On the nature of organic matter from natural and contaminated materials

isolation methods, characterisation and application to geochemical modelling

Promotoren:

Prof. Dr. R.N.J. Comans
Hoogleraar Milieugeochemie, Wageningen Universiteit

Prof. Dr. W.H. van Riemsdijk
Hoogleraar Bodemscheikunde en Chemische Bodemkwaliteit, Wageningen Universiteit

Promotiecommissie:

Prof. Dr. T.H. Christensen (*Technical University of Denmark*)
Prof. Dr. J.P. Gustafsson (*Royal Institute of Technology, KTH, Zweden*)
Prof. Dr. A.A. Koelmans (*Wageningen Universiteit*)
Prof. Dr. E. Smolders (*Katholieke Universiteit Leuven, België*)

Dit onderzoek is uitgevoerd binnen de onderzoekschool SENSE.

On the nature of organic matter from natural and contaminated materials

isolation methods, characterisation and application to geochemical modelling

André van Zomeren

PROEFSCHRIFT
Ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van Wageningen Universiteit,
Prof. Dr. M.J. Kropff,
in het openbaar te verdedigen
op vrijdag 10 oktober 2008
des namiddags te half twee in de Aula.

On the nature of organic matter from natural and contaminated materials
Van Zomeren, A.
Thesis, Energy research Centre of the Netherlands, The Netherlands

ISBN: 978-90-8504-993-7

CONTENTS

Chapter 1 Introduction and outline of this thesis 3

Chapter 2 Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash. 17
Environmental Science & Technology, 2004, 38, 3927-3932.

Chapter 3 Development of an automated system for isolation and purification of humic substances. 39
Analytical and Bioanalytical Chemistry, 2008, 391, 2365-2370.

Chapter 4 Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch procedure. 59
Environmental Science & Technology, 2007, 41, 6755-6761.

Chapter 5 Effect of accelerated aging of MSWI bottom ash on the leaching mechanisms of copper and molybdenum. 97
Environmental Science & Technology, 2006, 40, 4481-4487.

Chapter 6 Carbon speciation in municipal solid waste incinerator (MSWI) bottom ash in relation to facilitated metal leaching. 123
Submitted.

Chapter 7 Proton binding properties of humic substances originating from natural and contaminated materials. 141
Submitted.

Summary and synthesis 165

Samenvatting en synthese 173

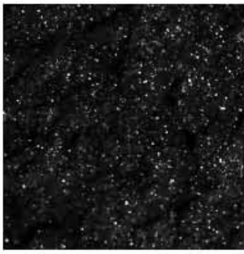
Dankwoord 183

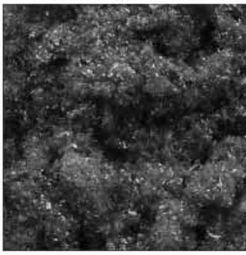
Curriculum vitae 187

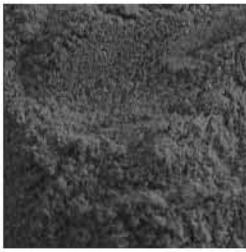
List of publications 191

CHAPTER 1

INTRODUCTION AND OUTLINE OF THESIS







1.1 Background

Natural organic matter (NOM) is the material that is formed after the natural decomposition and transformation of dead plant and animal matter. The fresh organic matter (e.g. plant or animal debris) is decomposed by microbial activity. As such, NOM is found everywhere in the natural environment: in soils, surface water and oceans. Due to its abundance at the earth's surface, the production and decomposition of NOM plays an important role in the global carbon cycling. In soil systems, NOM has an extremely important influence on essential properties like soil structure, water retention, nutrient availability and binding of contaminants (Hayes and Swift, 1990; Swift, 1996). In water systems (e.g. surface or river water), NOM is important in many (bio)-chemical processes and the geochemical cycling of elements/nutrients. A further introduction on the NOM sub fractions is given in paragraph 1.2.

Due to the importance of NOM in soils for agricultural production, research on its chemical and physical properties and classification dates back many centuries. Numerous laboratory procedures and classifications have been developed to relate organic matter properties to plant growth and soil fertility. However, since the growing public and political awareness of environmental pollution in the 1960s, the properties of NOM (especially humic substances, see paragraph 1.2) have increasingly been investigated in the context of its interactions with potentially toxic compounds such as heavy metals and pesticides. Already in the 19th century, the German scientist Sprengel made the first phenomenological observations that natural organic matter is able to complex heavy metals. From the 1960s onwards, scientists started to gain more extensive data on the strong interaction of heavy metals with NOM in natural soils and aquatic environments. At present, the important influence of NOM on the mobility of such potentially toxic compounds in the environment is widely acknowledged by the scientific community.

Waste materials do often also contain organic matter, and in addition, high contents of potentially toxic contaminants such as heavy metals. In many countries, waste materials are increasingly being recycled in construction works (e.g. in road foundations, embankments and sound barriers). The potential environmental risk associated with the re-use of waste materials in such applications depends on the extent to which contaminants can be released as a result of "leaching". Leaching is the release of contaminants from the solid phase (e.g. a waste material) to the water phase with which the material may be in contact (e.g., percolating rainwater).

The legislative framework in the Netherlands is also based on maximum allowable leaching limits for contaminants and was implemented to protect the environment against pollution as a result of application of (secondary) building materials in construction works. Since January 2008, application of (secondary) building materials is regulated in the Soil Protection Act. This regulation replaces the earlier Building Materials Decree.

In some materials, the leaching of certain contaminants does not comply with the regulatory criteria. For specific materials (e.g. municipal solid waste incineration bottom ash), it was thought that organic matter in these waste materials played an important role in the enhanced metal leaching, particularly copper (e.g. Chandler *et al.*, 1997; Meima *et al.*, 1999). These developments have increased the interest in organic matter characterisation in (contaminated) waste materials.

Since many applications of waste materials in construction have service life times of many decades, it is important to characterise the properties of organic matter in (contaminated) waste materials in the context of long-term environmental risk assessment of waste applications as a building materials. In addition, this knowledge can contribute to the development of waste treatment technologies, e.g. to improve the leaching properties of waste materials. Knowledge of the fundamental binding properties of NOM with respect to contaminants can also be specifically used for the development of (geochemical) models to predict the (long-term) leaching behaviour of waste materials.

The significant model development and the enormous gain in calculation capacity of modern computers made it possible to perform extensive model calculations of the behaviour of materials under different environmental scenarios. Recently, multiple binding models and associated generic binding parameters have been combined to a more complete “multi-surface” geochemical model (Dijkstra, 2007). This multi-surface model includes speciation calculations taking into account the inorganic chemistry, the adsorption of contaminants to Fe/Al-(hydr-)oxides, humic and fulvic acids and interactions with clay minerals in one single assessment. Using this approach, geochemical models can describe the dominant interactions that contaminants undergo in both natural and waste environments. These models can be used to assess important chemical/physical processes that determine the (time dependent) emission of contaminants.

1.2 Natural organic matter

Natural organic matter (NOM) is very heterogeneous in its nature and therefore complex to study. Various classifications of NOM are used and these are all based on operational definitions. In the next section, a background is given on the history of organic matter research and the various operational definitions used over time (paragraph 1.3*)*. It is important to note that the terminology that is used does not represent pure compounds. Each class of organic matter consists of highly complex and heterogeneous mixtures of organic molecules.

Natural organic matter is known to include a broad spectrum of organic constituents, many of which have their counterparts in biological tissues, and each with different chemical and physical properties. Two major types of compounds can be distinguished:

- *Humic substances*: a series of unidentifiable organic compounds of relatively high-molecular-weight. They are brown to black in colour and formed by secondary synthesis reactions. The term "humic substances" is used as a generic name, but many scientist discriminate between humic- and fulvic acids (HA and FA, respectively) based on their dissolution properties in alkaline and acid solutions. Humic acids are generally dark-brown to black in colour and have a relatively high molecular weight (several thousand to several hundred thousand atomic mass units (AMU), depending on the applied analysis techniques). Fulvic acids are light yellow to golden brown in colour and have molecular weights ranging from several hundred to about ten thousand AMU. The basis of this classification is also used throughout this thesis.

- *Non-humic substances*: all identifiable biochemical organic molecules that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fatty acids etc.

A classical fractionation of natural organic matter is to identify HA and FA based on their dissolution properties in alkaline and acid solutions, as is discussed in detail by Stevenson (1982). The basis of this classification is also used throughout this thesis. A simplified scheme of the operational definition of humic substances (HS) is given in Figure 1.

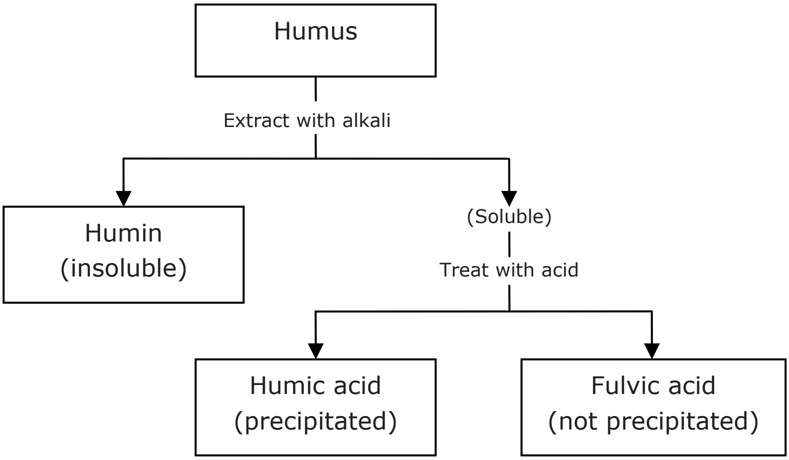


Figure 1. Classification of humic substances (modified after Stevenson, 1982).

Various attempts have been made to elucidate the chemical structure of HS. However, because of the heterogeneous nature of these compounds, it is impossible to precisely define their molecular structures but application of advanced spectroscopic techniques has revealed parts of these structures. This information has inspired scientists to propose overall chemical structures for HA and FA molecules.

An example of some important trends in properties of HA, FA and humin are represented in Figure 2. Humin is black in colour, highly polymerized, aromatic in nature and with high molecular weights. Humic acids are generally dark-brown to black in colour and have a relatively high molecular weight. Reported molecular weights range from several thousand to several hundred thousand AMU, depending on the analysis techniques that have been applied. Fulvic acids are light yellow to golden brown in colour and have molecular weights ranging from several hundred to about ten thousand AMU (Egeberg *et al.*, 2002; Schnitzer and Khan, 1972; Stevenson, 1982).

Other typical chemical properties of HA are a relatively high carbon content (±62%) and relatively low oxygen content (±30%) in comparison with FA (±55% C and 45% O). Fulvic acids are considered to be build up of relatively small building blocks of aromatic compounds with more functional groups (particularly carboxylic) compared to HA. They are supposed to be held together by H-bonds. The charge of HA and FA is caused by deprotonation of the carboxylic and phenolic groups on the molecules. These charged functional groups can subsequently complex heavy metals (and other cations), thereby increasing the solubility of these contaminants.

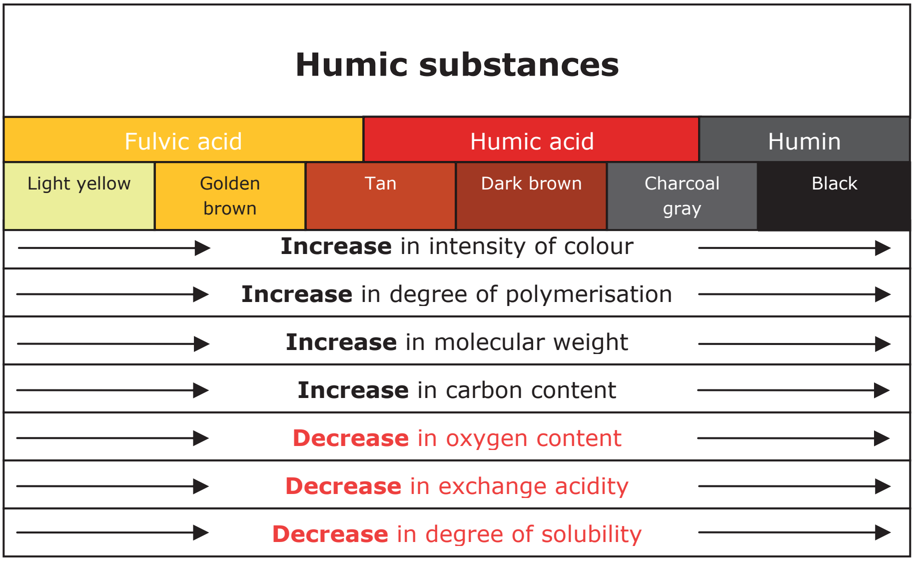


Figure 2. General properties of humic substances.

1.3 History of organic matter research

The study of natural organic matter properties often requires the isolation and purification of organic matter. This historical overview of HS research serves to point out the complexity of the study of these compounds, mainly due to the operational definitions of HS. This section is largely summarised from the extensive reviews of Waksman (1936), Kononova (1961), Odèn (1919) and from the summary given by Stevenson (1982).

The term "humus" dates back to the Roman period, but the Romans used this term frequently to designate the soil as a whole. "Humus" has had varied usage, principally because very little was known about the complicated processes that lead to the formation of the dark coloured organic substances in soils, composts and in water basins. The earliest reported attempts to isolate NOM from soil dates back to 1786. The German scientist Franz Karl Achard found that an extraction of soil with an alkaline extractant resulted in a dark coloured eluate. When this eluate was subsequently acidified, part of the extracted material precipitated. The precipitated material was called HA. He also found that larger amounts of HS could be extracted with alkali from lower layers in the peat, as opposed to the less decomposed organic matter in the upper layers (Achard, 1786).

In 1826, Sprengel was the first scientist who extracted HA from peat by a preceding acid extraction before an alkaline extraction. The alkaline extract was subsequently acidified again and the HA precipitated from the extract. The methods of Sprengel for extraction of HS from soils were generally adopted and are still the basis of many extraction procedures that are used today. Sprengel also extensively investigated the acidic nature of HS. He found that the acid precipitate gradually dissolved in water when the mineral acids were washed off. The dissolved HA subsequently precipitated upon addition of all mineral acids (except phosphoric acid), salts of alkali earths and heavy metals (except gold). These salts of HA were named “humates” and were the first phenomenological observations that NOM could bind heavy metals.

Later, investigations on the nature of HS were extended by Berzelius. In 1833, Berzelius introduced two new compounds which he named “crenic acid” and “apocrenic acid”, based on the dissolution behaviour of the alkaline extract when copper was added in a saturated acetic acid solution. A brown precipitate was formed, called “copper apocrenate”. When the remaining acetic acid solution (without the copper apocrenate) was neutralised, a second grayish green precipitate (“copper crenate”) formed. The precipitated copper complexes were decomposed with alkali. The free acids were called “apocrenic-“and “crenic acids”.

From 1839, Mulder (a pupil of Berzelius) believed that plant organic matter was first changed to “ulmic acid” and “ulmin” and that further oxidation led to the formation of “humic acid” and “humin”. The “humic acid” was subsequently further oxidised to “crenic acid” and finally to “apocrenic acid”. Mulder did also consider that, besides HS, various products of the decomposition of organic residues may also occur in the soil (e.g. leucine, butyric acid, valeric acid, formic acid and acetic acid). He recognised that these substances were easily decomposed and that concentrations were probably low.

The number of classification schemes for the isolation of new products from decomposing plant residues and soil increases significantly during the second half of the nineteenth century. In this period, scientists strongly believed that they could isolate distinct chemical compounds with different extraction methods. The large number of terms and definitions also led to growing confusion in the terminology of the isolated fractions. However, towards the end of the century, scientists realised that humus was a complex mixture of organic substances that were mostly colloidal in nature and contained weak acidic properties.

In the 20th century, more analytical techniques became available and this has led to much more knowledge of the extracted HS from natural materials. However, the “antique” principles of organic matter isolation and classification are still the basis for many procedures that are used today. The term “fulvic acid” was introduced by Odèn in 1919 as a generic term for the crenic and apocrenic acids earlier identified by Berzelius. He stated that a sensible name for those groups of acids was lacking. Since the crenic and apocrenic acids were pale yellow to gold-yellow in colour, he proposed the term “fulvic acid” (fulvus is the Latin word for yellow).

Presently, there is still no consensus as to how HA and FA should be operationally defined (Aiken, 1988; Clapp and Hayes, 1999; Hayes and Swift, 1990). According to aquatic scientists, HA is generally defined as the carbon fraction that precipitates below pH 2 (Clapp and Hayes, 1999; Hayes and Swift, 1990), whereas the methods of Thurman and Malcolm (Thurman and Malcolm, 1981) and Malcolm (Malcolm, 1991) use pH 1. Soil scientists generally define HA as the carbon fraction that precipitates below pH 1 (e.g. (Swift, 1996)). The definitions of FA also differ. Aquatic FA has previously been defined by adsorption on XAD-8 resin at pH 2 (Malcolm, 1991; Thurman and Malcolm, 1981), and soil FA by adsorption at pH 1 (Swift, 1996).

Numerous isolation and purification methods have been developed over the past decades (Aiken, 1985; Hayes, 1985; Leenheer, 1981; Swift, 1996; Thurman and Malcolm, 1981) and scientists now also use (polymeric) resins in preparative chromatography to adsorb specific organic matter classes (e.g. XAD-4, XAD-8 or DEAE-cellulose). Obviously, the developments in organic matter isolation and characterisation methods have enormously expanded and improved over time.

In the next paragraph, the specific aim and outline of this thesis on the characterisation of organic matter properties is addressed, to introduce the reader into the several chapters that will follow.

1.4 Aim and outline of this thesis

This thesis focuses on the development of methods for the isolation and characterisation of natural organic matter in general and organic matter in (contaminated) waste materials in particular. The overall purpose of this research is to develop a better understanding of the role of NOM with respect to the mobility of contaminants such as heavy metals in the environment.

The study of chemical properties of NOM often requires isolation and purification of different fractions of the organic matter. The advantage of purification is that it reduces the heterogeneity in the properties of NOM. As was reviewed in the previous paragraphs, numerous isolation and purification methods have been developed over the past decades to enable the further characterisation of organic matter properties. Although these procedures are well established and widely used by scientists, they all share the disadvantages that they are very laborious and primarily aimed on purification rather than quantification of the different fractions. Therefore, this thesis has a strong focus on developing analytical methods that enable an improved characterisation and quantification of the different fractions that are important for metal binding, preferably in a more time- efficient manner.

In **Chapter 2**, a competitive ligand exchange-solvent extraction method was used to measure Cu binding to DOC in leachates from municipal solid waste incinerator (MSWI) bottom ash. The copper binding properties of dissolved organic carbon were investigated with specific attention for the identification and quantification of the organic ligands.

Chapter 3 describes the development of an automated procedure to isolate and purify HA and FA from various materials. The conventional isolation and purification procedures share the disadvantage of being very laborious and time consuming. These disadvantages are largely overcome by automation and enabled gathering an extensive set of purified HA and FA samples from diverse origin for further characterisation purposes. The main objective for automation of the conventional procedure was to save a significant amount of labour and total throughput time in the performance of HA and FA isolation and purification. A better standardisation of HA and FA isolation and purification methods was aimed for by automating the procedure.

In **Chapter 4**, the development is described of a rapid batch method for the experimental characterisation and quantification of HS in natural and contaminated systems. In principle, the quantification of HS in the environment can be studied with the manual or the developed automated isolation and purification procedure (**chapter 3**). However, established models for calculation of metal binding to HS require only the concentrations of HA and/or FA as input. Therefore, conventional isolation and purification procedures are too elaborate for this type of application. The novelty of this method lies in the fact that it greatly facilitates the analysis of HA and FA concentrations (e.g. for use in geochemical modelling, **chapter 5**).

Based on results from previous chapters, “multi-surface” geochemical modelling of heavy metal leaching from MSWI bottom ash is used to develop a mechanistic insight into the beneficial effects of accelerated aging of MSWI bottom ash on the leaching of copper and molybdenum (**Chapter 5**). Therefore, the rapid batch procedure described in **Chapter 4** is used to characterise DOC quantitatively in terms of humic, fulvic and hydrophilic acids over a wide pH range. In addition, a new approach is developed to model the pH dependent leaching of fulvic acids from MSWI bottom ash based on adsorption to reactive Fe/Al-(hydr-)oxides. Subsequently, the role of the identified organic matter fractions in the leaching of Cu from MSWI bottom ash before and after accelerated ageing is investigated.

In **Chapter 6**, the total carbon speciation (inorganic, organic and elemental carbon) in MSWI bottom ash samples is studied to identify the amount and properties of the different carbon species present in MSWI bottom ash. The work specifically focuses on the amount of potentially leachable reactive carbon (i.e. HA and FA) because this fraction is important for the leaching properties of MSWI bottom ash. Moreover, information about HA and FA concentrations in the solid bottom ash matrix and in the leachate can be used in geochemical modelling for prediction of the long-term leaching behaviour of MSWI bottom ash. Based on these results, the relevance of measuring specific carbon species rather than LOI is addressed.

Chapter 7 describes a comparative study regarding the proton binding properties of the previously isolated and purified HS (**Chapter 3**). Binding models for HS, such as the NICA-Donnan model, have so far been developed and calibrated against organic matter from natural origin (e.g. soils and surface waters). In **Chapter 5,** the NICA-Donnan model was found to perform well when applied to a contaminated (waste) material, i.e. municipal solid waste incinerator (MSWI) bottom ash. However, the proton binding properties of HS originating from waste environments have not been analysed directly and demonstrated to fall within the observed range for natural materials. The aim of this study is to analyse the proton binding properties of humic and fulvic acid samples originating from secondary materials, waste materials and natural samples in order to assess whether the charge development of these HS can be described with generic NICA-Donnan parameters.

References

Achard, F. K. Chemische untersuchung des torfs, *Crell's Chem. Ann.*, **1786**, *2*, 391-403.

Aiken, G. R. Isolation and concentration techniques for aquatic humic substances. In *Humic substances in soil, sediment and water: geochemistry, isolation and characterization*; Aiken, G. R., Mc Knight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1985, pp 363-385.

Aiken, G. R. A critical evaluation of the use of macroporous resins for the isolation of aquatic humic substances. In *Humic substances and their role in the environment*; Frimmel, F. H., Christman, R. F., Eds.; John Wiley & Sons: New York, 1988, pp 15-28.

Chandler, A. J., Eighmy, T. T., Hartlen, J., Hjelmar, O., Kosson, D. S., Sawell, S. E., van der Sloot, H. A., Vehlow, J., *Municipal solid waste incinerator residues,* Elsevier: Amsterdam, 1997.

Clapp, C. E., Hayes, M. H. B. Sizes and shapes of humic substances, *Soil Sci.*, **1999**, *164*, 777-789.

Dijkstra, J. J. Development of a consistent geochemical modelling approach for leaching and reactive transport processes in contaminated materials. 1-192. 2007. Wageningen university.

Egeberg, P. K., Christy, A. A., Eikenes, M. The molecular size of natural organic matter (NOM) determined by diffusivimetry and seven other methods, *Water Res.*, **2002**, *36*, 925-932.

Hayes, M. H. B. Extraction of humic substances from soil. In *Humic substances in soil, sediment, and water: Geochemistry, isolation and characterization*; Aiken, G. R., Mc Knight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1985, pp 329-362.

Hayes, M. H. B., Swift, R. S. Genesis, isolation, composition and structures of soil humic substances. In *Soil colloids and their associations in aggregates*; de Boodt, M. F., Ed.; Plenum Press: New York, 1990, pp 245-305.

Kononova, M. M., *Soil organic matter,* Pergamon Press: Oxford, 1961.

Leenheer, J. A. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, *Environ. Sci. Technol.*, **1981**, *15*, 578-587.

Malcolm, R. L. Factors to be considered in the isolation and characterization of aquatic humic substances. In *Humic substances in the aquatic and terrestrial environment*; Boren, H., Allard, B., Eds.; Wiley: London, 1991, pp 369-391.

Meima, J. A., van Zomeren, A., Comans, R. N. J. Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates, *Environ. Sci. Technol.*, **1999**, *33*, 1424-1429.

Odén, S. Die huminsäuren; chemische, physikalische und bodenkundliche forschungen, *Fortschrittsberichte über Kolloide und Polymere*, **1919**, *11*, 75-260.

Schnitzer, M., Khan, S. U., *Humic substances in the environment,* Marcel Dekker, Inc.: New York, 1972.

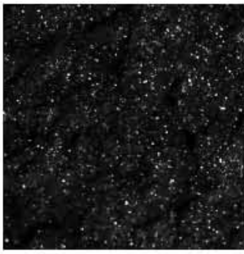
Stevenson, F. J., *Humus chemistry. Genesis, composition, reactions,* John Wiley & Sons: New York, 1982, pp 1-443.

Swift, R. S. Organic matter characterization. In *Methods of soil analysis. Part 3. Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996, pp 1011-1069.

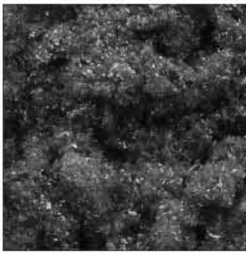
Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

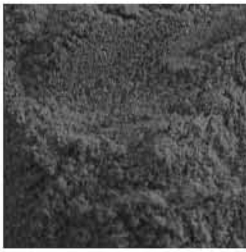
Waksman, S. A., *Humus; origin, chemical composition, and importance in nature,* Baillière, Tindall and Cox: London, 1936.

CHAPTER 2



CONTRIBUTION OF NATURAL ORGANIC MATTER TO COPPER LEACHING FROM MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH





Published in similar form as:
van Zomeren, A. and Comans, R.N.J., Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environmental Science & Technology*, **2004**, *38*, 3927-3932. Reproduced with permission. Copyright 2004, American Chemical Society.

CONTRIBUTION OF NATURAL ORGANIC MATTER TO COPPER LEACHING FROM MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH

André van Zomeren[1] *and Rob N.J. Comans*[1,2]

The leaching of heavy metals, such as copper, from municipal solid waste incinerator (MSWI) bottom ash is a concern in many countries and may inhibit the beneficial re-use of this secondary material. The enhanced leaching of copper from three MSWI bottom ash samples by dissolved organic carbon (DOC) was investigated with specific attention for the nature of the organic ligands. A Competitive Ligand Exchange-Solvent extraction (CLE-SE) method was used to measure Cu binding to DOC. Two types of binding sites for Cu were identified and geochemical modelling showed that the organically bound fraction varied from 82% to 100% between pH 6.6 to 10.6. Model calculations showed that complexation by previously identified aliphatic and aromatic acids was unable to explain the enhanced Cu leaching from the MSWI residues. High Performance Size Exclusion Chromatography (HPSEC) and the standard extraction procedure to isolate and purify natural organic matter revealed that about 0.5% of DOC consists of humic acids and 14.3-25.6% of fulvic acids. Calculated Cu binding isotherms based on these natural organic compounds, and the Non Ideal Competitive Adsorption-Donnan (NICA-Donnan) model, provide an adequate description of the organic Cu complexation in the bottom ash leachates. The results show that fulvic-acid type components exist in MSWI bottom ash leachates and are likely responsible for the generally observed enhanced Cu leaching from these residues. These findings enable the use of geochemical speciation programs which include models and intrinsic parameters for metal binding to natural organic matter, to predict Cu leaching from this widely produced waste material under variable environmental conditions (e.g. pH, ionic strength and concentrations of competing metals). The identified role of fulvic acids in the leaching of Cu and possibly other heavy metals can also be used in the development of techniques to improve the environmental quality of MSWI bottom ash.

---

[1] Energy Research Centre of The Netherlands.

[2] Wageningen University.

2.1 Introduction

Municipal solid waste incinerator (MSWI) bottom ash is produced world wide in large quantities and is generally re-used in construction or landfilled. The leaching of contaminants, such as heavy metals, oxyanions and salts, from these residues is a concern in many countries and may inhibit the potential re-use of MSWI bottom ash as a secondary building material. In the Netherlands, the leaching of particularly molybdenum and copper does not always comply with environmental regulations, which requires special (and expensive) measures to reduce contact with water. In order to understand the cause of the enhanced concentrations of these contaminants in MSWI bottom ash leachates, and to develop methods for improvement of the environmental quality of this residue, it is necessary to identify the underlying geochemical processes.

Several previous studies have pointed at the role of dissolved organic carbon (DOC) in facilitating the leaching of Cu from MSWI bottom ash (Chandler *et al.*, 1997; Comans *et al.*, 1993; Johnson *et al.*, 1995; Meima and Comans, 1999; van der Sloot *et al.*, 1992). In an earlier study we have determined conditional stability constants and binding capacities of organic ligands in MSWI bottom ash leachates to quantify the role of DOC in Cu leaching. It was demonstrated that, over a large pH range, 95-100% of Cu in the leachates was organically complexed (Meima *et al.*, 1999). A limitation of conditional stability constants is, however, that they are only valid at conditions close to those at which they are determined (e.g. pH, ionic strength and competitive ions). In order to enable the use of intrinsic thermodynamic binding constants, the nature of the organic ligands in the DOC pool needs to be known.

Ferrari *et al.* (2002) identified several aliphatic (lactic-, formic-, acetic-, oxalic- and maleic acid) and aromatic acids (terephthalic-, phthalic- and benzoic acid) in leachates from MSWI bottom ash, but these accounted for only 5-13% of DOC. Pavasars (1999) and Johansson *et al.* (2000) separated organic carbon on the basis of hydrophobicity and identified many different organic compounds in the isolated fractions. Also these compounds accounted for only a minor fraction of the DOC.

In the present study, we characterise the nature and Cu-binding properties of organic matter in MSWI bottom ash leachates in order to identify and quantify the relevant organic compounds with regard to enhanced copper leaching from these residues. We focus particularly on humic (HA) and/or fulvic (FA) acids, based on previous observations that a fraction of the DOC in MSWI bottom ash leachates is retained by XAD-8 resins (Johansson *et al.*, 2000; Pavasars, 1999), which are generally used for the isolation of HA and FA. These organic substances are known to have a very high affinity for Cu binding (Buffle, 1988; Croué *et al.*, 2003; Hering and Morel, 1988; Mantoura and Riley, 1975).

2.2 Materials and methods

2.2.1 Bottom ash samples

Three different bottom ash samples were used for this study. Bottom ash sample BA2 was taken from a Dutch MSWI in 1996. The sample was freshly produced and is atypical for a freshly produced bottom ash because of its low native pH (7.8) and high redox potential (344 mV). The large inorganic carbon content of this sample (6.7 g C/kg, relative to 0.6 g C/kg for sample QUE1 and 9.0 g C/kg for sample 1.5YR, see below) indicates that its low pH value is due to carbonation. The two other samples (QUE1 and 1.5YR) originate from a different Dutch MSWI and have been used in a previous study (Meima *et al.*, 1999). The QUE1 sample was taken directly after the material passed the quench tank. The 1.5YR sample was stored outside on a pile for 1.5 years and was sampled at the outer (carbonated) layer. In the laboratory, the samples were air dried and sieved through a 2 mm sieve and stored in a closed container under a N_2 atmosphere.

2.2.2 pH-static experiments

Bottom ash samples were leached at a liquid to solid (L/S) ratio of 5 L/kg for 24 hours at 20^{o}C in Teflon (PFA) reaction vessels. The pH was adjusted automatically by addition of 1 M HNO_3 and 1 M NaOH to the given setpoint. Finally, the suspensions were centrifuged (4649*g) and filtered (0.2 µm). The pH-stat procedure is described in more detail in Meima and Comans (Meima and Comans, 1997).

2.2.3 CLE-SE analysis

The Competitive Ligand Exchange Solvent Extraction (CLE-SE) analysis was originally developed by Moffett and Zika (1987) to study Cu-DOC binding in marine waters. We have adapted and slightly modified the procedure to enable its application to Cu complexation in (bottom ash) leachates. The method is based on the addition of a competitive ligand (acetylacetone, AcAc) that binds Cu and can be isolated by solvent extraction (toluene). The extracted $Cu(AcAc)_2$ complex was then quantitatively back extracted into 1 M HNO_3 and analysed by ICP-AES. Copper binding isotherms were measured by titration of the leachate with either additional Cu^{2+} or AcAc and subsequent CLE-SE analysis. Preliminary experiments showed that the organic ligands in the bottom ash leachates were already largely Cu-saturated and that only little additional Cu could be adsorbed. Therefore, most of the isotherm data were obtained by titration with AcAc, which desorbed Cu from the organic ligands. The CLE-SE data were fitted to a 2-site Langmuir isotherm by non-linear regression to estimate the affinity constants and site densities of the DOC. As discussed previously (Meima *et al.*, 1999), we have selected a 2-site rather than 3-site model, because the two extra parameters that would be required cannot be determined with sufficient accuracy. The 2-site isotherm was shown to describe the Cu binding very well at site saturations between 14 and 100%, i.e. the relevant range for the investigated bottom ash leachates. Therefore, we have excluded the data at the lower end of the isotherm (at Cu loadings < 14%) from the non-linear regression procedure. More details regarding the procedure, speciation calculations, and analyses can be found in Meima *et al.* (1999). The CLE-SE data for samples QUE1 and 1.5YR originate also from the latter study.

2.2.4 High performance size exclusion chromatography (HPSEC)

In order to obtain more insight in the nature of DOC in the bottom ash leachates, the molecular size distribution of DOC was measured by HPSEC. The system consisted of a HP 1100 liquid chromatograph with an isocratic pump and a variable wavelength detector (measurements at 254 nm). A Waters Protein PAK-125 modified silica column (7.8*300 mm) in combination with a guard column was used for analysis. The mobile phase consisted of a solution of 0.1 M NaCl, 2 mM NaH_2PO_4 and 2 mM K_2HPO_4 at pH 6.8.

2.2.5 Extraction of humic and fulvic acids

Humic and fulvic acids were extracted from leachates of the three bottom ash samples (leached at L/S=5, native pH) by adsorption/desorption steps on XAD-8 resins (Rohm & Haas Co., Philadelphia, PA) according to Thurman and Malcolm (1981). This procedure is widely accepted and currently recommended by the International Humic Substances Society (IHSS) for the extraction of soil and aquatic HA and FA. The lyophilized fractions were weighted and analysis of elemental composition was performed to check the purity.

2.2.6 Chemical equilibrium modelling

Additional information about the nature of DOC in leachates from MSWI bottom ash was obtained by chemical equilibrium modelling. The chemical equilibrium model ORCHESTRA (Meeussen, 2003) with the thermodynamic database from MINTEQA2 (Allison *et al.*, 1991) was used for the speciation calculations. The standard MINTEQA2 v3.11 database was modified according to Meima and Comans (1999).

First, calculations of Cu-binding to simple organic acids (acetic-, benzoic-, formic-, lactic-, maleic-, oxalic- and phthalic acid) identified in leachates from MSWI bottom ash (Ferrari *et al.*, 2002) were carried out. It is important to note that the sum of these identified organic acids comprised only about 25% of the DOC (Ferrari *et al.*, 2002). Affinity constants for the binding of Cu, Ca and H to formic-, lactic-, maleic- and oxalic acid, from Sillen and Martell (1964), were added to the MINTEQA2 database for this purpose. The input for the speciation calculations was the composition of the leachate (major and minor elements), one of the mentioned organic acids at a concentration equivalent to the total measured DOC concentration and AcAc used in the titration experiments.

Next, the NICA-Donnan model (Kinniburgh *et al.*, 1999) was incorporated in ORCHESTRA to calculate Cu binding to humic and fulvic acid. The recent generic binding parameters from Milne *et al.* (2003) were used for metal-ion and proton binding without any modifications. The NICA-Donnan model and the above parameter set do implicitly account for competition among trace metals and major cations in the leachates (such as Ca, Fe and Al) for the binding to DOC. Again, measured dissolved concentrations of major and minor elements in the leachate and the added AcAc concentrations were used as input, along with the measured concentrations of HA and FA extracted from the bottom ash leachates.

2.3 Results and discussion

2.3.1 CLE-SE analysis

Figure 1 shows isotherms for the binding of copper to DOC in leachates of MSWI bottom ash samples BA2, QUE1 and 1.5YR at different pH values, based on the CLE-SE analysis. Between pH 6.6 and 10.6 without added Cu or AcAC, Cu is leached from bottom ash in concentrations between 3.5 and 109 µmol/L (Table 1). Data analysis from preliminary experiments showed that the organic ligands in the bottom ash leachates were already largely saturated and only little additional Cu could be adsorbed by DOC (particularly for sample BA2). Desorbing the Cu from the organic ligands by increasing the AcAc concentration, therefore, generated most of the isotherm data in Figure 1.

It was not possible to estimate significant binding parameters for the lower affinity site (L_2) for sample BA2 at pH 7.9 and 6.6, because of the high capacity of the high affinity site (L_1) for this sample (Table 1), while Cu loadings at these pH values were limited by leachate saturation with respect to tenorite or $Cu(OH)_2$ (as indicated by MINTEQA2 calculations). Therefore, the isotherms of sample BA2 at these pH values have been fitted with a single binding site.

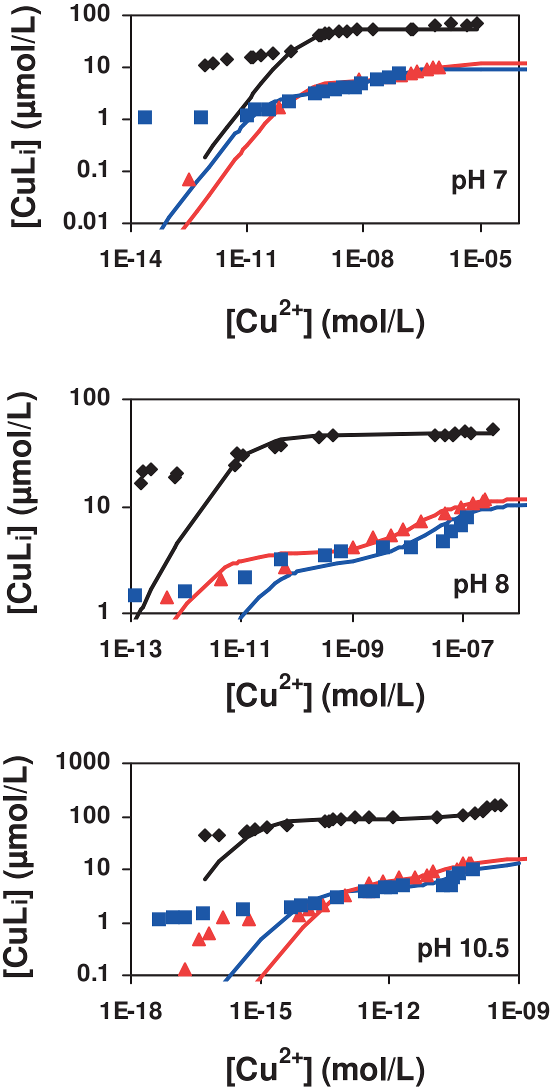


Figure 1. Measured isotherms of Cu binding to DOC in leachates from MSWI bottom ash samples BA2 (black diamonds), QUE1 (red triangles) and 1.5YR (blue squares). Data for sample QUE1 and 1.5YR were taken from Meima *et al.* (1999). The curves represent a two-site Langmuir isotherm fitted to the data (single site model for sample BA2 at pH 7.9 and 6.6). CuL_i indicates dissolved Cu bound to organic ligand L_i; Cu^{2+} indicates the free Cu^{2+} ion. It should be noted that, as discussed in the methods section, the isotherms have not been fitted to the data at the lower end of the isotherm.

Table 1 shows the measured parameters and ligand concentrations, affinity constants and site densities of the three bottom ash samples, calculated on the basis of a two-site Langmuir model (single site model for sample BA2 at pH 7.9 and 6.6). The calculated log K values for bottom ash sample BA2 are in good agreement with our earlier results (QUE1 and 1.5YR) for bottom ash samples from a different incinerator (Meima *et al.*, 1999). However, total ligand concentrations in leachates from BA2 are about one order of magnitude higher, consistent with the higher DOC concentrations of this sample.

Speciation calculations show that organic Cu complexation ranges from 82% to 100% of total dissolved Cu between pH 6.6 and 10.6. MINTEQA2 calculations show that the leaching of Cu from MSWI bottom ash is primarily controlled by the availability of the organic ligands, rather than by the available amount of copper in the bottom ash.

2.3.2 Chemical equilibrium modelling of Cu binding to aliphatic and aromatic acids

Ferrari *et al.* (2002) has identified several aliphatic and aromatic acids in MSWI bottom ash leachates, which are capable of binding Cu. In order to investigate whether these identified organic ligands can explain our CLE-SE titration data, we have calculated Cu binding isotherms for each of these acids at the measured DOC concentration (i.e. for each isotherm assuming that DOC consisted only of that particular organic acid).

Figure 2 shows the measured Cu-binding isotherms, obtained from the CLE-SE measurements of samples BA2, QUE1 and 1.5YR at the native pH of the leachate and isotherms calculated using MINTEQA2 on the basis of the identified acids. Clearly, the aliphatic and aromatic acids under-predict the measured Cu-binding to DOC by several orders of magnitude for each of the three samples. Therefore, other as yet unidentified organic ligands in the DOC pool must be responsible for the measured Cu complexation and the resulting facilitated leaching from MSWI bottom ash.

Table 1. Results from CLE-SE analysis of leachates from MSWI bottom ash samples BA2, QUE1 and 1.5YR at three pH values. Data for sample QUE1 and 1.5YR were taken from Meima *et al.* (1999). $[L_{1,2}]_T$ is the calculated total ligand concentration (expressed as μmol Cu/L) for the binding sites, log $K_{cond(1,2)}$ is the calculated conditional affinity constant and $S_{1,2}$ is the calculated site density (expressed as mol Cu/kg C). These parameters are calculated by fitting a two-site Langmuir model to the isotherm data shown in Figure 1.

Sample	**BA2**			**QUE1**			**1.5YR**		
pH	**10.6**	**7.9**	**6.6**	**10.5**	**8.2**	**7.1**	**10.2**	**8.2**	**7.5**
Calculated ligand concentrations and affinity constants based on a 2-site Langmuir model									
$[L_1]_T$ (μmol/L)	89	47	55	6	4	6	4	3	3
$[L_2]_T$ (μmol/L)	199	*	*	10	8	6	9	7	6
log $K_{cond(1)}$	15.2	11.2	9.6	13.2	11.7	9.8	14.1	10.6	10.6
log $K_{cond(2)}$	9.2	*	*	10.4	7.6	6.6	10.3	7.4	7.5
n	21	22	22	22	14	12	17	15	15
Direct measurements									
$[Cu]_T$ (μmol/L)	109.0	57.6	61.8	6.3	5.8	9.1	6.2	3.5	5.9
[DOC] (mg C/L)	290	206	225	89	103	109	26	15	16
Calculated site densities of DOC based on a two-site Langmuir model									
S_1 (mol/kg C)	0.31	0.17	0.23	0.07	0.04	0.05	0.15	0.20	0.21
S_2 (mol/kg C)	0.69	*	*	0.11	0.08	0.06	0.34	0.49	0.39
Calculated Cu-speciation based on a two-site Langmuir model									
CuL_1 (%)	82	82	89	95	64	60	65	86	56
CuL_2 (%)	14	*	*	5	35	32	32	13	39
Inorganic Cu (%)	4	18	11	0	1	8	3	1	5
Total (%)	100	100	100	100	100	100	100	100	100

*Isotherms have been fitted to a single site Langmuir model (see text for further details).

