MPEREEN TEKNILLINEN YLIOPISTO
MPERE UNIVERSITY OF TECHNOLOGY

kaisu 540 • Publication 540

Kati V   saari

Lead   and Ecotoxicity Tests as Methods for Classification and A   ssment of Environmental Hazard of Solid Wastes

Tampe   5

ABSTRACT

The importance of developing methods for the hazard assessment of solid wastes is steadily increasing worldwide. The main objective of this thesis was to develop a new approach to waste hazard classification that combines leaching and ecotoxicity tests, since the determination of total concentrations of substances in complex mixtures of unknown composition, which is a characteristic of many wastes, does not provide an accurate estimation of the overall environmental impact of solid wastes.

Chemical classification was carried out by comparing total concentrations of key hazardous substances in the wastes studied with the limit values set for hazardous wastes, and comparing the leached amounts of the substances with the limit values proposed by the EU. Four wastes studied from the metal and forest industries contained predominantly inorganic compounds and ten from the furniture and resin industries mainly aromatic or aliphatic organic compounds. Six soil samples contaminated by petroleum products were studied in order to evaluate their environmental hazard after remediation. Various types of leaching tests were used to study the leaching profiles of key hazardous substances in four predominantly inorganic wastes. One-stage or multi-stage batch leaching tests were also used to study the leaching of volatile organic compounds from the organic wastes and that of petroleum pro-ducts from the soil samples. The ecotoxicity of substances leached out from the wastes was studied from the eluates of batch leaching tests with different combinations of aquatic ecotoxicity tests: microbial tests, water flea and algal tests, electron transport assay (RET) and plant tests. In addition, the ecotoxicity of oil-contaminated soils was studied directly from solid materials with plant seed germination tests and enchytraeid worm survival and reproduction tests and the ecotoxicity of the organic wastes was investigated with a lettuce seed germination test before and after the leaching experiments.

The results of the present study proved that the environmental hazard of solid wastes and soil samples was underestimated when only the total concentrations of known key hazardous substances were analyzed. It was also found that the release of these substances should be determined in order to predict the long-term environmental impacts of solid wastes. It was also important to perform an availability test on the inorganic wastes in order to ascertain their resistance to acid attack. The batch leaching tests performed on the organic wastes and contaminated soil samples studied showed that these methods should be used to screen the water-leachable fraction of the key organic compounds. The differences between the chemical and ecotoxicological classification emphasized the need for ecotoxicity tests to complement chemical analyses in the hazard classification of wastes. For example, fly ash was classified as non-hazardous by chemical analyses but ecotoxicity assays proved that the batch leaching test eluates of this waste had high or very high aquatic toxicity ($10 < TU < 100$ and $TU > 100$). The organic wastes contained large amounts of compounds not identifiable with available chemical analyses. A more cost-effective and relevant estimation of the overall environmental hazard of complex mixtures of unknown substances in solid wastes and their eluates could be made with a combined solid-phase and liquid-phase approach using ecotoxicity assays and TOC analyses.

Based on the present study, the European batch leaching test method (EN-12457-2) was proposed for the combined chemical and ecotoxicological classification of substances leached out from inorganic and organic wastes and soils. Only then can ecotoxicity test results be compared with chemical analyses to improve hazard classification when selecting the best waste management alternative. The battery of toxicity tests should consist of cost-effective methods that are simple to perform, in which the volume required for analyses is minimized. According to this study, the luminescent bacteria test, MetPLATE and ToxiChromo tests, RET assay and onion root elongation test were the best choice. Wheat or lettuce seed germination tests are proposed for the determination of the ecotoxicity of solid wastes. The proposed terrestrial toxicity method for oil-contaminated soils was the Enchytraeid worm (*E. albidus)* survival test.

This study demonstrated that environmental hazard assessment of solid wastes based only on the chemical analyses of known key hazardous substances and available regulatory values was inadequate. The results showed that the criteria for both waste classification and management could be improved by setting criteria and limit values for ecotoxicity test results. A new screening approach and criteria for the evaluation of the environmental toxicity of wastes are presented. This approach would aid environmental authorities in making decisions on waste hazard classification and help waste producers to improve their processes and minimize the environmental impacts of wastes.

TIIVISTELMÄ

Ympäristölle haitallisten teollisuusjätteiden määrä kasvaa jatkuvasti, samoin tarve arvioida jätteiden ympäristövaarallisuutta. Tämän väitöskirjan tarkoituksena oli kehittää liukoisuus- ja toksisuustesteihin perustuva arviointimenetelmä jätteiden ongelmajäteluokittelun ja sijoitusvaihtoehtojen ratkaisujen tueksi. Yksittäisten kemiallisten kokonaispitoisuuksien analysoiminen monimutkaisista, usein koostumukseltaan tuntemattomista jätteistä ei ole riittävä tapa arvioida jätteiden ympäristövaarallisuutta.

Tässä työssä kemiallinen luokittelu tehtiin vertaamalla tutkituista jätteistä analysoitujen päähaitta-aineiden pitoisuuksia ongelmajätteiden raja-arvoihin sekä jätteistä tutkittujen liukenevien yhdisteiden määriä EU:ssa esitettyihin kaatopaikkasijoitusta koskeviin raja-arvoihin. Tutkituista jätenäytteistä neljä oli metalli- ja metsäteollisuuden jätteitä, jotka sisälsivät pääasiassa epäorgaanisia haitta-aineita. Näytteistä kymmenen oli huonekaluteollisuuden ja hartsin valmistuksen jätteitä, ja ne sisälsivät pääasiassa haihtuvia orgaanisia yhdisteitä. Kuusi näytettä oli peräisin entisen huoltoaseman pilaamasta maaperästä, ja ne sisälsivät öljyhiilivetyjä. Erilaisten liukoisuustestien avulla määritettiin merkittävimpien haitta-aineiden liukoisuus metalli- ja metsäteollisuuden jätteistä. Lisäksi yksi- ja monivaiheisilla ravistelutesteillä tutkittiin orgaanisten yhdisteiden liukenemista huonekalu- ja hartsiteollisuuden jätteistä sekä öljyhiilivedyillä pilaantuneista maanäytteistä. Jätteiden toksisuutta tutkittiin yksi- ja kaksivaiheisten ravistelutestien uutteista useilla erilaisilla ekotoksisuustesteillä. Lisäksi maanäytteiden toksisuus määritettiin suoraan kiinteistä maaperänäytteistä siementen itävyystesteillä sekä änkyrimatojen kuolevuus- ja lisääntymistesteillä. Salaatin siementen itävyystestiä käytettiin myös orgaanisia haitta-aineita sisältävien jätteiden toksisuuden määrittämiseen ennen ja jälkeen liukoisuustestausta.

Työn tulokset osoittivat, että jätteiden ympäristöhaitallisuutta aliarvioidaan, jos jätteistä analysoidaan ainoastaan niiden sisältämien päähaitta-aineiden pitoisuudet. Pitkäaikaisten ympäristöhaittojen selvittämiseksi jätteistä tulee tutkia myös haitta-aineiden liukeneminen. Maksimiliukoisuustestiä oli tärkeätä käyttää epäorgaanisille jätteille, jotta voitiin arvioida jätteiden kykyä vastustaa happamoitumista ja pH-muutosten vaikutusta haitta-aineiden liukenemiseen. Epäorgaanisille yhdisteille standardoidut ravistelutestit soveltuivat riittävän hyvin arvioimaan myös jätteistä liukenevien orgaanisten haihtuvien yhdisteiden haitallisuutta ympäristössä. Eroavuudet tutkittujen jätteiden kemiallisen luokittelun ja ekotoksisuuteen perustuvan luokittelun välillä osoittivat, että toksisuustestit täydensivät kemiallista analytiikkaa. Erityisen tärkeätä toksisuuden tutkiminen oli orgaanisia haitta-aineita sisältävistä jätteistä, koska ne sisälsivät tuntemattomia yhdisteitä eikä jätteiden koostumusta ja yhdisteiden liukoisuutta pystytty kemiallisesti analysoimalla selvittämään. Liukoisuus- ja toksisuustestien yhdistelmään perustuva arviointimenetelmä tarjosi edullisemman ja ympäristön kannalta merkityksellisemmän tavan arvioida jätteiden ympäristövaarallisuutta.

Tämän työn tulosten perusteella eurooppalaista ravistelutestiä neste/kiinteä-suhteessa 10 voidaan suositella uuttomenetelmäksi jätteistä liukenevien yhdisteiden toksisuuden määrittämiseen. Toksisuusmenetelmien tulisi olla helppokäyttöisiä ja edullisia sekä tarpeeksi herkkiä tunnistamaan sekä epäorgaanisten että orgaanisten yhdisteiden aiheuttamaa yleismyrkyllisyyttä. Työn tulosten perusteella jäteuutteiden toksisuus on suositeltavaa tutkia valobakteeritestillä, MetPLATE- tai ToxiChromotesteillä, RET-testillä sekä sipulin juurikasvunestymistestillä. Vehnän tai salaatin siementen itävyystestejä voidaan suositella käytettäväksi suoraan kiinteiden jätemateriaalien toksisuuden määrittämiseen. Lisäksi änkyrimatojen kuolevuustestiä voidaan suositella käytettäväksi öljyhiilivedyillä pilaantuneen maaperän jäteluokitteluun ja loppusijoitusvaihtoehtojen arvioimiseen.

Työn tulokset osoittivat, että pelkästään yksittäisten kemiallisten yhdisteiden analysointi ja pitoisuuksien vertaaminen käytettävissä oleviin raja-arvoihin ei riitä arvioitaessa jätteiden ympäristöhaittoja. Tässä työssä esitetään uusi toksisuus- ja liukoisuustestien yhdistelmään perustuva arviointitapa sekä perusteet toksisuustulosten tulkintaan, jotta jätehuoltoratkaisuihin liittyvä päätöksenteko olisi yksinkertaisempaa ja jätteiden loppusijoitus ympäristön kannalta turvallista.

PREFACE AND ACKNOWLEDGEMENTS

LIST OF ORIGINAL PAPERS

This thesis is based on the following original papers referred to, in this thesis, by the roman numerals:

I Vaajasaari, K., Ahtiainen, J., Nakari, T., Dahlbo, H. 2000. Hazard assessment of industrial waste leachability: chemical characterization and biotesting by routine effluent tests. *In:* Persoone, Janssen, De Coen (eds.). New Microbiotests for Routine Toxicity Screening and Biomonitoring, Kluwer Academic/Plenum Publishers, New York, 413–423.

II Joutti, A., Schultz, E., Tuukkanen, E., Vaajasaari, K. 2000. Determination of industrial waste leachates: toxicity detection with microbiotests and biochemical tests. *In:* Persoone, Janssen, De Coen (eds.). New Microbiotests for Routine Toxicity Screening and Biomonitoring, Kluwer Academic/Plenum Publishers, New York, 347–355.

III Schultz, E., Vaajasaari, K., Joutti, A., Ahtiainen, J. 2002. Toxicity of industrial wastes and waste leaching test eluates containing organic compounds. Ecotoxicol. Env. Saf. 52, 248–255.

IV Vaajasaari, K., Joutti, A., Schultz, E., Selonen, S., Westerholm, H. 2002. Comparisons of terrestrial and aquatic bioassays for oil-contaminated soil toxicity. JSS -J Soils & Sediments 2, 194–202.

V Vaajasaari, K., Kulovaara M., Joutti A., Schultz E., Soljamo K. 2004. Hazardous properties of paint residues from the furniture industry. J. Hazard. Mater. 106A, 71–79.

AUTHOR'S CONTRIBUTION

I   Kati Vaajasaari was responsible for most of the research planning and performed a part of the toxicity tests. She wrote the paper and is the corresponding author. The ecotoxicological results were jointly interpreted by Kati Vaajasaari and the co-authors.

II   Kati Vaajasaari was responsible for most of the research planning. She was responsible for writing and interpreting the results of the leaching studies. The ecotoxicological results were jointly interpreted with Kati Vaajasaari and the co-authors.

III   Kati Vaajasaari was responsible for the research planning and she performed a part of the toxicity tests. She interpreted and wrote the results of the leaching studies. The ecotoxicological results were jointly interpreted by Kati Vaajasaari and the co-authors.

IV   Kati Vaajasaari was responsible for the research planning and performed a part of the toxicity tests. She wrote the paper and is the corresponding author. The chemical and ecotoxicological results were jointly interpreted by Kati Vaajasaari and the co-authors.

V   Kati Vaajasaari was responsible for planning the research. She wrote the paper and is the corresponding author. The chemical and ecotoxicological results were jointly interpreted by Kati Vaajasaari and the co-authors.

DEFINITIONS AND ABBREVIATIONS

ANC	Acid neutralizing capacity
BTEX	Benzene, toluene, ethylbenzene and xylenes
CCA	Chromium copper arsenate, wood preservative
CEN/TC 292	European Committee for Standardization, Technical Committee for Characterization of Waste
COD	Chemical oxygen demand
DHM	Dissolved humic matter
DOC	Dissolved organic carbon
EC50	Median-effective concentration, i.e. concentration that causes 50 percent reduction of a certain effect on test organism
ELUATE	Water extract of the solid material performed by a leaching test method
EN	European standard of European Committee for Standardization CEN/TC 292
EPA	Environmental Protection Agency, USA
EWC	European waste code
GC-FID/MS	Gas chromatography accompanied with flame–ionization or mass spectrometer detector
H	Hazardous property of waste
ICP	Inductively coupled argon plasma spectrometry
LEACHATE	Liquid discharge of wastes, i.e. from landfills
LC50	Median-lethal concentration, i.e. concentration that causes 50 percent mortality of the test organism
LOI	Loss on ignition
L/S	Liquid-to-Solid-ratio in leaching test, l/kg
MTBE	Methyl-*tert*-butyl-ether, additive of gasoline
MSWI	Municipal Solid Waste Incineration
MSWIBA	Municipal Solid Waste Incineration Bottom Ash
PAHs	Polyaromatic hydrocarbons
PCBs	Polychlorinated biphenyls
RET	Reverse electron transport assay, an *in vitro* toxicity test
PP/V	Plasma Pyrolysis/Vitrification
prEN	Preliminary European standard of European Committee for Standardization CEN/TC 292
TAME	Tri-*amyl*-methyl-ether, additive of gasoline
TCLP	Toxicity Characteristics Leaching Procedure, USA EPA method
TOC	Total organic carbon
TU	Toxic Unit calculated by formula TU=100/EC50
VOCs	Volatile organic compounds
WG	Working group of European Committee for Standardization CEN/TC 292

TABLE OF CONTENTS

1 INTRODUCTION

1.1 Background

Development of methods for environmental hazard assessment of wastes has become a major issue worldwide due to the increasing amount of waste produced. The present European Union policy on hazard classification and landfill disposal of waste materials requires tighter control over the release of contaminants into the environment. Hazardous Waste Directive 1991/689/EC defines a set of 14 properties to be used in waste hazard classification (Official Journal of the European Communities 2000). According to EU Landfill Directive 1999/31/EC, the waste acceptance criteria impose requirements for waste classification and quality monitoring (Official Journal of the European Communities 2003). The basic requirements for waste classification are: (1) source and origin of the waste, (2) information about the waste producing process, (3) information on its composition and on its leaching behaviour and appearance. The previous regulations were introduced for non-household waste. The major limitations in decision-making on waste management alternatives have been a lack of harmonized technical testing solutions, classification criteria and the limit values of certain hazardous properties of waste materials, such as their ecotoxicity and the leaching of individual organic compounds. The importance of developing test methods for the hazard classification of wastes is steadily increasing in an attempt to comply with the demands set by the EU legislation. In recent years, there has been a lively debate in Europe about testing methods to assess the combined leaching and ecotoxicity of wastes (e.g. Lapa *et al.* 2002a).

Decisions on the hazardous properties of wastes are based on the total concentrations of hazardous substances. In order to determine the composition of wastes by chemical analyses, all the possible substances present in waste have to be identified. In practice, the background data available on the composition of wastes is often limited. Chemical analyses often focus on the determination of the concentrations of key hazardous substances. Thus, analyzing a limited set of key hazardous substances in matrices may not provide sufficient data to reflect the overall hazardous chemical composition of heterogeneous complex waste materials. Contaminated soils are also considered as waste when excavated from a site. The conventional treatment method for excavated contaminated soils is landfill disposal. So far, there are no uniform criteria for landfill disposal of contaminated soils. Decisions on the waste management of excavated soils are mainly based on the total concentrations of the key hazardous substances.

From an environmental hazard assessment perspective, the bioavailability of substances has to be distinguished from the total concentration of chemicals in wastes or in contaminated soils (Lanno *et al.* 2004). Chemical analyses cannot provide information about bioavailability, effects on biota, or interactions between chemicals (Turpeinen 2002). In addition, ecotoxicological properties are not easy to characterize or quantify using solely chemical data. This emphasizes the importance of studying the leaching and ecotoxicity properties of wastes complementary to the total concentrations of key hazardous substances.

Leaching tests and the chemical analyses of the resulting eluates can be used to identify one hazardous property of waste (H13) in Hazardous Waste Directive 1991/689/EC, i.e. substances that can cause harmful effects after disposal by yielding a leachate. Water is an important carrier of harmful compounds to the environment. Water is also the most common extraction liquid used in standardized leaching methods for waste materials (Van der Sloot *et al.* 1997). There are two main groups of standard leaching tests used for wastes: batch extraction tests and column tests. Special leaching test methods are used if there is a need to determine the influence of various factors, e.g. pH, redox potential, ionic strength, on leaching of contaminants from solid wastes (Van der Sloot *et al.* 1997).

Leaching of substances from solid waste at the landfill site depends on the quality of the waste material, the content of contaminants, the moisture or liquid content of the dumped waste, and on the reactions between the different waste materials (LaGrega *et al.* 2001). Liquid discharges from landfills, referred to here as landfill leachates, can be determined as a mixture of thousands of soluble and solid compounds. Heavy metal concentrations in landfill leachates are generally rather low, but a broad range of xenobiotic organic compounds has been detected in landfill leachates (Kjeldsen *et al.* 2002, Wintgens *et al.* 2003). As shown in the study of Paxéus (2000), more than 200 individual organic compounds and groups of compounds have been found in leachates from municipal landfills. Ecotoxicological assays measure the overall toxicity of complex mixtures of chemicals and are needed in order to obtain a more direct and integrated estimate of the harmful effects of contaminants arising from dumped wastes (Atwater *et al.* 1983, Devare and Bahadir 1994, Clément *et al.* 1996 and 1997).

The growing concern to predict the overall environmental hazard of wastes has led to a development of appropriate methods to measure the harmful properties of leached substances using a combination of chemical and ecotoxicological analyses. The sensitivity of ecotoxicity assays to various toxicants or mixtures of toxicants in the test material differs (Chapman 1995, Persoone *et al.* 2000). This realization has also led to the concept of using several bioassays to assess the environmental impacts of wastes with a battery-of-tests approach (e.g. Ferrari *et al.* 1999, Lapa *et al.* 2002a and b, Pŏllumaa 2004). According to Hazardous Waste Directive 1991/689/EC, ecotoxicity (H14) is one of the hazardous properties to be determined from wastes. In Finnish national landfill legislation (Council of State Decision 861/97, Annex II), the ecotoxicological properties of waste leachates are mentioned, but in the recently prepared waste acceptance criteria (Council Decision 2003/33/EC) of the EU Landfill Directive, there are no requirements or specific limit values for the ecotoxicity of waste eluates.

Most experience of leaching and ecotoxicity assays of solid wastes is still limited to characterizing inorganic wastes, e.g. waste incineration ashes (e.g. Fällman and Aurell 1996, Fällman 1997, Van der Sloot *et al.* 1997, Ferrari *et al.* 1999, Van der Sloot *et al.* 2001, Lapa *et al.* 2002a and b). In Europe, municipal solid wastes (MSW) and wastes from different industrial sectors are incinerated to a larger extent than in Finland. In 1997, the percentage of incinerated MSW out of the total amount of waste produced in Germany was 50 % and in Netherlands 62 %, while in France it was 30 % and in Finland 2 % (Laine-Ylijoki *et al.* 2005). The amount of bottom ash and fly ash produced annually is around 575 000 t to 814 000 t in Denmark, Germany, and Netherlands. It is to be expected that waste incineration and the amounts of ash produced will also increase in Finland.

There are also industrial sectors that produce wastes containing organic substances that are not incinerated. The waste acceptance criteria of the EU Landfill Directive have been established mainly for inorganic compounds and no leaching limit values are available for individual organic substances for non-hazardous or hazardous waste landfills (Official Journal of the European Communities 2003). In the European Standardization Committee working groups (CEN/TC 292), leaching tests have been developed for inorganic wastes, but so far no standardized or validated methods are available for wastes containing organic compounds. The batch and column leaching methods for inorganic compounds have been used to study leaching of organic substances, such as PCBs, PAHs, chlorophenols and petroleum products from contaminated soils (Rood *et al.* 1994, Wahlström *et al.* 1994, Hirner *et al.* 1998, Comans 2001, Wahlström *et al.* 2002, Yong-Jin and Masahiro 2003). However, there is still a need for the development of appropriate methods for combined leaching and ecotoxicity assays to determine the environmental hazard of wastes containing organic compounds.

1.2 Assessment of environmental hazard of wastes

1.2.1 Waste legislation demands for hazard classification and landfill disposal

The hazard classification of wastes should be done before decisions are made on waste management options, if it is suspected that the waste may possess any of the hazardous properties or if the classification of the waste is uncertain. In the EU waste legislation, the list of wastes and hazardous wastes is the basis for the hazard classification of waste materials (Official Journal of the European Communities 2000). According to this list, waste is classified as hazardous, if the concentrations of hazardous substances are such that the waste presents one or more of the 14 hazardous properties (H) listed in Annex III of the Hazardous Waste Directive (1991/689/EC). These hazardous properties are presented at the end of this thesis (see Appendix 1).

The Finnish national waste legislation is based on EU directives and regulations. The list of wastes and hazardous wastes is presented in the statutory regulations of the Finnish Ministry of Environment (1129/2001). For hazard classification, all the possible substances present in waste have to be identified on the basis of the hazardous properties (H) given in the waste decree (1128/2001, see Appendix 1). The waste hazard classification is based on the total concentrations of the hazardous substances and set according to the physical and chemical characteristics of chemicals and their hazard classification (statutes of the Finnish Ministry of Social Affairs and Health, 807/2001 and 624/2001). Generally, background information on the composition of wastes is collected from the waste producers. The physical and chemical characteristics of all the key hazardous substances are then evaluated from the different information sources for these chemicals (Dahlbo 2002).

Ecotoxic (H14) is one of the hazardous properties of wastes defined in the Hazardous Waste Directive (1991/689/EC). However, the directive does not refer to any specific methods or limit values for evaluating criterion (H14). The French Ministry of the Environment has proposed a methodology and limit values for aquatic ecotoxicity test results to assess the ecotoxicological properties of wastes. In this proposal, the ecotoxic (H14) property of waste of the European standard (EN-12457) batch leaching test eluates is determined by luminescent bacteria, water flea and algae tests (Ferrari *et al*. 1999, Békaert *et al*. 2002, Lapa *et al.* 2002a). A Spanish limit value for the ecotoxic (H14) property of waste is defined as the water flea immobilization test and the luminescent bacteria test performed on the eluates of the TCLP method (EPA 1990, Seco *et al*. 2003). The Finnish waste legislation does not yet refer to any specific test methods or limit values to determine the ecotoxic property of wastes (Dahlbo 2002). For an ecotoxic property (H14), the proposed limit value is set on the basis of the classification of chemicals with an ecotoxic property (see Appendix 1).

As mentioned above, leaching tests and the chemical analyses of the resulting eluates can be used to identify one hazardous property (H13) of waste. This property is defined in the Hazardous Waste Directive 1991/689/EC as " *substances that can cause harmful effects after disposal, of yielding another substance, e.g. leachate, which possesses a characteristic hazardous to humans or to the environment* ". According to EU regulations, the acceptance of wastes into landfills consists of (1) basic characterization, (2) compliance testing and (3) on-site verification (Official Journal of the European Communities 2003). The basic characterization tests focus on understanding the long-term leaching behaviour and the parameters influencing leaching (e.g. pH). When a waste has been determined to be acceptable for a landfill class of inert, non-hazardous or hazardous waste landfills on the strength of a basic characterization, the quality of the waste is determined by a compliance test periodically for waste streams that are produced regularly in the process (Official Journal of the European Communities 2003).

The EU criteria for landfills for non-hazardous waste are laid down only for inorganic wastes with low organic content, which is landfilled in the same cell with stable, non-reactive hazardous waste (Table 1). Member states may create subcategories of landfills for other non-hazardous wastes. Member states shall also determine the leaching test methods and corresponding leaching limit values (L/S-ratio 2 or/and 10 l/kg), which should be used. The proposed leaching limit values at L/S-ratio 10 l/kg are presented in Table 1. At the moment, this work is in process, and the changes to the Finnish national landfill legislation (861/1997) will not be announced until July 2005.

