

Long-Term Release of Iron-Cyanide Complexes from the Soils of a Manufactured Gas Plant Site

Magdalena Sut^{1*}, Thomas Fischer², Frank Reppmann³, Thomas Raab¹

¹Department of Geopedology and Landscape Development, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany; ²Central Analytical Laboratory, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany; ³Department of Soil Protection and Recultivation, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany.
Email: *sutmagda@tu-cottbus.de

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ABSTRACT

Iron-cyanide (Fe-CN) complexes have been detected at Manufactured Gas Plant sites (MGP) worldwide. The risk of groundwater contamination depends mainly on the dissolution of ferric ferrocyanide. In order to design effective remediation strategies, it is relevant to understand the contaminant's fate and transport in soil, and to quantify and mathematically model a release rate. The release of iron-cyanide complexes from four contaminated soils, originating from the former MGP in Cottbus, has been studied by using a column experiment. Results indicated that long-term cyanide (CN) release is governed by two phases: one readily dissolved and one strongly fixed. Different isotherm and kinetic equations were used to investigate the driving mechanisms for the ferric ferrocyanide release. Applying the isotherm equations assumed an approach by which two phases were separate in time, whereas the multiple first order equation considered simultaneous occurrence of both cyanide pools. Results indicated varying CN release rates according to the phase and soil. According to isotherm and kinetic models, the long-term iron cyanide release from the MGP soils is a complex phenomenon driven by various mechanisms parallelly involving desorption, diffusion and transport processes. Phase I (rapid release) is presumably mainly constrained by the transport process of readily dissolved iron-cyanide complexes combined with desorption of CN bound to reactive heterogeneous surfaces that are in direct contact with the aqueous phase (outer-sphere complexation). Phase II (limited rate) is presumably driven by the diffusion controlled processes involving dissolution of precipitated ferric ferrocyanide from the mineral or inner-sphere complexation of ferricyanides. CN release rates in phase I and II were mainly influenced by the pH, organic matter (OM) and the total CN content. The cyanide release rates increased with increasing pH, decreased with low initial CN concentration and were retarded by the increase in OM content.

Keywords: Prussian Blue; Elovich Equation; Freundlich Equation; Parabolic Diffusion Equation; Multiple First Order Equation

1. Introduction

Cyanide in the form of iron-cyanide (Fe-CN) complexes is a potentially toxic compound that once exposed to UV or visible light radiation, in solution, can be broken down to free cyanide (CN⁻ and HCN) [1]. Anthropogenic activities, like the process of gas purification after coal gasification in Manufactured Gas Plants (MGPs), yielded side products in the form of ferric ferrocyanide (Prussian Blue), leading possibly to the contamination of soil and groundwater. The manufactured gas was conducted through wood shavings, impregnated with hydrated iron

oxide, in order to remove hydrogen sulfide (H₂S) and hydrogen cyanide (HCN). When the iron oxide lost its absorbing capacity it was often deposited in the vicinities of MGP, which generated a potential environmental pollution due to high amounts of sulfur, tar and various complex iron-cyanides.

Knowledge concerning the behavior, particularly dissolution and desorption, of contaminants can help in reducing the extent of cleanup technologies. In order to design effective remediation strategies, it is relevant to understand contaminant fate and transport in soil, and to quantify and mathematically model the release rate [2]. The mobility of iron-cyanide complexes in soil is mainly

*Corresponding author.

governed by the characteristics of the soil solution (pH, pE), the presence of complexing cations (K^+ , Mn^{2+} , Fe^{2+} , etc.), the presence of UV light as well as the substrate composition and stratigraphy (e.g. clay content, hydrological barriers) of the site. Fe-cyanide complexes are negatively charged and can form inner-sphere complexes on positively charged surfaces, which makes adsorption on the soil particles a possible Fe-CN retention mechanism [3]. With decreasing pH the adsorption of iron-cyanide complexes on iron and aluminum oxides surfaces, which are positively charged under acidic conditions, increases. Hence, neutral and alkaline soils sorb CN anions to a lower extent than acidic soils. Depending on the pH, Fe-CN complexes can be adsorbed on the soil organic matter (SOM). According to Mansfeldt [4], the adsorption takes place through hydrogen bonds under acidic conditions and through charge transfers complexes under neutral to caustic conditions. Fuller [5] stated that the sorption of ferricyanide in soil is driven by the pH, iron-oxides and clay mineral content. According to Ohno [6] sorption of ferrocyanide was increased, when the pH of the soil decreased. Rennert and Mansfeldt [3] found that ferrocyanides adsorb on goethite surfaces rather than ferricyanides. Rennert and Mansfeldt [7] predicted that ferricyanide forms outer-sphere and weak inner-sphere surface complexes on goethite. According to them, ferrocyanide was sorbed inner-spherically and by precipitation of a Prussian Blue-like phase. Cheng and Huang [8] found that the adsorption of either ferrocyanide or ferricyanide complexes onto aluminum oxide is achieved through outer-sphere complexation. Ghosh *et al.* [9] carried out a column experiment, where both ferricyanide and ferrocyanide were not restrained by the sandy aquifer material.

Sorption of iron-cyanide complexes by soils, as shown above, is a subject that is studied in soil chemistry, but the reverse process (release/desorption) should be of an equal environmental interest, due to its practical importance. Column studies can provide key information concerning the mechanism of the iron-cyanide complexes dissolution or desorption. Release rate parameters can be estimated from the isotherms of the time dependent data using various mathematical models. The aim of this study was to use different isotherm and kinetic equations to investigate the phenomena of iron-cyanide complexes release from the MGP soils. Applying various models to the column experimental data, was believed to provide the knowledge whether the contaminant discharge is driven by the kinetics of desorption from the heterogeneous substrates (Elovich, Freundlich), the diffusion-controlled phenomena (Parabolic Diffusion Equation) or by the transport following Multiple First Order Equation. Additionally the influence of soils parameters such as pH, texture, OM content, initial CN concentrations on the iron-cyanide complexes release rate was studied.

