ECOLOGICAL REMEDIATION OF THE ŠOŠTANJ THERMAL POWER PLANT WITH RESPECT TO SUSTAINABLE DEVELOPMENT OF THE ŠALEK VALLEY, SLOVENIA

by

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The Šalek valley used to be exposed to huge amounts of pollutants due to its close vicinity to the largest Slovene thermal power plant of Šoštanj (ŠTPP). Due to large emissions of SO_2 and heavy metals as well as dumping of fly ash negative effects on the environment appeared (e.g. forest decline in area exposed to deposition of emission by the ŠTPP, pollution of lake Velenje and the river Paka). Therefore, several ecological remediation measures on the ŠTPP were implemented in the 1990s, and several research projects on reasons and effects of forest decline and degradation of environment began as well. A continuous and marked improving of the condition of both forest and freshwater ecosystems (of lake Velenje and the river Paka) after the installation of desulphurization devices on Units 4 and 5 of the ŠTPP and construction of a closed loop system for the ash transportation is emphasized in the present paper.

Key words: *remediation, Šoštanj thermal power plant, desulphurization devices, bioindication, Norway spruce needles, tree-rings, roe deer antlers*

Introduction

The Šoštanj Thermal Power Plant (ŠTPP), which is located at the bottom of the Šalek valley, in the north-central part of Slovenia, has been operated since 1956; total installed power of 755 MW was established in 1975 when Unit 5 was built. The ŠTPP is the largest producer of electricity in Slovenia, nowadays produces almost 30% of the electrical energy of the state. Due to large emissions of both SO_2 (in the period before installation of desulphurization devices emissions ranged from 80,516 t in year 1983 to 123,382 t in year 1995, tab. 1, and heavy metals (annual emissions reached up to 298 t of Zn, 60.6 t of Cr, 22.1 t of Pb, 4.5 t of As, 0.3 t of Hg, and 0.2 t of Cd) as well as dumping of fly ash (as a result of the combustion of lignite in the ŠTPP) pronounced negative effects on the environment appeared (*e. g.* forest decline in the emission area of the ŠTPP, pollution of the lake Velenje and the river Paka). Therefore, ecological remediation of the ŠTPP (desulphurization of exhaust gases; primary measures for reduction of

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Table 1. Annual emissions of SO_2, NO_x, CO, CO_2 and dust from the ŠTPP in the period 1991-2008 [1]

Year	SO_2 [t]	NO_x [t]	CO [t]	CO_2 [t]	Dust [t]
1991	80,390	11,057	440	3,142,725	7,495
1992	79,988	9,009	505	3,587,029	6,085
1993	86,101	9,770	523	3,731,473	8,121
1994	80,516	9,483	484	3,434,461	4,917
1995*	51,663	10,025	761	3,581,956	2,765
1996	51,804	10,154	626	3,287,774	1,845
1997	53,093	11,572	739	3,698,747	2,377
1998	55,053	11,963	734	3,821,570	2,316
1999	47,665	9,096	589	3,334,732	1,077
2000*	44,253	10,379	541	3,540,040	460
2001	18,071	11,403	693	3,887,053	467
2002	22,871	12,779	931	4,740,476	632
2003	13,334	10,936	1,033	4,366,652	480
2004	7,951	8,877	1,300	4,536,876	419
2005	10,341	9,054	1,236	4,622,632	332
2006	6,190	9,130	1,394	4,662,431	158
2007	5,450	8,600	1,269	4,906,889	262
2008	4,182	7,613	1,315	–	205

* Two desulphurization devices were installed in February 1995 and in November 2000

NO_x, reconstruction of electrostatic filters, construction of closed loop system for ash transport) started in the beginning of 1990s; moreover, profound research studies of reasons and effects of forest decline and degradation of environment began as well.

