



PM₁₀ and Elemental Concentrations in a Dismantling Plant for Waste of Electrical and Electronic Equipment in Greece

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ABSTRACT

Processing Waste of Electrical and Electronic Equipment (WEEE) causes serious environmental problems, especially when WEEE is processed in uncontrolled conditions. WEEE recycling under controlled conditions consists of the following major steps: disassembly, upgrading and refinement. Disassembly is usually done manually, and, at this stage, certain components (cases, external cables, cathode ray tubes [CRTs], printed circuit boards [PCBs], batteries etc.) are separated. This activity releases coarse and fine particles, which may also contain additional noxious substances, into the atmosphere. The current study determines the concentration of indoor PM₁₀ in a Greek plant for the dismantling and temporary storage of WEEE, based on a short-term sampling campaign. Elemental concentrations in the PM₁₀ have also been determined. Results show that the indoor PM₁₀ concentration in the disassembly area did not exceed the time-weighted average (TWA) for total particles set by Greek legislation or the 8-h TWA for total particles set by the Occupational Safety and Health Administration (OSHA). Nevertheless, these concentrations were higher than those measured in the ambient air of Greek cities. Regarding the measured elements, Zn, As, Br, Pb and Cd were quite enriched in PM₁₀, indicating significant indoor sources. Factor analysis of elements of possible anthropogenic origin showed a clear distinction between cathode ray tubes (CRT) and other possible sources. Finally, the risk assessment for metals of toxicological concern showed a non-negligible lifetime risk for 8-h workers. This is the first report of WEEE indoor air pollution in Greece and its associated origins and effects.

Keywords: Indoor air pollution; PM₁₀; WEEE recycling; Elemental composition; Disassembly.

INTRODUCTION

Management of Waste of Electrical and Electronic Equipment (WEEE) has been listed among the priority issues in European and national policies related to waste management (2003/108/EC, 2012/19/EU). WEEE management has become an urgent issue due to substances included in WEEE which are often hazardous as well as due to the increasing amounts of WEEE that are produced worldwide.

WEEE contain a high percentage of metals (approximately

60% w/w) as well as plastics (15%), cathode ray tubes (CRT) and liquid crystal display (12%), mixed materials of metal and plastics (5%) and many others (Makenji and Savage, 2012) which eventually may be released to the environment and become a threat to humans. In addition, dioxins may be formed as the original e-waste components are degraded (Swedish Environmental Protection Agency, 2011) and polybrominated diphenyl-ethers may be released from the surface of these e-products (Gou *et al.*, 2016).

The best option, both from an environmental and a recovery efficiency point of view, is to recycle the WEEE; however, the recycling process may also cause serious environmental problems, especially when taking place informally under uncontrolled conditions. Several research works have been published on the uncontrolled recycling of WEEE, and especially on case studies in developing countries (Deng *et al.*, 2006; Leung *et al.*, 2006; Huo *et al.*, 2007; Wong *et al.*, 2007; Leung *et al.*, 2008; Liu *et al.*, 2008; Xing *et al.*, 2009; Gu *et al.*, 2010; Sepúlveda *et al.*,

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2010; Chen *et al.*, 2011; Tsydenova and Bengtsson, 2011; Song and Li, 2014; Zheng *et al.*, 2016).

On the contrary, studies on WEEE recycling under controlled conditions in European factories adapted for this purpose are few (Julander *et al.*, 2014; Zimmermann *et al.*, 2014). It is obvious that recycling under controlled conditions is better from a risk perspective for the workers, the local residents, and the environment; nevertheless, risks may occur during these processes as well (Swedish Environmental Protection Agency, 2011).

In this framework, the current study was performed in an organized WEEE dismantling facility in Greece, with the objectives of: (i) determining the PM₁₀ concentrations, as well as the concentrations of selected elements found in PM₁₀, inside a WEEE manual dismantling and temporary-storage plant in Greece; (ii) estimating the possible origin of the different components of airborne particulate matter (PM); (iii) assessing the corresponding health risks for the workers.

This study aims at enriching our knowledge on the state of the art of organized WEEE recycling facilities in developed countries, as well as on the risks and problems that may arise from these activities. Finally, it may act as a database for further similar research in WEEE recycling processes and their environmental impact in Greece.

MATERIALS AND METHODS

Study Site and Production Process

The measurement campaign was carried out in a WEEE treatment plant, located in central Greece with a main dismantling area of 1344 m² and a maximum capacity of 3000 tn year⁻¹. The main activities taking place in the treatment plant are manual disassembly of the WEEE and removal of any hazardous substances, according to the Directive 2002/96/EU. The recycling stages in the treatment plant are: a) arrival and sorting of WEEE by category, b) WEEE processing (manual disassembly and remediation for the recovery of selective treatment substances such as PCB, capacitors, batteries, toners and cartridges etc.) and c) temporary storage and shipping to certified companies and treatment plants for further processing. WEEE categories treated in the treatment plant include: a) IT and telecommunications equipment such as PCs, monitors, printers, phones, etc.; b) consumer equipment such as TVs, radio-CD-DVD players, audio equipment, etc.; c) monitoring and control instruments such as smoke and movement detectors, control panels, measuring, weighing or adjusting appliances etc. (WEEE plant, personal communication).

Sample Collection and Analysis

Sampling campaigns were conducted during the months October and November of 2012. Climatological data for this time-period are given in Table 1 (National Observatory of Athens, 2018). The samples were collected in 11 different points in the WEEE treatment plant, 7 of which were located in the main dismantling area of the treatment plant, 2 were located in the offices of the administrative staff and 2 were located in the area surrounding the treatment plant. A layout of the treatment plant, including the sampling points

and the number of sampling dates in each point is shown in Fig. 1. Sampling points have been strategically chosen, in relation to the process that takes place near them. In Point 1, CRT glass remediation takes place; the tube is split into the electron gun part, the neck/funnel glass and the face plate glass. Each part is then further reduced into smaller parts. In Point 2, activities which precede the activities in Point 1 take place, namely dismantling of TV monitors into TV case part and remaining parts. The latter are then divided into CRT part and other subparts. In Point 3, various electronic equipment, small in size such as fans and mixing machines are dismantled. In Point 4, dismantling of PC monitors, CD players and cell phones take place. CRTs deriving from this process are also subsequently transported to Point 1. Photocopiers are dismantled in Point 5. Dismantling of PCBs takes place in Point 7 while Point 6 was next to the static PM sampler (Tecora Echo PM LVS) and the equipment conveyor belt. Points 9 and 8 are within the office spaces of the plant, which are adjacent to the dismantling area. Point 10 is on the outside, next to the back door of the plant, while Point 11 is also outside in the backyard 37 m from the plant. No mechanical ventilation exists in the treatment plant and the offices, and the rooms are naturally ventilated in daytime through open doors and windows. The WEEE treatment plant did not operate in the weekends.

