UNIVERSITY OF NOVA GORICA
GRADUATE SCHOOL

HISTORICAL BIOMONITORING OF HEAVY METAL POLLUTION IN THE VICINITY OF SLOVENE ROADS BY DETERMINATION OF METAL CONTENTS IN ANNUAL RINGS OF SELECTED TREE SPECIES

MASTER'S THESIS

Jure LAH

Mentor: doc. dr. Boštjan Pokorny

Nova Gorica, 2012

UNIVERZA V NOVI GORICI
FAKULTETA ZA ZNANOSTI O OKOLJU

RETROSPEKTIVNI BIOMONITORING SPREMEMB V ONESNAŽENOSTI OKOLJA S TEŽKIMI KOVINAMI V BLIŽINI PROMETNIC Z DOLOČITVIJO VSEBNOSTI KOVIN V BRANIKAH IZBRANIH DREVESNIH VRST

MAGISTRSKA NALOGA

Jure LAH

Mentor: doc. dr. Boštjan Pokorny

Nova Gorica, 2012

ABSTRACT

Trees are bioindicators capable of recording HM levels in the environment in the past. In this study Scots pine trees for the determination of long-term trends and silver birch and trembling poplar trees for the determination of pollution in the last three decades were sampled in three locations near roads in Slovenia. For the determination of historical trends of pollution the levels of Pb, Cd, Zn, Cr and Ni in sampled tree-rings were determined using inductively coupled plasma mass spectrometry (ICP-MS). Study demonstrates that tree-rings of fast growing diffuse porous broadleaf species, especially silver birch, could be successfully used in determination of trends of pollution with HM from road traffic. The trend of decrease in Pb levels in the last years was established at all locations, although it seems that also other sources of Pb had an important influence on the content of this metal in tree-rings. Despite of large emission of this element from road traffic it seems that the large proportion of it wasn't deposited in a form that is readily available for the uptake by the trees. In the heavily polluted Upper Meža valley, the levels of Pb are much higher, and in a non-polluted area of Kočevje lower than those measured at roadside locations. After the phase-out of Pb gasoline and other remediation measures for the reduction of air pollution, the levels of Pb in trees near roads have been reduced to similar levels than those found at non-polluted environment. A trend of increase in Cr levels is evident at all locations and in pine trees also well correlated with traffic indicators. It seems that after the phase out of Pb gasoline, Cr may be an important indicator of traffic pollution. The tree-ring width doesn't seem to influence the levels of HM in tree-rings. It is difficult to compare trees at different locations in the vicinity of roads because of numerous factors that influence the emissions, the distribution of pollutants and the uptake of HM. Levels of some HM could also be linked to same other indicators of general pollution like emissions and imissions of SO_2, dust emissions from TE-TOL, therefore one has to be very careful in the interpretations of the results of dendrochemical studies.

KEY WORDS: road traffic, pollution, heavy metals, Pb, Cd, Zn, Cr, Ni, tree-rings, bioindication, Scots pine, silver birch, trembling poplar, dendrochemistry

IZVLEČEK

Drevesa so bioindikatorji, ki lahko beležijo ravni težkih kovin (HM) v okolju, v katerem rastejo. V raziskavi so bile vzorčene 3 drevesne vrste: rdeči bor za določitev dolgoročnih trendov in breza ter trepetlika za določitev trendov onesnaženja v zadnjih treh desetletjih, na 3 lokacijah v bližini cest v Sloveniji. Za določitev zgodovinskih trendov onesnaženja so bile določene koncentracije Pb, Cd, Zn, Cr in Ni v branikah dreves s tehniko induktivno sklopljene plazme z masnospektrometrično detekcijo (ICP-MS). Izsledki raziskave kažejo, da so branike hitro rastočih listavcev z difuzno poroznim lesom, predvsem breza, primerne za določanje trendov onesnaženja s težkimi kovinami iz cestnega prometa. Trend zniževanja vsebnosti Pb v zadnjem obdobju je bil ugotovljen na vseh lokacijah, čeprav se zdi, da so tudi drugi viri imeli pomemben vpliv na ravni te kovine v branikah dreves. Kljub velikim emisijam te kovine zaradi prometa kaže, da glavnina Pb ni bila odložena v okolju v obliki, ki bi bila drevesom enostavno na voljo. Vsebnosti Pb v močno onesnaženi Mežiški dolini so mnogo večje kot na lokacijah ob cestah in v neonesnaženem okolju na območju Kočevja nižje kot ob cestah. Po opustitvi osvinčenega bencina in ostalih ukrepih za zmanjšanje onesnaženosti zraka se ravni Pb v drevesih bližajo ravnem, značilnim za neonesnaženo okolje. Trend povečevanja vsebnosti Cr je ugotovljen na vseh lokacijah in kaže v boru tudi dobro soodvisnost s podatki o prometu. Kaže, da bi lahko bil Cr najpomembnejši indikator onesnaženja zaradi prometa po opustitvi osvinčenega bencina. Ne kaže, da bi širina branik vplivala na koncentracije HM v lesu. Primerjava med drevesi na različnih lokacijah ob cestah je težavna zaradi množice dejavnikov, ki vplivajo na emisije, razširjanje in privzem HM v drevesa. Koncentracije nekaterih HM je mogoče povezati tudi z drugimi indikatorji splošne onesnaženosti okolja, kot so emisije in imisije SO_2, emisije praha iz TE-TOL, zato je potrebna posebna pazljivost pri interpretaciji rezultatov dendrokemijskih raziskav.

KLJUČNE BESEDE: cestni promet, onesnaževanje, težke kovine, Pb, Cd, Zn, Cr, Ni, drevesne branike, bioindikacija, rdeči bor, breza, trepetlika, dendrokemija

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ABBREVIATIONS AND SYMBOLS

HM	-	heavy metals - elements in a context that is used in biological and environmental studies and is not in total accordance with the pure phisio-chemical definition by which heavy metals are those metals with specific gravity greater than 4,5 g/cm^3 (for more information see Wittig, 1993; Duffus, 2002)
ICP-MS	-	inductively coupled plasma mass spectrometry
RM	-	reference material
LOQ	-	limit of quantification
ARSO	-	Slovenian environment agency
CERCLA	-	Comprehensive Environmental Response, Compensation, and Liability Act
SURS	-	Statistical office of the Republic of Slovenia
TE-TOL	-	remote heating and thermal power plant in Ljubljana
PLDP	-	average annual daily traffic
N	-	number of analysed pairs

1 INTRODUCTION

Transport, especially road transport, has been becoming cleaner during the last two decades because of increasingly strict emission standards for the different transport modes. Nevertheless, air quality in cities usually does not meet the limit values set by European regulation and still has a major negative impact on human health (EEA report 2006). Heavy metals are long-term contaminants with the ability to accumulate in soil and plants and have no natural way to be removed (Butkus and Baltrenaite, 2007). Historically, the rate of heavy metal emissions has been low due to the low volatility of most metals (except mercury) and/or due to low industrial activity. However in 19th and 20th century, increasing human (industrial) activity has substantially enhanced emissions and therefore increased metal concentrations in the atmosphere and in atmospheric deposition (Valiulis et al., 2002). Since emissions from industry and other point sources have decreased substantially in last decades, the diffuse sources are becoming increasingly relevant. Road traffic is one of the major sources of disperse pollution with heavy metals (Hjortenkrans et al., 2006). The main sources of heavy metals near roads represent emissions of exhaust gasses, brake wear, tire wear and wear due to friction of mechanical parts. Historically lead was the most important heavy metal associated with road traffic and originated mainly from vehicle exhaust (Legret and Pagotto, 2000), but after the phase-out of leaded gasoline its emissions have been decreasing significantly (Rode et al., 2010).

Due to the lack of data from the past it is almost impossible to reliable assess trends in environmental pollution merely by comparing historical and recent data on emission/deposition rates or on pollutant's contents in different (a)biotic media. Retrospective approach by employing suitable historical biomonitoring tools (species, organs, tissues) therefore represents the only possibility for relevant post-hoc determination of pre-industrial concentrations of pollutants in selected part of the biota, which is often a prerequisite for comparing recent environmental burdens with (otherwise unknown) baseline values; moreover, it also allows the assessment of effectiveness of different ecological remediation measures done for reducing the release of toxic substances into the environment (Pokorny et al., 2004).

A bioindicator is an organism which reacts to specific environmental dynamics with observable and measurable changes. By observing and measuring the changes a conclusion as to the kind of pollution (e.g. heavy metal), its source (e.g. from road traffic) and possibly its intensity (given as the relationship between degree of pollution and observable measurable changes of the bioindicator) can be drawn (Markert, 1993).

Retrospectivity is one of the main advantages of biomonitoring and can not be achieved with classical methods of instrumental monitoring (Pokorny, 2003) and it is necessary for the assessment of efficiency of different mitigation measures that were carried out in the past (e.g. phase-out of leaded gasoline, construction of purification devices on point sources) (Poličnik et al., 2009).

For historical biomonitoring of trace metal pollution, dendrochemistry, a method of chemical analysis of tree-rings, was developed in the past decades. In climates characterized by distinct seasons of growth and dormancy, trees develop annual growth rings in the wood. It is thus possible to accurately date the rings. Trace metals are transported through the water conducting tissue of the rings and accumulated in the wood (Hagemeyer, 1993). In dendrochemistry, the growth rings of different age are collected and their trace elements content is analyzed in order to get a chronological record of the element composition of the trees environment. It is assumed that when annual rings lose function, they isolate a relative record of the sap chemistry and the elements uptaken from the environment are deposited only in currently growing parts of the tree (Nabais et al., 1999).

Dendrochemistry seems to be suitable for historical biomonitoring of heavy metal pollution near roads because trees meet some demands for ideal passive accumulative biomonitors as described by Wittig (1993). They commonly grow in the vicinity of roads, their age and distance from the road can be accurately determined, they are easy to sample and there is no problem with their determination. Their susceptibility for historical biomonitoring of heavy metals uptake has been more or less successfully determined in many studies (e.g. Watmough and Hutchinson, 1996, 2002; Watmough et al., 1998; Patrick and Farmer, 2006; Padilla and Anderson, 2002; Bellis et al., 2002; Cheng et al, 2007), but careful selection of the most suitable tree species for a given task is very important (Poličnik et al., 2009).

The purpose of this study is to determine temporal differences (trends) in levels of lead (Pb), and also some other traffic related heavy metals (cadmium (Cd), zinc (Zn), chromium (Cr), and nickel (Ni)), in annual tree-rings of selected tree species, sampled at the vicinity of major roads in Slovenia, and to determine whether road traffic characteristics (or other known factors, e.g. emissions from relevant point sources, overall emissions in Slovenia) are reflected in levels of heavy metals in tree-rings.

Main research goals were as follows:

(a) Retrospective determination of trends of heavy metal environmental pollution near road sections with high traffic densities in Slovenia.

(b) Comparison of trends in environmental pollution and temporary ecosystem heavy metal load: (i) among individual major road sections in Slovenia; (ii) with traffic characteristics at the selected road sections, (iii) with available data for environmental pollution.

(c) Determination whether trees could be successfully used for reconstruction of trends of pollution with heavy metals from road traffic.

(d) Determination whether major decrease of Pb emissions from road traffic is reflected in tree-ring levels of this heavy metal.

(e) Comparison of tree-ring's heavy metal levels near roads with other Slovene studies of metal contents in tree-rings.

2 LITERATURE REVIEW

Contamination of the earth's ecosystems by potentially toxic metals/metalloids is a global problem. It will likely grow with our planet's increasing populations and their requirements for natural resources (e.g. water, food, energy, waste disposal sites) and metal based goods. The health impacts of pollution from ingestion of heavy metals/metalloids via respiration, food, and drinking water are most often long-term and manifest themselves in many ways. These include, for example, diminution of mental acuity, loss of motor control, critical organ dysfunction, cancer, chronic illnesses and concomitant suffering, incapacitation, and finally death (Siegel, 2002).

Historically, emissions from industry and other point sources were of most acute concern, but since these emissions have decreased to less than one tenth of their previous levels, research into diffuse sources has become increasingly relevant. Several studies of metal flows in the anthroposphere point to the traffic sector as a major contributor of diffuse metal emissions (Hjortenkarans et al., 2006).

Regarding data of U.S Environmental Protection Agency, the World Health Organization and the Arctic Monitoring and Assessment Programme, metals/metalloids that are potentially toxic to life forms are As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Ti, Tl, V and Zn (Siegel, 2002).

There are several heavy metals that are micronutrients (As, Co, Cr, Cu, Fe, Mn, Mo, Se, V, Zn) essential to maintain a good health status in humans and other organisms. Non-essential heavy metals are Be, Cd, Hg, (Ni*), Pb, Sb, (Sn*) and Ti. However Ni and Sn may potentially be essential micronutrients (Siegel, 2002).

2.1 Road traffic contamination with heavy metals

2.1.1 Emissions of heavy metals due to road traffic and presence of a road

The main processes by which vehicles disseminate pollutants into the environment are combustion processes, the wear of cars (engine, tyres, brakes), leaking of oil and coolants, and corrosion (Van Bohem and Van de Laak, 2003). While emissions control regulation has led to a substantial reduction in exhaust emissions from road traffic, currently non-exhaust emissions from road vehicles are unabated (EEA, 2009). Lead is (was) released in combustion processes, zinc is derived from tyre dust (zinc is a catalyst used in the manufacture of tyres), and copper is derived from the corrosion of radiators and brakes; the other heavy metals have mixed origins (Van Bohem and Van de Laak, 2003). The origin of Zn associated with road traffic is also corrosion of crash barriers (Legret and Pagotto, 1999)

The most important traffic related heavy metals nowadays are Cu, Pb and Zn (Legret and Pagotto, 1999). Brake linings are an important source of heavy metals (mainly Cu, Zn and Pb), and regarding fuels, only leaded gasoline is (used to be) an important source of metals (ibid). Historically lead was the most important heavy metal associated with road traffic, but after the phase-out of leaded gasoline its emissions in Slovenia decreased significantly (Rode et al., 2010). Other metals of concern for emissions from road traffic are Cd, Cr, Cu, Ni, Pb, Sb and Zn for brake wear, Zn and traces of Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni and Pb for tyres, and Cd, Cr, Cu, Ni, Pb and V for exhaust fumes from combustion of fossil fuels, respectively (Hjortenkrans et al., 2006). In a study conducted using mosses in tunnel experiment in Vienna (Zechmeister et al., 2006) Ba, Cu, Mo, Pb, S, Sb and Zn have been found to be the indicators of road traffic pollution.

An assessment of emissions of heavy metals from road traffic (Table 1) was made in the Netherlands and shows assessed national emissions from road traffic in tons per year based on a car fleet of six million vehicles (Van Bohem and Van de Laak, 2003).

Table 1*: Calculated emission of heavy metals by road traffic per emission source (tons/year) in the Netherlands (Van Bohem and Van de Laak, 2003)*

Element	Exhaust	Oil leaks	Tyres	Brakes	Radiator	Total
Arsenic	0.17	0.015	0.013	0.004	/	0.199
Cadmium	1.2	0.002	0.73	/	/	1.932
Chromium	1.7	0.014	2.6	0.518	/	4.832
Copper	0.25	0.061	3.65	9.072	50.910	63.943
Lead	240	1.96	/	0.022	0.072	242.054
Nickel	1.7	0.007	2.48	0.285	0.192	4.664
Zinc	2.3	1.49	175	0.117	0.168	179.075

The number of registered vehicles in Slovenia has risen from less than 5,000 vehicles in the year 1946 to 0.46 million in 1980 and to 1.28 million vehicles in 2007 (SURS, 2011).

Not only emissions from the traffic affect the quantities of emitted pollutants from the road; also the diffuse atmospheric deposition on the road segment has some influence on the overall emissions (Steiner et al., 2007).

The outputs (emissions) from the road into the road shoulder can be divided into the following categories (Van Bohem and Van de Laak 2003; Steiner et al. 2007; see also Figure 1):

(a)Road runoff: Water that runs off a road surface can convey some of the pollutants in a dissolved or suspended form to the roadside. Most metals and almost all polycyclic aromatic hydrocarbons (PAHs) are bonded to the silt that is flushed off roads. The quantity of rainwater that runs off varies between 20% and 80%. The runoff depends on the degree of evaporation, spray and pool formation, type of road (inclinations), and especially the type of road surface used (drainage asphalt…). When running off, the rainwater dissolves particles and soluble substances; approximately 6%–9% of the total dissolved substances originate from the rainwater itself. High concentrations of dangerous substances in runoff are formed especially in the first flush after a dry period.

(b) Spray: this refers to the splash water from traffic activity during rain events (wet spray), or in a dry condition (dry spray) which is emitted to the road shoulder. In both cases, a large part lands on or in the immediate vicinity of the roadside. The range of the spray depends on local conditions and can be determined from measurements of heavy metals in the road shoulder.

(c) Drift: drift (long-distance atmospheric spray) is caused by particulate emissions blown by the wind and deposited to the soil up to relatively large distances from the road (several hundreds of meters). Drift occurs during both dry and wet weather.

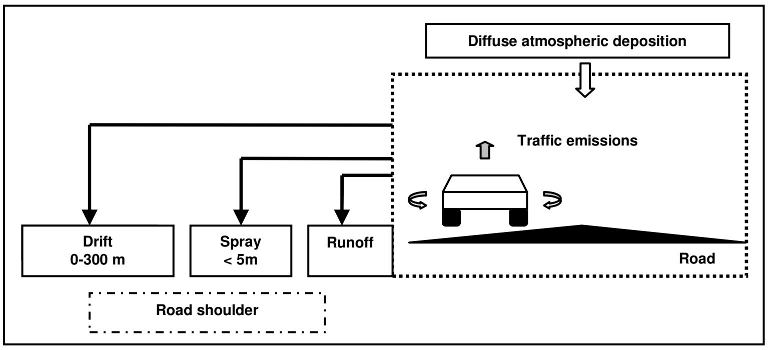

Figure 1: *Scheme of emissions from the road (modified from Steiner et al., 2007)*

Additional sources of emissions that originate from road traffic and from the existence of roads are: (a) Emissions from road "furniture" (mainly Zn from crash barriers and to a lesser degree road signs and portals) and road surfaces due to erosion of materials that make up the road surface. Leaching of chemicals due to weathering of roads can occur, especially when road construction contains secondary material. (b) Means and materials of winter maintenance: compared to other sources, this contamination by heavy metals is very limited; however, de-icing salt contains highly soluble NaCl, and this may influence the flow and bioavailability of several metals. (c) Road accidents, litter, leaks, and herbicides and pesticides: Chemicals can spread into the environment due to car accidents. Although highly unpredictable in nature, the effects can be serious, depending on the chemical compounds involved. Solid litter may or may not break down, and leaks from vehicle lubrication and hydraulic systems can also cause pollution (Van Bohem and Van de Laak, 2003).

2.1.2 Pollution: how far from the road

Depending on the size of the particles (Van Bohem and Van de Laak, 2003), metallic particles released by motor vehicles may remain in the air for some time, but most of them get deposited on the roadside soils and vegetation close to the road is able to accumulate heavy metals and their compounds. Metals can be deposited on plant surfaces by rain and dust, but indirect effects of air pollution through the uptake from soil are also of great importance, because these soils are continually exposed to both wet and dry deposition of trace elements. Urban soils and roadside soils can receive large inputs of trace metals from different anthropogenic sources, but primarily from motor vehicle emissions (Jozic et al., 2008).

Depending on the pollutant and the properties of the soil, the pollutants will bond to the soil (accumulate) or percolate into the soil and end up in the groundwater. If the soil becomes saturated with pollutants, they may percolate into to deeper parts of the soil and, in the long to very long term, into the groundwater. The contamination is especially present close to the road and to a depth of approximately 40 cm. At a distance of approximately 10 m from the road, the quality of the soil is comparable to the background quality of the soil. In the top layer of the soil, and in the case of older roads the concentrations of single substances (Pb, Zn, PAH) usually exceed the target values, and in some cases even the intervention values (Van Bohem and Van de Laak, 2003).

In a study in Brisbane, Australia, it was concluded that total lead concentrations in roadside soils of tree major roads (28,000 – 121,000 vehicles per day) were between 400 to 900 folds higher than at the background site (20 km away from urban activities). Concentrations decreased with increasing distance and with increasing depth from which soil samples were taken. Concentrations at 5 m from the road in three studied locations were 15, 13 and 2.3 folds lower and at 25 m 44, 115 and 13 folds lower than those at 0 m distance, respectively. The largest concentrations were found near the road that had the highest number of vehicles and also no kerbing or channelling which allowed road runoff waters to wash the pollutants directly to roadside soil. The authors also found that the rapid reduction of total lead levels with the depth was in close relation with the rapid decrease of both organic carbon and calcium carbonate in soil (Al-Chalabi and Hawker, 2000).

Results of a case study performed at Burgdorf, Switzerland, show that between 36% and 65% of Cd, Cr, Cu, Pb and Zn are present in runoff and spray, and between 35% and 64% are dispersed diffusely in the environment (defined as drift). The runoff infiltrates into the vegetated road shoulder up to a distance of approximately 1 m from the road. The distribution of spray shows a maximum at 1 m and decreases steadily up to a distance of 5 m (Steiner et al., 2007).

In a study of Zn, Pb and Cd content in meadow plants and mosses along M3 motorway in Hungary, the authors also found a reduction of pollution with increased distance from the road (samples at 5, 10, 25, 50 and 100 m distance from the road were analyzed), and the greatest leap in concentrations was between 5 and 10 m distance (Naszradi et al., 2004).

Near Slovenian roads two studies regarding soil and plant contamination with heavy metals (Zn, Pb, Cd and Cr) were made in the process of environmental assessment for constructions of new highway. Soil and plant samples were taken at the distances of 2, 5, 10, 25 and 50 m from existing two-line motorway on the sections Vrba – Peračica and Naklo – Kranj east. Higher concentrations of HM in soil and plants were established for only some of the metals at some locations at the sampling locations distances from the road that didn't exceed 10 m. The reduction of concentrations with distance was established mainly for Pb (Sušin and Žnidaršic-Pongrac, 1999).

In a study of snow contamination near Ljubljana bypass, that was conducted in winter 2003/2004, the authors found that the average deposited amounts of heavy metals measured in snowpack after a 3 week dry period, decreased with increasing distance from the road edge. The highest amounts were measured in samples up to a distance of 10 m, at larger distances amounts were near the background values. The results for some of the studied contaminants are presented in the Table 2. Authors also found that the amounts of Pb were much lower than those measured in a study conducted in the year 1985, due to the phase-out of leaded gasoline (Švegl et al., 2004).

Table 2: *Average amounts of deposited heavy metals measured in snowpack at different distances from the edge of Ljubljana bypass (Švegl et al., 2004)*

Heavy metal	**Average amounts of metals per week [mg/(m^{2}week] at different distances**				
	3 m	**5 m**	**10 m**	**15 m**	**30 m**
Pb	15	13	5	3	2
Zn	40	43	12	4	3
Cd	23	22	3	1	0.9
Cu	0.43	0.32	0.09	0.02	0.01
Ni	14	13	4.5	0.9	0.8

Particles from road traffic are emitted in different fractions. In a study of emissions from two tunnels in Milwaukee (Lough at al., 2005) emission factors for road traffic in fine PM2.5 and coarse PM10 particulate matter were calculated. The most abundant elements emitted in PM10 in the tunnel were iron (Fe, average 4.5 +/- 1.7% of PM10 mass), calcium (Ca, 4.2 +/- 0.9%), silicon (Si, 3.9 +/- 0.8%), sodium (Na, 2.2 +/- 0.8%), magnesium (Mg, 1.1 +/-0.2%), sulphur (S, 0.84 +/- 0.26%), aluminium (Al, 0.69 +/-0.24%), and potassium (K, 0.41 +/-0.10%), respectively. The sum of these eight elements accounted for an average 94 +/-1% of the total PM10 emission of 42 measured elements. They were also present in PM2.5 in much lower amounts and were significantly different from zero in PM2.5 in only a few tests. These elements are major components of crustal materials and soil and are predominantly attributed to resuspension of road dust due to the large amounts present in PM10 (Lough et al., 2005). Significant emissions of barium (Ba) zinc (Zn), copper (Cu), antimony (Sb), and lead (Pb) were also detected in PM10 in all tests. Although the sum of these five elements did not exceed 1% of PM10 mass, they may be important for health effects and can provide some indications of the sources of particulate matter emissions, such as brake wear. The established emission rates ($\mu g\ km^{-1}\ veh^{-1}$) for Zn and Cu were around 30% higher in PM10 than in PM2.5 fraction (Lough et al., 2005). The analysis in the study of traffic generated particulate matter in Copenhagen (Wahlin et al., 2006) showed that particles created by bake abrasion have aerodynamic diameters in the inhalable size range around 2.8 µm. This particle diameter is common mass median for a long list of heavy metals that are apportioned to the brake sources: Cr, Fe, Cu, Zn, Zr, Mo, Sn, Sb, Ba and Pb. Other significant contributions of Al, Si, K, Ca, Ti, Mn, Fe, Zn and Sr, mostly in the coarse particle fraction, are apportioned to the road/tyres source (ibid).

2.2 Road traffic emission factors

Brake lining wear is a major source of metals like zinc, copper, barium, and lead (Westerlund et al., 2001, op. cit. Laschober, 2004), and motor oils are commonly considered as important sources of Zn (Cadle et al., 2001, op. cit. Laschober, 2004). Mechanical abrasion of the car body can also emit particles containing zinc, nickel and other alloy components of steel. Another potential source for metal emissions is the resuspension of soil and road dust (Laschober et al., 2004).

Average emission factors per vehicle per kilometre of some heavy metals that were established in a study of particulate emissions from tunnels in Austria (Laschober et al., 2004) are stated in Table 3.

Table 3: *Average emission factors in µg vehicle^{-1} km^{-1} (Laschober et al., 2004)*

	Mean (AV)	SD	Workday	SD	Weekend	SD
Zn	34.2	29.9	33.4	28.9	36.1	31.9
Cu	30.2	20.2	32.3	20.7	25.7	15.8
Pb	9.5	6.7	9.5	6.3	9.5	7.1
Ni	1.8	2.1	1.8	2.0	2.3	3.2
V	1.0	0.7	1.0	0.7	1.1	0.7

AV average; SD standard deviation

In the Table 4 total emissions of heavy metals per source from road traffic in Denmark in the year 2007 are presented (Winther and Slentø, 2010). It can be seen that nowadays brake wear is the most important source of heavy metals. The three elements that are emitted in the greatest amounts are Cu, Zn and Pb. Brake wear is responsible for 100% of Cu emissions, for 95% of Pb emissions and for 39% of Zn emissions, for which also tyre wear (33%) and engine oil (28%) are important sources.

Set in relation to a revised Danish emission budget, road transport (emission shares in brackets) is a key source for Cu (95%), Zn (54%) and Pb (53%) and of some relevance for Cr (15%). For the remaining emission components, road transport is only a minor source of emission.

Table 4: *Total heavy metal emissions (kg) per source category for Denmark in 2007 (modified from Winther and Slentø, 2010)*

	Fuel		Engine oil		Tyre wear		Brake wear		Road		Total
As	0.8	9.9%	0.0	0.0%	0.8	9.9%	6.5	80.2%	0.0	0,0%	8.1
Cd	0.5	1.0%	39.4	82.6%	2.5	5.2%	5.2	10.9%	0.1	0,2%	47.7
Cr	31.6	16.0%	65.0	33.0%	3.4	1.7%	74.5	37.8%	22.7	11,5%	197.2
Cu	21.7	0.0%	106.5	0.2%	14.8	0.0%	51624.6	99.7%	11.4	0,0%	51779.0
Hg	28.0	99.6%	0.0	0.0%	0.0	0.0%	0.0	0.0%	0.1	0,4%	28.1
Ni	4.5	2.8%	39.4	24.9%	24.2	15.3%	72.1	45.5%	18.2	11,5%	158.4
Pb	3.3	0.0%	173.5	2.5%	76.3	1.1%	6682.2	95.6%	53.8	0,8%	6989.1
Se	0.6	1.8%	0.0	0.0%	18.9	58.2%	13.0	40.0%	0.0	0,0%	32.5
Zn	101.0	0.4%	7876.2	27.6%	9491.7	33.2%	11000.9	38.5%	86.5	0,3%	28556.3

On the basis of Danish inventory values (Winther and Slentø, 2010), the emission factors, expressed as equivalent fuel content, were determined for the calculation of emissions in COPERT 4.0 v9.0 (a software program for the calculation of emissions from the road transport sector). Emission factors from the description prepared by Gkatzoflias et al. (2011) are stated in Table 5. Equivalent fuel content factors express the emissions of heavy metals as a function of fuel usage, where beside emissions that come directly from the combustion of fuel, also other sources of exhaust emissions are taken into account (i.e. lube oil and engine wear emissions). It is important to emphasize that there is a lack of reliable information regarding metal emission rates, therefore the determination of HM emissions from road vehicles is a procedure associated with large uncertainties.

Table 5: *Emission factors of heavy metals given as equivalent fuel content factors for gasoline, diesel and gas powered vehicles (modified from Gkatzoflias et al., 2011)*

Metal	Gasoline (ppb)	Diesel (ppb)	CNG and LPG (ppb)
Cd	10.8	8.7	10.6
Hg	8.7	5.3	0.0
Pb	33.2	52.1	31.6
As	0.3	0.1	0.0
Cr	15.9	30	9.3
Cu	41.8	21.2	37.3
Ni	13	8.8	10.7
Se	0.2	0.1	0.0
Zn	2164	1738	2130

LPG - Liquefied petroleum gas
CNG - Compressed natural gas

The assessment of emissions from different road traffic sources was made in a study of emissions by highway runoff waters (Legret and Pagotto, 2000). The authors stated that the amount of matter from tyre wear is 68 mg/veh./km, and twice the quantity for heavy lorries; the amount of brake wear approximately 20 mg/veh./km for cars, 29 mg/veh./km for light good vehicles and 47 mg/veh./km for heavy lorries. Lead originated mainly from the combustion of leaded fuel. The total estimated loads of heavy metal emissions for the year 1997-1998 on a highway in France with 24,000 vehicles of daily traffic (7% of heavy lorries) are stated in Table 6.

Table 6: *The total estimated loads of heavy metals in 1997-1998 (Legret and Pagotto, 2000)*

Metal	Estimated yearly load
Cd	2
Cr	24
Cu	16000
Ni	99
Pb	7700
Zn	7300

There is a general agreement in the literature, that 75% of Pb contained in gasoline is emitted into the atmosphere, while 25% remains in the engine, as Pb adhering to engine-exhaust surfaces (15%) and Pb remaining in the lubrication oil (10%) (Mielke et al., 2010; Legret and Pagotto, 2000).

2.3 Selected heavy metals, their sources and their uptake characteristics

For the purpose of this study heavy metals that could have road traffic related origin regarding the results in the available literature were selected. Selected heavy metals were lead (Pb), cadmium (Cd), zinc (Zn), chromium (Cr) and nickel (Ni).

2.3.1 Lead

Lead is a naturally occurring bluish-gray metal found in small amounts in the earth's crust. Lead can be found in all parts of our environment. Much of it comes from human activities including burning fossil fuels, mining, and manufacturing. It has many different uses. It is used in antiknock agents, in the production of batteries, ammunition, metal products (solder and pipes), and devices to shield X-rays, glassware and ceramics, plastics, in alloys, cable sheathings, pipes or tubing. Because of health concerns, lead from paints and ceramic products, caulking, and pipe solder has been dramatically reduced in recent years. On the CERCLA Priority List of Hazardous Substances it is ranked as the second most hazardous substance (Agency for Toxic Substances and Disease Registry, Priority list 2007).

