

Determination of historical emission of heavy metals into the atmosphere: Celje case study

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Received: 11 October 2007 / Accepted: 19 November 2007 / Published online: 5 December 2007
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Abstract The research shows that in the Celje area (Slovenia), the historical anthropogenical emissions are 1,712 tons of Zn and 9.1 tons of Cd. For Zn, this value represents approximately 0.3% of the total Zn production in that area. Close to the former zinc smelting plant, the “Zn precipitation” has been estimated to be up to 0.036 mm. The 100-year Zn production left behind a heavily contaminated area with maximum concentrations of Zn of up to 5.6% in attic dust and 0.85% in the soil, and 456 mg/kg of Cd in attic dust and 59.1 mg/kg in the soil. The calculation of historical emissions is based on the data of heavy metals concentration in the attic dust at 98 sampling points and on the data from 19 measurement sites of the weight of total monthly air deposit. The main idea behind determining past emissions is that when the weight of the deposited dust on a small area is multiplied by the concentration of the element in that area, the mass of the pollutant which has been transported to the place of interest by air can be calculated. If we sum up all the weight over the whole geochemical anomaly, we get the quantity of historical emissions.

Keywords Heavy metals · Attic dust · Air deposit · Celje · Emissions · Numerical methods

Introduction

Past environmental studies (Lobnik et al. 1989; Šajn 1999, 2005) show that the environment of Celje (Fig. 1) is

strongly contaminated with heavy metals, especially with those connected to the 100-year tradition of Zn smelting between 1874 and 1970. Before World War I there were 12 operational furnaces, which used pyrometallurgical processing of the sphalerite ore from nearby mines and imported ore from the Trepča mine (Serbia). A rough estimation from historical statistical almanacs is that, in Celje 580,000 tons of raw Zn waste produced. Nowadays Cinkarna Celje (former zinc smelting company) produces different chemical and metallurgical products. The titanium dioxide production plant has caused recent emissions of titanium into the atmosphere (Šajn 2005). Besides the zinc smelting plant, we also have to take into consideration the nearby Štore ironworks, which has been operational since 1861. But nevertheless, the Zn and Cd emissions from the ironworks are not comparable in sense of their quantities with the Zn and Cd emissions from the Cinkarna Celje plant.

Due to lack of different past environmental data and the wide spatial spread of the pollution, which extends to more than 35 km away (Žibret and Šajn 2005), the following question arises: what amount of heavy metals has been taken into the environment of Celje by emissions into the air? Because of a very low natural geochemical background, the majority of heavy metals in the soils in Celje are the consequence of airborne particle sedimentation, which has been the carrier of heavy metals. The main source of particles in the atmosphere was the Zn smelting operations. However, the amount of emissions of heavy metals that entered the air during the historic time of Zn production was unknown.

The town of Celje lies in the relatively young, tectonically formed Celje basin with a west–east extension. It is filled with Holocene alluvium. The altitude is between 240 and 260 m above sea level. To the north of the basin, on

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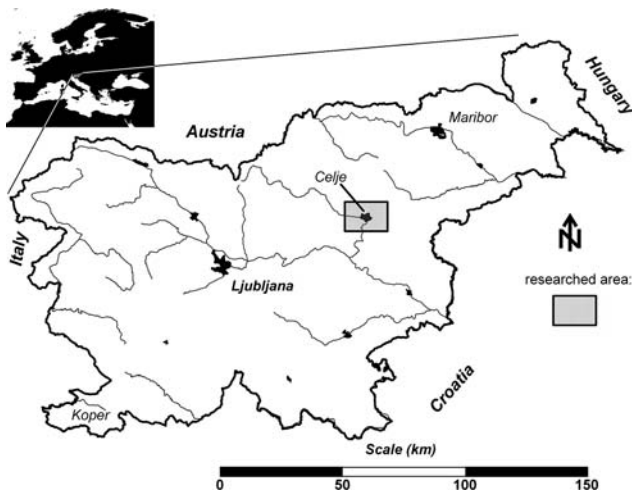


