

Analysis of Fire Debris after Tyre Fires and Fires in Electrical and Electronics Waste

BRANDFORSK project 633-051



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Abstract

According to Swedish and European law electric and electronic waste and used tyres are not allowed to be placed in landfills. The waste should be collected and recycled in some way. Instead the waste is stored at different places, e.g. recycling station. Large amount of stored good imply large potential risk in case of fire. In this work the fire debris after fires in tyres or electric and electronic equipments were analysed.

Eight fire tests, four with each type of waste, were performed beneath an industry calorimeter. The set-up was varied to study the influence of for example the ventilation condition, i.e. how easily the air could reach the centre of the fire, had on the results. Tests were performed with and without water application. After the tests the fire residue was analysed for polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzodioxins and furans (PCDD/PCDF), polybrominated dibenzodioxins and furans (PBDD/PBDF), selected brominated flame retardants, and metals and other selected elements. This report contains the results from these analyses. When applicable, the results have been compared to limit values for contaminated soil. The tests show that the concentrations of contaminants in the fire residue will vary with the storage configuration and whether water application is used or not.

Key words: fire debris, electrical and electronics waste, tyre fire, PCDD/F, PBDD/F, PAH, metals, brominated flame retardants

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Preface

This work was sponsored by BRANDFORSK (The Swedish Fire Research Board; project number 633-051). The fire experiments were performed within a larger project sponsored by the Swedish Rescue Services Agency.

The technicians at SP Fire Technology are acknowledged for their good and efficient way of performing the fire tests. El-Kretsen AB, the City of Borås, Svensk Däckåtervinning AB, and RagnSells assisted both with information and help to obtain the tyres and electrical and electronic equipments used as fuel in the fire tests. For this assistance these organizations are acknowledged.

The reference group for this project was the same as for the project sponsored by the Swedish Rescue Services Agency. The members of the reference group were:
Ann Lundström, Environmental authorities of the City of Göteborg (Miljöförvaltningen, Göteborg)
Ingela Höök, The County Administration of Västra Götaland (Länsstyrelsen i Västra Götalands län)
Måns Krook, The fire department of Malmö (Malmö Brandkår)
Niklas Johansson, Swedish Environmental Protection Agency (Naturvårdsverket)
Peter Andersson, The Swedish Fire Protection Association (Svenska brandförsvarsföreningen)

Sammanfattning

Allt fler material och produkter blir förbjudna att lägga på deponier. I stället skall de återanvändas eller återvinnas på något sätt. Detta innebär att det skapas många mellanlager där använda produkter samlas i väntan på att transporteras till nästa steg i återvinningskedjan. Sådana lager innebär en brandrisk och detta kan också innebära en hälso- och miljörisk beroende på vilka ämnen som produceras i branden.

I det aktuella arbetet ansågs två produkttyper speciellt intressanta att studera: bildäck respektive elektrisk och elektronisk utrustning. Inom ramen för ett större projekt analyserades brandrök och släckvatten för att kartlägga utsläppen från bränder i de nämnda produkttyperna. Dessa resultat rapporteras separat. I denna rapport presenteras analyser av brandrester från brandförsök med bildäck respektive elektrisk och elektronisk utrustning. Fyra brandförsök genomfördes med varje produkttyp. Inom varje grupp varierades den experimentella uppställningen. Dessutom genomfördes försöken med eller utan vattenbegjutning.

De ämnen som analyserades för var polycykliska aromatiska kolväten (PAH), polyklorerade dibensodioxiner och dibensofuraner (PCDD/PCDF), polybromerade dibensodioxiner och dibensofuraner (PBDD/PBDF), bromerade flamskyddsmedel samt metaller och några andra utvalda grundämnen. Denna rapport innehåller resultaten från dessa analyser. I vissa relevanta fall har resultaten jämförts med gränsvärden för förorenad mark. Försöken visar att koncentrationerna av föroreningar varierar med experimentell uppställning och är beroende av om vatten påförs eller inte.

Nomenclature

DS	Dry substance
EE	Electrical and electronics waste
GC	Gas chromatography
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectroscopy
HRR	Heat release rate
ICP	Inductively coupled plasma
MS	Mass spectroscopy
PAH	Polycyclic aromatic hydrocarbon
PBDD	Polybrominated dibenzo-p-dioxin
PBDF	Polybrominated dibenzofuran
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran

1 Introduction

Since the first of July 2001 a company that sells electrical or electronic equipment (abbreviated EE in the rest of this document) in Sweden has the responsibility to arrange that the products are properly disposed at the end of their useful life-cycle [1-3]. Many producers or trade organisations have joined the organisation El-Kretsen, who is responsible for collecting and recycling such waste. After collection the waste is sorted and dismantled so that environmentally hazardous components or materials are destroyed or safely contained while other materials are recycled in some way.

One result of this system is that a large amount of EE-waste is collected and stored at different places, both at special recycling stations and at dismantling companies. Large amounts of stored goods imply a large potential risk in case of fire. In the case of EE-waste it can also mean an increased environmental risk due to some specific components of the waste. To assess to what extent species, hazardous to the environment, are produced and spread during a fire in EE-waste, a series of fire tests with EE-waste was performed. The waste used in these tests is described in the next section.

Similarly, there is a regulation in Sweden since 1994 [4] saying that anyone that professionally produces, imports or sells tyres is responsible for retrieval and disposal of used tyres in an environmentally friendly way. This is administrated by Svensk Däckåtervinning AB (SDAB) and performed by its entrepreneur Ragn-Sells. After the 1st of July 2002 landfilling of whole used tyres (excluding bicycle tyres and tyres larger than 1400 mm) is not allowed in Sweden [5]. According to an EU directive, after 1 July 2003, whole tyres are not allowed to be placed in landfills and after 1 July 2006, chunked or shredded tyres are not allowed to be placed in landfills [6]. Even if this means fewer tyres in landfills, there are many small and a number of large storage sites for used or shredded tyres, before the tyres are transported to the next stage in the recycling chain. This means a potential fire hazard that is of interest to study and there are examples of fires that have already occurred in such storage sites.

This report contains information on and results from a series of tests with fires involving EE-waste and tyres, individually. In total eight tests were performed, four with each type of product. Within each group of tests the experimental set-up (which affected the ventilation conditions) was varied. Tests were also performed with and without water application. The full details of the tests and results from gas analyses and analyses of the run-off water are presented elsewhere [7, 8]. This report focuses on the results of analyses of the fire debris from the two different product types.

There are several reasons for performing analyses of the fire debris. In a clean-up situation after a fire it is important to be able to characterize the debris, both for the safety of the personnel and for information regarding appropriate disposal of the debris. Analyses of the debris can also give clues to other possible emissions (to air or run-off water). From a scientific point of view the analyses of the fire debris are interesting for comparisons with analyses of the fire gases and run-off water. This would give a more holistic view of the situation and variations in the relative distribution of different species between the different matrices (gas, water, and debris) could be identified.

2 Commodities

2.1 EE-waste

Fifteen cages of EE-waste were delivered to SP. The waste was contained in cages from El-Kretsen and had a total weight of 5100 kg. From the delivered EE-waste, representative and similar waste loads were selected for four different tests. The waste used in the four tests is described in Table 2.1.

Table 2.1 EE-waste used in each test (kg).