In the US, lead was introduced as an anti-knock additive after the ban of benzene in 1950s, which previously made up several percent of the fuel. Ironically, benzene was banned due to concerns about its toxicity (Mielke et al., 2010).

Some uses through which Pb can be introduced to the environment:

In 1991 the main source for Pb emissions in Slovenia was road transport with a share of around 92.8%. Other important sources were production processes with a share of 3.1%, and other transport with a share of 3.7% (Rode et al., 2010). The emissions of lead in Slovenia were dramatically reduced in the year 1995, because the new regulation regarding the quality of liquid fuels came into force. In Slovenia, leaded fuel was banned in the year 2001 (MOP ARSO 2002). The ban in 2001 resulted in additional reduction of lead emissions. Total Pb emissions in Slovenia were reduced from 312 tons/year in 1993 to around 14 tons/year in 2002 (Table 7; Rode et al., 2010).

The total amount of emitted lead in Slovenia had been reduced from 347 t/year in 1990 to 15 t/year in 2008, which represents a reduction of more than 95% (Table 7).

In 2008, the main sources for Pb emissions in Slovenia were production processes with a share of 77.5%, road transport with a share of 20.0% and combustion in energy 1.5% (Rode et al., 2010).

In the Table 8 levels of allowed Pb content in gasoline for individual periods are stated. Leaded gasoline was phased out in some other countries in the following years: Austria 1993; Germany 1996; Denmark 1995; Slovakia 1994; Japan 1980; Canada 1993; Sweden 1995; United States 1996, respectively (OECD Phasing Lead…, 1999). In Figure 2 the total emissions of Pb for road transport in the years 1980 – 2008 are presented. The values were calculated using COPERT III methodology and are published in the Informative inventory report 2010 for Slovenia - Submission under the UNECE Convention on Long-range Transboundary Air Pollution (Rode et al., 2010).

Table 7: *National total emissions and emissions trend for Pb in Slovenia (1990-2008) (modified from Rode et al., 2010)*

Year	Emissions of Pb
1990	347
1991	301
1992	295
1993	312
1994	311
1995	198
1996	83
1997	72
1998	57
1999	49
2000	42
2001	24
2002	14
2003	13
2004	14
2005	13
2006	14
2007	14
2008	15
Reduction trend	95.69%

__Table 8:__ Levels of lead content in gasoline (modified from Rode et al., 2010)

Fuel	Period	Lead [g/L]
Gasoline Leaded	1980-1994	0.6
	1995	0.4
	1996-2001	0.15
Gasoline Unleaded	1986-1994	0.026
	1995-2001	0.013
	2002-2008	0.005

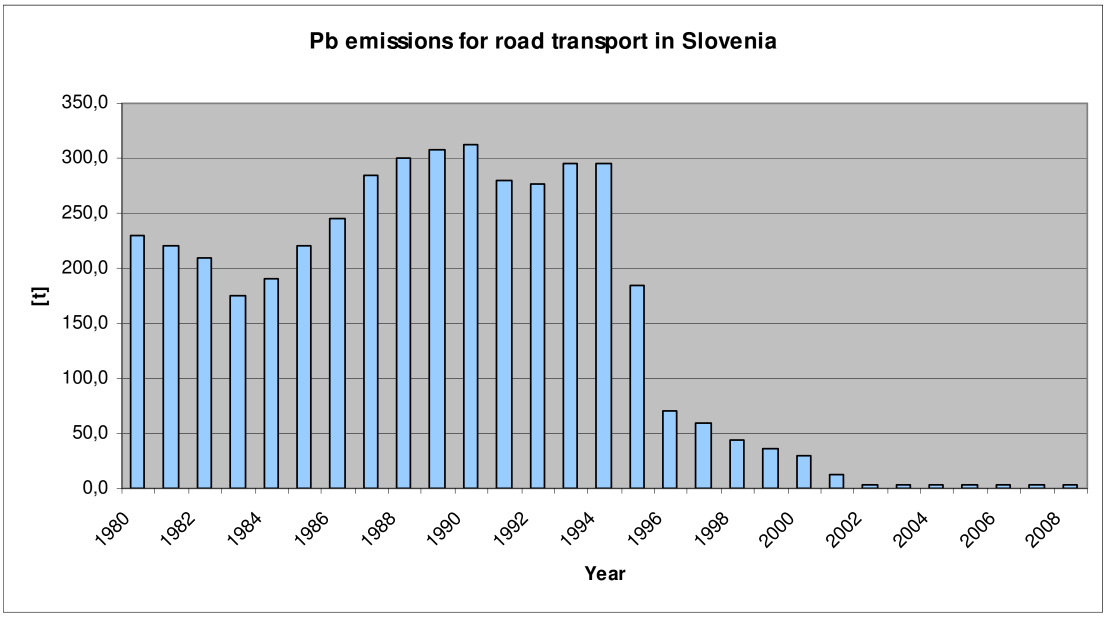

__Figure 2:__ Pb emissions (t) for road transport in years 1980−2008 (modified from Rode et al., 2010)

Plant uptake of Pb is probably passive. The translocation from roots to other plant parts is low. Aerial deposition and foliar uptake may contribute significantly to leafy conditions. Uptake is promoted by anaerobic conditions (e.g. by flooding), low pH, low organic levels, low phosphate concentrations. In soils, this metal is largely immobile with a long half-life time due to adsorption to soil clays, phosphates, sulphates, carbonates, hydroxides and organic matter. High soil concentrations may inhibit microbial processes and reduce decomposition processes (Strait and Stumm, 1993).

Although its emissions had been drastically reduced, lead is regarding data from Winther and Slentø (2010) technical report of heavy metal emission from road traffic, still an important metal associated mainly with brake wear. As regarding the total national emitted quantities of heavy metals in Denmark, it is on the third place after Zn and Cu (ibid). The main vehicle exhaust sources of Pb nowadays are main bearings and rod bearings, bushings and lead solder (Gkatzoflias et al., 2011).

Even though Pb fuel has been phased out, exterior soils still represent an enormous reservoir of Pb (Mielke et al., 2010), and resuspension of urban soil is nowadays still an important source of Pb (Lough et al., 2005; Mielke at al., 2010; Aberg et al., 1999). Using Rhododendron leaves as bioindicator Suzuki et al. (2009) suggested that yellow paint is the main source of roadside lead pollution, and based on the isotopic ratio of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, that lead-containing products from automobiles, such as wheel balance weights, might contribute to traffic related lead pollution.

Lead is emitted to the atmosphere on fine particles which can be transported within air masses on very long distances, e.g. from regions in mid latitudes to the Arctic and Antarctica (Aberg et al., 1999).

Regarding the total quantities of HM from road traffic assessed in Denmark (Winther and Slentø, 2010) Pb is nowadays besides Cu and Zn the third most abundant HM associated with road traffic, contributing to 7.9% of the total emitted quantities of HM from road traffic.

2.3.2 Cadmium

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide). On the CERCLA Priority List of Hazardous Substances it is ranked as the seventh most hazardous substance (Agency for Toxic Substances and Disease Registry, Priority list 2007).

All soils and rocks, including coal and mineral fertilizers, contain some cadmium. Most cadmium used in the United States is extracted during the production of other metals like zinc, lead, and copper. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings, and plastics (Siegel, 2002).

<u>Some uses through which Cd can be introduced to the environment:</u>
Sources of contamination are Ni/Cd batteries, pigments, anti-corrosive coatings of metals, plastic stabilizers, alloys, coal combustion, neutron absorber in nuclear reactors (Siegel, 2002).
Plant uptake can occur passively as well as metabolically. Within plants, it is very mobile. In the soil, it occurs in the divalent state and forms complex ions and organic chelates. It is easily absorbed by clay and organic matter. Its uptake is promoted by pH levels below 6 and restrained by pH values above 7. Zn, Cu and Se seem to reduce Cd uptake or toxicity. It is easily transported to different plants parts; highest concentrations are found in the roots and in parts of the leaves (Strait and Stumm, 1993).

The emissions of Cd in Slovenia have been decreasing. From 1990 – 2008, the total emitted quantities had been reduced from 0.84 t/year to 0.48 t/year (Table 9). Even though the reduction is substantial, it is not as drastic as in the case of Pb. Also the total amount of emitted Cd is much smaller than the emitted amount of Pb.

Only a small proportion (1-4%) of emitted Cd originates from the road traffic. Assessed emissions of Cd from road traffic are shown in Figure 3.

Table 9: *National total emissions and emissions trend for Cd in Slovenia (1990-2008) (modified from Rode et al., 2010)*

Year	Emissions of Cd
1990	0.842
1991	0.722
1992	0.682
1993	0.679
1994	0.681
1995	0.685
1996	0.675
1997	0.598
1998	0.577
1999	0.550
2000	0.540
2001	0.505
2002	0.478
2003	0.454
2004	0.437
2005	0.447
2006	0.462
2007	0.449
2008	0.478
Reduction trend	43.22%

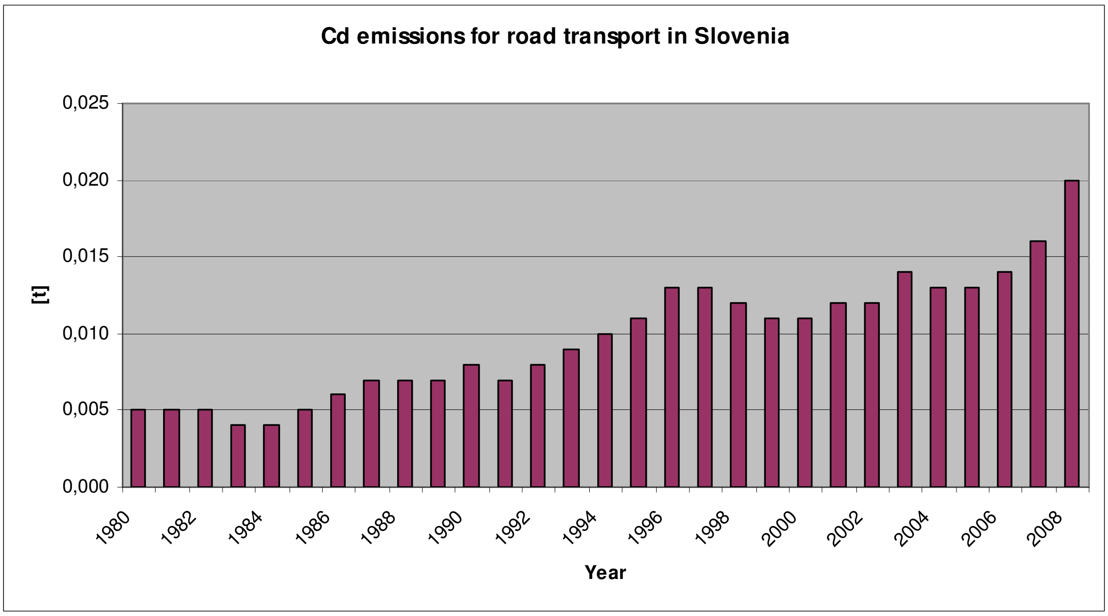

Figure 3: *Cd emissions (t) for road transport in years 1980−2008 (modified from Rode et al., 2010)*

Regarding the total quantities of HM from road traffic assessed in Denmark (Winther and Slentø, 2010), Cd contributes 0.05% of the total emitted quantities of HM, and its main source is engine oil.

2.3.3 Zinc

Zinc is one of the most common elements in the earth's crust. It is found in air, soil, and water, and is present in all foods. Pure zinc is a bluish-white shiny metal. On the CERCLA Priority List of Hazardous Substances it is ranked as the 74th most hazardous substance. Zinc has many commercial uses as coatings to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass, and bronze. A zinc and copper alloy is used to make pennies in the United States (Agency for Toxic Substances and Disease Registry, Priority list 2007).

Some uses through which Zn can be introduced to the environment:
Zinc alloys (bronze, brass), anti-corrosion coating, batteries, cans, PVC stabilizers, precipitating Au from cyanide solution, in medicines and chemicals, rubber industry, paints, soldering and welding fluxes (Siegel, 2002)

Plant uptake is readily as hydrated Zn^{2+}, organic chelates and also adsorbed on Fe and Mn oxides. It is rather soluble in soil solutions and very mobile in acid soils. Uptake is promoted by low soil pH, restrained by high soil pH, high clay content, high phosphate concentration, and high cation exchange capacity. It is easily allocated to different plant parts (Strait and Stumm, 1993).

Regarding the total quantities of HM from road traffic assessed in Denmark (Winther and Slentø, 2010) Zn is nowadays besides Cu the most abundant HM associated with road traffic contributing to 32.5% of the total emitted quantities. Its main sources are tyre wear, engine oil and brake wear, respectively. However Gkatzoflias et al. (2011) stated that the main vehicle exhaust source of Zn are anti wear lube oil additives.

2.3.4 Chromium

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are chromium(0), chromium(III), and chromium(VI). No taste or odour is associated with chromium compounds. On the CERCLA Priority List of Hazardous Substances it is ranked as the 77-th most hazardous substance (Agency for Toxic Substances and Disease Registry, Priority list 2007).

<u>Some uses through which Cr can be introduced to the environment:</u>
Manufacturing of ferro – alloys (special steels), plating operations, pigments, textiles and leather tanning, passivate the corrosion of cooling circuits, wood treatment, audio, video and data storage (Siegel, 2002).

Plant uptake occurs easiest as hexavalent chromate (CrO_4^{2-}), which however is rapidly reduced to Cr^{3+} in all soils. This latter is usually precipitated in soils; it is mobile only in very acid environments. The trivalent form is absorbed little by the roots. The translocation of chromium from roots to other plant parts is low (Strait and Stumm, 1993).

Regarding the assessment of HM emitted from road traffic Denmark (Winther and Slentø, 2010), emissions of Cr nowadays contribute to 0.2% of the total emitted quantities of HM. Its main sources are brake wear and engine oil, in a smaller proportion also fuel and road abrasion. Suzuki et al. (2009) suggested that asphalt pavement dust contributes to traffic related Cr pollution. Moreover, Gkatzoflias et al. (2011) stated that the main vehicle exhaust sources of Cr are engine wear, manifold wear, rings, (cylinder) liners, exhaust valves, shaft plating, and stainless steel alloy.

2.3.5 Nickel

Nickel is a very abundant natural element. Pure nickel is a hard, silvery-white metal. Nickel can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. These alloys are used to make coins, jewellery, and items such as valves and heat exchangers. Most nickel is used to make stainless steel. On the CERCLA Priority List of Hazardous Substances it is ranked as the 53rd most hazardous substance (Agency for Toxic Substances and Disease Registry, Priority list 2007).

Some uses through which Ni can be introduced to the environment:

As an alloy in the steel industry, electroplating, Ni/Cd batteries, arc-welding rods, pigments for paints and ceramics, surgical and dental prostheses, moulds for ceramic and glass containers, computer components, catalysts (Siegel, 2002).

Plant uptake in different soluble forms (possibly soluble organic chelates and possibly also adsorbed on oxides), possibly in part active uptake. Uptake is promoted by pH below 6, restrained by lime, iron and phosphate. In the soil, it can co-precipitate with iron and manganese. It is readily adsorbed by organic matter. A moderate translocation from roots to other plant parts is found (Strait and Stumm 1993).

Regarding the assessment of HM emitted from road traffic in Denmark (Winther and Slentø, 2010), emissions of Ni nowadays contribute to 0.18% of the total emitted quantities of HM. The most important source is brake wear, followed by engine oil. Tyre wear and road abrasion contribute 15% and 11% of total Ni emissions, respectively. Gkatzoflias et al. (2011) stated that the main vehicle exhaust sources of Ni are manifold wear, valve plating, steel alloy from crankshaft and camshaft.

2.4 Biomonitoring and bioindication

(The contents of this chapter is mostly summarized from Wittig (1993), unless stated otherwise)

Biomonitoring, in general sense, may be defined as the use of bio-organisms or their parts to obtain (quantitative) information on certain characteristics of the biosphere (Wolterbeek, 2002). Biomonitoring and bioindication are terms that are often used as synonyms, but on the other hand the difference is described by some authors: Bioindicator »gives information« on the quality of its environment while a biomonitor quantifies the quality of its environment. Bioindication is sometimes used for qualitative and/or »freeze-frame« recording, where biomonitoring is used for quantitative and/or continuous observation. For example, the difference between bioindication and biomonitoring is the same as between a photograph and a film (Wittig, 1993). Bioaccumulation is the ability of living organisms to accumulate elements in concentrations higher than the median for species in unpolluted environment (Majestrik and Lepsova, 1993).

Within plants we can differentiate between (Madejon et al., 2004):

1. Excluders, that have a low uptake of trace elements, by active exclusion in the roots, even at high external concentrations in the soil solution
2. Accumulators, that are able to tolerate high concentrations of trace elements in their tissues, and this accumulation can be produced even at low external concentrations in the soil solution.
3. Indicators that have a relatively constant root uptake over a wide gradient of trace elements in the soil. As a consequence they show a linear relationship between the concentrations in the plant tissues and in the soil.

A bioindicator is an organism which reacts to specific environmental dynamics with observable and measurable changes. By observing and measuring changes a conclusion as to the kind of pollution (e.g. heavy metal), its source and possibly its intensity (given as the relationship between degree of pollution and observable measurable changes of the bioindicator) can be drawn. If the method is highly standardized, the bioindicator can be used for biomonitoring, i.e. for the quantification of the pollution as the function of time and origin. Biomonitoring can therefore be used to quantify the quality of our environment (Markert, 1993).

We can differentiate between sensitive bioindicators and accumulative bioindicators, but this classification should be used with care, because a sensitive bioindicator can have accumulating properties for the substances monitored and vice versa (Markert, 1993).

Passive biomonitoring is the method when already existing organisms in the investigation area are used for observation and measuring, in contrast with active biomonitoring that is based on organisms which naturally do not exist in the area to be investigated. For active biomonitoring organisms have to be transferred into the test area (e.g. from the laboratory) and are exposed to the pollution for a defined period of time (Markert B., 1993).

A quantification of the pollution (biomonitoring) can be obtained by (Wittig, 1993):

- comparing different heavily polluted areas with each other,
- investigating longer time series (historical monitoring),
- comparing data with given »normal« values (reference values),
- comparing determinations in air dust or precipitation with values evaluated by using the biomonitor.

Some demands must be fulfilled by an acceptable bioindicator as follows (Wittig, 1993):

- present in large amounts,
- widely distributed over the globe,
- easy to identify and to sample,
- analyzable according to the standard analytical methods presently available.

The main advantages of biomonitoring in relation to instrumental monitoring are:

- Especially in cases where many measurements in different locations are to be undertaken, the bioindicators are more practical

- Living organisms take into account the actual response of organisms (or population) to environmental variables, including other pollutants with which interactions may occur.

Advantages of biomonitoring:

- interception included
- retrospective
- low cost
- great availability
- no servicing
- independent of power source
- not attracting vandalism
- biological relevance
- synergistic (antagonistic) effects included.

Advantages of instrumental monitoring are in the fields of: response independent of other factors, standardization, reproducibility, exact readings, specific reaction, and differentiation between airborne and soil borne substances.

Because contaminants are often mutually correlated, due to their origin from the same source, in some cases biomonitoring of a single contaminant can provide information on the degree and extent of the general soil pollution (Madejon et al., 2006).

The best indicator plants for service as biomonitors should incorporate a metal in proportion, or nearly so, to its concentration in soils and soil waters and have a sufficient geographic distribution to allow good density sampling. Some plants can over accumulate or can discriminate against uptake of some metals that could be harmful to them (Siegel, 2002).

One of the main advantages of bioindication is the ability of retrospective analyses (Poličnik et al., 2007). Because of the lack of data from the past it is almost impossible to assess the past trends of pollution with only present imission measurements. The knowledge on historical changes (trends) in environmental pollution is necessary for monitoring and evaluation of improvement measures that were conducted for reducing influence of different chemical agents on biota (e.g. introduction of unleaded fuel). From this respect, annual tree-rings are a very useful tool for retrospective assessment of trends and changes in environmental pollution and also for determination of the most important pollution sources in a given time period (Poličnik et al., 2007).

Metal content in plants is influenced by several factors such as pollution intensity, climatic and environmental conditions, soil properties, leaf size and orientation, surface structure, age of needles, and the plants genotype ability to accumulate and dislocate metals (Jozic et al., 2008). Areas with plant cover accumulate heavy metals four times more than bare ones, 90%+ of the metals are retained by plants and only 10% go to the lower horizons in the ruderal ecosystems (Ozturk, 1993).

Numerous reports of the use of different plant species in biomonitoring heavy metals caused by atmospheric deposition have been published. But the use of the most suitable plant species depends on the task to be solved, on its capacity to accumulate metal pollutants and also on its distribution in the area to be investigated (Jozic et al., 2008).

Historical change in heavy metal pollution can be recorded by determination of metal contents in several sets of samples/archives, such as: (i) lake sediments; (ii) peat bogs; (iii) bivalve shells; (iv) human teeth; (v) deer antlers; and (vi) tree-rings, i.e. annual increments of wood, with incorporated bark pockets (Poličnik et al., 2011). However, most of these archives have some disadvantages, such as dispersal and translocation of heavy metals between adjoining layers, difficulties with collecting samples, secondary contamination during natural/artificial preservation or correct dating of samples (Pokorny et al., 2009).

2.5 Dendrochemistry

In climates characterized by distinct seasons of growth and dormancy, trees develop annual growth rings in the wood. On cross-sections of trunks the rings are easy to recognize in many species. Such rings are the results of rhythmic activity of the cambium, which is the meristem that forms wood tissue. While the cambium is active between spring and late summer, a mantle of new wood is formed on the outside of the whole stem. In autumn and winter, during the dormant season, the cambium is inactive until next spring. These rhythmic fluctuations in cell division activity cause the development of growth rings (Hagemeyer, 1993).

The method of biomonitoring of trace metal pollution by chemical analysis of tree-rings was termed dendroanalysis for the first time in the work published by Gilboy 1976 and Taut in 1978 (Hagemeyer, 1993).

In temperate regions trees usually produce one growth ring every year. It is thus possible to accurately date the rings. Trace metals are transported through the water conducting tissue of the rings and accumulated in the wood. The growth rings of different age are collected and their trace elements content is analyzed in order to get a chronological record of the element composition of the trees environment. It is assumed that when annual rings lose function, they isolate a relative record of the sap chemistry and the elements uptaken from the environment are deposited only in currently growing parts of the tree (Nabais et al., 1999).

The basic procedure of dendrochemistry is as follows (Hagemeyer, 1993):

1. Selection of appropriate trees in places where environmental pollution is investigated.
2. Sampling of wood with the help of increment borer, usually at breast height in horizontal direction.
3. The core is then divided into sections of one or several annual increments.
4. Analysis of increments.
5. Analytical results are usually plotted along time axis with the age of the wood samples.

The basic assumptions of the method are (Hagemeyer, 1993):

1. A distinct and constant relation must exist between the element concentration in the environment and the amount incorporated in wood tissue.
2. Incorporation of the investigated element into certain annual rings must occur only within a limited period of time.
3. It should be known to which rings the element is transported, either only to the outermost and youngest ring or to a number of older rings, as well.
4. After incorporation of the element in annual ring no subsequent remobilization and retranslocation should occur.
5. The radial distribution pattern of an element in the trunk wood should be stable over a long period of time (temporal stability).
6. Radial distribution patterns of a certain element should be similar in different parts of the same tree (spatial stability).

Within a plant, elemental uptake from the environment may occur via the roots, foliage or stem, with subsequent transport through the phloem and into the xylem (Watt et al., 2007).

2.5.1 Uptake of heavy metals by the roots

The uptake of water in plants is always from the compartments of high water potential (as in the soil and the root) to the compartments of low water potential (as in leaves and air). In bulk transport phenomena metal and non-metal ions may be transported within the water system. Metal uptake depends on the uptake capacity and the growth characteristics of the root system (when the roots don't have the capacity to grow, they would rapidly deplete the soil adjacent to their surface) (Strait and Stumm, 1993).

Soil is the main source of trace elements for plants both as micronutrients and pollutants. Some exceptions are in situations of heavy atmospheric deposition of pollutants or from flooding by contaminated waters. Soil conditions play a crucial role in trace element behaviour. It can be generalized that in well-aerated (oxidizing) acid soils, several trace metals, especially Cd and Zn, are easily mobile and available to plants, while in poorly aerated (reducing) neutral or alkaline soils, metals are substantially less available (Kabata-Pendias, 2004).

Water and ions taken up by the root are transported by the xylem system to different parts of the shoot. This transport does not consist of living cells, but allows free movement of the solvent and the solute. In contrast, the phloem is a living tissue (of highly modified cells, however), that translocates the products of photosynthesis from assimilating leaves to areas of growth and storage, including the root system, but also redistributes plant growth regulators and various other compounds thought the plant. In the xylem, heavy metals will usually only be transported, if special chelates are formed, e.g., by citrate (Strait and Stumm, 1993).

It currently seems that uptake by the roots only occurs in the free ionic form for the majority of metals and uptake mechanisms, such as active or passive transport processes (Strait and Stumm, 1993). Uptake by the roots seems to be the most important uptake path for heavy metals (Watt et al., 2007).

Physical states of contaminants in soil and sediments that affect potentially toxic metals chemical reactivity, mobility and bioavailability are (Siegel, 2002):

- particulate pollutant (mixed with particles of soil),
- liquid film (on the particles of soil),
- adsorbed contaminant (on the particles of soil),
- absorbed contaminant (in the particles of soil),
- contaminant as liquid phase in pores (of particles of soil),
- contaminant as a solid phase in pores (of particles of soil).

Trees are not passive monitors of their environment, and the uptake and immobilization of metals is unique to individual trees of the same species and depends on local attributes of the soil, hydrology and canopy structure as well as physical characteristics of the individual tree (Watmough and Hutchinson, 2003).

In regard of dendrochemical studies, three major types of wood may be distinguished (Hagemeyer, 1993):

- conifer wood with a comparatively simple structure,

- ring porous wood,
- diffuse porous wood with many transitional types.

In coniferous wood the water movement passes through several annual rings in the outer part of the stem. This means that incoming elements from the roots, will reach several rings at the same time, thus, rendering a year-to year chronology almost impossible. Similar pattern of water movement is found in diffuse porous wood of angiosperms. On the other hand, in ring porous wood of e.g. *Quercus, Ulmus* or *Faxinus*, water movement is largely confined to the outermost and youngest annual ring (Hagemeyer, 1993). But the findings of some more recent studies state the opposite and recommend the usage of some conifers (i.e. Scots pine) and also diffuse porous broadleaf species (silver birch, trembling poplar) as the most suitable tree species for historical monitoring (Poličnik et al., 2007). In literature, pine trees are one of the most commonly used tree species for this purpose (Butkus and Baltrenaite, 2007; Watmough and Hutchinson, 2002; Watmough and Hutchinson, 1996; Padilla and Anderson, 2002; Lageard et al., 2008; Garbe-Schonberg et al., 1997; Medeiros et al., 2008; Bindler et al., 2004). Apart from different pine species diffuse porous broadleaf species (sycamore, birch, poplar) are often successfully used in biomonitoring studies (Patrick and Farmer, 2006; Butkus and Baltrenaite, 2007; Garbe-Schonberg et al., 1997; Madejon et al., 2004).

2.5.2 Uptake of heavy metals trough the bark

There are, still, other pathways for mineral elements to enter a tree besides the roots. Laboratory experiments with Pb isotopes demonstrated a penetration of this element through the bark of trees and a subsequent translocation into the wood seems possible. Moreover, uptake by leaves may occur and the elements can eventually reach the stem wood trough phloem transport. Uptake along different pathways may result in radial distribution patterns which are directly related to the environmental availability of the minerals. The time passing between emissions of the element into the environment and its uptake by the tree will differ for the described pathways. Whereas direct uptake into the leaves may start almost instantly, a much longer time is required until the metal cations have passed through a soil system to reach the roots (Strait and Stumm, 1993).

Uptake trough the bark is suggested in many studies (Watmough and Hutchinson, 2002; Lageard et al., 2008; Garbe-Schonberg et al., 1997; Suzuki et al., 2009; Watmough and Hutchinson, 1999).

2.5.3 The atmospheric – foliar uptake path of heavy metals

Uptake of elements from the environment is possible also via the foliar surface. Passage trough the cuticle is possible only by diffusion. Some herbicides and even nutrients are applied on leaf surfaces, and can enter the plant by this path. Foliar deposition of lead has been reported to occur to a great extent due to anthropogenic aerosols, but the extent and the mechanism of uptake by the plant leaves is a matter of debate (Strait and Stumm, 1993).

Uptake trough the leaves or needles is suggested in studies conducted by Lageard et al. (2008) and Madejon et al. (2004).

2.5.4 Can dendrochemistry provide a record of environmental pollution?

Monitoring of trace metal pollution using tree-rings has been controversial for several decades. Several studies have shown that dendrochemistry shows a good record of past pollution but several studies also state the opposite. The reasons for this polarization steam from our general inability to address several fundamental questions. What are the contaminant pathways of metal within the tree-soil-groundwater-atmosphere system? Is the uptake of nonessential metals proportional to ambient levels in the immediate environment of the tree? Once taken up into the stem wood, do the metals stay where they first interact with the xylem tissues or are they mobile? And finally, how long are these complex biogeochemical signals preserved within the stem wood? (Brabander et al., 1999).

In a study undertaken by Wickern and Breckle (1983) (op cit. Hagemeyer, 1993) radial distribution patterns of Pb in oak trees (*Quercus robur*) along a highway were compared with the number of cars. In the period from 1955 to 1972 a steady increase in Pb concentrations correlated well with estimated Pb emissions. After that time Pb content of gasoline was reduced by law in Germany. This caused a drop of concentrations in xylem of oak trees. If allowance was made for a 2-3 year delay in Pb transport from the source of emission into the wood, a significant correlation between Pb emissions and contents in xylem rings of oak was found (oak is a ring-porous, heartwood forming tree).

Also a study conducted by Ragsdale and Berish (1988) (op cit. Hagemeyer, 1993) in Georgia USA founds a general increase in Pb concentrations in tree-rings of hickory trees (*Carya sp*.) near a highway, followed by a significant decline in rings formed after the introduction of unleaded gasoline. The same pattern was found also in a tree from an urban park area, but the concentrations of Pb near the road were much higher. The authors found that trees respond surprisingly fast to changes in ambient Pb levels and assumed that this may indicate that the Pb uptake occurred, at least, partly through the leaves.

Studying tree-rings of sycamore trees near a metal refinery at Prescot north-west England Watmough and Hutchinson (1996) found, that the Pb contents in tree-rings were much higher at the reference location (Croxteth) even though Pb levels in soil and bark samples were much higher at Prescot, but at both locations they found a similar steady decline in Pb contents after 1970. The probable cause for this trend was stated as the reduction in coal usage and the increase in the use of unleaded petrol. The higher contents at the reference location were interpreted as due to the Pb deposition at Croxteth that is typical for urban UK, also due to less competition with other aerially deposited cations. Following reduced emissions at Prescot, the Pb in xylem increased relative to levels at Croxteth, which the authors attributed to the possible Pb mobilization in soil. Changes in Cd contents in tree-rings accurately reflected changes in Cd deposition, implying very little lateral movement of Cd between rings. For Cu, Fe and Ni the trend of increase toward the bark was established. The conclusion was that sycamore tree-rings accurately reflect changes in atmospheric metal deposition, although it is unclear whether metal contents in xylem originate directly from atmospheric uptake or via uptake from soil or both.

