



Article

Tin and Antimony as Soil Pollutants along Railway Lines—A Case Study from North-Western Croatia

Zvezdana Stančić ^{1,*} , Željka Fiket ² and Andreja Vuger ¹

¹ Faculty of Geotechnical Engineering, University of Zagreb, Hallerova aleja 7, HR-42000 Varaždin, Croatia; andrejavuger@gmail.com

² Division for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia; zeljka.fiket@irb.hr

* Correspondence: zvstan@gfv.hr; Tel.: +385-42-408-947

Abstract: The aim of this study was to determine the extent and patterns of antimony and tin contamination in soils along railway lines, as there are very few data in the literature on this subject. The study was conducted in north-western Croatia. Total and bioavailable concentrations of Sn and Sb were detected using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The following results were obtained: total concentrations of Sb ranged from 0.98 to 52.0 mg/kg and of Sn from 3.04 mg/kg to 97.6 mg/kg. The soil samples showed pronounced Sb and Sn enrichment, up to 87 and 33 times the median value for European soils, respectively. In contrast to the total concentrations, the bioavailable concentrations showed relatively low values. For Sn, the percentage of total content ranged from 0.001 to 0.021%, while for Sb it ranged from 0.001 to 0.136%. Statistical data analysis suggests that the distribution of Sb and Sn in soils near railway lines is influenced by the functional use of the site, distance from the tracks, topography, age of the railway line, and also by soil properties such as soil texture, humus content, and soil pH. This study demonstrates that rail transport is a source of soil pollution with Sn and Sb. The origin of Sb and Sn enrichment is abrasion by brakes, rails, wheels, freight losses, exhaust gasses, etc. Both elements in soils along railway lines pose an environmental risk to humans, agricultural production, and wildlife, and therefore further detailed studies are required.

Keywords: antimony; tin; railway; soil; pollution; bioavailability; Croatia



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1. Introduction

The development of transportation, industry, power generation, and agriculture are crucial factors in the economic progress of any country. Unfortunately, such progress is associated with increasing pollution and often leads to the contamination of various components of the environment. Among the most commonly studied inorganic pollutants are heavy metals and metalloids (hereafter referred to as HMs). While some HMs, such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) are frequently the subject of research, antimony (Sb) and tin (Sn) are rarely analysed, although they are frequently used in everyday products.

Antimony is used mainly as a flame retardant (Sb₂O₃) in textiles, paper, plastics and adhesives, and in brake linings; in alloys (as a hardener of Pb in Pb acid batteries, cable sheathing, bullets, component in semiconductors, bearings); as stabilisers and catalysts in plastic manufacturing (PET); as rubber compounds; as additives in tire vulcanisation; as pigments in paints and varnishes; in ceramics manufacturing (opacifiers in enamels); in glass manufacturing; as losses; as abrasives; as antiparasitics; and in chemicals for ore dressing, and others [1–3].

Tin is used extensively for protective coatings (tinning) on steel to prevent corrosion, especially in food and beverage cans; in electrical solders (for joining pipes, electrical,

and electronic equipment); in the manufacture of alloys (e.g., bronze is about 90% Cu and 10% Sn, pewter contains about 85% Sn), some of which are used in the manufacture of brakes, landing gear, and engine parts in the automotive and aerospace industries; in additives in foodstuffs and toothpaste (SnCl_2); in the manufacture of organotin compounds, which have a wide range of uses, including heat stabilisers in PVC (66%), catalysts, and various biocides; in glass treatment; and in various other chemicals [1,4].

Consequently, both elements are released into the environment through various pathways, including mining, ore transportation, smelting, manufacturing and use of their products, disposal of wastes and sludges, wastewater [2,5–8], and so on. As a result, Sn and Sb accumulate in the pedosphere, hydrosphere, and biosphere.

One of the sources of pollution with Sb and Sn is rail transport. Both elements are released in various ways, e.g., dust emissions, freight losses, exhaust fumes, and the use of herbicides [9,10]. According to Burkhardt et al. [10], particulate matter is the dominant source of HMs in rail transport, and several authors have studied this issue [11–13]. Ultimately, everything enters the soil by wet or dry deposition and leaching. In the available literature, there are only three studies in which Sb and/or Sn were determined in the soil along railway lines [14–16]. However, there are studies that have investigated the presence of other HMs in soils along railway lines, in Canada [17,18], China [19–26], Czech Republic [27], Germany [28], India [29], Ghana [30], Lithuania [31,32], Poland [14–16,33–41], Russia [42,43], Serbia [44], and Ukraine [45–48], most of them including fewer than 10 elements, usually Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn.

Both trace elements, Sn and Sb are toxic to humans and living organisms in certain chemical forms [49,50]. In the case of Sn, the most dangerous organic compounds (e.g., organotin) are outlined in Alloway [4], while in the case of Sb, Sb (III) is more toxic than Sb (V) [2]. Detailed descriptions of chemical forms, processes, mobility, bioavailability, and toxicity in soil can be found for Sb in Adriano [1], Filella et al. [2,5], Clemente [3], Herath et al. [51], and Bagherifam et al. [8], and for Sn in Adriano [1], Rüdell [52], and Alloway [4].

In addition to HMs, railroads also emit various other types of pollutants, such as polycyclic aromatic hydrocarbons (PAHs) from creosote and lubricants, polychlorinated biphenyls (PCBs), various hydrocarbons, herbicides, phenols, gasolines, and mineral oils [40,53–59]. There are studies demonstrating the synergistic effect of several pollutants together, which can be toxic to organisms even at low concentrations below permissible levels [40]. In addition, railroads are a source of other negative impacts: noise, vibration, and light pollution. Thus, recent extensive studies in Europe conducted by Eze et al. [60] have shown that railway traffic, especially long-term exposure to noise and air pollution, affects human health and causes DNA methylation, which is associated with inflammation and immune responses, thus accelerating biological aging and causing various diseases (respiratory, cardiovascular, and others). In addition to the negative impacts of rail traffic on human health, numerous negative impacts on ecosystems and wildlife have also been confirmed [61].

This study was conducted because the railway network is widespread worldwide and very little is known about Sb and Sn in the soil along railway lines. In order to increase the knowledge about antimony and tin, rare trace elements emitted by railway traffic, the main objectives of this work are: (a) to determine the Sb and Sn content in soils along the railway lines in north-western Croatia, (b) to identify the contamination patterns, (c) to study the bioavailable concentrations of Sn and Sb in soils, and (d) to determine their possible sources.

2. Materials and Methods

2.1. Study Area

The study covers the north-western part of Croatia (Figure 1a), the most densely populated part of the country with a well-developed railway network. Sampling was carried out along three railway lines: Zagreb Main Station–Varaždin (104 km), Varaždin–

for loading and unloading passengers and freight. According to the topography, the sites are subdivided into: (i) above the tracks, (ii) at track level, and (iii) below the track level.

2.3. Soil Properties Analysis

The following analyses of the soil properties were performed: determination of soil texture [64], classification into texture classes [65], measurement of soil pH [66], determination of humus content using the Tjurin method [67], and classification of soils according to humus content [68].

Determination of soil texture: to 10 g of an air-dried soil fraction (<2 mm particles), 25 mL of 0.1 M sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \times 10\text{H}_2\text{O}$) was added, shaken, and left overnight. The next day, the fractions were separated by wet sieving through 212 μm and 63 μm hole size sieves: coarse sand (2.0–0.2 mm) and fine sand (0.2–0.063 mm). A glass cylinder containing soil particles <63 μm was filled up to 1000 mL with distilled water, the content was shaken, and after 4 min and 48 s of sedimentation, 10 mL of the soil suspension was pipetted from a depth of 10 cm and the fraction <20 μm was obtained; after 4 h of sedimentation, 10 mL of suspension was pipetted again from a 5-cm depth, and the fraction <2 μm was obtained. All separated fractions were dried in a thermostat at 105 °C to a constant mass, weighed, and the percentages of all fractions were calculated.