Item	Test 1	Test 2	Test 3	Test 4
3 Vacuum cleaners (incl. one cordless)	14.636	14.094	15.93	15.142
1 Micro wave	16.64	16.722	15.07	12.698
5 Coffee machines/Electric kettles	4.336	6.02	5.986	5.438
1 Toaster	0.942	1.698	1.572	1.328
2 Electric mixers	1.876	2.23	2.21	2.066
1 Electric apparatus for cutting grass	1.74	3.286	1.418	1.304
2 Computers (desk tops)	18.37	18.156	20.026	19.128
1 Lap top (L) / Scanner (S)	8.516 L	3.094 L	3.594 S	5.742 S
2 Monitors	31.302	31.178	31.686	33.66
2 Printers	12.602	12.76	11.586	12.292
2 keyboards	1.986	3.342	2.676	2.496
1 video recorder	3.652	4.71	5.958	6.62
2 DVD/CD players	8.928	7.12	7.252	8.334
3 portable Radio/CD players	7.934	8.082	8.1	8.156
1 Speaker	2.072	2.102	4.254	4.312
2 Telephones, cord connected	1.738	2.204	2.182	1.774
3 Television sets	105.132	105.626	102.89	101.91
Total	242.402	242.424	242.39	242.40

After weighing all the items to be used in the fire tests, the waste was distributed into four cages from El-Kretsen. The waste was placed in a similar way in each cage in the four separate tests. Each cage contained a combustible board as the bottom. The weight of the board (excluding the piece removed to allow the ignition flame from the burner to enter the cage) was approximately 12 kg. This weight is not included in the total weight given in Table 2.1. The inner dimensions of the cages were (l × b × h) 152 cm × 109 cm × 106.5 cm. The total height (including stands) of a cage was 120.5 cm.

2.2 Tyres

For the tests with tyres, SDAB allowed SP to use some of their collected tyres for research purposes and Ragn-Sells delivered approximately 200 tyres. Among these tyres most were car tyres, but some were larger tyres or motorcycle tyres. From the delivered tyres, whole car tyres, as similar to each other in size as possible, were selected for the four tests.

3 Experimental set-up

In each test with EE-waste the cage with waste was placed on a large square steel pan 2 m × 2 m. The pan had a 3 cm high rim around the sides. The purpose of the pan was to collect melting plastic. The pan was placed on a stand connected to load cells (see Figure 3.1). There was a square hole in the pan under which a square propane burner was positioned. During the tests with extinguishment, the pan also collected the water, but to decrease the effect on the load cells, holes were drilled near the four corners of the pan during the first test with extinguishment (Test 2) and the water was then collected in small steel pans beneath the holes. The whole set up was contained inside a concrete pan (3 m × 4 m) for additional collection of spill water.

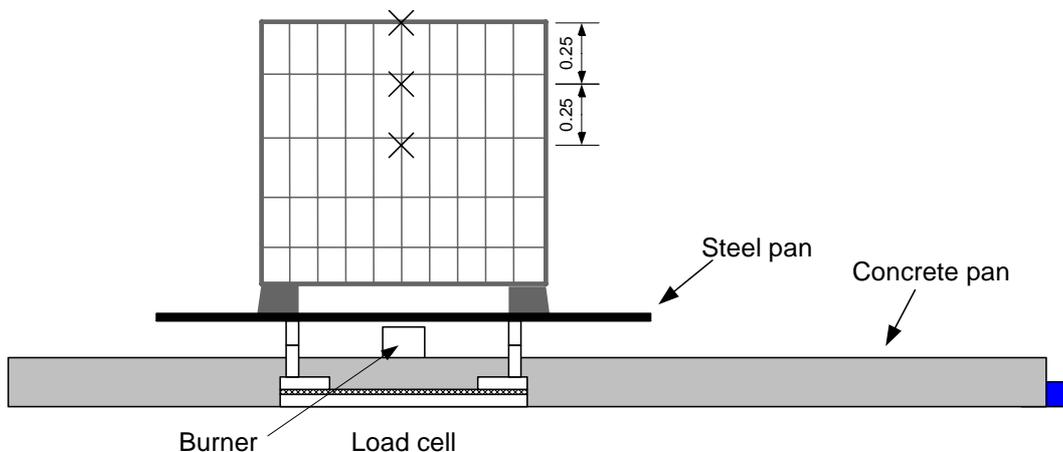


Figure 3.1 The experimental set-up with the cage with electronic waste on the metal pan placed on load cells. The waste was ignited with the help of a propane burner. In case of extinguishment, the water was collected in a concrete pool. The symbol × represents thermocouples.

The gas temperature was measured at three different positions, in the centre of the cage at three different heights. The thermocouples (type K, 0,25 mm) were positioned at the top level of the cage and 0.25 m and 0.5 m below this level (see Figure 3.1).

In the tests with used tyres, two different experimental set-ups were used, denoted: *heap* and *pile*. Both set-ups represent common ways to store used tyres. There are also other types of storage, e.g. container, but since that type of storage was not found to be as common as the other two it was not investigated in the experimental series.

In both set-ups, used the tyres were positioned on a steel pan, 2 m × 2 m. The steel pan was placed on steel beams lying on load cells (see Figure 3.2 and Figure 3.3). The whole set-up was positioned above a concrete pool (3 m × 4 m) to collect the extinguishing water, with the load cells placed on each side of the concrete pan. The load of tyres consisted of 32 used tyres in all tests. The tyres available varied somewhat in size, but tyres as similar as possible were selected for the tests. In the tests with *heaped* arrangement, the tyres were placed in several layers in the same way in each test. The total weight of the tyres for each test is presented in Table 3.1. Each tyre contained two rings of steel wire. The shape and weight of these varied, but the weight of each ring was approximately 150 g. This means that 9 kg to 10 kg in each tyre load consisted of incombustible steel wire.

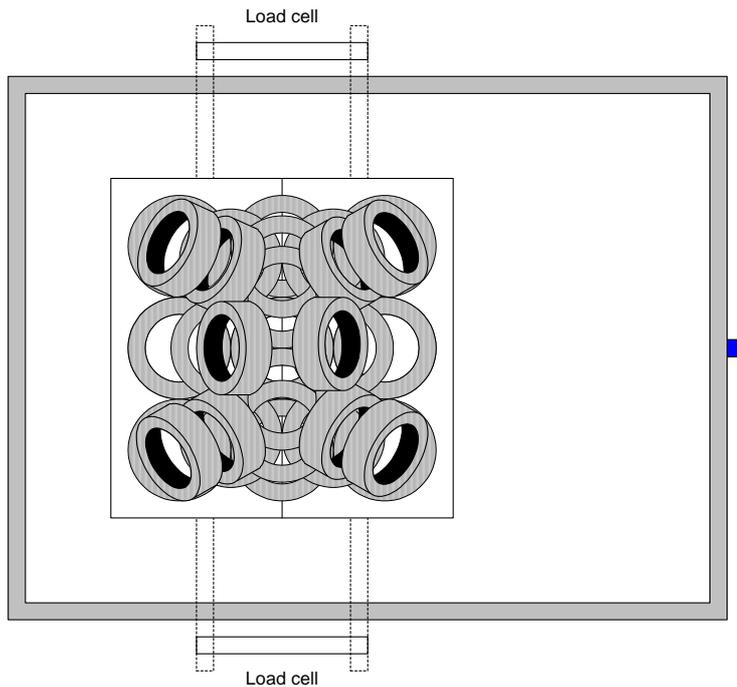


Figure 3.2 Experimental set-up for the heap of tyres.

