

Technical Note

Cyanide extraction from contaminated soil: a method comparison

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ABSTRACT

Soils on sites of former manufactured gas plants are usually contaminated with iron-cyanide complexes. We investigated the extraction of cyanide from 23 contaminated soils by three methods, which are prescribed by the German Federal Soil Protection Act and Ordinance: the soil-saturation extract with water, SSE, with a very narrow soil:solution ratio; the so-called S4 water extract with a soil:solution ratio of 1:10; and 1M NH₄NO₃ extracts with a soil:solution ratio of 1:2.5. Highest cyanide concentrations were found in the SSEs ranging from 0.1 to 70.5mg/l. However, percental cyanide extraction was lowest in these extracts. Cyanide concentration and percental extraction obtained by the three methods were correlated among the methods with squared correlation coefficients ranging from 0.45 to 0.80. The relationship between extract pH and cyanide extraction was weak. As the results differed among the methods, they cannot be regarded as equivalent with respect to cyanide extraction. Due to the narrow soil:solution ratio, the longer reaction time of 48h, and the strongest similarity between soil and extract pH, we recommend the SSE method to investigate cyanide extraction from contaminated soil. © 2004 SDU. All rights reserved.

Keywords: Cyanide; Extraction; Contaminated soil; Manufactured gas plant

1. INTRODUCTION

The presence of cyanide, CN, in soil and ground water is caused predominantly by anthropogenic inputs, because cyanide from natural sources is readily consumed by soil microorganisms (Knowles, 1976). Cyanide-containing compounds occurring in the soil environment originate from industrial processes such as coal gasification (Shifrin *et al.*, 1996), electroplating (Mohler, 1969), gold mining (Boucabeille *et al.*, 1994), pig iron production (Mansfeldt and Dohrmann, 2001), and paper recycling (Mansfeldt, 2001) or the use of road salt (Paschka *et al.*, 1999). Sites of former manufactured gas plants, MGP, or coke ovens are widespread in many industrialised countries and in soils on these sites, cyanide is present as the ferric ferrocyanide Berlin Blue, Fe₄[Fe(CN)₆]₃, and dissolved iron-cyanide complexes, [Fe(CN)₆]^{3-/4-} (Meeussen, 1992; Mansfeldt *et al.*, 1998). The total cyanide concentrations in these soils are up to 115g/kg (Fowler *et al.*, 1994) and up to 85mg/l in the ground water of these sites (Ferguson *et al.*, 2003). In soil extracts of a MGP site soil, cyanide complexes of Fe, Cu, and Ni as well as thiocyanate, SCN⁻, have been detected with ferrocyanide, [Fe(CN)₆]⁴⁻, as the dominant species (Theis *et al.*, 1994). Free cyanide, HCN_{g, aq} and CN⁻_{aq}, were not detected. However, there is no standard procedure to extract particularly cyanide in order to predict possible contamination of the seepage and ground water with cyanide, and, generally, investigations on extractable cyanide from soil have been rarely carried out (Kjeldsen, 1999). Therefore, the aim of this study was to investigate and to compare the cyanide extraction from contaminated MGP site soils by three methods using batch experiments.

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2. EXPERIMENTAL

2.1. Soil samples and methods of cyanide extraction

Twenty-three samples were taken from seven former MGP or coke oven sites in Northrhine-Westphalia, Germany, during remediation campaigns. The samples were dried at 60°C and sieved to 2mm. Two of the extraction methods used are prescribed by the German Federal Soil Protection Act and Ordinance (BBodSchV, 1999), the soil-saturation extract, SSE, and the S4 extract. Extractions with 1M NH₄NO₃ were carried out for comparison, as this method may be used alternatively.

SSE: According to BBodSchV (1999), about 180g dried soil was wetted with de-mineralised water in triplicate until the water capacity was reached approximately. After stirring with a glass rod, the samples were left standing for 24h at 5°C. The samples were then transferred to centrifuge tubes, and de-mineralised water was added until the samples began to flow. They were stirred again and then they were left standing for an additional 24h at 5°C. After centrifugation for 30min, the supernatant was filtered (membrane filtration, 0.45µm cellulose nitrate filter). As the water additions differed between the samples, soil:solution ratios ranged from 1:0.2 to 1:1.6.

S4 extract: According to DEV (1984), 50g dried soil and 500ml de-mineralised water (soil:solution ratio 1:10) were shaken end-over for 24h in 1000ml polyethylene bottles in triplicate. Subsequently, the phases were separated by filtration as described above.

