean.

Because of our interest in the behavior of cyanide in the most contaminated spots on the sites, we decided to compare the two highest concentrations of total cyanide measured in the groundwater at each of these sites. Total cyanide concentrations in these groundwater samples were generally measured according to the Dutch standard method (NEN 6489), which is based on a manual acidic distillation procedure followed by colorimetric determination of cyanide. The maximum total cyanide concentrations found in the contaminated soils varied from approximately 0.30 g kg^{-1} to 10.0 g kg^{-1}.

Investigation of Contaminated Soil Sites

We sampled the soil at four of the contaminated sites and we determined the distribution of pH, pe, and cyanide in soil profiles. We selected two sites with a sandy soil, and presumably a low pH, (A, B) and two sites with a calcareous clay soil and presumably a high pH (C, D). However, the soil profile at one of the alkaline sites (D) appeared to be recently disturbed by human activities, so it was impossible to relate the present spatial distribution of cyanide to its leaching behavior. Of the remaining three sites, the soil was sampled with a hand auger, at two locations about 2 m apart from each other, and at 5 to 10 depths until the groundwater level was reached. The samples of about 0.5 kg each were directly stored in air-tight bottles and processed within 48 h. To prevent effects of air on the redox status and pH as much as possible, the samples were not dried before the extractions. The mass water content was analyzed separately.

The total cyanide content of these soil samples was determined by extracting 5 g of the samples in duplicate with 50 mL of 0.25 *M* NaOH on a boiling water bath (3 h) (Meeussen et al., 1992b). In order to estimate the concentrations of cyanide present in the soil solution under field conditions, 20.0 g of soil was equilibrated for 5 d with 80 mL 0.01 *M* $CaCl_2$, as an alternative soil solution. The extracts were analyzed for pH, pe, and for total dissolved cyanide. The pH of the solutions was determined with a combined glass/calomel electrode, and redox potentials were measured with a platinum electrode and a calomel reference electrode.

Samples of the groundwater were obtained by centrifuging the deepest (water saturated) soil sample from each profile. In these samples the total concentration of dissolved cyanide was measured by an automated spectrophotometric method (Meeussen et al., 1989), after centrifugation for 20 min at 32 600 × *g*.

The pH and pe as measured in the soil extracts combined with the total cyanide content of the soil samples at different depths were used to calculate the concentration of dissolved iron cyanide in equilibrium with Prussian blue and iron (hydr)oxide. The calculations were done with the ECOSAT model using the same input data as for the previous calculations, except that in this case the measured total amount of iron cyanide in the soil was used.

RESULTS AND DISCUSSION

Calculation of Dissolved Iron Cyanide Concentrations in Equilibrium with Prussian Blue and Iron (Hydr)Oxide

The calculated total concentration of dissolved iron cyanide in equilibrium with both Prussian blue and $Fe(OH)_3(s)$ is shown in Fig. 1 as a function of pH and pe. The solid curves connect the points with equal total con-

centrations of dissolved iron cyanide complexes. Although Prussian blue is known as only slightly soluble, it appears from Fig. 1 that the solubility of Prussian blue depends strongly on pH and redox potential. At pH levels higher than 7, the concentration of total $Fe(CN)_6$ in equilibrium with Prussian blue would be greater than 1 mol L^{-1}, regardless of the pe, which implies that Prussian blue will not precipitate under such conditions. At pH levels occurring in acidic soils, the solubility of Prussian blue is much lower. At pH 4 and pe 10, only about 10 to 7 mol L^{-1} of iron cyanide would be in equilibrium with precipitated Prussian blue (Fig. 1).

In mildly reduced to oxidized soils (pH + pe ranging from ca. 11–18; Lindsay, 1979) the overall dissolution reaction of Prussian blue is:

$$Fe_4(Fe(CN)_6)_3(s) + 12H_2O + 3e^- \rightarrow 4Fe(OH)_3(s) + 3Fe(CN)_6^{3-} + 12H^+ \quad [1]$$

This reaction causes the equilibrium concentration of dissolved iron cyanide complexes to be proportional to 4 pH + pe, which implies that at a constant pe the iron cyanide concentration increases by a factor of 104 with a one unit increase of the pH. On the other hand, at a constant pH level, the solubility of iron cyanide decreases by a factor of 10 when the pe decreases one unit. At lower redox potentials (pe < ca. 7), and Ca^{2+} concentrations occurring in soil water ($Ca^{2+} > 10^{-4}$ mol L^{-1}) the overall dissolution reaction of Prussian blue becomes:

$$Fe_4(Fe(CN)_6)_3(s) + 3Ca^{2+} + 12H_2O \rightarrow 4Fe(OH)_3(s) + 3CaFe(CN)_6^{2-} + 12H^+ \quad [2]$$

In this reaction, no electrons are involved, which makes the solubility of iron cyanide independent of the pe, as is shown by the vertical parts of the curves in Fig. 1.