Determination of soil reaction: it was carried out in (i) a water eluate of the soil samples ($\text{pH}_{\text{H}_2\text{O}}$), and (ii) a mixture of soil and potassium chloride solution (pH_{KCl}). To each 10 g of the soil sample, 25 mL of deionised water and 25 mL of 1 M KCl solution were added. The prepared samples were mixed with a magnetic stirrer for 15 min. Then, the soil reaction was measured using a pH meter, SensION156, HACH. Before evaluation, the pH meter was calibrated with standard buffer solutions whose pH values were 4.0, 7.0, and 10.0.

Humus determination in soil: 0.1–0.5 g of air-dried soil samples were weighed, and 10 mL of 0.067 M potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and 0.1 g of silver sulphate (Ag_2SO_4) were added to the sample. All were mixed and boiled in a digester for 5 min. The cooled sample was filled up to a volume of 150 mL with distilled water. Then, 2 mL of a mixture of concentrated sulphate (H_2SO_4) and phosphoric acid (H_3PO_4) and 8 drops of the indicator diphenylamine sulfonic acid ($\text{C}_{12}\text{H}_{11}\text{NNaO}_3\text{S}$) were added. The sample was then mixed and titrated with a solution of 0.1 M Mohr's salt ($\text{Fe}(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$) until a green colour appeared. The mass fraction of humus (w) was calculated using Equation (1):

$$W_{\text{humus}}(\%) = \frac{(\text{Mohr salt depleted for blank titration (mL)} - \text{Mohr salt depleted for sample titration (mL)}) \times 0.0005172 \text{ g}}{\text{soil sample mass (g)}} \quad (1)$$

2.4. Sample Preparation for Analysis of Bioavailable and Total Sb and Sn Concentrations

For the determination of bioavailable Sb and Sn concentrations, a single-step extraction method [69] was used. To 1.5 g of soil sample, 15 mL of 0.01 M calcium chloride (CaCl_2 , Sigma Aldrich, St. Louis, MO, USA) was added. The solution was shaken on a shaker for 2 h, then centrifuged at 4000 rpm for 10 min, filtered through 0.45 μm membrane filter paper, and acidified with 0.5% nitric acid (HNO_3 , sp.).

To analyse the total content of Sb and Sn in the soil, subsamples (0.05 g) of the soils were subjected to total digestion in a microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure consisting of digestion with a mixture of 4 mL nitric acid (HNO_3 , 65%, pro analysi, Kemika, Zagreb, Croatia)—1 mL hydrochloric acid (HCl , 36.5%, pro analysis, Kemika, Zagreb, Croatia)—1 mL hydrofluoric acid (HF , 48%, pro analysi, Kemika, Zagreb, Croatia) followed by the addition of 6 mL of boric acid (H_3BO_3 , Fluka, Steinheim, Switzerland) [70]. After digestion, the soil samples were further diluted 10-fold, acidified with 2% (*v/v*) HNO_3 (65%, supra pur, Fluka, Steinheim, Switzerland), and indium (In , 1 $\mu\text{g}/\text{L}$) was added as the internal standard.

2.5. HR-ICP-MS Analysis

The analysis of all prepared solutions (single-step extracts and total digests) was performed using High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). The typical instrument conditions and measurement parameters used throughout the work were reported earlier [70]. Standards for multielement analysis were prepared by the appropriate dilution of standard solutions for Sn (1.000 \pm 0.002 g/L, Analytika, Prague, Czech Republic) and Sb (1.000 \pm 0.002 g/L, Analytika, Prague, Czech Republic). The quality control of the analytical procedure was performed by a simultaneous analysis of the blank and the certified reference material for soil (NCS DC 77302, also known as GBW 07410, China National Analysis Center for Iron and Steel, Beijing, China). A good agreement between the analysed and the certified concentrations within their analytical uncertainties (\pm 10%) for both measured elements was obtained [70].

2.6. Statistical Analysis

Data were statistically processed using STATISTICA 7.0 (StatSoft, Inc., Tulsa, OK, USA). Multivariate principal component analysis (PCA) was performed on the data matrix consisting of Sb and Sn concentrations, grain size fractions, texture, humus content, and pH (pH_{H2O} and pH_{KCl}). Differences between groups (distance to railroad tracks, topography, function, and age) were tested using the Kruskal–Wallis analysis of variance (ANOVA), followed by a pairwise comparison using Dunn’s method, with the significance level set at $p < 0.05$.

To determine the extent of site contamination with Sn and Sb, the contamination factors (CFs) (ratio of metal concentration in the sampled soil to background concentration in uncontaminated soil) were calculated using Equation (2):

$$CF = \frac{c \text{ (metal measured)}}{c \text{ (metal background)}} \quad (2)$$

3. Results and Discussion

3.1. Distribution of Sb and Sn in Soil Near Railway Tracks

The total concentrations of Sn in soils along the railway lines in north-western Croatia ranged from 3.04 mg/kg to 97.6 mg/kg (Table 1). The highest Sn content was found at Zaprešić railway station. For Sb, the total soil concentrations ranged from 0.98 to 52.0 mg/kg. The highest Sb content was found in the soil of Konjščina station.

Table 1. Total concentrations of Sn and Sb in soils from north-western Croatia, humus content, soil reaction, and soil texture. Abbreviations: I—loam, IP—loamy sand, P—sand, PI—sandy loam, Pr—silt, PrGl—silty clay loam, and PrI—silty loam.

No. of Locality	Locality	Sn (mg/kg)	Sb (mg/kg)	Humus (%)	pH _{H2O}	pH _{KCl}	Texture Class
1	Golubovec	3.98	1.21	2.7	6.8	6.2	PrI
2	Lepoglava	14.5	8.71	8.7	7.1	6.7	PI
3	Kaniža	7.90	0.98	4.5	7.1	6.6	PrI
4	Ivanec	8.25	1.50	6.2	7.3	6.7	PrI
5	Ivanec	7.88	5.07	8.8	7.3	6.9	PI
6	Novo Cerje	14.3	6.02	9.2	7.3	6.7	PrI
7	Novo Cerje	9.31	1.59	3.9	7.2	6.2	Pr
8	Gojanec	7.10	1.11	8.2	7.3	6.8	PI
9	Donji Kučan	7.04	1.18	4.0	7.3	6.8	PI
10	Jalžabet	7.25	1.65	5.4	7.4	6.7	PrI
11	Martijanec	7.06	1.72	4.8	6.9	6.0	PrI
12	Ludbreg	18.8	8.92	10.9	7.1	6.8	PI
13	Ludbreg	16.2	8.62	5.2	7.6	7.3	IP
14	Varaždin	52.6	27.4	8.5	7.7	7.1	PI
15	Varaždin	14.2	9.09	2.7	8.1	7.9	PI
16	Varaždin	30.7	21.4	17.7	7.8	7.1	PI
17	Varaždin-Turčin	6.63	1.06	1.2	7.7	6.8	I

Table 1. Cont.

