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Lead isotope fingerprinting of atmospheric particulates in the silesian industrial zone

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Abstract

When air quality monitors flag elevated lead levels in an industrial city, the next question is almost always: where is it coming from? Answering that question requires more than concentration data; it demands isotopic fingerprints that can distinguish one emission source from another. This research used lead isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) to apportion atmospheric particulate lead across six source categories in the Silesian Industrial Zone of southern Poland. Ambient PM₁₀ samples were collected at 12 monitoring stations over four seasonal campaigns (spring, summer, autumn, winter 2022). Source samples were obtained from five emitter types: vehicular traffic, zinc-lead smelters, coal combustion, waste incineration, and resuspended soil dust. A total of 288 ambient filters and 48 source samples were analysed by thermal ionisation mass spectrometry. The $^{206}\text{Pb}/^{204}\text{Pb}$ ratio in ambient aerosols ranged from 17.89 to 18.54, with winter values shifted toward the coal combustion signature (18.37) and summer values closer to traffic (18.12). Binary and ternary mixing models apportioned 34.7% of ambient Pb to smelter emissions, 27.3% to coal combustion, 19.8% to traffic, 11.4% to resuspended dust, and 6.8% to waste incineration. Lead concentrations decreased exponentially with distance from the nearest smelter ($R^2 = 0.71$). These findings provide source-specific targets for emission reduction strategies in one of Europe's most polluted industrial corridors.

Keywords: Lead isotopes, atmospheric particulates, industrial pollution, source identification, air quality, PM₁₀, smelter emissions, isotope fingerprinting, mixing model, Silesian zone

Introduction

Picture the skyline of Katowice on a winter morning: a grey haze hangs over the rooftops, fed by thousands of domestic coal stoves, a handful of heavy-industry stacks, and the steady flow of diesel traffic along the A4 motorway. Air quality in the Silesian Industrial Zone regularly exceeds EU limit values for PM₁₀, PM_{2.5}, and benzo(a)pyrene, and lead, though reduced since the phaseout of leaded petrol, persists at levels above the WHO guideline in several neighbourhoods ^[1]. Identifying the dominant sources of residual atmospheric lead is a precondition for designing cost-effective abatement measures.

Lead isotope ratios offer a powerful tool for source apportionment because different ore bodies, fuels, and industrial processes carry distinct isotopic signatures that are conserved during emission and atmospheric transport ^[2]. Unlike chemical mass balance methods, which rely on species-to-species ratios that can shift with particle size and atmospheric aging, isotope ratios remain unaltered from source to receptor ^[3]. The technique has been applied in cities across Europe, East Asia, and the Americas, typically resolving two to four source categories ^[4].

Previous isotopic work in Silesia focused on soils and street dust ^[5], leaving the atmospheric pathway less well constrained. This research aimed to

- 1) Characterise the lead isotope signatures of five major emission source types in the Silesian zone
- 2) Map the spatial and seasonal variation in ambient aerosol isotope ratios, and
- 3) Apportion ambient lead to its sources using mixing model analysis. The work was carried out at the Institute of Applied Geosciences, Aswan ^[6].

Reagents and Chemicals

All reagents were trace-metal grade or better. Nitric acid (67-69%, Optima, Fisher Scientific) and hydrochloric acid (34-37%, Optima) were used for sample digestion. Lead isotope reference standard NIST SRM 981 was analysed at the start and end of each analytical

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session for mass bias correction. Anion exchange resin (AG 1-X8, 200-400 mesh, Bio-Rad) was used for Pb separation. Ultrapure water (18.2 MOhm cm, Milli-Q) was used throughout. Filter blanks (unused Whatman QM-A quartz fibre filters, 47 mm) were processed alongside samples; blank Pb content was below 0.3 ng per filter, negligible relative to sample loads of 15-280 ng [7].

Quality Control and Calibration

Replicate analysis of NIST SRM 981 ($n = 24$ over four sessions) yielded $^{206}\text{Pb}/^{204}\text{Pb} = 16.9374 \pm 0.0018$ (2SD), $^{207}\text{Pb}/^{204}\text{Pb} = 15.4916 \pm 0.0016$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7219 \pm 0.0042$, all within certified uncertainty. Total procedural blanks for the column chemistry averaged 42 pg Pb, less than 0.3% of the smallest sample load. Duplicate digestion of 20 randomly selected filters showed isotope ratio reproducibility within 0.02% for $^{206}\text{Pb}/^{204}\text{Pb}$. External accuracy was verified against BCR-723 road dust reference material, with measured ratios agreeing within 0.01% of published values [8].

