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MEASUREMENT OF POLYCHLORINATED DIBENZO-*p*-DIOXIN AND DIBENZOFURAN EMISSION FROM EAF STEEL MAKING PROCES

BADANIA EMISJI WIELOCHLORKOWYCH DIBENZO-*p*-DIOKSYN I DIBENZOFURANÓW Z PROCESU WYTWARZANIA STALI W PIECU ŁUKOWYM

Electric arc furnace (EAF) steel manufacturing is an important recycling activity which contributes to the recovery of steel resources and steel scrap/waste minimization. Because of the content of plastics, coatings and paintings as well as other nonferrous materials in the charge during melting, a strong emission of pollutants, including polluting substance group consists of persistent organic pollutions (POPs) represented by polycyclic aromatic hydrocarbon (PAH), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) occurs.

This study was set out to investigate emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) from the stack of a new electric-arc furnace-dust treatment plant installed during modernisation of the Melt Shop in CMC SISAK d.o.o., Croatia. Obtained results have been compared with previously obtained results of PCDDs/Fs emission measurements from the old electric-arc furnace dust treatment without dust drop-out box, as well as quenching tower.

The total PCDDs/Fs concentration in the stack off gases of both electric arc furnaces EAF A and EAF B were 0.2098 and 0.022603 ng I-TEQ/Nm^3 respectively, and these results are close to previous obtained results by other authors. The calculated values of the emission factors for PCDDs/Fs calculated on the basis of measured PCDDs/Fs concentration in the stack off gases in 2008 and 2011 were 1.09 and 0.22 ng I-TEQ/ ton steel, respectively.

Keywords: persistent organic pollutions, EAF, PCDDs/Fs, dioxin

Produkcja stali w piecu łukowym (EAF) jest ważnym elementem recykling stali co przyczynia się do odbudowy zasobów stali i wykorzystania złomu i odpadów stalowych. Ze względu na zawartość tworzyw sztucznych, powłok i farb, jak również innych materiałów niezależnych we wsadzie, podczas topienia występuje silna emisja zanieczyszczeń, w tym grupy substancji składającej się z trwałych zanieczyszczeń organicznych (POP) takich jak wielopierścieniowe węglowodory aromatyczne (PAH), wielochlorowe bifenyle (PCB), wielochlorowe dibenzo-[1,4]-dioksyny (PCDD) i wielochlorowe dibenzofurany (PCDF).

Celem pracy jest zbadanie emisji wielochlorowych dibenzo-[1,4]-dioksyn i dibenzofuranów z nowego układu odpylania zainstalowanego w piecu łukowym w trakcie modernizacji huty CMC Sisak w Chorwacji. Uzyskane wyniki porównano z poprzednio uzyskanymi wynikami pomiarów emisji dioksyn i dibenzofuranów ze starego układu oczyszczania pyłów z pieca łukowego.

Całkowite stężenie dioksyn i dibenzofuranów w gazach odlotowych z pieców łukowych A i B wynosi odpowiednio 0,2098 i 0,022603 ng I-TEQ/Nm^3, i te wyniki są zbliżone do poprzednich uzyskanych wyników przez innych autorów. Obliczone wartości wskaźników emisji dioksyn i dibenzofuranów na podstawie zmierzonych koncentracji dioksyn i dibenzofuranów w gazach odlotowych w 2008 i 2011 wynosiły odpowiednio 1,09 i 0,22 ng I-TEQ / tonę stali.

1. Introduction

The biggest polluters among metallurgical facilities include coking plants, iron ore sintering and agglomeration plants, blast furnaces, steel mills, non-ferrous and light metal production and processing facilities. Emissions into air and water from these plants and installations include significant volumes of gaseous and solid polluting substances, such as sulfur and carbon oxide, fluorides, ammonia, benzene, heavy metals, phenols, cyanides, oil and grease, slag, used refractory material, metallic scrapings, sludge, dust, and scale. There are also relatively small pollutions with long-lasting effects that

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are hazardous, even in their low concentrations, and they rarely receive due attention.

This polluting substance group consists of persistent organic pollutions represented by polycyclic aromatic hydrocarbon (PAH), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). These compounds are the least explored of all known pollutants generated in the metallurgical processes, in terms of the impact of their emissions on the environment.

PCDDs and PCDFs, or as they are commonly referred to, PCDDs/Fs, fall into the group of persistent organic pollutants (POPs) and impose a great risk for the living environment (Fig. 1). These compounds are not produced as standard chemicals, except for very small quantities for research purposes or as chemically pure substances, but are generated in various chemical processes in the manufacture of chlorine compounds, pulp and paper mills, or processes that require high temperatures (waste incineration, metallurgical processes in iron and steel and light metal industry, cement manufacture, etc.). The generation of these compounds requires carbon, oxygen and chlorine, as well as metallic catalysts and adequate temperature. The optimal temperature range for pyrosynthesis of these compounds is between 400 and 700°C.
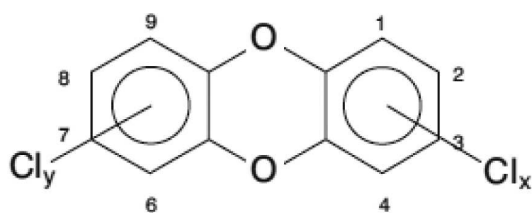
Polychlorinated Dibenzo-*p*-dioxins, **PCDD**
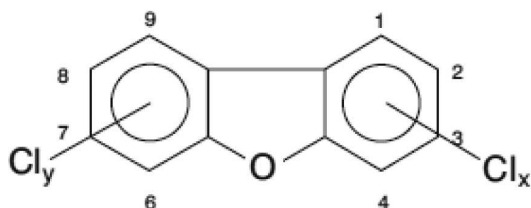
Polychlorinated Dibenzofurans, **PCDF**

Fig. 1. Structural formula of PCDD and PCDF

PCDDs/Fs as environment pollutants aroused interest of scientists during the mid-60ies of the past century when they were identified as the cause of *Kanemi Yusho* disease in Japan [1], and in the mid-70ies when they emerged as undesirable by-products in a misguided production process for 2,4,5-trichlorinephenols, causing an environmental pollution incident in Seveso, Italy

(Mazalović et al. [2]). In the late 1970ies, Olie *et al.* [3] for the first time identified PCDDs/Fs in emissions from a municipal waste incineration plant. Since that incident, these compounds have ever more frequently become the research subject of various environmental studies. According to Potykus and Joas [4]; Mc Kay [5]; and Pereira [6], elementary physical and chemical characteristics of PCDDs/Fs and their extremely adverse impact on human health stimulated the research of their origin and distribution in the environment.

