PCDDs/Fs Pollution from Metallurgical Processes in the Town of Sisak, Croatia

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PCDDs/Fs POLLUTION FROM METALLURGICAL PROCESSES IN THE TOWN OF SISAK, CROATIA

ZANIECZYSZCZENIA PCDD/PCDF Z TECHNOLOGII METALURGICZNYCH W MIEŚCIE SISAK W CHORWACJI

In order to calculate the emission of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes located in the town of Sisak, Croatia, this research has built on experiences from developed countries, where the emission factor values from individual metallurgical processes have been taken from the reference data and used for the estimate of the emission of these pollutions in the European countries. The calculation of the emission polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from metallurgical processes located in the town of Sisak took into account annual outputs of sinter, pig iron, steel blooms and steel billets, as well as steel casts.

The metallurgical processes installed in the town of Sisak between 1950 and 2010 emitted from Q_{I-TEQ} =17 mg a^{-1} PCDDs/Fs in 2001 to Q_{I-TEQ} =5823 mg a^{-1} in 1989, depending on the activity of these processes. Within the observed period, the largest source of PCDDs/Fs emission was the iron ore sintering plant. Within the observed timeframe, the town of Sisak did not experience any excessive air, soil or water pollution by polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from the local metallurgical processes.

Keywords: dioxin, furan, emission, metallurgical processes

W celu obliczenia emisji wielochlorowych dibenzo-[1,4]-dioksyn (PCDD) i wielochlorowych dibenzofuranów (PCDF) z technologii metalurgicznych w miejscowości Sisak, Chorwacja, badaniaprzedstawione w tej pracy oparte zostały nadoświadczeniach z krajów rozwiniętych, gdzie wartości wskaźnika emisji z poszczególnych technologii metalurgicznych, zostały wzięte z danych referencyjnych i użyte w celu oszacowania emisji tych zanieczyszczeń w krajach europejskich. W obliczeniach emisji wielochlorowych dibenzo-[1,4]-dioksyn i wielochlorowych dibenzofuranów z technologii metalurgicznych w miejscowości Sisak wzięto pod uwagę roczną produkcję spieku, surówki i odlewów.

Technologie metalurgiczne zainstalowane w mieście Sisak pomiędzy 1950 a 2010 rokiem emitowały od QI-TEQ = 17 mg a-1 PCDD/PCDF w 2001 r. do QI-TEQ = 5823 mg a-1 w 1989 roku, w zależności od aktywności tych procesów. W obserwowanym okresie, największym źródłem emisji PCDD/PCDF było spiekanie rudy żelaza. W obserwowanym czasie, miasto Sisak nie odczuwało nadmierne zanieczyszczenia powietrza, gleby lub wody przez polichlorowane dibenzo-p-dioksyny i polichlorowanych dibenzofuranów z lokalnych technologii metalurgicznych.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), often commonly denotated as PCDDs/Fs, belong to a group of persistent organic pollutants (POPs) and represent a major hazard for the living environment. Although these compounds are not produced directly, apart from very small amounts for research purposes or as chemically pure substances, they represent a hazard to the environment precisely because they are generated in various chemical processes in chlorine compounds industry, pulp and paper industry or industrial processes taking place under high temperatures. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are emitted in the air as undesired by-products from metallurgical processes and often adsorbed by dust particles. Due to the natural motion of air masses they can thus be transported to relatively large distances from the primary source of pollution. On their way, they can be easily washed out by precipitations and end up in soil, ground water, and sediments.

The most significant source of PCDDs/Fs among metallurgical processes located in the town of Sisak was the process of iron ore sintering for the production of pig iron in blast furnaces. Their concentration in off gases from sintering process usually ranges from γ_{I-TEQ} = 0.5 to 5 ng Nm^{-3}[1-3]. As the amount of off gases developed within the sintering process is ~2100 Nm^3t^{-1} sinter, it allows calculation of the PCDDs/Fs amount developing per tonne of produced sinter and it ranges from m = 1 to 10 μg I-TEQ, where it can sometimes take up the value exceeding γ_{I-TEQ} =20 ng Nm^{-3} [4]. According to the reference data [1], off gases coming out from blast furnaces in the environment were accompanied by PCDDs/Fs,

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the amounts of which ranged from m_{I-TEQ} from <1.1 to 4.3 ng t^{-1} pig iron.

As opposed to the procedure of steel production by oxygen converter, in terms of PCDDs/Fs emission, steel production in electric arc furnaces is much more relevant because it uses steel scrap as charge, and steel scrap is almost always polluted with various inorganic and organic substances [5].