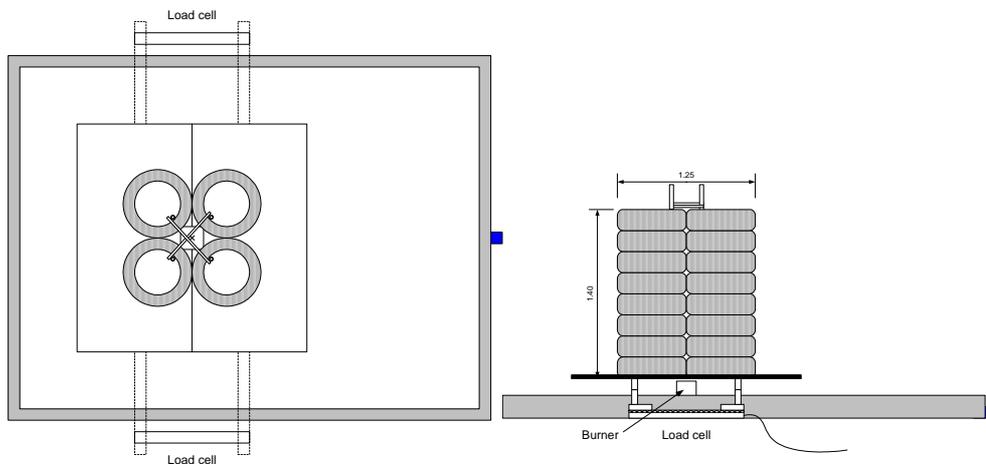


Figure 3.3 Experimental set-up of the pile of tyres.

Table 3.1 Total weight of tyres in each test.

Test id	Type of set-up	Weight [kg]
T5	Heap	245.6
T6	Heap	247
T7	Heap	239.2
T8	Pile	245.9

A square gas (propane) burner (17 cm × 17 cm) was placed in the concrete pool and ignited the commodities through a hole (22 cm × 22 cm) in the bottom of the steal pan. A piece of Promatect® board ran in tracks on the bottom of the steal pan. This was used for covering the hole in the bottom after the gas burner was switched off.

4 Experimental procedure

Each test started with background measurements for two minutes with the time resolved gas analysers. After this period the gas burner was ignited (time zero) and was let burn for two minutes to ignite the fuel load. After the gas burner had been switched off, the hole in the steel pan was closed using the Promatect board. At this time the accumulating gas sampling was started (see references [7, 8]), if the test did not include water application. In the case where water application was included, the accumulating gas sampling was started when the water application was started. The time the accumulating gas sampling was ended depended on the type of species being analysed and how much gas had been collected. More information on the gas sampling and results from the gas analyses are given elsewhere [7, 8].

Water application was used in four of the tests. This is described further in Section 5

After each test, representative samples of fire debris were collected and sent for analysis. Included in the analyses were:

- polychlorinated dibenzodioxins and furans (PCDD/PCDF), analysed using high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS),
- polycyclic aromatic hydrocarbons (PAH), analysed using gas chromatography and mass spectrometry (GC/MS),
- polybrominated dibenzodioxins and furans (PBDD/PBDF), analysed using HRGC/HRMS,
- selected brominated flame retardants, analysed using GC/MS,
- and metals and other selected elements, analysed using inductively coupled plasma and mass spectrometry (ICP-MS).

A limited number of the samples were analysed directly after the tests. The results from these analyses are denoted "December 2004", while the rest were frozen and analysed in June, 2005.

5 Water application

A water applicator with nine nozzles was used for the water application. The nozzles were positioned in three rows with three nozzles in each row. The distance between the rows and between the nozzles in each row was 45 cm. The applicator was placed so that the openings of the nozzles were situated 20 cm above the highest point of the set-up (the top of the cage in the case of EE-waste and the top tyre in the heap of tyres). A total water flow of 5 L/min was used. A calibration test showed that the water density on a plane 20 cm beneath the nozzles was approximately 2 L/m²/min. The water flow rate was chosen to affect the fire but not to extinguish it. The reason for this strategy was to be able to collect extinguishing water that has been affected by the combustion. The water density is also representative for what can be assumed to be the case when fighting a fire from a distance.

In test T2 approximately 150 L water was used during the water applicator phase and 6.7 L for the manual extinguishment. The corresponding values for T4 were 150 L and 8.1 L, respectively. In test T6, some of the nozzles were not functioning correctly, i.e. they did not give the correct spray pattern. The water, however, ended up at the fuel; it was only the total spray pattern that differed from the one in the case of correct nozzle function. In test T6 approximately 140 L water was used during the water applicator phase and 98 L for the manual extinguishment. The corresponding values for T7 were 140 L and 42.3 L, respectively. The values 140 L and 150 L, respectively, are based on the calibration values (5 L/min).

6 Results

6.1 Heat release rate and temperature

Time resolved results of HRR and gas temperatures for the tests with EE-waste and tyres are presented elsewhere by Lönnermark and Blomqvist [7, 8]. However, in Table 6.1 and Table 6.2 the maximum HRR and maximum gas temperatures are presented.

Table 6.1 Maximum HRR and maximum gas temperatures at different heights during the tests with EE-waste; height 0 corresponds to a height 1 m above the steel pan.

Test	HRR _{max} [kW]	T _{max,-50cm} [°C]	T _{max,-25cm} [°C]	T _{max,0cm} [°C]
T1	1950	1127	1144	1270
T2	1824	1187	1227	1197
T3	1622	1012	937	959
T4	1718	1081	1094	1222

Table 6.2 Maximum HRR and maximum gas temperatures at different heights during the tests with tyres; height 0 corresponds in tests T5 to T7 to a height 1 m above the steel plate and in T8 to a height 1.40 m above the steel pan.

Test	HRR _{max} [kW]		T _{max,-25cm} [°C]	T _{max,0cm} [°C]
T5	3722	-	1246	1292
T6	3609	-	1318	1363
T7	3686	-	1275	1141
		T _{max,-65cm} [°C]	T _{max,-40cm} [°C]	T _{max,0cm} [°C]
T8	3607	1072	1231	1057

In most of the tests the time resolved temperature measurements at the different heights showed rather similar results. The differences in maximum values at the different heights as presented in Table 6.1 and Table 6.2 do not really represent the general situation in a test. Instead the values are better used to compare between the different tests. In two of the tests (T3 and T8), however, the differences in temperatures between the different heights were relatively large [7, 8].

6.2 Mass loss

The mass loss was registered using load cells during the tests and for the tests without extinguishment during the sampling period (T1, T3, T5 and T8), the evaluation is straight forward. The consumed mass during a certain time period could be taken directly from the difference in the load cell signal. The application of water/foam complicates the situation. The load cell signal was first used together with information about the amount of applied water, the fire intensity, and visual observations to estimate the consumed mass for these time periods. However, when these values were used to calculate heats of combustion it was seen that the estimated mass losses probably were too small. Instead average values of the heat of combustion were used to estimate the mass loss during the time periods of water application. These estimated mass losses contain a larger inherent uncertainty compared to the cases without water application, but they are assumed to be sufficiently valid to provide interesting information for the calculation of yield [7, 8]. The measured and estimated mass losses for the main part of the tests are summarized in Table 6.3.

Table 6.3 Mass losses (in kg) during the entire tests. The time periods (in min) within the parenthesis are given from ignition. The starting time of the interval is taken when the ignition burner was switched off.

Tests	Mass loss [kg]
T1	70.9 (2-40)
T2	28.5 (2-33)
T3	62.1 (2-50)
T4	35.1 (2-28)
T5	112 (2-41)
T6	118.1 (2-40)
T7	115.9 (2-40)
T8	118 (2-43)

6.3 Analyses of fire debris

In this section the concentration of different species in the fire debris is presented. Most of the results are presented in tables, but some comparisons are also presented graphically.

