TRENDS IN ELEMENTAL CONCENTRATIONS OF TREE RINGS FROM THE SIBERIAN ARCTIC

Short Title: Changing chemistry of Siberian Arctic trees: a possible consequence of pollution and permafrost thawing.

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Abstract

The biogeochemistry and ecology of the Arctic environment have been heavily impacted by anthropogenic pollution and climate change. We examined long-term changes in wood chemistry of the dominant tree species of Siberian forests with inductively coupled plasma mass spectrometry analysis to study interaction between climate change and environmental trace elements. Variance and correspondence of 26 element concentrations of larch tree rings from the Taymyr Peninsula were statistically analyzed from AD 1300 to 2000. Unexpectedly, the tree rings reveal pronounced depletion of xylem Ca and Mg concentrations and enrichment of P, K, Mn, Rb, Sr and Ba concentrations after ca. 1950. The significant trends are unprecedented for the last 700 years, but the environmental mechanism triggering the change is not obvious. We hypothesize that the declining xylem calcium and manganese is a response to soil acidification from to air pollution as seen in experimental acidification elsewhere. The increase of P, K, and Mn concentrations, however, seems more likely a result of changes in root efficiency and excess water-soluble minerals liberated by the permafrost thaw and warming temperatures. Changes in wood chemistry altered by soil nutrient availability may signal mounting stress on arctic vegetation.

Introduction

Warming of the Siberian Arctic over the 20th century has triggered an increase of tree cover as tree line has expanded both northward and upwards (Kharuk *et al* 2006, Kirdyanov *et al* 2012, Golubeva *et al* 2013). Under some circumstances, however, the fragile balance of health and productivity of northern forest ecosystems has been adversely impacted by the climate change (e.g., Lloyd *et al* 2011) and pollution loading (e.g., Nilsson *et al* 1998; Kirdyanov *et al* 2014). To date many studies report profound impact of permafrost thawing on biogeochemical cycling and unexpected environmental feedbacks (e.g., Shur and Jorgenson 2007, Yarie and Van Cleve 2010, Keuper *et al* 2012, Iijima *et al* 2013). Moisture stress from the deepening of the active melting layer of permafrost soils contributes to unusual decline in forest growth in the high north (Barber *et al* 2000, Girardin *et al* 2014). Other studies show that active permafrost thawing could damage the boreal trees through acidification of the environment and soil in particular (Shortle *et al* 1997, Nilsson *et al* 1998, Shur and Jorgenson 2007, Rice and Herman 2011). The global acceleration of nitrification and anthropogenic acidification along with surface deposition of contaminants during industrial times greatly alters biogeochemistry of Arctic ecosystems as well (Galloway *et al* 2003, Smith *et al* 2011). The acid compounds induced by air pollution over the Arctic are well documented since the 1970s as a result of industrial pollution originating in mid-latitudes (AMAP Assessment 2006). However, pollution over the Arctic has been present much earlier than the historical records suggest. According to Law and Stohl (2007), pilots observed “widespread haze” over the North American Arctic in the 1950s. The effect of soil leaching related to nitrification is a well-documented phenomenon in Arctic and boreal ecosystems (Van Miegroet and Cole 1984, Sverdrup *et al* 1994). In cold environments, deposition of acid anions, such as sulfate and nitrate, affects intake of important macronutrients such as Ca, P, Mn and K by trees (Agren *et al* 2012). Additionally, surface water enriched with HNO_3 (nitric acid) triggers both the leaching and transport of base cation Ca^{2+}, K^+ and Mg^{2+} within the entire soil profile and leads to their depletion from the exchangeable pool available for tree uptake (Hogberg *et al* 2006). Thereby, the long-term (decadal) alterations of soil mineral composition clearly impact the relationship of exchangeable elements between soil and trees, and Siberian boreal forests are subject to these types of chemical alterations. Despite the significance of these affects, little is understood about the chemical relationship between trees and soils beyond the industrial period of the Modern Era.

Understanding of current forest conditions with respect to the possible influence of climate change and large–scale air pollution can be improved with knowledge of the history of biogeochemistry changes, which may in principle be accomplished using proxy archives such as tree rings (Hughes *et al* 1980). Tree-ring records are an established proxy of atmospheric pollution and soil and water contamination (Hall *et al* 1975, Baes III and McLaughlin 1984, Guyette *et al* 1992, Padilla and Anderson 2002, Kuang *et al* 2008). Tree-ring chemistry addresses to dynamics of stem element concentrations, which can be used as diagnostic markers of environmental change including soil chemistry. The aforementioned applications of tree rings have been successful in reconstructing soil pH and atmospheric pollution, and monitoring sulfur deposition and metal contamination (e.g., Guyette and Cutter 1993, Lei Chen *et al* 2010, Doucet *et al* 2012). Experimental acidification of soil and vegetation suggest that ratios of molar elements in tree rings (such as Ca/Mg, Mg/Mn or Ca/Al) may be more diagnostic for environmental effects than xylem elemental concentrations alone (DeWalle *et al* 1999, Kuang *et al* 2008).

Unfortunately, definitive understanding of unfolding impacts of atmospheric acidification and climate warming is often limited by the lack of long-term data on soil pH and nutrients uptake by trees. This deficiency prevents element trend comparisons earlier than the Modern Era warming and preindustrial times. Recent expanded application of inductively coupled plasma mass spectrometry has significantly increased the length of observations for trace elements from tree rings. Still, there are few records exceeding 100 years. The longest trace element tree-ring record known to us goes back to the mid-1600s (Padilla and Anderson 2002).

