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Effect of Humic Substances on Cu (II) Solubility in Kaolin-Sand Soil

by

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Short title: Copper mobility in humic kaolin-sand soil

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Abstract

The type and amount of organic matter present in industrially contaminated soils will influence the risk they pose. Previous studies have shown the importance of humic and fulvic acids (important components of soil organic matter) in increasing the solubility of toxic metals but were not carried out using toxic metal levels and the pH range typical of industrially contaminated soils. This study investigated of the influence of three humic substances (humates, fulvates and humins) on the solubility of copper(II) ions in kaolinitic soil spiked with Cu at levels representative of industrially contaminated soil.

Humates, fulvates and humin were extracted from Irish moss peat, and controlled pH batch leaching tests were conducted on an artificial kaolin-sand soil that was spiked with each. Further leaching tests were conducted on soil spiked with each humic substance and copper nitrate. Dissolved organic contents were determined by titration and total and free aqueous copper concentrations in the leachate were measured using AAS and ion selective electrode potentiometry respectively (dissolved complexed copper levels were determined by difference).

It was found that humates and fulvates are partially sorbed by the soil, probably by chemisorption on positively charged gibbsite (Al-hydroxide) sites in the kaolinite. The addition of 340 mg/kg Cu(II) ions did not significantly affect the amount of humate or fulvate sorbed. Dissolved humates and fulvates form soluble complexes with copper over the pH range 3 to 11. However, in the presence of kaolinite, soluble copper humates and fulvates are unable to compete with the kaolinite for Cu ions at pH 6 to 7. Above pH 8, humate and fulvate complexes are the only forms of dissolved Cu. Humin is largely insoluble and has little effect on Cu mobility between

pH 2 and 12. The implication of this study is that measurement of total soil organic content and water leaching tests should be a standard part of contaminated site investigation.

1. Introduction.

The soils at many old industrial sites are contaminated with metals because of the release of raw materials, process chemicals, finished products and wastes from the industrial processes. Elevated concentrations of many metals in soils can be phytotoxic or hazardous to human and animal health, and they must therefore be regarded as a potential source of harm. Current engineering practice for determining how contaminated soils are treated/categorised, disposed of, or reused still depends largely on comparison of contaminant levels in the soil with generic values (e.g. the UK guideline values for redevelopment of contaminated land: ICRCL, 1987). However, this approach fails to recognise that the hazard posed by a particular contaminant depends on both solubility and bio-availability. A better understanding of toxic metal speciation in contaminated soils is required if contaminated land management strategies are to be based on risk.

There have been many studies investigating toxic metal mobility in the soil and aquatic environment (see e.g. Dalang *et al.*, 1984; Weber, 1988; Zhou et al., 1994; Spark *et al.*, 1997; Temminghoff *et al*. 1997; Dwane and Tipping, 1998; Du *et al.*, 1999; Jelinek *et al.*, 1999; West *et al*. 1999). These studies show that the solubility and mobility of toxic metals is strongly influenced by the amount and type of humic substances (HS) present in soils, river sediments and aquifers. In particular, soluble humic substances such as humic and fulvic acids can increase the solubility of toxic metals such as copper and nickel in neutral

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and alkaline conditions. This is because humic substances contain a variety of functional groups such as carboxyl, hydroxyl and amino groups, which can complex metal cations in various ways (see Stevenson 1994). Hence toxic metal solubility depends on pH, the type of organic matter present, the stability of any dissolved organo-metal complexes, and interaction of both the metal ions and these complexes with the soil minerals.

Humic substances are produced by microbial degradation of plant and animal residues, and represent a range of chemical compounds whose detailed structures are not known. Humic substances can be classified, according to their variation in solubility with pH, into three fractions: humic acids (HA), fulvic acids (FA) and humin. Humic acids are completely soluble above pH 12, but precipitate between pH 12 and 2. Humic acids and fulvic acids are thought to have molecular weight averages of 50,000 to 100,000 and 500 to 2000 Daltons respectively (de Nobili and Chen, 1999), and FA has a higher proportion of hydrophilic to hydrophobic functional groups than HA (Stevenson, 1994). This makes fulvates soluble over the pH range 2 to 12. In contrast, humins are usually insoluble, but can be dissolved using strong acids at elevated temperatures (Yong and Mourato, 1988; Wu, 2000). Humins are high molecular weight polymers (Stevenson, 1994), with a lower proportion of functional groups than HA and FA.

Soluble humic substances have the potential to form complexes with toxic metals. However previous studies of soil systems were not aimed at evaluating risk from contaminated soils, and the levels of toxic metals used were rather low compared with those at industrially contaminated sites. Hence the extent to which these complexes form and sorb to the inorganic solids in such soils is unknown. Furthermore

industrially contaminated soils exhibit a wide range of pH, and many remediation

technologies (such as lime and cement stabilisation) alter the pH, but the pH

dependence of metal-humic-soil interactions have not been widely reported. Hence

the aim of this study was to investigate the influence of humic acid, fulvic acid, and

humins on copper(II) solubility in kaolin-sand soils contaminated to typical 'industrial

site' levels over the pH range 2-10.

2. Materials and Methods

Humic substance extraction

Humic substances were extracted from Irish Moss Peat (supplied by Erin Horticulture

Ltd, Ireland). Extraction and purification of humic and fulvic acids were carried out

following the procedure of Stevenson (1994). Humin was isolated using a technique

modified from that of Yong and Mourato (1988), where the peat was treated using 1M

HCl at a temperature of 60-65°C for 12 hours followed by 24 hours shaking and

centrifugation at 1,550g for 15 minutes. The resulting supernatant was adjusted to pH

10 using 4M NaOH, and the humin precipitate removed by further centrifugation

(Wu, 2000). The extracted samples of HA, FA and humin were stored at 4°C

(samples for elemental analysis were dried at 60°C).

Elemental composition of humic substances

Elemental analysis of the humic substance samples was conducted using a Gas

Chromatographic Elemental Analyzer (Carlo Erba Model 1106), see Table 1 (the

oxygen and inorganic components were not measured). Similar elementary

compositions were measured for reference humic and fulvic acids supplied by

International Society of Humic Substances analysed by the same method. Standard

humin was not available but the fraction defined here as humin had a greater proportion of carbon, but less nitrogen and sulfur than both humic and fulvic acids.

Variation in humic acid solubility with pH

The pH of a 10 g/L solution of HA was adjusted from its initial value of around 2.5 to pH 12 using 0.5 M NaOH. After 6 hours, any residue was separated by centrifugation, dried at 70 °C and weighed. The pH of the supernatant was then reduced by about 2 pH units using 1M HCl, and the procedure repeated until the pH was about 2.

