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Hazardous properties of paint residues from the furniture industry

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Abstract

The objective of this study was to screen nine excess paint residues for environmental hazard and to evaluate their disposability in a non-hazardous or hazardous-waste landfill. These residues were produced in the process of spray-painting furniture. Residues were classified according to their leaching and ecotoxicological properties. Leaching properties were determined with the European standard SFS-EN 12457-2 leaching-test. The toxicity of the leaching-test eluates was measured with plant-, bacteria- and enzyme-inhibition bioassays. Total organic carbon, formaldehyde and solvent concentrations in the solid wastes and in the leaching-test eluates were analysed. It seemed likely that leached formaldehyde caused very high acute toxicity in leaching-test eluates of the dry-booth residues. This hypothesis was based on the fact that the formaldehyde concentrations in the leaching-test eluates of the dry-booth residues were 62–75 times higher than the EC_{50} value reported in the literature for formaldehyde. The results of the water-curtain booth residues showed that the samples with the highest TOC and aromatic solvent concentrations were also the most toxic. The studied excess paint residues were complex organic mixtures and contained large amounts of compounds not identifiable from chemical data. Therefore, the evaluation of the hazard based solely on available chemical data is unlikely to be sufficient, as evidenced by our study. Our results show that harmful compounds remain in the solid waste and the toxicity results of their leaching-test eluates show that toxicity may leach from residues in contact with water at landfill sites. They also confirm the benefit of combining chemical and ecotoxicological assays in assessing the potential environmental hazard of complex organic mixtures found in wastes.

Keywords: Leaching-test; Ecotoxicological test; Organic waste; Furniture industry paint residue; Landfill disposal

1. Introduction

According to the EU Landfill Directive (1999/31/EC), the waste acceptance criteria assess requirements for waste classification and quality monitoring. The basic requirements in the landfill directive for characterisation of waste are: source and origin of the waste, information about the process producing the waste, data on its composition and on its leaching behaviour and appearance. In general, to obtain the information about latter requirements waste must be tested. For hazardous wastes the hazard properties should be evaluated according to Hazardous Waste Directive 1991/689/EEC. Hazardous Waste Directive defines a set of 14 properties allowing waste classification. This evaluation is based on the total concentrations of inorganic or organic pollutants in wastes. “Ecotoxic” (H14) is one of the hazardous properties defined in Hazardous Waste Directive (1991/689/EEC) in Annex III. However, this H14 criterion “ecotoxic” does not refer to specific methods. Owing to the hazardous properties of wastes, concern about and need for assessing the potential environmental hazard (H14 = “ecotoxic”) has led to development of appropriate methods for measuring leaching and the ecotoxicological properties of waste materials [1–4].

In Finland, a part of problems for acceptance of wastes at landfills are related to industrial sectors that produce wastes containing organic compounds. Landfill criteria for wastes have been established mainly for inorganic compounds. In addition, testing methods for leaching of organic compounds are limited. In working groups of the European standardisation committee CEN/TC 292, WG 2 and WG 6, leaching-tests have been developed for inorganic wastes, but no standardised or validated methods are available for

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wastes containing organic pollutants. The number of studies concerning the leaching properties of organic compounds from industrial wastes is very limited, e.g. [14,15]; but in the study of Paxéus [16] more than 200 individual organic compounds and groups of compounds have been found in leachates from three municipal landfills in the Göteborg region (Sweden). Therefore, there is also a need to develop leaching methods for organic compounds in wastes. If the chemical composition of the waste material is complex and not well-known, the ecotoxicological tests, according to our previous study [4], could be used in combination with chemical analyses to help the waste classification and to assess the potential environmental hazard of complex organic mixtures found in wastes.

In several studies the toxicity of landfill leachates has been characterised, e.g. [5–8], but a combination of leaching and toxicity assays for industrial solid waste is quite new branch of research [1,9–13]. The ecotoxicological characterisation of wastes has been identified as a priority in France, and the development to assess the methodology for ecotoxicological properties of raw wastes and their eluates has been studied [1]. The test methodology is based on toxicity testing of raw waste and waste eluates obtained from the leaching-test [1].

