



Unleaded gasoline as a significant source of Pb emissions in the Subarctic



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H I G H L I G H T S

- Unleaded gasoline and diesel remain a source of atmospheric Pb.
- Lichens were suitable bioindicators for this purpose.
- Snow and lichen samples exhibited different contamination pathways and sources.

A R T I C L E I N F O

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After the phasing out of leaded gasoline, Pb emissions to the atmosphere dramatically decreased, and other sources became more significant. The contribution of unleaded gasoline has not been sufficiently recognized; therefore, we evaluated the impact of Pb from unleaded gasoline in a relatively pristine area in Subarctic NE Norway. The influence of different endmembers (Ni slag and concentrate from the Nikel smelter in Russia, PM₁₀ filters, and traffic) on the overall Pb emissions was determined using various environmental samples (snow, lichens, and topsoils) and Pb isotope tracing. We found a strong relationship between Pb in snow and the Ni smelter. However, lichen samples and most of the topsoils were contaminated by Pb originating from the current use of unleaded gasoline originating from Russia. Historical leaded and recent unleaded gasoline are fully distinguishable using Pb isotopes, as unleaded gasoline is characterized by a low radiogenic composition ($^{206}\text{Pb}/^{207}\text{Pb} = 1.098$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.060$) and remains an unneglectable source of Pb in the region.

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1. Introduction

Air pollution by metals (i.e., Pb, Cd, Hg, and Zn) has been of great interest in the past two decades. Metals in the atmosphere are to a great extent associated with solid particles with diameters in the range of several tenths to 10 μm (Nriagu, 1980). The transportation of metal-bearing particles over long distances is feasible despite the

highly variable residence time of the finer particles (Simonetti et al., 2003).

Many forms of Pb are highly toxic, and exposure to an organism can lead to severe physiological and neurological effects. One of the primary input pathways to the organism is by respiration, and particles with relatively small diameters (less than 10 μm) are deposited in the lungs. Since the 1940s, tetraethyl lead (TEL) has been added into gasoline as an antiknock additive (Adriano, 2001). Leaded gasoline became a major source of Pb in the atmosphere with its maximum contribution in the 1970s (Nriagu, 1989), and

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the phasing out of leaded gasoline increased the relative proportion of other Pb sources in the atmosphere (mining and smelting activities, combustion of fossil fuels, etc.) (Véron et al., 1999). As expected, the phasing out of leaded gasoline decreased dramatically the concentration of Pb in Europe, Northern America and Asia (Li et al., 2009; Annibaldi et al., 2009; Novák et al., 2003; Čimová et al., 2016).

However, several authors have referred to unleaded gasoline as a new considerable anthropogenic source of lead emitting to the atmosphere (Yao et al., 2015; Shiel et al., 2012). For instance, Shiel et al., (2012) found that according to the Canadian Statistics report, unleaded gasoline consumption accounts for 8.4% of the total Pb emissions from fossil fuels (i.e., petroleum products and coal). Another source of Pb could be from the use of avgas (aviation gasoline) in spark-ignited internal combustion engines of small general aircrafts (personal aircrafts, seaplanes, crop dusters and bush planes) (Shiel et al., 2012). Similar to leaded gasoline, TEL is added to avgas, which is produced by only a few companies worldwide (Shiel et al., 2012).

Lead isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb are well known as a “fingerprint” tool for tracing the sources of Pb pollution (Komárek et al., 2008). Generally, European and U.S. leaded gasoline differed in Pb isotopes. While TEL added to European leaded gasoline originated from Australia (Broken Hill deposit) and was characterized by lower radiogenic values ($^{206}\text{Pb}/^{207}\text{Pb}$ from 1.03 to 1.10), the U.S. leaded gasoline was more radiogenic (Mississippi Valley ore deposit, $^{206}\text{Pb}/^{207}\text{Pb}$ from 1.31 to 1.35) (Komárek et al., 2008).

Some authors have still observed low radiogenic Pb values in urban and traffic areas (Cloquet et al., 2006; Simonetti et al., 2003; Doucet and Carignan, 2001). Cloquet et al., (2006) attributed this fact to re-deposition of “older” Pb originating from leaded gasoline. Simonetti et al., (2003) observed lichen samples in NW North America and found an isotope range of $^{206}\text{Pb}/^{207}\text{Pb}$ from 1.15 to 1.17 of unclear origin. Similarly, Doucet and Carignan (2001) presented an average industrial Pb-signal around $^{206}\text{Pb}/^{207}\text{Pb} = 1.15$ in France and attributed the source to a waste incinerator in Geneva, Switzerland.

