A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 53 2008 Issue 2

T. SOFILIĆ*, A. RASTOVČAN-MIOČ**, Z. ŠMIT***

POLYCHLORINATED DIBENZO-*p*-DIOXIN AND DIBENZOFURAN EMISSIONS FROM CROATIAN METALLURGICAL INDUSTRY

EMISJA POLICHLOROWANYCH DIBENZO-*p*-DIOKSYN I DIBENZOFURANÓW W CHORWACKIM PRZEMYŚLE HUTNICZYM

The group of pollutants consists of persistent organic pollutions represented by polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans. These are the least explored of all known pollutants generated in metallurgical processes, in terms of the impact of their emissions to the environment.

Based on the experience of industrialized countries which at the same time are the largest iron and steel manufacturers, the potential emissions of dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes during the 1990–2005 period in Croatia were estimated.

The estimated total emission of dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes to the environment during the 1990–2005 period in Croatia was 4.681g I-TEQ, while annual emission in the same period ranged from 0.886g I-TEQ a^{-1} in 1990 to 0.159g I-TEQ a^{-1} in 1995. Emissions of these compounds from metallurgical processes that were active in the less recent past were also calculated and the values recorded for the 1950–2005 period ranged from 5.853g I-TEQ a^{-1} in 1975 to 0.159g I-TEQ a^{-1} in 1995.

Keywords: PCDDs; PCDFs; Emission; Metallurgy

Grupa zanieczyszczeń złożonych z trwałych związków organicznych reprezentowanych przez wielopierścieniowe węglowodory aromatyczne, polichlorowane bifenyle, polichlorowane dibenzo-*p*-dioksyny i dibenzofurany są najmniej zbadanymi zanieczyszczeniami wytwarzanymi w procesach metalurgicznych pod względem wpływu ich emisji na środowisko. W oparciu o doświadczenie uprzemysłowionych krajów, które równocześnie są największymi producentami żelaza i stali, oszacowano potencjalną emisję dibenzo-*p*-dioksyn i polichlorowanych dibenzofuranów w okresie 1990–2005 w Chorwacji. Szacunkowa całkowita emisja dibenzo-*p*-dioksyn i polichlorowanych dibenzofuranów do środowiska z procesów metalurgicznych w latach 1990–2005 w Chorwacji wyniosła 4.681g I-TEQ, podczas gdy roczna emisja w tym samym okresie wahała się w granicach od 0.886g I-TEQ a^{-1} w 1990 do 0.159g I-TEQ a^{-1} w 1995. Emisja tych związków z procesów metalurgicznych, które były czynne w niedalekiej przeszłości również była obliczona, a zarejestrowane wartości z okresu 1950–2005 wahały się od 5.853g I-TEQ a^{-1} w 1975 do 0.159g I-TEQ a^{-1} w 1995.

1. Introduction

The biggest polluters among metallurgical facilities include coking plants, iron ore sintering and agglomeration plants, thermal power 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. Depending on the technology used, the most frequent pollutants include dust, SO_2, NO_x, NH_3, H_2SO_4, HCl, HF, HCN, H_2S, CO, CO_2, CH_4, heavy metals (Hg, Pb, Cr, Ni, Zn, Cd, Cu), benzene, phenol, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), cyanides, oil and grease, suspended substances, etc. Metallurgical plants burden the environment with by-products, i.e. various technological wastes (both hazardous and non-hazardous), which are usually disposed on their own untilled and unregulated landfills. Most frequently, the disposed waste material includes unprocessed slag, used refractory material, metallic scrapings, various sludge materials, dust from smoke gases, scale, etc.

* CMC SISAK D.O.O., BOŽIDARA ADŽIJE 19, SISAK, CROATIA
** UNIVERSITY OF ZAGREB, FACULTY OF METALLURGY, ALEJA NARODNIH HEROJA 3, SISAK, CROATIA
*** ZAGREB PUBLIC HEALTH INSTITUTE, MIROGOJSKA CESTA 16, ZAGREB, CROATIA

In terms of their impact on the environment, PCDDs and PCDFs, highly toxic chemicals, are the least researched of all pollutants emitted from the metallurgical processes.

2. Sources of PCDDs and PCDFs

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. 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.

PCDDs/Fs as environment pollutants aroused interest of scientists in 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] identified for the first time PCDDs/Fs in the emission from a municipal waste incineration plant. Since that time, these compounds have been ever more frequently the subject of research in various environmental studies. According to Potykus and Joas [4]; Mc Kay [5]; and Pereira [6], the 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 according to 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 (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 (TEQ) in correlation to 2,3,7,8-tetrachlorinedibenzodioxin (TCDD).

3. Emission of PCDDS/FS from metallurgical processes

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 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 how to develop a strategy to reduce these emissions.

According Anderson and Fischer [7] in most of industrialized countries in the world, in Europe and even in Croatia, an inventory of PCDDs/Fs was conducted in the mid-1990s, revealing the largest quantities of PCDDs/Fs to be emitted to the atmosphere from the sources in Japan (3,981g I-TEQ a^{-1}), China (2,773g I-TEQ a^{-1}) and the USA (2,744g I-TEQ a^{-1}). This was primarily caused by emissions from a large number of municipal waste incineration plants applying obsolete incineration techniques.