In previous studies we have evaluated the suitability of different leaching-tests and ecotoxicological tests in order to discover useful combination of test methods for classifying and assessing the environmental hazard of inorganic or organic industrial wastes to be disposed of to a landfill [2–4]. In this study, we concentrated on the hazard assessment of the excess paint residues which were produced in the process of spray-painting furniture. Four of these residues were collected from dry booths and the other five from water-curtain booths. The lacquers or paints used in the Finnish furniture industry are so-called acid-curable two-component lacquers or paints. These kinds of paints and lacquers are used mainly in Skandinavia. In other parts of the Europe, on the other hand, the paints and lacquers are mainly cellulose- and urethane-based, respectively. At present, the furniture industry is developing surface-paint processes to minimise production of the waste that improve the recovery of lacquers or paints use in spraying.

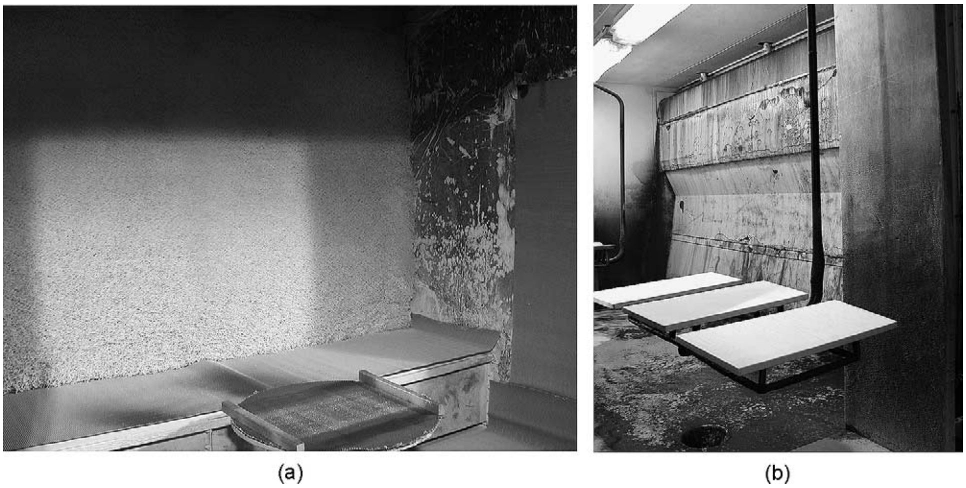
The aim of this study was to determine the environmental hazard of nine excess paint residues and to evaluate their disposability in either non-hazardous or hazardous-waste landfill. The residues were classified according to their leaching and ecotoxicological properties. Leaching properties were determined with the European standard SFS-EN 12457-2 leaching-test method. Total organic carbon (TOC) content, formaldehyde and solvent concentrations in solid wastes and in their leaching-test eluates were analysed. The toxicity of the leaching-test eluates was determined with assays of plant-, bacteria- and enzyme-inhibition.

Another objective of this study was to evaluate the use of simple pre-treatment methods for decreasing the hazardous properties of paint residues before their disposal to landfills. One major problem with water-curtain booth residues is their high free liquid content (around 30%). In the current Finnish landfill regulations it is prohibited to dispose of liquid wastes in a landfill. Therefore, one water-curtain booth residue was pre-treated in order to reduce the liquid content. For another water-curtain booth residue, the hazard was decreased by changing the raw materials in the spray-painting process. The leaching and ecotoxicological test results were used for comparison of the hazard reduction in untreated and treated residues.

2. Materials and methods

2.1. Description of waste materials

Excess paint residues were collected in eight different furniture factories. These residues are produced in the process of spray-painting furniture. Four of the residues (samples A–D) were collected from dry booths and the other five (samples E–I) from water-curtain booths (Fig. 1).



(a) (b)

Fig. 1. A dry-booth (a) and a water-curtain booth (b) used in spray painting of furniture in which the excess paint residues are produced.

The lacquers or paints used in these furniture factories were so-called acid-curable two-component lacquers or paints. Only the raw materials of paints and lacquers in the spray-painting process of Factory C were different from those used in the other dry-booth processes (samples A, B and D).

The information of the composition of paints and lacquers were collected from the material safety data sheets received from the paint producers. There is a limit for concentration above which chemical has to be mentioned in the material safety data sheets. Formaldehyde is used in so-called acid-curable two-component lacquers or paints, but in material safety data sheets, the content of formaldehyde needs not to be mentioned. In this study, the formaldehyde concentrations were analysed due to the information received from the producers of paints and lacquers.