The limit values for the total content of a few organic substances are set only for inert wastes (Table 1). Pre-treated hazardous wastes, acceptable at landfills for non-hazardous waste, must meet the limit values for total organic carbon (TOC) content in the solid waste and the limit values for inorganic compounds leached from waste. For hazardous waste landfill, additional criteria for the latter consist of the determination of either loss on ignition (LOI) or TOC in the solid waste (Official Journal of the European Communities 2003).

Table 1. The EU criteria for acceptance of waste at landfills. The proposed leaching limit values of substances calculated at a liquid to solid ratio 10 l/kg and the limit values of certain parameters in solid waste.

Component	Inert waste landfill	Non-hazardous waste landfill, waste with low organic content and non-reactive hazardous waste	Hazardous waste landfill
LEACHED amount	**mg/kg dry weight**		
Arsenic	0.5	2.0	25
Barium	20	100	300
Cadmium	0.04	1.0	5.0
Chromium total	0.5	10	70
Copper	2.0	50	100
Mercury	0.01	0.2	2.0
Molybdenum	0.5	10	30
Nickel	0.4	10	40
Lead	0.5	10	50
Antimony	0.06	0.7	5.0
Selenium	0.1	0.5	7.0
Zinc	4.0	50	200
Chloride	800	15000	25000
Fluoride	10	150	500
Sulphate	1000	20000	50000
Phenol index	1.0	-	-
Dissolved organic carbon (DOC)	500	800	1000
Total dissolved solid (TDS)	4000	60000	100000
SOLID waste	**mg/kg dry weight**		
Total organic carbon (TOC)	30000	50000	60000
Loss on ignition (LOI)		-	100000
Sum of BTEX compounds	6.0	-	-
Polychlorinated biphenyls (PCBs 7 congeners)	1.0	-	-
Mineral oil (C10 to C40)	500	-	-
pH	-	minimum 6	-
Acid neutralizing capacity (ANC)	-	to be evaluated	to be evaluated

– limit value not set, BTEX= sum of benzene, toluene, ethylbenzene and xylenes

1.2.2 Methods for environmental hazard assessment

1.2.2.1 Leaching tests

The general purpose of leaching tests is to determine the short-term and/or long-term leaching of contaminants from wastes in different areas – e.g. waste treatment and disposal, soil clean-up and the reuse of secondary materials in construction (Van der Sloot *et al.* 1997). The modelling of release rates is used to predict the long-term release of contaminants in a given scenario relating to the utilization or disposal of materials (Van der Sloot 1996 and 2002, Van der Sloot *et al.* 2001). The short-term and/or long-term leaching behaviour are determined by the column, i.e. percolation test, or the multi-stage batch leaching tests (Table 2). The influence of various factors, e.g. pH, redox potential, ionic strength on leaching of contaminants, is determined by pH static batch leaching tests or other special leaching test methods (Fällman and Aurell 1996, Fällman 1997, Van der Sloot *et al.* 2001, Van der Sloot 2002).

The physical form of waste materials can be either granular or monolithic. The leaching test methods are divided into procedures for which equilibrium or equilibrium-like conditions are assumed and test procedures performed under non-equilibrium conditions, known as dynamic leaching tests (Van der Sloot 1997, Kylefors *et al.* 2003). Dynamic tests, or tank tests (e.g. a Dutch method NEN 7345), are methods used for monolithic materials or stabilized granular materials. In these methods no equilibrium is reached and the rate of the release is measured as the diffusion of contaminants from a monolithic material measured in mg/m^2s. The steady state between the solid and liquid phases needs to be attained within the contact time of the test. The column test (i.e. percolation test) and batch leaching tests, either single or multiple, are examples of the most commonly used equilibrium-like test methods for granular wastes and sludge (Table 2). The equilibrium-like leaching tests can become dynamic, when the particle size of the sample is large and the contact time is too short in batch extraction, and also when flow rates are high in column tests (Van der Sloot *et al.* 1997).

In the Technical Committees of the European Standardization Organisation Committee (CEN/TC 292), the leaching tests for granular and monolithic wastes are being standardized or are under preparation (Table 2). For basic characterization of wastes, preliminary standards for determining pH related leaching are the ANC test and the pH static test (prCEN/TS 14429), which are under approval in 2005 in working group WG6 of CEN/TC 292. Leaching tests have been developed for inorganic wastes in CEN/TC 292 (CEN/TC 292–Work programme 2004). No standardized or validated methods are available for wastes containing organic compounds. The leaching methods for inorganic compounds, described in Table 2, have been used to develop leaching tests for organic compounds. Special test conditions are needed to prevent volatilization, adsorption and degradation of organic compounds during testing. Zero-headspace vessels will be required to avoid losses of volatile compounds during testing and during the separation procedure of the eluates (Van der Sloot *et al.* 1997). The test equipment materials and filters, and test conditions such as contact time, extraction liquid, and an eluate separation technique have been studied in order to use batch and column leaching methods meant for inorganic compounds for e.g. polyaromatic hydrocarbons (PAHs), volatile BTEX compounds, oil and chlorophenols in soils (Rood *et al.* 1994, Wahlström *et al.* 1994, Hirner et al. 1998, Comans 2001, Wahlström *et al.* 2002, Yong-Jin and Masahiro 2003).

Table 2. Different leaching test methods for granular wastes.

Type of test	Principle of the method	Usage of the method	Examples of test procedures and state of CEN/TC 292 standardization
Column leaching tests (also called as percolation test)	Up-flow (or down-flow) percolation test in which waste material is packed into a column and demineralized water is pumped through a waste material. Eluates are collected in fractions at different L/S-ratios: 0.1-10 l/kg. Particle size is normally < 4 mm and a contact time > 21 days	Used for regulatory purposes to simulate leaching of inorganic substances in short and medium term (<50 years) European standard (TS 14405) is used for basic characterization of wastes to be deposited in a landfill (2003/33/EC)	Up-flow tests: NEN 7343 (Netherlands, 1995) TS 14405 (technical standard of CEN/TC 292) Down-flow test : under development in CEN/TC 292
Batch leaching tests	Procedure in which waste is brought into contact with a leachant (demineralized water or acetic acid in the TCLP method) in a closed or open vessel and agitated for a period ranging from hours to several days. Method can be one-stage (24 h), or multi-stage (2 to 5 days) in which the procedure is repeated with fresh leachant each time. L/S ratio can vary from 2 to 20 l/kg. Particle size is normally between < 4 or < 10 mm.	European standard method is used as a compliance test for granular wastes and sludge in waste landfill acceptance criteria (2003/33/EC). The multi-stage method (e.g. NEN 7349) is considered to represent leaching over a very long time scale or an immediate high dilution	NEN 7349 (Netherlands, 1995) EN 12457-1-4 (European standard of CEN/TC 292) TCLP 1311 (USA EPA, 1990) NT ENVIR 005 (Nordtest method, 1998) NT ENVIR 002 (Nordtest method, 1995)
Availability tests	Single or multi-stage batch leaching tests carried out at high L/S-ratios (50 to 200 l/kg) with small particle size (<100-200 μm) under pH-static conditions at one or two pH-values (e.g. pH 4 and 7 in method NEN 7341)	Method to indicate what quantity of a particular component may leach out from a material under extreme conditions (very long time, dispersed material, full oxidation and loss of acid neutralizing capacity (ANC). ANC specifies the degree how a material may offer resistance to acid attack.	NEN 7341 (Netherlands, 1992) Acid and base neutralization capacity test (ANC) (under development in CEN/TC 292) NT ENVIR 003 (Nordtest method, 1995)
pH static tests	Single batch leaching test in which pH is maintained constant through automated addition of acid or base. L/S-ratio in CEN/TC 292 draft method is 10 l/kg and the leachant is demineralized water. Contact is 48 h at each pH-value (between pH range 4–12)	Used to describe how leaching of inorganic substances is dependent on pH and often used for input to hydro–geochemical models. Method can be used for basic characterization of wastes in waste landfill acceptance criteria (2003/33/EC)	prCEN/TS 14429 (standard draft under approval in CEN/TC 292) prEN 14997 leaching behaviour tests - Influence of pH on leaching with continuous pH-control (standard draft under approval in CEN/TC 292)

The pH dependence leaching test is needed in the basic characterization of municipal solid waste incineration (MSWI) residues in order to understand how the pH (pH-range 2–12) affected on the leachability of metals and to compare the leaching behaviour within one and the same type of MSWI residue (Van der Sloot *et al.* 2001).

The availability test is used to determine the availability of substances that may occur over a long or very long period of time, over hundreds of years, from a test material under extreme conditions. The acid neutralizing capacity (ANC), which describes the resistance of a material to acid attack, can be calculated from the test data (method NEN 7341) using the following equation (1):

$$ANC = [V_1 + V_2] / [m_1 [1 - (g_{105} + g_{40})] \, c(HNO_3)] \qquad (1)$$

where,

ANC	Acid neutralizing capacity, mol/kg
V_1	added volume of nitric acid in the first stage of the test, ml
V_2	added volume of nitric acid in the second stage of the test, ml
m_1	quantity of material to be extracted, g
g_{105}	humidity content of material determined at 105 ^{o}C, g/g
g_{40}	humidity content of material determined at 40 ^{o}C, g/g
$c(HNO_3)$	molarity of the added nitric acid, mol/l

Leaching test results are commonly presented in cumulative leached amounts of the substances as a function of the liquid/solid-ratio (L/S) of the leaching test performed. The rate of release can be determined from the leached amount of studied substance, when both serial and single batch leaching tests and a percolation test are performed on the same waste material, with the results being presented as a function of the liquid-solid ratio. When the release of the substance is compared to the total available amount of substance in the waste material, the shape of the curve can be used to describe the release profile (Van der Sloot *et al.* 1997). Figure 1 illustrates the general types of release pattern, as presented by Van der Sloot *et al.* (1997): " *Typical releases are described as: wash out (**A**), intermediate release (**B**) and slow release (**C**). A decrease in availability due to slow mineral formation or sorption reactions is described by curve **D**, an increase in release due to changes in pH or redox potential with time by curve **E** and a decrease in release due to changes in chemical conditions by curve **F**. "*
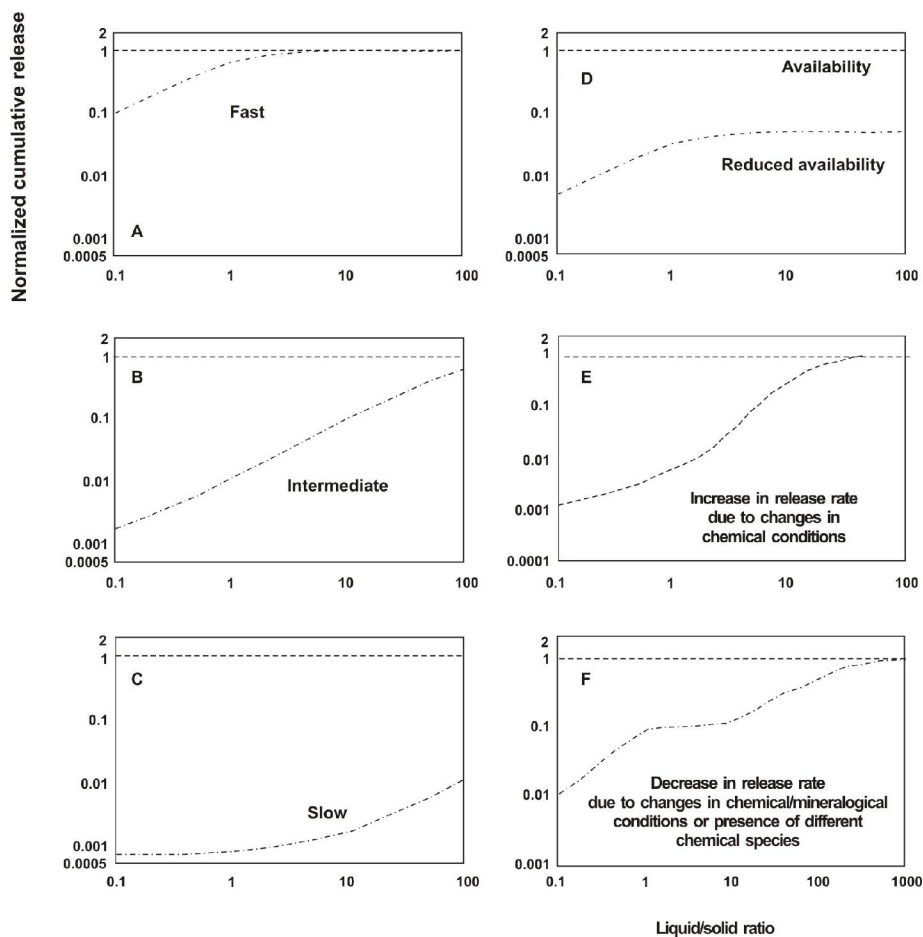
Figure 1. Examples of leaching patterns for cumulative releases shown as a function of L/S. Reprinted from Van der Sloot *et al.* (1997, p. 156) with copyright (2005) permission from Elsevier.

The overall composition of wastes has to be identified before identifying which substances are determined from leaching test eluates. In addition to harmful compounds, other substances that have an effect on leaching also need to be evaluated. Examples of such substances are chloride, sulphate and dissolved organic carbon (DOC). Chloride ions, sulphate and organic matter can form complexes with heavy metals, e.g. cadmium, and increase the leaching of metals from waste materials (Van der Sloot *et al.* 1997, Van der Sloot *et al.* 2001). In addition, the physical properties of waste matrices, e.g. porosity, structure and interactions between contaminants and waste constituents affect the movement of metals or other substances into the aquatic ecosystems (McLean and Bledsoe 1992, Van der Sloot *et al.* 1997). The interactions of contaminants with clay or with organic matter have an effect on the adsorption or complexation of contaminants, i.e. metals or polyaromatic hydrocarbons (PAHs) in soils (McLean and Bledsoe 1992, Hirner *et al.* 1998, Yong-Jin and Masahiro 2003). When studying the leaching properties of organic compounds, the following chemical properties are dominant: water solubility, vapour pressure, volatilization, degradation, biodegradation, and half-life (Wahlström *et al.* 1994).

1.2.2.2 Ecotoxicity tests

Ecotoxicity tests are designed to determine whether chemicals are present in toxic amounts in water ecosystems, sediments or soils (Chapman 1995). Determination of certain set of pollutants in complex mixtures of unknown composition, which is a characteristic of many wastes, does not allow a relevant estimation of the overall environmental hazard of wastes. The protocols used in regulatory decisions on the cleanup of contaminated soils or the hazard classification of solid wastes rely on total chemical concentrations, where the aim is to extract all of the pollutant from the sample. In addition, chemical analyses often focus on the determination of the known key hazardous substances in solid materials. The measurement of the total concentrations of substances in solid wastes or soils is useful for determining the level of contamination and for measuring any net change in concentrations over time. However, the bioavailability and impact of chemicals on organisms is related to leaching, exposure, and uptake by organisms, and their effects on critical biological functions, rather than on total concentrations of contaminants (Lanno *et al.* 2004). In wastes or in contaminated soils, the bioavailability is dependent on various parameters, e.g. water solubility, waterlogging, pH, redox conditions, microbial activity, chemical interactions between chemical species, and the production of metabolites (Ruokolainen *et al.* 2000, Turpeinen 2002). Several studies have shown that the toxicity of metal compounds and arsenic in general is highly dependent on their state of oxidation (Pantsar-Kallio and Manninen 1997, Villaescusa *et al.* 1997, Ruokolainen *et al.* 2000, Turpeinen 2002). These factors cannot be evaluated with total chemical concentrations of individual substances.

Ecotoxicity tests can be applied to wastes to identify their hazardous properties for classification purposes (i.e. hazardous/non-hazardous waste or waste acceptance to different landfills). Classification of waste materials with ecotoxicity tests should be independent of an exposure scenario. For classification purposes, more important is to use a standardized procedure to obtain comparable test results. Ecotoxicity tests should be used as complementary tools for hazard classification of wastes when there is not enough background information about the composition of wastes to perform qualitative or quantitative chemical analyses. Ecotoxicity tests can also be applied to wastes or contaminated soils to assess the risk related to a site-specific exposure scenario (e.g. waste deposit in stockpiles or landfills, soil clean-up, re-use of waste materials) in which the transfer of contaminants via the food chain and to surface and ground water is taken into account. Both the hazard classification and risk assessment approach should focus on testing toxicity with both terrestrial and aquatic organisms (Ferrari *et al.* 1999, Juvonen *et al.* 2000, Schultz *et al.* 2004).

Three aspects must be considered when using ecotoxicity tests: (1) the organism exposed (2) the test medium studied (waste, soil, sediment, water) and (3) the measured characteristics i.e. death, growth, reproduction, enzyme activity and mobility or other activities that are used as endpoints. Depending on the test exposure time and measured endpoint, ecotoxicity tests can be acute, sub-chronic or chronic (Calow 1993). In general, the test results of aquatic or direct solid-phase assays are determined, e.g. as EC50 or LC50 values, which means a concentration of the matrix studied that causes a 50 % reduction of the measured effect on a test organism. Nowadays, in many studies the toxicity test results are transformed into Toxicity Units (TU) (Clément *et al.* 1996 and 1997, Persoone *et al.* 2000). L(E)C50 values of the waste samples or their eluates are expressed as volume percentages. These values are transformed into Toxic Units (TU) using equation (2):

$$TU = [1/EC50] \times 100 \qquad \text{or} \qquad TU = [1/LC50] \, 100 \qquad\qquad (2)$$

where,

TU   Toxic Unit
EC50   Median effective concentration, dilution-%
LC50   Median lethal concentration, dilution-%

The toxicity of solid samples is tested from aqueous extracts or directly from the solid material (Fig. 2). A lack of accepted or standardized extraction methods for waste or soil samples has led to the observation that results of different toxicity studies are not always comparable (Peijnenburg *et al.* 2002). At present, international Standardization Organizations (ISO/TC 190, CEN/TC 292) are developing extraction or leaching test methods also for aquatic ecotoxicological tests of solid samples. The proposed method (prEN 14735) in CEN/TC 292 for preparation of waste samples for ecotoxicity tests is a water batch extraction using an L/S-ratio of 10:1. The biological testing methods for assessing the ecotoxicity of contaminated soils and soil materials are under development in the Standardization Committee of ISO/190 Soil Quality.
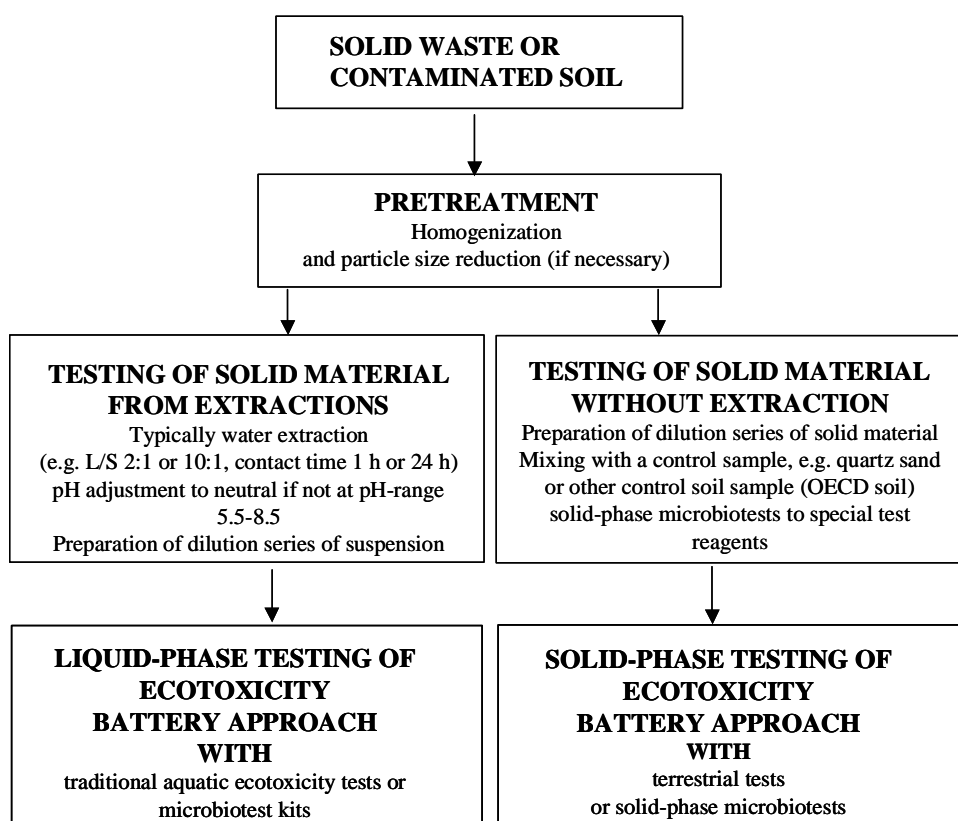

Figure 2. Principal methodology for liquid-phase or solid-phase testing of toxicity of solid waste materials.

1.2.3 Properties affecting leaching

1.2.3.1 Effects of pH

The pH value is one of the most important controlling factors in the leaching of inorganic waste materials (Van der Sloot *et al.* 1997 and 2001, Viguri *et al.* 2000). In many batch leaching tests, the pH is not controlled and is therefore dictated by the pH of the waste material (Viguri *et al.* 2000). At low or moderate L/S values (2 to 20 l/kg), the pH of the eluate is controlled by the solid phase, and the composition of the eluate is independent of the composition of the leachant. In pH-dependence tests, e.g. the availability test, ANC test or pH-static test, the leaching behaviour of the contaminant is studied in a controlled pH (Fällman and Aurell 1996, Fällman 1997, Van der Sloot 2002, Hage and Mulder 2004).

With an increasing pH (pH-range 7–10), the leaching of cationic metals from soil or mineral waste materials is decreased. In the pH-static leaching test performed on brick industry residues, leaching of zinc increased at acidic pH values and decreased at a pH range of 7–12 (Hage and Mulder 2004). In municipal solid waste incineration (MSWI) bottom ash and fly ash, the leachability of zinc increased, when the pH was decreased to below 7.5 (Van der Sloot 2002). The pH together with increased chloride concentration strongly affects the leachability of cadmium from fly ash or bottom ash. Cadmium forms soluble complexes with chloride, increasing the mobility of cadmium from soils or mineral granular wastes (McLean and Bledsoe 1992, Van der Sloot *et al.* 1997). Under acidic conditions (pH less than 5) almost all the cadmium present in MSWI residues was leachable and the amount released reflected the total concentration of cadmium in the material (Van der Sloot *et al.* 2001). At pH 10, the leached amount of cadmium increased from around 0.001 mg/kg to 5 mg/kg when the chloride concentration was increased from 50 mg/kg to 50 000 mg/kg (Van der Sloot *et al.* 2001). The oxyanions, e.g. molybdenum, vanadium and chromium, often show maximum leachability from soils and mineral waste materials between the neutral pH to alkaline pH 10 (McLean and Bledsoe 1992, Van der Sloot *et al.* 1997, Van der Sloot 2002).

Under highly alkaline conditions (pH 12–13), the leachability of hydrophobic organic compounds from soils, e.g. PCBs and PAHs, has been shown to increase. This is partly due to the breakdown of humic material in the soil (Wahlström *et al.* 1994 and 2002). PCBs and PAHs have the tendency to bind to dissolved humic matter (DHM), which is potentially dissolved and leached out at higher pH levels. Hirner *et al.* (1998) also reported a higher leaching ratio for soils spiked with PAHs, PCBs and phenol at pH 10 than at a lower pH level. The leachability of phenanthrene and pyrene from sandy soils of low organic content was found to be independent of the pH values 3, 5, 7, 9 and 11 (Yong-Jin and Masahiro 2003). The difference in results of the above studies may be due to differences in the dissolved organic matter content of the studied soil material. The sorption of chlorophenols onto the soil is dependent on the pH of the soil. The water solubility of pentachlorophenol at pH 8 was 420-440 times higher than at pH 5 (Wahlström *et al.* 2002). The pH-static test at pH 8 or pH 10 was considered to be suitable for studying the leaching behaviour of chlorophenols from soil samples (Wahlström *et al.* 2002).

1.2.3.2 Liquid to solid ratio

Liquid to solid ratios (L/S) vary in batch leaching tests between 2–100 l/kg (see Table 2). In practice, the L/S ratio of 2 l/kg is considered to be the minimum ratio to obtain a sufficient amount of liquid for analysis (Van der Sloot *et al.* 1997). An increased L/S ratio improves the possibilities for potentially soluble material to dissolve out of the waste material (Kylefors *et al.* 2003). The lower the L/S ratio, the better it simulates the leaching conditions in the field situation (Van der Sloot *et al.* 1997). If the L/S ratio is increased, the contact time needed to

achieve equilibrium conditions may increase, or it may affect the chemical reaction between the extraction liquid and the waste material (Fällman and Aurell 1996).