A Tecora Echo PM LVS sampler was used for the gravimetric determination of PM₁₀ mass concentration in the indoor air of the main dismantling area of the WEEE treatment plant. The sampler operated for 4 hours a day, during working hours. The sampling period was selected such as to prevent overloading of the collected filter samples. The sampler operated at a flow rate of 2.3 m³ h⁻¹, in accordance with the sampling procedure standardized in EN 12341: 1998. The samples were collected on Teflon (Zefluor) filters, 47 mm in diameter and with 2.0 μm pore size. In order to determine PM₁₀ concentrations, filters were equilibrated before and after sampling for at least 24 hours at controlled conditions (20 ± 1°C and 50 ± 5% relative humidity) and were then weighed with the use of a microbalance (d = 0.01 mg). The samples were then analyzed for major and trace elements, by Electrothermal Atomic Absorption Spectroscopy (ET-AAS) and X-ray Fluorescence (XRF). A total number of 10 filters were collected and subsequently analyzed. Details on both analytical techniques are given below.

In addition, two real-time monitors, MIE Thermo Personal DataRAM™ pDR-1000AN and pDR-1200 Particulate Monitors, were used for the determination of PM₁₀ mass concentration inside and outside the WEEE treatment plant. μIE Thermo Personal DataRAM™ pDR-1000AN was used for the determination of PM₁₀ mass concentration at seven different sites inside the WEEE treatment plant. The other monitor was used for the determination of PM₁₀ mass concentration at the other four different sites, two at the offices and two outside the treatment plant. The two monitors were operating 24 h a day, giving data per 30 sec. Raw data collected by the real-time monitors were calibrated based on gravimetric measurements. Specifically, the real-time concentration data recorded inside the dismantling

Table 1. (a) Climatological data from 25 to 31 of October 2012; (b) Climatological data from 1 to 14 of November 2012.

(a)

TEMPERATURE (°C), RAIN (mm), WIND SPEED (km h ⁻¹)										
DAY	MEAN TEMP	HIGH	TIME	LOW	TIME	RAIN	AVG WIND SPEED	HIGH	TIME	DOM DIR
25	15.5	22.7	15:50	9.8	6:50	0.0	0.0	8.0	13:40	NE
26	16.1	24.5	16:10	10.2	7:20	0.0	0.2	8.0	16:30	ENE
27	14.2	16.3	15:40	11.1	7:50	4.4	0.2	8.0	12:30	NNE
28	18.2	23.1	13:10	14.3	2:00	3.2	0.2	9.7	12:20	NNE
29	19.0	24.9	14:20	15.4	0:00	11.8	1.3	38.6	2:50	SSW
30	15.4	20.8	14:30	11.0	23:40	0.8	1.4	27.4	1:00	SW
31	13.7	19.6	14:30	8.2	7:20	0.0	0.2	8.0	12:00	ENE

(b)

TEMPERATURE (°C), RAIN (mm), WIND SPEED (km h ⁻¹)										
DAY	MEAN TEMP	HIGH	TIME	LOW	TIME	RAIN	AVG WIND SPEED	HIGH	TIME	DOM DIR
1	14.6	17.9	13:50	12.6	23:30	13.8	0.3	33.8	14:50	ENE
2	14.6	20.3	15:00	11.4	8:10	0.0	0.2	6.4	10:50	NE
3	15.7	22.6	15:00	10.4	7:00	0.0	0.0	4.8	0:30	NE
4	15.2	20.8	14:30	11.6	7:30	0.0	0.0	6.4	7:10	ENE
5	16.3	23.0	14:00	11.7	7:40	0.0	0.0	6.4	9:50	ENE
6	20.7	28.1	14:10	15.7	2:10	0.0	1.3	20.9	13:40	SSW
7	17.0	21.7	12:20	12.1	22:50	3.8	1.6	24.1	23:50	WSW
8	12.4	16.5	15:00	7.4	0:00	0.0	1.6	24.1	2:50	NE
9	10.2	16.8	15:10	4.4	5:40	0.0	0.2	6.4	15:10	ENE
10	11.2	18.5	14:20	5.7	6:00	0.0	0.6	12.9	13:20	NE
11	10.8	16.9	14:20	6.1	7:20	0.0	0.0	6.4	0:50	ESE
12	10.9	17.3	15:10	5.6	7:30	0.0	0.0	6.4	13:50	WSW
13	11.3	18.1	14:50	6.6	7:10	0.0	0.0	6.4	14:50	WSW
14	10.3	13.2	13:20	6.3	7:20	0.0	0.0	6.4	10:30	NE

area were averaged over the sampling period of the PM sampler and were compared to the corresponding gravimetric measurements. A very good correlation was observed (Pearson coefficient = 0.82). The linear regression equation that was obtained, was used for the calibration of the indoor concentration data. Ambient real-time concentrations were calibrated based on concurrent gravimetric and real-time measurements conducted in the ambient atmosphere in previous experiments (unpublished data). A different calibration equation was used for indoor and outdoor data, since the aerosol composition and size distribution both play a major role in determining the relationship between gravimetric and real-time measurements and these aerosol properties may vary significantly between the indoor and outdoor environments (Diapouli *et al.*, 2008).

X-ray Fluorescence (XRF)

The collected PM₁₀ samples were analysed for 19 elements (µg, Al, Si, S, P, Cl, Ca, K, Ti, Mn, Fe, Cu, Zn, As, Br, Sr, Sn, Ba and Pb) by means of energy dispersive X-Ray Fluorescence (ED-XRF). ED-XRF analysis was performed applying a “thin-layer” measurement on Ø 25 mm disks cut from each Teflon filter. Details on ED-XRF instrumentation, calibration method, detection limits and

overall precision are provided in Grigoratos *et al.* (2014). The analytical data were validated using the NIST 2783 Standard Reference Material (Air particulate on filter media) and single-element XRF Calibration Standards obtained from Micromatter™. Duplicate ED-XRF analyses were performed for about 10% of all ambient samples according to standard operating procedures (Grigoratos *et al.*, 2014).