We hypothesize that xylem trace element concentrations may show long-term changes in nutrient uptake by trees, which would provide evidence of interaction between climate change, pollution and environmental trace elements. We developed highly resolved and replicated records of trace element concentrations from larch tree rings and analyzed their variance and relationships extending back 700 years. The main goal of this study was to see whether xylem chemistry shows variability as potentially related to long-term nutrient availability in arctic soils prior to the Industrial Revolution and during the Modern Era warming. We apply Principal Component analysis to the long tree-ring series, i.e., series that can capture changes that have taken place over several decades to one hundred or more years, which assesses non-linear inter-correlation between various xylem trace elements. Further, use of ‘long-term’ scale refers to changes that have taken place over several decades to one hundred or more years. The results are discussed in relation to regional climate change and global acidification of the Arctic environment as well as pollutant emissions of north Siberian origin.

Materials and Methods

Site settings

The tree-ring site is located in the Kotuy River catchment near but outside of a 85-km zone of direct contamination impact of the Norilsk Nickel smelting complex, the largest pollutant of heavy metals and SO_4-S in the world since the 1950s. The studied area is the northernmost limit of tree growth in the world, on the Taymyr Peninsula of Eurasia (figure 1). The forest-tundra ecotone is widespread with thermokarst lakes and meandering streams draining polygonal tundra soils. Vegetation cover is sparse (less than 30%). Larch is the dominant conifer species of the Siberian forest-tundra and boreal forest. The age of mature larch trees (*Larix gmelinii* Rupr.) ranges from 100 to 550 years. Tree-ring growth of larch at the site is strongly limited by June-July temperature variability (Naurzbaev and Vaganov 2000). The growing season extends for only ca. 2.5 months, with mean annual temperature -13.5°C at the Khatanga weather station. Because larch is a deciduous coniferous tree, foliage is retained only during the short growing season. Overall, the larch matches optimal conditions for dendrochemistry, which ideally include a long-lived tree species, conifer, wide range of geographical distribution, distinct heartwood, a low number of rings in sapwood and low heartwood moisture content (Cutter and Guyette 1993).

Shallow soil is developed on frost-shattered limestone debris and fluvial silt and loamy to sandy sediments mixed with coarse gravel on the solifluction slopes. On average, the soils are dry and maximum thaw depth is up to 60 cm (authors V. Shishov and A. Knorre personal field observation), although the water table is close to the surface (ca. 40 cm). Typical polygonal tundra soil is low in organic matter content, gleying and acidification (Goryachkin 2010). At Taymyr, wet-setting soils are near neutral (pH 7.3) on average but soils from dry settings are slightly acidic (pH 5.3) (Schmidt 1999). The tree-ring upland site has relatively dry conditions.

At the continental scale, this area is transitional between the extremely flat Western Siberian plain and the higher relief of Eastern Siberia. The terrain encompasses a rolling plain between the Byrranga Mountains to the north and the North Siberian Lowland to the south. The elevation rises southwest to northeast from 160 m a.s.l. on the flood plains of the Kotuy River to 350 m a.s.l. in the mountains. Atmospheric circulation over the area depends on seasonal buildup of the Siberian High and the Siberian Low as well as the Arctic front, which play a key role in atmospheric circulation for the entire Eurasian continent (Shahgedanova 2002). The constraints of regional topography and the prevailing surface winds (westerlies) result in open-air transport into the area from both the west and south. The prevailing wind vectors change from the west to southwest direction during summer and the south-southwest direction during winter.

Tree-ring sampling

Sixteen larch cross-sections (*Larix gmelinii*) were selected from several hundred tree-ring specimens originally collected for a dendroclimatic study (Naurzbaev and Vaganov 2000). These were gathered from the forest-tundra ecotone along a 36-km

Kotuy River transect between 70°53′N 102°55′ E (350 m a.s.l.) and 70°37′N 103°23′ E (160-350 m a.s.l.). The original collection sought vigorous-looking trees with full foliage with no evidence of anthropogenic wounding or fire scars. Our subsampling selected individuals with large growth rings to provide the minimum 100 mg of material per ring group for analysis. The crossdated tree rings are combined into a tree-ring chronology with four-tree replication for any given year from AD 1300 to 2000 (figure 2). The collected wood cross-sections were dried at room temperature several weeks. Small radial blocks ca. 1-cm wide by 1-cm thick were cut from the cross-sections. The rings were separated into 5-year and 10-year groups with a mass of dry wood at least 100 mg. In most cases 10-year groups were isolated, which determined decadal resolution of the resulting tree-ring records.

Analytical analysis

Chemical pre-treatment of wood and analytical measurements were done at the Limnological Institute SBRAS (Irkutsk, RU). The subsampled wood was digested in nitric acid (HNO_3) according to the methods described by Sheppard *et al* (2008). The chemical concentrations of 26 elements (Li, B, Na, Mg, Al, Si, P, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Ag, Cd, Sn, I, Ba, Pb and Bi) were measured on an Agilent 7500 quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS). We did not measure concentrations of nitrogen and sulfur because pretreatment of the wood samples involved nitrogen (HNO_3), and the carrier gas (argon) used in measurements contained small amount of sulfur. Vigorous measures for quality control and reliable element detection included use of stainless-steel scalpels for ring separation, work in a cleanroom environment with sterile chemical dishes and tubes, regular calibration checks of ICP-MS operational parameters and replicated measurements (Dahlquist and Knoll 1978, Sheppard *et al* 2008). The measurements were replicated 3 to 6 times for each sample to heighten the measuring accuracy of element detection.

For calibration of mass-spectrometer measurements, we used a multi-element standard solution “2A Standard” ([Ag], [Al], [Ba], [Ca], [Cr], [Cu], [Fe], [K], [Mg], [Mn], [Na], [Ni], [Rb], [Sr] and [Zn]= 10.08 ppb). Additionally a standard of Lake Baikal water was used (Na, Mg, Si, S, Cl, K, Ca) as described in Suturin *et al* (2003). Uncertainties of metal concentration measurements (Na, Mg, Al, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Bi) in excess of 0.1 ppb (or 0.05 ppm referenced to the mass of dry wood sample) were no more ±30% uncertainty. Measurements of other elements such as B, Si, P, Cl, Zr, Ag, Cd, Sn and I have an uncertainty slightly higher than ±30%. All the results for element concentrations were measured in ppb (μg/kg) referenced to the mass of initially dry wood sample prior to adding acid. More details on analytical methods used for determination of the tree-ring measurements of element concentrations can be found in Grachev *et al* (2013).