Fig. 1 Location of studied area

raised hilly terrain, are young Plio-Quaternary clay and sand sediments, Oligocene andesite tuffs, tuffites, claystones, conglomerates, marls and sandstones and Miocene sandy marls, conglomerates, sandstones and limestones. The old basis of Cenozoic sediments is mainly carbonatic Triassic rocks with keratophyre intrusions. The hills to the south of the Celje basin are made of Mesozoic rocks and can be macrotectonically placed in the Sava folds region (Buser 1977; Fig. 2).

The 30-year annual average climatic parameters show that the temperature inversion lasts for 95.2 days,

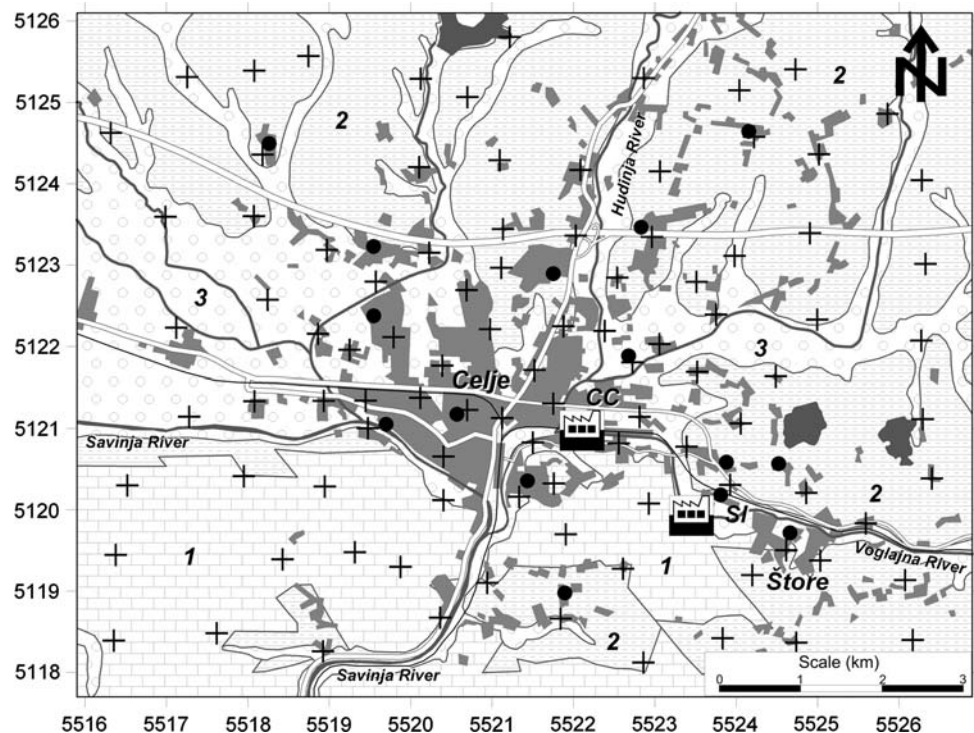
especially between September and January, the precipitation is 1,146 mm, and the average temperature is 9.1°C. Celje gets 1,655 h of annual solar insolation. The wind rose shows that the dominant wind directions are SW and NE, with an average velocity of 2 m/s and 32.1% of the year is calm (Cegnar 2003).

The community of Celje has a population of 48,081 (Dolenc 2003) and an area of 95 km². The industry is concentrated approximately 2 km NE from the city center. The main industries, chemical and metallurgical, are dominated by Cinkarna Celje (metallurgical and chemical products) and Železarna Štore (iron smelter).