According to the European Hazardous Waste List 2001/118/EC, excess paint residues from dry booths are classified by the EWC code 08 01 11 and water-curtain booth residues by the EWC code 08 01 15. Paint residues are classified as hazardous waste if their concentrations of organic solvents or other hazardous compounds exceed the limits set for the hazardous properties of Council Directive 91/689/EEC in Annex III. These properties are derived from the directive 67/548/EEC on dangerous substances. In Table 1 is presented the hazardous properties of the organic compounds, and their limit values according to Annex III which were analysed from these residues. In this study, we concentrated to evaluate the ecotoxic property (H14) of the residues with leaching and toxicity assays.

Examples of both spray-painting booths are illustrated in Fig. 1. The amount of excess paint in the spray-painting process can be as high as 80% of the total amount of paint or varnish used for surface treatment. In the spray-painting process, the piece of furniture hangs in the front of the booth, and the paint or varnish is sprayed on the surface manually or by robots. In the dry booths, the excess paint residue is collected in a carton or fibre filter placed at the back-wall of the booth. In water-curtain booths, water is flowing continuously in the booth collecting the excess paint, which with the help of chemicals is then precipitated into the water pool of the booth. The water-curtain booth residues were porous and amorphous material which contained 20–30 wt.% free liquid. Before laboratory analyses, the liquid phase was decanted from the solid matter. The moisture of the water-curtain residues after liquid separation was between 63 and 68%. The dry-booth residues were homogenous powders and their moisture content varied between 2.3 and 5%.

Two of the water-curtain booth residues were pre-treated: sample I by filtering in a simple open-air fibreglass filter bag for 14 days to reduce the free liquid content (sample I_{after}). This filtering was an experiment to find out a simple method to reduce the amount of waste by separating the liquid phase from the solid phase at source. The volatilisation was not taken into account during the experiment. Sample F was pre-treated by changing the paints or lacquers in the spray-painting process to the raw materials which contained lower concentrations of aromatic solvents (sample F_{after}).

2.2. Leaching studies and chemical analyses

Solid residues were stored in glass jars at +4 °C and analysed within 1 week of the sampling. Before chemical analyses and leaching-test experiments, the paint residues of the water-curtain booth residues were decanted to separate the free liquid phase from the solid phase. The toxicity assays and the chemical analyses of these two phases were carried out separately.

The European standard SFS-EN 12457-2 aimed at compliance testing of waste destined for landfill, was used to study the leaching properties of organic compounds in the excess paint residues [17]. For leaching studies, the moisture of the paint residues was determined before an amount corresponding to 100 g of dry weight was weighed into a 1000 ml glass flask. Water was then added to obtain a liquid to solid (L/S) ratio of 10:1. The mixture was shaken by end-over-end rotation at 10 rpm for 24 h. After this, the mixture was filtered (Whatman (GF/C), pore size: 1.2 μm) and used for chemical and ecotoxicological analyses.

For chemical analyses, the leaching-test eluates and the liquid phase samples were transferred to headspace crimp top vials and stored at +4 °C. The amount of organic solvents in samples was determined by gas chromatography

Table 1
The chemicals analysed from the residues, and their hazardous properties and limits set in the Hazardous Waste Directive (91/689/EEC) in Annex III

CAS number	Chemical	Hazardous property	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	Toluene	Harmful H5	250,000
100-41-4	Ethylbenzene	Highly flammable H3-A	–
1330-20-7	Xylenes	Harmful H5	250,000
64742-95-6	Aromatic hydrocarbon solvent	Ecotoxic H14	2,500

(GC–MS, HP 6890 + 5973). The total concentrations of solvents in solid samples were analysed from methanol extracts, which were further diluted with water when needed. The amounts of organic solvents in leaching-test eluates and in the liquid phases separated from the water-curtain paint residues were determined either as such or after dilution with water. An aliquot of 10 ml was studied using headspace autosampling at 80 °C according to the ISO 11423-1 standard. The chromatographic separation was performed on an HP-5M column (length: 30 m) and the GC-furnace temperature was raised from 30 to 270 °C. Identification was based on mass spectral interpretation and comparison with model compounds.