Statistical Analysis

Concentrations of the tree-ring elements vary significantly because of differences in their chemical properties and biochemical cycling (figure S1). Before applying statistical comparison we normalized the time series to their mean and standard deviation with the formula:

$$Z_c = \frac{c - \bar{c}}{\sigma_c},$$

where Z_c = standardized value with mean=0 and standard deviation=1; c = the measured concentration; $\bar{c}$ = mean (or average); σ_c = standard deviation. To detect differences between sets of normalized and averaged time series of 26 tree-ring elements, a cluster analysis was applied (Spath 1980), which is routinely used in tree-ring studies to segregate a common signal within a multivariate dataset (Fritts 1974, Shishov and Vaganov 2010). A hierarchical tree approach agglomerated a possible number of clusters. Optimal distance between clusters was measured with Pearson correlation via the Ward's method (Ward 1963). The amalgamation rule used in the Ward's method analyzes a relationship between group variance and minimizes the sum of squares of neighboring clusters. The K-means method defined the structure of our time series classification (MacQueen 1967).

Further examination of variance relationships retained by a clustered set of element concentrations was performed using Principal Component analysis (PCA), also commonly used for tree-ring data (LaMarche and Fritts 1971). Factor loadings of principal components were calculated with the Varimax (orthogonal) rotation method to maximize variance of loadings across a correlated assemblage of variables (Jolliffe 2002). All calculations were done in *Statistica 8.0 software* (*www.statsoft.com*).

Results

Pearson correlation analysis between monthly precipitation and temperature from the nearby Khatanga weather station (download http://meteo.ru/data_temperat_precipitation/) for the interval AD 1936-2000 and 26 element tree-ring series shows no significant correlations, confirming our assumption that the tree-ring element series is an independent environmental proxy. Both linear and non-linear interactions in variability of the normalized element tree-ring records were evaluated in two steps (table 1). First, the cluster analysis of element tree-ring variables identified four classes within which element concentrations are most interrelated through last 700 years. Number of element tree-ring series included in a cluster varies from four to ten. Second, PCA was implemented for the tree-ring variables from each cluster. This quantified a common domain of signals recorded across the elemental concentrations previously selected by clusters.

The first two clusters (cluster #1 and #2) captured the variation of concentrations of biologically essential trace elements and metals: the Fe, Zr, Cd, Sn, ^{208}Pb assemblage and the Li, B, Na, Al, Cr, Ni, Cu, Zn, Ag, I assemblage, respectively. These elements show no changes in their concentrations with time. Two other clusters (cluster #3 and #4) contain both macro- and micronutrient elements that have steadily changed their concentrations after ca. AD 1950 (table 2). The means and standard deviations of the principal components of these two clusters compared between intervals AD 1305-1900 and 1900-1995 are significantly different.

The third cluster (#3) has two principal components that explain 56% and 26% of common variance (table 1). Concentrations of ^{209}Bi, Cl and Si from the first principle component (PC1) of this cluster show no significant trend, but the second PC with P concentration shows a positive trend (table 2, figure 3 a-b). The phosphorous signal accounts for the highest loading in the second PC variance (0.8) and reveals significant P increase in tree rings formed over sixty years after ca. 1940.

Three principal components obtained from the fourth cluster (#4) demonstrate trends over the most recent 50 years of the tree-ring records. The three PCs explained 45%, 27% and 12% of common variance within the cluster #4 element set composed of

Mg, K, Ca, Mn, Rb, Sr, and Ba (table 1). The first PC of this cluster connects dominant variance between Mg and Ca records and shows a negative trend (table 2, figure 3c) suggesting depletion of these two elements. In contrast, the second and third PCs have positive trends after the 1950s and integrate signals across the Mn and Rb group and the K, Sr, and Ba group of tree-ring records, respectively (table 2, figure 3d-e). The positive trends suggest enrichment of exchangeable P, Mn and K in the soils, which have the highest factor loadings in the groups. In contrast, the negative trend probably is consistent with protracted depletion of exchangeable Ca and Mg from the soil.

The elemental concentration changes through time are large and statistically significant. The wood chemistry indicates a ten-fold and a three-fold increase in P and K concentrations, respectively, and a three-fold reduction in Ca and Mg concentrations (figure S1). Notably, the timing of the nutrient shift correlates between various elements and the peak concentrations appear during the last few decades of the records (1970-2000). This timing would seem consistent with observations related to higher cation mobility in sapwood – living xylem tissue where water conductivity takes place (Helmisaari and Siltala 1989, Smith *et al* 2009). However, the observed trends extend beyond the 10-15 year sapwood segment. Moreover, the tree-ring records have two segments with sapwood, i.e., ca. AD 1875-1900 and 1975-2000, the first of which is in the 19th century (figure 2) and does not show the concentration change. Although some elements such as P and K accumulate in sapwood through function of protoplasts (Smith and Shortle 1994), we do not attribute the 20th century increase to this effect, because we do not see the same trend in the 19th century sapwood for this species. Thus, the relationship of element concentrations in the last few decades, which were detected with the cluster and PC analysis, is capturing recent real dynamic changes, and it is not a heartwood-sapwood artifact. We believe that the chemical signal of low Ca-Mg versus high P-Mn-K in the larch tree rings relates and mirrors the availability of these exchangeable minerals in soil. However, more than one environmental factor may be prompting the long-term changes in soil and larch chemistry after ca. 1950.