No. of Locality	Locality	Sn (mg/kg)	Sb (mg/kg)	Humus (%)	pH _{H2O}	pH _{KCl}	Texture Class
18	Tomaševac-Križanec	8.26	1.54	3.1	7.6	6.7	Prl
19	Krušljevec	7.80	2.06	4.1	7.7	7.1	IP
20	Presečno-Novi Marof	7.89	1.25	2.5	7.9	7.3	I
21	Novi Marof	8.11	2.94	14.7	7.7	6.8	Pl
22	Mađarevo-Topličica	6.98	1.35	2.6	7.9	7.4	IP
23	Podrute	20.5	17.9	8.0	7.8	7.4	Prl
24	Podrute	9.08	3.84	5.4	7.8	7.1	Prl
25	Podrute-Budinščina	6.54	1.36	5.5	7.7	7.2	Pl
26	Budinščina	14.9	8.90	12.9	7.7	7.1	Pl
27	Hrašćina Trgovišće	7.81	2.13	15.5	7.5	6.9	PrGI
28	Konjšćina	8.96	52.0	9.5	7.6	7.3	Pl
29	Donji Lipovec	9.17	1.25	1.9	7.4	5.8	Pr
30	Zlatar Bistrica	7.25	2.00	7.0	7.3	6.7	Prl
31	Zlatar Bistrica	12.0	4.33	5.1	6.7	6.8	Prl
32	Lovrečan-Poznanovec	9.07	2.28	7.1	6.8	6.8	I
33	Zagreb, Main station	8.20	4.61	4.9	7.1	7.1	Prl
34	Zagreb, Main station	27.4	11.0	9.2	7.1	7.0	Prl
35	Zagreb, Main station	6.90	5.49	4.1	7.4	7.5	P
36	Zagreb, Western station	10.7	5.83	5.1	7.5	7.3	IP
37	Zagreb, Western station	3.25	3.10	1.0	7.7	7.6	P
38	Kustošija-Zagreb, Main station	5.58	4.06	8.6	7.5	7.2	P
39	Vrapče	6.77	3.95	5.3	7.8	7.2	Prl
40	Podsused	34.1	25.5	14.0	7.7	7.0	Pl
41	Podsused	3.94	2.34	5.5	7.7	7.4	Pl
42	Zaprešić	28.4	16.7	15.7	7.8	7.0	Pl
43	Zaprešić	12.4	5.92	9.2	7.7	7.1	Pl
44	Zaprešić	97.6	13.3	15.0	7.7	7.1	Pl
45	Novi Dvori	4.31	1.95	8.7	7.6	7.1	I
46	Novi Dvori-Zaprešić	6.80	4.45	9.5	7.7	6.8	I
47	Pojatno	5.38	2.80	7.4	7.6	6.9	I
48	Kupljenovo	3.04	2.49	4.6	7.9	7.2	I
49	Luka	9.62	7.41	10.9	7.8	7.2	IP
50	Žeinci	61.4	43.2	11.5	7.6	7.0	I
51	Vekiko Trgovišće	20.7	25.3	13.1	7.7	7.0	I
52	Vekiko Trgovišće	4.55	1.54	4.3	7.8	7.1	Prl
53	Zabok	6.22	2.17	7.8	7.8	7.0	Prl
54	Zabok	3.83	2.89	9.3	7.8	7.0	PI
55	Hum Lug	4.88	3.40	6.2	7.7	7.1	PI
56	Dubrava Zabočka	6.50	2.79	7.0	7.4	6.9	Prl
57	Špičkovina	6.12	4.53	3.2	7.8	7.5	IP
58	Poznanovec- Bedekovčina	6.23	2.97	6.9	7.6	7.1	Prl
59	Bedekovčina	6.52	2.89	8.3	7.8	7.1	I
60	Bedekovčina	13.3	2.85	4.4	7.9	7.1	I
	Average	13.2	7.13	7.3			
	Median	7.89	3.04	7.0			
	Maximum	97.6	52.0	17.7	8.05	7.90	
	Minimum	3.04	0.98	1.00	6.70	5.84	
	Background sample	4.13	1.67				

Tin and antimony are naturally present in soil in certain amounts. According to the Geochemical Atlas of Europe [71], the median for Sb and Sn in European topsoil is 0.6 mg/kg and 3 mg/kg, respectively. According to the same literature source, the soils in north-eastern Croatia contain between 0.83 and 1.46 mg/kg Sb, and between 4.00 and 7.00 mg/kg Sn. In fact, the Sb and Sn contents in the studied soils in the north-western part of Croatia range from the minimum values close to the medians reported for European soils to the maximum values of 52.0 mg/kg for Sb and 97.6 mg/kg for Sn, with RSDs of 139% and 117%, respectively. At the sites where the highest CF values were established, the concentrations of Sb and Sn in the soil were 87 and 33 times higher, respectively, than the median value for European soils; 36 and 14 times higher, respectively, than the lowest

value reported for north-eastern Croatia; and 31 and 24 times higher, respectively, than the background value for the study area (Table S1). The obtained data indicate not only a great variability of Sb and Sn content, but also an exceptional enrichment of the soil with Sb and Sn at certain sites.

In the present study, total concentrations of Sb exceeded the upper limit for regional soils in a total of 51 samples and in 16 sites by a factor of 5 or more [71]. A similar situation was observed for Sn, where the content above the upper limit for regional soils [71] was measured at 39 sites, although this factor was higher than 5 at only 3 sites (Table S1).

To our knowledge, the data for Sb and Sn in soils near railway lines include only three studies conducted in Poland (Table S2). Specifically, Dzierżanowski and Gawroński [14] investigated Sn and Sb concentrations between railway stations in the suburbs of Warsaw. Measurements were performed in situ with XRF instruments, and due to the high detection limits (18 mg/kg and 218 mg/kg for Sn and Sb, respectively), Sn and Sb were not detected. Wiłkomirski et al. [15] carried out investigations in the area of four railway stations in north-eastern Poland (Białystok, Sokółka, Hajnówka, and Kuźnica)—Sb was not determined, and the maximum value of Sn was 23 mg/kg. Staszewski et al. [16] conducted a study in northern Poland, at the Łława Główna railway junction. The concentrations of Sn were 2–5 times higher than those of the control samples, with the highest value of 33 mg/kg, while Sb was not included in the study. A comparison of the data from our study and the cited studies from Poland shows the highest recorded values for Sn in soils near railway lines in Croatia, while for Sb, the lack of data precludes further comparison.

Although the rail network is quite widespread worldwide, studies of HMs along railways, especially compared to urban and industrial areas, are relatively rare, which may be partly because they are considered trivial [19]. Wiłkomirski et al. [59] pointed out that there are surprisingly few reports in the scientific literature describing environmental problems caused by rail transport. Similarly, Popp and Boyle [72] highlighted that there is a conspicuous lack of research related to railways and their impacts on wildlife.