Copper(II) complexation by humate

To investigate the extent of copper(II) complexation by humate (in the absence of clay), a Cu^{2+} solution (made with copper nitrate) was mixed with HA solution to create 1:1, 2:1, 5:1, 10:1 and 17:1 HA:Cu systems by mass. The pH of the 2:1, 5:1, 10:1 and 17:1 HA:Cu systems were adjusted to pH 2 using 5% nitric acid, and left for 6 hours, which was found to be sufficient to establish equilibrium between free cupric ions and those bound by HA and/or by hydroxyl ions. Then the level of free cupric ions was then directly measured using an ISE25 Cu-ion selective electrode (ISE) supplied by Radiometer Ltd. The ISE was calibrated for the pore solution following a procedure similar to those of Town and Powell (1993), Temminghoff *et al.* (1997) and Robertson and Leckie (1999). It has been established that in the absence of complexed copper, the ISE measurement was within 0.5mg/l of the AAS copper level. Once the initial free copper level of each system had been determined, the pH was adjusted by 1 pH unit using 0.5 M NaOH and the measurement repeated (after 6 hour equilibration period) until it was 11. The HA-Cu 1:1 system was studied in greater detail, with total copper levels measured using a Varian Spectra (AA-10) Flame

Atomic Absorption Spectrometer as well as free Cu (II) using the ion selective electrode. Here, twelve different samples were used so that the liquid phase could be sampled, with the pH of each being adjusted directly to the specified value.

Batch extraction tests on humic soil

A kaolin-sand soil was prepared by consolidating a 4:1 w/w mixture of Speswhite kaolin and the 0.1 mm to 2 mm size fraction of Sherburn yellow building sand (see Table 2). These are processed minerals that are essentially free of organic matter. A slurry was mixed at 100% moisture content with either a solution containing a humic substance (i.e. HA, FA or humin), copper (II) nitrate, or a solution of each. Specimens were prepared with two levels of each humic substance: HA and humin at 1 and 10 g/kg, and FA at 0.5 and 1g/kg. Copper was added at a level of 338 mg/kg (the UK guideline value for Cu in contaminated soil is 130 mg/kg; ICRCL, 1987). The three-component systems (i.e. Cu-HS-clay) were formed by adding the humic substance first, to simulate the situation where natural humic soils are contaminated with copper. The slurries were consolidated under 18.4 kNm^{-2} for 48 hours, which resulted in moisture contents in the range of 60 to 68%.

Water extraction tests were conducted by adding distilled water to samples of consolidated soil at liquid to solid ratio of 10:1. Then the pH was adjusted to values between 2 and 11 using either HNO_3 or NaOH. The resulting suspensions were agitated with ultrasound for one hour and shaken for 24 hours. The supernatant was filtered at 0.45 μm (using Whatman Puradisc 25PP disposable filters), stored at 4°C, analysed for total copper by AAS, for free copper using the ion selective electrode, and for DOC by oxidation and titration following the procedure of Wilson (1959). A

leaching test was conducted on a blank specimen (i.e. containing no added humic substance) to correct the DOC content for the consumption of the oxidizing agent by non-DOC components.

3. Results

Copper speciation in Cu-humate systems

The influence of humate on copper speciation in the absence of kaolinite is shown in Figure 1a. Over 90% of the total Cu existed as free Cu (II) at pH below 4 in the solution with no humate. As pH increased above 4, free Cu (II) decreased quickly from 80% at pH 4.5 to 10% of the total at pH 6.0, and then more gradually to below the detection limit at pH 7. This behaviour is consistent with the thermodynamically stable forms of Cu(II) in aqueous conditions, i.e. free aqueous Cu^{2+} ions below pH 4, with CuO or $Cu(OH)_2$ precipitating between pH 4 and 7 (Pourbaix, 1966). In the HA-Cu 1:1 system, the free Cu(II) level represented 95% of the total at pH 2.5, decreased to 50% at pH 4.5 and to zero at pH 7. This behaviour showed that where humates were present, and the pH was less than 7, concentrations of free aqueous Cu^{2+} were less than without HA.

Dissolved copper humate species (determined by the difference between total dissolved and free aqueous copper) were present in the pH range of 3 to 11 (Figure 1a). From pH 6 to 11, Cu-humate species dominated the dissolved copper (i.e. overall, copper solubility was enhanced by humate). The remainder of the copper was in the solid phase probably as hydrolysed species, e.g. $Cu(OH)_2$. However, in the pH range 3-5 the concentrations of total dissolved copper were smaller in the HA-Cu 1:1

system than in the system containing Cu only, probably because some Cu was trapped in solid phase humates (hence humate did not enhance overall copper solubility).

The effect of increasing the HA:Cu ratio on the amount of free Cu in solution is shown in Figure 1b. Around pH 2, most of the Cu was free for all HA:Cu ratios less than 10:1. In the pH range 3-6, the free Cu level decreased with increasing HA:Cu ratio. At all HA:Cu ratios free Cu was undetectable by pH 7. Note that there is some doubt about the validity of the data for the larger HA:Cu ratios, as organic colloids such as precipitated colloidal HA can clog the membranes of both the ion selective and reference electrodes (Rundle, 2000).

Humic substance solubility behaviour

The variation in humate solubility with pH is shown in Figure 2. The amount of soluble humate rose from zero at pH 2 to 55% of the total at pH 5, and then increased to 97% at pH 7.5. Figure 3 shows the concentrations of DOC at various pH for humic acid in the presence of kaolin-sand soil (both with and without copper). With kaolinite present, only a small amount (5-25 mg/L) of DOC leached from the HA-containing mixtures between pH 2 and 7. Within this pH range, the soil spiked with 1g HA per kg soil revealed similar humate leaching to that with the 10 g HA/kg. These levels are less than those that can be inferred from Figure 2 for a system with no kaolinite present[4]. When the pH was greater than 8, more humate was leached. In the soil spiked with 1g HA per kg leaching increased at pH 8.5 and all was leached by

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[4] Humic acids are a range of similar compounds with varying precipitation pHs. Provided each humic acid compound completely dissolves above its precipitation pH, then the data shown in Figure 2 can be applied to systems with different levels of HA.

pH 9[5]. In the soil spiked with 10 g HA per kg, humate leaching increased sharply at pH 8, however only about 60% of the total was leached by pH 11. Failure to leach all of the humate by pH 11 may indicate that there were slow reaction kinetics for humate desorption from kaolinite. Figure 3 also shows that no significant difference in DOC was detected between soils with humate alone and those containing both humate and Cu. It can be concluded that kaolinite reduced humate solubility markedly over the pH range 3-8, and this process was largely unaffected by the introduction of copper(II) ions.