The total concentrations of formaldehyde in solid wastes and in the leaching-test eluates were analysed photometrically according to standard SFS-EN 4996. The total organic carbon (TOC) content of the solid samples was analysed by a LECO CNS-2000 analyser (LECO Corporation Svenska AB, Sweden) according to draft prEN 13137 and the TOC of the water eluates by a Unicarbo Universal Carbon Analyser according to standard SFS-EN 1484.

2.3. Ecotoxicological tests

Toxicity of the leaching-test eluates was determined by luminescent bacteria, in vitro enzyme inhibition assay (RET) and plant-root growth test (Table 2). The same tests were also used in our previous study for wastes containing organic compounds [4]. Toxicity data were compared to the chemical concentrations of the analysed organic compounds in the leaching-test eluates. Toxicity of the liquid phase samples of the water-curtain booth residues was determined only by luminescent bacteria test.

In order to compare the toxicity of the original waste material to the remaining waste after the leaching procedure, a lettuce seed germination test was performed for solid samples before and after the leaching-test SFS-EN 12457-2 (Table 2). Toxicity of the pre-treated residues (F_{after} and I_{after}) was determined only from the leaching-test eluates.

For lettuce (*Lactuca sativa*) seed germination test, the solid waste material was ground in a mortar. Samples were diluted with crushed quartz to achieve concentrations varying from 50 to 0.8%. For germination test 100 g of sample, sample dilution or crushed quartz (=control) was layered on plastic Petri dishes and the area of the dishes was divided by plastic strips into four sectors. Twenty-five seeds were placed into each sector. The seeds were covered with 90 g of quartz sand, and the dishes were moistened with 30 ml of deionised water. The test dishes were incubated in dark for 2 days and in light–dark (16:8 h) cycle for additional days at 20 °C. At the end of the test, the mean percentages of the germinated seeds were calculated and compared to the mean of the controls.

For ecotoxicological tests, the eluates were stored frozen in glass flasks and solid samples in glass jars at +4 °C. Before the ecotoxicity tests, the pH of the samples was adjusted with 0.5 M HCl or NaOH to pH 6–8. EC_{50} values were calculated from the results of the aquatic toxicity by regression analysis and converted to Toxic Units (TU) using the formula $TU = 100/EC_{50}$. The reference chemicals were used for the quality control of the aquatic toxicity tests. The accuracy of the assays expressed as the percentage coefficient of variation (CV%) for the luminescent bacteria test was 12% ($n = 10$) for 3,5-dichlorophenol. For the RET assay it was 11% for $ZnCl_2$ ($n = 9$) and 7% for 3,5-dichlorophenol ($n = 5$). In addition, for the onion growth inhibition assay it was 19% ($n = 6$) for $CuSO_4$.

3. Results and discussion

3.1. Solvents in residues

The results showed that the dry-booth residues contained mainly aliphatic solvents, whereas the main constituents in water-curtain booth residues were aromatics (Table 3). The aromatic solvent concentrations in the dry-booth residues were clearly smaller than those in the water-curtain booth residues. Conversely, the dry-booth residues contained

Table 2
Chararcteristics of the acute toxicity tests used for the leaching-test eluates of excess paint residues

Test method	Test organism	End-point	Duration	Standard or reference method
Luminescent bacteria test	Freeze-dried bacteria (*Vibrio fischeri*, NRRL B-11177) BioTox^{TM}-reagents (Aboatox Oy, Finland)	Inhibition of bioluminescence measured by 1253-luminometer (Bio-Orbit, Finland)	30 min	[18]
Reverse electron transport (RET) assay	Sub-mitochondrial particles prepared from isolated beef heart mitochondria	Enzyme activity measured kinetically at 340 nm in a microplate reader (iEMS, Ascent, Labsystems, Finland)	10 min	[19]
Plant root growth test	Bulbs of a commercial variety of common onion (*Allium cepa*)	Root growth inhibition measured as the average length of root bundles	4 days	[20]
Seed germination test	Lettuce (*Lactuca sativa*)	Inhibition of germination measured by calculating the germinated seeds, the health of the seedlings and roots	5 days	A modification of US EPA method [21]

Seed germination test was performed on solid residues before and after the leaching-test.