Electrothermal Atomic Absorption Spectrometer (ET-AAS)

The remaining part of the PM₁₀ filters was analysed by ET-AAS by a Varian 220 spectrometer equipped with a GTA 110 graphite furnace, for the determination of V, Cr, Co, Cd and Ni. Lab and field filter blanks were also prepared and analyzed together with the samples, and the concentrations measured were subtracted from sample measurements (Karanasiou *et al.*, 2005). Details on the analytical procedure followed are provided in Diapouli *et al.* (2017) and Manousakas *et al.* (2014). The analytical data were validated using the NIST 1648 Standard Reference Material. Standards for calibration were obtained from Merck and solutions were prepared by adding ultrapure water from a Millipore Milli-Q System. Palladium was

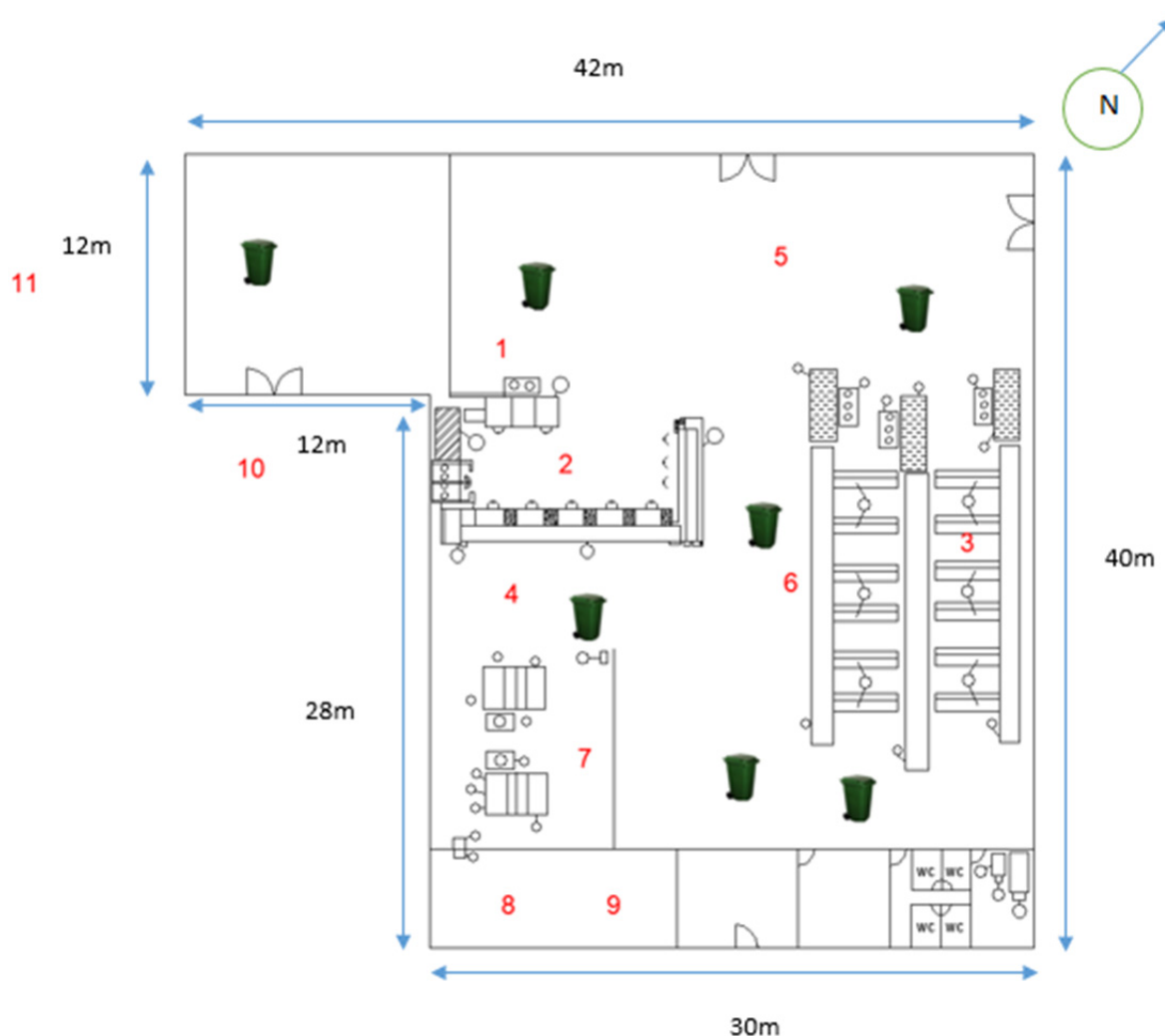


Fig. 1. Layout of the treatment plant together with sampling points. Key: point 1 (2 days): CRT glass remediation; point 2 (5 days): Dismantling of TV monitors; point 3 (3 days): Dismantling of small equipment; point 4 (4 days): Dismantling of PCs monitors and cell phones; Point 5 (4 days): Dismantling of photocopiers; point 6 (1 day): conveyor belt; point 7 (3 days): Dismantling of Printed Circuit Boards; point 8,9 (3 days each): administrative offices; point 10 (2 days): plant backyard; point 11(2 days): plant backyard.

used as modifier for Cd (as Pd, 10 g L⁻¹) and Mg for V (as Mg(NO₃)₂, 10 g L⁻¹). All modifiers were of suprapure grade and were obtained from Merck. Hollow cathode lamps were used as radiation sources for all elements. ET-AAS conditions were carefully optimized for the compensation or elimination of interferences (Karanasiou *et al.*, 2009). Detection limits for the different elements were calculated based on field blank filters and were in the range 0.1 ng m⁻³ (Cd) to 6.8 ng m⁻³ (V).

Calculation of Enrichment Factor

In order to calculate the contribution of natural or anthropogenic sources, the enrichment factor was used (Baeyens and Dedeurwaerder, 1991). The general formula to express the enrichment factor (EF) is:

$$EF = \frac{(X/Y)_{AIR}}{(X/Y)_{CRUST}} \quad (1)$$

where *EF* is the enrichment factor of element *X*, *Y* is the reference element of crustal material, X/Y_{AIR} is the concentration ratio of *X* to *Y* in air sample, and X/Y_{CRUST} is the concentration ratio of *X* to *Y* in the crust (Mason, 1966). If *EF* approaches unity, crustal soils are likely the predominant source for element *X*. If *EF* is > 5, the element *X* may have a significant fraction contributed by non-crustal sources (Gao *et al.*, 2002). *EF* was calculated for 22 elements, Mg, Si, Al, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Sn, Ba, Pb, Cd, Cr, with Al used as the reference element for crustal material. Values for crustal material were obtained from Mason (1966). Due to the low number of observations above the limit of quantification, V and Co were excluded from this analysis.