The concentrations of different PAHs in the fire debris from the fires in EE-waste are presented in Table 6.4. Corresponding values for the fires in tyres are presented in Table 6.5. In Figure 6.1 the analysed concentrations are compared to values for contaminated soil. The values selected for the comparison correspond to the limit between “moderately serious” and “serious” contamination of soil [9].

Table 6.4 PAH in the fire debris from electronic waste (mg/kg DS).

Species	T1	T2	T3	T4
Benzo(a)anthracene	27	2.8	0.3	2.1
Benzo(a)pyrene	<0.03	1.6	0.11	0.87
Benzo(b)fluoranthene	<0.03	4.2	0.46	2.0
Benzo(k)fluoranthene	<0.03	1.2	0.27	0.40
Chrysene/Triphenylene	0.051	5.6	0.72	3.8
Dibenzo(a,h)anthracene	<0.03	0.43	<0.1	0.28
Indeno(1,2,3-cd)pyrene	<0.03	1.3	0.12	0.73
PAH, total carcinogenic	27	17	2.0	10
Acenaphtene	0.20	0.50	0.36	0.46
Acenaphtylene	<0.03	4.4	0.52	1.8
Anthracene	0.057	6.5	0.67	3.9
Benzo(ghi)perylene	<0.03	0.80	<0.1	0.39
Phenanthrene	0.27	34	1.8	19
Fluoranthene	0.040	10	0.72	5.3
Fluorene	0.051	4.4	0.22	2.1
Naphtalene	65	32	31	110
Pyrene	<0.03	6.4	0.41	3.3
PAH, total others	66	99	36	150

Table 6.5 PAH in the fire debris from tyres (mg/kg DS).

Species	T5	T6	T7	T8
Benzo(a)anthracene	0.62	6.6	5.3	<0.1
Benzo(a)pyrene	0.67	5.9	6.1	<0.1
Benzo(b)fluoranthene	1.2	6.6	6.8	<0.1
Benzo(k)fluoranthene	0.22	1.5	2.0	<0.1
Chrysene/Triphenylene	1.6	11	7.4	<0.1
Dibenzo(a,h)anthracene	0.28	1.4	1.1	<0.1
Indeno(1,2,3-cd)pyrene	0.83	4.6	4.6	<0.1
PAH, total carcinogenic	5.4	38	33	<0.15
Acenaphtene	37	8.1	24	1.6
Acenaphtylene	2.0	5.6	6.8	1.4
Anthracene	5.1	10	12	3.4
Benzo(ghi)perylene	2.9	11	12	<0.1
Phenanthrene	5.2	34	35	2.2
Fluoranthene	2.1	15	15	<0.1
Fluorene	2.8	9.8	11	<0.1
Naphtalene	67	78	63	110
Pyrene	3.5	30	25	880
PAH, total others	130	200	200	1000

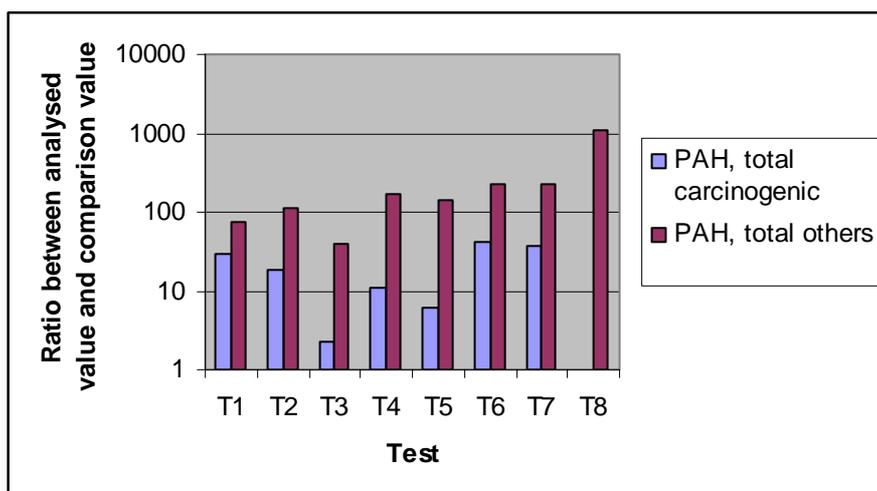


Figure 6.1 Ratio of concentration in the fire debris and limits between “moderately serious” and “serious” for contaminated soil for PAHs. The limit values are taken from reference [9].

The fire debris was analysed for PCDD/F and for two of the tests (T1 and T4) two samples were taken and analysed on different occasions (December 2004 and June 2005, respectively). The concentrations of different congeners for the different samples are presented as absolute concentrations in Table 6.6 and Table 6.7, and as relative occurrence in Table 6.9 and Figure 6.3. Most of the analyses were performed in June 2005 and the results from these analyses are also presented as absolute concentration (see Table 6.7 and Table 6.8) and in relative terms (see Table 6.10, Figure 6.4, and Figure 6.5).

Table 6.6 Chlorinated dioxins and furans in the fire debris (analysed in December 2004).

Congener	Concentration (ng/kg DS)	
	T1	T4
2378 TCDD	<3	4.3
12378 PeCDD	<2	7.7
123478 HxCDD	<1	3.0
123678 HxCDD	<1	4.5
123789 HxCDD	<1	4.1
1234678 HpCDD	2.4	9.3
OCDD	2.5	6.0
2378 TCDF	140	140
12378 PeCDF	150	88
23478 PeCDF	100	76
123478 HxCDF	62	69
123678 HxCDF	69	94
123789 HxCDF	36	33
234678 HxCDF	51	89
1234678 HpCDF	45	130
1234789 HpCDF	23	36
OCDF	11	71
TCDD-ekv I-TEQ Lower Bound	94	96
TCDD-ekv I-TEQ Upper Bound	98	96

Table 6.7 Chlorinated dioxins and furans in the fire debris from EE-waste (analysed in June 2005).

Congener	Concentration (ng/kg DS)			
	T1	T2	T3	T4
2378 TCDD	2.1	110	11	8.8
12378 PeCDD	2.5	310	6.8	17
123478 HxCDD	<2	210	3.3	6.0
123678 HxCDD	<2	330	3.8	10
123789 HxCDD	<2	280	12	7.7
1234678 HpCDD	2.3	1400	20	21
OCDD	3.6	1500	120	15
2378 TCDF	10	960	12	270
12378 PeCDF	11	1200	8.7	250
23478 PeCDF	15	1900	11	290
123478 HxCDF	5.9	1700	15	140
123678 HxCDF	6.9	1800	11	170
123789 HxCDF	2.7	480	6.1	38
234678 HxCDF	5.4	1800	9.4	140
1234678 HpCDF	5.9	5100	36	220
1234789 HpCDF	2.7	980	12	33
OCDF	3.5	3500	100	120
TCDD-ekv I-TEQ Lower Bound	15	2100	29	260
TCDD-ekv I-TEQ Upper Bound	15	2100	29	260

Table 6.8 Chlorinated dioxins and furans in the fire debris from tyres (analysed in June 2005).