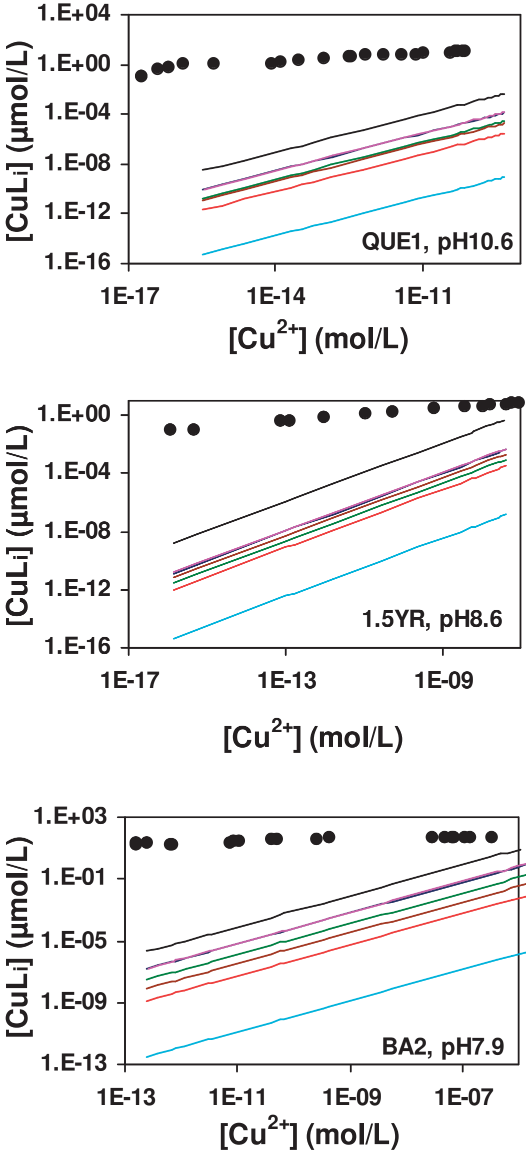


Figure 2. Measured (•) and calculated isotherms of copper binding to DOC in MSWI bottom ash leachates at their native pH. The calculated isotherms are based on identified aliphatic and aromatic acids in MSWI bottom ash by Ferrari *et al.* (2002). From top to bottom: oxalic acid (black), formic acid (pink), acetic acid (dark blue), benzoic acid (green), maleic acid (brown), lactic acid (red), and phthalic acid (light blue). Measured Cu-binding isotherms from samples QUE1 and 1.5YR are taken from Meima *et al.* (1999).

2.3.3 Molecular weight analysis of dissolved organic carbon by HPSEC

Figure 3 shows HPSEC chromatograms of the leachates of the three MSWI bottom ash samples, as well as that of a purified soil humic (HA) and fulvic (FA) acid. The leachates show a heterogeneous size distribution of the DOC macromolecules. The differences in peak heights are mainly related to DOC concentrations, which are higher for the samples QUE1 and BA2 than for the weathered bottom ash sample 1.5YR. The results clearly demonstrate that, in addition to a large contribution of relatively low molecular material (which elutes later from the SEC column), DOC in all bottom ash samples contains a fraction with the same retention time of 9.7 minutes as that of purified fulvic acid (Figure 3). Furthermore, Figure 3 shows that it is unlikely that this peak is related to HA, which elutes predominantly between 6 and 9 minutes. The main peak in the bottom ash leachates (at 10.3 minutes) represents the hydrophilic organic acids obtained from the IHSS extraction procedure (Thurman and Malcolm, 1981) that we use below to further characterise DOC (Table 2) and, more specifically, those identified by Ferrari *et al.* (2002).

The peak at around 12 minutes mainly represents the (UV absorbing) inorganic ions in the leachates (leachate retention time in the column is 12 minutes). These findings suggest that fulvic acid may be present in the leachates and are consistent with earlier findings of Pavasars (Pavasars, 1999) who concluded, based on adsorption of DOC on XAD-8 and XAD-4 columns, UV/VIS measurements and HPSEC analyses, that a high-molecular weight, possibly humic-like fraction is present in aqueous bottom ash extracts.

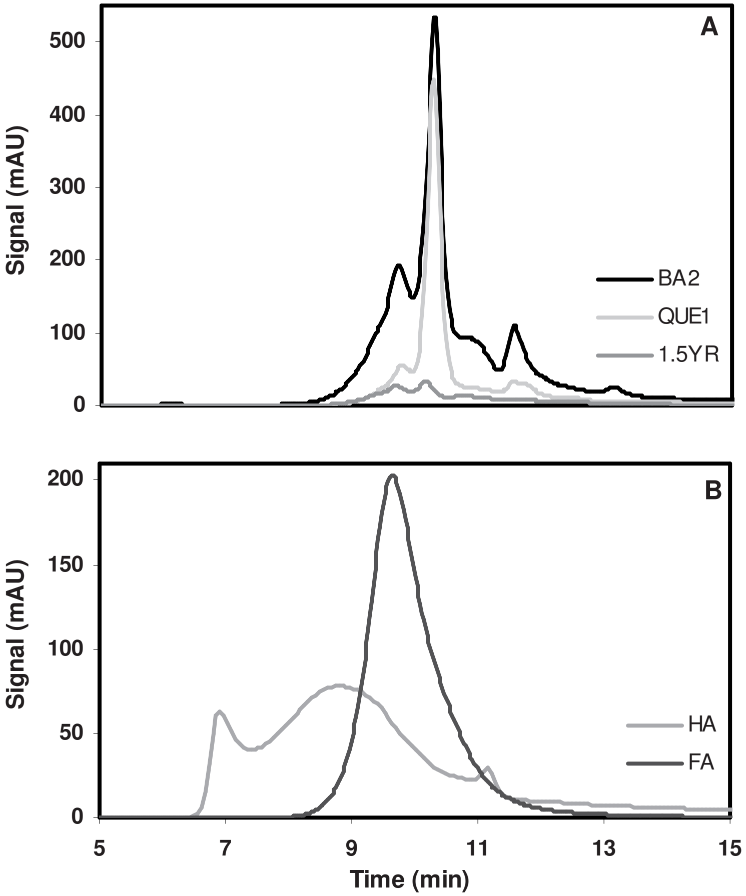


Figure 3. HPSEC chromatograms of different MSWI bottom ash leachates (A) and of a soil humic (HA) and fulvic (FA) acid (B), isolated and purified according to Thurman and Malcolm (1981). Sample QUE1 is a fresh bottom ash, whereas samples BA2 and 1.5YR are carbonated.

2.3.4 Extraction of humic and fulvic acids from MSWI bottom ash leachates

To identify and quantify the leachable fractions of humic acid (HA), fulvic acid (FA) and hydrophilic organic carbon (Hy), leaching tests of the bottom ash samples at their native pH and a liquid/solid (L/S) ratio of 5 L/kg were performed. The filtered (0.2 µm) leachates were subsequently subjected to the

IHSS extraction procedure (Thurman and Malcolm, 1981). The resulting characterisation of the leached organic carbon species is shown in Table 2.

It is clear that the organic carbon speciation is very similar for all samples. The DOC consists mainly of hydrophilic organic carbon, containing smaller organic acids such as those identified by Ferrari *et al.* (2002), with up to about 25% FA and minor amounts of HA. Pavasars (1999) estimated, based on XAD-8 extractions and HPSEC, that 23% of DOC in Swedish MSWI bottom ash leachates consisted of a high-molecular weight, possibly humic-like material. Ma *et al.* (2001) have studied the distribution of hydrophilic, fulvic and humic acids in both natural waters and wastewater. They found that in natural waters 54-68% of the DOC was FA, 14-29% HA and 9-30% Hy. Our leachate analyses are similar in that the relative concentration of FA (14-26% of the DOC) is much greater than that of HA (0.3-0.6%). Also similar to our observations, Ma *et al.* (2001) found for their wastewater sample that HA concentrations were extremely low and that the Hy fraction was dominant (Hy:FA:HA = 56:43:1, cf. Table 2). The purity of the FA ranges from 84-94% based on the sum of C, H, N, O and S analysis in the isolated fractions. Because of the very low yield of the HA extraction it was not possible to measure the elemental composition of these fractions.

Recent results from a parallel study (van Zomeren and Comans, 2003) indicate that relatively large amounts of HA and FA (200-400 mg HA/kg bottom ash and 400 mg FA/kg bottom ash) are present in the solid bottom ash matrices. These findings indicate that natural organic matter in these residues constitutes an important source for the long term leaching of reactive DOC and associated contaminants such as Cu.

Table 2. Carbon speciation in leachates (L/S=5, native pH) from MSWI bottom ash samples.

Sample	**pH**	**DOC (mg C/L)**	**HA (%DOC)**	**FA (%DOC)**	**Purity FA (%C,H,N,O,S)**	**Hy (%DOC)**
QUE1	10.39	87.2	0.3	16.9	94	82.8
1.5YR	8.63	15.2	0.6	14.3	84	85.1
BA2	7.88	214.1	0.5	25.6	94	73.9

2.3.5 Chemical equilibrium modelling of Cu binding to humic and fulvic acids

Based on the identified amounts of FA and HA in the bottom ash leachates (Table 2), we have tried to predict the Cu binding isotherms obtained by CLE-SE with the NICA-Donnan model for natural organic matter (Kinniburgh *et al.*, 1999). Figure 4 shows the CLE-SE measurements and the isotherms predicted by the NICA-Donnan model. The NICA-Donnan isotherms based on the measured concentrations of HA and FA in the leachates, are in much better agreement with the measurements than the isotherms based on aliphatic and aromatic acids (Figure 2). Considering that no parameters have been fitted to the data, the NICA-Donnan model describes the binding of Cu to DOC in the fresh bottom ash sample QUE1 very well, over most of the measured range of free Cu^{2+} concentrations and at each of the three pH-values. The model under-predicts the organic Cu complexation in the leachates from the carbonated bottom ash samples 1.5YR and BA2 by up to more than an order of magnitude. However, the slopes of the isotherms approximate the measurements much better than those of the previously identified aliphatic and aromatic acids (Figure 2).

It is also noteworthy that, except at pH 7.5 for sample 1.5YR, the NICA-Donnan model predicts the Cu binding to DOC in general adequately (i.e. well within one order of magnitude) at the original free Cu^{2+} concentrations in the leachates, indicated by the open squares in Figure 4. The deviation between model and data occurs particularly towards low Cu^{2+} concentrations. This part of the isotherm was obtained by stripping (i.e. desorbing) most of the originally DOC-bound Cu by the large added concentrations of the competing AcAc ligand, while the high end of the isotherm was obtained by addition of Cu^{2+} at relatively low AcAc concentrations. Possibly, this observation is related to slow desorption kinetics, although preliminary CLE-SE experiments with longer equilibration times (up to 24 hours) have shown no difference. Alternatively, the observed difference between model and data may be caused by deviating binding properties of the fulvic acids in the MSWI bottom ash leachates, relative to the generic properties derived by Milne *et al.* (2003) for natural fulvic acids.

The observation that the NICA-Donnan model describes the Cu binding to DOC much better in the leachates of fresh (QUE1) relative to carbonated (1.5YR and BA2) bottom ash, does not appear to be related to differences in the proportion of dissolved humic and fulvic acids (Table 2). We are presently isolating relatively large amounts of these humic substances from various fresh and aged MSWI bottom ash samples to investigate the possible variability in their binding properties. In addition, we cannot exclude at present that the large hydrophilic fraction of the DOC in bottom ash leachates, particularly from carbonated bottom ash, contains organic acids with a substantially larger Cu binding affinity than those that have been identified previously (Figure 2). Further research in this area is needed to fully resolve this issue. We emphasize, however, that the NICA-Donnan model with generic binding parameters for (natural) humic and fulvic acids already provides an adequate description of the DOC-enhanced leaching of Cu from MSWI bottom ash. It is also interesting to note at this point that the NICA-Donnan model does also closely predict our conditional binding constants log $K_{cond(1)}$ and log $K_{cond(2)}$, at the conditions of the CLE-SE experiments (Table 1); the differences are within 1.6 log units, except for log $K_{cond(1)}$ in sample 1.5 YR at pH 8.2 (2.3 log units). In addition, the site densities reported in Table 1 are also of the same order as the generic site densities that have been derived for FA (Milne *et al.*, 2003). We believe that this demonstrates the consistency between our earlier discrete 2-site approach and the NICA-Donnan model.

The results presented in Figure 4, strongly suggest that fulvic-acid like components present in MSWI bottom ash leachates are responsible for the observed enhanced Cu leaching from these residues. These findings enable the use of chemical speciation programs that include models and intrinsic parameters for metal binding to natural organic matter to predict Cu leaching from this widely produced incineration residue under variable environmental conditions (such as pH, ionic strength and concentrations of competing metals). Clearly, more research is needed to investigate the relative importance of HA and FA, and their specific binding properties, for heavy metal leaching from MSWI bottom ash world-wide. However, our results are generalised by the studies of Pavasars (1999) and Ferrari *et al.* (2002) on Swedish and Swiss bottom ash, respectively, in that high-molecular weight DOC components have been identified. As it is generally believed that humic substances are only slowly degradable (Pettersson *et al.*, 1994; Pettersson and Allard, 1991), further research to enhance the quality of MSWI bottom ash as a secondary building material should focus on the main sources of HA and FA in MSWI bottom ash and on their (thermal) decomposition during or after the incineration process. Results from laboratory experiments do indeed suggest that Cu leaching can be drastically reduced when bottom ash is subjected to a longer residence time in the incinerator (van der Sloot *et al.*, 2000).

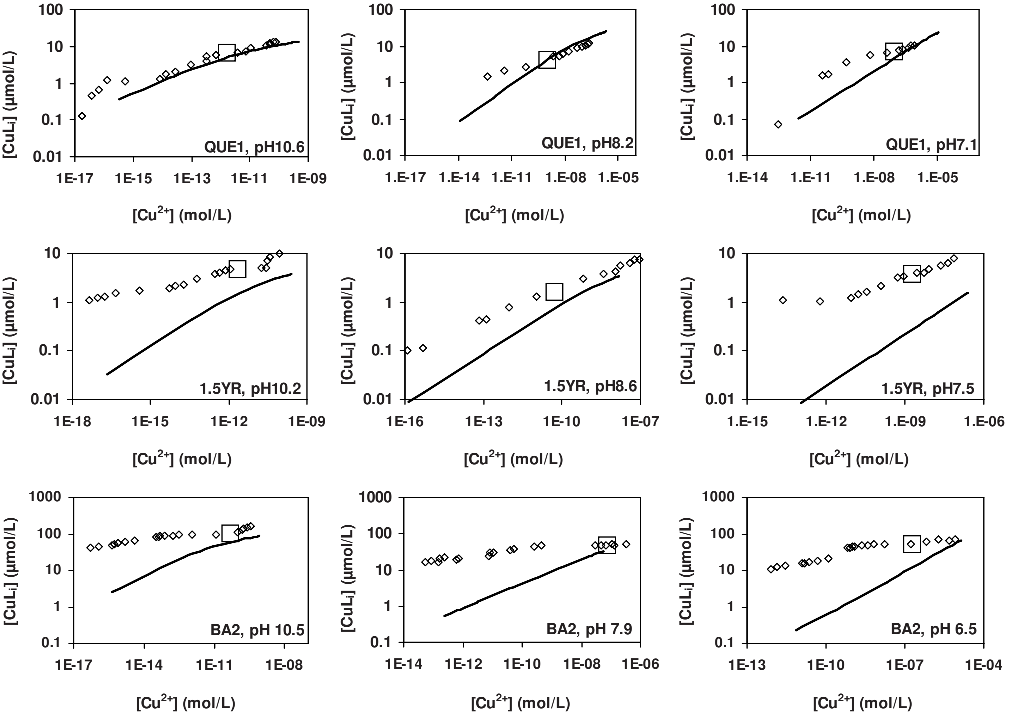


Figure 4. Measured isotherms (◇) and calculated isotherms based on the NICA-Donnan model and measured concentrations of humic and fulvic acids (line), for Cu binding to DOC from three MSWI bottom ash samples. The large open squares (□) approximate the conditions in the original leachates (minimum amount of AcAc and no added copper).

Acknowledgements

We thank Esther van der Weij-Zuiver for her careful work on the extraction of humic and fulvic acids. Joris J. Dijkstra is thanked for critically reading earlier versions of this manuscript and his assistance with the chemical equilibrium modelling. This work was partially funded by the Ministry of Spatial Planning, Housing and the Environment as part of the environmental research program of ECN.

References

Allison, J. D., Brown, D. S., and Novo-Gradac, K. J. *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: version 3.11 user's manual,* EPA/600/3-91/021, 1991.

Buffle, J., *Complexation reactions in aquatic systems; An analytical approach,* Ellis Horwood limited: Chicester, 1988, pp 1-692.

Chandler, A. J., Eighmy, T. T., Hartlen, J., Hjelmar, O., Kosson, D. S., Sawell, S. E., van der Sloot, H. A., Vehlow, J., *Municipal solid waste incinerator residues,* Elsevier: Amsterdam, 1997.

Comans, R. N. J., van der Sloot, H. A., and Bonouvrie, P. A. Geochemical reactions controlling the solubility of major and trace elements during leaching of municipal solid waste incinerator residues. (Municipal Waste Combustion Conference), 667. 1993. Williamsburg, V.A.

Croué, J. P., Benedetti, M. F., Violleau, D., Leenheer, J. A. Characterization and copper binding of humic and nonhumic organic matter isolated from the south platte river: evidence for the presence of nitrogenous binding site, *Environ. Sci. Technol.*, **2003**, *37*, 328-336.

Ferrari, S., Belevi, H., Baccini, P. Chemical speciation of carbon in municipal solid waste incinerator residues, *Waste Manage.*, **2002**, *22*, 303-314.

Hering, J. G., Morel, F. M. M. Humic acid complexation of calcium and copper, *Environ. Sci. Technol.*, **1988**, *22*, 1234-1237.

Johansson, I., Pavasars, I., Boren, H., Allard, B. Analysis of water leachable organic components in incineration residues, *International Journal of Environmental Analytical Chemistry*, **2000**, *78*, 305-313.

Johnson, C. A., Kersten, M., and Moore, C. Leaching behavior and solubility controlling solid phases of trace elements in municipal solid waste incinerator ash and cement stabilized solid wastes. (Proceedings of the international symposium on bulk 'inert' waste: An opportunity for use), 129-134. 1995. Proceedings of the international symposium on bulk 'inert' waste: An opportunity for use, Leeds.

Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K., Borkovec, M., Benedetti, M. F., Avena, M. J. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *Colloids Surf. A*, **1999**, *151*, 147-166.

Ma, H., Allen, H. E., Yin, Y. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent, *Water Res.*, **2001**, *35*, 985-996.

Mantoura, R. F. C., Riley, J. P. The use of gel filtration in the study of metal binding by humic acids and related compounds, *Anal. Chim. Acta*, **1975**, *78*, 193-200.

Meeussen, J. C. L. ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models, *Environ. Sci. Technol.*, **2003**, *37*, 1175-1182.

Meima, J. A., Comans, R. N. J. Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **1997**, *31*, 1269-1276.

Meima, J. A., Comans, R. N. J. The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering, *Appl. Geochem.*, **1999**, *14*, 159-171.

Meima, J. A., van Zomeren, A., Comans, R. N. J. Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates, *Environ. Sci. Technol.*, **1999**, *33*, 1424-1429.

Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances, *Environ. Sci. Technol.*, **2003**, *37*, 958-971.

Moffett, J. W., Zika, R. G. Solvent extraction of copper acetylacetonate in studies of copper (II) speciation in seawater, *Mar. Chem.*, **1987**, *21*, 301-313.

Pavasars, I. Characterisation of organic substances in waste materials under alkaline conditions. 1999. Ph.D. Dissertation, Linkopping university, Sweden.

Pettersson, C., Allard, B. Dating of groundwaters by 14C-analysis of dissolved humic substances. In *Humic substances in the aquatic and terrestrial environment*; Allard, B., Boren, H., Grimvall, A., Eds.; Springer: Heidelberg, 1991, pp 134-141.

Pettersson, C., Ephraim, J. H., Allard, B. On the composition and properties of humic substances isolated from deep groundwater and surface waters, *Org. Geochem.*, **1994**, *21*, 443-451.

Sillen, L. G., Martell, A. E., *Stability Constants of Metal-Ion Complexes,* The chemical society, Burlington House, W.1: London, 1964.

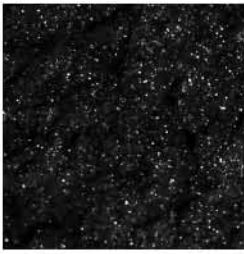
Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

van der Sloot, H. A., Comans, R. N. J., Eighmy, T. T., and Kosson, D. S. *Interpretation of MSWI residue leaching data in relation to utilization & disposal,* ECN-RX--92-051, 1992.

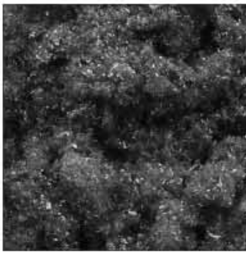
van der Sloot, H. A., Hoede, D., and van Zomeren, A. *Koper uitloging uit HVC bodemas in relatie tot de mate van uitbrand,* ECN-CX--00-136, 2000.

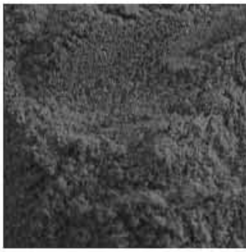
van Zomeren, A. and Comans, R. N. J. Speciation and characterisation of organic carbon in municipal solid waste incinerator (MSWI) bottom ash. Ortiz de Urbina, G. and Goumans, J. J. J. M. (5), 657-666. 2003. San Sebastian, Spain. Wascon 2003, Progress on the road to sustainability.

CHAPTER 3



DEVELOPMENT OF AN AUTOMATED SYSTEM FOR ISOLATION AND PURIFICATION OF HUMIC SUBSTANCES





Published in similar form as:
van Zomeren, A., van der Weij-Zuiver, E. and Comans, R.N.J., Development of an automated system for isolation and purification of humic substances, *Analytical and Bioanalytical Chemistry*, **2008**, 391, vol. 6, 2365-2370.

DEVELOPMENT OF AN AUTOMATED SYSTEM FOR ISOLATION AND PURIFICATION OF HUMIC SUBSTANCES

André van Zomeren[1]*, Esther van der Weij-Zuiver*[2] *and Rob N.J. Comans*[1,3]

Characterisation of humic substances (HS) in environmental samples generally involves labor-intensive and time-consuming isolation and purification procedures. In this paper, the development of an automated system for HS isolation and purification is described. The novelty of the developed system lies in the way the multiple liquids and columns used in the isolation/purification procedure are handled in both forward and back-elution mode by solenoid valves. The automated procedure significantly reduces the total throughput time needed, from 6–7 days to 48 h, and the amount of labor to obtain purified HS for further characterisation. Chemical characterisation of purified HS showed that results were in good agreement with previously published values for HS from a variety of sources, including the IHSS standard HS collection. It was also shown that the general properties of HS were consistent among the different source materials (soil, waste, aquatic) used in this study. The developed system greatly facilitates isolation and characterisation of HS and reduces the risk of potential (time-dependent) alteration of HS properties in the manual procedure.

---

[1] Energy Research Centre of The Netherlands.

[2] Chefaro Nederland B.V.

[3] Wageningen University.

3.1 Introduction

Natural organic matter (NOM) in the environment can be of plant, animal or microbial origin and may range from relatively fresh to highly decomposed and transformed. NOM plays an important role in, for example, soil properties such as cation exchange capacity, soil structure, water entry and retention, nutrient cycling, binding of heavy metals and organic micropollutants (Hayes and Swift, 1990; Swift, 1996). The study of these properties often requires isolation and purification of organic matter.

Currently, the International Humic Substances Society (IHSS) uses the adapted fractionation method of Aiken (Aiken, 1985), earlier described in detail by Thurman and Malcolm (Thurman and Malcolm, 1981), for the isolation and purification of humic- (HA) and fulvic acid (FA) standards from aqueous samples, and the method of Swift (Swift, 1996) for solid source materials. These methods are based on the precipitation of HA at pH 1 or 2 and the adsorption of HA and/or FA on the macroporous XAD-8 resin. Adsorbed HS are subsequently desorbed with 0.1 M NaOH and cations are removed by a cation exchange resin. The reader is referred to (Aiken, 1985; Leenheer, 1981; Swift, 1996; Thurman and Malcolm, 1981) for detailed descriptions of the isolation methods. Although these procedures are well established and widely used by scientists, they all share the disadvantage of being very laborious, particularly due to the manual handling of the multiple liquids and columns that are required.

This paper describes the development of an automated system to perform isolation and purification of HS, especially from solid source materials. The setup of the system is very flexible and easy to modify, which allows methods that involve HA separation after prior preconcentration and purification (e.g. Thurman and Malcolm (Thurman and Malcolm, 1981) and Leenheer (Leenheer, 1981)). However, these methods then involve an intermediate HA separation by acidification and centrifugation. The novelty of the method lies in the automated handling of the multiple liquids and columns, required in the isolation/purification procedure, in both forward and back elution mode. The particular experimental set up allows the procedure to be executed with only a single pump and flowmeter. Our main objective for automation of the IHSS procedure was to save a significant amount of labour and total throughput time in the performance of HS isolation and purification. By automating the procedure, we also aim for a better standardisation of the HS isolation and purification methods.

3.2 Materials and methods

3.2.1 Reagents

All reagents used were of analytical grade quality. Double demineralised water (nanopure) was used for subsequent preparation of reagents. Every new batch of XAD-8 (Amberlite) was first cleaned to remove organic impurities by five consecutive 24 hour extractions with 0.1 M HCl and 0.1 M NaOH. Fine floating particles were removed by decantation.

The XAD-8 and the cation exchange resin (Biorad AG-MP-50, 100-200 mesh) resin were thoroughly cleaned by soxhlet extractions with acetonitrile and methanol, each for 24 hours. The cleaned resins were stored in methanol until use.

3.2.2 Samples

The automated procedure was performed (according to Swift, 1996) on a peat (Devoke UK), a compost sample, a landfill waste mixture and a sample of municipal solid waste incineration (MSWI) bottom ash. Moreover, HS from four aquatic samples, a landfill leachate, influent and effluent water from a landfill water treatment plant and water from a DOC rich pond in a nature reserve (Zwanenwater, NL), were isolated and purified according to Thurman and Malcolm (Thurman and Malcolm, 1981). All purified HS (except from MSWI bottom ash) have also been characterised by van Zomeren and Comans (2007).

3.2.3 Hardware

The experimental setup of the procedure is outlined in Figure 1. The lines in the scheme represent Teflon tubing (FEP, 1/8” O.D., 1/16” I.D.), connected to several 2-way (Takasago, type, 24 V DC) and 3-way solenoid valves (Furon, model 1101493, 24 V DC) by Omnifit PEEK fitting nuts (part 2222) and grippers (part 2312). All valves and fraction collector positions of the system were named and used in the database (see Software) to specify their function (see Table 1 and Table 2). The position of the fraction collector is denoted with F1-10 (Fraction).The 2-way valves that control the liquid to be pumped were named I1-12 (input). The system contains two blocks (Takasago, MTV-2-6NMFG-1, 24 V DC) with 6 solenoid valves (manifolds). Additionally, two manifolds (Takasago, MTV-2-5NMFG-1, 24 V DC) with 5 valves on top and below the columns were named CA1-5 and CB1-5 (Column), respectively. The system was developed to perform the isolation and purification procedures of Swift (1996), Thurman and Malcolm (1981) and Leenheer (1981). Therefore, the connections and liquids for all of these methods are addressed in Figure 1 (e.g. liquid inputs I8, I9 and I12).

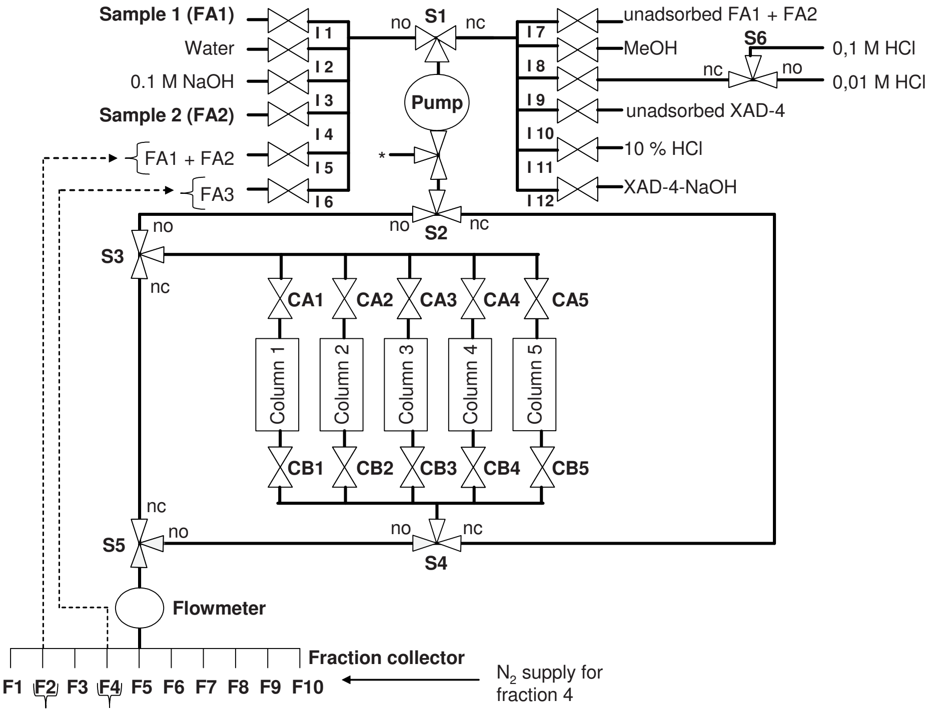


Figure 1. Schematic representation of the automated isolation and purification system. * marks the manual option (Omnifit manual 3-way connector, part: 1102) to de-aerate the tubing and the pump before each experiment. Dashed lines mark connections from fractions that are first produced (F2 and F4) in the procedure and that are later used in subsequent elution steps (FA1+FA2 and FA3). N_2 gas was supplied to the eluate FA3 (fraction 4) until it was purified by the cation exchange resin. Sample vessels F2 (containing 6 M HCl and concentrated HF) and F4 were placed on a magnetic stirrer with a Teflon coated magnet to homogenise the solution.

The six 3-way valves (S1-6, Switch) were used to reverse the flow to perform back elution during recovery of the purified HS. The normally open (no) and normally closed (nc) position on the valves is noted in Figure 1. Glass columns (Omnifit 2.5 cm I.D.* 40 cm for XAD-8 and Omnifit 1.5 cm I.D.*40 cm for AG-MP-50) were used and the adjustable endpieces (6265NS and 6465NS) were equipped with 100 µm PTFE frits (6243NS).

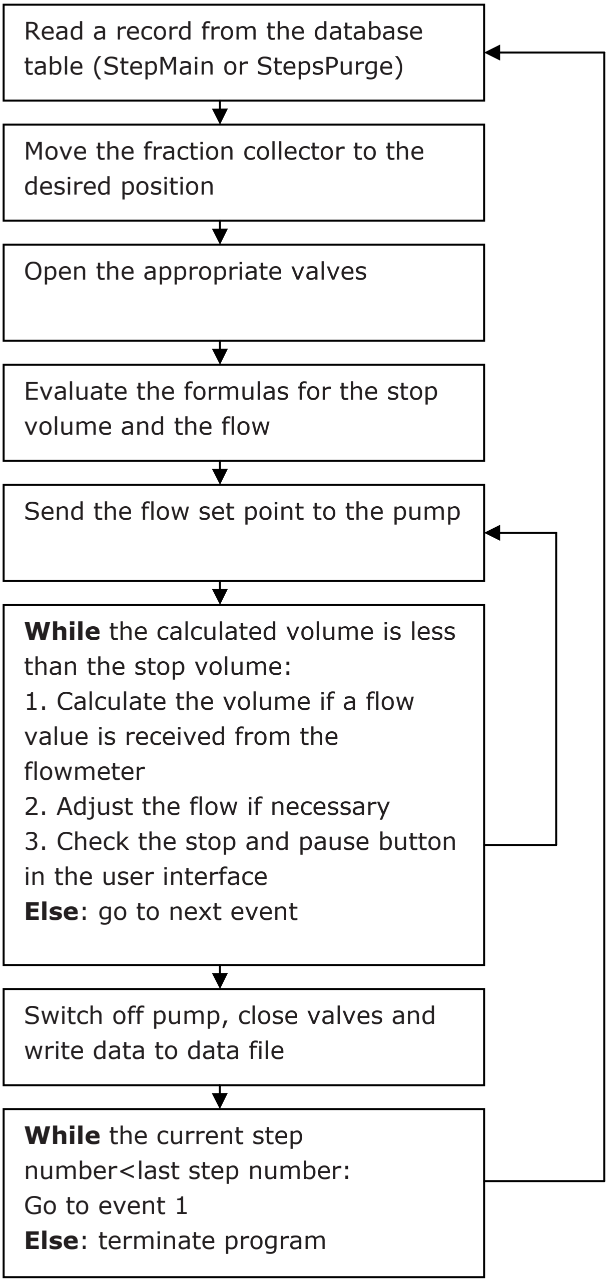
All liquids were pumped (ProMinent Verder B.V., Type: GALA 1602TTT000UA-002000) after the appropriate set of valves was opened (see Table 1 and Table 2). To reduce pressure pulses from the pump, either a silicone tubing (0.7 mm I.D., 1 mm O.D.) or a special crimped flexible PTFE tubing (3 mm I.D., 5.5 mm O.D., Polyfluor, NL) can be installed behind the pump. The flow was measured with a liquid flowmeter (G.J.C. Instruments, model 5025500) and adjusted to the set point value by the software. A home made rotating fraction collector collected the eluates in the various bottles using a stepper motor (Astrosyn, Y129, art. 586389, 12 V DC, 0.16 A). The home position (fraction number 1) was determined with an inductive sensor (Balluff, BES 516-3005-E4-C-PU-05).

Table 1. Procedure statements used in the isolation and purification procedure of Swift (1996). The steps are executed sequentially until the stop volume is reached. Sample (FA1/FA2) and column volumes (CV<n>) are entered in the user interface, the flow (FL<n>) is derived from that (default: 5 CV/hr). Column number, fraction number and deviation in the stop volume (%) are given per step.

Step	Description	Stop Volume	Column	Fraction	Flow	Deviation
1	Pumping water through column 4 (i2)	20*cv4	4	3	fl4	5
2	Pumping 10% HCl through column 4 (i11)	15*cv4	4	3	0.6*fl4	5
3	Pumping water through column 1 (i2)	20*cv1	1	3	fl1	5
4	Pumping water through column 2 (i2)	20*cv2	2	3	fl2	5
5	Pumping water through column 3 (i2)	20*cv3	3	3	fl3	5
6	Pumping 0.01 M HCl through column 1 (i8)	1.5*cv1	1	3	fl1	5
7	Pumping FA1 through column 1 (i1)	0.95*FA1	1	1	fl1	5
8	Pumping 0.65 columnvolumes of water through column 1 (i2)	0.65*cv1	1	1	fl1	5
9	Back-eluting with 1.5 columnvolume of 0.1 M NaOH (i3)	1.5*cv1	1	2	fl1	5
10	Back-eluting with 3.5 columnvolumes of water (i2)	3.5*cv1	1	2	fl1	5
11	Pumping 0.01 M HCl through column 2 (i8)	1.5*cv2	2	3	fl2	5
12	Pumping FA2 through column 2 (i4)	0.98*FA2	2	6	fl2	5
13	Pumping 0.65 columnvolumes of water through column 2 (i2)	0.65*cv2	2	6	fl2	5
14	Back-eluting with 1.5 columnvolume 0.1 M NaOH (i3)	1.5*cv2	2	2	fl2	5
15	Back-eluting with 3.5 columnvolumes of water (i2)	3.5*cv2	2	2	fl2	5
16	Pumping 0.01 M HCl through column 3 (i8)	1.5*cv3	3	3	fl3	5
17	Pumping FA1+FA2 through column 3 (i5)	4.9*(cv1+cv2)	3	1	fl3	5
18	Pumping 0.65 columnvolumes of water through column 3 (i2)	0.65*cv3	3	1	fl3	5
19	Back-eluting with 1.5 columnvolume 0.1 M NaOH (i3)	1.5*cv3	3	4	fl3	5
20	Back-eluting with 3.5 columnvolumes of water (i2)	3.5*cv3	3	4	fl3	5
21	Pumping water through column 4 (i2)	20*cv4	4	3	fl4	5
22	Pumping FA3 through column 4 (i6)	4.9*(cv3)	4	5	fl4	5
23	Pumping 2 columnvolumes of water through column 4 (i2)	2*cv4	4	5	fl4	5

Table 2. Modbus addresses and status of the solenoid valves in each step of the isolation and purification procedure according to Swift (1996). The grey cells indicate that the appropriate valve is opened during the specific step in the procedure.

Modbus Address	22	23	24	25	26	27	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Step/Valve	S1	S2	S3	S4	S5	S6	I1	I2	I3	I4	I5	I6	I7	I8	I9	I10	I11	I12	CA1	CA2	CA3	CA4	CA5	CB1	CB2	CB3	CB4	CB5
1								▨														▨					▨	
2	▨																▨					▨					▨	
3								▨											▨					▨				
4								▨												▨					▨			
5								▨													▨					▨		
6	▨														▨				▨					▨				
7							▨												▨					▨				
8								▨											▨					▨				
9		▨	▨	▨	▨				▨										▨					▨				
10		▨	▨	▨	▨			▨											▨					▨				
11	▨														▨					▨					▨			
12										▨										▨					▨			
13								▨												▨					▨			
14		▨	▨	▨	▨				▨											▨					▨			
15		▨	▨	▨	▨			▨												▨					▨			
16	▨														▨						▨					▨		
17											▨										▨					▨		
18								▨													▨					▨		
19		▨	▨	▨	▨				▨												▨					▨		
20		▨	▨	▨	▨			▨													▨					▨		
21								▨														▨					▨	
22												▨										▨					▨	
23								▨														▨					▨	



Read a record from the database table (StepMain or StepsPurge)

Move the fraction collector to the desired position

Open the appropriate valves

Evaluate the formulas for the stop volume and the flow

Send the flow set point to the pump

While the calculated volume is less than the stop volume:
1. Calculate the volume if a flow value is received from the flowmeter
2. Adjust the flow if necessary
3. Check the stop and pause button in the user interface
Else: go to next event

Switch off pump, close valves and write data to data file

While the current step number<last step number:
Go to event 1
Else: terminate program

Figure 2. Flow diagram showing the sequence of events during the execution of a typical experiment. The data used in the sequence are read from Table 1. The flow is adjusted by addition or subtraction of the offset in the flow (set point flow – actual flow). The experiment can be stopped or paused in the user interface at any time during the experiment.

3.2.4 Communications

The data I/O system contains several modules (Wago) for control of the valves, pump, inductive sensor and stepper motor. All modules and their functions are specified in Table S1, the connections are shown in Figure S1. The I/O modules were connected to the fieldbus network system (Modbus/RS232 communication) by a fieldbus controller (750-814), which was connected to COM1 of the PC. The second serial port of the PC (COM2) was used to communicate with the liquid flowmeter (RS232).

3.2.5 Software

The software was developed to control the pump, valves, flow meter and fraction collector and includes a user interface to specify experiments. During the experiment, the current status of each step is displayed and the user is allowed to stop or pause the experiment. Liquid volumes, elapsed time, flow and experiment set points are written to a data file. A Flow diagram showing the sequence of events during the execution of a typical experiment is shown in Figure 2. The software can be obtained from the authors at no charge.

The experimental configuration, procedure definitions (Table 1) and Modbus protocol register addresses (Table 2) were stored in a MS Access database.

3.2.6 Elemental analysis of purified HS

The elemental composition (CHNO) of the purified HS (after drying at 110 ^{o}C) was analyzed with a Carlo Erba FLASH EA 1112 element analyzer. Elemental S was determined by ICP-AES after digestion in $HNO_3/HClO_4$. The water content of the HS was determined separately on ‘as stored’ samples by a Karl Fischer titration. The ash content was determined by subtraction of the total C, H, N, O and S content from 100%.

3.3 Results and discussion

3.3.1 Performance characteristics of the automated procedure

The total throughput time of the automated system is about 48 hours when a sample is isolated according to Swift (1996). Since the automated procedure also continues during the night, the purification process is finished after two working days. It is obvious that a significant additional amount of time is saved on checking/adjusting the experimental progress. It is noted that time saving only occurs in the column operation procedure itself, since the several sample extractions (acid and base) before the column procedure and the subsequent freeze drying of the obtained FA product are identical to the manual procedure.

Without the intention to compare specifically with the manual procedure, we have tested the accuracy of the purified FA amounts in a duplicate isolation experiment with the compost sample. It was found that the differences were within 5% (3701 and 3586 mg FA/kg), suggesting an excellent experimental performance.

Results of the automated procedure are in good agreement with those obtained by a recently developed rapid batch procedure for quantification of HS (van Zomeren and Comans, 2007). The recovery of HA and FA was found to be dependent on the extraction conditions, in particular pH, HS concentration and resin loading. Since these conditions do not differ between the manual and automated procedure, the HS recovery of both procedures will be identical. Moreover, automation of the isolation procedure also overcomes practical problems in the planning of the experimental work. When the IHSS method (Swift, 1996) is performed manually, the total throughput time is about 6-7 days. Therefore, it is almost inevitable that the semi-purified HS are subjected to prolonged standing in acid or base. It has been found that FA storage in acidic solutions may induce polymerisation, whereas storage in alkaline solutions can also lead to significant alteration of the organic matter characteristics (Stevenson, 1982). In addition, adsorbed HS might remain on the XAD-8 resin overnight before being desorbed. This is also unwanted because of resin bleeding (Aiken, 1988; Malcolm, 1991), that will be higher at increasing contact times. Therefore, we suggest that the original properties of FA are better retained by the new automated system.

3.3.2 Practical considerations

Before the experiment, air is manually removed from the tubing with a syringe (at point * in Figure 1) and by bypassing the columns with a manually operated 3-way valve. When running experiments at flow rates above about 10 mL/min, degassing the demineralised water in an ultrasonic water bath is recommended.

The first purified alkaline FA extract (steps 9, 10, 14 and 15 in Table 1) is immediately acidified with 6 M HCl (added manually to bottle F2 before start of the procedure) to prevent possible auto-oxidation of the alkaline FA extract. Concentrated HF can be applied to reduce the ash content of the FA, yet there is still debate about its effects on the properties of purified FA (Stevenson, 1982). To prevent possible damage of the flowmeter (which contains a glass measuring tube), concentrated HF is added by a home made semi-floating vessel which is designed such that the HF is added after about half of the total eluted volume has entered the collection bottle.

3.3.3 Chemical characterisation of purified HS

Relevant properties of the samples that have been isolated and purified with the new automated procedure are summarised in Table 3. These results are generally in good agreement with other published values for HS from a variety of sources, including standard HS from the IHSS (Chin *et al.*, 1994; Ma *et al.*, 2001; Steelink, 1985). Given the heterogeneous nature of HS, we conclude that the automated procedure provides purified HS fractions that are comparable to those obtained with the manual procedure. In addition, the results in Table 3 show that the general properties of HA and FA are consistent among the different (soil, waste, aquatic) source materials.

Table 3. Chemical composition (based on dry matter and ash free basis) in %w/w and UV/VIS characteristics of isolated and purified HA and FA from various sources.

Sample	ε [a] (L(mole C)$^{-1}$cm^{-1})	Aromaticity[b] (%)	E4/E6	C (%)	O (%)	H (%)	N (%)	S (%)	sum CHNOS	H_2O (%)	Ash (%)	O/C[c]	H/C[c]
Compost HA	532.2	33.3	6.9	56.0	30.9	5.1	7.5	<0.5	99.5	8.5	7.4	0.41	1.10
Compost FA	31.6	8.3	na	53.8	34.8	5.1	5.0	<0.5	98.6	5.5	11.7	0.49	1.14
Peat HA	390.8	26.3	5.2	55.3	34.8	5.9	3.8	<0.1	99.8	6.8	4.5	0.47	1.27
Peat FA	381.1	25.8	16.0[d]	52.9	39.6	4.8	1.5	<0.1	98.9	9.0	10.3	0.56	1.10
Landfill waste HA	426.5	28.1	16.0[d]	56.2	30.7	6.0	5.5	1.5	99.9	4.4	2.4	0.41	1.28
Landfill waste FA	285.5	21.0	6.3	54.6	35.5	5.3	2.2	1.8	99.3	8.5	7.7	0.49	1.16
MSWI bottom ash HA	na	na	na	64.4	21.6	7.0	6.2	na	99.3	8.9	8.3	0.25	1.31
MSWI bottom ash FA	na	na	na	53.3	38.3	5.3	3.1	na	99.9	8.5	3.1	0.54	1.18
Effluent HA	348.4	24.2	17.3[d]	56.4	31.2	5.5	5.4	na	98.5	9.9	12.2	0.41	1.17
Effluent FA	255.6	19.5	na	55.7	34.6	5.8	2.0	1.5	99.5	5.8	6.0	0.47	1.24
Influent HA	272.7	20.4	9.5	58.9	28.4	6.0	3.7	2.3	99.4	5.8	6.7	0.36	1.23
Influent FA	168.8	15.2	na	59.6	30.4	6.5	1.4	1.7	99.6	6.5	5.3	0.38	1.31
Leachate HA	318.3	22.7	6.3	na	na	na	na	na	na	na	na	na	na
Leachate FA	151.1	14.3	na	57.6	32.1	6.3	0.9	2.7	99.6	7.2	5.1	0.42	1.31
Zwanenwater HA	na	na	na	53.5	37.7	4.5	2.7	1.5	99.9	7.9	3.0	0.53	1.01
Zwanenwater FA	na	na	na	52.7	40.0	4.3	1.5	1.4	99.8	7.9	3.4	0.57	0.98

[a] Measured at 280 nm, based on the molar mass of carbon. [b] Based on UV absorption at 280 nm, according to Chin *et al.* (1994).
[c] atomic ratio. [d] Relatively high ratio due to very low absorption at 665nm.