Kakareka and Kukharchyk [6] 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 offers variable data between m = 0.07 and 20 μg I-TEQ t^{-1} of steel on the emission factor values for PCDDs/Fs from the electric arc furnace process [7-12].

For the purpose of estimating PCDDs/Fs emission from metallurgical processes, in this study we have consulted the experience from industrialized countries. For the emission factor in individual processes, we used reference values suggested by a group of experts on emission estimate for this kind of pollution in European countries according to [6] i.e. we used emission factor m = 15 μg I-TEQ t^{-1} of sinter for sintering, m = 0.03 μg I-TEQ t^{-1} of pig iron for blast furnace, m = 2 μg I-TEQ t^{-1} of steel cast for casting and m = 2 μg I-TEQ t^{-1} of crude steel for EAF.

The calculation of PCDDs/Fs emission estimate from metallurgical processes (iron and steel making) took into consideration the output of OHF steel and EAF steel produced at Sisak melt shop, whereas the foundries were represented by the available data on the production in steel castings.

Since the available literature does not provide information on PCDDs/Fs emission factor from open-hearth furnace 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.

2. Results and discussion

2.1. Environment pollution around the town of Sisak by PCDDs/Fs from local metallurgical industry

Environment pollution around the town of Sisak begins with the development of iron and steel making industries in the town of Sisak that represents the center of the Croatian metallurgical industry, started with the construction of the blast furnace in the 1938. The pig iron output in 1939 was 3,736 t [13] and only one year later it already amounted to 19,561 t. After World War II, the output increased to around 100,000 t (1951) and reached 200,000 t in the early 1970s. The pig iron production was shut down in 1991.

For the purpose of pig iron production, the Sisak iron works built their own iron ore agglomeration and sintering plant, which was being developed and improved along with the blast furnace operation and was working continuously with an annual output of as much as 300,000 t until it was shut down in 1990.

According to Čepo [14], the production of steel billets and steel casts in Sisak started in 1954, when approximately 7,000 t of open-hearth furnace (OHF) steel and 2400 steel casts were produced. Ten years later, the output of steel produced by OHF process was 164,000 t, and in the mid-1970s it was 285,000 t. The production of steel casts at Sisak foundry was between 12,300 t in 1974 and only 615 t in 2010. The electric arc furnace was introduced in Sisak in 1966 with the annual output of EAF steel between 103,000 t in 2010 and 6,711 t in 2001.

In order to obtain better insight into the pollution status of the environment around the town of Sisak, and to calculate the emission of PCDDs/Fs from metallurgical processes in the town of Sisak, this research has built on experiences from developed countries, whereas the emission factor values from individual processes have been taken from the reference data [6] proposed by a group of experts for the estimate of the emission of these pollutions in the European countries. The calculation of the emission of PCDDs/Fs from metallurgical processes located in the town of Sisak took into account annual output of sinter, pig iron, crude steel and steel casts, Figure 1.

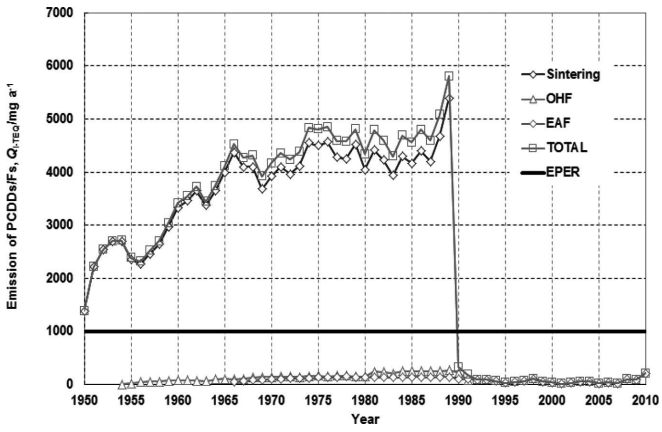

Fig. 1. Tendencies of PCDDs/Fs emission out of the metallurgical processes in the town of Sisak between 1950-2010

The metallurgical processes installed in the town of Sisak between 1950 and 2010 emitted from Q_{I-TEQ} =17 mg a^{-1} PCDDs/Fs in 2001 to Q_{I-TEQ} =5823 mg a^{-1} in 1989, depending on the activity of these processes. Within the observed period, the largest source of PCDD/Fs emission was the iron ore sintering plant. It is estimated that this plant accounted for 93% of the total emissions from the Sisak metallurgical processes, whereas the blast furnace and foundry emitted insignificant values (<1%) and were therefore ignored for the purpose of this paper.