A combination of a low pH with a low redox potential considerably increases the solubility of iron (Schwab and Lindsay, 1983). Therefore, iron (hydr)oxide will not precipitate when Prussian blue dissolves under such conditions. The dissolution reaction then becomes:

$$Fe_4(Fe(CN)_6)_3(s) + 3Ca^{2+} + 4\,e^- \rightarrow 4Fe^{2+} + 3CaFe(CN)_6^{2-} \quad [3]$$

In this reaction, no protons are produced or consumed, which makes the solubility of Prussian blue independent of the pH, shown by the horizontal parts of the curves in Fig. 1. The remaining pe dependence is the result of the produced electrons.

In general, when Prussian blue precipitates in soils, iron originating from iron (hydr)oxide is incorporated into Prussian blue. On the contrary, in case of dissolution of Prussian blue, iron hydroxide will be formed. Therefore, equilibrium concentrations of iron cyanide complexes do not only depend on the solubility of Prussian blue, but also on the solubility of iron (hydr)oxide.

According to the calculations, it is likely that Prussian blue will not precipitate in alkaline soils at the iron cyanide concentrations found on contaminated soil sites (Fig. 2). Therefore, iron cyanide complexes should be rather mobile in soils with a high pH, and high cyanide concentrations can be expected in groundwater.

In acidic soils, precipitation of Prussian blue is likely according to the calculations. This will considerably decrease the concentrations in the groundwater and reduce the mobility of iron cyanide complexes in such soils.

Inventory of Available Data

The results of the investigation of the two highest total cyanide concentrations found in the groundwater at contaminated sites (all former gasworks sites) revealed a large contrast between the sites located on the higher sandy (presumably acidic) soils and the sites located on the lower clay (presumably alkaline) soils (Fig. 2). Although the actual pH of the sites was not determined, and cyanide concentrations in the groundwater may also be influenced by groundwater depth, total amounts of cyanide and hydrology, the results strongly indicate the existence of large differ-

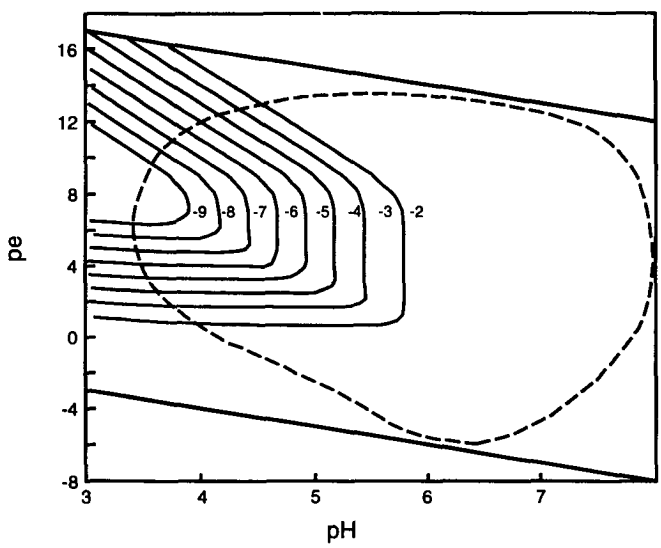

Fig. 1. Calculated concentration of total $Fe(CN)_6$ in log mol L^{-1} in equilibrium with Prussian blue and iron (hydr)oxide as a function of pH and pe. The diagonal solid lines enclose the area where water is thermodynamically stable, and the dotted circle roughly encloses the conditions occurring in natural soils (Lindsay, 1979).