The first document to address the environmental degradation of the Celje area was the forestry report from 1933. It reported shriveling in two-thirds of the trees. Between the end of the Second World War and the closure of the zinc smelting plants, the main emphasis was placed on the problems of SO₂ emissions and the monitoring of its concentration (Domitrovič-Uranjek 1990). In that period, the maximum concentration of SO₂ was 2,056 µg/m³, during the winter of 1968 (Verhovnik 1970). Only one research addressed the problem of heavy metal pollution (Planinšek 1972) in that time. The author concluded that the only source of Pb and Zn in the atmosphere of Celje were the furnaces for pyrometallurgical processing of the sphalerite ore.

The systematic measurement of the weight of air deposits started in 1989 (Stergar 2001; ZZV CE 2000). The

Fig. 2 Simplified geological map of the Celje area (1 Mesozoic rocks of Sava folds, 2 Oligocene; Miocene and Pliocene sediments, 3 Quaternary alluvial deposits), locations of sampling points of attic dust (crosses), locations of measurement spots for air deposit (circles; map shows all locations on presented area, four locations outside that area are not shown) and locations of past Cinkarna Celje zinc smelter (CC) and present location of Štore Ironworks (SI). Numbers on the left and bottom side are Gauss-Kruger coordinates in km



number, locations of monitoring sites and the duration of measurements have changed several times (min = 2, max = 15), but average weights can be used regardless. No other historical data about the quantity and composition of airborne particles are available.

Many authors have addressed the problem of determining the historical rate of pollution and have also used different media. Birch et al. (1996) used lake sediments as a record of the regional anthropogenic heavy metals intake into the atmosphere in the past 50–100 years. Dai et al. (2007) used marine sediments when they addressed the problem of the influence of present and historical wastewater discharge into the rivers and sea, and also the usage of the sea as a waste dump. Marine sediments were used to trace historical heavy metal pollution in the period 1910–2003. Heim et al. (2004) used floodplain sediments as an indicator of past pollution caused by municipal effluents, industrial sewage, wastewater discharge, incomplete combustion and intensive agriculture. The sediments were dated back to the year 1935. Meybeck et al. (2007) used different media as indicators of past pollution caused by the Paris megacity population, for different time periods: flood plain sediments for the period between 1930 and 2000 and suspended particulate matter as a more recent indicator (1983–2003). Attic dust has been recognized as a historical record of past air pollution by Ilacqua et al. (2003) and Cizdziel and Hodge (2000).

Materials and methods

Attic dust is a very suitable material for the research of past anthropogenic emissions because the everyday residential activities have almost no effect on attics and dust is usually preserved as electrostatically bound material to the wood on the lee of the attics. Concentrations of heavy metals in the air load, which have been deposited in the soil can be determined from the concentrations of heavy metals in the attic dust of old houses, located nearby. Because of the fact that in the wider Celje area there are a lot of houses more than 150 years old and that these houses are not concentrated just in the city center, but also in many other locations, such as old farms or vineyard cottages, attic dust has been chosen as the best indicator for the determination of historical deposit of heavy metals from the atmosphere. Dust has been sampled in the houses built before the beginning of the Zn smelting operations (1870). The second criteria was that the house must have the original wooden beams and the attics had not been used as storage for crops or hay or used as living space. The age of the house was determined on the basis of conversations with the owners of the object. The usage of wooden nails instead of iron ones in construction was also a good indicator of the appropriate house age.

The attic dust provided us with data about the concentration of elements in the historical atmospheric deposit on the area. The missing data for calculating past air emissions is the weight of the deposit that was deposited on the place during the selected period of time. With that data, the quantity of deposited element on a selected area (i.e. m²) can be concluded by multiplying the concentration of that element with the weight of material (Eq. 1).

$$m_{el.} = c_{el.} \cdot m \tag{1}$$

- $m_{el.}$ – mass of the deposited element on the selected area;
- $c_{el.}$ – average concentration of the element in the deposited dust in the selected period of time on the selected area;
- m – mass of the deposited dust in the selected period of time on the selected area.