In a study of trees at a park close to the centre of a large town Watmough and Hutchinson (2002) found, that the peak levels in Scots pine coincided with other chemical changes in wood that are associated with heartwood formation, and concluded that peaks in Pb contents are most likely due to the Pb accumulation in heartwood, possibly by radial translocation of Pb in ray parenchyma cells. The authors stated similar findings of Pb accumulation in heartwood for English oak. In sycamore (a diffuse porous wood) tree-rings the authors found a sharp decrease after the year 1985 which coincides with the introduction of unleaded gasoline and reduction of Pb content in leaded gasoline in 1986, and stated that such sharp decrease can not be due to the decrease of Pb in surface soil (the path from surface soil via the roots should be the main source of Pb in wood). The authors also suggested the possibility, that the changes in wood Pb reflect changes in Pb deposition due to direct uptake of atmospherically deposited Pb. The authors found that the changes in the isotopic ratio of $^{206}Pb/^{207}Pb$ are similar to those found in peat, sediment and aerosol samples from other studies, but the magnitude of changes is much lower, so they estimated that only 20% of the total Pb in sycamore is derived from gasoline. But as a more likely explanation of the decreasing contents after 1985, the authors stated that diffuse porous wood could accumulate Pb over a number of years, (a 10 years old ring would accumulate Pb for 10 years), and such uptake pattern would result in lower Pb levels in the outer tree-rings. The peak mean (n=8) measured contents were about 5 mg/kg.

Patrick and Farmer (2006) analyzed tree-rings from seven sycamore trees near Loch Lomond, Scotland an area with no point sources of Pb emissions, and compared the $^{206}Pb/^{207}Pb$ isotopic ratios with those from lake sediment. Two of the seven sycamores showed the same pattern as the lake sediment, two showed some similarity but only in parts of their profiles, the other trees showed relatively constant ratios over the entire time period or exhibited the opposite trend. The range of Pb contents was from 0.32 mg/kg - 12.3 mg/kg, mean 1.38-6.64 mg/kg. Tree cores were also taken from two areas with former lead mining and smelting activities (Wanlockhead and Tyndrum). The tree cores from Wanlockhead generally showed elevated Pb levels that decreased with time and distance from the lead mine, and the characteristic Pb isotopic ratio was established in trees closer to the mine. The range of Pb contents for the trees that were 3 or less km from the mine works was 2.2-244 mg/kg, mean contents 24.6 – 107 mg/kg. The sycamores from Tyndrum also showed elevated Pb levels that decreased with time. The authors concluded that sycamore tree-rings are not suitable for obtaining historical records of Pb deposition in areas with no large local lead input, but can reveal some information about the temporal and spatial influence of point source emitters.

When comparing the two studies (Watmough and Hutchinson, 2002 and Patrick and Farmer, 2006) we can see that in the 6 of the 7 sycamores from Loch Lomond the trend of decreasing levels can be seen between the last three (3) 5-year samples, so the conclusion that Pb is accumulated in tree-rings over a number of years, could be correct.

In a study of tree-rings of a more than 350 years old ponderosa pine (*Pinus ponderosa*) the authors found that the most regional, local, small scale environmental changes did not seem to impact the elemental concentrations within the tree. Arsenic, used as an insecticide in a local apple orchards did not occur in the tree above detection limits, also local road building and increase in petroleum combustion/automobiles in the region did not cause Pb to occur in the tree above detection limits, ore smelters in western Washington with peak emissions in the early/mid 1900s did not increase cadmium, lead, zinc, copper contents in wood (Padilla K.L, Anderson K.A, 2002).

Measuring historical changes in sugar maple (Watmough et al., 1998), the authors found that changes in Pb contents on a site near a highway increased sharply with the construction of a new highway in 1940 and increased vehicle usage, the decline during the 1960's and 1970's occurred prior to the recorded decline in ambient Pb concentrations in the atmosphere of Ontario, which began around 1972. The authors concluded that the phase-out of Pb gasoline may contribute to the latter part of the decline in Pb levels, although the decline may be initiated as a result of road alternations or some other unknown factors. It was also found that Cr was slightly higher in wood formed between 1940 and 1960, originating probably from vehicle emissions as it coincides with the peaking Pb concentrations, or from a steel works which operates in the area. The authors stated that highways appear to be the main source of trace metals into the chosen woodlands, although Pb in soil and tree-rings does appear to be a more general marker of urbanization.

In Japan, Bellis et al. (2002) analyzed tree-rings and bark pockets of 250-year-old *Quercus crispula* in Nikko National Park and found that bark pockets were more effective than annual rings for recording historical change in airborne Pb pollution. The Pb levels in tree-rings ranged from 0.01 to 0.1 mg/kg, and there was no significant change in concentration with time.

Study of tree-rings as an archive of volcanic cation deposition (Watt et al., 2007) found that core sections taken from two diametrically opposite halves of the same tree show very little correlation and hence the results depend on the orientation of the sampled core.

In study of arsenic (As) in tree-rings at a highly contaminated site, Cheng et al. (2007) found that there are systematically higher As concentrations in narrow rings produced during low-growth years and that the rings with higher concentrations also contained more As overall, and that the pattern shows that As is probably transported in all sapwood rings, rather than in the cambium only. Also Fischer et al. (2002) in a study of lead and calcium in American beech found that Pb contents correlated negatively with ring width. The rise of Pb levels in 1920 corresponded well with the introduction of leaded fuel in 1923. The authors stated that dendrochemistry appears to be an effective tool for determining temporal trends within environmental samples.

There is a general agreement that element mobility within a tree is different for different tree species and also different for different elements. Also availability of some elements is different then others. Cd and Zn are rather mobile in soils and thus readily available to the plants; on the other hand, Cu, As and Pb tend to accumulate in the roots and are scarcely translocated into aboveground organs (Madejon et al., 2004). The pool of available elements is composed of those ions present in the soil solution, as well as those that are readily solubilised and are therefore able to move into the plant.

In a study of red spruce tree-rings, Watmough and Hutchinson (1996) found that large reductions in Cu and Cd deposition were accompanied with a steep decline in Cd contents in the outer rings of trees close to the metal refinery at Prescot, northwest England.

Using tree-rings of *Pinus halepensis* (Pantera et al., 2007) it was found that radial distribution of concentrations in annual rings provides adequate information that in most of the cases can be related to the history of the tree. Indeed Medeiros et al. (2008) found that the quantity of Pb detected in the *Araucaria columnaris* indicates its presence in a 30-year growth period.

It can be resumed that not all tree species are suitable for dendrochemical studies, but if careful sampling strategies are used and suitable tree species are chosen, the chemical analysis of tree-rings can provide information concerning historical changes in soil and atmospheric trace metal levels unavailable from any other source (Watmough,1999).

A complex study of suitable tree species for dendrochemical studies of pollution with trace elements was conducted near large point sources in Slovenia by Poličnik et al. (2007) where 8 different tree species (European larch, Norway spruce, Scots pine, chestnut, sessile oak, silver birch, trembling poplar and common beech) were analyzed regarding temporal trends of heavy metal contents (Pb, Cd). Authors found that temporal trends of HM contents and also absolute HM levels are not the same in different tree species. Because of the high levels of Pb in Scots pine, strong correlations between concentrations and emissions from large point sources, strong correlations between concentrations and imissions at sampled locations and polinomic trend of concentrations in tree-rings (corresponding the polinomic trend of emissions) the authors concluded that this species is the most suitable for temporal analysis. Authors found that also European larch, silver birch, trembling poplar and common beech may be suitable for this purpose. On the contrary, chestnut and oak (species with ring porous wood) are not suitable for retrospective analysis. Coniferous trees and broadleaves with diffuse porous wood were found to be more suitable indicators. The priority list of suitable tree species was suggested as follows:

1. Scots pine, 2. European larch, 3. Trembling poplar, 4. Silver birch, 5. Common beech, respectively (Poličnik et al., 2007).

Regarding the results of a comprehensive dendrochemical study of common trees in Slovenia (Poličnik et al., 2007), Scots pine as long-living species and silver birch and trembling poplar as fast growing species were selected for the purpose of this study, because they were found to be the most suitable, and also present along majority of Slovene roads.

3 MATERIALS AND METHODS

3.1 Study sites

In the study, three road sections with heavy traffic loads were selected, for which traffic data for long-term was available. These sections were Lenart – Gornja Radgona, Miklavž – Hajdina and Škofljica – Rašica. The micro locations were selected by the presence of the suitable tree species (Scotch pine and trembling poplar or silver birch). The locations Miklavž, Spodnja Ščavnica and Vrh nad Želimljami were studied (Table 10). In Table 11, the sampled trees, their distance from the road edge, age and diameter are listed.

Table 10: *The studied locations and average daily traffic in years 1975 and 2007*

Road	Section		Site	km	Average daily traffic volume	
					1975	2007
G1-1	1400	Miklavž - Hajdina	Miklavž	0.940	6,719	18,536
G1-3	0315	Lenart – G. Radgona	Spodnja Ščavnica	11.970	1,852	9,641
G2-106	0261	Škofljica - Rašica	Vrh nad Želimljami	8.850	1,932	8,347

Table 11: *Sampled trees and their characteristics*

Location	English name	Latin name	Age of the tree	Diameter [cm]	Distance from the road [m]
Miklavž	Scots pine	*Pinus sylvestris*	1911-2007	39.5	7.5
Miklavž	Silver birch	*Betula pendula*	1978-2007	32.4	15
Sp. Ščavnica	Scots pine	*Pinus sylvestris*	1886-2007	50.9	7
Sp. Ščavnica	Silver birch	*Betula pendula*	1989-2007	19.7	20
Vrh nad Želimljami	Scots pine	*Pinus sylvestris*	1928-2007	48.8	20
Vrh nad Želimljami	Trembling poplar	*Populus tremula*	1981-2007	26.3	20

3.1.1 Study site Miklavž

The site Miklavž (Table 12) is situated on the northern part of the village Miklavž at the border with the town Maribor on the section of the main road G1-1 between Maribor and Ptuj; section 1400 Miklavž – Hajdina at approximately km 0.940, where the pine tree was sampled. The silver birch was sampled at km 0.440. The centre of the town Maribor is about 5.5 km in the NNW direction.

Table 12: *Study site Miklavž on the main road Miklavž - Hajdina*

Location	Miklavž
Road Number	G1-1
Section number	1400
Section name	Miklavž - Hajdina
Km	0.940
GKY	553225 (Pine);
GKX	152453 (Pine);
Altitude	265
Meteorological station	Maribor - airport
Tree species	Scots pine, silver birch

This is a road with heavy transit traffic and also with a lot of regional traffic because of the vicinity of town Maribor. The new highway, to which the majority of traffic from this road has been redirected, was opened in summer 2009.

The road at this location has a gradient of 0.5% and the runoff waters are channelized. The Scots pine was sampled at a distance of 7.5 m on the left side of the road; the distance from birch that was sampled on the right side to the road edge was 15 m. In Figure 4 and Figure 5, the location of sampled Scots pine and silver birch are presented.

On the Figure 4 the spots where individual trees were sampled are marked with an arrow. The top arrow is representing the spot where silver birch was sampled, the bottom one is the location of the pine tree. At this site the representative trees of the two species could not be found at the exact same location, so the two sampled trees were about 500 m apart.

The average daily traffic volumes for this road had been ranging between 6,719 vehicles per day in the year 1975 up to 18,536 vehicles in the year 2007. A decrease in traffic volumes is recorded in the year 1991 and 1992 but in the year 1997 the number of vehicles again reached the levels recorded in the year 1990 and has been steadily increasing ever since (Figure 6).

The nearest and most relevant meteorological station for the site Miklavž is Maribor – airport, which is about 4 km south from the location of sampling. The prevailing winds recorded in the years 2000 – 2010 for this location are N and SSW winds (Figure 7).

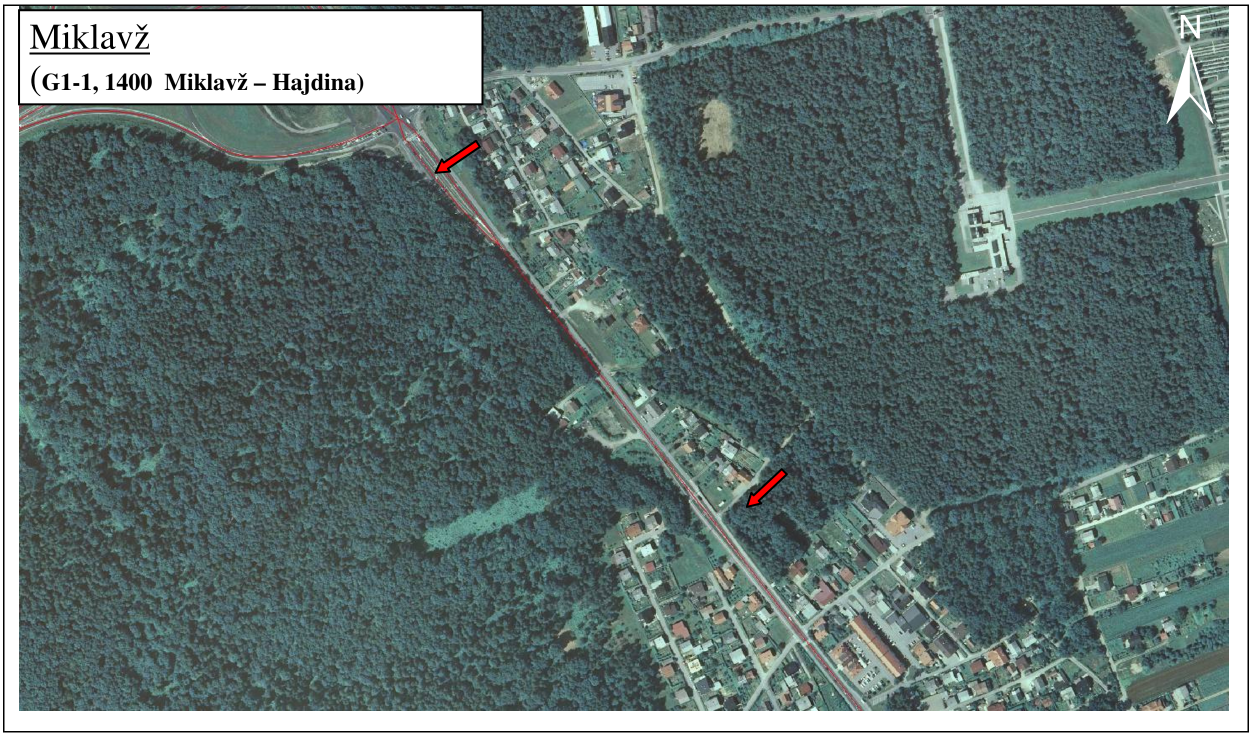

Figure 4: *The micro locations of sampled trees in Miklavž*

Figure 5: *Location of the sampled Scots pine on the right (photo: J. Lah)*

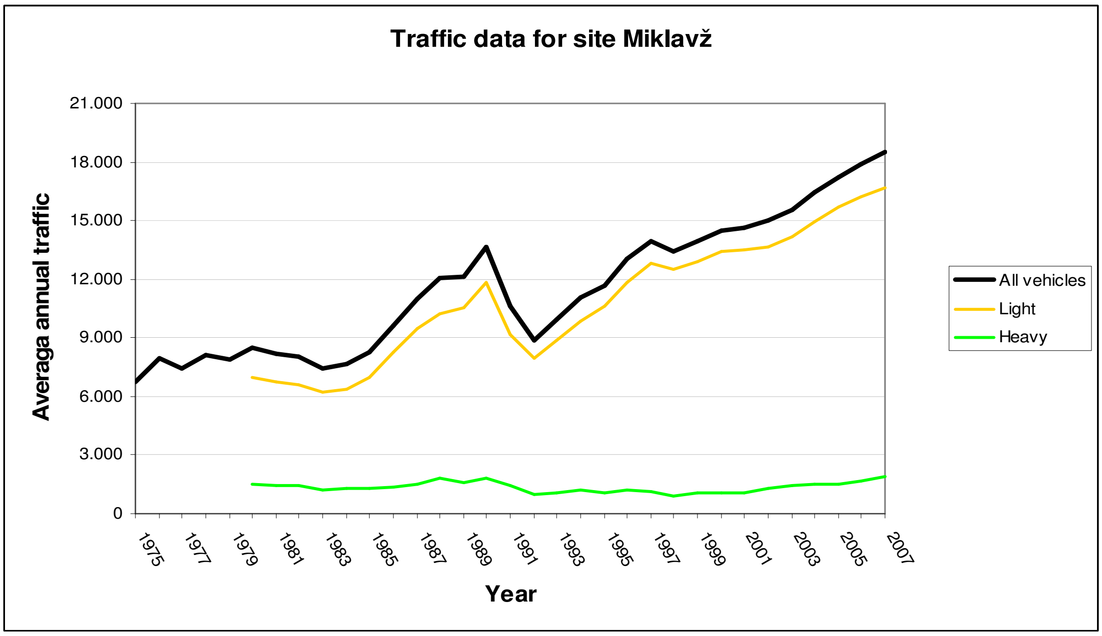

Figure 6: *Traffic data for the road Miklavž – Hajdina from 1975 – 2007*

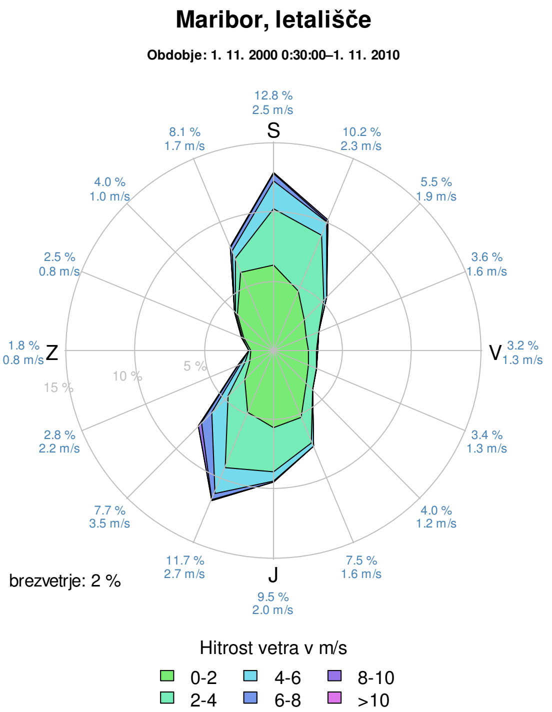

Figure 7: *Wind rose for the meteorological station Maribor (source MOP ARSO)*

3.1.2 Study site Spodnja Ščavnica

The site Spodnja Ščavnica (Table 13) is situated on the southern part of the village Spodnja Ščavnica on the section of main road G1-3 Pesnica – Lendava, section 0315 Lenart – Gornja Radgona at approximately km 11.970. The nearest bigger settlement is Gornja Radgona which is about 6 km in the NE direction.

Table 13: *Study site Spodnja Ščavnica on the main road Lenart – Gornja Radgona*

Location	Spodnja Ščavnica
Road Number	G1-3
Section number	0315
Section name	Lenart – Gornja Radgona
Km	11.970
GKY	570927
GKX	167427
Altitude	228 m
Meteorological station	Radenci
Tree species	Scots pine, silver birch

This road represented the main connection between Maribor and Hungarian border and connects towns Maribor, Gornja Radgona, Murska Sobota and Lendava. It is a road with heavy traffic volume that especially increased in the last years after the access of Republic of Slovenia in the European Union and more when Romania and Bulgaria joined the EU. The new highway, to which the majority of traffic from this road has been redirected, was opened in autumn 2008.

The road at this location has a gradient of 6% and the runoff waters are drained in the roadside ditch. The Scots pine was sampled at a distance of 7 m on the right side of the road; the distance to the birch that was sampled on the left side was 20 m. In Figure 8 and Figure 9 the location of sampled trees is presented.

The average annual traffic volumes for this road had been ranging from 1,852 in 1975 to 9,641 vehicles per day in 2007. As can be seen in the Figure 10, the increase of traffic was relatively constant, but larger increase of heavy vehicles in 2004 and the years after is recorded.

The nearest relevant meteorological station for location Spodnja Ščavnica is meteorological station Radenci, which is about 9 km east from the location of sampling. The prevailing winds recorded in the years 2000 – 2010 for this location are NW and SSW winds (Figure 11).

Figure 8: *The micro location of sampled trees in Spodnja Ščavnica*

Figure 9: *Location of the sampled Scots pine (right) and silver birch (left) (photo: J. Lah)*

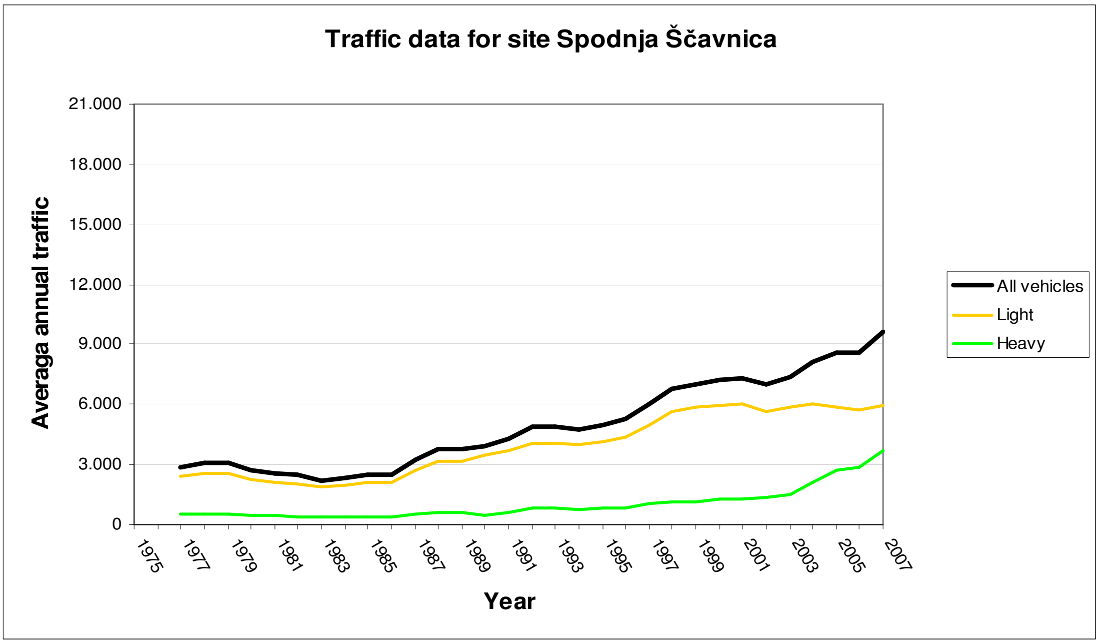

Figure 10: *Traffic data for site Spodnja Ščavnica*

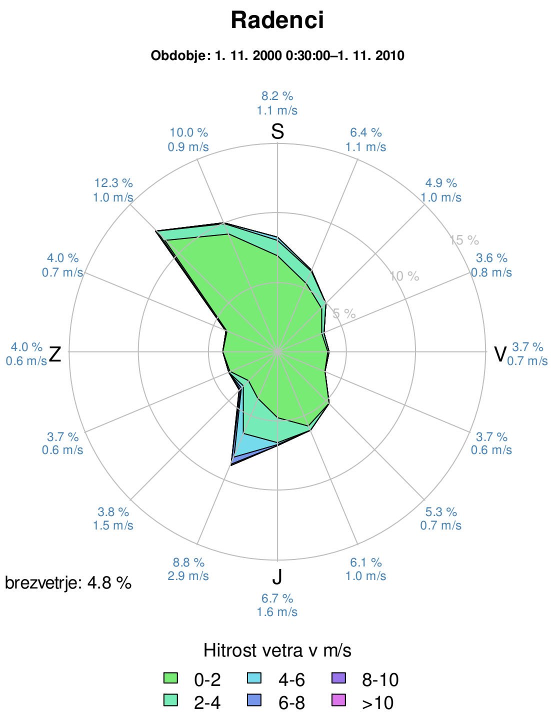

Figure 11: *Wind rose for the meteorological station Radenci (source MOP ARSO)*

3.1.3 Study site Vrh nad Želimljami

The site Vrh nad Želimljami (Table 14) is situated on the main road G2-106, section 0261 Škofljica – Rašica at approximately km 8.850, near the smaller village Vrh nad Želimljami and is about 18 km away from the town centre of Ljubljana which is in the NNW direction. This road represents the main connection between Ljubljana and Kočevje.

Table 14: *Study site Vrh nad Želimljami on the main road Škofljica - Rašica*

Location	Vrh nad Želimljami
Road Number	G2-104
Section number	0261
Section name	Škofljica - Rašica
Km	8.850
GKY	468575
GKX	84613
Altitude	505 m
Meteorological station	Ljubljana
Tree species	Scots pine, trembling poplar

The road at this location has a gradient of 2% and the runoff waters are drained over the roads embankments. The Scots pine and trembling poplar were sampled at a distance of 20 m on the right side of the road (Figure 12 and Figure 13).

The average daily traffic volumes for this road are ranging between 1,932 vehicles per day in the year 1975 up to 8,943 vehicles in the year 2007. As can be seen in the Figure 14, the increase of traffic trough the years had been relatively constant.

The most relevant meteorological station for the prevailing winds is the station Ljubljana – Bežigrad where NE and SW winds are prevailing (Figure 15). This meteorological station is situated in the centre of Ljubljana, about 18 km in the SSE direction.

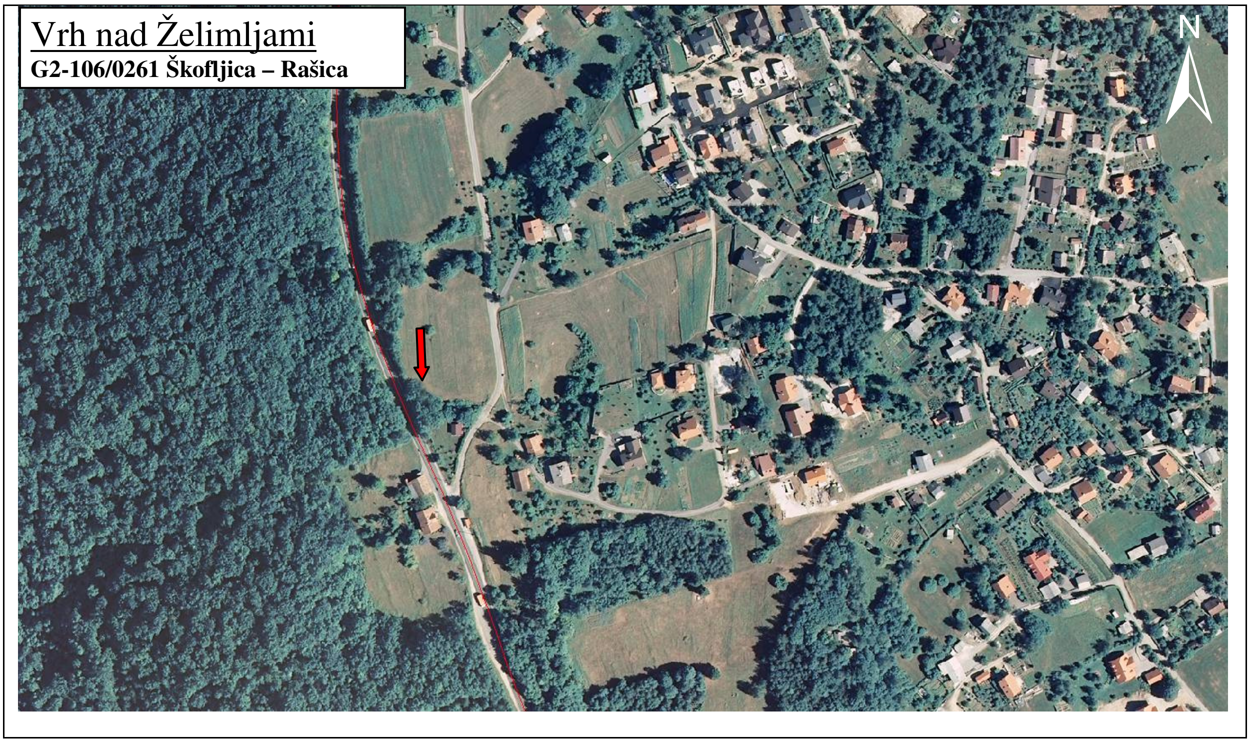

Figure 12: *The micro location of sampled trees at sampling location Vrh nad Želimljami*

Figure 13: *Location of the sampled Scots pine and trembling poplar on the right (photo: J. Lah)*

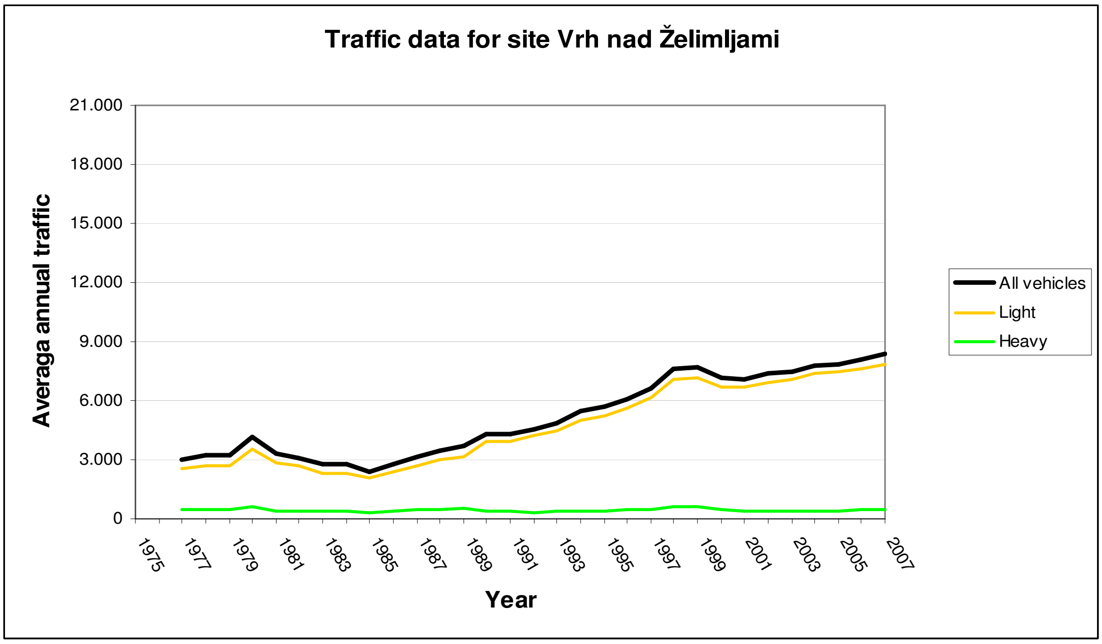

Figure 14: *Traffic data for site Vrh nad Želimljami*

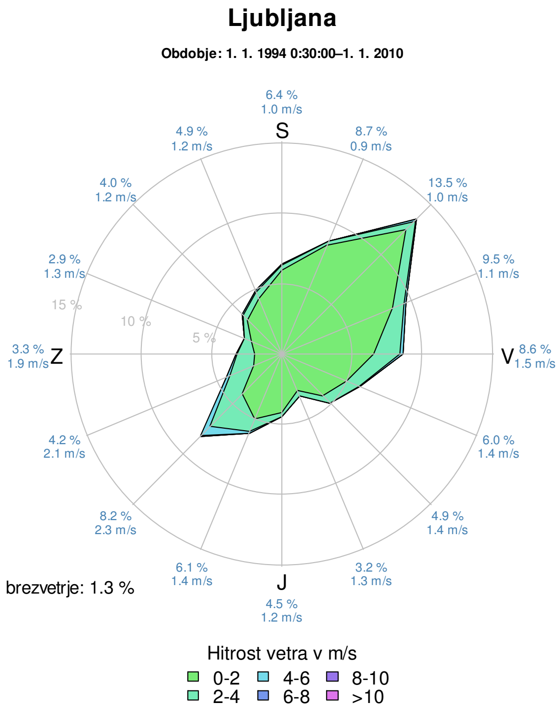

Figure 15: *Wind rose for the meteorological station Ljubljana (source MOP ARSO)*

3.2 Description of selected tree species

For the sampling and analysis two types of trees were selected at each location; one as a representative of long-living species (Scots pine - *Pinus sylvestris* L.) and one as a representative of fast-growing pioneer species (silver birch - *Betula pendula* R. or trembling poplar – *Populus tremula* L.). The selected tree species are presented in Figure 16.