Discussion

On one hand, the overall bulk quantity of elements in soils, contributed from various sources and processes can influence the concentration of elements in tree rings. Baseline concentrations of many elements available to plants in soils derive from weathering of the local bedrock. However, element concentrations can sometimes be greatly enhanced by airborne transport of natural and anthropogenic atmospheric inputs (Nriagu 1989, Law and Stohl 2007). There are more than a few varied forest locations where evidence of changing soil chemical composition and soil pH correlated with tree-ring element concentrations and pollution in the late 20th century (e.g., Johnson *et al* 2008, Chen *et al* 2010).

On the other hand, the elemental composition of tree rings is further determined by processes affecting availability and uptake of elements. The availability of nutrients to trees is a function of total concentration in soil solution, which will be influenced by both soil pH and soil mineral exchangeable pool (Berthrong *et al* 2009). The input of H^+ during acid deposition can alter the chemistry of soils by altering weathering, cation exchange, and mobility and availability of ions in the soil (e.g., Lawrence *et al* 1995, DeHayes *et al* 1999). Excess acidity may adversely affect plant nutrition if it contributes to uptake of excess toxic metals or to deficiency of essential nutrient cations such as calcium and potassium (Hirschi 2004, Lautner and Fromm 2009). Soil acidification (low soil pH) can decrease exchangeable Ca as acid-liberated Al cations occupy cation-exchange sites on clays and displace the atmospheric-origin base cations (e.g., Ca, K, Mg, Mn) from the soil exchange complex, contributing to their leaching out of the soil column (Warby *et al* 2009). The observed negative trend in the wood Ca and Mg concentrations at the tree-ring site may be signaling these soil acidification effects on base-cation loss. The observed increase of xylem Mn concentration can indicate ongoing soil acidification as well. Reconstructions of soil pH with tree rings suggest that xylem concentration of Mn correlates negatively with soil pH (Kogelmann and Sharpe 2006), so the acidity may be mobilizing Mn that might otherwise by locked up in mineral oxides. Like Mn, Ba concentration in trees also has a negative relationship with soil pH (Barber 1984) and is used to monitor sulfur deposition into soils (Guyette and Cutter 1994). The largest local source of sulfur deposition, the Norilsk smelting complex, is about 500 km west of the tree-ring site. The area of larch dieback impacted by the Norilsk pollution has been increasing for the last 50 years and presently reached ca. 85 km from Norilsk (Ivshin and Shiyatov 1996, Voronin and Ziganshin 1999, Kirdyanov et al 2014). There is no direct evidence of detrimental effects of the Norilsk pollution on the forest (Golubeva *et al* 2013) although modeled trajectories indicate active delivery of airborne sulfur to the site at times (figure S2). Historically, the smelting complex started operating since 1950s, the metal production tripled between the 1960s and 1980s. In 1983 the emissions of sulfur dioxide and mineral dust from the Norilsk metal production complex reached a maximum of 2483 thousand tons and 73.7 thousand tons, respectively (Doklad 2010). During the more recent 1990-1999 decade, Norilsk Nickel production released an average of 2066.5 thousand tons of sulfur dioxide and 25.5 thousand tons of particles into the air each year (Doklad 2010). Thus, the modification of tree nutrient cycling at the studied site may signals the soil pH variation and may link to consequences of both global and local sources of Arctic acidification after 1950.

However, the elevation of xylem K, P, Rb and Sr concentrations in the tree-ring records is puzzling. The K^+ activity in soils with low pH should be reduced by availability of Al cations, similar to Ca and Mg. Nor should high P be expected in most arctic soils with low fertility because of low mobility and availability of this element to plants (Burton *et al* 2002). It therefore seems likely that the interrelated concentration of these elements is driven by a mechanism apart from soil acidification. Acquisition of phosphorous by trees mainly occurs through diffusion (Barber 1984) and changes in larch root morphology and absorption efficiency would be the prime suspect for the upsurge. Root-induced increase of soluble P, K and Rb in alkaline or slightly acid soils has been reported as function of both decreasing soil pH (acidification) and the warming air temperature (Hinsinger 2001, Burton *et al* 2002, Ruess *et al* 2006). Considering the fact that climate of the Taymyr Peninsula has been warming steadily since 1880 (figure 4) several factors may contribute to the root-induced mineral modification, including ongoing thaw of permafrost soils and deepening of its active layer (Fedotov *et al* 2012). Permafrost thawing contributes to release of old carbon accumulated over thousands of years and changes the net carbon exchange in the Arctic and boreal forest (Hobbie *et al* 2002, Schuur *et al* 2009). Obviously, this alters the exchangeable pools of soluble minerals in soils. Even so the rate of release of base cations from the permafrost thaw is controversial (Keuper *et al* 2012), the thawing and associated nutrient release are coupled with tree nutrient uptake (Hobbie et al 2002, Herzschuh *et al* 2013). To date many studies report significant impact of both drought and moisture excess on the soil exchangeable cation pool throughout the soil profile in the Arctic caused by climate warming (e.g., Kreuzwieser and Gessler 2010). There could be additional causes of the observed trends in the elemental concentrations of our tree-ring records.