Congener	Concentration (ng/kg DS)			
	T5	T6	T7	T8
2378 TCDD	3.8	2.2	4.7	20
12378 PeCDD	<2	4.3	4.0	7.2
123478 HxCDD	7.5	2.8	3.5	13
123678 HxCDD	12	10	4.9	20
123789 HxCDD	14	13	14	39
1234678 HpCDD	16	33	20	51
OCDD	29	29	12	650
2378 TCDF	3.0	<2	3.3	7.8
12378 PeCDF	5.7	4.4	8.1	14
23478 PeCDF	8.6	3.2	6.9	29.7
123478 HxCDF	12	6.1	11	15
123678 HxCDF	10	2.2	8.4	15
123789 HxCDF	7.7	3.2	3.8	6.6
234678 HxCDF	13	3.0	6.9	4.5
1234678 HpCDF	20	10	21	120
1234789 HpCDF	14	4.2	8.2	2.9
OCDF	22	9.3	13	640
TCDD-ekv I-TEQ Lower Bound	17	11	17	44
TCDD-ekv I-TEQ Upper Bound	18	11	17	44

In Figure 6.2 the analysed concentrations of PCDD/F expressed as toxic equivalents are compared to values for contaminated soil. The values selected for the comparison correspond to the limit between “moderately serious” and “serious” contamination of soil [9].

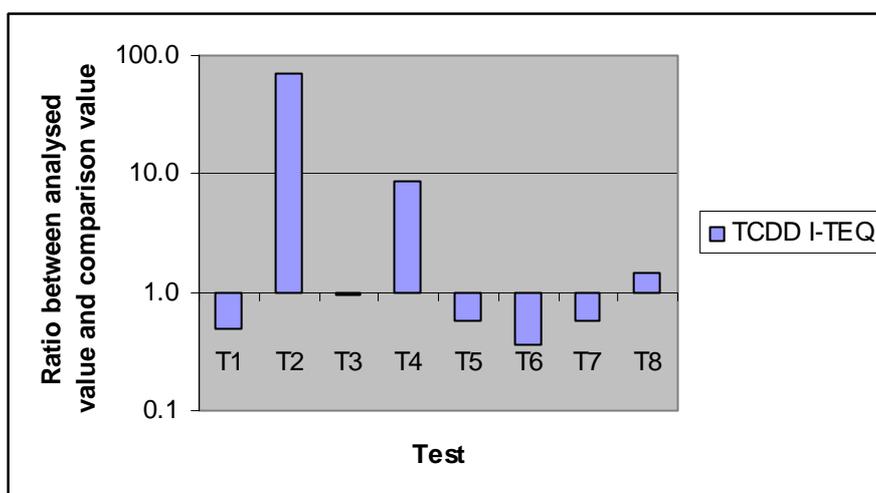


Figure 6.2 Ratio of concentration in the fire debris and limits between “moderately serious” and “serious” for contaminated soil for TCDD I-TEQ. The limit values are taken from reference [9].

Table 6.9 Relative occurrence (in %) of different congeners of chlorinated dioxins and furans in the fire debris from the EE-waste (analysed in December 2004 and June 2005, respectively).

Congener	Relative occurrence (%)			
	T1 Dec 04	T1 June 05	T4 Dec 04	T4 June 05
2378 TCDD	<0.4	2.5	0.5	0.5
12378 PeCDD	<0.3	2.9	0.9	1.0
123478 HxCDD	<0.1	<2.3	0.3	0.3
123678 HxCDD	<0.1	<2.3	0.5	0.6
123789 HxCDD	<0.1	<2.3	0.5	0.4
1234678 HpCDD	0.3	2.7	1.1	1.2
OCDD	0.4	4.2	0.7	0.9
2378 TCDF	20	12	16	15
12378 PeCDF	21	13	10	14
23478 PeCDF	14	18	8.8	17
123478 HxCDF	8.9	6.9	8.0	8.0
123678 HxCDF	9.9	8.1	11	9.7
123789 HxCDF	5.1	3.2	3.8	2.2
234678 HxCDF	7.3	6.3	10	8.0
1234678 HpCDF	6.4	6.9	15	13
1234789 HpCDF	3.3	3.2	4.2	1.9
OCDF	1.6	4.1	8.2	6.8
Total	100	100	100	100

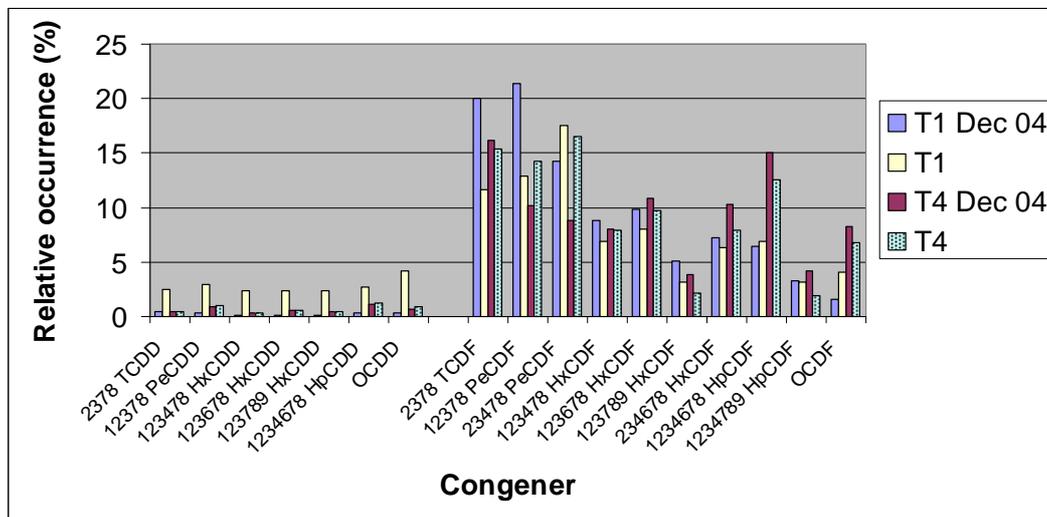


Figure 6.3 Relative occurrence of different PCDD/F congeners: comparison of different samples.

Table 6.10 Relative occurrence (in %) of different congeners of chlorinated dioxins and furans in the fire debris.

Congener	Relative occurrence (%)							
	T1	T2	T3	T4	T5	T6	T7	T8
2378 TCDD	2.5	0.5	2.8	0.5	1.9	1.6	3.1	1.2
12378 PeCDD	2.9	1.3	1.7	1.0	<1.0	3.0	2.6	0.4
123478 HxCDD	<2.3	0.9	0.8	0.3	3.7	2.0	2.3	0.8
123678 HxCDD	<2.3	1.4	1.0	0.6	6.0	7.0	3.2	1.2
123789 HxCDD	<2.3	1.2	3.0	0.4	7.0	9.2	9.1	2.4
1234678 HpCDD	2.7	5.9	5.0	1.2	8.0	23	13	3.1
OCDD	4.2	6.4	30	0.9	14	20	7.8	39
2378 TCDF	12	4.1	3.0	15	1.5	1.4	2.1	0.5
12378 PeCDF	13	5.1	2.2	14	2.8	3.1	5.3	0.8
23478 PeCDF	18	8.1	2.8	17	4.3	2.3	4.5	1.8
123478 HxCDF	6.9	7.2	3.8	8.0	6.0	4.3	7.2	0.9
123678 HxCDF	8.1	7.6	2.8	9.7	5.0	1.6	5.5	0.9
123789 HxCDF	3.2	2.0	1.5	2.2	3.8	2.3	2.5	0.4
234678 HxCDF	6.3	7.6	2.4	8.0	6.5	2.1	4.5	0.3
1234678 HpCDF	6.9	22	9.0	13	10	7.0	14	7.2
1234789 HpCDF	3.2	4.2	3.0	1.9	7.0	3.0	5.3	0.2
OCDF	4.1	15	25	6.8	11	6.6	8.5	39
Total	100	100	100	100	100	100	100	100

