Chapter 3
Multiple-Phase Evaluation of Copper Geochemistry

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3.1 Geological Aspects

3.1.1 Geogenesis

Considerations given to the Earth's geochemical structure might be referred to one of the most widely recognised hypotheses on its creation, i.e., initially the Earth was a melted mass having been maintained in its semifluid state by bombing planetoids. The chemistry of the Earth at the early forming stage was similar to an average compound of meteorites with the predominance of magnesium and iron silicates, nickel-bearing iron in the metallic state and numerous other elements. Referring to the commonly agreed threshold of 0.01 %, elements such as O, Si, Al, Fe, Ca, Na, Mg, K, C are considered as major since their concentrations are higher than this value. In the case of Ni, Zn, Cu, Co, Pb, Sn, As and Mo, their level is below 0.01% mm^{-1} and they are designated as rare earth metals or trace elements. Copper levels in the rocks of the Earth's crust are estimated to range from 5 to 100 mg kg^{-1},

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with the average of 55 mg kg^{-1} (Konstantynowicz 1979; Kabata-Pendias and Pendias 1999).

Copper as free metal is rarely encountered in the environment. Due to its chemical affinity for sulphur, copper is classified as the so-called chalcophylic elements and is mostly found in the form of sulphide minerals. In terms of usefulness, the greatest significance is attributed to chalcopyrite $CuFeS_2$, chalcocite Cu_2S and bornite Cu_5FeS_4. These minerals originate from magma processes whose quantitative predominance in nature is recognised, although the richest concentrations of copper are related to its secondary concentration at the weathering stage (Polański and Smulikowski 1969). Copper, being a weak basic oxide, forms also minerals of hydroxycarbonate nature with high utility significance such as azurite $Cu_3(CO_3)_2(OH)_2$ and malachite $Cu_2CO_3(OH)_2$. In this case they are mainly found in sedimentary rocks as products of hydrothermal transformations.

3.1.2 Geological CO_2 Sequestration Mediated Mineral Solubilisation

Processes of rock and minerals' weathering in conditions of underground injection of CO_2 to deep geological structures are considered to be new and of local character. In fact, these practices have occurred in different parts of our globe for over 40 years (Drobek et al. 2008). Carbon dioxide injection to deep geological structures including uncultivated saline aquifers initiates chemical processes in the pattern: CO_2-rock, CO_2-brine and brine (saturated CO_2)-rock, resulting in chemical changes of both underground waters and surrounding rocks. The effect of the diphasic system of CO_2-brine on geological milieu is based on bicarbonate balance according to the following reactions:

$$H_2CO_3 + Ca^{2+} \rightarrow CaCO_3 + 2H^+ \tag{3.1}$$

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{3.2}$$

A targeted example of such process is the surface aquifer of copper deposits in the Legnicko-Glogowski Okręg Miedziowy (LGOM, Poland) with average amounts of chalcophylic elements Cu 0.08, Zn 0.50 and Pb 0.045 mg dm^{-3} (Wilk and Bocheńska 2003). For metals of similar concentrations in the places of carbon dioxide injection in underground waters, copper and other metals will precipitate in the form of virtually dissoluble or hardly soluble hydroxycarbonate salts which are subject to the process of secondary dissolving, due to hydrogeochemical balance (Drobek et al. 2008).

The effect of two-phase brine (saturated CO_2)-rock system on geological environment is a subsequent mechanism of chemical processes occurring during CO_2 deposition under the ground. Carbonate minerals will gradually dissolve causing an increase in permeability of the surrounding rocks; thus, in the environment of brine supersaturated with carbon dioxide, precipitation of metals including dissoluble and hardly soluble copper hydroxycarbonates will take place. In this case the bicarbonate balance in brine environment will be again a potential source of co-precipitation of the hydroxycarbonate form of copper, loamy minerals and silicate (Huijgen et al. 2006; Ibsen and Jacobsen 1996).

The reported cases of chemical processes accompanying CO_2 injection to deep geological structures point out that such anthropogenic interference into the environment may generate changes in the forms of elements' mineralogy, copper among others. Taking into account great dispersions of copper in the Earth's crust, these processes are rather of local character and their magnitude should not generate significant changes in the environment at present.

3.2 Solid-Soil Solution Interface: Processes and Evaluation

Soil in its whole entity is one of the more complex naturally formed medium. The heterogeneity of its constituents, their mutual interactions and last but not the least the direct or indirect influence of external factors make this complexity quite unbelievable to define. In all natural heterogeneous soil environments, the following generalised mechanisms and phenomena occur simultaneously: (a) dissolution, (b) adsorption/desorption, (c) complexation, (d) migration, (e) precipitation, (f) occlusion, (g) diffusion, (h) absorption by microbiota and (i) volatilisation. The developments in soil chemistry started with the pioneering studies of Thomas Way on Base Exchange published in 1850 as *On the Power of Soils to Absorb Manure* (Forrester and Giles 1971). Detailed informations on geochemical reactions are reported by Gapon (1933), Gaines and Thomas (1953), Sokołowska (1989), Sposito (1984), Sparks (1989), Mulder and Cresser (1994) and Barrow (1999).

Soil chemistry has traditionally focused on the chemical reactions in soils that affect plant growth and plant nutrition. However, as concerns increased about inorganic and organic contaminants in water and soil, the emphasis of soil chemistry is now on environmental soil chemistry. This holds to the definition suggested by McBride (1994) and Sparks (1995) as the study of chemical reactions between soils and environmentally important plant nutrients, radionuclides, heavy metals and organic chemicals.

Environmental concern in the 1970s led to the adaptation of simulative/predictive models for metals solid-phase/aqueous-phase interactions and their probable behaviour in natural environments. Transport of heavy metals and copper among others through soil layers has long presented great interest to both environmental and soils scientists (Murali and Aylmore 1983a, b; Ogwada and Sparks 1986; Diatta et al. 2000). The complexity of the soil matrix makes it difficult to selectively choose interactions, which mostly contribute to the adsorption of a specific metal (Diatta et al. 2012). This problem creates more difficulty in the process of formulating meaningful soil models for the prediction of metal transport.

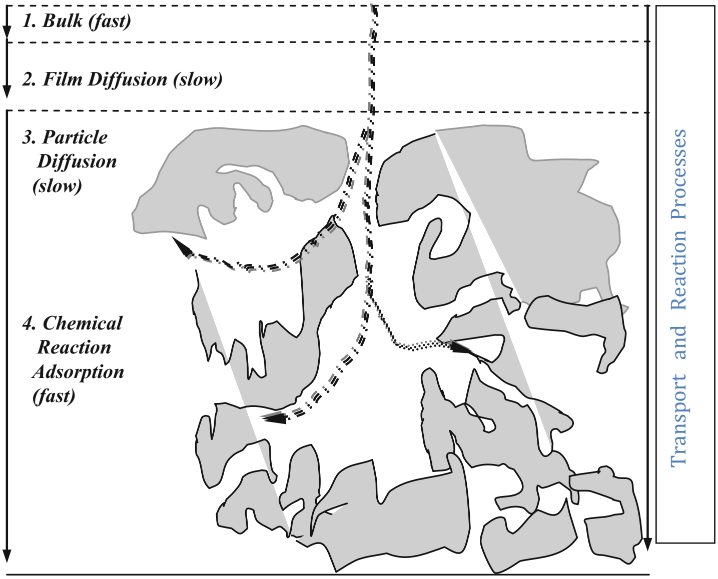


Fig. 3.1 Rate-determining steps in soil chemical reactions (Weber 1984 with permission from ASCE)

Most of soil chemical reactions are time dependent and may differ notably in rates. The frequently concerned mechanisms of ion movement through soil layer are diffusion-based processes, the rates of which are closely related to the homogeneity and heterogeneity of the systems (Lai and Mortland 1968; Sparks 2000). The following illustration (Weber 1984) shows rate-determining steps of soil chemical processes (Fig. 3.1):

There are three basic ways to determine rate constants (Skopp 1986; Sparks 1989, 1995). The first is the use of initial rates by plotting the concentration of a reactant or product over a short reaction time period during which the concentrations of the reactants change so little that the instantaneous rate is hardly affected. The second way is by directly applying integrated equations and graphing the data, and the last one is by using the nonlinear least square analysis.

In recent years, research on metal (copper among others) adsorption/desorption processes has been based mainly on the study of equilibrium conditions. The kinetic approach of these processes in soil systems is also reported (Bunzl et al. 1976; Elkhatib et al. 1992; Violante et al. 2008). The kinetics of metal adsorption (copper among others) at its first phase is found to be basically influenced by sorbent amounts, types and pH as well (Basta and Tabatabai 1992). The impact of organic matter on the kinetics of copper sorption by peat humic substances was extensively reported by Sapek (1976). The author reported that the time course of these processes is partly attributed to the occurrence of specific high- and low-energy adsorbing sites at the surface of soil organic colloids. It is of common view that the pool of high-energy sites is more developed than that expected for the low energy one. This acts as a limiting factor during adsorption process. At a longer time, more and more other low-energy sites become successively saturated (Tiller et al. 1984). On the basis of kinetic studies, it was formulated that kinetic adsorption is characterised by a two-phase process, a rapid exchange followed by a slower reaction of copper ions with organic sorbents (Sapek and Zebrowski 1976; Boehringer 1980; Aringhieri et al. 1985).

The reaction rate theory assumes that colliding molecules (e.g. reactions between solution ions and ions adsorbed in the exchange complex) must be in a high-energy state before a reaction can occur. This energy of activation is of van der Waals repulsive forces that take place as two ions approach each other (Sparks 1989). Then the energy of activation may be considered as a measure of the magnitude of the forces to be overcome during the process of adsorption/desorption. Thermodynamic approach can predict only the final state of a soil system from an initial nonequilibrium state and has been used to characterise exchange equilibria on clay and soil particle surfaces (El-Sayed et al. 1970). An alternative that should be examined is the use of kinetics to follow the course of adsorption/desorption reactions. This technique has the potential of providing both the mechanistic and thermodynamic informations. However, application of kinetic theory to determine thermodynamic parameters (e.g. for phosphorus and potassium) has received more attention (Evans and Jurinak 1976; Pavlatou and Polyzopoulos 1988; Ogwada and Sparks 1986; Liu and Huang 2000; Zhang et al. 2000) than for heavy metals (El-Sayed et al. 1970; Elkhatib et al. 1993).