Correlations between PM₁₀ Values and between elements Found in PM₁₀

Correlations for 8-h PM₁₀ mean concentrations (working

hours) between dismantling area and office area were explored, using Pearson product-moment correlation coefficient, for the days that simultaneous measurements were available (7 days in total) on SPSS22 (IBM, Armonk, NY, USA).

Principal component analysis (PCA) was used to identify the underlying latent factor structure of the PM₁₀ data for the elements of probable anthropogenic origin that are also of toxicological concern: Mn, Ni, As, Sr, Sn, Pb, Cr and Cd. PCA was conducted using maximum likelihood estimation and oblimin rotation. The assumption of homoscedasticity of variance was assessed with Bartlett's test of sphericity.

Human Risk Assessment for Elements Found in PM₁₀

Non-carcinogenic health risk assessment for inhalation exposure was calculated for a number of elements of toxicological concern, namely Pb, As, Cd, Ni, Sn Cr and Mn, according to Li *et al.* (2013). Inhalation exposure concentration was calculated according to the formula

$$C_{\text{inh}} (\text{mg kg}^{-1} \text{ d}^{-1}) = CA \times IR \times t \times EF \times ED / (BW \times AT) \quad (2)$$

with

CA = elemental concentration (mg m⁻³), IR = Inhalation rate (1.3 m³ h⁻¹), t = Daily exposure time span (8 h d⁻¹), EF = exposure frequency (250 d y⁻¹), ED = exposure duration (25 y), AT = averaging time (9125 d), BW = body weight (70 kg).

Calculated C_{inh} were subsequently divided by a reference dose (RfD) to yield a non-cancer hazard quotient (HQ):

$$HQ = C / \text{RfD} \quad (3)$$

RfDs for Ni, Mn, Cd, Cr and As were derived from IRIS database (USEPA, 2017); RfD for Pb was the one used in Qu *et al.* (2012); Sn RfD was derived from the subchronic MRL for inorganic tin (ATSDR, 2005).

Finally, the hazard index (HI) was calculated as the sum of HQs:

$$HI = \sum HQ_i \quad (4)$$

where i corresponds to different contaminants. HI ≤ 1 indicates no adverse health effects whereas HI > 1 indicates likely adverse health effects.

Carcinogenic risk assessment was performed for the metals As, Ni, Cr and Cd according to the formula (Lau *et al.*, 2014):

$$\text{Cancer risk} = \text{IUR} \times \text{EC} \quad (5)$$

where IUR = inhalation unit risk from IRIS database (USEPA, 2017) and

$$\text{EC} (\mu\text{g m}^{-3}) = CA \times t \times EF \times ED / \text{AT} \quad (6)$$

where AT = averaging time (613,200 h)

In order to minimize the uncertainties associated with

the calculation of risk, Monte Carlo simulation technique was used, considering 1,000 iterations. A probabilistic distribution of HQ values and of cancer risk was obtained as simulation result.

RESULTS AND DISCUSSION

PM₁₀ Concentrations

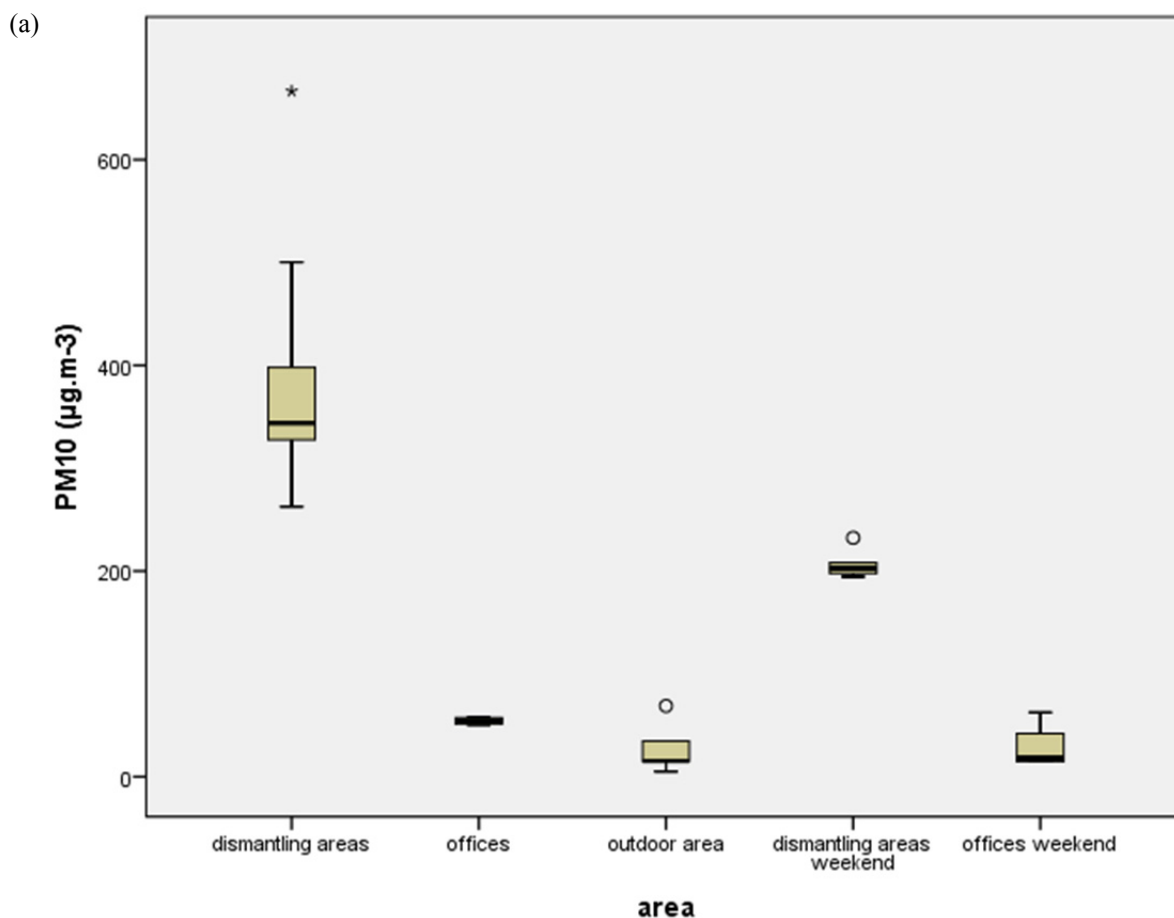
The analysis of the collected data showed that the WEEE dismantling activities resulted in elevated mass concentrations in the indoor environment based on the pDR continuous measurements. 8-h indoor PM₁₀ mass concentrations during working hours are summarized in Fig. 2(b).