The estimated signature of multidecadal changes in the cycling of major tree nutrients Ca, Mg, K, P and Mn) is important to monitoring of health and productivity of the Siberian forests. The signature suggests nutrient stress on the larch that can be directly linked to reducing resistance of trees to environmental stress, mainly because of Ca depletion. The role of calcium, phosphorous and potassium for wood formation is well-recognized and a direct relationship between the cambial concentrations of these nutrients and uptake from soils is confirmed by many plant physiology studies (e.g. McClenahen *et al* 1989, Barrelet *et al* 2006, Fromm 2010). Calcium particularly plays a role in regulating physiological and structural processes related to tree growth and its response to environmental stress (Lauther and Fromm 2010). Long-term calcium decrease in the tree nutrient points to weakening tree vigor and stand-level water stress (Sudachkova *et al* 2002). It has even been reported that larch regeneration is common and no visible forest decline was found in the Taymyr, except within a 85-km radius of the Norilsk smelting complex (Ivshin and Shiyatov 1996, Voronin and Ziganshin 1999, Zhulidov *et al* 2011, Kirdyanov *et al* 2014). Calcium depletion over a long period can negatively impact xylem development, particularly lignification of secondary cell wall and length of tracheid (Hirschuk 2004), which compromises integrity of wood against decay resistance and other environmental stressors (Cronan and Grigal 1995). This pathway affects not only mechanical properties of the timber but most importantly reduces cambial activity at the beginning of the growing season (Shortle *et al* 1997). The maximum latewood density of tree-ring records of the same area (Kotuy River catchment) shows a steady decline after AD 1950 (author A. Kirdyanov, personal observation). It is possible the recent density reduction was caused by the altered chemistry of the trees. The observed wood chemistry change may also bring particular insights to the divergence problem (Briffa *et al* 1998) in dendroclimatology (disagreement between tree-ring growth and summer temperature observations in boreal forests after 1950), but it needs further testing.

In conclusion, the 700-year tree-ring records of elemental concentrations from the Taimyr Peninsula indicate steep changes in tree-ring concentrations of P, Ca, Mg, Mn, K, Rb, Sr and Ba after ca. AD 1950. The negative trend in tree uptake of soluble Ca^+-Mg^+ and the positive trends in soluble P, and Mn+-Rb+ and K^+-Sr^+-Ba^+ elements suggest ecologically important changes in biogeochemical cycling of major nutrients available to the trees, which could be at least identified through the elemental composition of tree rings. The signal of low Ca-Mg and high P-Mn-K exposes a diagnostic relationship between concentrations of these elements, and supports the value of tree rings in addressing how the concentrations of nutrient elements in soils have changed with time. Although we have no soil chemistry measurements, the long-term trends in our data may be a consequence of pH fluctuations of permafrost soil with increasing soil acidity at decadal resolution in this region and interactions of permafrost thawing with forest and thaw lakes. Our tree-ring records of wood chemistry are linked to changes in atmospheric chemistry driven by both climate changes and Arctic pollution. Because of the extremely high magnitude of the assessed signal and the timing of changes in the elemental concentrations of tree rings, we think that changes in the wood and soil chemistry were predominantly triggered by anthropogenic factors.

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Table 1.

Results of cluster and principal component (PC) analysis of 26 tree-ring element chronologies for the period 1300-2000 (701 yrs).

PC#	Eigenvalue	Total Variance %	Cumulative eigenvalue	Cumulative variance, %
Cluster #1: Fe, Zr, Cd, Sn, ^{208}Pb				
1	1.43	28.54	1.427	28.54
2	1.14	22.85	2.57	51.39
3	0.96	19.19	3.53	70.59
4	0.88	17.57	4.41	88.16
Cluster #2: Li, B, Na, Al, Cr, Ni, Cu, Zn, Ag, I				
1	3.87	38.74	3.87	38.74
2	1.82	18.22	5.69	56.96
3	1.39	13.96	7.09	70.92
4	0.84	8.35	7.93	79.26
Cluster #3: Si, P, Cl, ^{209}Bi				
1	2.23	55.69	2.23	55.69
2	1.03	25.65	3.25	81.34
Cluster #4: Mg, K, Ca, Mn, Rb,Sr, Ba				
1	3.17	45.25	3.17	45.25
2	1.89	27.0	5.06	72.25
3	0.83	11.89	5.89	84.14

Table 2.

Factor loadings for each PC from cluster #3 and #4 with detected long-term trend after ca. AD 1950. Each PC denotes a sign of the fitted trends (distance-weighted least squares) at 95% confidence interval tested with one-way ANOVA modeling. Bold font marks significant coefficients of correlation.

Elements Cluster 3	**PC1**	**PC 2**	**Elements Cluster 4**	**PC 1**	**PC 2**	**PC3**
	No Trend	**Positive trend**		**Negative Trend**	**Positive Trend**	**Positive Trend**
Si	**0.32**	0.27	Mg	**0.41**	0.05	-0.10
P	-0.16	**0.80**	K	-0.20	0.08	**0.62**
Cl	**0.40**	0.07	Ca	**0.51**	0.07	-0.29
^{209}Bi	**0.51**	-0.39	Mn	0.19	**0.55**	-0.33
			Rb	-0.14	**0.45**	0.15
			Sr	0.09	-0.14	**0.42**
			Ba	0.07	-0.22	**0.35**

Figure Legends

Figure 1. Remote location of the tree-ring site (triangle) in pristine forest-tundra ecotone of Taymyr Peninsula and the Norilsk Nickel mining & smelting site (star). Lower right insert is a world map denoting the study location (Downloaded from demis.nl).