An increase in the L/S ratio from 100 to 200 decreased the leaching of iron and cadmium from MSWI bottom ash while the leaching of heavy metals, i.e. copper, chromium and lead increased (Fällman 1997). The higher dilution ratio might have introduced other reactions between the eluate and air. Iron could have been oxidized to a higher extent at the higher L/S ratio. Another objection to the increase in the L/S ratio was that the risk of reaching the detection limits for the analysis methods for certain elements was increased and the information on the amount of leached substances would then have been lost (Fällman 1997). As an example of organic compounds, different liquid to solid ratios (5:1–100:1) had no effect on the leaching of PAHs from sandy soils of a granular shape with a low porosity and a low organic content (Yong-Jin and Masahiro 2003).

1.2.3.3 Contact time, mixing and particle size

The contact time is dependent on the leaching method to be performed. In batch leaching tests, the contact time can vary from a few hours to a few days (Table 2). It is important that the contact time between water and the waste material is sufficient to achieve equilibrium/steady-state conditions during the batch leaching test (Kylefors *et al.* 2003). The mixing in batch leaching tests is commonly done by end-over-end rotation or by mixing with a magnetic stirrer (e.g. EN–12457, NEN 7341). In the percolation test, mixing is done to simulate percolation of rainfall by pumping the extraction liquid either down-flow or up-flow through a granular material packed into a column (e.g. Dutch method NEN 7343). In this percolation test, the equilibrium conditions are controlled by the flow rate. If the flow rates are too high, the column test can be changed to a dynamic, non-equilibrium method (Van der Sloot *et al.* 1997).

In general, the smaller the particle size, the larger the surface area of the particles in contact with water, producing higher leachability of the contaminants from the solid material. Usually, the particle size of the waste material is reduced to 4 mm (e.g. EN–12457), and an availability test to less than 0.125 mm (NEN 7341) in order to perform a leaching test. The morphology of the particles and the particle size distribution of the sample have an influence on the mobility and adsorption of metals onto the particles. It has been shown that the total concentrations of heavy metals like Cu, Ni, Pb, Zn and Cr in fly ash from coal combustion and from pulverized coal combustion with lime injection fly ash have increased 5- to 7-fold with a decreasing particle size from 250 μm to under 5 μm (Davison *et al.* 1974, Lecuyer *et al.* 1996), thus probably increasing the leaching of metals from smaller particles.

The contact time and particle size are dependent on each other. The contact time needs to be increased if the particle size is higher than in the standard leaching test procedure (Janusa *et al.* 1998, Kylefors *et al.* 2003). Fällman (1997) has studied the optimal contact time to modify the standard method of the availability test (method NEN 7341 in Table 2) to study the leaching of substances from bottom ash. The most important parameters for the availability test are the contact time, particle size and the L/S ratio. A contact time of 3 hours in the standard method of this test was too short to achieve equilibrium–like conditions in the second step, and so an increase of the contact time to 18 hours was proposed in the second step together with particle size fraction of 95 % less than 0.125 mm and L/S of 100 in both two steps (Fällman 1997).

A contact time of 48 h increased the leaching of phenanthrene and pyrene from spiked sandy soils together with an increase in temperature (22-55 ^{0}C) and an increase in the content of dissolved humic matter (DHM) added to the leachate (Yong-Jin and Masahiro 2003). No

significant differences were found in the amount of chlorophenols and oil leached out from contaminated soils in batch extraction tests of between 2–7 days (one- or two-stage methods of EN-12457 and pH-static test). A contact time of one to two days was sufficient for chlorophenols (Wahlström *et al.* 1994). Photodegradation of chlorophenols was avoided by using brown glass vessels and the biodegradation of PAH compounds was prevented by adding copper sulphate to the leachate (Wahlström *et al.* 1994 and Comans 2001).

1.2.3.4 Extraction liquid

Water is the most commonly used extraction liquid for solid samples because it is the main carrier of contaminants in field conditions (Van der Sloot e*t al.* 1997, Maxam *et al.* 2000). Some artificial salt solutions or seawater has been used when the evaluation of leaching has been related to the disposal or utilization of test material in the marine environment. One example is the wood preservative (e.g. CCA) treated materials used in seawater constructions (Lebow *et al.* 1999, Hingston *et al.* 2001). If more aggressive extraction liquids are used, the leachant together with higher L/S values and pH affects the leaching conditions (Van der Sloot *et al.* 1997). In the TCLP leaching test method, 0.1 mol/*l* acetic acid water solution is used for classifying wastes as either hazardous or non-hazardous (EPA 1990). However, this method has been criticized, because acetic acid interferes with chemical and ecotoxicological analyses (Jenner and Janssen-Mommen 1989, Peterson *et al.* 1990, Goergen *et al.* 1992). The TCLP method has been developed for cationic metals and can cause the reduction of chromium (VI) which leads to the false measurement of the leachability of Cr(VI). Mclean and Bledsoe (1992) also criticized the use of TCLP because acetic acid does not occur in nature and therefore it is not an appropriate extraction liquid for soil samples. However, during anaerobic degradation of organic matter, in the acetogenesis phase, volatile fatty acids and ethanol are produced and transformed into acetate, carbon dioxide and hydrogen by acidogeneous bacteria (Van der Sloot *et al.* 1997).

The evaluation of the leaching of hydrophobic organic compounds (e.g. PAHs and PCBs) from solid material should be based on aqueous acidic solutions similar to those occurring in nature (Hirner *et al.* 1998). Naturally acidic lakes and humic waters in mires are examples of naturally acidic solutions in which the original pH is <5.3 (Forsius *et al.* 1990, Tahvanainen 2003). Most of the PAHs and the PCBs associate with dissolved humic matter (DHM) in natural eluates, and the mobility of these substances is underestimated when using only a batch leaching test with distilled water (Hirner *et al.* 1998, Yong-Jin and Masahiro 2003). For instance, the recovery efficiency of PAHs from compost water extraction was 7 % while from distilled water extraction it was less than 1 % (Hirner *et al.* 1998). Because the addition of natural DHM to the extraction liquid can differ depending on the origin of the organic matter and the separation technique, an alternative reagent with an effect similar to that of DHM should be used as an extraction liquid for hydrophobic organic compounds (i.e. PAHs) from soils (Yong-Jin and Masahiro 2003). It has been suggested that the leaching tests performed for hydrophobic compounds should incorporate the solubilizing effects of amphiphilic substances (Hirner *et al.* 1998). With reference to this, sodium dodecyl sulphate (SDS) at a concentration of 1.9 g/l has proven an effective leachant. One technique that has been proposed to study leaching of PAHs from solid waste materials is an alkaline leachant (pH 12) into which DHM is added in the form of Aldrich humic acid at a concentration of 1000 mg/l in an availability test (L/S 100 l/kg, contact time 48 h) (Comans 2001). This availability test also seemed to be a promising tool for rough estimations of the leaching behaviour of PCBs from contaminated soils (Wahlström *et al.* 2002).

1.2.3.5 Separation of eluates

The eluates of leaching tests are usually separated from waste material by vacuum or pressure filtration. In general, a membrane filter with a pore size of 0.45 μm is used for separation. It is necessary to use glass fiber filters to avoid the absorption of hydrophobic and low soluble organic compounds into the filter matrix (Van der Sloot *et al.* 1997). In addition, centrifugation has been used for oil-hydrocarbons instead of filtering to separate the eluate from the solid phase (Wahlström *et al.* 1994, Juvonen *et al.* 2000). Wahlström *et al.* (1994) used Teflon column and glass vessels in the leaching experiments on PAHs. Glass vessels were better than Teflon vessels for studying the leaching properties of PCBs (Rood *et al.* 1994). The filter material had a great impact on concentration losses during separation. The best filter material for PCBs was regenerated cellulose, and glass fiber filters could be used for pre-filtering. Glassware or stainless steel should be used to minimize the sorption of chlorophenol compounds onto the walls of test vessels in batch leaching tests (Wahlström *et al.* 2002).

1.2.4 Ecotoxicity testing of waste materials
1.2.4.1 Ecotoxicological response to toxicants in an aquatic environment

In principle, ecotoxicity tests may be carried out at any level in the biological hierarchy, but there is no universal test that can detect all toxicants or assess a wide range of ecotoxicological effects from complex waste mixtures. This has led to the concept of using several bioassays for assessing the environmental impacts of leachates or waste eluates with a battery-of-tests approach (e.g. Clément *et al.* 1996 and 1997, Ferrari *et al.* 1999).

The sensitivity of aquatic toxicity assays for different substances varies (Table 3). When selecting appropriate bioassays, it is important to know their sensitivities and relevance to the purpose they are used for (Bitton *et al.* 1994, Chapman 1995). For example, the metal-specific microbial enzyme assay, MetPLATE™, is not useful for determining the toxicity of waste eluates containing mainly organic compounds.

Table 3. Aquatic toxicity of some inorganic and organic compounds to different test organisms and submitochondrial particles. Toxicity is expressed as LC50 or EC50 values in mg/l.

Test organism and exposure time / Compound	Bacteria *Vibrio fischeri* (15 min) [1 and 2]	Bacteria *Pseudomonas putida* (48 h) [3]	Water flea *Daphnia magna* (48 h) [1,3,4]	Green algae *Pseudokirchneriella subcapitata* (72 h) [3,4,5]	Rainbow trout *Oncorhynchus mykiss* (96 h) [1,3,4]	Duckweed *Lemna minor* (96 h) [6]	Onion *Allium cepa* (2-3 d) [7]	Submitochondrial particles from beef heart mitochondria RET or ETR-assay (10 min) [2]	Bacterial mutant *Esherichia coli* MetPLATE™ (4-5 h) [1]
As(III) or As (VI)	2810	-	7.4[3]	-	-	-	4.18	44.5	-
Cd	19-220	-	0.041-1.9	0.06	0.15-2.5	0.2	5.68	0.52	0.029
Cr(III) or Cr(VI)	13	-	0.10-1.8	0.3	11	35	-	33	6.9
Cu	0.076-3.8	0.03	0.02-0.093	0.1	0.25	1.1	0.3	0.3	0.22
Pb	1.7-30	-	3.6	1.0	8.0	8	-	2	10
Hg	0.029-0.05	-	0.0052-0.21	0.02	0.033-0.2	-	0.90	0.13	0.038
Ni	251[2]	-	7.6	0.012[3]	36	0.45	2.2	2.2	0.97
Zn	33[2]	-	0.54-5.1	0.20	0.55-2.2	10	-	1.7	0.11
Formaldehyde	8.5	14	2[3]	2.5	24.1	-	-	21 (ETR)	>1000
Methanol	320000[2]	6600	>10000[3]	8000[3]	10000-30000[3]	-	-	41700	-
Toluene	18	29	4.3-60[4]	105[4]	24-1340[4]	-	-	133 (ETR)	-
Pentachlorophenol	0.9-1.1	-	0.1-0.48	-	0.24	0.09[3]	-	0.081	>500
Xylenes	16[2]	-	1.3-1000[4]	55[4]	11-37[4]	-	74	19.6	-

Bitton et al. 1994[1], Read et al. 1998[2], Nikunen et al. 2000[3], Betton 1994[4], Persoone 1998[5], Wuncheng 1991[6], Fiskesjö 1997[7]

RET= reverse electron transport assay, ETR = electron transport assay

1.2.4.2 Ecotoxicity testing of waste eluates

Aquatic toxicity assays can be divided into test methods using (1) micro-organisms and sub-cellular components (e.g. enzymes), (2) plants and algae, and (3) invertebrates and fish (Calow 1993). Fish and Daphnids have been the most used aquatic toxicity test organisms in the past. Nowadays, the requirement for multitrophic and cost-effective toxicity testing has driven the development of biotests from macrobiotests to the use of microbiotests. These methods have been developed in order to make biotesting easier (Ahtiainen 2003). There are several commercial microbial test methods to assess the toxicity of water, wastewater and soil, sediment or waste extracts, of which the Microtox test (*Vibrio fischeri* luminescence inhibition assay) is the most well known (Bitton *et al.* 1994, Persoone *et al.* 2000, Ahtiainen 2003).

In several studies the toxicity of landfill leachates has been characterized either by microbes, algae and/or crustaceans (Atwater *et al*. 1983, Devare and Bahadir 1994, Clément *et al.* 1996 and 1997). There are still rather few studies on the hazard classification of solid wastes in which a combination of leaching and ecotoxicity tests has been used. The most common ecotoxicity assays performed on waste eluates have been the luminescent bacteria, green algae and water flea tests (Table 4). Currently, most of the toxicity measurements of waste or soil eluates are still based on a single-test approach, and only a few of them have used direct toxicity measurements of solid matter (Table 4). In all the studies referred to in Table 4, the importance of combined chemical and ecotoxicological classification of waste eluates was stressed, since these give a more direct and integrated estimate of the environmental hazard of waste materials.

Table 4. Examples of studies in which combined leaching and ecotoxicity tests have been used for hazard classification of solid wastes.

WASTE MATERIAL	Liquid-phase ecotoxicity tests					Solid-phase tests	Reference
	Bacterial luminescence ($V.fischeri$)	Water flea immobilization ($D.magna$)	Algae growth ($P.subcapitata$)	Plant test	Microbiotests or enzyme assays	Plant tests	
Extraction method	**TCLP method (EPA 1990) or a modification of EPA method (L/S 20, leachant: acetic acid solution)**						
Tannery wastes	x	x					Fernandez-Sempere *et al.* 1997, Font *et al.* 1998
Residues from waste battery recycling process	x						Coya *et al.* 2000
Municipal solid waste (MSW) and industrial waste incineration bottom ash and fly ash	x						Ibanez *et al.* 2000
Foundry sludge from iron industry	x						Ruiz *et al.* 2000
Adhesive solvent wastes from footwear industry	x	x					Sabater and Martinez 2001
Metal industry wastes	x						Ruiz *et al.* 2002 Seco *et al.* 2003
Extraction method	**European batch leaching test EN-12457-2 or EN-12457-4 (L/S 10, leachant: demineralized water)**						
Municipal solid waste incineration (MSWI) bottom ash	x	$D.magna$ and *Ceriodaphnia dubia* survival and reproduction tests (21 and 7 days)	x	Plant germination and biomass weight oats (*Avena sativa*), Chinese cabbage (*Brassica campestris*), lettuce (*Lactuca sativa*)	Oxidant enzyme activity assays of three plants (superoxide dismutase, catalase, peroxidase, glutathione reductase)	plant germination, fresh weight and oxidant enzyme activity assays	Ferrari *et al.* 1999
Residues from mechanical-biological treatment of MSW	x	x	x	Root growth of cress (*Lepidium sativum*)	Commercial microbial algal and daphnia tests (AlgalTox, and DaphTox)		Latif and Zach 2000
MSWI bottom ash from various incineration plants	x	x	x (incubation 5 days)	Lettuce seed germination			Lapa *et al.* 2002a
Soils, MSW wastes and MSWI bottom ash treated by plasma pyrolysis/ vitrification (PP/V)	x		x	Lettuce seed germination			Lapa *et al.* 2002b

17

The sensitivity of the ecotoxicity tests varied depending on the test organism and the chemical composition of the waste material under study. The algal growth inhibition test proved to be the most sensitive test over the luminescent bacteria and the water flea tests in detecting the toxicity of municipal solid waste incineration bottom ash (Ferrari *et al.* 1999, Lapa *et al.* 2002a). Ceriodaphnids (*C.dubia*) were more sensitive than the daphnids (*D.magna*) of the microcrustacean chronic tests performed on the MSWIBA (Ferrari *et al*. 1999). The water flea (*D.magna*) test was more sensitive than the algal test in detecting the toxicity of the eluates of mechanical-biologically treated municipal solid waste, probably due to the high ammonia content of these eluates (Latif and Zach 2000). The lettuce seed germination tests showed a non-toxic response to the MSWIBA eluates while these eluates were clearly toxic to the algae, luminescent bacteria and water fleas (Lapa *et al.* 2002a). The phytotoxicity test results of one MSWIBA proved that plant tests (oats, Chinese cabbage and lettuce) should be applied directly to the solid material rather than to water eluates (Ferrari *et al*. 1999). In contrast to seed germination in chromated copper arsenate (CCA) contaminated soil, the soil water eluates clearly inhibited plant growth of duckweed and onion (Schultz *et al*. 2004).

The luminescent bacteria test has proven to be more sensitive to organic than to inorganic compounds (see Table 3). This might explain why it has also proved a feasible screening method for measuring the acute toxicity of oil-contaminated soil or waste samples either from the soil extracts or directly from the soil suspensions (Dorn *et al*. 1998, Mearns *et al*. 1998, Juvonen *et al*. 2000, Plaza *et al*. 2005). The RET test has been shown to be as sensitive as luminescent bacteria in monitoring the toxicity reduction of water eluates of oily waste during the composting process (Juvonen *et al.* 2000). Certain properties of organic compounds (e.g. petroleum products), such as the anticipated low water solubility and volatilization, might have limited the use of aquatic ecotoxicity assays for petroleum products. The losses of volatile compounds by evaporation and adsorption of petroleum hydrocarbons on the test vessels during ecotoxicity assays might decrease the toxicity, although false conclusions of the toxic effects of petroleum products can be made (Betton *et al*. 1994, Mearns *et al.* 1998).

1.2.4.3 Ecotoxicity testing of solid wastes

Solid-phase direct toxicity tests mean that the measurement of toxicity is performed directly from the solid material without any extraction of the soil or waste sample to an aquatic medium. The solid-phase approach has not been applied to any great extent in the hazard classification purposes of wastes. Plant tests (oats, Chinese cabbage, and lettuce) have been the most common of the terrestrial ecotoxicity tests on wastes (Ferrari *et al*. 1999). With reference to this, plant oxidant enzyme assays were shown to be more sensitive endpoint than plant growth and seed germination. In the European Standardization Committee (CEN/TC 292), a standard proposal has been made for hazard classification of waste that rely on both aquatic and terrestrial tests.

The standardized terrestrial soil animal tests, e.g. the mortality and reproduction of earthworms (*Eisenia fetida*, ISO 11268-1 and 2, OECD 207) and enchytraeid worms (*Enchytraeus albidus,* ISO 16837, OECD 220) have been used successfully in monitoring the remediation actions or screening of oil-contaminated soils (Salanitro *et al*. 1997, Dorn *et al*. 1998, Saterback *et al*. 1999 and 2000, Dorn and Salanitro 2000, Juvonen *et al*. 2000). The reproduction test is a chronic test, and therefore more sensitive than the acute mortality test (Saterbak *et al*. 1999, Juvonen *et al*. 2000, Didden and Römbke 2001). Salanitro *et al.* (1997) showed in their bioremediation studies of oil-contaminated soil that the earthworm survival test was more sensitive and less variable than the luminescent bacteria test.

The earthworm survival test and the plant seed germination tests have been proposed for the environmental hazard classification of oil-contaminated soils, because the effects of the soil types and duration of the contamination cannot be predicted using only chemical analyses and the equilibrium-partitioning theory or ecotoxicity tests on soil extracts (Saterbak *et al.* 1999). In addition, the phytotoxicity of soil samples cannot be predicted from the total concentrations of oil hydrocarbons because it varies with the oil and the soil type and within the plant species (Salanitro *et al.* 1997). The ecotoxicity of soil samples have often been studied using artificially contaminated samples, which is why the results are not easily comparable to the bioavailability or the toxicity of the contaminants in aged soils (e.g. Salanitro *et al.* 1997, Dorn *et al.* 1998). For example, weathered oil products have proven less toxic to plants than freshly polluted products in soils (Trapp *et al.* 2001). Therefore, terrestrial ecotoxicity tests should also be applied to field soils and toxicity test results should be integrated in the environmental risk assessment of contaminated sites (Saterbak *et al.* 1999 and 2000).

In order to make biotesting easier and more cost-effective, more rapid methods than the terrestrial ecotoxicity tests, for instance, are needed for soil remediation and waste hazard classification purposes. In this regard, the direct contact method based on the luminescent bacteria test has been used for contaminated soils, sludge and sediments (Brouwer *et al.* 1990, Dutka *et al.* 1996, Lappalainen *et al.* 1999, Lappalainen 2001). Juvonen *et al.* (2000) concluded that the luminescent bacteria test, especially the new FLASH method for soil suspensions, was the only sufficiently sensitive screening test for monitoring the entire composting process of oily waste from a former oil refinery landfill (Juvonen *et al.* 2000). The FLASH method was also proposed for the study of the particle-bound toxicity of solid residues and soils contaminated by solid waste (semicoke) leachates from the oil shale industry (Põllumaa 2004).

1.2.5 Waste classification based on ecotoxicity

At the moment, there is no generally accepted toxicity classification system in the EU that could be used for determining the ecotoxicity of wastes. New test procedures and limit values to evaluate the ecotoxic property (H14) of wastes have been proposed in France and Spain (Ferrari *et al.* 1999, Lapa *et al.* 2002a, Seco *et al.* 2003). In the French proposal, the limit values for the ecotoxicity classification of waste are set for water fleas (*Daphnia magna*), luminescent bacteria (*Vibrio fischeri*) and algae (*Pseudokirchneriella subcapitata*) tests performed on European batch leaching test (EN-12457-2) eluates. In Spanish legislation, a limit value for the ecotoxic (H14) property of waste is defined as the water flea immobilization (*D.magna*) and the luminescent bacteria (*V.fischeri*) test performed on the eluates of the TCLP method (EPA 1990).

Table 5. Test procedure and limit values for the ecotoxic property (H14) of wastes in France.

Extraction method for solid waste	Ecotoxicity tests and limit values for test results of the eluates			Reference
European standard batch leaching test (EN-12457-2) L/S–ratio 10:1 Extraction medium: Demineralized water	Water flea immobilization test (*Daphnia magna*) Incubation: 48 h	Luminescent bacteria test (*Vibrio fischeri*) Incubation: 30 min	Algal growth inhibition test (*Pseudokirchneriell a subcapitata*) Incubation: 72 h	Lapa *et al.* (2002a)
Limit value EC50 (vol-%) TU= 100/EC50	≤ 10 ≥ 10	≤ 10 ≥ 10	≤ 0.1 (EC 20) ≥ 1000 (EC20)	

The ecotoxicity test methods for the French proposal were selected for three reasons: (1) the test species are representative of different trophic levels, (2) the methods are standardized, and (3) they are used world-wide. The limit values for different ecotoxicity test results differ, probably because the sensitivity of the test species to different pollutants varies, also shown in Table 3. Moreover, the algal test is a short-chronic assay and the EC20 values are used instead of an EC50 value.

One waste toxicity classification system (TCS), first introduced by Persoone (1999), has been used to classify the ecotoxicity of waste incineration ash (Lapa *et al.* 2002a). In the TCS, the determination and quantification of the acute toxicity of the waste eluates is done with a battery of ecotoxicity tests. The proposed system is based on two values: an acute toxicity ranking in toxicity classes, and a weight score for each toxicity class. The aim of this method is to combine the results of a battery of tests into one unique value of toxicity. In the TCS system, the results obtained with each ecotoxicity test are transformed into Toxic Units (TU). The samples are classified into one of the following categories on the basis of the highest number of TU found in one of the ecotoxicity tests (Persoone 1999 cited at Lapa *et al.* 2002a):

"**Class I: no acute toxicity** = If the result of one toxicity test of the battery is TU < 1, the **test score for this result is 1**.

Class II: significant acute toxicity = If the test result of the toxicity test is $1 < TU < 10$, the **test score for the test result is 2**.

Class III: high acute toxicity = If the test result of the toxicity test is $10 < TU < 100$, the **test score is 3**.

Class IV: very high acute toxicity = If the test result of the toxicity test is TU > 100, **the test score is 4.**

A weight score is calculated for each toxicity class, to indicate the quantitative importance (weight) of the toxicity in the class using the formula:

$$\text{Class weight score} = \frac{\sum \text{test score}}{n} \qquad (3)$$

n   number of tests performed

The weight score is expressed in % using the formula

$$\text{Class weight score in \%} = \frac{\text{Class weight score x 100}}{\text{Maximum test score of the battery}} \qquad (4)$$

The closer this weighted score percentage value is to 100 %, the lower the variability of biological responses of the test results of the test battery. "

2 AIMS OF THE PRESENT WORK

The main aim of this thesis was to study the use of combined leaching and ecotoxicity tests for hazard assessment of solid wastes. Currently, decisions on the hazardous properties of solid wastes, e.g. the ecotoxic property (H14), are based on the total concentrations of key hazardous substances. In addition, the proposed criteria for waste acceptance to landfills in the EU do not set any limit values for individual leachable organic compounds. So far, there are no uniform criteria for landfill disposal of excavated oil-contaminated soils. Determination of a limited set of substances in complex mixtures of unknown composition, which is a characteristic of many wastes, does not provide an accurate estimation of the overall environmental hazard of wastes. Therefore, a provisional hazard screening approach for solid wastes using combined chemical and ecotoxicological classification was proposed.