The EU directive 2000/479/EC proscribes keeping the European Pollutant Emission Register (EPER) in the EU. Sources with annual PCDDs/Fs emission above Q_{I-TEQ} =1 g a^{-1} are considered significant sources of emissions [15]. The iron ore sintering plant, which has been shut down in the meantime, was the only metallurgical process in the town of Sisak that belonged to this category.

2.2. Distribution of PCDDs/Fs from metallurgical processes

Metallurgical processes in Sisak's metallurgical processes emitted PCDDs/Fs from six stationary point sources: stack of the sintering plant, two stacks of the open-hearth furnaces,

EAF's stack, the blast furnace stack, and the foundry EAF stack. The blast furnace stack and the foundry EAF stack were not even considered in this paper due their irrelevant amounts as sources PCDDs/Fs.

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, climatologic features, geographical characteristics of the source location, as well as ground configuration.

The emission conditions relevant for the distribution of pollution include the type of construction of the stack (height and cross-section), flow rate and volume, and the temperature of the stack gases. 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.

Dispersion of PCDDs/Fs emitted in the air from industrial zone i.e. metallurgical processes, calculated with the dispersion model of the US Environmental Protection Agency, was for the purposes of this paper called SCREEN3 [16]. 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 [17].

The imission concentrations of PCDDs/Fs were calculated within the 20 km radius around the sintering plant at the centre as the most significant point source of emissions, for worst-case weather conditions implying atmospheric stability class *F* and wind rate 1 m s $^{-1}$.

Basic input values for calculation by SCREEN3 model within the 20 km radius around the PCDDs/Fs sources of emissions are displayed in Table 1.

TABLE 1

Basic input values for SCREEN3 model

Emission source	Emission (g s^{-1})	Stack height (m)	Stack inside diameter (m)	Stack gas temperature (K)	Stack gas flow rate (m^3h^{-1})
Sintering	2.08E-7	70	5,1	543	480000
OHF	2.48E-8	68	2	743	60000
EAF	5.60E-9	26	1	323	38000

The imission calculation used continuous annual emissions of PCDDs/Fs from individual metallurgical processes for every year between 1950 and 2010. The worst case of annual imission was in the year with the highest total PCDDs/Fs emission (1989), as Figure 2 below shows.

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 contingency imission values to the maximum distance of 20 km in steps of 100 m.

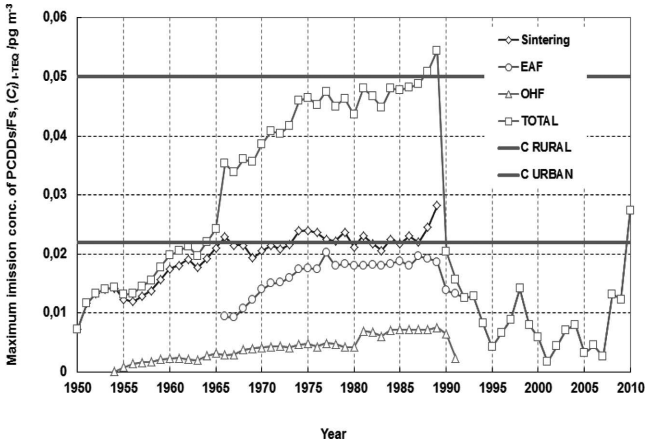

Fig. 2. Annual imission concentrations between 1950 and 2010

Maximal hourly imission concentration values and their distance from the source for individual source emissions are displayed in Table 2, and the profiles of maximum hourly, while average annual concentrations of PCDDs/Fs depending on the distance are given in Figures 3.

TABLE 2

Maximal hourly concentrations and their distances from the sources

Emission source	Maximal hourly imission concentration (μg m^{-3})	Distance from source (m)
Sintering	3.53 E-7	3885
OHF	9.50 E-8	736
EAF	2.33 E-7	200

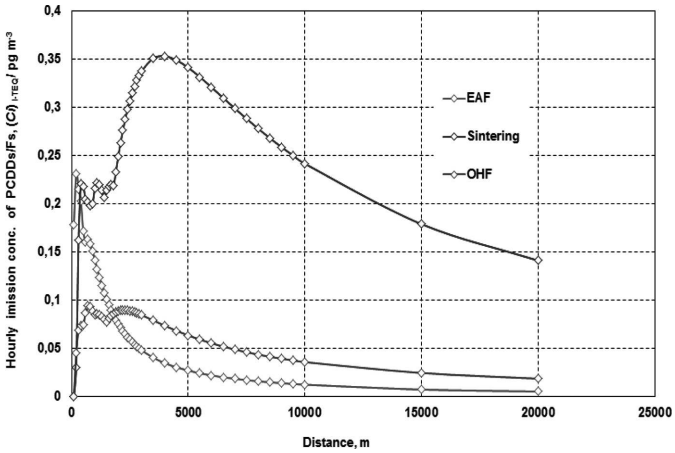

Fig. 3. Dependence of the hourly imission concentration profiles (C_I) PCDDs/Fs on the distance from the source in the year with the highest total emission (1989)

Average annual imission concentration values and their distance from the sources emissions are displayed in Table 3. The profiles of annual concentrations of PCDDs/Fs depending on the distance are given on Figure 4.