Comparing soil contamination with Sb and Sn along the railway lines in this study with other sources of pollution, the highest levels were measured near mining and smelting areas [2]. Examples: 6.4–21775 mg/kg Sb near old Sb–Au and As–Au mines in NW Portugal [73]; 10.3–1200 mg/kg Sb in a former Sb mining and smelting area in SW Scotland in the UK [74]; 11.9–710 mg/kg Sb near former As–Cu, Pb–Cu–As and Sb–Pb mining sites in the UK [75]; 527–11798 mg/kg Sb in an active Sb mining area in China [76]. Similarly, very high Sb levels, in the range of 35–17500 mg/kg, have been measured in shooting areas in slope substrate (non-natural soil) in Switzerland [77]. Very high levels of Sb (1.6–368 mg/kg) and Sn (3.2–115 mg/kg) were also found in an abandoned wastewater reservoir in China [78]. Furthermore, in urban and industrial areas, especially along busy roads, concentrations of Sb and Sn are elevated compared to the background levels in soil. Examples: the average value of 5.2 mg/kg Sb was found in soils near road intersections in the city of Bratislava in the Slovak Republic [79]; 5–70 mg/kg Sb at busy road intersections in three cities (Prague, Ostrava, České Budějovice) in the Czech Republic [80]; 0.5–6.2 mg/kg Sb along roads in the south of Cologne (Klettenberg and Raderthal) in Germany [81]; up to 8 mg/kg Sb along two highways (near Kalmar and Varberg) in southern Sweden [82]; 6.8–15 mg/kg Sn along rural roads and highways (between Nigde and Adana) in Turkey [83]; up to 5 mg/kg Sb along highways (between Curitiba and Ponta Grossa) in Brazil [84]; and 0.3–34.2 mg/kg Sb in roadside soils in Shanghai, China [85]. It is evident that, in this study, the measured Sb concentrations at larger and busier railway stations were higher than most of the measured values along roads. For Sn, there are relatively few data in the literature. Thus, although thousands of articles have been published on the pollution of soils with metals and metalloids in places with different anthropogenic influences around the world, neither Sb nor Sn have yet been identified as pollutants along railway lines.

Croatian regulations [86–89] define the maximum permissible concentrations of some HMs, but Sn and Sb are not included in this list. According to the European Chemicals Agency [90,91], antimony is recognised as a toxic element, while tin is not considered

harmful to humans or the environment. In addition, antimony is listed on the Priority Pollutant List of the USA [92]. Some developed countries set maximum permissible levels for both elements in soil. According to the Dutch standards [93], the intervention value for Sb in soil is 22 mg/kg, and the indicative level for severe contamination for Sn in soil is 900 mg/kg.

3.2. Bioavailable Concentrations of Sn and Sb in Soils

In our study, the bioavailable concentrations of Sn in the soil samples range from 0.0004 to 0.0015 mg/kg with a percentage of total concentration ranging from 0.001 to 0.021%, while for Sb, the bioavailable concentrations range from 0.001 to 0.136 mg/kg with a percentage ranging from 0.01 to 0.35% (Table S3). It follows that a very small fraction of the total concentration of both elements is in the form of a bioavailable fraction.

When we compare the bioavailable and total concentrations of Sn and Sb in the soil, we can see that these two elements behave differently (Figure 2). For Sb, an increase in the bioavailable concentration was observed with increasing total concentration in soil, whereas for Sn, bioavailable concentrations were similar regardless of the total concentration of Sn in soil.

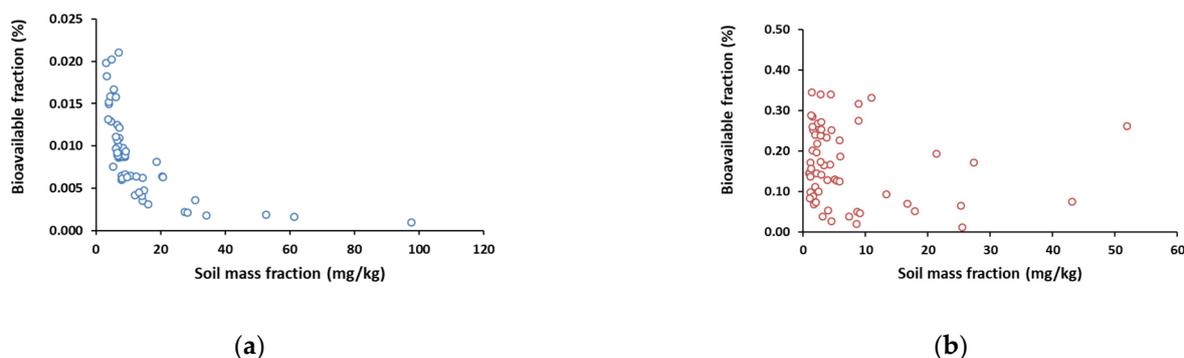


Figure 2. Dependence of the bioavailable concentration (%) and the total concentration of each element in the soil for (a) Sn, and (b) Sb.

Bioavailable concentrations of the elements in soil are considered to be available to living organisms [94] and are a better indication of their potential toxic or nutritional effects than total concentrations. In addition to bioavailability, which is the term most commonly used in the literature, the term bioaccessibility is also used (a search on 15 November 2021 found 118676 results for “bioavailability” and 6463 results for “bioaccessibility” in the Web of Science Core Collection). Bagherifam et al. [8] offer several definitions for both terms. One is “bioaccessibility includes what is actually bioavailable now and what is potentially bioavailable”.

The bioavailable or bioaccessible concentrations of elements are influenced by many environmental factors. The most important factors affecting the bioavailability of Sb are: soil chemical composition, Fe and Mn oxides, aging, disturbance factors, metalloid source, and particle size [8]; organic matter [95]; organically complexed iron [96]; the synergistic effect of iron and nitrate (Fe(II) + NO₃⁻) [97]; soil pH, sand and clay content, total phosphate, amorphous and crystalloid Fe, Mn and Al oxides [98]; naturally occurring precipitation and adsorption processes [51]; and microorganisms [99]. From all of this, it follows that many factors, both researched and unexplored, influence the bioavailability of Sb.

There are several laboratory methods for determining the bioavailability of HMs in soil and their modifications. Bagherifam et al. [8] described and classified the methods into three groups (soil pore water, single-step extraction, sequential extraction) and emphasised that there is a significant gap in the knowledge about the bioaccessibility of Sb in soils.

In this study, the single-step extraction method using CaCl₂ was used [69]. The applicability of the method was confirmed by Houba et al. [100,101], Sahuquillo et al. [102],

and Pueyo et al. [103], but the bioavailable concentrations of Sn and Sb were not determined in any of the mentioned works.

The data on the bioavailable concentrations of Sb in the literature are very heterogeneous [8,51]. It is obvious that they partly depend on the extraction method [8,104]. Here are some examples of measured bioavailable Sb concentrations expressed as a percentage of the total content determined by different single-step extraction methods, including water dissolution: 0–42% with a mean value of 2.5% [75], 0.01–8.8% *w/w* [74], 0.6–10.2% [76], and 2.08–11.9% [98]. Moreover, Nakamaru and Martín Peinado [95] obtained values between 0.075 and 0.42% of total Sb when extracted with CaCl₂, which is in agreement with the results of this work. It is also interesting to note that Ettler et al. [104] determined the bioavailability of Sb using five single-step extraction methods (H₂O, 0.01 M CaCl₂, 1 M NH₄NO₃, 0.005 M DTPA, and 0.1 M Na₂HPO₄), with the highest extractivities observed for Na₂HPO₄ with up to 9% of total Sb, while other methods gave values of <2%, including the CaCl₂ used in our study. Furthermore, in studies where the sequential extraction of Sb was applied [105–107], data were obtained for each step of the analysis and are difficult to compare when different methods or modifications thereof are used.

The bioavailable concentrations of Sb are obviously low, but their negative effects on organisms have been shown: for the abundance, diversity, and functionality of soil microbes, especially in alkaline soils [105]; toxicity to agricultural crops, e.g., spinach (*Ipomoea aquatica*) [106] and barley [98]; accumulation in rice grains and risk to human health [97]; and acute toxicity to earthworms (*Eisenia fetida*) [107].

A literature search revealed very few data on bioavailable Sn concentrations [52,108], no work was found using the same methodology as in our study, and bioavailable Sn concentrations appear to be low in most cases. Bureć-Drewniak et al. [108] investigated the bioavailable concentrations of Sn in soil using the sequential extraction method (BCR), and the results showed the minimal bioavailability of Sn (numbers not given). Despite the low values, Wang et al. [78] found that bioavailable forms of Sn, together with Ti, Cr, and Co, play an essential role in shaping the microbial community structure.