3.4 Conclusions

The presented automated system greatly facilitates the isolation and characterisation of HS. The system significantly reduces the total needed throughput time, from 6-7 days to 48 hours, and also the amount of labor to obtain purified HS for further characterisation. The properties of purified HS obtained with the automated procedure are comparable to published values for HS from a variety of sources, including standard HS from the IHSS. Our results also show that the general properties of HA and FA are consistent among the different (soil, waste, aquatic) source materials used in this study. Automation of the isolation and purification procedure reduces the risk of alterations in HS properties resulting from potentially prolonged standing of HS in acid and/or base or effects from resin bleeding. Therefore, it is concluded that the presented automated procedure allows for a better standardisation of HS isolation and purification methods because of the standard operating protocol facilitated by the software.

Acknowledgements

D. Hoede, F. Kuijper, R. de Moel, R. van Rossum and T. Schrijver are thanked for their significant technical contributions and J.P. Pinheiro for critically reading earlier versions of the manuscript. This work was partly funded by the Ministry of Spatial Planning, Housing and the Environment as part of ECN's environmental research program.

References

Aiken, G. R. Isolation and concentration techniques for aquatic humic substances. In *Humic substances in soil, sediment and water: geochemistry, isolation and characterization*; Aiken, G. R., Mc Knight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1985, pp 363-385.

Aiken, G. R. A critical evaluation of the use of macroporous resins for the isolation of aquatic humic substances. In *Humic substances and their role in the environment*; Frimmel, F. H., Christman, R. F., Eds.; John Wiley & Sons: New York, 1988, pp 15-28.

Chin, Y. P., Aiken, G. R., O'Loughlin, E. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances, *Environ. Sci. Technol.*, **1994**, *28*, 1853-1858.

Hayes, M. H. B., Swift, R. S. Genesis, isolation, composition and structures of soil humic substances. In *Soil colloids and their associations in aggregates*; de Boodt, M. F., Ed.; Plenum Press: New York, 1990, pp 245-305.

Leenheer, J. A. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, *Environ. Sci. Technol.*, **1981**, *15*, 578-587.

Ma, H., Allen, H. E., Yin, Y. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent, *Water Res.*, **2001**, *35*, 985-996.

Malcolm, R. L. Factors to be considered in the isolation and characterization of aquatic humic substances. In *Humic substances in the aquatic and terrestrial environment*; Boren, H., Allard, B., Eds.; Wiley: London, 1991, pp 369-391.

Steelink, C. Implications of elemental characteristics of humic substances. In *Humic substances in soil, sediment, and water; geochemistry, isolation, and characterization*; Aiken, G. R., Mc Knight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley & Sons: New York, 1985, pp 457-476.

Stevenson, F. J., *Humus chemistry. Genesis, composition, reactions,* John Wiley & Sons: New York, 1982, pp 1-443.

Swift, R. S. Organic matter characterization. In *Methods of soil analysis. Part 3. Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996, pp 1011-1069.

Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

van Zomeren, A., Comans, R. N. J. Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch procedure, *Environ. Sci. Technol.*, **2007**, *41*, 6755-6761.

SUPPORTING INFORMATION

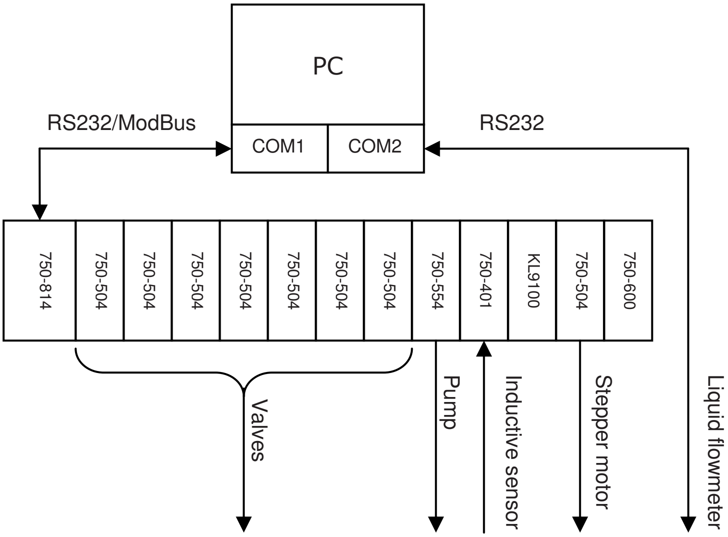
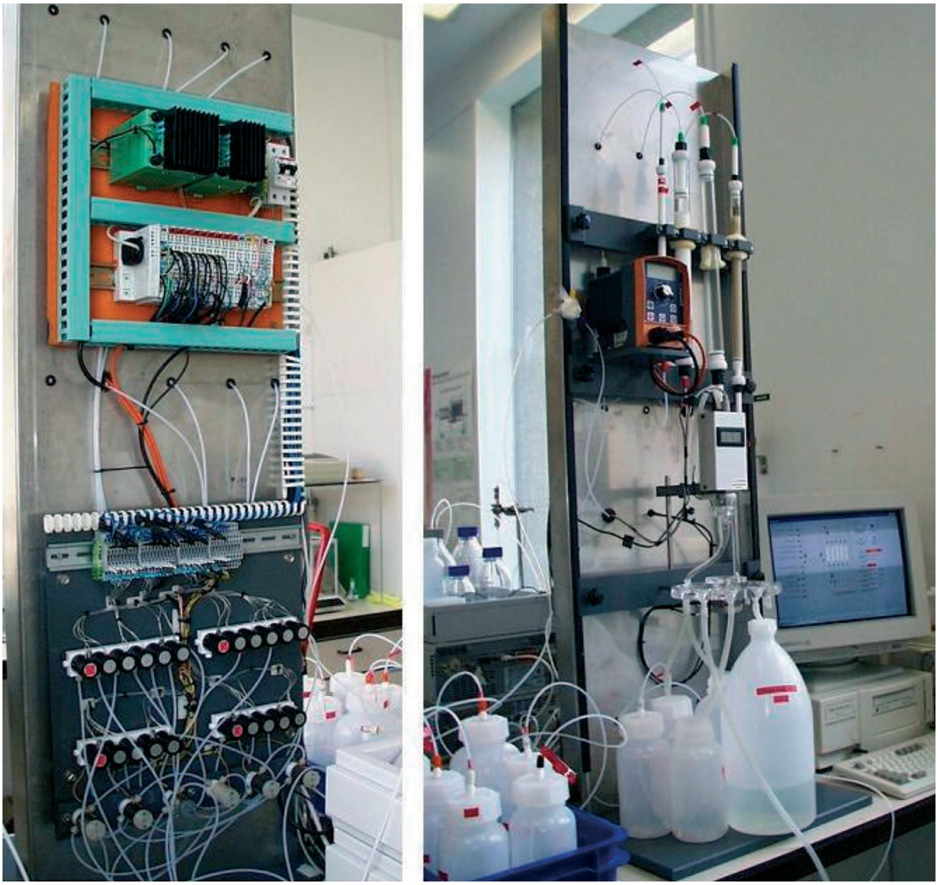


Figure S1. Hardware configuration of the automated isolation and purification system

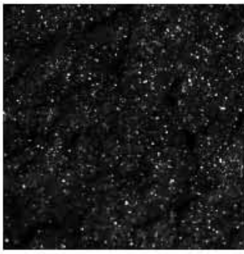
Table S1. Specifications of the data I/O system used in the automated isolation procedure

# of components	**Name**	**Type**	**Function**
1	Modbus fieldbus coupler	750-814	Connects WAGO-I/O-SYSTEM as slave to MODBUS fieldbus.
7	Digital output module	750-504	Valve control
1	Digital output module	750-504	Stepper motor control
1	Digital input module	750-401	Inductive sensor control
1	Analog output module (4-20 mA)	750-554	Pump control
1	Voltage supply terminal (Beckhoff)	KL9100	General power supply
1	End module	750-600	Completes internal I/O data circuit

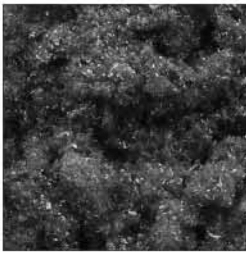
Photograph of the rear (left) and front (right) of the automated system for isolation and purification of humic substances.

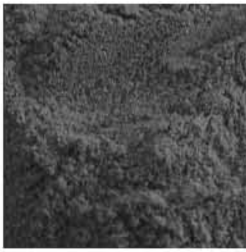


CHAPTER 4



MEASUREMENT OF HUMIC AND FULVIC ACID CONCENTRATIONS AND DISSOLUTION PROPERTIES BY A RAPID BATCH PROCEDURE





Published in similar form as:

van Zomeren, A. and Comans, R.N.J., Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch method, *Environmental Science & Technology*, **2007**, 41, 6755-6761. Reproduced with permission.

MEASUREMENT OF HUMIC AND FULVIC ACID CONCENTRATIONS AND DISSOLUTION PROPERTIES BY A RAPID BATCH PROCEDURE

André van Zomeren[1] *and Rob N.J. Comans*[1,2]

Although humic substances (HS) strongly facilitate the transport of metals and hydrophobic organic contaminants in environmental systems, their measurement is hampered by the time-consuming nature of currently available methods for their isolation and purification. We present and apply a new rapid batch method to measure humic (HA) and fulvic (FA) acid concentrations and dissolution properties in both solid and aqueous samples. The method is compared with the conventional procedures and is shown to substantially facilitate HS concentration measurements, particularly for applications such as geochemical modelling where HS purification is not required. The new method can be performed within 1.5-4 hours per sample and multiple samples can be processed simultaneously, while the conventional procedures typically require approximately 40 hours for a single sample. In addition, specific dissolution properties of HS are identified and are consistent with recent views on the molecular structure of HS that emphasize molecular interactions of smaller entities over distinct macromolecular components. Because the principles of the new method are essentially the same as those of generally accepted conventional procedures, the identified HA and FA properties are of general importance for the interpretation of the environmental occurrence and behaviour of HS.

---

[1] Energy Research Centre of The Netherlands.

[2] Wageningen University.

4.1 Introduction

The mobility of contaminants in natural and waste environments is strongly influenced by adsorption to humic (HA) and fulvic (FA) acids (Burkhard, 2000; Milne *et al.*, 2003). Understanding and modelling the interactions between contaminants and humic substances (HS) is of crucial importance for environmental risk assessment, as the release of heavy metals and hydrophobic organic contaminants can be enhanced by orders of magnitude due to HS complexation.

Recently, "generic" binding constants have been developed (Milne *et al.*, 2003) to describe the binding of a wide range of metals to HS by the thermodynamically consistent semi-empirical NICA-Donnan model (Kinniburgh *et al.*, 1999). This model has been successfully applied to describe the speciation of metals in soils (Dijkstra *et al.*, 2004; Weng *et al.*, 2003) and waste materials (Dijkstra *et al.*, 2006; van Zomeren and Comans, 2004). Similarly, partition coefficients have been compiled for hydrophobic organic contaminants between DOC, HA, FA and water (Burkhard, 2000). Because such models require HA and/or FA concentrations as input, the experimental characterisation and quantification of HS in natural and contaminated systems is needed.

Humic substances are operationally defined by specific isolation procedures, as discussed in detail by Stevenson (1982). This operational definition inevitably makes HA and FA quantification dependent on the extraction procedure rather than an intrinsic property of the HS. Therefore, it is likely that specific conditions in the isolation procedure (that affect the chemical behaviour of HS) can change their classification in terms of HA and FA. Nevertheless, numerous methods have been developed for the isolation, purification and quantification of HS (Aiken, 1985; Hayes, 1985; Leenheer, 1981; Swift, 1996; Thurman and Malcolm, 1981). Currently, the International Humic Substances Society (IHSS) uses the adapted extraction scheme of Aiken (1985), earlier described in detail by Thurman and Malcolm (1981), for the isolation and purification of HA and FA from aqueous samples, and the method of Swift (1996) for solid materials. Both procedures are widely used by scientists but are laborious, and are primarily aimed at isolating and purifying sufficient amounts of HA and FA for characterisation studies. However, in many studies, such as in geochemical modelling of contaminant mobility or carbon cycling in aquatic systems, knowledge of only the HA and FA *concentrations* in the solid material and/or solution is required. The current isolation and purification procedures are too elaborate to allow frequent measurements for these purposes.

In addition to isolation methods, spectroscopic techniques are being used to analyse HS, which are particularly suitable for characterisation of the chemical and molecular composition. However, quantitative analysis of specific HS subfractions in various environments is limited by the variable relationships between spectroscopic properties and the carbon content of these subfractions (Stevenson, 1982).

Our goal was to develop a rapid batch procedure to quantify HA and FA concentrations in both aquatic samples and solid materials based on the widely accepted procedures described in Thurman and Malcolm (1981) and Swift (1996), respectively. In addition, specific dissolution properties of HS are identified that have general relevance for the environmental behaviour of HS. These new findings are interpreted in terms of recent views on the molecular structure of HS.

Models for metal complexation with HA and FA, such as the NICA-Donnan model (Kinniburgh *et al.*, 1999) and Model VI (Tipping, 1998), generally rely on parameters obtained from experiments with HA and FA as isolated by the methods of Thurman and Malcolm (1981) and Swift (1996), supporting the choice of these conventional isolation procedures as the basis for the rapid batch method. The distinction between HA and FA is relevant in geochemical modelling studies as these components have different binding properties for heavy metals and hydrophobic organic contaminants (Milne *et al.*, 2003; Stevenson, 1982). Finally, the new batch method also distinguishes the hydrophilic acids (Hy) as defined by Thurman and Malcolm (1981) and Swift (1996), as well as the hydrophobic neutral organic matter (HON) as defined by Leenheer (1981). For the specific properties of Hy and HON, we refer to these previous studies.

4.2 Materials and methods

Two sets of experiments and samples have been used for the two major aims of this study; i.e. (1) the development of the new batch procedure and its comparison with the conventional methods for the isolation and purification of HS in aquatic and solid samples, and (2) the study of the recovery and dissolution properties of HS. The samples that have been used for these two specific objectives are described first, followed by the experimental details of the batch procedure. Finally, the specific experiments and samples are described that are used for the comparison of the batch and conventional methods and for the HS recovery and dissolution properties.

4.2.1 Samples

A comparison between the batch method and the conventional isolation and purification methods of Thurman and Malcolm (Thurman and Malcolm, 1981) and Swift (Swift, 1996) was performed with samples from both aquatic and solid environments, respectively. Four aquatic samples have been used, a landfill leachate, influent and effluent water from a landfill water treatment plant and water from a DOC rich pond in a nature reserve (Zwanenwater, NL). The solid samples consist of a peat (Devoke UK), compost and a landfill waste mixture (consisting mainly of soil remediation sludge, contaminated soil, industrial sludge and construction and demolition waste). The landfill sample has been extensively characterised in a project on sustainable landfilling (Mathlener *et al.*, 2006).

Because of our goal to distinguish between the HA and FA sub-fractions, the experiments to investigate the recovery and dissolution properties of HS require previously isolated and purified HA and FA. For this purpose, previously isolated and purified HA and FA (using the conventional methods) from the above mentioned aquatic and solid samples were used. In addition, Purified Elliot soil HA and FA and Suwannee river HA were used. These samples are defined by the IHSS as standard HS and were obtained from the IHSS. Solutions of these previously purified HS were prepared by HA/FA dissolution in demineralised water. The pH was raised to >10 with 0.1 M NaOH (under N_2) to enhance HS dissolution. Solutions were equilibrated 15-20 hours by continuous end over end tumbling (20 rpm) before being filtered (0.45 µm membrane filter).

4.2.2 Preparation of DAX-8 and XAD-8 resin

Various documented methods for HS isolation and purification make use of XAD-8 resin to adsorb HA and/or FA (Aiken, 1985; Hayes, 1985; Leenheer, 1981; Swift, 1996; Thurman and Malcolm, 1981). This resin is no longer commercially available; therefore, the comparability of the substitute resin DAX-8 (McDonald *et al.*, 2004) was tested. The results are given in the supporting information.

Every new resin batch was first cleaned to remove organic impurities with five 0.1 M HCl extractions (24 hours). The solution was renewed after each extraction. This cycle was repeated with 0.1 M NaOH. Then, the resin was thoroughly cleaned by soxhlet extractions with acetonitrile and methanol, each for 24 hours. The cleaned resin was stored in methanol. Prior to use, the methanol was removed by placing the resin in a büchner funnel with a Whatman 41 filter and washing under vacuum with water having a volume 20 times that of the resin. Subsequently, the resin was similarly rinsed with 0.1 M HCl having 10 times the resin volume. It was found that 250 g of resin could be cleaned sufficiently by rinsing with 2 L demineralised water and 1 L of 0.1 M HCl. This cleaning sequence was used to obtain a DOC free (DOC generally < 2 mg C/L) and acidic (pH 1) resin for experimental use. The molecular size of the residual DOC in cleaned DAX-8 was <100 Dalton, based on high performance size exclusion chromatography. We believe that the residual DOC originates from resin bleeding rather than from residual FA.

The average moisture content ($\mathrm{Moist}_{\mathrm{DAX}}$) of the cleaned moist resin was 60.3±3.4% (n=5). Small changes in moisture content have a limited effect on the final results, so this average value was used to correct the measured FA and Hy concentrations for the resin's water content.

4.2.3 Batch procedure for determining dissolved HA, FA and Hy concentrations

Figure 1 shows a schematic overview of the procedure. About 50 mL of a sample solution (V_1) was adjusted to pH 1 with 6 M HCl (V_2) to precipitate the dissolved HA. After standing overnight the suspension was centrifuged (10 minutes, 3000*g*). The supernatant was decanted (V_3, the difference between V_1 and V_3 is the water volume retained in the HA pellet) and subsampled for DOC analysis (representing the sum of dissolved FA, Hy and HON, $\mathrm{DOC}_{\mathrm{FAHyHON}}$) using a Shimadzu 5000A TOC analyser. 10 g of cleaned DAX-8 resin ($W_{\mathrm{DAX,L}}$) was added to the remaining supernatant ($V_{4,L}$, this is essentially V_3 minus the volume taken for DOC analysis) to adsorb the FA (and HON) fraction. After one hour of equilibration by continuous tumbling, the suspension was filtered and a subsample of the solution was taken for DOC analysis ($\mathrm{DOC}_{\mathrm{HY}}$). Experimental verification for the optimum amount of DAX-8 and the equilibration time required is provided in the supporting information, Figures S1 and S2 respectively.

In order to desorb FA, the resin was equilibrated in four subsequent steps (1 hour each) with 20 mL of 0.1 M KOH ($V_{11,i}$). Preliminary experiments have shown that for a quantitative desorption, the suspension pH should be >11 (adjusted with 1 M KOH if necessary) and that four desorption steps were required for the highest FA concentration in this study (~400 mg C/L). DOC was analysed in the eluates ($\mathrm{DOC}_{\mathrm{FA},i}$). HON was quantified as the difference between the amount of adsorbed FA+HON and the amount of desorbed FA. Meanwhile, the pellet of precipitated HA was dissolved in 0.1 M KOH (V_5) and analysed for DOC (DOC_{HA}).

A blank experiment to determine the DOC contribution from DAX-8 was performed for each batch of cleaned resin. Ten grams of moist DAX-8 resin ($W_{DAX,BL}$) were added to 50 mL of 0.1 M HCl ($V_{4,BL}$) after previous DOC analysis (DOC_{Bl1}). After one hour of equilibration by continuous tumbling, the resin was allowed to settle for 5 minutes and DOC was measured (DOC_{Bl2}). The equations for the calculation of dissolved HA, FA and Hy concentrations are given in the Supporting Information.

4.2.4 Batch procedure for determining the total HA, FA and Hy content in solid source materials

A schematic overview of the procedure is given in Figure 1. About 20 g (M_{Wet}) of sample (moisture content is measured separately, $Moist_{Samp.}$) was acidified to pH 1-2 with 1 M HCl. The solution volume was then adjusted to 200 mL (L/S=10) with 0.1 M HCl and the total volume of added HCl (1 and 0.1 M) was recorded (V_6). This suspension was equilibrated by continuous tumbling in a closed container (polycarbonate) for 1 hour and centrifuged (3000*g*, 10 minutes). Then, the supernatant (named $FAHyHON_1$ because it contains FA, Hy and HON from this first extraction) was removed (V_7) from the residue by decantation and stored for DAX-8 treatment.

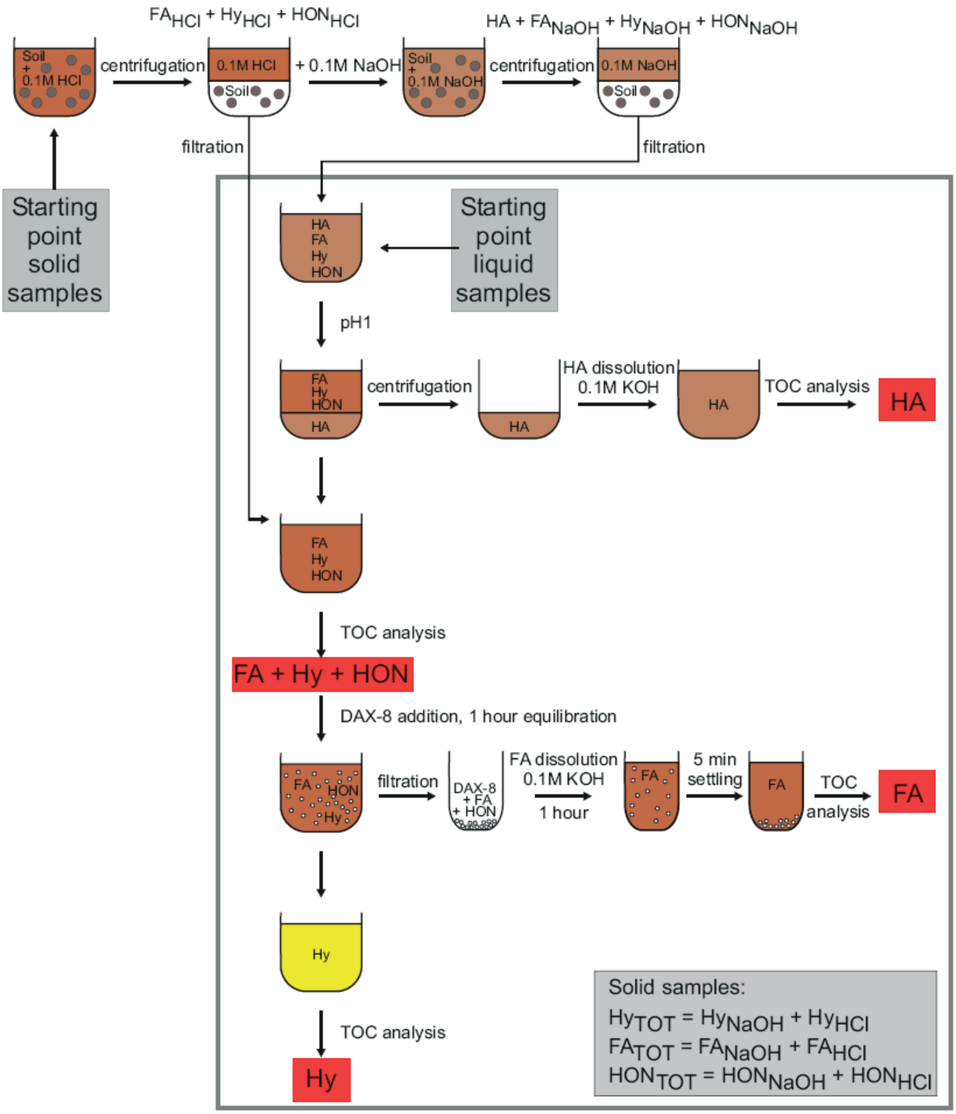


Figure 1. Schematic representation of the batch procedure for determining HA, FA and Hy concentrations in aqueous and solid samples. The gray line indicates the procedure for aqueous samples.

The soil residue was neutralised with 1 M NaOH to pH = 7.0 and thereafter 0.1 M NaOH was added under a N_2 atmosphere to a final volume of 200 mL (L/S=10). The final pH was ≥12 to ensure high HA solubility. The suspension was equilibrated overnight by continuous tumbling in a closed container (polycarbonate), and then centrifuged (3000*g*, 10 minutes) and decanted (volume of decanted eluate is recorded, V_1). Subsequently, the supernatant was acidified to precipitate HA. 6 M HCl (V_2) was added with constant stirring until pH 1.0 was reached. The suspension was allowed to stand overnight and centrifuged (3000*g*, 10 minutes) after which the supernatant was decanted (V_8, this volume was needed to correct for the water volume retained in the HA pellet). The solution (named $FAHyHON_2$ because it contains FA, Hy and HON from this second extraction) was stored for treatment with DAX-8. The precipitated HA were re-dissolved in 0.1 M KOH (V_5) for DOC analysis (DOC_{HA}).

FA, HON and Hy concentrations were determined by equilibration with suspended DAX-8. Firstly, the stored solutions ($FAHyHON_{1,2}$) were filtered (0.45 µm membrane filter) and analysed for DOC ($DOC_{FAHyHON1,2}$). Next, 50 mL aliquots ($V_{4,i}$) of the filtered solutions were transferred to polycarbonate containers and 10 g of moist DAX-8 ($W_{DAX,i}$) was added to both samples. After one-hour equilibration by continuous tumbling, the suspensions were filtered and DOC was measured in both solutions ($DOC_{Hy1,2}$). The FA was desorbed from the resin with 0.1 M KOH ($V_{9,10}$) as described above for aqueous samples. DOC was analysed in the eluates ($DOC_{FA,i}$). HON was quantified as the difference between the total amount of adsorbed FA+HON and the amount of desorbed FA. Finally, a blank experiment was also performed as described previously. The equations for calculating the total HA, FA and Hy contents of solid materials are given in the supporting information.

4.2.5 Comparison of conventional and batch procedure

The batch method for aquatic HS concentrations and the conventional extraction and purification methods (Swift, 1996; Thurman and Malcolm, 1981) were performed on all aquatic and solid environmental samples. For all samples, the concentrations of HA, FA and Hy were compared. The concentrations of HON from both procedures were only available for the Zwanenwater sample.

4.2.6 Recovery and dissolution properties of previously purified HS

Solutions of previously purified HS from Elliot soil, peat and compost were prepared with concentrations ranging from 7.6 to 104.9 mg C/L (HA) and 8.5 to 98.2 mg C/L (FA), and were combined to obtain mixtures with similar HA and FA concentrations. As will be discussed in the results, HA recovery was variable and particularly low at lower HA concentrations. This feature was studied in more detail by recovery experiments. Solutions (100 mg C/L) were prepared from purified Elliot soil, peat, compost, landfill waste mixture, landfill leachate, Zwanenwater and Suwannee River HA, and were diluted to give solutions with HA concentrations of between 0.5 and 100 mg C/L. These samples were analysed by the batch procedure and results were compared to the initially prepared HA concentrations.

4.3 Results and discussion

4.3.1 Comparison of batch procedure with conventional isolation and purification procedures

Table 1 shows the HA, FA, Hy and HON concentrations obtained using the conventional extraction methods (Swift, 1996; Thurman and Malcolm, 1981) and the new batch method. The amounts of HA, FA and Hy isolated by the conventional procedure for solid source materials are in good agreement with those of the batch method for two of the three samples. The peat sample was initially stored at -18^{o}C until it was used for HS isolation with the conventional procedure and was then further stored at 4^{o}C in the dark for 3 years until it was used in the batch procedure. This difference may have led to the deviant results as storage conditions have been shown to influence DOC composition (Zsolnay, 2003).

The conventionally isolated HA concentrations in liquid samples are generally about 2.5-3 times higher than those measured with the batch procedure. During the development of the batch procedure, we observed a strong increase in the recovery of previously purified HA at concentrations up to approximately 50 mg C/L, which is investigated in separate experiments discussed below. In the batch procedure, HA is immediately precipitated, whereas in the conventional procedure for liquid samples HA (and FA) is pre-concentrated on XAD-8 before precipitation at pH 1. This pre-concentration of HA is, therefore, believed to result in the observed higher HA recovery in the conventional procedure.

The HON fraction in the Zwanenwater sample, which has been measured with both the conventional and batch procedure, is very similar for both methods. The conventionally isolated FA concentrations in liquid samples are about a factor 2 lower than those measured with the batch method. This difference is partially exaggerated because the HON fraction was not estimated in these (initial) experiments. As a result, the reported FA, except for the Zwanenwater sample, is in fact the sum of FA and HON. However, FA does also appear to be incompletely retained by the XAD-8 columns in the conventional procedure. The Zwanenwater sample shows that approximately 22 mg C/L was not retained on XAD-8 and measured as Hy, which is supported by the observation that Hy is generally about 1.5-2.5 times higher in the conventional procedure.

Table 1 also shows that incomplete retention of FA occurs in the conventional procedure for aquatic samples but not, or only to a limited extent, in that for solid samples. This observation is consistent with the differences in the procedures for aquatic (Thurman and Malcolm, 1981) and solid samples (Swift, 1996), particularly the ratio of sample volume to column size (i.e. column loading) and pH (pH=1 for solid, and pH=2 for aquatic samples). The adsorption efficiency of FA on XAD-8 is known to increase strongly with decreasing pH (Aiken *et al.*, 1979). The relatively high sample volume and pH used for aquatic samples may cause a lower retention on XAD-8 and, hence, a higher breakthrough relative to the conditions used for solid samples. In the batch procedure, we have chosen relatively large amounts of DAX-8 to reduce the risk of overloading the resin. These differences in isolation approaches among different fields of science show a clear need for standardisation of methods to enable more comparable results.

4.3.2 Recovery of previously purified HS

Previously isolated and purified (dissolved) HA and FA are required to investigate the recovery of these HS in the batch procedure. Therefore, mixtures of re-dissolved HA and FA were analysed. The results, shown in Table 2, indicate that the reproducibility is good, especially considering the heterogeneous nature of HS, the different steps in the procedure, and the subtraction of different DOC concentrations in the calculations (see supporting information). The overall mass balance (calculated as the sum of HA, FA and Hy compared to total DOC) is good (average=90±9%, n=44).

Table 1. Comparison of results for conventional IHSS extraction and purification method and developed batch method for solid source materials and aquatic samples.

Sample code	Matrix	Method[1]	HA[2]	FA[2]	Hy	HON	Sum
Compost	Solid	B	43.3	1.7	5.7	2.3	53.1
		C	43.7	1.7	5.7	n.a.	51.1
Peat	Solid	B	168.3	3.9	27.9	9.6	209.7
		C	113.9	2.8	8.4	n.a.	125.1
Landfill waste	Solid	B	6.1	0.7	2.1	1.6	10.4
		C	5.6	0.9	2.1	n.a.	8.5
Effluent	Liquid	B	0.7	93.1[4]	40.3	n.a.	134.1
(DOC=150 mg C/L)		C	2.0	46.2	67.8	n.a.	116.0
Influent	Liquid	B	1.6	124.4[4]	51.7	n.a.	177.7
(DOC=202 mg C/L)		C	4.8	72.7	46.0	n.a.	123.5
Leachate	Liquid	B	0.9	137.5[4]	46.1	n.a.	184.4
(DOC=199 mg C/L)		C	3.0	66.2	88.5	n.a.	157.7
Zwanenwater water	Liquid	B	8.0	34.5	14.0	10.3	66.8
(DOC = 71.7 mg C/L)		C	9.2[3]	12.3	35.0	9.6	66.0

[1] B = batch method (average from duplicate analysis; Zwanenwater triplicate analysis), C = conventional method (single analysis, Concentration C calculated with elemental composition of the purified HA or FA), [2] Solid samples are reported in g C/kg d.m., liquid samples are reported in mg C/L, [3] Lower recovery due to multiple washing steps to remove chloride, [4] result of FA+HON.

Table 2 also shows that the HA and FA recoveries are highly variable (61.4-102.9% and 67.8-116.2%, respectively) and that the differences are much greater than the coefficient of variation. As the initial HS concentrations increased, the HA recovery increased while FA recovery decreased. Furthermore, solutions from purified peat and compost HS containing low FA concentrations show recoveries significantly higher than 100%, which indicate an apparent lack of distinction between HA and FA at low concentrations. These observations have been examined in detail in further experiments that are discussed in the following section.

Table 2. Duplicate analysis of previously isolated and purified HA and FA mixtures with the batch procedure . Measurements were performed at concentrations of about 100 mg C/L (high) and about 10 mg C/L (low).

Sample		**Theoretical concentrations (mg C/L)**		**Measured concentrations (mg C/L)**		**Recovery**	
	No.	HA	FA	HA	FA	HA (%)	FA (%)
Elliot soil *(high)*	1	104.9	85.1	105.1	60.8	100.2	71.5
	2	104.9	85.1	108.0	57.7	102.9	67.8
Coefficient of variation (%)				***1.9***	***3.8***		
Elliot soil *(low)*	1	10.5	8.5	8.0	7.0	76.6	82.7
	2	10.5	8.5	7.7	7.8	73.2	91.6
Coefficient of variation (%)				***3.2***	***7.2***		
Peat *(high)*	1	75.5	98.2	52.5	88.9	69.6	90.6
	2	75.5	98.2	58.5	91.4	77.6	93.1
Coefficient of variation (%)				***7.7***	***1.9***		
Peat *(low)*	1	7.6	9.8	4.6	10.8	61.4	110.0
	2	7.6	9.8	4.8	10.4	63.5	105.5
Coefficient of variation (%)				***2.4***	***3.0***		
Compost *(high)*	1	99.1	89.1	92.2	84.1	93.0	94.3
	2	99.1	89.1	91.4	85.1	92.2	95.4
Coefficient of variation (%)				***0.6***	***0.9***		
Compost *(low)*	1	10.0	8.9	6.4	10.3	64.3	116.2
	2	10.0	8.9	6.4	9.9	64.0	110.9
Coefficient of variation (%)				***0.4***	***3.3***		

4.3.3 Dissolution properties of HA and FA

Additional experiments were performed to investigate HA recovery as a function of the initial HA concentration. Previously isolated and purified HA from various sources were dissolved (0.5 to 100 mg C/L), and subjected to the batch procedure (Figure 2).

Figure 2A reveals two remarkable features. Firstly, HA recovery decreases markedly at concentrations below about 50 mg C/L; this is consistent for all samples, despite the different HA sources. These concentrations are relevant as they are often found in natural and waste environments. Experiments with Elliot soil HA, applying high-speed centrifugation (6000*g*, 20 minutes) to enhance separation between the liquid and the acid precipitate, showed the same recovery pattern, which was reconfirmed by centrifugation at 16.000*g* (data not shown).

Figure 2B and C illustrate that at low concentrations the unrecovered HA fraction (Figure 2A) is predominantly measured as FA, consistent with the hydrophobic properties of HA and FA which results in a high affinity of both fractions for adsorption to DAX-8. These results are in agreement with Evans (Evans, 1959) who also found an apparent conversion of HA to FA (at HA concentrations of 400-1300 mg C/L). Evans (Evans, 1959) also observed that ~50% of previously purified HA was precipitated in 0.1 M HCl, increasing to a maximum of ~60% in > 0.2 M HCl. Preliminary precipitation experiments with Elliot soil HA (16 mg C/L) at pH 0.5 and 0 also showed a 10% increase in HA recovery compared to pH 1 (data not shown). These observations suggest that incomplete recoveries are related to a general HA property and are not an artefact of the method.

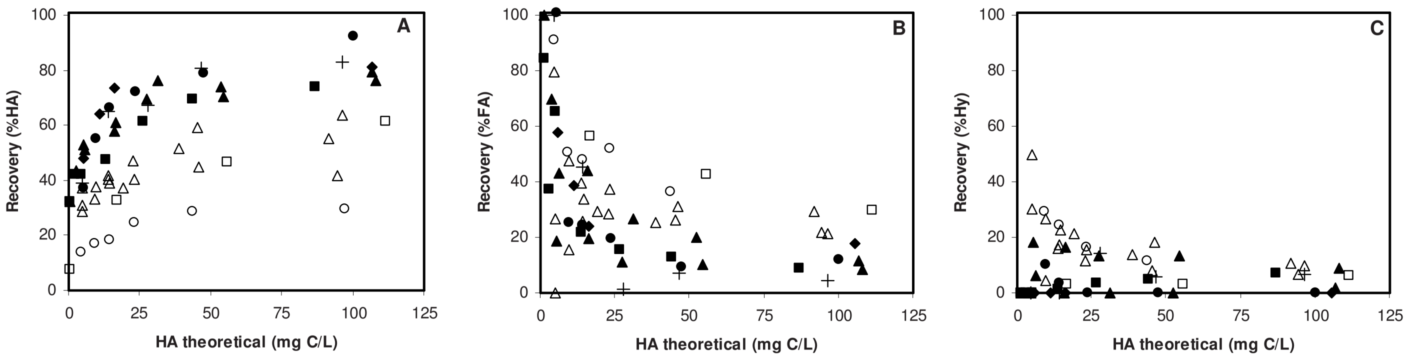


Figure 2. Recovery of purified HA as a function of the initial theoretical HA concentration for the peat (■), Elliot soil (▲), Elliot soil after high-speed centrifugation (◆), compost (●) and the landfill waste mixture (+) solid source materials (Part A). The open symbols represent isolated aquatic HA: Suwannee river (○), Landfill leachate (□) and Zwanenwater (△).Parts B and C show the percentage of DOC (originating from HA) measured as FA and Hy, respectively, as a function of the initial HA concentration. HON was measured in Elliot soil and Zwanenwater HA and found to be lower than the detection limit.

There is presently no consensus as to how HA and FA should be operationally defined (Aiken, 1988; Clapp and Hayes, 1999; Hayes and Swift, 1990). According to aquatic scientists, HA is generally defined as the carbon fraction that precipitates below pH 2 (Clapp and Hayes, 1999; Hayes and Swift, 1990), whereas the methods of Thurman and Malcolm (Thurman and Malcolm, 1981) and Malcolm (Malcolm, 1991) use pH 1. Soil scientists generally define HA as the carbon fraction that precipitates below pH 1 (e.g. (Swift, 1996)). The definitions of FA also differ. Aquatic FA has previously been defined by adsorption on XAD-8 resin at pH 2 (Malcolm, 1991; Thurman and Malcolm, 1981), and soil FA by adsorption at pH 1 (Swift, 1996). We have chosen acidification to pH 1, which enhances HA precipitation due to the higher degree of protonation and increases FA hydrophobicity and subsequent binding to XAD-8 (Aiken *et al.*, 1979).

The recovery patterns shown in Figure 2 are consistent with the recent view that humic substances are in fact dynamic, supramolecular, associations of relatively low molecular mass components. Stabilised by hydrophobic interactions and hydrogen bonds (Sutton and Sposito, 2005; Wershaw, 2004) (and references therein), the size of these aggregates has been shown to increase with the HA concentration, while hydrophobic regions form at low pH and disperse towards high pH (Sutton and Sposito, 2005). Our observations of a concentration-dependent flocculation of HA and, at low concentrations, the apparent lack of distinction from FA, are in support of this new view on HS, which emphasizes molecular interactions over (chemically distinct) molecular components.

In addition to HA aggregate formation being a function of pH, ionic strength and metal concentrations (Avena and Wilkinson, 2002; Clapp and Hayes, 1999; piccolo, 2001; Swift, 1999; Temminghoff *et al.*, 1998; Weng *et al.*, 2002), the colloid concentration is an important factor in HA aggregation and flocculation (Stevenson, 1982; Wershaw, 1999). The colloid aggregation rate depends largely on colloid collision frequency (Stumm and Morgan, 1981), which decreases at low HA concentrations. The observed incomplete HA precipitation at low concentrations suggests a limited HA aggregation, which may be due to an insufficient colloid collision frequency and resulting aggregate size.
The second feature observed in Figure 2A is that the maximum recoveries of HA remain, also at the higher concentrations, significantly lower than 100%, while the recoveries are distinctly lower for HA isolated from aquatic samples than for HA from solid materials and the remaining DOC is predominantly measured as FA. These distinct trends in the precipitation recoveries are consistent with the more aromatic character of HA from soils, relative to aquatic HA (Visser, 1983). In addition to the concentration dependent

flocculation of previously purified HA at low pH that is consistent with the theory of HA being dynamic, supramolecular, associations of smaller entities, we postulate that the unrecovered ~20% (solid samples) to ~50% (aquatic samples) reflects a very soluble fraction that results from the conventional isolation and purification procedure. Originally, HA was precipitated from the source material by acidification in the presence of di- and trivalent cations, which induce HA precipitation (Temminghoff *et al.*, 1998; Weng *et al.*, 2002). As the purification procedure removes these cations, HA becomes fully protonated. Re-acidification of the purified HA in the absence of multivalent cations may then result in a HA fraction that remains soluble in the fully protonated state. Evans (Evans, 1959) has also observed an incomplete recovery of similarly purified HA by precipitation in 0.1 M HCl. We have been unable to explain the < 100% recoveries of HA solely on the basis of its electrostatic properties, using the model of Lumsdon (Lumsdon, 2004).
The relatively high HA recoveries from solutions also containing FA (Table 2), as compared to the recoveries of pure HA (Figure 2A), suggest that some FA is measured as HA. Stevenson (Stevenson, 1982) has pointed out that FA can assume HA characteristics after prolonged standing at both high and low pH. The latter might have occurred in the experiments with HA and FA mixtures which then led to aggregation and precipitation and, hence, to the apparent conversion of FA to HA (Table 2).

Additional experiments (see Supporting Information) were performed with HA isolated from compost, to characterise the fractions obtained at different concentrations in the batch method (Figure 2). The results revealed no significant differences in size and chemical composition between the HA fractions that were precipitated at different HA concentrations (0.5-100 mg C/L).

In light of the observed partial conversions between HA and FA, it is important to emphasize that acidification of alkaline extracts should not be regarded as a means of separating fundamentally different components, but rather as a way to fractionate HA (Kononova, 1966). Although HA and FA exhibit consistent differences in their elemental composition and properties, it has been shown that each fraction contains intermediate forms that have characteristics overlapping the other (Kononova, 1966; Stevenson, 1982). As such, these observations are also in line with the recent view of HS being supramolecular arrangements of smaller molecules (Sutton and Sposito, 2005; Wershaw, 2004) (and references therein), which emphasizes molecular interactions over chemically distinct molecular components. Our results are also in agreement with this view. It should be stressed that while considering these overlapping properties, which can hamper the quantitative interpretation of separation results, it is nevertheless important to fractionate HA and FA for environmental risk assessment studies since HA and FA possess different metal binding properties (Milne *et al.*, 2003).

The observed low HA recovery at concentrations below approximately 50 mg C/L has to be taken into account when the batch procedure is applied to environmental samples. Pre-concentration of HA (and FA) on DAX-8 prior to performing the method was investigated in preliminary investigations, but was found to be only partly successful. Pre-concentration by a factor of 5 to 10 is practically feasible but generally too low to significantly concentrate HA to above 50 mg C/L (plateau in Figure 2A) before the HA precipitation step. These limitations are related to the amount/volume of DAX-8 required to bind all HA and FA, while these fractions must be desorbed in a small volume of 0.1 M KOH, relative to the original sample volume, to obtain the necessary pre-concentration. Alternatively, HA pre-concentration by low temperature rotary film evaporation may be applied. This method has recently been developed for the concentration of aquatic humic substances (Thacker *et al.*, 2005). Without pre-concentration one might apply the empirical relationship between the measured HA concentration and precipitation efficiency according to Figure S3, while correcting the measured FA concentration for the difference. This relationship may be further developed by additional measurements.