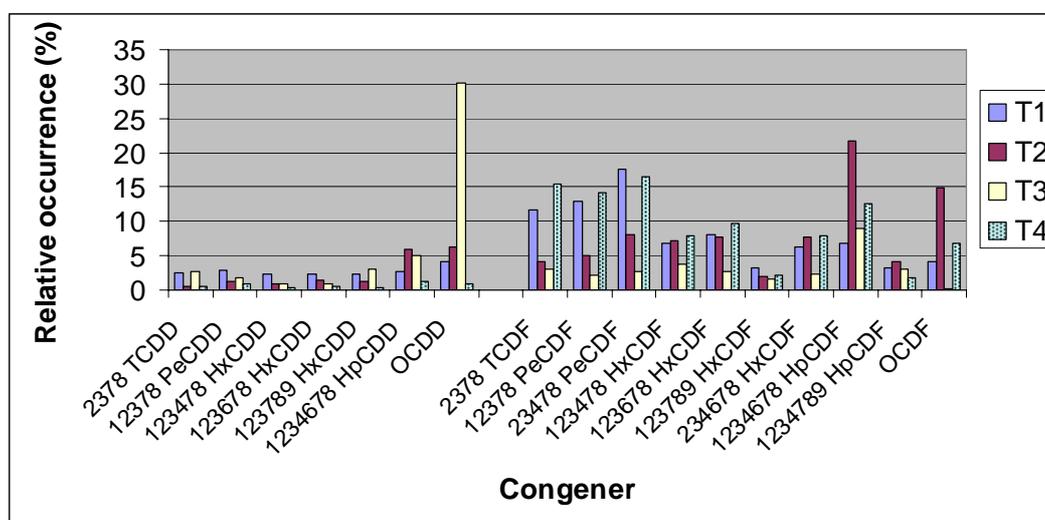


Figure 6.4 Relative occurrence of different PCDD/F congeners: comparison of different tests with EE-waste.

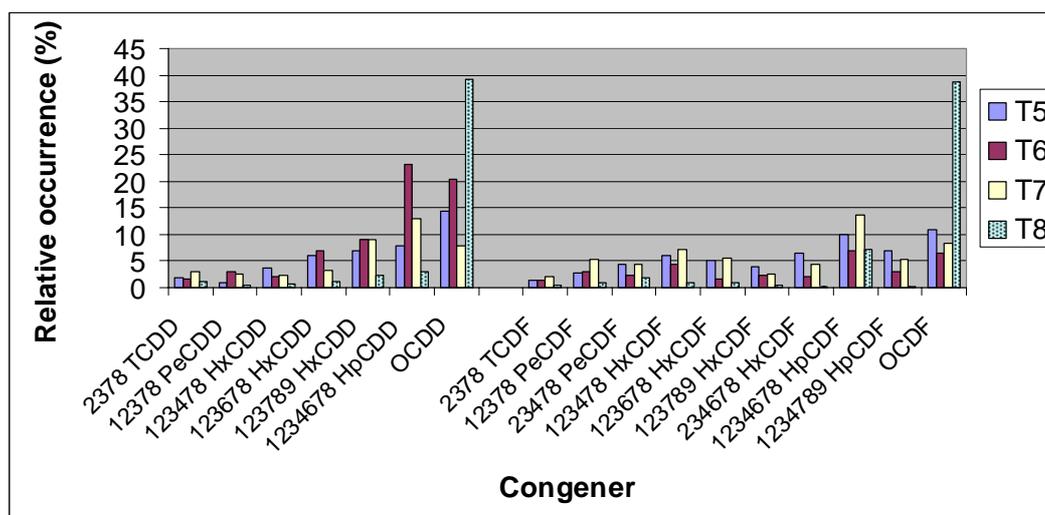


Figure 6.5 Relative occurrence of different PCDD/F congeners: comparison of different tests with tyres.

The samples of fire debris from two of the tests with EE-waste were analysed for two types of brominated compounds: brominated flame retardants and brominated dioxins and furans (PBDD/F). The results from these analyses are presented in Table 6.11 and Table 6.12.

Table 6.11 Brominated flame retardants in the fire debris from the EE-waste ($\mu\text{g}/\text{kg DS}$).

Species	T1	T4	T4/T1
2,2',4,4'-TeBDE, #47	33	310	9.4
2,2',4,4',6-PnBDE, #100	2.6	100	38
2,2',4,4',5-PnBDE, #99	14	290	21
2,2',3,4,4'-PnBDE, #85	<1	56	
2,2',4,4',5,6'-HxBDE, #154	1.4	160	114
2,2',4,4',5,5'-HxBDE, #153	<1	78	
2,2',3,4,4',5'-HxBDE, #138	<1	14	
DekaBDE, #209	<2	11	
Tetrabromobisphenol A (TBBP A)	18	810	45
2,4,6-Tribromophenol	170	760	4.5

Table 6.12 Brominated dioxins and furans in the fire debris from EE-waste.

Congener	Concentration (ng/kg DS)		
	T1	T4	T4/T1
2378 TBrDD	<10	910	
2378 TBrDF	320	8400	26
12378 PeBrDD	8.5	330	39
12378 PeBrDF	71	850	12
23478 PeBrDF	91	3100	34
123478/123678 HxBrDD	<30	170	
123789 HxBrDD	<100	120	
123478 HxBrDF	91	780	8.6
1234678 HpBrDF	<100	160	

In Table 6.13 concentration in the EE-waste fire debris of metals often used to define contamination of soil are presented. The concentrations are in Figure 6.6 compared to the limit values between the intervals for contamination denominated “moderately serious” and “serious”, respectively [9]. Note that Cr (VI) not has been analysed explicitly, but it is total chromium that is compared.

Table 6.13 Concentration in the debris from test T1 to T4 of metals often used to define contamination of soil [$\mu\text{g}/\text{kg}$].

Element	T1	T2	T3	T4
Arsenic, As	970	2100	11000	<56
Lead, Pb	11000000	530000	2100000	6500000
Cadmium, Cd	6000	21000	<53	640000
Cobalt, Co	2600	3700	92000	2700
Copper, Cu	86000000	14000000	42000000	28000000
Chromium, Cr	34000	1000000	28000	6100
Mercury, Hg	51	160	<53	<56
Nickel, Ni	930000	11000	490000	23000
Vanadium, V	3100	100000	14000	890
Zinc, Zn	3300000	4200000	2200000	1700000