Soil spiked with both levels of fulvic acids (FA) showed that the amount of fulvate leached was larger at higher pH, with 100% leached around pH 11 (see Figure 4). As fulvates are soluble across the pH range, this showed that kaolinite can reduce fulvate solubility by up to 75%. Comparison between the 1g/L data in Figures 3 and 4 showed that there was little difference between humate and fulvate in the amount leached.

Little humin was leached from the soil spiked with 1g humin per kg soil (Figure 5). However, the soil spiked with 10 g humin per kg leached some humin (less than 10% of the total), especially in alkaline conditions. Nevertheless, the amount of DOC leached in humin-spiked soil was small compared with those from HA and FA spiked soils, indicating that humins were relatively immobile (indeed, the measured DOC probably represents impurities in the humin).

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[5] The total amount of organic carbon available was found from the amount of humic substance added, and the proportion of carbon present in each humic substance (Table 1). It was assumed that no humic substances were lost during consolidation.

Copper speciation in Cu-HS-kaolin soils

In the absence of humate, dissolved copper in kaolin-sand soil was about 75% of the total at pH 3, decreasing with increasing pH to less than the detection limit of the analytical technique (AAS) of 0.1 mg/L at all pH values greater than 6.5 (Figure 6a). These levels were less than those for copper in free solution (Figure 1a), which indicates that the clay sorbed the copper. In acidic conditions, humate enhanced copper leaching from the kaolin-sand soil by about 5% of the total present (this difference represents about 15 times the detection limit of the analytical technique). In alkaline conditions, no detectable leaching occurs without humic substance. However, in the system with 10 g HA per kg soil, about 15% of the total Cu was leached at pH 8.5, and 45 % at pH 11.

The copper leaching behaviour of soil spiked with FA shows a similar pattern to that spiked with HA (see Figure 7a). Fulvate increased Cu mobility more than humate in the acidic and neutral pH range, but produced a similar amount of leaching in alkaline conditions. For example, in soils spiked with 1g FA per kg, about 2 % Cu was leached at pH 7, and 14 % at pH 11, compared to less than 1% at pH 7 and 11% at pH 11 in soils spiked with 1 g HA per kg. In contrast, humin had little effect on the amount of Cu leached under acidic and neutral conditions, although about 15% of the Cu was leached from the 10g humin/kg soil in alkaline conditions (Figure 8a). These data suggest that humate and fulvate can enhance mobility of copper greatly in alkaline conditions, but also that humate and especially fulvate can enhance mobility signficantly in the pH range commonly found in the natural environment (pH 5-9).

The levels of free aqueous Cu (II) ions and dissolved copper humates are shown in Figure 6b. At about pH 2 aqueous copper was largely uncomplexed (probably as a result of H^+ competition for binding sites on humate), whereas around pH 4 the dissolved copper consisted of free and complexed copper, with free cupric ions being dominant. Free Cu was undetectable at pH 6, and as a result dissolved complexed Cu was relatively important. At about pH 7 dissolved complexed Cu was also undetectable. In alkaline conditions, dissolved copper was present almost entirely as copper humate complexes.

The levels of free aqueous Cu (II) ions and of dissolved complexed Cu in soils containing fulvate and humin are shown in Figures 7b and 8b respectively. The trends in the fulvate and humin data were similar to those for humate, except the concentrations of dissolved complex were slightly greater for fulvate, and smaller for humin, than humate. This probably reflects the relative functionality of each humic substance.

4. Discussion

The humate studied consists of a family of substances which precipitated at pH values between 7 and 2 (60% is soluble at pH 4), see Figure 2. The presence of a kaolin-sand soil reduced the humate concentration in the aqueous phase when the pH was less than 8 (Figure 3). This reduction shows that kaolin is capable of sorbing negatively charged humate species under neutral and acid conditions, and suggests that humate sorption occurs on positively charged protonated gibbsite (aluminium hydroxide) sites on kaolinite, which become neutralized by about pH 8 (Schulthess and Huang, 1991; Greenland, 1970). When copper was added to a kaolin-sand soil

containing humate it made no difference to humate sorption, probably because it sorbed onto negatively charged sites on the faces of the particles.

The tests performed here and elsewhere (Schnitzer and Khan 1972) indicate that in the absence of soil, fulvates are fully soluble over the range pH 2 to 12. Du *et al.* (1999) inferred from acid titrations that fulvic acid was protonated below pH 4 and was sorbed by illite as neutral molecules (i.e. physisorption). They found that there was little fulvate absorption on illite above pH 4 (less than 20%). Zhou et al. (1994), suggested a similar physisorption mechanism operates between fulvate and vermiculite. However in this study, where kaolinite was used, about half of the fulvate was still sorbed to the clay at pH 8. A significant difference between kaolinite and illite/vermiculite is the higher availability of positively charged gibbsite sites below pH 8 because kaolinite is a 1:1 layer mineral (illite and vermiculite are 2:1 layer minerals and the gibbsite layer is less exposed). Fulvate therefore interacts more strongly and over a larger pH range with kaolinite than illite, probably because it chemisorbs to kaolin (like humate).

This study has shown that humic acid has little copper binding ability at about pH 2 (Figure 1a). Town and Powell (1993) reported a similar result for humate and copper (II) ions, suggesting that copper humate complexes do not form at pH 2 because of strong competition of H^+ for COOH binding sites. At pH 4 about 10% of the copper was in dissolved copper(II) humate complexes, and in the absence of clay, this level only varied slightly between pH 4 and 11. This was despite further humate dissolution above pH 4 (see Figure 2). The fact that this humate dissolution did not result in increased dissolved complexed copper, suggests that in the system studied

copper was unavailable for complexation, probably because of Cu^{2+} hydrolysis (which begins above pH 4; Pourbaix, 1966).

In the presence of kaolinitic soil, complexed Cu(II) in solution was not detectable in neutral conditions, although there were humates or fulvates in solution. This shows that kaolinite can compete strongly with humic substances for Cu(II) in neutral pH conditions, possibly because copper can form particularly stable partially hydrolyzed surface coatings on kaolinite in this pH range (Hunter and James, 1992).