A number of models have been elaborated for describing adsorption/desorption reactions of various elements in soils (Gapon 1933; Stawiński 1977; Mattigod and Sposito 1979; Kinniburgh 1986; Amacher et al. 1986; Sokołowska 1989; Dube et al. 2001; Diatta et al. 2003). The most well-known sorption models may be classified into two groups: (1) models which take account of electrostatic forces and bonding and (2) models which do not include these parameters. Models of the first group have some bug: they are complicated—it means that they require many parameters at the beginning of modelling—or they are simply physical equalisations of transport inside the soil profile without consideration of interaction between contaminants and soil matrix. To the second group belong the classical models, i.e. Freundlich and Langmuir isotherms with their suggestive extensions (Veith and Sposito 1977; Sposito 1982, 1984; Sparks 1995; Sarbak 2000). These isotherms are generally based on the amount of adsorbed element (quantity) plotted against its equilibrium concentration (intensity) and the resulting slopes and intercepts to be indicative of various soil sorption/desorption parameters (Fig. 3.2).

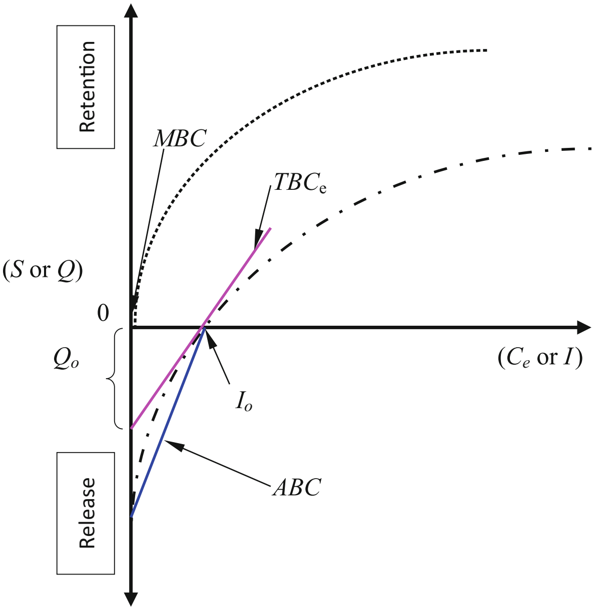


Fig. 3.2 Schematic representation of various sorption and buffering parameters that could be characterised during equilibration studies. S = amount retained (i.e. adsorbed) or released (desorbed). Q = quantity, Q_o = intercept on the Q axis of the TBC_e tangent, C_e = equilibrium concentration, I = intensity, I_o = no retention (i.e. adsorption) and no release (desorption), MBC = maximum buffering capacity ($C_e \to 0$), TBC_e = tangential buffering capacity, ABC = average buffering capacity

3.3 Copper Status in Contaminated and Uncontaminated Soils

Dynamic development of civilisation during the past century led to excessive accumulation of heavy metals, among others copper, in the environment, creating serious ecological problems. Gradual increase of soil contamination with copper and its relative mobility in the environment threatens with the risk of this metal introduction into trophic cycle (Kabata-Pendias 1978; Markert and Friese 2000; Markert et al. 2003; Nriagu et al. 2012). Several phosphate fertilisers and pests' products contain copper either as impurity or as active constituent (Alloway 1995; Robert 1996), but one of the major copper pollution sources is attributed to mining activity and dust emissions from metallurgical industries (Geiger et al 1993; Kabata-Pendias A. 1993; Grzebisz and Chudziński 1996; Diatta et al. 2000).

Heavy metals (copper among others) are ubiquitous and fundamental components of life on Earth and part of all food chain. Because their levels in soils naturally range between 0.1 and 100.0 mg kg^{-1} (Cox 1989; Baker 1990; Kabata-Pendias and Pendias 1992), they are also called "trace elements" (Adriano 1986; Duffus 2002). Some metals such as copper and zinc are essential to life, but in high concentrations, however, the same metals can exhibit toxicity effects. The natural concentration of copper in soil solution is found to be very low, being in the range of 1×10^{-8} to 60×10^{-8} moles dm^{-3}. Hodgson et al. (1966) reported that more than 98 % of soil solution copper was complexed with organic matter and more strongly bound to organic matter than are other micronutrient cations like Zn^{2+} and

Mn^{2+}. The affinity to organic matter regulates Cu mobility and availability in the soil. In a fractionation study of Cu in soils, McLaren and Crawford (1973a, b) have found that a high proportion of total copper was in occluded or lattice form. Irrespective of the forms in which copper may occur, its behaviour and shift from natural copper nontoxicity to anthropogenic copper toxicity are intrinsically related to metal specificity and man activities (Adriano 1986; Kabata-Pendias 1993; Chudziński 1995; Prasad 2008).

The behaviour of heavy metals and copper among others is governed mainly by two groups of adversely acting phenomena. The first group involves processes such as: sorption of copper by soil mineral and organic sorptive complex, precipitation of insoluble compounds and biogenic accumulation, which aim at reducing copper solubility and mobility (Adriano 1986; Brümmer et al. 1986; Logan 1990). The second group consists of processes that tend to increase copper mobility, i.e. desorption, solubility and mineralisation of organic compounds (Ram and Verloo 1985). Copper solubility and desorption in soil systems are generally strengthened by a decrease of pH (Lindsay 1979) which increases its activity manifold than for soil with neutral or weakly acid soils (Xian and Shokohifard 1989; Msaky and Calvet 1990; McBride 2001).

Copper retention by the organo-mineral soil complex has been a topic of several reports (McLaren and Crawford 1973a, b; Cavallaro and McBride 1978; Sapek and Sapek 1980; Logan et al. 1997; Diatta et al. 2000). Several works dealt with copper organic complexes of soil systems in which the organic part is quite dominating. Clay minerals are also potential binding agents for copper as they exhibit large specific surface area and enhanced cation exchange capacity. In general clay minerals are found to possess both a pH-dependent and permanent negative surface charge, which is among others a resultant of isomorphous substitution. The permanent charge is for the most part compensated by cations intercalated in the interstitial space (McBride 1994; Sparks 1995). Therefore, the metal cations bound in such a way can readily be exchanged by other cations, e.g. Ca^{2+}, Mg^{2+} and NH_4^+ (Van Bladel et al. 1993).

The mechanisms of copper adsorption are pH dependent and may additionally depend on the concentrations of copper in the soil solution. At relatively high pH and low copper concentrations, specific adsorption is often the predominant binding mechanism (McBride 1989; Diatta et al. 2004, 2012). Surface complex is thought to occur via interaction of a surface functional group with an ion or molecule present in the soil solution, which creates a stable molecular entity. If water molecule is present between the surface functional group and the bound ion or molecule, the surface complex is termed outer sphere (Sposito 1984). If there is not a water molecule present between the ion or molecule and the surface functional group to which it is bound, this is an inner sphere complex. It is important to note that inner sphere complexes can be monodentate (metal is bound to only one oxygen) and bidentate (metal is bound to two oxygens) as illustrated below (Fig. 3.3).

The prediction of the mobility of metals in soils may also be assessed by simulative natural diffusion studies (Helios-Rybicka and Jędrzejczyk 1995) or desorption. It is often observed that desorption is a more difficult process than

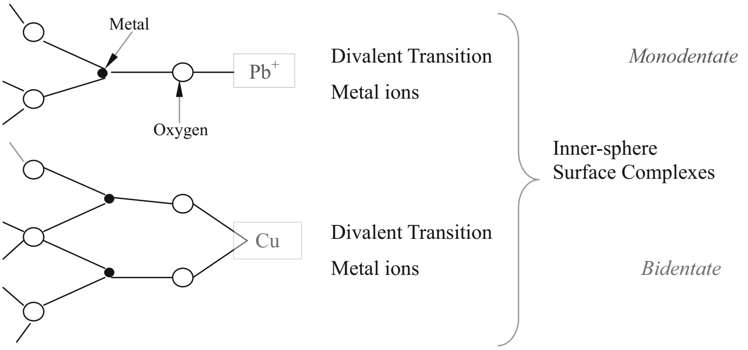


Fig. 3.3 Illustration of surface complexes' formation between inorganic ions and hydroxyl groups of an oxide surface (with permission from Elsevier for Sparks 1995: Environmental Soil Chemistry, p. 99–139)

adsorption and that the adsorbate is not entirely desorbed. So the reactions (adsorption process) appear to be irreversible. Ion exchange is in essence a reversible reaction in which cations are stoichiometrically exchanged between the electrolyte solution and the surface phase of the exchanger material. Exchange irreversibility is sometimes observed and has been attributed to colloidal aggregation and the formation of quasi-crystals (Van Bladel and Laudelout 1967), which could make exchange sites inaccessible. Such apparent irreversibility is commonly referred to as hysteresis that means adsorption and desorption isotherms corresponding to the forward and backward reaction would not coincide (Verburg and Baveye 1994). Hysteresis is often reported for soil-pesticide interactions (Barriuso et al. 1994; Zhu and Selim 2000) and also for metal reactions with soils or soil components (Ainstworth et al. 1994).

Informations about hysteretic behaviour of copper in soils are scarce. Schultz et al. (1987) reported about a substantial hysteresis in the desorption of Cu, Ni, Pb and Zn and Cr sorbed to hydrous ferric oxide. They found that the magnitude of the hysteresis was dependent on pH at which the adsorption process took place and the length of time of contact of sorbent-solute prior to initiation of the desorption process. However, Maqueda et al. (1998) have found that copper desorption isotherms on a montmorillonite showed a very high hysteresis, and in the same order a substantial sorption/desorption hysteresis was also observed by Wu et al. (1999), who reported that Cu has formed high-energy bonds with organic matter and layer silicate surfaces.