NH₄NO₃ extract: According to DEV (1997), about 20g soil was suspended in 50ml 1M NH₄NO₃ (soil:solution ratio 1:2.5) in 100ml polyethylene bottles and shaken horizontally for 24h at room temperature in triplicate. The phases were separated as described above.

2.2. Analyses

Soil pH was measured potentiometrically with a WTW pH 90 (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) in 0.01M CaCl₂ with a soil:solution ratio of 1:2.5. Extract pH was measured with the same equipment. Total cyanide (CN_T) in soils and soil extracts was analysed by micro-distillation (Eppendorf-Netheler-Hinz, Hamburg, Germany) and subsequent spectrophotometrical detection (Lambda 2, Perkin-Elmer, Überlingen, Germany) at 600nm according to Mansfeldt and Biernath (2000). Nearly identical results are obtained by the micro-distillation technique compared to the distillation technique prescribed by the German Federal Soil Protection Act and Ordinance (Mansfeldt and Biernath, 2000). The presence of free cyanide was checked by spectrophotometry without previous distillation of the filtrates.

3. RESULTS AND DISCUSSION

Soil chemical properties and the results of the extractions are summarised in Table 1.

Table 1
Sample properties and cyanide extraction from 23 contaminated soils by three methods (SSE, soil-saturation extracts with water; S4, S4 water extracts; NH₄NO₃, extracted by 1M NH₄NO₃).

Sample	Depth (cm)	pH	CN _T (mg/kg)	Extracts								
				SSE			S4			NH ₄ NO ₃		
				pH	CN _{extr} (mg/l)	% _{extr}	pH	CN _{extr} (mg/l)	% _{extr}	pH	CN _{extr} (mg/l)	% _{extr}
#2017	20 - 40	3.0	410	3.4	1.22	0.1	4.2	0.44	1.1	3.0	0.76	0.7
#2043	80 - 120	3.1	43	3.5	0.57	0.9	4.2	0.13	3.0	3.5	0.63	5.9
#2044	80 - 100	3.1	82	3.7	0.34	0.2	4.5	0.12	1.5	3.3	0.87	4.2
#2070	250	4.7	418	4.6	4.66	0.3	7.5	1.19	2.8	4.3	0.74	0.7
#2071	450	4.8	733	4.9	0.15	< 0.1	6.6	0.08	0.1	5.3	0.14	0.1
#2136	surface	2.2	66,760	2.0	0.61	< 0.1	2.6	0.22	< 0.1	2.1	0.88	< 0.1
#2137	40 - 60	2.6	82	2.4	0.24	0.1	3.1	0.05	0.6	2.7	0.10	0.5
#2138	60 - 100	2.6	30	2.4	0.12	0.2	3.0	0.02	0.7	2.6	0.12	1.6
#2139	surface	3.8	2,510	4.0	3.90	0.1	5.0	6.79	2.7	3.6	0.63	0.1
#2140	80 - 100	3.4	19	3.8	2.10	5.0	4.5	0.44	22.7	3.5	2.00	41.2
#2146	surface	2.1	70,450	2.2	2.55	< 0.1	2.3	1.42	< 0.1	-	4.01	< 0.1
#2147	50	2.6	4,690	2.6	0.66	< 0.1	3.5	0.12	< 0.1	2.6	0.42	< 0.1
#2150	surface	6.3	195	5.8	50	5.5	4.6	2.31	11.8	5.6	5.49	11.3
#2151	surface	6.5	852	5.2	60.4	1.5	5.0	2.16	2.5	5.9	6.36	3.0
#2152	surface	4.9	380	5.4	2.97	0.2	4.8	0.32	0.8	5.7	0.43	0.5
#2154	50	2.6	6,530	1.9	0.14	< 0.1	3.0	0.13	< 0.1	2.6	0.31	< 0.1
#2155	50	2.2	13,150	1.9	0.16	0.9	2.7	0.80	0.1	2.3	0.24	< 0.1
#2156	300	5.7	2,500	5.6	10.3	0.1	6.6	2.36	0.9	5.7	1.52	0.2

continued (Table 1)

Sample	Depth (cm)	pH	CN _r (mg/kg)	Extracts								
				SSE			S4			NH ₄ NO ₃		
				pH	CN _{extr} (mg/l)	% _{extr}	pH	CN _{extr} (mg/l)	% _{extr}	pH	CN _{extr} (mg/l)	% _{extr}
#2157	300	8.0	1,570	7.4	70.5	1.4	7.9	68.5	43.6	7.4	8.08	2.1
#2158	550	7.4	795	7.4	36	2.5	7.8	3.01	3.8	7.3	3.85	1.9
#2160	675	7.4	9	7.4	1.14	5.3	7.7	0.13	15.3	7.3	0.16	7.5
#2161	675	7.4	59	7.4	5.82	4.7	7.7	0.40	6.8	7.2	1.30	8.8
#2162	700	7.3	23	7.6	1.94	4.2	7.7	0.27	11.7	7.2	0.43	7.5