4.3.4 Method application and relevance

Geochemical speciation calculations based on generic parameters for cation binding to HS (Milne *et al.*, 2003) are sensitive to the assumed composition of the HS in terms of HA and/or FA. Consequently, these assumptions can lead to significant differences in predicted metal speciation and mobility. For example, Kalis *et al.* (2006) have recently shown that calculations of metal speciation in the River Rhine depend strongly on assumptions regarding the composition of organic matter and concluded that it is important to obtain a better insight into the DOC composition.

The developed batch procedure is designed to measure HA, FA, Hy and HON concentrations in both solid and aqueous samples. As such, it is a good alternative to the elaborate conventional isolation and purification procedures (e.g. Swift, 1996; Thurman and Malcolm, 1981). The application of this procedure to previously isolated and purified HS has led to fundamental insights into the dissolution/precipitation properties and the resulting classification in terms of HA and FA. These insights are also relevant for the application and interpretation of conventional extraction and purification procedures. Moreover, the new method can contribute to the development and validation of new mechanistic models for the adsorption of HS to reactive surfaces (Weng *et al.*, 2006). The new batch method can be performed within 1.5-4 hours per sample (see Table S6 in supporting information), is easy to perform and multiple samples can be processed simultaneously. The conventional procedure would typically require approximately 40 hours for a single sample. Therefore, the new batch method substantially facilitates HS concentration measurements, particularly for applications where HS purification is not required (e.g. Dijkstra *et al.*, 2004).

Acknowledgements

We thank Esther van der Weij-Zuiver and Petra Bonouvrie for their precise experimental work. Hans Meeussen, Chanelle Carter and four anonymous reviewers have provided valuable comments that have improved our manuscript substantially. This work was partly funded by the Ministry of Spatial Planning, Housing and the Environment as part of ECN's environmental research program.

Annex 4.1 Supporting information

General correction factors for the calculations of HA, FA, Hy and HON in liquid and solid samples:

Correction factor for acid addition used in HA precipitation:

$$f_1 = \frac{(V_1 + V_2)}{V_1}$$

Where:

V_1 = sample volume used for determination of HA, FA, Hy and HON in liquid samples (mL); Volume after alkaline extraction, centrifugation and decantation for determination of HA, FA, Hy and HON in solid samples.

V_2 = added volume of HCl for precipitation of HA (mL).

Correction factors for moisture content from DAX-8. $f_{2,i}$ can be used for liquid samples ($i=_{L}$), solid materials ($i=_{FAHyHON1}$ and $i=_{FAHyHON2}$) and the blank experiments ($i=_{BL}$):

$$f_{2,i} = \frac{W_{DAX,i} * Moist_{DAX} * 0.01}{V_{4,i}} + 1$$

Where:

$W_{DAX,i}$ = wet weight of DAX-8 applied for adsorption of FA or used in the blank experiment (g)*.

$Moist_{DAX}$ = moisture content of the cleaned DAX-8 (%).

$V_{4,i}$ = sample volume taken into account for the DAX-8 adsorption experiment (mL) after removal of HA or the amount of 0.1 M HCl used in the blank experiment*. $i=_{L}$ for liquid samples, $i=_{FAHyHON1}$ and $i=_{FAHyHON2}$ for solid materials and $i=_{BL}$ in the blank experiments.

* For simplicity, it is recommended that both $W_{DAX,i}$ and $V_{4,i}$ are kept constant (10 g and 50 mL, respectively) in both the samples (i=L, FAHyHON1 and FAHyHON2) and the blank experiments (i=BL). In that case, the factor $f_{2,i}$ will be constant in all of the calculations.

DOC contribution of DAX-8 in blank experiment (mg C/L):

$$Bl_{DAX} = (DOC_{BL2} * f_{2,BL} - DOC_{BL1})$$

Where:

DOC_{BL1} = DOC concentration in the 0.1 M HCl solution used in the blank experiment (mg C/L), When DOC_{BL1}<DTL, DOC_{BL1}=0.

DOC_{BL2} = DOC concentration in the 0.1 M HCl in the blank experiment after one hour of equilibration with DAX-8 (mg C/L).

Equations for the calculation of dissolved HA, FA, Hy and HON concentrations:

Concentration of HA in solution (mg C/L) corrected for DOC concentration of remaining water in HA pellet after centrifugation (containing small concentration of FA+ Hy). Only apply correction if V_1 - V_3 > 0:

$$HA = \frac{DOC_{HA} * V_5}{V_1} - \frac{((V_1 - V_3) * DOC_{FAHyHON} * f_1)}{1000}$$

Where:

DOC_{HA} = measured DOC concentration of HA (mg C/L).

V_5 = added volume of KOH to dissolve the HA fraction (mL).

V_3 = volume of supernatant after acid precipitation and centrifugation (mL).

$DOC_{FAHyHON}$ = measured DOC concentration of the sample after removal of HA (mg C/L).

Concentration of Hy in solution (mg C/L):

$$Hy = DOC_{Hy} * f_{2,L} - Bl_{DAX}$$

Where:

DOC_{Hy} = measured DOC concentration of the sample after equilibration with DAX-8 (mg C/L).

Concentration of FA+HON in solution (mg C/L):

$$[FA + HON] = (DOC_{FAHyHON} * f_1) - Hy$$

Concentration of DOC_{FA} after correction of blank DAX-8 contribution (mg C/L). Only apply if $DOC_{FA,measured,i}$ – DOC_{BlDAX} > 0, else 0 is used:

$$DOC_{FA,i} = DOC_{FA,measured,i} - DOC_{BlDAX}$$

Where:

$DOC_{FA,measured,i}$ = DOC concentration(s) in 0.1 M KOH after dissolution of FA from DAX-8 in liquid samples (mg C/L). DOC concentrations are registered separately (*i*=1-4).

Concentration of FA in solution (mg C/L):

$$FA = \frac{\sum_{i=1}^{4} DOC_{FA,i} * V_{11,i}}{V_{4,L}}$$

Where:

$V_{11,i}$ = added volume(s) of KOH to dissolve FA from DAX-8 in liquid samples. Volumes are registered separately (*i*= 1-4).

Concentration of HON in solution (mg C/L):

$$HON = [FA + HON] - FA$$

Equations for the calculation of total HA, FA, Hy and HON concentrations in solid samples:

Dry sample weight (g):

$$M_{Dry} = M_{Wet} * (100 - Moist_{Samp.})/100$$

Where:

M_{wet} = wet sample weight (g).

$Moist_{Samp.}$ = moisture content of the sample (%).

Sample moisture (mL) :

$$V_M = (\frac{Moist_{Samp.}}{100} * M_{Wet})$$

Volume correction for acid addition (V_2) and the water volume retained in the pellet containing the HA (V_1 - V_8) (mL). Only apply correction if $V_A > 0$:

$$V_A = V_1 + V_2 - V_8$$

Where:

V_8 = recovered supernatant after the HA removal (mL).

V_1 = recovered supernatant after the 0.1 M NaOH extraction (mL).

V_2 = added volume 6 M HCl (mL).

Calculation of Hy_1 (mg/kg d.m.):

$$Hy_1 = \frac{(f_{2,FAHy1} * DOC_{Hy1} - Bl_{DAX}) * V_7}{M_{Dry}}$$

Where:

V_7 = recovered supernatant after the 0.1 M HCl extraction (mL).

DOC_{Hy1} = measured DOC concentration in the 0.1 M HCl extract after equilibration with DAX-8 (mg C/L).

Calculation of FA+HON_1 (mg/kg d.m.):

$$[FA + HON]_1 = \frac{DOC_{FAHyHON1} * V_7}{M_{Dry}} - Hy_1$$

Where:

$DOC_{FAHyHON1}$ = DOC concentration in the recovered supernatant after the 0.1 M HCl extraction (mg C/L).

Calculation of FA_1 (mg/kg d.m.):

$$FA_1 = \frac{\sum_{i=1}^{4} DOC_{FA1,i} * V_{9,i}}{M_{dry}}$$

Where:

V_9 = added volume(s) of KOH to dissolve FA from DAX-8, 0.1 M HCl extract. Volumes are registered separately (*i*= 1-4).

DOC_{FA1} = DOC concentration(s) in 0.1 M KOH after dissolution of FA from DAX-8 in the 0.1 M HCl extract (mg C/L). DOC concentrations are registered separately (*i*= 1-4).

Calculation of Hy_2 (mg/kg d.m.):

$$Hy_2 = \frac{(DOC_{Hy2} * f_{2,FAHy2} - Bl_{DAX}) * (V_M + V_6)}{M_{Dry}}$$

Where:

V_6 = added volume of 1 and 0.1 M HCl to acidify the sample to a pH of 1 (mL).

DOC_{Hy2} = measured DOC concentration in the extract after HA removal and the equilibration with DAX-8 (mg C/L).

Calculation of FA+HON_2 (mg/kg d.m.):

$$[FA + HON]_2 = \frac{DOC_{FAHyHON2} * (V_M + V_6) * f_1}{M_{Dry}} - Hy_2$$

Where:

$DOC_{FAHyHON2}$ = DOC concentration in the recovered supernatant after the HA removal (mg C/L).

Calculation of FA_2 (mg/kg d.m.):

$$FA_2 = \frac{\sum_{i=1}^{4} DOC_{FA2,i} * V_{10,i}}{M_{dry}}$$

Where:

V_{10} = added volume(s) of KOH to dissolve FA from DAX-8, 0.1 M NaOH extract. Volumes are registered separately (*i*= 1-4).

DOC_{FA2} = DOC concentration(s) in 0.1 M KOH after dissolution of FA from DAX-8 in the 0.1 M NaOH extract (mg C/L). DOC concentrations are registered separately (*i*= 1-4).

Hy content (mg/kg d.m.):

$$Hy = Hy_1 + Hy_2$$

FA content (mg/kg d.m.):

$$FA = FA_1 + FA_2$$

Calculation of HON (mg/kg d.m.):

$$HON = [FA + HON]_1 + [FA + HON]_2 - FA$$

HA content (mg/kg d.m.):

$$HA = \frac{(DOC_{HA} * (V_A + V_5) - DOC_{FAHyHON2} * f_1 * V_A) * (V_M + V_6)}{M_{Dry} * V_1}$$

Where:

V_5 = added volume of KOH to dissolve the HA fraction (mL).

DOC_{HA} = measured DOC concentration of HA (mg C/L).

A4.1.1 Preliminary investigations of DAX-8 and XAD-8 performance

The adsorption of FA on XAD-8 and DAX-8 was studied at different resin additions and the adsorption time was measured. Moreover, the reversibility of the adsorption process was measured because FA are generally identified on the basis of their adsorption and subsequent desorption from XAD-8 (Aiken *et al.*, 1979; Hayes and Swift, 1990; Swift, 1996; Thurman and Malcolm, 1981). The results of these preliminary investigations are given in Figure S1 and S2. It should be noted that that the DAX-8 resin tends to adsorb slightly greater amounts (up to 5%) of FA as compared to XAD-8. These results are consistent with Peuravuori *et al.* (2002). They concluded that the XAD-8 and DAX-8 resins isolate mixtures of components with generally similar structural compositions, although the content of aliphatics within the extracted HS is slightly greater for DAX-8. It should be noted that Peuravuori *et al.* (2002) have based their results on mixtures of HA and FA, whereas we only focus on the equivalency for FA sorption and desorption. We conclude that XAD-8 and DAX-8 are equivalent with regard to the estimation of FA concentrations and that the use of this procedure with DAX-8 is compatible with the standard procedures recommended by the IHSS.

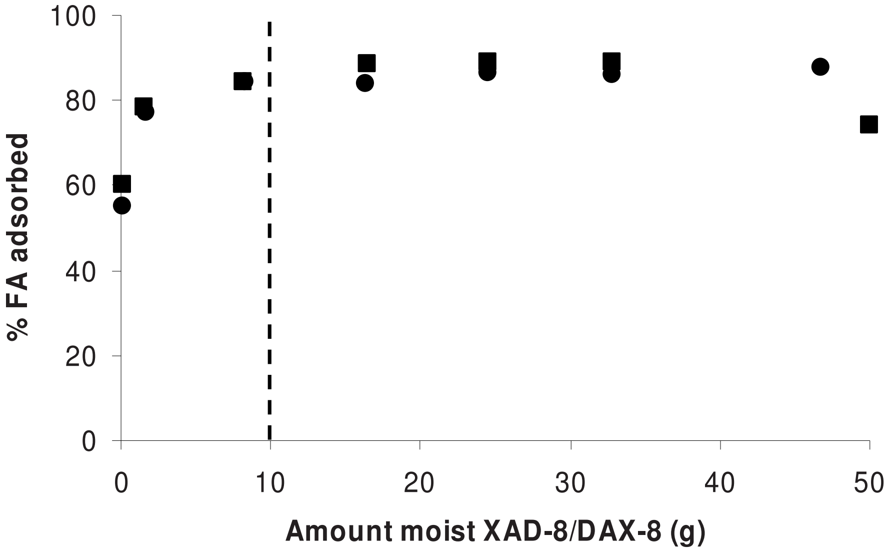


Figure S1. Adsorption of Elliot soil FA (28 mg C/L) as a function of the amount of XAD-8 or DAX-8 resin (moist). The circles represent experiments with XAD-8 resin, squares show the results with DAX-8 resin. The vertical line indicates the amount of resin selected for the standard procedure.

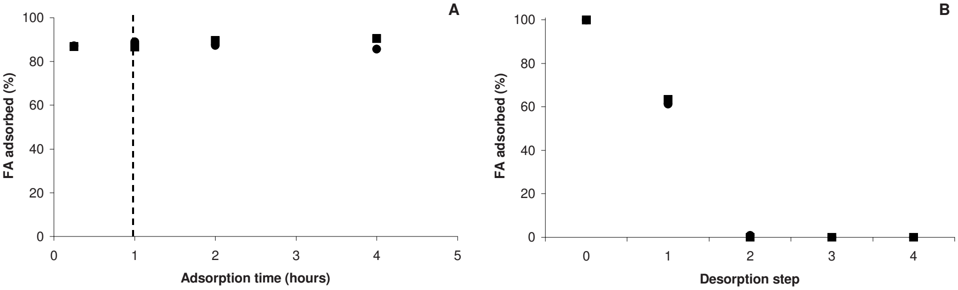


Figure S2. Adsorption of FA as a function of time (A) and the desorption characteristics of XAD-8 and DAX-8 (B) for Elliot soil FA (28 mg C/L). The experiments were performed with 10 g of moist resin for 50 mL of sample solution. The vertical line indicates the selected adsorption time for the standard procedure.

A4.1.2 Concentration dependent precipitation behaviour of HA

Figure S3 reflects the HA recovery from precipitation as a function of the measured HA concentrations. The fitted relationships for solid and aquatic HA can be used to approximately account for the precipitation efficiency. Please note that these general relationships might not be adequate enough in specific samples.

A4.1.3 Chemical characterisation of HA precipitates obtained at different concentrations

Additional experiments were performed with HA isolated from compost, to chemically characterise the fractions obtained at different concentrations in the batch method. HA fractions precipitated at five different initial concentrations (10-100 mg C/L) were again purified by dialysis, freeze-dried and chemically characterised by HPSEC, UV/VIS absorbance (254 to 665 nm) and elemental analysis (C, H, N, O). The results are shown in Table S4 and S5. The HPSEC chromatograms are shown in Figure S4.

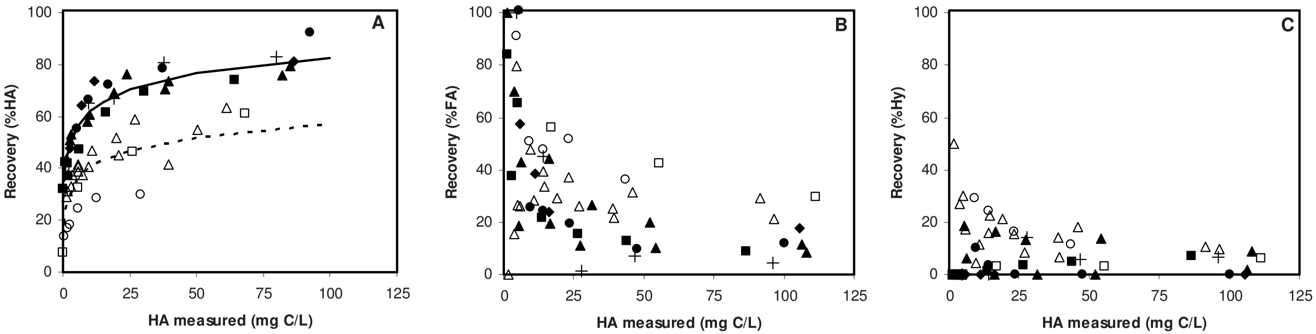


Figure S3. Recovery of purified HA as a function of the **measured** HA concentration for the peat (■), Elliot soil (▲), Elliot soil after high-speed centrifugation (◆), compost (●) and the landfill waste mixture (+) solid source materials (Part A). The open symbols represent isolated aquatic HA: Suwannee river (○), Landfill leachate (□) and Zwanenwater (△). The solid line is the fitted curve ($y=10.46Ln(x)+32.93$, $r^2=0.86$, $n=38$) based on all data from peat, soil, compost and the landfill waste mixture derived HA, the dashed line is the fitted HA concentration dependency ($y=8.28Ln(x)+12.88$, $r^2=0.52$, $n=27$) based on the data from three aquatic HA samples. Parts B and C show the percentage of DOC (originating from HA) measured as FA and Hy, respectively, as a function of the measured HA concentration. HON was not detected in these samples.

Table S4. UV/VIS characteristics of previously purified compost HA (original) and re-precipitated compost HA samples that were subsequently dissolved at different concentrations. E3/E4 is the ratio between absorption at 300 nm and 400 nm, E4/E6 is the ratio between absorption at 465 nm and 665 nm. Aromaticity (Aromat.) was calculated from the absorbance at 254nm according to Chin *et al.* (1994).

Precipitation concentration	DOC (mg C/L)	254nm (abs)	280nm (abs)	300nm (abs)	400nm (abs)	465nm (abs)	665nm (abs)	E3/E4 (-)	E4/E6 (-)	ε (254)*	Aromat. (%)
Original	15.1	0.767	0.668	0.577	0.233	0.124	0.018	2.5	6.9	611	33.3
10 mg C/L	13.5	0.731	0.626	0.541	0.235	0.142	0.058	2.3	2.5	556	34.5
20 mg C/L	15.2	0.769	0.677	0.585	0.261	0.154	0.058	2.2	2.7	534	33.4
30 mg C/L	13.6	0.743	0.645	0.553	0.25	0.145	0.054	2.2	2.7	568	35.1
50 mg C/L	14.4	0.767	0.675	0.584	0.25	0.145	0.055	2.3	2.6	561	34.8
100 mg C/L	14.7	0.803	0.703	0.608	0.255	0.15	0.058	2.4	2.6	572	35.4

*In L(mole C)$^{-1}$cm^{-1}

The E4/E6 ratio seems to be higher in the original sample, this property is not reflected in the other isolates. It is unclear why the absorbance of the original sample at 665 nm is relatively low in comparison with all other results, although it should be noted that very little absorption is measured at this wavelength. The other chemical properties seem to be well comparable with each other amongst all samples. The HPSEC chromatograms (Figure S4) show (other than the peak height due to different concentrations) no significant differences in the apparent molecular size distribution. It is therefore concluded that these techniques reveal no significant differences between the HA fractions that were precipitated from low to high concentrations (0.5-100 mg C/L).

Table S5. Elemental analysis of previously purified compost HA (original) and re-precipitated compost HA samples that were subsequently dissolved at different concentrations. Elemental composition was determined on dry matter basis. The original material was isolated and purified with the conventional isolation procedure.

Precipitation concentration	**C (%)**	**H (%)**	**N (%)**	**O (%)**	**Sum CHNO (%)**	**O/C Ratio (-)**
Original	55.78	4.82	7.77	27.71	96.1	0.61
10 mg C/L	53.31	4.46	6.84	29.17	93.8	0.53
20 mg C/L	54.52	4.83	7.4	29.04	95.8	0.57
30 mg C/L	53.35	4.74	7.26	20.55	85.9	0.56
50 mg C/L	53.86	4.77	7.19	27.1	92.9	0.55
100 mg C/L	54.27	4.79	7.3	27.12	93.5	0.61

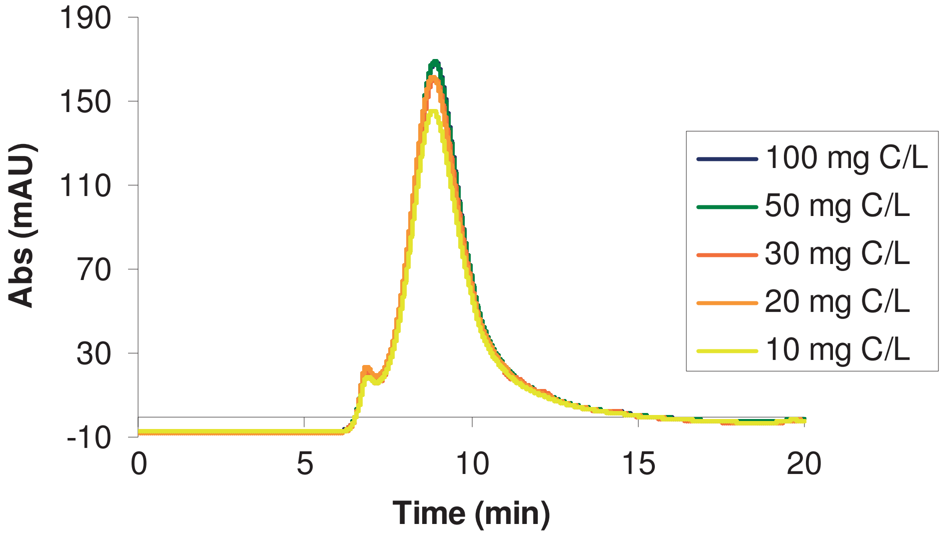


Figure S4. HPSEC chromatograms of previously purified compost HA (original) and re-precipitated compost HA samples that were subsequently dissolved at different concentrations.

A4.1.4 Labour intensity and throughput time of the batch and conventional procedures

The labour intensity of the batch procedures (for solid and aquatic samples) was compared with that of the conventional procedures. In addition to the labour time, the total throughput time of both procedures was compared (Table S6). It is shown that the total throughput time of the conventional procedures for isolation and purification of soil and aquatic samples is of the order of several weeks. This is largely related to the dialysis and freeze drying steps in the conventional procedures. The batch methods have a total throughput time of about 1-2 days. It should be noted that the conventional procedures are mainly developed to isolate the HS for further characterisation studies. If one would be interested in the concentrations of the specific HS only, DOC can be measured in the samples after the column elution steps of the conventional procedures (Swift, 1996; Thurman and Malcolm, 1981). This would eliminate the need for further dialysis and freeze drying. However, the throughput time would still be a factor of 3-6 longer than with the batch method.

The labour time of the procedures is also compared in Table S6. The conventional procedures are very labour intensive and require about 40 hours of work for one sample (depending on the specific laboratory infrastructure and equipment). The batch procedures can be performed within 1.5-4 hours for one sample. It should also be noted that the number of samples that can be handled simultaneously can be easily extended with the batch procedures. For example, about 10 aquatic samples or about 5 solid samples can be processed simultaneously. The labour time per sample is then even further reduced.

Table S6. Comparison of total throughput time and labour time for the conventional isolation and purification procedures and the batch method based on the processing of one sample.

Procedure	Throughput time isolation (days)	Throughput time dialysis/freeze drying (days)	Labour time isolation (hours)	Labour time dialysis and freeze drying (hours)	Total labor time (hours)
Conventional aquatic	6	7	40	1	**41**
Batch aquatic	1	-	1.5-3	-	**1.5-3**
Conventional solid	6	21	40	2	**42**
Batch solid	2	-	2-4	-	**2-4**

References

Aiken, G. R. Isolation and concentration techniques for aquatic humic substances. In *Humic substances in soil, sediment and water: geochemistry, isolation and characterization*; Aiken, G. R., Mc Knight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1985, pp 363-385.

Aiken, G. R. A critical evaluation of the use of macroporous resins for the isolation of aquatic humic substances. In *Humic substances and their role in the environment*; Frimmel, F. H., Christman, R. F., Eds.; John Wiley & Sons: New York, 1988, pp 15-28.

Aiken, G. R., Thurman, E. M., Malcolm, R. L. Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution, *Anal. Chem.*, **1979**, *51*, 1799-1803.

Avena, M. J., Wilkinson, K. J. Disaggregation kinetics of a peat humic acid: mechanism and pH effects, *Environ. Sci. Technol.*, **2002**, *36*, 5100-5105.

Burkhard, L. P. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals, *Environ. Sci. Technol.*, **2000**, *34*, 4663-4668.

Chin, Y. P., Aiken, G. R., O'Loughlin, E. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances, *Environ. Sci. Technol.*, **1994**, *28*, 1853-1858.

Clapp, C. E., Hayes, M. H. B. Sizes and shapes of humic substances, *Soil Sci.*, **1999**, *164*, 777-789.

Dijkstra, J. J., Meeussen, J. C. L., Comans, R. N. J. Leaching of heavy metals from contaminated soils; an experimental and modelling study, *Environ. Sci. Technol.*, **2004**, *38*, 4390-4395.

Dijkstra, J. J., van Zomeren, A., Meeussen, J. C. L., Comans, R. N. J. Effect of Accelerated Aging of MSWI Bottom Ash on the Leaching Mechanisms of Copper and Molybdenum, *Environ. Sci. Technol.*, **2006**, *40*, 4481-4487.

Evans, L. T. The use of chelating reagents and alkaline solutions in soil organic matter extraction, *J. Soil Sci.*, **1959**, *10*, 110-118.

Hayes, M. H. B. Extraction of humic substances from soil. In *Humic substances in soil, sediment, and water: Geochemistry, isolation and characterization*; Aiken, G. R., Mc Knight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1985, pp 329-362.

Hayes, M. H. B., Swift, R. S. Genesis, isolation, composition and structures of soil humic substances. In *Soil colloids and their associations in aggregates*; de Boodt, M. F., Ed.; Plenum Press: New York, 1990, pp 245-305.

Kalis, E. J. J., Weng, L., Dousma, F., Temminghoff, E. J. M., van Riemsdijk, W. H. Measuring free metal ion concentrations in situ in natural waters using the Donnan membrane technique, *Environ. Sci. Technol.*, **2006**, *40*, 955-961.

Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K., Borkovec, M., Benedetti, M. F., Avena, M. J. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *Colloids Surf. A*, **1999**, *151*, 147-166.

Kononova, M. M., *Soil organic matter,* Pergamon Press: Oxford, 1966.

Leenheer, J. A. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, *Environ. Sci. Technol.*, **1981**, *15*, 578-587.

Lumsdon, D. G. Partitioning of organic carbon, aluminium and cadmium between solid and solution in soils: application of a mineral-humic particle additivity model, *Eur. J. Soil Sci.*, **2004**, *55*, 271-285.

Malcolm, R. L. Factors to be considered in the isolation and characterization of aquatic humic substances. In *Humic substances in the aquatic and terrestrial environment*; Boren, H., Allard, B., Eds.; Wiley: London, 1991, pp 369-391.

Mathlener, R. A., Heimovaara, T., Oonk, H., Luning, L., van der Sloot, H. A., and van Zomeren, A. *Opening the black box, process-based design criteria to eliminate aftercare of landfills,* ISBN-10: 90-73573-30-0, Dutch sustainable landfill foundation, 2006.

McDonald, S., Bishop, A. G., Prenzler, P. D., Robards, K. Analytical chemistry of freshwater humic substances, *Anal. Chim. Acta*, **2004**, *527*, 105-124.

Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances, *Environ. Sci. Technol.*, **2003**, *37*, 958-971.

Peuravuori, J., Lehtonen, T., Pihlaja, K. Sorption of aquatic humic matter by DAX-8 and XAD-8 resins - Comparative study using pyrolysis gas chromatography
5, *Anal. Chim. Acta*, **2002**, *471*, 219-226.

piccolo, A. The supramolecular structure of humic substances, *Soil Sci.*, **2001**, *166*, 810-832.

Stevenson, F. J., *Humus chemistry. Genesis, composition, reactions,* John Wiley & Sons: New York, 1982, pp 1-443.

Stumm, W., Morgan, J. J., *Aquatic Chemistry; An introduction emphasizing chemical equilibria in natural waters,* John Wiley & Sons: New York, 1981.

Sutton, R., Sposito, G. Molecular Structure in Soil Humic Substances: The New View, *Environ. Sci. Technol.*, **2005**, *39*, 9009-9015.

Swift, R. S. Organic matter characterization. In *Methods of soil analysis. Part 3. Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996, pp 1011-1069.

Swift, R. S. Macromolecular properties of soil humic substances: Fact, fiction, and opinion, *Soil Sci.*, **1999**, *164*, 790-802.

Temminghoff, E. J. M., van der Zee, S. E. A. T. M., de Haan, F. A. M. Effects of dissolved organic matter on the mobility of copper in a contaminated sandy soil, *Eur. J. Soil Sci.*, **1998**, *49*, 617-628.

Thacker, S. A., Tipping, E., Baker, A., Gondar, D. Development and application of functional assays for freshwater dissolved organic matter, *Water Res.*, **2005**, *39*, 4559-4573.

Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

Tipping, E. Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances, *Aquat. Geochem.*, **1998**, *4*, 3-48.

van Zomeren, A., Comans, R. N. J. Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **2004**, *38*, 3927-3932.

Visser, S. A. Application of van Krevelen's graphical-statistical method for the study of aquatic humic material, *Environ. Sci. Technol.*, **1983**, *17*, 412-417.

Weng, L., Temminghoff, E. J. M., Lofts, S., Tipping, E., van Riemsdijk, W. H. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil, *Environ. Sci. Technol.*, **2003**, *36*, 4804-4810.

Weng, L., Temminghoff, E. J. M., van Riemsdijk, W. H. Interpretation of humic acid coagulation and soluble soil organic matter using a calculated electrostatic potential, *Eur. J. Soil Sci.*, **2002**, *53*, 575-587.

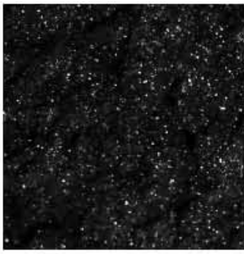
Weng, L., van Riemsdijk, W. H., Hiemstra, T. Adsorption free energy of variable-charge nanoparticles to a charged surface in relation to the change of the average chemical state of the particles, *Langmuir*, **2006**, *22*, 389-397.

Wershaw, R. L. Molecular aggregation of humic substances, *Soil Sci.*, **1999**, *164*, 803-813.

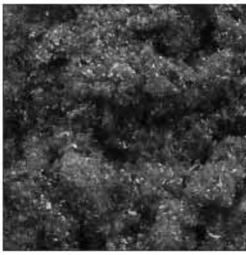
Wershaw, R. L. *Evaluation of conceptual models of natural organic matter (humus) from a consideration of the chemical and biochemical processes of humification,* Report 2004-5121, U.S. Geological survey, Denver, CO, 2004.

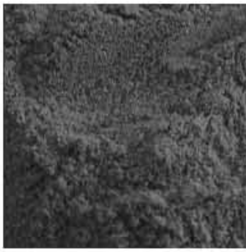
Zsolnay, A. Dissolved organic matter: artefacts, definitions, and functions, *Geoderma*, **2003**, *113*, 187-209.

CHAPTER 5



EFFECT OF ACCELERATED AGING OF MSWI BOTTOM ASH ON THE LEACHING MECHANISMS OF COPPER AND MOLYBDENUM





Published in similar form as:

Dijkstra, J.J., van Zomeren, A., Meeussen, J.C.L., Comans, R.N.J., Effect of accelerated aging of MSWI bottom ash on the leaching mechanisms of copper and molybdenum. *Environmental Science and Technology*, **2006**, 40, 4481-4487. Reproduced with permission. Copyright 2006, American Chemical Society.

EFFECT OF ACCELERATED AGING OF MSWI BOTTOM ASH ON THE LEACHING MECHANISMS OF COPPER AND MOLYBDENUM

Joris J. Dijkstra[1], *André van Zomeren*[1], *Johannes C.L. Meeussen*[1] *and Rob N.J. Comans*[1,2]

The effect of accelerated aging of MSWI bottom ash on the leaching of Cu and Mo was studied using a “multisurface” modelling approach, based on surface complexation to iron/aluminum (hydr)oxides, mineral dissolution/precipitation, and metal complexation by humic substances. A novel experimental method allowed us to identify that the solid/liquid partitioning of fulvic acids (FA) quantitatively explains the observed beneficial effect of accelerated aging on the leaching of Cu. Our results suggest that iron/aluminum (hydr)oxides are the major reactive surfaces that retain fulvic acid in the bottom ash matrix, of which the aluminum (hydr)oxides were found to increase after aging. A new modelling approach, based on the surface complexation of FA on iron/aluminum (hydr)oxides is developed to describe the pH-dependent leaching of FA from MSWI bottom ash. Accelerated aging results in enhanced adsorption of FA to (neoformed) iron/aluminum (hydr)oxides, leading to a significant decrease in the leaching of FA and associated Cu. Accelerated aging was also found to reduce the leaching of Mo, which is also attributed to enhanced adsorption to (neoformed) iron/aluminum (hydr)oxides. These findings provide important new insights that may help to improve accelerated aging technology.

---

[1] Energy Research Centre of The Netherlands.

[2] Wageningen University.

5.1 Introduction

Municipal Solid Waste Incinerator (MSWI) bottom ash, the major waste stream originating from the incineration of municipal solid waste, is considerably enriched in potentially toxic trace elements compared to its parent material (Chandler *et al.*, 1997). The material, when either re-used or disposed, can be qualified as a potential risk to the environment, depending on the availability of the contaminants for leaching. MSWI bottom ash is re-used as a construction material in many countries, but its application is often restricted by regulatory limits based on its leaching potential. In the Netherlands, the leaching of particularly Cu and Mo are critical with respect to environmental regulations (e.g., Dutch Building Materials decree (1995)).

MSWI bottom ash, being a high temperature product, is thermodynamically unstable under atmospheric conditions and is therefore subject to similar weathering processes as observed in natural equivalents such as volcanic ashes (e.g. Zevenbergen *et al.*, 1994). The uptake of atmospheric CO_2 is the primary weathering reaction of MSWI bottom ash and generally leads to a decreased leachability of a number of critical metal contaminants (e.g. Chimenos *et al.*, 2000; Meima and Comans, 1999; van Gerven *et al.*, 2005). Accelerating the natural weathering process of MSWI bottom ash by optimizing parameters such as CO_2 pressure and humidity have been demonstrated to be a potentially promising technology, both with respect to improved leaching properties as well as to reduce CO_2 emissions from industrial sources (e.g. Rendek *et al.*, 2006; van Gerven *et al.*, 2005 and references therein). Therefore, an improved understanding of the processes and parameters that control the leaching of contaminants before and after accelerated aging may contribute to further development of this technology.

Recently, natural humic substances (humic (HA) and fulvic acid (FA)) have been identified in MSWI bottom ash and their leaching has been shown to constitute the key process responsible for the facilitated leaching of copper and possibly other metals (van Zomeren and Comans, 2004). At present, no knowledge exists on the processes controlling the leaching of humic substances from MSWI bottom ash, and their relation with contaminant leaching.

The objective of this paper is to provide a mechanistic insight in the effects of accelerated aging on the leaching of Cu and Mo as typical and important metal and oxyanionic contaminants in MSWI bottom ash. We focus particularly on the potentially important factors that influence the leaching of these contaminants, particularly pH-control, the contents of reactive surfaces in the bottom ash matrix and the quantities and composition of dissolved organic carbon (DOC). Given the key role of DOC in facilitating the leaching of Cu and possibly other metals, DOC is characterised in terms of humic, fulvic and hydrophilic acids over a wide pH-range, in order to identify the processes controlling the solid/liquid partitioning of these reactive organic ligands. With an independently determined set of analytical parameters, we attempt to predict the leaching of Cu and Mo over a wide pH-range, both before and after accelerated aging, using a "multisurface" modelling approach (i.e. adsorption processes to (hydr)oxide surfaces and humic substances). Model results are used to gain further insight in the major chemical factors that control the leaching of contaminants such as Cu and Mo in MSWI bottom ash treated by accelerated aging. A novel approach is developed to model the pH-dependent leaching of fulvic acid from MSWI bottom ash, being the major process controlling the leaching of Cu and possibly other metals.

5.2 Materials and methods

5.2.1 MSWI Bottom ash samples

A batch of about 900 tons (by weight) of freshly quenched MSWI bottom ash was treated by accelerated aging early 2004. Before the treatment, the ashes were sieved to a particle size of <4 cm, and metal parts were removed. The treatment was carried out in a large indoor facility using air enriched with carbon dioxide (pCO_2 = 0.1 bar). Before the start of the treatment and after 24 hours of treatment, samples were taken at different depths within the bottom ash heap (in the surface, in the middle and at the bottom) and mixed. Until further treatment, the samples were stored for about 2 weeks at 4 °C. Prior to the leaching and extraction experiments, the samples were dried at 40 °C and sieved to pass a < 4 mm stainless steel sieve, yielding about 43% of the initial dry sample weight for both the fresh and the aged material. Sieving was preferred over size-reduction to prevent breaking-up of (weathered) grains and the creation of fresh surfaces.

5.2.2 Batch pH-static leaching experiments

Leaching experiments were carried out on individual subsamples that were each equilibrated for 48 h, as prescribed by the European standard for the pH-static test TS14497 (CEN/TC292, 2006), at a specific pH value between pH 2 and 12 (including the native pH of the bottom ash samples that was not adjusted). 25 g of dry bottom ash was suspended in 250 g Nanopure demineralised water (a liquid to solid (L/S) ratio of 10 L/kg) in acid-cleaned 300 mL PTFE vessels, under continuous stirring at 20 °C. The pH of the different suspensions was controlled using solutions of 1 M HNO_3 and NaOH (analytical grade) and a computerised pH-stat system. The suspensions were in contact with the atmosphere. After the equilibration period, the suspensions were filtered through 0.2 µm membrane filters. The clear filtrates were acidified with concentrated HNO_3 (suprapure) and analyzed by ICP-AES to obtain solution concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, V, and Zn. It was assumed that total S and P as measured by ICP-AES equated to SO_4^{2-} and PO_4^{3-}, respectively. A carbon analyser (Shimadzu) was used to determine dissolved inorganic and organic carbon in non-acidified fractions. Chloride was determined by ion chromatography (IC).

It has recently been shown that pH-concentration patterns, particularly of dissolved organic carbon (DOC), may be influenced by leaching kinetics (Dijkstra *et al.*, 2006). Therefore, we have included independent experiments at selected pH values with a longer equilibration time of 168 h.

5.2.3 Selective chemical extractions

Independent estimates of the amount of reactive surfaces present in the bottom ash matrix, which are required for sorption modelling, were made by selective chemical extractions. The solid and dissolved organic carbon in the samples was characterised quantitatively in terms of three fractions, i.e. HA, FA and hydrophilic acids (denoted by HY) by a batch procedure (van Zomeren and Comans, 2007) derived from the method currently recommended by the International Humic Substances Society (IHHS) (Swift, 1996; Thurman and Malcolm, 1981). The amount of amorphous and crystalline iron (hydr)oxides in the bottom ash matrix was estimated by a dithionite extraction described in Kostka and Luther III (1994), and will be referred to as Fe-DITH. The portion of amorphous iron (hydr)oxides was estimated by an ascorbate extraction (Kostka and Luther III, 1994), and will be referred to as Fe-ASC. The amount of amorphous aluminum (hydr)oxides was estimated by an oxalate extraction according to Blakemore *et al.* (1987) and will be referred to as Al-OX.

5.2.4 Geochemical modelling

The analytical leaching data are compared to geochemical modelling predictions based on the solubility of minerals, sorption to (hydr)oxide minerals and FA/HA in the solid and solution phase. A similar modelling approach was followed by Dijkstra *et al.* (2006) to which the reader is referred for further detail. In short, mineral saturation indices (SI), solution speciation, solubility of minerals and sorption processes were calculated with the ORCHESTRA (Meeussen, 2003) modelling framework, in which we incorporated the different sub-models described below. Inorganic speciation and mineral solubility was calculated using thermodynamic data from MINTEQA2 (version 3.11) (Allison *et al.*, 1991), with modifications listed in Dijkstra *et al.* (2002). Specific and non-specific sorption of protons and ions to HA and FA was modelled with the NICA-Donnan model (Kinniburgh *et al.*, 1999) using the set of “generic” binding parameters of Milne *et al.* (2003). It was assumed that 50% of FA and HA consists of carbon (de Wit, 1992).

Dissolved element concentrations corresponding with solubility control by an infinite amount of a selected mineral was calculated according to the "infinite solid approach" as outlined by Meima and Comans (1997). We used the Generalized Two Layer Model (GTLM) of Dzombak and Morel (1990) for modelling surface complexation of ions to Hydrous Ferric Oxide (HFO). In accordance with Meima and Comans (1998), amorphous aluminum (hydr)oxides present in the bottom ash matrix were considered as potentially important sorbent minerals, for which HFO was taken as a surrogate sorbent in the model. The reason for this approach is the absence of a complete and systematic database for sorption reactions on aluminum (hydr)oxides. For detail and justification of this approach the reader is referred to Meima and Comans (1998). HFO was also used as a surrogate sorbent mineral for crystalline iron (hydr)oxide surfaces, however, site densities were calculated using a lower specific surface area of 100 m^2/g (Hiemstra *et al.*, 1989). Low pH (pH 2) extracts were used to estimate concentrations of Cu available for adsorption, and alkaline pH (pH 12) extracts to estimate concentrations of Mo that are available for adsorption, respectively, assuming complete desorption at these pH values (Meima and Comans, 1998). Component activities were calculated with the Davies equation and a moderately oxidizing environment was assumed (pH + pe = 15), in accordance with measured redox potentials in similar MSWI bottom ash samples (Meima and Comans, 1997). The sorption equilibrium was calculated simultaneously for Cu and Mo, in the presence of solution concentrations of a broad range of elements (Na, K, Ca, Mg, Mn, Al, Si, Fe, Ba, Sr, SO_4^{2-}, PO_4^{3-}, Cl, CO_3^{2-}, Ni, Zn, Cd and Pb), which were fixed in the model at their measured values at each pH value to fully account for competitive adsorption on iron- and aluminum (hydr)oxide surfaces, HA and FA.

5.3 Results and discussion

Results of the pH-static leaching experiments, selective chemical extractions and geochemical modelling are discussed in detail below. We focus on potentially important factors that influence the leaching of Cu and Mo, particularly pH-control, the contents of reactive surfaces in the bottom ash matrix and the quantities and composition of dissolved organic carbon (DOC).

5.3.1 pH-dependent leaching data

Measured concentrations of Cu, Mo and DOC in leachates as a function of pH are shown in Figure 1, along with predicted concentrations based on geochemical modelling. Additional graphs are presented in the Supporting Information for the important major elements Ca, Al and SO_4^{2-} (Figure S1). In comparing the pH-dependent leaching data with modelling results, it should be noted that in cases where the "infinite solids approach" (Meima and Comans, 1997) has been used, leaching may be overpredicted at pH values where mineral solubility is high relative to the maximum leachable amount of elements (i.e. the "availability", as estimated by the amounts leached at pH 2 and 12 for cations and anions, respectively).

For an adequate assessment of the result of the treatment with respect to the leaching under field conditions, leached concentrations should be compared particularly at the native pH values of the fresh and aged sample (pH 11.1 and 8.6, respectively). When judged in this way, the aging process leads to a reduction of the Cu leaching by a factor of 3 and of Mo by about a factor of 1.5 (see also Supporting Information for a linear plot of measured concentrations in this particular pH range).