As opposed to these very large volumes of PCDDs/Fs that were emitted into the environment, other countries in the world and in Europe, according to Pulles *et al.* [8], accounted for lower emissions in 1990, e.g. Germany 1,196g I-TEQ a^{-1}, Belgium 625g I-TEQ a^{-1}, Italy 504g I-TEQ a^{-1}, Hungary 157g I-TEQ a^{-1}, whereas the estimated emissions in Croatia ranged from 179g I-TEQ a^{-1} in 1990 to 109g I-TEQ a^{-1} in 2000. In order to perform a more detailed analysis of PCDDs/Fs emission values, it is necessary to know the types and number of sources of these pollutions for each country individually as well as their shares in total emissions at the national level.

According to literature data on European countries, i.e. Quass *et al*. [9,10]; Mc Kay [5] and Paradiž and Dilara [11], it is obvious that in terms of total PCDDs/Fs emission to the atmosphere, the processes of municipal and hospital waste incineration, the manufacture of sintered iron ore, forest fires, the manufacture of non-ferrous metals from scrap raw material, wood and coal fire places in households, electric steel making processes, etc. account for the largest share (relative significance).

Quass *et al*. [9, 10] have also presented an estimate of total PCDDs/Fs emission in EU15 countries along with Norway and Switzerland for 2005, compared to the inventory results from 1995 and 2000, and to the share of individual sources of these pollutions in their total emission, indicating the contribution of metallurgi-

cal processes like iron ore sintering, steel making and non-ferrous and light metal production from scrap raw material in the total PCDDs/Fs emission to be highly significant. The relative significance of individual metallurgical processes varies from country to country, depending on the installed capacities of individual technological processes as well as on their annual output levels.

Pulles *et al*. [8] have made an estimate of reduced PCDDs/Fs emissions in 2005 as compared to 1995 in 17 European countries (EU15, Norway and Switzerland), ranging from 3% to >90%, depending on the source. The exceptions were the emissions from electric steel making process that were estimated to have increased by 13%. According to Quass *et al*. [9, 10]; Paradiž and Dilara [11], PCDDs/Fs emissions from metallurgical processes, including non-ferrous metal production processes from scrap material, accounted for 25% of total dioxin emissions in EU15 in 1985, to rise to 32% ten years later.

The most significant source of PCDDs/Fs among metallurgical processes definitely is sintering of iron ore intended for pig iron production in blast furnaces. Smoke gases produced in the iron ore sintering contain solid substances, heavy metals, gaseous pollutants such as HCl, HF, NO_x, SO_2, CO, CO_2, volatile organic compounds, PAH, PCB and PCDDs/Fs. According to Tan and Neuschutz [12] the PCDDs/Fs develop in the sintering process in the temperature range from 250 to 450°C and their concentration in stack gases, according to Buekenes *et al*. [13] and Wang *et al*. [14] is usually between 0.5 and 5 ng I-TEQ/Nm^3. As the volume of stack gases produced in the sintering process is ~2100 Nm^3/t of sintered material, one can calculate the volume of PCDDs/Fs produced per tonne of produced sintered material and it ranges from 1 to 10 μg I-TEQ, but sometimes it can take up a value, (Quass *et al*. [9]), exceeding 20 ng I-TEQ $N^{-1}m^{-3}$.

If the sintering process is the largest source of PCDDs/Fs among iron and steel making processes, the pig iron production process in blast furnaces is then the smallest source. According to reference data [15] for 2001 in EU15 countries, stack gases from blast furnaces, in addition to dust, sulfur, nitrogen and carbon compounds, were emitted to the environment along with PCDDs/Fs in a quantity of <0.0011 to 0.0043 μg I-TEQ $t^{-1}$of pig iron. Using such pig iron for converter 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. Namely, the converter steel production process generated PCDDs/Fs and their emission, according to the same reference source [15], range from <0.001 to 0.060 μg I-TEQ t^{-1} of steel. Although the emission of PCDDs/Fs from oxygen converters is much lower than the emission from an electric arc furnace, one has to bear in mind that the converter steel making process accounts for ~60% of output in EU15 countries, i.e. ~95.5 mil tonnes in 2003, since Gojić [16]. On this ground, one can calculate, i.e. estimate the quantity of PCDDs/Fs burdening the environment that year.

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%), almost always polluted with various inorganic and organic substances.

Although electric arc furnace is not an incineration plant for these inorganic and organic substances, they are burned during steel scrap melting. According Gojić [16], steel scrap is categorized on the market according to the European Scrap Grading System (ESGS) into quality categories or classes depending on physical and chemical properties. According to Baillet [17], organic and inorganic pollution content in steel scrap is lower than 1.4% in the E1 steel scrap category (light steel scrap prepared for charging, without Cu, Sn, Pb and their alloys, thickness <6 mm) and EHRB steel scrap category (old or new scrap prepared for charging, without Cu, Sn, Pb and their alloys, max. dimensions 1.5×0.5×0.5 m) and 1% in E3 (heavy scrap prepared for charging, including pipes, hollow profiles, without Cu, Sn, Pb and their alloys, thickness >6 mm).

Due to the presence of organic pollution, EAF and its 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", various organic molecules occur and/or decompose during melting and refining processes but many molecules also leave the reactor and pollute the environment.

Birat *et al*. [18] 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 with steel scrap into electric arc furnace and on thermodynamic conditions inside the EAF and the stack gas drainage system.

Emission factor is the number that designates the mass of emitted PCDDs/Fs per operation unit – in this case product mass unit. Kakareka and Kukharchyk [19]

offer different data on emission factors for PCDDs/Fs from EAF 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.

