Postprint: Heavy Metal Enrichment in Picea schrenkiana Needles Along Roadsides in Mining Areas

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Abstract

Mining and mineral product transportation processes can cause heavy metal pollution to the environment and pose risks to organisms. To quantitatively characterize the degree of heavy metal pollution on both sides of roads in the Aiergou mining area and clarify the absorption and enrichment effects of Schrenk' s spruce needles on heavy metals, we collected Schrenk' s spruce needle and soil samples, measured the contents of lead (Pb), zinc (Zn), cadmium (Cd), arsenic (As), copper (Cu), and chromium (Cr), and analyzed the enrichment effects and spatial variation characteristics of heavy metals. The results showed that: (1) The contents of heavy metals in Schrenk' s spruce needles and soil differed significantly ($P < 0.05$), with Pb content in needles being significantly higher than other heavy metals ($P < 0.05$), reaching an average of 86.28 g/g; Zn and Cu in soil exceeded the Grade I limits of the national soil quality standard, while As was 41% higher than the Grade III limit; (2) Using heavy metals in soil and Schrenk' s spruce needles from the background area (Banfanggou Forest Farm) as evaluation criteria, the comprehensive pollution index of heavy metals in Schrenk' s spruce needles in the study area was 2.05, indicating moderate pollution, with As and Pb having relatively high single-item pollution indices of 3.65 and 2.57, respectively. The comprehensive pollution index of heavy metals in soil in the study area was 1.69, indicating slight pollution; (3) With increasing distance, except for Pb content in both soil and needles showing a negative linear decrease, As and Cu both showed an initial increase followed by a decrease; Cr and Zn in soil gradually increased, while Cr in needles gradually decreased and Zn showed little change; (4) Redundancy Analysis (RDA) results showed that Cu, As, and Pb in soil were positively correlated with the diameter at breast height (DBH) and tree height of dead Schrenk' s spruce trees, while Cr and Zn were negatively correlated with these parameters. Mining and transportation have already affected soil and the growth of Schrenk's spruce, and this

study provides valuable insights for the ecological restoration and conservation of Tianshan Schrenk' s spruce forests.

Full Text

Accumulation of Heavy Metals in *Picea schrenkiana* Leaves Growing on Roadsides in a Mining Area

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Abstract

Mining and the transportation of mineral products can contaminate the environment with heavy metals, which accumulate in organisms and pose significant ecological risks. To quantify heavy metal pollution along roadsides in the Aiergou mining area and investigate the accumulation characteristics in *Picea schrenkiana* leaves, we collected leaf and soil samples at distances of 0–500 m perpendicular to the road. The contents of As, Cd, Cr, Cu, Pb, and Zn were measured to analyze enrichment effects and spatial differentiation patterns. Results showed that heavy metal contents in soils and leaves varied significantly ($P < 0.05$). Pb content in leaves averaged 86.28 g/g, significantly higher than other heavy metals ($P < 0.05$). Cu and Zn contents exceeded the first-level limits of the Chinese Environmental Quality Standard for Soils, while As was 41% higher than the third-level limit. The comprehensive pollution index of heavy metals in leaves was 2.05, indicating moderate pollution, with single pollution indexes for As and Pb reaching 3.65 and 2.57, respectively. The soil pollution index was 1.69, indicating light pollution. As distance from the road increased, Pb content in soil and leaves decreased following a negative linear gradient ($P < 0.05$), while As and Cu contents first increased then decreased. Soil Cr and Zn contents increased gradually with distance, whereas leaf Cr decreased gradually and Zn remained stable. Redundancy analysis (RDA) revealed that soil As, Cu, and Pb were positively correlated with diameter at breast height (DBH) and height of dead trees, while Cr and Zn showed negative correlations. Mining and transportation activities have thus affected soil and *P. schrenkiana* growth in the study area, making ecological restoration and conservation critical.