Several authors provided another possible explanation for the source of low radiogenic Pb values after the phasing out of leaded gasoline (Shiel et al., 2012; Yao et al., 2015). Shiel et al., (2012) found a Pb composition in oysters from British Columbia similar to road dust and lichen samples described in the work by Simonetti et al., (2003). They reported that this composition is representative of the average modern Pb isotopic signature of unleaded gasoline and diesel fuel, however the authors did not provide direct analytical evidence for this statement. Another group of authors (Yao et al., 2015) measured Pb isotope composition in unleaded gasoline (octane numbers of 92, 95, 98) and diesel from local suppliers in Taipei, Taiwan. The average Pb isotope composition found in vehicle exhaust ($^{206}\text{Pb}/^{207}\text{Pb} = 1.148$) overlapped with reported aerosol data, while the Pb isotope composition in unleaded gasoline and diesel fell within the ranges of 1.139–1.152 and 1.144–1.157, respectively (Yao et al., 2015).

Considering that direct evidences of Pb input from unleaded gasoline is missing and questionable, we decided to report Pb isotope data from various environmental samples (snow, lichen, moss, soil and aerosol - particulate matter, specifically PM_{10}) originating from NE Norway to show the impact of unleaded gasoline combustion in a relatively simple environment with only a few Pb endmembers. Snow, lichen and soil samples were further used to describe contamination pathways of Pb emissions from local dispersed and remote sources and we revised the idea of resuspension of the “old” gasoline lead in the environment.

2. Materials and methods

2.1. Study area and sources of contamination

The sampling network covers approximately 2000 square kilometres in north-eastern (NE) Norway, near the Norwegian-Russian border. The region is known for the largest remaining area of primeval pine forest in Norway, an offshoot of the Siberian taiga (Fig. 1). The study area is dominated by birch forests and low-productivity pine forests. The annual average temperature is $-1\text{ }^{\circ}\text{C}$, the annual precipitation is 400–500 mm/year, and the elevation is between approximately 80 and 280 m a.s.l. (Räisänen et al., 1997). There are two important non-ferrous metal processing plants, the Nickel smelter (5 km from the border) and an ore enrichment plant in Zapolyarny (15 km from the border). The facilities emit SO_2 and risk elements, mainly Ni and Cu. Additionally, these types of industries remain a huge source of SO_2 and a wide range of elements: Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Sr, Th, Tl, Zn and others (Reimann et al., 1996).

In total, 17 sampling sites were chosen. The sampling sites can be divided into 3 transects. The transects go approximately 50 km south-west (transect 1; sites 1, 2, 3, 4, and 5), 90 km north-west (transect 2; sites 6, 7, 8, 9, and 13) and 40 km north-east (transect 3; sites 10, 11, 12, 14, 15, 16, and 17) from the Nickel smelter. The prevailing wind direction is north, north-east (N,NE) (Fig. 1).

2.2. Sampling and sample treatment

The sampling was performed in March 2015 (snow and lichens) and August 2015 (soil profiles and bedrock). Snow and lichens were collected at each site (1–17), soil profiles and bedrock were only collected at selected sites of each transect (1, 4, 5, 6, 7, 8, 13, 15, and 17). Moreover, PM_{10} fraction was provided by the Norwegian Institute for Air Research, from two monitoring stations, and included atmospheric deposition data from January and March 2015. The PM_{10} samples came from monitoring stations in Svanvik (3 m above the ground near site 5) and in Karpdalen (1.5 m above the ground near site 15). Finally, representative samples of the smelter slag and the feeding material (Ni-ore concentrate) were obtained for the analysis of Pb isotope composition.

Approximately 2 L of fresh snow was collected directly to a polypropylene bottle. Snow was collected in duplicate, and the sampling points were within 50–100 m from each other. Only visually clean and fresh snow was collected to avoid collecting ground vegetation or ice layers. Only *Hypogymnia physodes* and *Melanohalea olivacea*, two foliose species, occurred within the study area. Approximately 30 thalli of each species were cut from several tree branches and trunks using a ceramic knife and stored in paper bags. The aboveground part of the moss *Polytrichum commune* was collected at each sampling site and stored in paper bags. Samples of soil profiles were collected from a 1 x 1-m-wide pit sectioned into 3 or 4 parts according to the natural development and visible changes within the profile down to the mineral horizon. The top surface composed of fresh litter or grass cover was removed. Bedrock samples were collected using a geological hammer. Each sample consisted of 5–7 rock fragments.

All the samples were homogenized and decomposed in a mixture of acids (HNO_3 , HCl, and HF) to obtain a liquid sample. The appropriate analytical procedure for each sample type is given in supplementary file (Table S1).

