Validation and verification of emission factors in the heavy metal emission determination for the Slovenian Thermal Power Plants (TPP) and a comparison of the metal content in flue gases and ambient air

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Abstract

In signing the Protocol On Heavy Metals (HM) in 1998, Slovenia committed itself towards HM emission reduction. Apart from targeting HM emission reduction, the Protocol also binds its member countries to report on their HM emission rates. In Slovenia, the responsibility for HM emission registering and reporting is with the Environmental Agency of the Republic of Slovenia. For that purpose, preliminary estimates of the Pb, Cd and Hg emission rates have been made in compliance with the 'OSPARCOM–HELCOM UNECE Emission Inventory of Heavy Metals and Persistent Organic Pollutants'.

In 2000 the Milan Vidmar Electric Power Research Institute began monitoring HM emissions, together with dust emitted from the TPP. Last year, our measurements of the dust concentrations were made with a cascade impactor to determine the HM concentrations for individual granulation. In 2003, our monitoring of the HM concentrations was expanded to also include ambient air measurements in the surrounding of the TPP.

While monitoring the HM concentrations for individual granulation, which we performed in compliance with the national as well as the European legislation, our emphasis was on the PM10 and PM2,5.

We follow two objectives. The first one is validation and verification of emission factors that we use for HM emission calculations. The second one is to detect the influence of the emitted ash on the particle concentration in the surrounding ambient air, on their granulation and HM content.
Keywords: emission factors, heavy metals, dust composition, elemental concentrations, antropogenic activity, thermal power plant.

1 Introduction

Aerosolic particles are involved in many physical-chemical processes in the atmosphere. They affect visibility, take part in transformations of gaseous pollutants as well as in formation of acid components. Various epidemologic studies have shown the relationship between the increased particle concentrations of 10 μm (PM10) and the increased illnesses of the respiratory and cardiovascular system. The impact of aerosols on the human health mostly depends on the size and composition of particles.

Dust and with it trace elements are released into the atmosphere both from natural and anthropogenic sources.

Particles of natural sources are mostly the consequence of the erosion of the earth's crust and the wind activity on the sea surface.

Resuspended surface dust largely contributes to the total natural emissions. A large contribution of trace elements such as Cr, Mn, V and to the lesser extent Cu, Mo, Ni and Zn are found in resuspended dust [1,2].

Antropogenic sources are the ones that contribute to the air stressing with solid particles, i.e. transport, thermal power plants and other industrial plants and facilities. A large antropogenic source of particulate emissions is the combustion of fossil fuels. The contribution to the trace elements from those sources depends mainly to the fossil fuel used.

One of the largest stationary sources of particulate are power plants. Coal combustion in power plants gives rise to the emissions of primary (direct emissions) and secondary (small particles formed by the condensation of compounds volatilesed during the combustion) particulate pollutants. Emission of pollutants depends on coal quality, combustion technology and gas cleaning system. The majority of particles resulting from these emissions are usually of the order from 0,1 to 10 μm. The distance those particles travel before they are removed from the air by settling or by precipitation depends on their physical characteristics and the weather conditions. The size, density and shape influence the rate at which particles settle. Aerosols often function as condensation nuclei for cloud formation and are washed out with rain.

Metals (commonly referred to as heavy metals) bound in most fossil fuels are liberated during combustion and may be released to the atmosphere on particles or as vapours. Metals which are of most concern with respect to fossil fuel utilisation are As, B, Cd, Hg, Mo, Pb, Se, Cr, Cu, Ni, V and Zn. Some of these metals are very toxic, especially if they are present in sufficient quantities.

Most of heavy metals considered (As, Cd, Cr, Hg, Ni, Pb) are normally released as compounds (e.g. oxides, chlorides) in association with particulates. Only Hg is present in the vapour phase. Less volatile elements tend to condense onto the surface of smaller particles in the flue gas stream.

For the evaluation of the environmental impact of the power plants, specific studies including transport, transformation and deposition of contaminants depending on regional climatic conditions should be taken into account [1,2,3].

In compliance with international obligations, Slovenia prepares, on the annual basis, State Emission Inventories (SEI). Emission data are for each year reported to the United Nations Economic Commission for Europe. Within the scope of this database, evidence is of heavy metals (Cd, Hg, and Pb) maintained. Calculations of these emissions are based on emission factors taken from the OSPARCOM-HELCOM methodology (Technical Paper to the OSPARCOM-HELCOM UNECE Emission Inventory (Emission Factors Manual PARCOM-ATMOS). These emission factors do not include specifics of individual technologies. In order to assure more accurate SEI data, verification of emission factors is a prerequisite.