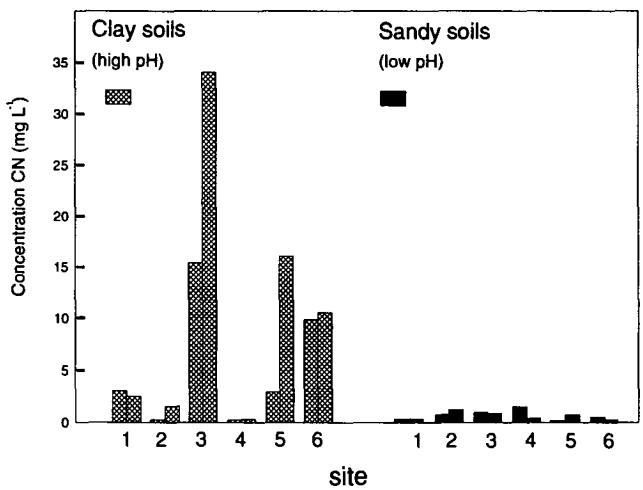

Fig. 2. Two highest concentrations per site of total dissolved iron cyanide complexes found in the groundwater on six contaminated soil sites with a high pH (left), and six contaminated sites with a low pH (right).

ences in concentrations of dissolved cyanide between alkaline and acidic sites. The maximum concentrations found on the acidic sites (ca. 10–5 mol L^{-1}; Fig. 2) would correspond with a pH of the soil water of about 5.2 at pe 4 (relatively reduced), or about pH 4.5 at pe 12 (relatively oxidized) (Fig. 1). This agreed well with the presumed pH levels on these sites.

Although the concentrations observed on the acidic sites were much lower than at the alkaline sites, they still exceeded the Dutch quality standard for total cyanide concentrations (0.2 mg L^{-1}) in groundwater. Apparently, the solubility of Prussian blue in acidic soils was not low enough to prevent unacceptable cyanide concentrations to occur in groundwater. However, a new groundwater standard has been proposed that allows a total cyanide concentration of 8 mg L^{-1}. If this standard becomes effective, it will probably only be exceeded in the groundwater of alkaline soil sites.

Investigation of Contaminated Sites

Acidic Sites

The pH in the profiles of the soil on the acidic sites (A and B) varied from 3.5 to 5.5. In combination with the pe, which varied between 6 and 11 (Fig. 3 and 4). Under these conditions, Prussian blue is only slightly soluble ($<10^{-4}$ mol L^{-1}) (Fig. 1). Considering the total cyanide content, precipitated Prussian blue was probably present in the soil samples.

The distribution of the total amount of cyanide in the two soil profiles was more or less similar at each site, but larger differences existed between sites A and B. The highest