The literature also offers variable data on the emission factor values for PCDDs/Fs from the electric arc furnace process. There are a number of PCDDs/Fs inventories conducted at the national levels, containing data on their measured or calculated emission factors from EAF steel making processes, varying from country to country, resulting from the production output and EAF process applied. Differences were also recorded in the emission factor values between inventories within the same country, that were conducted at time intervals of one to several years, also being a result of the mentioned factors.

According to Kakareka and Kukharchyk [19], the value of the emission factor for PCDDs/Fs in 1996 was 1.15 μg I-TEQ t^{-1} steel scrap in Germany, whereas in Great Britain it varied from 0.7 to 10 μg I-TEQ t^{-1} steel scrap. In Japan, the emission factor value from EAFs in 1997 was 5.46 μg I-TEQ t^{-1} steel [20], to decrease to 3.83 μg I-TEQ t^{-1} steel in the very next year. According to Lemmon [21], the PCDDs/Fs emission factor in Canada in 1998 was 2.14 μg I-TEQ $t^{-1}$of EAF steel. In China it ranged from 0.2 to 20 μg I-TEQ t^{-1} of EAF steel since Jin *et al*. [22]. The PCDDs/Fs emission factor in some EU countries [23]was between 0.07 and 9 μg I-TEQ $t^{-1}$of steel, in New Zeland (Buckland *et al*. [24]) from 0.98 to 0.37 μg I-TEQ t^{-1} steel, and in Portugal from 0.23 to 1.43μg I-TEQ t^{-1} steel [25].

The production of metallurgical coke is also considered a metallurgical process that is a common component of integrated iron works, taking a very important place in the process chain from iron ore to finished steel products. The coke produced is used in iron and steel metallurgy, i.e. in sintering processes, in blast-furnace pig iron production, and in steel making processes, steel foundries, other casting processes, etc.

Environmental pollution caused by the coking process consists of ammonia, coke gas, tar, phenols, benzene, toluene, xylene, pyridine, sulphur (IV) oxide, and nitrogen oxides. Apart from the mentioned polluting substances, the coking process includes pollution with PCDDs/Fs. The impact of the coking process on the total emission of PCDDs/Fs has not yet been systematically examined.

As opposed to the sintering process, and even steel making process, literature data on measuring emissions of PCDDs/Fs from the coking process are rather scarce. According to Anderson and Fisher [7], the emission factor for PCDDs/Fs from coke making in Great Britain between 1995 and 1998 ranged from <0.001 to 0.12 ng I-TEQ $N^{-1}m^{-3}$ of waste gases. According to Kakareka and Kukharchyk [19], the PCDDs/Fs emission factor value in the Netherlands in 1994 was 0.23 μg I-TEQ t^{-1} coke, whereas the calculation of the emission factor in other European countries was based on the value of 0.25 μg I-TEQ t^{-1} coke. Jin *et al*. [22] report on the emission factor for PCDDs/Fs of 0.3 μg I-TEQ t^{-1}coke in China in 2002, and Bawden *et al*. [26] on the PCDDs/Fs emission factor of 0.3 μg I-TEQ t^{-1} coke in Australia in 2003, whereas the report on PCDDs/Fs emission in Hong Kong in 2000 states an emission factor of as much as 0.3g I-TEQ t^{-1}coke [27].

Metallurgical processes relevant for the PCDDs/Fs emission to the environment, in addition to the already mentioned metallurgical coke production, iron ore sintering, and iron/steel production and their castings, also include production of both heavy and light non-ferrous metals and their alloys from scrap material such as metal scrap, dust, slag, sludge, etc.

On metallurgical waste processing for the purpose of secondary recovery of Zn, Al, Pb, Cu, Cd, Ni, and their alloys, there is a wide application field for pyrometallurgical processes, e.g., high-temperature processing of EAF dust with Waelz's method according Cruells *et al*. [28]; Dutrizac and Chen [29]; Ferenzi *et al*. [30]; Czernecki *et al*. [31]. This process is most widely represented of all pyrometallurgical processes and accounts for the most frequently used zinc recycling technology from EAF dust and other zinc-bearing waste material (for example, sludge from zinc electrolysis).

Besides Waelz furnace, there are a number of other furnace types that are used in various secondary recovering of Al, Pb, Cu, Cd, Ni, etc. from so-called scrap materials that are rich with in metals (metal scrap, slag, dust, sludge). These processes of secondary recovery of light and non-ferrous metals have been included in the previously conducted inventories of PCDDs/Fs emission into the environment in many countries, whereby the calculation of emissions used different values of emission factors expressed in different measuring units (μg I-TEQ t^{-1}, μg I-TEQ $N^{-1}m^{-3}$, μg I-TEQ m^{-3}).

Due to the presence of various organic admixtures in these processes like plastic, dye, dissolving agents, and the application of technological additives like salt (NaCl, KCl,...) PCDDs/Fs often occur in waste gases. 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. Therefore, the calculation of PCDDs/Fs emission from various industrial secondary recovery processes for Al, Cu, Cd, Pb, etc. uses various emission factors. Thus, emission factors for, e.g. PCDDs/Fs emission into the atmosphere from copper production can range from

0.01 μg I-TEQ t^{-1} (all primary copper production processes) through 50 μg I-TEQ t^{-1} (secondary copper recovery with controlled waste gas discharge) all the way to 800 μg I-TEQ t^{-1} (secondary copper recovery without emission control).