Slovenia has three large thermal power plants (TPP). A combined heat and power plant (CHPP) of Ljubljana located in the its capital, Trbovlje thermal power plant situated 60 km south-east from Ljubljana, and Šoštanj TPP located at the distance of 100 km from Ljubljana.

Brown coal and lignite are the primary fuels utilised in these power plants. Oil is used only to starting boilers.

2 Legal basis

In the time we are living in, the open environmental issues are being copped with by every country and its government. The same applies of course also to Slovenia. One of the conditions for being allowed access to the EU for Slovenia was to adopt all the EU environmental legislation.

Operation of the Slovenian TPPs must be harmonised with emission as well as immission environmental legal stipulations. One such legally bound obligation is to monitor, in addition to other emission parametrs, also emissions monitoring of dust, PM10 and HM as well as immission monitoring of air particles (TSP, PM10, PM2,5) and HM. Environmental monitoring in the TPP's, either of the emission or immission type, is performed by the Milan Vidmar Electric Power Research Institute of Ljubljana.

Monitoring heavy metal emissions, especially Cd, Pb and Hg, caused by the human activities, is imposed also by the Protocol on Heavy Metals to the 1979 Convention on Large Transboundary, which Slovenia ratified on February 9, 2004.

This Protocol binds the member countries to minimise emissions of each of the three metals on the level of the set reference year. The specified limit emission values from the major stationary emission sources are to be achieved within two years for new plants and facilities and within the period of eight years for the existing ones counting from the date of the protocol validity.

3 Technical characteristics of the observed TPP'S and properties of the used fuel

Emissions of dust, PM 10 and HM mainly depend on coal quality and combustion technology, including also the used techniques to reduce emission.

In tables below there are some basic specifications about the Šoštanj and Trbovlje TPP's and the Ljubljana CHPP (thermal inputs, year of the construction, used techniques to reduce emissions, used coal).

The fuel used in two of the observed TPP's is domestic coal. The Šoštanj TPP uses lignite from the Velenje coalmine and the Trbovlje TPP uses brown coal from the Trbovlje – Hrastnik coal mine. The Ljubljana CHPP uses Indonesian coal.

Table 1: Technical characteristics of the Šoštanj TPP.

Unit	Combustion techniques	Year of construction completion	Thermal input power (MW)	Used coal	Techniques to reduce emission
Unit 1	SULZER lignite-fired-pulverised	1956	105	lignite	ESPs FGD Primary measures
Unit 2	SULZER lignite-fired-pulverised	1956	105	lignite	ESPs FGD Primary measures
Unit 3/1	SULZER lignite-fired-pulverised	1960	125	lignite	ESPs FGD Primary measures
Unit 3/2	SULZER lignite-fired-pulverised	1960	125	lignite	ESPs FGD Primary measures
Unit 4	BABCOCK lignite-fired-pulverised	1971	740	lignite	ESPs FGD Primary measures
Unit 5	SULZER lignite-fired-pulverised	1977	920	lignite	ESPs FGD Primary measures

ESPs…electrostatic precipitators
FGD ... wet lime/limestone scrubber to reduce sulphur oxide emissions
Primary measures …to reduce NOx emissions

Table 2: Technical characteristics of the Ljubljana CHPP.

Unit	Combustion techniques	Year of construction completion	Thermal input power (MW)	Used coal	Techniques to reduce emission
Unit 1	GANZ Budapest lignite-fired-pulverised	1967	137	Brown coal	FF / Primary measures
Unit 2	GANZ Budapest lignite-fired-pulverised	1967	137	Brown coal	FF / Primary measures
Unit 3	ĐURO Đakovič lignite-fired-pulverised	1984	207	Brown coal	ESPs / Primary measures

ESPs…electrostatic precipitators
FF.......fabric filter
Primary measures...to reduce NOx emissions

Table 3: Technical characteristics of the Trbovlje TPP.

Unit	Combustion techniques	The year of construction completion	Thermal input power (MW)	Used coal	Techniques to reduce emission
Unit 4	RAFAKO (OP - 380 b) lignite-fired-pulverised	1968	350	Brown coal	ESPs / Primary measures

ESPs…electrostatic precipitators
Primary measures...to reduce NOx emissions

As volatile metal elements are enriched in the fine-grained particulate material carried downstream of the chamber, emissions of these elements depend more on the efficiency of the gas cleaning system than upon the method of fuel conversion. Control technologies capable of removing a large portion of certain metals from flue gas can generally be divided into two categories:

- techniques that are commonly used to remove particulates, SOx or NOx emission and
- techniques that have been developed to express trace elements from the flue gas [3].