At first, due to the fact that there was no unique technology and no sufficient information needed for toxicity assessment of PCDDs/Fs, and since Potykus and Joas [4], a number of different methods were developed at national levels. The purpose of adopting a unique international factor of equivalent toxicity (I-TEF) was to achieve a higher level of uniformity and comparability of results defining PCDDs/Fs content in samples of different materials of different origin. Today, the analysis of PCDDs/Fs in various samples commonly includes 17 compounds (7 PCDDs and 10 PCDFs) and their level in the sample is described as toxic equivalent (I-TEQ) in correlation to 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD).

Due to the great risk of PCDDs/Fs accumulation in the natural environment, and in an attempt to prevent environmental pollution with these compounds from various emitters, many countries have made an inventory of industrial sources [7-11] and their emission to the environment in order to achieve better understanding of how individual sources participate in the total emission of PCDDs/Fs and to develop a strategy of reduction of these emissions.

Municipal solid waste incinerators and iron and steel plants represent major sources of atmospheric pollution by PCDDs/Fs [9-14]. With the progressive abatement of emissions from municipal solid waste incinerators, the iron and steel industries are now becoming major contributors to the global atmospheric pollution by PCDDs/Fs [7, 15].

The most significant source of PCDDs/Fs among metallurgical processes is definitely sintering of iron ore intended for pig iron production in blast furnaces. If the sintering process is the largest source of PCDDs/Fs among iron and steel making processes, then the pig iron production process in blast furnaces is the smallest source. Using such pig iron as converter in steel production continues the series of technological processes for production of finished steel products that are increasingly demanded on the world market, burdening the environment further with toxic dioxins and furans.

As opposed to this steel making process, PCDDs/Fs emissions are more significantly generated in the EAF

steel making processes using steel scrap as charge (often as much as 100%), which is almost always polluted with various inorganic and organic substances. Due to the presence of organic pollution, EAF and its dust treatment plant, as well as stack gas drainage system, under specific thermodynamic conditions become a very complex reactor where pyrolysis and pyrosynthesis occur, generating dioxins, furans, and other organic compounds. Inside this "reactor" many PCDDs/Fs molecules occur and/or decompose during melting and refinement processes but many of them also leave the reactor and pollute the environment and the human impact of these pollutants is still of concern because of their ability to bio-accumulate in the food chain and then in human fat tissue.

EAF steel manufacturing is a batch process which can result in fluctuating emissions during heating of the charge and from heat to heat. Gas handling systems for steel manufacturing EAFs vary from facility to facility, both in configuration and design and these factors contribute to a varying PCDDs/Fs concentration in process off-gases.

In recent years, more new and existing electric arc furnaces have been equipped with a system for dust treatment in the off-gas in order to remove the particulate matter from the gas stream and avoid reformation of PCDDs/Fs before it is exhausted to the environment.

The project of modernisation of the Melt Shop in CMC Sisak d.o.o., which was conducted with the purpose of increasing the annual steel production, was completed in the year 2010. This project, among others, included the installation of new EAF of 60 t (EAF B) capacity, as well as the construction of ladle furnace (LF) in the place of the current 30 t EAF (EAF A); canopy hood for EAF and LF off-gasses collection; EAF off gases post combustion; the system for PCDDs/Fs synthesis prevention; new bag house for EAF off gasses filtration; etc.

The constructed and installed new system for off gas pretreatment provides complete post combustion of off gases, collection of large size dust particles in dust drop-out box, as well as subsequent quenching of the off-gases in quenching tower to avoid the *'de novo'* synthesis of PCDDs/Fs. The cooled and treated primary off gas is then mixed with secondary off gas, after which it passes through a fabric filter where the fine particles are removed.

The present work was initially motivated by the installation of a new EAF dust treatment plant developed by TECOAER - StG Group S.p.A., Italy. The paper discusses the PCDDs/Fs emission concentration in off gases from old electric arc furnace (EAF A) dedusting plant without off gases pretreatment as well as the newly installed electric arc furnace (EAF B) dedusting plant with off-gases pretreatment i.e. with a dust drop-out box and quenching tower installed between the EAF and bag filters.

2. Experimental

The first electric arc furnace (EAF A) investigated in this study was an old 30 tonne furnace conducted by a filter bag house produced by SOP Krško, Slovenia, designed for the flow rate of 56.000 Nm^3/h as major air pollution control device. From this furnace the stack off gases are emitted via a 26 m height stack. New pulse jet filter bag house installed in CMC Sisak d.o.o., Croatia, where a 60 tons electric arc furnace (EAF B) was installed, is designed for the flow rate of 900.000 Nm^3/h from the EAF primary line and a total capacity from the secondary line of 1.000.000 m^3/h. The stack flue gases from EAF B are emitted via a 30 m height stack.

