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Ecotoxicity of cyanide complexes in industrially contaminated soils

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ABSTRACT

This study deals with acute and chronic ecotoxicity of leachates from industrially contaminated soils. Analyses focused on cyanides (complex and free forms) to study their possible involvement in leachates toxicity. No acute toxicity on the Microtox and 48 h-*Daphnia magna* tests was found in leachates collected over 18 months, but a high chronic toxicity was recorded on the reproduction of *Ceriodaphnia dubia* (EC50-7 d = 0.31 ± 0.07%) and on the algal growth of *Pseudokirchneriella subcapitata* (EC50-72 h = 0.27 ± 0.09%). Ceriodaphnids were as sensitive to free cyanide as to complex forms (EC50-7 d as CN^- = 98 μg/L, 194 μg/L and 216 μg/L for KCN, $Fe(CN)_6K_3$ and $Fe(CN)_6K_4$, respectively). The EC50-72 h of KCN to *P. subcapitata* (116 μg/L) as CN^- was also of the same level as the EC50-72 h of potassium ferricyanide (127 μg/L) and ferrocyanide (267 μg/L). Complex cyanides explained a major part of the toxicity of leachates of the soil. On the other hand, cyanide complexes had no effect on survival of the earthworm *Eisenia fetida* up to 131 mg CN^-/kg, while potassium cyanide was highly toxic [EC50-14 d as CN^- = 74 μg/kg soil].

Thermodesorption treatment eliminated a majority of cyanides from the soil and generated much less toxic leachates. Complex cyanides must be integrated into environmental studies to assess the impact of multi-contaminated soils.

1. Introduction

Past industrial activities, such as mining, coal and iron exploitation for energy or steel production, have generated wastelands and historically contaminated soils in most developed countries. In Europe, vast programs have been launched to inventory contaminated sites and define action plans for management and treatment. National inventories indicate that metals, hydrocarbons and mineral oils are the harmful contaminants most frequently found in soil and groundwater at investigated sites. The north-east of France with its past activities of coal and iron extraction, is especially concerned as it has multiple-contaminated soils with high levels of metals and organic pollutants such as polycyclic aromatic hydrocarbons (PAHs).

In a previous work, a multidisciplinary and long term study was carried out to assess the fate and environmental impact of contaminants from a coke plant soil. A field pilot study was designed to evaluate the efficiency of phytoremediation and thermodesorption. Thermodesorption was carried out to eliminate the major part of PAHs, which are considered as pollutants of high concern due to their carcinogenic properties. Investigations targeted metals and polycyclic aromatic hydrocarbons specifically to determine their mobility and their toxicity in untreated and treated soils. An integrated approach associating physicochemical analyses and ecotoxicity studies was applied for risk assessment.

Results indicated that the bioavailability of PAHs and metals was low in these aged soils [1]. No toxicity was recorded on invertebrate terrestrial species despite high levels of metals and hydrocarbons in the untreated soil [2]. On the other hand, high chronic toxicity of soil leachates was recorded on freshwater microalgae and microinvertebrates. In contrast, leachates of the thermodesorbed soil were much less toxic. As the thermal treatment eliminated most PAHs from the soil (Table 1), these pollutants were suspected of being responsible for aquatic toxicity recorded in leachates of the untreated soil. Yet, none the 16 PAH pollutants measured in leachates, nor metals could explain toxicity to aquatic species of the untreated and phytoremediated soils [3]. Therefore, further investigations appeared necessary to identify soil pollutants harmful to aquatic life.

The present study was undertaken over 18 months after the previous investigations reported above. It aimed to characterize the unknown pollutants responsible for leachate toxicity and thermodegradable. A review of the processes applied in coke plants led us to consider cyanide complexes resulting from waste and gas purification by iron treatment as possible contaminants responsible for the toxicity to microalgae and microinvertebrates.

Ferro- and ferricyanide complexes constitute the major forms of cyanides in soils as a result of wastes produced after iron

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Table 1
The main physico-chemical characteristics of both contaminated soils before and after thermal desorption (mean ± sd, standard deviation).

	Untreated soil		Thermodesorbed soil	
	Mean	sd	Mean	sd
Soil texture				
Clay %	12.8	0.2	10.4	0.05
Silt %	23.9	1.5	19.4	0.1
Sand %	64.8	1.7	70.1	0.21
pH	7.10	0.03	7.38	0.01
C/N	26		62.0	1.4
Organic carbon %	7.25	0.25	5.8	0.2
Organic matter %	12.5	0.4	10.1	0.4
Heavy metals (mg/kg soil d.w.)				
Arsenic (As)	60.75	6.13	74.50	5.45
Cadmium (Cd)	2.72	0.06	2.14	0.08
Chromium (Cr)	346	24	393.75	23.08
Cobalt (Co)	27.3	0.7	27.18	0.17
Copper (Cu)	104.5	8	109.25	1.71
Mercury (Hg)	4.0	0.7	1.54	0.24
Nickel (Ni)	155	91	102.25	2.06
Lead (Pb)	669	26	672.75	23.04
Zinc (Zn)	2647	143	2745.00	26.46
PAHs (mg/kg soil d.w.)				
Naphthalene	31	5	2.9	0.5
Acenaphthylene	1.7	0.2	2.9	0.1
Acenaphtene	84	58	0.8	0.04
Fluorene	59	25	2.6	0.1
Phenanthrene	173	55	9.3	0.3
Anthracene	62	10	6.4	0.1
Fluoranthene	260	55	15.7	0.4
Pyrene	203	35	10.6	0.4
Benzo[a]anthracene	125	18	8.2	0.3
Chrysene	108	13	5.4	0.5
Benzo[b]fluoranthene	107	14	9.1	0.5
Benzo[k]fluoranthene	63	8	3.7	0.8
Benzo[a]pyrene	107	14	8.2	0.5
Dibenzo[a,h]anthracene	12	2	4.9	0.1
Benzo[g,h,i]perylene	66	7	4.9	0.2
Indeno[1,2,3-cd]pyrene	77	11	10.7	0.4
Σ 16 PAH US-EPA	1539	314	106.3	3.6