3.2.1 Scots pine (*Pinus sylvestris* L.)

Pinus sylvestris is an evergreen coniferous tree growing up to 30 (40) m in height and 1 m trunk diameter when mature. It is the most frequent species of pine in Slovenia that populates the regions by the Drava and Sava River, Ljubljana basin, it is frequent in Goričko, Slovenske gorice, Haloze, Posotelje, in Bela Krajina, Litijsko hribovje, it also grows on the slopes of the mountain ranges and some parts of the Alpine world, for example in the Polhov Gradec hills. It is very adaptable and modest tree species, which grows in habitats that have low nutrient levels. Though it can also grow elsewhere, its preferred habitats are those with moist and acid, dry and acid and dry and alkaline soils. The lifespan of Scots pine is normally 150–300 years (Brus, 2004).

Scots pine as a coniferous tree has a comparatively simple structure of wood (Hagemeyer, 1993). Coniferous trees produce a single cell type, the tracheid, that carries out the functions of both support and water conduction. It has a structure with large diameter, thin-walled tracheids in the early wood and decidedly thicker-walled, smaller-diameter tracheids in the latewood (Jagels, 2006). Scots pine is a species that has a pronounced heartwood/sapwood boundary.

Pines are suitable for dendrochemical studies because they have a low number of sapwood rings, which enhance element mobility trough water conduction, and cations are bound to cell wall structures, with mobility strongly influenced by cation exchange reactions (Watt et al., 2007) and they show no detrimental effect from increment boring.

3.2.2 Silver birch (*Betula pendula* Roth)

Birch is up to 30 m high and up to 0.6 m thick deciduous tree with a rare, narrowly conical and a wider, often irregular crown in a greater age. It is a modest tree species. It prefers to grow in a light, fresh, deep, sandy loam and acidic soil. It is a pioneer species with short, up to 100 years-long lifespan that naturally grows throughout Slovenia; it is only rare in the Mediterranean world (Brus, 2004).

Silver birch has a diffuse porous wood type. Diffuse-porous hardwoods have similar size vessels arranged in various patterns throughout the growth ring, but typically in a relatively uniform distribution of pores, as apposed to ring porous woods, for which clustered large pores (vessels) at the beginning of the growing season followed by more scattered, smaller diameter pores embedded in fibbers in the latewood are characteristic (Jagels, 2006). Birch has 1.7 - 4 folds more fine roots which play a fundamental role in nutrient uptake and 2.2 folds more large roots than pine (Butkus and Baltrenaite, 2007).

3.2.3 Trembling poplar (*Populus tremula* L.)

Trembling poplar is up to 30 m high and 1 m thick deciduous tree with light, illuminated, often irregular rounded crown and a shallow but very wide forked root system. It is a very modest tree species that grows best in fresh, light and rich sandy loamy soil, but tolerates very well all other types of soil. It is naturally spread across Slovenia, from lowlands to the subalpine zone, sometimes even to the forest frontier. It is only rare in the Mediterranean world. It is a short-lived tree species as the tree begins to rot already at the age of 60 years (Brus, 2004). Trembling poplar is also a representative of trees with diffuse porous type of wood.

Scots pine (*Pinus sylvestris* L.)	
Silver birch (*Betula pendula* Roth)	
Trembling poplar (*Populus tremula* L.)	

Figure 16: *Selected tree species (photo: B. Pokorny)*

3.3 Sample collection, preparation and analysis

All trees were sampled in September 2007. Trees that grow closest to the road were selected for the sampling and analysis. The micro sites for sampling were selected by the appearance of Scots pine that grew closest to the road. At each location samples were taken from Scots pine, as a representative of long-living species for the assessment of long-term trends and from one of the representatives of fast-growing pioneer species (birch or trembling poplar) for the assessment of trends in the last couple of decades. Tree cores were taken at breast height (1.3 m above the ground) from the road facing aspect of each tree (Figure 17), using a 12-mm steel increment borer (Haglof) (Figure 18 - left). The diameter of each of the sampled trees was measured (Figure 19) with a girth measuring tape (Figure 18 - right) that measures the diameter from the circumference of the tree.

Sampled increments (Figure 20) were immediately sealed in dry plastic tubes and after the transport stored at -10°C prior to analysis. Because the cores from Scots pine trees were used to determine a long time temporal variability of HM pollution, they were divided into 5-year increments and the cores from silver birch and trembling poplar that were used to determine the yearly trends in the last couple of decades, were divided in 1-year increments. For the purpose of statistical analysis (the comparison of tree-ring width and their HM contents) the width of the samples (representing 5-year or 1-year ring width) was measured with a caliper. Increments were separated using stainless steel chisel (Stubai) and stainless-steel knife (Stubai) and placed in glass containers and dried at 36°C to constant weight (until the difference between two sequential weightings in a 4 hour interval was smaller than 0.1% of the last measured mass).

Figure 17: *Sampling of tree core from Scots pine (left) and birch (right) (photo: J. Lah)*

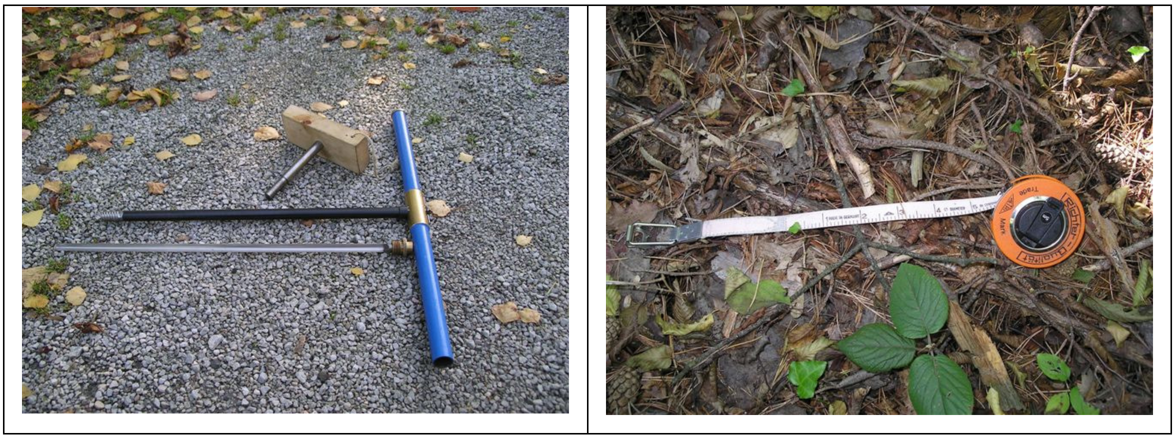

Figure 18: *Steel increment borer used for sampling (left) and girth measuring tape (right) (photo: J. Lah)*

Figure 19: *Measuring the diameter of birch (left) and pine (right) (photo: J. Lah)*

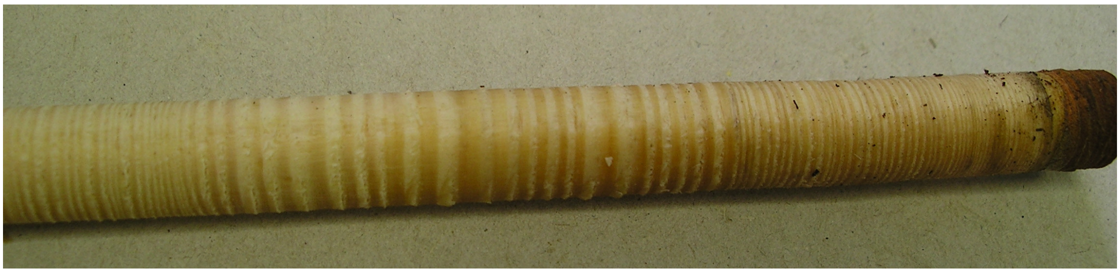

Figure 20: *Increment sample from Scots pine (photo: J. Lah)*

Determination of HM contents in tree-ring samples was made by the chemical laboratory in Erico institute Velenje.

A Milestone Ethos Plus microwave digestion system was used for pressurized wet digestion of samples with concentrated HNO_3. Using this method the samples were digested in a short period of time due to local superheating. Temperature programme of the microwave was as follows:

- from the start up to 5 minutes it heats to 60 ºC,
- from 5 to 7 minutes it heats to 200 ºC,
- in the next 45 minutes it maintains 200 ºC.

From digestion containers (teflon containers) the samples were quantitatively transferred to 25 mL laboratory flasks and diluted with ultrapure water. For some of the smallest samples 10 mL laboratory flasks were used. Before the analysis samples were filtered through the 0.45 µm membrane filters Chromafil RC-45/25 (Macherey Nagel, Germany).

The contents of heavy metals in samples were determined using an inductively coupled plasma mass spectrometer (ICP-MS Agilent 7500).

The contents of heavy metals, that may have origin in road traffic pollution, were determined. Selected metals were Pb, Cd, Zn, Cr, and Ni, respectively.

3.4 Measurement uncertainty and limit of quantification (LOQ)

(The measurement uncertainty and LOQ were determined by the chemical laboratory in Erico institute Velenje that conducted the chemical analysis).

Measurement uncertainty was determined by combining the contributions of precision and trueness study. Due to a small real sample amount the repeatability test was performed on a sample of wood, grinded (cut) to a size <1 mm, homogenized and analyzed in 10 parallel determinations, carrying out complete application of the method (pressurized microwave digestion and ICP-MS measurement, respectively). For trueness checking of the method the analysis of the reference material IAEA-336 (Trace and minor elements in lichen) was used. The material was analyzed at the method development and validation and during the analyses of the real samples. The results of expanded measurement uncertainty (*U*) and limits of quantification (*LOQ*) for analyzed heavy metals are presented in Table 15.

Table 15: *Expanded measurement uncertainty and limit of quantification for analyzed heavy metals*

	Cd	Pb	Cr	Ni	Zn	unit
U	33	30	33	44	23	%
LOQ_{inst}	0.10	0.10	0.10	0.10	1.00	µg/L
LOQ	0.01	0.01	0.01	0.01	0.1	mg/kg

LOQ_{inst} corresponds to instrumental limits, achieved by ICP-MS measurement. *LOQ* for solid sample in Table 15 is calculated for the sample amount of 0.25 g and dilution to 25 mL. The exact LOQ for each sample (generally rounded to 2 decimal places) is presented in annex C.

3.5 Traffic at the selected sampling sites

Traffic data were obtained from the Slovenian Roads Agency, which is a body within the Ministry of Transport that, among other tasks, also organizes and performs automatic and manual traffic counts and keeps record of traffic data for past years. Traffic data is published by the Slovenian Roads Agency in a yearly publication "Promet". The traffic data for selected road sections were available for a period 1975 - 2007, with the exceptions of the year 1976, for which no traffic data for sites Spodnja Ščavnica and Vrh nad Želimljami could be obtained, and for site Miklavž, only total annual traffic was available for the years 1976 – 1979 (there was no separate data for light and heavy vehicles for that period). The traffic data for study sites are presented in Table 16.

Table 16: *Annual volume of traffic for the locations Spodnja Ščavnica, Miklavž and Vrh nad Želimljami, given as all vehicles, light vehicles (<3,5 t), and heavy vehicles (>3,5 t) respectively*

Year	Sp. Ščavnica		Site Nr.85		Miklavž		Site Nr.		Vrh nad		Site Nr. 117	
	All	Light	Heavy		All	Light	Heavy		All	Light	Heavy	
	PLDP		PLDP	%	PLDP		PLDP	%	PLDP		PLDP	%
1975	1,852	1,448	404	22	6,719	5,404	1,315	20	1.932	1.583	349	18
1976	/	/	/	/	7,985	/	/	/	/	/	/	/
1977	2,888	2,393	496	17	7,452	/	/	/	3.004	2.552	453	15
1978	3,100	2,567	533	17	8,138	/	/	/	3.200	2.720	480	15
1979	3,100	2,567	533	17	7,919	/	/	/	3.200	2.720	480	15
1980	2,710	2,256	456	17	8,523	6,997	1,526	18	4.130	3.541	589	14
1981	2,577	2,144	433	17	8,179	6,714	1,465	18	3.274	2.864	410	13
1982	2,450	2,037	413	17	8,017	6,561	1,456	18	3.112	2.722	390	13
1983	2,203	1,849	354	16	7,433	6,201	1,232	17	2.737	2.346	391	14
1984	2,345	1,991	354	15	7,629	6,364	1,265	17	2.737	2.346	391	14
1985	2,510	2,131	379	15	8,266	6,996	1,270	15	2.407	2.065	342	14
1986	2,510	2,131	379	15	9,635	8,300	1,335	14	2.769	2.375	394	14
1987	3,212	2,692	520	16	10,989	9,510	1,479	13	3.157	2.708	449	14
1988	3,801	3,186	615	16	12,076	10,231	1,845	15	3.473	2.979	494	14
1989	3,801	3,186	615	16	12,143	10,552	1,591	13	3.716	3.188	528	14
1990	3,919	3,500	419	11	13,634	11,832	1,802	13	4.346	3.940	406	9
1991	4,268	3,675	593	14	10,605	9,140	1,465	14	4.346	3.940	406	9
1992	4,899	4,096	803	16	8,889	7,930	959	11	4.563	4.232	331	7
1993	4,900	4,097	803	16	9,900	8,832	1,068	11	4.840	4.489	351	7
1994	4,751	3,972	779	16	11,089	9,893	1,196	11	5.428	5.034	394	7
1995	4,989	4,146	818	16	11,678	10,576	1,090	9	5.699	5.268	414	7
1996	5,238	4,380	859	16	13,072	11,851	1,220	9	6.040	5.602	438	7
1997	6,039	4,965	1,074	18	13,934	12,809	1,125	8	6.644	6.163	481	7
1998	6,747	5,635	1,132	17	13,390	12,542	880	7	7.621	7.055	596	8
1999	6,970	5,857	1,134	16	13,936	12,906	1,030	7	7.730	7.155	605	8
2000	7,200	5,918	1,282	18	14,486	13,404	1,082	7	7.129	6.681	448	6
2001	7,300	6,000	1,300	18	14,613	13,523	1,090	7	7.087	6.675	412	6
2002	7,020	5,664	1,356	19	14,975	13,678	1,297	9	7.379	6.961	418	6
2003	7,368	5,870	1,498	20	15,574	14,141	1,433	9	7.476	7.072	404	5
2004	8,139	6,018	2,121	26	16,453	14,951	1,502	9	7.757	7.353	404	5
2005	8,594	5,889	2,705	31	17,238	15,691	1,547	9	7.864	7.451	413	5
2006	8,593	5,698	2,895	34	17,890	16,203	1,687	9	8.095	7.626	469	6
2007	9,641	5,917	3,724	39	18,536	16,646	1,890	10	8.347	7.854	493	6

PLDP – average annual daily traffic (number of vehicles)
% – percentage of heavy vehicles in the total number of vehicles
Site Nr. – number of the traffic counting site of the Slovenian Roads Agency
/ – no data available

3.6 Statistical methods

To test the dependency of heavy metal concentrations in tree-rings with other parameters taken from the literature (Pb, Cd emissions in Slovenia, emissions of other pollutants in Slovenia or from point sources, imissions of pollution indicators) or assessed in this research (emissions of Pb by road traffic, growth ring width) the Pearson's correlation coefficients (r) between parameters were calculated. Statistical analysis was carried out using a computer program Statistica for Windows 8.0 (StatSoft, Inc., 2007). The limit for statistical significance was set at $p < 0.05$. Nevertheless, correlations with $r > 0.8$ are described as strong, correlations with r between 0.6 and 0.8 are described as moderate, whereas correlations with $r < 0.6$ are described as weak and are considered irrelevant even in the case of their statistical significance ($p < 0.05$).

4 RESULTS AND DISCUSSION

In the study, trends of changes in contents of selected heavy metals in samples from individual tree species, which represent a time period of their growth, were established. Long-term trends were established in 5-year samples of tree-rings of Scots pine and short-term trends were established in 1-year samples of tree-rings of silver birch or trembling poplar. Contents and trends were compared among different tree species at the same location and among different locations.

Comparison was also made with known yearly traffic volumes for the roads at the study locations, with assessed emissions of Pb for individual road segment and also with known data for emission and deposition of different pollutants in Slovenia.

A comparison with levels of Pb and Cd in a study of chemistry of tree-rings at several polluted and unpolluted locations in Slovenia (Poličnik et al., 2007) is also presented.

4.1 Assessment of Pb and Cr emissions at the selected sampling sites

For the comparison of concentrations obtained in tree-rings, the rough assessment of lead and chromium emissions trends produced by road traffic at selected sampling sites was calculated. All calculations have been made for the purpose of statistical analysis and comparison of trends. Regarding the purpose and because of the lack of exact data, some simplifications had to be made, which are described in the following text.

4.1.1 Assessment of Pb emissions

The calculation was made from the average yearly amount of passenger vehicles (light vehicles) at selected road sections, average fuel consumption per kilometre, maximal allowed concentrations of Pb in leaded gasoline, share of gasoline powered vehicles and the ratio between the amounts of total sold leaded/unleaded gasoline in Slovenia for individual years. In the assessment only passenger vehicles are taken into account.

The formula used for the assessment is stated below:

$$E_{Pb}/km = A \times B \times EF \times G\,((L \times C_{Pb}) + (U \times C)) \qquad \text{(equation 1)}$$

Where:

E_{Pb}/km – Assessed emissions of Pb per kilometre of individual road section
A – Number of vehicles (traffic data for individual road section)
B – Average fuel consumption per km
EF – Emission factor – ratio of exhaust emitted Pb (0.75)
G – Share of gasoline powered vehicles
L – Share of vehicles using leaded gasoline
C_{Pb} – Concentration of Pb in leaded gasoline
U – Share of vehicles using unleaded gasoline
C – Concentration of Pb in unleaded gasoline

The formula takes into account that 75% of the lead contained in the fuel is emitted into the air, which is a commonly accepted factor for lead emissions by exhaust fumes from road traffic (Corinair, 2007). Assessment of the average fuel consumption is based on the data for average fuel consumption for new cars from 1980 – 1995 for Austria (ECMT, 2001), time shifted for 7 years which is the approximation of average age of passenger vehicles in Slovenia (ARSO KOS, 2011) and linearly interpolated for the years, for which no data was available. Linear interpolation is made on the basis of the last 3 available years. Concentrations of Pb in leaded and unleaded gasoline were taken from Table 8, which states the maximum allowed levels of lead content in gasoline for individual years.

The assessment of the share of gasoline powered passenger vehicles was made on the basis of data from Ministry of the interior (MNZ) that was available for the period from 1992 – 2007 (SURS, 2011). The data shows that the share of gasoline powered passenger vehicles has been decreasing from 0.92 in the year 1992 to 0.72 in the year 2007. For the years 1980 – 1991 the assessment has been made with linear interpolation of the data for the last 4 available years (1992-1995) so the share used in calculation is ranging from 0.94 in the year 1980 to 0.72 in the year 2007, respectively.

The assessment of share of vehicles using leaded/unleaded fuel has been made on the basis of the data for the total sold quantities of leaded/unleaded fuel in Slovenia. The share of leaded gasoline was 1.00 for the years 1980 – 1988, and had decreased till 0.00 in the year 2002 (MOP ARSO, 2002).

The assessed emissions of Pb from road traffic are about three folds higher at location Miklavž compared to Spodnja Ščavnica and Želimlje. The emissions at location Miklavž have been steeply decreasing after the year 1991 (because of the decreased traffic at this location), and also due to the increased usage of unleaded fuel. At other two locations only a minor decrease has been recorded from 1990 – 1995, followed by the largest decrease after 1995 at all locations, due to the new limit values for Pb content in gasoline (Figure 21).

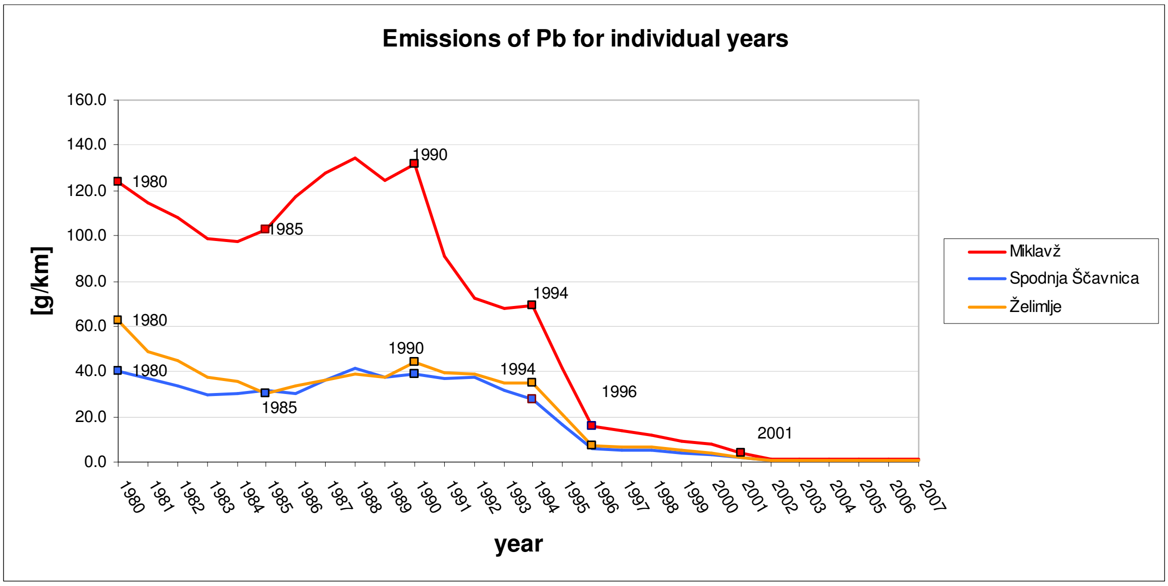

Figure 21: *The assessment of trends of Pb emissions from road traffic in grams per kilometre of road [g/km] for sites Miklavž, Spodnja Ščavnica and Želimlje in years 1980 – 2007*

4.1.2 Assessment of Cr emissions

The calculation was made from the average yearly amount of vehicles (light and heavy vehicles) at selected road sections, estimated fuel consumption per kilometre, emission factors for gasoline and diesel fuel, share of gasoline and diesel powered vehicles for both categories (light/heavy). The formula used for the assessment is stated below:

$$E_{Cr}/km = (A_L \times FC_L \times G_L + A_H \times FC_H \times G_H) \times EF_{GASOLINE} + (A_L \times FC_L \times D_L + A_H \times FC_H \times D_H) \times EF_{DIESEL} \quad \text{(equation 2)}$$

Where:

E_{Cr}/km	–	Assessed emissions of Cr per kilometre of individual road section
A_L	–	Number of light vehicles (traffic data for individual road section)
A_H	–	Number of heavy vehicles (traffic data for individual road section)
FC_L	–	Estimated fuel consumption per km for light vehicles
FC_H	–	Estimated fuel consumption per km for heavy vehicles
$EF_{GASOLINE}$	–	Emission factor for gasoline powered vehicles
EF_{DIESEL}	–	Emission factor for diesel powered vehicles
G_L	–	Share of gasoline powered light vehicles
G_H	–	Share of gasoline powered heavy vehicles
D_L	–	Share of diesel powered light vehicles
D_H	–	Share of diesel powered heavy vehicles

Emission factors that were used for assessment of Cr emissions were prepared for COPERT 4 v9.0 (a software program for the calculation of emissions from the road transport sector) and are taken from the description made by Gkatzoflias et al. (2011) (Table 5). It is important to emphasize that there is a lack of reliable information regarding metal emission rates and so the determination of HM emissions from road vehicles is a procedure associated with large uncertainties (ibid.).

Assessment of the average fuel consumption for light vehicles and of the share of gasoline powered vehicles is the same as described in the previous chapter about Pb emissions (4.1.1), for heavy vehicles an estimated fuel usage of 30 L/km in 1980 to 25 L/km in 2007 was used.

The results are presented in the following figures (Figure 22; Figure 23; Figure 24), a cubic trendline (Emission trend) is fitted to the data for totall emission (Emission ALL) at each location.

The assessed emissions of Cr from road traffic at location Miklavž were from 2.88 g/km to 4.33 g/km in the year 1990, when the first peak in emissions is reached, followed by a decrease to the lowest value of 2.73 g/km in the year 1992. After that time the assessed emissions were increasing and they reached the highest value of 6.43 g/km in 2007 which is the last year of assessment (Figure 22).

The assessed emissions of Cr at location Spodnja Ščavnica were about 3 folds lower than at Miklavž and were around 1 g/km (0.86-1.15 g/km) in the years till 1987. After that assessed emissions were increasing with a small decrease in 1989 and 1994. From 1994 (1.32 g/km) the emissions were rapidly increasing and they reached a value of 2.00 g/km in 1998. In the following years the emissions were relatively constant with a small decrease in 2002 (1.97 g/km) followed by a steady increase till the highest value of 2.30 g/km in 2007 (Figure 23).

Also the assessed emissions of Cr from road traffic at location Vrh nad Želimljami were about 2-3 folds lower than at Miklavž and were decreasing in the years 1980 (1.81 g/km) till 1985 when the lowest value (0.90 g/km) is assessed. After that year the emissions had been increasing with a small peak in 1990 (1.44 g/km) till 1998

(2.50 g/km) and 1999 (2.48 g/km). The peak is followed by a decrease till 2001 (2.27 g/km), after that year the emissions had been constantly increasing till the last year (2007) when the highest value is assessed (3.03 g/km) (Figure 24).

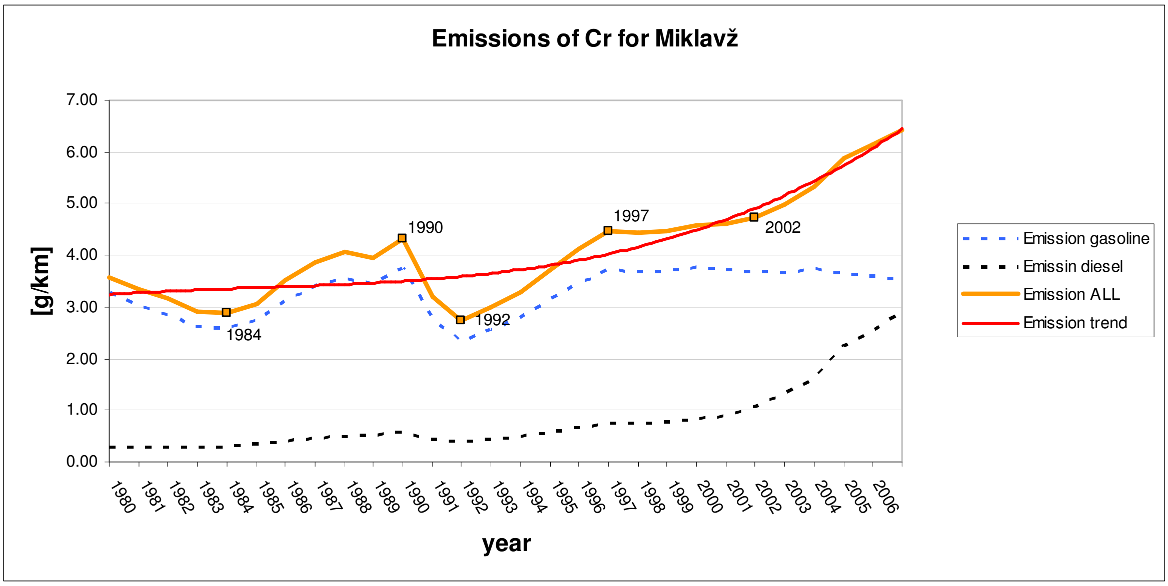

Figure 22: *The assessment of trends of Cr emissions from road traffic in grams per kilometre of road [g/km] for site Miklavž, in years 1980 - 2007*

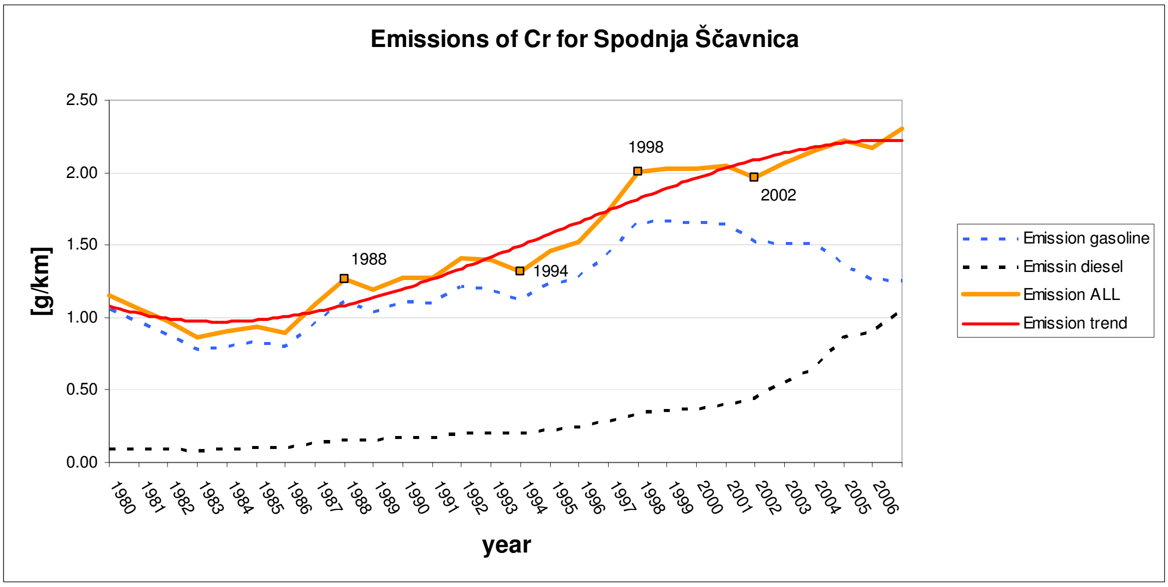

Figure 23: *The assessment of trends of Cr emissions from road traffic in grams per kilometre of road [g/km] for site Spodnja Ščavnica in years 1980 - 2007*

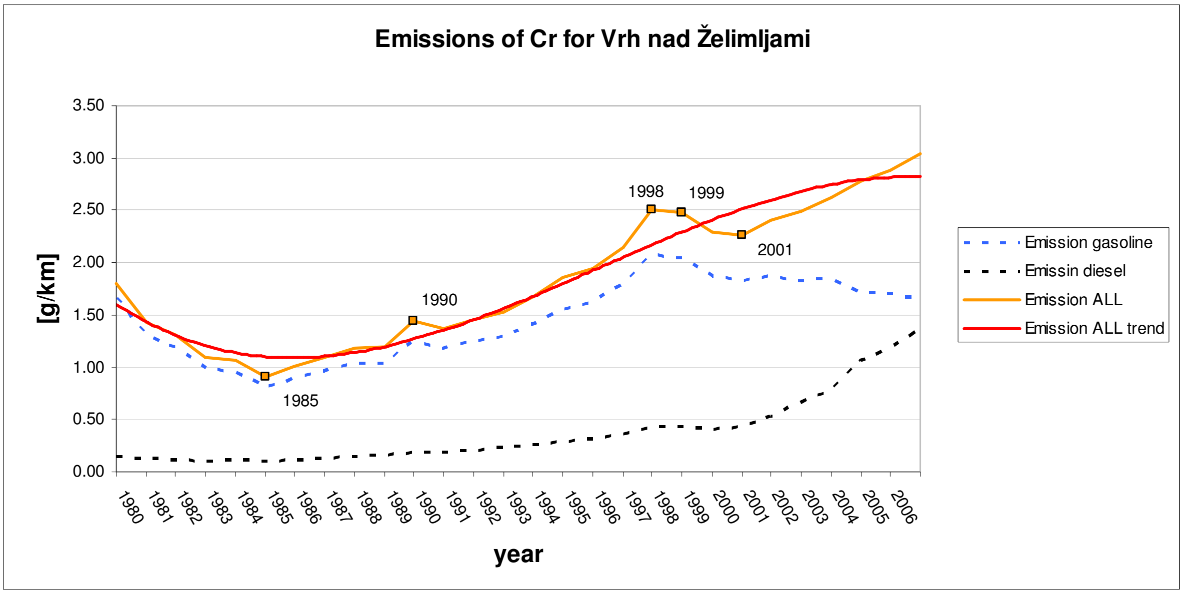

Figure 24: *The assessment of trends of Cr emissions from road traffic in grams per kilometre of road [g/km] for site Vrh nad Želimljami in years 1980 - 2007*

4.2 Temporal trends in heavy metal levels in tree-rings

Temporal changes in contents of HM in tree-rings are presented for studied sampling sites Miklavž, Spodnja Ščavnica, and Vrh nad Želimljami. For each site, long-term temporal variability of HM contents in annual growth rings of long-living species (Scots pine) and short term variability for representatives of fast growing species (silver birch or trembling poplar) are presented. The trends are presented as scaterplots; a cubic curve is fitted to the data of HM content.