Studies were made of four waste materials from the metal and forest industries containing predominantly inorganic compounds (I–II) and ten waste materials from the furniture and resin industries containing mainly aromatic or aliphatic organic compounds (III–V). Six oil-contaminated soil samples from a former petrol station were studied in order to evaluate their environmental hazard after remediation (IV). Chemical classification was carried out to determine the key hazardous substances in the solid wastes and the leaching properties of these substances were studied. The ecotoxicity of the substances leached out from the solid wastes and soil samples was determined from the eluates of one-stage and/or multi-stage batch leaching tests with a battery of aquatic ecotoxicity tests (I-V). In addition, the ecotoxicity of the solid organic wastes and oil-contaminated soil samples was studied directly from the solid phase with terrestrial tests (III-V).

The main goals of this thesis were:

1. To determine the leaching patterns of key hazardous substances in wastes containing predominantly inorganic substances and to evaluate the need for pH-controlled leaching methods (I).
2. To evaluate the applicability of combined leaching and ecotoxicity tests for the hazard classification of predominantly inorganic wastes (I-II).
3. To evaluate the applicability of solid-phase ecotoxicity assays to complement chemical analyses of complex mixtures of organic contaminants in solid wastes and oil-contaminated soil samples (III–V).
4. To evaluate the suitability of combined leaching and ecotoxicity tests for the hazard classification of volatile organic compounds in solid wastes and of petroleum products in contaminated soil samples (III–V).
5. To propose a provisional hazard screening approach for solid wastes using combined chemical and ecotoxicological classification (I–V).

3 MATERIALS AND METHODS

3.1 Description of the waste materials

Six different types of inorganic and organic waste materials and six oil-contaminated soil samples were used (Table 6). Four predominantly inorganic waste materials (fly ash, jarosite, metal blade waste and de-inking waste) produced in the Finnish metal and forest industry were chosen because of the high amounts produced (I and II). Two of these inorganic wastes contained also partially organic substances: metal-blade waste containing organic-based metal working liquid and de-inking waste organic matter originating from paper recycling. These two wastes were considered in this thesis to belong to a group of inorganic wastes. Eight paint

residues and one varnish residue from the furniture industry and a process waste from the urea-formaldehyde resin production were chosen, because these types of waste materials are produced in significant amounts in various small or medium-sized Finnish industries, but their waste management and hazard classification from the regulatory point of view is unclear (III and V). Six contaminated soil samples were collected from an excavated soil mass from a former petrol station (Taivalkoski, Finland). The soil samples were chosen because the determination of the landfill disposal of excavated soils has been mainly based on the total concentrations of key hazardous substances. The leaching and the ecotoxicity tests were applied for the hazard classification of excavated contaminated soils (IV).

The process data and the safety data sheets of the process chemicals were used as background information on the chemical composition of the wastes. This data was collected from the waste producers. The planning of testing procedures and analyses consisted of determining: (1) the type and origin of waste, (2) the amount of waste, and (3) the concentrations of key hazardous substances in the waste material. The sampling place and the pre-treatment and preservation of the waste materials before laboratory analyses are presented in Table 6.

Table 6. The waste materials used in this study and their European Waste Code (EWC): Origin of the waste materials and the amount produced annually in Finland, sampling, pre-treatment and preservation before laboratory analyses.

Waste	European Waste Code (EWC)	Origin and average amount produced	Sampling place and sampling procedure	Pretreatment and preservation
Papers I and II				
Metal blade waste	Either non-hazardous(**) 120101 or hazardous (*) 120120	Waste resulting from the machining of metal blades which contained metal working fluid Average annual amount of waste produced 200-250 t/a	Composite sample from different metal grinding machines	Mixing 4 °C
Fly ash	Either non-hazardous(**) 100117 or hazardous (*) 110116	Fly ash of a fluidized bed reactor from a peat and coal-fired power plant, incinerating waste water treatment sludge from a mill producing viscose fibers Average annual amount of waste produced 7500 t/a	Three sub-samples collected from the fluidized bed reactor during three days	Combination of three separate sub-samples into one composite sample Mixing and mechanical crushing (2mm) 4 °C
De-inking waste	Non-hazardous 030305	Three types of waste from the de-inking process of the secondary pulp production: (a) assorted household paper (b) wood–containing white household paper (c) white wood–free paper Average annual amount of waste produced 40 000 t/a	Three waste samples were collected from the belt filter press	Combination of three separate sub-samples into one composite sample Mixing and mechanical crushing (2mm) -20 °C
Jarosite	Hazardous 110202	By-product from a mill producing nickel and cobalt products Average annual amount of waste produced 50 000 t/a	Sample was collected from the belt conveyor after the iron purification process	Mechanical mixing and crushing (2mm) drying to room temperature 4 °C

Papers III and V)				
Paint or varnish residues from the furniture industry	Dry booth residues: either hazardous 080111 (*), (***) or non-hazardous 080112 (**) Water-curtain booth residues: either hazardous 080115 (*) or non-hazardous 080116 (**)	Residues from the spray painting of furniture. In this process, the piece of furniture hangs in the front of the booth, and the paint or varnish is sprayed on the surface of the piece manually or by robots. In dry booths, excess paint residue is collected by a carton or fibre filter placed at the back-wall of the booth. In water-curtain booths, water flows continuously into the booth collecting the excess paint, which with the help of chemicals is then deposited into the water pool of the booth. Annual amount of wastes produced vary among factories from ≤ 10 to 200 t/a, Total amount of paint residues produced in Finland is around 1000 t.	Samples were collected from the water pool of a water-curtain booth and from the filters of a dry booth	Dry booth residues Mixing No other pretreatment The liquid phase of the water-curtain booth residue (20−30 w -%) was decanted from the solid matter before laboratory analyses Samples were stored in glass jars at 4 °C and analysed within one week of sampling.
Urea-formaldehyde resin waste	Either non-hazardous or hazardous 080499 (***)	Process waste was generated in different parts of urea-formaldehyde resin production; mainly in the purification of resin- producing reactors Average annual amount of resin waste produced is around 500 t	Composite sample was collected from waste containers	Mixing and mechanical crushing (2 mm) 4 °C
Paper IV				
Oil contaminated soil samples	Either non-hazardous 170504 (**) or hazardous 170503 (*)	Six soil samples with different concentrations of petroleum products and a background sample were collected at a former petrol station, which had been in active use from 1965 to 1997. Annual amount of excavated contaminated soil is around 500 000 t. The average amount of excavated oil-contaminated soil mass in Finland is 41 000 t (1997-2003)	Sampling was done at the beginning of remediation actions as six independent composite samples from different parts of the excavated soil mass and a background sample were chosen for this study.	No pretreatment Samples were stored in glass jars at 4 °C and -20 °C

(*) The concentrations of hazardous substances in the matrix exceed the limit value set for hazardous properties (H) for wastes

(**) The concentrations of the hazardous substances in the matrix are below the limit values set for the hazardous properties (H) for wastes

(***) The EWC code is different in paper III for paint residue and urea-formaldehyde resin waste, due to changes in the Hazardous Waste and Waste List published by the Finnish Ministry of Environment (decision 867/1996, amendment 1129/2001).

3.2 Leaching tests on waste and soil samples

The leaching tests used in this study and their main characteristics are listed in Table 7. Wastes were mainly studied using one-stage and multi-stage batch leaching tests (I–V). During the present work, the standardization of the European compliance leaching test SFS-EN 12457-(1-4) was completed (cited in Papers I–III as CEN-test or prEN-12457). The former one-stage method of DIN 38414 referred to Papers I and II has been renamed as European standard of SFS-EN–12457-4. In the present work, a three-stage method of DIN 38414-S4 was used (cited as the DIN test in Papers I and II). The TCLP method and the availability test (NEN 7341) were used to evaluate the leachability of substances from predominantly inorganic wastes at maximum leaching conditions, i.e. acidic extraction liquid, small particle size and lost acid-neutralizing capacity (I and II, Table 7). A column test (NEN 7343) was used to simulate the percolation of inorganic substances and TOC from the wastes (I-II).

Table 7. The main characteristics of the standardized leaching test methods used in the present study.

The standard of the method	SFS-EN 12457-2	SFS-EN 12457-3	SFS-EN 12457-4	DIN-38414-S4	NEN 7349	TCLP Method 1311	NEN 7343	NEN 7341
The type of the method	batch extraction	batch extraction	batch extraction	batch extraction	batch extraction	batch extraction	column test	availability test
Origin	CEN/TC 292	CEN/TC 292	CEN/TC 292, former one-stage method of DIN 38414-S4	Germany	Netherlands	USA EPA	Netherlands, European technical standard of CEN/TC 292 TS14405 ready	Netherlands, European standard (ANC-test) of CEN/TC 292 under development
Usage	compliance test for wastes			multi-stage batch leaching test to study long-term leaching properties		batch leaching test for hazardous waste classification	basic characterization test for wastes	leaching of a particular component from a material under extreme conditions
Particle size, mm	< 4	< 4	< 10	< 10	< 4	< 10	< 4	< 0.125
Amount of solid, g	100	100	100	100	40	> 100	500 - 800	16
Extraction liquid	de-ionized water	de-ionized water	de-ionized water	de-ionized water	de-ionized water adjusted to pH 4	acetic acid solution pH 2.88 or 4.93	de-ionized water adjusted to pH 4	de-ionized water adjusted to pH 4 and pH 7 (eluates from two separate extractions combined)
Number of steps	1	2	1	3	5	1	7	2
L/S -ratio/step, l/kg								
I step	10	2	10	10	20	20	0.1	50
II step		8		10	20		0.1	50
III step				10	20		0.3	
IV step					20		0.5	
V step					20		1	
VI step							3	
VII step							5	
Cumulative L/S -ratio, l/kg	10	10	10	30	100	20	10	100
Method of agitation	rotation end over end	rotation end over end	rotation end over end	rotation end over end	rotation end over end	rotation end over end	up-flow percolation flow rate 3.7-7.4 ml/h	magnetic stirring
Rotation speed, rpm	10	10	10	10	10	30	-	-
Contact time, h	24	first step 6 second step 18	24	24	23	18	11-25 d	3
Filter pore size, μm	0.45	0.45	0.45	0.45	0.45	0.6-0.8	0.45	0.45
Method used in paper of this study	I-V	I-III	I-II	I-II	I-IV	I-II	I	I-II
Ecotoxicity determined from studied waste eluates	x	x	x (only jarosite eluates)	x (only jarosite eluates)	x (I and II, only jarosite eluates)	x	-	x (only jarosite eluates)

For the batch leaching studies, the moisture of the waste material was determined before an amount corresponding to the mass of the dry weight given in the standard procedure was weighed into a test vessel. The extraction liquid was then added to obtain a given liquid-to-solid (L/S) ratio (Table 7). The mixture was agitated for a certain time period. After that, the liquid phase of the mixture was separated by filtration and used for the chemical and ecotoxicological analyses.

In the column test (NEN 7343), an amount of the sample corresponding to a given mass of dry weight was packed to fill up the column (Table 7). The extraction liquid was then pumped up-stream through the sample. The flow rate was chosen depending on the moisture content of the waste material. The output of the pump (l/h) should correspond to the value 1/50 (kg h/l) multiplied by the dry mass of the material (kg). Filters were placed into the lower and upper part of the column: Whatman paper filters, and membrane filters (poresize of 0.45 μm) in the lower part, and two glass fiber GF/A (poresize of 1.6 μm) and membrane filters in the upper part. The eluates were collected at different liquid-to-solid (L/S) ratios (Table 7). The concentrations of substances analyzed from the leaching tests eluates were expressed as the leached amounts (mg/kg) relative to the total mass of the test sample.

3.2.1 Chemical analyses

The methods of chemical analyses of solid wastes and their leaching test eluates are summarized in Table 8.

Table 8. Chemical analyses of waste and soil samples and their leaching test eluates.

Compound	Method	Paper/ Matrix
Inorganic compounds		
Al, Cd, Co, Mo, Ni, Zn, Cr, Cu, V, Pb	Solid samples were extracted by microwave–assisted acid digestion using a modification of EPA method 3051.	IV/ solid samples
	Soil acid extracts and leaching test eluates were analysed by inductively coupled argon plasma spectrometry (ICP-MS)	I and II/ leaching test eluates
Sulphate Chloride	Sulphate concentrations were determined nephelometrically according to standard SFS 5738	I and II/ leaching test eluates
	Chloride concentrations were determined by Mohr titration according to standard SFS 3006	
Organic compounds		
Total organic carbon content (TOC)	TOC was analysed with an elemental analyser (LECO CNS 2000) according to standard SFS-EN 13137	III–V / solid samples
Dissolved organic carbon (DOC)	DOC was determined by infra–red spectroscopy according to standard SFS-EN 1484	I, II, III, and V /leaching test eluates

| Mineral oil
MTBE, TAME
Benzene
Toluene
Ethylbenzene
Xylenes | Mineral oil concentrations were determined from carbon tetra-chloride extractions of the soil samples and metal blade waste eluates by infra–red spectroscopy according to standard SFS 3010

Petroleum hydrocarbons (C_{10}-C_{40}) were determined from di-chloromethane extractions of the soil samples by gas chromatography accompanied with flame-ionization detector (GC-FID)

BTEX compounds were determined from methanol extractions of the soil samples by gas chromatography (GC-MS) using the headspace technique | IV/solid samples I and II /leaching test eluates of the metal blade waste |
| Xylenes
Ethylbenzene
Toluene
Aromatic hydrocarbon solvent (CAS number 64742-95-6)
Isobutanol
1-Butanol
Isopropanol
Ethylacetate
Butylacetate

Formaldehyde
Methanol | Organic solvents in solid wastes were extracted to methanol. These extractions and the leaching test eluates were analysed with a GC-MS or -FID detector using the headspace technique. Identification was based on mass spectral interpretation and comparison with model compounds

Formaldehyde in waste eluates was determined photometrically according to standard SFS 4996

Methanol was determined from water extractions of the solid waste. The extractions and the leaching test eluates were analyzed with a GC-FID using the headspace technique | III and V / solid samples and leaching test eluates |

3.2.2 Ecotoxicity assays and biodegradation studies

The main characteristics of the aquatic and the terrestrial ecotoxicity assays used in this study are summarized in Table 9. The aquatic toxicity was mainly measured from the eluates of the batch leaching tests: SFS-EN 12457 and NEN 7349, and in Papers I and II, additionally from the TCLP test eluates. The leaching methods used for ecotoxicity assays are presented in Table 7. Both the aquatic and the terrestrial toxicity tests were applied to the oil contaminated soil samples (IV). In addition, a terrestrial toxicity test – a lettuce seed germination test – was performed on the solid furniture residues and the resin waste before and after the leaching test (III and V). The biodegradability of the solid wastes and the leaching test eluates was measured with the ISO 14593 test method from one furniture residue and the resin waste (III). In this method, the samples were incubated in a mineral medium with the sample as the sole carbon source at a 20 mg/l concentration for 28 days. The inoculum was activated sludge diluted to 4 mg/l suspended solid. Aniline was used as a readily degradable reference substance, which showed at least 60 % CO_2 evolution compared to the original theoretical TOC.

The eluates were stored frozen and the solid samples were kept in a refrigerator, and analyzed within one week of sampling. The pH of the eluates was adjusted to neutral with 0.5 M HCl or NaOH if it was not between 6 and 8.5. The results of the toxicity tests were given either as inhibition percentages or as EC50 or LC50 values. These values were calculated from the inhibition percentages of each eluate or soil dilution. When the EC50 values were presented they were converted into Toxic Units (TU). The toxicity classification system (TCS), presented in the literature review, was used to combine the aquatic toxicity results of a battery into one unique value of toxicity.

The reverse electron transport assay (RET) was chosen because it is a quick method and gives direct measures of acute toxicity, data that can be correlated with acute toxicities in whole organisms (Read *et al.* 1998). This method resembles microbial tests, but is an *in vitro* test

using sub-mitochondrial particles prepared from isolated beef heart mitochondria (Table 9). Because the functional units (respiration, enzyme functions, membrane transport) are often similar in different species, *in vitro* screening tests are relevant methods to be used to determine the environmental hazard of pollutants (Read *et al.* 1998). The RET test has been proved to correlate well with toxicity tests, such as luminescent bacteria and fish (rainbow trout), water flea and algal tests as shown in the chapter 1.2.4.2 in Table 3.

Table 9. Ecotoxicological test methods used in this study for wastes and oil-contaminated soil samples. The approximate minimum sample volume needed to perform the tests is also presented.

Aquatic tests performed on batch leaching test eluates					
Type of test	Organism	Endpoint	Exposure time and minimum requirement of sample	Standard or reference method	Paper
Commercial microbiotest Luminescent bacteria test	Freeze-dried bacteria (*Vibrio fischeri*) (NRRL B-11177) BioTox™–reagents	Inhibition of bioluminescence measured by Bio-Orbit 1253 Luminometer EC50 value	30 min < 20 ml	ISO SFS-EN 11348-3 (1999)	I–V
Algal growth inhibition test	Microalgae (*Pseudokirchneriella subcapitata*)	Inhibition of growth measured as fluorescence by Sequoia –Turner 450 Digital Fluorometer EC50 value	72 h 500-1000 ml	ISO SFS-EN 28692 (1993) OECD guideline (201)	I
Water flea immobilization test	Freshwater invertebrate (*Daphnia magna*)	Inhibition of mobilization measured as the number of immobilized water fleas EC50 value	48 h 500-1000 ml	ISO 6341 (1996) OECD guideline (202)	I
Bacterial growth inhibition test Microbiotest	Bacteria (*Pseudomonas putida*)	Inhibition of cell multiplication measured as turbidity with an automated Bioscreen C ® analyser EC50 value	48 h 100 ml	A modification of ISO 10712 (1995)	I
Reverse electron transport assay, RET *in vitro* test	Sub-mitochondrial particles prepared from isolated beef heart mitochondria	Inhibition of enzyme activity measured kinetically at 340 nm in a micro-plate reader Inhibition % (paper II) EC50 value	10 min ≤ 20 ml	Read *et al.* (1998)	II–V
Seed germination test performed on a filter paper	Barley (*Hordeum vulgare*) Spinach (*Spinacia oleracea*) Red clover (*Trifolium pratense*)	Inhibition of germination measured as the number of germinated seeds Inhibition %	3 d 100 ml	Kós *et al.* (1995)	II
Plant root elongation test	Onion (*Allium cepa*)	Inhibition of root growth measured as average length of root bundles EC50 value	4 d ≤ 100 ml	Fiskesjö (1997)	III–V

Plant growth inhibition test	Duckweed (*Lemna minor*)	Inhibition of growth measured as the number of fronds, fresh weight and chlorophyll-*a* concentration ≤ 100 ml Inhibition %	3–5 d ≤ 100 ml	ISO/DIS 20079 OECD guideline (221)	II and IV
Commercial microbial enzyme assays ToxiChromotest, ToxiChromoPAD	Mutant strain of bacteria (*Escherichia coli*)	Inhibition of *de novo* synthesis of *β*-galactosidase measured visually or spectrophotometrically Inhibition % (Paper II) EC50 value	6 h ≤ 20 ml	Manufacturer's instructions Group 206 Technologies, Gainesville FL, USA	II and III
Commercial microbial enzyme assays for heavy metals MetPLATE MetPAD	Mutant strain of bacteria (*Escherichia coli*)	Inhibition of activity of *β*-galactosidase measured visually or spectrophotometrically Inhibition %	4–5 h ≤ 20 ml	Manufacturer's instructions Group 206 Technologies, Gainesville FL, USA	II
Terrestrial tests performed on solid waste and soil samples					
Plant seed germination assays	Lettuce (*Lactuca sativa*) Wheat * (*Triticum aestivum*) Cress * (*Lepidium sativum*) Red clover * (*Trifolium pratense*)	Inhibition of seed germination measured as the number of germinated seeds Inhibition %	5–7 d 1 kg	A modification of method US-EPA 600/3-88-029 (1989) and Stephenson *et al.* (2000)	III–V IV*
Survival and reproduction of soil animal	Enchytraeid worms (*Enchytraeus albidus*)	Mortality measured as the number of death adults LC50 value Inhibition of reproduction measured as the number of juveniles EC50 value	21 d 6 weeks >1 kg	A modification of ISO 16387 (2000)	IV
Plant growth inhibition assay	Onion (*Allium cepa*)	Root growth inhibition measured as shoot weights Inhibition %	14 d 1 kg	Fiskesjö (1997)	IV

4 RESULTS AND DISCUSSION

4.1 Environmental hazard of predominantly inorganic wastes (I and II)

The environmental hazard of predominantly inorganic wastes from the metal and forest industries was studied using combined leaching and ecotoxicity tests. The metal-blade waste and the de-inking waste contained also organic material; the former contained organic-based metal working liquid and the latter organic matter from paper recycling. The leaching patterns of key hazardous substances of the wastes were determined with column and batch leaching tests and the need for pH-controlled leaching (availability test NEN 7341) was determined. Chemical classification of wastes was done by comparing the leached amount of substances with the leaching limit values proposed by the EU (Official Journal of the European Communities 2003). Ecotoxicological classification was carried out using the toxicity classification system (TCS). Finally, the requirements for a battery of ecotoxicity assays to complement chemical analyses of the batch leaching tests (EN-12457 and TCLP tests) were determined.

4.1.1 Selection of key hazardous substances

The key hazardous substances were selected based on the background knowledge of each waste material. Total concentrations of cadmium, nickel and cobalt in the jarosite were high (Cd and Ni 1400 mg/kg and Co 2700 mg/kg), and cadmium was chosen as a key hazardous substance in this study. The high oil content of the metal working fluid was the key hazardous substance in the metal blade waste. The TOC content was selected as a key hazardous substance in the de-inking waste because the total metal concentrations in the waste were low (Zn 50–140 mg/kg, Cr 20–25 mg/kg and Pb 5–12 mg/kg). The key hazardous substance in the fly ash was the high zinc concentration (74 000 mg/kg) because the studied fly ash was produced in a peat and coal-fired power plant, which also incinerated the sludge from the wastewater treatment plant. This wastewater was produced in the fibre producing process in which zinc sulphate was used as a process chemical.

4.1.2 Leaching patterns of key hazardous substances

The leaching patterns of key hazardous substances of studied wastes are presented in Fig. 3. The cumulative leached amounts of the key hazardous substance from single and multi-stage batch leaching tests and a column test were presented as a function of the L/S ratios and used to describe the release patterns. The leaching patterns of the key hazardous substances were compared with the general leaching patterns described by Van der Sloot *et al.* 1997 (see Fig. 1). Ideally, the total content or the leached amount in the availability test (i.e. NEN 7341) should represent the asymptote for the leaching curves of the both batch and column test results (Van der Sloot *et al.* 1997).
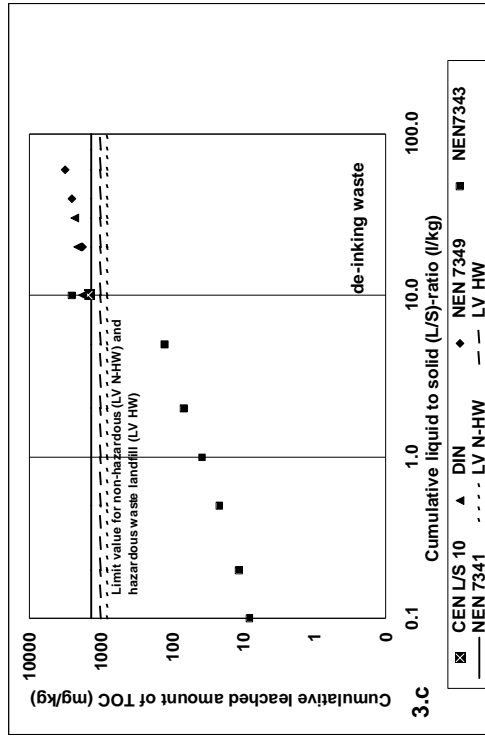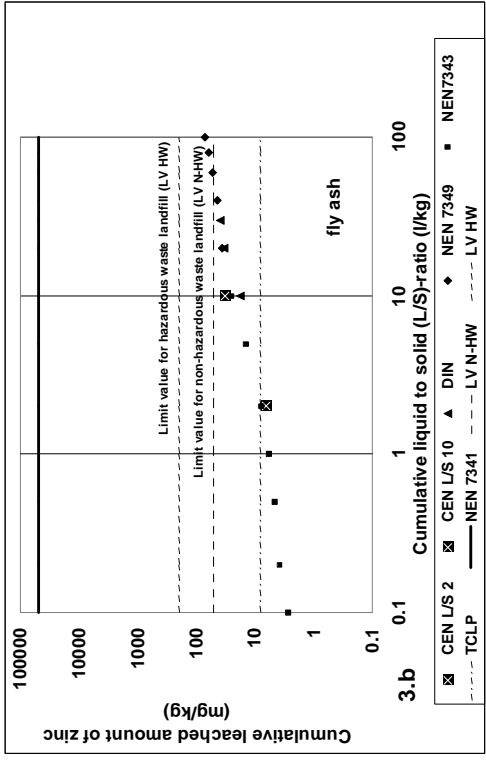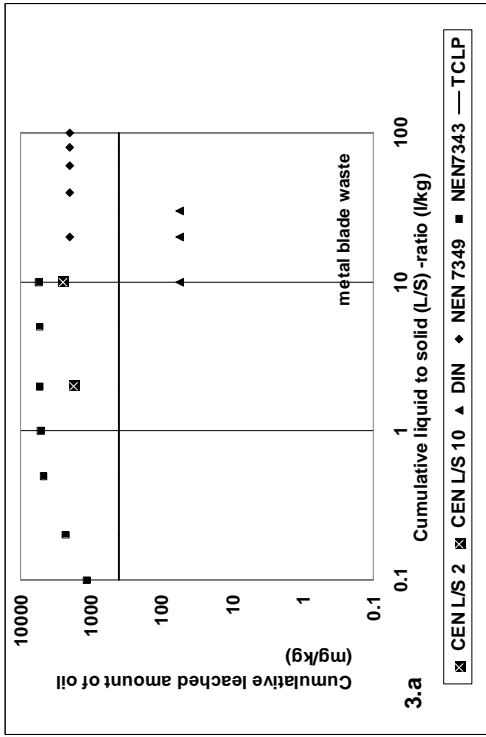
Figure 3. Leaching patterns of the key hazardous substances; (3.a) release of oil from the metal blade waste; (3.b.) release of zinc from the fly ash; (3.c) release of TOC from the de-inking waste; and (3.d.) release of cadmium from jarosite. CEN I= EN-12457-3, two-stage method cumulative L/S ratio 10-30; CEN II = EN-12457-2, one-stage method L/S ratio 10:1; DIN = DIN 38414 S4 three-stage method cumulative L/S-ratios 20-100. TCLP= Toxicity leaching test procedure (EPA 1990), L/S ratio 20:1; NEN 7341 = availability test, cumulative L/S ratio 100, NEN 7343 = column test, cumulative L/S-ratios 0.1, 0.2, 0.5, 1, 2, 5, and 10.