A reduction of negative impacts on the environment represents the basis for sustainable development of the Šalek valley, where a severe anthropogenic impact resulted in marked pollution of ecosystems. Therefore, temporal trends in the stage of environmental pollution in terrestrial ecosystems have been continuously assessed by employment of several bioindicators, such as Norway spruce needles, tree-rings and roe deer antlers [2-5]; moreover, monitoring programmes of the quality/pollution of freshwater ecosystems (Velenje lake and Paka river) have also been performed since early 1990s [6-8]. In the present paper, determination of efficiency of desulphurization devices being constructed on the ŠTTP on the vitality of forest ecosystems is emphasised. Apart from this, temporal change of pH, which reflects pollution with calcium hydroxide and carbonate due to flay ash transport into the Velenje lake, is also presented.

Material and methods

Study area

The ŠTPP is located at the bottom of the Šalek valley, at an altitude of 370 m, in the north-central part of Slovenia, in the alpine and pre-alpine vegetation province with moderate continental climate. Prevailing winds are from the west and east, which has an important impact on the distribution of pollutants in the area. In this respect it is important that the ground layer of the frequent thermal inversions usually does not exceed 100 m, which is far below the height of the power station chimneys. Therefore, pollutants are spread over the hilly margins up to 1100 m above sea level, where the upper inversion layer occurs. The selected sampling sites (tab. 2) differ regarding altitude, distance, and direction from the ŠTTP.

Table 2. Description of sampling sites, where spruce needles, tree-rings and roe deer antlers were used as historical bioindicators of changes in environmental pollution

Sampling site	Distance from the ŠTPP [m]	Direction from the ŠTPP	Altitude [m]	Spruce needles	Tree-rings	Roe deer antlers
Slatine	5,900	SE	310-400			+
Lajše	3,700	SW	400	+		
Topolšica	5,400	NW	400	+		
Laze	5,700	SE	460	+		
Veliki vrh	3,500	SW	570	+	+	+
Skorno	4,000	W	350-710			+
Lubela	5,300	NE	700		+	
Graška gora	7,600	NE	730	+		
Gora Oljka	5,000	SW	730			+
Zavodnje	7,600	NW	760	+	+	
Paški Kozjak	10,500	E	900		+	
Brneško sedlo	18,100	NE	1,030	+		
Kramarica	12,700	NW	1,070	+		
Kope	17,500	NE	1,400	+		
Smrekovec	14,600	NW	1,555	+		

The Velenje lake, which is the biggest lake in the Šalek valley, is situated in the central part of the valley in the former basin of the river Lepena along its affluent Sopota. It appeared after the Second Word War due to coal-mining. The surface of the lake is 1.35 km^2, the volume 25 million m^3, and the depth near 70 m. This subsidence lake was used as a reservoir for ash and ash transport water from the ŠTPP from early 1980s to the middle of 1990s [9].

Sampling procedures

Ascorbic acid (vitamin C), photosynthetic pigments (chlorophyll a, b), and total sulphur content were measured in current-year needles of spruce (*Picea abies* (L.) Karst.) in the period 1991-2008 to assess the physiological state of spruce-trees and consequently the condition of forest ecosystem. Sampling of current-year needles of Norway spruce were carried out following the procedure described in the ICP recommendation [10]. Five vital trees in the age of 60-100 years were selected per site; from each tree we collected needles from the seventh spindle of branches from the top. Branches were cut off and left overnight in the dark at 4 °C for further processing of needles. Needles were frozen in liquid nitrogen and lyophilized prior to analyses.

Tree-rings (annual increments of wood) of Scots pine (*Pinus sylvestris* L.) as the most suitable tree species for historical biomonitoring of ambient pollution with Cd and Pb in Slovenia [11] were sampled at four locations in the Šalek valley (tab. 2) by special forestry drill (Suunto) at the breath height of four different trees (one per location). For reconstruction of temporal trends, annual tree-rings were dated and separated on 5-years intervals later in the laboratory.

Antlers of 129 roe deer (*Capreolus capreolus*) bucks, shot in the period 1961-2004, were collected in four areas of the Šalek valley (tab. 2) from local hunters owning trophies at their homes. Bone samples were taken following the method described by [12, 13]. To eliminate the possibility of secondary contamination, antlers were thoroughly cleaned with a nylon brush; moreover, the bone surface was removed by grinding. Afterwards, a hole was drilled into the back of each beam approximately 1.5 cm above the antler-pedicle junction, using a tungsten-carbide cutter fitted to a hand-held electric drill. Between 1 and 3 g of bone powder were collected from both antlers of an individual.