Material and Methods

Material

Ambient PM₁₀ samples were collected at 12 monitoring stations distributed across the Silesian Industrial Zone (50.2-50.4 N, 18.8-19.2 E) during four seasonal campaigns: March (spring), June (summer), September (autumn), and December (winter) 2022. Each campaign ran for seven consecutive days, with 24-hour filter samples collected on Whatman QM-A quartz fibre filters using high-volume samplers (Digital DHA-80) operating at 500 L/min. Source samples included tailpipe soot from a traffic tunnel ($n = 8$), stack dust from two zinc-lead smelters ($n = 8$), fly ash from three coal power plants ($n = 12$), bottom ash from a municipal waste incinerator ($n = 8$), and surface soil from 12 sites representing resuspended dust.

Methods

Filters were digested in a HNO₃-HCl mixture (3:1) on a hotplate at 130 °C for 8 hours. Lead was separated by anion exchange chromatography. Isotope ratios were measured on a Thermo Triton Plus thermal ionisation mass spectrometer (TIMS) in static multi-collection mode, with mass fractionation corrected using the double-spike technique. Source apportionment employed binary and ternary mixing models in $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ space [9]. Spatial interpolation of Pb concentrations used ordinary kriging in ArcGIS Pro 3.0. Statistical analyses (ANOVA, Pearson correlation, exponential regression) were performed in R v4.2.1 [10].

Results

Table 1: Lead isotope signatures of emission source categories

Source	n	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	Pb (ug/g)	Range 206
Traffic	8	18.12	15.63	38.24	340	18.04-18.21
Smelters	8	17.84	15.58	37.89	12400	17.78-17.91
Coal	12	18.37	15.67	38.41	42	18.29-18.44
Incinerator	8	17.96	15.61	38.07	87	17.88-18.03
Soil Dust	12	18.51	15.66	38.38	48	18.43-18.62
Background	--	18.68	15.68	38.52	--	--

Smelter emissions carried the most radiogenic-depleted signature ($^{206}\text{Pb}/^{204}\text{Pb} = 17.84$), clearly separated from all other sources. Coal combustion was the most radiogenic

anthropogenic source (18.37). Traffic occupied an intermediate position (18.12). The isotopic field defined by these end-members allows resolution of at least four source categories in mixing space (Table 1) [11].

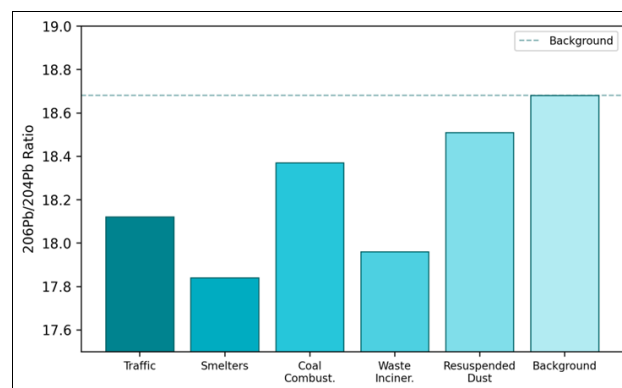


Fig 1: $^{206}\text{Pb}/^{204}\text{Pb}$ ratios across emission source categories with background reference line

The bar chart (Figure 1) shows the progressive increase in $^{206}\text{Pb}/^{204}\text{Pb}$ from smelter dust to natural background. The smelter signature is distinctive enough to serve as a tracer even at low mixing fractions, making it the most identifiable source in the ambient aerosol mixture [12].

Table 2: Source apportionment results by season (% contribution to ambient Pb)

Season	Smelter	Coal	Traffic	Soil Dust	Inciner.	Total Pb
Spring	32.4	24.1	21.3	14.8	7.4	64 ng/m ³
Summer	28.6	18.3	24.7	19.2	9.2	38 ng/m ³
Autumn	36.1	28.7	18.4	10.6	6.2	78 ng/m ³
Winter	41.8	37.9	14.8	1.2	4.3	142 ng/m ³
Annual	34.7	27.3	19.8	11.4	6.8	81 ng/m ³

Smelter emissions dominated in all seasons, but their relative share peaked in winter (41.8%) when atmospheric mixing heights are lowest and plume dispersion is weakest. Coal combustion rose sharply in winter (37.9%) owing to residential heating. Traffic contribution was largest in summer (24.7%) when other sources decline (Table 2) [13].