2.3. Pb concentration and isotope analysis

Concentration of Pb was determined by an inductively coupled plasma-mass spectrometer (ICP MS, iCAP Q, Thermo Fisher

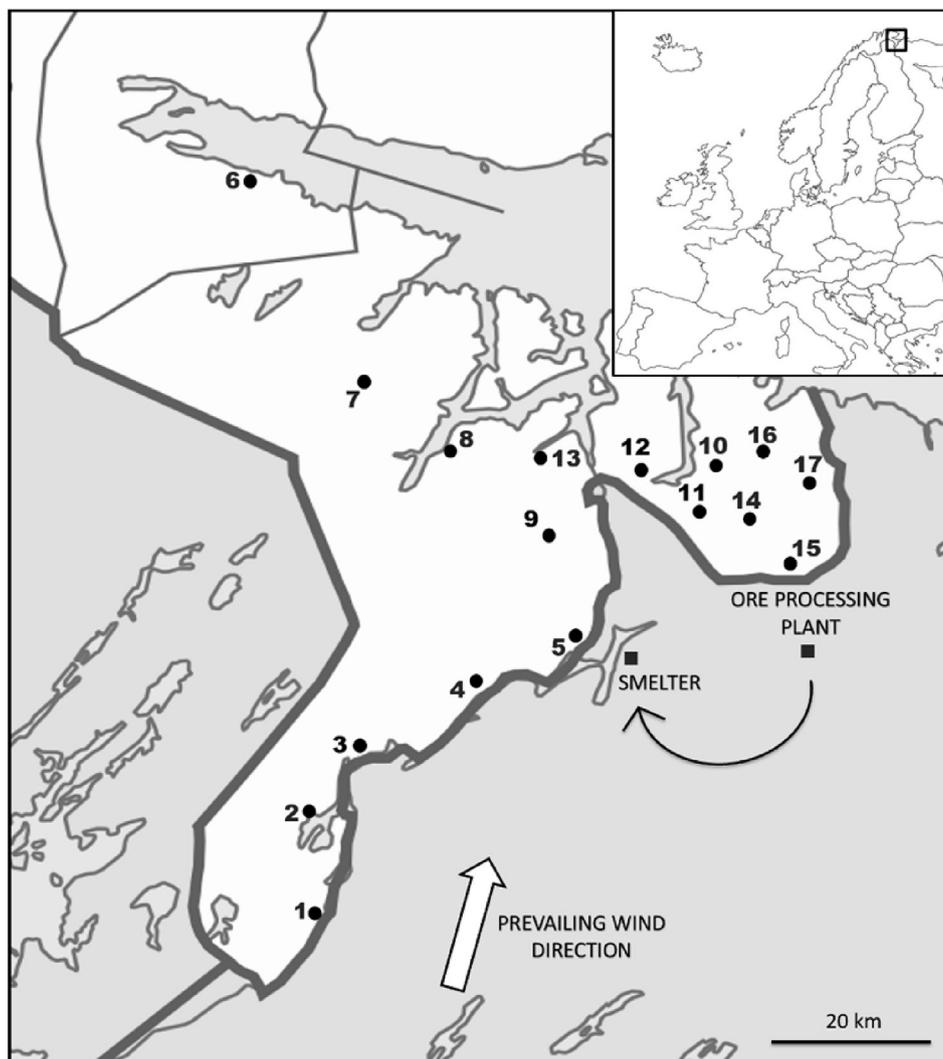


Fig. 1. Study area and sampling sites.

Scientific, Germany) using an aqueous calibration standard CertiPUR (Merck, Germany). The drift of an analytical signal was corrected using In as an internal standard.

Pb isotope ratios presented here were measured using ICP MS. Raw $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ were measured and the data were corrected according to instrumental mass bias. The correction was done on the basis of the standard–sample bracketing technique using SRM NIST 981 (common lead). Ten replicates were measured for each standard and sample measurement (120 sweeps for each measurement).

2.4. QA/QC procedures

The quality control procedures consisted of measurements of sample replicates and triplicates and certified reference materials. To ensure the accuracy of the analytical process, we used the certified reference materials as follow: BCR-482 Lichen (IRMM, Belgium), SRM 1640a Natural Water (NIST, USA) and SRM 2710a Montana I Soil (NIST, USA). The recovery of Pb certified reference values was within the range of 89–111% for all the materials used. Internal reproducibility for concentration and isotope measurements was better than 3 and 0.4% for all standards and sample analyses, respectively. The external reproducibility (between

sample replicates and triplicates) was better than 15%. The method quantification limit (MQL) calculated based on all steps of analytical procedure was 13 ng L^{-1} and $6 \mu\text{g kg}^{-1}$, for liquid (snow) and solid (soil, bedrock and lichen) samples, respectively.