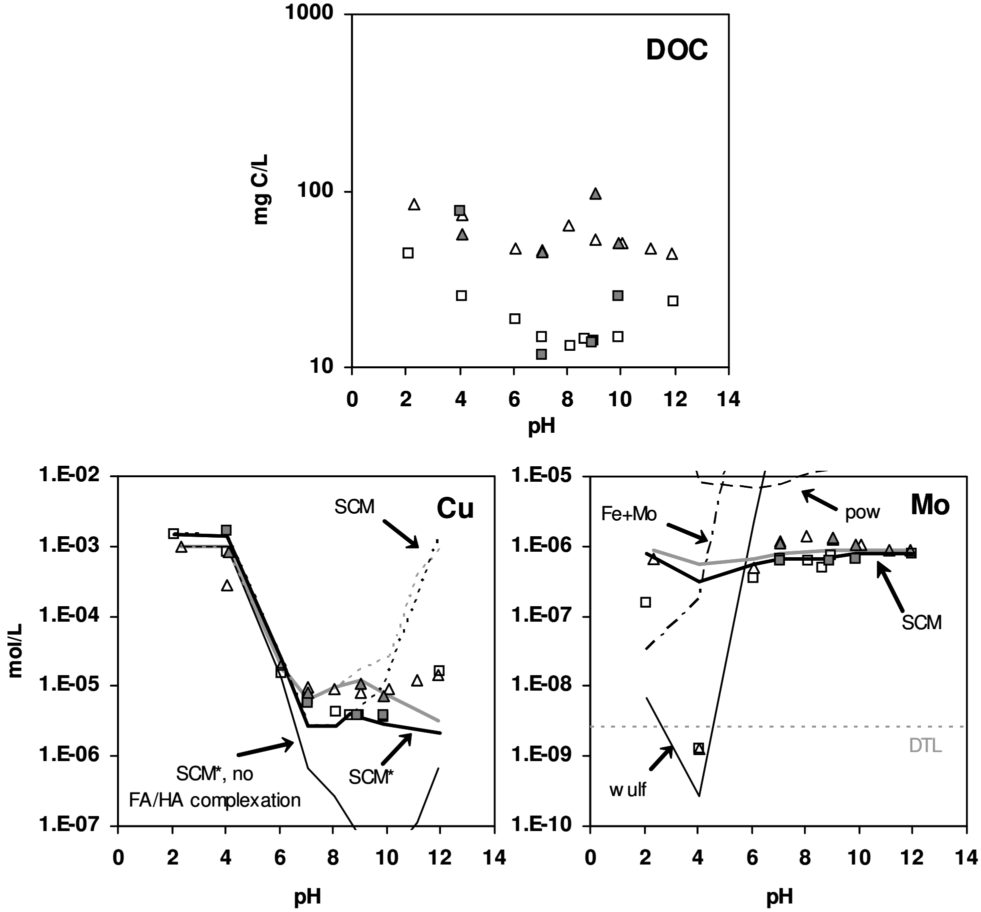


Figure 1. Leached concentrations of Cu, Mo and dissolved organic carbon (DOC) as a function of pH, for the fresh and aged sample (fresh = triangles, aged = squares; closed symbols are independent experiments obtained after a longer equilibration time of 168 h) shown together with model predictions. Grey model curves refer to model predictions of the fresh sample, black to the samples treated by accelerated aging. Abbreviations of model predictions are "SCM" = surface complexation to Fe/Al (hydr)oxides, "SCM*" = surface complexation to Fe/Al (hydr)oxides with $Cu(OH)_2(s)$ allowed to precipitate. In the panel for Cu, also a model scenario is shown for SCM* without FA/HA complexation in solution (for clarity only shown for the aged sample). Panel for Mo: "pow" = powellite, "Fe+Mo" = ferrihydrite + $Fe_2MoO_4(s)$, "wulf" = wulfenite (model curves for these minerals are only shown for the aged sample); DTL = Detection Limit.

5.3.2 Native pH and major element leaching

The "native" pH of the fresh sample is about 11.1 and has decreased to 8.6 in the aged sample (Table 1). The native pH of the fresh sample is consistent with the coexistence of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O$), $Al(OH)_3$ and gypsum ($CaSO_4:2H_2O$), which results in a pH of 10-11, depending on the degree of undersaturation of gypsum (Meima and Comans, 1997). The native pH of the aged sample (8.6) is typical for weathered MSWI bottom ash (Johnson *et al.*, 1995; Meima and Comans, 1997). The observed changes in the pH-dependent leaching patterns of important major elements (Ca, SO_4^{2-}) after the accelerated aging of the bottom ash (see Supporting Information) are consistent with the processes identified previously for naturally aged bottom ash (Meima and Comans, 1997).

Table 1. Native pH and results of the selective chemical extractions of the MSWI bottom ash samples used in this study [a].

	Fresh	*Aged*
Native pH [b]	11.1	8.6
Fe-ASC (g Fe/kg dry ash) [c]	1.6 ± 0.1	1.6 ± 0.1
Fe-DITH (g Fe/kg dry ash) [c]	8.7 ± 0.5	9.4 ± 0.4
Al-OX (g Al/kg dry ash) [c]	4.8 ± 0.2	6.2 ± 0.2

[a] Values represent the mean ± standard deviation of experiments carried out in triplicate (*n*=3).

[b] Measured pH in L/S=10 (L/kg) bottom ash suspensions after a 48–hour equilibration period in the pH stat vessels without acid/base dosage.

[c] Fe extracted by ascorbic acid or dithionite extraction (denoted with Fe-ASC and Fe-DITH, respectively), Al extracted by oxalate extraction (denoted with Al-OX), see text.

5.3.3 Reactive surfaces present in the bottom ash matrix

Table 1 shows the estimated contents of iron/aluminum (hydr)oxides before and after the treatment, which are needed as input in the adsorption models to predict the leaching of Cu and Mo. A clear increase in Fe-ASC and Fe-DITH was not observed (Table 1). However, Al-OX has increased considerably by about 1.4 g Al/kg (Table 1), equivalent to 4 g $Al(OH)_3$/kg. This value is consistent with the amount estimated from the observed release of SO_4^{2-} after aging. Assuming that this release results from the dissolution of ettringite, the simultaneous release of Al would result in the formation of 3.6 g $Al(OH)_3$/kg (see Supporting Information for further detail).

5.3.4 Leaching and characterisation of Dissolved Organic Carbon (DOC)

DOC concentrations show a slight pH-dependency and have consistently decreased after the treatment (Figure 1). Figure 2 shows the measured composition of DOC with respect to the quantities of humic substances (FA and HA) and hydrophilic acids (HY) as a function of pH. Figure 2 also includes the total extractable amounts of these substances from the samples. Results are shown for equilibration times of 48 hours and 168 hours. Generally, the major fraction of DOC is composed of HY, with a FA contribution of between 10 and 40%. Virtually no dissolved HA was detected in both samples (Figure 2). Below we focus on the leaching behaviour of FA, which is thought to play a key role in the facilitated leaching of Cu from MSWI bottom ash leachates (van Zomeren and Comans, 2004).

The primary effect of the accelerated aging treatment on DOC is a strong decrease of FA concentrations over almost the entire pH range. Degradation of FA is unlikely to be the process responsible for the observed differences, as 1) the total extracted amounts of FA hardly changed after treatment (Figure 2); 2) humic substances have been shown to be only slowly degradable with ^{14}C-ages of up to several thousands of years (Pettersson *et al.*, 1994). Therefore, the decrease of FA concentrations after accelerated aging is more likely explained by stronger adsorption to the bottom ash matrix, presumably to reactive surfaces formed during the aging process such as iron/aluminum (hydr)oxide surfaces (Table 1).

Leached FA concentrations show a pH-dependency consistent with adsorption of anionic species to (hydr)oxide surfaces, i.e. strong adsorption (low solution concentrations) at low pH and a decreasing adsorption (i.e. increasing solution concentrations) towards higher pH values (Filius *et al.*, 2000; Strathmann and Myneni, 2005). At pH 2, solution concentrations of FA increase again, consistent with protonation of the carboxylic groups of FA in this pH range, as well as the enhanced dissolution of iron/aluminum (hydr)oxide surfaces at low pH. At pH 2 and pH > 8 in the fresh sample, leached FA concentrations are similar to the measured total FA content, suggesting virtually complete FA desorption at these pH values. Leached FA concentrations in the aged sample are less than 50% of the total content, indicating that most of the FA content remains adsorbed to the solid phase over the full pH range. The stronger adsorption of FA in the aged sample is consistent with the larger aluminum (hydr)oxide content of this sample, as reflected by Al-OX in Table 1. An increase of the amount of reactive surface area would result in an increased adsorption of FA towards higher pH values. This feature has been observed for

FA sorption on goethite (Strathmann and Myneni, 2005), and is also clearly visible in the pH dependency of FA concentrations before and after aging (Figure 2). In our data, these features are more strongly pronounced in the data collected after an equilibration time of 168 hours (Figure 2), indicating a potential role of kinetics in the process that controls the leaching of FA.

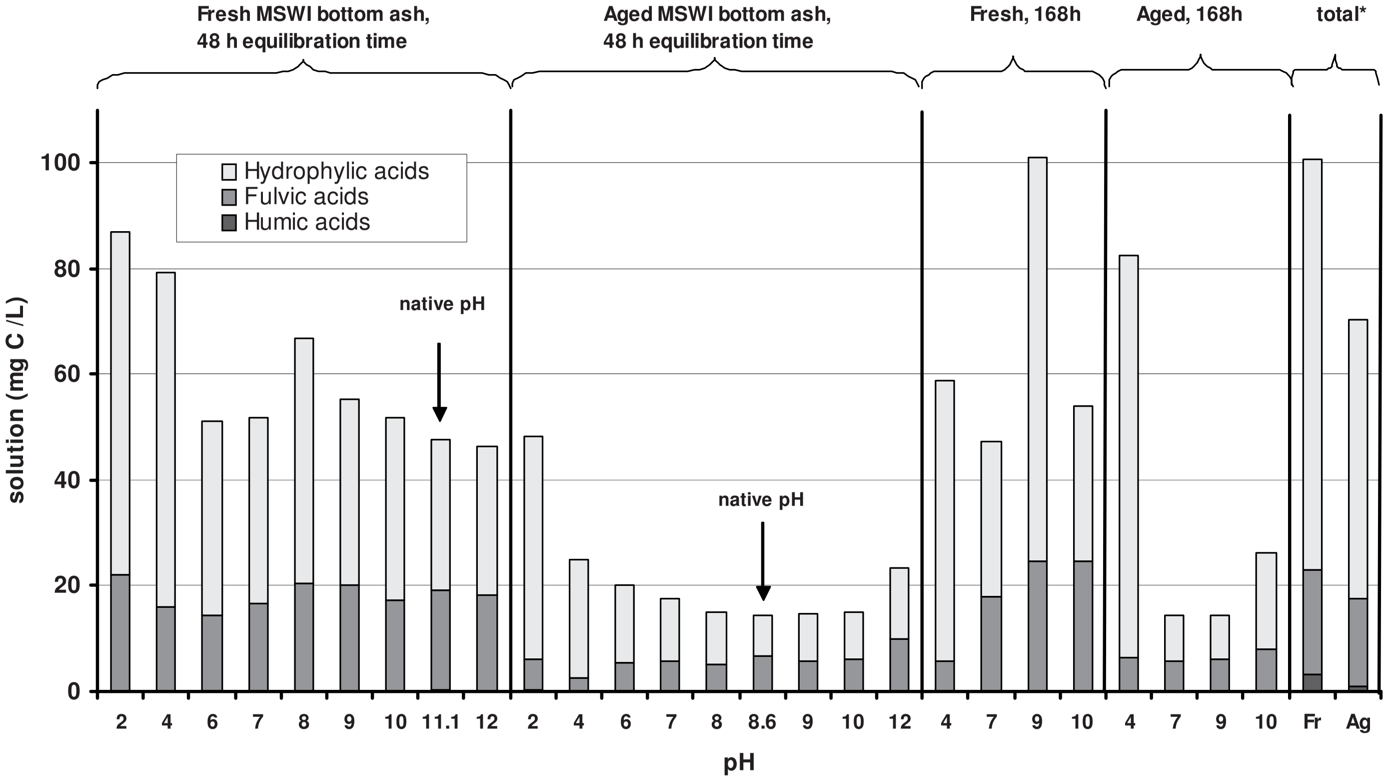


Figure 2. Results of the characterisation of organic carbon present in the fresh and aged MSWI bottom ash samples with respect to hydrophilic acids, fulvic acids and humic acids. Results are shown for the standard equilibration time of 48 h and for 168 h (the latter at selected pH values). Arrows indicate the "native" pH of the samples. Total concentrations measured in the samples are shown for comparison (Fr = fresh, Ag = aged) and are expressed in the same units as the dissolved concentrations (mg C/L).

5.3.5 Adsorption of fulvic acid on iron- and aluminium (hydr)oxides

Given the key role of FA in controlling the leaching of Cu and possibly other metals, it is important to further identify the processes that control the pH-dependent leaching of FA from fresh and aged MSWI bottom ash. Therefore, we have developed a modelling approach based on the surface complexation of FA on iron- and aluminium (hydr)oxides. This approach is derived from that of Filius *et al.* (2000) for FA adsorption on goethite (α-FeOOH). The first step in our approach was to describe the pH dependent charging behaviour of FA in solution by eight discrete protonation reactions, following Filius *et al.* (2000). Like these authors, we also assume a molar weight of 1000 g FA/mol (1 mg FA/L ~ 10^{-6} mol/L).

Next, we have derived surface complexation parameters for FA adsorption to iron- and aluminum (hydr)oxides in the untreated MSWI bottom ash sample by defining surface complexation reactions, largely following the approach of Dzombak and Morel (1990) for anionic species. The following surface complexation reactions were considered:

$$\equiv FeOH + 0.25\ FA^{-8} = \equiv FeOHFA_{0.25}^{-2} \qquad [1]$$

$$\equiv FeOH + 0.25\ FA^{-8} + H^+ = \equiv FeFA_{0.25}^{-1} + H_2O \qquad [2]$$

$$\equiv FeOH + 0.25\ FA^{-8} + 2H^+ = \equiv FeFA_{0.25}H^0 + H_2O \qquad [3]$$

In reactions 1-3, ≡FeOH are the sites on the (hydr)oxide surface and $\equiv FeOHFA_{0.25}^{-2}$, $\equiv FeFA_{0.25}^{-1}$ and $\equiv FeFA_{0.25}H^0$ are the adsorbed species, which differ in their degree of protonation. Note that each of the adsorbed species describes the adsorption of ¼ FA molecule, i.e. one adsorbed FA molecule occupies 4 ≡FeOH sites, in line with the approach of Filius *et al.* (2000). As the fully deprotonated FA species has a charge of –8 eq/kg (the sum of carboxylic and phenolic groups of FA, see Filius *et al.*, (2000)), we model, for reasons of simplicity, the adsorption of ¼ FA molecule to each ≡FeOH site as a divalent anion (0.25*-8 = -2 eq/kg).

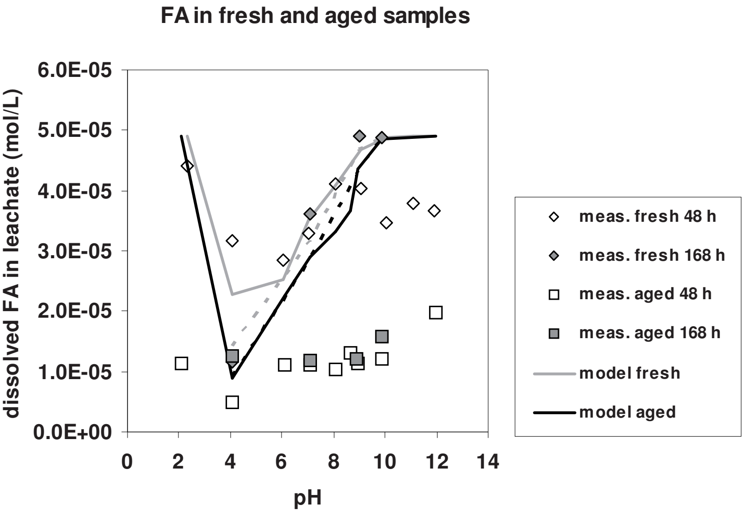


Figure 3. Measured FA concentrations in the bottom ash leachates and model curves based on surface complexation of FA to (hydr)oxide surface (see text for details). The dashed lines are obtained with the same parameters but are calculated for the leachates equilibrated for 168 h.

Reactions 2 and 3 were found to be sufficient to describe the leaching of FA in the fresh bottom ash sample over the full pH range (Figure 3). The amount of FA extracted at pH 12 after 168 h was taken as the total sorbate concentration, while the same sorbent concentration was used as described for the geochemical modelling approach in the Methods section. The log K values were fitted manually until an adequate description of the FA leaching in the fresh sample was obtained. The only fitting parameters are the log K values of reactions 2 and 3, which were found to be +10.48 and +17, respectively. Note that our log K values for FA adsorption to the iron- and aluminium (hydr)oxide surface are conditional, as they include the effects of leached cations on the speciation and binding properties of FA. These effects are negligible in the system of Filius *et al.* (2000) that only contained FA, goethite and an inert electrolyte.

Figure 3 shows that pH dependent leaching of FA from the fresh bottom ash is adequately described. We note that the difference in the predicted pH dependent FA leaching after 48 and 168 h is caused by the lower competition by phosphate and sulphate at the longer reaction time. Although the leaching behaviour of FA can be described by surface complexation, the model does not predict the observed strong decrease of FA concentrations after aging, in particular at higher pH values. Possibly, the properties of the (neoformed) reactive surfaces in the aged bottom ash differ from those in the fresh material (e.g., a higher reactivity than currently assumed in the model) and/or the representation of FA speciation in our model is too simple (e.g., interactions with cations other than H^+). Important new insights in the binding of humic substances to (hydr)oxide minerals have been made by Filius *et al.* (2003) and recently by Weng *et al.* (2006), which may contribute to further identification of the mechanisms controlling the solid/solution partitioning of FA in materials such as MSWI bottom ash.

5.3.6 Copper

Leached concentrations of Cu follow a strong pH-dependency in the acidic-neutral pH range and a weaker pH-dependency towards higher pH values. Compared to the fresh sample, a consistently lower Cu leaching is observed in the aged sample between pH 6 and 10 (Figure 1), indicating that the effect of aging is not exclusively the result of the pH decrease from pH 11.1 to 8.6.

Model predictions based on surface complexation on iron/aluminum (hydr)oxides and complexation with the measured concentrations of FA in solution, denoted with SCM in Figure 1, are generally adequate up to pH 9 for both the fresh and the aged sample. However, strong overestimates of leached concentrations are found at pH 12. Although kinetic experiments with MSWI bottom ash have shown that Cu concentrations at pH 12 slowly increase beyond 48 hours (Dijkstra *et al.*, 2006), we consider this time effect to be too small to explain the large discrepancy between the model and the data at pH 12. In this high pH region (hydr)oxide minerals such as $Cu(OH)_2(s)$ and tenorite (CuO), which have been found in MSWI bottom ash (e.g. Meima and Comans, 1999 and references therein), become oversaturated and are expected to precipitate. Therefore, an alternative surface complexation scenario is shown in which $Cu(OH)_2(s)$ is allowed to precipitate as soon as it becomes oversaturated (denoted with SCM* in Figure 1). This model scenario provides an excellent description of Cu leaching up to pH 10, but still underestimates Cu leaching somewhat at higher pH values (Figure 1). Model scenarios based solely on the solubility of a number of common Cu carbonates and (hydr)oxide phases, calculated by the “infinite solid approach” (Meima and Comans, 1997), provide less adequate predictions as these generally fail to explain Cu leaching both at low and/or high pH (see model predictions for tenorite, $Cu(OH)_2(s)$, malachite ($Cu_2(OH)_2CO_3$) and azurite ($Cu_3(OH)_2(CO_3)_2$ in the Supporting Information).

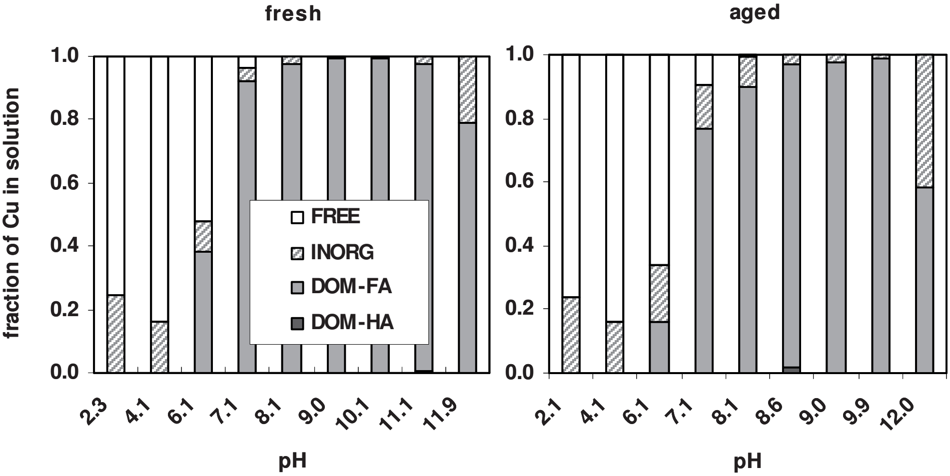


Figure 4. Calculation of the solution speciation of Cu among the different surfaces considered in the model shown for the fresh and aged sample. "DOM-FA" = bound to Fulvic Acids, "DOM-HA" = bound to Humic Acids, "Inorg" = inorganic complexes such as Cl and OH species; Free = free ions (Cu^{2+}). This figure complements predicted Cu concentrations based on the model scenario referred to as SCM* in Figure 1, see text.

With the model we are able to investigate the relative importance of the different solution species of Cu as a function of pH, as is shown in Figure 4 for the SCM* model scenario. The solution speciation is subdivided into "complexed with FA", "complexed with HA", "inorganic complexes" and "free metal" (Me^{2+}). At values of pH 6 and lower, Cu is mainly present in its free ionic form (Cu^{2+}). Above pH 7, the binding of Cu to FA is by far the dominant solution complexation reaction in both the fresh and the aged sample. The strong predominance of organically bound Cu species at the natural pH of the samples is in agreement with earlier studies based on measurements and modelling (Meima *et al.*, 1999; van Zomeren and Comans, 2004), but the strong complexation extends to both lower and higher pH values as well. When interactions with dissolved FA are neglected in the geochemical modelling calculations (shown for the SCM* model scenario in Figure 1), Cu leaching is underestimated by up to several orders of magnitude in the relevant pH range. These calculations clearly show that the leaching of Cu from MSWI bottom ash is primarily controlled by the availability and reactivity of humic substances present in the MSWI bottom ash matrix. As a consequence, the positive effect of accelerated aging on the leaching of Cu is primarily caused by the changed leaching behaviour of FA, which is in turn most likely caused by an enhanced adsorption to (neoformed) iron/aluminum (hydr)oxides.

5.3.7 Molybdenum

The leaching of Mo between pH 6 and 10 has decreased significantly after ageing (Figure 1). Processes controlling the leaching of Mo from MSWI bottom ash have been discussed in previous publications (Dijkstra *et al.*, 2006; Johnson *et al.*, 1996; Meima and Comans, 1999), from which we show a number of potentially solubility controlling minerals in Figure 1, i.e. $Fe_2(MoO_4)_3$, wulfenite ($PbMoO_4$), and powellite ($CaMoO_4$). Figure 1 also shows predictions based on the surface complexation of for MoO_4^{-2} on iron/aluminum (hydr)oxides. Wulfenite can explain the measured concentrations below pH 6, but the leaching in the more relevant pH range between pH 8 and 11 can only be explained on the basis of the weak surface complexation of molybdate (MoO_4^{-2}) on iron/aluminum (hydr)oxides.

The measured beneficial effect of aging on the Mo concentrations between pH 8 and 11 is also predicted by the adsorption of molybdate (MoO_4^{-2}) to the increased amounts of iron/aluminum (hydr)oxides, albeit to a much lesser extent (Figure 1). It should be noted that the adsorption parameters for MoO_4^{-2} to HFO have been estimated by a Linear Free Energy Relationship (LFER) (Dzombak and Morel, 1990) and are, therefore, uncertain. However, in line with our findings regarding the adsorption of FA to the solid phase, the difference between the modelled and measured effect of aging is possibly related to different properties of the (neoformed) reactive surfaces in the aged bottom ash. Although the current model cannot fully account for the reduced leaching of Mo after accelerated aging, we conclude that this positive effect is the result of a stronger Mo adsorption to (neoformed) iron/aluminum (hydr)oxides. These findings are consistent with earlier observations based on the carbonation of MSWI bottom ash leachates (Meima *et al.*, 2002).

This study lends mechanistic support for the sustainability of the observed beneficial effect of accelerated aging on the leaching of Cu and Mo from MSWI bottom ash. This work provides important new insights that may help to improve accelerated aging technology, particularly the notion that the facilitated leaching of Cu and possibly other metals is predominantly controlled by the adsorption properties of fulvic acid in MSWI bottom ash. Our results suggest that iron/aluminum (hydr)oxides are the major reactive surfaces that retain fulvic acid in this matrix, of which the aluminum (hydr)oxides have been shown to increase after aging. The observed amount of neoformed Al(hydr)oxides is probably close to the maximum that can be reached by accelerated aging, given that the dissolution of ettringite, which is believed to be the major Al source in fresh bottom ash, is complete at the final pH of 8.6. Therefore, the effect of this treatment may be optimised by the addition of reactive minerals such as iron/aluminum (hydr)oxides, that can further enhance the adsorption of humic substances, associated trace contaminants and oxyanions such as MoO_4^{-2}.

Acknowledgements

This work was partially funded by the Ministry of Housing, Spatial Planning and the Environment as part of the environmental research program of ECN. The authors acknowledge Petra Bonouvrie and Esther van der Weij-Zuiver for their careful experimental work.

A5.1 Supporting Information

Major element leaching before/after accelerated ageing; linear concentration-pH plots for Cu, Mo and SO_4, model predictions for common Cu-carbonates and hydroxides.

Major element leaching before and after accelerated aging

The pH dependent leaching pattern of Ca is an indicator for the degree of aging (Johnson *et al.*, 1995; Meima and Comans, 1997). In the fresh bottom ash Ca leaching is adequately described by the solubility of gypsum in the pH range 2-9 and ettringite above pH 9. After treatment, the Ca leaching pattern has clearly shifted towards the theoretical solubility curve of calcite (Figure S1), in particular above pH 7 where calcite is less soluble than both gypsum and ettringite. This difference results from the reaction of gypsum and ettringite with carbon dioxide, during which calcite is produced (see below). Figure S1 also includes the pH dependent leaching pattern of Ca from a MSWI bottom ash sample that has been in outside storage for 1.5 years (data from ref. 1), showing a stronger similarity with the theoretical solubility curve of calcite than the sample treated by accelerated aging. This observation suggests that the aging process in the treated sample is not complete. The oversaturation of calcite in our leachates ($SI_{calcite}$ ~ 1.1 – 1.4 above pH 8) is commonly observed in leachates from incineration residues and natural waters (see Chandler *et al.*, 1997 and references therein).

In the pH range above pH 9, the leaching of SO_4 has strongly increased after treatment (Figure 1). This process can be explained by the reaction between ettringite and dissolved CO_2(g), leading to the formation of calcite and $Al(OH)_3$(s):

$$Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O + 6CO_2(g) \leftrightarrow 6CaCO_3(s) + 2Al(OH)_3(s) + 3SO_4^{-2} + 6H^+ + 32H_2O$$

The above equation shows that the conversion of ettringite leads to the release of SO_4^{-2}. The released SO_4^{-2} may be controlled by more soluble minerals at high pH such as hydrocalumites (Reardon and Della Valle, 1997), and may be used to estimate the minimum amounts of reaction products formed after aging. The increase of SO_4^{-2} amounts to 6.83 mM (derived from Figure S1), indicating that 13.66 mM of calcite has formed ~ 13.7 g calcite/kg dry ash (1 mol SO_4^{-2} ~ 2 mol calcite, L/S ratio = 10 L/kg). Similarly, it can be estimated that 3.6 g $Al(OH)_3$(s)/kg has formed. Both in the fresh and the aged sample, the leaching of Al largely follows the pH-dependent solubility behaviour characteristic for aluminum (hydr)oxides (Figure S1).

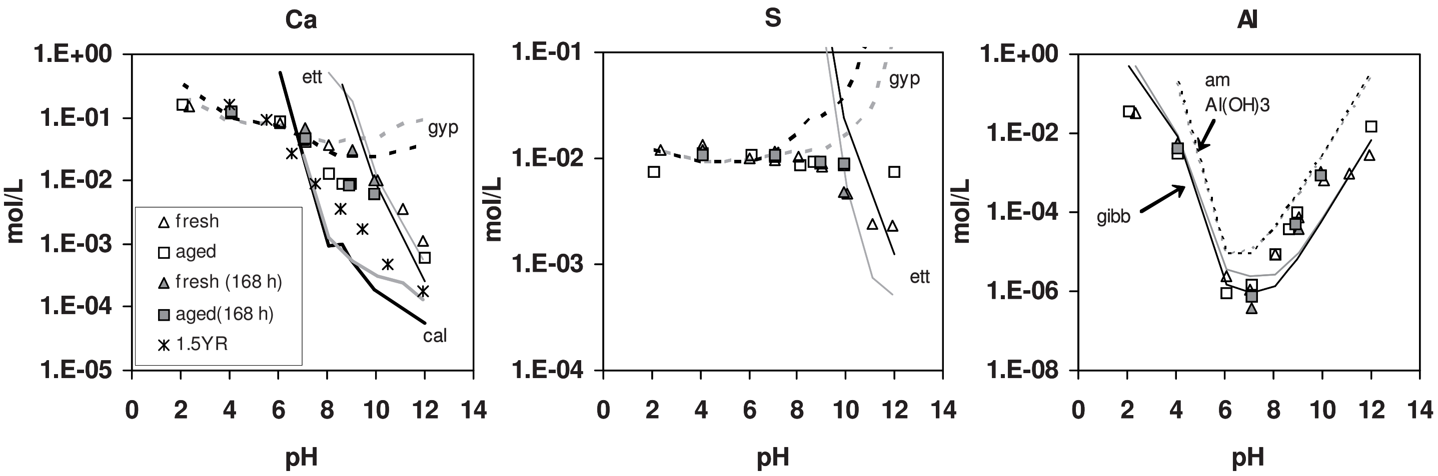


Figure S1. Leached concentrations and model predictions as a function of pH of Ca, SO_4^{-2} and Al from the fresh sample and the sample treated by accelerated aging (fresh = triangles, aged = squares; closed symbols are independent experiments obtained after a longer equilibration time of 168 h). The Ca panel includes the leaching pattern for a naturally aged sample (1.5YR, see text for further explanation). Grey model curves refer to model predictions of the fresh sample, black to the aged samples treated by accelerated aging. Abbreviations of model predictions are ett = ettringite, gyp = gypsum, cal = calcite, gibb = gibbsite, am $Al(OH)_3$ = amorphous $Al(OH)_3$.

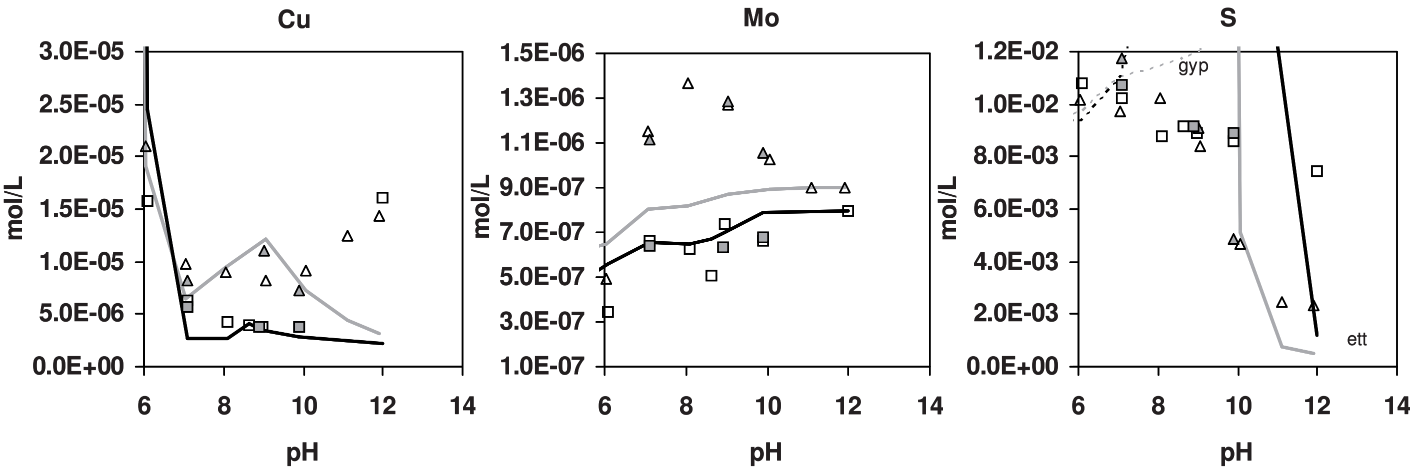


Figure S2. pH versus concentrations of Cu, Mo and SO_4 plotted on a linear scale in the pH-range 6 – 12 (fresh = triangles, aged = squares; closed symbols are independent experiments obtained after a longer equilibration time of 168 h). The data is identical to that of Figure 1 in the main text that covers the whole pH range (pH 2 – 12) and in which concentrations are plotted on a log scale to account for the log-scale concentration differences over the full pH range. Grey model curves refer to the fresh sample, black model curves to the aged sample. The model scenarios shown are for Cu: surface complexation to (hydr)oxides, precipitation of $Cu(OH)_2(s)$ and complexation of Cu to fulvic acids in solution; For Mo: surface complexation to (hydr)oxides; For SO_4^{-2}: solubility of gypsum and ettringite. For detail see main text and (for SO_4^{-2}) text on the first pages of this supporting information.

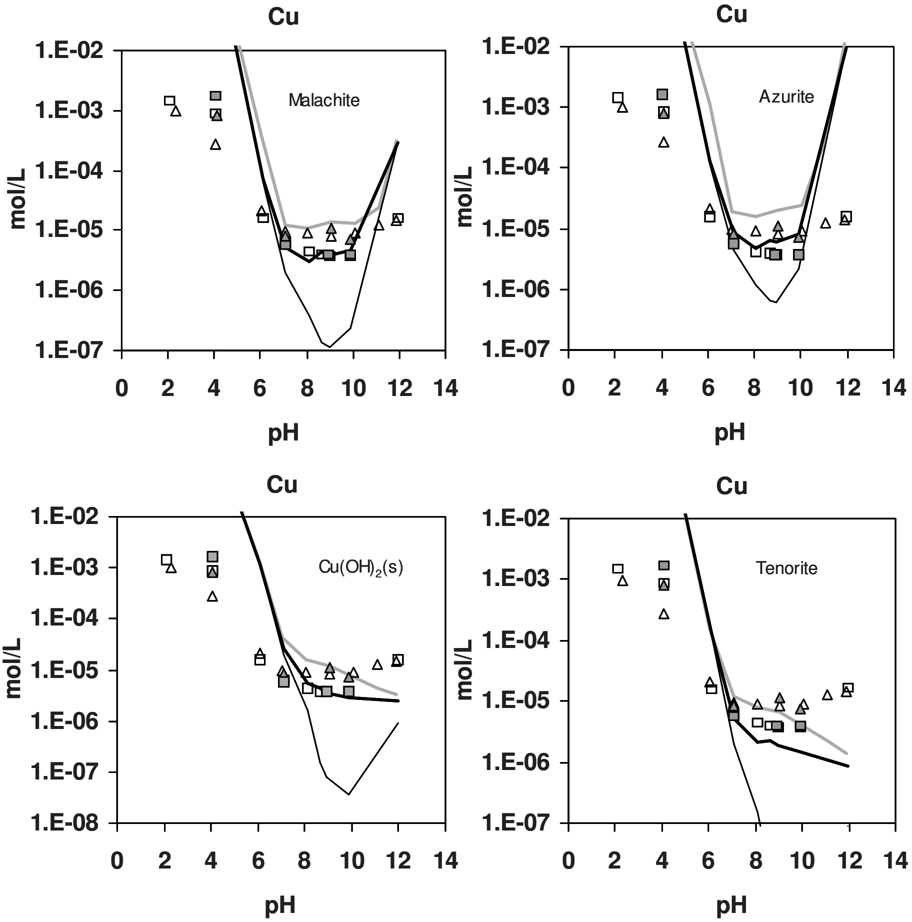


Figure S3. Leached concentrations and model predictions as a function of pH of Cu from the fresh and aged sample (fresh = triangles, aged = squares; closed symbols are independent experiments obtained after a longer equilibration time of 168 h) for different mineral phases. Grey model curves refer to model predictions of the fresh sample, black to the aged samples. Thin black curves illustrate the model scenarios in which interactions with dissolved humic acids (HA) and fulvic acids (FA) were not taken into account, in order to demonstrate the importance of these ligands for copper binding in MSWI bottom ash leachates (for clarity only shown for the aged sample).

References

Dutch Building Materials decree. Besluit van 23 november 1995, houdende regels met betrekking tot het op of in de bodem of in het oppervlaktewater gebruiken van bouwstoffen (Bouwstoffenbesluit bodem- en oppervlaktewaterenbescherming). Staatsblad van het Koninkrijk der Nederlanden 567, 1-92. 1995.

Allison, J. D., Brown, D. S., and Novo-Gradac, K. J. *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: version 3.11 user's manual,* EPA/600/3-91/021, 1991.

Blakemore, L. C., Searle, P. L., and Daly, B K *Methods for chemical analysis of soils,* Sci. rep. 80, NZ Soil Bureau, 1987.

CEN/TC292. Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with continuous pH-control. CEN/TS 14997. 2006.

Chandler, A. J., Eighmy, T. T., Hartlen, J., Hjelmar, O., Kosson, D. S., Sawell, S. E., van der Sloot, H. A., Vehlow, J., *Municipal solid waste incinerator residues,* Elsevier: Amsterdam, 1997.

Chimenos, J. M., Fernandez, A. I., Nadal, R., Espiell, F. Short-term natural weathering of MSWI bottom ash, *J. Hazard. Mater.*, **2000**, *79*, 287-299.

de Wit, J. C. M. Proton and metal ion binding by humic substances. 1992. Wageningen University, Dept. Soil Quality.

Dijkstra, J. J., van der Sloot, H. A., Comans, R. N. J. Process identification and model development of contaminant transport in MSWI bottom ash, *Waste Manage.*, **2002**, *22*, 531-541.

Dijkstra, J. J., van der Sloot, H. A., Comans, R. N. J. The leaching of major and trace elements from MSWI bottom ash as a function of pH and time, *Appl. Geochem.*, **2006**, *21*, 335-351.

Dzombak, D. A., Morel, F. M. M., *Surface complexation modeling: hydrous ferric oxide,* John Wiley & Sons, Inc.: New York, 1990.

Filius, J. D., Lumsdon, D. G., Meeussen, J. C. L., Hiemstra, T., van Riemsdijk, W. H. Adsorption of fulvic acid on goethite, *Geochim. Cosmochim. Acta*, **2000**, *64*, 51-60.

Filius, J. D., Meeussen, J. C. L., Lumsdon, D. G., Hiemstra, T., van Riemsdijk, W. H. Modeling the binding of fulvic acid by goethite: The speciation of adsorbed FA molecules, *Geochim. Cosmochim. Acta*, **2003**, *67*, 1463-1474.

Hiemstra, T., de Wit, J. C. M., van Riemsdijk, W. H. Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: a new approach, II.

application to varous important (hydr)oxides, *J Colloid Interface Sci.*, **1989**, *133*, 105-117.

Johnson, C. A., Brandenberger, S., Baccini, P. Acid neutralizing capacity of municipal waste incinerator bottom ash, *Environ. Sci. Technol.*, **1995**, *29*, 142-147.

Johnson, C. A., Kersten, M., Ziegler, F., Moor, H. C. Leaching behaviour and solubility-controlling solid phases of heavy metals in municipal solid waste incinerator ash, *Waste Manage.*, **1996**, *16*, 129-134.

Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K., Borkovec, M., Benedetti, M. F., Avena, M. J. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *Colloids Surf. A*, **1999**, *151*, 147-166.

Kostka, J. E., Luther III, G. W. Partitioning and speciation of solid phase iron in saltmarsh sediments, *Geochim. Cosmochim. Acta*, **1994**, *58*, 1701-1710.

Meeussen, J. C. L. ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models, *Environ. Sci. Technol.*, **2003**, *37*, 1175-1182.

Meima, J. A., Comans, R. N. J. Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **1997**, *31*, 1269-1276.

Meima, J. A., Comans, R. N. J. Application of surface complexation/precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **1998**, *32*, 688-693.

Meima, J. A., Comans, R. N. J. The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering, *Appl. Geochem.*, **1999**, *14*, 159-171.

Meima, J. A., van der Weijden, R. D., Eighmy, T. T., Comans, R. N. J. Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum, *Appl. Geochem.*, **2002**, *17*, 1503-1513.

Meima, J. A., van Zomeren, A., Comans, R. N. J. Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates, *Environ. Sci. Technol.*, **1999**, *33*, 1424-1429.

Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances, *Environ. Sci. Technol.*, **2003**, *37*, 958-971.

Pettersson, C., Ephraim, J. H., Allard, B. On the composition and properties of humic substances isolated from deep groundwater and surface waters, *Org. Geochem.*, **1994**, *21*, 443-451.

Reardon, E. J., Della Valle, S. Anion sequestering by the formation of anionic clays: lime treatment of fly ash slurries, *Environ. Sci. Technol.*, **1997**, *31*, 1218-1223.

Rendek, E., Ducom, G., Germain, P. Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash, *J. Hazard. Mater.*, **2006**, *128*, 73-79.

Strathmann, T. J., Myneni, S. C. B. Effect of soil fulvic acid on nickel(II) sorption and bonding at the aqueous-boehmite (g-AlOOH) interface, *Environ. Sci. Technol.*, **2005**, *39*, 4027-4034.

Swift, R. S. Organic matter characterization. In *Methods of soil analysis. Part 3. Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996, pp 1011-1069.

Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

van Gerven, T., van Keer, E., Arickx, S., Jaspers, M., Wauters, G., Vandecasteele, C. Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling, *Waste Manage.*, **2005**, *25*, 291-300.

van Zomeren, A., Comans, R. N. J. Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **2004**, *38*, 3927-3932.

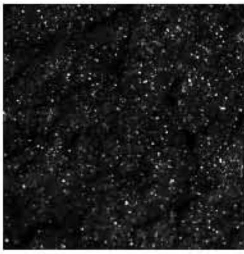
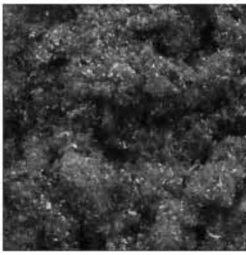
van Zomeren, A., Comans, R. N. J. Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch procedure, *Environ. Sci. Technol.*, **2007**, *41*, 6755-6761.

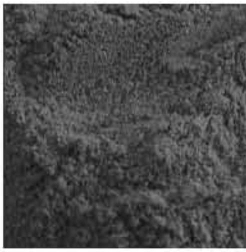
Weng, L. P., van Riemsdijk, W. H., Hiemstra, T. Adsorption free energy of variable-charge nanoparticles to a charged surface in relation to the change of the average chemical state of the particles, *Langmuir*, **2006**, *22*, 389-397.

Zevenbergen, C., Vander Wood, T., Bradley, J. P., Van der Broeck, P. F. C. W., Orbons, A. J., van Reeuwijk, L. P. Morphological and chemical properties of MSWI bottom ash with respect to the glassy constituents, *Hazardous waste and hazardous materials*, **1994**, *11*, 371-383.

CHAPTER 6

CARBON SPECIATION IN MUNICIPAL SOLID WASTE INCINERATOR (MSWI) BOTTOM ASH IN RELATION TO FACILITATED METAL LEACHING




van Zomeren, A. and Comans, R.N.J., Carbon speciation in municipal solid waste incinerator (MSWI) bottom ash in relation to facilitated metal leaching. *Submitted*, **2008**.

CARBON SPECIATION IN MUNICIPAL SOLID WASTE INCINERATOR (MSWI) BOTTOM ASH IN RELATION TO FACILITATED METAL LEACHING

André van Zomeren[1] *and Rob N.J. Comans*[1,2]

The release of inorganic and organic contaminants from municipal solid waste incinerator (MSWI) bottom ash is controlled to a large extent by the release of dissolved organic carbon (DOC), and in particular by the reactive humic (HA) and fulvic acids (FA) subfractions of DOC. The properties of organic matter contributing to the release of DOC, HA and FA are, therefore, important for environmental risk assessment. In this study we have quantitatively measured the carbon speciation, and its relation with the leaching of Cu, in three fresh and carbonated MSWI bottom ash samples. Results show that up to only 25% of LOI consists of organic carbon (OC), while about 15% of OC in the three samples consists of HA and FA. Since only these small reactive carbon fractions contribute to enhanced metal leaching from MSWI bottom ash, we conclude that LOI measurements are insufficiently discriminative for a quantitative assessment of environmentally relevant organic carbon species in MSWI bottom ash. In addition, only the hydrophilic organic carbon fraction is probably prone to gas production (CO_2/CH_4) by biodegradation in disposal scenarios. Up to 50% of DOC in MSWI bottom ash leachates was identified as fulvic acid (FA). This value is substantially higher than previously estimated for these MSWI bottom ash samples and is consistent with the higher recovery of the new method that was applied. The results of this study imply that dedicated methods, focusing on specific carbon fractions, are more appropriate for assessment of environmentally relevant organic carbon species than the measurement of LOI. These methods may greatly improve the assessment of the long-term environmental properties of bottom ash in utilisation or disposal scenarios.