3.3. Properties That Affect the Content of Sn and Sb in the Soil

The content of HMs, including Sb and Sn, in soil is influenced by both natural and anthropogenic factors, where natural factors include physical, chemical, biological, and climatic factors, while anthropogenic factors refer to various types of pollution and degradation.

3.3.1. Influence of Soil Properties

In the studied soils, the humus content ranges from 1.0% to 17.7%, with an average of 7.3% (Table 1). Most of the samples—namely, 30—belong to very humus rich soil (class range: 5.1–10%), 12 samples to quite humus rich soil (3.1–5%), 11 samples to very high humus rich soil (10.1–30%), 4 samples to medium humus rich soil (2.1–3%), 2 samples to low humus rich soil (1.1–2.0), and 1 sample to very low humus rich soil (0.6–1.0) [89].

Soil pH_{H₂O} ranged from 6.7 to 8.05; out of the 60 samples, 37 samples were slightly alkaline (pH 7.6–8.1) and 23 samples were neutral (pH 6.5–7.5), while pH_{KCl} ranged from 5.48 to 7.9.

The studied soils were classified into the following textural classes: sandy loam (19 samples), silty loam (18 samples), loam (11 samples), loamy sand (6 samples), sand (3 samples), silt (2 samples) and silty clay loam (1 sample) (Table 1 and Table S4 in Supplementary Materials).

In order to identify the role of different natural factors (grain size distribution, texture, humus content, pH) affecting the content of Sb and Sn in the studied soils, their relationship was examined using principal component analysis (PCA). The eigenvalues of the first four principal components (PCs) were larger than 1, indicating their significance and explaining 75.4% of the total variability among 11 variables. The first component (PC1) contributed 34.5%, while the second, the third, and the fourth corresponded to 17.6%, 13.2%, and 10.3%,

respectively, of the total variance of the data set. The results of the PCA are presented on the PCA loading plots (Figure 3a,b), illustrating the orientation of the variables with respect to the principal components. On the PC1 vs. PC2 plot (Figure 3a), the highest negative PC1 loadings exhibited fine and coarse silt (-0.84 and 0.80 , respectively), while coarse sand content and pH_{KCl} displayed positive PC1 loadings (0.93 and 0.81 , respectively). The humus, Sb, and Sn content exhibited the greatest negative effect on PC2 (from -0.82 to -0.71), whereas none of the studied parameters showed positive values (>0.5) with respect to this component. On the PC3 vs. PC4 plot (Figure 3b), the highest negative PC3 loadings exhibited texture (-0.66), whereas fine sand displayed a positive PC3 loading (0.51). The pH and ΔpH exhibited the greatest positive effect on PC4 (0.70 and 0.71 , respectively), whereas none of the studied parameters showed negative (<-0.5) values with respect to this component.

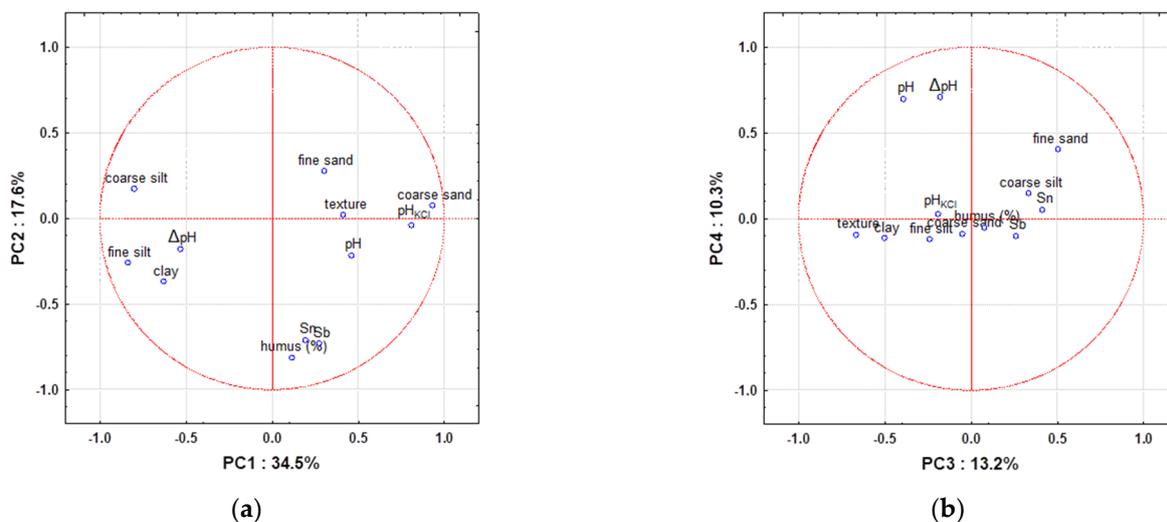


Figure 3. Principal component analysis: (a) PC1-PC2 and (b) PC3-PC4 loading plot.

According to Figure 3a, the variation of the data is mainly influenced by the soil texture, especially by the ratio of finer (coarse silt, fine silt, and clay) and larger fractions (coarse sand) in the soil itself. While the influence of the finest fraction of soil as a metal carrier is well known [109], the results show the significant influence of the largest fraction on the distribution of Sb and Sn. To some extent, this is to be expected, as the soil texture near railway embankments is not entirely of natural origin, i.e., formed by the decomposition of the parent substrate. This is because there are ballast stones on the railway embankments, and as the distance from the tracks increases, this material is replaced by natural soil. The next factor affecting the content of Sb and Sn in the studied soils is the humus content (Figure 3a). This is consistent with previous findings indicating higher adsorption of metals in soils with higher organic matter content and cation exchange capacity [109,110]. As can be seen in Figure 3b, the factors affecting the variance of the data are the texture (class) and the pH of the soil.

3.3.2. Influence of Distance from Railway

One of the factors affecting the total concentrations of Sn and Sb in the topsoil is the distance of the sampling sites from the railway as a linear source of pollution. Different authors have studied HMs' gradients at different distances from the tracks, e.g., Baltrenas et al. [31] at 1, 2, 3, 5, 10, 15, 25, 50, and 75 m; Bobryk [45] and Bobryk et al. [46] at 0, 25, 50, 100, and 250 m; Chen et al. [19,20] at 1, 5, 15, 20, and 50 m; Liu et al. [22] at 2, 10, 25, 50, 100, and 150 m; Ma et al. [23] at 0, 10, 20, 30, 50, 100, 200, 300, and 500 m from the track edge; Malawska and Wiłkomirski [34] at 0, 15, 30, 50, and 100 m; Mazur et al. [36] at 2, 10, 20, and 30 m from the railway line; Meng et al. [24] at 5, 10, 25, 50, 100, and 150 m; Radziemska

et al. [38] at 1, 10, 20, and 30 m from the railway line; Samarska and Zelenko [48] at 5, 10, 15, 20, 30, 50, and 100 m; Šeda et al. [27] at 1.5, 3, 10, and 25 m; Stojic et al. [44] at 0.03–4.19 km from the railway; Vaiškūnaitė and Jasiūnienė [32] at 1, 5, 10, 15, and 25 m from the sleepers; Zhang et al. [25] at 2, 5, 10, 20, 30, 50, 60, 70, 80, 100, 150, and 200 m from the railway; and Zhang et al. [26] at 2, 5, 10, 20, 30, 50, 60, 70, 80, 100, and 150 m from the embankment bottom. In most of the reported studies and for most of the studied chemical elements, the general conclusion is that their total concentrations decrease with increasing distance from the railway tracks. The results of this study are consistent with these observations. In fact, the measured Sb and Sn content in the soil showed a decrease with increasing distance from the tracks, although this decrease was not linear (Figure 4a,b). When the samples were classified by distance into the following categories: 1 m, 1–2 m, 2–3 m, 3–5 m, and 5–10 m (Figure 5a,b), a statistically significant difference ($p < 0.05$) was only found between the above groups for Sb. Moreover, for both elements, an initial decrease in the content was followed by an increase (at a distance of 2–3 m) and a further decrease.