TABLE 3
Average annual imision concentrations and their distances from the sources

Emission source	Average annual imission concentration (μg m^{-3})	Distance from source (m)
Sintering	2.824 E-8	3885
OHF	7.60 E-9	736
EAF	1.864 E-8	200

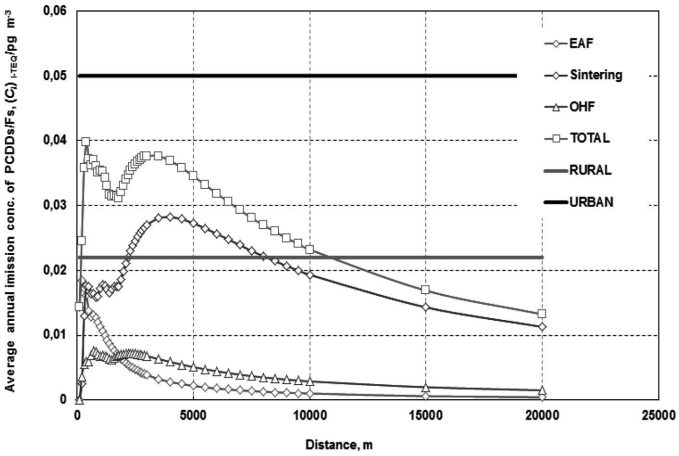

Fig. 4. Dependence of the annual imission concentration profiles (C_I) PCDDs/Fs on the distance from the source in the year with the highest total emission (1989)

Since neither the limit hourly value for PCDDs/Fs nor the limit annual air quality values have 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 and therefore the comparisons in this work were based on the measured values of imission concentrations of PCDDs/Fs in the USA [18] and Germany [18], in rural regions of which $(C_I)_{I-TEQ}$ = 0.022 pg m^{-3} and in urban areas $(C_I)_{I-TEQ}$ = 0.05 pg m^{-3}.

Figure 4 shows that the estimated value of the annual concentration of PCDDs/Fs never exceeded the amount of $(C_I)_{I-TEQ}$ = 0.05 pg m^{-3} even in the year with the highest emissions of these compounds from metallurgical processes.

Zones of the strongest impact of PCDDs/Fs emission from individual metallurgical processes in town of Sisak during observed period are shown in Figure 5.

3. Conclusion

This paper has calculated and estimated the emission values of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans to the environment from metallurgical processes in the town of Sisak, Croatia between 1950 and 2010.