treatment in coke and gas manufacture plants [4]. These complexes are persistent, while subjected to decomposition in UV light [5]. They are non-mobile in acidic soils, but their solubility increases with neutralisation and alkalinisation of soils [6]. They are far less toxic to mammals compared with free cyanide, even at high levels of exposure [7,8]. Yet, little is known of their toxicity to invertebrates.

In the present study, cyanides were analyzed in leachates from untreated and thermodesorbed soils generated by rainwaters in situ collected over eighteen months. Both acute and chronic bioassays were used to assess ecotoxicity of leachates. The Microtox and 48 h-*Daphnia magna* tests were applied for acute effects. Chronic toxicity to freshwater species was evaluated by population growth of the microalgae (*Pseudokirchneriella subcapitata*) and by reproduction of the microinvertebrates (*Ceriodaphnia dubia*). In parallel, chronic toxicity of cyanide chemicals (free and complex cyanides) to these aquatic species was assessed in order to study the plausibility of cyanide involvement in leachate aquatic toxicity. Potassium ferrocyanide and potassium ferricyanide were studied as models of soluble complex cyanides released from alkaline soils, and potassium cyanide as a model of free cyanide. Toxicity of these compounds to earthworms (*Eisenia fetida*) was also evaluated to provide information about the sensitivity of terrestrial species to cyanides that is lacking in data bases.

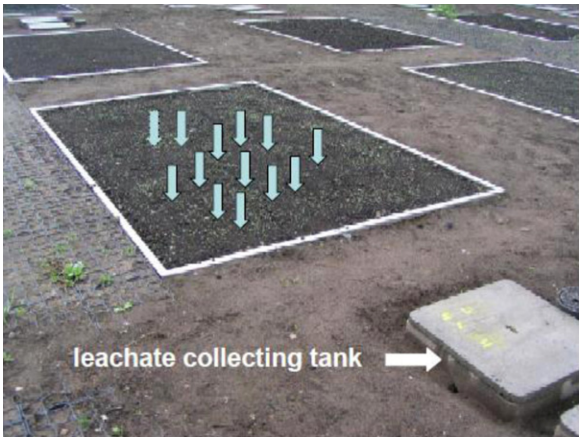

Fig. 1. Photo of a soil plot (2 m wide × 3 m long × 0.7 m deep) connected to a tank allowing the collection of leachates generated by rain water percolating through the tested soil (GISFI experimental station).

The present ecotoxicity results support the conclusions that cyanide complexes are the main pollutants responsible for aquatic toxicity recorded in soil leachates. This work underlines the high risk of soils contaminated with these complexes for environmental and human health, once conditions favoring their mobility and decomposition are met. This study points to the need to include cyanide complexes in the list of priority pollutants in routine analyses of industrially contaminated soils and their leachates, especially in the case of soils selected for requalification.

2. Materials and methods

2.1. Sampling and analyses

A multicontaminated soil was excavated from a former coking plant in the Lorraine Region (north eastern France) in 2004. Part of the soil (30 tons) was treated by thermo desorption at a temperature of 650 °C in a mobile unit. The untreated soil and the thermodesorbed soil were transferred to the experimental station of GISFI (group for integrated studies on industrial wastelands), located at Homécourt in the same country (49°2136N, 5°99608E) (http://www.gisfi.fr). Several tons of the soils (thermodesorbed or untreated) were homogenized, sieved at 80 mm mesh size, and used to fill in situ lysimeter plots in 2005.

Each lysimeter plot (2 m width × 3 m length × 0.7 m depth) was equipped with a system allowing the collection of leaching water in a stainless steel tank (Fig. 1). The leaching water collection tanks were emptied every week or after abundant rain so as to ensure that fresh leachates would be sampled for analyses in the following days. Leachates collected were stored in the dark at 4 °C until physicochemical and ecotoxicological analyses were undertaken within 48 h. After decantation and filtration through 0.7 mm porosity glass filters, leachates were analyzed for organic and inorganic contaminants including total and free cyanides and for ecotoxicity bioassays carried out on the same samples.

Representative soil samplings were carried out for analyses; soils were mixed and sieved at 4 mm for contaminant analyses.

2.2. Chemical characterisation

The PAH congeners (US-EPA) were analyzed in soil samples and leachates according to the AFNOR XP X33-012 [9] and the NF EN ISO 17993 [10] standard methods, respectively, using fluorimetric detection. Acenaphthylene was quantified using diode array. Total PAH concentrations reported in the present study corresponded to the sum of the concentrations of the 16 PAHs analyzed. Heavy metals in soils and leachates were analyzed as described in Bonnard et al. [11]. Cyanide concentrations were measured in soil samples according to ISO 11262 [12] and in leachates according to ISO 14403