4.2.1 Study site Miklavž

4.2.1.1 Heavy metal contents in 5-years increments of Scots pine in the period 1911-2007

In tree-rings of Scots pine in Miklavž (Figure 25) the long-term trend of increasing concentrations of majority of heavy metals can be established, with the exception of cadmium (Cd), where a trend of decreasing concentrations begun in 1956 and the lowest measured concentrations were in the period from 1976 to 1986.

The levels of Pb were relatively constant during the period from 1911 to 1961, with a small increase in tree-rings formed after the Second World War (samples for the years after 1946). After the year 1961 the levels begun to gradually increase, but the rapid increase in Pb contents began after 1981. The highest measured level was established in the last sample (2006-2007). The increase of contents corresponds with the trend of increasing road traffic and motorization that began in the beginning of the 1980's. Even though the overall emissions of Pb in Slovenia rapidly decreased after the introduction and growing usage of unleaded fuel and after stricter limits for the Pb content in gasoline were adopted in 1995 (Rode et al., 2010), no decrease in lead levels could be seen in Scots pine from this location. This could mean that the environment is still polluted with lead and the transport of this metal to tree-rings still takes place. As stated in a research by Mielke at al. (2010), even though Pb fuel has been phased out, exterior soils represent an enormous reservoir of Pb. Also, due to the structure of wood in coniferous trees, water and nutrient conductivity is not restricted to only one, the most outer tree-ring, therefore it is suggested that heavy metals are also transported in more than one ring at the time (Hagemeyer, 1993). This may cause that the tree-ring fixation of heavy metals in the last couple of sampled rings would differ from the overall trend in the whole period of growth.

Other possibility is that other traffic or non-traffic related sources may be the prevailing source of lead that is readily available to the pine tree at this location. The quantity of Pb deposited in an annual growth ring represents the readily bound (ionic form) fraction and not the total transportable quantity of Pb (Nabais et al., 1999). The contents in tree-rings are most probably a result of different pathways trough which heavy metals enter the tree (by thee roots, by direct air deposition trough the bark, trough the leaves/needles), and different forms of each pollutant have different uptake and binding characteristics. Free Pb ions bind more readily to woody tissue than complexed Pb (Lepp and Dollard 1974, op cit Nabais et al., 1999). One of the pathways or forms could prevail in a certain time period. Regarding study of emissions of heavy metals in road traffic conducted in Denmark (Winther and Slentø, 2010), lead is still an important pollutant, originating mainly from brake wear, and Suzuki et al. (2009) suggested that also yellow paint and lead components of automobiles like wheel balance weights are an important source of Pb near roads. Because of soil characteristics, it could take some time for the Pb to be readily available to the tree roots (Kabata-Pendias, 2004); this time delay could be more pronounced in pine tree due to its root characteristics. Pine tends to produce deeper roots and less fine roots than birch (Butkus and Baltrenaite, 2007). Birch tends to produce shallow roots that spread over a large area; on a healthy birch, roots will spread to a distance of at least twice the tree's height (Johnson, 1993).

It is important to state that in the case of Scots pine, only two 5-year samples (1996-2000 and 2001-2005) and one 2-year sample (2006-2007) were analyzed after the year 1995, in which the first restrictions in the process of leaded gasoline phase-out were adopted. The cause for the highest levels of heavy metals in the outer most (2-year) sample may also be from the contamination with a small amount of bark that could be partially present in the last analyzed sample (the bark might contain greater concentrations of HM due to direct atmospheric deposition). Contamination of the outer most rings from bark tissue was also suggested in a study made by Watmough and Hutchinson (1996).

A clear trend of increasing levels of chromium (Cr) that could be also associated with the increasing road traffic can be seen in tree-rings formed after 1986. Moreover, also the levels of nickel (Ni) have been rising with a similar pattern. A trend of increase for Zn is also present; although the increase is not so evident, because some relatively high levels were also recorded in the samples from the period 1941-1950. Ni and Zn are elements that are (after Cu) emitted from road traffic in the largest quantities (Winther and Slento, 2010), but because they are essential elements, their concentrations could also point to the physiological processes in the tree. Strong correlations were established between traffic parameters and concentrations of Cr in Scots pine (Table 26).

The changes of Pb, Cr and Ni levels at sampling site Miklavž may be linked to the increasing traffic on the road between Maribor and Ptuj, which is relevant to this location, and also on other roads in an urbanized area nearby. The location is situated about 5.5 km from the centre of the town Maribor, the second largest town in Slovenia, which also generates a lot of local traffic (on other roads in the town) and also other possible sources of pollution with heavy metals (industry, local fireplaces).

Levels of Cd were relatively constant in the first six samples, dated in the period 1911 – 1935. In samples from the years 1941-1945 and 1946-1950 the maximum levels were measured, and after that levels rapidly decreased till the period 1981-1990 when minimum levels were recorded. In samples from the last 17 years, levels have been slowly increasing. Cd is the only element for which an obvious decrease in levels is recorded in Scots pine from Miklavž in the whole study period, with a slight increase in the period of the last 17 years, which corresponds with the increase of all other measured elements in recent decades. This may point to a conclusion that levels of heavy metals tend to increase towards the bark, but this explanation is less likely regarding the findings of some other authors which pointed to an increase in the opposite direction, that is that the contents of HM are likely to be higher towards the stem centre (in the heartwood) because of an possible mechanism of sapwood detoxification (Stewart 1966, op cit Nabais et al., 1999).

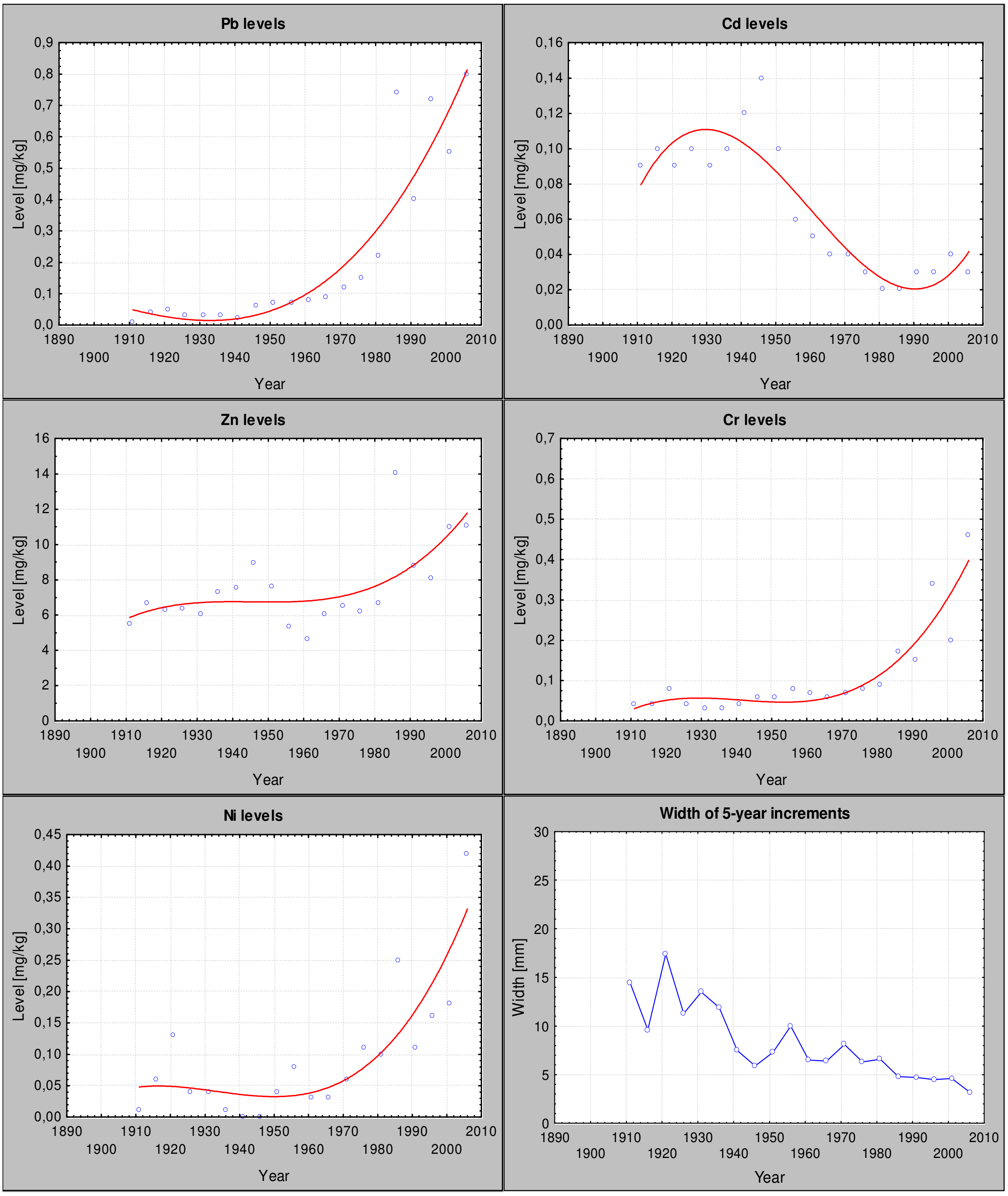

Figure 25: *Long-term temporal variability of heavy metal concentrations [mg/kg] and width of 5-year increments [mm] of Scots pine, Miklavž (period 1911 - 2007)*

4.2.1.2 Heavy metal contents in annual tree-rings of silver birch in the period 1978-2007

In tree-rings of silver birch in Miklavž (Figure 26) levels of lead (Pb) had been increasing till the year 1989, remained constant till 1993, and since then have been decreasing rapidly. A clear trend of decrease from 1994 till 2007 was established. Temporal trend of decrease in lead contents in silver birch after the year 1994 is accordant to the expectations for the indication of Pb pollution in trees. A well pronounced decrease of Pb content in tree-rings that grew after the stricter regulations regarding Pb content in gasoline were adopted in 1995, is accordant to the assessed decrease in traffic related emissions of Pb in Republic of Slovenia (Figure 2), but if we look at the assessed trend of emissions from road Miklavž – Hajdina (Figure 21), the decrease in tree-rings took place some years later. On the road Miklavž - Hajdina an important decrease in traffic volumes after the year 1990 took place because of the war in the Balkans, which limited the transit in this traffic corridor. In comparison to the year 1990 (13,634 vehicles), the traffic decreased for about 45% in the year 1992 (8,889 vehicles), and didn't grow back to the 1990 level, till the year 1997 (13,934 vehicles). This is the main cause for the decrease in the assessed emissions in chapter 4.1.1, but the effect of this decrease in transit traffic regarding the emissions in the sampling location is most likely overestimated. The sampling location is situated at the beginning of a relatively long road section, just outside the town Maribor, where we can expect a more pronounced effect of local traffic that is not recorded in the traffic counter which is situated in the village Starše, about 10 km away from the sampling location. Unfortunately the traffic data for the first subsection of this road, the subsection trough settlement Miklavž (0 – 3 km), is only available for the years after 2001; however the comparison of the traffic volumes from 2001 - 2007 shows that there was about 4,000 (20-30%) more light vehicles in the first subsection of this road than on the counting site in Starše. Also if we presume that nearby town of Maribor had an effect on higher background levels of Pb at the sampling location, the decrease in emissions from a single road could have a less important effect.

The maximal levels of lead in silver birch are higher than those measured in Scots pine. Results show that silver birch seems to be more appropriate tree species than Scots pine for the indication of Pb emissions from the road traffic. This is in agreement with the findings of some previous studies which found that diffuse porous broadleaves appear to be better indicators of metal deposition than conifers or ring porous broadleaves (Watmough and Hutchinson, 1996). It is important to state that sampled trees at this site were note found at exactly the same location, but were about 550 m apart. In birches the uptake of pollutants trough the bark due to direct atmospherical deposition (Watmough and Hutchinson, 2002) is more likely to occur due to its structure (the bark of silver birch is thin and gentle). A fact that points to the uptake from the bark as the most important pathway for Pb entering tree-rings is also the drastic decrease in Pb levels in tree-rings formed after the year 1994. Such drastic decrease is unlikely if the Pb would mainly enter the wood trough the contaminated soil (Watmough and Hutchinson, 2002). Strong correlation between assessed emissions of Pb from road traffic and levels in tree-rings was found (Table 17) which confirms a potential of silver birch for biomonitoring of heavy metal pollution even on a yearly basis.

Levels of Pb in annual tree-rings of silver birch and assessed yearly emissions of Pb from road traffic have been compared using Pearson's simple correlation (r). Correlations were tested between the assessed emissions and the levels in tree-rings that grew in the same years (Emission -0 years), and also by applying a time shift scenario with assumption that the changes of emissions are resulted in tree-ring that grew some years later (Emissions -3 years; Emission -5 years; Emission -7 years). A scenario of -3 year time shift for example means that the emissions of Pb are not compared to the Pb levels in the tree-rings that grew in the same year, but to the concentrations that are measured in tree-rings that grew three years after. Strong statistically significant correlations were established at $p<0.001$ for all calculated scenarios, although the largest coefficient ($r = 0.95$) is found at a 3 year time shift, which means that it takes 3 years before tree-rings react to the traffic emitted content of Pb. Similar time delay in trees responses was also recorded by Aznar et al. (2008). Correlations between emissions and Pb levels are presented in Table 17.

Table 17: *Correlations between assessed yearly emissions of Pb from road traffic and Pb levels in annual tree-rings of silver birch at location Miklavž (Pearson's "r" and "p" are presented)*

	N	Emission (-0 years)	N	Emission (-3 years)	N	Emission (-5 years)	N	Emission (-7 years)
Miklavž	28	0.80	25	0.95	23	0.90	21	0.80
		$p < 0.001$		$p < 0.001$		$p < 0.001$		$p < 0.001$

N – Number of analysed pairs

A clear trend of increase in levels of chromium (Cr) after the year 2000 was found (Figure 26), which is similar than the increase found in Scots pine, which had begun some years earlier (the Scots pine is used for determination of long-term trends). The increase of concentrations in silver birch in the last years corresponds to the increase in the assessed emissions (Figure 22). It is interesting that the lowest Cr content in silver birch from Miklavž was measured in tree-ring from the year 1992, when also the assessment of emissions shows the lowest value, but the differences are low and regarding the range of measurement uncertainty might as well be coincidental. On the other hand relatively high contents of Cr in tree-rings from 1981 and 1982 and relatively low content in 2005 cannot be explained with the assessed trend of emissions.

Regarding the decrease in Pb concentrations and increase in Cr concentrations (which can also be associated with road traffic) it seems that silver birch corresponds well to pollution from road traffic. Positive correlations were established between concentrations of Cr and traffic parameters (Table 27), but with rather low coefficients that are considered very weak ($r = 0.44 – 0.56$).

A clear trend of decrease in cadmium (Cd) levels is seen, and a trend of decrease could also be seen for zinc (Zn), but the differences in concentrations are not that significant.

For Ni, slightly higher levels are measured in some of the samples of the last 7 years, but the trend of increase is not that clear as for Cr. Because higher concentrations are established only in the last couple of years, and because the levels in this period vary significantly, it is not very likely that Ni levels in tree-rings of silver birch adequately reflect the changes in road traffic pollution. Also the differences in levels of Cd and Zn are most likely not associated with road traffic pollution and may be the result of physiological processes in the tree or of some other factors that have an influence on three ring contents of HM.

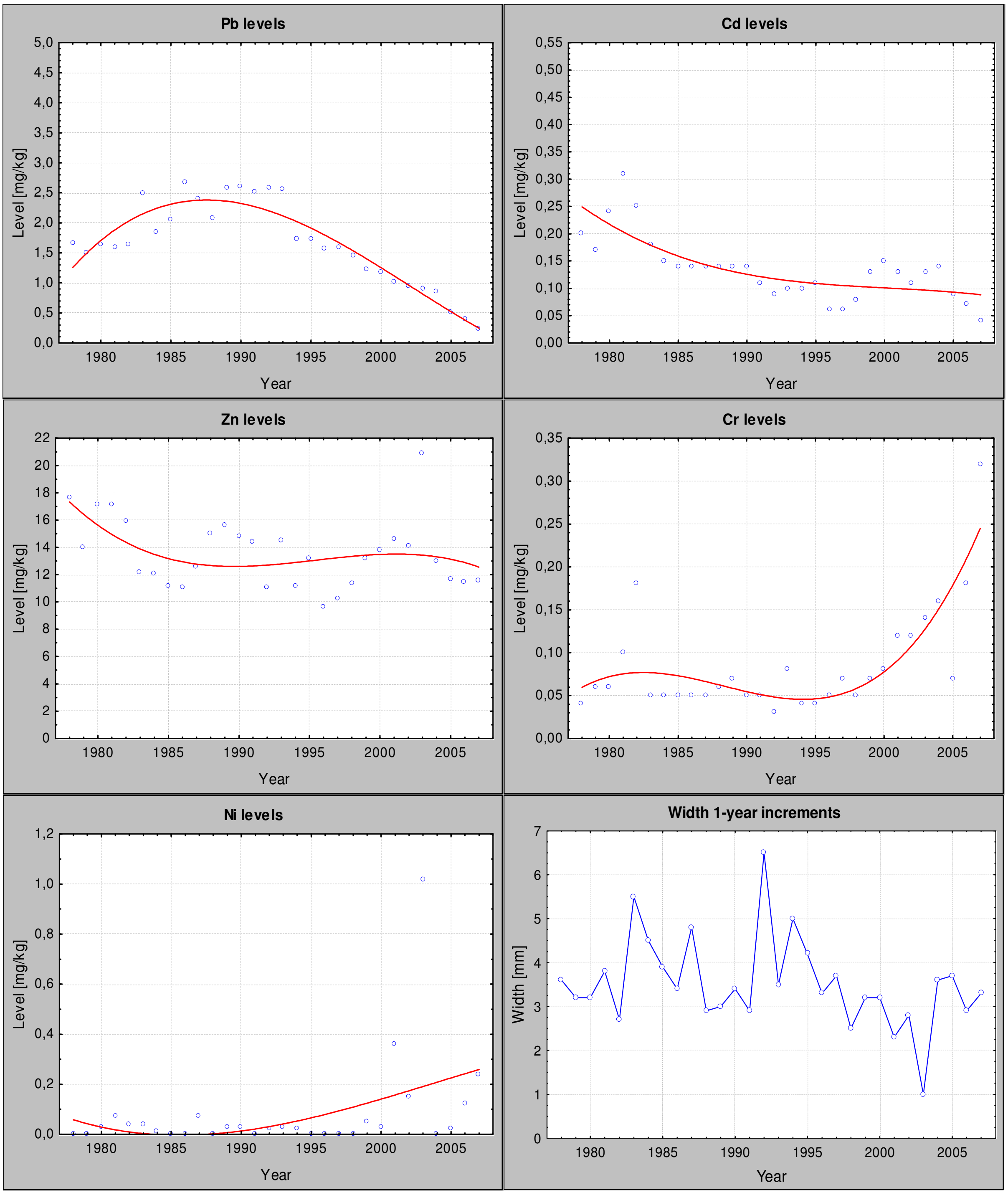

Figure 26: *Variability of heavy metal content in annual tree-rings [mg/kg] and width of 1-year increments [mm] of silver birch, Miklavž in the last three decades*

4.2.2 Study site Spodnja Ščavnica

4.2.2.1 Heavy metal contents in 5-years increments of Scots pine in the period 1896-2007

In tree-rings of Scots pine at the location Spodnja Ščavnica (Figure 27), Pb levels were found to be increasing till the rings that grew from 1931-1936; after that time, Pb content has been decreasing and was below the limit of quantification in the last 4 samples (1991-2007). This trend cannot be linked to the road traffic pollution with Pb. The absolute measured levels of Pb till the 1970's are higher than levels in the same period measured in Scots pine at location Miklavž, in the samples for the periods 1971-1981 the levels are comparable, but opposed to Miklavž, where an increase after the 1980's is recorded, Pb levels in Spodnja Ščavnica have been decreasing in the later samples. The trend of decrease from the highest measured levels in the sample for the period 1916-1920 could point to a conclusion that Pb is accumulated in heartwood with a similar pattern that was established in a study made by Watmough and Hutchinson (2002). It seems that Pb emitted from the traffic is not accurately reflected in the concentrations in tree-rings from Scots pine at this location. Watmough and Hutchinson (1999) suggested, that Pb (and Cd) taken up by roots (of sacred fir) accumulate in the heartwood, whereas Pb (and Cd) entering trough the bark are transported readily to a much lesser extent and more accurately record changes in trace metal deposition. The less pronounced uptake trough the bark may also be the explanation for the trend found at this location, since the sampled tree was at a bit higher level (about 1 m higher) than the road, and the vegetation around the sampled tree was denser. Both factors could limit the absorption of trace metals trough the bark. Possible translocations of metals to the heartwood is more likely because also Cd concentrations followed a similar pattern of higher concentrations in the early years of growth that decrease towards the bark. The traffic volume at this location is also much lower than in Miklavž (the total amount of light vehicles in the period 1978 – 2007 was almost 3-folds lower), and the assessed quantities of emitted Pb were also about 3-folds lower. Because the Pb concentrations in the wood are most likely the sum of element entering via the roots and those entering trough the bark (Watmough and Hutchinson 2002), 3-folds lower emissions could result that the uptake trough the bark wouldn't play an important role in regard to the uptake by the roots that can point to the concentrations in the trees natural environment.

The trend of concentrations of Cr shows a similar pattern than established for the location Miklavž. Levels at Spodnja Ščavnica were relatively constant, with a slight increase in the rings formed from 1961-1970, decreased in the next 5-year sample and slowly increased till 1990. In the following years, a very pronounced increase, similar to one at Miklavž, was established. Strong correlations between Cr concentrations and traffic parameters were established, but the level of significance is somewhat lower in comparison with Miklavž (Table 26).

The trend of Zn and Ni, for which higher concentrations were measured in some of the samples from the last 17 years, could point to the conclusion that these elements tend to accumulate in the most outer rings. As Zn and Ni are essential elements, their distribution could be more affected by biological processes in the tree in comparison to other metals investigated in this study. However, trend of increase of both elements is less pronounced than in Miklavž (chapter 4.2.1.1 and Figure 25).

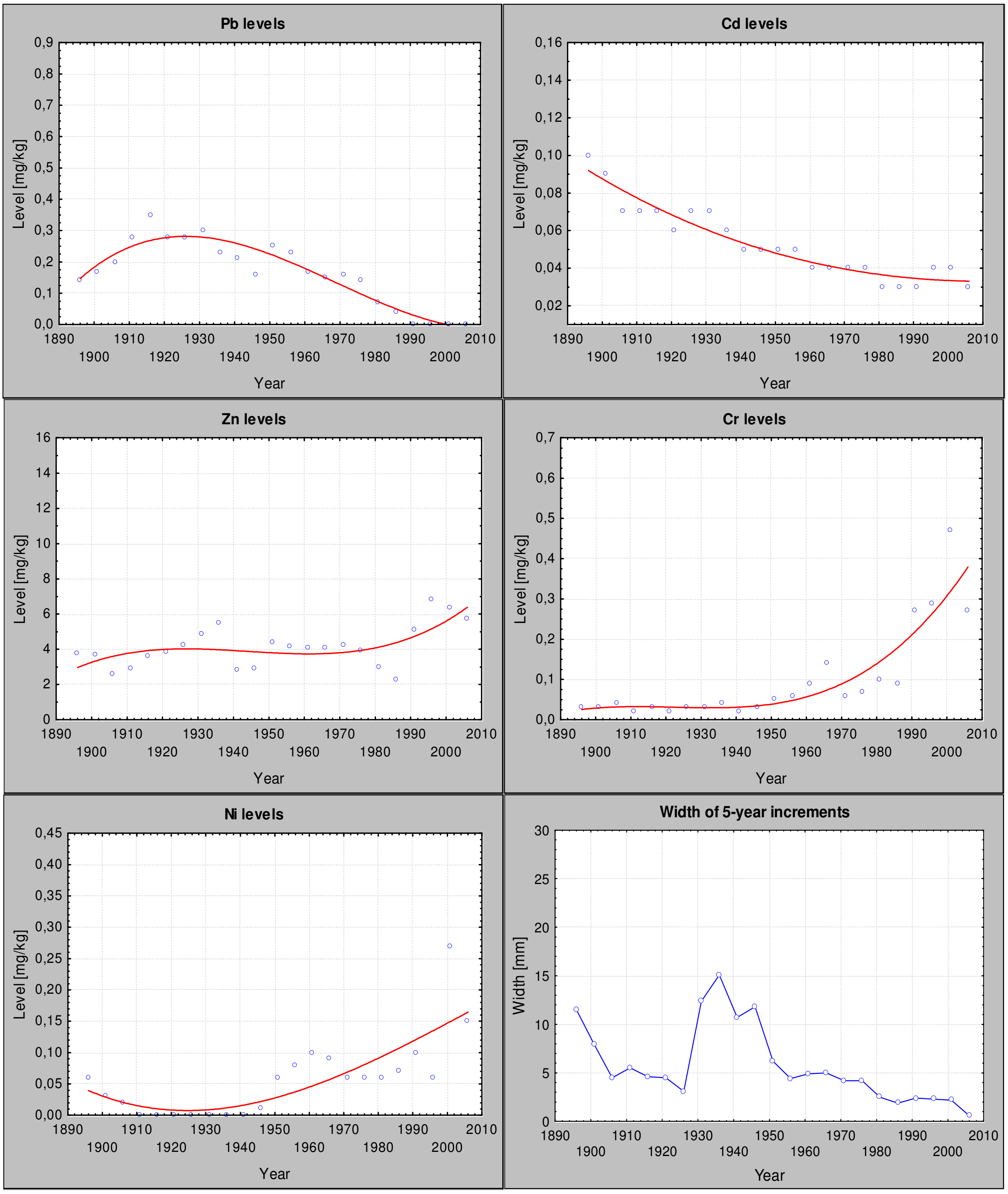

Figure 27: *Long-term temporal variability of heavy metal contents [mg/kg] and width of 5-year increments [mm] in Scots pine, Spodnja Ščavnica (period 1896 – 2007)*

4.2.2.2 Heavy metal contents in annual tree-rings of silver birch in the period 1990-2007

In silver birch from Spodnja Ščavnica (Figure 28) which, regarding results in location Miklavž, seems to be a better indicator of lead pollution as Scots pine, the trend of decrease of Pb levels started in the year 2000, some years later than in Miklavž, and the levels have been decreasing ever since. The explanation for a delay in the reduction in contents of Pb in the wood samples, that is established some years after the phase-out of leaded gasoline, might be the ability of humus and litter acting as a buffer (Aznar J-C, et al. 2008), which results in a certain time delay between changes in emissions and tree responses – tree-ring fixation of heavy metals. Also overall lower emission due to less traffic on this road section (and hence also smaller changes in studied period) may cause that the reduction is less apparent. It is interesting that although the concentrations begun to decrease at this location not before the year 2000, the absolute concentrations in this period (2000 – 2007) are very similar in Miklavž and Spodnja Ščavnica. In Miklavž the Pb content fell from 1.17 mg/kg in 2000, to 0.52 mg/kg in 2005, and to 0.24 mg/kg in 2007. In Spodnja Ščavnica the concentration in 2000 was 1.08 mg/kg, than 0.66 mg/kg in 2005, 0.51 mg/kg in 2006 and 0.52 mg/kg in 2007, respectively. This later reaction of the birch in Spodnja Ščavnica could point to the conclusion that was also a finding of some other authors (e.g. Patrick and Farmer, 2006) that trees are more suitable for the historical biomonitoring of heavy metals at locations with larger emissions.

However, it should also be emphasized that due to a younger birch sampled at this location, we do not have a record for the years before 1990, and it is also possible that a very young tree would react differently in the first couple of years of its life.

Similar as at the location Miklavž, we also tried to find any correlation between Pb contents in annual tree-rings of silver birch and assessed yearly emissions of Pb at this road section. At this location a strong positive correlation was established for time shift of 7 years ($r = 0.83$; $p < 0.001$), and for a time shift of 5 years also moderate positive correlation that could be considered as relevant. For a time shift of 3 years low correlation coefficient cannot be considered as relevant. On the contrary, no statistically significant correlations were found for scenario without any time shift (i.e. by comparing Pb contents and emissions in the same year). A greater time shift for this location could be due to the fact that the location is closest to the Hungarian boarder on the V. pan-European traffic corridor (Kiev – Venice) and could be influenced by a greater percentage of traffic from some Eastern European countries that phased out leaded gasoline some years later than Slovenia an also had higher maximal allowed content of Pb in leaded fuel. Correlation coefficients are presented in Table 18.

Table 18: *Correlations between assessed yearly emissions of Pb from road traffic and Pb levels in tree-rings of silver birch at location Spodnja Ščavnica (Pearson's "r" and "p" are presented)*

	N	**Emission (-0 years)**	**N**	**Emission (-3years)**	**N**	**Emission (-5years)**	**N**	**Emission (-7years)**
Spodnja Ščavnica	18	0.36	18	0.51	18	0.66	18	0.83
		NS		$p < 0.05$		$p < 0.01$		$p < 0.001$

N – Number of analysed pairs; NS - not significant

Levels of Cr have been increasing in the last years (since 2004), but similar concentrations are also found in the oldest rings (from 1988), so a clear trend of increase could not be established. Similar course of concentration trend is also found for Ni. No statistically significant correlation between traffic parameters and levels of Cr was found, except for moderate correlation with the number of heavy vehicles with r = 0.66 (Table 27). There are not many similarities between assessed Cr emissions (Figure 23) and Cr content in tree-rings of silver birch, except that the concentrations are rising in the samples from 2004 – 2007 but the differences in concentrations are much more pronounced than the differences in assessed Cr emissions for these years.