2.1. Sampling

Measurements were made in off gases from dedusting systems both for old and new systems. The isokinetic sampling equipment was a Zambelli 6000 Isoplus, according to ISO 9096:2003. The same standard was used for the selection of measurement points on stack after the bag filters. A partial volume of the flue gas was extracted via a glass tube from the off gas duct and led into collection system, as showed in Fig. 2.
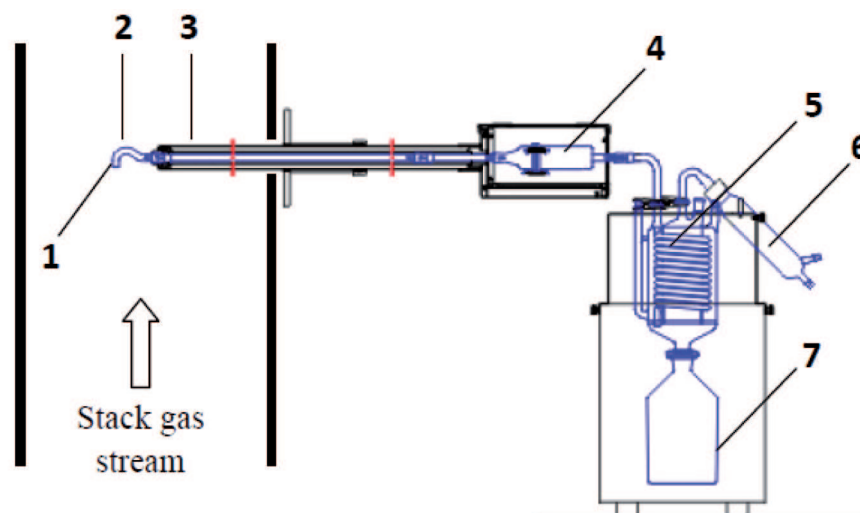
Fig. 2. Shematic presentation of the samplimg apparatus (1-nozzle; 2-glass connection; 3-heated probe; 4-filter with sampling standard solution; 5-condenser; 6-solid adsorber with XAD-2; 7- condensate bottle)

The values of determined concentrations of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from off gases are based on sample collected during six hours on the old system (EAF A), resulting in the sampled volume 2.85 Nm^3; and on sample collected during six hours on the new system (EAF B), resulting in an sampled volume 4.70 Nm^3. In general, the ranges of the main parameters in old and new system during samplimg were: waste gas temperature 343 and 320 K; pressure 1015 and 1024 hPa; moisture content 2.0 and 1.0%; O$_2$ content 20.6 and 21.0%, gas velocity 24.2 and 10.34 m/s respectively.

Bot the EAF A and EAF B stack flue gases sampling were carried out using EN 1948-1:2006 method for sampling from Stationary source emissions for determining the mass concetration of PCDDs/PCDFs and dioxin-like PCBs [16].

2.2. PCDDs/Fs Analyses

All chemical analyses were conducted by an accredited laboratory, the Institute of Public Health in Maribor, Slovenia, certified by the Slovenian Accreditation for analyzing PCDDs/Fs. Stack emission testing was carried out using EN 1948-2:2006 and EN 1948-3:2006 methods for determining polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from stationary sources [17,18].

The sampling tests were made over 6 h, using the procedure described above, and no significant changes in temperature, pressure and flow were observed during the sampling operations. Limit of Detection (LD) for PCDFs/PCDDs, calculated for stack gas samples was 0,001 – 0,005 ng I-TEQ/Nm^3 in gas sample.

3. Results and discusion

3.1. PCDDs/Fs Concentrations in the Stack Flue Gas from EAF A

The measured PCDDs/Fs concentrations in the stack flue gases of EAF A are listed in Table 1. The obtained PCDDs/Fs congener concentration ranged from 0.0039 (1,2,3,4,7,8,9- HpCDF) to 3.3895 (OCDF) ng/Nm^3, while the corresponding toxic equivalency quantity values ranged from 0.00004 to 0.00339 ng I-TEQ/Nm^3. The total PCDDs/Fs concentration in the stack flue gases of EAF A was 0.2098 ng I-TEQ/Nm^3. This result for total PCDDs/Fs concentrations in the stack flue gases of EAF is close to previous obtained results (0.28 ng I-TEQ/Nm^3) by Lee et all [19] or results (0.35ng I-TEQ/Nm^3) by Chang et all [20]. The congeners 1,2,3,7,8-PeCDD, OCDD, 2,3,7,8-TCDF and OCDF are the major contributors of the dioxin concentration.

PCDDs/Fs are generated as well by the combustion of organochlorinated compounds catalysed by metals (e.g. Cu) at low temperatures (250-500°C) that may be present in the charge, as well as by *'de novo'* synthesis [21]. Due to the presence of various organic admixtures in these processes, such as plastic, dye, dissolving agents, and technological additives like alkali chlorides, PCDDs/Fs often occur in waste gases and the generated volumes of PCDDs/Fs depend on the type of the scrap material used in the process, thermodynamic process conditions, and the waste gas treatment systems installed. Steel scrap is categorized on the market according to the European Scrap Grading System (ESGS) into quality categories or classes [22] depending on physical and chemical properties. According to Baillet [23], organic and inorganic pollution present in steel scrap is lower

TABLE 1

PCDDs/Fs mass concentration and toxic equivalency quantity (I-TEQ) from EAF A

PCDDs/Fs	I-TEF*	EAF A	
		mass concentration, γ_{I-TEQ} [ng/Nm³]	toxic equivalency quantity, I-TEQ [ng/Nm³]
2,3,7,8-TCDD	1	0.0060	0.0060
1,2,3,7,8-PeCDD	0.5	0.0667	0.0334
1,2,3,4,7,8-HxCDD	0.1	0.0112	0.00112
1,2,3,6,7,8- HxCDD	0.1	0.0302	0.00302
1,2,3,7,8,9- HxCDD	0.1	0.0330	0.00330
1,2,3,4,6,7,8-HpCDD	0.01	0.0154	0.00015
OCDD	0.001	0.7987	0.00080
2,3,7,8-TCDF	0.1	0.3511	0.0351
1,2,3,7,8-PeCDF	0.05	0.2563	0.0128
2,3,4,7,8- PeCDF	0.5	0.1826	0.0913
1,2,3,4,7,8-HxCDF	0.1	0.0737	0.0074
1,2,3,6,7,8- HxCDF	0.1	0.0737	0.00737
2,3,4,6,7,8- HxCDF	0.1	0.0348	0.0035
1,2,3,7,8,9- HxCDF	0.1	0.0074	0.00074
1,2,3,4,6,7,8-HpCDF	0.01	0.0527	0.00053
1,2,3,4,7,8,9- HpCDF	0.01	0.0039	0.00004
OCDF	0.001	3.3895	0.00339
T O T A L	–	–	**0.2098**

* I-TEF – International Toxicity Equivalency Factor used to calculate the toxicity weighting of dioxin concentrations

than 1.4% and 1% in the E1 and E3 steel scrap category, respectively.