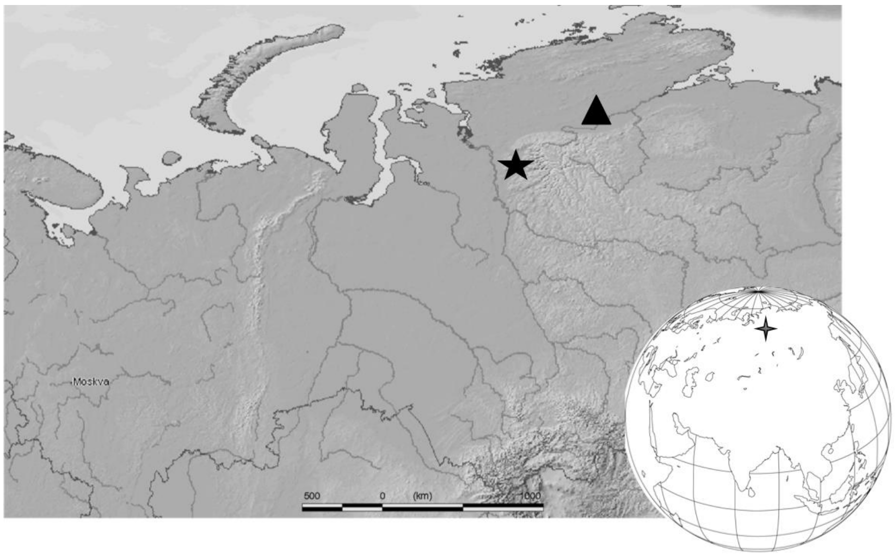


Figure 2. Segment length of tree-ring series from this study. Line represents a tree specimen. Shaded area shows the tree sapwood (about 15 outer rings with functioning vascular tissue) in two segment groups around the 1890s and 1990s. Notice that the sapwood ca.1890 is outside of the discussed trends in the tree-ring element concentrations. This proves that the trends not being the result of the mobility of elements within the sapwood and/or between the sapwood and the heartwood.

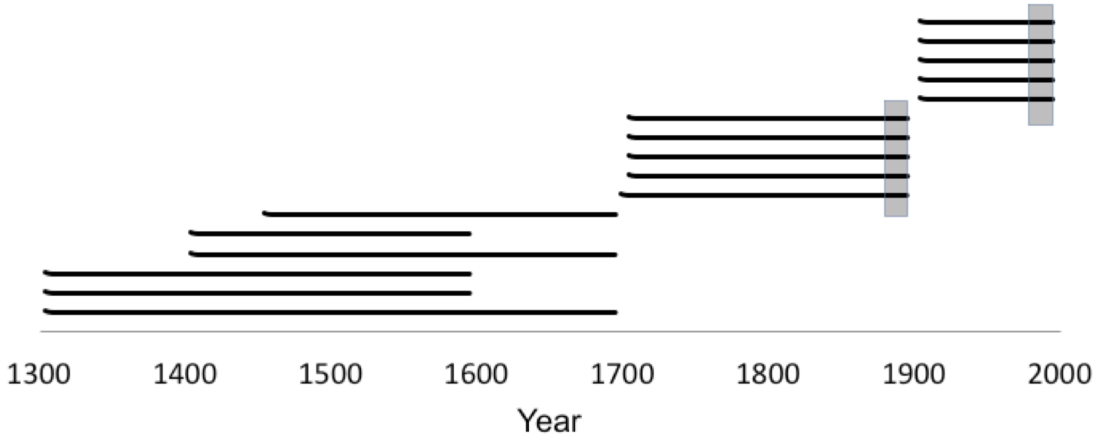


Figure 3. Long-term variations of element concentrations in the tree rings from AD 1300 to 2000 (700 years) contributing to the principal components of cluster #3 ((a) PC1, (b)

PC2)) and cluster #4 ((c) PC1, (d) PC2, (e) PC3) where the trends are observed. Thin lines represent normalized element concentrations of the tree specimens. The trend line (thick line) after 1900 is estimated with distance-weighted least squares fitted fitting described by McLain (1974). See Table 1 for cluster's statistics and Table 2 for factor loadings of PCs from cluster #3 and #4. Elements of major contribution to the PC variance are denoted on the left.