3.4 Site-Specific Copper Geochemistry: A Case Study

3.4.1 Site Characterisation and Soil Sampling Procedure

The study area is located in the Głogów proglacial stream valley (N 51°41′03″ and E 15°57′12″) situated between Sudetes (North) and the Małopolska Plateau (South) (Kondracki 1978). Soil samplings were performed within the years 2000–2001. The investigated area is represented by two major soil groups: Fluvisols and Luvisols (WRB 1998), as reported in Table 3.1. The Głogów copper smelter (GCS) was established in the 1970s, and the primary cause of high metal accumulation was the emission of dusts and gases by smelters. In the 1970s the Głogów copper smelter annually discharged into the atmosphere over 15,000 tons of dusts containing heavy metals, sulfuric acid and sulphur dioxide, and from early 1990s a rapid reduction of dust emissions occurred. Copper content of dust discharges amounted to 2,968, 204, 23, 9.7 tons for the years 1980, 1990, 2000 and 2012, respectively (www.kghm.pl/index. Access 20.07.2014).

These tremendous amounts of copper accumulated progressively in soils for many years, and their negative environmental impact is still lasting. The zone mostly contaminated by heavy metals (copper mainly) was taken out of agricultural utilisation and afforested (poplars and maples), establishing since 1987 the "sanitary belt". Earlier investigations carried out in this area showed a copper distribution pattern consistent with the wind rose, where southwest (SW) and west (W) winds—referring to Głogów copper smelter position—were dominating (Kabata-Pendias 1978; Grzebisz et al. 1997; Geochemical Atlas 1999) (Fig. 3.4).

It should be mentioned in the past all soils of the area under study were arable, some have currently changed management purposes. Since most of sampling sites were located in arable soils, the sampling depth of 0–20 cm was applied due to agricultural practices. The same sampling depth was considered also for sampling sites other than those under agricultural practices.

3.4.2 Physical and Chemical Soil Tests

Prior to basic analyses, soil samples were air-dried and crushed to pass through a 1 mm mesh sieve. Total copper (Cu_{Tot}) content was determined in soil samples (International Standard 1995). On the basis of total copper content (Cu_{Tot}), it was decided to elaborate a "consensual" share of soils into two operational groups: Group I represents the moderate and highly contaminated soils (from the sanitary belt) with total copper content varying from 76.1 to 334.0 mg kg^{-1}, except one soil sample with Cu_{Tot} of 1,048 mg kg^{-1}. To the group I belong soil Nos. 1–8 considered as contaminated. The group II consists of soils collected beyond the "Sanitary Belt", where Cu_{Tot} was below 30.0 mg kg^{-1}. The mentioned group involved soil Nos. 9–16 and is designated as uncontaminated (Table 3.2). Copper from soils was

Table 3.1 Sampling sites, positioning towards the Głogów copper smelter and soils' taxonomical description

Soil sample (No.)	Distance from the main emitter (km)	Position towards the main emitter	Sampling site[a]	Particle size (mm)			Soil texture[b]	WRB (1998)[c]	Locality
				Sand (1.0–0.05)	Silt (0.05–0.002) (g kg^{-1})	Clay (<0.002)			
1	5.0	E	A	660	220	120	Sandy loam	Calci-Stagnic Luvisols	Rapocin
2	1.5	S	Fa	820	130	50	Loamy sand	Haplic Luvisols	Zukowice
3	3.5	NW	A	860	120	20	Loamy sand	Gleyic Fluvisols	Wróblin Głogowski
4	4.0	E	A	460	490	50	Sandy loam	Gleyic Fluvisols	Biechów
5	4.8	NE	Fa	420	420	160	Loam	Molli-Gleyic Fluvisols	Bogomice
6	4.0	NE	M	780	190	30	Loamy sand	Gleyic Fluvisols	Bogomice
7	3.5	NE	M	560	360	80	Sandy loam	Haplic Luvisols	Bogomice
8	0.5	NE	Fo	790	180	30	Loamy sand	Dystri-Gleyic Fluvisols	Sanitary belt
9	8.0	SW	A	820	160	20	Loamy sand	Gleyic Fluvisols	Domanice
10	7.5	W	M	750	160	90	Sandy loam	Stagnic Luvisols	Brzeg Głogowski
11	9.0	E	A	820	130	50	Loamy sand	Haplic Luvisols	Serby
12	7.0	E	A	750	210	40	Loamy sand	Gleyic Fluvisols	Grodziec Mały

13	7.0	W	A	790	160	50	Loamy sand	Calci-Stagnic Luvisols	Brzeg Głogowski
14	8.5	E	A	820	140	40	Loamy sand	Albic Luvisols	Serby
15	8.5	W	M	900	80	20	Sand	Areni-Gleyic Fluvisols	Kromolin
16	6.0	SE	A	770	140	90	Sandy loam	Stagni-Cutanic Luvisols	Brzostów

RED line for delimitating the group I (contaminated) from the and II (uncontaminated)

[a] *A* arable, *Fa* fallow, *Fo* forest, *M* meadow

[b] Soil taxonomy. USDA (1975)

[c] WRB-84, World Soil Resources Reports, FAO-ISSIC-ISRIC (1998)

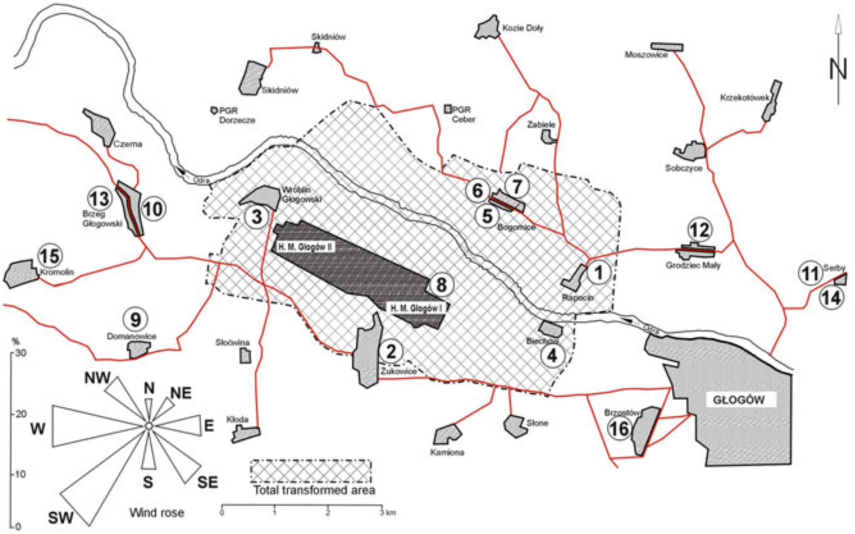


Fig. 3.4 Spatial location of sampling sites (*numbers in circles*) within the investigated area

additionally extracted by using DTPA solution (diethylenetriaminepentaacetic acid) (Lindsay and Norvell 1978; Kociałkowski et al. 1999). Copper in filtrates was determined by the FAAS method (Flame Atomic Absorption Spectrometry, Varian SpectrAA 250 plus).

Particle-size distribution was determined according to the method of Bouyoucos-Casagrande (Ryan et al. 2001). The texture classes were established according to USDA classification (Soil Taxonomy 1975) on the basis of the following separates: sand (1.0–0.05 mm), silt (0.05–0.002 mm) and clay (<0.002 mm). Organic carbon was determined by the dichromate wet oxidative method (Nelson and Sommers 1996) and soil pH potentiometrically, according to Polish Standard (1994). Soil samples were additionally analysed for carbonate content (Loeppert and Suarez 1996), whereas the cation exchange capacity (CEC) was assessed by the barium chloride method as suggested by Hendershot and Duquette (1986). The cation exchange capacity of the soils was obtained by summation of exchangeable alkaline cations and acidity according to Thomas (1982). The specific surface area (SSA) of the soils was determined according to the ethylene glycol monoethyl ether (EGME) procedure, whereas the external surface area was measured by the BET method (Gregg and Sing 1967; Carter et al. 1986; de Jong 1999).

Table 3.2 Some physical and chemical properties of investigated soils

Soil texture	pH ($CaCl_2$)	Total copper (Cu_{Tot})	Cu-DTPA	C_{org} ($g\ kg^{-1}$)	SSA_{EGME}[a] ($m^2\ g^{-1}$)	SSA_{BET}[b] ($m^2\ g^{-1}$)	SSA_{INT}[c] ($m^2\ g^{-1}$)	CEC[d] ($cmol_c\ kg^{-1}$)	$CaCO_3$ (%)
Sandy loam (1)	7.3	76.1	16.5	6.5	25.9	6.7	19.1	15.0	4.6
Loamy sand (2)	6.5	79.5	22.0	8.9	14.7	1.3	13.4	11.7	–[e]
Loamy sand (3)	6.4	84.9	27.7	6.8	15.5	3.4	12.1	13.4	–
Sandy loam (4)	6.8	117.8	40.3	9.9	37.4	4.3	33.2	13.2	–
Loam (5)	6.9	162.8	52.3	18.3	72.0	17.1	54.9	21.8	–
Loamy sand (6)	6.6	235.3	93.2	7.7	13.6	1.6	12.0	11.7	–
Sandy loam (7)	6.9	334.0	131.5	14.9	25.2	3.9	21.3	17.5	–
Loamy sand (8)	5.0	1048.0	472.2	5.6	9.4	2.1	7.4	9.8	–
Loamy sand (9)	7.0	22.3	6.8	8.9	15.7	1.5	14.2	11.3	–
Sandy loam (10)	7.3	22.6	5.0	9.4	26.9	4.9	22.0	14.5	0.6
Loamy sand (11)	6.2	23.1	5.2	5.8	9.4	2.6	6.9	9.6	–
Loamy sand (12)	7.6	23.4	3.5	12.0	37.4	10.1	27.3	17.5	2.2
Loamy sand (13)	7.4	25.6	7. 7	8.8	16.9	2.5	14.4	12.9	0.9
Loamy sand (14)	5.1	26.0	5.9	12.2	17.5	1.4	16.0	11.6	–

(continued)

Table 3.2 (continued)

Soil texture	pH ($CaCl_2$)	Total copper (Cu_{Tot})	Cu-DTPA	C_{org} (g kg^{-1})	SSA_{EGME}[a] (m^2 g^{-1})	SSA_{BET}[b] (m^2 g^{-1})	SSA_{INT}[c] (m^2 g^{-1})	CEC[d] ($cmol_c$ kg^{-1})	$CaCO_3$ (%)
Sand (15)	6.4	28.2	9.0	8.1	8.4	1.1	7.3	10.1	–
Sandy loam (16)	6.8	28.5	10.9	9.0	26.2	4.0	22.2	12.2	–