30

The leaching of oil from the metal blade waste was fast. The oil in the metal working liquid washed out of the waste and emulsified with the extraction liquid, i.e. water (Fig 3.a). The leached amounts of oil varied among the leaching tests (Fig. 3.a). The filtration of the eluates might have caused the variability of the oil concentrations. The leached amount of oil from the batch and column tests was not compared with the available amount of oil determined by the availability test because it was technically impossible to perform the availability test (NEN 7341) on the metal blade waste due to the magnetic characteristics of this material.

The leaching of TOC from the de-inking waste represented an intermediate leaching pattern in which, at the end of the experiment (L/S 10 and 100), the leached amount of TOC started to approach the available fraction, indicating a release controlled by the solubility (Fig. 3.c). The result of the TCLP test was not presented for the de-inking waste because acetic acid used as an extraction liquid in the TCLP method disturbed the determination of DOC content in the TCLP eluate.

The leaching pattern of the fly ash identified a relatively slow, solubility-controlled release of zinc (Fig.3.b) because the leached amount of zinc in the batch and column test experiments was considerably lower than the available amount of zinc determined by the availability test (NEN 7341). This was due to the fact that the fly ash was a strongly alkaline material with a moderately high acid-neutralizing capacity (5.39 mol/kg, determined by the equation (1) presented in the literature review). The leachability of zinc was increased when the pH was decreased to acidic in the availability test (Fig. 4). The original pH of the solid waste was a decisive factor affecting the pH of leaching test eluates in batch extraction tests and column test experiments. Therefore, the test eluates of the fly ash remained alkaline after the leaching experiments (Fig. 4).

The leaching of cadmium from the jarosite was fast because the leached amount of cadmium reached the available amount in the batch and column test experiments compared with the result of the availability test (Fig. 3.d). The jarosite was an acidic waste material with a relatively low acid-neutralizing capacity (0.019 mol/kg). The change in the leaching conditions, such as different L/S ratios and the number of extraction steps, affected the leachability of zinc more than the pH did (Fig. 4).
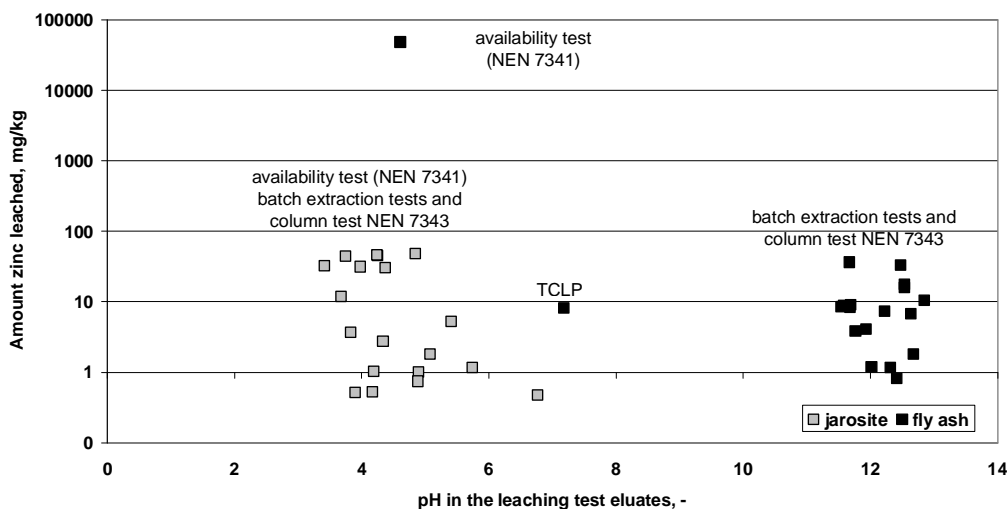
Figure 4. Amount of zinc leached from the jarosite and fly ash at different pH values in the end of batch leaching (L/S = 2 and L/S = 10–20) and column (L/S = 0.1–5) tests and the availability test conditions (L/S = 50). The original data is presented in Paper I and Vaajasaari *et al.* 1997.
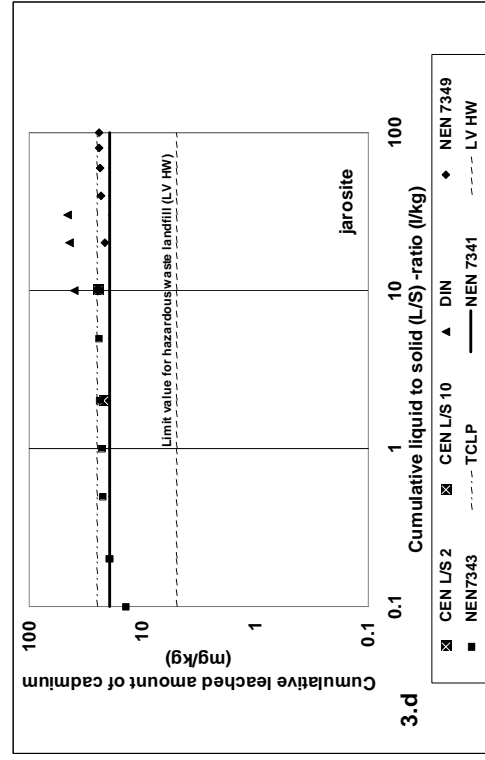
The leaching patterns of the key hazardous substances showed that the release of the contaminants was dependent on the physical and chemical characteristics of the waste material. The availability test (NEN 7341) results described what was the total leachable amount of a selected key hazardous substance under conditions, which favour release (dispersed material, high L/S ratio, pH, and lost acid neutralizing capacity). The resistance of materials to acid attack (acid neutralizing capacity) was moderately high in the fly ash compared with the jarosite. The results showed that the batch extraction tests and column test were not sufficient as such to study the leaching properties of inorganic waste materials with a strong acid-neutralizing capacity. It was important to perform pH-controlled leaching experiments on the inorganic wastes in order to know how the changes of pH in the surrounding environment affect the leachability of substances. If the fly ash is put into an acidic environment, i.e. landfilled in the same cell with the jarosite, the leaching of zinc may be dramatically increased. The change of pH in a landfill environment may also occur due to natural acid formation during anaerobic microbial degradation. During the re-use and long-term storage of wastes, acidification might be resulting from sulphide oxidation, buffering capacity of natural waters, acid rain and atmospheric CO_2 (Van der Sloot *et al.* 2001).

4.1.3 Applicability of combined leaching and ecotoxicity tests for predominantly inorganic waste eluates

A study was made of the ecotoxicological classification of predominantly inorganic waste eluates using a battery of traditional acute toxicity tests, and the toxicity classification (TCS) system (Table 10). In addition, the ecotoxicity of the waste eluates was studied using commercial microbial enzyme assays, the duckweed growth inhibition test, and the RET assay (Table 11). An evaluation was made of the sensitivity of ecotoxicity tests and the applicability of batch leaching tests (EN-12457 and TCLP) for the preparation of waste samples for ecotoxicity tests.

The sensitivity order of the ecotoxicity tests for predominantly inorganic waste eluates according to decreased toxicity was as follows: (1) the algal growth inhibition test (*P. subcapitata)*, (2) water flea immobilization test (*D.magna)*, (3) luminescent bacteria test (*V.fischeri)* and (4) bacterial (*P.putida)* growth inhibition test (Table 10). In the previous ecotoxicity studies on MSWI bottom ash*,* the algal growth inhibition test has also proven a more sensitive test than the luminescent bacteria and water flea tests (Ferrari *et al.* 1999, Lapa *et al.* 2002a).

A class weight score was calculated for each toxicity test result according to the toxicity classification (TCS) system (Table 10). The closer the class weight score percentage value to 100 %, the lower the variability of biological responses of the results of the battery of tests (Table 10). The bacterial tests were the least sensitive tests for detecting toxicity in the fly ash and jarosite eluates. Therefore, the class weight scores (%) were the lowest for these waste eluates (Table 10). Plant seed germination tests were not particularly sensitive and were regarded as unsuitable for this purpose (Table 4 in Paper II). According to Ferrari *et al.* (1999), plant seed germination tests performed on MSWI bottom ash were more sensitive for solid-phase than water eluates.

Table 10. Toxicity classification of predominantly inorganic waste eluates based on the toxicity classification system (TCS). The data was recalculated (TU =100/EC50) from the results presented in Fig. 2 in Paper I.

Waste and the leaching test	Luminescent bacteria test (*V.fischeri*)	Test score	Bacterial growth inhibition test (*P.putida*)	Test score	Water flea immobilisation test (*D. magna*)	Test score	Algal growth inhibition test (*P.supcapitata*)	Test score	Class weight score	Class weight score	Toxicity classification
Metal blade waste	TU	-	TU	-	TU	-	TU	-	-	%	
CEN I	63	3	3.3	2	33	3	17	3	2.8	92	high acute toxicity
CEN II	2.8	2	<1	1	6.6	2	5.6	2	1.8	88	significant acute toxicity
TCLP	2.9	2	5.6	2	35	3	29	3	2.5	83	high acute toxicity
Fly ash											
CEN I	<1	1	<1	1	13	3	33	3	2.0	67	high acute toxicity
CEN II	<1	1	<1	1	6.1	2	33	3	1.8	58	high acute toxicity
TCLP	202	4	40	3	56	3	100	3	3.3	81	very high acute toxicity
De-inking waste											
CEN I (L/S 10)	<1	1	<1	1	<1	1	<1	1	1.0	100	no acute toxicity
TCLP	<1	1	7.7	2	3.0	2	6.7	2	1.8	88	significant acute toxicity
Jarosite											
CEN I	106	4	100	3	143	4	100	4	3.8	94	very high acute toxicity
CEN II	6.3	2	25	3	17	3	100	4	3.0	75	very high acute toxicity
TCLP	<1	1	<1	1	77	3	100	4	2.3	56	very high acute toxicity
TCLP extraction liquid	3.0	2	2.1	2	1.8	2	6.3	2	2.0	100	significant acute toxicity

CEN I= European standard batch leaching test EN-12457-3, first step L/S 2:1; CEN II = European standard batch leaching test EN-12457-3, second step L/S 8:1; TCLP= Toxicity leaching test procedure (EPA 1990); CEN I (L/S 10) = European standard batch leaching test EN-12457-2, L/S 10:1

The sensitivity of commercial microbiotests was selective depending on the chemical composition of the waste eluates (Table 11). The metal-specific microbial tests (MetPLATE and the MetPAD) displayed none or lower inhibition for de-inking waste and metal blade waste eluates than for fly ash and jarosite eluates (Table 11). The microbial colorimetric assay (ToxiChromotest) is known to be sensitive to both inorganic and organic compounds (Bitton *et al.* 1994). This might explain why the response of the ToxiChromotest was higher to the CEN I eluate of metal blade waste than to fly ash (Table 11). The metal concentrations in these eluates were at the same level but the metal blade waste eluate contained organic–based metal working fluid.

Table 11. Toxicity of predominantly inorganic waste eluates determined with commercial microbiotests, the duckweed growth inhibition test, and the RET test (Figs. 2 and 3 in Paper II). Results are expressed as inhibition percentages (I-%) for undiluted (100 %) or diluted (50 %) extracts.

Waste and the leaching test	MetPLATE	MetPAD	ToxiChromotest	Duckweed (*Lemna minor*) growth inhibition	RET
Metal blade waste	I-% (undiluted sample)	I-% (undiluted sample)	I-% (undiluted sample)	I-% (sample diluted at ratio 2:1)	I-% (sample diluted at ratio 2:1)
CEN I	0*	20	100	100	91
CEN II	0*	10	5	0*	93
TCLP	0*	20	100	99	88
Fly ash					
CEN I	100	50	0	49	52
CEN II	75	40	0	48	52
TCLP	44	40	100	75	100
De-inking waste					
CEN I (L/S 10)	0	0	0	13	0*
TCLP	-	-	-	-	25
Jarosite					
CEN I	83	40	100	100	-
CEN II	78	50	100	93	97
TCLP	91	30	100	100	100
TCLP extraction liquid	61	-	100	88	0*

 - = not determined; * = measured effect in eluate sample was higher than in the control sample; CEN I= European standard batch leaching test EN-12457-3, first step L/S 2:1; CEN II = European standard batch leaching test EN-12457-3, second step L/S 8:1; TCLP= Toxicity leaching test procedure (EPA 1990); CEN I (L/S 10) = European standard batch leaching test EN-12457-2, L/S 10:1

A comparison was made of the applicability of two batch leaching tests (EN-12457 and TCLP) for the preparation of waste samples for ecotoxicological tests. The European standard leaching test (EN-12457-2 or 3) was proposed as an extraction method for ecotoxicity tests. The TCLP method was regarded as unsuitable for use in the toxicity assays because the pure TCLP extraction liquid (acetic acid) was classified as having significant acute toxicity (class weight score 100 %) with one exception, the RET test (Tables 10 and 11). The same observation has been made earlier by Jenner & Janssen-Mommen (1989) and Peterson *et al.*(1990).

4.1.4 Ecotoxicity assays to complement chemical analyses in the hazard classification of predominantly inorganic wastes

The chemical classification of jarosite showed that the leached amounts of nickel, copper and cadmium were high and exceeded the limit values set for a hazardous waste landfill in the EU (Table 12). The amount of nickel leached in the batch leaching tests and in the column test (NEN 7343) was between 160 and 430 mg/kg, while the proposed limit value for hazardous waste is 40 mg/kg. The amount of cadmium leached was five to seven times the proposed limit value for hazardous waste. The batch leaching test (EN-12457-3) eluates of the jarosite were also classified as very highly toxic (TU >100) to all the test biota, confirming the conclusions drawn from the chemical classification (Tables 10 and 13).

Table 12. Comparison of inorganic substances and TOC content leached from studied wastes with the limit values proposed by the EU for non-hazardous and hazardous waste landfills at L/S 10 l/kg. Original data presented in Paper I and Vaajasaari *et al.* 1997.

Component	Waste materials (I and II)				EU waste acceptance criteria (2003/33/EC) Leached amounts at L/S 10 mg/kg	
	Metal blade waste	Fly ash	Jarosite	De-inking waste	Non-hazardous waste landfill	Hazardous waste landfill
	Amount of substances leached at L/S 10 l/kg determined by the batch extraction (EN-12457-2 or -3) and column test (NEN 7343)				(inorganic waste with low organic content)	
	mg/kg dry weight				mg/kg dry weight	mg/kg dry weight
Arsenic	0.001	0.08	0.07 - 0.3	0.1	2	25
Cadmium	0.02 - 0.03	0.005	**24**	0.001	1.0	5.0
Chromium total	0.04	0.1 - 0.6	0.3 - 0.9	0.1	10	70
Copper	0.1 - 0.2	0.01	**96 - 160**	0.02 - 0.03	50	100
Molybdenum	3.4 - 4.8	3.1 -3.7	0.04 - 0.1	0.06 - 0.11	10	30
Nickel	0.37 - 1.3	0.3 - 0.8	**160 - 430**	0.1 - 0.3	10	40
Lead	0.02 - 0.05	0.1 - 0.9	0.01	0.002	10	50
Zinc	1.0 - 1.8	25 - 32	**45 - 50**	0.4 - 0.8	50	200
Chloride	-	3600 - 8300	11 - 20	24 - 38	15000	25000
Sulphate	-	11000 - 13000	16000 - 17000	4800	20000	50000
Mineral oil	2500 - 5400	-	-	-	-	-
DOC content	**4800 - 5600**	33 - 50	19 - 32	**1500 - 2500**	800	1000

- not determined

The chemical classification showed that the fly ash could be deposited in a non-hazardous waste landfill (Table 12). According to ecotoxicological classification, the batch leaching test eluates of the fly ash were classified as having very high (TU>100) or high acute toxicity (10<TU<100, Table 10). In addition, the availability test results showed that the leaching of zinc and sulphate from the fly ash increased in an acidic environment to 48 000 mg/kg and 37 000 mg/kg, respectively (Fig. 4 and Vaajasaari *et al.* 1997). Therefore, additional information on the pH-dependence of leaching (the availability test NEN 7341) and ecotoxicity tests was needed in order to evaluate the overall environmental hazard presented by the fly ash. The results strongly suggested that ecotoxicity tests should be integrated for hazard classification in decision-making of landfill disposability (Table 13).

The amount of metals leached from the metal blade waste did not exceed the proposed limit values set for a non-hazardous waste (Table 12). No leaching limit values for mineral oil have been set within the EU. The only possible way to evaluate the hazardous properties of this waste material was to compare the amount of TOC leached from the waste with the limit value of DOC content set for different landfill classes (Table 12). These limit values were

exceeded in the batch leaching tests and column test (NEN 7343) experiments. According to this study, the metal blade waste would be considered unsuitable for a non-hazardous waste landfill before the removal of the metal working fluid. This was based on the fact that the leaching test eluates of the CEN and TCLP tests with the highest oil concentrations were also the most toxic to all the test biota (Tables 10 and 11).

The chemical classification of the de-inking waste showed that the amount of TOC leached in the column and batch leaching tests exceeded the limit value of DOC set for a non-hazardous and hazardous waste landfill (Table 12). However, the de-inking waste eluate of the European batch leaching test (EN-12457-2) was classified non-toxic (TU<1) to all the test biota (Tables 10 and 11). Therefore, the de-inking waste was considered suitable for disposal in a non-hazardous waste landfill.

A battery of ecotoxicity tests was proposed for the hazard classification of the wastes studied that contained either inorganic or both inorganic and organic substances (Table 13). According to this hazard classification, chemical and ecotoxicological analyses should be performed from the same water extractions (Table 13). Only then can the toxicity test results be compared with chemical analyses to improve the hazard classification. If both chemical and ecotoxicological analyses are to be measured, the volume of eluate obtained in the leaching experiments is a limiting factor. Therefore, it would be more practical to use a battery of ecotoxicity tests in which the need for sample volume is minimized to < 100 ml. Microbiotests seemed the best choice in this regard (see Table 9). In commercial microbial tests (e.g. luminescent bacteria, MetPLATE, and MetPAD), the minimum requirement for the sample volume is less than 20 ml. In the traditional versions of water flea immobilization and algal growth inhibition tests, the sample volume required to perform the test can be from 500 to 1000 ml. Therefore, the algal and water flea tests were not proposed for inclusion (Table 13). However, the new microbiotest applications of these methods could be useful (Persoone *et al.* 2000). The luminescent bacteria, MetPLATE/ToxiChromotest and RET tests were proposed for use as screening tests for both basic characterization and compliance testing of wastes (Table 13). The MetPLATE test is a metal-specific assay that can be used as a selective method to identify the toxicity caused by inorganic compounds in waste materials with unknown composition of both organic and inorganic substances.

Table 13. Chemical and ecotoxicological classification of predominantly inorganic wastes and a proposal for a combined leaching and ecotoxicity approach for hazard classification.

Waste	Key hazardous substances leached	Ecotoxicological classification (SFS-EN 12457-3 eluates)	Chemical classification compared with the EU waste acceptance criteria
metal blade waste	TOC mineral oil in metal working fluid	**high and significant toxicity** (TU 17-63 and <1-6.6) (88-92 %)*	TOC exceeded the limit values for non-hazardous and hazardous waste landfill **no set leaching limit value for mineral oil disposed in a non-hazardous and hazardous waste landfill**
fly ash	zinc and sulphate	**high acute toxicity** (TU 6.1-33) (58-67 %)*	**suitable** for disposal in a **non-hazardous waste landfill** **leaching of zinc and sulphate clearly increased in acidic environment** no set limit value for pH-dependence leaching **resistance to acid attack was moderately high (ANC 5.39 mol/kg)**
de-inking waste	TOC	**non-toxic** (TU <1) (100 %)*	TOC exceeded the limit values for non-hazardous and hazardous waste landfill
jarosite	cadmium, nickel, copper	**very high acute toxicity** (TU 17-143) (75-94 %)*	leached amounts of key hazardous substances exceeded the limit values for a hazardous waste landfill **resistance to acid attack was low (ANC 0.019 mol/kg)**
Proposal for a combined leaching and ecotoxicity approach: <u>Leaching test:</u> European batch leaching test (EN 12457-2 or 3) <u>Proposed battery of tests:</u> luminescent bacteria test, MetPLATE/ToxiChromotest and RET assay (**)		<u>Five most sensitive tests</u> (1) Algal test, (2) water flea test, (3) luminescent bacteria test, (4) MetPLATE/ToxiChromotest and (5) RET assay	

( )* =The closer the weighted class score percentage value to 100 %, the lower the variability of biological responses of the results of the tests (algal test, water flea test, luminescent bacteria test, *P.putida* test); (**) = only the microbiotest versions of algal or water flea tests were proposed for the battery

4.2 Environmental hazard of organic wastes (III and V)

Environmental hazard classification of organic wastes from the furniture and resin industries was studied using combined leaching and ecotoxicity tests. Chemical classification was carried out comparing total concentrations of key hazardous substances in the wastes with the limit values set for hazardous wastes in EU in the Hazardous Waste Directive (91/689/EEC) and Finnish waste legislation (waste decree 1128/2001). Leaching of the key hazardous substances was studied with standardized single and multi-stage batch leaching tests (EN-12457-2 and -3 and NEN 7349) and the applicability of these methods for volatile organic compounds was then evaluated. Ecotoxicological classification was carried out for solid organic wastes with the terrestrial lettuce seed germination test and their leaching test eluates with a battery of aquatic toxicity tests. A TCS system was used to combine the aquatic ecotoxicity results of the test battery into one unique value.

4.2.1 Chemical and ecotoxicological classification of solid organic wastes

The chemical classification was carried out by analyzing the key hazardous substances from furniture industry paint residues and comparing the total concentrations with the limit values set for hazardous waste in EU and Finnish waste legislation (Tables 14 and 15). The total concentrations of known key hazardous substances in paint residues did not exceed the limit values set for hazardous wastes (Table 15). The limit value for the ecotoxic property (H14) in hazardous waste (2 500 mg/kg) for special aromatic hydrocarbon solvent (CAS-number 64742-95-6), used in paint products, was exceeded in one water-curtain booth (F) residue (Table 14). The TOC limit value for hazardous waste landfill in the EU waste acceptance criteria (60 000 mg/kg) was exceeded in all paint residues (Tables 14 and 15). The paint residues also contained large amounts of unknown compounds, since the TOC of analyzed key hazardous substances, calculated as carbon, constituted only 0.3–14 % of the total TOC content of the residues.

Table 14. Composition of the dry-booth (A─D) and water-curtain booth (E─H) paint residues (Table 3 in V). The varnish residue was renamed as sample I (Table 2 in III). Concentrations which exceeded the limit values set for hazardous waste (see Table 15 and Appendix 1) are **bolded**.