---

[1] Energy Research Centre of The Netherlands.

[2] Wageningen University.

6.1 Introduction

Incineration plays a major role in the management of municipal solid waste in many countries. Therefore, large quantities of municipal solid waste incinerator (MSWI) bottom ash are produced. These residues are generally landfilled or re-used as secondary construction materials in road constructions (Chandler *et al.*, 1997). The leaching of contaminants (metals, oxyanions and salts) from MSWI bottom ash may possibly inhibit its application as a construction material. In The Netherlands, the release of copper and molybdenum from MSWI bottom ash is of particular concern in view of current limit values.

Several studies have pointed to the role of dissolved organic carbon (DOC) in facilitating the leaching of copper from MSWI bottom ash (Chandler *et al.*, 1997; Comans *et al.*, 1993; Dijkstra *et al.*, 2006; Johnson *et al.*, 1995; Meima *et al.*, 1999; van der Sloot *et al.*, 1992; van Zomeren and Comans, 2004). DOC is a sum parameter for all dissolved organic carbon compounds. Humic- (HA) and fulvic acids (FA) have been identified as important DOC sub-fractions contributing to the complexation of contaminants (Stevenson, 1982). Pavasars (1999) estimated, based on XAD-8 extractions and high performance size exclusion chromatography, that 23% of DOC in Swedish MSWI bottom ash leachates consisted of a high-molecular weight, possibly humic-like material. Recently, we have determined that 80-100% of the leached copper is bound to FA. The hydrophilic organic carbon (Hy) fraction in MSWI bottom ash leachates (generally > 50% of the DOC) is, therefore, considered to be of minor importance for the enhanced leaching of heavy metals (Dijkstra *et al.*, 2006; van Zomeren and Comans, 2004). Therefore, the specific properties of organic carbon in the solid MSWI bottom ash matrix that contribute to the leaching of DOC and associated contaminants are important for environmental risk assessment of these materials.

In addition to the complexation properties of organic carbon, there is also an increasing interest in the stability of organic carbon in soil and waste materials, e.g. in the context of carbon sequestration in soils and landfilling of organic waste. The development of methods to assess the degradability and solubility of organic matter is currently being considered in technical standardisation committees within CEN and ISO. Recently, methods to assess reactive and inert carbon species have been developed (Comans *et al.*, 2004) and are currently being standardised in The Netherlands (NVN 7391 and NVN 7392).

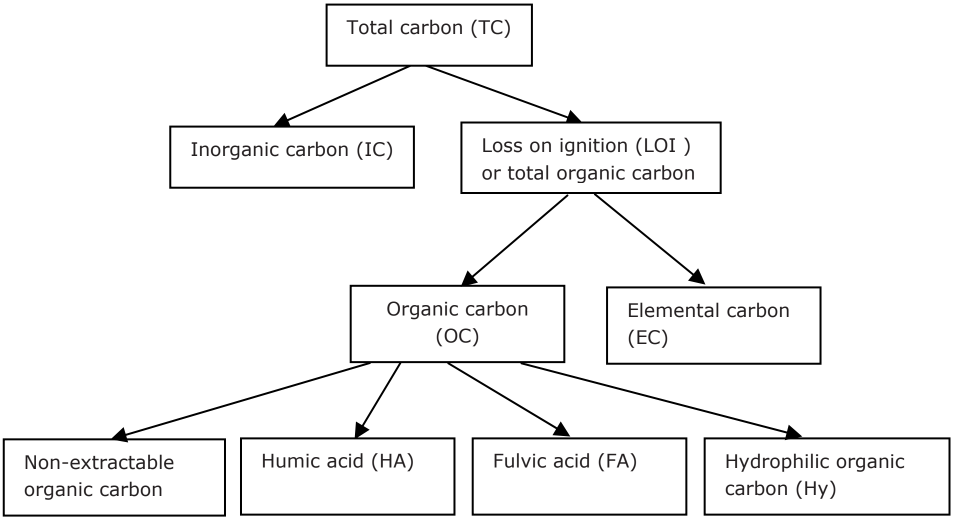


Figure 1. Schematic representation of carbon speciation in MSWI bottom ash. TOC is used rather than LOI, because TOC analysis specifically quantifies the amount of carbon. Measurement of TOC or LOI estimates the amount of OC and EC together, while only OC (especially HA and FA) is important with regard to enhanced metal leaching from these materials. The hydrophilic organic carbon (Hy) fraction is probably more prone to gas production (CO_2/CH_4) by biodegradation and is believed to be of less importance with respect to metal complexation. The remaining part of carbon is defined as the non-extractable organic carbon fraction (NEOC).

Figure 1 defines measurable carbon species that are relevant for the environmental carbon properties that have been reviewed above, i.e., reactivity for metal complexation, solubility and degradability. The objective of this study is to quantify these species in MSWI bottom ash, with specific emphasis on the reactive carbon fractions (i.e. HA and FA) relevant for the long-term leaching behaviour of this waste material. As shown in Figure 1, total carbon (TC) in the solid matrix includes inorganic carbon (IC) and total organic carbon (TOC), the latter is generally approximated by loss on ignition (LOI), which is not necessarily solely related to carbon; in general, natural organic matter consists of about 50% C by weight (Stevenson, 1982). TOC (or LOI) is made up of elemental carbon (EC) and organic carbon (OC). Elemental carbon is a product of incomplete combustion; it has a high molecular weight, very few functional groups and is insoluble in water (Ferrari *et al.*, 2002). It is believed that EC does not contribute significantly to the production of DOC and, hence, the facilitated leaching of contaminants. However, these hydrophobic carbon species can possibly bind organic micro pollutants to the solid matrix. Organic carbon (OC) represents the amount of potentially reactive carbon that may be degraded, contribute to DOC formation and/or facilitate contaminant leaching. The potentially leachable carbon fraction can be divided into humic acids (HA), fulvic acids (FA), hydrophobic neutral (HON) organic carbon and other organic substances, which will be referred to as “hydrophilic organic carbon” (Hy). In fact, Hy is defined here as DOC that is not identified as HA, FA or HON and can be made up of, e.g., small aliphatic acids or carbohydrates. The remaining part of (insoluble) OC is defined as non-extractable (i.e. by acid or base) organic carbon (NEOC) and can be of diverse origin (e.g. paper, plastics, wood).

Based on the carbon species defined in Figure 1, we have selected and applied specific methods to quantify these species in MWSI bottom ash. We have determined the following carbon fractions in three fresh and carbonated MSWI bottom ash samples: TC, IC, EC, OC, LOI, HA, FA, Hy and NEOC. The relevance of measuring specific carbon species rather than LOI will be addressed with regard to the environmental properties of bottom ash.

6.2 Materials and methods

6.2.1 MSWI bottom ash samples

Three MSWI bottom ash samples were derived from two Dutch MSW incinerators, 1 and 2. The sample QUE1 was taken directly after the material passed the quench tank in MSWI 1. In the laboratory, the sample was air dried, crushed and sieved through a 2 mm sieve and stored in a closed container. The second sample from MSWI 1 (1.5YR), was taken after a storage period of 1.5 years in open atmosphere on a heap. The sample was taken from the outer layer of the heap, and was air-dried and sieved (<2 mm). This sample was not ground to prevent the breaking up of weathered grains and the creation of fresh surfaces. Both samples were used in an earlier study on characterisation of the leaching behaviour of MSWI bottom ash (Meima and Comans, 1997; Meima and Comans, 1999) and for the characterisation of DOC in leachates (van Zomeren and Comans, 2004).

Bottom ash sample BA2 was taken from MSWI 2 in 1996. The sample was freshly produced and is atypical for a freshly produced bottom ash because of its low native pH (7.8) and high redox potential (+344 mV) that develops in contact with water. In the laboratory, the sample was air dried, sieved through a 2 mm sieve and stored in a closed container. The leaching behaviour of this sample was studied by Dijkstra *et al.* (2002) and DOC in leachates was characterised according to van Zomeren and Comans (2007). All samples were stored in the dark under a nitrogen atmosphere.

Leaching experiments, LOI and moisture content analysis were performed using the <2mm bottom ash samples. Due to the small sample sizes required for TGA-MS, TIC/TOC and elemental analysis, a further size reduction (<100 μm) of sub samples for these analyses was necessary to reduce errors due to sample heterogeneity. In addition, all samples were analysed five times. The results were averaged and the standard deviation was calculated.

6.2.2 Moisture content and loss on ignition (LOI)

Crushed and sieved sub-samples (about 2 gram, <100 μm) were dried in an oven at 105 ^{o}C for 24 hours to determine the moisture content. Subsequently, the samples were heated at 550 ^{o}C for 4 hours to determine LOI. Moisture content and LOI were determined gravimetrically.

6.2.3 Total, inorganic and organic carbon measurements

Total carbon, total organic carbon (TOC) and total inorganic carbon (TIC) in the solid matrix was measured with a Shimadzu solid sample module coupled to a Shimadzu TOC 5000A analyzer. About 100 mg of sample was weighed and TC was measured by catalytic combustion at 900 ^{o}C. Next, TIC was measured by H_3PO_4 addition to decompose carbonate and TOC was subsequently quantified by subtraction of TC and TIC.

DOC in the bottom ash leachates (see section “Leaching experiments” below) was measured with a Shimadzu TOC 5000A TOC analyser. DOC was measured as the difference between total dissolved carbon (catalytic combustion at 680 ^{o}C) and inorganic carbon (acidification with H_3PO_4). The evolved gasses from the total content analysis (TC and TIC) and from the liquid samples (total dissolved carbon and dissolved inorganic carbon, DIC) were detected for CO_2 by a non-dispersive infrared detector.

Total Carbon (TC) in the bottom ash matrix was also measured with a Carlo Erba FLASH EA 1112 element analyser. About 20 mg MSWI bottom ash was weighed in a tin cup and the sample was combusted at 1700 ^{o}C. The evolved CO_2 was detected with a katharometer.

6.2.4 Thermal Gravimetrical Analysis-Mass Spectrometry (TGA-MS)

TGA-MS analysis was performed with a Mettler-Toledo TGA/SDTA 851e system coupled to a Quadrupole mass-spectrometer (Pfeiffer, Thermostar). 10-30 mg bottom ash was weighed in a ceramic cup and heated from 25-900 ^{o}C under an oxygen atmosphere at a heating rate of 40 ^{o}C/min. Three different carbon species were derived from TGA-MS analysis on the basis of their thermal stability; OC, EC and IC. A temperature program (Table 1) was used in order to obtain a good peak separation. Preliminary experiments have shown that an isothermal equilibration time of 15 minutes at the reaction temperatures of OC, EC and IC (Table 1) was sufficient to completely separate the subsequent weight loss steps and the evolved gas peaks. The weight loss was recorded by the TGA microbalance. The MS simultaneously monitored the evolved gasses for CO_2 and H_2O. The CO_2 peak areas were determined by integration, the amount of evolved carbon was calculated from a calibration line based on the decomposition of $CaCO_3$ standards. The H_2O peaks were only used qualitatively to identify the carbon species.

Table 1. Temperature program for TGA-MS analysis. The heating rate was 40 °C/min in each dynamic heating step. Isothermal time steps were included to ensure complete reactions and hence separation of all processes.

Step	Temperature range (°C)	Isothermal time (min)
1	25-150	-
2	150	15
3	150-350	-
4	350	15
5	350-550	-
6	550	15
7	550-900	-

6.2.5 Leaching experiments

Leaching experiments were carried out by adding the MSWI bottom ash samples to demineralised water at a liquid to solid ratio (L/S) of 5 L/kg. The samples were leached, without pH adjustment, for 24 hours, while being continuously agitated in an end-over- end shaker. After 24 hours, pH was measured and the eluates were centrifuged and filtered (0.2 µm).

6.2.6 Determination of HA, FA and Hy concentrations

Concentrations of humic- (HA) and fulvic acids (FA) and the remaining more hydrophilic organic carbon (Hy) were measured in leachates and in the total solid matrix of the three bottom ash samples. The organic matter was fractionated using a new rapid batch procedure (van Zomeren and Comans, 2007) based on generally applied isolation/purification procedures for HA and FA determination in liquid samples (Thurman and Malcolm, 1981) and solid source materials (Swift, 1996). These procedures are also used by the International Humic Substances Society (IHSS) to isolate standard HA and FA samples from solid and liquid source materials. In short, the rapid batch procedure involves isolation of HA at pH 1 and the subsequent adsorption of FA (and HON) onto DAX-8 resin. The concentrations of HA, FA and Hy are determined by direct DOC measurements (HA and Hy) or by the difference between two DOC measurements (FA). The HON fraction was not separately determined in this study and is included in the reported FA concentrations.

6.3 Results and discussion

6.3.1 Total organic, elemental and inorganic carbon analysis

Figure 2 displays a typical result from TGA-MS analysis (sample BA2). Sample moisture and crystal water is released at temperatures up to 150 ^oC, as evidenced by the weight loss in combination with the large H_2O peak from the MS. Organic carbon is combusted at 350 ^oC, releasing both CO_2 and H_2O, while at 550 ^oC the elemental carbon content is converted, predominantly to CO_2 . Elemental carbon mainly consists of carbon with only minor amounts of functional groups, which is reflected in the small H_2O peak accompanying the CO_2 peak. The temperature for EC combustion appears lower than expected but experiments with mixtures of bottom ash and activated carbon showed that this fraction is indeed combusted at 550 ^oC (whereas pure activated carbon was combusted at about 750 ^oC). This observation is consistent with the work of Ferrari *et al.* (Ferrari *et al.*, 2002) who suggest that metals or metal oxides in the bottom ash matrix catalyse the combustion of EC. Finally, at about 730 ^oC, inorganic carbon (from $CaCO_3$) decomposes, which results in the release of solely CO_2. Preliminary experiments showed that this CO_2 peak disappears when the samples were treated with acid before analysis. Figure 2 shows that the conventional LOI (or TOC) method (combustion at 550 ^oC) determines the weight loss of both OC, which is primarily combusted at 350 ^oC, and EC (combustion at 550 ^oC).

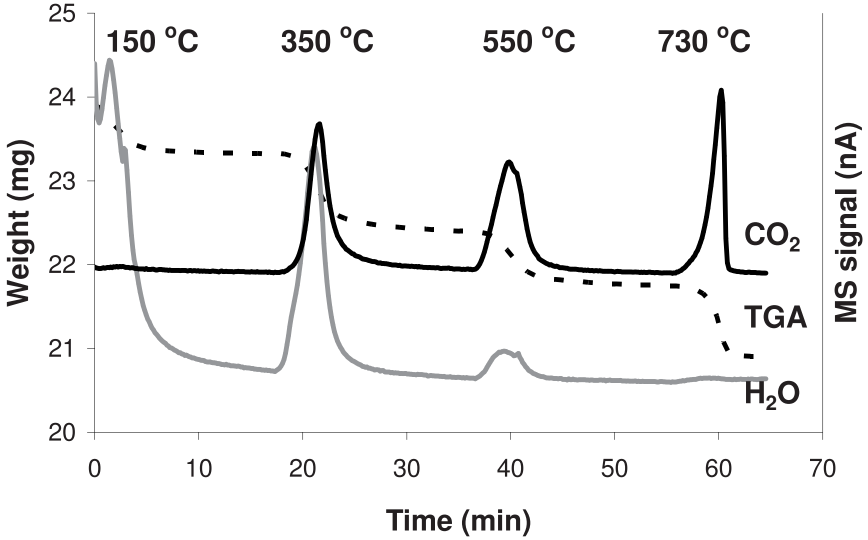


Figure 2. TGA-MS result from analysis on MSWI bottom ash sample BA2. Four weight loss steps are visible from the TGA curve (dotted line) and are identified by the simultaneous release of CO_2 (black line) and/or H_2O (gray line): moisture (150 °C), Organic carbon (350 °C), Elemental carbon (550 °C) and Inorganic carbon (730 °C). The heating rate was 40 °C/min and isothermal time steps (Table 1) were included to ensure complete reactions and good separation of MS peaks.

Table 2 shows the results of TC, TOC and LOI in the three MSWI bottom ash samples. Total Carbon (TC) measured by TGA-MS (as the sum of OC, EC and IC) is in reasonably good agreement with the results measured by elemental analysis and by the TOC analyser (solid sample module), especially considering the larger standard deviations in the TGA-MS analysis. The measured TOC concentrations for sample QUE1 and 1.5YR are similar whereas TOC in sample BA2 is 40-90% higher. The measured TOC concentrations by both TGA-MS and the TOC analyser are in reasonably good agreement.

Table 2. Total carbon (TC), total organic carbon (TOC, sum of organic and elemental carbon) and loss on ignition (LOI) measurements in three MSWI bottom ash samples. All results are in gram C per kg dm, except for LOI which is calculated in gram weight loss per kg dm.

Parameter	Technique	n	QUE1	1.5YR	BA2
TC	Element analyser	3	25.20±0.00	31.85±0.21	43.05±0.35
TC	TGA-MS	5	19.64±4.13	29.03±5.97	43.38±7.59
TC	TOC analyser	1	24.16	30.70	41.38
TOC	TGA-MS	5	17.63±3.95	17.86±4.30	32.60±6.04
TOC	TOC analyser	1	20.13	19.86	29.44
LOI	TGA-MS	5	28.64±1.25	31.82±0.58	62.72±0.77
LOI	Gravimetric	3	31.83±0.12	40.99±0.64	76.72±0.32

The total carbon and the organic carbon speciation (see Figure 1) in the solid materials is presented graphically in Figure 3. All samples have comparable EC concentrations, which might be related to similar combustion conditions as suggested by Rubli *et al.* (2003). EC accounts for a relatively large part of LOI (and TOC) in the samples, consistent with the observations of Ferrari *et al.* (2002) and Rubli *et al.* (2003). LOI is often measured in incineration plants to determine the degree of mineralisation of the solid bottom ash matrix (Chandler *et al.*, 1997). High mineralisation is targeted because organics can adversely influence (e.g. by facilitating the leaching of contaminants and/or by CO_2/CH_4 gas formation) the long-term behaviour of incinerator residues (Rubli *et al.*, 2003). Given the large contribution of (relatively inert) EC to LOI, we conclude that LOI measurements are insufficiently discriminative for a quantitative assessment of environmentally relevant organic carbon species in MSWI bottom ash.

The IC concentration in the carbonated samples 1.5YR and BA2 is similar and significantly higher than that in the fresh bottom ash sample (QUE1), as a result of carbonation during storage in the open air. The total carbon speciation is quite different in the three samples. The OC concentrations are similar for the samples QUE1 and 1.5YR, but OC in sample BA2 is significantly higher. We conclude that TGA-MS analysis provides detailed information with regard to the speciation of both organic and inorganic carbon in waste materials.

6.3.2 Organic carbon speciation measurements

The carbon speciation in the OC fraction is further detailed in terms of humic (HA), fulvic (FA) and hydrophilic acids (Hy) in Figure 3. The total HA and FA content, i.e. the subfractions that are particularly relevant for the enhanced leaching of metals, is about 15% of OC in each of the three samples (Figure 3). It is observed that the sum of HA, FA and Hy is not equal to the total OC fraction as measured by TGA-MS. The amount of carbon that is not extracted in the method for determination of HA, FA and Hy is defined here as NEOC (see also Figure 1). This fraction accounts for a relatively large part of the OC. It is noted that it cannot be excluded that part of NEOC may still consist of HA and/or FA. Li *et al.* (2002) have shown that only 29% of the total HA in a peat soil is extracted in the first alkaline extraction step of the IHSS procedure and that four sequential steps were required to extract more than 90%. However, in an earlier study (Comans *et al.*, 2004), we have found that in MSWI bottom ash 90% of the HA fraction is already extracted in the first extraction step. Therefore, we conclude that the NEOC fraction in MSWI bottom ash predominantly consists of other carbon species than HA, FA, and Hy. These species are probably strongly hydrophobic (e.g. plastics).

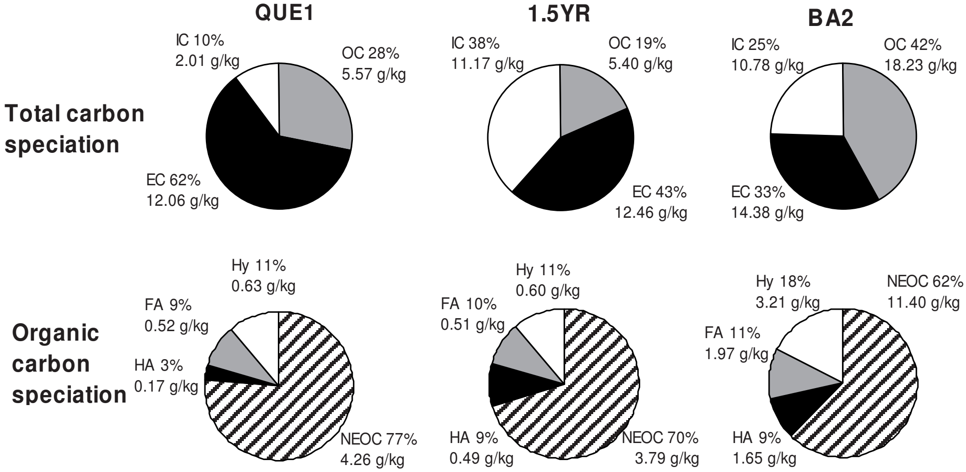


Figure 3. Carbon speciation (total content) in three MSWI bottom ash samples according to the diagram shown in Figure 1 (g C/kg dry bottom ash). NEOC is calculated as OC-(HA+FA+Hy).

6.3.3 Dissolved organic carbon characterisation

The carbon speciation (HA, FA and Hy concentrations) in leachates (L/S=5, native pH) from MSWI bottom ash was analysed by a new rapid batch method (van Zomeren and Comans, 2007). Table 3 shows that about 50% of DOC in the leachates is present as FA, while HA accounts for only a small percentage of total DOC. Accurate determination of FA is important for assessment of Cu leaching from MSWI bottom ash. The measured FA concentrations in this study are significantly greater than those reported earlier (i.e. 15-20% of DOC) by van Zomeren and Comans (2004), based on the conventional isolation procedure for aquatic samples. This observation is consistent with the higher dissolved FA recovery of the new method (van Zomeren and Comans, 2007), that was applied in this study. In principle, the reported FA concentrations in this study might include a hydrophobic neutral (HON) carbon fraction (not determined). However, preliminary experiments using several water samples taken from different bottom ash leachates (e.g. quench tank and seepage water) in an incineration plant, indicate that HON is of minor importance in this matrix (10-30% of FA).

Table 3. Cu leaching (van Zomeren and Comans, 2004) and dissolved organic carbon species determined in three MSWI bottom ash leachates (L/S=5) without pH adjustment. The total amount of reactive Fe- and Al-(hydr-)oxides is expressed in terms of hydrous ferric oxide (HFO) in g HFO/L.

Sample	**pH** (-)	**Cu** (mg/kg)	**DOC** (g C/kg)	**HA** (g C/kg)	**FA** (g C/kg)	**Hy** (g C/kg)	**HFO** (g HFO/L)
QUE1	10.39	2.00	0.52	0.003	0.29	0.23	2.53*
1.5YR	8.63	1.11	0.12	0.002	0.06	0.07	5.24*
BA2	7.79	18.3	1.08	0.007	0.48	0.59	7.88#

*Meima & Comans (1999); #Dijkstra *et al.* (2002)

Van Zomeren and Comans (2004) have found that the complexation of Cu by DOC in MSWI bottom ash could not be fully explained by their earlier estimate of the FA fraction (i.e. 15-25% of DOC). We suggest that our new FA measurements (Table 3) can better explain the earlier measurements and further modelling work is planned to re-interpret these results.

Olsson *et al.* (2007) conclude that the hydrophilic carbon fraction controls the complexation of Cu in MSWI bottom ash leachates by >95%. In a recent study (van Zomeren and Comans, 2007), we have found that the hydrophilic carbon fraction obtained with the conventional column elution procedures for aquatic samples (e.g. Leenheer, 1981; Swift, 1996; Thurman and Malcolm, 1981) contains a substantial part of FA-like substances. The hydrophilic carbon fraction in leachates from MSWI bottom ash determined by Olsson *et al.* (2007) was based on Leenheer (1981). Therefore, their observed Cu complexation is likely to be at least partly controlled by these FA-like substances. We conclude that the operational character of humic substances needs to be considered carefully in the interpretation of reactive organic matter fractions and their effect on copper leaching.

6.3.4 Leaching mechanisms of HA and FA in MSWI bottom ash samples

When the leached concentrations of HA, FA and Hy (Table 3) are compared to the total amounts of each component in the solid matrix (Figure 3), it is clear that, respectively, only a minor to moderate percentage of HA and FA in the bottom ash samples is leached under the prevailing conditions (between pH 8 and 10.5 for the three bottom ash samples). The low leachability of HA from bottom ash is attributed to the presence of relatively high amounts of di- and trivalent ions (e.g. Ca, Al and Fe), which have been shown to precipitate HA due to charge neutralisation and subsequent coagulation (Temminghoff *et al.*, 1998; Weng *et al.*, 2002).

The FA leaching in sample 1.5YR is considerably lower (Table 3) than in the fresh bottom ash from the same incinerator (QUE1). The incomplete leaching of FA from the bottom ash samples is attributed to FA adsorption to reactive Fe and Al (hydr)oxide surfaces (HFO) in the bottom ash matrix, albeit with limited affinity at these moderately alkaline pH values (Dijkstra *et al.*, 2006). Table 3 does also shows a lower leaching of Hy from 1.5 YR, relative to the fresh bottom ash. Measurements of Dijkstra *et al.* (2006) show that the lower leaching of Hy from carbonated bottom ash is likely caused by leaching and/or degradation.

6.4 Conclusions

In this study, the carbon speciation of two freshly produced MSWI bottom ash samples and a 1.5 year old MSWI bottom ash sample from two different MSW incinerators was measured in both the solid materials and the leachates at native pH. Our results show that up to only 25% of LOI consists of organic carbon (OC), while about 15% of OC in the three samples consists of HA and

FA. Since only these small reactive carbon fractions contribute to enhanced metal leaching from MSWI bottom ash, we conclude that LOI measurements are insufficiently discriminative for a quantitative assessment of environmentally relevant organic carbon species in MSWI bottom ash. With regard to the improvement of the environmental properties of MSWI bottom ash, optimisation of the incineration process should focus first of all on minimisation of the OC content since this fraction contains the humic (HA) and fulvic (FA) acids that significantly enhance contaminant leaching from these residues. In addition, only the hydrophilic organic carbon fraction is probably prone to gas production (CO_2/CH_4) by biodegradation in disposal scenarios. We have shown that dedicated methods, focusing on the relevant carbon fractions, are more appropriate than the measurement of LOI.

Up to 50% of DOC in the leachates at the native pH of the bottom ash samples consists of FA, with a minor contribution of HA. This value is substantially higher than previously estimated for these MSWI bottom ash samples and is consistent with the higher recovery of the new method that was applied. The observed lower leaching of FA from aged bottom ash, attributed to a stronger binding to reactive Fe and Al (hydr)oxide surfaces in the solid matrix, may also be considered in treatments to improve the environmental quality of MSWI bottom ash.

The identified speciation of organic carbon in both the solid phase and the leachates of MSWI bottom ash can contribute substantially to improve the assessment of the long-term environmental behaviour of bottom ash in utilisation or disposal scenarios.

Acknowledgements

We thank Esther van der Weij-Zuiver for her work on the HA, FA and Hy extractions. Wouter Huijgen is thanked for the stimulating discussions on the TGA-MS method development. This work was partly funded by the Ministry of Spatial Planning, Housing and the Environment as part of the environmental research program of ECN.

References

Chandler, A. J., Eighmy, T. T., Hartlen, J., Hjelmar, O., Kosson, D. S., Sawell, S. E., van der Sloot, H. A., Vehlow, J., *Municipal solid waste incinerator residues*; Elsevier: Amsterdam, 1997.

Comans, R. N. J., Steketee, J. J., van Zomeren, A., and Zuiver, E. *Bepalingsmethoden voor reaktieve en inerte vormen van koolstof in grond, bouw- en afvalstoffen (ANVM project 247)*; ECN-C--03-127; 2004.

Comans, R. N. J., van der Sloot, H. A., and Bonouvrie, P. A. Geochemical reactions controlling the solubility of major and trace elements during leaching of municipal solid waste incinerator residues. (Municipal Waste Combustion Conference), 667. 1993. Williamsburg, V.A.

Dijkstra, J. J., van der Sloot, H. A., Comans, R. N. J. Process identification and model development of contaminant transport in MSWI bottom ash, *Waste Man.*, **2002**, *22*, 531-541.

Dijkstra, J. J., van Zomeren, A., Meeussen, J. C. L., Comans, R. N. J. Effect of Accelerated Aging of MSWI Bottom Ash on the Leaching Mechanisms of Copper and Molybdenum, *Environ. Sci. Technol.*, **2006**, *40*, 4481-4487.

Ferrari, S., Belevi, H., Baccini, P. Chemical speciation of carbon in municipal solid waste incinerator residues, *Waste Man.*, **2002**, *22*, 303-314.

Johnson, C. A., Kersten, M., and Moore, C. Leaching behavior and solubility controlling solid phases of trace elements in municipal solid waste incinerator ash and cement stabilized solid wastes. (Proceedings of the international symposium on bulk 'inert' waste: An opportunity for use), 129-134. 1995. Proceedings of the international symposium on bulk 'inert' waste: An opportunity for use, Leeds.

Leenheer, J. A. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, *Environ. Sci. Technol.*, **1981**, *15*, 578-587.

Li, L., Sheng, G., Fu, J., Peng, P., and Huang, W. Characterization of humic acids progressively base extracted from Pahokee peat. 207-209. 2002. Proceedings of the International Humic Substances Society Twentieth Anniversary Conference, July 21-26, 2002, Boston, USA. IHSS 20th anniversary conference, Humic acids: nature's most versatile materials.

Meima, J. A., Comans, R. N. J. Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **1997**, *31*, 1269-1276.

Meima, J. A., Comans, R. N. J. The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering, *Applied geochemistry*, **1999**, *14*, 159-171.

Meima, J. A., van Zomeren, A., Comans, R. N. J. Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates, *Environ. Sci. Technol.*, **1999**, *33*, 1424-1429.

Olsson, S., vanSchaik, J. W. J., Gustafsson, J. P., Kleja, D. B., vanHees, P. A. W. Copper(II) Binding to Dissolved Organic Matter Fractions in Municipal Solid Waste Incinerator Bottom Ash Leachate, *Environ. Sci. Technol.*, **2007**, *41*, 4286-4291.

Pavasars, I. Characterisation of organic substances in waste materials under alkaline conditions. 1999. Ph.D. Dissertation, Linkopping university, Sweden.

Rubli, S., Belevi, H., Baccini, P. Optimizing municipal solid waste combustion through organic and elemental carbon as indicators, *Environ. Sci. Technol.*, **2003**, *37*, 1025-1030.

Stevenson, F. J., *Humus chemistry. Genesis, composition, reactions*; John Wiley & Sons: New York, 1982, pp 1-443.

Swift, R. S. Organic matter characterization. In *Methods of soil analysis. Part 3. Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996; pp 1011-1069.

Temminghoff, E. J. M., van der Zee, S. E. A. T. M., de Haan, F. A. M. Effects of dissolved organic matter on the mobility of copper in a contaminated sandy soil, *Eur. J. Soil Sci.*, **1998**, *49*, 617-628.

Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

van der Sloot, H. A., Comans, R. N. J., Eighmy, T. T., and Kosson, D. S. *Interpretation of MSWI residue leaching data in relation to utilization & disposal*; ECN-RX--92-051; 1992.

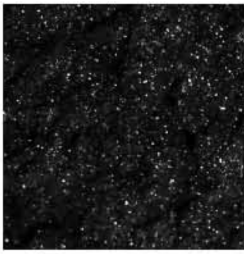
van Zomeren, A., Comans, R. N. J. Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **2004**, *38*, 3927-3932.

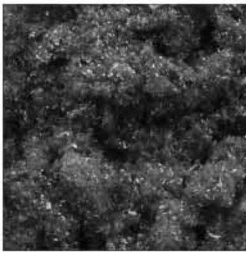
van Zomeren, A., Comans, R. N. J. Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch procedure, *Environ. Sci. Technol.*, **2007**, *41*, 6755-6761.

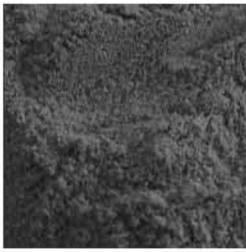
Weng, L., Temminghoff, E. J. M., van Riemsdijk, W. H. Interpretation of humic acid coagulation and soluble soil organic matter using a calculated electrostatic potential, *Eur. J. Soil Sci.*, **2002**, *53*, 575-587.

CHAPTER 7

PROTON BINDING PROPERTIES OF HUMIC SUBSTANCES ORIGINATING FROM NATURAL AND CONTAMINATED MATERIALS







van Zomeren, A., Costa, A., Pinheiro, J.P. and Comans, R.N.J., Proton binding properties of humic substances originating from natural and contaminated materials, *submitted*, **2008**.

PROTON BINDING PROPERTIES OF HUMIC SUBSTANCES ORIGINATING FROM NATURAL AND CONTAMINATED MATERIALS

André van Zomeren[1]*, Amélia Costa*[2]*, Jose Paulo Pinheiro*[2] *and Rob N.J. Comans*[1,3]

Humic substances (HS) are ubiquitous organic constituents in soil and water and can strongly adsorb contaminants in natural and waste environments. Therefore, understanding and modelling contaminant-HS interactions is a key issue in environmental risk assessment. Current binding models for HS, such as the NICA-Donnan model are developed and calibrated against organic matter from natural origin (e.g. soils and surface water). The aim of this study is to analyse the proton binding properties of humic and fulvic acid samples originating from secondary materials, waste materials and natural samples in order to assess whether the charge development of these HS can be described with generic NICA-Donnan parameters. New proton binding parameters are presented for HS isolated from several natural and contaminated (waste) materials. These parameters are shown to be similar to those of HS originating from natural environments, suggesting that the NICA-Donnan model and generic binding parameters are adequate to describe proton binding to HS in both natural and contaminated materials. These findings widen the range of environments to which the NICA-Donnan model can be applied and justifies its use in geochemical speciation modelling of metal mobility in contaminated (waste) materials.

---

[1] Energy Research Centre of The Netherlands.

[2] Universidade do Algarve.

[3] Wageningen University.

7.1 Introduction

Humic substances (HS) are important soil and fresh water components that are formed by microbial degradation of plant and animal tissue. Several methods have been developed to extract HS from soil/ water and to fractionate these into humic (HA) and fulvic acids (FA), thus allowing the characterisation of their chemical properties (Stevenson, 1982). Humic and fulvic acids can strongly influence the mobility of contaminants in natural and waste environments by adsorption (Milne *et al.*, 2003; Stevenson, 1982). Understanding and modelling contaminant-HS interactions is of crucial importance for environmental risk assessment as the release of heavy metals (and organic micropollutants) can be enhanced by orders of magnitude due to complexation with HS.

Several binding models have been developed to calculate the adsorption of contaminants to HA and FA (e.g. Kinniburgh *et al.*, 1999; Tipping, 1998). Currently, two discrete site models, Model VI (Tipping, 1998) and the Stockholm humic model (Gustafson, 2001) and a continuous distribution model, the NICA-Donnan model (Kinniburgh *et al.*, 1999) are frequently used to describe proton and metal adsorption to HA and FA. The NICA-Donnan model has been successfully applied to describe the speciation of metals in soil (Dijkstra *et al.*, 2004; Weng *et al.*, 2003) as well as waste materials (Dijkstra *et al.*, 2006; van der Sloot *et al.*, 2007; van Zomeren and Comans, 2004) and is also used in this study.

Models that describe binding of metals to HS require adsorption parameters (e.g. binding capacity and affinity) and the concentrations of HS in the studied system. Concentrations of HS can be quantitatively measured using the method developed by van Zomeren and Comans (2007). Milne *et al.* have developed "generic" NICA-Donnan adsorption parameters for the binding of protons (Milne *et al.*, 2001) and metals (Milne *et al.*, 2003) to HS. These adsorption parameters and the concentrations of HS are important input parameters in speciation and transport models applied to soil and waste materials (e.g. Dijkstra *et al.*, 2004; van Zomeren and Comans, 2004).

Recently, new legislative emission limits were derived in the Netherlands for the application of (secondary) building materials. In this assessment, the chemical speciation code ORCHESTRA (Meeussen, 2003) was used with the NICA-Donnan model (among other adsorption models for inorganic surfaces) and the generic binding parameters. The limit values were derived from ORCHESTRA predictions of the long-term reactive transport of leached contaminants in the soil and groundwater (Verschoor *et al.*, 2006). This development shows the increasing importance of geochemical speciation models for environmental risk assessment of contaminated materials. Since binding models for HS are calibrated against natural organic matter (e.g. soils and surface waters) this example illustrates the need for validation of model applications in situations outside the calibrated range.

The generic dataset from Milne *et al.* (2001) contains proton binding data for natural organic matter from 24 HA titrations and 25 FA titrations (including two samples from groundwater polluted by landfill leachate). The NICA-Donnan model has been shown to perform well when applied to contaminated (waste) materials such as municipal solid waste incinerator (MSWI) bottom ash (Dijkstra *et al.*, 2006; van Zomeren and Comans, 2004), contaminated soil (Dijkstra *et al.*, 2004), predominantly inorganic waste (van Zomeren and van der Sloot, 2006) and compost (unpublished results). However, the proton binding properties of HS originating from waste environments have not been analysed directly and demonstrated to fall within the observed range for natural materials.

In this study proton binding titrations are performed on HA and FA samples isolated from secondary materials, waste materials and natural samples. The natural samples serve as a reference for the applied procedure and comparison with literature values. The results are compared to calculated proton titrations using the generic NICA-Donnan parameters. In addition, new proton binding parameters are derived for these materials by fitting the NICA-Donnan model to the data. This work validates the extended application of the generic proton binding parameters to contaminated environments and particularly secondary and waste materials.

7.1.1 Derivation of NICA-Donnan parameters

In this study, we use the NICA-Donnan model to describe the proton binding to HS, as proposed by Milne *et al.* (2001). A detailed description and background of the NICA-Donnan model can be found elsewhere (Avena *et al.*, 1999; Benedetti *et al.*, 1995; Benedetti *et al.*, 1996b; Kinniburgh *et al.*, 1999; Milne *et al.*, 2001). The NICA Donnan model for proton binding to HS is given in Equation 1 (Milne *et al.*, 2001).

$$Q_H = Q_{\max,1H} \cdot \frac{\{\tilde{K}_{H1} \cdot [H]_S\}^{m_1}}{1 + \{\tilde{K}_{H1} \cdot [H]_S\}^{m_1}} + Q_{\max,2H} \cdot \frac{\{\tilde{K}_{H2} \cdot [H]_S\}^{m_2}}{1 + \{\tilde{K}_{H2} \cdot [H]_S\}^{m_2}} \qquad (1)$$

The subscripts 1 and 2 denote the carboxylic and the phenolic type of binding sites, respectively. Q_H is the total amount of protons bound to the HS (mol/kg), $Q_{max,iH}$ is the total number of available proton binding sites for each type of binding sites. The median value of the affinity distribution for protons is given by $\tilde{K}$, $[H]_S$ is the concentration of protons in the Donnan phase and m_i is a measure of the apparent heterogeneity of the HS.

The separate intrinsic and electrostatic affinities can be calculated from the proton binding curves at different ionic strengths. For this purpose, a model is needed that accounts for the drop in the electrostatic potential between the binding sites and the bulk solution. In the Donnan model, HS in solution are assumed to have an open gel-like structure that behaves as an electrically neutral entity permeable to electrolyte ions. All charges of the HS are neutralized by counter- and co-ions within the Donnan volume. The potential is constant within the gel phase and is zero outside of the gel phase. The Donnan model is an approximation that has been demonstrated to explain the electrostatic interactions involved in cation binding to HS (Benedetti *et al.*, 1996a). Although this model is a strong simplification of reality, its advantage is that electrostatic interactions are explicitly taken into account with only one adjustable parameter (ψ_D).

The Donnan volume (L/kg) can be estimated using the empirical relationship (equation 2) derived by Benedetti *et al.* (1996a). The parameter *b* is an empirical parameter that describes the variation of the Donnan volume with the ionic strength ($[I]$). The value of *b* is a property of the HS and is fitted using the titration curves obtained at different ionic strength. Normally, *b* is a positive number between 0 and 1.

$$\log V_D = b\cdot(1 - \log[I]) - 1 \qquad (2)$$

To calculate the concentration of protons within the Donnan phase ($[H]_S$), the potential (ψ_D) needs to be calculated for each ionic strength using the Donnan volume (V_D). The derivation of the formula to calculate the charge density in the Donnan phase (ρ_D) at each point of the titration curve from the electroneutrality condition is described elsewhere (Avena *et al.*, 1999). The potential ψ_D (in Volt) can be calculated by solving equation 3 (Avena *et al.*, 1999), resulting in equation 4.

$$\rho_D = -2 \cdot F \cdot c_{salt} \cdot z_{salt} \cdot SINH \cdot \left(\frac{z_{salt} \cdot F \cdot \psi_D}{R \cdot T} \right) \qquad (3)$$

$$\psi_D = \frac{R \cdot T}{z_{salt} \cdot F} \cdot ASINH\left(\frac{Q}{2 \cdot z_{salt} \cdot V_D \cdot c_{salt}}\right) \tag{4}$$

Where R is the gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), T is the temperature (K), z_{salt} is the charge number of the electrolyte, F is the Faraday constant ($C \cdot mol^{-1}$), Q is the measured charge (mol/kg) at each point and c_{salt} is the concentration (mol/L) of the background electrolyte. The concentration of protons in the bulk solution ($[H]$) and in the Donnan phase ($[H]_S$) are related by a Boltzmann factor that includes the potential (ψ_D) in Volt within the gel phase:

$$[H]_S = [H] \cdot \exp\left(\frac{-F \cdot \psi_D}{R \cdot T}\right) \tag{5}$$

Using this information it is possible to transform the measured binding or charging curves as a function of solution pH, to binding as a function of (calculated) Donnan pH. This approach has the advantage that theoretically the curves measured at different ionic strengths should merge into a single "master curve". This master curve only includes the intrinsic or chemical binding properties and not the electrostatic part. The reader is referred to de Wit *et al.* (1990) for further reading on the master curve approach.

7.2 Materials and methods

7.2.1 Samples

HA and FA were isolated from five solid samples (Table 1) according to the method of Swift (1996) and from three aquatic samples according to Thurman and Malcolm (1981). All samples were processed using an automated procedure for the isolation and purification of HS (van Zomeren *et al.*, 2008). Purified Minnesota peat FA was obtained from the International Humic Substances Society (IHSS) (art. 1R107F). The purified HS were freeze-dried and stored in a desiccator until use.

Table 1. Sample origin and isolation methods used for the samples in this study. HS from the landfill leachate, compost, effluent and Zwanenwater are also characterised in van Zomeren and Comans (2007). HA and or FA refers to the specific HS fraction used in this study. The isolation method refers to the method of Swift (1996) (S) for solid samples and to the method of Thurman and Malcolm (1981) (T) for liquid samples.