In the tests conducted here, there was dissolved complexed copper in kaolinitic soil under alkaline conditions. This shows that neither the clay nor hydroxyl ions can scavenge copper from dissolved humic complexes in alkaline conditions. However, the tests conducted were unable to show whether the copper complexation occurred in alkaline conditions. This is because the specimens were initially acidic, and the pH was then increased rapidly by the addition of an alkali (NaOH). Thus the possibility that the humic complex formed in acidic conditions, and persisted during the period of pH adjustment, cannot be eliminated.

Implications for soil risk assessment

The type and amount of humic substances present will influence the risk from soils contaminated with toxic metals. Although metal toxicity is reduced when metals are present as organic complexes rather than as free aqueous ions (Weber, 1988), these complexes can still possess significant toxicity, and they can be very much more soluble in natural waters than free aqueous ions. The solubility and mobility of copper is enhanced in neutral and alkaline conditions in the presence of humate and fulvate

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(the same is true of other toxic metals e.g. Pb, Cd, Zn, Ni). Although this study has shown that both humate and fulvate are largely sorbed by kaolinite below pH 8, a portion remains mobile, and this was enough to enhance Cu mobility compared with that in inorganic soils. Mobility could be enhanced further in carbonate rich soils which are slightly alkaline.

At industrially contaminated sites the exact composition of the soils organic matter will be unknown, but is likely to include humates and fulvates. It is therefore clear that measuring the total toxic metal concentrations and soil pH are inadequate for establishing the solubility, and therefore the potential mobility of the toxic metals at such sites. Thus it is recommended that as a minimum, total organic carbon content is also measured, and if this is significant then a standard water leaching test (such as that described by Lewin *et al.*, 1994) is also conducted, and the leachate analysed. This will not establish the speciation of the toxic metal, but will give a clear indication of the proportion of the toxic metal that can be dissolved. This is often sufficient for most sites. However, if the speciation of the dissolved metal is important (e.g. when evaluating the potential impact on aquatic ecosystems), then it can be deduced from the DOC and known complexation behaviour of the metal.

This study has also shown that soil organic matter has the potential to be detrimental to the effectiveness of remediation technologies such as lime stabilisation that partially rely on alklaline conditions to immobilise heavy metals. This is because soil minerals fail to fully sorb metal-humic complexes in alkaline conditions.

Conclusions

In a kaolin-sand soil containing single humic substances and spiked with Cu(II) ions to levels representative of industrially contaminated soils:

- Humates and fulvates are sorbed by kaolin-sand soil, especially below pH 8. The mechanism is probably chemisorption on positively charged gibbsite (Al-hydroxide) sites in kaolinite, which deprotonate above pH 8. This contrasts with relatively weak sorption of humic substances on illite and vermiculite reported in the literature. In this study the addition of 340 mg/kg Cu(II) ions to kaolin-sand soil did not significantly affect the amount of humate or fulvate sorbed to the kaolinite.

- Humates and fulvates form dissolved complexes with copper over the pH range 3 to 11 (their carboxyl groups protonate between pH 4 and 2). In the presence of kaolinite, soluble copper humates and fulvates are not present around pH 6 to 7 (although humates and fulvates remain in solution). This is because humates and fulvates are unable to compete with the kaolinite for Cu ions in this pH range (Cu species form partially hydrolysed species that interact strongly with kaolinite surfaces between pH 6 and 7). Above pH 8, humate and fulvate complexes are the only forms of dissolved Cu.

- Humin is largely insoluble and has little effect on Cu mobility between pH 2 and 12. This relative inertness results from its lack of functional groups compared with humate and fulvate.

- The implication of this study is that total organic content and water leaching tests should be a standard part of contaminated site investigation.

Acknowledgements

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Table 1 Elemental composition of humic substances.

Humic substance	Element (wt%)			
	C	N	H	S
Reference humic acids *	53	6.60	3.32	0.48
Reference fulvic acids*	47	4.50	3.10	0.35
Humin	57	1.38	4.56	0.28
Humic acids	51	5.91	4.00	0.41
Fulvic acids	45	3.95	3.18	0.40

* Sample supplied by International Society for Humic Substances


Table 2 Properties of Speswhite Kaolinite and Sherburn Sand.

Speswhite Kaolinite		Sherburn Sand	
Mineralogical Composition [a]		Chemical Composition [c]	
Kaolinite	94%	Silica	90 %
Mica	4%	Ferric oxide	0.64 %
Montmorillonite	1%	Aluminium	4.56 %
Feldspar and quartz	1%	Magnesia	0.45 %
Surface area (m^2g^{-1})	14.0	Lime	0.33 %
Percentage of particles(<2μm)[b]	80%	Percentage of particles	
Plastic limit [b]	38%	>2mm	1 %
Liquid limit [b]	80%	<100 μm	10 %
Cation exchange capacity		Specific Gravity [c]	2.67
(meq/100g pH7)	4-5		

[a] McGuffog, ECC International Ltd (personal communication)

[b] Al-Tabbaa (1987)