Red line delimitates group I (contaminated) and group II (uncontaminated) soils

[a] Specific surface area: EGME—ethylene glycol monoethyl ether

[b] BET—Brunauer, Emmett and Teller N_2 adsorption

[c] INT—Internal surface area ([a]EGME – [b]BET)

[d] Cation exchange capacity according to $BaCl_2$ method (Hendershot and Duquette 1986)

[e] Not detected

3.4.3 Dynamic Phase Evaluation of Copper in Soils

3.4.3.1 Batch Tests

Copper concentrations of 0.2, 0.4, 0.6, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8 and 3.2 $\text{mmol}_\text{c}\,\text{dm}^{-3}$ designated as initial solutions (C_i) were prepared by dissolving appropriate amounts of $Cu(NO_3)_2 \cdot 3H_2O$ p.a. in 0.010 mole $Ca(NO_3)_2 \cdot 4H_2O$ (p.a.) as a background electrolyte. The use of 0.010 mole $Ca(NO_3)_2 \cdot 4H_2O$ was an attempt to approximate the electrolyte environment of soils in the field (Jopony and Young 1994). Nitrate was chosen because of its poor ability to complex metallic cations (Sillén and Martell 1971). Solutions were added to homogenised soils at soil/solution ratios (*w*/*v*) of 1:25 into a series of polyethylene centrifuge tubes and shaken in a rotative shaker for 2 h. Suspensions were allowed to equilibrate for 22 h after which filtration followed. The concentrations of Cu of the filtrates at equilibrium concentration (C_e) were determined by FAAS method (Flame Atomic Absorption Spectrometry, Varian SpectrAA 250 plus). The solid-phase Cu was calculated as the difference between the initial Cu concentration (C_i) and that remaining in the solution after equilibration (i.e. C_e) accordingly:

$$S = (C_i - C_e)\,V/W \tag{3.3}$$

where

S—amount of Cu adsorbed ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)
C_i—initial Cu concentration in solution before reaction ($\text{mmol}_\text{c}\,\text{dm}^{-3}$)
C_e—equilibrium Cu concentration in solution after reaction ($\text{mmol}_\text{c}\,\text{dm}^{-3}$)
V—volume of the solution (dm^3)
W—weight of soil sample (kg)

Langmuir and Freundlich adsorption constants were computed by using Sorption Softwares (IZOTERMY© 1993), especially elaborated for sorption studies.

3.4.3.2 Kinetics of Copper Adsorption and Desorption

Studies on the kinetics of adsorption were carried out using soil samples described earlier. Prior to these studies, soil samples were separated into two sets on the basis of copper equilibrium concentrations (C_e) at the highest initial copper concentration (C_i) as indicated in Table 3.3.

Appropriate triplicate 1.00 g of soil samples were placed in 100 cm^3 polyethylene centrifuge tubes and equilibrated with 50 cm^3 of 0.8, 1.6, 2.4 and 3.2 $\text{mmol}_\text{c}\,\text{dm}^{-3}$ as solution of $Cu(NO_3)_2 \cdot 3H_2O$ in 0.010 mole $Ca(NO_3)_2 \cdot 4H_2O$ used as a background electrolyte to reduce variability and simulate natural soil conditions (Table 3.4). The suspensions were vigorously shaken for 30 s at the beginning of the kinetic experiment to ensure a uniform mixture and allowed to settle for 96 h (whole kinetic adsorption time) at temperature conditions of 21.0 °C (294 K). Two (2) cm^3 aliquots for Cu determination (FAAS method) were collected

Table 3.3 Soil/solution ratios (kinetic studies) applied for appropriate soils on the basis of Cu equilibrium concentration (C_e) at the highest initial copper concentration (C_i)

Soil number	Ratio (soil/solution) (g cm^{-3})	Equilibrium concentration (C_e, mmol$_c$ dm^{-3}) at $C_i = 3.2$ mmol$_c$ dm^{-3}
1, 5, 7, 10, 12, 13	1/50	$C_e < 0.5$
2, 3, 4, 6, 8, 9, 11, 14, 15, 16	1/25	$C_e > 0.5$

Table 3.4 Amounts of copper adsorbed (%, mean value) at the end of 8 h of kinetic studies

	Initial copper concentration (C_i, mmol$_c$ dm^{-3})			
Soils	0.8	1.6	2.4	3.2
Contaminated	93	88	85	84
Soil no. 8	76	57	51	45
Uncontaminated	90	85	84	78
Soil no. 15	60	51	47	48

at the following time intervals: 0.5, 2, 8, 24, 48, 72 and 96 h. Amounts of Cu adsorbed during the adsorption kinetic phases were calculated by using Eq. (3.3).

The kinetics of desorption studies started immediately at the end of the kinetics of adsorption and were conducted on all samples used above. The supernatants at 96 h (end of kinetic adsorption study) were centrifuged at 4,000 rpm for 5 min, 5 cm^3 aliquots were collected, and the remaining decant was discarded. The polyethylene centrifuge tubes with soil samples were weighted and 50 cm^3 of 0.010 mole $Ca(NO_3)_2 \cdot 4H_2O$ Cu-free solution was placed after which the suspensions were shaken for 30 min. After this time the suspensions were centrifuged and 5 cm^3 aliquots were collected for Cu analysis. This step was repeated six more times using 0.010 mole $Ca(NO_3)_2 \cdot 4H_2O$ Cu-free solution. Amounts of copper desorbed at each desorption stage were calculated on the basis of the amounts of copper initially adsorbed (at $t = 96$ h).

3.4.3.3 Langmuir and Freundlich Models (Isotherms)

Solute adsorption mechanisms at solid surfaces are observed to bear several shapes basically divided into four main classes, namely, *S*, *L*, *H* and *C*, as widely outlined by Giles et al. (1960). With an *S*-type isotherm, the slope initially increases with adsorbate concentration, but eventually decreases and becomes zero as vacant adsorbent sites are occupied. The L-type (Langmuir) isotherm is characterised by a decreasing slope as concentration increases since vacant adsorption sites decrease as the adsorbent surface becomes covered. The *H*-type (high affinity) isotherm is indicative of strong adsorbate-adsorbent interactions such as inner sphere complexes. The *C*-type isotherms are indicative of a partitioning mechanism whereby adsorbate ions or molecules are linearly distributed or partitioned between the solid phase (adsorbent) and the solution phase without any specific bonding between the adsorbent and adsorbate.

Of these classes, the *L*-type isotherm is described mathematically by the Langmuir equation (Sposito 1984), as follows:

$$S = \frac{a_{\max} \cdot b \ \ C_e}{1 + b \ \ C_e} \tag{3.4}$$

where

S—amount of Cu adsorbed ($\mathrm{mmol_c\,kg^{-1}}$)
C_e—equilibrium Cu concentration in solution after reaction ($\mathrm{mmol_c\,dm^{-3}}$)
$a_{\max}$—adsorption maximum ($\mathrm{mmol_c\,kg^{-1}}$)
b—bonding term relative to interaction energies ($\mathrm{dm^3\ mmol_c{}^{-1}}$)

In the linear form, Eq. (3.4) may be rewritten as follows:

$$\frac{C_e}{S} = \frac{1}{a_{\max} \cdot b} + \frac{C_e}{a_{\max}} \tag{3.5}$$

where

$a_{\max} \cdot b$ expresses the maximal buffering capacity (*MBC*, $\mathrm{dm^3\,kg^{-1}}$) exhibited by an adsorbent (soil) for a given adsorbate (Cu) when the equilibrium concentration is very low (tends to 0). The slope is equal to $\frac{1}{a_{\max}}$ and the intercept (when C_e tends closely to 0) is expressed by $\frac{1}{a_{\max} \cdot b}$. The value of the Langmuir term related to the interaction energies (b) may be calculated from the ratio of the slope and the intercept and is equal to $\frac{\text{slope}}{\text{intercept}}$ Diatta (2002). It is noteworthy that the calculation of the maximum sorption capacity $a_{\max}$ can involve errors of 50 % and more (Harter 1984) if the isotherm does not have correct Langmuir shape and only low concentration data (Schulthess and Dey 1996) is used for the calculation.

The Freundlich isotherm as an empirical equation is given by

$$S = K_F \ \ C_e{}^m \tag{3.6}$$

where

K_F—Freundlich partition constant ($\mathrm{dm^3\ kg^{-1}}$)
C_e—equilibrium Cu concentration in solution after reaction ($\mathrm{mmol_c\,dm^{-3}}$)
m—sorption constant (shape intensity factor, dimensionless) expressing the slope of the adsorption isotherm. This positive-valued empirical constant is reported to lie between 0 and 1 (Elzinger et al. 1999; Diatta et al. 2003). By taking the log of Eq. (3.6), the linear form of the Freundlich equation is obtained as

$$\log S = \log K_F + m \log C_e \tag{3.7}$$

3.4.3.4 Sorption and Surface Charge Densities

Adsorption and desorption processes predominantly occur at surfaces of organic and inorganic colloids. Therefore, the expression of these processes in terms of "concentration" of substances (e.g. ions) per unit area may give more practical approach. Copper sorption densities at any point were calculated as reported by Schulte and Beese (1994) and Zehetner and Wenzel (2000):

$$\mathrm{SD_{SSA}} = \frac{SN_\mathrm{A}}{\mathrm{SSA}} \tag{3.8}$$

where

$\mathrm{SD_{SSA}}$—sorption density based on the specific surface area (ions $\mathrm{m^{-2}}$)
S—amount of Cu adsorbed ($\mathrm{mmol_c\,kg^{-1}}$)
N_A**—**Avogadro's number (6.023×10^{23} ions $\mathrm{mol^{-1}}$)
SSA**—**specific surface area ($\mathrm{m^2\,g^{-1}}$)