Sample	TOC	Formaldehyde	Iso-propanol	Iso-butanol	1-Butanol	Butyl acetate	Ethyl acetate	Toluene	Ethyl benzene	Xylenes	Aromatic hydrocarbon solvent
A	**510**	9200	1700	400	2800	600	n.d.	153	4.7	28	6.4
B	**480**	8600	500	6900	3500	980	n.d.	41	32	250	n.d.
C	**510**	44	n.d.	n.d.	n.d.	1600	150	290	51	330	29
D	**520**	9600	1700	200	12000	2900	120	n.d.	43	440	n.d.
E	**420**	27	n.d.	n.d.	n.d.	n.d.	n.d.	5700	4300	22000	290
F	**410**	110	n.d.	n.d.	3600	7200	480	6000	13000	40000	**84000**
G	**550**	41	n.d.	n.d.	n.d.	350	n.d.	8300	25	180	180
H	**420**	120	n.d.	n.d.	n.d.	n.d.	n.d.	14	160	480	480
I	**258**	-	-	3200	-	200	-	1300	1300	7500	-

Composition of dry-booth and water-curtain booth residues, mg/kg; TOC in g/kg

n.d. = not detected, - = not determined

The limit values for hazardous properties in wastes are set according to the chemical hazard classification (see Appendix 1). Toluene and xylenes were classified as harmful chemicals (statute of the Finnish Ministry of Social Affairs and Health 624/2001). The sum of toluene and ethylbenzene concentrations in the solid wastes can be as high as 250 000 mg/kg before the organic paint residues are classified as hazardous (Table 15).

Table 15. The hazardous properties and limit values of the key hazardous substances analyzed from the furniture industry paint residues based on the Hazardous Waste Directive (91/689/EEC) and the waste decree of the Finnish Ministry of Environment (1128/2001).

CAS number	Chemical	Hazardous property (H)	Limit value mg/kg
50-00-0	formaldehyde	carcinogenic H7	10 000
71-36-3	1-butanol	irritant H4, flammable H3-B	100 000 -
123-86-4	butylacetate	flammable H3-B	-
141-78-6	ethylacetate	irritant H4, highly flammable H3-A	200 000 -
108-88-3 100-41-4	toluene ethylbenzene	harmful H5, highly flammable H3-A	250 000 -
1330-20-7	xylenes	harmful H5	250 000
64742-95-6	aromatic hydrocarbon solvent	ecotoxic H14	2500
Limit value for hazardous waste landfill (2003/33/EC)		**TOC content in solid waste**	**60 000**

- limit value not set, to be evaluated or tested

The solid-phase ecotoxicity of the paint residues and one varnish residue was studied using the lettuce seed germination test. The dry-booth (A─D) and water-curtain booth (E─H) paint residues clearly inhibited lettuce seed germination and should be classified as hazardous waste (Table 16). The seed germination of lettuce was markedly inhibited (EC50 value 3 %) by one water-curtain booth varnish residue (III renamed as sample I in Table 14). This residue also contained components that were only slowly degradable either as solids or as water eluates (Fig. 2 in Paper III). The germination test results of paint residues also showed that all the dry-booth (A-D) and water-curtain (E-H) booth residues remained toxic after the leaching test (Table 16). The seed germination test showed that the hazard posed by the waste materials was underestimated by measuring only the total concentrations of individual key hazardous substances in the paint residues. The combined chemical and ecotoxicological classification of eight paint residues from different furniture factories also showed that the environmental hazard of the same waste type differed (Tables 14 and 16). The hazardous properties of the paint residues apparently varied due to the differences in spray paint compositions and their physical appearance. The water-curtain booth residues were porous and amorphous material while the dry-booth residues were homogenous powders.

Table 16. The toxicity of dry-booth (A—D) and water-curtain booth (E—H) paint residues to lettuce seed germination before and after the leaching test (EN-12457-2). The original data is presented in Table 9 in V.

Test concentration dry weight %	Lettuce seed germination test, inhibition %							
	Toxicity of the residues before the leaching test							
	A	B	C	D	E	F	G	H
1.6	100	100	0*	100	0*	6	0*	0*
3.1	100	100	0	100	4	0 *	0*	3
6.3	100	100	0*	100	4	14	22	0
12.5	100	100	14	100	6	27	22	11
Test concentration dry weight %	Toxicity of the residues after the leaching test							
	A	B	C	D	E	F	G	H
0.8	-	-		4	-	-	-	0*
1.6	-	-	3	37	-	-	-	19
3.1	92	-	3	95	-	-	0	0
6.3	-	-	5	100	0	9	-	5
12.5	100	100	21	100	0	40	-	-
25	100	100	34	100	89	71	-	-
50	100	100	-	-	-	-	100	100

- = not determined, * = seed germination in sample dilution was higher than in the control sample
In control samples (quartz sand) the number of germinated seeds was 36-39 out of 40

The environmental hazard classification of solid resin waste was studied using both chemical and ecotoxicological analyses. The key hazardous substances in the resin waste were methanol and formaldehyde. The TOC content was at a level of 240 g/kg (III). The methanol content (660 mg/kg) in the solid resin waste was analyzed from the water extract. It was impossible to determine formaldehyde from the solid material because its heterogeneous form would have led to unreliable analytical results. Therefore, the concentrations of the key hazardous substances could not be compared with the limit values for hazardous waste. The results of the seed germination test proved that the toxicity to lettuce seed germination of this waste remained unchanged (EC50 value 11%) even after the leaching test experiments. In addition, the solid resin waste was non-degradable in the standard test (ISO 14593), compared with the readily degradable aniline used as a reference chemical (Fig. 2 in Paper III). The solid resin waste was classified as ecotoxic (H14) using the seed germination and biodegradation tests. The environmental hazard of resin waste could not be evaluated unless the ecotoxicity of the solid material was measured first.

4.2.2 Applicability of leaching tests for volatile organic compounds

Studies were made of the leaching of the key hazardous substances from the organic wastes from the furniture and resin industries, and the applicability of standardized batch leaching tests (EN-12457-2 and -3 and NEN 7349) for volatile organic compounds. Methanol was readily released from the resin waste because it was washed out after the first step of the multi-stage batch extractions (Fig. 5). The multi-stage leaching tests (EN-12457-3 and NEN 7349) reflect leachability over hundreds of years (Van der Sloot *et al.* 2001). The results of the multistage batch extractions showed that the varnish residue would continue to release less water-soluble compounds, e.g. ethylbenzene and toluene, at a relatively constant level for a long period of time (Fig. 5).
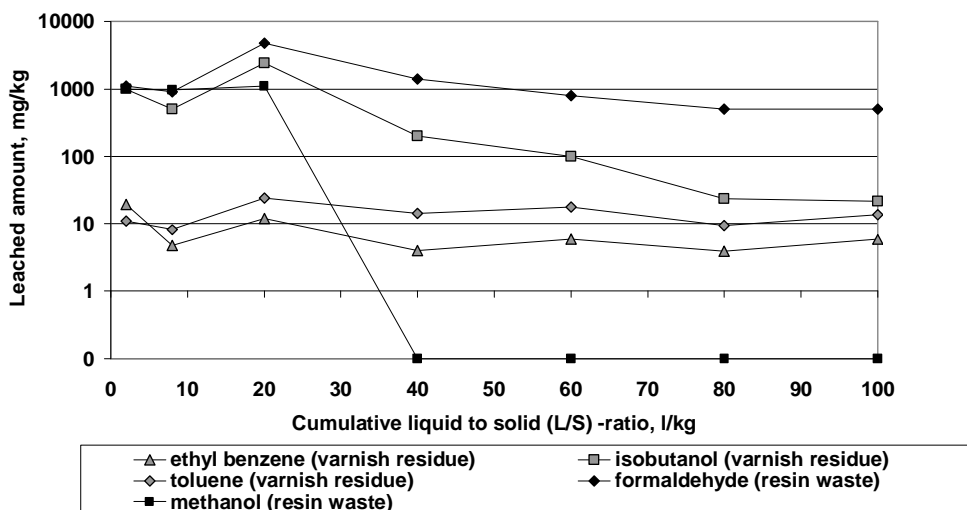
Figure 5. Release of selected organic compounds from varnish residue and resin waste in two-stage (SFS-EN 12457-3, L/S 2 and 10) and five-stage (NEN 7349, L/S 20-100) batch extractions (Table 2 in III).

The eluates of the dry-booth (A-D) residues contained more easily leachable polar organic compounds than the water-curtain (E-I) booth residues (Table 17). The latter residues contained more organic compounds that were not identifiable with quantitative chemical analyses. Therefore, the leached amount of the known key hazardous substances in the water-curtain booth residues calculated as carbon, constituted only 10–38 % of the DOC content analyzed from the leaching test eluates. Butanol leached out readily (70–80%) in comparison with the total concentrations in the dry-booth paint residues (Tables 14 and 17). Formaldehyde was also easily water-leachable from the dry-booth residues (A, B and D). The amount of formaldehyde leached from the paint residues was 80-90 % of the total concentration and was released slowly from a paint-binding (amino resin) agent (Tables 14 and 17). Isobutanol and 1-butanol were not detected in solid water curtain booth residues (E, G and H in Table 14) but significant concentrations (460–930 mg/kg) were determined from the leaching test eluates (Table 17). The physical form of the water-curtain booth residues was porous and amorphous and contained liquid that formed a separate phase from the solid matter during storage. Therefore, reproducible sampling of water-curtain booth residues for chemical analyses and leaching studies was difficult, and might be one reason for the lower concentrations of aliphatic organic compounds in the solid residue, compared with the leaching test eluates.

Table 17. Organic compounds leached in the SFS-EN 12457-2 leaching test from the dry-booth (A─D) and water-curtain booth (E─H) residues (Table 4 in V). Leached amounts were calculated as mg/kg. Varnish residue is renamed sample I in this table (Table 2 in III).

Sample	Formaldehyde	Iso-propanol	Iso-butanol	1-Butanol	Butyl acetate	Ethyl acetate	Toluene	Ethyl benzene	Xylenes	Aromatic hydrocarbon solvent
A	5300	340	6200	3300	180	360	5	n.d.	0.3	n.d.
B	6900	520	11000	3400	310	n.d.	0.2	0.5	2.0	n.d.
C	n.d.	n.d.	n.d.	n.d.	410	n.d.	5	0.4	3.0	n.d.
D	6400	690	n.d.	9600	910	46	n.d.	0.7	6.0	n.d.
E	-	520	280	460	n.d.	n.d.	110	30	170	0.6
F	-	350	2200	4400	1700	290	80	43	230	57
G	-	130	110	930	37	40	160	0.1	0.15	n.d.
H	-	47	290	820	n.d.	n.d.	0.3	2.0	11	0.9
I*	-	-	2400	-	<50	-	10	10	65	-
I**	-	-	2400	-	<50	-	36	42	220	-

n.d. = not detected; - = not determined; * = glass vessel, ** = headspace vessel

Losses of volatile organic compounds were studied using the EN-12457-2 method with two different kinds of extraction vessels: a glass bottle and a vacuum headspace extraction vessel. The leachable concentrations of volatile organic compounds from one varnish residue (sample I) were lower in the glass bottle than in the headspace vessel. The effect was dependent on the compound, the lowest (5 %) value obtained for toluene and the highest (24 %) for xylenes (III and Table 17). Losses of volatile organic compounds could be avoided by using a zero-headspace extraction vessel in the leaching procedure. In addition, the pre-treatment of the samples should be minimized, and solid waste and eluate samples should be stored frozen and analyzed within a week of sampling (see Table 6).

The leaching tests performed on the organic wastes studied showed that these methods should be used to screen the water leachable fraction of the key hazardous substances when selecting the best waste management alternative. Standardized column tests have also been used to study the leaching of BTEX compounds from contaminated soils (Wahlström *et al.* 1994). However, as stated by Wahlström *et al.* (1994), the degradation and volatilization of BTEX compounds need to be controlled by conducting the leaching experiments in darkness at a low temperature (5 $^{\circ}$C) and collecting the eluates on a carbon adsorption tube for further chemical analysis.

4.2.3 Ecotoxicological classification of organic waste eluates

The ecotoxicological classification of the batch leaching test (EN-12457-2/-3 and NEN 7349) eluates of the organic wastes was carried out using a battery of aquatic toxicity tests and the RET assay (Tables 18–20). The toxicity of the eluates from the resin waste and the one water–curtain booth varnish residue decreased substantially during the multi-stage (NEN 7349) method, but the eluates still remained toxic after the last step of the batch extraction and a marked inhibition was recorded in the luminescent bacteria and RET tests (Tables 18 and 19). The ecotoxicological classification of the eluates from multi-stage leaching tests showed that the resin waste and one of the water–curtain booth varnish residues might continue to release toxic compounds for a long period of time (see also Fig. 5).

Table 18. Toxicity classification of the resin waste eluates determined with three toxicity tests and the RET test based on the TCS system. Data was recalculated (TU=100/EC50) from the results presented in Table 3 in Paper III.

Leaching test	Formaldehyde concentration of the eluate	Luminescent bacteria test (*V.fischeri*)	Test score	RET test	Test score	Onion root elongation test (*A.cepa*)	Test score	ToxichromoPAD	Test score	Class weight score	Class weight score	Toxicity classification
	mg/kg	TU	-	TU	-	TU	-	TU	-	-	%	
CEN I L/S 2	1100	81	3	15	3	-	-	20	3	3.0	100	high acute toxicity
CEN II, L/S 8	1900	19	3	23	3	-	-	5.3	2	2.7	89	high acute toxicity
NEN 7349 1.step	4800	15	3	3.4	2	4.8	2	10	2	2.3	75	high acute toxicity
NEN 7349 2.step	1400	2.8	2	1.5	2	<1	1	<1	1	1.5	75	significant acute toxicity
NEN 7349 3.step	800	4.1	2	1.5	2	<1	1	<1	1	1.5	75	significant acute toxicity
NEN 7349 4.step	500	2.5	2	1.5	2	<1	1	<1	1	1.5	75	significant acute toxicity
NEN 7349 5.step	500	2.1	2	1.5	2	<1	1	<1	1	1.5	75	significant acute toxicity

- = not determined; CEN I L/S 2= European standard batch leaching test EN-12457-3, first step ; CEN II L/S 8 = European standard batch leaching test EN-12457-3, second step ; NEN 7349, L/S 20 = five-stage batch leaching test, 1.–5. steps

A study was made into the possibility that toxicity in the varnish residue eluates might have been caused by some unknown compounds rather than the key hazardous substances analyzed from the eluates. The highest concentrations of individual organic compounds (5.5–500 mg/l) and DOC (24000 mg/l) were detected in the two-stage CEN test eluates of the varnish residue at an L/S ratio of 2:1 (Table 2 in III). These eluates were also the most toxic to all the test biota (Table 19). However, when a pure organic solvent mixture of isobutanol (500 mg/l), xylenes (48 mg/l), toluene (5.5 mg/l) and ethylbenzene (9.6 mg/l) with the same concentrations as in the varnish residue eluate were prepared and tested for toxicity with luminescent bacteria and RET inhibition, no toxic effect was observed. Therefore, it was reasonable to conclude that the toxicity in the varnish residue eluates was probably due instead to some other toxic compounds that co-eluted with the known key hazardous substances rather than the key compounds themselves. The latter observation emphasized the need for ecotoxicity assays to complement chemical analyses in the hazard classification of complex mixture of substances in waste matrices.

Table 19. Toxicity classification of the varnish residue eluates (sample I in Table 14) determined with three toxicity tests and the RET test based on the TCS system. Data was recalculated (TU=100/EC50) from the results presented in Table 3 in Paper III.

Leaching test	DOC content of the eluate	Luminescent bacteria test (*V.fischeri*)	Test score	RET test	Test score	Onion root elongation test (*A.cepa*)	Test score	ToxichromoPAD	Test score	Class weight score	Class weight score	Toxicity classification
	mg/kg	TU	-	TU	-	TU	-	TU	-	-	%	
CEN I L/S 2	48400	625	4	1250	4	143	4	167	4	4.0	100	very high acute toxicity
CEN II, L/S 8	12500	345	4	400	4	25	3	33	3	3.5	88	very high acute toxicity
CEN I, L/S 10	49300	249	4	250	4	25	3	29	3	3.5	88	very high acute toxicity
NEN 7349 1.step	61200	278	4	250	4	13	3	18	3	3.5	88	very high acute toxicity
NEN 7349 2.step	5800	147	4	83	3	3.3	2	2.0	2	2.8	69	very high acute toxicity
NEN 7349 3.step	2400	45	3	32	3	2.9	2	1	1	2.3	75	high acute toxicity
NEN 7349 4.step	1400	22	3	11	3	1	1	1	1	2.0	67	high acute toxicity
NEN 7349 5.step	800	7.8	2	5.0	2	1	1	1	1	1.5	75	significant acute toxicity

CEN I, L/S 2 = European standard batch leaching test EN-12457-3, first step; CEN II, L/S 8 = European standard batch leaching test EN-12457-3, second step ; CEN II, L/S 10 = European standard batch leaching test EN-12457-2; NEN 7349, L/s 20 = five-stage batch leaching test, 1.–5. steps

Toxicity was compared among eight paint residues from different furniture factories. The dry-booth residues were more toxic than the water-curtain booth residues (Table 20). The dry-booth residue eluates contained high levels of formaldehyde (Table 17). The formaldehyde content of the dry-booth residues explained the ecotoxicity of the paint to a great extent. One dry-booth residue (C) did not contain formaldehyde and was far less toxic than the other residues (Table 20). This hypothesis was also based on the fact that formaldehyde concentrations in the leaching test eluates of other dry-booth residues (530–690 mg/l) were 62-75 times higher than the EC50 value reported for formaldehyde (Kaiser and Devillers 1994 and V). On the other hand, the concentrations of the aliphatic and aromatic compounds of these residues were lower than the EC50 values reported by Kaiser and Devillers (1994). The water-curtain booth residues (E and F) with the highest leached DOC concentrations were classified as highly toxic, while the two with the lowest concentrations were classified as having a significant acute toxicity (Table 20).

Table 20. Toxicity classification of the dry-booth (A-D) and water-curtain (E-H) booth residue eluates determined with two toxicity tests and the RET test based on the TCS system. Data was recalculated (TU =100/EC50) from the results presented in Table 7 in Paper V.

Waste	DOC content of the eluate	Luminescent bacteria test (*V.fischeri*)	Test score	RET test	Test score	Onion root elongation test (*A.cepa*)	Test score	Class weight score	Class weight score	Toxicity classification
dry-booth residues	mg/kg	TU	-	TU		TU	-	-	%	
sample A	21000	238	4	25	3	15	3	3.3	83	very high acute toxicity
sample B	18000	244	4	28	3	21	3	3.3	83	very high acute toxicity
sample C	1800	4.6	2	1.6	2	<1	1	1.7	83	significant acute toxicity
sample D	21000	250	4	28	3	14	3	3.3	83	very high acute toxicity
water-curtain booth residues										
sample E	12000	48	3	2.0	2	3.6	2	2.3	78	high acute toxicity
sample F	20000	22	3	3.2	2	4.5	2	2.3	78	high acute toxicity
sample G	11000	4.4	2	<1	1	1.7	2	1.7	83	significant acute toxicity
sample H	5700	8.1	2	<1	1	3.6	2	1.7	83	significant acute toxicity

n.d = not detected, - = not determined

4.2.4 Ecotoxicity tests to complement chemical analyses in hazard classification of organic wastes

A comparison was made between chemical and ecotoxicological classification results in the hazard classification of organic wastes. According to the chemical classification, the organic wastes were not classified as hazardous when the concentrations of known key hazardous substances were compared with the limit values set for hazardous wastes in the EU and Finnish waste legislation (Tables 14 and 15). Only one paint residue (F) exceeding the limit value for the ecotoxic property (H14) was classified as hazardous waste. TOC analyses from solid paint residues and resin waste also showed that these wastes contained unknown substances not identifiable solely with chemical analyses. Therefore, the hazard classification based on the chemical analyses of the total chemical concentrations of known key hazardous substances was insufficient. The ecotoxicological classification using lettuce seed germination tests clearly showed that paint residues and resin waste should be classified as hazardous with the ecotoxic (H14) property (Table 16 and III). The lettuce seed germination tests of the paint residues produced in different furniture factories also showed that the same waste type could be screened more simply by the ecotoxicity assays than with chemical analyses of key hazardous substances (Table 22). The differences in the chemical and ecotoxicological classification emphasized the need for ecotoxicity tests to complement chemical analyses in the hazard classification of wastes which also contain unknown organic compounds not identifiable solely with chemical analyses (Table 22).

The ecotoxicity tests to complement the chemical analyses of the leaching test eluates of organic wastes were evaluated. The chemical hazard classification of the leaching test (EN-12457 and NEN 7349) eluates of organic wastes was impossible due to a lack of leaching limit values for non-hazardous or hazardous landfills in the EU (Council Decision 2003/33/EC). Only the DOC concentrations in the eluates suggested that the resin waste and paint residues should not be landfilled in either a non-hazardous or hazardous waste landfill. Significant correlation of toxicity with chemical concentrations is often used as a sign of successful evaluation. However, a comparison of the concentrations of individual compounds with a database of their toxicity did not give any information on the overall toxicity of the complex mixtures of substances leaching from wastes without measuring toxicity (III and V). The organic waste eluates also contained unknown toxic compounds not identifiable with quantitative chemical analyses. In addition, ecotoxicity tests only measured overall toxicity but the identification of the chemicals causing the effects remained unresolved. In order to make a chemical identification of compounds causing toxicity, a fractionation procedure combined with toxicity tests and chemical analyses (toxicity identification evaluation, TIE) would be of great value. However, this is a complicated and expensive approach, and beyond the scope of hazard screening for wastes. Nevertheless, the screening of the environmental hazard of organic waste eluates with combined ecotoxicity and chemical analyses was possible using DOC concentration levels. When the DOC concentrations and the ecotoxicity of the one- and two-stage batch extractions (EN-12457) were transformed to logarithmic values, the relationship showed relatively good linear correlation (Table 21).

Table 21. The linear correlation matrix of the logarithmic DOC concentrations (mg/l) and ecotoxicity (TU=100/EC50) from paint residues and resin waste eluates. The number of observations was n=13 (original data is presented in III and V).

	DOC concentration (log mg/l)	Onion root elongation test (log TU)	Luminescent bacteria test (log TU)	RET test (log TU)
DOC concentration (log mg/l)	1.0000			
Onion root elongation test (log TU)	0.8835	1.0000		
Luminescent bacteria test (log TU)	0.7288	0.9084	1.0000	
RET test (log TU)	0.7061	0.9355	0.8711	1.0000

The sensitivity of the ecotoxicity and RET tests were evaluated from their toxicity responses to the paint residue and resin waste eluates, and the requirements for a battery of toxicity tests for hazard classification were proposed (Table 22). The aquatic toxicity results with different test organisms showed similar effects for the paint residue and resin waste eluates. The weighted class score percentages calculated with the TCS system varied between 78 and 100 %, indicating relatively low variability in the biological responses of the toxicity results of the test battery (Table 22). The luminescent bacteria have proven to be much more sensitive to organic than to inorganic toxicants (Bitton *et al.* 1994). It was also the most sensitive bioassay applied to all paint residue and resin waste eluates (Tables 18─20). The experience gained from the sensitivity of toxicity tests (Table 18) gave the opportunity to choose the most sensitive bioassays for a continued survey of paint residues (Table 20). The ToxiChromoPAD test was rejected from the battery of toxicity tests, because it was not as cost-effective for these kinds of waste materials as the luminescent bacteria (= BioTox™), RET and *Allium cepa* tests. The onion root elongation test was chosen instead of the ToxiChromoPAD test, because it is a simple and easy test to perform and gives relevant information on toxicity to plants.

Table 22. The chemical and ecotoxicological classification of organic wastes and a proposal for a combined solid-phase and liquid-phase ecotoxicity approach for hazard classification.