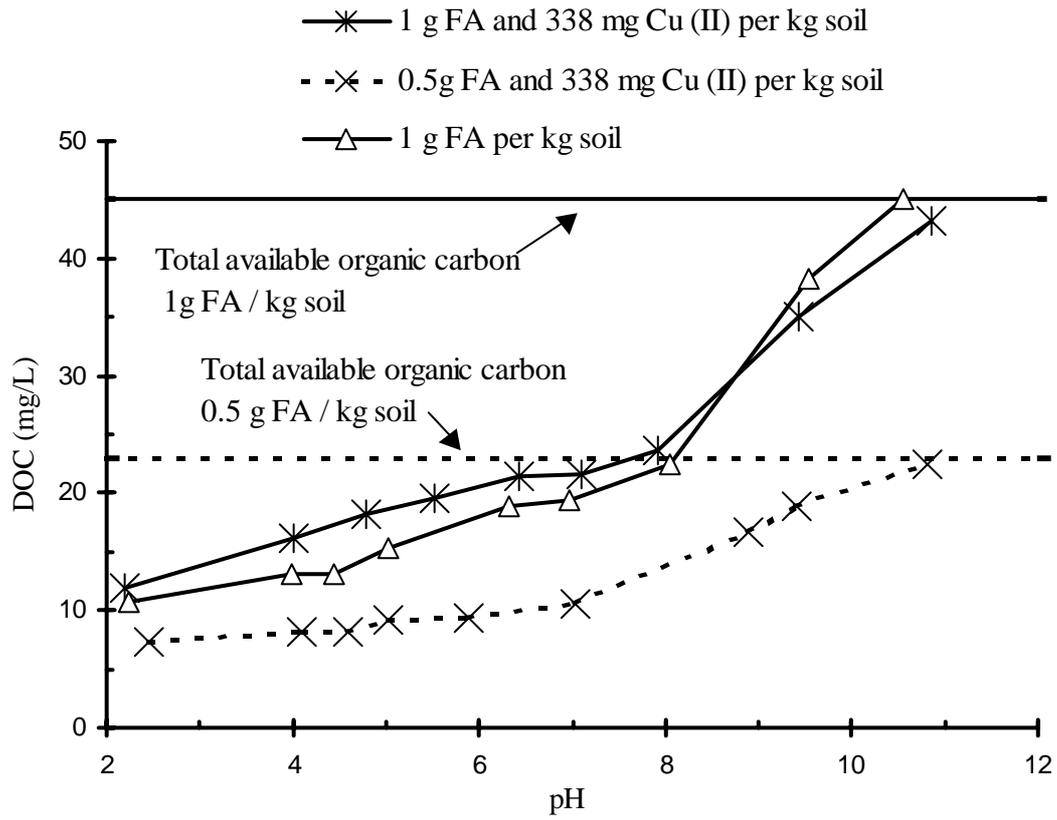[c] Tom Langton and Son Ltd, Leeds, UK

a)

b)
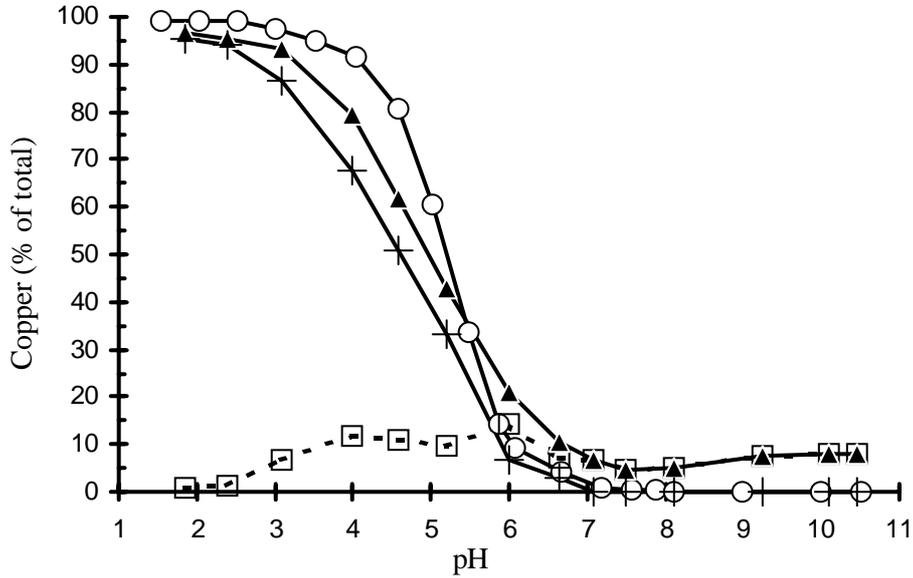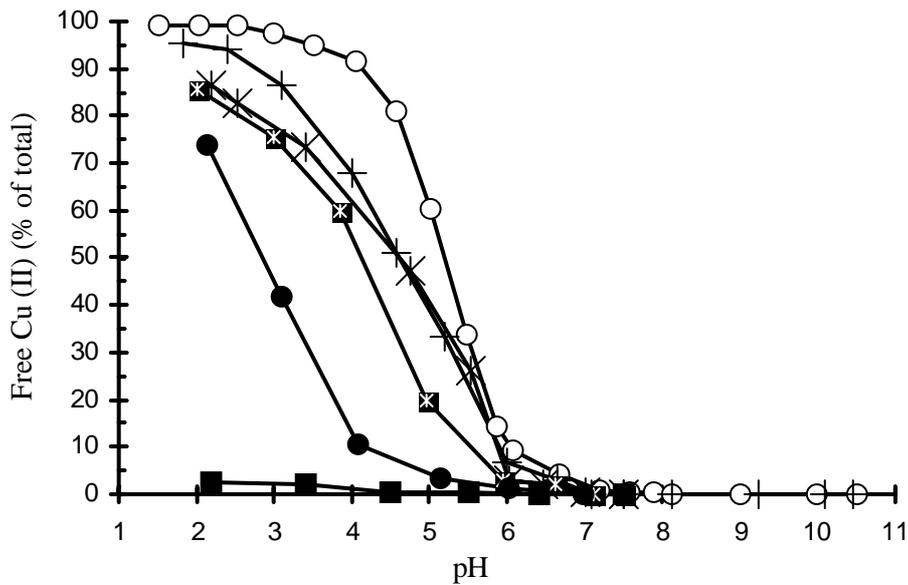
Figure 1. Influence of HA on Cu speciation a) Cu alone and HA:Cu 1:1 system b) free Cu(II) at all HA:Cu