Birat *et al*. [24] have presented that 1g of organic pollution contained in steel scrap can produce around 10^{-1}g of volatile organic compounds, around 10^{-2}g of specific compounds designated as BTEX (benzene, toluene, ethyl benzene, and xylene isomers), around 10^{-3}g PAH, around 10^{-5}g chlorinated benzenes and chlorinated phenols, and perhaps around 10^{-10}g of PCDDs/Fs. The actual composition of the generated organic compounds depends on the nature of organic material charged into EAF with steel scrap and on thermodynamic conditions inside the EAF and the stack gas drainage system.

In oder to reduce PCDDs/Fs in the total off-gas (primary and secondary emissions), primary and secondary measures can be applied.

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of PCDDs/Fs. Primary measures include use of less contaminated input scrap or pre-cleaning of the scrap, as well as effective process control. The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDDs/Fs during incomplete combustion or by 'de no-

vo' synthesis. Feed material should be classified according to composition and possible contaminants. Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDDs/Fs generation, such as maintaining furnace temperature above 850°C in order to destroy PCDDs/Fs.

Secondary measures are pollution control techniques and these methods do not eliminate the generation of PCDDs/Fs, but serve as means to contain and prevent emissions. Secondary measures include off-gas post combustion to destroy PCDDs/Fs, as well as their precursors; quick cooling of the waste gases in the quenching chamber to avoid reformation of PCDDs/Fs; using new fabric filters for dust collection which can easily provide dust concentration in the clean gas and injection of lignite or activated carbon in the off-gas flux system to reduce the PCDDs/Fs by adsorption on a solid phase.

3.2. PCDDs/PCDFs emissions from EAF B

The new EAF B plant extracts the emissions of an 60 tone electric arc furnace by the fourth hole of the furnace roof. EAF primary off-gas (melting, refining) is exhausted through the furnace roof into water cooled elbow and ductwork. A dust drop-out box is typically pro-

vided to ensure complete collection of large size dust. In EAF B plant off gas treatment systems, a drop-out box is installed after the furnace elbow to trap the coarser dust particles and liquid slag droplets. The hot off gas stream (typically up to 1.000°C) contains significant portions of CO gas which combusts upon contact with inducted ambient air.

Simultaneously, the inherent volatile organic components and dioxin — arising from the organic substances contained in the charged scrap are partially destroyed depending on the prevailing gas temperature. To avoid the *'de novo'* synthesis of PCDDs/Fs, it is essential to have a rapid cooling (quenching) of the fumes as soon as possible after dust drop-out box to a temperature of below 250°C at which all risk of 'de novo' synthesis is excluded.

In our case, this cooling is obtained by water injection in a quenching tower. Figure 3 shows the photo of an EAF applying complete collection of large size dust particles in dust drop-out box and subsequent quenching of the off-gas in quenching tower. After cooling, these primary fumes are mixed with the so-called secondary fumes coming from the melt-shop building and so obtained the combined off-gas flux is then treated in the bagfilter. A bagfilter with appropriately selected bag ma-

terial is used to remove the particulate matter from the gas stream before it is exhausted to the environment.

3.3. PCDDs/Fs Concentrations in the Stack Flue Gas from EAF B

The measured PCDDs/Fs concentrations in the stack flue gases of EAF B are listed in Table 2. The obtained PCDDs/Fs congener concentration ranged from 0.0009 (2,3,7,8-TCDD and 1,2,3,4,7,8,9-HpCDF) to 0,0617 (2,3,7,8-TCDF) ng/Nm^3, while the corresponding I-TEQ value ranged from 0.000851 and 0.000085 ng I-TEQ/Nm^3 of 2,3,7,8-TCDD and 1,2,3,7,8,9- Hx-CDD respectively, to 0.006171 ng I-TEQ/Nm^3 of 2,3,7,8-TCDF. The total PCDDs/Fs concentration in the stack flue gases of EAF B was 0.022603 ng I-TEQ/Nm^3. These results for total PCDDs/Fs concentrations in the stack flue gases of EAF B are in line with previous results presented by other authors [25-27].

The congeners 2,3,4,7,8-PeCDF, 2,3,7,8-TCDF and 1,2,3,7,8-PeCDD are the major contributors of the PCDDs/Fs concentration in the stack flue gases of EAF B. In addition, the PCDFs are the major contributors of PCDDs/PCDFs, because the PCDDs/PCDFs I-TEQ ratio is <1.
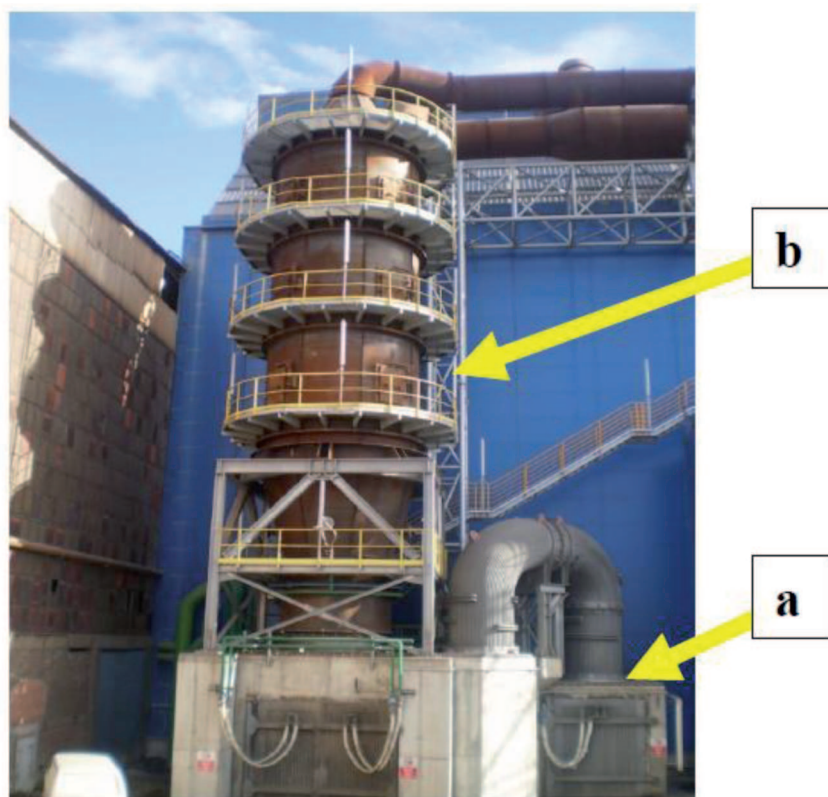