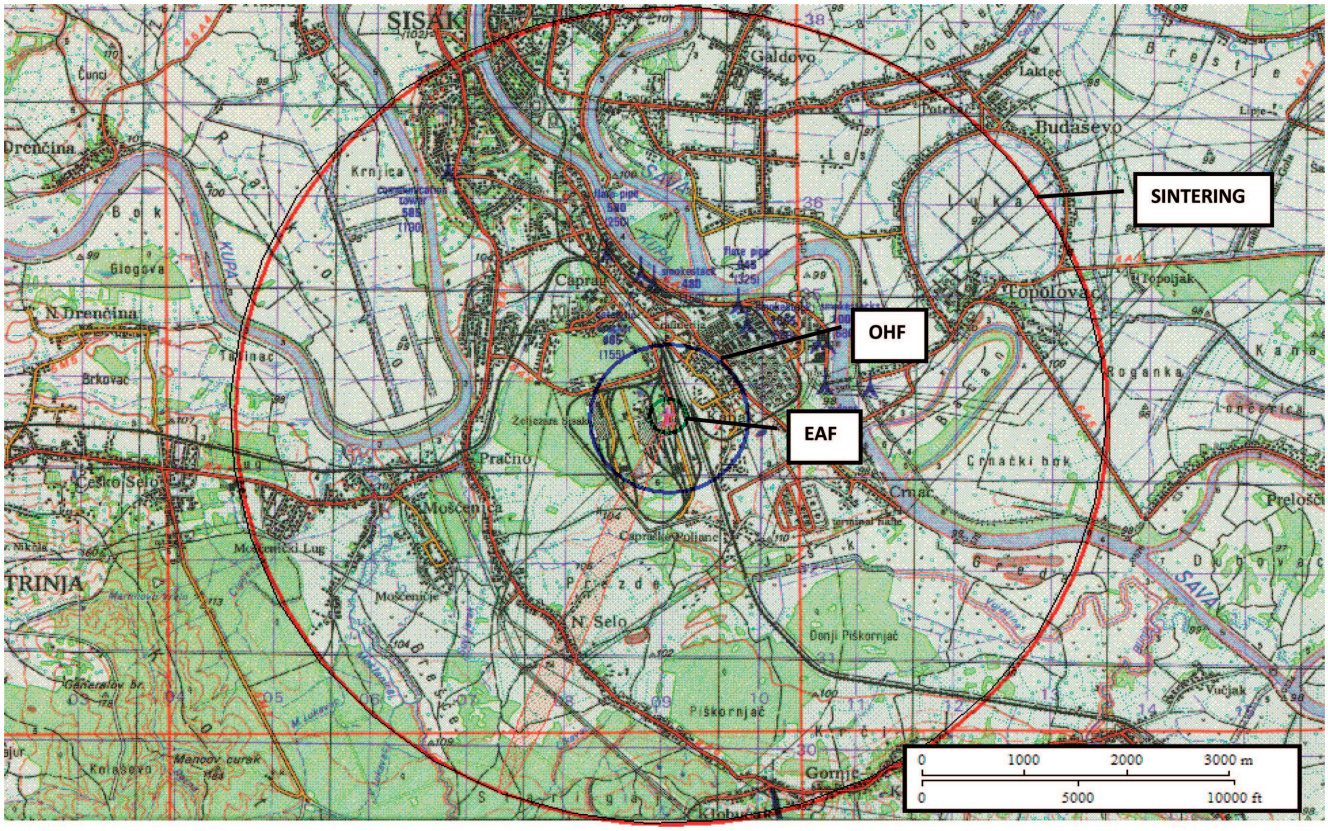

Fig. 5. Zones of the strongest impact of PCDDs/Fs emission from individual metallurgical processes in the town of Sisak 1950-2010

Calculated emission values of these compounds from all metallurgical processes installed in the town of Sisak ranged from Q_{I-TEQ} = 5823 mg a^{-1} in 1989 to Q_{I-TEQ} = 17 mg a^{-1} in 2001 as a result of sinter production, which represented the largest source of emissions of these compounds among all metallurgical processes active at the time.

The imission concentrations of PCDDs/Fs were calculated within the 20 km radius around the sintering plant at the centre as the most significant point source of emissions, for worst-case weather conditions. The imission calculation was based on the continuous annual PCDDs/Fs emissions between 1950 and 2010, and the worst-case example for 1989, the year with the highest total PCDDs/Fs emissions from the Sisak's metallurgical processes was displayed.

The obtained values of maximal hourly imission concentration of PCDDs/Fs and their distance from the source were $(C_I)_{I-TEQ}$ = 2.33 E-7μg m^{-3} and 200 m (EAF); $(C_I)_{I-TEQ}$ = 9.5 E-8 μg m^{-3} and 736 m (OHF), and $(C_I)_{I-TEQ}$ =3.53 E-7μg m^{-3} and 3885 m (sintering).

The obtained values of average annual imission concentration of PCDDs/Fs and their distance from the source were $(C_I)_{I-TEQ}$ = 1.864 E-8 μg m^{-3} and 200 m (EAF); $(C_I)_{I-TEQ}$ = 7.60 E-9 μg m^{-3} and 736 m (OHF), and $(C_I)_{I-TEQ}$ = 2.824 E-8 μg m^{-3} and 3885 m (sintering).

Within the observed period (1950-2010) there was no excessive air pollution in the town of Sisak due to PCDDs/Fs emissions from metallurgical processes. It should be duly noted that the metallurgical processes (especially sintering) were probably the most significant, but not the only sources of PCDDs/Fs emissions in and around the town of Sisak. In order to obtain a complete picture of the total load upon the Sisak environment with the said pollutions, one also needs to estimate pollution from other industrial and non-industrial sources of PCDDs/Fs in the town of Sisak that were active in the observed period such as traffic, domestic fireplaces, fires, oil refinery, thermal power plants, etc.

These results will contribute to the fulfilment of the action plan to reduce and annihilate the release of PCDDs/Fs as by-products to the environment, which is in line with the goals defined by the National Implementation Plan of the Stockholm Convention.

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