Cd contents in tree-rings of silver birch from this location were the highest in the oldest couple of tree-rings (period 1990-1993) followed by a well-pronounced decrease in the year 1994. A similar (although less pronounced) pattern at the beginning of the growth period (period 1978-1982) is also recorded in silver birch from Miklavž. This may point to a conclusion that silver birch is more susceptible to Cd uptake in the beginning of its growth period.

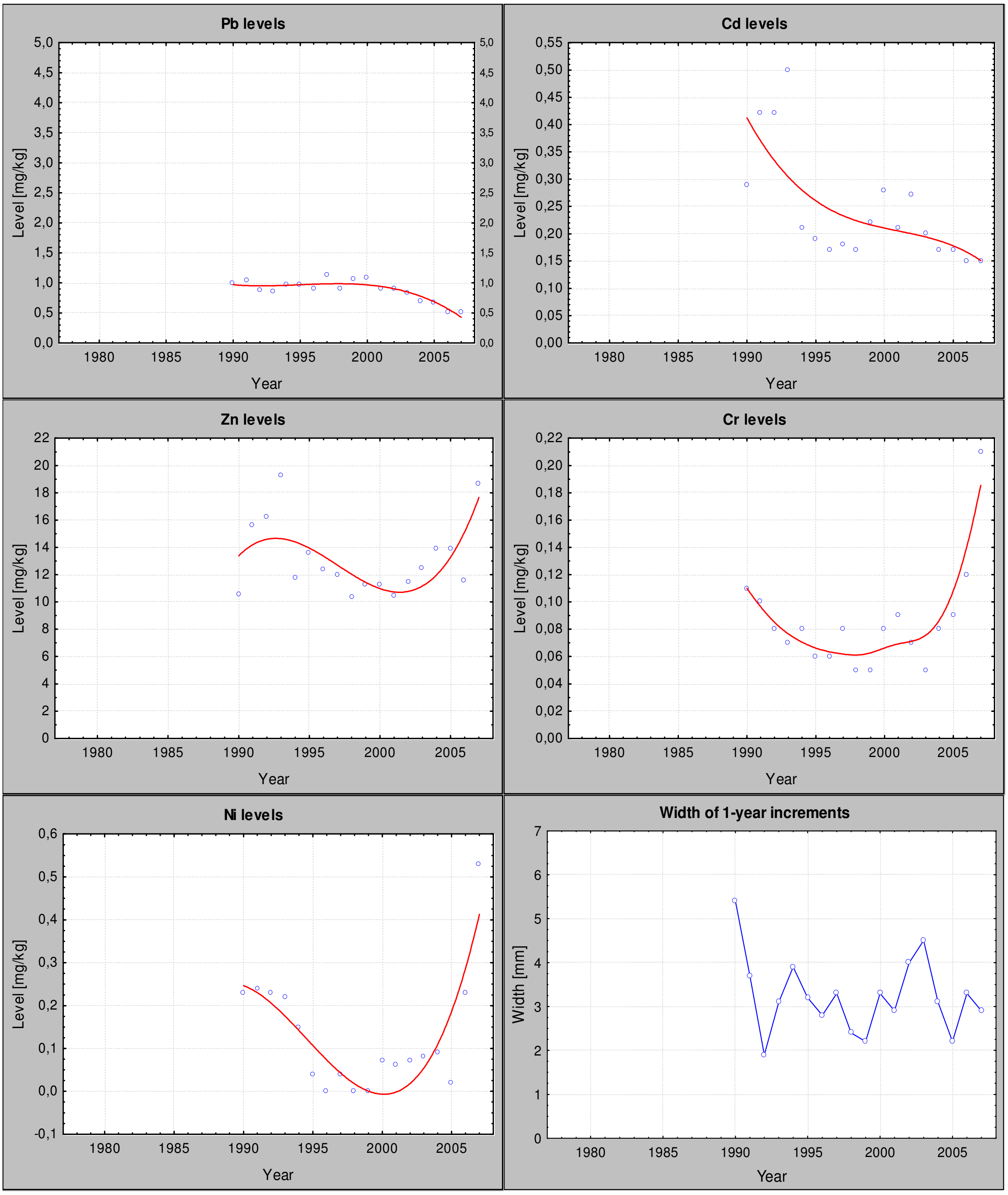

Figure 28: *Variability of heavy metal content in annual tree-rings [mg/kg] and width of 1-year increments [mm] of silver birch, Spodnja Ščavnica in the last two decades*

4.2.3 Study site Vrh nad Želimljami

4.2.3.1 Heavy metal contents in 5-years increments of Scots pine in the period 1928-2007

The concentrations of Pb in Scots pine at location Vrh nad Želimljami (Figure 29) are the highest and are about one order of magnitude higher compared to the other studied sites. The concentrations in the years after 1981 have been rising and the peak was reached in the sample for the period 1996-2001, which is followed by a decrease in the last two samples. The decrease in the last two samples (2001-2007) is recorded later than it would be expected if we compare Pb levels with the decrease of Pb emissions from road transport in RS (Figure 2) where the most drastic decrease was assessed in the years from 1994-1996. However some similarities of both trends are seen, that is an increase in the 1980 and a decrease some years after the phase-out of leaded gasoline.

In comparison to assessment of emissions from the road Škofljica – Rašica (Figure 21), where a decrease in the early 1980s, followed by a relatively low increase from 1985-1991, and also a low decrease till 1995 followed by a drastic decrease in the following years was assessed, some similarity could only be found in the decrease of Pb levels in the last two tree-ring samples (2001 – 2007).

The Pb concentrations at this location are very high in comparison to other two locations, which couldn't be explained only by local emissions from one road, which should emit quantities of Pb similar to those at Spodnja Ščavnica. Because the area of the sampled tree is not densely populated, the possible source of Pb could be a greater pollution in a broader region of the Ljubljana basin, which generates pollution from other sources (e.g. local fireplaces and point emission sources). This explanation is less likely regarding the prevailing NE and SW winds in Ljubljana. Another explanation is that the Pb concentrations were influenced by other factors, for example as a result of much greater mobilization of this element in the soil at a certain time period. A greater mobilization could be due to the decrease of soil pH. Regarding Strait and Stumm (1993), the uptake of Pb is promoted by anaerobic conditions (e.g. by flooding), low pH, low organic levels, low phosphate concentrations. However, no data on soil characteristics were available for the purpose of this study, in which the focus was to establish temporal trends of environmental pollution merely by using tree-rings, as well as to obtain a quick idea whether tree-rings could be useful historical bioindicator of ambient pollution in the vicinity of roads. But it is clear that for following studies, soil characteristics, should also be taken into consideration.

A very clear trend of decrease of Cd levels is established for the whole period of growth. The trend of decrease at this location is the most pronounced, but also at other two locations a clear trend of decrease is obvious for this element.

Similar as at other locations and trees, the increase in concentrations of Cr is evident, but only in the last two samples. Strong to moderate correlations at $p < 0.05$ were established between all traffic parameters and Cr concentrations except with the volume of heavy vehicles (Table 26).

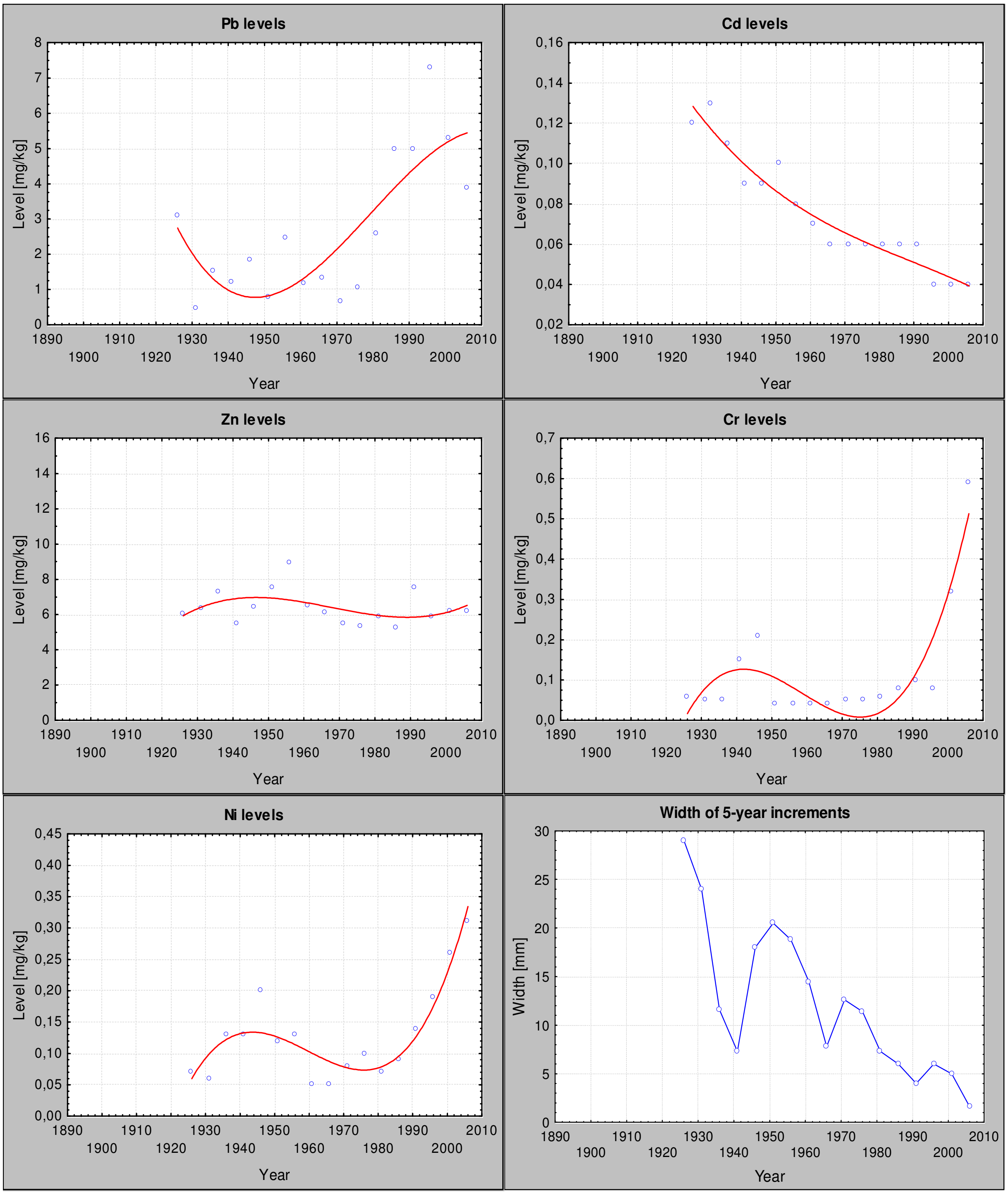

Figure 29: *Long-term temporal variability of heavy metal concentrations [mg/kg] and width of 5-year increments [mm] in Scots pine in Vrh nad Želimljami (period 1928 – 2007)*

4.2.3.2 Heavy metal contents in annual tree-rings of trembling poplar in the period 1981-2007

In trembling poplar that was sampled at location Vrh nad Želimljami (Figure 30), there is no decrease in contents of Pb in tree-rings that grew after the phase-out of lead in 1995. The highest levels were measured in the oldest rings that grew in the beginning of 1980’s, followed by a rapid decrease till the beginning of the 1990’s. After that time the levels remained more or less constant. The mean concentrations in the period 1981 – 1989 at this location are about 4-folds higher than the mean measured in Miklavž (due to a younger tree sampled at Spodnja Ščavnica no data for this period is available). In the period 2000-2007, the mean concentrations at all three locations are much more similar. However, it should be stressed that silver birch was used as a key species in other two locations; therefore this comparison is rather of only informative value.

The decrease of Pb levels in the 1980’s corresponds with the time in which also the assessment of emissions from the road Škofljica – Rašica shows some decrease; however, lack of the decrease in Pb levels after the phase out of leaded gasoline points to a conclusion that Pb contents in tree-rings at this location were largely influenced by some other sources of Pb contamination. Higher Pb contents point to a conclusion that the emissions from this road section did not represent an important source of Pb pollution in the area. Therefore, due to a relatively small contribution from the road emissions, the reduction of traffic-related emissions could not be well pronounced in the tree-ring contents of Pb. The same conclusion regarding the probable sources of Pb in tree-rings is also suggested regarding the trend of Pb levels in Scots pine from this location (4.2.3.1). The variability of contents in the whole period and between consecutive years is also much higher than in the trees sampled at other two locations. This could point to conclusion that due to higher levels in the earliest years the possible radial transport in this tree masked the influence of Pb emitted from road traffic (the total concentrations in the latest years are similar to those found at other two locations, where a reduction in the last years could be established). The possible other sources of Pb at this location could be the pollution in a broader region of Ljubljana basin, due to emissions from individual heating facilities and emissions from some point sources (e.g. remote heating and thermal power plant in Ljubljana - TE-TOL). The decrease of Pb in the 1980's could be due to the remediation measures made on point sources in Ljubljana basin that could have the dominant effect on (high) Pb levels in tree-rings at this location. The correlations between Pb contents and some indicators of pollution could support this conclusion. Especially for dust emissions from TE-TOL a strong correlation ($r = 0.84$; $p < 0.001$) was found, for other parameters (SO_2 emissions from TE-TOL, emissions of SO_2 in RS, imissions of SO_2 measured at Ljubljana–Bežigrad meteorological station) also some moderate correlation was established (Table 30, Table 32).

When comparing Pb content in annual tree-rings of trembling poplar with assessed yearly traffic emissions of Pb at this road section (by the same approach as explained for silver birch in location Miklavž), at this location correlations have been established at $p<0.01$ for no time shift (-0 years) and for time shift of (-)3 years but the coefficient of positive correlation are rather low and all around $r = 0.5$ that shouldn't be considered as relevant (Table 17).

Table 19: *Correlations between assessed yearly emissions of Pb from road traffic and Pb contents in annual tree-rings of trembling poplar at location Vrh nad Želimljami (Pearson's correlation coefficients r and p are presented)*

	N	Emission (-0 years)	N	Emission (-3 years)	N	Emission (-5 years)	N	Emission (-7 years)
Želimlje	27	0.51	25	0.52	23	0.53	21	0.52
		p < 0.01		p < 0.01		p < 0.05		p < 0.05

N – Number of analysed pairs

Sharma and Dubey (2005) found that high levels of Pb in the soil cause imbalances of mineral nutrients in growing plants, Pb can block the entry of cations (K^{+}, Ca^{2+}, Mn^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}). From the graphs for location Vrh nad Želimljami (Figure 30) it can be seen that the time of decrease of Pb levels corresponds with the increase of Zn levels in trembling poplar, but such a decrease is not evident in Scots pine (Figure 29). The graph for trembling poplar shows that Pb could have an influence on plant cations uptake. This influence is not pronounced on the both other locations where Pb levels in tree-rings were much lower. Nevertheless, the correlations between Pb levels in the whole sampling period and concentrations of other HM do not support the assumption that Pb influenced the uptake of other metals (Table 22, Table 25).

The trend of decreasing Pb concentrations in fast growing trees is visible at all three locations. The decrease is most accordant with expectations in tree-rings of silver birch from Maribor. In tree-rings from silver birch from Spodnja Ščavnica the decrease took place some years after the drastic reduction in emissions from road traffic and in tree-rings from trembling poplar from Vrh nad Želimljami some years prior to this reduction. There are no other similarities in the trends of Pb levels in Scots pines, except that the highest levels in Maribor and Vrh nad Želimljami were measured in the last 5 samples (years 1986-2007). In Spodnja Ščavnica which is the only location where a well pronounced Pb decrease in Scots Pine was recorded, the lowest levels were recorded in the last samples, in the years from 1991-2007 even below the limit of quantification. It is also visible that higher concentrations of lead are recorded in fast growing trees (birch, poplar) than in Scots pine. This could be due to the fast growing characteristics of these species (the fast growth could generate faster absorption of trace elements), depth, distribution and density of the trees roots and most likely due to the different uptake characteristics of different tree species (root uptake, uptake trough the bark, uptake trough the leaves/needles).

In trembling poplar at location Vrh nad Želimljami, Cr levels also seem to rise in the last years. Correlations with all traffic parameters seem to be positive but the coefficients are rather low (r = 0.41-0.44) and shouldn't be considered as very relevant (Table 27).

The overall trend of Cr contents in tree-rings and the trend of assessed emissions (Figure 24) show some similarities. The highest contents of Cr in some of the trembling poplar samples of the last years (2004, 2005 and 2007) corresponds to the highest assessed emissions, but the differences in individual samples between sequential years are sometimes unusual. Some very high levels were recorded in the years 1983, 1996 and 1997 and lower level in the year 2006 that could question the accuracy of the established trend of increase in the last years. It is important to state that the differences in assessed emissions are not as drastic as the differences in measured tree-ring levels which is unusual (one would expect that the differences in emissions would be less pronounced in tree-rings). An interesting issue is that (much) higher levels in tree-rings from the years 1996-1997 come in about the same years when a small peak in emissions has been assessed (1998-1999), but this is most likely a coincidence.

The variability of HM contents between consecutive years, especially of Cr and Ni, in trembling poplar sampled at Vrh nad Želimljami is much higher than in the trees sampled at other two locations. This is somehow unusual but relatively large differences are also recorded in some other studies, also when analysing 5-year samples that mask the differences between consecutive years. For example when analysing 5-year samples Watmough et al. (1999) found large differences for Ni and Zn in sacred fir; Watmough et al. (1998) for Cr and Cd in sugar maple; Patric and Farmer (2006) for Pb, also Butkus and Beltranaite (2007) found large differences between consecutive (3-year) samples of birch for Cr and Nabais et al. (1999) in 1-year samples of oak tree for Cd. The cause of differences could also be an experimental error (for example error in dilution, quantitative transfer, weighing) but this is not very likely because the differences are not recorded in the same years.

A trend of increase in Cr concentrations is evident at all locations. This is somehow surprising because of it's relatively lower total emitted quantities in comparison to Cu, Zn and Pb (Winther and Slento, 2010), but it is nevertheless the fourth element regarding its quantities emitted from road traffic. Its influence from the traffic could be more pronounced due to the fact that it doesn't have such historical peaks (as in the case of Pb) and it is not an essential element to plants (as Zn). Due to the findings of this study Cr could be considered as the most important indicator of traffic influence in the road environment; indeed, it seems that tree-ring analysis may be particularly useful for determining historical trends of Cr pollution.

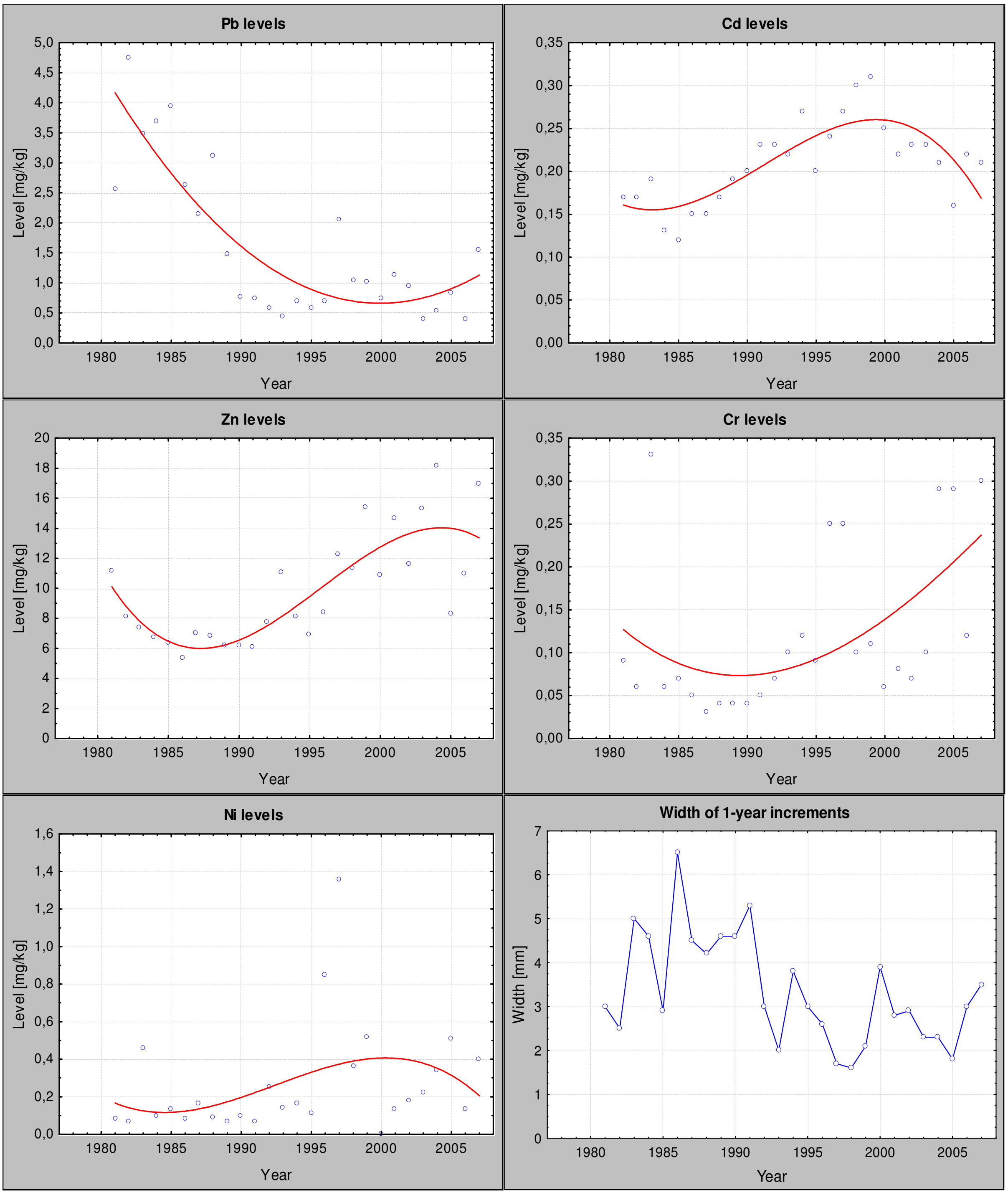

Figure 30: *Variability of heavy metal levels [mg/kg] and width of 1-year increments [mm] in trembling poplar, Vrh nad Želimljami (period 1981-2007)*

4.3 Comparison among heavy metal levels in tree-rings and influence of increment width

Different HM could come from the same sources and therefore, their content in tree-ring may follow a similar pattern. Also as discussed in chapter 4.2.3.2, some heavy metals may influence the uptake of others, so correlations between elements may exist. Tree-ring width is also a factor that may have an influence on HM contents in the wood. Wider rings could contain lower levels of HM due to the dilution effect, on the other hand during more intensive growth; the trees take up more nutrients and potentially also more contaminants.

To test the correlation between levels ob different HM in tree-ring samples and the correlation between levels and increment width Pearson's correlation coefficients (r) have been calculated. The results for each site and tree species are presented in the following tables (Table 20; Table 21; Table 22; Table 23; Table 24; Table 25).

The coefficients of correlation between different HM in fast growing trees are rather low and mostly on the border or bellow the level at which we could describe that the correlation is relevant ($r = 0.6$). Only between Cr and Ni a strong positive correlation was established ($r = 0.87$. $p < 0.001$). Also between Zn and Pb no correlation has been found, not even at location Vrh nad Želimljami where the graphed data pointed to a possible negative correlation between these two elements.

There is no unambiguous conclusion possible regarding the correlation of tree-ring width and heavy metal concentrations. Most of the results show that correlation is not statistically significant (16/30), and only 1 out of 30 results shows a strong correlation (Cd and 5 year increment width in Scots pine from Vrh nad Želimljami). Also the results for negative correlation that are statistically significant show low coefficients, and only 1 comparison out of 30 exceeds the limit at which the correlations could be considered as relevant ($r = -0,66$; $p < 0.01$ for Pb and 5-year increment width in Scots pine from Miklavž).

Cr and Ni are strongly correlated (r = 0.87 – 0.89; p < 0.001) in all pine trees and in silver birch from Spodnja Ščavnica. The correlation is also positive in silver birch from Vrh nad Želimljami (r = 0.68; p < 0.001). The positive correlation of these two elements is interesting and could point to a conclusion that both metals come from the same source. Although the reason might be also contamination with the tools used for collection and preparation of the samples (increment borer, chisel), it should be emphasised that also the emissions of both metals from the traffic have similar origin. Indeed, both Cr and Ni are attributed to the wear of engine parts (e.g. manifold, valves, and shafts, respectively) (Gkatzoflias et al., 2011).

Table 20: *Correlation between levels of different HM and increment width in silver birch at location Miklavž (N = 30; Pearson's "r" and "p" are presented)*

Birch	Cd	Zn	Cr	Ni	Increment width
Pb	0.21^{NS}	$-0{,}018^{NS}$	-0.66^{***}	-0.38^{*}	0.43^{*}
Cd		0.61^{***}	-0.12^{NS}	$-0{,}06^{NS}$	-0.01^{NS}
Zn			0.11^{NS}	0.53^{**}	-0.51^{**}
Cr				0.40^{*}	-0.39^{*}
Ni					-0.53^{*}

* p < 0.05; ** p < 0.01; *** p < 0.001; NS – not statistically significant

Table 21: *Correlation between levels of different HM and increment width in silver birch at location Spodnja Ščavnica (N = 18; Pearson's "r" and "p" are presented)*

Birch	Cd	Zn	Cr	Ni	Increment width
Pb	0.33^{NS}	-0.37^{NS}	-0.57^{*}	-0.47^{*}	0.20^{NS}
Cd		0.49^{*}	-0.12^{NS}	0.26^{NS}	0.06^{NS}
Zn			0.43^{NS}	0.65^{**}	-0.25^{NS}
Cr				0.87^{***}	0.07^{NS}
Ni					0.17^{NS}

* p < 0.05; ** p < 0.01; *** p < 0.001; NS – not statistically significant

Table 22: *Correlation between levels of different HM and increment width in trembling poplar at location Vrh nad Želimljami (N = 27; Pearson's "r" and "p" are presented)*

Poplar	Cd	Zn	Cr	Ni	Increment width
Pb	-0.62^{***}	-0.37^{NS}	-0.10^{NS}	-0.08^{NS}	0.28^{NS}
Cd		0.49^{**}	0.15^{NS}	0.40^{*}	-0.43^{*}
Zn			0.42^{*}	0.28^{NS}	-0.58^{**}
Cr				0.68^{***}	-0.32^{NS}
Ni					-0.45^{*}

* p < 0.05; ** p < 0.01; *** p < 0.001; NS – not statistically significant

Table 23: *Correlation between levels of different HM and increment width in Scots pine at location Miklavž (N = 20; Pearson's "r" and "p" are presented)*

Pine	Cd	Zn	Cr	Ni	Increment width
Pb	-0.66**	0.80***	0.90***	0.87***	-0.66**
Cd		-0.28^{NS}	-0.55**	-0.60**	0.53*
Zn			0.59**	0.69***	-0.56*
Cr				0.89***	-0.57**
Ni					-0.45*

* p < 0.05; ** p < 0.01; *** p < 0.001; NS – not statistically significant

Table 24: *Correlation between levels of different HM and increment width in Scots pine at location Spodnja Ščavnica (N = 24; Pearson's "r" and "p" are presented)*

Pine	Cd	Zn	Cr	Ni	Increment width
Pb	0.60**	-0.34^{NS}	-0.78***	-0.68***	0.33^{NS}
Cd		-0.16^{NS}	-0.58**	-0.57**	0.27N^{S}
Zn			0.63***	0.37^{NS}	-0.19^{NS}
Cr				0.87***	-0.29^{NS}
Ni					-0.14^{NS}

- p < 0.05; ** p < 0.01; *** p < 0.001; NS – not statistically significant

Table 25: *Correlation between levels of different HM and increment width in Scots pine at location Vrh nad Želimljami (N = 17; Pearson's "r" and "p" are presented)*

Pine	Cd	Zn	Cr	Ni	Increment width
Pb	-0.57*	-0.06^{NS}	0.33^{NS}	0.52*	-0.50*
Cd		0.27^{NS}	-0.41^{NS}	-0.44^{NS}	0.82***
Zn			-0.12^{NS}	-0.08^{NS}	0.28^{NS}
Cr				0.87***	-0.45^{NS}
Ni					-0.45^{NS}

* p < 0.05; ** p < 0.01; *** p < 0.001; NS – not statistically significant

4.4 Comparison of traffic parameters and levels of Cr in tree-rings

From the graphs presented in chapter 4.1 it seems that Cr levels in tree-rings correspond with the increasing traffic loads. The concentrations of chromium are increasing in all three locations in pine and both fast growing tree species. Because such unambiguous trend is not evident for other studied metals and because Cr as a non-essential element with no known historical peaks in emissions (as in the case of Pb) could be an indicator of traffic pollution, only Cr levels were tested for correlation with traffic parameters. Correlations are presented in Table 26 for Scots pine, and for fast growing species in Table 27.

The Cr levels in tree-rings correspond well to the increasing traffic loads in the last years. For Scots pine, even though the number of samples that could be compared to road traffic parameters is relatively low (due to the analysis of 5-year increments), strong correlations were established at all three locations with all traffic parameters except with heavy vehicles. For fast growing trees (i.e. for comparison, made on a yearly basis), the correlation coefficients at statistically significant level (where they do exist) are low and could not be considered as very relevant.

Due to the existence of positive correlations of Cr levels in tree-rings of Scots pine with traffic parameters at all locations after the phase-out of leaded gasoline, Cr contents in tree-rings of Scots pine seem to be an important indicator of traffic pollution.

Since Cr is an element that is not source specific and the main source of its emissions form road traffic is abrasion of mechanical parts, the relevance of these findings should be tested in further studies. However, we can not absolutely eliminate a possibility that a source of Cr in analysed increment samples could also be contamination with metal tools that were used for sampling and preparation of samples as described in chapter 4.3.

Table 26: *Correlation (Pearson's "r") between traffic parameters and levels of Cr in long-living trees (Scots pine)*

Traffic parameters	Levels of Cr in Scots pine								
	N	Miklavž		N	Spodnja Ščavnica		N	Vrh nad Želimljami	
Vehicles RS	7	0.85	*	7	0.83	*	7	0.84	*
Vehicles ALL		0.88	**		0.80	*		0.77	*
Vehicles Light		0.88	**		0.89	**		0.78	*
Vehicles Heavy		0.27	NS		0.56	NS		0.11	NS

N – Number of analysed pairs; * p < 0.05; ** p < 0.01; NS – not statistically significant
Vehicles RS – total number of registered vehicles in Slovenia; Vehicles ALL, Light, Heavy – traffic volume on relevant road sections

Table 27: *Correlation (Pearson's "r") between traffic parameters and levels of Cr in fast growing trees (silver birch and trembling poplar)*

Traffic parameters	Levels of Cr in Silver birch/Trembling poplar								
	N	Miklavž		N	Spodnja Ščavnica		N	Vrh nad Želimljami	
Vehicles RS	30	0.55	**	18	0.32	NS	27	0.44	*
Vehicles ALL		0.56	**		0.40	NS		0.41	*
Vehicles Light		0.53	**		0.08	NS		0.41	*
Vehicles Heavy		0.44	*		0.66	**		0.04	NS

N – number of analysed pairs; * p < 0.05; ** p < 0.01; NS – not statistically significant
Vehicles RS – total number of registered vehicles in Slovenia; Vehicles ALL, Light, Heavy – traffic volume on relevant road sections

4.5 Comparison of Pb and Cd levels in tree-rings with emissions of Pb and Cd in Slovenia

The data on the overall emissions of Pb and Cd in Slovenia and their share resulting from road traffic were assessed for the purpose of submission under the UNECE Convention on Long-range Transboundary Air Pollution in Slovenian's Annual Emissions Inventory Report (IIR). The data used in this study was taken from the publication Informative inventory report 2010 for Slovenia (Rode et al., 2010). Data for Pb from the traffic were available for period after the year 1980 and the data for total Pb emissions in Slovenija for the period after 1990.