Chemical analysis

Ascorbic acid and photosynthetic pigments were analised by high performance liquid chromatography [14-17], and total sulphur by colorimetric titration using an AOK-S (adsorbed organic halogens) analyser [18]. Heavy metal contents were determined in tree rings (Cd, Pb) and in roe deer anters (Pb). Microwave digestion system (Milestone, Ethos plus) was used for the wet digestion of samples. Bone and wood samples (1.5000 ± 0.0010 g) were weighed into the microwave vessels to which 10 ml of conc. HNO_3 and 2 ml of H_2O_2 were added. After digestion, samples were diluted to 50 ml with double deionized water (Barnstead Nanopure Infinity system). Inductively coupled plasma mass spectrometry (ICP-MS Agilent 7500 c) was used for Pb and Cd determination. Levels of fluorides in roe deer antlers were determined by combined dry and acid combustion in solution with the use of an ion-selective electrode (Metrohm 6.0258).

Statistical analysis

Statistica for Windows 7.1 software package [19] was used for all statistical analyses; the limit of statistical significance was set at $p < 0.05$. All results regarding Norway spruce needles represent annual mean values, calculated on the basis of data provided for selected five spruce trees per sampling site, sampled at ten locations in the emission area of the ŠTPP in the period 1991-2008. Existence of correlations between different variables was tested by calculating the *Spearman rank coefficients*. In the following sections, all results are given either as mg/g (total sulphur, ascorbic acid, and pigment content) or as mg/kg (Pb, Cd, and F content) on a dry weight basis. Heavy metal levels in tree-rings and roe deer antlers had a non-normal distribution; therefore, non-parametric methods were used. Kruskal-Wallis analysis of variance (ANOVA) was employed to test the differences in Pb levels in roe deer antlers among 10-year intervals.

Results and discussion

Total sulphur content in Norway spruce needles

Exposures of the environment of the Šalek valley to sulphur were assessed by measuring the total sulphur content in spruce needles. The average annual sulphur content in needles was directly correlated with the average annual emissions of SO_2 in the period 1991-2008 (R =

$= 0.91$, $P < 0.001$, $N = 17$). Analysis of single year needles indicated that sulphur content is highest at sites close to the power plant (*e. g.* Veliki vrh, Topolšica, Lajše), and where altitude coincides with that of frequent thermal inversions (*e. g.* Zavodnje) [2, 20, 21].

From the sulphur content in needles it is possible to draw only partial conclusions about the physiological state of spruce trees. The classes of total sulphur content in spruce needles used in Austria [22] were accepted and modified by the Slovenian Forestry Institute to estimate forest condition/decline [23]. According to total sulphur content, each tree was assigned to one of four classes. Needles assigned in the first class contain the natural level of sulphur (<0.97 mg/g); needles in the second class have an increased sulphur content, but a defoliation of the crown is not expected (0.97-1.24 mg/g); in the third (1.24-1.58 mg/g) and fourth classes (>1.58 mg/g) damages to needles are more frequent and pronounced [23].

By measuring the content of sulphur in Norway spruce needles in the period 1991-2008 the efficiency of desulphurization devices on the ŠTPP was confirmed. Indeed, the mean annual level of total sulphur has been continuously decreasing, dropping from the fourth class (>1.58 mg/g) in the period before installation of the desulphurization device on Unit 4 of the ŠTTP (before 1995) to the third class before the construction of similar device in 2000, and then to the first class (<0.97 mg/g; natural content of sulphur) after 2005. Significantly, in this year SO_2 emissions from the ŠTPP were for the first time in the study period below 10,000 t per year (fig. 1).