2. Materials and Methods

2.1. Field Data

Field data on total and dissolved cyanide content of the soils, pH, EC, OM were obtained by sampling the site of a former MGP in Cottbus ($51^{\circ}45,161'N$; $14^{\circ}18,529'E$). The investigation field covers an area of 2500 m² and is relatively flat. The annual average temperature is 8.8°C and average annual precipitation sum is 589 mm [10]. The local climate is characterized as humid continental [11]. Own pre-studies show that the groundwater table is situated at a depth about 7 m below the surface and the soil pH varies between 3.2 and 7.7 [12]. The top soil layer is composed of varying fractions of sand, coal, slag and organic matter (up to 0.5 m deep). The deeper soil (0.5 - 2.0 m) has a sandy texture (texture classes according to German classification system).

Gas works produced a variety of largely hazardous waste products (like iron-cyanide complexes) that were used as a filling material contaminating the surrounding field. Soils (labeled A, B, C and D) used in the column experiment originate from the former MGP site in Cottbus. Soils A, C and D are the top soils (up to 0.5 m deep), whereas soil B was the lower sandy layer (0.5 - 1.5 m deep) of soil A. Selected chemical and physical properties of the investigated soils are presented in **Table 1**.

Grain size analysis was performed by sieving (>20 µm) and X-ray granulometry (XRG) using the SediGraph 5120TM particle-size analyzer [13]. Organic matter was determined with the Loss on Ignition method (LOI). pH and EC were studied with a bench pH/mV meter MultiLab 540 (WTW). Total and water soluble cyanide (**Table 1**) determination was performed according to the micro dist procedure US QuickChem Method 10-204-00-1-X [15]. After distillation cyanide was determined with the flow injection analyzer (FIA Compact, MLE) [16]. The detection limit for both (total and water soluble CN) extractions is 0.02 mg·l⁻¹ of cyanide in analyte.

2.2. Column Experiment (Dissolution/Desorption)

The release of iron-cyanide complexes from the MGP soils (A, B, C and D) was studied by conducting laboratory column experiments at constant flow rates under unsaturated conditions [14]. Eight percolation columns (two replicates for each soil) were constructed from Plexiglas[®] (ID 5.4 cm, height 30 cm) and positioned perpendicular to each other. A peristaltic pump fed distilled water to each column, in the beginning of the experiment at a flow rate of 20 ml·h⁻¹ once per day. Introduced soil was homogenized by hand and each column was loaded with ≈ 700 g of field fresh soil. The system was daily percolated with distilled water and the obtained

Table 1. Selected chemical and physical properties of the investigated soils [14].

Soil	Soil characteristic	OM	Water content	Tot. CN conc.	Tot. water soluble CN conc.	pH	EC	Clay	Silt	Sand
		(%)	(%)	(mg·kg ⁻¹)	(mg·kg ⁻¹)		(μS·cm ⁻¹)	(%)	(%)	(%)
A	top soil	3.4	12.6	875	148	7.6	1455	9.0	14.1	76.9
B	0.5 - 1.5 m deep	1.2	6.4	401	26	5.9	2041	11.8	17.6	70.6
C	top soil	3.1	12.9	1718	21	5.0	2253	7.4	15.2	77.4
D	top soil	4.2	10.6	40	0.6	7.7	780	8.0	14.1	77.9

leachate was subsequently analyzed with the FIA. The experimental set up is shown in **Figure 1**.

2.3. Isotherm Equations

Three isotherm models were applied to the CN experimental data in order to better understand the release process of iron-cyanide complexes from the MGP soils with the varying pH, OM content, CN concentration and soil texture. The gathered data were computed according to the following equations that often describe time-dependent data sufficiently [17].

2.3.1. Elovich Equation [17]

The Elovich equation is generally considered an empirical equation. It has been used in the soil chemistry to describe the kinetics of sorption and desorption of various inorganic materials on the soil [18], and the soil chemical reaction rates [19,20].

$$q = (1/\alpha) \cdot \ln(a \cdot \alpha) + (1/\alpha) \cdot \ln t \quad (1)$$

where:

q —the amount of released CN in time t (mg·CN·kg⁻¹);
 α —a release constant (mg·CN·kg⁻¹·day⁻¹); and
 a —a constant related to the initial velocity of the reaction (mg·CN·kg⁻¹).

Plot of “ q ” vs. “ $\ln t$ ” gives a linear relationship with the slope of $(1/\alpha)$ and the intercept of $(1/\alpha) \cdot \ln(a \cdot \alpha)$.

2.3.2. Parabolic Diffusion Equation [21]

The parabolic diffusion equation is often used to indicate that diffusion-controlled phenomena are rate limited. The diffusion models have been developed to predict the dynamic character of release and have been successfully used to describe for example metal reactions on soil and soil constituents [22].

$$q = a + K_d \cdot t^{1/2} \quad (2)$$

where:

q —the amount of released CN in time t (mg·CN·kg⁻¹);
 a —constant (mg·CN·kg⁻¹); and
 K_d —apparent diffusion rate constant (mg·CN·kg⁻¹·day^{-1/2}).

Plot of “ q ” vs. “ $t^{1/2}$ ” gives linear relationship if the reaction confirms the parabolic diffusion law. The “ a ” and

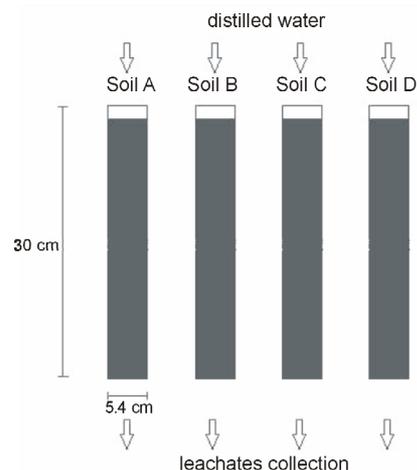


Figure 1. Scheme of the column experiment set-up.