In their calculations of PCDDs/Fs emission from secondary production in Europe, Kakareka and Kukharchyk[19]applied the values of 200 μg I-TEQ t^{-1} (Cu); 50 μg I-TEQ t^{-1} (Al) and 20 μg I-TEQ t^{-1} (Pb). In the same paper they quote the previously used values of PCDDs/Fs emission factors from secondary aluminum recovery processes, where, depending on the procedure applied, the values in 1998 ranged from 0.1 to 14 ng I-TEQ m^{-3}waste gas. According to the measurements conducted in Germany in 1996, the emission of PCDDs/Fs from secondary aluminum recovery processes varied from 0.01 μg I-TEQ t^{-1} to 167 μg-TEQ t^{-1}, and 42 μg I-TEQ t^{-1}were accepted as the mean value. At the same time, the USA applied the emission factor 13.1 μg I-TEQ t^{-1}waste used as scrap material for aluminum, whereas the calculation of PCDDs/Fs emission into the atmosphere in Croatia according Jerman [32] in 2001 used the values of 50 μg I-TEQ t^{-1} for Cu, 35 μg I-TEQ t^{-1} for Al and 8 μg I-TEQ t^{-1} for Pb.

4. Emission of PCDDs/Fs from Croatian metallurgical processes

The production of metals and metallic castings rank very high on the list of industrial processes that are considered stationary emitters of PCDDs/Fs.

According to the literature data available, i.e. national inventory of PCDDs/Fs in Croatia [33, 34], the estimated total emission of these compounds into the environment between 1990 and 2000 ranged from 95 to 179g I-TEQ a^{-1}, of which some 80% are the result of wood burning and combustion of wooden waste derivatives in households and industry, 11% results from industrial combustion, and 5% from industrial processes. The question is what was the share of emissions from metallurgical processes of coke processing, pig iron production, ferrous and non-ferrous castings, and steel production in this period?

Although Croatia never counted as a big metal and metallic product manufacturer, it is by all means necessary, for the purpose of better understanding of the situation with environmental pollution in Croatia, as well as for the understanding of the PCDDs/Fs behavior in the interaction with the environment, to determine the potential burden to the environment by these compounds from metallurgical processes the activity of which stopped in the previous time period, as well as from the processes that burden the environment with their activities and emissions today.

The development of iron and steel making processes in Croatia started in the 1930ies. The pig iron output in 1939 was 3,736 t [35] and only one year later it was 19,561 t. After the World War II, the output increased to around 100,000 t (1951) and reached 200,000 t in the early 1970ies. The pig iron production was shut down in 1991.

For the purpose of pig iron production, the iron works built their own iron ore agglomeration and sintering plant, that was being developed and improved along with the blast furnace operation and was working continuously with an annual output of as much as 500,000 until it was shut down in 1990.

According to Čepo [36] the production of steel in Sisak started in 1954, when some 7,000 tonnes of open-hearth (OH) steel were produced. Ten years later, the output was 164,000 t, and in the mid-1970ies it was 285,000 t. The electric arc furnace was introduced in Sisak in 1966 and in Split in 1971, with the annual output of EAF steel in Croatia between 189,457 t in 1989 and 43,380 t in 2002.

Croatia started its own production of metallurgical coke in 1978 with an average annual production of 680,000 t until the plant was shut down in 1993.

Although the foundries in Croatia have a very long tradition. According Budić *et al*. [37] many Croatian foundries had a small production capacity and their total annual output was between ~8,000 t (1939) and ~125,000 t (1986), whereas the total output in 2005 was ~62,000 t of all kinds of castings. The iron-based castings accounted for the majority of the castings produced (~90%) up to 1990, when this proportion started to change in favor of non-ferrous castings that reached ~30% in 2005.

Literature data on the measurements of PCDDs/Fs emission into the atmosphere from individual metallurgical processes imply that different results were caused by the charge material properties and the process itself (properties of raw material used in the process, thermodynamic conditions of the process, installed waste gas treatment systems, etc.). For these reasons, the systematization and classification of emission factors for PCDDs/Fs emission from different industrial processes, including metallurgical processes, have been initiated. Thus, for example, in order to calculate PCDDs/Fs emission from the coking process one can apply values of emission factors from 3 μg I-TEQ t^{-1} and 0.3 μg I-TEQ t^{-1}; iron ore sintering process 20 μg I-TEQ t^{-1}, 4 μg I-TEQ t^{-1} and 0.3 μg I-TEQ t^{-1}; iron and steel production 10 μg I-TEQ t^{-1}, 4.3 μg I-TEQ t^{-1}, 3 μg I-TEQ t^{-1}, 1 μg I-TEQ t^{-1}, 0.1 μg I-TEQ t^{-1}, 0.03 μg I-TEQ t^{-1}

and 0.01 μg I-TEQ t^{-1}; production of Cu and Cu-alloys 800 μg I-TEQ t^{-1}, 50 μg I-TEQ t^{-1}, 5 μg I-TEQ t^{-1}, 0.03 μg I-TEQ t^{-1}, and 0.01 μg I-TEQ t^{-1}; production of Al and Al-alloys 150 μg I-TEQ t^{-1}, 35 μg I-TEQ t^{-1}, 10 μg I-TEQ t^{-1}, and 1 μg I-TEQ t^{-1}; production of Zn and Zn-alloys 1000 μg I-TEQ t^{-1},100 μg I-TEQ t^{-1}, 5 μg I-TEQ t^{-1}, 1 μg I-TEQ t^{-1}, 0.3 μg I-TEQ t^{-1}, and 0.1 μg I-TEQ t^{-1}; production of Pb and Pb-alloys 80 μg I-TEQ t^{-1}, 8 μg I-TEQ t^{-1}, and 0.5 μg I-TEQ t^{-1}, production of Mg 250 μg I-TEQ t^{-1} and 50 μg I-TEQ t^{-1}; production of Ni 100 μg I-TEQ t^{-1} and 2 μg I-TEQ t^{-1}.