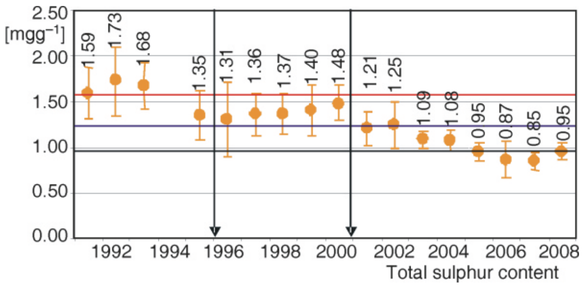

Figure 1. Mean annual concentrations of total sulphur in current-year needles from spruce, sampled in the period 1991-2008 in the emission area of the ŠTPP. Arrows mark years in which desulphurization devices were installed (Unit 4 in February 1995, and Unit 5 in November 2000). The marginal levels for total classes of sulphur contents are presented with lines

The physiological status of Norway spruce

Physiological condition of spruce trees, sampled in the area influenced by the ŠTPP, was investigated by determination of contents of vitamin C and photosynthetic pigments in current-year Norway spruce needles. Mean annual concentrations of vitamin C are presented in fig. 2. As a rule, the defence mechanism of plants and consequently content of vitamin C in their tissues should increase with increasing air pollution [24-27]. However, in the period of the largest emissions of sulphur dioxide (1991-1994), the lowest mean concentrations of vitamin C in spruce nee-

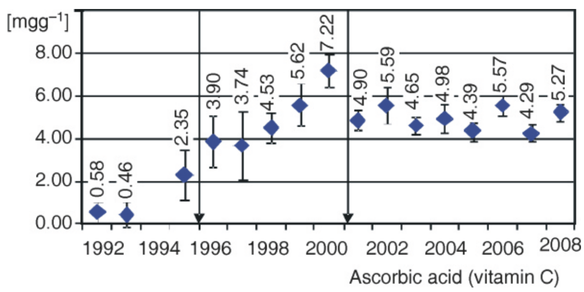

Figure 2. Mean content of vitamin C in current-year needles of spruce located in the emission area of the ŠTPP in the period 1992-2008. Arrows marked years in which desulphurization devices were installed (Unit 4 in February 1995 and Unit 5 in November 2000)

dles were found (fig. 2). Immediately after the first significant reduction of SO_2 emissions in 1995, contents of vitamin C in needles started increasing and reached the peak in 2000, although emissions remained almost unchanged in that period. Such a trend is comparable with some previous studies from highly polluted areas [28-30]. If spruces trees were exposed to high SO_2 emissions for a long time, the antioxidant defence mechanism would be damaged and the content of vitamin C would not increase as expected. In our study area, previous huge emissions of SO_2 were firstly significantly reduced after the installation of the desulphurization device on the Unit 4 of the ŠTPP in February 1995. Therefore, it is most likely that after a long lasting stress in 1980's and early 1990's the defence mechanism in spruce needles has started repairing and the normal mechanism of formation of antioxidant has been re-establishing after the implementation of this mitigation measure. After the second significant reduction of emissions of SO_2 (after the installation of the desulphurization device on the Unit 5 of the ŠTPP in November 2000) contents of vitamin C immediately drastically diminished, and remained almost unchanged afterwards (fig. 2).

In order to assess the health status of investigated trees we also measured the content of photosynthetic pigments, since oxidative stress tends to reduce chlorophyll (especially chlorophyll a) content. Mean annual concentrations of total chlorophyll (a + b) in current-year needles are shown in fig. 3. A very clear increase of spruce vitality after 1995 was confirmed; indeed, after this year a total chlorophyll content generally exceeded the limit value of 1.5 mg/g (indicating tree injury) [31]. Presumably, decrease of the total pigment contents in years 1996, 1997, and 2002 were not correlated with air pollution; rather, a lower vitality of trees (*i. e.* lower contents of pigment) in these three years reflects the impact of some climatic stress (*e. g.* high summer temperature and drought in years 1996 and 2002).