“ K_d ” parameters are determined from the intercept and the slope of the function respectively.

2.3.3. Freundlich Equation [23]

Freundlich equation is generally considered an empirical relationship describing the adsorption of solutes from a liquid to a solid surface, and have been widely applied to experimental data. Elkhatib *et al.* [24] used a modified Freundlich equation to describe the kinetics of lead and copper desorption [25] from soils.

$$q = k \cdot t^v \quad (3)$$

where:

q —the amount of released CN in time t (mg·CN·kg⁻¹);
 k —release rate coefficient (day⁻¹);
 t —reaction time (day); and
 v —a constant.

The Freundlich isotherm is a power function, where “ k ” and “ v ” are constants that can be determined from the coefficient and the exponent respectively.

2.4. Kinetic Equation

Transport models assuming chemically controlled non-equilibrium, which describes the kinetic of a release or dissociation reactions is often defined as a first order reaction [26]. The heterogeneity of a system as well as the controlling mechanism of the release process (such as

mass transfer or chemical reaction) determines the rate constants that are required to describe the experimental data.

First Order Equation [27]

Release kinetics based on the first order equation, where the total released amount (q) within a certain time (t), is expressed by the following equation:

$$q = q_0 \cdot (1 - e^{-kt}) \tag{4}$$

where:

q —the amount of released CN in time t ($\text{mg} \cdot \text{CN} \cdot \text{kg}^{-1}$);

q_0 —the amount of CN released at equilibrium ($\text{mg} \cdot \text{CN} \cdot \text{kg}^{-1}$); and

k —apparent release rate coefficient (day^{-1}).

Assuming that CN release is constrained by more than one pool, total released CN amount should be expressed as:

$$q_{tot} = q_1 + q_2 \tag{5}$$

where:

q_{tot} —is the total amount of released CN in time t ($\text{mg} \cdot \text{CN} \cdot \text{kg}^{-1}$);

q_1 —is the fast releasing CN pool ($\text{mg} \cdot \text{CN} \cdot \text{kg}^{-1}$); and

q_2 —is the stronger fixed CN pool ($\text{mg} \cdot \text{CN} \cdot \text{kg}^{-1}$).

The release kinetics for two pools concept (one readily and one slowly liberating) can be expressed using the multiple first order rate equation, where each pool has its capacity and rate constant:

$$q = q_1 \cdot (1 - e^{-k_1t}) + q_2 \cdot (1 - e^{-k_2t}) \tag{6}$$

Numerical parameters (k) fit was based on least sum of squares.

2.5. Statistical Analysis

The predictive performances of the developed models were assessed by adjusted correlation coefficient (R^2), standard error (SE) and the probability value (p), using the analysis of variance (ANOVA).

3. Results

3.1. Column Experiment

Release of cyanide from MGP soils (A, B, C and D), was investigated with the soil column experiment. The CN release rate was studied for four soils with different pH's and textures (Table 1). According to Bodenkundliche Kartieranleitung [28], soil A and B are medium loamy sandsoils (SI3), whereas soils C and D are characterized as weak loamy sand soils (SI2). Figure 2 represents the relation of the released cyanide, plotted cumulatively, vs. release time. Figure 2 indicates that long-term CN release from soil can be described using two separate cyanide pools: one available and one strongly fixed. The amount of released cyanide representing each pool was visually obtained from the graph (Figure 2).

It is assumed that amount of cyanide in the column leachates is influenced by mobilization of readily soluble

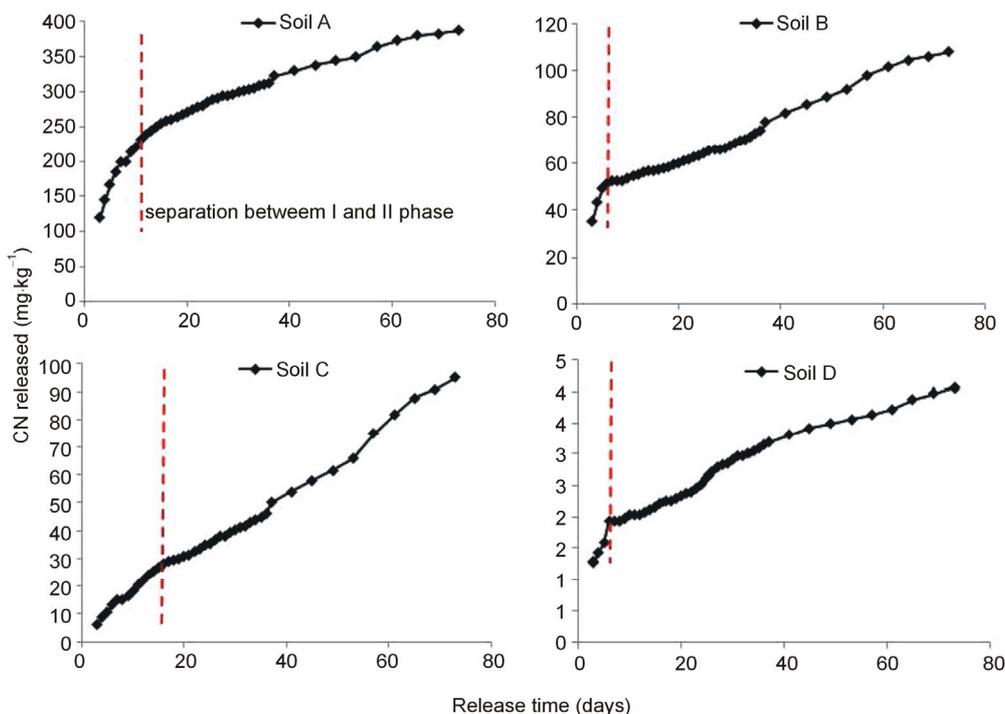


Figure 2. Cumulative CN release curves for the four investigated soils [14].

hexacyanoferrate (phase I) and slow dissolution of ferric ferrocyanide (phase II) [29]. The kinetics of CN release will be based on deriving a constant release rate for each phase, based on the continuously measured CN rerelease as a function of time.