Table 3
Composition of the dry-booth (A–D) and water-curtain booth (E–H) residues presented as mg/kgTS

Sample	Composition of dry-booth and water-curtain booth residues (mg/kgTS TOC in g/kgTS)										
	TOC	Formaldehyde	Isopropanol	Isobutanol	1-Butanol	Butylacetate	Ethylacetate	Toluene	Ethylbenzene	Xylenes	Aromatic hydrocarbon solvent
A	510	9,200	1,700	400	2,800	600	n.d.	*153*	*4.7*	*28*	*6.4*
B	480	8,600	500	6,900	3,500	980	n.d.	*41*	*32*	*250*	*n.d.*
C	510	44	n.d.	n.d.	n.d.	1,600	150	*290*	*51*	*330*	*29*
D	520	9,600	1,700	200	12,000	2,900	120	*n.d.*	*43*	*440*	*n.d.*
E	420	27	n.d.	n.d.	n.d.	n.d.	n.d.	*5,700*	*4,300*	*22,000*	*290*
F	410	110	n.d.	n.d.	3,600	7,200	480	*6,000*	*13,000*	*40,000*	*84,000*
G	550	41	n.d.	n.d.	n.d.	350	n.d.	*8,300*	*25*	*180*	*180*
H	420	120	n.d.	n.d.	n.d.	n.d.	n.d.	*14*	*160*	*480*	*480*

TOC is presented in g/kgTS. Aromatic solvents presented in italics. n.d.: not detected.

higher amounts of formaldehyde than the water-curtain booth residues did, except the sample from Factory C which contained only a small amount of formaldehyde. The main aliphatic solvents in dry-booth residues were isobutanol, isopropanol, 1-butanol and ethyl- and butylacetate. In the water-curtain booth residues the main aromatic solvents were toluene, xylenes, ethylbenzene and a mixture of aromatic hydrocarbon solvent.

TOC content did not differ much between dry and water-curtain booth residues (Table 3). It is obvious that organic residues contained large amounts of unknown compounds, since the TOC of analysed compounds calculated as carbon constituted only 0.3–14% of the total TOC.

In the dry-booth residues, 1-butanol and isobutanol were leached easily (70–80%) when the leached amounts of these compounds are compared with the total concentration (Table 4). Formaldehyde was also easily water soluble (leached amount 80–90% of the total concentration). Because the formaldehyde concentration was much more lower in the wet residues than in the dry residues (Table 3), formaldehyde concentrations were not determined from the leaching-test eluates of the water-curtain booth residues.

The aromatic solvents of the water-curtain booth residues were almost insoluble in water (Table 4). The liquid phase of the water-curtain booth residues was analysed separately from the solid phase (Table 5). Water-soluble aliphatic solvents were found in the liquid phase rather than in the solid phase of the water-curtain booth residues. Even though these aliphatic solvents were not detected in solid water-curtain booth residues, significant concentrations of the aliphatic compounds were found in the leaching-test eluates of these residues (Tables 3 and 4). The physical

Table 4
Organic compounds leached in the SFS-EN 12457-2 leaching-test from the dry-booth (A–D) and water-curtain booth (E–H) residues

Sample	Formaldehyde	Isopropanol	Isobutanol	1-Butanol	Butylacetate	Ethylacetate	Toluene	Ethylbenzene	Xylenes	Aromatic hydrocarbon solvent
A	5,300	340	6,200	3,300	180	360	*5*	*n.d.*	*0.3*	*n.d.*
B	6,900	520	11,000	3,400	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	6,400	690	n.d.	9,600	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	2,200	4,400	1,700	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*

Leached amounts were calculated as mg/kgTS. Aromatic solvents presented in italics. n.d.: not detected; –: not determined.

Table 5
Solvent concentrations of the liquid phase of the water-curtain booth residues (in mg/l)

Sample	Isopropanol	Isobutanol	1-Butanol	Butylacetate	Ethylacetate	Toluene	Ethylbenzene	Xylenes	Aromatic hydrocarbon solvent
E	46	200	100	n.d.	n.d.	*19*	*7.7*	*33*	*0.3*
F	70	2500	1100	360	34	*8.7*	*6.8*	*39*	*10.0*
G	58	56	380	4.4	6.4	*58*	*0.2*	*0.6*	*0.9*
H	130	80	330	n.d.	n.d.	*0.04*	*0.7*	*3.9*	*0.7*

Aromatic solvents presented in italics. n.d.: not detected.