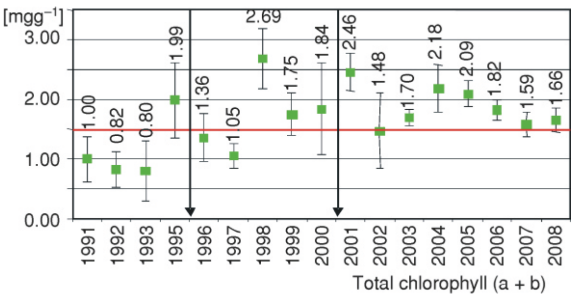

Figure 3. Mean annual concentrations of total chlorophyll (a + b) in current-year needles of spruce located in the emission area of the ŠTPP in the period 1991-2008. The horizontal line represents the limit value (1.5 mg/g). Arrows marked years in which desulphurization devices were installed (Unit 4 in February 1995 and Unit 5 in November 2000)

Tree rings as a historical bioindicator of heavy metal pollution

Annual rings of different tree species were employed for retrospective reconstruction of trends in environmental pollution with Pb and Cd in the Šalek valley [5]. Remediation measures made at the ŠTPP have contributed to a great decrease of emissions and to important reduction in pollution; consequently, pronounced decrease in Cd content (and to a leaser degree also in Pb content) in tree rings grown in years after the construction of flue-gas cleaning devices on the ŠTPP chimneys were found in several tree species (*e. g.* Norway spruce, European larch, trembling poplar, common birch, and Scots pine; fig. 4).

Among these species, Scots pine was selected as the most suitable retrospective bioindicator for assessing trends in environmental pollution with Cd and Pb due to existence of highly significant positive correlations between annual SO_2 or dust emission from the ŠTPP and Cd/Pb contents in annual rings of the species [11].

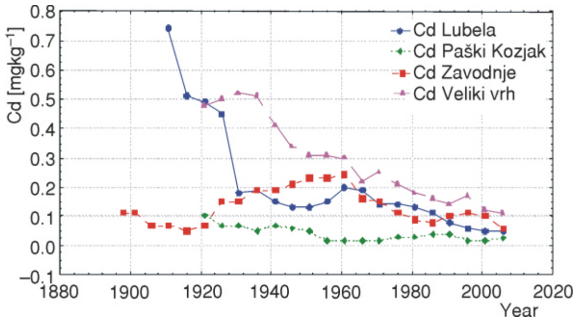

Figure 4. Cd contents in tree-rings of Scots pine from the Šalek valley [5]

Roe deer antlers as a historical bioindicator of lead and fluorides pollution

Roe deer antlers are a useful tool for historical biomonitoring since they accumulate potential bone-seeking pollutants and are kept as trophies in well-dated collections [4, 32-34]. For reconstruction of historical trends in environmental pollution with Pb and fluorides, their contents were measured in 129 antlers of roe deer, shot in the period 1961-2004 in the Šalek valley. The following conclusions were made [33, 34]: (a) The highest Pb and fluorides concetrations were determined in samples from the middle of the 20th century (Pb: $\bar{a}$ = 4.21 2.57 mg/kg, max. = 7.28 mg/kg; fluorides: mean = 1453 113 mg/kg, max. = 2590 mg/kg), and the lowest in the period 2000-2004 (Pb: mean = 0.58 0.11 mg/kg, max. = 1.25 mg/kg; fluorides: mean = 500 113 mg/kg, max. = 1010 mg/kg). (b) A continuous decline of Pb and fluorides contents in roe deer antlers confirmed efficiency of remediation measures for reduction of environmental pollution (*e. g*. construction of remote heating system in 1970s; introduction of unleaded petrol in 1990s, and especially installation of desulphuriza tion devices on the ŠTPP in the end of 1990s; fig. 5). (c) Existence of strong correlations between annual emissions of SO_2 and annual Pb or fluorides levels in roe deer antlers confirmed that remediation measures being made on the ŠTPP have importantly contributed to a lower exposure of wildlife in the Šalek valley.