Sample name	**HA/FA**	**Origin**	**Isolation method**
Bottom ash BE 2005	FA	Freshly produced bottom ash from Belgium MSWI*, taken in 2005.	S
Bottom ash BE 2007	HA, FA	Freshly produced bottom ash from Belgium MSWI*, taken in 2007.	S
Bottom ash NL 2005	HA, FA	Freshly produced bottom ash from Dutch MSWI*, taken in 2005.	S
Compost	HA, FA	Compost from source separated municipal solid waste	S
Effluent	HA, FA	Purified leachate from waste water treatment plant at Dutch landfill	T
Landfill leachate	HA, FA	Leachate from a predominantly inorganic waste landfill in the Netherlands	T
Min. peat	FA	IHSS standard FA	S
Zwanenwater	HA, FA	DOC-rich pond in Dutch nature reserve	T

*Municipal Solid Waste Incinerator

7.2.2 Potentiometric titrations

Humic substances dissolution

Potentiometric titrations were performed using an automated titration set up in accordance with Kinniburgh *et al.* (1995). The samples (10 mg) were dissolved in about 5 mL demineralised water and 250 µL 0.20 M NaOH (carbonate-free, see below) was added under N_2 (99.999% N_2) to enhance dissolution. Subsequently, 500 µL of 0.10 M HNO_3 was added to re-establish the natural starting pH of the samples. The total volume was adjusted to 10 mL with demineralised water. A sample from the stock solution (1000 mg HS/L) was used immediately for the first titration. The remainder was stored in the dark at 4 ^{o}C. All three titrations (see below) were completed within one week from the preparation of the stock solution.

Preparation of carbonate-free NaOH
Carbonate-free base solution (0.02 M) was prepared weekly. Demineralised water was first boiled for 20 minutes to remove dissolved CO_2. 20 mL of a 0.2 M NaOH stock solution (Merck, cat. Nr. 1.09140.1000, stored under N_2) was added to 180 mL boiled demineralised water under a N_2 atmosphere. The solution was stored in a plastic container which was placed in a glass desiccator according to the specifications described in Kinniburgh and Milne (1992). The exact base concentration was measured by duplicate acid/base titrations with a calibrated 0.143 M HNO_3 solution.

pH electrode calibrations
The pH was measured with a Radiometer combination pH electrode (Ag/AgCl, pHC3006-9). The pH electrode was calibrated in duplicate before and after each HS titration in a $NaNO_3$ electrolyte solution (0.01 M, 0.03 M, 0.1 M or 0.3 M, depending on the ionic strength of the sample titration) that was pre-adjusted to pH 3 with HNO_3 (Lopez *et al.*, 2003). Generally, 20-25 fixed doses (50 μL) of 0.1 M HNO_3 were added and the electrode response was recorded. Linear regression was used to obtain the electrode slope and offset. It was found that the reproducibility of the titrations was affected by differences in the slope of the pH calibration line, especially at pH values <5 and >8.5. Therefore, the slope of the electrode should not deviate by more than 0.3 mV/pH between two calibrations to limit experimental errors in the titration experiments. Calibrations were repeated until the difference between the slopes was within 0.3 mV/pH.

Titration of HA and FA samples
Titrations with HA and FA samples were performed at 25 °C using three different ionic strengths (ranging from 0.01 M to 0.3 M). The sample (1 mL) was transferred from the stock solution into the titration vessel. Demineralised water and 1 M $NaNO_3$ were subsequently added to a total volume of 25 mL to obtain a final HS concentration of 40 mg/L at the appropriate ionic strength.

The titrations were performed by subsequent additions of 10 μL 0.02 M NaOH under a N_2 atmosphere. The electrode drift criterion was set to 0.4 mV/min, with a maximum stabilization time of 5 min. Titrations were stopped when the EMF was -200 mV since the analytical errors increase exponentially at higher pH values (Milne *et al.*, 2001). A typical titration experiment took about 2-3 hours.

7.3 Results and discussion

The experimental data for proton binding by HA and FA at different ionic strengths are presented in Figure 1 and Figure 2, respectively. The solid lines in the graphs represent the calculated titration curves based on the NICA-Donnan model using the generic parameters (Milne *et al.*, 2001). Calculations were performed using the geochemical speciation code ORCHESTRA (Meeussen, 2003). In general, the titration curves show a clear and consistent increase of charge as a function of the pH and the ionic strength. These observations are in agreement with results obtained with HA and FA from different origins by other authors (e.g. Fiol *et al.*, 1999; Lopez *et al.*, 2003; Milne *et al.*, 2001; Plaza *et al.*, 2005). The charge of our FA samples is generally higher than that of the corresponding HA samples from the same origin, consistent with the results of Milne *et al.* (2001).

Figure 1 and Figure 2 show that the experimental data for HA and FA are generally in reasonable accordance with the proton binding curves calculated with the generic binding parameters. The compost, the two MSWI bottom ash HA samples and the Belgian MSWI bottom ash FA sample (2005), show a relatively large deviation from the generic proton binding curves compared to the other samples.

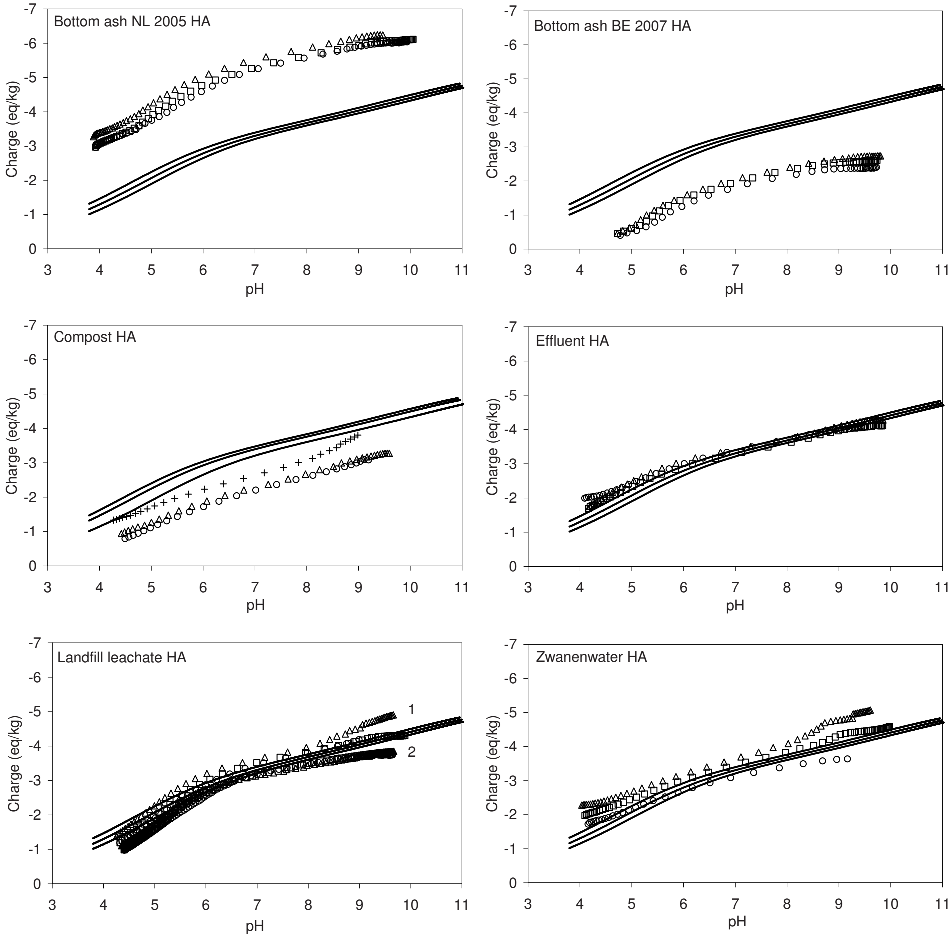


Figure 1. Experimental data for proton binding by HA expressed as the negative charge as a function of pH at I = 0.01 M (○), 0.03 M (□), 0.1 M (Δ) and/or 0.3 M (+).The landfill leachate HA sample was titrated in duplicate as indicated by number 1 and 2 in the graph. The solid lines represent the calculated titration curves at the appropriate ionic strength (lowest line represents lowest ionic strength) using the NICA-Donnan model with the generic proton binding parameters.

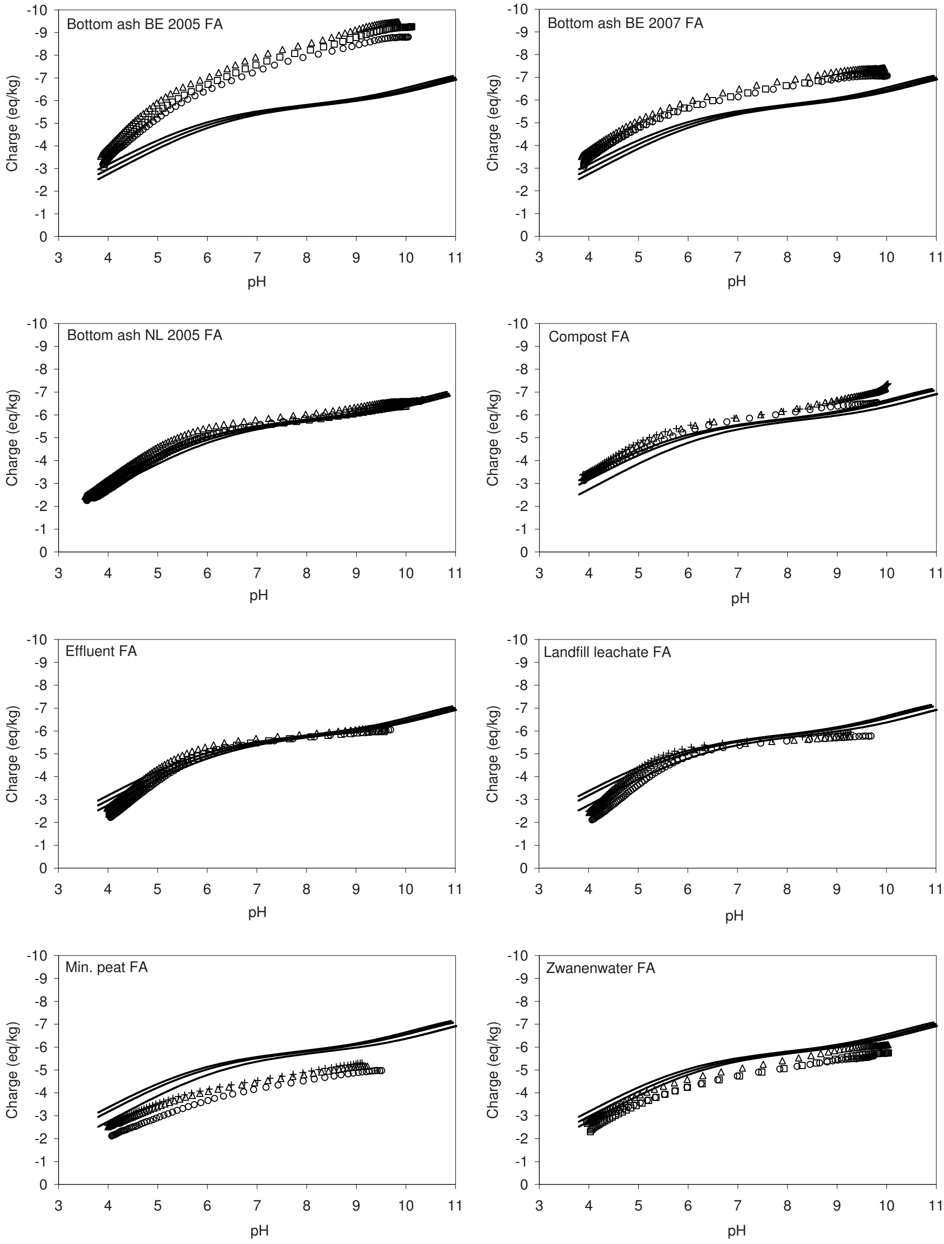


Figure 2. Experimental data for proton binding by FA expressed as the negative charge as a function of pH at I = 0.01 M (○), 0.03 M (□), 0.1 M (Δ) and/or 0.3 M (+). The solid lines represent the calculated titration curve at the appropriate ionic strength using the NICA-Donnan model with the generic proton binding parameters.

All experimental proton binding data from HA and FA at various ionic strengths (0.01-0.3 M) have been plotted together in Figure 3, to directly compare the measured charge development as a function of pH with the titration data of natural HS compiled by Milne *et al.* (2001). The experimental titration data for the samples from this study do largely fall within the range of data for natural HS. The measured titration curves for Belgian bottom ash (2005) FA and the Dutch bottom ash HA deviate from the upper limit observed for the natural materials. It is important to note that Milne *et al.* (2001) found titration curves for a single sample (i.e., Laurentian soil fulvic acid), obtained by different authors, situated both at the upper and lower limit of the compiled dataset. Although the reasons for this large variation are unclear (Milne *et al.*, 2001), this observation demonstrates that an individual HS sample can have proton binding properties varying over the entire range shown in Figure 3.

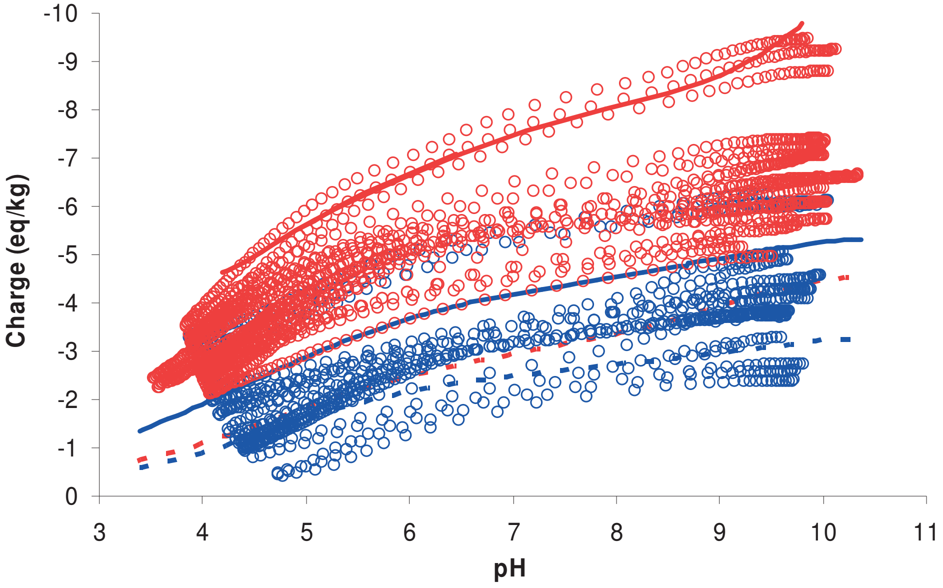


Figure 3. Comparison of all experimental data for proton binding by HA (blue symbols) and FA (red symbols) expressed as the negative charge as a function of pH. The blue (HA) and red (FA) lines represent the lowest (dashed) and highest (solid) observed proton binding curves from Milne *et al.* (2001).

Calculation of NICA-Donnan proton binding parameters

A better description of the titration data and new (intrinsic) proton binding parameters, particularly for the HA and FA from waste environments, can be obtained when fitting the measurements to the NICA-Donnan model. The proton binding parameters have been derived using the master curve approach and by fitting the master curve to the NICA model by iterative minimisation of the sum of squares with the Levenberg-Marquardt approach. The fitted master curves (negative charge versus Donnan pH) are presented in Figure 4 and Figure 5 and show a good match with the data for all samples.

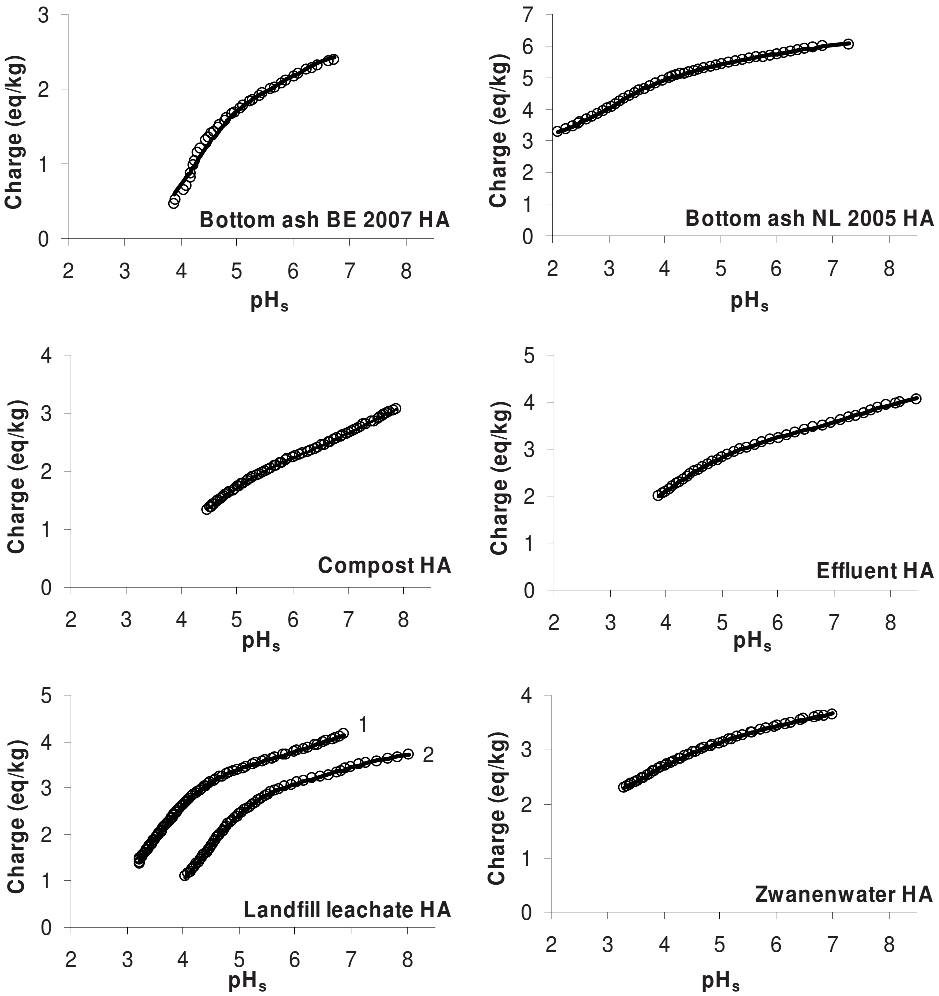


Figure 4. Master curves for HA samples (○) expressed as the negative charge as a function of Donnan pH (pH$_s$). Only part of the data is shown for reasons of clarity. The solid line represents the fitted master curve from which the NICA parameters have been derived (Table 2).

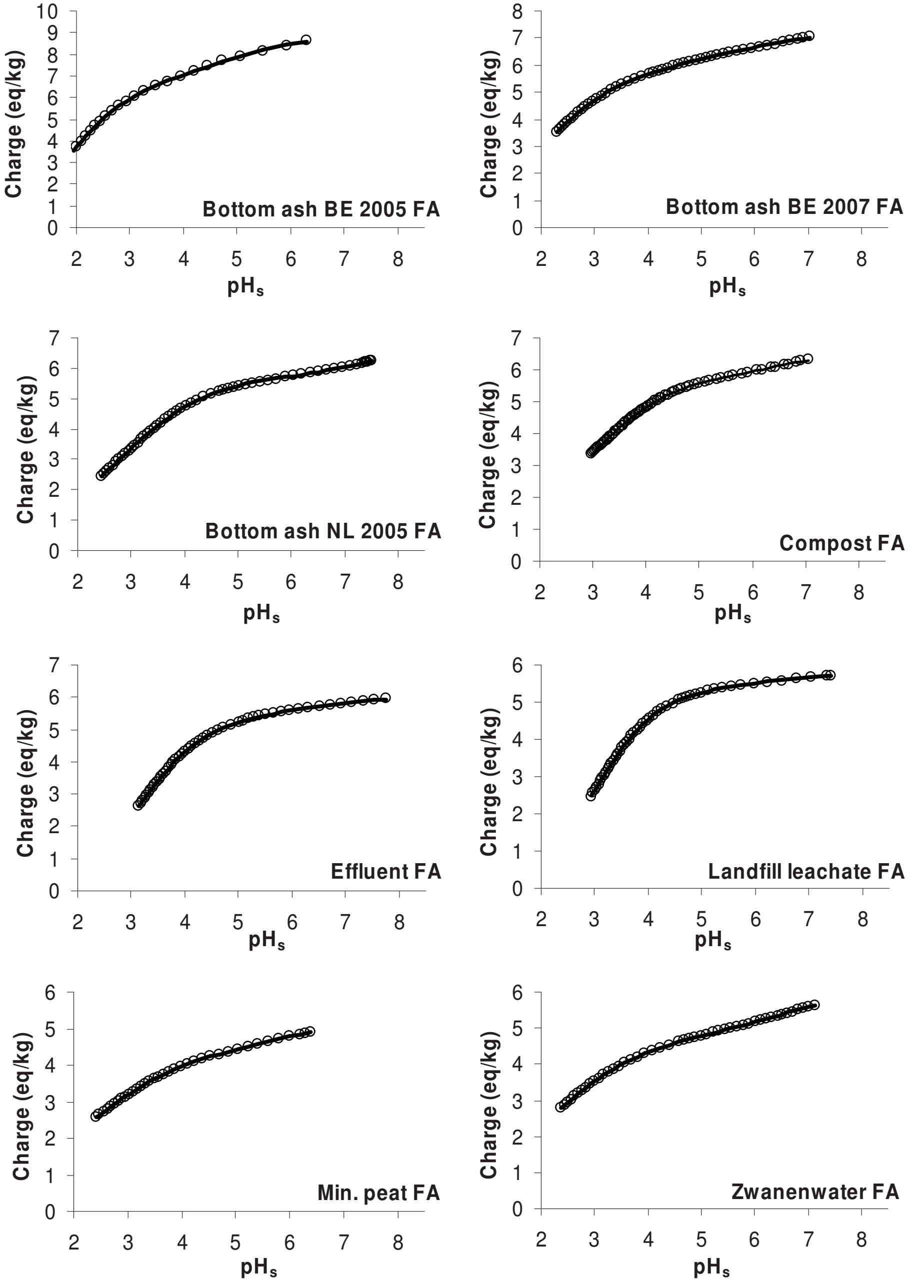


Figure 5. Master curves for FA samples (○) expressed as the negative charge as a function of Donnan pH (pH_s). Only part of the data is shown for reasons of clarity. The solid line represents the fitted master curve from which the NICA-Donnan parameters have been derived (Table 2).

Table 2 shows the optimised NICA-Donnan parameters for the individual HA and FA samples. These values are compared to the generic parameters and the observed range described by Milne *et al.* (2001). The large values of the determination coefficient (R^2) and the small residual mean square errors (RMSE) indicate that the NICA-Donnan model fits very well to the experimental data for the HS samples. Considering the distinct sources of our HS, which differ from those described by Milne *et al.* (2001), we emphasize that the obtained proton binding parameters are generally in agreement with the range of the generic data.

Some results shown in Table 2 warrant specific consideration. The proton binding parameters for the Dutch bottom ash HA exhibit the largest deviations from the generic values as well as from the parameters obtained for the other waste and natural HA samples. All parameters for this sample, except $Q_{max2,H}$, are consistently found outside the range of the generic parameters.

In addition, a relatively low log $K_{2,H}$ is observed for all of our (natural and waste derived) FA samples as well as for Zwanenwater HA. We note that the apparent deviation in this parameter is found for both natural and waste derived HS. Specifically, Minnesota peat FA and Zwanenwater HA and FA show log $K_{2,H}$ values outside the range for the natural materials considered by Milne *et al.* (2001). Therefore, the relatively low log $K_{2,H}$ values do not seem to be related to the source of the HS. Given also that our experimental approach is very similar to the methods on which the data compiled by Milne et al. (2001) are based, we ascribe these deviating results by differences in the parameter estimation procedures (see below).

Table 2. Proton binding data for HA and FA samples. Values in bold are outside the observed range of the generic dataset by Milne *et al.* (2001). Q_{max} is reported in eq/kg. *generic value was used.

Humic acid	**Log $K_{1,H}$**	**$Q_{max1,H}$#**	**m_1**	**Log $K_{2,H}$**	**$Q_{max2,H}$#**	**m_2**	**Q_{tot}**	**b**	**RMSE**	**R^2**
generic	2.93	3.15	0.5	8	2.55	0.26	5.7	0.49	0.127	0.9890
min	1.99	1.93	0.38	6.06	0.76	0.14	3.45	0.21	0.012	0.9547
max	3.9	4.73	0.89	10.06	5.39	0.86	9.15	0.84	0.175	0.9999
Compost	**4.29**	2.43	0.53	7.38	0.93	0.79	**3.36**	0.75	0.006	0.9999
Effluent	3.57	3.42	0.46	7.58	0.85	0.68	4.26	**0.86**	0.004	0.99996
Landfill leachate (1)	3.43	3.52	0.80	6.44	0.92	0.74	4.44	0.55	0.008	0.9999
Landfill leachate (2)	**4.40**	3.17	0.84	7.02	**0.60**	**0.93**	3.77	**0.87**	0.012	0.9998
MSWI Bottom ash NL 2005	**1.54**	**5.83**	**0.15**	**3.14**	0.98	**1.00**	6.81	0.43	0.013	0.9998
MSWI Bottom ash BE 2007	**4.24**	1.95	**1.00**	6.11	**0.60**	**1.00**	**2.55**	0.53	0.070	0.9848
Zwanenwater	2.76	3.86	**0.15**	**3.64**	**0.52**	0.82	4.37	0.49*	0.004	0.9999
Fulvic acid	**Log $K_{1,H}$**	**$Q_{max1,H}$**	**m_1**	**Log $K_{2,H}$**	**$Q_{max2,H}$**	**m_2**	**Q_{tot}**	**b**	**RMSE**	**R^2**
generic	2.34	5.88	0.38	8.6	1.86	0.53	7.74	0.57	0.123	0.9920
min	2	2.64	0.27	7.19	0.55	0.17	4.73	0.29	0.016	0.9802
max	3.81	8.76	0.65	10.91	7.77	0.96	13.14	0.94	0.153	0.9997
Compost	2.74	6.02	0.50	**7.00**	0.71	0.91	6.73	0.75	0.010	0.9999
Effluent	3.18	5.39	**0.71**	**6.42**	0.68	0.50	6.07	0.76	0.008	0.9999
Landfill leachate	3.02	5.35	**0.75**	**6.08**	**0.42**	0.58	5.77	0.67	0.007	0.9999
Minnesota peat	2.20	4.66	0.42	**5.88**	**0.44**	0.91	5.10	0.38	0.009	0.9998
MSWI Bottom ash NL 2005	2.72	5.81	0.50	**7.15**	0.67	0.87	6.48	0.72	0.011	0.9999
MSWI Bottom ash BE 2007	**1.99**	5.92	0.55	**5.74**	1.39	0.46	7.31	0.52	0.009	0.9999
MSWI Bottom ash BE 2005	2.07	3.28	**1.00**	**3.34**	6.60	0.21	9.88	0.39	0.025	0.9997
Zwanenwater	2.08	4.79	0.48	**6.50**	1.25	0.51	6.04	0.40	0.007	0.9999

In order to test this hypothesis, we have fitted titration data of two Laurentian soil FA samples (FH-02 and FH-23) that are included in the dataset compiled by Milne *et al.* (2001). While the proton binding parameters for the low affinity site were found to be very similar, the parameters for the high affinity site were considerably different (FH-02: log $K_{2,H}$=7.6 vs 9.4, $Q_{max2,H}$=0.6 vs 2.6, m_2=0.9 vs 0.5; FH-23: log $K_{2,H}$=6.2 vs 7.3, $Q_{max2,H}$=3.7 vs 7.8, m_2=0.3 vs 0.2). We have also obtained substantially lower RMSE and higher R^2 values than those reported by Milne *et al.* (2001). Given that the NICA model requires six parameters to be fitted simultaneously, one might question the uniqueness of the parameter optimisation results. However, in testing the sensitivity of the fit to individual parameter values, we have found that the three parameters for the carboxylic sites are relatively insensitive to the parameters for the phenolic sites and vice versa. Nevertheless, it should be noted that the parameter values for the phenolic sites are determined by only a small fraction of the titration data (i.e., those at high pH) and, hence, that these values have more uncertainty than those for the carboxylic sites. This effect may be more noticeable by the relatively low HS concentrations that were available for our titrations, given that higher concentrations allow for titrations up to higher pH values.

Several other proton binding parameters for HA and FA show values that are generally about 10-20% outside of the reported range. These deviations appear to be randomly divided among all samples and parameters. Given the heterogeneous nature of HS, we do not take this relatively small deviation as an indication for significant differences in the chemical properties of these HS. In addition, the observed *b* values in our study are in good agreement with the range that has been found for HA and FA from natural environments (Milne *et al.*, 2001), indicating that the electrostatic interactions in our samples are also comparable to those found in natural humic substances.

It has been shown that the source of HS (e.g. aquatic or soil derived) can also contribute to differences in proton binding parameters. Ritchie and Perdue (2003) have found that the carboxylic contents of HS decrease in the order terrestrial FA > aquatic FA >aquatic HA > terrestrial HA. When we consider our compost, Minnesota peat and the bottom ash samples as terrestrial and the other samples as aquatic HS, the carboxylic contents ($Q_{max1,H}$) of our samples do (except for Minnesota peat and bottom ash BE 2005 FA) also follow the same sequence as observed by Ritchie and Perdue (2003). This relation appears to hold also for the generic dataset in that the $Q_{max1,H}$ values of FA are generally higher than those of HA.

Based on the discussion above and the heterogeneous character of HS, we conclude that the proton binding properties of the HS that we have isolated from waste materials are similar to those of HS originating from natural environments. Therefore, we suggest that the NICA-Donnan model and generic proton binding parameters are adequate to describe the proton binding to HS in both natural and contaminated materials. Given that metals compete with protons for the same binding sites and that this process can also be described by the NICA-Donnan model, we conclude that this model with the generic binding parameters for protons (Milne *et al.*, 2001) and metals (Milne *et al.*, 2003) can also be used for the geochemical speciation modelling of metal mobility in natural and contaminated (waste) materials. These findings widen the range of environments to which the NICA-Donnan model can be applied.

Acknowledgements

Stefanie Arickx is acknowledged for kindly providing the Belgium MSWI bottom ash HS samples. Hans Meeussen is thanked for critically reading earlier versions of this manuscript and for his assistance with ORCHESTRA calculations. This work was partly funded by the Ministry of Spatial Planning, Housing and the Environment as part of ECN's environmental research program.

References

Avena, M. J., Koopal, L. K., van Riemsdijk, W. H. Proton binding to humic acids: electrostatic and intrinsic interactions, *J Colloid Interface Sci.*, **1999**, *217*, 37-48.

Benedetti, M. F., Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K. Metal ion binding to humic substances: Application of the Non-Ideal Competitive Adsorption Model, *Environ. Sci. Technol.*, **1995**, *29*, 446-457.

Benedetti, M. F., van Riemsdijk, W. H., Koopal, L. K. Humic substances considered as a heterogeneous Donnan gel phase, *Environ. Sci. Technol.*, **1996a**, *30*, 1805-1813.

Benedetti, M. F., van Riemsdijk, W. H., Koopal, L. K., Kinniburgh, D. G., Gooddy, D. C., Milne, C. J. Metal ion binding by natural organic matter: From the model to the field, *Geochim. Cosmochim. Acta*, **1996b**, *60*, 2503-2513.

de Wit, J. C. M., van Riemsdijk, W. H., Koopal, L. K. Analysis of ion binding on humic substances and the determination of intrinsic affinity distributions, *Anal. Chim. Acta*, **1990**, *232*, 189-207.

Dijkstra, J. J., Meeussen, J. C. L., Comans, R. N. J. Leaching of heavy metals from contaminated soils; an experimental and modelling study, *Environ. Sci. Technol.*, **2004**, *38*, 4390-4395.

Dijkstra, J. J., van Zomeren, A., Meeussen, J. C. L., Comans, R. N. J. Effect of Accelerated Aging of MSWI Bottom Ash on the Leaching Mechanisms of Copper and Molybdenum, *Environ. Sci. Technol.*, **2006**, *40*, 4481-4487.

Fiol, S., Lopez, R., Ramos, A., Antelo, J. M., Arce, F. Study of the acid-base properties of three fulvic acids extracted from different horizons of a soil, *Anal. Chim. Acta*, **1999**, *385*, 443-449.

Gustafson, J. P. Modeling the acid-base properties and metal complexation of humic substances with the stockholm humic model, *J Colloid Interface Sci.*, **2001**, *244*, 102-112.

Kinniburgh, D. G. and Milne, C. J. *Guide to the Wallingford titrator,* Technical Report WD/92/14, 1992.

Kinniburgh, D. G., Milne, C. J., Venema, P. Design and construction of a personal-computer-based automatic titrator, *Soil Sci. Soc. Am. J.*, **1995**, *59*, 417-422.

Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K., Borkovec, M., Benedetti, M. F., Avena, M. J. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *Colloids Surf. A*, **1999**, *151*, 147-166.

Lopez, R., Fiol, S., Antelo, J. M., Arce, F. Analysis of the effect of concentration on the acid-base properties of soil fulvic acid. Conformational changes, *Colloids Surf. A*, **2003**, *226*, 1-8.

Meeussen, J. C. L. ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models, *Environ. Sci. Technol.*, **2003**, *37*, 1175-1182.

Milne, C. J., Kinniburgh, D. G., Tipping, E. Generic NICA-Donnan model parameters for proton binding by humic substances, *Environ. Sci. Technol.*, **2001**, *35*, 2049-2059.

Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances, *Environ. Sci. Technol.*, **2003**, *37*, 958-971.

Plaza, C., Brunetti, G., Senesi, N., Polo, A. Proton Binding to Humic Acids from Organic Amendments and Amended Soils by the NICA-Donnan Model, *Environ. Sci. Technol.*, **2005**, *39*, 6692-6697.

Ritchie, J. D., Perdue, E. M. Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter, *Geochim. Cosmochim. Acta*, **2003**, *67*, 85-96.

Stevenson, F. J., *Humus chemistry. Genesis, composition, reactions,* John Wiley & Sons: New York, 1982, pp 1-443.

Swift, R. S. Organic matter characterization. In *Methods of soil analysis. Part 3. Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996, pp 1011-1069.

Thurman, E. M., Malcolm, R. L. Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.*, **1981**, *15*, 463-466.

Tipping, E. Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances, *Aquat. Geochem.*, **1998**, *4*, 3-48.

van der Sloot, H. A., van Zomeren, A., Meeussen, J. C. L., Seignette, P., Bleijerveld, R. Interpretation of test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal, *J. Hazard. Mater.*, **2007**, *141*, 354-369.

van Zomeren, A., Comans, R. N. J. Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **2004**, *38*, 3927-3932.

van Zomeren, A., Comans, R. N. J. Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch procedure, *Environ. Sci. Technol.*, **2007**, *41*, 6755-6761.

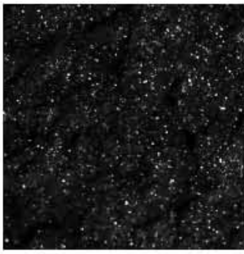
van Zomeren, A. and van der Sloot, H. A. *Equistort, stortplaats voor overwegend anorganisch afval,* ISBN-10: 90-73573-33-5, Dutch sustainable landfill foundation, 2006.

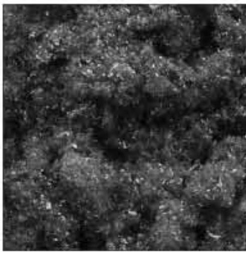
van Zomeren, A., van der Weij-Zuiver, E., Comans, R. N. J. Development of an automated system for the isolation and purification of humic substances, *submitted*, **2008**.

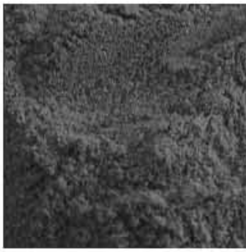
Verschoor, A. J., Lijzen, J. P. A., van den Broek, H. H., Cleven, R. F. M. J., Comans, R. N. J., Dijkstra, J. J., and Vermij, P. H. M. *Kritische emissiewaarden voor bouwstoffen; milieuhygienische onderbouwing en consequenties voor bouwmaterialen,* RIVM report 711701043/2006, 2006.

Weng, L., Temminghoff, E. J. M., Lofts, S., Tipping, E., van Riemsdijk, W. H. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil, *Environ. Sci. Technol.*, **2003**, *36*, 4804-4810.

SUMMARY AND SYNTHESIS







SUMMARY

Natural organic matter (NOM) is the material that is formed after the natural decomposition and transformation of dead plant and animal matter. The fresh organic matter (e.g. plant leaves or animal debris) is decomposed and transformed by microbial activity. As such, NOM is found everywhere in the natural environment; in soils, surface water and oceans. Due to its abundance at the earth's surface, the production and decomposition of NOM plays an important role in the global carbon cycling. In soil systems, NOM has an extremely important influence on essential properties like soil structure, water retention, nutrient availability and binding of contaminants. In water systems (e.g. surface or river water), NOM is important in many (bio)-chemical processes and the geochemical cycling of elements/nutrients.

Due to the importance of NOM in soils for agricultural production, research on its chemical and physical properties and classification dates back many centuries. Numerous laboratory procedures and classifications have been developed to relate organic matter properties to plant growth and soil fertility. However, since the growing public and political awareness of environmental pollution in the 1960s, the properties of NOM (especially humic substances, see below) have increasingly been investigated in the context of its interactions with potentially toxic compounds such as heavy metals and pesticides. Although the first phenomenological observations that natural organic matter can bind heavy metals have already been made in the 19th century, scientists started to gain more extensive data on the strong interaction of heavy metals with NOM in natural soils and aquatic environments during the past decades. At present, the important influence of NOM on the mobility of such potentially toxic compounds in the environment is widely acknowledged by the scientific community.

Waste materials do often also contain organic matter, and in addition, high contents of potentially toxic contaminants such as heavy metals. In many countries, waste materials are increasingly being recycled in construction works (e.g. in road foundations, embankments and sound barriers). The potential environmental risk associated with the re-use of waste materials in such applications depends on the extent to which contaminants can be released as a result of "leaching". Leaching is the release of contaminants from the solid phase (e.g. a waste material) to the water phase with which the material may be in contact (e.g., percolating rainwater). The leaching of contaminants such as heavy metals can be strongly enhanced by complexes with (soluble) organic matter. Therefore, it is important to characterise the properties of organic matter in (contaminated) waste materials in the context of long-term risk assessment of waste applications in construction. In addition, this knowledge can contribute to the development of waste treatment technologies, e.g., to improve the leaching properties of waste materials. Knowledge of the fundamental binding properties of NOM with respect to contaminants can also be specifically used for the development of models to predict the (long-term) leaching behaviour of waste materials.

Natural organic matter is known to include a broad spectrum of organic constituents, many of which have their counterparts in biological tissues, and each with different chemical and physical properties. Two major types of compounds can be distinguished:

- *Humic substances*: a series of unidentifiable organic compounds of relatively high-molecular-weight. They are brown to black in colour and formed by secondary synthesis reactions. The term "humic substances" is used as a generic name, but many scientist discriminate between humic- and fulvic acids (HA and FA, respectively) based on their dissolution properties in alkaline and acid solutions. Humic acids are generally dark-brown to black in colour and have a relatively high molecular weight (several thousand to several hundred thousand atomic mass units (AMU), depending on the applied analysis techniques). Fulvic acids are light yellow to golden brown in colour and have molecular weights ranging from several hundred to about ten thousand AMU. The basis of this classification is also used throughout this thesis.

- *Non-humic substances*: all identifiable (biochemical) organic molecules that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fatty acids etc.

This thesis focuses on the development of methods for the isolation and characterisation of natural organic matter in general and organic matter in (contaminated) waste materials in particular. The overall purpose of this research is to develop a better understanding of the role of NOM with respect to the mobility of contaminants such as heavy metals in the environment.

The main difficulty of studying humic substances is that these substances are very heterogeneous by their nature. Various classifications of humic substances are used in the scientific literature and these are all based on operational definitions. There is still no consensus today as to how HA and FA should be operationally defined. It is important to note that the terminology that is being used does not represent pure compounds. Each class of the humic substances consists of highly complex and heterogeneous mixtures of organic molecules.

The study of chemical properties of NOM often requires isolation and purification of different fractions of the organic matter. The advantage of purification is that it reduces the heterogeneity in the properties of NOM. Numerous isolation and purification methods have been developed over the past decades to enable the further characterisation of organic matter properties. Although these procedures are well established and widely used by scientists, they all share the disadvantages that they are very laborious and primarily aimed on purification rather than quantification of the different fractions. Therefore, this thesis has a strong focus on developing analytical methods that enable an improved characterisation and quantification of the different fractions that are important for metal binding, preferably in a more time- efficient manner.

In **Chapter 2**, a Competitive Ligand Exchange-Solvent extraction (CLE-SE) method was used to measure Cu binding to DOC in leachates from municipal solid waste incinerator (MSWI) bottom ash. The copper binding properties of dissolved organic carbon (DOC) were investigated with specific attention for the identification and quantification of the organic ligands. Evidence was found for an important role of fulvic acids (FA) in the strongly enhanced leaching of Cu from MSWI bottom ash. This work implies that the complexation of contaminants with natural organic matter is an important process in these relatively inorganic waste materials.

Chapter 3 describes the development of an automated procedure to isolate and purify HA and FA from various materials. The conventional (manual) isolation and purification procedures that are widely used by scientists, share the disadvantage of being very laborious and time consuming. These disadvantages are largely overcome by automation and enabled to gather an extensive set of purified HA and FA samples from diverse origin for further characterisation purposes. The main objective for automation of the conventional procedure was to save a significant amount of labour and total throughput time in the performance of HA and FA isolation and purification. The novelty of the method lies in the automated handling of the multiple liquids and columns, required in the isolation/purification procedure, in both forward and back elution mode. By automating the procedure, better standardisation of HA and FA isolation and purification methods is feasible. The automated procedure significantly reduces the total throughput time needed, from 6–7 days to 48 h, and the amount of labour to obtain purified HS for further characterisation.

In **chapter 4**, the development is described of a rapid batch method for the experimental characterisation and quantification of HS in natural and contaminated systems. In principle, the quantification of HS in the environment can be studied with the manual or the developed automated isolation and purification procedure (**chapter 3**). However, the established models for calculation of metal binding to HS require absolute concentrations of HA and/or FA as input. The conventional isolation and purification procedures are too elaborate (and mainly focussed on purification) for this type of application. Because the principles of the new batch method are essentially the same as those of the well-known conventional isolation and purification procedures, the HA and FA properties identified in this study are, therefore, of general importance for the interpretation of the occurrence and behaviour of HS in the environment. The novelty of this method lies in the fact that it greatly facilitates the analysis of HA and FA concentrations (e.g. for use in geochemical modelling, **chapter 5**). The new method can be performed within 1.5-4 hours per sample and multiple samples can be processed simultaneously, while the conventional procedures typically require approximately 40 hours for a single sample.

Based on results from previous chapters, “multi-surface” geochemical modelling of heavy metal leaching from MSWI bottom ash was used to develop a mechanistic insight into the beneficial effects of accelerated aging of MSWI bottom ash on the leaching of copper and molybdenum (**Chapter 5**). Therefore, the rapid batch procedure described in **Chapter 4** is used to characterise DOC quantitatively in terms of humic, fulvic and hydrophilic acids over a wide pH range. Important processes controlling the solid/liquid partitioning of humic and fulvic acids and their role in the effects of aging on contaminant leaching are identified. In addition, a new approach is developed to model the pH dependent leaching of fulvic acids from MSWI bottom ash based on adsorption to reactive Fe/Al-(hydr-)oxides. This chapter shows that accelerated ageing results in enhanced adsorption of FA to reactive Fe/Al-(hydr-)oxides, leading to a significant decrease in the leaching of both FA and associated Cu.

In **Chapter 6**, the carbon speciation (inorganic, organic and elemental carbon) in MSWI bottom ash samples is studied to identify the amount and properties of the different carbon species present in MSWI bottom ash. The carbon speciation was quantitatively measured (partly based on the method described in **Chapter 4**), and its relation with the leaching of Cu, in fresh and carbonated MSWI bottom ash. Results show that up to only 25% of loss on ignition (LOI) consists of organic carbon (OC), while about 15% of organic carbon (OC) in the three samples consists of HA and FA. Since only these small reactive carbon fractions contribute to enhanced metal leaching from MSWI bottom ash, it is concluded that LOI measurements are insufficiently discriminative for a quantitative assessment of environmentally relevant organic carbon species in MSWI bottom ash. The results of this study imply that dedicated methods, focusing on specific carbon fractions, are more appropriate for assessment of environmentally relevant organic carbon species than the measurement of LOI. These methods may greatly improve the assessment of the long-term environmental properties of bottom ash in utilisation or disposal scenarios.