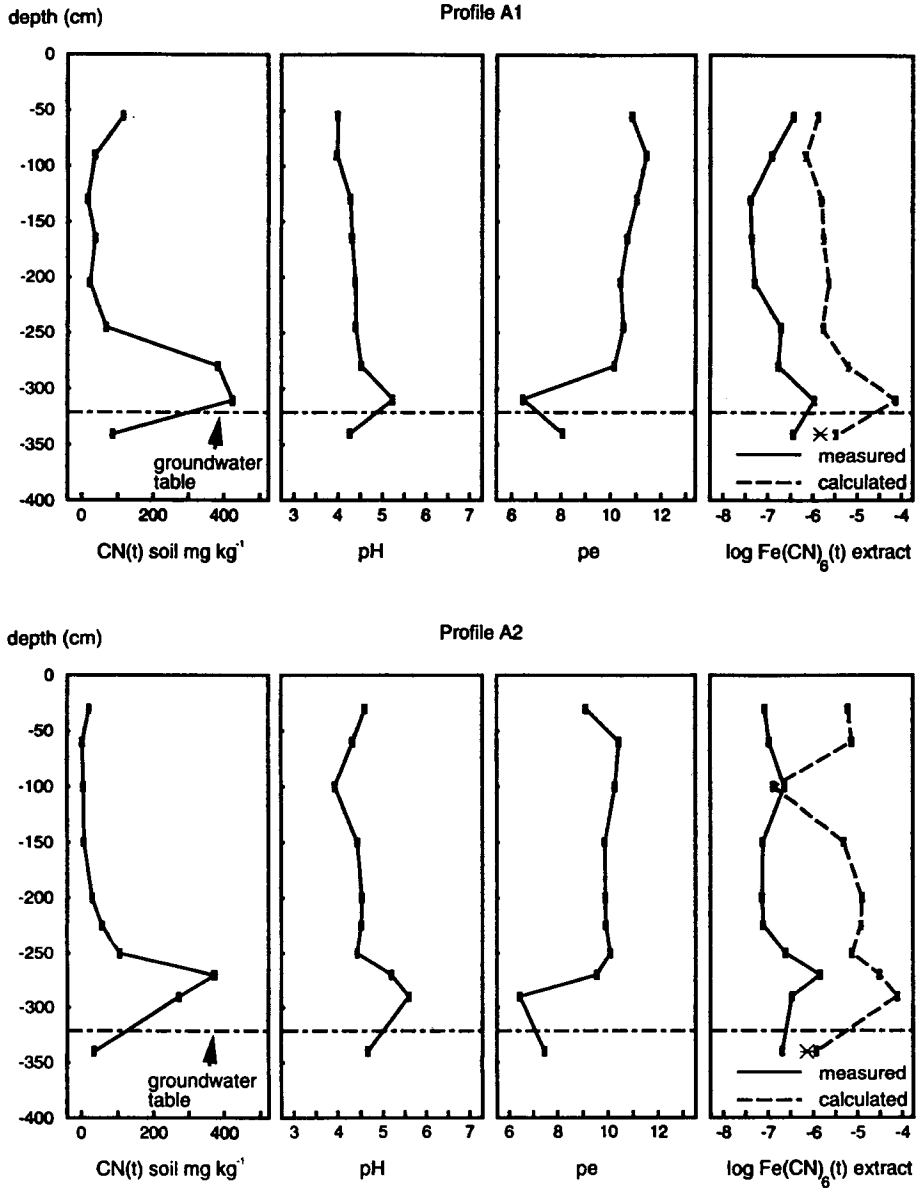

Fig. 3. Profiles (A1 and A2) of total cyanide concentrations (CN(t)) in the soil, of pH, pe, and total dissolved iron cyanide in the soil extracts and the iron cyanide concentration measured in the groundwater (*) of Site A.

cyanide concentrations were found at site A, at a depth of ca. 3.0 m, which was clearly indicated by a blue-colored soil layer. In general, this color was apparent when samples contained more than about 100 mg kg^{-1} of cyanide. The blue layer was located just on top of the water-saturated zone, which was present at about 3.2 m at the time of sampling (Fig. 3). However, according to the presence of soil material with a reduced appearance, the depth of this zone probably varies from about 2.8 m to 3.2 m because of seasonal influences.

The highest cyanide concentrations at Site B were of the same order as those found at Site A, but they were detected at a depth of about 1 to 1.5 m. The soil layer with the highest cyanide concentrations also had a blue appearance. In the first profile at Site B (B1), an increase of the cyanide concentration was also observed in the upper area of the saturated zone as was observed at Site A. Although not as profound as that at Site A, Prussian blue was visible in the soil samples. At Site B, the saturated zone is present at a depth of about 3.5 m with a seasonal variation of less then 0.5 m.

The differences between sites A and B, with respect to depth where the maximum amount of cyanide was detected, might be the result of different site histories. Although the deeper soil profiles at both sites were likely undisturbed, it was possible that at Site A, a contaminated upper soil layer was removed and that the present contamination of the soil is the result of leaching of cyanide from that layer. Cyanide-containing solid wastes were present at Site B, at a depth of 0 to 1.2 m, while such residual wastes were absent at Site A.