Sorption processes, especially non-specific adsorption through ion exchange, are influenced by the surface charge, of which *CEC* is a measure. The surface charge density (*SCD*) as pointed out by Poonia and Talibudeen (1977) and Laird et al. (1992) is expressed as follows:

$$\mathrm{SCD} = \frac{\mathrm{CEC}}{\mathrm{SSA}} \tag{3.9}$$

where

SCD—surface charge density ($\mathrm{mmol_c\,m^{-2}}$)
CEC—cation exchange capacity ($\mathrm{cmol_c\,kg^{-1}}$)

By dividing $\mathrm{SD_{SSA}}$ (Eq. 3.8) by the surface charge density (SCD), we obtain the charge-based sorption density ($\mathrm{SD_{CEC}}$):

$$\mathrm{SD_{CEC}} = \frac{SN_\mathrm{A}}{\mathrm{CEC}} \tag{3.10}$$

where
$\mathrm{SD_{CEC}}$—charge-based sorption density (ions $\mathrm{mol_c}^{-1}$)

3.4.3.5 Development of the Simplified Elovich Equation

The simplest form of Elovich equation (Allen and Scaife 1966) is generally expressed as

$$\frac{dS}{dt} = \alpha \exp^{(-\beta S)} \tag{3.11}$$

where S is the amount of Cu adsorbed at time t and α and β are constants during one experiment. The constant α can be regarded as initial rate since $\frac{dS}{dt} \rightarrow \alpha$ as $S \rightarrow 0$, i.e. a rapid adsorption not governed by the exponential law (Low 1960). The integrated form of the Eq. (3.11) gives

$$S = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t + t_o) \tag{3.12}$$

in which t_o is the integration constant for which sometimes the symbol k is given (to avoid confusion with the time variable). Assuming $t_o \approx 0$ indicates that no other processes besides Elovichian ones are occurring, that is, the boundary condition $S = 0$ at $t = 0$ applies (Allen and Scaife 1966; Sparks 1989). In this case the assumption $t_o \approx 0$ leads directly to the simplified equation:

$$S = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{3.13}$$

Chien and Clayton (1980) reached the simplified Eq. (3.13) by obtaining the form:

$$S = \frac{1}{\beta}\ln(1 + \alpha\beta t) \tag{3.14}$$

from Eq. (3.12), by first assuming that the boundary condition $S = 0$ at $t = 0$ applies and then by making the assumption that $\alpha\beta t \gg 1$.

However, as pointed out by Allen and Scaife (1966), t_o can never be exactly zero without loss of the physical significance of Eq. (3.11). If this approximation is used, important information may be lost. Equation (3.13) was used to test the applicability of the simplified Elovich equation for the kinetics of Cu adsorption and desorption of the soils. Thus, a plot of S versus ln t should give a linear relationship with the slope of $\frac{1}{\beta}$ and intercept of $\frac{1}{\beta}\ln(\alpha\beta)$.

3.4.3.6 Kinetics of Copper Adsorption and Desorption and Hysteresis Approach

It was assumed that copper adsorption during the kinetic course should be monitored at some selected time intervals by sampling given equilibrium solution volumes for Cu determination. Therefore, it should be necessary to correct for this volume loss in the calculation of the amount of metal adsorbed at each subsequent sampling time (Amacher et al. 1986) as shown below:

$$\Delta S_{\text{kin}} = \left(C_{e\,\text{prev}} - C_{e\ \text{pres}}\right)\ \frac{(V - vn)}{W} \tag{3.15}$$

and

$$S_{\text{kin}} = S_{\text{prev}} + \Delta S_{\text{kin}} \tag{3.16}$$

where

ΔS_{kin}—change in amount of Cu adsorbed by the soil from one sampling time to the next ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)
S_{kin}—amount of Cu adsorbed by the soil at each sampling time ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)
$C_{e\ \text{prev}}$—concentration of Cu in solution at previous sampling time ($\text{mmol}_\text{c}\,\text{dm}^{-3}$)
$C_{e\ \text{pres}}$—concentration of Cu in solution at present sampling time ($\text{mmol}_\text{c}\,\text{dm}^{-3}$)
V—initial total solution volume (dm^3)
v—volume of solution removed at each sampling time for Cu determination (dm^3)
n—number of times sampled
S_{prev}—amount of Cu adsorbed by the soil at previous sampling time ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)

Copper partition parameters during the kinetics of the adsorption phase were calculated at each sampling time on the basis of Freundlich equation:

$$S_{\text{kin}} = K_{\text{kin-ads}} C_e{}^{N_{\text{kin-ads}}} \tag{3.17}$$

where

$K_{\text{kin-ads}}$—Freundlich partition parameter for copper kinetics of adsorption ($\text{dm}^3\ \text{kg}^{-1}$)
$N_{\text{kin-ads}}$—empirical kinetics of adsorption parameter (dimensionless)

It was assumed that the starting point of the desorption isotherm is a point on the adsorption isotherm and that Freundlich adsorption and desorption coefficients are not independent as outlined by O'Connor et al. (1980) and Laird et al. (1992). Then:

$$S_{\text{kin-max}} = K_{\text{kin-ads}}(C_{e\text{-max}})^{N_{\text{kin-ads}}} = K_{\text{kin-des}}(C_{e\text{-max}})^{N_{\text{kin-des}}} \tag{3.18}$$

where

$S_{\text{kin-max}}$—amount of Cu adsorbed at the end of kinetic adsorption process (i.e. $t = 96$ h) ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)
$C_{e\text{-max}}$—equilibrium copper concentration at the end of kinetic adsorption process (i.e. $t = 96$ h) ($\text{mmol}_\text{c}\ \text{dm}^{-3}$)

By solving Eq. (3.18) for $K_{\text{kin-des}}$, it comes

$$K_{\text{kin-des}} = K_{\text{kin-ads}}\, C_{e\text{-max}}{}^{N_{\text{kin-ads}}(1 - N_{\text{kin-des}}/N_{\text{kin-ads}})} \tag{3.19}$$

where

$K_{\text{kin-des}}$—Freundlich partition constant for copper kinetics of desorption ($\text{dm}^3\ \text{kg}^{-1}$)
$N_{\text{kin-des}}$—empirical kinetics of desorption constant (dimensionless)

By taking into account the amount of copper adsorbed, Eq. (3.19) bears the form

$$K_{\text{kin-des}} = K_{\text{kin-ads}}{}^{N_{\text{kin-des}}/N_{\text{kin-ads}}}\, S_{\text{max}}{}^{(1-N_{\text{kin-des}}/N_{\text{kin-ads}})} \tag{3.20}$$

The ratio of Freundlich exponents ($N_{\text{kin-des}}/N_{\text{kin-ads}}$) gives an indication of adsorption/desorption hysteresis (O'Connor et al. 1980).

3.4.3.7 Activation Energies: Processes Evaluation

All adsorption and desorption kinetic studies were run in triplicate under isothermal conditions at 294 K. Activation energies were calculated based on the simplified Elovich equation using the following relationship as reported by Pavlatou and Polyzopoulos (1988) and Zhang et al. (2000):

$$E_{\text{aa/ad}} = \frac{S_{\text{kin}}RT}{E_{\text{slope}}} \tag{3.21}$$

where

$E_{\text{aa/ad}}$—activation energy for kinetics of Cu adsorption/desorption processes (J mol^{-1})
S_{kin}—amount of Cu adsorbed or desorbed during the kinetic study ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)
R—gas constant ($8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$)
T—absolute temperature (273 K)
E_{slope}—slope of the simplified Elovich linear part of S_{kin} versus ln t plots for Cu adsorption and desorption processes ($\text{mmol}_\text{c}\,\text{kg}^{-1}$)

3.5 Evaluation and Quantification

The basic physical and chemical properties of investigated soils are reported in Tables 3.1 and 3.2. Contaminated soils (Nos. 1–8) were predominantly neutral to alkaline with pH ranging from 6.4 to 7.3 (except for soil Nos. 8 with pH = 5.0). Organic carbon (C_{org}) content fluctuated within the range 5.6–18.3 g kg^{-1}, whereas the specific surface area (SSA_{EGME}), external (SSA_{BET}) and internal (SSA_{INT}), varied from 9.4 to 72.0, 1.3 to 17.1 and 7.1 to 54.9 $\text{m}^2\ \text{g}^{-1}$, respectively. Soil particle distribution showed a general prevalence of the sand fraction varying from 420 to 860 g kg^{-1} over the silt and clay ones. Clay fractions were relatively low and were in the range 20–160 g kg^{-1} in which most of soils were characterised by clay content below 100 g kg^{-1}. The particle distribution and the relatively low organic carbon content promoted a cation exchange capacity (CEC), which varied from 9.8

to 21.8 $\mathrm{cmol_c\,kg^{-1}}$ with quite all soils characterised by a CEC higher than 10.0 $\mathrm{cmol_c\,kg^{-1}}$ (except for soils No. 8).

Most of uncontaminated soils (Nos. 9–16) were slightly alkaline but their pH values fluctuated from pH 5.1 to 7.6. The organic carbon content ranged within the interval 5.8–12.2 g $\mathrm{kg^{-1}}$, where 75 % of soil samples did not exceed 10.0 g $\mathrm{kg^{-1}}$. The clay fraction content of soils was below 100 g $\mathrm{kg^{-1}}$ (from 20 to 90 g $\mathrm{kg^{-1}}$) with a relatively high content of the sand fraction varying from 750 to 900 g $\mathrm{kg^{-1}}$. About 75 % of soils were characterised by CEC values higher than 10.0 $\mathrm{cmol_c\,kg^{-1}}$ and relatively high specific surface area ($\mathrm{SSA_{EGME}}$) with 75 % of soils possessing more than 15.0 $\mathrm{m^2\,g^{-1}}$. The occurrence of carbonates in some soils could be attributed to frequent liming in order to reduce acidity.