However, spatially speaking, both the concentrations of elements and the weight of the deposited material change from place to place. This is why we have to define the functions, which spatially describe that change (Eqs. 2, 3).

$$c_{el.} = f(x, y) \tag{2}$$

$$m = g(x, y) \tag{3}$$

Equations 2 and 3 can fit into Eq. 1 to get Eq. 4, which represents the spatial changing of the mass of the emitted element on the selected area in the defined period of time in the relation to the spatial coordinates x and y .

$$m_{el.}(x, y) = f(x, y) \cdot g(x, y) \tag{4}$$

When we define the functions $f(x,y)$ and $g(x,y)$, the solution to the problem can be reached with the help of calculus. The total mass of the emitted element from the historical source of pollution can be calculated by integrating the function that describes the spatial changing of the mass of the deposited element (Eq. 5). x and y are geographical coordinates. They can be coordinates from the locally defined Euclidean coordinate system or simply the Gauss-Kruger coordinates.

$$\begin{aligned} m_{tot} &= \int_{x_{min}}^{x_{max}} \int_{y_{min}}^{y_{max}} m_{el.}(x, y) \cdot dx \cdot dy \\ &= \int_{x_{min}}^{x_{max}} \int_{y_{min}}^{y_{max}} f(x, y) \cdot g(x, y) \cdot dx \cdot dy \end{aligned} \tag{5}$$

- m_{tot} – complete emissions of the element emitted from the source of pollution.

With this method we can also separate the natural and anthropogenic parts simply by changing the function of the spatial concentration of the specific element with the estimation of the natural geochemical background (symbol »k« in Eqs. 6, 7) for that element, which might be a

constant value, when addressing the problems on a smaller scale. When the geochemical background is not constant and changes spatially, then the appropriate function has to be considered.

$$m(x, y) = k \cdot g(x, y) \quad (6)$$

$$\begin{aligned} m_{\text{tot}} &= \int_{x_{\min}}^{x_{\max}} \int_{y_{\min}}^{y_{\max}} m_{\text{el}}(x, y) \cdot dx \cdot dy \\ &= \int_{x_{\min}}^{x_{\max}} \int_{y_{\min}}^{y_{\max}} k \cdot g(x, y) \cdot dx \cdot dy \end{aligned} \quad (7)$$

The problem of mathematically expressing functions $f(x, y)$ and $g(x, y)$ can be solved with the help of numerical methods. With them we can also bypass the problem of integrability. Although we are operating with continuous functions, we can use matrices (grids) of data. In this case, we can exchange the differentials of the spatial coordinates with the grid spacing values (Eqs. 8, 9) and integrals with the sum of multiplied values (Eq. 10). In this way the problem can be easily solved with the appropriate software, i.e. Excel, Matlab, Surfer, etc. When calculating natural input with a constant geochemical background, Eq. 11 can be used.

$$dx = \Delta x \quad (8)$$

$$dy = \Delta y \quad (9)$$

$$m_{\text{tot}} = \sum_{x=x_{\min}}^{x_{\max}} \sum_{y=y_{\min}}^{y_{\max}} m_{\text{tot.}}(x, y) \cdot c_{\text{el}}(x, y) \cdot \Delta x \cdot \Delta y \quad (10)$$

$$m_{\text{tot}} = \sum_{x=x_{\min}}^{x_{\max}} \sum_{y=y_{\min}}^{y_{\max}} m_{\text{tot.}}(x, y) \cdot k \cdot \Delta x \cdot \Delta y \quad (11)$$

Before fitting the data into Eq. 10, the grids have to be prepared first. With them we can also correct any geometrical irregularities of the sampling positions and fill in the gaps of missing data. The data are usually not correctly spatially placed and the values are not always spatially dense enough. The grid eliminates these two problems. The gridding yields spatially regular values from spatially non-regular data.