To test the correlation between Pb (Table 28) and Cd (Table 29) levels in tree-ring samples of fast growing trees with the emissions of these two elements in Slovenia, Pearson's correlation coefficient (r) was used.

As we would expect because Pb from the traffic formed a vast majority of the overall emissions of this element, a similar pattern between the two parameters of emissions (emissions of Pb from the traffic in RS and overall emissions of Pb in RS) is evident. For Pb, high correlations between both emissions of this element in Slovenia (from the traffic and overall emissions of Pb) were established for the sampling site Miklavž, but not for the other two sites where no statistically significant correlation could be established. A discussion about possible reasons for the lack of correlation is given in the chapter 4.2, where the trends of changes in concentrations are described.

For Cd originated from the traffic moderate negative correlation was found for the location Miklavž and strong negative correlation for Spodnja Ščavnica; on the contrary, moderate positive correlation was found at Vrh nad Želimljami. Regarding the opposing results and because Cd from the traffic formed only a small proportion of the total emitted quantities of this element in RS the chance that the positive correlations is relevant is very slim. For the total emitted quantities in RS only at the site Spodnja Ščavnica some (moderate) correlation was found. Therefore the levels of Cd in tree-rings in trees near roads don't seem to reliably reflect the emitted quantities of this HM from the traffic.

Table 28: *Correlation between emissions of Pb in Slovenia and its levels in tree-rings of fast growing trees (silver birch and trembling poplar)*

Emissions	**Levels of HM in Silver birch/Trembling poplar**								
	N	**Mi_Pb**	**p**	**N**	**SS_Pb**	**p**	**N**	**Ze_Pb**	**p**
RS_Pb	18	0.90	<0.001	18	0.38	NS	18	-0.28	NS
RS_Traffic_Pb	28	0.88	<0.001	17	0.38	NS	27	0.32	NS

N – number of analysed pairs; NS – not statistically significant; Mi - Miklavž; SS - Spodnja Ščavnica; Z - Vrh nad Želimljami

Table 29*: Correlation between emissions of Cd in Slovenia and its concentration in tree-rings of fast growing trees (silver birch and trembling poplar)*

Emissions	**Levels of HM in Silver birch/Trembling poplar**								
	N	**Mi_Cd**	**p**	**N**	**SS_Cd**	**p**	**N**	**Ze_Cd**	**p**
RS_Cd	18	0.07	NS	17	0.53	<0.05	18	-0.12	NS
RS_Traffic_Cd	28	-0.69	<0.001	17	-0.80	<0.001	27	0.58	<0.01

N – number of analysed pairs; NS – not statistically significant; Mi - Miklavž; SS - Spodnja Ščavnica; Z - Vrh nad Želimljami

4.6 Comparison of Pb and Cd levels in tree-rings with indicators of pollution

As discussed previously (chapter 4.2), there are other possible sources that may have an influence on HM levels in tree-rings. Although gasoline combustion was the source to which the majority of emitted Pb was attributed, beside metal production processes also coal combustion was one of the sources of Pb entering the atmosphere. Pb from coal combustion is mainly bound to particles and released to the atmosphere in the form of fly ash (Final review UNEP). The emissions of fly ash were reduced with the introduction of cleaner fuels and flue gas purifying systems on point emission sources and with the use of alternative technologies in residential combustion (e.g. gas, oil). In the previous decades also pollution with SO_2 mainly declined due to the introduction of quality fuels and mitigation measures on point emission sources. Because SO_2 emission and imissions data were available for a relatively long period of time and because in a previous study (Poličnik et al., 2007) highly positive correlation was found between Pb contents in tree-rings (Scots pine and silver birch) and SO_2 emissions from the Thermal power plant of Šoštanj and also with SO_2 imissions at the sites of sampling, exsistence of these correlations was also tested in this study.

To test the exsistence of correlation between Pb (Table 30) and Cd (Table 31) contents in tree-ring samples with indicators of general pollution in the period of their growth, data on HM contents in tree-rings were compared with data on emissions of SO_2 in Slovenia and with available imissions data (index of pollution with acid gasses ($I(SO_2)$)) at Ljubljana Bežigrad (for site Vrh nad Želimljami) and at Maribor-centre (for site Miklavž)). Unfortunatelly, imission data were available for locations relatively remote to sampling sites (Vrh nad Želimljami – Ljubljana Bežigrad: 18 km; Miklavž – Maribor centre: 4 km); however, the comparisons were made with the assumption that the trends are similar in a broader environment.

Calculated emissions of SO_2 were available for the whole period (1980-2007) (Rode et al., 2010), and the data for imissions ($I(SO_2)$) for the period from 1980 – 1997 (Figure 31 and Figure 32). The correlations with imissions were not calculated for

Spodnja Ščavnica because there was no available data. For the comparison Pearson's correlation coefficients (r) were calculated.

For the site Vrh nad Želimljami also correlations with SO_2 and dust emissions from TE-TOL (Figure 33) were calculated. The results are presented in Table 32.

Positive correlation between Pb concentrations and imissions of ($I(SO_2)$) as an indicator of general pollution in Ljubljana was found for the site Vrh nad Želimljami, but no correlation could be established between concentrations in Miklavž and imissions in Maribor – centre. Positive correlations between concentrations of Pb and total emissions of SO_2 in RS were found for all three locations and for Vrh nad Želimljami also with emissions of SO_2 from TE-TOL. For Vrh nad Želimljami also strong positive correlation with dust emissions from TE-TOL was found ($r = 0.84$; $p<0.001$). Positive correlations for all four indicators of pollution for Vrh nad Želimljami could point to a conclusion that the concentrations of Pb in tree-rings at this location were influenced by regional pollution in Ljubljana basin as discussed in the chapter about the trends of changes in concentrations (chapter 4.2.3.2). The correlations between Cd concentrations and pollution indicators (imissions and emission) were positive for the site Miklavž, but negative for the site Vrh nad Želimljami. It doesn't seem very likely that the correlations between Cd and SO_2 are relevant in the assessment of trends of this element in tree-rings, because the Cd emissions followed quite a different pattern than the emissions of SO_2. Moreover, contrary to Pb which is rather very immobile in the soil, uptake of Cd from soil to roots and following transportation along the tree may be very high (Kabata-Pendias, 2004), which importantly mask the influence of Cd annual emissions on Cd levels in tree-rings.

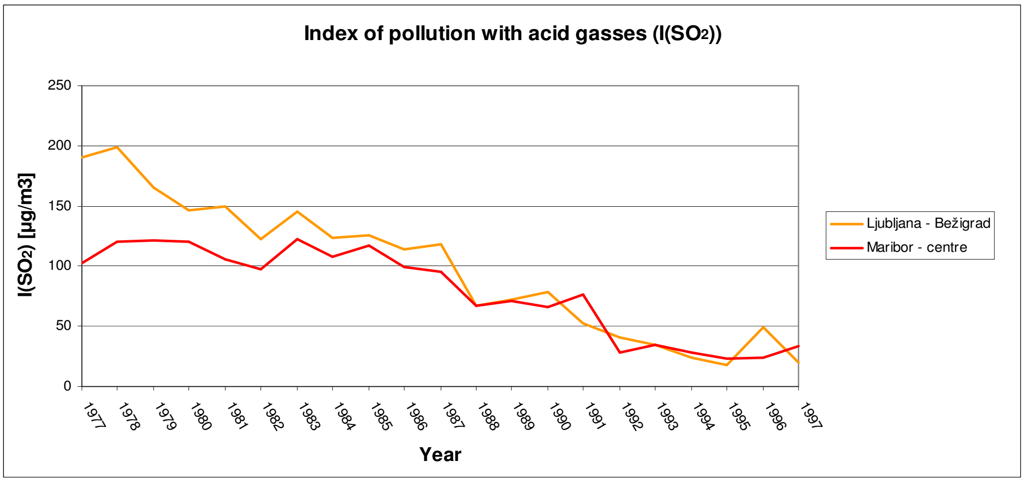

Figure 31: *Trend of imissions (as index of air pollution with acid gases ($I(SO_2)$) for Ljubljana - Bežigrad and Maribor – centre (data from: Onesnaženost zraka v Sloveniji v letu 1997)*

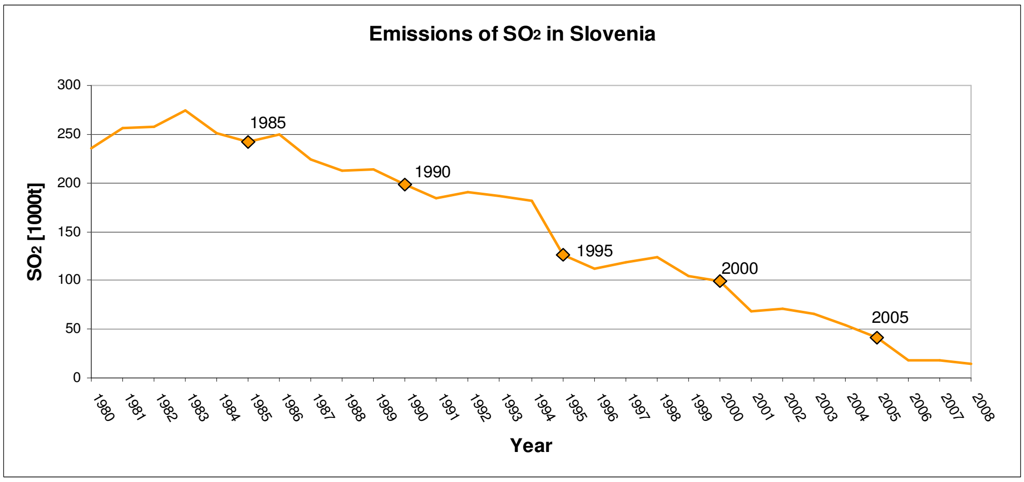

Figure 32: *Total emissions of SO_2 in Slovenia (data from Rode et al., 2010)*

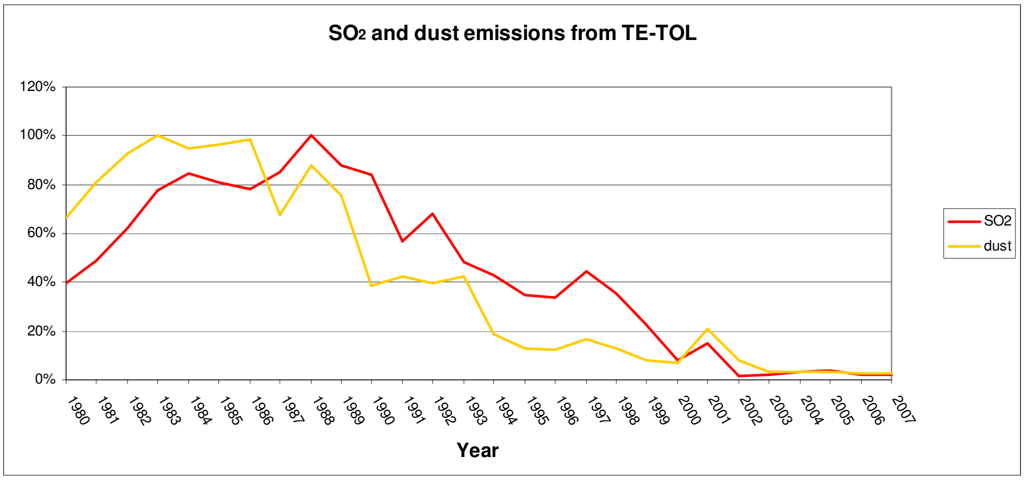

Figure 33: *Trend of SO_2 and dust emissions from TE-TOL (data from Pregledi proizvodnje in emisij 1980 – 2008. TE-TOL)*

Table 30: *Correlation between levels of Pb in tree-rings and imissions ($I(SO_2)$) and emissions of SO_2 in Slovenia*

Emissions/ Imissions	Levels of HM in silver birch/trembling poplar								
	N	Mi_Pb	p	N	SS_Pb	p	N	Z_Pb	p
Imission_SO_2	18	0.06	NS	/	/	/	17	0.77	<0.001
RS Em_SO_2	28	0.82	<0.001	18	0.66	p<0.01	27	0.69	<0.001

N – number of analysed pairs; NS – not statistically significant; Mi - Miklavž; SS - Spodnja Ščavnica; Z - Vrh nad Želimljami

Table 31: *Correlation between levels of Cd in tree-rings and imissions ($I(SO_2)$) and emissions of SO_2 in Slovenia*

Emissions/ Imissions	Levels of HM in silver birch/trembling poplar								
	N	Mi_Cd	p		SS_ Cd	p		Z_Cd	p
Imission_SO_2	18	0.72	<0.001	/	/	/	17	-0.79	<0.001
RS Em_SO_2	28	0.62	<0.001	18	0.70	<0.01	27	-0.49	<0.01

N – number of analysed pairs; Mi - Miklavž; SS - Spodnja Ščavnica; Z - Vrh nad Želimljami

Table 32: *Correlation between concentration of Cd and Pb and emissions of SO_2 and dust from TE-TOL for location Vrh nad Želimljami*

Emissions	Levels of HM in trembling poplar					
	N	Z_Pb	p	N	Z_Cd	p
TE-TOL_SO_2	27	0,60	<0.001	27	-0,50	<0.01
TE-TOL_dust	27	0,84	<0.001	27	-0,70	<0.001

N – number of analysed pairs; Z - Vrh nad Želimljami

4.7 Comparison of Pb and Cd levels in tree-rings with other Slovene studies

To compare the trends of Pb and Cd contents in tree-rings at studied road locations, with the results obtained at other locations in Slovenia, the data from the research conducted by Poličnik et al. (2009) was used. The comparison of trends of Pb and Cd contents in Scots pine tree-rings is presented for the locations at Upper Meža valley, as a heavily polluted area with history of Pb mining and smelting and for a reference location in Kočevje region as a non-polluted area.

Pb emissions from mining and smelting are a well-known source of pollution with this heavy metal. Upper Meža valley is the most polluted area in Slovenia and maybe also in Europe. The first document about Pb mining is from the year 1424, and after the joining of small mines, the year 1893 is considered as the beginning of mining and smelting operation in this area (SVO RS, 2009). The pollution and its effect have been discussed in many studies (e.g. Pokorny, 2000; Pokorny and Ribarič-Lasnik, 2000; Pokorny et al., 2009; Al-Sayegh-Petkovšek and Pokorny, 2011; Ribarič-Lasnik et al., 1999). The locations of sampling at Upper Meža valley are Pikovo, Kavšakov vrh and Peca.

The comparison of trends of Pb levels from a heavily polluted Upper Meža valley (Pikovo, Kavšakov vrh and Peca; Poličnik et al., 2009) and those from road locations (Figure 34) shows that roadside locations (Miklavž and Spodnja Ščavnica) are much less polluted than the environment near historical lead smelting operations. The levels at Vrh nad Želimljami are more comparable but generally lower then at the heavily polluted sites.

Also the concentrations of Cd are lower than those at locations Kavšakov vrh and Peca. At Pikovo in the Upper Meža valley are a bit lower than at roadside locations.

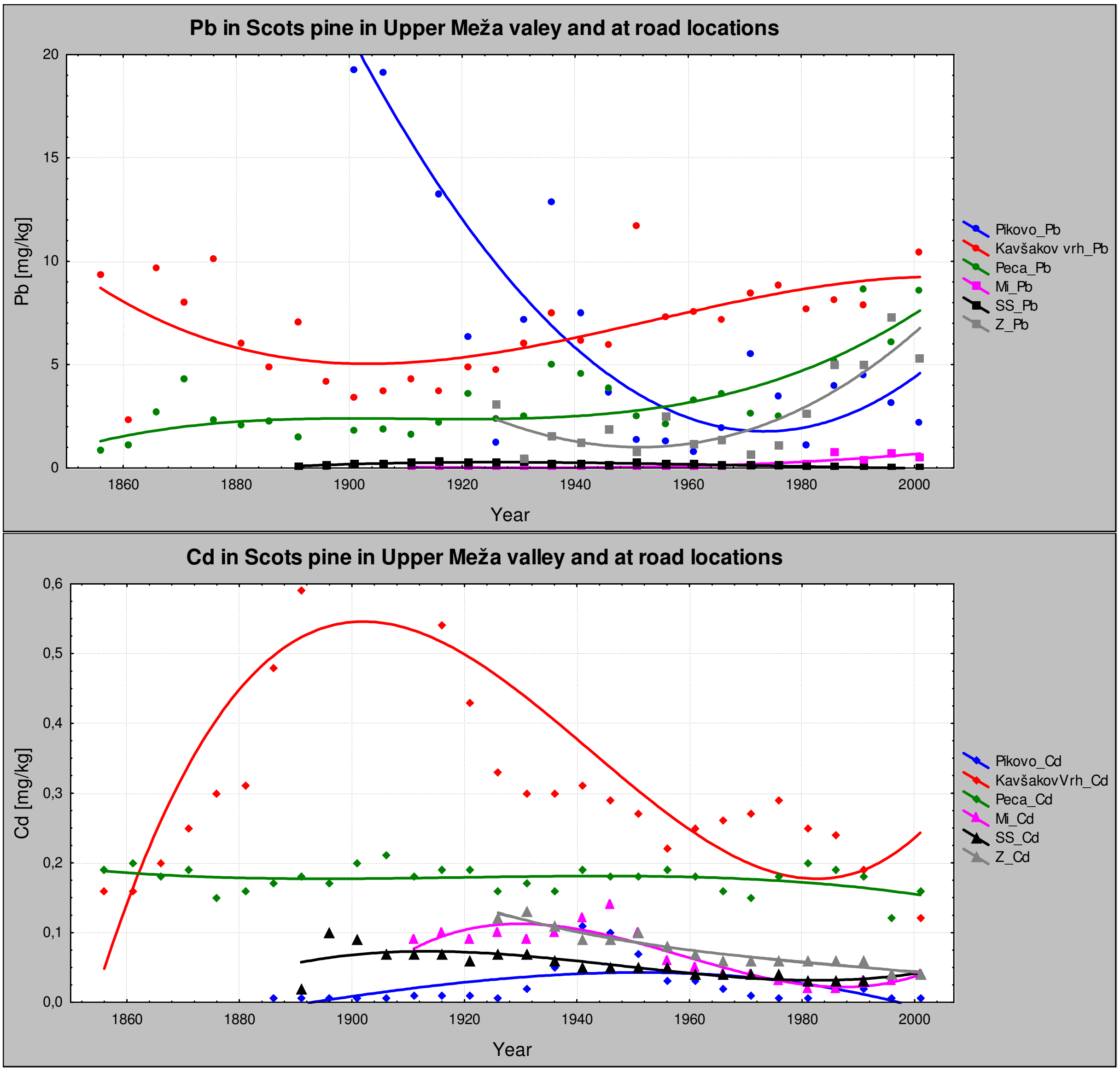

Figure 34: *Comparison of concentrations of Pb (top) and Cd (bottom) measured in Scots pine trees in Upper Meža valley (Pikovo, Kavšakov vrh, Peca; data from Poličnik et al., 2009) and at road locations (Mi-Miklavž, SS-Spodnja Ščavnica, Z-Vrh nad Želimljami)*

For the comparison of trends of Pb and Cd contents from road locations with an unpolluted area, the data for HM contents in trembling poplar from location Rajhenav forest in Kočevje region were used (Poličnik et al., 2009). The comparison of trends shows that Cd concentrations in trees near roads are very similar to those at unpolluted location. It can be concluded again that traffic doesn't seem to be reflected in Cd concentrations in tree-rings. The concentrations of Pb are clearly higher near roads than in the unpolluted environment, but after the phase-out of Pb (and other remediation measures being made on majority of point emission sources both in Slovenia and Europe) their values have been largely reduced and are approaching the values measured in unpolluted Rajhenav (Figure 35).

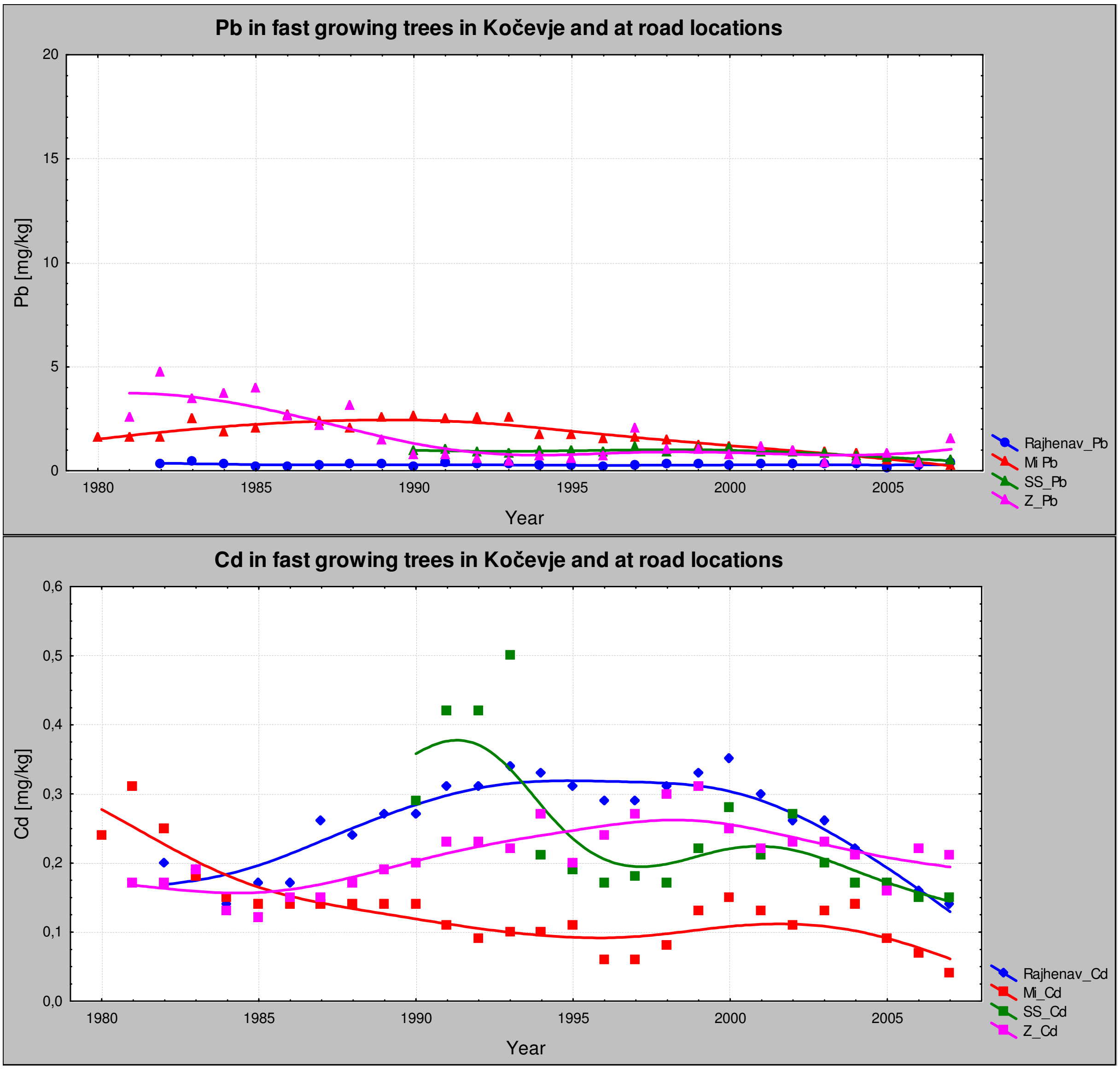

Figure 35: *Comparison of concentrations of Pb (top) and Cd (bottom) measured in fast growing trees in Kočevje (Rajhenav forest; data form Poličnik et al., 2009) and at road locations (Mi-Miklavž, SS-Spodnja Ščavnica, Z-Vrh nad Želimljami)*

It can be resumed that tree-ring levels of some heavy metals at certain locations could be linked to the road traffic emissions (for example Pb and Cr concentrations), but it is more likely that these levels are a result of all sources (traffic and non-traffic related) that exist in the broader surroundings of the studied locations and not only of one road in the vicinity of which the samples were taken. The method of dendrochemical biomonitoring of heavy metals is less suitable for monitoring of emissions/pollution originated from road traffic on the scale of one road, because it is extremely difficult to find suitable trees near roads that could be directly comparable.

It is known that lead containing dust particles deposit quickly in the near vicinity of the road and therefore contribute to accumulation of lead on the roadside soil surface. Because the direct impact of road pollution is largely reduced with the distance from the road (Al-Chalabi and Hawker, 2000), it is important to compare the samples taken from the same distance. In the case of dendrochemistry, this goal is hard to achieve, due to the natural pattern of the position of trees that are used as passive monitors (the trees are not deliberately planted for the purpose of dendrochemical studies).

The distribution of concentrations at the different distances could also be influenced by the meteorological conditions at the individual sites, mainly wind speeds and directions and also by the traffic speeds, because higher speeds of traffic produce higher turbulences that have an influence to where the particles are deposited (directly on the road surface, near or further from the road). Also the soil pH and the contents of organic matter (both have an influence in metal mobility and may effect concentrations of exchangeable metal forms) may vary widely among soils and with depth.

Every road has different elements that could largely influence metal emissions to the nearby trees. Such elements are embankments, road gradient, different drainage systems. Also the trees growing very near the road could be largely influenced by road works that are conducted during road reconstructions or road maintenance. The road works could also damage the root system of the tree that spreads over a large area, which could alter the results.

All these factors make it difficult to compare trees among different sampling sites near roads.

Some of the metal content in the trees also comes from the natural content of the soil at the individual location; Bindler et al. (2004) found that 10 - 30% of the tree-ring Pb is derived from the underlying mineral soil (the levels of Pb in tree-rings in that study were all <1 mg/kg and generally <0.1 mg/kg). This complicates the comparison of the different sites. So it is not necessary that higher levels measured in a tree also correspond with the higher emissions at a certain location. The higher levels could come from the natural background and also, when the natural background levels are high, the emissions will have a smaller influence on metal levels in tree-rings.

Also the accumulation of metals in the soil may result in a certain time shift between the time of high emission and the years of higher levels in tree-rings.

Nevertheless, results show that Pb concentrations in tree-rings of silver birch at Miklavž and with a certain time shift in Spodnja Ščavnica are correlated to the Pb emissions in Slovenia that have been drastically reduced after the year 1994, when the new order on Pb fuel contents was adopted. So it appears that tree-rings of properly selected tree species may be used as bioindicators of changes in a larger area, but historical monitoring with dendrochemistry is less suitable for modelling and comparing emissions from one road because of the numerous factors that could influence the concentrations in annual rings.

Although there are some drawbacks regarding the use of dendrochemical records for the assessment of past trends of pollution, properly selected species might be taken into considerations for the purpose of assessment of past trends of pollution near roads. Even though suitable trees that grow close to the roads are also sometimes hard to find, and their uptake characteristics could be influenced by road works or some other usually unknown local factors, other bioindicators that are commonly used for the purpose of historical monitoring at the large (regional) spatial scale are even more limited. Other commonly used biomonitors (lake sediments, peat bogs, bivalve shells, human teeth, deer antlers) are mainly suitable for the assessment of historical trends in a broader region. Another possible medium that shows some good results in incorporating the past trends of pollution from traffic are bark pockets (Bellis et al., 2002; Satake et al., 1996), but this media also lacks one of the main characteristics for a suitable biomonitor of local pollution from the road, that is it's presence in large amounts, and finding a suitable bark pocket near a certain road would most probably be a very difficult task (if possible at all).

5 CONCLUSIONS

Tree-rings are, due to their availability, ease of sampling and possibility for accurate dating of samples, probably the most suitable bioindicator for the assessment of historical trends of traffic pollution (at least with some heavy metals, particularly Cr and probably also Pb) near roads.

The uptake of HM is not the same in different tree species that were sampled at the same locations. Study demonstrates that tree-rings of fast growing diffuse porous broadleaf species, especially silver birch, may be successfully used in determination of trends of pollution with heavy metals from road traffic. With the use of silver birch and trembling poplar a trend of decrease in Pb levels in the last years was established at all locations, although it seems that also other sources of Pb had an important (and even more pronounced) influence on the levels of this metal in tree-rings. Despite of large emission of this element it seems that the large proportion of it wasn't deposited in a form that is readily available for the uptake by the trees. In the heavily polluted Upper Meža valley, the concentrations of Pb are much higher, and in a non-polluted area of Kočevje lower than those measured at roadside locations (see and compare also Poličnik et al., 2009, Lah et al., 2008). After the phase-out of Pb gasoline and other remediation measures for the reduction of air pollution, the levels of Pb in trees near roads are reduced to similar levels than those found at non-polluted environment.

A trend of increase in Cr concentrations is evident at all locations and in pine trees also well correlated with traffic indicators. The correlations with traffic parameters at all locations show that after the phase-out of leaded gasoline, Cr seems to be an important indicator of traffic pollution. Regarding the findings of this study, Cr could be considered as the most important indicator of traffic influence in the road environment.

The tree-ring width doesn't seem to influence the concentrations of HM in tree-rings.

It is difficult to compare trees at different locations in the vicinity of roads because of numerous factors that influence the emissions, the distribution of pollutants and the uptake of HM.

Concentrations of some HM could also be linked to some other indicators of general pollution like emissions and imissions of SO2, therefore one has to be very careful in the interpretations of the results of dendrochemical studies.

As guidance for further dendrochemical analysis of HM it would be advisable to carry out pedologic analysis at growing sites of trees and analysis of HM content in soil. For the purpose of testing the relevance of results also analysis of parallel samples taken from the same tree would be proposed and in the case of Pb also analysis of isotopic ratio to define the source of Pb content in tree-rings.

6 SUMMARY

Road traffic is one of the major sources of disperse pollution with heavy metals. The main sources of heavy metals near roads represent emissions of exhaust gasses, brake wear, tire wear and wear due to friction of mechanical parts. Historically Pb was the most important heavy metal associated with road traffic and originated mainly from vehicle exhaust, but also other heavy metals (HM) were and are nowadays still emitted from road traffic.

Trees are bioindicators capable of recording HM levels in the environment in the past. In this study Scots pine trees for the determination of long-term trends (the oldest rings of Scots pine from Spodnja Ščavnica were from 1889) and of silver birch and trembling poplar trees for the determination of pollution in the last three decades were sampled in three locations (Miklavž, Spodnja Ščavnica and Vrh nad Želimljami) near roads in Slovenia.

Tree cores were taken at breast height (1.3 m above the ground) from the road facing aspect of each tree. For the determination of historical trends of pollution the 5-year samples of Scots pine and yearly samples of silver birch and trembling poplar were analysed. The contents of Pb, Cd, Zn, Cr and Ni in tree-ring samples were determined using inductively coupled plasma mass spectrometry (ICP-MS).

The results of HM content in tree-rings were plotted along time axis for a presentation of trends of HM in the period of the trees growth. The results were compared with other available data (emissions, imissions, traffic) using Pearson's correlation. For the purpose of statistical analysis and comparison of trends, Pb and Cr emissions from studied road locations were also calculated.

Study demonstrates that tree-rings of fast growing diffuse porous broadleaf species, especially silver birch, could be successfully used in determination of trends of pollution with HM from road traffic. The trend of decrease in Pb levels in the last years was established at all locations, although it seems that also other sources of Pb had an important influence on the content of this metal in tree-rings. Despite of large emission of this element from road traffic it seems that the large proportion of it wasn't deposited in a form that is readily available for the uptake by the trees.