3. Results and discussion

3.1. Pb concentrations in snow samples

Gregurek et al., (1998) distinguish between snowmelt (dissolved metals defined by $0.45 \mu\text{m}$ filter porosity) and the filter residue (solid particles). We measured the total amount of metals in snow samples to avoid potential loss of analyte due to the fact that metal concentrations in snow is generally at ppb levels and snow melting can take place over 24 h. During that time, a certain amount of metals can adsorb on the PET wall. However, the slight acidification of snowmelt prevents sorption, and causes leaching of the particle surface and therefore, an overestimation of the snow melt metal fraction.

We summarize the snow and lichen concentrations in Table 1. The snow concentrations are relatively uniform and vary between $18 \mu\text{g L}^{-1}$ (# 1) and approximately $64 \mu\text{g L}^{-1}$ (# 17). The relatively higher Pb concentrations in snow samples were detected at

Table 1
Pb concentrations in snow and lichen samples (mean \pm 2SD).

Site	Snow ($\mu\text{g L}^{-1}$)	Lichen (mg kg^{-1}) <i>Melanohalea</i>	<i>Hypogymnia physodes</i>
1	18.0 \pm 5.66	3.04 \pm 0.81	3.51 \pm 0.32
2	22.0 \pm 7.07	3.71 \pm 1.20	0.23 \pm 0.28
3	18.0 \pm 2.83	3.55 \pm 0.52	3.81 \pm 0.75
4	48.5 \pm 16.3	4.69 \pm 0.36	24.9 \pm 10.8
5	22.5 \pm 2.12	6.53 \pm 3.36	2.89 \pm 1.23
6	28.1 \pm 8.49	2.96 \pm 0.19	1.80 \pm 0.42
7	15.5 \pm 9.90	2.08 \pm 0.14	8.11 \pm 0.04
8	30.5 \pm 9.19	22.07 \pm 27.8	5.54 \pm 2.59
9	49.4 \pm 10.9	8.69 \pm 8.0	30.2 \pm 35.8
10	43.1 \pm 5.66	2.20 \pm 0.20	5.59 \pm 0.24
11	34.5 \pm 4.95	3.28 \pm 0.37	6.25 \pm 4.22
12	27.5 \pm 9.19	3.24 \pm 0.07	8.16 \pm 0.49
13	41.2 \pm 5.66	6.77 \pm 0.81	12.0 \pm 3.39
14	32.8 \pm 9.90	n.a.	n.a.
15	21.5 \pm 4.95	5.11 \pm 0.39	7.69 \pm 0.12
16	55.5 \pm 12.0	6.29 \pm 0.49	5.91 \pm 0.13
17	63.5 \pm 16.3	4.60 \pm 0.39	7.63 \pm 1.27

sampling points very close to highly frequented roads. We found $48.5 \mu\text{g L}^{-1}$ at sampling points # 4 and # 9, both on the local road of 885 connecting the southern and northern parts of the area and at # 13, which is near to the city of Kirkenes. Additionally, higher Pb concentrations were detected at points #10, 11, 16 and 17 (the highest Pb concentration was $63.5 \mu\text{g L}^{-1}$) (Table 1). This north-eastern area is a military border area frequented by military vehicles and snowmobiles or can be related to the emissions from the smelter and ore processing plant with a prevailing wind direction from the south.

Gregurek et al., (1998) analysed snow pack samples from the vicinity of the Ni smelter in Monchegorsk (Russia), an area more than 200 km southeast from our sampling points. If we compare Pb concentrations in snow melt and filter residues with the study by Gregurek et al., (1998), we can observe comparable results (several tens of $\mu\text{g L}^{-1}$) at those points of relatively low Pb concentrations (points 1–3, 5–8, 12, and 15). This fact means that the Russian Ni industry is not the main source of Pb contamination in this area. Reimann et al., (1996) characterized industrial emissions near the cities of Nikel and Zapoljarnyj (very close to our sampling points). They found that the Pb concentrations, even in the sub-ppb levels, were much lower than both the concentrations from Gregurek et al., (1998) and the concentrations from this study. According to the Reimann et al., (1996) the Pb emissions came from the Ni smelter but the level of contamination was very low. The differences in our and earlier results by Reimann et al., (1996) could be due to different sampling strategies. We were focused on sampling points near highly frequented roads, while Reimann et al., (1996) sampled more remote open areas.