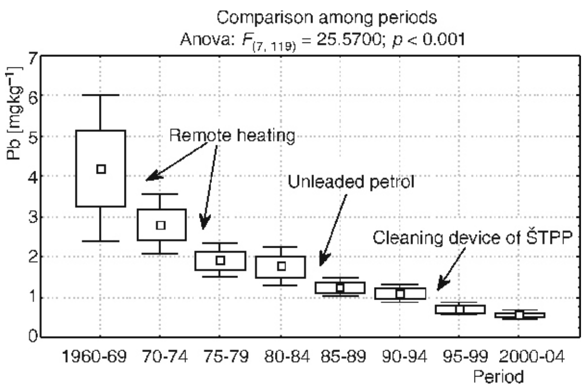

Figure 5. Deacrease of Pb content with SD in roe deer antlers from the Šalek valley (1961-2004) [3]

The Velenje lake

Due to electricity production and coal-mining in the Šalek valley the surface of valley has subsided, the depressions that formed have a volume of 1000 million m^3 until now; therefore, three subsidence lakes originated. The Velenje lake was used as a reservoir for ash from the ŠTPP, therefore water became polluted with calcium hydroxide and carbonate, and the pH of the

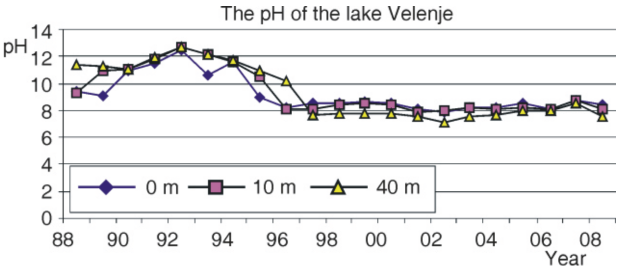

Figure 6. pH value of the Velenje lake, measured on the surface (0 m), at depths of 10 m and 40 m, in the period from 1988 to 2008

lake was around 12 (!); moreover, the run-off from the Velenje lake caused deposition of limestone in the river Paka. High alkalinity of water of the lake did not enable organisms to survive in such an environment. Since a closed loop system for ash transportation was built in 1994 pollution of the Velenje lake and the Paka river has stopped. Indeed, the abiotic conditions improved in a way that allowed organisms to again live in the lake (alkalinity diminished soon after the construction of the closed loop system, and the pH value remained between 8 and 9), and it has been recolonized by algae, fishes, frogs, macrophytes, and other organisms. There, fishes of several species contain very low amount of heavy metals nowadays, indicating that the quality of the surface waters in the Šalek valley is pretty high [6, 8, 9, 35].

Conclusions

On the basis of presented data the most significant findings and conclusions are as follows.

After the installation of desulphurization devices on Units 4 and 5 previous extremely high SO_2 and dust emissions have been dramatically reduced. Lower exposure to ambient pollution results in better vitality of Norway spruce trees, as well as in rising of their defence capabilities. The biomonitoring of total sulphur levels in spruce needles, which reflects the exposure of spruce trees to SO_2 emissions, confirmed the efficiency of desulphurization devices on the ŠTPP. Indeed, the mean annual content of total sulphur has decreased from the fourth class (>1.58 mg/g) in the period before the installation of the desulphurization device on Unit 4 of the ŠTTP to the first class (<0.97 mg/g) after 2005, and needles of Norway spruce from the Šalek valley nowadays contain only natural amounts of sulphur.

By using retrospective bioindicators (tree-rings and roe deer antlers) a reconstruction of trends in environmental pollution with heavy metals and some other toxic substances (*e. g.* fluorides) can be made. Both Pb and fluorides contents in roe deer antlers and Cd/Pb levels in annual tree-rings confirmed that the remediation measures of the ŠTPP reduced the environmental pollution with these substances, and also that exposure of ecosystems to toxic substances has been significantly decreased in the last decade.

With the reconstruction of flay ash transport system (closed water cycle) in 1994 the pollution of the Velenje lake and the Paka river has stopped. The lake became alive again (alkalinity diminished and pH value has remained between 8 and 9), and it has been recolonized by algae, fishes, frogs, macrophytes, and other organisms.

Ecological remediation of the ŠTPP evidently reduced the environmental pollution in this part of Slovenia and enabled a sustainable development of the Šalek valley, which used to be polluted with different inorganic toxic substances in the past [2, 9, 34, 36, 37]. Therefore, mitigation approach being employed in the Šalek valley and particularly on the ŠTPP (together with several essential up-following biomonitoring programmes) should represent the model approach for reducing the man-made pollution in the emission areas of thermal power plants, with the aim to improve the quality of live of citizens as well.

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