Keywords: heavy metals; enrichment; pollution index; *Picea schrenkiana*; Tianshan Mountains

Introduction

With continuous industrial development, waste emissions have caused severe ecological damage, with heavy metal pollution being particularly concerning [1]. Heavy metals diffuse through the atmosphere and soil [2-4], exhibiting concealment, long-term persistence, and irreversibility in the environment [5]. Their presence and migration significantly impact the physiological activities and health of humans, animals, and plants [6]. Mineral mining represents a major source of heavy metal pollution [7], as extraction and smelting expose deep underground minerals to the surface, increasing the flux of heavy metal release [8] and causing strong ecological hazards [9-11]. While most research has focused on heavy metal pollution assessment and ecological impacts in mining areas, transport processes have been largely overlooked [9,12-13]. Studies confirm that traffic increases heavy metal content in roadside soil and plants [14], affecting seed germination and physiological-biochemical indicators [15-16]. Due to plant-specific differences and varying toxicity effects of heavy metal elements, adaptation processes and mechanisms are extremely complex [17-18]. Some species like *Pterocarya stenoptera* and *Camellia oleifera* exhibit hyperaccumulation capabilities that can remediate environments [17-18], while heavy metal stress negatively affects vegetation such as *Poa pratensis* and *Lolium perenne*, impacting seed germination, cell structure, and physiological processes [19].

The Tianshan Mountains are dominated by pure *Picea schrenkiana* forests, which play a crucial role in maintaining ecosystem functions on the northern slopes [20]. Aiergou is rich in coking coal, and dust and exhaust from mining and transport contain substantial heavy metals that disperse into the environment and accumulate in *P. schrenkiana* tissues. As the primary organ for photosynthesis and assimilation, leaves are vital to plant life cycles [14]. However, research on heavy metal absorption and enrichment in *P. schrenkiana* leaves, particularly in the Aiergou mining area, remains unreported. This study collected *P. schrenkiana* leaf and soil samples along roadsides in Aiergou to test heavy metal contents, evaluate pollution levels, and analyze spatial distribution patterns, providing a basis for health maintenance of Tianshan *P. schrenkiana* forests and sustainable mining development.

1. Study Area Overview

Aiergou is located in the mid-mountain zone of the northern Tianshan slope (44°11 -44°39 N, 82°15 -82°57 E) at elevations of 2000-3000 m. The region has a temperate continental climate with large diurnal temperature variations, an annual average temperature of 2-3°C, extreme minimum temperature of -30.2°C, and extreme maximum of 30.5°C. Precipitation is 120-180 mm, far less than evaporation (2000-3000 mm). Winter snowfall is minimal with little snow accumulation in the valley. The forest zone is dominated by pure *P. schrenkiana* stands, with understory shrubs including *Cotoneaster melanocarpus*, *Berberis heteropoda*, *Rosa spinosissima*, *Spiraea hypericifolia*, *Lonicera hispida*, and *Juniperus pseudosabina*. Herbaceous plants mainly comprise *Geranium rotundifolium*, *Alchemilla tianschanica*, and *Aegopodium podagraria*. Soils are mountainous gray-brown forest soils [16] with organic matter content of 189.3 g/kg (30-35%). The upper Aiergou is primarily pastoral, while the middle-lower reaches constitute the mining area, creating a typical natural pastoral-industrial transition zone. Xinjiang Coking Coal Group conducts mining activities in the lower valley, with nearby limestone processing plants and residential areas for coal mine workers. The main road runs along the mountain valley, with *P. schrenkiana* forests distributed on both sides. Frequent mining and transport activities have caused severe pollution, with numerous spruce trees showing yellowing leaves or death, severely impacting community growth and development.

2. Field Investigation and Sampling

Sampling transects were established perpendicular to the Aiergou road at both sides. At distances of 50, 100, 200, 300, and 500 m from the road, DBH and height of dead trees within sampling point ranges were measured using diameter tapes and height meters. Since *P. schrenkiana* distributes on both road sides, leaf samples were collected from trees with consistent growth at each sampling point from the canopy layer (4–6 m) and mixed as one sample. Surface soil (0–10 cm) was collected simultaneously at each point. Using the same method, background leaf and soil samples were collected at Banfanggou Forest Farm, approximately 50 km south of Ürümqi, representing pristine conditions. [Figure 1: see original paper] shows the sampling point map.

3. Sample Testing and Analysis

Aiergou primarily produces coking coal. According to Bai Xiangfei et al. [21], mining and transport cause high accumulation of heavy metals including Cu, Pb, As, Cd, Cr, and Zn in roadside soil and plants [14,22]. Therefore, this study focused on Pb, Cd, Zn, Cr, Cu, Zn, Pb, Cr, Cd, and As. Leaf samples were cleaned, oven-dried to constant weight, and pulverized. Soil samples were air-dried and sieved to 0.149 mm. Measurement methods followed national standards (Table 1). The enrichment coefficient, an indicator of plant heavy metal accumulation capacity (larger values indicate stronger enrichment) [25], was calculated as:

$$\text{Enrichment Coefficient} = \frac{C_i}{S_i}$$

where C_i is the measured heavy metal content in plant leaves and S_i is the measured content in soil at the sampling point.