In the heavily polluted Upper Meža valley, the levels of Pb are much higher, and in a non-polluted area of Kočevje lower than those measured at roadside locations. After the phase-out of Pb gasoline and other remediation measures for the reduction of air pollution, the concentrations of Pb in fast growing trees near roads have been reduced to similar levels than those found at non-polluted environment. A trend of increase in Cr levels is evident at all locations and in pine trees also well correlated with traffic indicators. It seems that after the phase out of Pb gasoline, Cr may be an important indicator of traffic pollution. The tree-ring width doesn't seem to influence the concentrations of HM in tree-rings.

It is difficult to compare trees at different locations in the vicinity of roads because of numerous factors that influence the emissions, the distribution of pollutants and the uptake of HM. Levels of some HM could also be linked to same other indicators of general pollution like emissions and imissions of SO_2, therefore one has to be very careful in the interpretations of the results of dendrochemical studies.

POVZETEK:

Promet je pomemben vir disperznega onesnaževanja s težkimi kovinami. Glavne vire težkih kovin ob cestah predstavljajo emisije izpušnih plinov, obraba zavor, obraba pnevmatik in obraba zaradi trenja mehanskih delov. V preteklosti je bila najpomembnejša težka kovina povezana s cestnim prometom svinec, ki je v glavnem izviral iz izpušnih plinov, vendar cestni promet tako danes kot v preteklosti povzroča tudi emisije drugih težkih kovin.

Drevesa so bioindikatorji, ki lahko beležijo koncentracije težkih kovin (HM) v okolju, v katerem rastejo. V raziskavi so bile vzorčene 3 drevesne vrste: rdeči bor za določitev dolgoročnih trendov (najstarejše branike bora vzorčenega v Spodnji Ščavnici so bile iz leta 1889) in breza ter trepetlika za določitev trendov onesnaženja v zadnjih treh desetletjih, na 3 lokacijah (Miklavž, Spodnja Ščavnica in Vrh nad Želimljami) v bližini cest v Sloveniji.

Drevesni izvrtki so bili odvzeti v prsni višini (1,3 m) v smeri proti cesti. Za določitev zgodovinskih trendov onesnaženja so bili analizirani 5 letni vzorci branik bora in letni vzorci branik breze in trepetlike. Vsebnost Pb, Cd, Zn, Cr in Ni v vzorcih branik je bila določena s tehniko induktivno sklopljene plazme z masnospektrometrično detekcijo (ICP-MS).

Za prikaz časovnega poteka trendov vsebnosti težkih kovin v branikah v času rasti posameznih dreves, so bili rezultati vsebnosti prikazani na časovni osi. Rezultati so bili primerjani z ostalimi razpoložljivimi podatki (o emisijah, imisijah, prometu) z uporabo Pearsonove korelacije. Za potrebe statistične analize in primerjave trendov so bile ocenjene tudi emisije svinca in kroma iz prometa za posamezen cestni odsek.

Izsledki raziskave kažejo, da so branike hitro rastočih listavcev z difuzno poroznim lesom, predvsem breza, primerne za določanje trendov onesnaženja s težkimi kovinami iz cestnega prometa. Trend zniževanja vsebnosti Pb v zadnjem obdobju je bil ugotovljen na vseh lokacijah, čeprav se zdi, da so tudi drugi viri imeli pomemben vpliv na ravni te kovine v branikah dreves. Kljub velikim emisijam te kovine zaradi prometa kaže, da glavnina Pb ni bila odložena v okolju v obliki, ki bi bila drevesom enostavno na voljo.

Koncentracije v močno onesnaženi Mežiški dolini so mnogo večje kot na lokacijah ob cestah in v neonesnaženem okolju na območju Kočevja nižje kot ob cestah. Po opustitvi osvinčenega bencina in ostalih ukrepih za zmanjšanje onesnaženosti zraka se ravni Pb v hitrorastočih drevesih bližajo ravnem, značilnim za neonesnaženo okolje. Trend povečevanja vsebnosti Cr je ugotovljen na vseh lokacijah in v boru kaže dobro soodvisnost s podatki o prometu. Kaže, da bi lahko bil Cr najpomembnejši indikator onesnaženja zaradi prometa po opustitvi osvinčenega bencina. Ne kaže, da bi širina branik vplivala na koncentracije HM v lesu.

Primerjava med drevesi na različnih lokacijah ob cestah je težavna zaradi množice dejavnikov, ki vplivajo na emisije, razširjanje in privzem HM v drevesa. Koncentracije nekaterih HM je mogoče povezati tudi z drugimi indikatorji splošne onesnaženosti okolja, kot so emisije in imisije SO_2, zato je potrebna posebna pazljivost pri interpretaciji rezultatov dendrokemijskih raziskav.

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ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to my mentor doc. dr. Boštjan Pokorny for his effort to help me, to point my thoughts in the right direction and for his encouragement, patience, remarks and comments in a number of consultations. I would also like to thank other co-workers at Erico institute, especially dr. Helena Poličnik, for their help with the gathering of literature and with the gathering, preparation and analysis of samples.

I'm also grateful to the members of the commission: prof. dr. Mladen Franko, doc. dr. Tom Levanič and prof. dr. Pierluigi Barbieri for their evaluation and comments that helped me to improve my work.

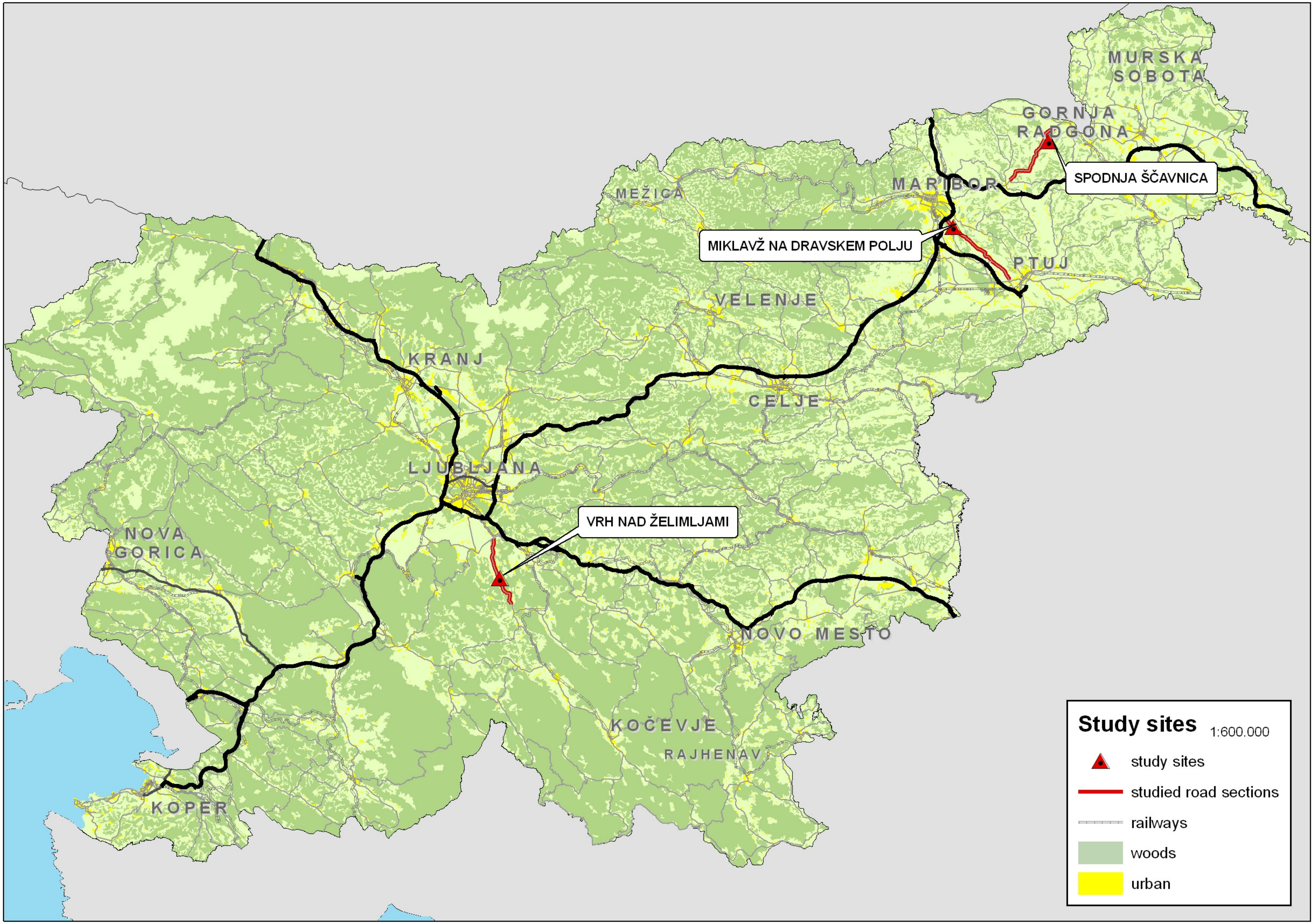
This thesis would not have been possible without my boss mag. Barbara Likar and other colleagues at work that encouraged me to point my effort in finishing it, and without the Ministry of transport, Slovenian roads agency.

I would also like to thank my family: Klavdija and our children Maša and Matevž; and my parents for the support they provided and for helping me to find some time to work on this project. Without their love and encouragement, I would not have finished this thesis.

ANNEXES

ANNEX A: Yearly traffic and the assessment of trends of Pb emissions from road traffic in grams per kilometre of road for sites Miklavž, Spodnja Ščavnica and Vrh nad Želimljami

	Miklavž		Spodnja Ščavnica		Vrh nad Želimljami	
Year	Yearly traffic [vehicles/day]	Emission of Pb per year [g/km]	Yearly traffic [vehicles/day]	Emission of Pb per year [g/km]	Yearly traffic [vehicles/day]	Emission of Pb per year [g/km]
1980	6,997	123.6	2,256	39.9	3,541	62.6
1981	6,714	114.6	2,144	36.6	2,864	48.9
1982	6,561	108.1	2,037	33.6	2,722	44.8
1983	6,201	98.5	1,849	29.4	2,346	37.3
1984	6,364	97.3	1,991	30.4	2,346	35.9
1985	6,996	102.9	2,131	31.3	2,065	30.4
1986	8,300	117.2	2,131	30.1	2,375	33.5
1987	9,510	128.0	2,692	36.2	2,708	36.5
1988	10,231	134.2	3,186	41.8	2,979	39.1
1989	10,552	124.7	3,186	37.6	3,188	37.7
1990	11,832	131.7	3,500	39.0	3,940	43.9
1991	9,140	91.1	3,675	36.6	3,940	39.3
1992	7,930	72.5	4,096	37.5	4,232	38.7
1993	8,832	68.1	4,097	31.6	4,489	34.6
1994	9,893	68.9	3,972	27.7	5,034	35.0
1995	10,576	41.7	4,146	16.3	5,268	20.8
1996	11,851	15.6	4,380	5.8	5,602	7.4
1997	12,809	14.0	4,965	5.4	6,163	6.7
1998	12,542	12.1	5,635	5.4	7,055	6.8
1999	12,906	9.4	5,857	4.2	7,155	5.2
2000	13,404	8.1	5,918	3.6	6,681	4.0
2001	13,523	3.9	6,000	1.7	6,675	1.9
2002	13,678	1.3	5,664	0.5	6,961	0.7
2003	14,141	1.3	5,870	0.6	7,072	0.7
2004	14,951	1.4	6,018	0.6	7,353	0.7
2005	15,691	1.5	5,889	0.6	7,451	0.7
2006	16,203	1.5	5,698	0.5	7,626	0.7
2007	16,646	1.5	5,917	0.5	7,854	0.7



MURSKA SOBOTA
GORNJA RADGONA
SPODNJA ŠČAVNICA
MARIBOR
MEŽICA
MIKLAVŽ NA DRAVSKEM POLJU
PTUJ
VELENJE
KRANJ
CELJE
LJUBLJANA
VRH NAD ŽELIMLJAMI
NOVA GORICA
NOVO MESTO
KOČEVJE
RAJHENAV
KOPER
Study sites
1:600.000
study sites
studied road sections
railways
woods
urban

ANNEX C: Heavy metal contents in tree-rings

for sites Miklavž, Spodnja Ščavnica and Vrh nad Želimljami

Location	Tree species	Year	Pb	Cd	Zn	Cr	Ni	Incr. width	Sample mass	Dilution volume	LOQ Pb	LOQ Cd	LOQ Zn	LOQ Cr	LOQ Ni
			[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/k	[mm]	[g]	[mL]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg
Miklavž	*Pinus sylvestris*	1911	0.01	0.09	5.47	0.04	0.01	14.5	0.4961	25	0.01	0.01	0.05	0.01	0.01
		1916	0.04	0.1	6.64	0.04	0.06	9.6	0.4949	25	0.01	0.01	0.05	0.01	0.01
		1921	0.05	0.09	6.3	0.08	0.13	17.4	0.4962	25	0.01	0.01	0.05	0.01	0.01
		1926	0.03	0.1	6.33	0.04	0.04	11.3	0.4907	25	0.01	0.01	0.05	0.01	0.01
		1931	0.03	0.09	6.05	0.03	0.04	13.5	0.4944	25	0.01	0.01	0.05	0.01	0.01
		1936	0.03	0.1	7.27	0.03	0.01	11.9	0.4905	25	0.01	0.01	0.05	0.01	0.01
		1941	0.02	0.12	7.54	0.04	<0.01	7.5	0.4255	25	0.01	0.01	0.06	0.01	0.01
		1946	0.06	0.14	8.92	0.06	<0.01	5.9	0.3563	25	0.01	0.01	0.07	0.01	0.01
		1951	0.07	0.1	7.63	0.06	0.04	7.3	0.3551	25	0.01	0.01	0.07	0.01	0.01
		1956	0.07	0.06	5.32	0.08	0.08	10	0.5003	25	0.005	0.005	0.05	0.005	0.005
		1961	0.08	0.05	4.64	0.07	0.03	6.5	0.3367	25	0.01	0.01	0.07	0.01	0.01
		1966	0.09	0.04	6.06	0.06	0.03	6.4	0.3347	25	0.01	0.01	0.07	0.01	0.01
		1971	0.12	0.04	6.5	0.07	0.06	8.1	0.4023	25	0.01	0.01	0.06	0.01	0.01
		1976	0.15	0.03	6.2	0.08	0.11	6.3	0.3202	25	0.01	0.01	0.08	0.01	0.01
		1981	0.22	0.02	6.66	0.09	0.1	6.6	0.317	25	0.01	0.01	0.08	0.01	0.01
		1986	0.74	0.02	14.07	0.17	0.25	4.8	0.2387	25	0.01	0.01	0.10	0.01	0.01
		1991	0.4	0.03	8.77	0.15	0.11	4.7	0.2171	25	0.01	0.01	0.12	0.01	0.01
		1996	0.72	0.03	8.1	0.34	0.16	4.5	0.2147	25	0.01	0.01	0.12	0.01	0.01
		2001	0.55	0.04	10.95	0.2	0.18	4.6	0.214	25	0.01	0.01	0.12	0.01	0.01
		2006	0.8	0.03	11.1	0.46	0.42	3.2	0.1658	25	0.02	0.02	0.15	0.02	0.02
	Betula pendula	1978	1.67	0.2	17.64	0.04	<0.01	3.6	0.2124	25	0.01	0.01	0.12	0.01	0.01
		1979	1.51	0.17	13.95	0.06	<0.01	3.2	0.1894	25	0.01	0.01	0.13	0.01	0.01
		1980	1.63	0.24	17.09	0.06	0.03	3.2	0.1908	25	0.01	0.01	0.13	0.01	0.01
		1981	1.58	0.31	17.13	0.1	0.07	3.8	0.2471	25	0.01	0.01	0.10	0.01	0.01
		1982	1.63	0.25	15.88	0.18	0.04	2.7	0.1491	25	0.02	0.02	0.17	0.02	0.02
		1983	2.48	0.18	12.19	0.05	0.04	5.5	0.3508	25	0.01	0.01	0.07	0.01	0.01
		1984	1.85	0.15	12.04	0.05	0.01	4.5	0.2616	25	0.01	0.01	0.10	0.01	0.01
		1985	2.05	0.14	11.14	0.05	<0.01	3.9	0.2358	25	0.01	0.01	0.11	0.01	0.01
		1986	2.67	0.14	11.04	0.05	<0.01	3.4	0.2013	25	0.01	0.01	0.12	0.01	0.01
		1987	2.4	0.14	12.58	0.05	0.07	4.8	0.2886	25	0.01	0.01	0.09	0.01	0.01
		1988	2.08	0.14	14.99	0.06	<0.01	2.9	0.1276	25	0.02	0.02	0.20	0.02	0.02
		1989	2.58	0.14	15.64	0.07	0.03	3	0.1973	25	0.01	0.01	0.13	0.01	0.01
		1990	2.61	0.14	14.83	0.05	0.03	3.4	0.2175	25	0.01	0.01	0.11	0.01	0.01
		1991	2.52	0.11	14.38	0.05	<0.01	2.9	0.1971	25	0.01	0.01	0.13	0.01	0.01
		1992	2.59	0.09	11.02	0.03	0.02	6.5	0.4071	25	0.01	0.01	0.06	0.01	0.01
		1993	2.56	0.1	14.46	0.08	0.03	3.5	0.1926	25	0.01	0.01	0.13	0.01	0.01
		1994	1.72	0.1	11.19	0.04	0.02	5	0.3072	25	0.01	0.01	0.08	0.01	0.01
		1995	1.74	0.11	13.14	0.04	<0.01	4.2	0.2827	25	0.01	0.01	0.09	0.01	0.01
		1996	1.56	0.06	9.61	0.05	<0.01	3.3	0.2273	25	0.01	0.01	0.11	0.01	0.01
		1997	1.59	0.06	10.25	0.07	<0.01	3.7	0.2493	25	0.01	0.01	0.10	0.01	0.01
		1998	1.45	0.08	11.4	0.05	<0.01	2.5	0.1885	25	0.01	0.01	0.13	0.01	0.01
		1999	1.23	0.13	13.22	0.07	0.05	3.2	0.2101	25	0.01	0.01	0.12	0.01	0.01
		2000	1.17	0.15	13.82	0.08	0.03	3.2	0.1997	25	0.01	0.01	0.13	0.01	0.01
		2001	1.01	0.13	14.6	0.12	0.36	2.3	0.1597	25	0.02	0.02	0.16	0.02	0.02
		2002	0.95	0.11	14.06	0.12	0.15	2.8	0.1737	25	0.01	0.01	0.14	0.01	0.01
		2003	0.89	0.13	20.93	0.14	1.02	1	0.082	25	0.03	0.03	0.30	0.03	0.03
		2004	0.85	0.14	12.95	0.16	<0.01	3.6	0.2383	25	0.01	0.01	0.10	0.01	0.01
		2005	0.52	0.09	11.67	0.07	0.02	3.7	0.2211	25	0.01	0.01	0.11	0.01	0.01
		2006	0.4	0.07	11.48	0.18	0.12	2.9	0.1795	25	0.01	0.01	0.14	0.01	0.01
		2007	0.24	0.04	11.6	0.32	0.24	3.3	0.1929	25	0.01	0.01	0.13	0.01	0.01

<0.01* - below LOQ

Incr. width – width of analyzed 1-year/5-year increment

LOQ – level of quantification (the results are generally rounded to 2 decimal places)

Location	Tree species	Year	Pb	Cd	Zn	Cr	Ni	Incr. width	Sample mass	Dilution volume	LOQ Pb	LOQ Cd	LOQ Zn	LOQ Cr	LOQ Ni
			[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mm]	[g]	[mL]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg	[mg/k
Spodnja Ščavnica	*Pinus sylvestris*	1896	0.14	0.1	3.73	0.03	0.06	11.5	0.5	25	0.01	0.01	0.05	0.01	0.01
		1901	0.17	0.09	3.68	0.03	0.03	7.9	0.3955	25	0.01	0.01	0.06	0.01	0.01
		1906	0.2	0.07	2.62	0.04	0.02	4.5	0.2436	25	0.01	0.01	0.10	0.01	0.01
		1911	0.28	0.07	2.91	0.02	<0.01*	5.5	0.3123	25	0.01	0.01	0.08	0.01	0.01
		1916	0.35	0.07	3.63	0.03	<0.01*	4.6	0.2542	25	0.01	0.01	0.10	0.01	0.01
		1921	0.28	0.06	3.83	0.02	<0.01*	4.5	0.2487	25	0.01	0.01	0.10	0.01	0.01
		1926	0.28	0.07	4.2	0.03	<0.01*	3.1	0.2088	25	0.01	0.01	0.12	0.01	0.01
		1931	0.3	0.07	4.86	0.03	<0.01*	12.4	0.5008	25	0.005	0.005	0.05	0.005	0.005
		1936	0.23	0.06	5.46	0.04	<0.01*	15.1	0.4968	25	0.01	0.01	0.05	0.01	0.01
		1941	0.21	0.05	2.86	0.02	<0.01*	10.7	0.4897	25	0.01	0.01	0.05	0.01	0.01
		1946	0.16	0.05	2.89	0.03	0.01	11.8	0.4983	25	0.01	0.01	0.05	0.01	0.01
		1951	0.25	0.05	4.42	0.05	0.06	6.2	0.3999	25	0.01	0.01	0.06	0.01	0.01
		1956	0.23	0.05	4.14	0.06	0.08	4.4	0.2699	25	0.01	0.01	0.09	0.01	0.01
		1961	0.17	0.04	4.05	0.09	0.1	4.9	0.2916	25	0.01	0.01	0.09	0.01	0.01
		1966	0.15	0.04	4.09	0.14	0.09	5	0.3181	25	0.01	0.01	0.08	0.01	0.01
		1971	0.16	0.04	4.24	0.06	0.06	4.2	0.2827	25	0.01	0.01	0.09	0.01	0.01
		1976	0.14	0.04	3.91	0.07	0.06	4.2	0.2655	25	0.01	0.01	0.09	0.01	0.01
		1981	0.07	0.03	2.97	0.1	0.06	2.5	0.1531	25	0.02	0.02	0.16	0.02	0.02
		1986	0.04	0.03	2.29	0.09	0.07	1.9	0.0905	25	0.03	0.03	0.28	0.03	0.03
		1991	<0.01*	0.03	5.09	0.27	0.1	2.4	0.1308	25	0.02	0.02	0.19	0.02	0.02
		1996	<0.01*	0.04	6.85	0.29	0.06	2.3	0.1235	25	0.02	0.02	0.20	0.02	0.02
		2001	<0.01*	0.04	6.34	0.47	0.27	2.2	0.0939	10	0.01	0.01	0.11	0.01	0.01
		2006	<0.01*	0.03	5.69	0.27	0.15	0.6	0.0285	10	0.04	0.04	0.35	0.04	0.04
	Betula pendula	1990	0.99	0.29	10.5	0.11	0.23	5.4	0.3258	25	0.01	0.01	0.08	0.01	0.01
		1991	1.04	0.42	15.59	0.1	0.24	3.7	0.2185	25	0.01	0.01	0.11	0.01	0.01
		1992	0.87	0.42	16.18	0.08	0.23	1.9	0.1082	25	0.02	0.02	0.23	0.02	0.02
		1993	0.86	0.5	19.26	0.07	0.22	3.1	0.2015	25	0.01	0.01	0.12	0.01	0.01
		1994	0.98	0.21	11.79	0.08	0.15	3.9	0.2531	25	0.01	0.01	0.10	0.01	0.01
		1995	0.97	0.19	13.54	0.06	0.04	3.2	0.1653	25	0.02	0.02	0.15	0.02	0.02
		1996	0.89	0.17	12.41	0.06	<0.01*	2.8	0.163	25	0.02	0.02	0.15	0.02	0.02
		1997	1.13	0.18	11.93	0.08	0.04	3.3	0.2096	25	0.01	0.01	0.12	0.01	0.01
		1998	0.9	0.17	10.36	0.05	<0.01*	2.4	0.1528	25	0.02	0.02	0.16	0.02	0.02
		1999	1.07	0.22	11.24	0.05	<0.01*	2.2	0.144	25	0.02	0.02	0.17	0.02	0.02
		2000	1.08	0.28	11.23	0.08	0.07	3.3	0.2315	25	0.01	0.01	0.11	0.01	0.01
		2001	0.89	0.21	10.43	0.09	0.06	2.9	0.1736	25	0.01	0.01	0.14	0.01	0.01
		2002	0.9	0.27	11.47	0.07	0.07	4	0.2494	25	0.01	0.01	0.10	0.01	0.01
		2003	0.84	0.2	12.48	0.05	0.08	4.5	0.3047	25	0.01	0.01	0.08	0.01	0.01
		2004	0.7	0.17	13.89	0.08	0.09	3.1	0.1966	25	0.01	0.01	0.13	0.01	0.01
		2005	0.66	0.17	13.85	0.09	0.02	2.2	0.1411	25	0.02	0.02	0.18	0.02	0.02
		2006	0.51	0.15	11.6	0.12	0.23	3.3	0.2163	25	0.01	0.01	0.12	0.01	0.01
		2007	0.52	0.15	18.68	0.21	0.53	2.9	0.1709	25	0.01	0.01	0.15	0.01	0.01

<0.01* - below LOQ

Incr. width – width of analyzed 1-year/5-year increment

LOQ – level of quantification (the results are generally rounded to 2 decimal places)

Location	Tree species	Year	Pb	Cd	Zn	Cr	Ni	Incr. width	Sample mass	Dilution volume	LOQ Pb	LOQ Cd	LOQ Zn	LOQ Cr	LOQ Ni
			[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mm]	[g]	[mL]	[mg/kg	[mg/kg	[mg/kg]	[mg/kg]	[mg/kg
Vrh nad Želimljami	*Pinus sylvestris*	1928	3.08	0.12	6.07	0.06	0.07	29	0.4935	25	0.01	0.01	0.05	0.01	0.01
		1931	0.48	0.13	6.34	0.05	0.06	24	0.4932	25	0.01	0.01	0.05	0.01	0.01
		1936	1.54	0.11	7.3	0.05	0.13	11.6	0.4908	25	0.01	0.01	0.05	0.01	0.01
		1941	1.23	0.09	5.46	0.15	0.13	7.3	0.497	25	0.01	0.01	0.05	0.01	0.01
		1946	1.86	0.09	6.45	0.21	0.2	18	0.4898	25	0.01	0.01	0.05	0.01	0.01
		1951	0.77	0.1	7.52	0.04	0.12	20.5	0.4975	25	0.01	0.01	0.05	0.01	0.01
		1956	2.49	0.08	8.97	0.04	0.13	18.8	0.4913	25	0.01	0.01	0.05	0.01	0.01
		1961	1.18	0.07	6.54	0.04	0.05	14.5	0.4993	25	0.01	0.01	0.05	0.01	0.01
		1966	1.32	0.06	6.13	0.04	0.05	7.8	0.4964	25	0.01	0.01	0.05	0.01	0.01
		1971	0.67	0.06	5.48	0.05	0.08	12.6	0.4853	25	0.01	0.01	0.05	0.01	0.01
		1976	1.07	0.06	5.33	0.05	0.1	11.4	0.4937	25	0.01	0.01	0.05	0.01	0.01
		1981	2.6	0.06	5.9	0.06	0.07	7.3	0.3982	25	0.01	0.01	0.06	0.01	0.01
		1986	5	0.06	5.26	0.08	0.09	6	0.3325	25	0.01	0.01	0.08	0.01	0.01
		1991	4.99	0.06	7.55	0.1	0.14	4	0.2179	25	0.01	0.01	0.11	0.01	0.01
		1996	7.29	0.04	5.86	0.08	0.19	6	0.3433	25	0.01	0.01	0.07	0.01	0.01
		2001	5.28	0.04	6.19	0.32	0.26	5	0.2699	25	0.01	0.01	0.09	0.01	0.01
		2006	3.88	0.04	6.2	0.59	0.31	1.6	0.0733	10	0.01	0.01	0.14	0.01	0.01
	Populus tremula	1981	2.55	0.17	11.18	0.09	0.08	3	0.0823	25	0.03	0.03	0.30	0.03	0.03
		1982	4.74	0.17	8.07	0.06	0.07	2.5	0.2301	25	0.01	0.01	0.11	0.01	0.01
		1983	3.48	0.19	7.36	0.33	0.46	5	0.4371	25	0.01	0.01	0.06	0.01	0.01
		1984	3.69	0.13	6.73	0.06	0.1	4.6	0.3488	25	0.01	0.01	0.07	0.01	0.01
		1985	3.94	0.12	6.33	0.07	0.13	2.9	0.2297	25	0.01	0.01	0.11	0.01	0.01
		1986	2.62	0.15	5.32	0.05	0.08	6.5	0.4246	25	0.01	0.01	0.06	0.01	0.01
		1987	2.15	0.15	7.05	0.03	0.16	4.5	0.3121	25	0.01	0.01	0.08	0.01	0.01
		1988	3.11	0.17	6.85	0.04	0.09	4.2	0.2913	25	0.01	0.01	0.09	0.01	0.01
		1989	1.48	0.19	6.2	0.04	0.07	4.6	0.2754	25	0.01	0.01	0.09	0.01	0.01
		1990	0.76	0.2	6.22	0.04	0.1	4.6	0.2372	25	0.01	0.01	0.11	0.01	0.01
		1991	0.74	0.23	6.06	0.05	0.07	5.3	0.3203	25	0.01	0.01	0.08	0.01	0.01
		1992	0.58	0.23	7.73	0.07	0.25	3	0.1811	25	0.01	0.01	0.14	0.01	0.01
		1993	0.44	0.22	11.05	0.1	0.14	2	0.1422	25	0.02	0.02	0.18	0.02	0.02
		1994	0.7	0.27	8.08	0.12	0.16	3.8	0.2144	25	0.01	0.01	0.12	0.01	0.01
		1995	0.57	0.2	6.93	0.09	0.11	3	0.2183	25	0.01	0.01	0.11	0.01	0.01
		1996	0.7	0.24	8.4	0.25	0.85	2.6	0.1426	25	0.02	0.02	0.18	0.02	0.02
		1997	2.06	0.27	12.22	0.25	1.36	1.7	0.1031	25	0.02	0.02	0.24	0.02	0.02
		1998	1.04	0.3	11.34	0.1	0.36	1.6	0.1035	25	0.02	0.02	0.24	0.02	0.02
		1999	1.02	0.31	15.36	0.11	0.52	2.1	0.1188	25	0.02	0.02	0.21	0.02	0.02
		2000	0.74	0.25	10.86	0.06	<0.01*	3.9	0.2254	25	0.01	0.01	0.11	0.01	0.01
		2001	1.14	0.22	14.7	0.08	0.13	2.8	0.1278	25	0.02	0.02	0.20	0.02	0.02
		2002	0.95	0.23	11.61	0.07	0.18	2.9	0.1526	25	0.02	0.02	0.16	0.02	0.02
		2003	0.39	0.23	15.35	0.1	0.22	2.3	0.1207	25	0.02	0.02	0.21	0.02	0.02
		2004	0.53	0.21	18.16	0.29	0.34	2.3	0.1034	25	0.02	0.02	0.24	0.02	0.02
		2005	0.82	0.16	8.31	0.29	0.51	1.8	0.0779	10	0.01	0.01	0.13	0.01	0.01
		2006	0.4	0.22	10.96	0.12	0.13	3	0.1644	25	0.02	0.02	0.15	0.02	0.02
		2007	1.54	0.21	16.99	0.3	0.4	3.5	0.1732	25	0.01	0.01	0.14	0.01	0.01

<0.01* - below LOQ
Incr. width – width of analyzed 1-year/5-year increment
LOQ – level of quantification (the results are generally rounded to 2 decimal places)