3.2. Pb concentrations in lichen samples

The Pb concentration in both lichen species *Hypogymnia physodes* and *Melanohalea olivacea* are highly heterogeneous at some sampling points (# 4, 5, 8, 9, 11 and 13) (Table 1). Generally, at sampling points less exposed to emissions from highly frequented roads (# 1–3, 6 and 7), the sample replicates were more consistent (Table 1). We increased the amount of well-homogenized samples from the previous 250 mg–500 mg, which is the maximum mass usable for the EPA 3051 method using microwave digestion, but without any substantial effect on Pb concentrations heterogeneity. When considering, for instance, Pb concentration in *Melanohalea olivacea* at # 8 (22.1 mg kg^{-1}), the range was from 2.41 to 42 mg kg^{-1} , with a difference of

approximately 40 mg kg^{-1} . The Pb aliquot related to 0.5 g of the sample is $20 \mu\text{g}$. In the case of PbO, it is $21.5 \mu\text{g}$ absolutely. From the density of PbO (9.53 g cm^{-3}), we can further calculate the diameter of a theoretical spherical particle, which is equal to $1.6 \mu\text{m}$. In other words, only one spherical particle with the diameter of $1.6 \mu\text{m}$ can influence the above-mentioned range of Pb concentration in a lichen sample. Therefore, an efficient sample homogenization in such cases is almost impossible.

Our lichen data correspond well with the earlier work by Äyräs et al., (1997), which addressed the monitoring of terrestrial moss in northern Finland, Norway and Russia. Pb concentrations in their study varied between 0.8 and 29.4 mg kg^{-1} , and the authors attributed the sources of Pb to local mines, industry and traffic. They found higher Pb concentrations in the vicinities of cities, such as Nikel, Murmansk and Monchegorsk, and on the Norwegian side near local traffic centres, i.e., near the Norwegian-Finnish border (the main E6 road, close to our sampling points # 7 and 8, where we detected elevated Pb concentrations in snow and lichen samples, Table 1). Haack et al., (2004) analysed topsoils, mineral soil horizons, moss samples and melted snow. Using a coupled Pb concentration/stable isotope analyses they proved that Pb from Nikel and Zapolarnyi is probably not a major contributor.

We found elevated Pb concentrations in lichen samples near frequented roads, mainly at sampling point # 4, 8, 9 and 13. Point # 13 is near the city Kirkenes. At points # 8, 9, and 13 we measured higher Pb concentrations in snow samples (Table 1). Conversely, the highest Pb level in snow was at sampling point # 17 where only moderate Pb concentrations in lichen samples were found (Table 1). While snow reflects only current emissions, lichens integrate information of several years. We can therefore assume that traffic in the northeastern area (points # 11–17) is not so frequent compared to the westernmost region, and the surrounding points # 8, 9, and 13. However, during winter periods, military traffic is more likely responsible for Pb concentrations in the snow.

3.3. Pb concentrations in soil samples

We measured Pb concentrations in soils at sampling points where the soils had developed (points # 1, 4–8, 13, 15, and 17) (Fig. 1 and Table 2). Pb concentrations in topsoil layers varied by one order of magnitude from 15.4 (# 17) to 164 mg kg^{-1} (# 4). We found relatively higher Pb values at some sampling points (Table 1) compared to earlier works. For example, Räisänen et al., (1997) included in their study a sampling point at Skellbekken that corresponds to our sampling point # 4, while Räisänen et al., (1997) and Reimann et al., (1997) found Pb concentrations of approximately 15 mg kg^{-1} , we observed a value more than 10 times higher (Table 2). Haack et al., (2004) had a sampling network with a larger grid and their sampling points did not overlap with ours but the highest value in their study was approximately 43 mg Pb kg^{-1} at the Russian site (almost 200 km south from our nearest sampling point # 1).

Our sampling strategy was adapted to prove the importance of traffic for the Pb emissions in this Subarctic area. Therefore, we designed the sampling points systematically near highly frequented roads (Fig. 1) contrary to other studies (Räisänen et al., 1997; Haack et al., 2004; Reimann et al., 1997). Points # 1, 4 and 8 closer to higher traffic had higher Pb concentrations in the topsoil; the other sites, # 15 and 17, were influenced only by the Ni smelter and ore processing plant (Fig. 1), and the Pb concentrations were significantly lower (Table 2). Therefore, our findings are congruent with the findings by Äyräs et al., (1997) that the Russian metallurgical activities are of minor importance in terms of Pb emissions.

Table 2
Basic soil characteristics, total Pb concentration and local geology at the sampling points (mean \pm 2SD).