Measurement method and reference standard for heavy metals in *P. schrenkiana* leaves and soil

Test items	Measurement method	Reference standard
Cu, Zn in leaves	Graphite furnace atomic absorption spectrometry	GB/T 5009.12–1996
Cd, Cr in leaves	Perchloric acid digestion	GB 7887–87
Cu, Zn in soil	Graphite furnace atomic absorption spectrometry	Terrestrial biological community investigation and analysis [24]
Pb, Cd in soil	Diethyldithiocarbamate silver spectrophotometry	GB/T 5009.11–1996
As in soil	Extraction flame atomic absorption spectrometry (KI-MIBK)	GB/T 17134–1997
Cr in soil	Flame atomic absorption spectrometry	GB/T 17138–1997
Pb in soil	Flame atomic absorption spectrometry	GB/T 17140–1997
Zn in soil	Flame atomic absorption spectrometry	GB/T 17137–1997

4. Data Statistics and Analysis

Pollution index calculation formulas follow [26]:

$$P_i = \frac{C_i}{B_i}$$

where P_i is the single pollution index, C_i is the measured value, and B_i is the evaluation standard. The comprehensive pollution index $P_{综}$ is calculated as:

$$P_{综} = \sqrt{\frac{[\max(P_i)]^2 + [\text{average}(P_i)]^2}{2}}$$

This study used measured heavy metal contents in *P. schrenkiana* leaves and soil from the background area (Banfanggou Forest Farm Tianshan Forest Ecosystem Research Station) as evaluation standards. Interpretation: $P_{综} \leq 1.0$ indicates clean; $1.0 < P_{综} \leq 2.0$ light pollution; $2.0 < P_{综} \leq 3.0$ moderate pollution; $P_{综} > 3.0$ heavy pollution.

Basic statistical parameters were calculated using Excel 2013. Variance analysis (one-way ANOVA) and multiple comparisons (LSD) were performed in SPSS 17.0 to analyze differences in heavy metal contents across distances. Nonlinear regression in Origin 9.0 was used to fit heavy metal content versus distance, selecting optimal models based on coefficient of determination and significance level. Detrended correspondence analysis (DCA) was conducted in Canoco 4.5, and redundancy analysis (RDA) was used to explore relationships between leaf heavy metal contents and soil heavy metals.

1. Soil Heavy Metal Content and Pollution Assessment

Basic characteristics of soil heavy metal contents are shown in Table 2. The average Zn content was 128.04 g/g, exceeding the first-level limit of the national soil quality standard (82.21–149.55 g/g). Average Cr and As contents were 47.13 and 42.61 g/g, respectively, also exceeding first-level limits. As was 41% higher than the third-level limit (43.17 g/g). The coefficient of variation for all six heavy metals ranged 0.11–0.25, indicating moderate variation. Using Banfanggou Forest Farm background values as standards, the single pollution indexes were 1.72, 2.97, and 1.63 for Zn, As, and Pb, respectively, all indicating moderate pollution. The comprehensive soil pollution index was 1.69, indicating light pollution.

Statistical description of heavy metals in soil (g/g)

Parameter	Zn	Cr	As	Cu	Pb	Cd
Maximum	204.86	63.77	55.15	33.05	42.61	14.32
Minimum	82.21	39.94	27.33	14.32	16.51	10.92
Mean	128.04	47.13	42.61	23.12	30.22	12.01
Standard deviation	57.21	10.92	14.32	5.57	11.24	1.95
Coefficient of Variation	0.25	0.23	0.25	0.24	0.22	0.11
Background value	57.21	43.17	27.33	14.32	16.51	10.92
Pollution index	1.72	1.09	1.56	1.61	1.83	1.10
Comprehensive pollution index	1.69					

2. Heavy Metal Content in *Picea schrenkiana* Leaves and Pollution Assessment

Basic characteristics of leaf heavy metal contents are shown in Table 3. Pb content was highest with an average of 86.28 g/g, significantly higher than other metals ($P < 0.05$). Cu and As contents were 31.31 and 11.24 g/g, respectively. The coefficient of variation for Pb was 0.18 (moderate variation), while others showed moderate to heavy variation (0.11–0.28). Using background values, the pollution indexes were 3.65 for As (heavy pollution), 2.57 for Pb (moderate pollution), and 1.63 for Cu (light pollution). Cd showed minimal pollution (0.17). The comprehensive pollution index in leaves was 2.05, indicating moderate pollution from mining activities.