While there are no universally accepted upper limits for PM₁₀ mass concentration for the indoor air of different environments, there are quite a few recommendations for Occupational Exposure Limits (OELs). According to the Greek legislation, TWA concentration for total particles emitted during the production phase should not exceed 100 × 10³ μg m⁻³. This limit involves both the indoor and the outdoor environments (Glytsos *et al.*, 2013). Furthermore, OSHA 8-h TWA limit is 15 × 10³ μg m⁻³ for total particulate matter. As such the indoor PM₁₀ concentration in the dismantling area (based on the 8-h average concentrations) did not exceed the above limits.

Kim *et al.* (2015) conducted a U.S.-based study on an e-waste recycling facility that utilized mechanical processing in three lines. In this study they found that the PM₁₀ concentration in two size reduction lines ("low density e-waste" and "high density e-waste", employing various size reduction methods) was 439 ± 233 μg m⁻³ and 543 ± 67 μg m⁻³ respectively, while in CRT disassembly line the respective concentration was 535 ± 165 μg m⁻³. In general, the PM concentration is expected to be increased when size reduction operations are performed comparing to dismantling operation (Tsydenova and Bengtsson, 2011).

Our results of the 8-h PM₁₀ mean concentration are comparable with the results of Fang *et al.* (2013) who measured an average PM₁₀ concentration of 360.4 μg m⁻³ in the mechanical workshop of a licensed and permitted enterprise of waste TV recycling, located in the industrial zone of Shanghai, processing 740,000 television sets per year. Xue *et al.* (2012) reported slightly lower PM₁₀ levels (202.0 μg m⁻³) in a PCB qualified recycling plant located in Jiangsu, China, processing up to 600 kg PCBs per hour. Song *et al.* (2015) measured Total Suspended Particles (TSP) concentrations in the CRT and PCB workshops of a mobile waste recycling plant processing up to 48,000 units per year, equal to 246.5 μg m⁻³ and 650.7 μg m⁻³, respectively.

It is expected that PM concentration will be increased during working hours in relation to non-working hours and weekends inside the recycling plant. The daily periodicity inside the dismantling area is clearly depicted with the concentration increasing in the beginning of the shift at 07:00 in the morning and decreasing after the end of the shift at 16:00 in the afternoon as shown in Fig. 3. The results indicate that there is no clear association between the activity that was taking place and the variability of



(b)

PM ₁₀ ($\mu\text{g m}^{-3}$)	Dismantling areas	Offices	Outdoor area	Dismantling areas (weekend)	Offices (weekend)
average \pm SDEV	382.4 \pm 104.8	54.3 \pm 5.3	27.8 \pm 25.4	206.4 \pm 13.8	28.4 \pm 23.0
median (min–max)	343.8 (262.5–666.7)	55.0 (47.9–59.4)	15.3 (5.0–68.9)	202.7 (194.6–232.3)	18.2 (14.5–62.5)
10 th –90 th percentile	291.7–282.8	49.2–58.9	9.0–55.2	196.2–220.2	14.7–50.1

Fig. 2. (a) Boxplots of indoor and outdoor 8-h concentrations of PM₁₀ ($\mu\text{g m}^{-3}$), during working hours (08:00–16:00). Extreme points are indicated with an asterisk; (b) Statistical data of indoor and outdoor 8-h concentrations of PM₁₀ ($\mu\text{g m}^{-3}$), during working hours (08:00–16:00).

PM₁₀ concentrations, which however were different from day to day. Consistent with the results of Kim *et al.* (2015), the fluctuations of PM₁₀ were associated with both PM₁₀ emissions and resuspension of dust, since forklifts and collection bins were in constant motion during working hours.

Regarding the PM₁₀ levels in the administrative office, the values were lower but comparable to other occupational areas of increased PM₁₀ concentrations in Greece, such as offices or mixed office-lab rooms and photocopying places in Thessaloniki (75 \pm 43 $\mu\text{g m}^{-3}$) (Gemenetzi *et al.*, 2006) and to concentrations found in school classrooms in residential areas in Athens (80–100 $\mu\text{g m}^{-3}$) (Diapouli *et al.*, 2007). No correlation was found between daily 8-h PM₁₀ mean concentrations in main dismantling area and in offices ($R = 0.74$, $p = 0.072$).

Since the main equipment in the administrative office were

two computers and smoking was not permitted it can be assumed that the main source of PM₁₀ was the resuspension of dust from people's movements. No direct comparison can be made with the outdoor PM₁₀ concentration, since indoor and outdoor concentrations were measured on different days. In any case, the plant is situated in the countryside, next to a fairly busy National Road that connects two mainland cities in central Greece, both of which have exhibited elevated PM₁₀ due to increased car traffic (Papamanolis, 2015). It is possible that some enrichment of offices and the dismantling area with outdoor PM₁₀ due to traffic may have taken place. However, wind velocity was quite low for the dates of measurements as shown in Table 1.

PM₁₀ Elemental Composition

The elemental concentrations associated to indoor PM₁₀ are given in Table 2. The OSHA, NIOSH and Greek