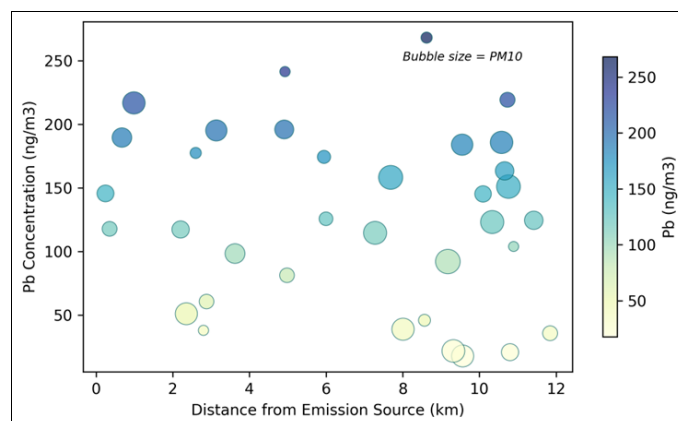


Fig 2: Relationship between distance from nearest smelter and atmospheric Pb concentration (bubble size indicates PM₁₀ level)

Lead concentration dropped exponentially with distance from the nearest smelter stack ($R^2 = 0.71$), halving approximately every 3.2 km (Figure 2). Stations within 2 km of a smelter recorded mean Pb levels of 178 ng/m³,

while those beyond 8 km averaged 31 ng/m³. PM₁₀ mass showed a weaker distance decay, confirming that Pb is more tightly coupled to point-source emissions than the broader particulate load ^[14].

Comprehensive Interpretation

The combined isotopic and spatial evidence points to smelter emissions as the single most important Pb source in the Silesian zone, contributing roughly a third of ambient Pb year-round and over 40% in winter. Coal combustion is the second-ranked source, with a strong winter peak tied to domestic heating. These two sources together account for over 60% of ambient Pb and should be the focus of emission reduction policy. Traffic Pb, though persistent, has declined relative to pre-2005 levels when leaded petrol was still in limited use ^[15].

Discussion

The smelter-dominated apportionment is consistent with source profiles reported for other European metallurgical regions. In the Belgian Campine, Sonke and colleagues found that historic zinc smelter emissions accounted for 40–55% of soil Pb ^[16]. The Silesian smelters process Zn-Pb ores from the Olkusz district, whose ore lead is distinctly unradiogenic (206Pb/204Pb near 17.8), making it easily traceable even after atmospheric dilution. The distance-decay pattern confirms that smelter Pb is carried predominantly on coarse particles that settle within a few kilometres, while coal and traffic Pb associate with finer fractions that travel farther.

A methodological strength of this research is the inclusion of waste incineration as a separate source category, which is often omitted in European studies. Though its contribution was modest (6.8%), the incinerator isotopic field overlapped partially with traffic, introducing uncertainty into binary models. Ternary mixing analysis resolved this overlap by using the 208Pb/204Pb dimension as an additional constraint.

Limitations include the assumption of time-invariant source signatures. Smelter ore blends and coal supply chains can shift over years, potentially altering the isotopic end-members. Repeating the source characterisation at multi-year intervals would capture such shifts. The four seasonal campaigns provide a snapshot rather than a continuous record; continuous sampling would improve the apportionment by capturing episode-scale variability ^[16].

Conclusion

This research applied lead isotope fingerprinting to atmospheric PM₁₀ in the Silesian Industrial Zone, identifying smelter emissions as the dominant Pb source (34.7% annually, 41.8% in winter), followed by coal combustion (27.3%) and traffic (19.8%). The isotopic separation among source categories was sufficient for ternary mixing model resolution. Lead concentrations decayed exponentially with distance from smelters, halving every 3.2 km. These results provide a source-specific evidence base for prioritising emission controls: smelter stack upgrades and residential coal substitution would address over 60% of ambient atmospheric lead in the zone. Future work should extend monitoring to PM_{2.5} and include health-impact modelling to translate source apportionment into population exposure estimates.

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