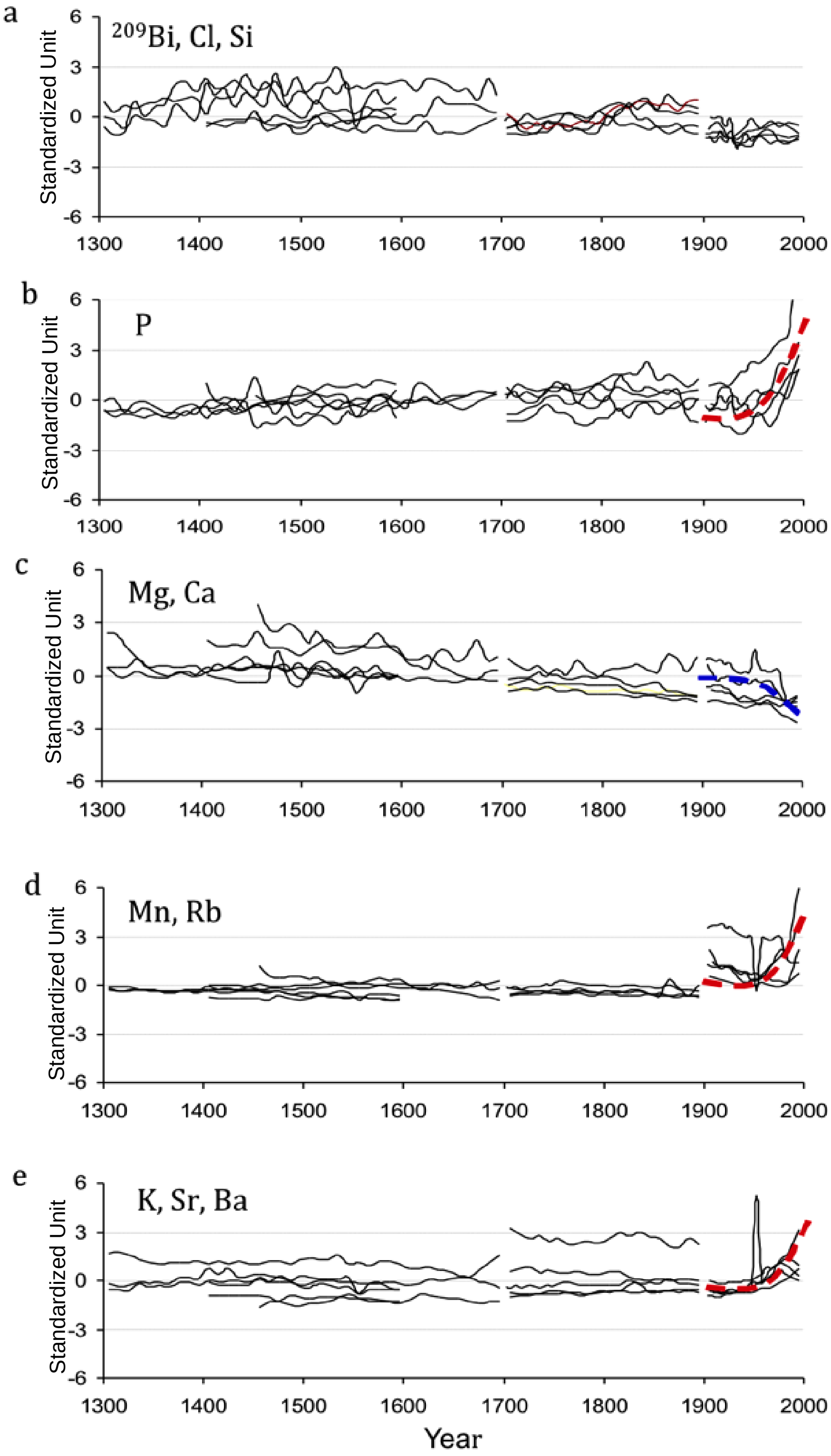
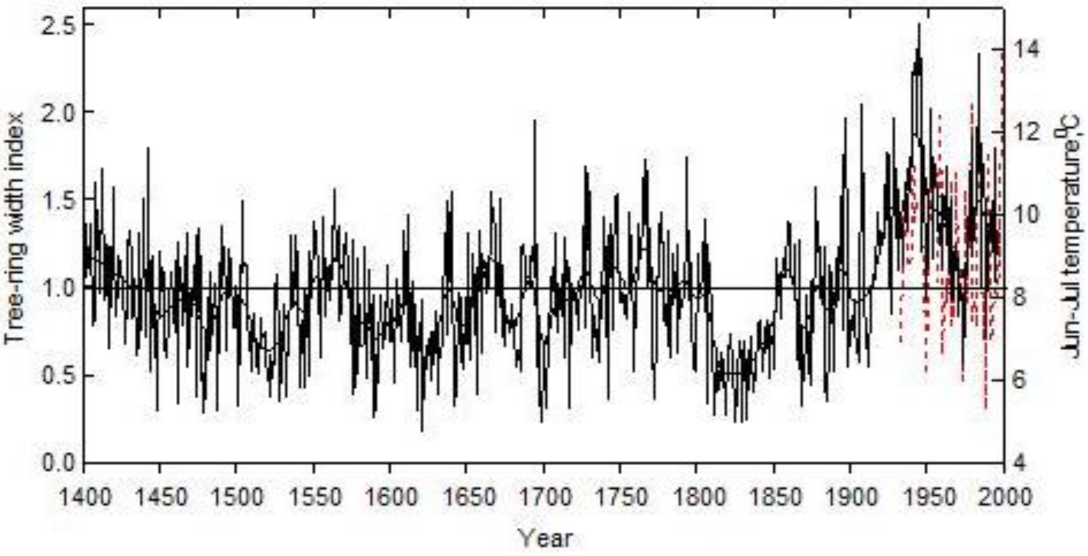

a
^{209}Bi, Cl, Si
b
P
c
Mg, Ca
d
Mn, Rb
e
K, Sr, Ba
Standardized Unit
6
3
0
-3
-6
1300
1400
1500
1600
1700
1800
1900
2000
Year

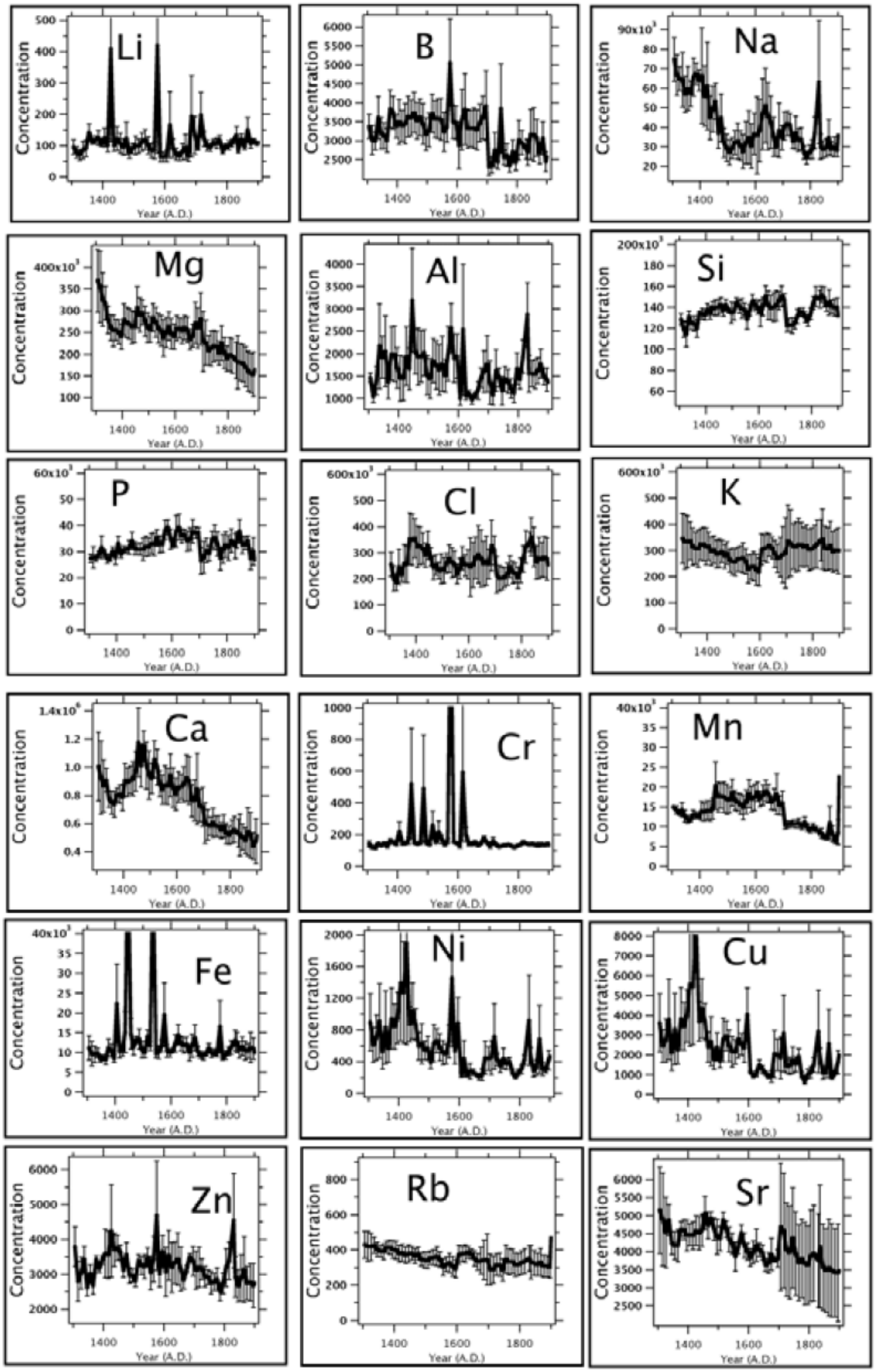
Figure 4. Tree-ring width chronology of larch from Taymyr (Briffa et al. 2008) that includes the tree specimens used in this study. Variability of the tree-ring indices corresponds to June and July temperature. Red dotted line shows mean June –July temperature observations from Khatanga weather station for interval 1934-2000. Thick black line is 20-year low-pass filter curve of tree-ring indices. The plot shows the reduced tree-ring width growth during the Little Ice Age and the increased growth since the mid 1850 induced by the Modern Era warming.