Fig. 3. Photo of instaled dust drop-out box (a) and quenching tower (b); EAF B system

TABLE 2

PCDDs/Fs mass concentration and toxic equivalency quantity (I-TEQ) from EAF B

PCDDs/Fs	I-TEF*	EAF B	
		mass concentration, γ_{I-TEQ} [ng/Nm^3]	toxic equivalency quantity, I-TEQ [ng/Nm^3]
2,3,7,8-TCDD	1	0.0009	0.000851
1,2,3,7,8-PeCDD	0.5	0.0055	0.002766
1,2,3,4,7,8-HxCDD	0.1	0.0011	0.000106
1,2,3,6,7,8- HxCDD	0.1	0.0015	0.000149
1,2,3,7,8,9- HxCDD	0.1	0.0009	0.000085
1,2,3,4,6,7,8-HpCDD	0.01	<0.0011	<0.000011
OCDD	0.001	0.0013	0.000001
2,3,7,8-TCDF	0.1	0.0617	0.006171
1,2,3,7,8-PeCDF	0.05	0.0134	0.000670
2,3,4,7,8- PeCDF	0.5	0.0206	0.010321
1,2,3,4,7,8-HxCDF	0.1	0.0055	0.000553
1,2,3,6,7,8- HxCDF	0.1	0.0045	0.000447
2,3,4,6,7,8- HxCDF	0.1	0.0043	0.000426
1,2,3,7,8,9- HxCDF	0.1	0.0002	0.000021
1,2,3,4,6,7,8-HpCDF	0.01	0.0034	0.000034
1,2,3,4,7,8,9- HpCDF	0.01	<0.0011	<0.000011
OCDF	0.001	<0.0011	<0.000001
T O T A L	–	–	**0.022603**

<Values below limit of detection were not taken into account.

3.4. Emission Factors of PCDDs/Fs

Emission factor is the number that designates the mass of emitted PCDDs/Fs per operating unit – in this case product mass unit. Literature offers various data on the emission factor values for PCDDs/Fs from the electric arc furnace process, depending on the steel scrap purity, i.e. organic pollution contained in it, as well as on the additional equipment installed in some EAF systems. According to Lemmon [28], the PCDDs/Fs emission factor in Canada in 1998 was 2.14 μg I-TEQ/t of EAF steel. In China it ranged from 0.2 to 20 μg I-TEQ/t of EAF steel since Jin *et al.* [29]. The PCDDs/Fs emission factor in some EU countries [11, 30, 31] was between 0.02 and 9 μg I-TEQ/t EAF steel, in New Zeland (Buckland *et al.* [32]) from 0.98 to 0.37 μg I-TEQ/t EAF steel and in Taiwan from 1.84-2.443μg I-TEQ/t EAF steel [33].

The average flow rate of the EAF A stack flue gas during the sampling periods was 52412 Nm^3/h. Therefore, the estimated emission rate of PCDDs/Fs of the stack flue gas was 10996 ng I-TEQ/h. By taking the production rates of steel (30 ton/heat; tap to tap time was 3.2 hours) during the sampling periods into account, the calculated emission factors for the point source were 1.09 μg I-TEQ /ton steel.

The average flow rate of the EAF B stack flue gas during the sampling periods was 579266 Nm^3/h. Therefore, the estimated emission rate of PCDDs/Fs of the stack flue gas was 13323 ng I-TEQ/h. By taking the production rates of steel (60 ton/heat; tap to tap time was 1 hour) during the sampling periods into account, the calculated emission factors for this point source were 0.22 μg I-TEQ /ton steel. The obtained emission factors values are consistent with previous results presented by other authors [29-33] and can be used as contribution to establish the Croatian PCDDs/Fs inventory.

3.5. Distribution of PCDDs/Fs from EAF steel making process at CMC Sisak d.o.o.

After the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans have been emitted to the atmosphere, they disperse in the environment and their concentration always dilutes in the ground level of the atmosphere (imission), accompanied by both dry and wet sedimentation and absorption in plants and ground. Their distribution depends on the emitting conditions, climato-logic features, geographical characteristics of the source location, and ground configuration. The emission conditions relevant for the distribution of pollution include

the type of construction of the smokestack (height and cross-section), flow rate and volume, and temperature of the smoke gases in the stack. Climatologic elements that the distribution depends on include atmospheric stability, air temperature, vertical temperature gradient, wind rate and direction, mixing layer height, and vertical wind profile.

Several different mathematical models are applied for simulation of dispersion of emitted polluting substances on a regional or local level. The models are based on the Euler-Lagranger regional dispersion model and Gauss local dispersion model. Depending on the modelling purpose, one applies calculations of ground level concentrations of harmful substances with different levels of accuracy, from a relatively rough estimate to reliable accuracy.