Extracts of the soil samples from sites A and B con-

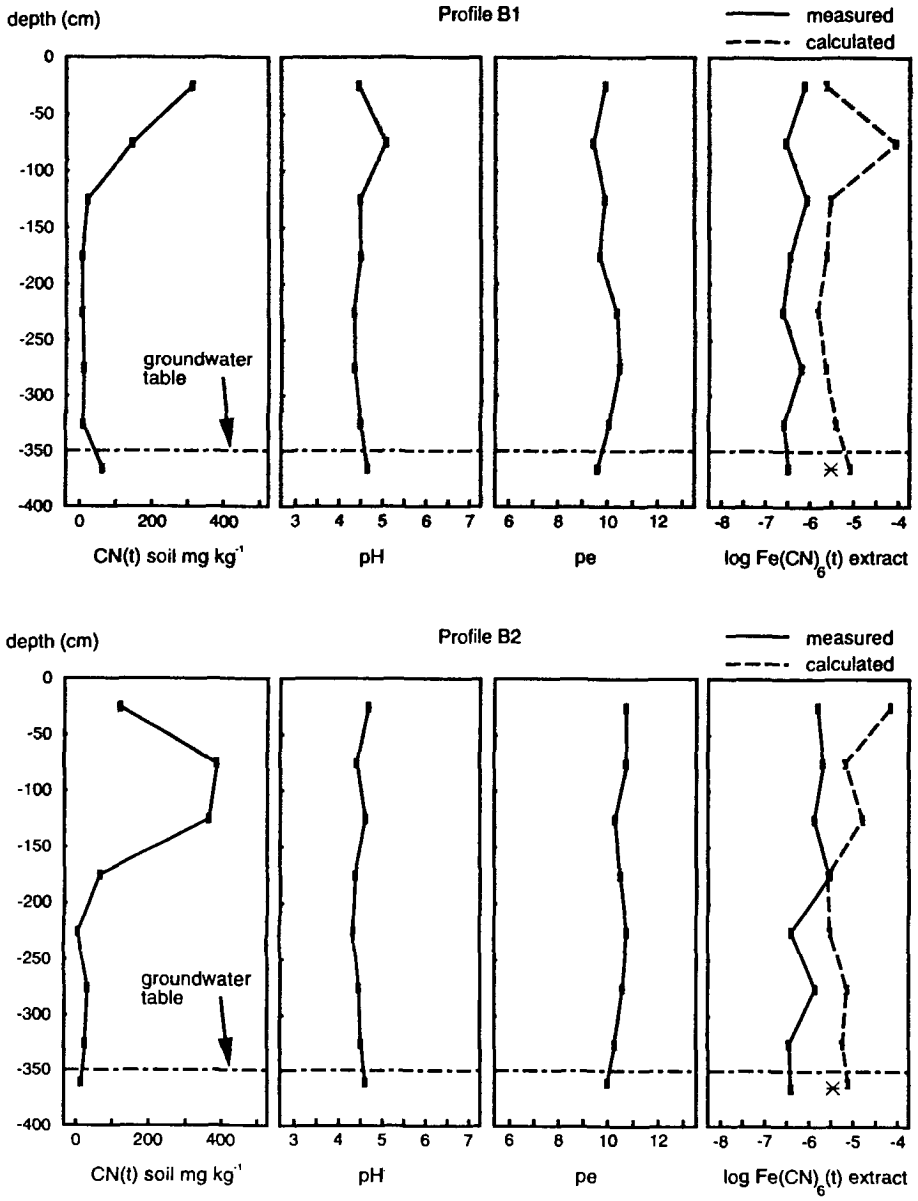

Fig. 4. Profiles (B1 and B2) of total cyanide concentrations (CN(t)) in the soil, of pH, pe, and total dissolved iron cyanide in the soil extracts and the iron cyanide concentration measured in the groundwater (*) of Site B.

tained only a very small percentage of the cyanide, varying from about 0.1 to 5% of the total amount present in the sample. This, combined with the blue color of part of the samples, indicated the presence of precipitated Prussian blue. Only low concentrations of total $Fe(CN)_6$ will be present at equilibrium with this precipitate under acidic conditions (Fig. 1). This agreed with the low total $Fe(CN)_6$ concentrations measured in the extracts. In most cases, the calculated cyanide concentrations appeared to be greater than the concentrations measured in the extracts (Figs. 3 and 4). This discrepancy can be explained if it is assumed that complete equilibrium between the extracts and the Prussian blue was not reached within the extraction time of 5 d. Although the accuracy of the calculations is limited because of a high sensitivity for small deviations of pH and pe, it was remarkable that the calculated concentrations showed a great resemblance with the concentrations observed directly in the groundwater. This indicates that the situation in the field probably was closer to equilibrium with Prussian blue than were the soil extracts.

If the mobility of cyanide in the field is indeed largely governed by equilibrium with Prussian blue, its mobility will strongly depend on pH and pe, but also on the concentration of cyanide in the soil. At concentrations below the solubility of Prussian blue, cyanide could be quite mobile. For example, this may occur after initial dissolution of cyanide from Prussian blue present in waste material. If the pH and pe do not change after dissolution, the dissolved cyanide has no tendency to precipitate during transport in soil. Precipitation will only happen at a decrease of the solubility of Prussian blue because of a change in pH or pe. This process might be an explanation for the observed accumulation of Prussian blue in the soil profiles at the beginning of the reduced zone. In those profiles, a lower solubility of Prussian blue was calculated for the saturated zone compared with the soil layer above this zone. According to the observed color of the soil samples, the mean groundwater height corresponded well with the zone where cyanide had accumulated.