For the purpose of estimating PCDDs/Fs emission from metallurgical processes, in this study we consulted the experience from industrialized countries.

For the emission factor in individual processes, we used reference values suggested by group of experts on emission estimate for this kind of pollution in European countries according Kakareka and Kukharchyk [19]. The calculation of PCDDs/Fs emission estimate from metallurgical processes (iron and steel making) took into consideration the output of OH steel and EAF steel produced at Sisak Steelworks and EAF steel produced at Split Steelworks, whereas the foundries were represented by the available data on the production in all foundries making grey, nodular, tempered, and steel castings as well as non-ferrous and light metal castings.

As Croatian steelworks use pure steel scrap, the calculations in this study were based on the emission factor values lower than those used for calculation in the Dioxins and Furans Inventory in the Republic of Croatia according Jerman [32].

Since the available literature does not provide information on PCDDs/Fs emission factor from open-hearth steel production, the calculation of PCDDs/Fs emission from this metallurgical process in this study was based on the information on the share of steel scrap from 30% to 45% in the open-hearth furnace charge. Based on this, the activity of open-hearth process was corrected and the emission factor of 2 μg I-TEQ t^{-1} was applied in the calculation.

For the calculation of PCDDs/Fs emission from non-ferrous casting processes (Al, Zn, Cu and their alloys) we used the reference emission factor value of 1 μg-TEQ t^{-1} [38], considering the fact that the Croatian non-ferrous foundries use highly pure metal scrap.

In the time period covered by the 1stnational inventory (1990–2000), Croatia produced a total of approximately 1.83 mil t of metallurgical coke, ~236,000 t of pig iron, ~432,000 t of iron cast (grey cast, nodular cast, tempered cast, and steel cast), ~99,000 t of non-ferrous cast, ~347,000 t of open-hearth steel, and ~942,000 t of EAF steel (Table 1). Should reference values according Kakareka and Kukharchyk [19] for PCDDs/Fs emission factors be applied to these operations, we come to amounts of 0.159g I-TEQ a^{-1} in 1995 to 0.943g I-TEQ a^{-1} in 1990. The calculated values of PCDDs/Fs emissions from metallurgical processes in Croatia between 1990 and 2000 corresponded to the shares of 0.14% to 0.52% in their total emission to the environment.

Between 1990 and 2000, the calculated emission values from EAF steel production only, within the total PCDDs/Fs emission in Croatia, ranged from 0.091g I-TEQ a^{-1} in 1995 to up to 0.342g I-TEQ a^{-1} in 1990, when 171,138 t of EAF steel were produced. These values accounted for 0.10% to 0.20 % of total PCDDs/Fs emission to the environment.

If the calculated value of PCDDs/Fs emission from EAF steel production, amounting to 0.143g I-TEQ in 2000, is compared to the total emission of 4.97g I-TEQ from the manufacture processes in Croatia that year, the share of the emission from the EAF procedure in the total emission from the manufacture processes is about 3%, which is consistent with the respective figures reported for some other countries (Quass et al. [9]).

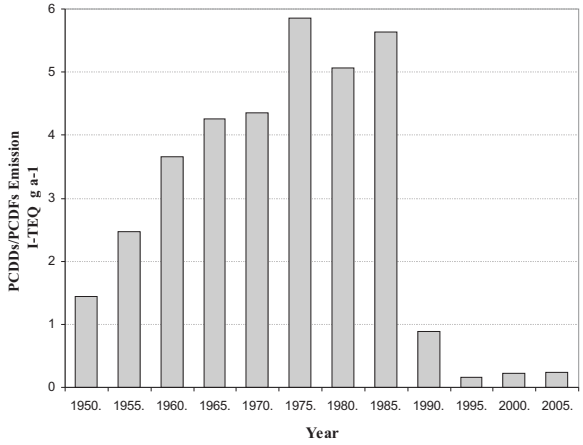

Fig. 1. Emission of PCDDs/Fs from Croatian metallurgical processes between 1950 and 2005

Between 1990 and 2000, i.e. time period covered by the 1st national inventory, the emissions from iron cast manufacturing, which included grey cast, nodular cast, tempered cast and steel cast in the present study, ranged from 62 mg I-TEQ a^{-1} in 1995 to up to 157 mg I-TEQ a^{-1} in 1990, (Table 2). The calculated PCDDs/Fs emission values from non-ferrous cast manufacture in the same time period ranged from 5mg I-TEQ a^{-1} in 1993 to up to 14mg I-TEQ a^{-1} in 1990. Between 2001 and 2005, the annual output of non-ferrous castings increased from ~10,600 t in 2001 to ~18,000 t in 2005. Therefore, the calculated values of PCDDs/Fs emission grew in the same time interval from 11 mg I-TEQ a^{-1} to 18 mg I-TEQ a^{-1}.