Dispersal of PCDDs/Fs emitted in the air from EAF A and EAF B dedusting plants were, in this paper, cal-culated with the dispersion model of the US Environmental Protection Agency, called SCREEN3 [34]. The model estimates pollution concentrations from air pollution sources under a wide range of meteorological conditions. SCREEN3 is a Gaussian plume dispersion model which takes into account the physical factors of each particular air pollution source including emission rate, stack height and diameter, and gas exit velocity and temperature. The imission concentrations of PCDDs/Fs from observed staks were calculated within the 5 km radius around the Melt Shop at the centre of emissions, for worst-case weather conditions implying atmospheric stability class F and wind rate 1.0 m s^{-1}.

Basic input values for calculation by SCREEN3 model within the 5 km radius around the Melt Shop at the centre of emissions are displayed in Table 3.

TABLE 3

Basic input values for SCREEN3 model

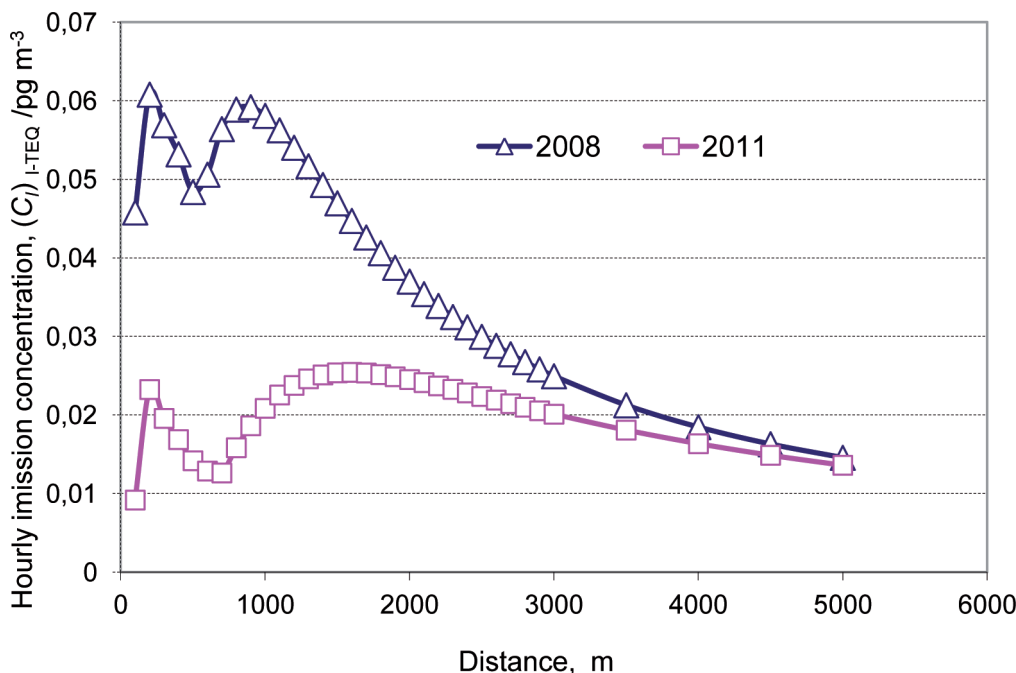| Source/Year	Emission, Q (g s^{-1})	Stack height, h_s (m)	Stak inside diameter, d_s (m)	Stack gas temperature, T_s (K)	Stack gas flow rate, V (m s^{-1})
EAF A/2008	3.05E-9	26	1	343	24.2
EAF B/2011	3.64E-9	30	4.85	320	10.34

Fig. 4. Dependence of the hourly imission concentration profile (C_I) PCDDs/Fs on the distance from the source

The result of the calculation using the SCREEN3 model are hourly PCDDs/Fs imission concentration values (C_I) and their dependence on the distance from the source, as well as the distance of maximal hourly values. They are presented as contigency imission values to the maximum distance of 5 km in steps of 100 m.

Maximal hourly imission concentration values and their distance from the sources emissions are displayed in Table 4. The profiles of hourly concentrations of PCDDs/Fs depending on the distance are given on Figures 4.

TABLE 4

Maximal hourly imision concentrations and their distances from the sources

Source/Year	Maximal annual imission concentration, C_I (pg m^{-3})	Distance from source (m)
EAF A/2008	6.10E-2	178
EAF B/2011	2.54E-2	1589

Maximal annual imission concentration values and their distance from the sources emissions are displayed in Table 5. The profiles of annual concentrations of PCDDs/Fs depending on the distance are given on Figure 5.

TABLE 5

Maximal annual imision concentrations and their distances from the sources

Source/Year	Maximal annual imission concentration, C_I (pg m^{-3})	Distance from source (m)
EAF A/2008	4.86E-3	178
EAF B/2011	2.04E-3	1589