3.2. Isotherm Models

Modeling of the CN release experimental data using isotherm equations assumes that the above mentioned two phase approach is separate in time and that phase I precedes phase II. Treating the processes separately, intent to derive the cyanide release rates for each phase.

3.2.1. Elovich Equation

The empirical equation [19] was used to describe the CN release rate from the MGP soils (A, B, C and D) in the column experiment. **Figure 3** demonstrates the Elovich equation plots of released CN vs. \ln of reaction time obtained for phase I and phase II. In **Figure 3** it can be noticed that a linear relationship exists between the released CN “ q ” and \ln of release time “ \ln (release time)” for both phases in all investigated soils.

The Elovich equation parameters, determined from the slope and intercept of the linear plots, are given in **Tables 2** and **3**. In the Elovich equation a decrease in “ α ” values and increase in “ a ” values would increase the reaction rates [22]; [30]. Regression analysis (**Table 2**) indicated significant (<0.01) correlation in all investigated soil.

The Elovich equation parameters for phase II are listed in **Table 3**. Regression analysis (**Table 3**) indicated significant (<0.01) correlation in all investigated soils. As indicated by the regression analysis, the Elovich equation resulted to be adequate for describing the kinetics of CN release from contaminated soils in a column experiment. Moreover, the Elovich equation provides a very good fit ($R^2 > 0.95$) for phase I and a good fit ($R^2 > 0.84$) for phase II of CN release.

3.2.2. Parabolic Diffusion

The parabolic diffusion equation was subsequently used to describe the CN release from the contaminated soils (A, B, C and D) in the column experiment. A parabolic diffusion plot of CN release vs. $t^{1/2}$ is shown in **Figure 4**. The parabolic diffusion equation parameters, determined from the slope and intercept of the linear plots, are given in **Tables 4** and **5**.

Regression analysis for phase I (**Table 4**) indicated significant (<0.01) correlation and high correlation coefficient (>0.91) in all investigated soil. In phase II (**Table 5**), regression analysis demonstrates significant (<0.01) correlation in all investigated soil, as well as high correlation coefficient (>0.97) and low SE.

Table 2. The Elovich equation parameters and correlation coefficients for phase I CN release in the MGP soils.

Soil	Phase I		R^2	SE	p
	α	a			
	mg·CN·kg ⁻¹ ·day ⁻¹	mg·CN·kg ⁻¹			
A	0.01	125.00	0.99	3.29	<0.01
B	0.05	39.92	0.96	1.54	<0.01
C	0.07	5.82	0.98	1.37	<0.01
D	2.02	2.21	0.98	0.03	<0.01

Table 3. The Elovich equation parameters and correlation coefficients for phase II CN release in the MGP soils.

Soil	Phase II		R^2	SE	p
	α	a			
	mg·CN·kg ⁻¹ ·day ⁻¹	mg·CN·kg ⁻¹			
A	0.01	88.99	0.98	4.46	<0.01
B	0.04	15.77	0.85	5.72	<0.01
C	0.02	3.79	0.96	3.81	<0.01
D	1.27	0.58	0.93	0.08	<0.01

Table 4. The parabolic diffusion equation parameters and correlation coefficients for phase I CN release in the MGP soils.

Soil	Phase I		R^2	SE	p
	K_d	a			
	mg·CN·kg ⁻¹ ·day ^{-1/2}	mg·CN·kg ⁻¹			
A	83.00	69.63	0.94	4.96	<0.01
B	32.18	35.81	0.99	0.81	<0.01
C	10.03	5.57	0.99	0.77	<0.01
D	0.54	0.02	0.92	0.11	<0.01

Table 5. The parabolic diffusion equation parameters and correlation coefficients for phase II CN release in the MGP soils.

Soil	Phase II		R^2	SE	p
	K_d	a			
	mg·CN·kg ⁻¹ ·day ^{-1/2}	mg·CN·kg ⁻¹			
A	29.30	139.92	0.99	2.26	<0.01
B	10.29	15.98	0.94	3.60	<0.01
C	17.12	53.96	0.98	2.60	<0.01
D	0.26	0.95	0.97	0.05	<0.01

3.2.3. Freundlich Equation

The Freundlich equation was also used to describe the CN release from the MGP soils in a column experiment. The Freundlich isotherm is a power function, where “ v ” and “ k ” are constants. Isotherms of this form have been