Site	Depth	pH	Fe _{ox}	Mn _{ox}	Al _{ox}	Pb _{TOT}	Geological description
1	0–8	4.8	0.05	26.3	0.01	70.3 \pm 10.6	peat (over 0.5 m)/glacifluvial and beach sediments/gneiss; granitic gneiss
	23-x	5.4	0.09	50.3	0.01	37.9 \pm 10.1	
4	0–2	4.0	0.29	30.7	0.15	164 \pm 10.5	moraine material (over 0.5 m)/ metamorphosed basalt and andesite
	2-x	4.4	0.30	0.97	0.03	65.3 \pm 58.4	
5	0–5	3.7	0.15	7.56	0.06	100 \pm 3.91	moraine material (over 0.5 m) / granitic gneiss
	45-x	5.3	0.35	0.95	0.19	24.9 \pm 5.03	
6	0–2	4.6	0.10	0.86	0.01	25.0 \pm 2.79	migmatitic, tonalitic and granodioritic gneiss
	20-x	5.3	0.64	4.05	0.23	29.0 \pm 5.61	
7	0–2	5.4	0.14	81.0	0.01	64.1 \pm 68.1	peat (over 0.5 m)/moraine material (up to 0.5 m)/gneiss; amphibolite
	23-x	5.7	0.12	29.5	0.04	42.1 \pm 16.5	
8	0–2	5.0	3.45	26.2	0.68	114 \pm 6.34	marine sediments (over 0.5 m) /tonalitic and granodioritic gneiss
	2-x	5.3	1.37	44.4	1.36	32.8 \pm 7.56	
13	0–5	4.1	0.02	0.84	0.02	19.0 \pm 5.29	marine sediments (over 0.5 m) /granitic gneiss
	10-x	4.4	0.15	0.77	0.11	22.3 \pm 6.14	
15	0–10	4.7	0.08	2.31	0.02	17.1 \pm 5.09	moraine material (over 0.5 m)/ granite („spotted granite“)
	25-x	4.8	0.29	1.53	0.03	24.2 \pm 9.46	
17	0–15	4.7	0.57	0.23	0.64	15.4 \pm 3.42	moraine material (over 0.5 m)/ monzonite
	35-x	5.1	0.38	3.55	0.17	20.1 \pm 5.07	

3.4. Pb isotope composition in snow, lichen and soil samples

The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios were measured to determine the contributions of separate Pb sources. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio found in snow samples varied from 1.131 (# 16) to 1.209 (# 6) (Fig. 2). The continuous snow cover limits possible particle resuspension, as shown from the comparison of Pb isotope composition in topsoils and snow at sampling points # 1, 4, 6, 7, 13 and 15. We further hypothesize that mainly heavier particles from the nearest point sources can contaminate the surface of the snow cover and that the Pb isotope composition should reflect their contribution (Francová et al., 2017). In our study area, there are only two potential main sources of Pb contamination: Russian metal-lurgy and traffic.

We were not able to obtain fly ash from the Nickel smelter, but we sampled the Ni concentrate from the Ni ore and Ni slag from the Ni ore processing plant. Instead of fly ash, we obtained the PM₁₀ fraction (<10 μm) of particulate matter from the atmospheric aerosol from two sampling points near the Ni smelter (# 5) and near the ore processing plant (# 15). The Pb isotope composition of the potential endmembers is presented in Table 3. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Ni concentrate and slag were homogenous with values

of 1.150 and 1.146 for concentrate and slag, respectively. This Pb isotope signature can be observed in lichen samples at points # 1, 2, 12, and 15–17 and in snow samples from points # 11–17 (Table 1, Fig. 2.). Sampling points # 1 and 2 could not have been easily contaminated by either the smelter or the ore processing plant because of the long distance and prevailing wind directions (Fig. 1). Therefore, the Pb isotope signal at the northeastern sampling points is more likely related to the metallurgical industry (Fig. 1).

This fact was further proven by the analyses of PM₁₀. Generally, Pb isotope signatures in PM₁₀ differ at both sampling points and different sampling times. PM₁₀ were sampled in January and March of 2015. While at some points we observed a homogenous (and the highest) Pb signature within both samples (# 5, $^{206}\text{Pb}/^{207}\text{Pb} = 1.189$, Table 3), at other sites (e.g., # 15), we obtained different values for January and March (Table 3). The PM₁₀, contrary to snow samples, contain particles with very long residence times in the atmosphere, and can be transported over long distances (Francová et al., 2017). Moreover, the credibility of PM₁₀ is related to the actual wind direction, thus the robustness of sampling replicas is limited.

The Pb isotope signatures of topsoils and environmental indicators are more or less congruent at most of the sites. For example, at point # 7, both snow and lichen samples differ from the topsoil, which is consistent with the mineral horizon. This fact can be explained either by the influence of the metallurgy or unleaded gasoline. The influence of the industry is unlikely due to the position of the sampling point and prevailing wind direction. Another explanation (and our hypothesis) can be related to the influence of unleaded gasoline to Pb emissions. We therefore analysed both gasoline and diesel from the local gasoline station in Kirkenes, Norway, and in Nikel, Russia (Table 3). The Pb in Russian unleaded gasoline, which is commonly used by the locals, is less radiogenic with $^{206}\text{Pb}/^{207}\text{Pb}$ at approximately 1.10 (Table 3). The difference in Pb isotope composition between topsoil and lichen samples at this locality excludes possible particle resuspension. The different bedrock or mineral Pb isotope composition is due to the complicated geological conditions characterized by deposition of secondary moraine material at most of the sampling points (Table 1).