Most samples were acid with pHs ranging from 2.1 to 8 due to the oxidation of reduced sulphur species to sulphuric acid, which is a common process occurring in MGP site soils (Environmental Resources Limited, 1987). Higher pH values (7.3 to 8) were found in the samples #2157 to #2162, which were taken from underlying calcareous cretaceous sediments. Cyanide contents in soil varied largely from 9 to 70,450mg/kg. Even in samples taken from depths >300cm, considerable cyanide concentrations have been detected (#2071, #2156 - #2162) indicating vertical transport of cyanide.

Soil pHs were reflected by extraction pHs in the case of SSE and NH₄NO₃ extracts (ΔpH 0.3). However, the pHs of the S4 extracts differed from soil pH with a maximum ΔpH of 2.8. Free cyanide was never found in the extracts as similarly reported by Theis *et al.* (1994). Cyanide concentration as well as percental extraction differed largely between the samples (Table 1) and between the methods used (Table 2).

Table 2

Statistical parameters of cyanide extraction from 23 contaminated soils by three methods (SSE, soil-saturation extracts with water; S4, S4 water extracts; NH₄NO₃, extracted by 1M NH₄NO₃).

	Concentration (mg/l)			Percent extracted		
	SSE	S4	NH ₄ NO ₃	SSE	S4	NH ₄ NO ₃
Arithmetic mean	11.1	4	1.7	1.4	5.8	4.3
Median	1.94	0.4	0.74	0.23	1.5	0.74
Minimum	0.12	0.02	0.10	0.0006	0.003	0.005
Maximum	70.5	68.5	8.08	5.5	43.6	41.2

Cyanide concentrations revealed a large variability ranging from 0.02 to 70.5mg/l. There was only one sample (#2138, S4 extract) not exceeding the German concentration limit for total cyanide in drinking-water, 50μg/l. The highest concentrations were found in the SSE, whereas percental extraction was lowest with the SSE.

Two samples (#2139 and #2157) revealed high cyanide concentrations in the S4 extracts only. These extracts were bluish indicating the presence of Berlin Blue colloids. The extracts of these samples obtained by the other two methods were colourless. As the extraction methods are used for the prediction of concentrations of dissolved species, these two samples were excluded from linear regression calculations.

Based on concentrations, the regression equations were

$$c(\text{SSE}) = -2.7 + 14.8 c(\text{S4}), r^2 = 0.62; \quad (1)$$

$$c(\text{SSE}) = -3.7 + 8.4 c(\text{NH}_4\text{NO}_3), r^2 = 0.80; \quad (2)$$

$$c(\text{S4}) = 0.2 + 1.6 c(\text{NH}_4\text{NO}_3), r^2 = 0.63, \quad (3)$$

where r^2 is the square of the regression coefficient r .

Based on percental extraction, the regression equations were

$$\% \text{ extracted (SSE)} = 0.3 + 0.3 \% \text{ extracted (S4)}, r^2 = 0.80; \quad (4)$$

$$\% \text{ extracted (SSE)} = 0.8 + 0.2 \% \text{ extracted (NH}_4\text{NO}_3), r^2 = 0.45; \quad (5)$$

$$\% \text{ extracted (S4)} = -0.7 + 1.3 \% \text{ extracted (NH}_4\text{NO}_3), r^2 = 0.77. \quad (6)$$

Transforming the data on a logarithmic scale did not improve the fits. The regression equations based on concentration data clearly demonstrated that the highest concentrations were found in soil-saturation extracts. Therefore, the SSE and the S4 method cannot be regarded as equivalent alternatives with respect to cyanide as laid down by the German Federal Soil Protection Act and Ordinance. One reason for the higher concentrations might be the longer reaction time, 48h altogether. Rate-limited desorption might explain the highest concentrations in the soil-saturation extracts, because these samples reacted for an additional 24h compared to the other methods. In column experiments, the desorption of iron-cyanide complexes from a MGP site soil was strongly rate-limited (Weigand *et al.*, 2001). This additionally has to be taken into account when judging the applicability of batch experiments to predictions of cyanide seepage water concentrations.