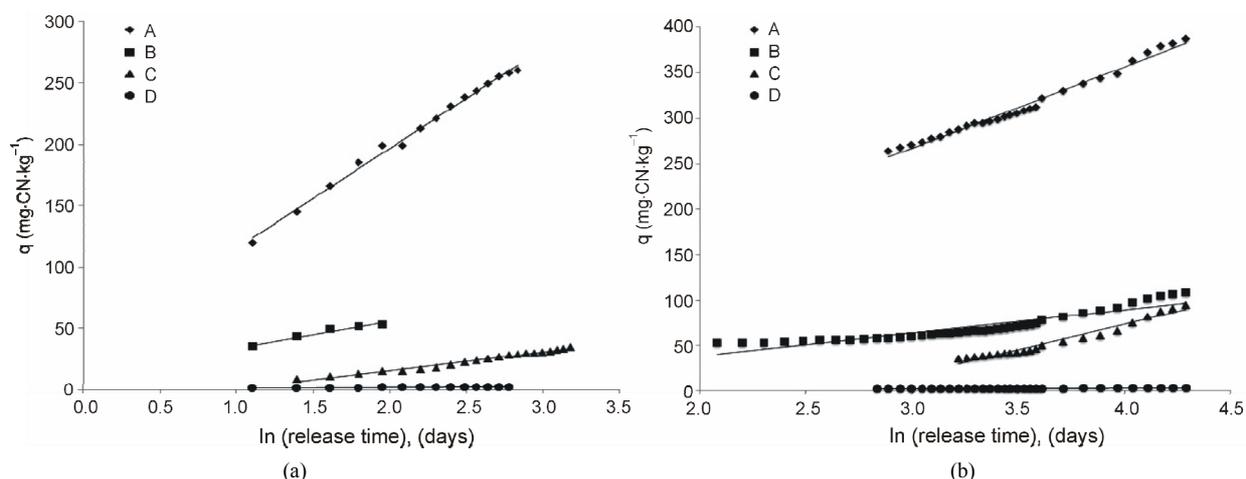


Figure 3. The Elovich equation plots for CN release from the MGP soils in (a) phase I and (b) phase II.

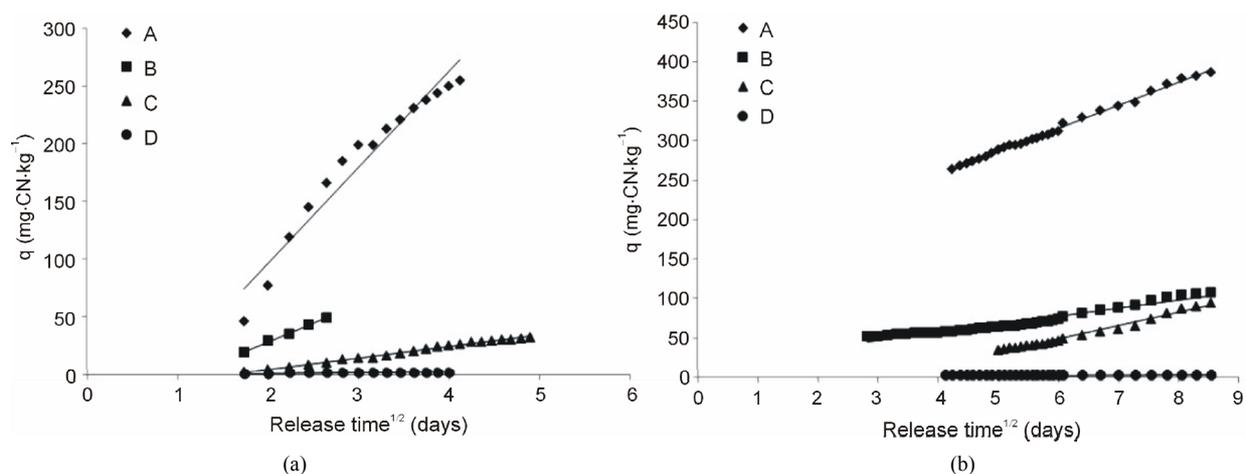


Figure 4. The parabolic diffusion equation plots for CN release from the MGP soils in (a) phase I and (b) phase II.

observed for a wide range of heterogeneous surfaces, including activated carbon, silica, clays, metals, and polymers [31]. The release of CN in phase I and II was well modeled by the Freundlich equation (Figure 5).

In both phases (I and II), a power function was able to fit the data with a high degree of correlation: $R^2 > 0.93$ and $R^2 > 0.90$ respectively. Regression analysis (Tables 6 and 7) indicated significant (<0.01) correlation in all investigated soil. The Freundlich equation proved to be successful in describing both phases in CN release from the MGP soils.

3.3. Kinetic Model

Another consideration assumes that release of iron-cyanide complexes is constrained by two phases that occur simultaneously, which would suggest non-equilibrium liberation. In this approach transport phenomena of phase I is not considered separately from the slow chemical reaction of phase II. For this approach, a modified first order equation was used. The total released CN amount

Table 6. The Freundlich equation parameters and correlation coefficients for phase I CN release in the MGP soils.

Soil	Phase I				
	$v \times 10^{-3}$	$\frac{k}{\text{day}^{-1}}$	R^2	SE	p
A	427.60	81.40	0.97	7.30	<0.01
B	477.30	21.77	0.94	2.00	<0.01
C	596.50	5.58	0.98	0.70	<0.01
D	295.40	0.94	0.97	0.04	<0.01

Table 7. Freundlich equation parameters and correlation coefficients for phase II CN release in the MGP soils.

Soil	Phase II				
	$v \times 10^{-3}$	$\frac{k}{\text{day}^{-1}}$	R^2	SE	p
A	278.40	117.00	0.99	3.60	<0.01
B	345.90	22.37	0.91	3.80	<0.01
C	948.70	1.60	0.99	2.70	<0.01
D	300.30	0.87	0.95	0.06	<0.01

was determined as a sum of phase I and phase II (Equation 6), where each phase had its capacity and rate constant.

Multiple First Order Equation

A multiple, two-component first-order equation was used to describe the CN release from the MGP soils in a column experiment. **Figure 6** represents fitted release curves for the investigated soils, the measured CN and the released quantities from both phases. **Figure 6** shows that the two-component first order model provides a good fit of the experimental data for soil A, B and D. The

multiple first order equation parameters and correlation coefficients are listed in **Table 8**. Applying this kinetic approach, it was assumed that each phase has its release rate (k), which is proportional to the amount present in a specific pool.