The first thing to consider is the spacing between different values inside grids. These values depend on the type of problem and on the quantity of data. For local anomalies the grid spacing can be between 10 and 100 m and for regional anomalies between 1 and 10 km. For calculating larger, continental anomalies this method is not suitable because these equations deal with Euclidean space, to which the Earth's surface does not conform to.

Before creating the grid, the limit points (x_{\min} , x_{\max} , y_{\min} , y_{\max}) have to be considered. When determining the total emissions from one source of pollution, the limit

values have to be set such that the grid covers the whole anomaly and there is no or minimum need for extrapolation. The difference between the minimum and maximum values has to be a multiple value of the grid spacing (Eqs. 12, 13), where N is any natural number.

$$x_{\max} - x_{\min} = N \cdot \Delta x \quad (12)$$

$$y_{\max} - y_{\min} = N \cdot \Delta y \quad (13)$$

The method of creating the grids is interpolation. The procedures used are triangulation with linear interpolation, the natural neighbor method or kriging method. The polynomial interpolation method is not useful because it is possible that in some cases it can return negative values of concentrations and also when extrapolating the values, they can grow intolerably large. The software useful for gridding is Matlab, Golden Software Surfer, AutoCAD Map, and so on.

The sampling of attic dust was performed in the year 2000. A 1 km sampling grid was placed on an 8×10 km wide area. In the Celje urban area, the grid was condensed so that additional sampling points were placed in the middle of the four points of the basic grid. The randomness of the sampling grid was ensured by placing the microlocation of the starting point randomly (Pirc 1993). The total number of samples taken was 80 samples from the basic grid, 15 sampling points from the condensed grid and 2 additional sampling points added after the field inspection (Fig. 2).

The attic dust was collected from intact wooden roof-supported construction tiles of at least 130-year-old houses. The dust was brushed from the wood at different locations inside the attic. Special attention was placed not to collect different coarse particles (i.e. pieces of bricks, sand....) and different plant remains (leaves, crop remains, hay, etc.). The laboratory preparation included drying at 303 K to remove atmospheric humidity, sowing (<0.125 mm) and chemical analyses after the total 4-acid digestion (HClO_4 , HNO_3 , HCl and HF at 200°C) by inductively coupled plasma mass spectrometry (ICP-MS). Concentrations of Hg had been determined with cold vapor atomic absorption spectrometry CV-AAS after aqua regia digestion (mixture HCl , HNO_3 and water at 95°C). The number of analyzed elements was 42. The laboratory, which did the analysis, was ACME Analytical Laboratories, Vancouver.

Results

The maximum concentrations of Zn and Pb in the soil can be expressed as percentage (0.86% Zn and 0.15% Pb) and the attic dust can be classified as Zn-rich ore with maximum concentrations of 5.63% close to the former location

of the zinc smelting plant. The maximum concentrations of Cd reach 59 mg/kg in the soil and 456 mg/kg in attic dust. In Celje, there are 17.9 km² of critically polluted soil because of high concentrations of Zn, 4 km² of critically polluted soil because of high concentrations of Cd and 3.8 km² of critically polluted soil because of high concentrations of Pb, according to the Slovenian legislation (OG RS 1996; Žibret 2002).

The weight of collected air deposit varies between 187 and 57 mg/m² per day with a median value of 101 mg/m² per day, measured at 19 different locations (Fig. 2). The numbers are expressed as the average value of annual averages. The maximum monthly value is 1,155, the minimum is 25 and the median value is 112 mg/m² per day (ZZV CE 2000). The working period of the zinc smelting plant had been 100 years. The weight of air deposit at each location has to be expressed for that period of time. That is why each number had to be multiplied by 100 (years) and 365 (days/year) and divided by 1,000 to get the appropriate values, in grams, of fallen dust per 100 years.