The differences between the S4 and the NH₄NO₃ extracts were smaller, but the correlation was weaker. Percental extraction by the SSE method was lower compared to the other methods, maybe it is because the samples were stirred, not shaken. Again, the results obtained by the S4 and the NH₄NO₃ method were

similar. The methods used differ in the soil:solution ratio and in the ionic composition of the extraction solution. Consequently, cyanide in the extracts should differ quantitatively as well as qualitatively. When investigating cyanide mobility in MGP site soils and ground waters, three major groups of cyanide have to be considered, free cyanide; anionic metal-cyanide complexes; and Berlin Blue colloids (Meeussen, 1992; Mansfeldt *et al.*, 1998). Cyanide species of these fractions differ in their toxicity and in their geochemical behaviour (Mansfeldt and Rennert, 2003).

Based on very similar adsorption behaviours of NO_3^- and Cl^- and analogous to the desorption of ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, from goethite by 1M NaCl (Rennert and Mansfeldt, 2002), only weakly bound cyanide species should be released into solution by 1M NH_4NO_3 . These species include at least iron-cyanide complexes except for ferrocyanide sorbed on iron oxides.

Generally, increasing electrolyte concentration decreases colloid release and transport (Kretzschmar and Sticher, 1998). This effect has been found for the release of Berlin Blue colloids from contaminated soil in column experiments (Mansfeldt *et al.*, 2004). Consequently, Berliner Blue colloids were extracted by the S4 method only (#2139 and #2157). Colloids were not mobilised by the SSE method, because the samples were not shaken.

Cyanide extraction did not depend strongly on pH (SSE, $r = 0.66$; S4, $r = 0.64$; NH_4NO_3 , $r = 0.54$) as shown in Figure 1.

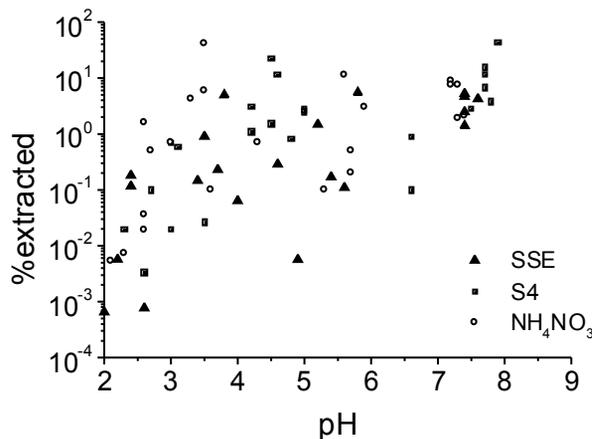


Figure 1. Relationship between pH and percental cyanide extraction from 23 contaminated soils by three methods (SSE, soil-solution extract with water; S4, S4 water extract; NH_4NO_3 , extraction with 1M NH_4NO_3)

However, pH has been found to be the master variable controlling dissolution of cyanide containing solid phases in soils on MGP sites (Meeussen *et al.*, 1990; Mansfeldt *et al.*, 1998). In these studies, dissolution and solubility have been investigated by raising the pH with alkali. This might explain the discrepancy to the results presented here, because we used equilibrium pHs for the regression analysis.

Neither did cyanide concentrations nor percental extraction depend on cyanide contents of the soils (r ranging from 0.05 to 0.17), which is consistent with the results of Meeussen *et al.* (1990).

4. CONCLUSIONS

The three methods used for cyanide extraction from contaminated soil are not equivalent, because the amounts of cyanide extracted from the same soil varied largely between the methods. Nevertheless, batch cyanide extractions are a useful tool to estimate total cyanide extraction from contaminated soils and sediments. However, it has to be taken into account that cyanide concentrations and speciation in the extracts depend on the method used. As shown above, different cyanide fractions were extracted including low toxic Berlin Blue colloids in the S4 extracts. Consequently, the determination of total cyanide concentrations in soil water does not necessarily predict acute and possible toxicity resulting from cyanide in MGP site soils.

We recommend to extract cyanide from contaminated soil using the SSE method, because i) the narrow soil:solution ratio is more realistic for soils than ratios of 1:10 or 1:2.5; ii) Berlin Blue colloids are not released from soil as the samples are not shaken; iii) the influence of the most important parameter controlling cyanide release, pH, is more significant compared to the other methods used; iv) soil and extract pH are very similar; and v) a reaction time of 48h seems to be more adequate than 24h due to rate-limited desorption of cyanide species.