Statistical description of heavy metals in *P. schrenkiana* leaves and DBH/height of dead trees

Parameter	Pb	Cr	Zn	Cu	As	Cd	DBH (cm)	Height (m)
Maximum	108.42	65.97	41.63	17.88	30.22	0.40	24.15	11.69
Minimum	50.21	24.15	19.17	11.24	19.17	0.11	10.98	6.63
Mean	86.28	41.63	31.31	15.36	24.15	0.17	17.88	9.87
Standard deviation	15.36	11.24	6.63	2.51	3.31	0.08	3.31	1.24
Coefficient of Variation	0.18	0.27	0.21	0.16	0.14	0.47	0.19	0.13
Background value	33.57	41.63	31.31	11.24	6.63	0.60	-	-
Pollution index	2.57	1.00	1.00	1.37	3.65	0.17	-	-
Comprehensive pollution index	2.05							

1. Spatial Distribution Characteristics of Heavy Metals in Leaves and Soil

Heavy metal content variations with distance are shown in [Figure 2: see original paper] and Table 4. Pb content in both leaves and soil showed negative linear decreases with distance ($P < 0.05$), fitting the equation y = -0.05x + 97.898 (R^2 = 0.858). Cr content in leaves decreased gradually with distance (y = -0.006x + 48.815, R^2 = 0.136), while Zn remained stable. As and Cu contents first increased then decreased, fitting cubic distributions. Soil Cr and Zn increased gradually with distance. Regression analysis showed significant relationships ($P < 0.05$) for most metals, with coefficients of determination ranging 0.136–0.858.

Regression analysis of heavy metal content and distance in *P. schrenkiana* leaves and soil

Heavy metal	Regression model	R^2	P
Leaves			
Pb	$y = -0.05x + 97.898$	0.858	<0.001
Cr	$y = -0.006x + 48.815$	0.136	0.112
Zn	$y = 0.002x + 31.12$	0.023	0.309
Cu	$y = 1.349\times10\ x^2 - 0.009x + 1.636$	0.468	0.001
As	$y = 9.395\times10\ x^3 - 0.0008x^2 + 0.083x + 17.085$	0.566	0.004
Cd	$y = 1.76\times10\ x^3 - 1.33\times10\ x^2 + 0.029x + 0.197$	0.407	0.008
Soil			
Pb	$y = -0.003x + 0.595$	0.609	<0.001
Cr	$y = 3.903\times10\ x^3 + 0.042x + 44.414$	0.559	0.001
Zn	$y = 3.138\times10\ x^3 + 0.008x + 102.77$	0.505	0.002

Heavy metal	Regression model	R^2	P
Cu	$y = 2.021\times10\ \ x^3 - 0.002x + 0.41$	0.255	0.036
As	$y = -1.149\times10\ \ x^3 + 0.002x + 22.472$	0.464	0.001
Cd	$y = -1.67\times10\ \ x^3 + 0.0002x + 0.19$	0.318	0.023

2. Enrichment Effect of Heavy Metals in *Picea schrenkiana* Leaves

The enrichment coefficient of *P. schrenkiana* leaves for soil heavy metals is shown in [Figure 3: see original paper]. Enrichment capacity varied significantly among metals, following the order: Pb > Cr > Zn > Cu > As. The enrichment coefficient for Pb was significantly higher (5.79, $P < 0.05$), indicating strong enrichment capacity and low-background-high-accumulation characteristics. Enrichment coefficients for Cu, As, Cr, and Zn were relatively low (0.0052–0.26).

3. Correlation Between Leaf Heavy Metal Content and Dead Tree Characteristics

RDA was used to explore relationships between leaf heavy metal contents, dead tree characteristics, and soil heavy metals. For leaf heavy metals, two ordination axes explained 71.6% of cumulative variance, with the first axis (eigenvalue 0.478) explaining 60.6% of variation. Soil Cu and Cr correlated strongly with the first axis, while the second axis correlated with leaf Pb, Cr, and Zn. Soil As, Cu, and Pb showed significant positive correlations with leaf content ($P < 0.01$). For dead tree characteristics, two axes explained 79.1% of variance. The first axis (eigenvalue 0.698) contributed most, showing that soil As, Cu, and Pb were positively correlated with DBH and height of dead trees, while Cr and Zn were negatively correlated ($P < 0.01$).