3.5. Pb source apportionment in the Norway/Russian/Finland border area

For a better representation of Pb source apportionment, we constructed a three isotope plot (Fig. 3) containing both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios. The addition of the ^{208}Pb isotope

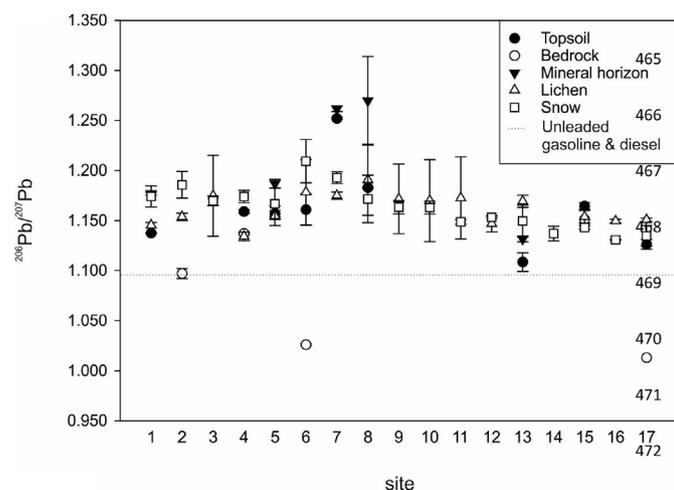


Fig. 2. $^{206}\text{Pb}/^{207}\text{Pb}$ isotope composition in samples of topsoil, bedrock, mineral horizon, lichen and snow. The dotted line represents unleaded gasoline/diesel from the Russian gas station.

Table 3
Pb concentration and isotope composition of endmembers. Results are given as mean \pm 2SD.

Sampling campaign 2015		$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Pb (mg kg ⁻¹)
PM ₁₀ (#5)	January	1.187 \pm 0.003	2.061 \pm 0.01	0.93 \pm 0.07
	February	1.190 \pm 0.005	2.064 \pm 0.006	0.74 \pm 0.04
PM ₁₀ (#15)	January	1.156 \pm 0.004	2.098 \pm 0.007	1.57 \pm 0.02
	February	1.177 \pm 0.006	2.074 \pm 0.01	1.75 \pm 0.03
Ni slag		1.150 \pm 0.003	2.101 \pm 0.008	36 \pm 0.09
Ni concentrate		1.146 \pm 0.002	2.100 \pm 0.009	n.d.
Unleaded gasoline - Russia		1.098 \pm 0.003	2.060 \pm 0.011	0.98 ^a \pm 0.1
Diesel - Russia		1.100 \pm 0.002	2.062 \pm 0.006	0.89 ^a \pm 0.1
Unleaded gasoline - Norway		1.148 \pm 0.003	2.124 \pm 0.008	0.38 ^a \pm 0.05
Diesel - Norway		1.153 \pm 0.006	2.129 \pm 0.009	0.50 ^a 0.05

n.d. – not detected.

^a mg L⁻¹.

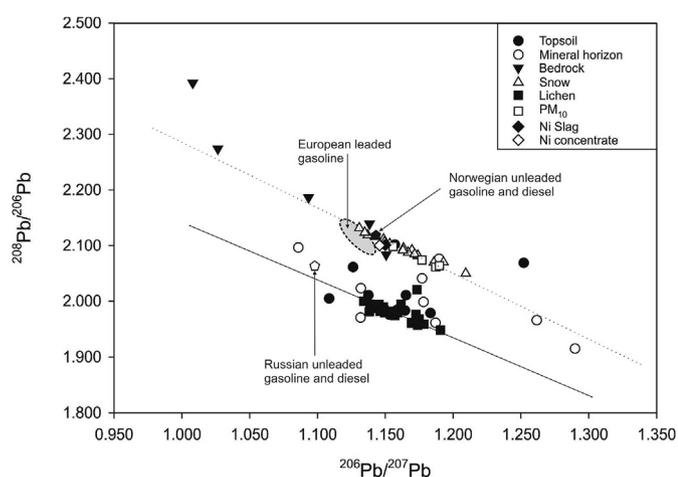


Fig. 3. Three isotope plot of $^{208}\text{Pb}/^{206}\text{Pb}$ against $^{206}\text{Pb}/^{207}\text{Pb}$ of natural samples (topsoil, mineral horizon, bedrock, snow, lichen) and endmembers (PM₁₀, Ni slag, Ni concentrate). The isotope signature of leaded gasoline is from Komárek et al. (2008). Lines on graph represent the two possible sources: dotted line – Russian nickel industry ($y = -1.04x + 3.3$; $R^2 = 0.98$); straight line – Russian unleaded gasoline and diesel ($y = -1.28x + 3.48$; $R^2 = 0.47$).

distributed our data into two main groups. The first group contains all of the snow samples, PM₁₀, Ni slag, concentrate and most of the bedrocks. The second contains most of the topsoils, lichens and data on unleaded gasoline (Fig. 3).