The geochemical maps and factor analysis show that the environment is most contaminated with Zn and Cd and is a consequence of the Zn smelter. These elements are also geochemically associated with Pb, Ag, As, Cu, Mo, S, Hg and Sb. The natural geochemical association consists of Al, Ce, K, La, Li, Rb, Sc and Th. A third geochemical association, which is not of natural origin (Ti, Nb), is the consequence of the recent production of titanium dioxide. The association of Co, Cr, Fe, Mn, and Ni is connected with the iron smelter in Štore (Šajn 2005).

The limit points were defined so that the majority of the whole geochemical anomaly has been covered. Also the sampling plan allowed us not to extrapolate more than several hundred meters. The border coordinates we chose were (Gauss-Kruger coordinates in meters): $X_{\min} = 5,515,900$; $X_{\max} = 5,526,900$; $Y_{\min} = 5,117,700$ and $Y_{\max} = 5,126,100$. Using these limit points, the majority of the geochemical anomaly has been covered by the grid (Fig. 3b). The differences in the minimum and maximum coordinates also allowed us to choose a variety of spacing values ΔX and ΔY (Eqs. 12, 13) used in Eq. 10. We tried different spacing values but the value $\Delta X = \Delta Y = 50$ m was a good compromise between the accuracy and speed of computation. The difference between a spacing value of 10 and 100 m means less than 1% difference in the final result on the Celje case study.

The next step was the creation of grids (Fig. 3). The grids were created using the method of triangulation with linear interpolation for all chemical elements and for the weight of air deposit. Figure 3 graphically represents the procedure of the historical emissions calculation. Figure 3a shows the 3D grid visualization of the quantities of measured weight of air deposit on 1 m² and recalculated

to 100-year period, expressed in tons. Two peaks are visible, one is in the measurement site inside the industrial zone (Celje—industrijska cona), and the second is nearby the Celje city centre (Celje—Lava). Figure 3b shows the visualization of the grid, which shows the spatial arrangement of Zn concentration in the attic dust, expressed in mg/kg. The highest concentrations are situated in the vicinity of the abandoned Zn smelter plants. The third grid visualization (Fig. 3c) shows the multiplication of each grid cell from Fig. 3a with appropriate grid cell from Fig. 3b. The volume of the obtained body represents the historical 100-year Zn emissions into the atmosphere, expressed in tons and can be calculated using the Eq. 10. The units on the x and y axes of Fig. 3a, b, c are grid units. Each grid unit or grid cell is 100 × 100 m wide.

The final results were obtained using the same procedure as shown in the Fig. 3 and are shown in Table 1. Equations 10 and 11 have been used. The values of the geochemical background (value k in the Eq. 11) had been obtained from a geochemical map of Slovenia (Šajn 1999).

Discussion

The proposed method works only if we make certain assumptions. They are:

- (1) The composition of attic dusts of old houses represents the average composition of particle emissions at the location of sampling.
- (2) The recent measurements of the weights of monthly deposited dust are comparable with the weight of monthly deposited dust, which might have fallen on the ground in the past.
- (3) The geochemical background in the Celje area is a constant value throughout the researched area.

The first assumption is likely correct because at the sampling points we chose houses which are older than the source of the pollution. However, the second assumption can be quite tricky because the quantity of emitted airborne particles can vary. The problem is that there were no available measurements of particle sedimentation in the period of Zn (and consequently also the maximum airborne particles) production between 1870 and 1970. The only option was to use the data of recent measurements, which have been conducted since 1989. Recent values are expected to be lower than the historical amount of particle sedimentation. Therefore, the calculated values might be lower than the actual ones. The third assumption is likely correct, because attic dust is, geochemically speaking, a much less variable medium than soil and also the researched area is small enough not to catch the regional variations.