REFERENCES

- BBodSchV, Verordnung zur Durchführung des Bundes-Bodenschutzgesetzes (Bundes-Bodenschutz- und Altlastenverordnung - BBodSchV). Bundesgesetzblatt 1999, I, 1554-1582.
- Boucabeille, C., Bories, A., Ollivier, P., Michel, G., Microbial degradation of metal complexed cyanides and thiocyanate from mining wastewaters. *Environmental Pollution*, 1994, 84, 59-67.
- DEV, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Schlamm und Sedimente (Gruppe S). Bestimmung der Eluierbarkeit mit Wasser (S4), DIN 38414, 1984, VCH, Weinheim, Germany.
- DEV, Extraktion von Spurenelementen mit Ammoniumnitratlösung, DIN 19730, 1997, VCH, Weinheim, Germany.
- Environmental Resources Limited, Problems Arising from the Redevelopment of Gas Works and Similar Sites, 1987, Department of the Environment, London, UK.
- Ferguson, A.S., Doherty, R., Larkin, M.J., Kalin, R.M., Irvine, V., Ofterdinger, U.S., Toxicity assessment of a former manufactured gas plant. *Bulletin of Environmental Contamination and Toxicology*, 2003, 71, 21-30.
- Fowler, G.D., Sollars, C.J., Ouki, S.K., Perry, R., Thermal conversion of gasworks contaminated soil into carbonaceous adsorbents. *Journal of Hazardous Materials*, 1994, 39, 281-300.
- Kjeldsen, P., Behaviour of cyanides in soil and groundwater: A review. *Water, Air, and Soil Pollution*, 1999, 115, 279-307.
- Knowles, C.J., Microorganisms and cyanide. *Bacteriological Reviews*, 1976, 40, 652-680.
- Kretzschmar, R. and Sticher, H., Colloid transport in natural porous media: Influence of surface chemistry and flow velocity. *Physics and Chemistry of the Earth*, 1998, 23, 133-139.
- Mansfeldt, T., Cyanide in paper de-inking sludge used as a soil amendment. *Journal of Plant Nutrition and Soil Science*, 2001, 164, 637-641.
- Mansfeldt, T. and Biernath, H., Determination of total cyanide in soils by micro-distillation. *Analytica Chimica Acta*, 2000, 406, 283-288.
- Mansfeldt, T. and Dohrmann, R., Identification of a crystalline cyanide-containing compound in blast furnace sludge deposits. *Journal of Environmental Quality*, 2001, 30, 1927-1932.
- Mansfeldt, T. and Rennert, T., Iron-cyanide complexes in soil and ground water. *Geochemical processes with long-term effects in anthropogenically affected seepage- and groundwater*, eds. H.D. Schulz and A. Haderer. Wiley-VCH, 2003, pp. 65-77.
- Mansfeldt, T., Gehrt, S.B., Friedl, J., Cyanides in a soil of a former coking plant site. *Zeitschrift für Pflanzenernährung und Bodenkunde*, 1998, 161, 229-234.
- Mansfeldt, T., Leyer, H., Barmettler, K., Kretzschmar, R., Cyanide leaching from soil developed from coking plant purifier waste as influenced by citrate. *Vadose Zone Journal*, 2004, 3, 471-479.
- Meeussen, J.C.L., Chemical speciation and behaviour of cyanide in contaminated soils. Ph.D. thesis, Wageningen Agricultural University, Wageningen, The Netherlands, 1992, 133 p.
- Meeussen, J.C.L., Keizer, M.G., van Riemsdijk, W.H., The solubility of iron-cyanide in soils. *Contaminated soil '90*, eds. F. Arendt, M. Hinsenveld and W.J. van den Brink. Kluwer Academic Publishers, Wageningen, 1990, pp. 367-374.
- Mohler, J.B., Electroplating and related processes. Chemical Publishing, New York, 1969, 311 p.
- Paschka, M.G., Ghosh, R.S., Dzombak, D.A., Potential water-quality effects from iron-cyanide anticaking agents in road salts. *Water Environment Research*, 1999, 71, 1235-1239.
- Rennert, T. and Mansfeldt, T., Sorption of iron-cyanide complexes on goethite in the presence of sulfate and desorption with phosphate and chloride. *Journal of Environmental Quality*, 2002, 31, 745-751.
- Shifrin, N.S., Beck, B.D., Gauthier, T.D., Chapnick, S.D., Goodman, G., Chemistry, toxicology, and human health risk of cyanide compounds in soils at former manufactured gas plant sites. *Regulatory Toxicology and Pharmacology*, 1996, 23, 106-116.
- Theis, T.L., Young, T.C., Huang, M., Knutsen, K.C., Leachate characteristics and composition of cyanide-bearing wastes from manufactured gas plants. *Environmental Science and Technology*, 1994, 28, 99-106.
- Weigand, H., Totsche, K.U., Mansfeldt, T., Kögel-Knabner, I., Release and mobility of polycyclic aromatic hydrocarbons and iron-cyanide complexes in contaminated soil. *Journal of Plant Nutrition and Soil Science*, 2001, 164, 643-649.