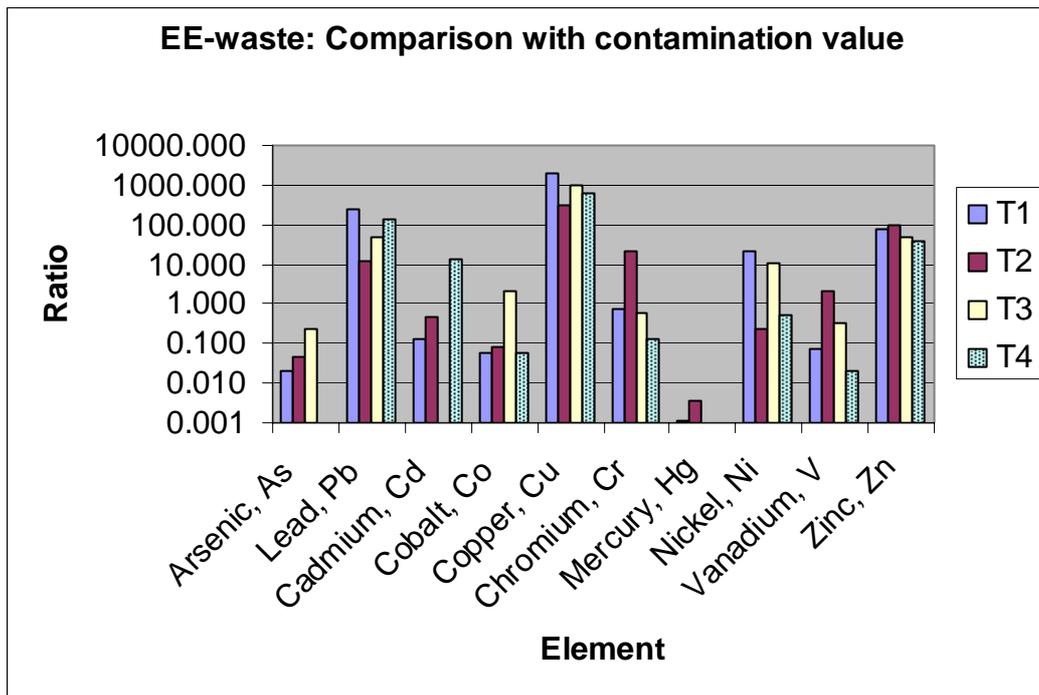


Figure 6.6 Ratio of concentration in the EE-waste fire debris and limits between “moderately serious” and “serious” for contaminated soil for selected elements. The limit values are taken from reference [9].

Table 6.14 Elements in the fire debris (except those reported in Table 6.13) from tests T1 to T4 [µg/kg].

Element ^{a)}	T1	T2	T3	T4
Aluminium, Al	14000000	>100000000	22000000	2800000
Antimony, Sb	130000	76000	140000	100000
Barium, Ba	200000	170000	500000	650000
Beryllium, Be	61	210	480	56
Boron, B	600000	750000	6200000	56000
Bromine, Br	25000000	8300000	8200000	49000000
Cerium, Ce	360	950	5500	390
Caesium, Cs	58	<53	2500	84
Dysprosium, Dy	<51	<53	360	<56
Erbium, Er	<51	<53	130	<56
Europium, Eu	56	110	130	56
Phosphorus, P	3400	7400	11000	5300
Gadolinium, Gd	<51	<53	440	<56
Gallium, Ga	1800	13000	5500	670
Gold, Au	410	<53	160	<56
Hafnium, Hf	<51	530	<53	<56
Indium, In	<51	110	520	450
Iron, Fe	40000000	5300000	3700000	2800000
Calcium, Ca	10000000	21000000	58000000	16000000
Potassium, K	490000	540000	1800000	5100000
Silicon, Si	7500	54000	12000	13000
Carbon, C	2700000	2300000	2200000	3100000
Lanthanum, La	360	790	3500	430
Lithium, Li	2600	2800	1900	1600
Magnesium, Mg	620000	610000	1300000	1200000
Manganese, Mn	170000	1700000	140000	250000
Molybdenum, Mo	920	11000	640	110
Sodium, Na	1300000	340000	1700000	730000
Neodymium, Nd	310	420	3200	220
Niobium, Nb	<51	630	<53	<56
Palladium, Pd	360	1400	320	<56
Praseodymium, Pr	100	160	850	56
Rubidium, Rb	870	1600	13000	7900
Samarium, Sm	51	110	640	<56
Selenium, Se	102	160	640	13000
Silver, Ag	4500	2700	20000	38000
Scandium, Sc	200	1200	1700	340
Strontium, Sr	32000	43000	460000	55000
Tin, Sn	2600000	130000	1300000	2000000
Terbium, Tb	<51	<53	53	<56
Thorium, Th	100	110	390	<56
Titanium, Ti	520000	580000	350000	260000
Uranium, U	100	160	800	<56
Bismuth, Bi	8100	6200	1700	<20000
Tungsten, W	<51	320	<53	<56
Ytterbium, Yb	<51	<53	160	<56
Yttrium, Y	1300	1600	3400	1200
Zirconium, Zr	460	52000	3100	110

a) Germanium, Holmium, Iridium, Iodine, Chlorine, Lutetium, Osmium, Platinum, Rhenium, Ruthenium, Sulfur, Thallium, Tantalum, Tellurium, and Thulium were also analysed for, but the concentrations were below the detections limits.

Table 6.15 Concentration in the debris from test T5 to T6 of metals often used to define contamination of soil [$\mu\text{g}/\text{kg}$].

Element ^{a)}	T5	T6	T7	T8
Arsenic, As	790	<49	540	340
Lead, Pb	32000	39000	78000	4600
Cadmium, Cd	1600	2200	6000	160
Cobalt, Co	240000	580000	410000	400000
Copper, Cu	92000	99000	200000	61000
Chromium, Cr	6400	7100	4800	3300
Nickel, Ni	<53	4700	1800	<54
Vanadium, V	1600	2500	1400	1700
Zinc, Zn	38000000	42000000	37000000	20000000

a) Mercury was also analysed for but the concentrations were below the detections limits.

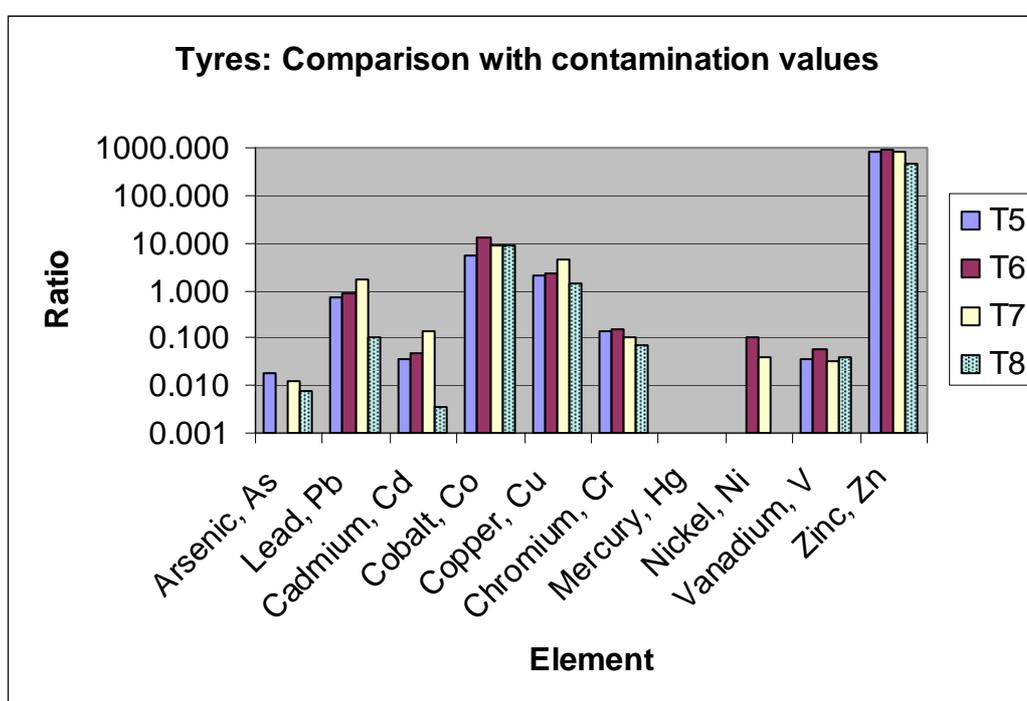


Figure 6.7 Ratio of concentration in the tyre fire debris and limits between “moderately serious” and “serious” for contaminated soil for selected elements. The concentrations of Mercury were below the detection limit and are therefore not included in the graph. The limit values are taken from reference [9].