ratios (total Cu is equivalent to 20 mg/L dissolved).
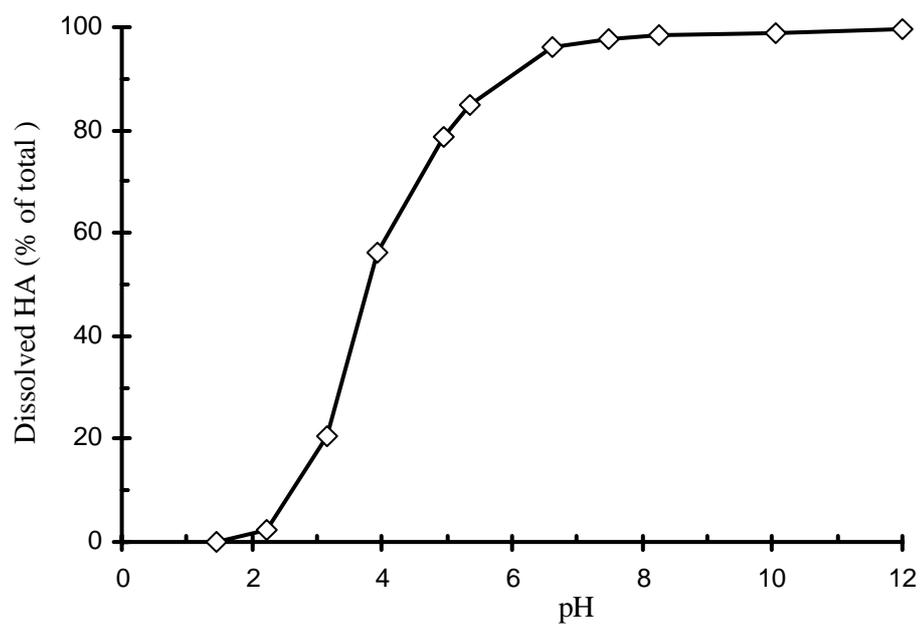
Figure 2. Humic acid solubility versus pH (HA concentration was initially 10 g/L).
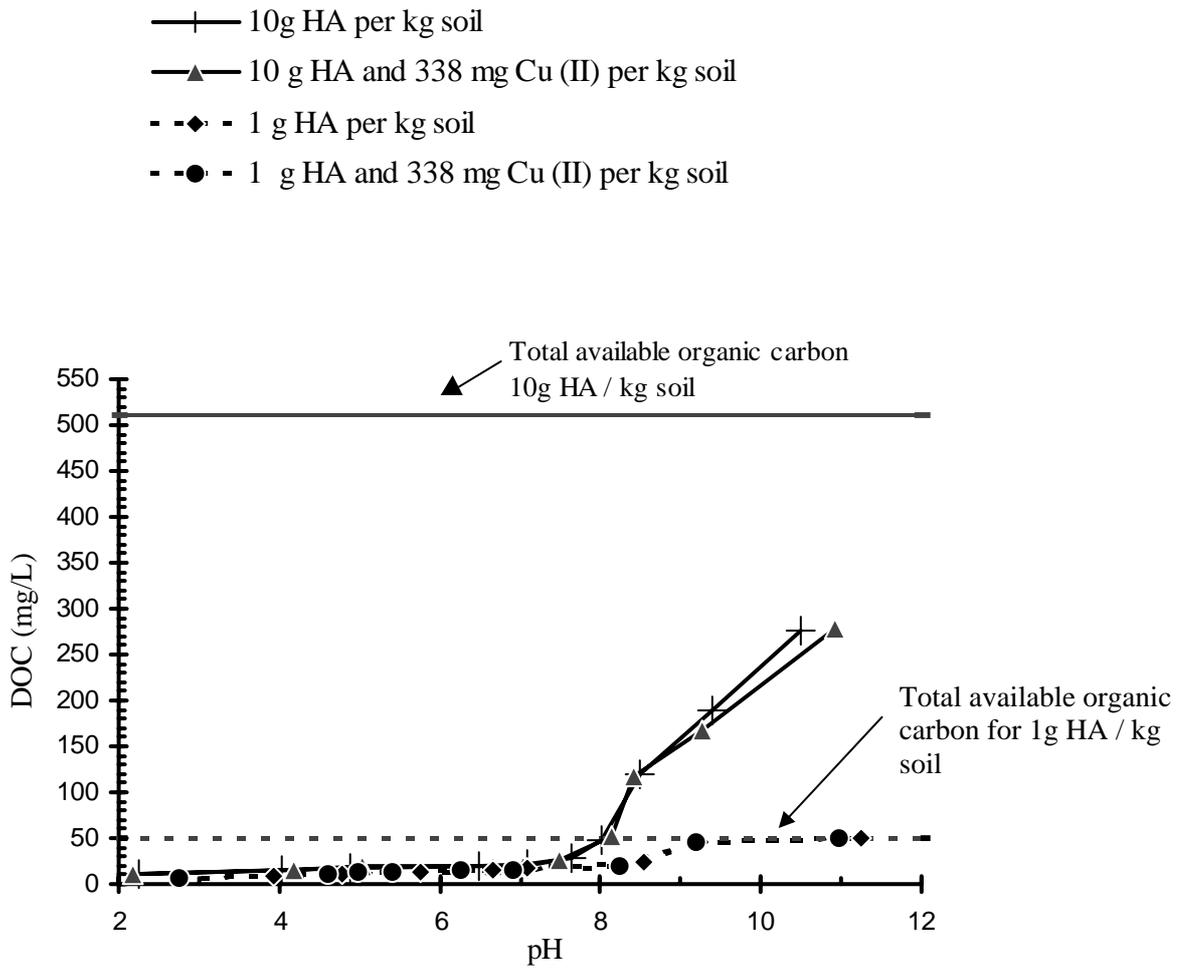
Figure 3. Humate leached from kaolin-sand soil.