Since neither the limit hourly value for PCDDs/Fs nor the limit annual air quality values have not been adopted yet, the averaging of the obtained hourly values to the time interval of one year allows us only to compare the averaged values to the usual measured average annual values. Reference data on imission concentrations of PCDDs/Fs in Croatia are rather deficient and unreliable. Therefore, comparisons in this work were based on the measured values of imission concentrations of PCDDs/Fs in the USA [35] and Germany [36], in rural regions $(C_I)_{I-TEQ} = 0.022$ pg m^{-3}, and in urban areas $(C_I)_{I-TEQ} = 0.05$ pg m^{-3}. The obtained results displayed in Table 4 shows that the estimated value of the maximum annual concentration of PCDDs/Fs never exceeded the amount of $(C_I)_{I-TEQ} = 0.022$ pg m^{-3}.
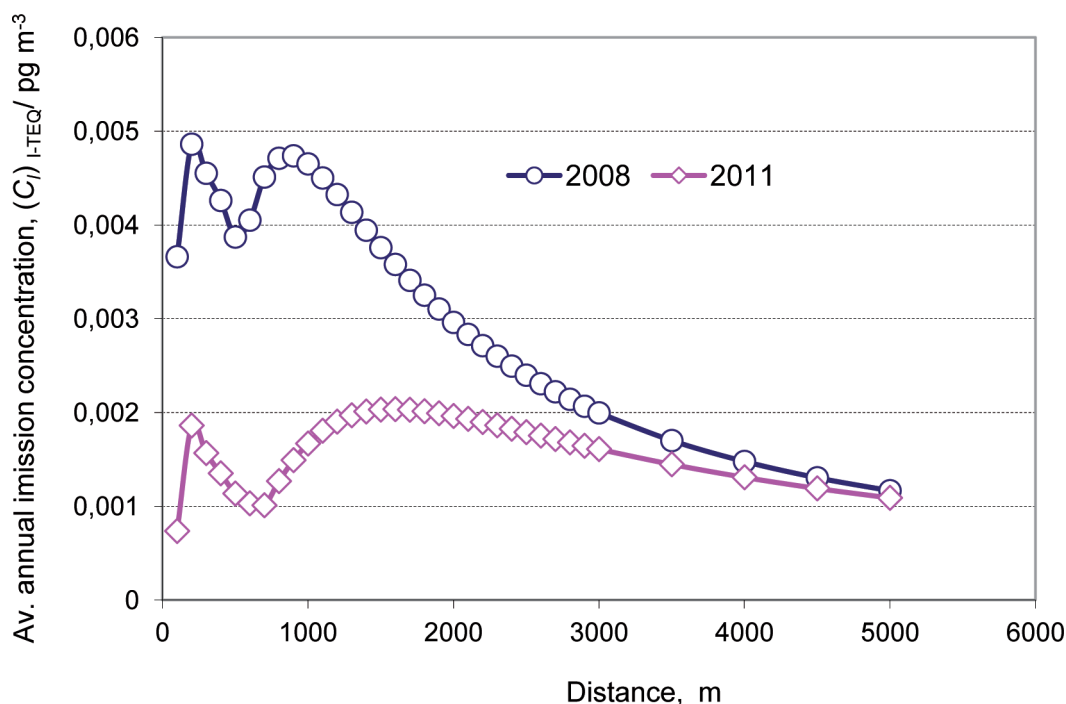
Fig. 5. Dependence of the annual imission concentration profile (C_I) PCDDs/Fs on the distance from the source

4. Conclusions

The total PCDDs/Fs concentration in the stack off gases of both electric arc furnaces EAF A and EAF B were 0.2098 and 0.022603 ng I-TEQ/Nm^3 respectively. These results are close to previously obtained results by other authors. The values of the emission factors for PCDDs/Fs calculated on the basis of measured PCDDs/Fs concentration in the stack off gases in 2008 and 2011 were 1.09 and 0.22 μg I-TEQ/ ton steel, respectively.

Reference data on imission concentrations of PCDDs/Fs in Croatia are rather deficient and unreliable. Therefore the comparison in this work was based on the measured values of imission concentrations of PCDDs/Fs in the USA and Germany, in rural regions $(C_I)_{I-TEQ}$ = 0.022 pg m^{-3}, and in urban areas $(C_I)_{I-TEQ}$ = 0.05 pg m^{-3}. The obtained results for 2008 and 2011 shows that the estimated value of the maximum annual concentration of PCDDs/Fs never exceeded the amount of $(C_I)_{I-TEQ}$ =0.022 pg m^{-3} (rural areas).

The Croatian Regulation on polluting emission limits from stationary sources to the atmosphere (Croatian Official Gazette No. 21/2007) prescribes the emission limit value for PCDDs/Fs in waste gas from waste incineration and cement production, i.e. co-incineration of waste, of 0.1ng I-TEQ/Nm^3. Since there are no separately prescribed emission limit values for PCDDs/Fs emission from metallurgical processes in Croatia, this value, which is equal to the IPPC BAT value for PCDDs/Fs from EAF, can be considered as the limit for emissions of these compounds and for Croatian electric arc furnace steel making processes.

The concentrations of PCDDs/Fs of the stack flue gas of the investigated EAF A and EAF B were 0.0226 ng I-TEQ/Nm^3, much lower than 0.1ng I-TEQ/Nm^3. Therefore, using air pollution control methods, such as dust drop-out box and quenching tower and bag filter, are sufficient to reduce PCDDs/Fs emissions from the above emission sources.

REFERENCES

[1] http://www.inet.hr/~priroda/dioksin.htm

[2] M. Mazalović, M. Kovčalija, Lj. Tinjić, E. Mazalović, Z. Žigić, L. Begić, S. Berbić, Sažetak današnjih spoznaja o dioksinima, Kem.Ind. **51**, 6, 267-280 (2002).

[3] K. Olie, P.L. Vermeulen, O. Hutzinger, Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components in the Netherlands, Chemosphere **6**, p.455 (1977).

[4] A. Potykus, R. Joas, Dioxins and PCBs: Environmental and Health Effects, Eds.: G. Chambers, Publishers: European Parliament, DG for Research, Directorate A, PE 168.400/Fin. St., June 2000, p.1,2,9.

[5] G. McKay, Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review, Chemical Engineerin Journal **86**, 343-368 (2002).

[6] M. de Souza Pereira, Polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and polychlorinated biphenyls (PCB): main sources, environmental behaviour and risk to man and biota. Quím. Nova **27**, 934-943 (2004).

[7] D.R. Anderson, R. Fisher, Sources of dioxines in the United Kingdom: the steel industry and other sources, Chemosphere **46**, 371-381 (2002).

[8] T. Pulles, U. Quass, K. Mareckova, C. Juery, Dioxin emissions in Candidate Countries, TNO-Environment, Energy and Process Innovation, TNO-Repoer R 2004/069, Appeldorn, The Netherlands, (2004).

[9] M.B. Chang, H.Ch. Huang, S.S. Tsai, K.H. Chi, G.P. Chang-Chien, Evaluation of the emission characteristics of PCDD/Fs from electric arc furnace, Chemosphere **62**, 1761-1773 (2006).