TABLE 1

Calculation of PCDDs/Fs emission from Croatian metallurgical processes between 1990 and 2005

Year	METALLURGICAL PROCESSES																	Total emission of PCDDs/Fs mg I-TEQ
	production of metallurgical coke			production of pig iron			production of iron cast[b]			production of non-ferrous cast			production of open-hearth steel			production of EAF steel			
	Production of t	□g I-TEQ t^{-1}	mg I-TEQ	Output t	□gI-TEQ t^{-1}	mg I-TEQ	Output t	□gI-TEQ t^{-1}	mg I-TEQ	Output t	□gI-TEQ t^{-1}	mg I-TEQ	Output t	□gI-TEQ t^{-1}	mg I-TEQ	Output t	□gI-TEQ t^{-1}	mg I-TEQ	
1990	556.084	0.25[a]	139	209.308	0.03	6	78.508	2[a]	157	13.836	1	14	253.161	2[a]	228[c]	171.138	2[a]	342	886
1991	441.584	0.25	110	25.713	0.03	1	47.650	2	95	12.381	1	12	94.165	2	85	119.734	2	239	542
1992	407.458	0.25	101	0	0.03	0	35.981	2	72	7.594	1	8	0	2	0	101.943	2	204	386
1993	421.569	0.25	105	0	0.03	0	34.868	2	70	5.130	1	5	0	2	0	74.082	2	148	328
1994	0	0.25	0	0	0.03	0	34.739	2	70	6.271	1	6	0	2	0	63.352	2	127	203
1995	0	0.25	0	0	0.03	0	31.208	2	62	6.301	1	6	0	2	0	45.371	2	91	159
1996	0	0.25	0	0	0.03	0	32.655	2	65	8.212	1	8	0	2	0	45.754	2	92	165
1997	0	0.25	0	0	0.03	0	33.519	2	67	9.071	1	9	0	2	0	69.932	2	140	216
1998	0	0.25	0	0	0.03	0	37.124	2	74	9.996	1	10	0	2	0	103.203	2	206	290
1999	0	0.25	0	0	0.03	0	33.110	2	66	9.058	1	9	0	2	0	76.832	2	154	229
2000	0	0.25	0	0	0.03	0	32.373	2	65	10.280	1	10	0	2	0	71.021	2	143	218
2001	0	0.25	0	0	0.03	0	39.056	2	78	10.578	1	11	0	2	0	57.993	2	116	205
2002	0	0.25	0	0	0.03	0	40.643	2	81	12.433	1	12	0	2	0	33.851	2	68	161
2003	0	0.25	0	0	0.03	0	40.575	2	81	12.876	1	13	0	2	0	43.380	2	86	181
2004	0	0.25	0	0	0.03	0	41.186	2	82	15.263	1	15	0	2	0	86.108	2	172	269
2005	0	0.25	0	0	0.03	0	43.827	2	87	17.960	1	18	0	2	0	68.901	2	138	243
Σ	1.826.695	0.25	455	235.021	0.03	7	637.022	2	1.272	167.240	1	166	347.326	2	313	1.232.592	2	2.466	4.681

[a]values from literature reports (Kakareka and Kukharchyk [19]; [b]grey, nodular, tempered, and steel cast; [c]according to the corrected amount of open-hearth steel

TABLE 2

Calculation of PCDDs/Fs emissions from Croatian non-ferrous and ferrous cast manufacture between 1990 and 2005

Year	METALLURGICAL PROCESSES						Total emission of PCDDs/Fs mg I-TEQ
	Production of non-ferrous cast			Production of ferrous cast			
	Output, t	□g I-TEQ t^{-1}	mg I-TEQ	Output, t	□g I-TEQ t^{-1}	mg I-TEQ	
1990	13.836	1**	14	78.508	2*	157	171
1991	12.381	1	12	47.650	2	95	107
1992	7.594	1	8	35.981	2	72	80
1993	5.130	1	5	34.868	2	70	75
1994	6.271	1	6	34.739	2	70	76
1995	6.301	1	6	31.208	2	62	68
1996	8.212	1	8	32.655	2	65	73
1997	9.071	1	9	33.519	2	67	76
1998	9.996	1	10	37.124	2	74	84
1999	9.058	1	9	33.110	2	66	75
2000	10.280	1	10	32.373	2	65	75
2001	10.578	1	11	39.056	2	78	89
2002	12.433	1	12	40.643	2	81	93
2003	12.876	1	13	40.575	2	81	94
2004	15.263	1	15	41.186	2	82	97
2005	17.960	1	18	43.827	2	87	105
Σ	167.240	1	167	637.022	2	1272	1438

*values from literature reports (Kakareka and Kukharchyk [19]; ferrous cast = grey, nodular, tempered, and steel cast;
**http//:www.europa.eu.int/comm/environment/dioxin/pdf/stage1/smelting_non_ferous_metals.pdf;
non-ferrous cast = Cu, Zn, and/or Al based cast

TABLE 3

Calculation of PCDDs/Fs emission from Croatian non-ferrous cast manufacture between 1990 and 2005