Waste	Key hazardous substances		Ecotoxicological classification (EN-12457-3 test)		Chemical classification versus ecotoxicological classification
	Solid	Leached	Solid	Eluate	
resin waste	formaldehyde methanol TOC	formaldehyde methanol TOC	**acute toxicity** (EC50 11 %, TU 9)	**high acute toxicity** (89-100 %)* (TU 15-81)	**-chemical classification** based on total chemical concentrations of known key hazardous substances **was insufficient**
dry booth paint residues (A, B and D)	formaldehyde 1-butanol butyl acetate isopropanol isobutanol toluene xylenes ethylbenzene TOC	formaldehyde 1-butanol butyl acetate ethyl acetate isopropanol isobutanol xylenes TOC	**very high acute toxicity** at test concentration 12.5 % (I-% 100)	**very high acute toxicity** (83 %)* (TU 25-250)	-formaldehyde was impossible to analyse from the solid resin waste and paint residues contained compounds not identifiable with chemical analyses
dry booth paint residue (C)	butyl acetate ethyl acetate toluene xylenes ethylbenzene aromatic hydrocarbon solvent TOC	butyl acetate toluene xylenes ethyl acetate TOC	**acute toxicity** at test concentration 12.5 % (I-% 14-21)	**significant acute toxicity** (83 %)* (TU 2-4.6)	-ecotoxicological classification using **seed germination assays** showed that **all organic wastes** should be classified as **hazardous** waste with the **ecotoxic** property (H14)
water-curtain booth paint residues (E and F)	1-butanol butyl acetate toluene ethyl benzene xylenes aromatic hydrocarbon solvent TOC	isopropanol isobutanol 1-butanol butyl acetate ethyl acetate toluene ethyl benzene xylenes aromatic hydrocarbon solvent TOC	**high acute toxicity** at test concentrations 12.5 and 25 % (I-% 6-89)	**high acute toxicity** (83 %)* (TU 22-48)	-TOC and DOC concentrations in all studied wastes exceeded the limit values for non-hazardous and hazardous waste landfills, **no leaching limit values are set for individual organic compounds**
water-curtain booth paint residues (G and H)	butyl acetate toluene ethyl benzene xylenes aromatic hydrocarbon solvent TOC	isopropanol isobutanol 1-butanol butyl acetate ethyl acetate toluene ethyl benzene xylenes TOC	**high acute toxicity** at test concentrations 12.5 and 50 % (I-% 11-100)	**significant acute toxicity** (78 %)* (TU 4.4-8.1)	**-combined leaching and toxicity results** showed clearly that the **DOC leached** from the wastes was **toxic** and multi-stage leaching test results of the varnish residue (I) and the resin waste **reflected the solubility of organic compounds over hundreds of years**
water-curtain booth varnish residue (I)	isobutanol 1-butanol butyl acetate toluene ethyl benzene xylenes TOC	isobutanol toluene ethyl benzene xylenes TOC	**high acute toxicity** (EC50 3 %, TU 33)	**very high acute toxicity** (88-100 %)* (TU 249-1250)	
Proposal for a combined solid-phase and liquid-phase ecotoxicity approach: Ecotoxicity of solid waste determined with lettuce seed germination test Ecotoxicity of SFS-EN 12457-2 leaching test eluates with luminescent bacteria test, RET assay and onion root elongation test					

* The closer the weighted class score percentage value to 100 %, the lower the variability in the biological responses of the test results of the test battery (luminescent bacteria test, RET assay and *Allium cepa* test and/or ToxiChromoPAD)

4.3 Environmental hazard of oil–contaminated soils (IV)

The environmental hazard classification of excavated oil–contaminated soil from a former petrol station was carried out using chemical and ecotoxicological analyses. To date, there is no uniform procedure or standards for landfill disposal of excavated oil-contaminated soils. Chemical classification was carried out comparing total concentrations of key hazardous substances in the soil samples with the limit values set for hazardous wastes in the EU and Finnish waste legislation (waste decree 1128/2001). Ecotoxicological classification of the oil-contaminated soil samples was carried out using a solid-phase and liquid-phase approach. The sensitivity of terrestrial and aquatic ecotoxicity assays was compared, and the applicability of three different extraction procedures (EN-12457, NEN 7349 and a batch extraction with a low L/S ratio 2:1 and short contact time 1h) in determining the aquatic toxicity of the soil eluates was evaluated.

4.3.1 Chemical and ecotoxicological classification of solid oil-contaminated soil samples

The key hazardous substances in the oil-contaminated soil samples were analyzed and the concentrations were compared with the limit values set for hazardous wastes in the EU and Finnish waste legislation (waste decree 1128/2001). The order of the samples according to decreasing concentrations of oil was as follows: 2 > 5 > 6 > 4 > 1 and 3 and BTEX concentrations: 2 > 5 > 4 > 1 > 6 > 3 (Table 23). Based on the Finnish waste legislation demands, the oil-contaminated soil samples were classified as hazardous if the mineral oil concentration in soil was over 10 000 mg/kg, or if the benzene concentration in soil exceeded the limit value of 1000 mg/kg. Only one soil sample (2) exceeded the limit value set for mineral oil (Table 23). The limit values for hazardous waste for BTEX compounds were not exceeded in the soil samples (see Table 15). None of the soil samples exceeded the limit values of TOC content of wastes set for a non-hazardous (50 000 mg/kg) or hazardous waste (60 000 mg/kg) landfill (Table 23).

Table 23. Concentrations of petroleum products in the oil-contaminated soil samples presented in mg/kg. Concentrations, which exceeded the limit values set for hazardous waste, are presented in bold.

Sample	Oil	MTBE	TAME	Benzene	Toluene	Ethyl benzene	m+p-Xylenes	o-Xylene	Sum of BTEX	TOC
1	2500	3.2	5.2	0.5	42	7.2	270	110	430	13000
2	**12000**	250	260	120	1100	170	690	230	2310	28000
3	2500	7.9	4.3	1.7	65	19	144	57	287	17000
4	2600	36	33	10	190	42	180	63	485	15000
5	6200	9.2	62	23	520	100	450	163	1256	9500
6	5500	0.01	5.3	3.5	110	34	170	63	381	16000
7 unpolluted control soil	nd	nd	nd	nd	0.01	<0.01	0.01	<0.01	0.01	2100

nd = not detected, MTBE = methyl-*tert*-butylether, TAME = metyl-*tert*-amylether

The ecotoxicity of oil-contaminated soil samples was determined with plant seed germination tests and the Enchytraeid worm (*E. albidus)* mortality and reproduction tests, and compared with the concentrations of the key hazardous substances (Tables 23 and 24). The ecotoxicity of the unpolluted control soil (sample 7) was not studied. The soil samples 2 and 3 were the most toxic to all the test organisms (Table 24). The concentrations of petroleum hydrocarbons were the highest in sample 2 and the lowest in sample 3 (Table 23). The other soil samples with oil concentrations of 2500–6200 mg/kg had no or only slightly adverse effects on

terrestrial organisms, with one exception, the *E. albidus* reproduction test (Table 24). Seed germination tests were less sensitive than the *E.albidus* assays. The order of the samples according to decreasing toxicity in EC50 values to reproduction of *E.albidus* was 3 > 2 > 6 > 5 > 4 > 1 and to seed germination: 3 > 2 > 6 > 1> 5, 4 (Table 24). It was reasonable to conclude that sample 3 contained unknown hazardous substances not identified with the chemical analyses of key compounds (Tables 23 and 24). The difference in the chemical and ecotoxicological classification order of the samples (e.g. sample 3) showed that terrestrial tests should be used in combination with chemical analyses for identifying whether the hazardous substances in the soil samples were present at an ecotoxic level (Table 25).

Table 24. Toxicity of the soil samples contaminated by petroleum products to terrestrial organisms. The original data is presented in Fig. 2 and 3 in Paper IV.

Soil sample	1	2	3	4	5	6
Test soil concentration, dry weight %	Seed germination of wheat (*Triticum aestivum*) , inhibition (%)					
50	10	25	21	5	5	10
100	5	85	89	0	5	15
	Seed germination of cress (*Lepidium sativum*), inhibition (%)					
50	0	7	31	0	0	0
100	3	37	76	0	0	7
	Seed germination of lettuce (*Lactuca sativa*), inhibition (%)					
50	0	0	48	0	0	4
100	0	34	83	0	0	7
	Survival of Enchytraeid worms (*Enchytraeus albidus*) , inhibition (%)					
100	93	100	100	53	77	47
	EC50 value dry weight %					
Survival of *E.albidus*	>50	31	28	>50	>50	>50
Reproduction of *E.albidus*	23	11	8	22	21	18

4.3.2 Applicability of combined leaching and ecotoxicity tests for petroleum products in soils

The applicability of three different extraction procedures (EN-12457-2, NEN 7349 and a batch extraction with a low L/S ratio 2:1 and contact time of 1h) in determining the environmental hazard of petroleum products in contaminated soils (samples 2, 4 and 6) was evaluated. The volatilization and anticipated low solubility of petroleum hydrocarbons in water had implications for the chemical analyses of the batch leaching test eluates. Petroleum hydrocarbons adsorbed onto the walls of test vessels and were emulsified with water, causing unreliable analytical results. However, these three different extraction methods could be used to screen the environmental impacts of petroleum products leaching from the soil samples by measuring the ecotoxicity with acute toxicity tests (Table 5 in Paper IV). Only the water leachable fractions of the petroleum products from soil sample 2 were toxic to all the test biota (*V.fischeri*, *L.minor* and *A.cepa*). Toxicity of the soil samples (2, 4 and 6) decreased gradually during the five-stage batch leaching test, but the last eluate of the sample 2 was still toxic (Table 5 in Paper IV). The different liquid to solid-ratio (L/S) of the extractions did not affect the response of the luminescent bacteria *(Vibrio fischeri)*. A modification of the ISO/TC 190 soil quality method using an L/S ratio of 2:1 was the more appropriate extraction method for the other toxicity tests: onion root elongation and *Lemna minor* growth inhibition tests. For ecotoxicity tests, it was proposed to use either simple water extraction (L/S 2:1, contact time 1 h) or batch leaching test (EN-12457-2). Juvonen *et al.* (2000) have earlier shown that the extraction method using the final L/S ratio of 1.5:1 and a short contact time was suitable for aquatic ecotoxity tests on oily compost wastes.

4.3.3 Ecotoxicity tests to complement chemical analyses in hazard classification of oil-contaminated soils

The use of ecotoxicity tests to complement chemical analyses in hazard classification of oil-contaminated soils was studied. The ecotoxicity test results suggested that both a solid- and liquid-phase approach were needed to complement chemical analyses in the hazard classification of excavated soils (Table 25). The sensitivity of toxicity tests to petroleum hydrocarbons was greater with terrestrial than with aquatic tests. The Enchytraeid worm (*E. albidus)* reproduction and survival tests were more sensitive terrestrial tests than plant seed germination assays for oil-contaminated soils. The reproduction test was more sensitive than the mortality test, because it is a chronic terrestrial test (Didden and Römbke 2001). However, according to this study, the reproduction test was regarded as unsuitable for use in waste hazard classification because it was too laborious and costly for routine use. Instead, it was proposed for use in risk assessment for contaminated soil sites. The survival of *E. albidus* and the wheat seed germination tests were useful in the waste hazard classification of excavated soils to complement chemical analyses of the key hazardous substances. The combined batch water extractions and ecotoxicity tests were needed for oil-contaminated soils to evaluate the toxic effects of the most water-soluble substances (e.g. MTBE and TAME) leaching from the soils to the aquatic environment (Table 25). The luminescent bacteria test was considered as the most advantageous screening method for basic characterization and quality monitoring of excavated oil-contaminated soil samples in deciding on their acceptance to landfills. As also stated by Juvonen *et al.* (2000), the luminescent bacteria test was rapid and sensitive as a screening test for monitoring the composting process of oily waste from both the waste suspensions and water eluates.

Table 25. The chemical and ecotoxicological classification of oil-contaminated soils and a proposal for a combined solid-phase and liquid-phase ecotoxicity approach for hazard classsification.

Waste	Key hazardous substances samples in decreasing order of total concentrations in soil	Ecotoxicological classification samples in decreasing order of toxicity		Chemical versus ecotoxicological classification
		Solid	Eluate	
Six soil samples collected at a former petrol station	oil concentration: **2** > 5 > 6 > 4 >1 and **3** sum of BTEX compounds: **2** > 5 > 4 > 1 > 6 > **3** TOC **2** > **3** > 6 >4 > 1 > 5	survival of *E.albidus* **3** > **2** > 1 > 5 > 4 > 6 **acute toxicity** (TU 3.2-3.6) reproduction of *E.albidus* **3** > **2** > 6 > 5 > 4 > 1 (TU 4.3 -12.5) **chronic toxicity** seed germination: **3** > **2** > 6 > 1 > 5, 4 **acute toxicity** (I-% 34-89)	luminescent bacteria test and onion root elongation test **2** > 4 > 6 **sample 2 had high acute toxicity** (TU 4-67)	-according to the total concentrations of the key hazardous substances in soils only sample 2 was classified as hazardous -all the samples had chronic toxicity samples 2 and 3 were the most toxic in both terrestrial and aquatic environment
Proposal for a combined solid-phase and liquid-phase ecotoxicity approach: Ecotoxicity of solid samples: wheat seed germination test survival test of *E. albidus* Eluates of batch leaching test (EN-12457 L/S 10): luminescent bacteria test				

4.4 Provisional hazard screening approach for solid wastes

A provisional hazard screening approach for solid wastes using combined chemical and ecotoxicological classification was proposed in order to improve waste hazard classification (Fig. 6). Currently, the evaluation of the ecotoxic property (H14) of wastes is based on the total concentrations of pollutants (Hazardous Waste Directive 1991/689/EC). The proposed criteria for waste acceptance of the EU Landfill Directive (2003/31/EC) do not set any limit values for individual leachable organic compounds. The only possibility to classify hazardous properties of organic compounds in solid wastes is based on the total organic carbon content in the solid matter or the leached amount of TOC in the leaching test eluates.

It was proposed to carry out screening of the environmental hazard of complex chemical mixtures in solid wastes using (1) chemical analyses of total concentrations of the key hazardous substances based on the background information of the wastes, (2) analysis of the TOC content in the solid material, and (3) ecotoxicity assays of solid matter using the seed germination test with wheat or lettuce (Fig. 6). In addition, the proposed terrestrial toxicity method for basic characterization of oil-contaminated soils was the Enchytraeid worm (*E. albidus)* survival test. Quartz sand was used as a control sample and dilution media for solid organic wastes, and OECD control soil for oil-contaminated soil samples (III–V).

The column test was used for leaching experiments of predominantly inorganic wastes when the annual amount of regularly produced waste exceeded 250 t (I and Table 6). pH static methods (availability test NEN 7341) needed to be performed for inorganic wastes when the leaching of substances was expected to increase due to changes in the surrounding pH (I). Use of the European batch leaching test method (EN-12457-2) was proposed for determining the chemical and ecotoxicological classification of substances leached out from inorganic and organic wastes and soils. The minimum requirement for eluate analyses should consist of: (1) potentially hazardous inorganic substances, (2) DOC concentrations, and (3) aquatic toxicity determined with a battery of ecotoxicity tests (Fig. 6). For waste management purposes, it was considered that the battery of toxicity tests should consist of cost-effective methods that are simple enough to perform, and methods in which the volume required for analyses is minimized to ≤ 100 ml. Toxicity tests should also be sensitive to both inorganic and organic substances. According to this study, the luminescent bacteria test, MetPLATE and ToxiChromotests, RET assay and onion root elongation test were the best choice. For quality control and monitoring purposes of the same waste type, it was considered sufficient to use one of the most sensitive toxicity tests of the battery (Fig. 6).

The results of this study illustrate that the criteria for both waste classification and management should also be improved by setting the criteria and limit values for ecotoxicity test results. Some efforts have been made in Europe to propose a test procedure and limit values to evaluate the ecotoxic property (H14) of hazardous wastes (Ferrari *et al.* 1999, Lapa *et al*. 2002a, Seco *et al*. 2003). In this study, the criteria for the evaluation of toxicity test results were proposed, modified from the toxicity classification system (TCS) first introduced by Persoone (1999, cited at Lapa *et al*. (2002a):

1. Waste is considered as **non-toxic**, if all the aquatic test results are TU ≤ 2 and inhibition for a strongest test dilution in aquatic and/or the terrestrial test dilution is I $\leq$ 20 %.
2. Waste has **acute toxicity**, if at least one of the aquatic test results is $2 \leq TU \leq 10$, and/or inhibition in the terrestrial test for the strongest test dilution is $20 \leq I\text{-}\% \leq 50$
3. Waste has **high acute toxicity**, if at least one of the aquatic test results is $10 \leq TU \leq$ 100, and/or inhibition in the terrestrial test for the strongest test dilution is I ≥ 50 %

4. Waste has **very high acute toxicity**, if all the aquatic test results are TU ≥ 100, and inhibition in the terrestrial test for the lowest test dilution is I ≥ 50 %
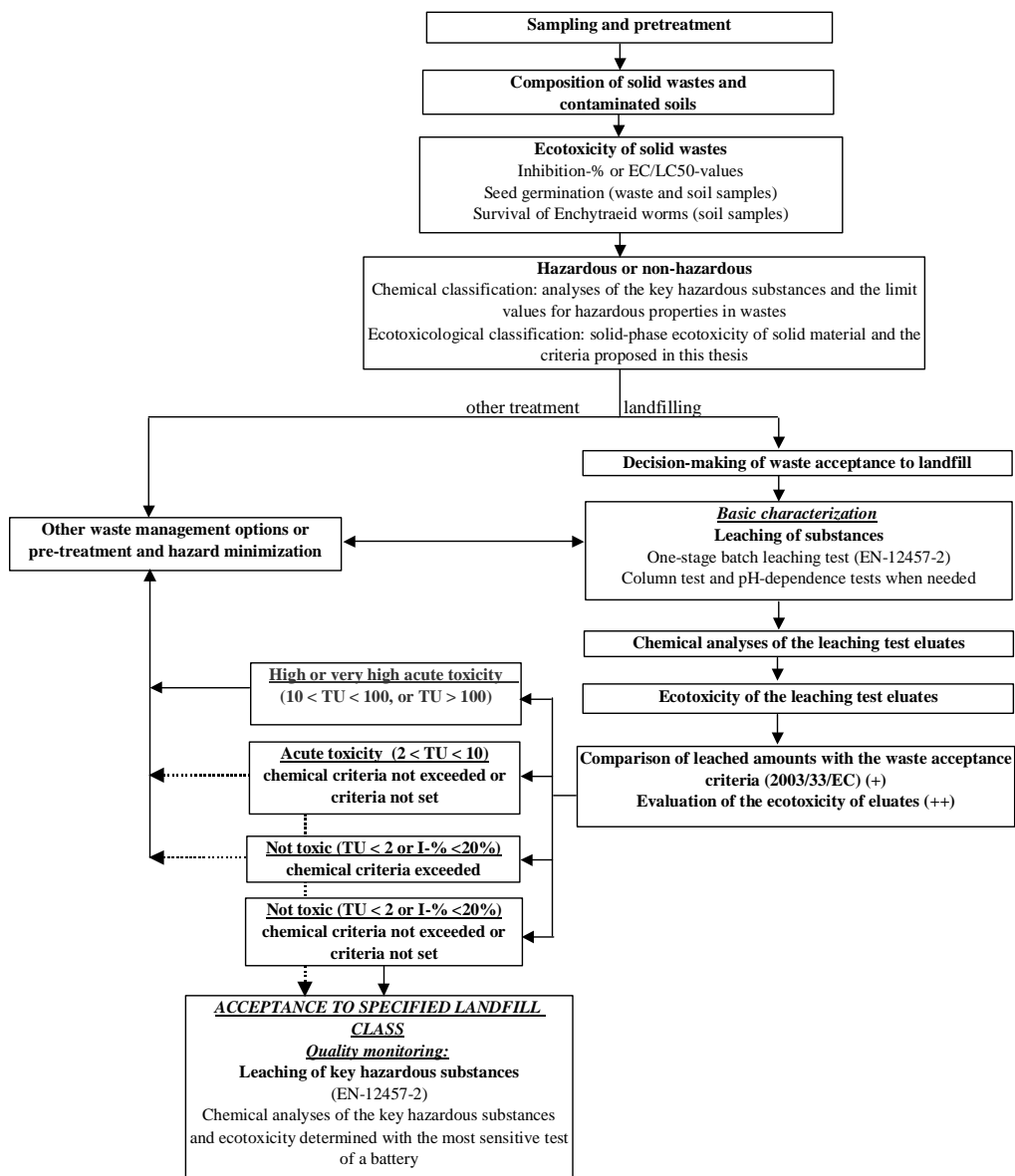
Eluate analysis: (based on the background knowledge of waste)
(+) minimum requirement for analyses of inorganic compounds: arsenic and heavy metals, chloride, fluoride, sulphate, and for analyses of organic compounds: DOC content
(++) Acute toxicity: e.g. the luminescent bacteria test, RET assay and onion root elongation test (and/or MetPLATE test or ToxiChromotest)

Figure 6. Proposed hazard screening approach for wastes or contaminated soils when deciding on their waste management.

5 CONCLUSIONS

A new combined leaching and ecotoxicity test approach was developed for the environmental hazard assessment of solid wastes. In addition, criteria for the evaluation of toxicity test results were proposed because there is at present no specified limit value in the EU for the ecotoxic property (H14) that could be used to evaluate the ecotoxicity of solid wastes or their eluates.

The results of this thesis showed that environmental hazard assessment of the solid wastes studied based only on chemical classification and the available limit values was highly unlikely to be sufficient (I–V). The organic wastes from the furniture and resin industries were not classified as hazardous when the concentrations of known key hazardous substances were compared with the limit values set for hazardous wastes. However, the lettuce seed germination tests clearly showed that these wastes should be classified ecotoxic (III and V). The ecotoxicity of the paint residues produced in different furniture factories and soil samples contaminated by petroleum products also showed that a more relevant estimation of the environmental hazard of the same waste type was attained using solid-phase ecotoxicity assays as opposed to total concentrations of known key hazardous substances (IV and V). It was proposed to determine the ecotoxicity of organic wastes using the lettuce seed germination test. The proposed terrestrial toxicity tests for oil-contaminated soils were the wheat seed germination test and Enchytraeid worm (*E. albidus)* survival test (IV).

The results of this study indicated that the release of contaminants should be determined in order to predict the long-term environmental impacts of solid wastes. A combination of column, batch leaching tests and an availability test could be used to describe the leaching patterns of key hazardous substances from predominantly inorganic wastes. The leaching profiles showed that it was important to perform an availability test for inorganic wastes in order to identify their resistance to acid attack (ANC), and how the pH affects the leachability of substances (I and II). The batch leaching tests (EN-12457 and NEN 7349) intended for inorganic substances were effective enough to evaluate the easily water-leachable fraction of volatile organic compounds from paint residues and resin waste (III and V).

This study also demonstrated that a combined chemical and ecotoxicological classification of substances leached out from inorganic and organic wastes and soils should be determined using the European batch leaching test method (EN-12457-2). Only then can the ecotoxicity test results be compared with chemical analyses to improve the hazard classification when selecting the best waste management alternative. The minimum requirement for eluate analyses should consist of: (1) potentially hazardous inorganic substances, (2) DOC concentrations, and (3) aquatic toxicity determined with a battery of ecotoxicity tests. According to this study, the luminescent bacteria test, MetPLATE and ToxiChromotests, RET assay and onion root elongation test would be the best choice.

The differences between the chemical and ecotoxicological classification results emphasized the need for ecotoxicity tests to complement chemical analyses. The need for an ecotoxicological classification of the leaching test eluates for wastes containing easily leachable inorganic substances, i.e. jarosite, was not as important as for fly ash with moderately high acid neutralizing capacity and a relatively slow release profile of a key hazardous substance, i.e. zinc (I and II). Jarosite was classified as hazardous with both chemical and ecotoxicological analyses. In contrast, the chemical classification of the leaching test eluates showed that fly ash could be deposited in a non-hazardous waste landfill but the eluates were classified as having very high (TU>100) or high acute toxicity (10<TU<100) with a battery of water flea immobilization, algal growth inhibition, luminescent bacteria, and bacterial (*P. putida*) growth inhibition tests.

The chemical classification of complex mixtures of organic substances leaching from solid wastes and soil samples was difficult due to the lack of leaching limit values in the EU criteria for waste acceptance to landfills. Comparison of the concentrations of individual compounds with a database of their toxicity did not give any information on the overall toxicity of complex mixtures of substances leaching from wastes without actually measuring toxicity from the waste eluates. The screening of the environmental hazard of batch leaching test eluates could be done using a battery of toxicity tests and DOC concentrations (I-III and V). The organic waste eluates from the furniture and resin industries contained unknown toxic compounds not identifiable with quantitative chemical analyses. When the DOC concentrations and the toxicity results from the luminescent bacteria, onion root elongation and RET tests were transformed to logarithmic values, the results showed relatively good linear correlation (r= 0.7061–0.8835).

The results of this thesis demonstrated that toxicity tests provide a promising, more relevant and cost-effective tool for the environmental hazard assessment of solid wastes and their leachates than chemical analyses of known key hazardous substances alone.

6 REFERENCES

Ahtiainen, J. 2003. Microbiological Tests and Measurements in the Assessment of Harmful Substances and Pollution. Academic Dissertation. Faculty of Agriculture and Forestry of University of Helsinki. 51pp.

Atwater, J.W., Jasper, S., Mavinic, D.S, Koch, F.A. 1993. Experiments using Daphnia to measure landfill leachate toxicity. Water Res. 17, 1855–1861.

Békaert, C., Ferrier, V., Marty, J., Pfohl-Leszkowicz, A., Bispo, A., Jourdain, M.J., Jauzein, M., Lambolez-Michel, L., Billard, H. 2002. Evaluation of toxic and genotoxic potential of stabilized industrial waste and contaminated soils. Waste Manage. 22, 241–247.

Betton, C.I. 1994. Oils and Hydrocarbons. In: Calow, P. (ed.), Handbook of Ecotoxicology, vol. 2. Blackwell Scientific Publications. University Press, Cambridge. Great Britain. pp. 244–263.

Bitton, G., Jung, K., Koopman, B. 1994. Evaluation of a microplate assay specific for heavy metal toxicity. Arch. Environ. Contam. Toxicol. 27, 25–28.

Brouwer, H., Murphy, T.P., McArdle, L. 1990. A sediment contact bioassay with *Photobacterium phosphoreum*. Environ. Toxicol. Chem. 9, 1353–1358.