The average copper content in uncontaminated soils around the world is estimated to vary from 20 to 30 mg $\mathrm{kg^{-1}}$, whereas in Poland the mean level is about 12 mg $\mathrm{kg^{-1}}$ (Kabata-Pendias and Pendias 1992). On the other hand, there is great concern of copper contamination from metal processing plants, where a site pollution of 1,400–3,700 mg Cu $\mathrm{kg^{-1}}$ in Ontario was reported by Freeman and Hutchinson (1980). Local copper pollution in Poland was also pointed out by Roszyk and Szerszeń (1988) at the surroundings of Legnica copper smelter, with a copper content ranging from 25 to 9,800 mg $\mathrm{kg^{-1}}$, and in the case of Głogów copper smelters, authors have reported a relatively lower level of 30–3,280 mg $\mathrm{kg^{-1}}$. Copper chemistry in soils is ruled by several factors which may be classified into two main groups: (1) soil properties, in which pH plays one of the key roles (Cavallaro and McBride 1980; Harter and Lehmann 1983; Msaky and Calvet 1990), organic matter and clay content (Eriksson 1988) and redox potential (McBride 1989; Diatta 2008), and (2) copper content and its forms such as $\mathrm{Cu^{2+}}$, $\mathrm{CuOH^{+}}$, $\mathrm{Cu(OH)_2}$, CuO, $\mathrm{CuCO_3}$ and $\mathrm{Cu(OH)_2CO_3}$ (Adriano 1986; McBride 1989).

The distribution of sorptive sites on soil colloids is generally not uniform (Sparks 1995; Wu et al. 1999; Diatta et al. 2000). For adsorption, cations are held either through electrostatic attraction, this giving rise to ion exchange with surrounding ions or by specific adsorption through surface complexation on organic and mineral substrates (Benjamin and Leckie 1981). The distribution of charges per square metre of the specific surface area (SSA) is reported in Table 3.5 for contaminated and uncontaminated soils.

As it could be observed, the higher the reactive surface, the apparently lower the number of free active sites, as pointed out especially for soils No. 4 and No. 5 (contaminated soils) with surface charge density ($\mathrm{SCD_{SSA}}$) amounting to 3.5 and 3.0×10^{-3} $\mathrm{mmol_c\,m^{-2}}$, characterised relatively by SSA of 37.4 and 72.0 $\mathrm{m^2\,g^{-1}}$, respectively. A reverse case occurred for soils No. 3, No. 6 and No. 8, which developed apparently higher $\mathrm{SCD_{SSA}}$, accordingly 8.7, 8.6 and 10.4×10^{-3} $\mathrm{mmol_c\,m^{-2}}$. If one considers the $\mathrm{SCD_{SSA}} = 5.0 \times 10^{-3}$ $\mathrm{mmol_c\,m^{-2}}$ as targeted reference, it comes out that only two contaminated soils should be tentatively classified as “highly” charged and the remaining as “moderately” charged. Uncontaminated soils behave similarly as the contaminated ones, that is, the lowest the specific surface area, the apparently highest the surface charge density as shown for soils No. 11 and No. 15 with proper $\mathrm{SCD_{SSA}}$ values of 10.2 and 12.0×10^{-3} $\mathrm{mmol_c\,m^{-2}}$. Referring to the targeted $\mathrm{SCD_{SSA}} = 5.0 \times 10^{-3}$ $\mathrm{mmol_c\,m^{-2}}$

Table 3.5 Specific surface area (SSA)-based surface charge density (SCD_{SSA}) of investigated soils

Soil texture	SCD_{SSA} (10^{-3} $mmol_c\,m^{-2}$)
Contaminated	
Sandy loam (1)	5.8
Loamy sand (2)	7.9
Loamy sand (3)	8.7
Sandy loam (4)	3.5
Loam (5)	3.0
Loamy sand (6)	8.6
Sandy loam (7)	6.9
Loamy sand (8)	10.4
Uncontaminated	
Loamy sand (9)	7.2
Sandy loam (10)	5.4
Loamy sand (11)	10.2
Loamy sand (12)	4.7
Loamy sand (13)	7.6
Loamy sand (14)	6.6
Sand (15)	12.0
Sandy loam (16)	4.7

as earlier reported, only two of eight soils, basically, i.e. No. 12 and No. 16 (and soil No. 10 inclusive), should be considered as “highly” charged in opposite to the “moderately” ones.

Plots of these sorption densities (SD) versus copper equilibrium concentration (C_e) resulted in at least one linear regression for most of the soils (Fig. 3.5a, b). Such plots are indicative of the occurrence of at least one pool of adsorption sites, the first highly energetic and the consecutive with lower adsorption energy.

The use of surface-based sorption density isotherms for heavy metal ecotoxicology assessment should be based on the relationship of metal ion densities at the soil colloid surface versus equilibrium concentration (C_e), as suggested by Schulte and Beese (1994) for Cd and Zehetner and Wenzel (2000) for Cu and Ni. In the current work, plots of SD_{SSA} versus C_e for the studied soils gave the best visualisation of copper adsorption process. A general analysis of plots revealed that the lower the SD_{SSA} and C_e, the highest the potential reactive sites for copper, and inversely. A simulative computation based on regressions of soils No. 1, No. 5 and No. 14, for instance, has shown that these soils attained a $C_e = 2.0$ $\mu mol_c\,dm^{-3}$ at an average SD_{SSA} of 1.2×10^{17} ions m^{-2} (soil No. 1), whereas for soils No. 5 and No. 14, it was 0.4×10^{17} and 2.3×10^{17} ions m^{-2}, respectively.

Practically a marked increase in the solution concentration following copper additions (for soils No. 1 and No. 5) is not to be expected as long as a targeted ion density (e.g. 2.3×10^{17} ions m^{-2} for soil No. 14) limit has not been reached. These approaches emphasise on the possibility of copper equilibrium monitoring based on sorption densities’ application.

Copper adsorption and its equilibrium concentrations, both equilibria are pH dependent, pointed out that soils exhibited in fact more charges than evaluated on

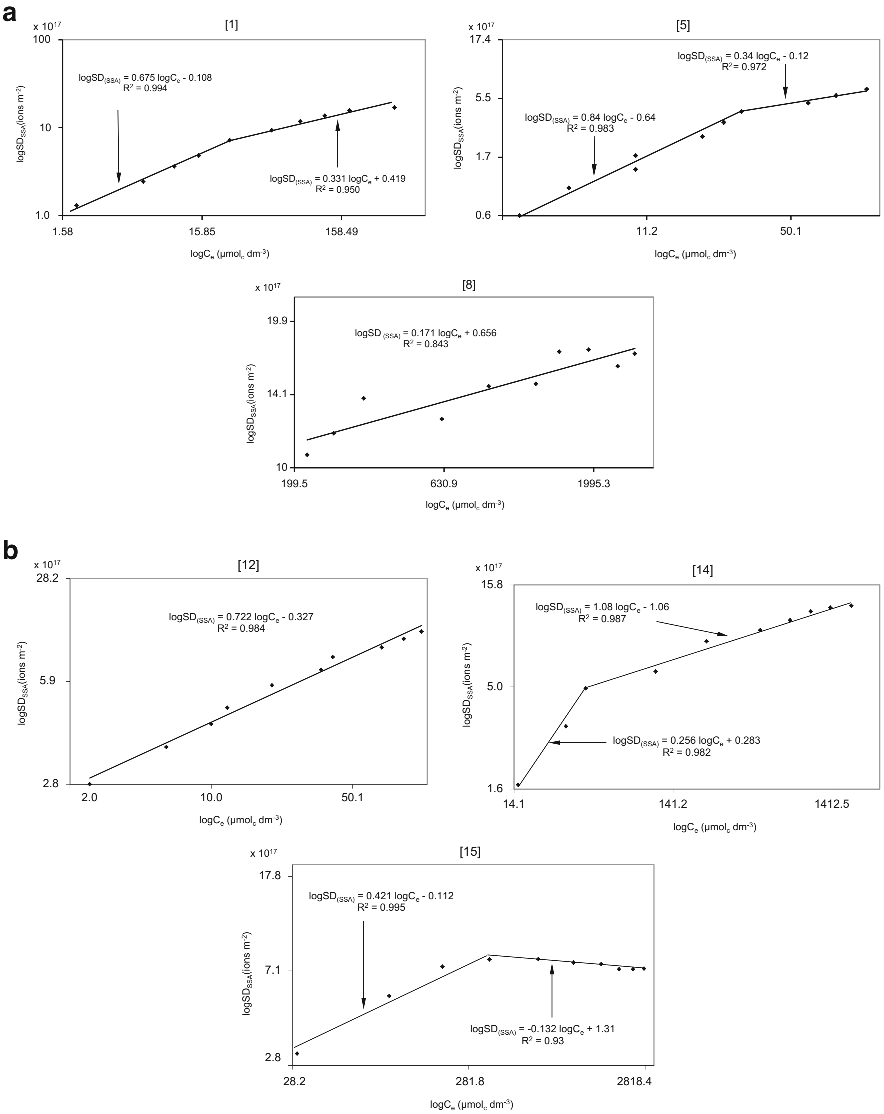
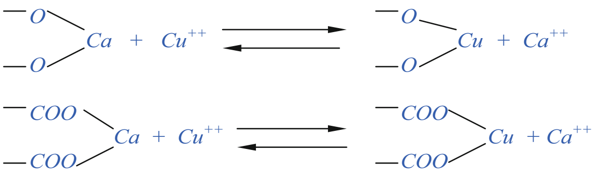
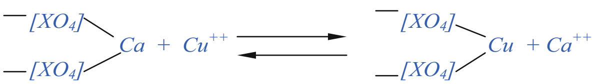


Fig. 3.5 Relationships between sorption density (SD$_{SSA}$) and Cu equilibrium concentrations (C$_e$) for selected (**a**) contaminated soils (Nos. 1, 5 and 8) and (**b**) uncontaminated soils (Nos. 12, 14 and 15)

the basis of SCD$_{SSA}$ (Table 3.5). Therefore the complex reaction of copper ions with deprotonated surface OH and COOH groups as bidentate and monodentate ligands could be expectable as pointed out by Schindler et al. (1976) and Davis and Leckie (1978). The adsorption of copper at energetically high sorptive sites can be formulated:



The saturation of the energetically high sorptive sites runs with the emergence of energetically low sorptive sites, and the latter ones may be presumably attributed to isomorphous substitution charge (Forbes et al. 1976; Bowden et al. 1977) as indicated below:



[XO_4]—exchange site due to isomorphous substitution charge, X to represent Si, Al

Such approach is in agreement with the reports of Msaky and Calvet (1990), who stated that copper adsorption systematically decreased as the surface coverage increased. So it may be deduced that copper ions were primarily attracted by high energetically charged sites, what coincided to the first intensive adsorption process leading to a marked removal of copper ions from the equilibrium solution. These sorption mechanisms showed some limitation of the formerly applied Langmuir and Freundlich isotherms for soil systems (Diatta et al. 2004, 2012).