Year	TYPE OF CAST									Total emission of PCDDs/Fs mg I-TEQ
	Cu - alloys/ cast			Zn - alloys/ cast			Al - alloys/ cast			
	Output, t	□g I-TEQ t^{-1}	mg I-TEQ	Output, t	□g I-TEQ t^{-1}	mg I-TEQ	Output, t	□g I-TEQ t^{-1}	mg I-TEQ	
1990	1,338	1**	1.338	1,266	1**	1.266	11,232	1**	11.232	13.836
1991	864	1	0.864	566	1	0.566	9,951	1	9.951	11.381
1992	1,128	1	1.128	478	1	0.478	5,988	1	5.988	7.594
1993	743	1	0.743	368	1	0.368	4,014	1	4.014	5.125
1994	1,030	1	1.030	443	1	0.443	4,981	1	4.981	6.454
1995	1,005	1	1.005	361	1	0.361	4,935	1	4.935	6.301
1996	1,039	1	1.039	461	1	0.461	6,711	1	6.711	8.211
1997	969	1	0.969	554	1	0.554	7,548	1	7.548	9.071
1998	1,296	1	1.296	583	1	0.583	8,117	1	8.117	9.996
1999	680	1	0.680	1,050	1	1.050	7,778	1	7.778	9.508
2000	624	1	0.624	758	1	0.758	8,898	1	8.898	10.280
2001	704	1	0.704	377	1	0.378	8,997	1	8.997	10.079
2002	603	1	0.603	580	1	0.580	9,907	1	9.907	11.090
2003	745	1	0.745	698	1	0.698	10,609	1	10.609	12.052
2004	687	1	0.687	468	1	0.468	12,940	1	12.940	14.095
2005	1,120	1	1.120	502	1	0.502	15,038	1	15.038	16.660
Σ	14,575	1	14.575	9,514	1	9.514	137,644	1	137.644	161.733

**http//:www.europa.eu.int/comm/environment/dioxin/pdf/stage1/smelting_non_ferous_metals.pdf

Between 1990 and 2000, the calculated emission values from non-ferrous casting ranged from 0.624 mg I-TEQ a^{-1} in 2000 to up to 1.338 mg I-TEQ a^{-1} in 1990 from Cu and Cu-alloy castings manufacture; from 0.361 mg I-TEQ a^{-1} in 1995 to 1.266 mg I-TEQ a^{-1} in 1990 from Zn and Zn-alloy castings manufacture; and from 4.014 mg I-TEQ a^{-1} in 1993 to 11.232 mg I-TEQ a^{-1} in 1990 from Al and Al-alloy castings manufacture, (Table 3).

The same methodology used to calculate the emission of PCDDs/Fs from the metallurgical processes that were active in the past yields the values for the 1960–2005 period from 5.853g I-TEQ in 1975 to 0.159g I-TEQ in 1995, figure 1. The variation in the calculated values of total emissions of PCDDs/Fs from metallurgical processes between 1990 and today has a negative tendency and it is a result of economic changes and restructuring in the Croatian metallurgical industry that started in the late 1980s and continued with war operations in the 1990s, when some metallurgical processes and facilities like sintering plant, blast furnaces, open-hearth furnaces, and coking plant were abandoned.

As the Croatian economic policy is oriented towards restructuring of the metallurgical industry, in particular steel and steel product manufacturing, it is necessary, regarding all future activities of reconstruction of these and other facilities or construction of new ones, to respect the principles of cleaner production and environmental requirements that are imposed to us as a future member of the European Union (e.g., IPPC Directive).

The Directive 96/61 EC on Integrated Pollution Prevention Control (IPPC) integrates the emission control with the overall impact that the industry has on the environment, and it is a very important document of EU legislation relevant for environmental protection that among other issues includes the control over PCDDs/Fs emission.

The Regulation on polluting emission limits to the atmosphere from stationary sources (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 m^{-3}. Since there are no separately prescribed limit values for PCDDs/Fs emission from metallurgical processes in Croatia, this value can be considered as the limit for emissions of these compounds and for metallurgical processes.

5. Conclusion

Emissions of dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes that were active in the less recent past in Croatia were calculated and the values recorded for the 1950-2005 period ranged from 5.853g I-TEQ a^{-1} in 1975 to 0.159g I-TEQ a^{-1} 1995.

The assessed total emission of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes to the environment between 1990 and 2000 in Croatia (1^{st} inventory period) was 3.622g I-TEQ, and the annual emission in the same period varied from 0.159g I-TEQ a^{-1} in 1995 to 0.886g I-TEQ a^{-1} in 1990.

Between 1990 and 2000, the calculated values of PCDDs/Fs emission from metal casting processes in Croatia varied from 68 mg I-TEQ a^{-1} in 1995 to 171 mg I-TEQ a^{-1} in 1990. The calculated total burden with these pollutants to the environment in the same period was 960 mg I-TEQ.

The non-ferrous casting processes emitted a total of 97 mg I-TEQ in the same period. Although this value represents a relatively low burden with dioxins and furans to the environment, it is certainly enough to imply the need to control the emissions of PCDDs/Fs from non-ferrous casting processes.

Although these calculated values of PCDDs/Fs emission do not represent significant shares in total emissions from metallurgical processes, i.e. in total emissions from the Croatian production processes, it is important to know the levels of these emissions and to try to maintain or even reduce them, in order to decrease the total emission of these hazardous substances into the environment.

The follow-up research of the impact of all existing active metallurgical processes on the total emission of PCDDs/Fs should include measurements of their emissions. For better understanding of the emission flows of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes it is necessary to determine the content of these compounds in all types of waste generated in the observed metallurgical processes and to select technical solutions to improve every single process and to reduce their emission to the environment.

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 (2002).

[3] K. Olie, P.L. Vermeulen, O. Hutzinger, Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components in the Netherlands, Chemosphere **6**, 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, 1,2,9.

[5] G. McKay, Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review, Chemical Engineerin Journal **86**, 343 (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 (2004).

[7] D.R. Anderson, R. Fisher, Sources of dioxines in the United Kingdom: the steel industry and other sources, Chemosphere **46**, 371 (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, February 2004.