Alkaline Site

The pH of the soil extracts from Site C varied from about 5.5 in the upper soil layer to about 7.2 in deeper layers. The pe of these extracts was lower and there was also a larger decrease in pe with depth compared with sites A and B. This was probably the result of the lower permeability of the clay soil compared with the sandy soils at sites A and B. The total cyanide concentrations found in the soil on Site C differed in several aspects from those found at sites A and B (Fig. 5). In the first place, the sampled profiles were not as deep as those at Site A and B because of the higher groundwater level (about 1.3 m). Furthermore, at Site C, the maximum cyanide concentrations

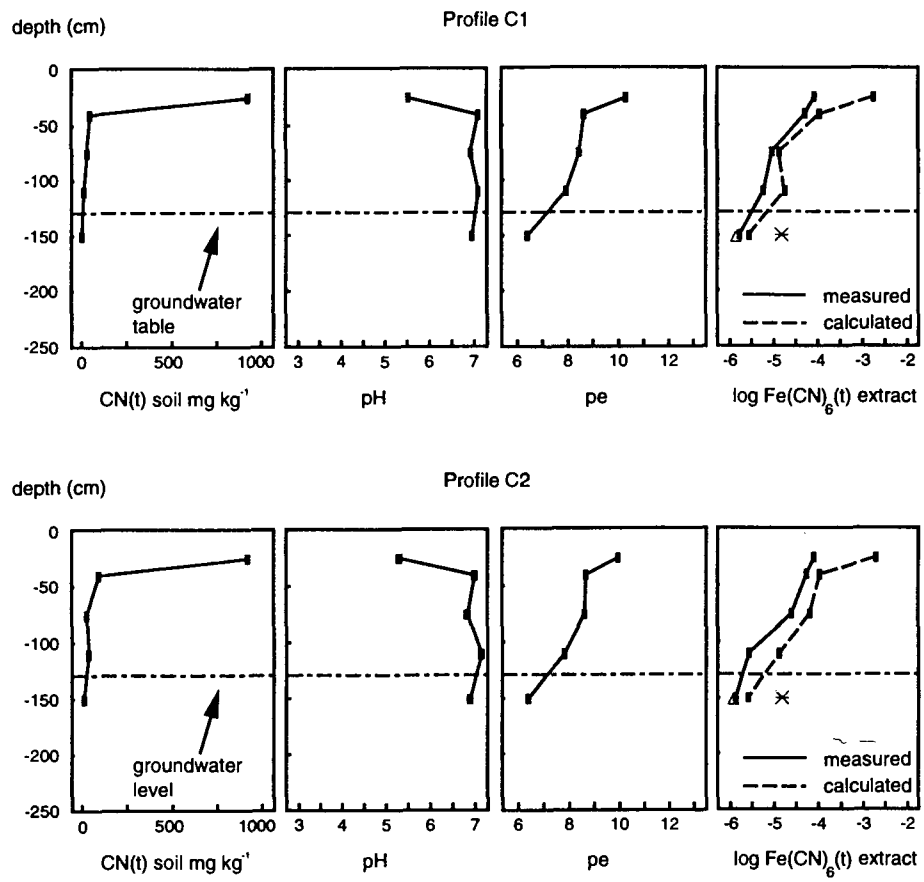

Fig. 5. Profiles (C1 and C2) of total cyanide concentrations (CN(t)) in the soil, of pH, pe, and total dissolved iron cyanide in the soil extracts and the iron cyanide concentration as measured in the groundwater (*) of Site C, and after correction for the dilution as applied in the extraction.

Table 2. Total cyanide concentrations in soil samples from Site C and percentage extracted with 0.01 *M* $CaCl_2$.

	Profile C1		Profile C2	
Depth	Total CN	Extracted	Total CN	Extracted
cm	mg kg^{-1}	%	mg kg^{-1}	%
−25	922	5.8	938	5.4
−40	58.6	58	52.4	66
−75	21.1	75	31.2	51
−110	29.6	36	16.4	27
−150	5.96	76	5.98	64

were present in a blue-colored top soil layer and the highest concentrations were about twice as high as those at Site A or B. The concentrations appeared to decrease sharply with depth. No accumulation of cyanide was observed in the saturated zone, which indicated that after initial dissolution of Prussian blue in the topsoil layer, precipitation did not occur during leaching in the profile.