Chapter 7 describes a comparative study regarding the proton binding properties of the previously isolated and purified HS (**Chapter 3**). Binding models for HS, such as the NICA-Donnan model, have so far been developed and calibrated against organic matter from natural origin (e.g. soils and surface waters). In **Chapter 5,** the NICA-Donnan model was found to perform well when applied to a contaminated (waste) material, i.e. municipal solid waste incinerator (MSWI) bottom ash. However, the proton binding properties of HS originating from waste environments have not been analysed directly and demonstrated to fall within the observed range for natural materials. The aim of this study is to analyse the proton binding properties of humic and fulvic acid samples originating from secondary materials, waste materials and natural samples in order to assess whether the charge development of these HS can be described with generic NICA-Donnan parameters. New proton binding parameters are presented for these HS and are shown to be similar to those of HS originating from natural environments. These results suggest that the NICA-Donnan model and generic binding parameters are adequate to describe proton binding to HS in both natural and contaminated materials. This finding widens the range of environments to which the NICA-Donnan model can be applied and justifies its use in geochemical speciation modelling of metal mobility in contaminated (waste) materials.

SYNTHESIS

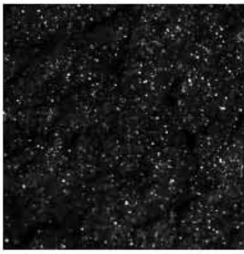
In this thesis, several analytical techniques have been developed and applied to characterise chemical properties of natural organic matter in relation to the complexation of heavy metals in natural and contaminated materials. Novel techniques have been developed, which have led to new insights in the role of organic matter in the facilitated leaching and transport of contaminants from waste materials.

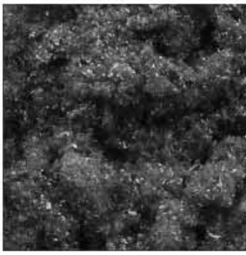
The identified role of fulvic acids in the leaching of Cu (**Chapter 2**) and the revealed leaching mechanism of fulvic acids in MSWI bottom ash (**Chapter 5**) can be used in the development of techniques to improve the environmental quality of this widely produced waste material. Moreover, a new technology for the emission reduction of organically complexed metals from waste materials has been developed and patented (WO2007035101) based on the knowledge from this thesis. These developments open the perspective to apply MSWI bottom ash more generally as a construction material without isolation measures, while complying with environmental criteria.

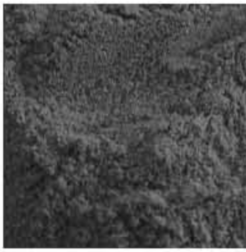
The developed batch method for rapid quantification of humic and fulvic acids (**Chapter 4**) is increasingly being used for organic matter characterisation. In addition, this method has now been proposed for international standardisation (ISO TC 190/SC7). New applications of this method include the assessment of the biodegradability of organic matter fractions in the fields of landfilling and agriculture, development of organic matter treatment technologies and improvement of our insight in processes contributing to global carbon cycling. Possibly, improved predictions of potential greenhouse gas emissions are feasible based on knowledge of the different organic matter fractions in specific environmental compartments.

The new insights into the reactivity of dissolved organic matter have contributed to the development of multiple binding models for predictions of (long-term) contaminant emissions from waste materials to soil and groundwater. Recently, new environmental criteria for the application of waste materials in construction, in the framework of the Dutch Soil Protection Act, have been established based on this modelling approach. Given that these models largely owe their predictive capabilities to the NICA-Donnan model, it is important to note that there is still very little information of the concentrations of (dissolved) organic matter and its subfractions in the natural environment. The rapid batch method described in **Chapter 4** can strongly facilitate routine measurement of these important parameters in monitoring programs.

SAMENVATTING EN SYNTHESE







SAMENVATTING

Natuurlijke organische stof (natural organic matter, NOM) is het materiaal dat gevormd wordt door de natuurlijke afbraak en omzetting van dood plantaardig en dierlijk materiaal. De verse organische stof (bijvoorbeeld bladeren van planten of weefselresten van dieren) wordt afgebroken en omgezet door microbiële activiteit. Natuurlijke organische stof komt daardoor overal voor in het milieu; in bodems, oppervlaktewater en oceanen. Doordat natuurlijke organische stof overal op aarde voorkomt, speelt de productie en afbraak ervan een belangrijke rol in de mondiale koolstof kringloop. In bodems is natuurlijke organische stof belangrijk voor essentiële bodemeigenschappen zoals bodemstructuur, water retentievermogen, beschikbaarheid van nutriënten en de binding van verontreinigingen. In watermilieus (bijvoorbeeld oppervlakte- of rivierwater) is natuurlijke organische stof belangrijk in vele (bio)-chemische processen en voor de geochemische kringloop van elementen/nutriënten.

Doordat organische stof zo belangrijk is in de landbouw (en dus voor de voedselproductie), wordt er al eeuwenlang onderzoek verricht naar de chemische en fysische eigenschappen en naar de classificatie van natuurlijke organische stof. In de loop van de tijd zijn vele laboratoriumprocedures en classificaties ontwikkeld om eigenschappen van natuurlijke organische stof te relateren aan plantengroei en bodemvruchtbaarheid. Echter, sinds de jaren ’60 groeide het publieke en politieke besef van (effecten van) milieuvervuiling. Sinds die tijd worden de eigenschappen van organische stof (in het bijzonder de zogenaamde humus bestanddelen, zie hieronder) in toenemende mate onderzocht in de context van interacties met potentieel giftige stoffen, zoals zware metalen en pesticiden. De eerste fenomenologische waarnemingen dat natuurlijke organische stof in staat is om zware metalen te binden werden al gedaan in de 19^{e} eeuw. Sinds enkele decennia zijn wetenschappers intensief bezig om meer uitgebreide data te verzamelen over de sterke binding van zware metalen aan organische stof. Tegenwoordig wordt de belangrijke invloed van organische stof op de mobiliteit van deze potentieel giftige stoffen in het milieu alom erkend door wetenschappers.

Afvalstoffen bevatten vaak ook organische stof en bovendien hoge concentraties aan potentiële giftige stoffen zoals zware metalen. In veel landen worden afvalstoffen in toenemende mate hergebruikt in bouwconstructies (bijvoorbeeld in wegfunderingen, ophogingen of geluidswallen). De potentiële milieurisico’s die samenhangen met hergebruik van afvalstoffen in zulke toepassingen hangen af van de mate waarin verontreinigingen zich kunnen verspreiden als gevolg van “uitloging”. Uitloging is het in oplossing gaan van stoffen vanuit een vaste matrix (bijvoorbeeld een afvalstof) naar de waterfase waar het materiaal mee in contact kan komen (bijvoorbeeld regenwater). De uitloging van verontreinigingen zoals zware metalen kan sterk verhoogd worden door binding met (opgeloste) organische stof. Het is daarom van belang om de eigenschappen van organische stof in (verontreinigde) afvalstoffen te karakteriseren in relatie tot het lange termijn risico van toepassing van deze materialen als bouwproduct. Daarnaast kan deze kennis bijdragen aan de ontwikkeling van technologieën voor afvalbehandeling, bijvoorbeeld om de uitloogeigenschappen van afvalstoffen te verbeteren. Kennis van de fundamentele bindingseigenschappen van metalen aan organische stof kan ook worden toegepast voor de ontwikkeling van modellen om het (lange termijn) uitlooggedrag van verontreinigingen te voorspellen.

Natuurlijke organische stof bevat een zeer breed spectrum van organische bestanddelen die veelal afkomstig zijn van biologische celmaterialen/weefsels. Al deze bestanddelen hebben elk verschillende chemische en fysische eigenschappen. Er kunnen twee belangrijke klassen van verbindingen onderscheiden worden:

- *Humus*: Een reeks van onidentificeerbare organische stoffen met een relatief hoge molecuulmassa. Deze organische stoffen zijn bruin tot zwart in kleur en worden gevormd door secundaire synthese reacties. De term “humus” wordt als een generieke naam gebruikt, veel wetenschappers maken onderscheid tussen humus- (humic acid, HA) en fulvozuren (fulvic acid, FA) op basis van de oplosbaarheid van deze componenten in loog en zuur. Humuszuren zijn over het algemeen donkerbruin tot zwart in kleur en hebben een relatief hoog molecuulgewicht (enkele duizenden tot enkele honderdduizenden atomaire massa-eenheden, afhankelijk van de toegepaste meetmethode). Fulvozuren zijn lichtgeel tot goudbruin in kleur en hebben een molecuulgewicht variërend van enkele honderden tot ongeveer tienduizend atomaire massa-eenheden. Deze classificatie wordt ook in dit proefschrift gebruikt.

- *Overige organische componenten*: Alle identificeerbare (biochemische) organische moleculen die in een van de categorieën van discrete stoffen geplaatst kunnen worden, zoals suikers, aminozuren, vetzuren etc.

Dit proefschrift focust zich op de ontwikkeling van methoden voor de isolatie en karakterisering van natuurlijke organische stof en in het bijzonder van organische stof in (verontreinigde) afvalstoffen. Het generieke doel van het onderzoek is om een beter begrip te ontwikkelen van de rol van natuurlijke organische stof in relatie tot de (verhoogde) mobiliteit van verontreinigingen (zoals zware metalen) in het milieu.

De grootste moeilijkheid bij het bestuderen van humus- en fulvozuren is dat deze verbindingen zeer heterogeen van aard zijn. In de wetenschappelijke literatuur worden verscheidene classificaties voor humus- en fulvozuren gebruikt en deze zijn allemaal gebaseerd op operationele definities. Er is vandaag de dag nog steeds geen consensus over hoe humus- en fulvozuren operationeel gedefinieerd moeten worden. Het is belangrijk om op te merken dat de humus componenten geen pure verbindingen zijn. Elke klasse van humus verbindingen (bijvoorbeeld humus- en fulvozuren) is zeer complex en bestaat uit heterogene mengsels van organische moleculen.

Onderzoek naar de chemische eigenschappen van natuurlijke organische stof vereist veelal de isolatie en zuivering van diverse fracties van de organische stof. Het voordeel van zuivering is dat de heterogeniteit in de eigenschappen van organische stof wordt gereduceerd. Er zijn de afgelopen decennia vele methoden ontwikkeld voor de isolatie en zuivering van natuurlijke organische stof. Deze methoden maken het mogelijk om de eigenschappen van de gezuiverde organische stof fracties te onderzoeken. Hoewel deze methoden veel gebruikt worden door wetenschappers, hebben ze allemaal het nadeel dat het zeer bewerkelijk en tijdrovend is om de humus- en fulvozuren te isoleren en te zuiveren. Bovendien zijn deze methoden voornamelijk gericht op zuivering en in veel mindere mate op de kwantificering van de verschillende organische stof fracties. Dit proefschrift heeft daarom een sterke focus op de ontwikkeling van analytische methoden die een verbeterde karakterisering en kwantificering van natuurlijke organische stof in relatie tot de binding van zware metalen mogelijk maken. Bij voorkeur zijn deze methoden ook minder bewerkelijk en daardoor makkelijker breed inzetbaar.

In **Hoofdstuk 2** is gebruik gemaakt van een competitieve ligand uitwisselingsmethode om de binding van koper aan opgeloste organische stof te meten in uitloogoplossingen van bodemas uit een afvalverbrandingsinstallatie (AVI). De bindingseigenschappen van organische stof zijn onderzocht met bijzondere aandacht voor de identificatie en kwantificering van de organische liganden. Er is bewijs gevonden dat fulvozuren de uitloging van koper sterk verhogen door binding aan dat metaal. Dit onderzoek impliceert dat de binding van verontreinigingen met natuurlijke organische stof een belangrijk proces is in deze relatief anorganische afvalstoffen.

Hoofdstuk 3 beschrijft de ontwikkeling van een geautomatiseerde procedure voor de isolatie en zuivering van humus- en fulvozuren uit verschillende materialen. De conventionele (handmatige) isolatie- en zuiveringsmethoden die veelvuldig gebruikt worden door wetenschappers hebben allemaal het nadeel dat deze zeer bewerkelijk en tijdrovend zijn. Deze nadelen worden grotendeels opgeheven door automatisering. Bovendien biedt de automatisering mogelijkheden om humus- en fulvozuren uit vele materialen te isoleren en te zuiveren voor verdere karakterisering van de chemische eigenschappen. Het voornaamste doel van de automatisering was om tijd te besparen bij de uitvoering van de procedure, zowel in arbeidstijd als de doorlooptijd van de methode. Het innovatieve van deze methode ligt in de efficiënte manier waarop de verschillende vloeistoffen en kolommen in verschillende richtingen aan te sturen zijn. Door automatisering van de procedure voor isolatie en zuivering van humus- en fulvozuren wordt het mogelijk om deze methode beter te standaardiseren. De nieuwe procedure reduceert de totaal benodigde tijd voor isolatie en zuivering van humus- en fulvozuren van 6-7 dagen naar 48 uur. Daarnaast wordt de benodigde arbeidstijd significant ingekort.

In **Hoofdstuk 4** wordt de ontwikkeling van een snelle methode voor de karakterisering en kwantificering van humus- en fulvozuren in natuurlijke en verontreinigde systemen beschreven. In principe kan de kwantificering van humus- en fulvozuren in verschillende monsters ook gedaan worden met de handmatige of de ontwikkelde geautomatiseerde procedure (**Hoofdstuk 3**). Echter, de ontwikkelde modellen voor berekening van de metaalbinding aan humus- en fulvozuren vereisen slechts de concentraties van deze stoffen als invoer. De conventionele procedures en zelfs de geautomatiseerde procedure zijn nog steeds te bewerkelijk voor dit doel. De principes van de snelle batch procedure zijn in essentie hetzelfde als die van de conventionele procedures. Daarom zijn de in dit hoofdstuk vastgestelde eigenschappen van humus- en fulvozuren van algemeen belang voor de interpretatie van het voorkomen en het gedrag van deze componenten in het milieu. De nieuwheid van deze methode ligt in het feit dat de procedure de kwantitatieve analyse van humus- en fulvozuur concentraties aanzienlijk makkelijker en sneller maakt (bijvoorbeeld voor toepassing in geochemische modellering, **Hoofdstuk 5**). De nieuwe methode kan worden uitgevoerd in ongeveer 1,5-4 uur (arbeidstijd) per monster en meerdere monsters kunnen tegelijkertijd worden opgewerkt. De conventionele procedures voor isolatie en zuivering van humus- en fulvozuren vragen ongeveer 40 uur arbeidstijd per monster en hierbij is het veelal niet mogelijk om meerdere monsters simultaan op te werken.

In **Hoofdstuk 5** is gebruik gemaakt van een geochemisch rekenmodel om de uitloging van zware metalen uit AVI-bodemas te beschrijven. In dit hoofdstuk is mechanistisch inzicht ontwikkeld omtrent de gunstige effecten van versnelde veroudering van AVI-bodemas op de uitloging van koper en molybdeen. De snelle batch methode die ontwikkeld is in **Hoofdstuk 4** is gebruikt om de opgeloste organische stof te kwantificeren over een breed pH-bereik in humus- en fulvozuren en de zogenaamde (relatief kleine) hydrofiele zuren. Hiermee zijn belangrijke processen geïdentificeerd die de verdeling van humus- en fulvozuren over de vaste stof en de uitloogvloeistof bepalen als gevolg van veroudering van de AVI-bodemas. Daarnaast is een nieuwe aanpak ontwikkeld om de pH-afhankelijke uitloging van fulvozuren uit AVI-bodemas te modelleren op basis van adsorptie aan reactieve ijzer/aluminium-(hydr-)oxiden. Dit hoofdstuk toont aan dat versnelde veroudering van AVI-bodemas leidt tot een toenemende adsorptie van fulvozuren aan de reactieve ijzer/aluminium-(hydr-)oxiden en daarmee een significante reductie van de uitloging van koper.

In **Hoofdstuk 6** is de koolstofspeciatie (anorganisch, organisch en elementair koolstof) in AVI-bodemas bestudeerd om de hoeveelheid en de eigenschappen van de verschillende koolstofvormen (species) te identificeren. De koolstofspeciatie is kwantitatief gemeten (gedeeltelijk gebaseerd op de methode beschreven in **Hoofdstuk 4**) om de relatie van de koolstofspecies met de uitloging van koper in verse en verouderde AVI-bodemas te bepalen. De resultaten laten zien dat slechts ongeveer 25% van het gloeiverlies bestaat uit organisch koolstof, de rest van het gloeiverlies is inert elementair koolstof. Het organisch koolstofgehalte bestaat vervolgens voor slechts ongeveer 15% uit humus- en fulvozuren. Omdat voornamelijk deze kleine fractie van organisch koolstof bijdraagt aan de verhoogde uitloging van zware metalen uit AVI-bodemas, wordt geconcludeerd dat metingen van gloeiverlies (momenteel een kwaliteitscontrole parameter) onvoldoende onderscheidend zijn voor een kwantitatieve bepaling van de relevante organisch koolstof species in AVI-bodemas. De resultaten van deze studie impliceren dat specifieke methoden voor de bepaling van relevante organisch koolstof species (humus- en fulvozuren) meer geschikt zijn dan de bepaling van gloeiverlies. Deze methoden kunnen de voorspeling van het lange termijn gedrag van AVI-bodemas in toepassingen of opslag waarschijnlijk aanzienlijk verbeteren.

Hoofdstuk 7 beschrijft een vergelijkende studie naar de proton bindingseigenschappen van de eerder geïsoleerde en gezuiverde humus- en fulvozuren (**Hoofdstuk 3**). Bindingsmodellen voor humus- en fulvozuren, zoals het NICA-Donnan model, zijn tot nu toe ontwikkeld en gekalibreerd met organische stof van natuurlijke herkomst (bijvoorbeeld bodems en oppervlaktewateren). In **Hoofdstuk 5** is al geconstateerd dat het NICA-Donnan model goed presteert wanneer het wordt toegepast op AVI-bodemas. De proton bindingseigenschappen van humus- en fulvozuren uit afvalstoffen zijn echter nog niet eerder direct gemeten om te demonstreren dat deze binnen het bereik van natuurlijke organische stof vallen. Het doel van deze studie is om de proton bindingseigenschappen van humus- en fulvozuren uit verschillende secundaire materialen, afvalstoffen en natuurlijke monsters te meten om vast te stellen of de ladingscurven van deze organische stoffen beschreven kunnen worden met de generieke parameters in het NICA-Donnan model. Er zijn nieuwe proton bindingsgegevens gerapporteerd en er is gevonden dat deze overeenstemmen met eerder gepubliceerde gegevens voor natuurlijke organische stof. De resultaten suggereren dat het NICA-Donnan model en de generieke bindingsparameters geschikt zijn om de protonbinding aan humus- en fulvozuren in zowel natuurlijke als verontreinigde (afval) materialen te beschrijven. Deze bevinding vergroot het bereik van de systemen/materialen waarop het NICA-Donnan model kan worden toegepast en het rechtvaardigt het gebruik van dit model voor geochemische speciatie modellering van de metaalmobiliteit in (verontreinigde) afvalstoffen.

SYNTHESE

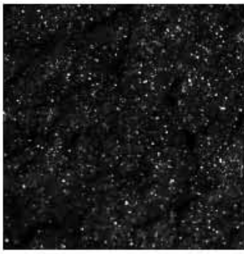
In dit proefschrift zijn verschillende analytische technieken ontwikkeld en toegepast om de chemische eigenschappen van natuurlijke organische stof te karakteriseren in relatie tot de binding van zware metalen in natuurlijke en verontreinigde materialen. Hiervoor zijn vernieuwende methoden ontwikkeld die hebben geleid tot nieuwe inzichten in de rol van organische stof bij de verhoogde uitloging en mobiliteit van verontreinigingen vanuit afvalstoffen.

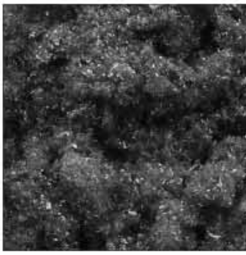
De geïdentificeerde rol van fulvozuren bij de uitloging van koper (**Hoofdstuk 2**) en de vastgestelde uitloogmechanismen van fulvozuren in AVI-bodemas (**Hoofdstuk 5**) kunnen worden gebruikt bij de ontwikkeling van technieken om de milieukwaliteit van dit veel geproduceerde materiaal te verbeteren. Op basis van de kennis uit dit proefschrift is ook een nieuwe technologie ontwikkeld voor de binding van organisch gebonden koper uit afvalstoffen om de koper uitloging aanzienlijk te verlagen. Er is inmiddels patent aangevraagd op deze technologie (WO2007035101). Deze ontwikkelingen openen het perspectief om AVI-bodemas zonder de noodzaak van aanvullende isolatiemaatregelen toe te passen als bouwmateriaal. Momenteel kan dit materiaal slechts met aanbreng van isolatievoorzieningen (folie afdichting) worden toegepast om aan de geldende eisen voor milieukwaliteit te voldoen.

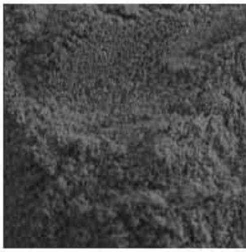
De ontwikkelde snelle batch procedure voor de kwantificering van humus- en fulvozuren (**Hoofdstuk 4**) wordt inmiddels steeds meer toegepast voor organische stof karakterisering. Bovendien is deze procedure voorgedragen voor internationale standaardisering in ISO kader (ISO TC 190/SC7). Nieuwe toepassingen van deze methode omvatten de bepaling van biologische afbreekbaarheid van organische stof fracties voor (organisch) afval op stortplaatsen en in de landbouw. De bredere toepassing van de snelle batchprocedure voor bepaling van humus- en fulvozuur concentraties kan het inzicht in processen die bijdragen aan het broeikaseffect verbeteren. Op basis van kennis van de verschillende organische stof fracties in specifieke milieucompartimenten, kunnen mogelijk verbeterde voorspellingen gedaan worden van potentiële broeikasgasemissies.

De nieuwe inzichten in de reactiviteit van organische stof hebben bijgedragen aan de ontwikkeling van gecombineerde modellen om de verspreiding van verontreinigingen vanuit afvalstoffen naar bodem en grondwater te voorspellen. Recentelijk zijn op basis van deze modelbenadering nieuwe milieucriteria vastgesteld voor de toepassing van afvalstoffen als bouwmateriaal (Besluit Bodemkwaliteit). Gezien het feit dat het NICA-Donnan model een belangrijke bijdrage levert aan de nauwkeurigheid van deze gecombineerde modellen, is het belangrijk op te merken dat er nog steeds erg weinig informatie beschikbaar is van de concentraties van humus- en fulvozuren in het milieu. De snelle batch methode die beschreven is in **Hoofdstuk 4** kan de routinematige bepaling van deze belangrijke parameters in monitoringprogramma’s aanzienlijk makkelijker maken.

DANKWOORD







DANKWOORD

Door de jaren heen ben ik de werkzaamheden rondom mijn proefschrift gaan beschouwen als mijn hobby. Mijn permanente positie als onderzoeker bij het ECN maakte de combinatie van projectwerk én proefschrift op zijn minst uitdagend. Nu is mijn hobby klaar, wie had dat ooit gedacht!

De geweldige begeleiding van Jeannet Meima en Rob Comans tijdens mijn HBO afstudeerperiode was de belangrijkste stimulans om later zelf ook echt de wetenschap te willen bedrijven. Ik kwam destijds als "broekie" met mijn resultaten bij ze en volgde dan vol bewondering de discussies over de betekenis van de resultaten. Ik vond het ongelooflijk dat er zoveel informatie in die getallen kon zitten! Dit werk leidde ook tot een co-auteurschap van een wetenschappelijk artikel. Tijdens mijn werk bij ECN kwam later het "wilde idee" om "gewoon" te proberen om een artikel te schrijven over mijn onderzoek, we zouden dan wel zien waar het schip zou stranden. Nou, dat heb ik geweten…

Rob zou mijn co-promotor worden en hij had ook Willem van Riemsdijk bereid gevonden om als promotor op te treden. Uiteindelijk zijn beiden promotor geworden en ben ik Willem dankbaar voor zijn vertrouwen en interesse in mijn werk. Rob, jou ben ik zeer dankbaar voor alle goede adviezen, hulp en het grote vertrouwen in mijn kunnen. Zonder jouw enorme drive en altijd positieve inslag had ik dit proefschrift niet kunnen voltooien. Je zeer kritische blik heeft er ook voor gezorgd dat mijn artikelen nu in toptijdschriften gepubliceerd zijn. Het kostte soms wat moeite, maar dan heb je ook wat!

Ik dank ook veel aan de inzet van de collega's bij het ECN. Allereerst mijn "lotgenoten" Joris Dijkstra en Wouter Huijgen, wij waren de drie musketiers van kamer 4. Bij jullie kon ik alles kwijt, alle leuke dingen van het werk en zeker ook de moeilijkheden die ik tijdens en naast het werk tegenkwam. We hadden het altijd vreselijk druk en eigenlijk nergens tijd voor, maar als ik een probleem had dan lag het werk direct stil en was er volle aandacht van jullie. Betere kamergenoten kan ik me niet wensen! Tevens denk ik met veel plezier terug aan de *PD-sessies*, waarbij ook de ex-collega's Patrick Cnubben en Hein de Wilde van de partij waren. Het bier vloeide dan altijd rijkelijk...

Hans van der Sloot, jij liet me zien hoe kennis direct toegepast kan worden en je opmerkingen waren vaak goed om zaken in breder perspectief te plaatsen. Mijn resultaten gingen ook direct de wereld rond op jouw missie om het uitloogwerk op de kaart te zetten. Dank hiervoor! Ik dank Hans Meeussen voor het regelmatig kritisch beoordelen van mijn manuscripten. Esther van der Weij, dank voor je geweldige hulp bij de ondersteuning op het laboratorium! Petra, wat zal ik zeggen? Jouw inzet, enthousiasme en nauwkeurigheid bij het uitvoeren van proeven is ongekend! Het is daarom logisch dat jij mijn paranimf bent en ik hoop dat we in de toekomst nog veel meer goed werk kunnen doen.

José Paulo Pinheiro, obrigado pela oportunidade que me deste para ficar na universidade em Portugal, aprendi muito contigo.

De collega's die iets verder van het proefschrift stonden, toonden ook veel belangstelling en hielpen me waar nodig: Remco Koper (altijd behulpzaam), Paul Seignette (leermeester databases) en oud-collega's Gerlinde Roskam (altijd vrolijk en hardwerkende promovenda), Arjan de Koning (gedreven promovendus en sportfanaat) en Dirk Hoede (voor jezelf op komen en af en toe flink brullen). Chanelle Carter, thanks for your English writing corrections and the joy you brought to ECN during your exchange. Verder ben ik Kees van der Klein en Jan-Willem Erisman zeer dankbaar, jullie hebben er altijd voor gezorgd dat de randvoorwaarden voor mijn werk en hobby goed geregeld waren.

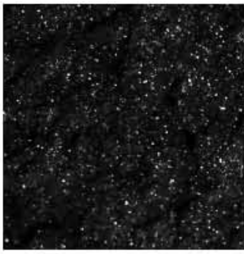
Mijn vrienden en kennissen buiten het werk hebben de afgelopen jaren niet altijd de aandacht gekregen die ze verdienden. Bedankt voor jullie geduld en begrip, ik zal de schade nu gaan inhalen! Wellicht is er nu zelfs ook weer tijd om eens hockeytraining bij te wonen…

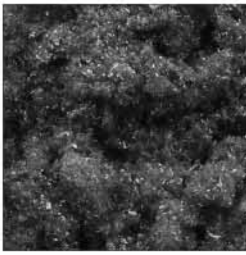
Judith, als buurmeisje van mij zijn we samen opgegroeid en hebben altijd lief en leed gedeeld, tot op de dag van vandaag. Jouw interesse in mijn promotie werkzaamheden was altijd groot en niet aflatend. In tijden dat ik twijfelde over de haalbaarheid van dit project, wist jij altijd een positieve draai aan de situatie te geven. Het is een eer dat jij mijn paranimf wilt zijn. Mark, ook jou ken ik al mijn hele leven en we hebben samen dus al veel meegemaakt. Het is daarom bijzonder voor me dat jij de omslag van dit boekje ontworpen hebt, bedankt.

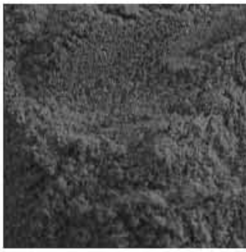
Papa en mama, als jullie me niet de kansen hadden gegund die ik gekregen heb dan was ik nooit zover gekomen. Dank voor de manier waarop jullie mij de nodige ondersteuning en vertrouwen hebben gegeven. Het is uiteindelijk toch nog goed gekomen met mij…

Tenslotte natuurlijk Annemiek, in plaats van te beginnen met danken kan ik beter eerst benadrukken dat jij een tomeloos geduld hebt met mij. Het was vaak niet makkelijk voor je om weer op de tweede plaats gezet te worden omdat ik in de avonduren of in het weekend weer allerlei resultaten voor dit boekje wilde uitwerken. Jouw begrip en vertrouwen hebben er aan bijgedragen dat het boekje nu toch echt af is. Bedankt voor je geduld en liefde!

CURRICULUM VITAE



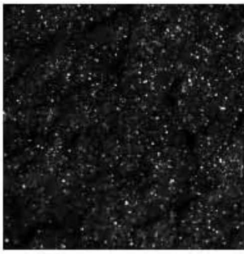


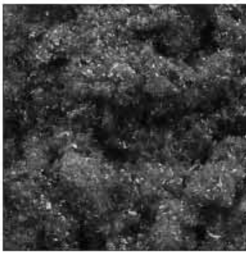


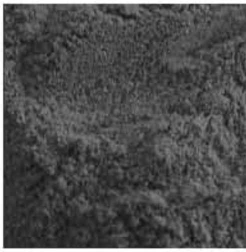
CURRICULUM VITAE

André van Zomeren was born in Alkmaar on June 4, 1973. He completed secondary school (MAVO) at the “don Bosco MAVO” in Heerhugowaard in 1989. From 1989 through 1993, he studied Analytical chemistry (specialisation: environmental chemistry) at the Backhuis Roozeboom institute (MLO) in Beverwijk. From 1993 to 1996 he studied environmental chemistry at the ”Hogeschool Alkmaar” (second specialisation was environmental management). He received his Bachelor’s degree on both specialisations in 1996. The subject of his graduate research project was the complexation of copper with dissolved organic carbon in leachates from municipal solid waste incineration bottom ash. In the same year, he got a temporary position as chemical analyst in the Environmental Risk Assessment group of the Energy research Centre of the Netherlands (ECN) in Petten. In that role, he contributed to numerous projects on the leaching behaviour of natural and waste materials. He also started the development of innovative analysis techniques for the characterisation of organic matter in these materials. He was project manager from 2000 onwards on various projects on the characterisation of waste materials and sustainable landfill concepts. He has also worked on the database model development and functionality of the ECN LeachXS^{TM} database/expert system. His Ph.D. research started around 2000 and was completed in 2008. In 2002, he received a permanent position at ECN as researcher/project manager. In January 2007, he became research scientist at the research institute.

LIST OF PUBLICATIONS







LIST OF PUBLICATIONS

PEER-REVIEWED PUBLICATIONS

Astrup, T., Cappai, G., Hjelmar, O., Kihl, A., Lechner, P., Mostbauer, P., Nyholm, M., Polettini, A., Pomi, R., van der Sloot, H. A., van Zomeren, A. Towards an improved understanding of the leaching behavior of MSWI residues - report on the 2nd meeting of the IWWG pHOENIX working group on "Management of municipal solid waste incineration residues", *Waste Man.*, **2004**, *24* , 529-530.

Carter, C. M., van der Sloot, H. A., Cooling, D., van Zomeren, A., Matheson, T. Characterization of untreated and neutralized bauxite residue for improved waste management, *Environ. Eng. Sci.*, **2008**, *25*, 475-488.

Dijkstra, J. J., van Zomeren, A., Meeussen, J. C. L., Comans, R. N. J. Effect of Accelerated Aging of MSWI Bottom Ash on the Leaching Mechanisms of Copper and Molybdenum, *Environ. Sci. Technol.*, **2006**, *40*, 4481-4487.

Meima, J. A., van Zomeren, A., Comans, R. N. J. Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates, *Environ. Sci. Technol.*, **1999**, *33*, 1424-1429.

van der Sloot, H. A., Meeussen, J. C. L., van Zomeren, A., Kosson, D. S. Developments in the characterisation of waste materials for environmental impact assessment purposes, *J. Geochem. Explor.*, **2006**, *88*, 72-76.

van der Sloot, H. A., van Zomeren, A., Meeussen, J. C. L., Seignette, P., Bleijerveld, R. Interpretation of test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal, *J. Hazard. Mater.*, **2007**, *141*, 354-369.

van Zomeren, A., Comans, R. N. J. Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.*, **2004**, *38*, 3927-3932.

van Zomeren, A., Comans, R. N. J. Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid batch procedure, *Environ. Sci. Technol.*, **2007**, *41*, 6755-6761.

van Zomeren, A., Comans, R. N. J. Carbon speciation and characterisation for improved understanding of the environmental behaviour of Municipal Solid Waste Incinerator (MSWI) bottom ash, *submitted*, **2008**.

van Zomeren, A., Costa, A., Pinheiro, J. P., Comans, R. N. J. Proton binding properties of humic substances originating from natural and contaminated materials, *submitted*, **2008a**.

van Zomeren, A., van der Weij-Zuiver, E., Comans, R. N. J. Development of an automated system for isolation and purification of humic substances, *Anal. Bioanal. Chem.*, **2008b**, *391*, 2365-2370.

BOOK CHAPTERS

Scharff, H., Oonk, H., Vroon, R., van der Sloot, H. A., van Zomeren, A., Hensen, A. Verbesserte methanoxidation durch zwangsbeluftung unter einer deponieabdeckung. In *Handbuch altlastensanierung und flachenmanagement*; C.F. Muller: 2003, pp 1-40.

van der Sloot, H. A., van Zomeren, A., Dijkstra, J. J., Meeussen, J. C. L., Comans, R. N. J., Scharff, H. Prediction of the leaching behaviour of waste mixtures by chemical speciation modelling. In *Landfill modelling*; Haarstrick, A., Reichel, T., Eds.; CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy: 2007.

van Zomeren, A., van der Sloot, H. A., Meeussen, J. C. L., Jacobs, J., Scharff, H. Prediction of the long-term leaching behaviour of a sustainable landfill containing predominantly inorganic waste. In *Landfill modelling*; Haarstrick, A., Reichel, T., Eds.; CISA Publisher: Padova, 2007.

CONFERENCE CONTRIBUTIONS

Astrup, T., Cappai, G., Lechner, P., Muntoni, A., polettini, A., Pomi, R., van Gerven, T., and van Zomeren, A. State-of-the-art and outlook on management of waste-to-energy bottom ashes. part 2: utilization. Cossu, R. and Stegmann, R. 101-102. 2007. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 11th international waste management and landfill symposium.

Carter, C. M., Cooling, D., Matheson, T., van der Sloot, H. A., and van Zomeren, A. New approach to leach testing of bauxite residue to support management decisions in view of beneficial application and storage. 2005. 7th International Alumina Quality Workshop, Perth, Australia 2005.

polettini, A., Astrup, T., Cappai, G., Lechner, P., Muntoni, A., Pomi, R., van Gerven, T., and van Zomeren, A. State-of-the-art and outlook on management of waste-to-energy bottom ashes. part 1: treatment. Cossu, R. and Stegmann, R. 99-100. 2007. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 11th international waste management and landfill symposium.

Rietra, R. P. J. J., van der Sloot, H. A., van Zomeren, A., and Bleijerveld, R. Integration of lab-scale testing and pilot scale monitoring of a stabilised waste landfill to reach sustainable landfill conditions. Christensen, T. H., Cossu, R., and Stegmann, R. 4, 243-250. 2001. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. Sardinia 2001, Eighth International waste management and landfill symposium.

Scharff, H., Jacobs, J., van der Sloot, H. A., and van Zomeren, A. Inorganic waste landfill and final storage quality. Cossu, R. and Stegmann, R. 147-148. 2007. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 11th international waste management and landfill symposium.

Scharff, H., Oonk, H., Vroon, R., van der Sloot, H. A., van Zomeren, A., and Hensen, A. Improved methane oxidation by means of forced aeration under a landfill cover. Christensen, T. H., Cossu, R., and Stegmann, R. 2, 555-564. 2001. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. Eighth International waste management and landfill symposium.

van der Sloot, H. A., Seignette, P., Comans, R. N. J., van Zomeren, A., Dijkstra, J. J., Meeussen, J. C. L., Kosson, D. S., and Hjelmar, O. Evaluation of environmental aspects of alternative materials using an integrated approach assisted by a database/expert system. 769-790. 2003a. University of Dundee, Dundee, Scotland. Conference on advances in waste management and recycling.

van der Sloot, H. A., van Zomeren, A., Dijkstra, J. J., Hoede, D., Jacobs, J., and Scharff, H. Prediction of long term leachate quality and chemical speciation for a predominantly inorganic waste landfill. Christensen, T. H., Cossu, R., and Stegmann, R. 2003b. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 9th international waste management and landfill symposium.

van der Sloot, H. A., van Zomeren, A., Dijkstra, J. J., Meeussen, J. C. L., Comans, R. N. J., and Scharff, H. Prediction of the leaching behaviour of waste mixtures by chemical speciation modelling based on a limited set of key parameters. Cossu, R. and Stegmann, R. 603-604. 2005. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 10th international waste management and landfill symposium.

van der Sloot, H. A.; van Zomeren, A.; Dijkstra, J. J.; Meeussen, J. C. L.; Comans, R. N. J.; Scharff, H. Prediction of the leaching behaviour of waste mixtures by chemical speciation modelling. In *Landfill modelling*; Haarstrick, A., Reichel, T., Eds.; CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy: 2007.

van der Sloot, H. A., van Zomeren, A., Rietra, R. P. J. J., Hoede, D., and Scharff, H. Integration of lab-scale testing, lysimeter studies and pilot scale monitoring of a predominantly inorganic waste landfill to reach sustainable landfill conditions. Christensen, T. H., Cossu, R., and Stegmann, R. 1, 255-264. 2001. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. Eighth International waste management and landfill symposium.

van Gerven, T., Astrup, T., Cappai, G., Lechner, P., Muntoni, A., polettini, A., Pomi, R., and van Zomeren, A. The Phoenix network on waste-to-energy residues. Cossu, R. and Stegmann, R. 2007. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 11th international waste management and landfill symposium.

van Zomeren, A. and Comans, R. N. J. Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash. (Proceedings of the International Humic Substances Society Twentieth Anniversary Conference, July 21-26, 2002, Boston, USA), 424-426. 2002. Boston (MA), USA. IHSS 20th anniversary conference, Humic acids: nature's most versatile materials.

van Zomeren, A. and Comans, R. N. J. Speciation and characterisation of organic carbon in municipal solid waste incinerator (MSWI) bottom ash. Ortiz de Urbina, G. and Goumans, J. J. J. M. (5), 657-666. 2003. San Sebastian, Spain. Wascon 2003, Progress on the road to sustainability.

van Zomeren, A., Comans, R. N. J., and van der Sloot, H. A. A rapid batch procedure for assessment of humic substances and biodegradable components of organic matter. Cossu, R. and Stegmann, R. 821-822. 2007. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 11th international waste management and landfill symposium.

van Zomeren, A., van der Sloot, H. A., Hoede, D., van Wetten, H., and Bleijerveld, R. Laboratory, pilot and field studies on stabilized waste produced at the VBM site for recipe development, quality control and support of regulation. Ortiz de Urbina, G. and Goumans, J. J. J. M. 2003a. San Sebastian, Spain. Wascon 2003 conference: Progress on the way to sustainability.

van Zomeren, A., van der Sloot, H. A., Meeussen, J. C. L., Jacobs, J., and Scharff, H. Prediction of the long-term leaching behaviour of a sustainable landfill containing predominantly inorganic waste. Cossu, R. and Stegmann, R. 831-832. 2005a. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 10th international waste management and landfill symposium.

van Zomeren, A., van der Weij-Zuiver, E., van der Sloot, H. A., van den Berg, P., and Bleijerveld, R. Environmental behaviour of a stabilised waste disposal in the framework of sustainable landfilling. Cossu, R. and Stegmann, R. 833-834. 2005b. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. 10th international waste management and landfill symposium.

van Zomeren, A., van Wetten, H., Dijkstra, J. J., van der Sloot, H. A., and Bleijerveld, R. Long term prediction of release from a stabilised waste monofill and identification of controlling factors. Christensen, T. H., Cossu, R., and Stegmann, R. 527. 2003b. S. Margherita di Pula, Cagliari, Italy, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy. Ninth International waste management and landfill symposium.

SELECTED OTHER PUBLICATIONS AND REPORTS

Comans, R. N. J., Filius, J., van Zomeren, A., and van der Sloot, H. A. *Karakterisering organische stof, Haalbaarheidsstudie naar genormaliseerde methoden voor de bepaling van de beschikbaarheid en rol van organische stof in grond, afval- en bouwstoffen m.b.t. verhoging van de uitloging van slecht water-oplosbare verontreinigingen*, ECN-C--00-060; ECN, 2000.

Comans, R. N. J., Geelhoed, P. A., van Zomeren, A., and Geusebroek, M. *Belang van opgeloste organische stof bij transport van contaminanten uit baggerspecie*, ECN-C--98-076, 1998.

Comans, R. N. J., Steketee, J. J., van Zomeren, A., and Zuiver, E. *Bepalingsmethoden voor reaktieve en inerte vormen van koolstof in grond, bouw- en afvalstoffen (ANVM project 247)*, ECN-C--03-127, 2004.

Erisman, J. W., Vermeulen, A. T., Geusebroek, M., van Zomeren, A., Comans, R. N. J., Bakker, F. P., Fonteyn, P., Mols, J. J., and Koeleman, M. *Dispersion and loads of pollutants to the verge of two highways in the Netherlands; Contribution to the POLMIT project*, ECN-C--99-100, 1999.

Mathlener, R. A., Heimovaara, T., Oonk, H., Luning, L., van der Sloot, H. A., and van Zomeren, A. *Opening the black box, process-based design criteria to eliminate aftercare of landfills*, ISBN-10: 90-73573-30-0, Dutch sustainable landfill foundation, 2006.

Moolenaar, S. W., Middeldorp, P. F., Zevenbergen, C., van Zomeren, A., Comans, R. N. J., and Bradly, J. P. *Retrospectief onderzoek aan archeologische resten naar de afbraak van PAK in grond en baggerspecie*, 98-1-19, 2001.

Schoknecht, U., Mathies, H., Morsing, N., Lindegaard, B., van der Sloot, H. A., van Zomeren, A., Deroubaix, G., Legay, S., Tadeo, J. L., Garcia-Valcarcel, A. I., Gigliotti, G., Zadra, C., Hajslova, J., Tomaniova, M., Wegner, R., and Bornkessel, C. *Inter-laboratory evaluation of laboratory test methods to estimate the leaching from treated wood*, 04/375757/C4, 2005.

van der Sloot, H. A., van Zomeren, A., de Nie, D. S., and Meeussen, J. C. L. *pH en redox effecten van bouwmaterialen*, ECN-E--07-093, 2007.

van Zomeren, A., Meeussen, J. C. L., Oonk, H., Luning, L., and van der Sloot, H. A. *Evaluation of geochemical and biochemical processes and release from landfills*, ISBN-10: 90-73573-34-3, Dutch sustainable landfill foundation, 2006.

van Zomeren, A. and van der Sloot, H. A. *Equistort, stortplaats voor overwegend anorganisch afval*, ISBN-10: 90-73573-33-5, Dutch sustainable landfill foundation, 2006a.

van Zomeren, A. and van der Sloot, H. A. *Monolith, stortplaats voor cement-gestabiliseerd gevaarlijk afval*, ISBN-10: 90-73573-32-7, Dutch sustainable landfill foundation, 2006b.

This research was partly funded by the Dutch Ministry of Housing, Spatial Planning and the Environment as part of ECN’s environmental research program.

Printed by Gildeprint B.V., Enschede, The Netherlands.

Cover: Photographs of isolated and purified humic- and fulvic acids from natural and contaminated materials. The sources of these humic substances are (from top to bottom):
-Fulvic acid from a landfill leachate in The Netherlands
-Humic acid from Suwannee river in the USA
-Fulvic acid from a Dutch municipal solid waste incinerator bottom ash sample
-Humic acid from municipal solid waste derived compost
-Humic acid from a landfill leachate in The Netherlands
-Fulvic acid from the nature reserve “Zwanenwater” in The Netherlands

Design cover: Mark de Jong