Regression analysis (**Table 8**) indicated significant (<0.01) correlation in all investigated soil. According to the correlation coefficient and standard error, a modified two-component first-order equation was successful in describing the experimental data from soil A, B and D. Slightly worse correlation was obtained for soil C ($R^2 = 0.89$; SE = 7.42).

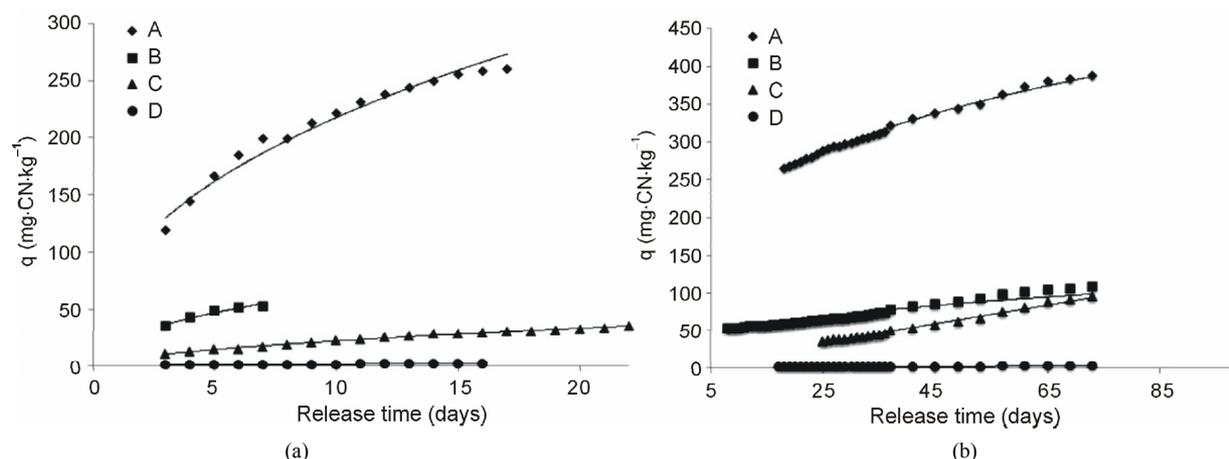


Figure 5. The Freundlich equation plots for CN release from the MGP soils in (a) phase I and (b) phase II.

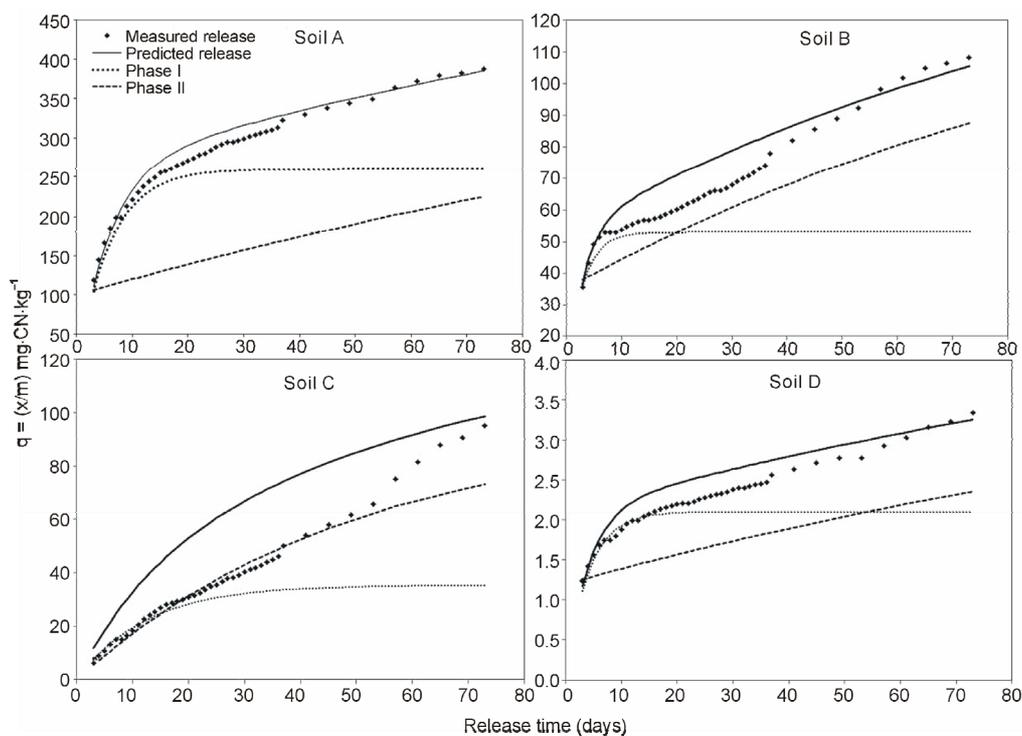


Figure 6. Cumulative measured CN release plots with predicted CN release, phase I and phase II, using the modified first order equation, for the MGP soils.

Table 8. The multiple first order equation parameters and correlation coefficients for CN release in the MGP soils.

Soil	Phase I	Phase II	R ²	SE	p
	k_1 day ⁻¹	k_2 day ⁻¹			
A	0.17	0.53×10^{-2}	0.97	9.28	<0.01
B	0.37	0.01	0.92	4.14	<0.01
C	0.08	0.01	0.89	7.42	<0.01
D	0.5×10^{-2}	0.25	0.94	0.10	<0.01

4. Discussion

In contaminated soils, on the sites of former MGPs, the mobility of iron-cyanide complexes is mainly governed by the dissolution and precipitation of ferric ferrocyanide and adsorption on soil minerals [32]. The purpose of our work was to gain better knowledge concerning the iron-cyanide complexes release from the MGP soils by applying various isotherm and kinetic equations. The column experiment simulated the experimental conditions relevant to anthropogenically altered soils. The approach presented here assumes that the release of iron-cyanide complexes is constrained by two phases. According to Aharoni *et al.* [23], the rate of release is rapid, when it is governed by the transport process taking place in the liquid phase, or diffusion in the bulk of the liquid, at the film adjacent to the solid particle, in liquid-filled pores, etc. Theis *et al.* [33] attributed quick and complete desorption of ferricyanide from goethite to outer-sphere complexation.