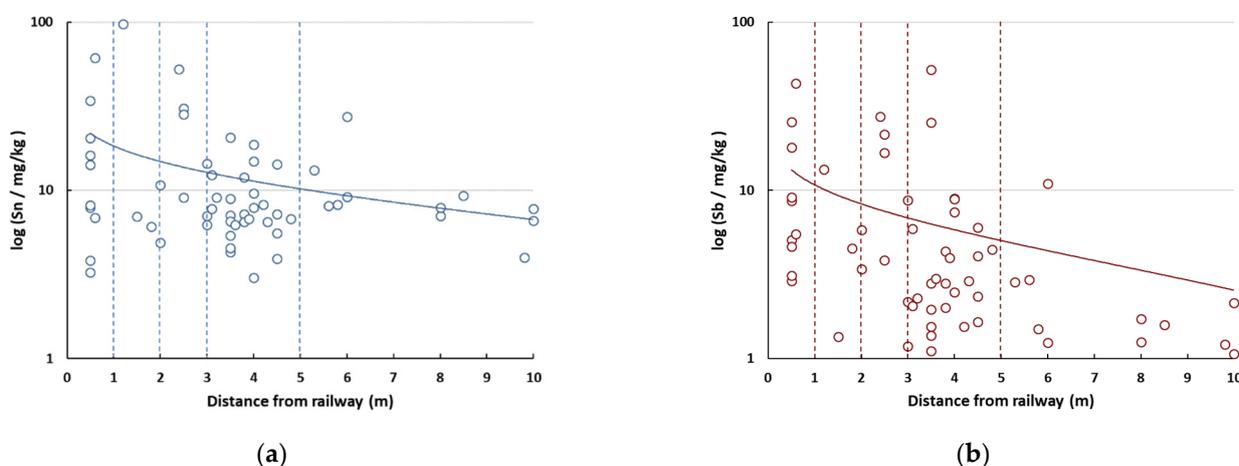


Figure 4. Dependence of the concentration of Sn (a) and Sb (b) in the soil, expressed in logarithmic form, and the distance of the sampling point from the railway tracks.

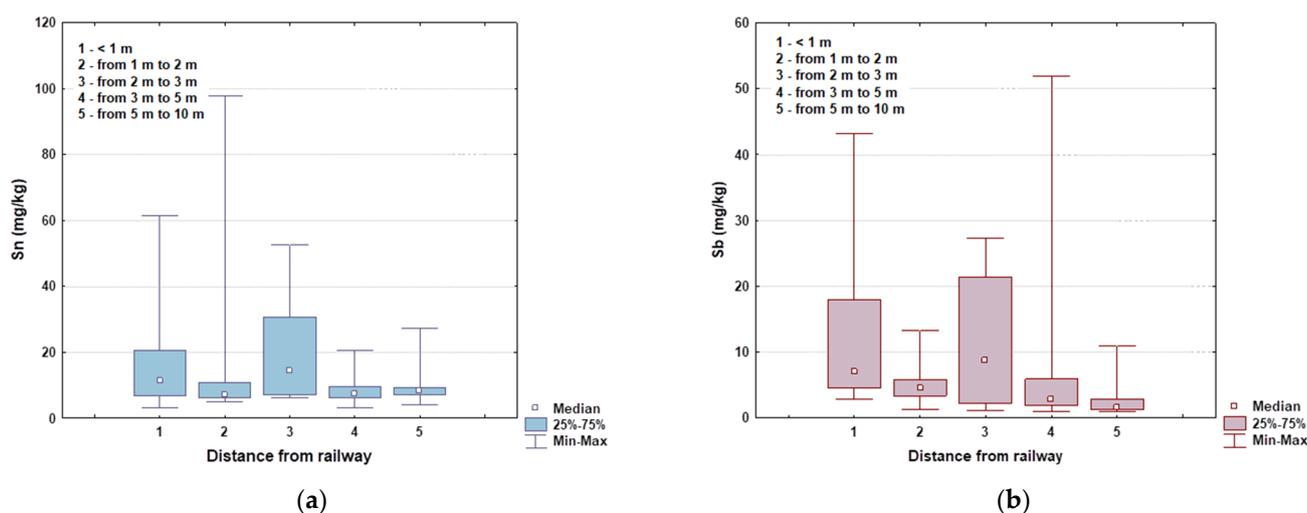


Figure 5. Dependence of concentration of Sn (a) and Sb (b) in soil and the distance categories of the sampling point from the railway tracks (boxplots were obtained by Kruskal–Wallis ANOVA followed by a pairwise comparison using Dunn’s method, with the significance level set at $p < 0.05$).

A similar observation was also made by other authors. According to Ma et al. [23], the highest contents for Ni, Cr, and Cu were measured at a distance of about 10–30 m. Mazur

et al. [36] recorded the highest Ni contents at a distance of 20 m, and for Cr and Co, at a distance of 10 or 20 m, depending on the study site. Meng et al. [24] found that Cd content increased between 5 and 50 m. A possible explanation for this distribution pattern is related to the exhaust gasses, which can migrate with the airflow and deposit off-track [23]. Based on the obtained results, different authors define safety distances for agricultural production. Šeda et al. [27] stated that the safety distance is about 10 m. Vaiškūnaitė and Jasiūnienė [32] defined the safety distance to the railway stations as 15 m, while Baltrenas et al. [31] indicated that it should be 15 m or more. In agreement with the study by Liu et al. [22], in China, areas within a distance of 15 m along railway lines are regulated as safety zones and the cultivation of crops is prohibited in this area. However, the authors emphasise that the influence of Mn, Zn, and Cd can extend beyond 15 m, so crops at these distances can still pose a potential risk of pollution from HMs. Meng et al. [24] stated that in China, crops and cropland should not be planted within 30 m of the railway line, and they suggested an even greater distance because the influence of HMs on soils can spread even further.

The study by Földi et al. [81] on the distribution of antimony in roadside soils in Germany also showed a decrease in Sb content with distance, down to natural background levels: 5.77 mg/kg (0.25 m), 3.65 mg/kg (10 m). In the same study, the authors found that the total Sb content also decreased significantly with soil depth.

3.3.3. Influence of Site Functionality

According to the results of this study, functional parts of railway infrastructure have a significant influence on Sn and Sb content in soil. As shown in Figure 6, for both elements, the lowest mean concentrations were measured along the lines between the stations, higher ones at the stops, even higher ones at the stations, and the highest ones at the major junction stations. In fact, the most polluted locations are near large junction stations such as Varaždin, Zagreb Main Station, and Zaprešić. Statistically, a significant difference ($p < 0.05$) was found between the sites in terms of functionality for Sb, while this was not the case for Sn.