Table 4 shows some of the coal characteristics affecting emissions.

Table 4: Properties of coal used in individual TPP.

	Šoštanj TPP	Trbovlje TPP	Lj. CHPP
moisture (%)	38.02 ± 0.39	21.15 ± 0.29	28.68 ± 0.25
ash (%)	17.33 ± 1.61	32.27 ± 1.00	2.17 ± 0.12
combustible (%)	44.24 ± 1.59	46.58 ± 1.18	69.15 ± 2.23
Calorific value (MJ/kg)	9.82 ± 0.31	11.19 ± 0.42	18.31 ± 0.62

4 Verification of heavy–metal (HM) emission factors

The main reasons for introducing monitoring of HM emission quantities are:

- monitoring of the HM content in exaust gases from TPP's is imposed by the law and Protocol on Heavy Metals,
- validation and verification of emission factors used for HM emission calculations.

4.1.1 Measuring principle

A known volume of flue gases is isokinetically extracted from a duct or chimney during a certain period of time at a controlled flow rate. The dust in the sampled gas volume is collected on a filter. The mass of the dust is determined by weighing. The filter is then recovered for analysis (digestion in a closed vessel).

4.1.2 Measuring equipment

The following is the main equipment used for gravimetrical determination of dust emission concentrations:

- GRAVIMAT tipa SHC 502, manufacturer SICK optic electronic, Germany (for flue gas extraction)
- Drayer SP-45 C, manufacturer Kambič, Lab equipment, Slovenia
- Balance AT 261, manufacturer Mettler-Toledo AG, Switzerland,
- PMA 10 (O2), manufacturer M&C Instruments and others.

Filters with collected dust are analysed with ICP-MS, the only exception is mercury.

4.1.3 Standards

To provide for appropriate results, various standards and guidelines are used:

- SIST ISO 9096:2003, Stationary source emissions – Manual for determination of mass concentration of particulate matter,

- prEN 14385, Air Quality – Stationary source emission – Determination of the total emission of specific elements,
- SIST EN 13211:2002, Air quality – Stationary source emissions – Manual for the method of determination of the concentration of total mercury and others.

4.2 Results of emission measurements

Average values for a three-year period (2001-2003) are given for the Cr, Ni, As, Cd, Pb and Hg emission concentrations for the Šoštanj and Trbovlje TPP's and the Ljubljana CHPP.

The measurement results for the Šoštanj TPP Unit 4 and Unit 5 (B 4,5) are joined together because they both use the same technniques to reduce emissions. Measurement results for the Unit 1, Unit 2, Unit 3/1 and Unit 3/2 (B 1, 2, 3/1, 3/2) are also joined together because the sampling point was behind the electrostatic precipitators. Flue gases from those four devices are then cleaned also with a FGD wet lime/limestone scrubber.

Measurements for all the three units of the Ljubljana CHPP were made in a common flue gas exhaust.

Table 5: Average emission concentrations.

Plant	Unit	Cr $\mu g/m^3$	Ni $\mu g/m^3$	As $\mu g/m^3$	Cd $\mu g/m^3$	Pb $\mu g/m^3$	Hg $\mu g/m^3$
Šoštanj TPP	U 4,5	3,95	1,05	2,52	0,1	1,00	0,06
	U 1,2,3/1,3/2	5,66	2,38	6,47	0,12	6,68	0,02
Trbovlje TPP	U4	7.43	3.99	1.,38	0.28	1.84	0.02
Ljubljana CHPP	U 1,2,3	6.04	7.19	5.36	1.22	6.45	0.75

4.3 Emissions and emission factors of HM

Figures 1, 2 and 3 serve as an example of shares of Cd, Hg and Pb emissions over individual sectors. An example is given for year 2002. The same situation is usually observed in other years. They are calculated on the basis of emission factors adopted from the OSPARCOM-HELCOM methodology.

TPP's contribute more than a half of the Hg emissions (53 %), more than a third of Cd emissions (35 %) and around 9% of Pb emissions.

Table 6 shows total values for a three-year period (2001-2003) for the Cd, Pb and Hg emissions for the Šoštanj and Trbovlje TPP's and the Ljubljana CHPP.