If the release rate is slow, it is probably limited by the process taking place in the solid phase. It can be constrained by the constant dissolution of the ferric ferrocyanide like precipitate, which according to Mansfeldt and Dohrmann [34] may originate from coprecipitation on the soil surface or from precipitation of iron-cyanide complexes with alkali and alkaline earth cations. Rennert and Mansfeldt [7]; [35] proposed that slow and incomplete desorption of ferrocyanide was attributed to inner-sphere surface complexation, which occurs through the formation of direct chemical bonds with the mineral surface, (typically with surface oxygen atoms), and by precipitation of a Prussian Blue-like phase on the goethite surface.

Pursuant to the results obtained in the column experiment (Figure 2), it is believed that the release of iron-cyanide complexes from the contaminated soils can be described using two separate cyanide pools: one available (like transport of readily dissolved hexacyanoferrate or desorption of weak outer-sphere complexation) and one strongly fixed (like dissolution of precipitate in from of ferric ferrocyanide or desorption of inner-sphere complexation). Applying the isotherm models to the column

experimental data required handling the phases separately in order to derive the release rate constants. Implementing the equations to the complete data set (Figure 2) resulted in very low correlations, which proves the hypothesis that the release of iron-cyanide complexes from the MGP soils is constrained by two phases.

The Elovich equation has been frequently used to study the chemical release processes and is suitable for systems with heterogeneous adsorbing surfaces [36]. The kinetic behavior of inorganic materials like metals (Pb and Cu) has been successfully described by the Elovich equation [22]; [23]. Mathematical analysis of the CN release data indicated that the Elovich equation is suitable to describe the kinetic behavior of iron-cyanide complexes in the MGP soils (Figure 3). In the Elovich equation, a decrease in “ α ” increases the reaction rate. In phase I (Table 2), the CN release rate increases with the increasing soil pH (Table 1), except for the soil D, where release rate is very low according to soil pH (7.7). The low release rate of soil D is most probably caused by the low total CN concentration (Table 1) hence, the cyanide release rate in phase I is influenced by the soil pH as well as the initial CN concentration in soil. Generally, in the desorption processes, one of the most important parameter is the initial pH value of the solution, which influences both the contaminant surface binding sites and the contaminant chemistry in water. Our findings are consistent with the study made by Ohno [6], who investigated sorption of ferrocyanide by five soils, where increasing sorption was observed with decreasing soil pH. In phase II, the relation of “ α ” and “ a ” values are analogous with the ones obtained for phase I, where the release rates for phase I are higher than for phase II. Low pH of the soil C (pH = 5) most probably reduces the amount of readily dissolved iron-cyanide complexes in the phase I, which results in only slightly higher “ α ” values for the phase II. Lower, but still significant, was the correlation in soil B (R² = 0.85), which may be affected by the low OM content (Table 1). On the other hand, depending on pH, the overall charge of SOM is either neutral or negative, hence the anion adsorption cannot be expected. However, Rennert and Mansfeldt [3] state that SOM promotes the sorption, hence the content of C_{org} is possibly enhancing the sorption of iron-cyanide complexes on soils. The suggested reaction for this process was the charge transfer complexes, formed by cyanide ion (CN⁻), via cyanide-N with quinone groups of humic acids [37].

Simultaneously, the parabolic diffusion equation was used to describe the CN release from the MGP soils. This model has been used by many scientists to characterize the diffusion-controlled phenomena in soil constituents and the release of ion in soil and soil minerals [38]. It assumes that described CN release is determined by the sum of various diffusion processes with different diffu-

sion coefficients and various particle sizes. Linear relationship visible in phase II indicates (**Figure 4**) that the parabolic equation adequately describes the CN release process, suggesting that phase II is driven by the diffusion of CN out of the mineral matrix. On the other hand, in phase I, the regression line for the soil A doesn't pass through the origin, suggesting that the diffusion is not the main driving mechanisms. Additionally, in phase I, the "a" value was determined from the y-intercept ($t = 0$). The intercept is most probably affected by the rapid CN release, which would be much slower if not influenced by the transport of already dissolved phase. The apparent CN diffusion rate coefficient " K_d " in the parabolic diffusion law is considered the measure of the relative rate of CN release [23]. The difference between the " K_d " values indicates that the release power of the soils is different. In phase I (**Table 4**), the " K_d " values for the studied soils were increasing with the increasing soil pH, except for the soil D, which despite of the alkaline character, indicated low CN release, most probably induced by low initial CN concentration. Soil B, despite of acidic character, indicated comparably high CN release rate, which can be attributed to the low OM content. The diffusion coefficient " K_d " is higher in sandy soils with lower organic matter. More heterogenic soils are more likely to have an increase in transport-limited process [23]. In phase II, the relative rate of CN release (K_d) seems to be affected by the CN concentration. Major decrease in " K_d " value can be noticed in soil A, despite of basic soil pH. Release rate in soil B also decreased, whereas in soil C, continuous release, comparable to the one obtained in phase I, can be observed (**Table 5**). Based on correlation coefficient it can be stated that the parabolic diffusion law effectively describes the phase II of CN release from the MGP soils. For the phase I, the results revealed ("a" value determined from the y-intercept) that the diffusion phenomena is not the driving mechanisms, however it doesn't imply that CN release does not include a slow diffusion reaction. It may rather indicate that the kinetics of this process shouldn't be considered separately from the transport phenomena. More study need to be done to determine whether CN release is driven by intraparticle diffusion, external-film diffusion or internal-pore diffusion.