Langmuir constants, i.e. $a_{\max}$ (adsorption maximum) and b (constant related to bonding energies) spread widely, mostly in the case of b values (Table 3.6). For contaminated soils, it was noted that the lowest b value was obtained for the soil No. 8 and accounted for 6.7 $dm^3\ mmol_c{}^{-1}$, whereas the highest one, amounting for 40.2 $dm^3\ mmol_c{}^{-1}$, was attributed to soil No. 7. It is also important to note that both $a_{\max}$ and b constants directly influence the whole soils' maximal buffering capacities (MBC) towards Cu. Soil No. 5 with the highest $a_{\max}$ (111.7 $mmol_c\,kg^{-1}$) was characterised by an MBC of 2,412 $dm^3\ kg^{-1}$ with a respective $b = 21.6$ $dm^3\ mmol_c{}^{-1}$, whereas soil No. 7 at $a_{\max} = 81.5$ $mmol_c\,kg^{-1}$ has developed the highest maximal buffering capacity of 3,276 $dm^3\ kg^{-1}$ (for $b = 40.2$ $dm^3\ mmol_c{}^{-1}$). Soil No. 8 deserves special attention, since all sorption constants are strikingly low as a result of combined low pH, organic carbon content (C_{org}) and specific surface area on one hand and high copper content (1,048.0 mg kg^{-1}), on the other hand. Uncontaminated soils were also characterised by a great variation of both Langmuir constants, which for adsorption maximum—$a_{\max}$—ranged from 14.0 to 115.1 $mmol_c\,kg^{-1}$ and for the bonding energy term, b, from 11.4 to 26.0 $dm^3\ mmol_c{}^{-1}$ and exceptionally to 236.6 $dm^3\ mmol_c{}^{-1}$, obtained for soil No. 15 with a resulting high buffering capacity (MBC = 2,454 $dm^3\ kg^{-1}$). Assuming that small amounts of copper should be strongly fixed by soil colloids, therefore, the notably low $a_{\max}$ simultaneously with high b explains the case encountered for this soil. The involved mechanisms

Table 3.6 Langmuir one-site and Freundlich adsorption parameters calculated for the contaminated and uncontaminated soils

Statistical description	Langmuir one-site				Freundlich		
	$a_{\max}$ (mmol$_c$ kg^{-1})	b (dm^3 mmol$_c$$^{-1}$)	MBC[a] (dm^3 kg^{-1})	R^2	K_F (dm^3 kg^{-1})	m[b] (dimensionless)	R^2
Contaminated							
Min	27.5	6.7	185.0	0.972	7.4	0.35	0.836
Max	111.7	40.2	3276.0	0.998	704.9	0.87	0.981
Mean	60.9	22.0	1492.0	0.993	166.2	0.51	0.915
SD	26.9	10.8	1087.7	0.009	230.9	0.18	0.046
Uncontaminated							
Min	10.4	11.4	408.0	0.975	10.3	0.17	0.825
Max	115.1	236.6	2454.0	0.998	569.4	0.84	0.966
Mean	54.2	47.4	1405.1	0.992	131.2	0.44	0.913
SD	33.6	76.6	764.8	0.009	184.7	0.21	0.052

SD standard deviation

[a] $a_{\max} \cdot b$ = MBC (Maximal Buffering Capacity)

[b] Adsorption constant

resulted basically from the heterogeneous character of soil sorptive surfaces (Sokołowska 1989; Sparks 1995; Diatta et al. 2003).

The Freundlich constant m expresses the intensity of isotherms slope (Table 3.6). Most of m values were $\ll 1$, that means isotherm shapes were less steepy (occurrence of curvature), typically for soils in which most of high energetic sorptive sites have been just occupied by copper ions, the remaining ones being characterised by low adsorption energies with increasing surface coverage. Such cases were frequently reported also for Langmuir isotherms (Wu et al. 1999). Since slope intensity clearly indicated differences in the capacities of soils for copper adsorption, it appeared necessary to find out any relationships which may be helpful in determining Cu adsorption maximum as equated below:

$$a_{\max} = 137.3\,m - 9.4, \quad R^2 = 0.82, \text{ for contaminated soils}$$

$$a_{\max} = 159.7\,m - 15.7, \quad R^2 = 0.98, \text{ for uncontaminated soils}$$

where $a_{\max}$ is the Langmuir adsorption maximum constant and m is the Freundlich slope intensity.

Table 3.7 Stepwise variable selection for simplified Elovich rate constant (β) versus selected soil properties for contaminated and uncontaminated soils

Simplified Elovich rate constant (β) for	Contaminated		Uncontaminated	
	Stepwise variable selection			
Adsorption at $^{a}C_i = 2.4$ mmol$_c$ dm^{-3}	$\beta = 0.01\,\mathrm{CEC} + 0.01\,\mathrm{Ca_{ex}} - 0.012\,C_{org} + 0.20\,\mathrm{pH} - 0.8$	$^{b}R^2 = 59$	$\beta = 0.04\,\mathrm{Ca_{ex}} - 0.10\,C_{org} - 0.09\,\mathrm{pH} - 0.005\,\mathrm{Clay} + 1.9$	$R^2 = 95$
Desorption at $C_i = 2.4$ mmol$_c$ dm^{-3}	$\beta = 0.02\,\mathrm{Ca_{ex}} - 0.01\,\mathrm{CEC} - 0.04\,C_{org} + 0.002\,\mathrm{Clay} + 0.6$	$R^2 = 91$	$\beta = 0.06\,\mathrm{CEC} - 0.06\,\mathrm{Ca_{ex}} - 0.11\,\mathrm{pH} - 0.004\,\mathrm{Clay} + 0.9$	$R^2 = 78$

[a] Initial copper concentration

[b] Coefficients of determination, R^2 (%)

3.6 Kinetic Reaction (Adsorption/Desorption) Rate Constants

Kinetics is the study of the time-dependent processes, which in heterogeneous systems such as soil components occur simultaneously and consecutively over a wide time scale (Amacher 1991). The time-interval set for kinetics of copper adsorption in this study ranged from 0.5 up to 96 h. The 8 h time used for the estimation showed that amounts of adsorbed copper varied from 84 to 93 % for contaminated soils (with 57 % for soil No. 8) and from 78 to 90 % for uncontaminated soils (with soil No. 15 about 52 %). Experimental data fitted the simplified Elovich equation that proves its utility for empirical prediction. According to Sparks (1989), the chemical significance of these constants has not been clearly resolved β constants, but they can be used for comparing adsorption rates in different soils (Chien and Clayton 1980; Elkhatib et al. 1992; Dang et al. 1994; Taylor et al. 1995).

The constants β calculated from the slopes $\frac{1}{\beta}$ of the Elovich equation were also a function of both soil textural group and initial copper concentration. The values of the slopes $\frac{1}{\beta}$ increased gradually when increasing copper concentrations in the solution with a simultaneous decrease of β values. When comparing contaminated and uncontaminated soils, it was found that the decrease in β between $C_i = 0.8$ and 1.6 mmol$_c$ dm^{-3} averaged 69 % in comparison with the relatively small decrease (31 %) observed between $C_i = 2.4$ and 3.2 mmol$_c$ dm^{-3}. The "sensitivity" of the slope and hence constants β relied on the degree of surface coverage by copper ions. The relatively high coefficients of determination (R^2) resulting from multiple variable interactions (Table 3.7) on the constant β pointed out the fact that copper chemistry of contaminated as well as uncontaminated soils should be similarly described by simplified Elovich equation, which is generally considered to characterise a number of different processes including bulk diffusion.

Table 3.8 Freundlich kinetic adsorption and desorption (at $C_i = 3.2$ mmol$_c$ Cu dm^{-3}) parameters at adsorption time $t = 96$ h and hysteresis indices based on the ratio of Freundlich exponents[a] for adsorption and desorption isotherms for contaminated and uncontaminated soils

Statistical description	Adsorption		Desorption		Hysteretic index
	$K_{\text{kin-ads}}$	$N_{\text{kin-ads}}$	$K_{\text{kin-des}}$	$N_{\text{kin-des}}$	($N_{\text{kin-des}}/N_{\text{kin-ads}}$)
Contaminated					
Min	8.0	0.20	6.8	0.37	1.21
Max	716.7	0.33	566.6	1.02	5.04
Mean	160.5	0.25	135.4	0.87	3.65
SD	235.2	0.05	184.0	0.22	1.33
Uncontaminated					
Min	12.8	0.21	11.2	0.60	1.78
Max	623.8	0.61	500.7	1.60	4.66
Mean	137.7	0.32	111.5	0.96	3.30
SD	203.0	0.14	162.3	0.31	1.13

SD standard deviation

[a] For $K_{\text{kin-ads}}$; $K_{\text{kin-des}}$; $N_{\text{kin-ads}}$; $N_{\text{kin-des}}$ parameters, refer to Eqs. (3.17, 3.19 and 3.20)

3.7 Hysteresis of Copper in Investigated Soils

Ion exchange reactions in soils are by nature reversible, but this reversibility may appear to be apparently irreversible (Van Bladel and Laudelout 1967), or quite irreversible, that means occurrence of hysteresis (Fripiat et al. 1965; Verburg and Baveye 1994; Zhu and Selim 2000). The total amount of copper desorbed at the end of the desorption process was relatively high and averaged 22 and 26 % at $C_i = 2.4$ and 3.2 mmol$_c$ dm^{-3}, respectively, for contaminated soils, except for soil No. 1, where copper was less desorbed (i.e. 6.0 and 10 % at the respective C_i levels). Interestingly higher desorption rates, i.e. 28 and 35 %, were obtained even for uncontaminated soils at $C_i = 2.4$ and 3.2 mmol$_c$ dm^{-3}, respectively, whereas soil No. 12 desorbed accordingly low copper in the order 4.0 and 8 %. On the other hand Wu et al. (1999) have found that 35 % of formerly adsorbed copper was desorbed from a fine clay fraction, while 27 and 25 % of copper were desorbed from medium and coarse clay, respectively. The relatively high levels of copper desorbed in the current study did not confirm the occurrence of any irreversibility (hysteresis) as earlier reported by Ainstworth et al. (1994). The presence of carbonates in the case of soils No. 1 and No. 12 resulted in a limited copper desorbability (i.e. limited irreversibility).