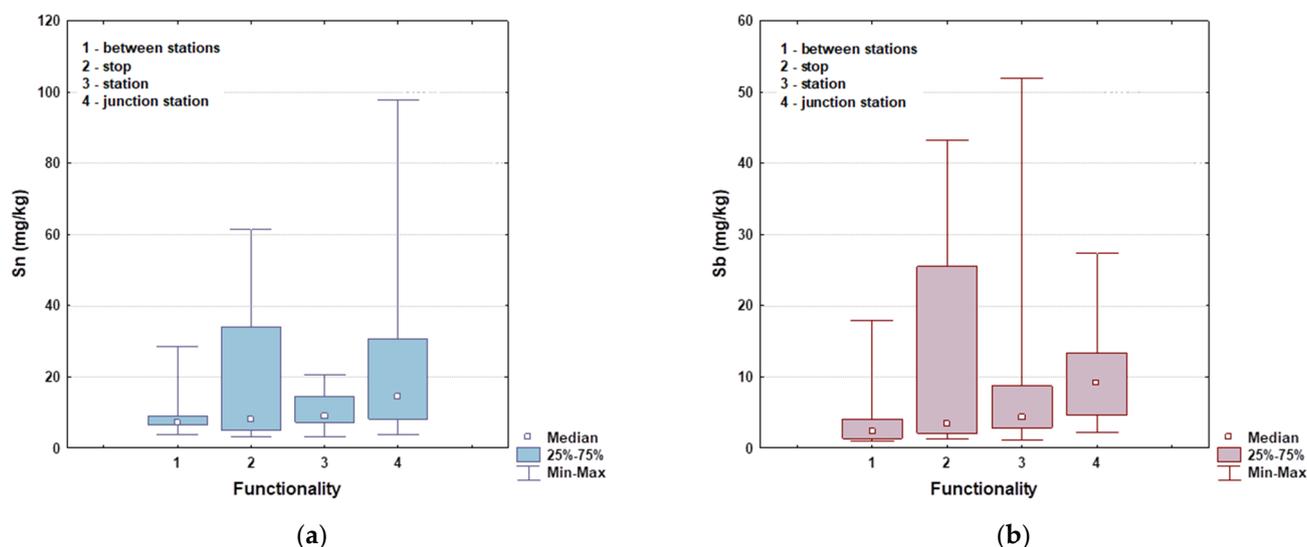


Figure 6. Dependence of concentration of Sn (a) and Sb (b) in soil and site functionality (boxplots were obtained by Kruskal–Wallis ANOVA followed by a pairwise comparison using Dunn’s method, with the significance level set at $p < 0.05$).

However, unexpectedly high levels of Sn (61.4 mg/kg) and Sb (43.2 mg/kg) were found in the soil of the Žeinci stop. A possible explanation is that, in the past, a large amount of cargo or some other substance (e.g., fuel) containing these two elements spilled at this site. It is also interesting that the highest Sb concentration (52.0 mg/kg) was found

at the Konjščina station, which could be the result of mining activities in the past, from 1885 to 1962. In the vicinity of Konjščina, lignite coal was mined, which is known to contain antimony, and the coal was loaded and unloaded near the soil sampling point.

The dependence of HM concentrations and the functional parts of the railway infrastructure has only been systematically studied by researchers from Poland. Malawska and Wiłkomirski [34], in their study, distinguished the following functional parts of junctions: loading ramp, platform area, vehicle cleaning facility, the siding, and parts along the tracks outside the stations. They found the highest contamination with HMs at the loading ramp, and the lowest along the tracks. The same authors, but in a different area [35], found the highest contamination at the cleaning bay and in the siding area. In the work of Wiłkomirski et al. [41], the highest HM levels were found at the siding and in the platform area. Mętrak et al. [37] did not find typical contamination profiles for the differently used areas of the railway, while Staszewski et al. [16] recorded the highest soil contamination in the platform area.

3.3.4. Influence of Site Topography

Although little studied, topography has a very important influence on the distribution of pollution. Liu et al. [22] indicated that the topographic profile influences the metal content and distribution pattern along the railway line. In their study, the elevated HM concentrations varied from 5 m to 100 m from the tracks, depending on the topography and elements.

In our study, the highest Sb and Sn soil contents were found in areas located at the same level as the railway line, while they were lower in locations either above or below the railway level (Figure 7a,b), confirming the influence of topography on their spatial distribution. Moreover, a statistically significant difference ($p < 0.05$) between sites in terms of topography was again found only for Sb. The sites above and below the railway lines are on slopes, where leaching of pollutants obviously occurs. Chen et al. [21] made the same observations and attributed them to leaching and erosion on slopes. Vo et al. [111] suggested storm water management as one of the possible solutions to prevent the spread of pollutants by railway lines.

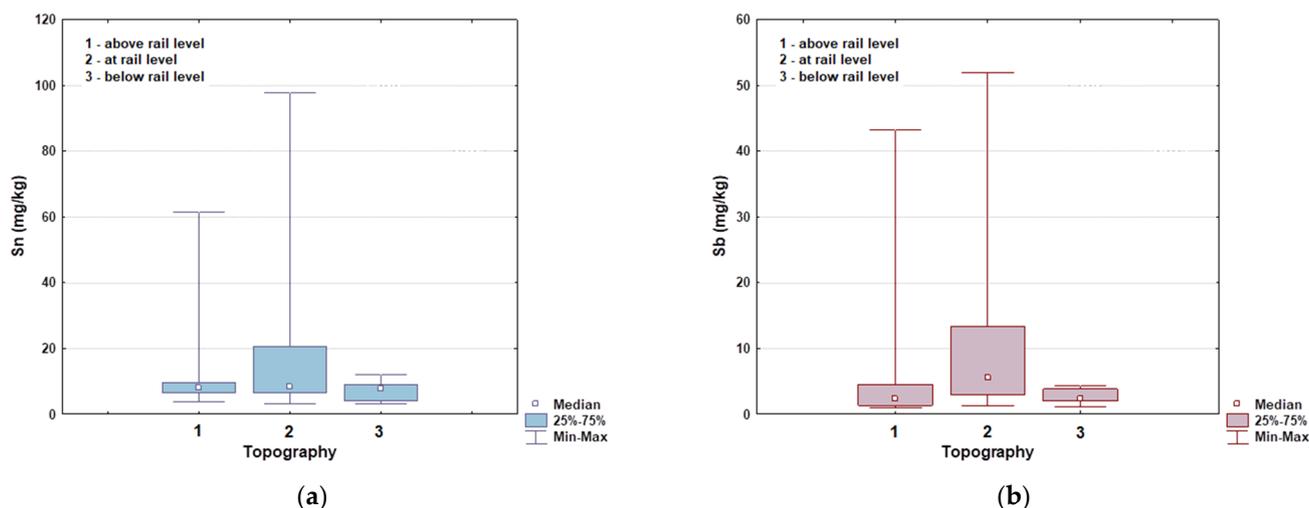


Figure 7. Dependence of concentration of Sn (a) and Sb (b) in soil and site topography (boxplots were obtained by Kruskal–Wallis ANOVA followed by a pairwise comparison using Dunn’s method, with the significance level set at $p < 0.05$).

3.3.5. Influence of Railway Age

According to statistical analysis, although both elements, Sb and Sn, have slightly higher values in soils sampled near older railway tracks (Figure 8a,b), the age of the

tracks, i.e., the time of pollutant accumulation, only has a statistically significant effect on Sb concentrations.