[10] U. Quass, M. Fermann, G. Broeker, The European Dioxin Emission Inventory Project – Final Results, Chemosphere **54**, 1319-1327 (2004).

[11] A. Grochowalski, C. Lassen, M. Holtzer, M. Sadowski, T. Hudyma, Determination of PCDDs, PCDFs, PCBs and HCB Emission from the Metallurgical Sector in Poland, Environ Sci Pollut Res Int. **14**, 5, 326-32 (2007).

[12] K. Everaert, J. Baeyens, The formation and emission of dioxins in large scale thermal processes. Chemosphere **46**, 439-448 (2002).

[13] R.K. Gilpin, D.J. Wagel, J.G. Solch, Production, distribution, and fate of polychlorinated dibenzo-pdioxins, dibenzofurans, and related organohalogens in the environment. In Dioxins and Health, eds. A Schecter and T.A. Gasiewicz, Hoboken: John Wiley & Sons, Inc., 55-87 (2003).

[14] D. Zook, R. Rappe, Environmental sources, distribution, and fate of polychlorinated dibenzodioxins, dibenzofurans and related organochlorines. In Dioxins and Health, ed. A. Schecter, New York: Plenum Press, 79-113 (1994).

[15] A. Buekenes, L. Stieglitz, K. Hell, H. Huang, P. Segres, Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry, Chemosphere **42**, 729-735 (2001).

[16] EN 1948-1:2006 Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 1: Sampling of PCDDs/PCDFs.

[17] EN 1948-2:2006 Stationary source emissions – Determination of mass concentration of PCDDs/PCDFs – Part 2: Extraction and clean-up of PCDDs/PCDFs.

[18] EN 1948-3:2006 Stationary source emissions – Determination of mass concentration of PCDDs/PCDFs – Part 3: Identification and quantification of PCDDs/PCDFs.

[19] W.S. L e e, G.P. C h a n g - C h i e n, L.C. W a n g, W.J. L e e, K.Y. W u, P.J. T s a i, Emission of Polychlorinated Dibenzo−p−dioxins and Dibenzofurans from Stack Gases of Electric Arc Furnaces and Secondary Aluminum Smelters. J. Air Waste Manage. Assoc. **55**, 219-226 (2005).

[20] M.B. C h a n g, H.C. H u a n g, S.S. T s a i, K.H. C h i, G.P. C h a n g - C h i e n, Evaluation of the characteristics of PCDD/Fs from electric arc furnaces; Chemosphere **62**, 1761-1773 (2006).

[21] T. O b e r g, Low temperature formation and degradation of chlorinated benzenes, PCDD and PCDF in dust from steel production, Science of the Total Environment 382, **1** (2007) 153-158. doi:10.1016/j.scitotenv.2007.03.015

[22] M. G o j i ć, Metalurgija čelika, Izd.: Denona d.o.o., Zagreb 2005.

[23] G. B a i l l e t, Pourquoi un nouveau referentiel europeeb des ferrailes? La Revue de Metallurgie-CIT, Avril, 399-410 (2001).

[24] J.P. B i r a t, A. A r i o n, M. F a r a l, F. B a r o n n e t, P-M. M a r q u a i r e, P. R a m b a u d, Abatement of organic emissions in EAF exhaust flue gas, La Revue de Metallurgie-CIT, Octobre, 839-854 (2001).

[25] Ch. P r ü m, Ch. W e r n e r, J. W i r l i n g, Reducing dioxin emissions in electric steel mills, MPT International **1**, 36-42 (2005).

[26] EUROPEAN COMMISSION, Integrated Pollution Prevention and Control (IPPC), Best Available Techniques Reference Document on the Production of Iron and Steel, December 2001, pp. 281.

[27] K.M. Y u, W.J. L e e, P.J. T s a i, K. F a n g, M. L i n, Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from both of point and area sources of an electric-arc furnace-dust treatment plant and their impacts to the vicinity environments, Chemosphere **80**, 1131-1136 (2010).

[28] W. L e m m o n, Standards pancanadiens relatifs aux dioxines et uax furannes, Reunion sur les standardsd'emission, Toronto, Novembre 1999.

[29] J. J i n, H. P e n g, T. X i a o y a n, An inventory of Potential PCDD and PCDF Emission Sources in the mainland of China, Organohalogen Compounds **66**, 852-858 (2004).

[30] UN ENVIRONMENT PROGRAMME, Standardized Toolkit for Identifiication and Qantification of Dioxin and Furan Releases, Prepared by UNEP Chemicals, Geneva, Switzerland, January 2001.

[31] M. C o u t i n h o, R. R o d r i g u e s, C. B o r r e g o, Caracterizacao das Emissoes Atmosfericas de Dioxina e Furanos em Portugal: 1999-2000, 1. Encontro Nacional de Dioxinas e Compostos Similares na Saude e no Ambiente: uma abordagem intersectorial. Lisboa, Portugal, 2003.

[32] S.J. B u c k l a n d, H.K. E l l i s, P. D y k e, New Zealand inventory of dioxin emission to air, land and water, and reservoir sources, Pbs. Ministry for the Environment, Wellington, March 2000.

[33] J.C. C h i u, Y.H. S h e n, H.W. L i, L.F. L i n, L.C. W a n g, G.P. C h a n g - C h i e n, Emissions of Polychlorinated Dibenzo−p−dioxins and Dibenzofurans from an Electric Arc Furnace, Secondary Aluminum Smelter, Crematory and Joss Paper Incinerators, Aerosol and Air Quality Research **11**, 13-20 (2011), doi: 10.4209/aaqr.2010.06.0051

[34] United States Environmental Protection Agency, SCREEN3 Dispersion Model, Version Dated 95250, September 1995.

[35] U.S. EPA (2000b). Dioxins Reassessment. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds. Levels of CDD, CDF and PCB congeners in environmental media and food.

[36] Compilation of EU Dioxin Exposure and Health Data, Task 6 – Trends, European Commission DG Environment, October 1999. http://ec.europa.eu/environment/dioxin/pdf/task6.pdf