Apart from the extracts of the samples of the upper soil layer, a much larger portion of the cyanide dissolved in the soil extracts (27–76%) when compared with both acidic soils (Table 2). Hence, the mobility of cyanide in this soil would be high, which is also illustrated by the high cyanide concentrations observed directly in the groundwater (indicated with asterisks in Fig. 5). In contrast with the acidic soils, the concentrations in the alkaline soil extract were strongly influenced by the total cyanide content of the soil.

According to solubility modeling, Prussian blue would completely dissolve at the pH and pe levels measured in the soil extracts. Nevertheless, solid Prussian blue appeared to be present in the upper layer of this soil. An explanation for this might be the fact that equilibrium between the soil material and the extracts was not reached within 5 d of extraction time.

Apart from a slow chemical dissolution reaction, rapid attainment of equilibrium might also be prevented by limited transport of ions to and from the dissolving Prussian blue. As illustrated by Eq. [1], protons are produced during the dissolution of Prussian blue. This causes solid Prussian blue to act as an effective low pH buffer. During dissolution a very local acidic environment might develop, in which Prussian blue would be less soluble when compared with the more alkaline soil solution. Under such conditions, the local pH and dissolution rate of Prussian blue would depend on the transport rate of protons away from, or base ions toward the dissolving solid phase. Apart from hydrological conditions, this transport rate would be governed by the pH and buffering capacity of the surrounding solution. The latter might be strongly influenced by the concentration of HCO_3^- in the soil solution. In such a way it is possible that Prussian blue would persist in soils although at the average pH of the soil it would dissolve.

Compared with field conditions, such transport rates are probably high during extraction of soil samples, due to the effect of mixing. This might have caused a relatively high dissolution rate when compared with the field situation, although this increased rate was apparently not rapid enough to reach equilibrium within 5 d (Table 2). The relatively low pH of the samples of the upper soil layer was probably caused by the dissolution of Prussian blue (Eq. [1]).

The iron cyanide leached from the dissolving Prussian blue in the upper soil layer will not have precipitated as Prussian blue again, at the pH and pe levels observed in the deeper soil layers. The calculations predicted that all the cyanide in these layers should be present in dissolved form. However, according to the measurements, a small part of the cyanide, especially when compared with the acidic soils, is present in soil solid phase (Table 1). According to the calculations, it is not likely that this is caused by reprecipitation of Prussian blue in the soil. Other possibilities are adsorption of iron cyanide by variable charge surfaces of the soil, or precipitation of some iron cyanide with other metals, like Pb^{2+} or Zn^{2+}, which are less soluble than Prussian blue at higher pH levels (Bellomo, 1970). Nevertheless, these processes appear to be far less effective as precipitation of Prussian blue. Iron cyanide, therefore, remains very soluble and therefore mobile in the alkaline soil. The concentrations reaching the groundwater in this soil are not determined by equilibrium with Prussian blue, but they might be regulated by the dissolution rate of this solid phase in the contaminated topsoil layer. The ability of solid Prussian blue to persist in alkaline soils, decades after disposal of waste material containing this substance, is possibly the result of the slow dissolution kinetics of this precipitate. More insight in these dissolution kinetics is needed for a better understanding of the solubility and mobility of cyanide in alkaline soil.

CONCLUSIONS

1. The large differences in mobility of cyanide between soil sites with different pH and pe could be quantitatively described by the solubility of Prussian blue.
2. The concentrations of cyanide as measured in the groundwater at contaminated acidic sites corresponded very well with the concentrations that were calculated based on equilibrium with Prussian blue.
3. Although precipitation of cyanide is possible in acidic soils, it still can reach groundwater in concentrations exceeding present Dutch soil quality standards.
4. According to theory, Prussian blue is very soluble in alkaline soils. The fact that this solid phase is still present decades after its discharge may be due to slow dissolution kinetics.
5. The concentrations of dissolved cyanide leaching from contaminated alkaline soils were not controlled by equilibrium with Prussian blue, but possibly by the dissolution kinetics of this precipitate.

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