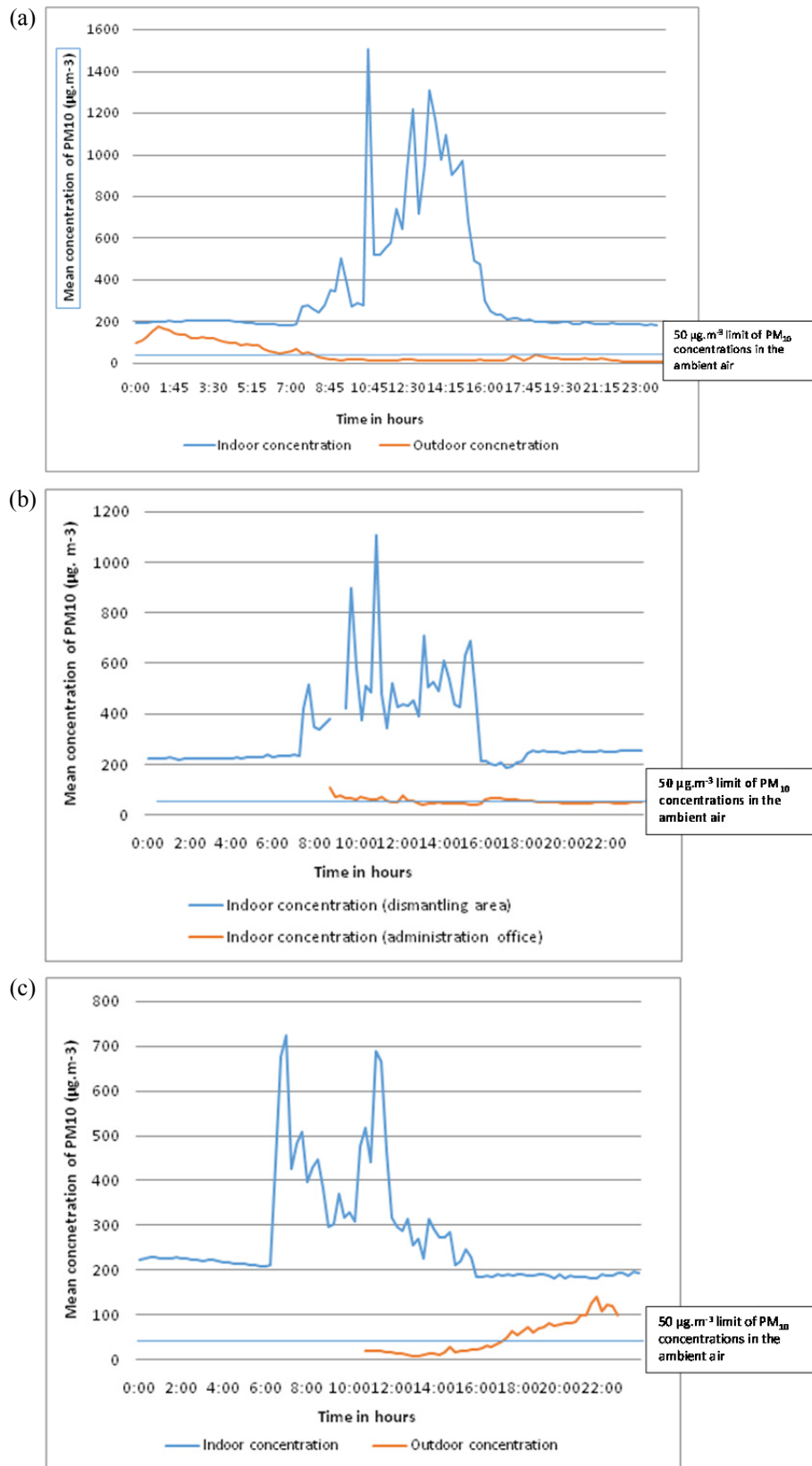


Fig. 3. Daily variation of mean concentrations of PM₁₀ in various sampling points. (a) Daily variation of indoor and outdoor mean concentrations of PM₁₀ (Tuesday 6/11/2012, points 1 and 11); (b) Daily variation of indoor mean concentrations of PM₁₀ (Friday 26/10/2012, points 2 and 8); (c) Daily variation of indoor and outdoor mean concentrations of PM₁₀ (Monday 5/11/2012, points 3 and 11); (d) Daily variation of indoor mean concentrations of PM₁₀ (Friday 2/11/2012, points 5 and 9); (e) Daily variation of indoor mean concentrations of PM₁₀ (Sunday 28/10/2012, points 2 and 8).

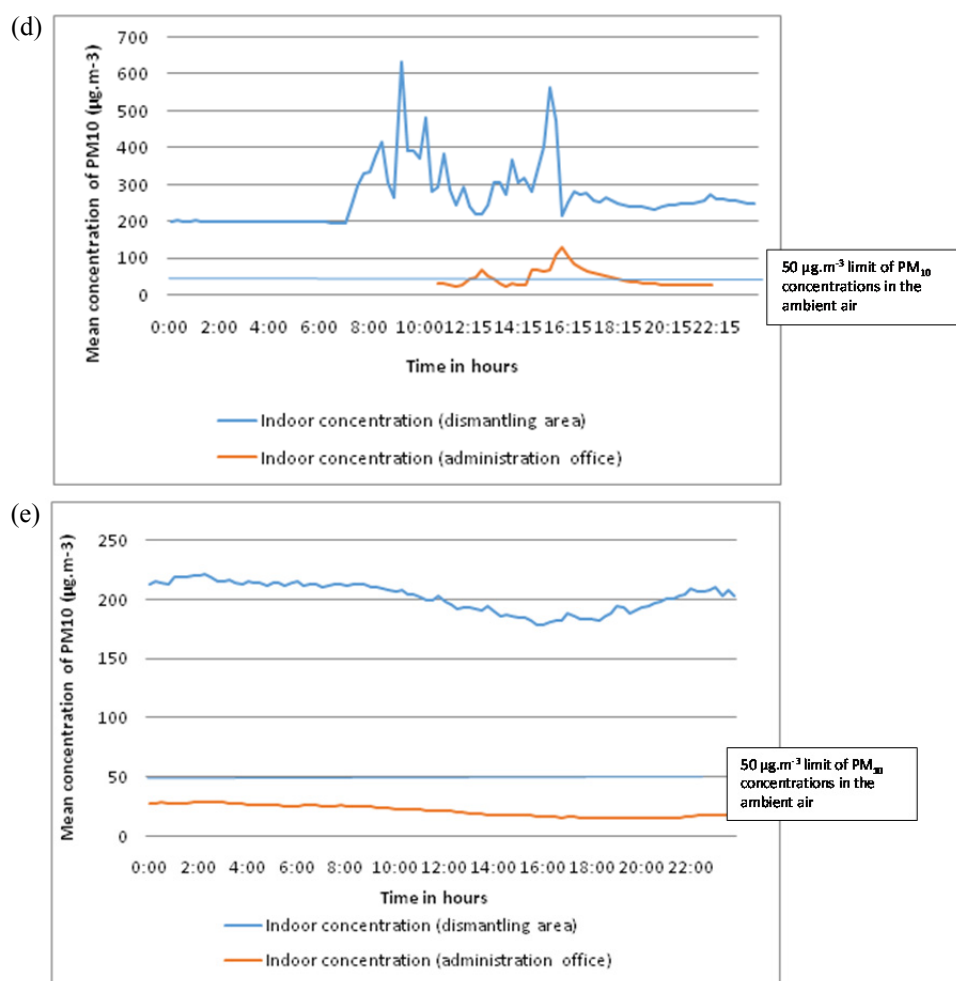


Fig. 3. (continued).