As seen from table 6, emissions obtained from the OSPARCOM – HELCOM emission factors are much higher than emissions obtained from measurements.

As seen from table 7, the OSPARCOM – HELCOM emission factors and emission factors obtained from measurements differ, too.

Emission factors obtained on the basis of measurements are the lowest for the Šoštanj TPP, in particular for Units 4 and 5 for which cleaning of flue gases is made also by using the FGD system. This finding does not apply to the Hg emission factor. We believe the reason for it is the fact that the Hg is in flue gases mainly present in its vapor phase, whereas measurements were made only for the emission concentrations of heavy metals emitted with dust. The fact that

Hg is in flue gases mostly present in its vapor phase is the main reason why we this year expanded sampling so as to include measurements of the total metal content.

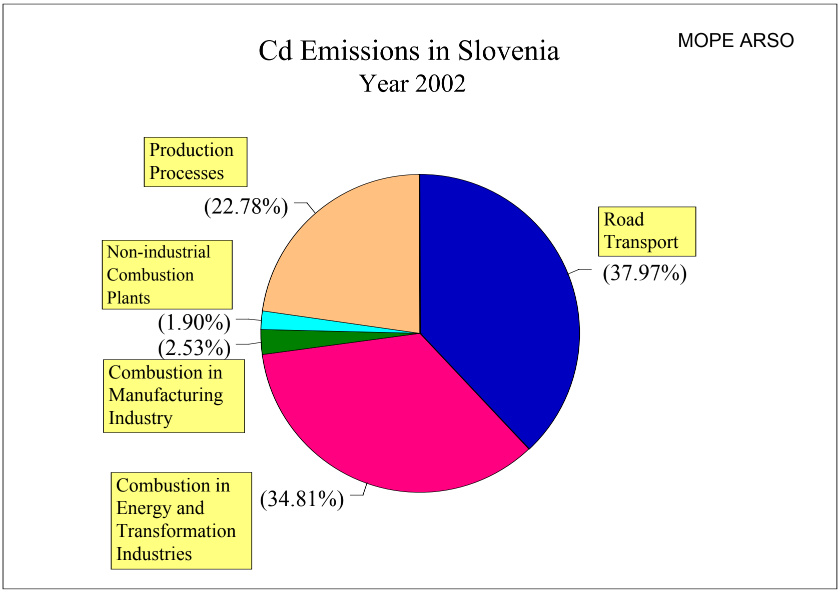

Figure 1: Share of Cd emissions in 2002 over individual sectors.

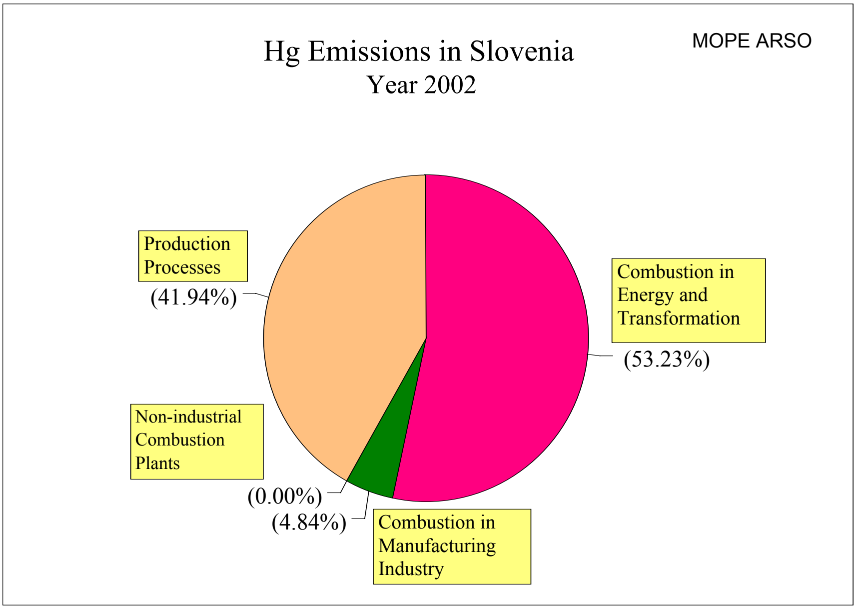

Figure 2: Share of Hg emissions in 2002 over individual sectors.