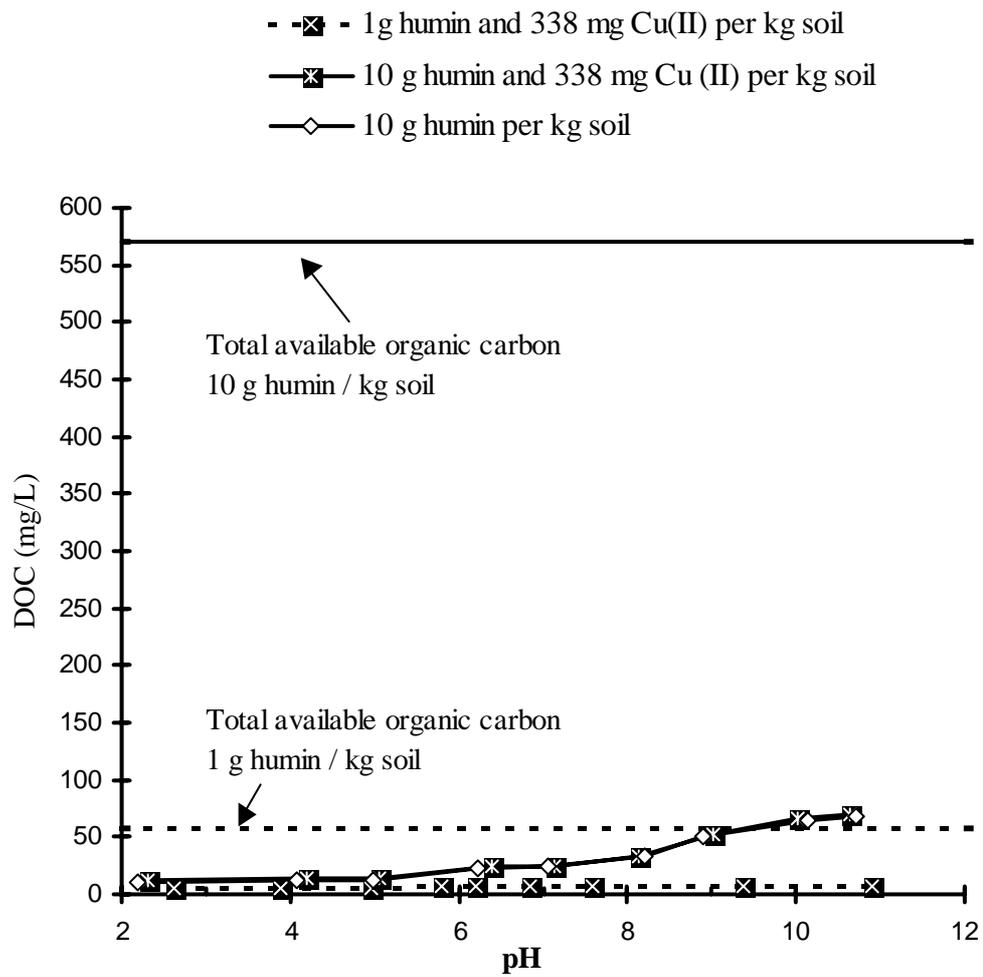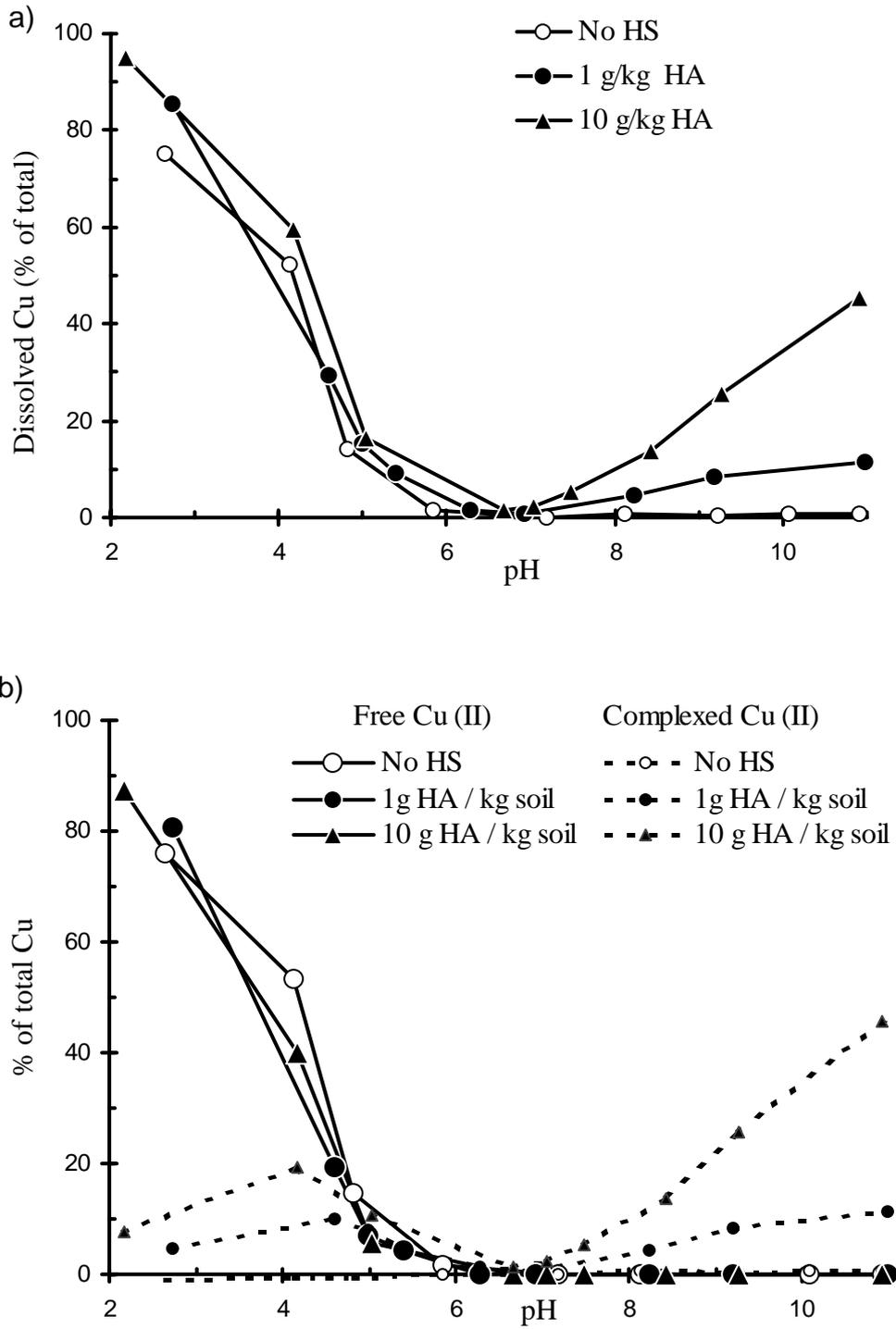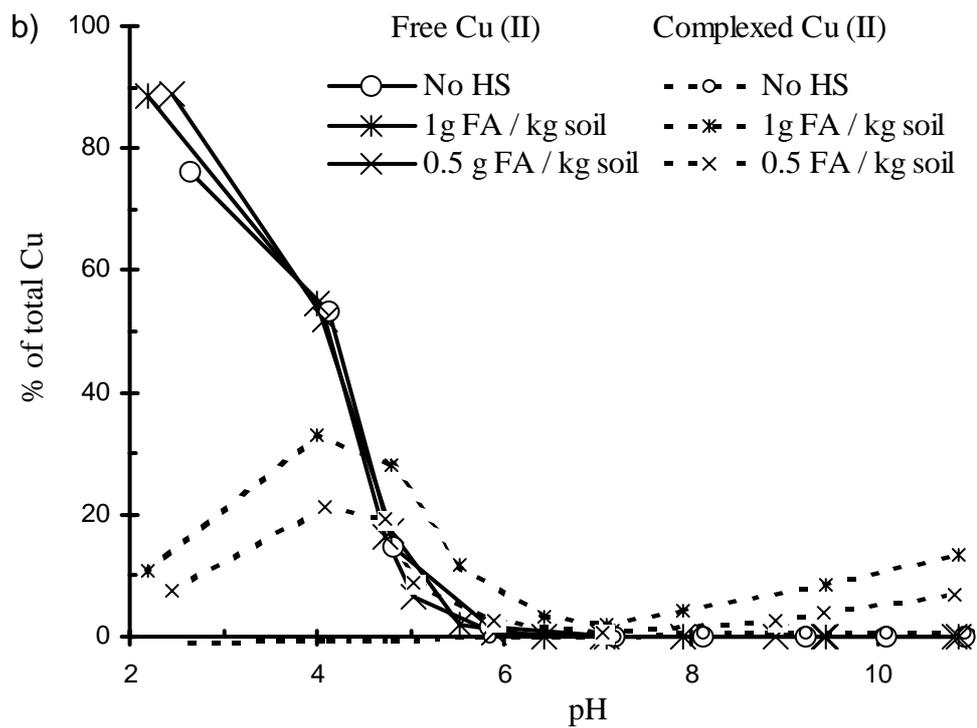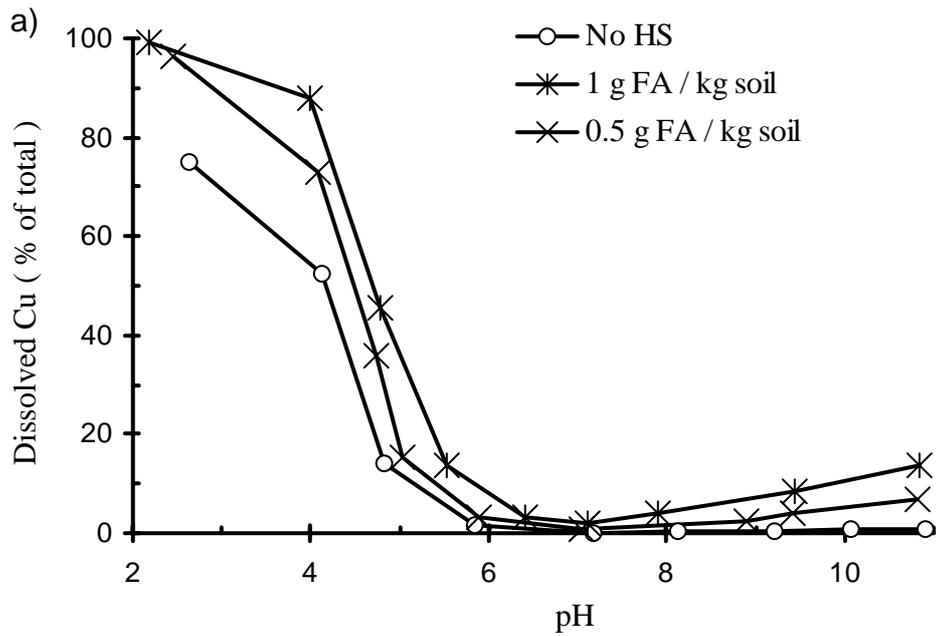**Figure 4. Fulvate leached from kaolin-sand soil.**
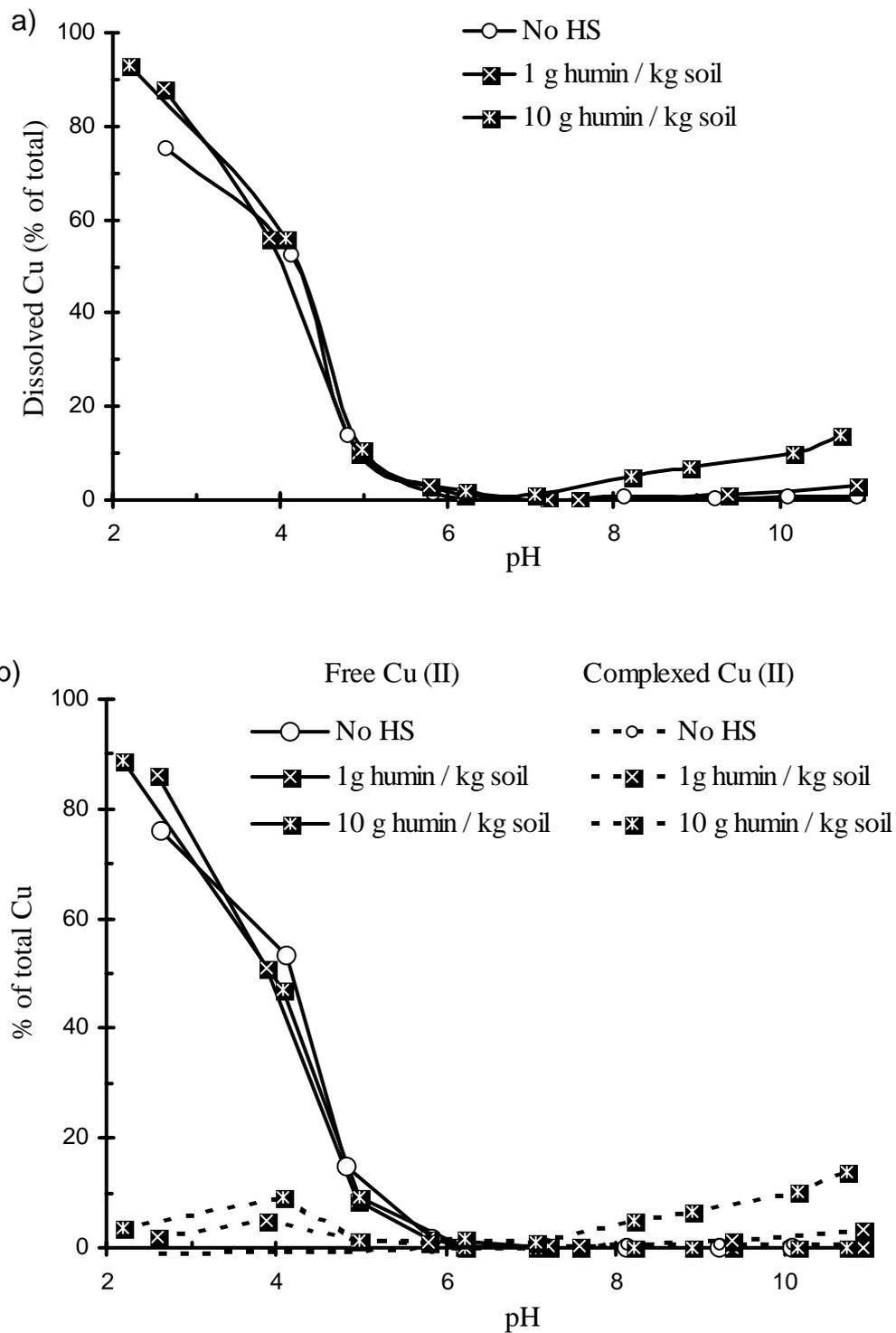
Figure 5. Humin leached from kaolin-sand soil.

Figure 6. Influence of humate on a) total dissolved copper and b) copper speciation, in leachate from kaolin-sand soil.

Figure 7 Influence of fulvate on a) total dissolved copper and b) copper speciation, in leachate from kaolin-sand soil.

**Figure 8 Influence of humin on a) total dissolved copper and
b) copper speciation, in leachate from kaolin-sand soil.**