Legislation Permissible Exposure Levels (PELs) of selected elements are presented in Table 3 and it can be seen that all elemental concentrations (based on 4-h average values) were lower than the corresponding 8-h TWA limit values. Ca was by far the most abundant element in the PM₁₀ size fraction (~60 µg m⁻³), followed by Fe (~13 µg m⁻³) and Si (~9 µg m⁻³). Si, Al, Mg, Fe, Ca, Ti and P are elements included in the earth's crust composition (Mason, 1966) so it may be assumed that these elements were most likely derived from resuspension of dust due to indoor human activities and the forklift's movement.

Regarding elements that are commonly found in WEEE, namely Pb, Ni, Cu, Cr, Mn, As and Zn (Andreola *et al.*, 2005; Mostaghel and Samuelsson, 2010; Nnorom *et al.*, 2011; Tsydenova and Bengtsson, 2011; Makenji and Savage, 2012; Dai *et al.*, 2015), these were also detected in PM₁₀ as shown in Table 2 but were all below the permissible exposure limits set by OSHA, NIOSH and the Greek legislation.

Consistent with other studies (Xue *et al.*, 2012; Julander *et al.*, 2014; Lau *et al.*, 2014; Kim *et al.*, 2015), Zn concentrations were the highest of all WEEE-related elements and Pb was the second highest. Concerning Pb, Cu, Mn, Fe, Ni, Ba and Cr concentrations, our results were within the range of values reported in Julander *et al.* (2014), Kim

et al. (2015) Lau *et al.* (2014) and Xue *et al.* (2012).

Focusing on the comparison of elemental concentrations between indoor PM₁₀ in the WEEE dismantling plant and typical ambient levels, As concentrations in indoor samples were 140 times higher and Pb concentrations were 40 times higher than these measured in the ambient air of the city of Volos (Emmanouil *et al.*, 2017). Significantly increased were also the indoor concentrations of Cu, Ni, Zn, Cd (> 10 times) and of Cr (> 5 times). Comparing with ambient elemental concentrations in the city of Thessaloniki, Greece (Diapouli *et al.*, 2017), Pb concentrations were found 150 times higher and As was 140 times higher. Pb is commonly the most enriched element in WEEE processes in comparison to ambient air concentrations (Kim *et al.*, 2015).

The enrichment factor with respect to the earth's crust composition was calculated for 22 elements (Mg, Si, Al, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Sn, Ba, Pb, Cd, Cr) found in the samples of indoor PM₁₀ in the WEEE recycling plant. Al was used as the reference element based on the chemical composition of the earth crust (Mason, 1966). The results (Table 4) suggest that P, S, Cl, Ca, Ni, Cu, Zn, As, Br, Sr, Sn, Pb, Cd and Cr were enriched indicating sources other than resuspension of dust; it can therefore be assumed that these elements derive

Table 2. Indoor elemental concentrations in PM₁₀ (ng m⁻³).

Elements	Arithmetic Mean	Standard Deviation	Min	Max
Mg	1795	545	599	2477
Al	4170	1544	1174	7071
Si	9060	2772	3383	13184
P	248	104	61	398
S	1522	621	393	2696
Cl	765	463	207	1729
K	3720	1517	1892	7433
Ca	60111	21021	22929	100399
Ti	794	228	507	1279
Mn	245	73	156	383
Fe	12974	4591	8403	22235
Ni	62	30	19	108
Cu	341	190	155	641
Zn	2568	683	1623	3707
As	274	68	189	409
Br	419	111	275	602
Sr	630	269	200	1126
Sn	38	28	2	84
Ba	77	54	11	179
Pb	1545	606	899	2780
Cd	21	15	5	57
Cr	51	24	25	107

Table 3. OSHA, NIOSH 8-h TWA exposure limits and Greek Legislation 15-minutes permissible exposure levels during working hours for selected elements of toxicological concern.

ELEMENT	OSHA PELs ^a	NIOSH RELs ^b	GREEK LEGISLATION ^c
Zn	15 × 10 ³ μg m ⁻³	5 × 10 ³ μg m ⁻³	-
Pb	50 μg m ⁻³	50 μg m ⁻³	-
Cu	1 × 10 ³ μg m ⁻³	1 × 10 ³ μg m ⁻³	1 × 10 ³ μg m ⁻³
As	10 μg m ⁻³	2 μg m ⁻³ (15 minutes)	100 μg m ⁻³
Mn	5 × 10 ³ μg m ⁻³	1 × 10 ³ μg m ⁻³	5 × 10 ³ μg m ⁻³
Ni	1 × 10 ³ μg m ⁻³	15 μg m ⁻³	1 × 10 ³ μg m ⁻³
Cr	500 μg m ⁻³	500 μg m ⁻³	1 × 10 ³ μg m ⁻³
Cd	5 μg m ⁻³		25 μg m ⁻³

^a Occupational Safety and Health Administration, 2017; ^b National Institute for Occupational Safety and Health;

^c Presidential Decree 90/1999.

Table 4. Enrichment factor results for certain elements in PM₁₀.

Element	EF	Element	EF
As	3000	Mn	4.63
Ba	3.30	Ni	11.5
Br	325	P	10.7
Ca	31.9	Pb	3700
Cd	2000	S	55.9
Cl	100	Si	0.64
Cr	65	Sn	26
Cu	140	Sr	27.9
Fe	4.98	Ti	3.46
K	2.73	Zn	762
Mg	1.68		

from the WEEE processed at the plant. These results are further corroborated from PCA for the elements of probable

anthropogenic origin that are also of toxicological concern (Mn, Ni, As, Sr, Sn, Pb, Cr, and Cd) as shown in Table 5. Results revealed the presence of 3 components with eigenvalues exceeding 1, explaining 45.0%, 26.7% and 16.5% of the variance respectively with a total of 88.2%. The rotated solution revealed the presence of a simple structure with all components showing a number of strong loadings and most variables located substantially on only one component. Pb, As, Cd and Sr loaded on Component 1 while Ni and Sn loaded on Component 2, and Cr, as well as Mn to an extent, loaded on Component 3. Sr is almost exclusively found in panels or screens of CRT (Andreola *et al.*, 2005) while Pb is also commonly—but not exclusively—found in the back funnels of CRTs (Mear *et al.*, 2007). Pb is still also found in PCBs (Tsydenova and Bengtsson, 2011), but in reducing trends (Lau *et al.*, 2014; Holgersson *et al.*, 2018), hence its negligible contribution to the two other components here. Cd is also found in older types of