[Figure 3: see original paper] The enrichment coefficient of heavy metal in *P. schrenkiana* leaves
[Figure 4: see original paper] Two-dimensional RDA ordination diagram of heavy metals in *P. schrenkiana* leaves and dead tree characteristics with soil heavy metals

The contribution rate and T-test of heavy metals in soil to ordination

Soil heavy metal	Leaf heavy metal contribution (%)	Dead tree characteristic contribution (%)	T-test (leaf)	T-test (dead tree)
As	2.162	0.815	7.622**	0.372
Cu	1.468	5.129	0.194	0.042
Pb	0.695	0.257	0.678	0.002
Cr	7.622	0.882	0.252	0.001
Zn	0.194	0.372	0.574	0.001

Soil heavy metal	Leaf heavy metal contribution (%)	Dead tree characteristic contribution (%)	T-test (leaf)	T-test (dead tree)
Cd	0.678	0.042	0.002	0.001

**$P < 0.01$

1. Heavy Metal Content and Environmental Quality Assessment in Aiergou Mining Area

Mining activities release substantial heavy metals [15], while vehicle exhaust, oil leaks, and metal friction further increase roadside heavy metal content [14]. Compared to background areas, *P. schrenkiana* leaves in Aiergou showed high As and Pb contents reaching moderate pollution levels. Pb and As primarily originate from road dust [27], while As accumulation from vehicle exhaust and water transport processes can inhibit plant growth and cause mortality [28,22]. The study area showed moderate pollution in leaves and light pollution in soils, with leaves more heavily polluted because mining-derived heavy metals deposit directly on plants and soil as particulates, while also being absorbed as aerosols through leaf stomata [29]. Therefore, leaf pollution index better characterizes the heavy metal pollution status in Aiergou.

2. Enrichment Effect of Heavy Metals in *Picea schrenkiana* Leaves

Heavy metal accumulation in plant leaves depends on genetic regulation and cellular structure, making adaptation mechanisms complex [29]. Different species and environments show varying accumulation capacities. In this study, *P. schrenkiana* leaves showed Pb enrichment coefficients of 5.79, significantly higher than other metals, but lower than some hyperaccumulator species [17,31]. The strong enrichment may relate to the Tianshan climate' s intense evaporation creating strong transpiration pull that drives heavy metal absorption. The low coefficients for other metals suggest *P. schrenkiana* employs exclusion strategies for most heavy metals while accumulating Pb. RDA showed strong correlations between soil Pb, Cu, Zn and leaf Pb, Cu, Zn, indicating composite effects in heavy metal uptake, though specific influencing factors require further study.

3. Spatial Distribution Characteristics of Heavy Metals

Heavy metal diffusion is influenced by particle size and wind direction. Pb showed negative linear decreases in both leaves and soil with distance, consistent with previous research [14]. However, aerosol particles are smaller and disperse more widely, causing leaf Pb to decrease faster than soil Pb. As and Cu showed initial increases then decreases, as aerosol-borne metals travel downwind before contacting soil and plants [35–36]. The steep mountain slopes along Aiergou roads may contribute to this pattern. Soil Cr and Zn increased gradually with distance, while leaf Cr decreased and Zn remained stable, suggesting leaf Cr and Zn originate primarily from atmospheric aerosol absorption through stomata rather than soil uptake [29,37].

4. Impact of Heavy Metal Pollution on *Picea schrenkiana* Growth

Heavy metal accumulation affects plant growth and development [28,38]. Soil As, Cu, and Pb showed positive correlations with dead tree DBH and height, while Cr and Zn were negatively correlated. The average DBH of dead trees was 24.15 cm with height of 11.69 m, indicating that heavy metals have negatively impacted *P. schrenkiana* survival and growth, as dead individuals are typically smaller trees [39]. To maintain forest health, we recommend: (1) strengthening supervision of mining transport vehicles; (2) timely road watering or hardening; and (3) promoting advanced mining technologies to reduce pollution.

Conclusion

Along roadsides in the Aiergou mining area, soils suffer light heavy metal pollution while *P. schrenkiana* leaves show moderate pollution, negatively affecting tree growth. The unique Tianshan climate, heavy metal contents, *P. schrenkiana* physiological characteristics, and metal interactions result in Pb enrichment coefficients of 5.97 in leaves, while other metals have coefficients < 0.26. Spatial distribution varies significantly across the 0–500 m transect: Pb decreases linearly with distance in both soil and leaves; As and Cu first increase then decrease; Cr and Zn in soil increase gradually while leaf Cr decreases and Zn remains stable. These findings provide crucial guidance for ecological restoration and conservation of *P. schrenkiana* forests in mining areas.

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Note: Figure translations are in progress. See original paper for figures.