Calow, P. (ed.) 1993. General Principles and Overview. In: Handbook of Ecotoxicology vol. 1, Blackwell Scientific Publications. University Press, Cambridge. Great Britain. pp. 1-5.

CEN/TC 292- Work Programme 2004. Cited at 12.5.2004. Available at: http://www.cenorm.be/CENORM/BusinessDomains/TechnicalCommitteesWorkshops/CENT echnicalCommittees/CENTechnicalCommittees.asp.

Chapman, P., M. 1995. Ecotoxicology and pollution - key Issues. Marine Pollution Bulletin 31, 167–177.

Clausen, A.C. 2000. CCA Removal from treated wood using a dual remediation process. Waste Manage. Res. 18, 485–488.

Clément, B., Persoone, G., Janssen, C., Le Du-Delepierre, A. 1996. Estimation of the hazard of landfills through toxicity testing of leachates. I. Determination of leachate toxicity with a battery of acute tests. Chemosphere 33, 2303–2320.

Clément, B., Janssen, R.C., Le Du-Delepierre, A. 1997. Estimation of hazard of landfills through toxicity testing of leachates. II. Comparison of physico-chemical characteristics of landfill leachates with their toxicity determined with a battery of tests. Chemosphere 35, 2783–2796.

Comans, R.N.J. (ed.) 2001. Development of standard leaching tests for organic pollutants in soils, sediments, and granular waste materials. Final report ECN-01-121. ECN Fossil fuels. Emission characterisation & reduction. Netherlands. 163 pp.

Coya, B., Maranon, E., Sastre, H. 2000. Ecotoxicity assessment of slag generated in the process of recycling lead from waste batteries. Resources, Conservation and Recycling 29, 291–300.

Dahlbo, H. 2002. Jätteen luokittelu ongelmajätteeksi – arvioinnin perusteet ja menetelmät (Classification of waste as hazardous waste – the basis and methods for evaluation). Environment Guide 98. Finnish Environment Institute. Helsinki. Finland. 160 pp. (In Finnish)

Davison, R.L., Natusch, D.F.S., Wallace, J.R. 1974. Trace elements in fly ash dependence of concentration on particle size. Environ. Sci. Technol. 8, 1107–1112.

De Jonge, H., Freijer, J.I., Verstraten, J.M., Westerveld, J. 1997. Relation between bioavailability and fuel oil hydrocarbon composition in contaminated soils. Sci. Technol. 31, 771–776.

Devare, M., Bahadir, M. 1994. Biological monitoring of landfill leachate using plants and luminescent bacteria. Chemosphere 28, 261–271.

Didden, W., Römbke, J. 2001. Enchytraeids as indicator organisms for chemical stress in terrestrial ecosystems. Ecotoxicol. Environ. Saf. 50, 25–43.

Dorn, P.B., Vipond, T.E., Salanitro, J.P., Wisniewski, H.L. 1998. Assessment of the acute toxicity of crude oils using earthworms, Microtox, and plants. Chemosphere 37, 845–860.

Dorn, P.B., Salanitro, J.P. 2000. Temporal ecological assessment of oil contaminated soils before and after bioremediation. Chemosphere 40, 419–426.

Dutka, B.J., McInnis, R., Jurkovic, A., Liu, D. 1996. Water and sediment ecotoxicity studies in Temuco and Rapel river basin, Chile. Environ. Toxicol. Water Qual. 11, 237–247.

EPA, 1990. Method 1311 Toxicity Characterization procedure (TCLP). Federal Register. Rules and Regulations. Vol. 55 (61). pp. 11863–11877.

EPA method 3051. Microwave assisted acid digestion of aqueous samples and extracts for total metals analysis by FLAA, furnace AA, ICP spectroscopy and ICP/MS spectrometry. Available at: http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3051.pdf.

Fernández-Sempere, J., Barrueso-Martínez, M.L., Font-Montesinos, R., Sabater-Lillo, M.C. 1997. Characterization of tannery wastes comparison of three leachability tests. J. Hazard. Mater. 54, 31–45.

Ferrari, B., Radetski, C.M., Veber, A-M., Ferard, J-F. 1999. Ecotoxicological assessment of solid wastes: A combined liquid- and solid-phase testing approach using a battery of bioassays and biomarkers. Environ. Toxicol. Chem. 18, 1195–1202.

Fiskesjö, G. 1997. Allium test for screening chemicals. In: Wang W. (ed), Plants for Environmental Studies, CRC Lewis Publishers. New York. pp. 307–334.

Font, R., Gomis, V., Fernandez, J., Sabater, M.C. 1998. Physico-chemical characterization and leaching of tannery wastes. Waste Manage. Res. 16, 139–149.

Forsius, M., Kämäri, J., Kortelainen, P., Mannio, J., Verta, M., Kinnunen, K. 1990. Statistical lake survey in Finland: Regional Estimates of lake acidification. In: Kauppi, P., Anttila, P., Kenttämies, K. (eds.). Acidification in Finland. Spinger-Verlag Berlin Heidelberg. pp. 759-781.

Fällman, A-M., Aurell, B. 1996. Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. Sci. Total Environ. 178, 71–84.

Fällman, A-M. 1997. Performance and design of the availability test for measurement of potentially leachable amounts from waste materials. Environ. Sci. Technol. 31, 735–744.

Goergen, M.G., Murshak, V.F., Roettger, P., Murshak, I., Edelman, D. 1992. ICP-MS analysis of toxic characteristics leaching procedure (TCLP) extract: Advantages and disadvantages. Atomic Spectroscopy 13, 11–18.

Hage, J.L.T., Mulder, E. 2004. Preliminary assessment of three new European leaching tests. Waste Manage. 24, 165–172.

Hingston, J.A., Collins, C.D., Murphy, R.J., Lester, J.N. 2001. Leaching of chromated copper arsenate wood preservatives: a review. Environ. Pollut. 111, 53–66.

Hirner, A.V., Pestke, F.M., Busche, U., Eckelhoff, A. 1998. Testing contaminant mobility in soils and waste materials. J. Geochem. Expl. 64, 127–132.

Ibánêz, R., Andrés, A., Viguri, J.R., Ortiz, I., Irabien, J.A. 2000. Characterisation and management of incinerator wastes. J. Hazard. Mater. A79, 215–227.

ISO 16837. Soil quality: Effects of pollutants on enchytraeidae (*Enchytraeus sp.*) Determination of effects on reproduction and survival. Geneve: International Organization for Standardisation.

Janusa, M.A., Bourgeois, J.C., Heard, G.E., Kliebert, N.M., Landry, A.A. 1998. Effects of particle size and contact time on the reliability of toxicity characteristic leaching procedure for solidified/stabilized waste. Microchem. J. 59, 326–332.

Jenner, H.A., Janssen-Mommen, J.P.M. 1989. Phytomonitoring of pulverized fuel ash leachates by the duckweed *Lemna minor*. Hydrobiologia 188/189, 361–366.

Juvonen, R., Martikainen, E., Schultz, E., Joutti, A., Ahtiainen, J., Lehtokari, M. 2000. A battery of toxicity tests as indicators of decontamination in composting oily wastes. Ecotoxicol. Environ. Saf. 47, 156–166.

Kaiser, K.L.E., Devillers, J. (eds.). 1994. Ecotoxicity of Chemicals to *Photobacterium phosphoreum*, Vol. 2. Gordon and Breach Science Publishers. OPA (Amsterdam) B.V. pp. 114–766.

Karius, V., Hamer, K. 2001. pH and grain-size variation in leaching tests with bricks made of harbour sediments compared to commercial bricks. Sci. Total Environ. 278, 73–85.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., Christensen, T.H. 2002. Present and long-term composition of MSW landfill leachate: a review. Critical reviews in Environ. Sci. Technol. 32, 297-336.

Knobeloch, L., Blondin, G., Harkin, J.M., 1994. A rapid bioassay for toxicity assessment of chemicals: Reverse electron transport. Environ. Toxicol. Water Qual. 9, 231–234.

Kõs, P., Gorzo, G., Suranyi, G., Boberly, G. 1995. Simple and efficient method for isolation and measurement of Cyanobacterial hepatoxins by plant tests (*Sinapis alba L.*). Anal. Biochem. 225, 49-53.

Kylefors, K., Andreas, L., Lagerkvist, A. 2003. A comparison of small-scale, pilot-scale and large-scale tests for predicting leaching behaviour of landfilled wastes. Waste Manage. 23, 45–59.

LaGrega, M.D., Buckingham, P.L., Evans, J.C. (eds.) 2001. Hazardous Waste Management 2nd edition. Environmental Resources Management. Mc-Graw Hill. Singapore. pp. 812–824.

Laine-Ylijoki, J., Mroueh, U.M., Vahanne, P., Wahlström, M., Vestola, E., Salonen, S., Havukainen, J. 2005. Yhdyskuntajätteiden termisen käsittelyn kuonista ja tuhkista hyötykäytettäviä ja loppusijoitettavia tuotteita - kansainvälinen esiselvitys (Current International Status of MSW Ashes and Slags). VTT bulletin 2291. Espoo. 83 pp. + App. 4 pp. (In Finnish)

Lanno, R., Wells, J., Conder, J., Bradham, K., Basta, N. 2004. The bioavailability of chemicals in soil for earthworms. Ecotoxicol. Environ. Saf. 57, 39–47.

Lapa, N., Barbosa, R., Morais, J., Mendes, B., Mėhu J., Santos Oliviera, J.F. 2002a. Ecotoxicological assessment of leachates from MSWI bottom ashes. Waste Manage. 22, 583–593.

Lapa, N., Santos Oliviera, J.F., Camacho, S.L., Circeo, L.J. 2002b. An ecotoxic risk assessment of residue materials produced by the plasma pyrolysis/vitrification (PP/V) process. Waste Manage. 22, 335–342.

Lappalainen, J., Juvonen, R., Vaajasaari, K., Karp, M. 1999. A new flash method for measuring the toxicity of solid and coloured samples. Chemosphere 38, 1069–1083.

Lappalainen, J. 2001. Improved Use and New Applications of Luminescent Bacteria. Academic Dissertation. University of Turku, Finland. 54pp.

Latif, M., Zach, A. 2000. Toxicity of treated residual wastes in Austria using different types of conventional assays and cost-effective microbiotests. In: Persoone, G., Janssen, C., De Coen, W. (Eds.). New Microbiotests for Routine Toxicity Screening and Biomonitoring. Kluwer Academic/Plenum Publishers. New York. pp. 367–383.

Lebow, S.T., Foster, D.O., Lebow, P.K. 1999. Release of copper, chromium and arsenic from treated southern pine exposed in seawater and freshwater. For. Prod. J. 49, 80–89.

Lecuyer, I., Bicocchi, S., Ausset, P., Lefevre, R. 1996. Physico-chemical characterization and leaching of desulphurization coal fly ash. Waste Manage. Res. 14, 15–28.

Maxam, G., Rila, J.-P., Dott, W., Eisentraeger, A. 2000. Use of bioassays for assessment of water extractable ecotoxic potential of soils. Ecotoxicol. Environ. Saf. 45, 240–246.

Mclean, J.E., Bledsoe, B.E. 1992. Behaviour of metals in soils. Ground water issue. EPA report/540/S-92/018. 20 pp.

Mearns, A.J. 1998. Oil spill treating agents: validation, and analysis of Salmonella mutagenicity test, In: Wells, P.G., Lee, K., Blaise, C. (eds.). Microscale Testing in Aquatic Toxicology. CRC Press LLC. United States of America. pp. 575-590.

NEN 7341, 1995. Leaching characteristics of solid earthy and stony building materials. Leaching tests. Determination of the availability of inorganic components for leaching. Nederlands Normalisatie-Instituut. 11 pp.

NEN 7343, 1995. NEN 7343– Leaching characteristic of solid earthy and stony building and waste materials. Leaching test. Determination of the leaching of inorganic components from granular materials with the column test. Delft: Nederlands Normalisatie-Instituut. 11 pp.

NEN 7349, 1995. Leaching characteristic of solid earthy and stony building and waste materials. Leaching test. Determination of the leaching of inorganic components from granular materials with the cascade test. Delft: Nederlands Normalisatie-Instituut, 11 pp.

Nikunen, E., Leinonen, R., Kemiläinen, B., Kultamaa, A. 2000. Environmental properties of chemicals vol. 1. Environment guide 71. Finnish Environment Institute. EDITA. Helsinki. 1165 pp.

OECD. 1984. Earthworm acute toxicity tests (no. 207); and Terrestrial plants, growth test (no. 208) adopted April 4, 1984. In OECD Guideline for testing of chemicals, OECD, Paris, France.

Official Journal of the European Communities 2000. 2000/532/EC: Commission Decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste. Official Journal L 226, 06/09/2000. 0003–0024. Cited at 11.12.2003. Available at: http://europa.eu.int/eur-lex/en/lif/reg/en_register_15103030.html

Official Journal of the European Communities 2003. 2003/33/EC: Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Official Journal L 11, 16/01/2003. 0027–0049. Cited at 11.01.2004. Available at: http://europa.eu.int/eur-lex/en/lif/reg/en_register_15103030.html.

Pantsar-Kallio, M., Manninen, P. 1997. Speciation of mobile arsenic in soil samples as a function of pH. Sci. Total Environ. 204, 193–200.

Paxéus, N. 2000. Organic compounds in municipal landfill leachates. Wat. Sci. Technol. 42 (7-8), 323–333.

Peijnenburg, W., Sneller, E., Sijm, D., Lijzen, J., Traas, T., Verbruggen, E. 2002. Implementation of bioavailability in standard setting and risk assessment. JSS– J Soils & Sediments 2, 169–171.

Pereira, C.F., Rodriguez-Pinero, M., Vale, J. 2001. Solidification/stabilization of electric arc furnace dust using coal fly ash. Analysis of the stabilization process. J. Hazard. Mater. B82, 183–195.

Persoone, G. 1998. Development and first validation of a "stock–culture free" algal microbiotest: the algaltoxkit. In: Wells, P.G, Lee, K., Blaise, C. (eds.). Microscale Testing in Aquatic Toxicology. CRC Press LLC. United States of America. pp. 311-323.

Persoone, G. 1999. Pollution Classification systems. October 1999. 6p.

Persoone, G., Janssen, C., De Coen, W. (Eds.) 2000. New Microbiotests for Routine Toxicity Screening and Biomonitoring. Kluwer Academic/Plenum Publishers. New York. 550 pp.

Peterson, S.A., Greene, J.G., Miller, W.M. 1990. Toxicological assessment of hazardous waste samples extracted with deionised water or sodium acetate (TCLP) leaching media. In: Friedman, D. (Ed.). Waste Testing and Quality Assurance Vol. 2. American Society for Testing and Materials (ASTM STP 1062). Philadelphia P.A. pp. 107–129.

Plaza, G., Nalecz-Jawecki, G., Ulfig, K., Brigmon, R.L. 2005. The application of bioassays as indicators of petroleum-contaminated soil remediation. Chemosphere 59, 289–296.

Põllumaa, L. 2004. Evaluation of Ecotoxicological Effects Related to Oil Shale Industry. Academic Dissertation. Tallinn University of Technology. Estonia. 50 pp.

Read, H., Harkin, J.M., Gustavson, K.E. 1998. Environmental applications with submitochondrial particles. In: Wells, P.G, Lee, K., Blaise, C. (eds.). Microscale Testing in Aquatic Toxicology. CRC Press LLC. United States of America. pp. 31–52.

Rixey, W.G., Garg, S., Nie, Y. 1999. Comparison of the fixed-bed and batch leaching characteristics of aromatic compounds in residually trapped crude oils and oily wastes. J. Hazard. Mater. B64, 137–156.

Rood, G.A., Broekman, M.H., Aalbers, Th.G. 1994. Investigating a leaching test for PCBs and organochlorine pesticides in waste and building materials. In: Gourmans, J.J.J.M., Van der Sloot, H.A., Aalbers, Th. G. (eds.). Environmental Aspects of Construction with Waste Materials. Elsevier Science B.V., Amsterdam. pp. 271‒280.

Ruiz, M.C., Viguri, J., Andrés, A., Coz, A., Irabien, A. 2002. Lagooning of wastes from iron activities: Characterisation and evaluation. Fresen. Environ. Bull. 11, 921–925.

Ruokolainen, M., Pantsar-Kallio, M., Haapa, A., Kairesalo, T. 2000. Leaching, runoff and speciation of arsenic in a laboratory mesocosm. Sci. Total Environ. 258, 139–147.

Sabater, M.C., Martínez, M.A. 2001. Toxicity and hazardous properties of solvent base adhesive wastes. Waste Manage. Res. 19, 442–449.

Salanitro, J.P., Dorn, P.B., Huesemann, M.H., Moore, K.O., Rhodes, L.M., Jackson R., Vipond T.E., Western, M.M., Wisniewski, H.L. 1997. Crude oil hydrocarbon bioremediation and soil ecotoxicity assessment. Environ. Sci. Technol. 31, 1769–1776.

Saterbak, A., Toy, R.J., Wong, D.C.L., McMain, B.J., Williams, M.P., Dorn, P.B., Brzuzy, L.P., Chai, E.Y., Salanitro, J.P. 1999. Ecotoxicological and analytical assessment of hydrocarbon-contaminated soils. Environ. Sci. Technol. 18, 1591–1607.

Saterbak, A., Toy, R.J., McMain, B.J., Williams, M.P., Dorn, P.B. 2000. Ecotoxicological and analytical assessment of effects of bioremediation on hydrocarbon-containing soils. Environ. Sci. Technol. 19, 2643–2652.

Schultz, E., Joutti, A., Räisänen, M.-L., Lintinen, P., Martikainen, E., Lehto, O. 2004. Extractability of metals and ecotoxicity of soils from two old wood impregnation sites in Finland. Sci. Total Environ. 326, 71–84.

Seco, J.I., Fernández-Pereira, C., Vale, J. 2003. A study of the leachate toxicity of metal-containing solid wastes using *Daphnia magna*. Ecotoxicol. Environ. Saf. 56, 339–350.

SFS 3006, 1982. Determination of chloride content of water. Potentiometric titration. Finnish Association of Standardisation. Helsinki. 6pp.

SFS 3010, 1980. Determination of oil and grease in water. Infrared spectrophotometric method. Finnish Association of Standardisation. Helsinki. 10 pp.

SFS 4996, 1987. Determination of Formaldehyde. Japanese method. Finnish Association of Standardisation. Helsinki. 6pp.

SFS 5738, 1992. Determination of sulfate in water. Nephelometric method. Finnish Association of Standardisation. Helsinki. 5 pp.

SFS-EN 1484, 1997. Water analysis, Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). European Committee for Standardization CEN/TC 292. 12 pp.

SFS-EN 12457-(1–4), 2001. Characterisation of waste, leaching. Compliance test for leaching of granular waste materials and sludges. European Committee for Standardization CEN/TC 292. 28 pp.

SFS-EN 13137, 2001. Determination of total organic carbon (TOC) in waste, sludges and sediments. European Committee for Standardization CEN/TC 292. 14 pp.

Stephenson, G.L., Koper, N., Atkonson, G.F., Solomon, K.R., Scroggins, R.P. 2000. Use of nonlinear regression techniques for describing concentration-response relationships of plant species exposed to contaminated site soils. Environ. Toxicol. Chem. 19, 2968–2981.

Tahvanainen, T., Tuomaala, T. 2003. The reliability of mire water pH measurements – a standard sampling protocol and implications to ecological theory. Wetlands 4, 701-708.

Trapp S., Köhler, A., Larsen, L., Zambrano, K.C., Karlson, U. 2001. Phytotoxicity of fresh and weathered diesel and gasoline to willow and poplar trees. JSS– J Soils & Sediments 1, 71–76.

Turpeinen, R. 2002. Interactions Between Metals, Microbes and Plants – Bioremediation of Arsenic and Lead Contaminated Soils. Academic Dissertation. The Department of Ecological and Environmental Sciences of University of Helsinki. 48 pp.

Vaajasaari, K., Dahlbo, H., Pönni, S., 1997. Liukoisuustestit jätteiden kaatopaikkakelpoisuuden määrittämisessä (Leaching tests as a method for determining the suitability of wastes for landfill disposal). Regional Environmental Publications 47. Regional Environmental Agency of Häme. Finland. 76 pp. (In Finnish)

Van der Sloot, H. 1996. Developments in evaluating environmental impact from utilization of bulk inert wastes using laboratory leaching tests and filed verification. Waste Manage. 16, 65–81.

Van der Sloot, H., Heasman L., Quevauviller P. (eds.) 1997. Harmonization of Leaching/Extraction Tests, Studies in Environmental Sciences 70. Elsevier Science B.V. Amsterdam. 281 pp.

Van der Sloot, H.A., Kosson, D.S., Hjelmar, O. 2001.Characteristics, treatment and utilization of residues from municipal waste incineration. Waste Manage. 21, 753–765.

Van der Sloot, H. 2002. Characterization of the leaching behaviour of concrete mortars and of cement-stabilized wastes with different waste loading for long term environmental assessment. Waste Manage. 22, 181–186.

Viguri, J., Andrés, R., Ibaňez, R., Puente, R., Irabien, A. 2000. Characterization of metal finishing sludges: influence of the pH. Journal of Hazardous Mat. A79, 63–75.

Villaescusa, I., Marti, S., Matas, C., Martinez, M., Ribŏ, J.M. 1997. Chromium (VI) toxicity to luminescent bacteria. Environ. Toxicol. Chem. 16, 871–874.

Wahlström, M., Thomassen, H., Flyvbjerg, J., Vetkamp, A.C., Oscarsson, C., Sundqvist, J.-O., Rood, G.A. 1994. Leaching of organic contaminants from contaminated soils and waste materials. In: Gourmans, J.J.J.M., Van der Sloot, H.A., Aalbers, Th. G. (eds.). Environmental Aspects of Construction with Waste Materials. Elsevier Science B.V. Amsterdam. pp. 257─270.

Wahlström, M., Laine-Ylijoki, J., Pihlajaniemi, M., Ojala, M. 2002. Leaching of PCBs and chlorophenols from contaminated soil and waste – Influence of leaching test characteristics. Presentation in 1st International Workshop on Groundwater Risk Assessment at Contaminated Sites. February 21-22, 2002. Tubingen, Germany. 5 pp.

Wintgens, T., Gallenkemper, M., Melin, T. 2003. Occurrence and removal of endocrine disrupters in landfill leachate treatment plants. Wat. Sci. Technol. 48 (3), 127–134.

Wuncheng, W. 1991. Literature review on higher plants for toxicity testing. Water, Air, and Soil Pollution 59, 381–400.

Yong-Jin, K., Masahiro, O. 2003. Leaching characteristics of polycyclic aromatic hydrocarbons (PAHs) from spiked sandy soils. Chemosphere 51, 387–395.

The hazardous properties of wastes adapted from Annex III of the Hazardous Waste Directive (1991/689/EC) and the limit values for hazardous properties in wastes (waste decree of the Finnish Ministry of the Environment 1128/2001).

Hazardous properties	Description	Limit value for the hazardous properties in wastes % dry weight
H1 Explosive	*Substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.*	-
H2 Oxidizing	*Substances and preparations which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances.*	-
H3-A Highly Flammable	*Liquid substances and preparations having a flash point below 21 °C (including extremely flammable liquids), or - substances and preparations which may become hot and finally catch fire in contact with, or solid substances and preparations which may readily catch fire after brief contact with a source of ignition, or - gaseous substances and preparations which are flammable in air at normal pressure, or - substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.*	-
H3-B Flammable	*Liquid substances and preparations having a flash point equal to or greater than 21 °C and less than or equal to 55 °C.*	-
H4 Irritant	*Non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.*	*10 % (Xi and R41) 20 % Xi(and R36, R37, R38)*
H5 Harmful	*Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.*	*25 % (Xn) 10% Xn (and R68) 10 % Xn (and R48)*
H6 Toxic	*Substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.*	*0.1 % (T and R23, R24, R25) 0.1 % (T+ and R39) 3% (T and R23, R24, R25) 1% (T and R39 or T and R48)*
H7 Carcinogenic	*Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.*	*0.1 % (Carc. Cat. I or 2 (T and R45, R49) 1 % Carc. Cat. 3 (Xn and R40)*
H8 Corrosive	*Substances and preparations which may destroy living tissue on contacts.*	*1 % (C and R35 or C and R34))*
H9 Infectious	*Substances containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.*	-
H10 Teratogenic	*Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence.*	*0.5 % Repr. Cat. 1 and 2 (T R60 and R61) 5 % Repr. Cat. 3 (T and R46)*
H11 Mutagenic	*Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.*	*0.1% Muta. Cat. 1 and 2 and R46 1% Muta. Cat. 3 and R68*
H12	*Substances and preparations which release toxic or very toxic gases in contact with water, air or an acid.*	-
H13	*Substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.*	*- (limit values set for inorganic components for hazardous waste landfill)*
H14 Ecotoxic	*Substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment.*	*-, recommended limit value in Finland 0.25 % (N and R51-53 or R50 or R53)*

- limit value not set , must be evaluated/tested