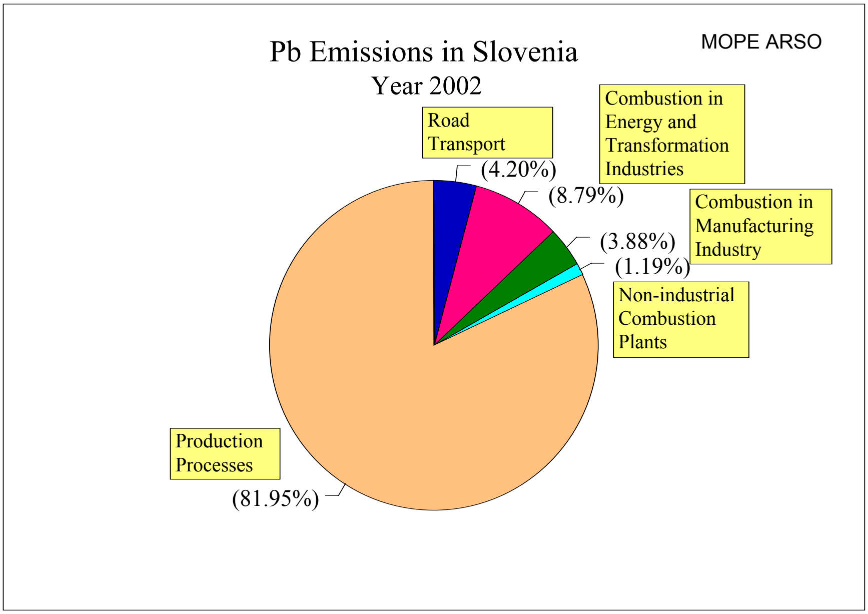

Figure 3: Share of Pb emissions in 2002 over individual sectors

Table 6: HM emission.

TPP/CHPP	Unit	Cd emissions (kg)		Hg emissions (kg)		Pb emissions (kg)	
		OHE	ME	OHE	ME	OHE	ME
Šoštanj TPP	Unit 4,5	999	4	600	2	1999	39
	Unit 1,2,3	241	1	145	1	482	52
Trbovlje TPP		192	3	115	1	384	110
Ljubljana CHPP		141	8	85	7	282	59

OHE... emissions of HM calculated on the basis of the OSPARCOM – HELCOM emission factors
ME..... emissions of HM calculated on the basis of the measurement emission factors

Table 7: HM emissions factors.

TPP/CHPP	Unit	Cd emission factors (g/t)		Hg emission factors (g/t)		Pb emission factors (g/t)	
		OHF	MF	OHF	MF	OHF	MF
Šoštanj TPP	Unit 4,5	0,1	3,73E-04	0,06	2,37E-04	0,2	3,88E-03
	Unit 1,2,3/1,3/2	0,1	4,57E-04	0,06	7,67E-05	0,2	2,56E-02
Trbovlje TPP		0,1	1,27E-03	0,06	9,00E-05	0,2	5,89E-02
Ljubljana CHPP		0,1	7,54E-03	0,06	4,74E-03	0,2	4,15E-02

OHF... OSPARCOM – HELCOM emission factors
MF..... emission factors obtained on the basis of measurements

5 Conclusion

Judging from the present measurement results of HM emissions emitted with dust, it is seen that emission factors obtained by using the OSPARCOM – HELCOM methodology are higher compared to emission factors obtained with emission measurements.

In as much as emission factors obtained on the basis of measurements of total metal emission concentrations are smaller than emission factors obtained by using the emission factor obtained with the OSPARCOM – HELCOM methodology, it would be reasonable to consider utilisation - for the needs of SEI as well as emission reporting – of emission factors obtained on the basis of measurements.

6 Future targets for the area of environmental monitoring

Two most important targets of our future work are:

- Obtaining information – by means of adequate sampling and chemical characterisation of aerosols over the various size classes (emission and imission monitoring) in combination with meteorological data and statistical processing - about impacts of individual TPP's on air pollution with solid particles over areas exposed to their impacts (ambient air pollution measurements with TSP have been performed for several years and PM10 pollution during the last three years. The first PM10 emission measurements started last year),
- In addition to determination of the pollution source impact on the environment - assessment on the basis of data about the toxic metal content of the potentially harmful effects of aerosols on the human health.

Future legal acts and protocols to be adopted for this field shall have to take into consideration complexity of interactions between the numerous pollutants. This will necessitate co-operation among various competent research institutions and introduction of the most recent results into the development of efficient strategies targeting at minimisation of environmentally negative impacts. One of the most problematic issues in this field is pollution with atmospheric solid particles.

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