Table 6.16 Elements in the fire debris (except those reported in Table 6.15) from tests T5 to T6 [$\mu\text{g}/\text{kg}$].

Element	T5	T6	T7	T8
Aluminium, Al	1700000	1100000	760000	550000
Antimony, Sb	740	1200	1400	1100
Barium, Ba	7900	6200	7700	35000
Beryllium, Be	<53	54	<56	<54
Boron, B	240000	34000	75000	11000
Bromine, Br	2700000	810000	2000000	1400000
Cerium, Ce	420	<49	320	380
Caesium, Cs	<53	49	<56	<54
Phosphorus, P	5000	5900	6000	4500
Gallium, Ga	420	380	270	<54
Indium, In	<53	98	78	<54
Iodine, I	<53	4700	1200	<54
Iron, Fe	8700000	2500000	1300000	6500000
Calcium, Ca	7100000	1700000	1500000	6200000
Potassium, K	740000	970000	640000	430000
Silicon, Si	8500	11000	7800	9800
Carbon, C	4000000	4200000	3300000	3100000
Lanthanum, La	740	540	540	1100
Lithium, Li	1800	4500	5300	3700
Magnesium, Mg	520000	630000	570000	630000
Manganese, Mn	51000	22000	12000	1000
Molybdenum, Mo	510	440	290	340
Sodium, Na	580000	600000	790000	40000
Neodymium, Nd	890	6700	1600	2000
Niobium, Nb	<53	49	<56	110
Praseodymium, Pr	110	98	120	160
Rhodium, Rh				
Rubidium, Rb	3000	2500	1900	1100
Selenium, Se	<53	390	<56	<54
Silver, Ag	620	490	<56	<54
Scandium, Sc	260	390	230	160
Strontium, Sr	6200	3600	2600	8000
Sulfur, S	1300000	1500000	1400000	1100000
Thallium, Tl	<53	49	<56	<54
Tin, Sn	5500	2100	1400	860
Thorium, Th	<53	98	<56	<54
Titanium, Ti	59000	51000	22000	47000
Uranium, U	160	98	67	<54
Tungsten, W	<53	390	<56	<54
Yttrium, Y	210	200	140	110
Zirconium, Zr	260	440	100	<54

a) Dysprosium, Erbium, Europium, Gadolinium, Germanium, Gold, Hafnium, Holmium, Iridium, Chlorine, Mercury, Lutetium, Osmium, Palladium, Platinum, Rhenium, Ruthenium, Samarium, Tantalum, Tellurium, Terbium, Thulium, Bismuth, and Ytterbium were also analysed for, but the concentrations were below the detections limits.

7 Discussion and conclusions

Analyses of the fire debris after eight fire tests have been presented. Two different fuels were used: EE-waste and used tyres. Differences due to variations in experimental set-up and between tests with or without water application are identified and discussed below.

It seems that the water application increased the concentration of **PAH** in the debris. This was the case both for EE-waste and tyres, but in the case of EE-waste the relative distribution between carcinogenic PAHs and other PAHs varied. The largest difference between tests was, however, between test T8 and the rest of the tyre tests. In tests T8, where a *pile* of tyres was used instead of a *heap*, the concentration of PAH was significantly higher. Another difference was that almost all of the PAHs in T8 consisted of naphthalene and pyrene and only small concentrations of some other non-carcinogenic PAHs. The concentrations of all carcinogenic PAHs were below the detection limit in test T8.

In all of the tests (except for carcinogenic PAHs in test T8) the concentrations of both the carcinogenic PAHs and others were higher, and in most cases much higher, than the selected values for contaminated soil.

Various comparisons are of interest concerning **PCDD/Fs**. For two of the tests (T1 and T4), two different samples were analysed, one in December 2004 and one in June 2005. For T1 the concentration of dioxins was approximately the same in the two samples. The concentration of furans was, however, approximately ten times higher in the first sample. For T4 the concentrations of both dioxins and furans were higher in the second sample. For both tests the relative concentration of each congener was, however, similar with both pairs of samples (see Table 6.9). The differences in PCDD/F concentrations found between the two samples taken from the same test can probably be attributed to concentration variations in the fire residues and not to changes in concentrations within the samples from December 04 to June 05 when the analyses of the two samples were made. This illustrates the problem with representative sample collection from inhomogeneous materials such as fire debris after fires in EE-waste. The relative occurrence of the different congeners is, however, approximately the same between the different samples. The exception is test T1 where relative occurrences of dioxin congeners in the sample analysed in June 2005 are higher than the corresponding congeners in the other samples.

When comparing the relative occurrences of different congeners for all tests a number of conclusions can be drawn. For the tests with EE-waste, furans were found in higher concentrations than dioxins. The only exception was in test T3 where a high amount of Octa-CDD was found. For the tyre fires the concentrations of dioxins and furans were closer to each other. A tendency towards higher concentration of highly chlorinated congeners can be seen. Specifically for test T8 high concentration of Octa-CDD and Octa-CDF was found.

For the EE-waste, the concentration of PCDD/Fs is highest in the tests with water application. In the tyre tests this effect could not be seen. However, the different experimental set-up in T8 increased the concentration of PCDD/Fs as was the case with PAH.

The calculated toxic equivalents (TCDD I-TEQ) for the eight tests were close to the selected values for contaminated soil (limit between “moderately serious” and “serious” [9]). Highest values were found in test T2 and T4.

EE-waste may contain different types of **brominated flame retardants**. Various polybrominated diphenylethers (PBDEs), tetrabromo bis-phenol A (TBBP-A) and 2,4,6-Tribromophenol were found both in T1 and T4 where analysis of these compounds was made. Further, high concentrations of bromine were found from all EE-tests. The presence of brominated flame retardants and bromine in the residues also indicates the presence of **PBDD/Fs**, which were found in the residues from both tests. The concentrations of brominated flame retardants and PBDD/Fs were higher in test T4 than in test T1, i.e. higher in the test with water application.

Many different **metals** were detected in the fire debris, both from the EE-waste tests and after the tyre tests. For some of the elements comparisons have been made with values for contaminated soil and this comparison shows that for the EE-waste some of the metal concentrations (lead, copper, and zinc) were much higher than the limit between “moderately serious” and “serious” for all tests, while some other metal concentrations were above the limit in one or two of the tests (cadmium, chromium, nickel, and vanadium). For the tyre fires the concentration of zinc was much higher than the limit in all four tests; the concentrations of cobalt and copper were also above the limit in all four tests, while the concentrations of lead were close to the limit and above the limit in one test (T7). High concentrations were also found for other metals, but these were not compared to contamination values.

Even if great efforts were made to obtain fuel load contents that were as similar as possible for each test, there may have been some differences in the fuel composition between the tests that can have affected the results. Further, the total amount of combustible material in the fuel load and the exact chemical composition was not analysed.

The spatial variations within the fire residues were not analysed. In the case of the tyre tests the fire residue was more homogenous than in the cages with EE-waste and therefore easier to extract samples from. The samples from the EE tests had to be taken as mixtures of debris from different positions in the cage to get a fairly representative sample. These samples were taken in the same way in each test.

Although some variation was found in the results of the analysis due to non-representative sampling, the test results give important information on the types of species that can be found in the debris after fires in EE-waste and tyres, respectively. The tests also show that the concentrations of contaminants in the fire residue will vary with the storage configuration and whether water application is used or not.

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