According to O'Connor et al. (1980) and Barriuso et al. (1994), if there is no hysteresis the ratio $N_{\text{kin-des}}/N_{\text{kin-ads}} = 1$ and $K_{\text{kin-ads}} > K_{\text{kin-des}}$ and in case of negative hysteresis, i.e. enhanced desorbability, the ratio $N_{\text{kin-des}}/N_{\text{kin-ads}} > 1$ and $K_{\text{kin-ads}} > K_{\text{kin-des}}$, as also observed in this study by the fact that the increase of $N_{\text{kin-des}}/N_{\text{kin-ads}}$ induced an increase of $K_{\text{kin-ads}}$ parameter (Table 3.8). Such conditions could explain the relatively high copper desorbability (exception for soils No. 1 and No. 12). As surface charge density (SCD$_{\text{SSA}}$) increases, the $N_{\text{kin-des}}/N_{\text{kin-ads}}$ ratio decreases, implying that copper was more tightly adsorbed by high charge density soil colloids than by low charge density ones (Wu et al. 1999; Diatta et al. 2002). This is evidenced by the negative slopes (SCD_{SSA} versus $N_{kin\text{-}des}/N_{kin\text{-}ads}$) as follows:

$$\mathrm{SCD_{SSA}} = -1.17\left(N_{\text{kin-des/kin-ads}}\right) + 11.12, \quad R^2 = 0.32, \text{ for contaminated soils}$$

$$\mathrm{SCD_{SSA}} = -1.77\left(N_{\text{kin-des/kin-ads}}\right) + 13.13, \quad R^2 = 0.57, \text{ for uncontaminated soils}$$

For $N_{kin\text{-}des}/N_{kin\text{-}ads}$ parameters, refer to Eqs. (3.17, 3.19 and 3.20).

Therefore, if we assume the pool of high-density charges to be pH dependent, since 88 % of contaminated as well as uncontaminated soils exhibited $pH > 6.0$, the high-density charges could probably be limited in number.

3.8 Activation Energies for Copper Geochemical Processes

The reaction rate theory assumes that colliding molecules (e.g. reactions between solution ions and ions held in the soil sorptive complex) must be in a high energy before a reaction occurs (El-Sayed et al. 1970; Diatta et al. 2000). This energy of activation measures the magnitude of the forces that must be overcome during the process of adsorption and desorption reactions (Elkhatib et al. 1993). Energies of activation for copper adsorption (E_{aa}) and desorption (E_{ad}) are grouped in three operational ranges, respectively, for C_i levels (0.8, 1.6, 3.2 $\mathrm{mmol_c\,dm^{-3}}$), both for contaminated and uncontaminated soils: $E_{aa} < 50$, $51 < E_{aa} < 150$, $E_{aa} > 151$ kJ $\mathrm{mol^{-1}}$, namely, range I (R_I), range II (R_{II}) and range III (R_{III}), respectively, as follows:

$C_i = 0.8\ \mathrm{mmol_c\,dm^{-3}}$	
Contaminated	12 % of soil belong to R_I, 63 % to R_{II} and 25 % to R_{III}
Uncontaminated	25 % of soils belong to R_I, 63 % to R_{II} and 12 % to R_{III}
$C_i = 1.6\ \mathrm{mmol_c\,dm^{-3}}$	
Contaminated	25 % of soils belong to R_I, 63 % to R_{II} and 12 % to R_{III}
Uncontaminated	63 % of soils belong to R_I, 25 % to R_{II} and 12 % to R_{III}
$C_i = 3.2\ \mathrm{mmol_c\,dm^{-3}}$	
Contaminated	75 % of soils belong to R_I, 25 % to R_{II}
Uncontaminated	100 % of soils belong to R_I

According to Barrow and Whelan (1989) and Barrow (1998), the E_{aa} for investigated reactions varied from 80 to 100 kJ $\mathrm{mol^{-1}}$. The activation energy of a diffusion-controlled process in a solution is about 25 kJ $\mathrm{mol^{-1}}$ (Sparks 1986). Activation energies for copper adsorption (E_{aa}) ranged from 11.81 to 453.81 kJ $\mathrm{mol^{-1}}$ and for copper desorption (E_{ad}), between 3.79 and 13.59 kJ $\mathrm{mol^{-1}}$ (Fig. 3.6a, b).

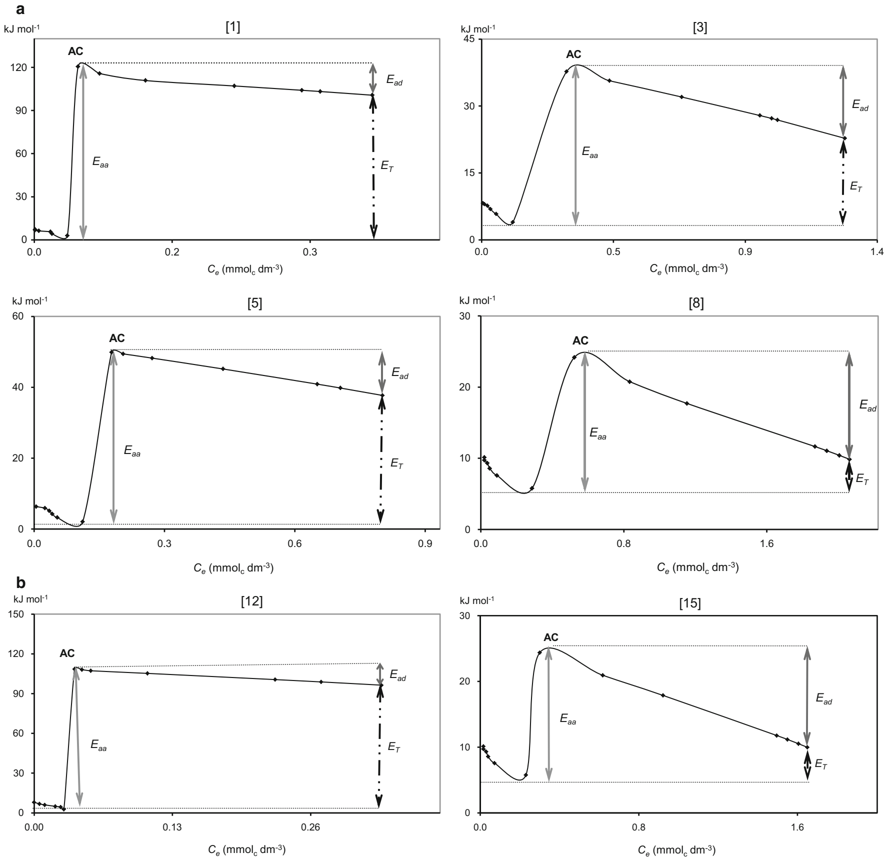


Fig. 3.6 (a) Energy flow for Cu adsorption/desorption at $C_i = 2.4$ mmol$_c$ dm^{-3}, AC = activated complex, E_{aa} and E_{ad} = adsorption and desorption activation energy, respectively. E_T = energy transfer (energy needed for Cu to move from the solution to the solid phase). (**a**) Contaminated soils (Nos. 1, 3, 5 and 8) and (**b**) Uncontaminated soils (Nos. 12 and 15)

The energy transfer (E_T) expresses a measure of the amount of energy needed to transfer copper ions from the solution to activated complex, i.e. soil solid state (Ogwada and Sparks 1986). The E_T value outcomes for soils No. 1 and No. 12 amounted for 97.78 and 93.65 kJ mol^{-1}, respectively, and were notably higher than those obtained for soils No. 3, No. 5, No. 8 and No. 15, amounting for 18.96, 39.71, 5.85 and 4.99 kJ mol^{-1}, respectively. A suggestive endothermic reaction could have been occurring in these soils. The endothermic nature of the reaction and the trend with surface coverage (a decrease of E_{aa} and E_{ad} with increasing initial copper concentration) may be attributed to the potential energy available for adsorption and the fact that most energetic sites were occupied first (Msaky and Calvet 1990). Since the latter become limited as surface coverage increases, adsorbed copper ions at lower interaction energy will be readily desorbable due to weak attraction. So relatively low energy is necessary for copper ions to transfer back to the ambient soil solution.

Investigated soils both contaminated and uncontaminated were mostly characterised by relatively weak buffering properties towards copper ions and should be managed with care: a reduction of copper inputs may increase its E_{ad} and as a result slow down copper transfer to soil solution. Mass transfer and diffusion reaction control seem to be of prime order. The multiple-phase evaluation pointed out in the current study showed the complexity of mechanisms involved in copper dynamics in soil systems.

3.9 Summary

Geochemical processes involve reactions which mediate and control the dissolution/release and (re)formation/sorption of mineral elements at geological as well as soil levels. The role of trace elements, copper among others, in soil chemical changes is still a matter of detailed studies. Copper-bearing minerals (chalcopyrite, $CuFeS_2$; chalcocite, Cu_2S, and bornite, Cu_5FeS_4) predominate in nature, although the richest Cu concentrations are related to the secondary weathering stage compounds [azurite, $Cu_3(CO_3)_2(OH)_2$, and malachite, $Cu_2CO_3(OH)_2$, for instance]. The release of Cu from these minerals may operate via CO_2 injection into deep geological structures or mining activities. The latter ones initiate slow or intensive spread of Cu compounds into the environment.

For decades, geochemists have been facing challenges related to the quantification of both natural (uncontaminated) and anthropogenic (contaminated) soil Cu concentrations. The current chapter was enriched with a case study which outlines in detail multiple steps involved in the evaluation of copper geochemical processes. The approach suggested herein takes into account the medium concentration, time dependency, model application and data fitting for Cu phase characterisation. Equilibria, exchange mechanisms, retention versus release, hysteresis as well as Cu complex formation (energy transfer) and the resulting (geo)environmental concerns were treated with substantial care.

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