Table 6
Solvent concentrations of two water-curtain booth residues before and after pre-treatment (mg/kgTS)

Sample	Isopropanol	Isobutanol	1-Butanol	Butylacetate	Ethylacetate	Toluene	Ethylbenzene	Xylenes	Aromatic hydrocarbon solvent
F_{before}	n.d.	n.d.	3,600	7,200	480	*6,000*	*13,000*	*40,000*	*84,000*
F_{after}	n.d.	1,800	2,100	20,000	n.d.	*130*	*290*	*1,700*	*2,800*
I_{before}	–	3,200	–	200	–	*1,300*	*1,300*	*7,500*	–
I_{after}	–	1,100	510	340	–	*410*	*1,700*	*8,400*	*7,900*

Aromatic solvents presented in italics. n.d.: not detected; –: not determined.

form of the water-curtain booth residues were porous and amorphous and they contained liquid that was separating by gravity from the solid matter during the storage. Therefore, the uniform sub-sampling of water-curtain booth residues for chemical analyses and leaching studies was difficult, and might be one reason for lower concentrations of aliphatic solvents in raw waste compared to leaching-test eluates. Another reason could be the loss of volatile organic solvents into the headspace of the jars during the storage.

The aromatic solvent concentrations of sample I_{after} was not reduced (Table 6), but one advantage of the pre-treatment was that the amount of the waste was diminished by separating around 40 wt.% of the free liquid from the waste. The concentrations of the aromatic solvents in sample F_{after} were decreased by changing the paints or lacquers in the spray-painting process. Only the amount of butylacetate was increased after the pre-treatment. Despite the fact that the aromatic hydrocarbon solvent concentration in sample F was decreased below the recommended limit value (2500 mg/kg) set for the ecotoxic property (H14) in Hazardous Waste Directive, the water eluates of these residues remained toxic after the pre-treatment (Table 7).

Table 7
Total organic carbon concentration (DOC) and toxicity (TU) of the leaching-test eluates of dry (A–D) and water-curtain booth (E–I) residues and the pre-treated water-curtain booth residues (F_{after} and I_{after})

Sample	DOC (mg/l)	Toxicity in Toxic Units ($TU = 100/EC_{50}$)			
		BioTox		RET	Onion
A	2100	238		25	15
B	1800	244		28	21
C	180	4.6		1.6	1.0
D	2100	250		28	14
E	1200	48	25[a]	2.0	3.6
F	2000	22	40[a]	3.2	4.5
G	1100	4.4	16[a]	<1.0	1.7
H	570	8.1	15[a]	<1.0	3.6
I	4900	333	–[b]	250	25
F_{after}	1500	16		4.5	4.2
I_{after}	1500	333		714	13

Toxicity of the liquid phase of water-booth residues was determined only to luminescent bacteria (BioTox).

[a] Toxicity of the liquid phase separated from the solid matter.

[b] Not determined.

3.2. Toxicity of the paint residues

The dry-booth residues, with the exception of the sample I, were clearly more toxic than the water-curtain booth residues (Table 7). All the toxicity tests—luminescent bacteria, RET, onion root growth and lettuce seed germination—led essentially to the same conclusion. The dry-booth residues contained high levels of formaldehyde (Table 3). It seems likely that leached formaldehyde caused also very high acute toxicity (Tables 4 and 7) in leaching-test eluates of the dry-booth residues. This hypothesis is based on that formaldehyde concentrations in the leaching-test eluates of the dry-booth residues were 62–75 times higher than the EC_{50} value in the literature [22] reported for formaldehyde (Table 8). On the other hand, aliphatic and aromatic solvent concentrations of these residues were lower than the EC_{50} values reported in the literature [22]. The sample of Factory C was clearly less toxic than other dry-booth residues (Table 7). This residue contained smaller amount of formaldehyde, but more aromatic solvents than other dry-booth residues (Table 3). Formaldehyde was not detected in the leaching-test eluates of sample C (Table 4). DOC of the sample C was also clearly lower than DOC of the other leaching-test eluates (Table 7). DOC concentrations in the leaching-test eluates did not differ much between other dry-booth residues.