Continuous snow cover limits resuspension, hence snow samples are distinguishable from lichen and topsoils, which have a large overlap in the Pb isotope composition (Fig. 3). According to Fig. 3, snow samples contained Pb derived from the metallurgical industry; however, for the topsoil and lichen, the prevailing source was Russian unleaded gasoline. We suggest that snow contains mainly those particles traveling through the atmosphere at relatively higher altitudes, where the dry deposition can be created. This can explain the same Pb isotope composition found in PM₁₀ samples, Ni products and waste materials, and snow samples. Topsoils and lichen samples from the vicinity of highly frequented roads contain particles from lower parts of the atmosphere coming primarily from vehicle exhausts.

Some authors attribute low-value radiogenic Pb found in environmental samples (i.e., moss and lichen samples) to resuspension of previously used leaded gasoline (Haack et al., 2004; Cloquet et al., 2006; Doucet and Carignan, 2001); however, this does not discredit the possibility of Pb contribution from unleaded gasoline. Shiel et al., (2012) suggested that unleaded gasoline is a source of Pb contamination of bivalves collected from western Canada (British Columbia); however, the authors do not present clear evidence for

this statement. They only suggest that the low radiogenic composition of Pb isotopes found in oyster samples are consistent with atmospheric aerosols reported by Simonetti et al., (2003) and in road dust analysed along two highways in British Columbia collected by Preciado et al., (2007). The authors presented low-value radiogenic isotope ratios different from those related to leaded gasoline found deeper in roadside soils; however, the Pb isotope composition of unleaded gasoline was only taken from Erel et al., (1997) as an average value of $^{206}\text{Pb}/^{207}\text{Pb}$ approximately 1.11. Additionally, Erel et al., (1997) did not present original data but referred to Monna et al., (1995) who characterized the automotive exhausts near a car parking. France completely phased out leaded gasoline by 2000 and their data represents thus effects from leaded gasoline.

From our observations, we were able to distinguish between two main sources of Pb in the study area: Ni metallurgy (Ni concentrate – $^{206}\text{Pb}/^{207}\text{Pb} = 1.146$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.100$, Fig. 3) and unleaded gasoline from Russia (Diesel – $^{206}\text{Pb}/^{207}\text{Pb} = 1.100$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.062$ and gasoline $^{206}\text{Pb}/^{207}\text{Pb} = 1.098$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.060$, Fig. 3). Although, the possibility is unlikely, the resuspension of “old” Pb from leaded gasoline should still be considered by taking into account the lichen lifetime (less than 5 years, Simonetti et al., 2003) and time since the phasing out of leaded gasoline. When we compared the two Pb sources in the Subarctic area, the predominant source near the frequented roads was the combustion of unleaded gasoline originating from Russia; otherwise, a more diffusive pattern was observed from the lichen data, and as the lichen approached closer to the snow line (Fig. 3) the mixing of these two sources increased.

Many authors suggest that after the phasing out of leaded gasoline, Pb from this source has had a negligible impact on the whole Pb emission budget. Haack et al., (2004) concluded that in the Arctic area, Pb derived from gasoline additives is overlapped by Pb from other local sources. Russian gasoline/diesel is widely used in NE Norway, especially due to its lower price. The concentrations of Pb in gasoline/diesel samples from Norway were significantly lower compared to Russian ones with a different isotope signature (Table 3), indicating that the influence of the Norwegian gasoline/diesel is negligible.

4. Conclusions

The study focused on the identification of Pb sources in NE Norway. Our hypothesis was that Pb originating from current unleaded gasoline and diesel could be an important source in an environment with few anthropogenic Pb sources. We analysed locally used unleaded gasoline samples for Pb isotope composition, and because the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio in the Russian samples is similar to the Pb additives in European leaded gasoline, we suggest

that conclusions based on resuspension of Pb from “old” gasoline determined from evidence of this isotope ratio, should be revised. Using suitable environmental indicators, we further traced Pb from the Ni metallurgy and combustion of unleaded gasoline. We describe the link between Pb isotope composition of unleaded gasoline and lichen within the majority of topsoil samples. The snow samples collected from the same localities were affected by metallurgy. Snow and lichen samples exhibited different contamination pathways and sources. Lichens integrated local dispersed sources, i.e., automotive; while snow integrated local point sources that emitted particles higher in the atmosphere.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2017.11.031>.

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