Table 5. Pattern and Structure Matrix for PCA with Oblimin Rotation for 3 Factor Solution for elements of toxicological concern.

elements	Pattern Coefficients			Structure Coefficients			Communalities
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3	
Pb	0.999			0.989			0.899
As	0.940			0.958			0.908
Cd	0.835			0.834			0.926
Sr	0.804	−0.494		0.817	−0.564		0.942
Ni		0.947			0.939		0.736
Sn		0.824			0.827		0.982
Cr			0.975			0.928	0.914
Mn		0.303	0.768		0.371	0.855	0.752
Variance (%)	Component 1		Component 2		Component 3		Cumulative
	45.0		26.7		16.5		88.2

CRTs in their phosphor coatings (Environment Policy Committee, 2003). Cd is also a material in PCBs (Tsydenova and Bengtsson, 2011) and it was detected in PCBs dust of disassembly workshops to smaller, but comparable concentrations to CRTs disassembly workshops (Song *et al.*, 2015). As is supposedly found in various metal alloys, and circuit boards (U.S. Geological Survey, 2014) and in older type CRTs (Nguemaleu and Montheu, 2014). Steel alloy elements such as Ni (U.S. Geological Survey, 2014) and Sn contributed to Component 2, and other steel alloy elements such as Mn (Dai *et al.*, 2015) and Cr (Kogel *et al.*, 2006) contributed to Component 3. Ni and Cr are found in PCBs (Tsydenova and Bengtsson, 2011).

Regarding the health impacts of occupational exposure (Table 6), non-carcinogenic risk assessment for the metals of toxicological concern shows non-acceptable risk based on the sum of HQs, for Pb, As, Cd, Ni, Sn, Cr and Mn, mainly due to the contribution of HQ of Pb, based on the quite conservative (and non-IRIS derived) RfD found in Qu *et al.* (2012). In agreement with our results, Pb was the main factor creating possible human health risk (out of Pb, Cu and Cd, based on dust concentrations) in a mobile e-waste recycling plant in China (Song *et al.*, 2015). Pb again was the metal contributing to unacceptable risk (out of Cu, Pb, Cr and Cd; based on dust concentrations), mainly through ingestion, in a PCB recycling factory (Xue *et al.*, 2012). The threat of Pb in recycling workers has also been highlighted in the study of Julander *et al.* (2014), in a formal recycling plant in Sweden.

Carcinogenic risk was also elevated and non-acceptable (one in a million chance of additional human cancer over a 70-year lifetime), based on inhalation exposure, due to all elements of concern (As, Ni, Cd and Cr). This is further corroborated by the probabilistic risk assessment of Li *et al.* (2013) in a vehicle-inspection line in China, with Ni concentrations comparable to ours (50.4 ng m⁻³, 100.2 ng m⁻³; gasoline and bus line respectively), As concentrations less than half of ours (33.9 ng m⁻³, 76.7 ng m⁻³; as before), Cd concentrations less than quarter of ours (2.7 ng m⁻³; as before) and Cr concentrations more than double than ours (266.2 ng m⁻³, 652.5 ng m⁻³; as before). In that study, the incremental life cancer risk (based on Ni, As, Co and Cd)

was within the 10⁻⁵ rate, for half of the exposed population, signifying unacceptable adverse health effects. Unacceptable risk (in the range of 10⁻⁴) was also recorded for the dismantling area of a formal e-waste plant in China, based on dust concentrations of Cd, Cr and Ni (Lau *et al.*, 2014). Limitations in the present risk assessment study, among others, include the inherent uncertainty in risk estimation (Li *et al.*, 2013), the variability in reference values (here selected preferentially from IRIS; Tier 1 according to USEPA, 2003) and the use of airborne particulates instead of surface and floor dust. More realistic risk assessment in the future should also include possible metal bioaccessibility in simulated fluids (Huang *et al.*, 2018).

CONCLUSIONS

A sampling campaign in a WEEE-disassembly plant in Greece showed elevated 8-h indoor PM₁₀ concentrations during working hours in relation to surrounding offices or ambient air in outdoor locations. These values did not exceed the limits set by OSHA, NIOSH or Greek legislation. Elemental analysis also revealed values below the corresponding limits set by OSHA, NIOSH or Greek legislation; however, significant enrichment due to WEEE disassembly and processing was evident for the majority of the analyzed elements, especially As, Pb, Cd and Zn. Furthermore, As concentrations in the indoor samples were 140 times higher and Pb concentrations were 40 times higher than those that have been measured in the ambient air of the nearby city of Volos. Compared to other WEEE, CRT processing seemed to release different elements into the ambient air, namely, Sr, which is almost exclusively found in CRTs; Pb, which is commonly found in the back funnels of CRTs; and Cd and As, which are found in older types of CRTs. A conservative risk assessment for selected elements revealed a non-negligible lifetime risk for the workers engaging in WEEE disassembly and processing, with the non-carcinogenic risk mainly being due to the Pb and the carcinogenic risk being due to all the elements of concern (As, Ni, Cd and Cr). More research on WEEE recycling in the EU is urgently needed.

Table 6. Calculated risk derived for each element of toxicological concern (Cr, Mn, Ni, Sn, Cd, Pb and As).

category	Cr		Mn		Ni		Sn		Cd		Pb		As				
	5%	mean	5%	mean	5%	mean	5%	mean	5%	mean	5%	mean	5%	mean			
HQ	3.62 E-4	1.69 E-3	9.22 E-5	1.77 E-4	2.66 E-4	5.47 E-5	3.12E -4	5.55 E-4	4.24 E-6	1.73 E-5	3.13 E-5	3.24 E-4	2.08 E-3	4.41 E-1	5.57 E-2	9.13 E-2	1.26 E-1
CR	1.26 E-5	4.96 E-5	2.39 E-7	1.20 E-6	2.19 E-6	4.62 E-7	3.02 E-6	6.59 E-6	5.94 E-5	9.49 E-5	1.34 E-4	5% CR	Mean CR	95% CR	5.77E-4	1.49E-4	2.28E-4

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