The water-curtain booth residues (E, F and I) with the highest leached TOC and aromatic solvent concentrations were the most toxic ones, while the two with the smallest concentrations had only slight acute toxicity (G and H) (Table 7). The reduction in DOC concentrations of pre-treated residues (F_{after} and I_{after}) did not decrease the toxicity. They remained toxic also after the pre-treatment.

The concentrations of xylenes in the leaching-test eluates of samples E and F were higher than the EC_{50} values reported in the literature (Table 8). Moreover, the concentration of butylacetate in the leaching-test eluate of sample F was higher than the known EC_{50} values reported in the literature (Table 8). There are only a few reported results of solvent toxicity to RET in the literature. However, the EC_{50} values for isopropanol, 1-butanol and xylenes, are very close to those of the luminescent bacteria (RET EC_{50} values 17.4, 4.26 and 19.6 mg/l, respectively) [19]. The onion growth inhibition test is a new method that has mainly been used to determine the toxicity of the inorganic rather than the organic compounds [20].

Table 8
Toxicity of the pure chemicals as EC_{50}-values [22] and the concentration intervals of the leaching-test eluates of dry and water-curtain booth residues and the concentration intervals of liquid phase of the water-curtain booth residues

CAS number	Chemical	Toxicity to *Vibrio fischeri* EC_{50} (mg/l)		Concentration intervals of the leaching-test eluates (mg/l)	Concentration intervals of the liquid phase of the water-curtain booth residues (mg/l)
		15 min	30 min		
50-00-0	Formaldehyde	8.5	8.5	530–690	
67-63-0	Isopropanol	31,500–42,000 (5 min)	–	4.7–52	46–130
78-83-1	Isobutanol	1,224	–	11–1,100	56–2,500
71-36-3	1-Butanol	2,818–3,690	3,710	46–440	100–1,100
123-86-4	Butylacetate	82.2–130	98.9	3.7–170	4.4–360
141-78-6	Ethylacetate	5,870	–	4.0–36	6.4–34
108-88-3	Toluene	28	23.1	0.02–16	0.04–58
100-41-4	Ethylbenzene	7.69	9.68	0.01–4.3	0.2–7.7
1330-20-7	Xylenes	16 (5 min)	–	0.02–23	0.6–39
95-47-6	*o*-Xylene	9.25	–		
108-38-3	*m*-Xylene	3.36	7.18		
106-42-3	*p*-Xylene	–	5.70		

The water-curtain booth residues contained free liquid which was decanted from the residues (E–H) before analyses. These liquid samples were more toxic to light bacteria (*Vibrio fischeri*) than were the leaching-test eluates of these residues (Table 7). This might be due to fact that more water-soluble compounds were detected in the liquid phase rather than in the leaching-test eluates (Table 8). The liquid separated from sample F was the most toxic one, and its aliphatic and aromatic solvent concentrations were the highest (Tables 5 and 7).

The results of combined toxicity and leaching-test assay showed that toxicity may leach from residues when they come into contact with water. The environmental hazard between dry and water-curtain booth residues was discovered only with toxicity assays. Samples could be arranged according to their decreasing toxicity in order: I > D > B > A > E > F > H > G > C. This screening describes directly how the ecotoxicological properties differed between the residues. Hazard ranking according to chemical analyses was not as clear. The residues contained large amounts of unknown compounds since the TOC of analysed compounds, calculated as carbon, constituted only 0.3–14% of the total TOC. Therefore, the evaluation of the hazard based solely on available chemical data is unlikely to be sufficient. Ecotoxicological tests measure only the overall toxicity of the complex mixtures of chemicals but identification of the chemicals causing the effects still remains unresolved. For the chemical identification of toxicity causing compounds, a fractionation procedure combined with toxicity tests and chemical analyses (toxicity identification evaluation, TIE) would be of value. However, it would have been a complicated and expensive approach, and beyond the purpose of this study.

New criteria for landfill disposal (Council Decision 2003/33/EC) in the EU Landfill Directive (1999/31/EC) do not set any limit values for leachable organic compounds or the ecotoxicity of waste eluates [23]. However, the DOC concentrations of the eluates suggested that the paint residues should not be landfilled. The comparisons between the ecotoxicolocigal and chemical results are probably best made using the DOC concentration levels.