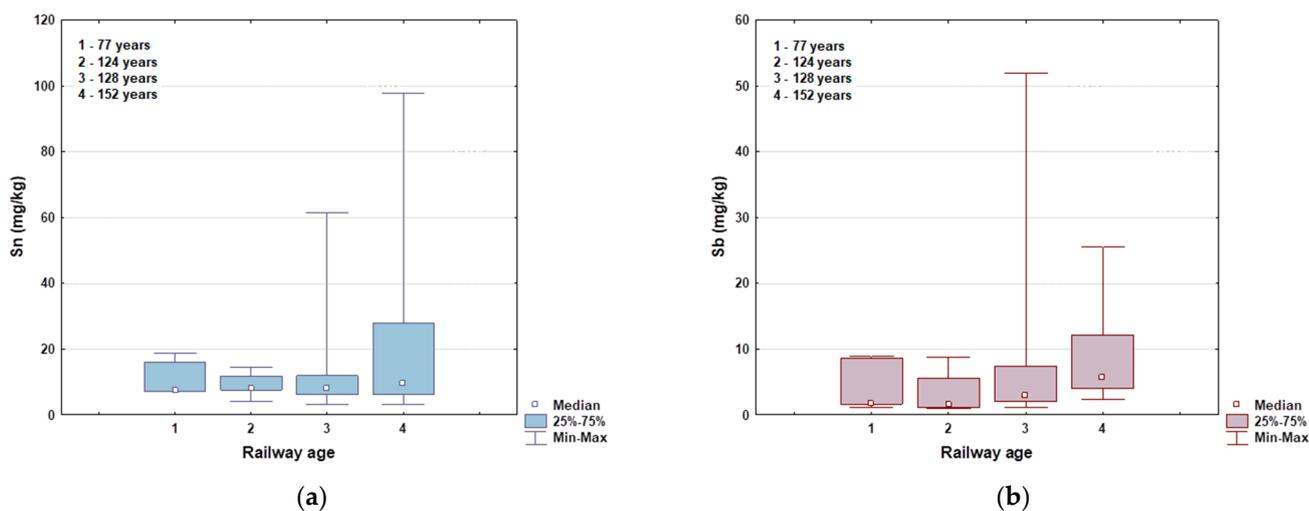


Figure 8. Dependence of concentration of Sn (a) and Sb (b) in soil and railway age (boxplots were obtained by Kruskal–Wallis ANOVA followed by a pairwise comparison using Dunn’s method, with the significance level set at $p < 0.05$).

Similar results were also obtained by other authors. Chen et al. [19] investigated the effect of railway operation time on contamination levels. Their results indicate an increase in contaminant concentrations (Cd and Pb) with the duration of railway operation. Wiłkomirski et al. [41] indicated a significant increase in PAH concentrations in comparative studies conducted in 1995 and 2008 (after 13 years) at the same sites, although the same was not observed for HM concentrations. In fact, elevated HM concentrations were only observed at some of the sites studied.

3.4. Anthropogenic Sources of Soil Pollution with Sn and Sb

Several authors cite dust released during railway operations as a significant source of Sb and Sn, as well as other HMs. For example, Chillrud et al. [9] studied steel dust in the form of particulate matter (PM) in the New York City subway, and found that levels of Fe, Mn, and Cr were more than 100 times higher than outdoors, while other elements, including Ag, Al, As, Cu, Sn, and Sb, were above median for outdoor air levels. Possible sources of these elements were suggested to be contact points of electrical relays and switches, composite metal breaker pads, and trace impurities in some types of steel.

Bukowiecki et al. [12] investigated outdoor air pollution with particulate matter (PM) emitted by freight and passenger trains in Zürich, Switzerland. Ten trace elements (Br, Ca, Cl, Cr, Cu, Fe, Mn, Pb, S, and Zn) were detected, of which Fe, Mn, and Cu were the main contributors. According to the authors, particulate emissions are caused by various forms of abrasion from rails, wheels, brakes, and the overhead line.

Burkhardt et al. [10] provided a calculation-based assessment of the main sources and quantities of pollutants from the Swiss Federal Railways (SBB) network in 2003. The main substances emitted by regular railway operations were metals (about 2270 t/year), hydrocarbons (1357 t/year), and herbicides (3.9 t/year). The authors indicated that particulate matter is the predominant form of pollution. Most particulate matter emissions are caused by the abrasion of brakes (73%), rails (21%), wheels (5%) and overhead lines (1%). In this context, the abrasion of sintered iron brakes, which may contain 0.09% Sn and 0.01% Sb, is considered a possible source of Sn and Sb.

In addition, Adriano [1] reported Zn–Sn and Cd–Sn alloys as commonly used coatings in hydraulic brakes. Research by Månsson et al. [112] in Stockholm, Sweden, also suggested that the main source of Sb emissions in an urban area is brake pad wear. Similarly,

Clemente [3] suggested that the use of Sb as a fire retardant in brake pads emits significant amounts from vehicles into the environment.

Besides PM, rail transport emits HMs in many other ways, including freight losses during transport, the use of herbicides, coal heating of wagons, exhaust gasses from locomotive engines, migration from wooden and reinforced concrete sleepers, from debris and ballast waste, and from rubbish discarded from trains and on platforms [47].

Additionally, Sn is released into the environment by burning fossil fuels (coal and oil) and exists in the atmosphere as gasses and vapours, and is bound to dust particles [49].

In this context, Staszewski et al. [16] pointed out that metal concentrations in soil near railway lines are higher than the corresponding levels along traffic roads and in urban centres. Consistent with this are the results of studies on HMs in dust (which enters the soil during dry and wet deposition) in various urban functional areas in the city of Shijiazhuang in northern China, which found that the area around the North Railway Station was among the most polluted [113]. Similar results were obtained from a study in the city of Varaždin in north-western Croatia (unpublished data), where the highest concentrations of HMs were found in the topsoil in the area of the railway station. According to this, railway stations in urban areas, which are very often located in city centres, are points of very high pollutant emissions that should not be neglected.

4. Conclusions

This article demonstrated that rail transport is a source of soil pollution with Sn and Sb. Soil samples collected along the railway lines in north-western Croatia showed significant enrichment of antimony and tin up to 31 and 24 times higher than background levels, respectively. The total concentrations of Sn ranged from 3.04 mg/kg to 97.6 mg/kg, and of Sb from 0.98 to 52.0 mg/kg.

In contrast to the total concentrations, very low bioavailable concentrations were measured; as a percentage of total concentrations, the values ranged from 0.001 to 0.021% for Sn, and from 0.01 to 0.35% for Sb.

The pollution patterns mostly show the highest concentrations in the soil near major (junction) railway stations; the concentrations decrease with distance from the railway, increase with the duration of railway operation, and the distribution is also influenced by the topography.

Regarding soil properties, the distribution of Sb and Sn is primarily determined by soil texture (especially the ratio of finer and larger fractions—ballast stones), followed by humus content and pH.

According to literature sources, particulate matter (dust) is the most important source of pollution with HMs, i.e., Sn and Sb, resulting from the abrasion of various moving parts such as brakes, wheels, and rails.

Following the above, soil contamination with Sn and Sb requires more detailed studies and the establishment of safety distances to ensure that rail impacts to humans, wildlife, agricultural production, and groundwater are minimised. It would also be desirable to establish maximum permissible concentrations through regulations and to implement protective measures such as the electrification of rail lines, selection of materials for rail transport, installation of artificial or living barriers, and management of surface runoff.

In future studies, more emphasis will be placed on the chemical forms of Sn and Sb in soil, including comprehensive testing of potential toxicity. We also plan to investigate the total and bioavailable concentrations of other HMs in the soil, the patterns of their distribution, and the content of HMs in the most abundant plant species along the railway lines.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/environments9010010/s1>, Table S1: Contamination factors (CFs) for each metalloid and sampling site, Table S2: Published research on Sn and Sb along the railway, Table S3: Bioavailable concentrations and percentage of bioavailable concentrations for Sn and Sb, Table S4. Proportions of soil fractions. References [14–16,71] are cited in the Supplementary Materials.

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