Subsequently, the release of CN from the MGP soil was described using the Freundlich equation. This power function exhibits increasing release rate with increasing time, but decreasing positive slope as time increases (**Figure 5**). The Freundlich equation is often used for heterogeneous surfaces and describes desorption from solid to the solutes in liquid and assumes that different sites with several adsorption energies are involved. Many organics and inorganics follow this type of behavior [19]; [23]. According to mathematical analysis (**Tables 6** and

7), the Freundlich reaction based model was successful in describing, both phase I and phase II, CN release from the MGP soils. The exception is phase I in soil A, where the regression line doesn't pass through the origin (**Figure 5**), suggesting that desorption is not the driving mechanism. Soil A is alkaline (pH = 7.6) and has high CN content, which would explain high amount of dissolved cyanide in the pore water and imply that the CN release in phase I is mainly constrained by the transport of readily dissolved compounds rather than desorption. The values of release rate coefficient " k ", in phase I and II, decrease with the decreasing soil pH, except for the soil D, where low " k " value might be a result of low CN concentration in soil.

Applying the isotherm equations to the column data was aimed at better understanding the mechanisms of the CN release that, prior to the kinetic study, was divided in two phases. This modeling approach assumed that phase I and phase II are separated in time. Results revealed various release rates in both phases, implying that the driving mechanisms are different. The column experimental data for phase II showed good correlation with the Elovich, Freundlich and Parabolic Diffusion Equations leading to inconclusive results about the driving mechanisms of the CN release. For the phase I, poor fitting of the regression line (Freundlich) and the negative intercept values (Parabolic diffusion), implied the transport of dissolved iron-cyanide complexes as the main process.

The First order equation was previously used by many researchers to describe time-dependent data [26]; [39]. This modeling approach assumes that both CN release phases occur simultaneously. The modified first order model well described the CN release data (**Table 8**), which is supported by the graphical test presented in **Figure 6**. This result suggests that the release of CN from the MGP soils followed the multiple first order kinetics. Worst graphical and regression correlation was obtained for soil C. The release of CN from soil C is almost linear, most probably due to low soil pH, constrained mainly by one strongly fixed pool. According to Meeussen *et al.* [40] the mobility of cyanide in the soil largely depends on pH. Under acidic conditions, solid iron-cyanide complexes in the form of precipitated Prussian Blue are likely to be expected. It could explain why the two-component approach didn't manage to describe the kinetics of CN release from the soil C. Due to the low pH, the amount of dissolved iron-cyanide complexes is relatively low, so the difference in the release rates for phase I and phase II is relatively small (**Table 8**).

Rate constants for each soil vary (**Table 8**), indicating the highest release rate in soil B for phase I and in soil D for phase II. The low initial release rate in phase I for soil C is consistent with the study made by Meeussen *et al.*

[40]. They stated that acidic character of soil will considerably decrease the CN concentration in groundwater and reduce the mobility of iron-cyanide complexes in such soils. High initial release rate (k_1) in soil B can be constrained by the low OM content, despite of a slightly acidic character of the soil. Using the multiple first order kinetic equation for modeling of the long-term cyanide release probably closer reflects the phenomena that occur in the MGP soils. It is more probable that the release of phase I and phase II appear simultaneously rather than completely separate in time.

5. Conclusions

The study of iron-cyanide complex release, in a column experiment, was conducted to investigate the long-term desorption or dissolution mechanisms. The research revealed that the cyanide liberation from the investigated MGP soils is driven by two phases. From the kinetic studies, it was observed that the cyanide release was initially rapid (phase I) followed by a much slower release rate (phase II). Most probably, one more fraction exists (an amount that is not released), but our experimental time scale didn't allow for that observation.

Modeling with isotherm equations, assuming that both phases are separate in time, delivered inconclusive results concerning the driving mechanisms for the cyanide release in phase II. The Elovich equation was in good agreement to describe the CN release in phase I and II, suggesting desorption from the heterogeneous surfaces to the liquid. Analogously good correlation was obtained by using the Freundlich equation, except for phase I in soil A, where too high CN content and alkaline pH imply transport of readily dissolved cyanide as a main driving release mechanism. The parabolic diffusion adequately describes the rate-limiting CN release (phase II), implying that it's driven by the diffusion of CN out of the mineral matrix. For phase I, obtained results imply that transport of dissolved cyanide is the main mechanisms. Indefinite results for phase II, obtained from applying the isotherm equations, most probably indicate that the long-term iron cyanide release from the MGP soils is a complex phenomenon driven by various mechanisms parallelly involving desorption, diffusion and dissolution processes.

The multiple first order equation assumed simultaneous occurrence of both phases and adequately described the CN release from soil A, B and D, except for the soil C, where due to it's acidic character, the CN mobility is most probably constrained by one strongly fixed pool. This non-equilibrium approach is considered to closer reflect the probable cyanide release mechanisms from the MGP soils.

Based on conducted isotherm and kinetic modeling, we attribute the fast release rate (phase I) to the transport

process of readily dissolved iron-cyanide complexes (hexacyanoferrates) that is taking place in the liquid phase combined with the desorption of CN bound to heterogeneous surfaces that are in direct contact with aqueous phase (outer-sphere complexation).

Mobility governed on the low release level (phase II) is probably controlled by the desorption, dissolution or diffusion processes, like the dissolution of precipitated ferric ferrocyanide or of inner-sphere complexed ferricyanides.

The iron-cyanide release rates for phase I and II, obtained in the kinetic modeling, revealed that the CN mobility is mainly influenced by the pH (which affects both the contaminant surface binding sites and the contaminant chemistry in water), by the initial CN concentration and by the possible sorption on soil organic matter. The cyanide release rates increased with the increasing pH, decreased with low initial CN concentration and was retarded by the increase in OM content.

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