Despite the fact that the water-curtain booth residues were less toxic to germination of lettuce seeds than the dry-booth residues were, the germination test results showed that all of the residues remained toxic after the leaching-test. Even though the leaching-test eluates of samples C, G and H were only slightly toxic to light bacteria, these residues were toxic and inhibited germination of lettuce seeds after the leaching-test (Table 9).

The combined leaching and ecotoxicity results proved that landfilling is not environmentally sound way of handling these kind of waste streams in the future. Toxicity of solid matter proved that harmful compounds will remain in solid

Table 9
Toxicity of the dry-booth (A–D) and the water-curtain booth (E–H) residues to lettuce-seed germination before and after the leaching-test

Test concentration (wt.%)	Germination test of lettuce, inhibition (%)							
	A	B	C	D	E	F	G	H
Toxicity of the residues before the leaching-test								
1.6	100	100	−6	100	−4	6	−3	−11
3.1	100	100	0	100	4	−1	−8	3
6.3	100	100	−8	100	4	14	22	0
12.5	100	100	14	100	6	27	22	11
Toxicity of the residues after the leaching-test								
0.8	–	–		4	–	–	–	−3
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	–	–
25.0	100	100	34	100	89	71	–	–
50.0	100	100	–	–	–	–	100	100

Results presented as a function of diluted concentration of the residue compared to the inhibition (%) of germinated seeds. –: Not determined.

waste, and the toxicity results of their leaching-test eluates showed that toxicity may leach from residues in contact with water at landfill sites.

The chemical concentrations of paint residues did not exceed the limit values set for hazardous wastes (Tables 1 and 3). Nevertheless, the studied residues and their water eluates were clearly ecotoxic and they should be classified as hazardous waste. However, the EU has not yet set a limit value for the ecotoxic property (H14) that could be used to evaluate the ecotoxicity test results of solid waste or their eluates. Also, as stated earlier in other ecotoxicological studies of wastes [1,24], further investigations of a useful battery of toxicity tests and limit values for ecotoxicological test results are necessary for the hazard evaluation of industrial wastes.

4. Conclusions

In many cases, there is a lack of overall background data on paint residue wastes. Therefore, co-operation between paint or lacquer producers, waste producers, environmental authorities, and waste researchers and laboratories is very important. For example, in this study the formaldehyde concentrations were analysed based on information received from the producers of paints and lacquers. Otherwise, this information would not have been available. However, this provided the most important information for the overall assessment of the chemical and ecotoxicological hazard of residues studied.

The studied excess paint residues were complex organic mixtures and contained large amounts of compounds not identifiable from chemical data. Therefore, the evaluation of the hazard based solely on available chemical data might not have been sufficient. This was confirmed by the toxicity assays which identified the environmental hazard of dry and water-curtain booth residues. However, the hazard ranking according to chemical analyses was not as clear. The results of our study demonstrate that ecotoxicological tests should be used in combination with chemical analyses to determine the waste classification, and to assess the potential environmental hazard of complex organic mixtures found in paint residue wastes.

The information of the ecotoxicological and leaching properties of excess paint residues produced in different spray-painting processes helps paint producers to develop their products and makes it possible for furniture producers to choose environmentally safer products. Furthermore, this hazard-screening approach will help furniture producers to improve the surface-paint process of furniture-making in order to minimise the amount and hazard of the wastes produced.

The results also proved that landfilling is not a suitable method of disposal for the paint residues produced in the furniture industry. For this type of organic wastes, a better alternative method of treatment could be incineration.

According to this study, the luminescent bacteria and the lettuce seed germination tests were simple and sensitive bioassays that are recommended for a test battery to estimate the ecotoxic property (H14) of complex organic wastes. However, further investigations of a useful battery of toxicity tests and limit values for ecotoxicological test results are necessary for the hazard evaluation of industrial wastes**.** Certain properties of organic compounds like volatilisation and anticipated low solubility of organic chemicals in water may have implications for chemical characterisation and performance of toxicity and leaching methods. The development of suitable leaching and toxicity methods for volatile organic compounds need to be investigated further.

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