[9] U. Quass, M. Fermann, G. Broeker, Assesment of dioxin emission until 2005, The European Dioxin Emission Inventory – Stage II, Volume 3, North Rhine Westphalia State Environment Agency end EC, Directorate General for Environment, Essen, Germany, December 2000, 25, 118.

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

[11] B. Paradiž, P. Dilara, Dioxin Emissions in the Candidate Countries: Sources, Emission Inventories, Reduction Policies and Measures, EUR 20779 EN , European Commission, Join Research Centre, Institute for Environment Sustainability, Emission and Health Unit, I-21020 Ispra (VA), Italy, 2003, 7.

[12] P. Tan, D. Neuschutz, Study on Polychlorinated Dibenzo-p-Dioxin/Furan Formation in Iron Sinterin Process, Metallurgical and Materials Transactions B, **35** B, 983 (2004).

[13] 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 (2001).

[14] T. Wang, D.R. Anderson, D. Thompson, M. Clench, R. Fisher, Studies into formation of dioxins in the iron and steel industry. 1. Characterisation of isomer profiles in particulate and gaseous emissions, Chemosphere **51**, 585 (2003).

[15] EUROPEAN COMMISSION, Integrated Pollution Prevention and Control (IPPC), Best Available Techniques Reference Document on the Production of Iron and Steel, December 2001, 12, 230.

[16] M. Gojić, Metalurgija čelika, Izd.: Denona d.o.o., Zagreb, 2005, 162-163, 205.

[17] G. Baillet, Pourquoi un nouveau referentiel europeeb des ferrailes? La Revue de Metallurgie-CIT, Avril (2001) 399.

[18] J-P. Birat, A. Arion, M. Faral, F. Baronnet, P-M. Marquaire, P. Rambaud, Abatement of organic emissions in EAF exhaust flue gas, La Revue de Metallurgie-CIT, Octobre (2001) 839.

[19] S. Kakareka, T. Kukharchyk, Expert Estimates of PCDD/F and PCB Emissions for some European Countries, Institute for Problems of Natural Resources Use and Ecology, Minsk, Belarus, MSC-E Technical Note 2/2002, June 2002, 13.

[20] htpp://www.kcn.ne.jp/~azuma/English/news/Nov1999/991116.html

[21] W. Lemmon, Standards pancanadiens relatifs aux dioxines et uax furannes, Reunion sur les standards d'emission, Toronto, Novembre 1999.

[22] J. Jin, H. Peng, T. Xiaoyan, An inventory of Potential PCDD and PCDF Emission Sources in the mainland of China, Organohalogen Compounds **66**, 852 (2004).

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

[24] S.J. Buckland, H.K. Ellis, P. Dyke, Nerw Zealand inventory of dioxin emission to air, land and water, and reservoir sources, Pbs. Ministry for the Environment, Wellington, March 2000.

[25] M. Coutinho, R. Rodrigues, C. Borrego, Caracterizacao das Emissoes Atmosfericas de Dioxina e Furanos em Portugal: 1999–2000, 1^o Encontro Nacional de Dioxinas e Compostos Similares na Saúde e no Ambiente: uma abordagem intersectorial. Lisboa, 2003, 245.

[26] K. Bawden, R. Ormerod, G. Starke, K. Zeise, Australian inventory of dioxin emissions, Technical report No. 3, Department of the Environment and Heritage, ISBNO 642 5495 8, May 2004.

[27] An Assessment of Dioxin Emission in Hong Kong: Final Report, Environmental Resources Management, Tsimshatsui Kowlon, Hong Kong, March 2000.

[28] M. Cruells, A. Roca, C. Nunez, Electric arc furnace dust: characterization and leaching with sulphuric acid, Hydrometallurgy **31**, 3 , 213 (1992).

[29] J.E. Dutrizac, T.T. Chen, The role of hydrometallurgy in the recycling of zinc, copper and lead, www.ams.tuke.sk/data/ams_online/1998/number1/mag01/mag01.pdf

[30] T. Ferenczi, A. Enyedi, L. Becze, T.I. Torok, J. Rozinyak, Acta Metallurgica Slovaca, **7**, 21 (2001).

[31] J. Czernecki, E. Stos, R. Prajsnar, M. Kwarcinski, Acta Metallurgica Slovaca, **7**, 6 (2001).

[32] M. Jerman, Inventarizacija dioksina i furana u Republici Hrvatskoj (sažetak), Ekonerg- Institut za energetiku i zaštitu okoliša d.o.o., Zagreb, listopad 2001, 31.

[33] htpp://www.cro-cpc.hr/projekti/pops/EA-Croatia.pdf

[34] http://www.msceast.org/pops/emission_pcddf.html

[35] Izvještaj o izvorima, raspodjeli i učincima POPs spojeva na okoliš i zdravlje ljudi, IMI HCČP-1, Institut za medicinska istraživanja i medicinu rada, Zagreb, rujan 2003, 7.

[36] Z. Č e p o, Željezara Sisak 1938–1978, Izdavač: SOUR MK-ŽS, Sisak 1978, 286.

[37] I. B u d i ć, Z. B o n a č i ć M a n d i n i ć, Osnove tehnologije kalupljenja, Izd.: Strojarski fakultet u Slavonskom Brodu, Slavonski Brod, 2004, 12.

[38] European Dioxin Inventory – Results 040309: Other – Installations for smelting and casting of non ferrous metals, europa.eu.int/comm/environment/dioxin/pdf/stage1/smelting_non_ferrous_metals.pdf

Received: 3 April 2008.