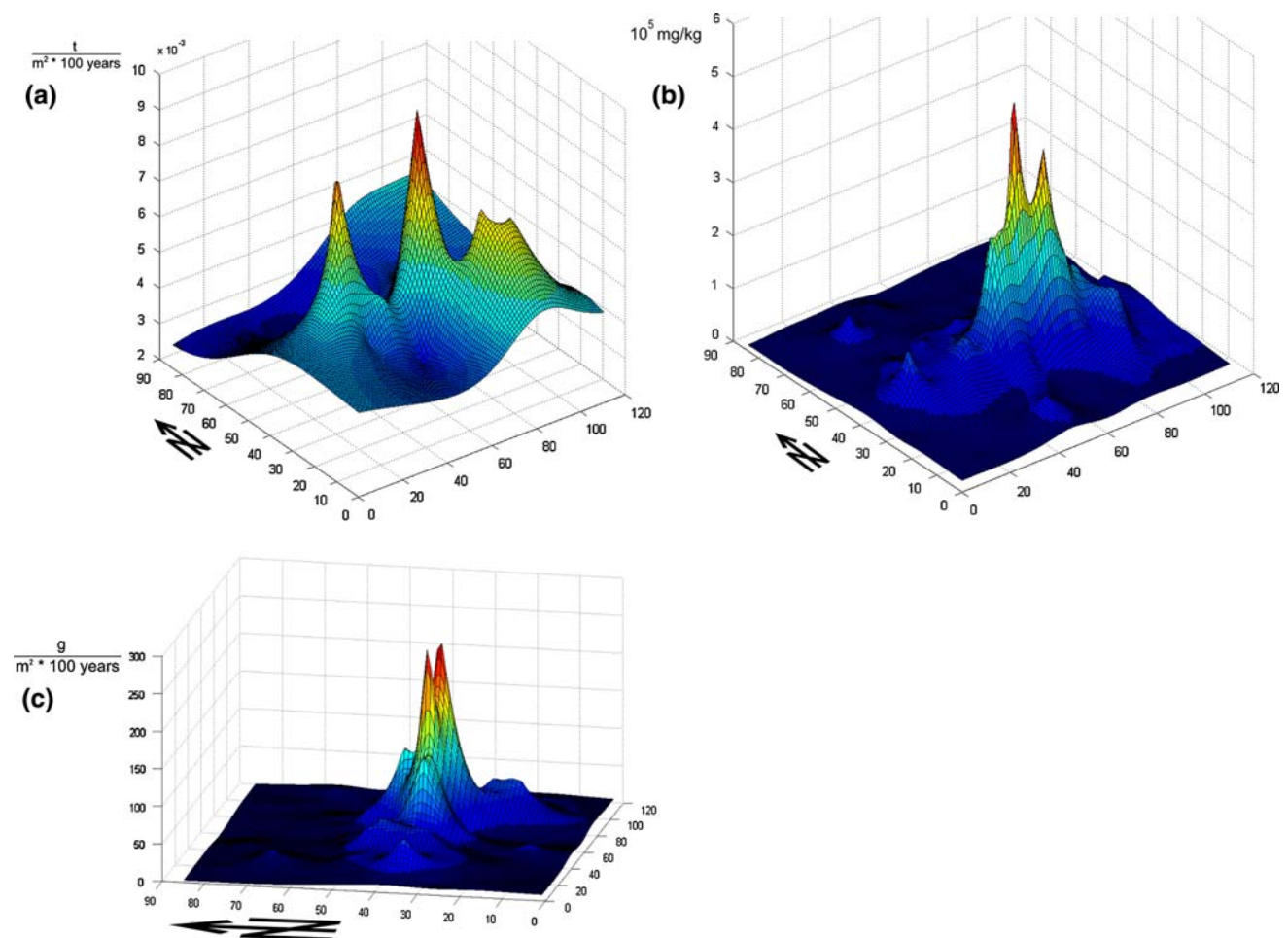


Fig. 3 Graphs of the grids used for calculation of the total emissions of zinc into the atmosphere in the Celje case study. **a** Weight of the sedimented dust in the 100-year period, expressed in tons per m^2 , **b** concentration of zinc in the attic dust, expressed in mg/kg ; **c** graph of

the multiplication of each cell from grid(a) and grid (b), expressed in grams per m^2 in the period of 100 years. The volume of the last body represents the complete emissions from the Cinkarna Zinc Smelter during its operational time

If we compare the results in Table 1, we see that all the elements from the geochemical association connected with Zn production (Zn and Cd) have the greatest anthropogenic/natural ratio with anthropogenic emissions more than six times than that of the natural. The environment is most contaminated with these two elements. On the other hand the elements, where geochemical distribution is mostly natural (Al, Na, Ti, Hg), show very low anthropogenic emissions compared to the natural ones. This is especially the case with aluminium and mercury. The elements probably connected with the pyrometallurgical processing of the sulphide ore (Cu, Pb) show a moderate anthropogenic/natural emissions ratio. The situation is similar with the elements connected with steel production at the nearby Štore steel plant (Ni, Sn). Data on the natural background in the attic dust for Fe and As are unavailable.

This method can be evaluated by comparing the anthropogenic emissions with the total production of Zn in

Cinkarna Celje. From historical data it can be concluded that 580,000 tons of raw Zn had been produced (Žibret 2002). This means that the calculated emissions into the air are 0.3% of the total production. The real quantity can be expected to be between 1 and 2% (Stergar 2001), which was the actual emission/production ratio for the furnace at the Štore Steelworks before installing the dust filters. A value lower than expected could be the consequence of the data about the weight of deposited air dust during the past period of maximum Zn production possibly being much higher than today. Nevertheless, it is believed that the numbers we got correctly represent only a scale factor, not exact emissions. However, production has been closed for 35 years and any estimation of emitted heavy metals into the atmosphere due to the production is better than nothing.

When taking into account the density of the Zn, which is $7,140 \text{ kg/m}^3$ and the maximum zinc deposition on 1 m^2 in 100 years (258 g/m^2), the additional conclusion about

Table 1 Basic nonparametric statistics, total, anthropogenic and natural emissions of different elements in the atmosphere during the period of zinc smelting in the researched area of Celje

	Min (mg/kg)	Max (mg/kg)	Md (mg/kg)	Back. (mg/kg)	Tot (t)	Anth. (t)	Nat. (t)	Anth./nat.
Al	18,000	54,000	33,000	25,100	12,930	1,388	11,540	0.120
As	6	482	36	–	16.1	–	–	–
Cd	2.3	456	24	3.8	10.46	9.102	1.353	6.73
Cu	48	1,086	157	71	65.61	44.55	21.05	2.17
Fe	12,000	150,000	33,000	–	15,270	–	–	–
Hg	0.11	4.59	0.545	1.5	0.288	0.039	0.248	0.157
Na	3,000	18,000	4,600	3,100	1,864	811.4	1,053	0.771
Ni	21	367	57	26	24.22	14.44	9.775	1.48
Pb	191	6,920	622	270	278.7	180.9	97.75	1.85
Sn	4.3	1,832	22	11	12.08	7.940	4.136	1.92
Ti	999	7,500	2,500	1,900	975.4	246.0	729.4	0.337
Zn	459	56,000	4,400	500	1,919	1,712	206.8	8.28

Min minimum value, *max* maximum value, *Md* median value, *back.* background value for the attic dust (Šajin 1999), *tot* total emissions of the element in the atmosphere, *anth.* anthropogenic input of the element in the atmosphere, *nat.* natural input of the element in the atmosphere, *A/N* ratio between anthropogenic and natural input of the element in the atmosphere

maximum “zinc precipitation” can be calculated using basic arithmetic operations. This value is 0.035 mm and this spot is located nearby the past zinc smelter plants.

The significance of this method is that it allows the determination of the historical emissions of the heavy metals into the atmosphere where almost no historical data on environmental emissions and monitoring are available. It gave good results comparing to the other possible ways of estimation of the atmosphere emissions of heavy metals based on the historical data about production.

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