Supplementary Data

Figure S1. The average values of raw element concentration measurements for the period from 1300 to 2000 (701 yrs). Error bars show two standard deviations of the mean values. The results for element concentrations are shown in ppb (µg/kg) referenced to the mass of initially dry wood sample prior to adding acid. The chemical concentrations of Li, B, Na, Mg, Al, Si, P, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Ag, Cd, Sn, I, Ba, Pb and Bi were measured on an Agilent 7500 quadrupole Inductively

Coupled Plasma Mass Spectrometer (ICP-MS). Detailed description of analytical methods used for the tree-ring measurements of element concentrations has been published in Grachev et al. (2013). Notice, we used normalized indices of tree-ring element concentrations in statistical calculations and interpretations.



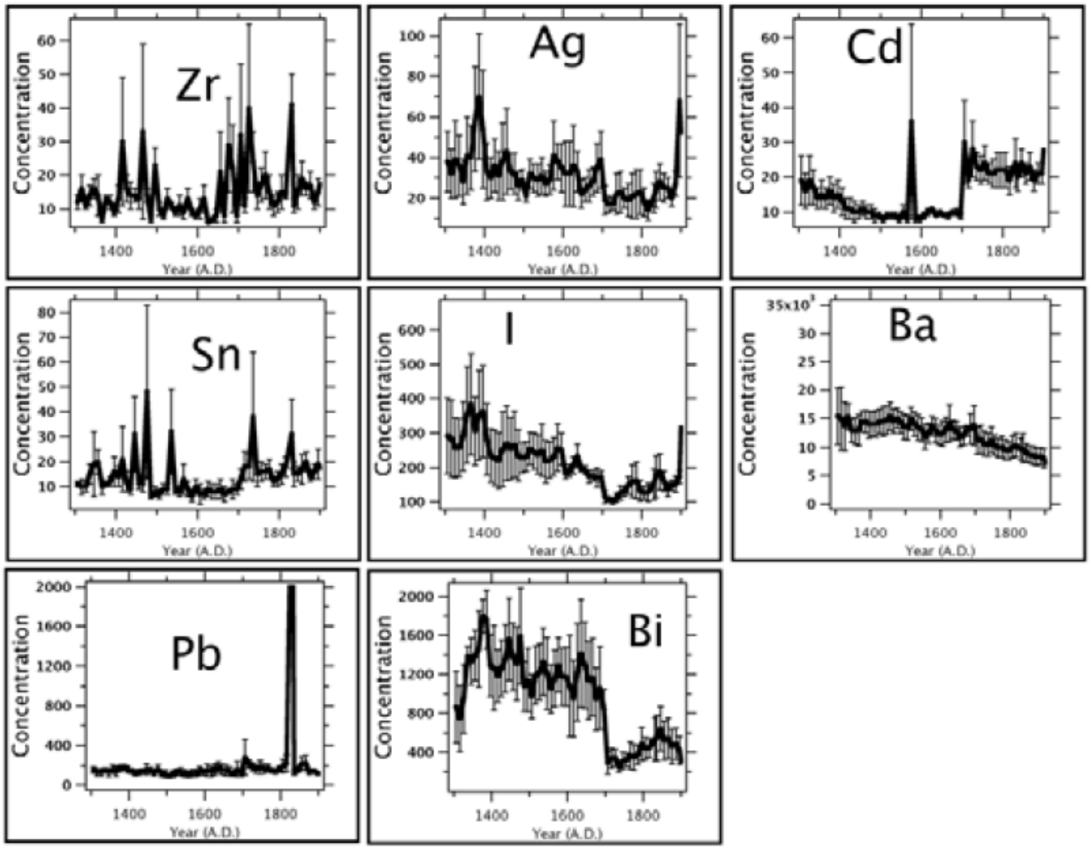
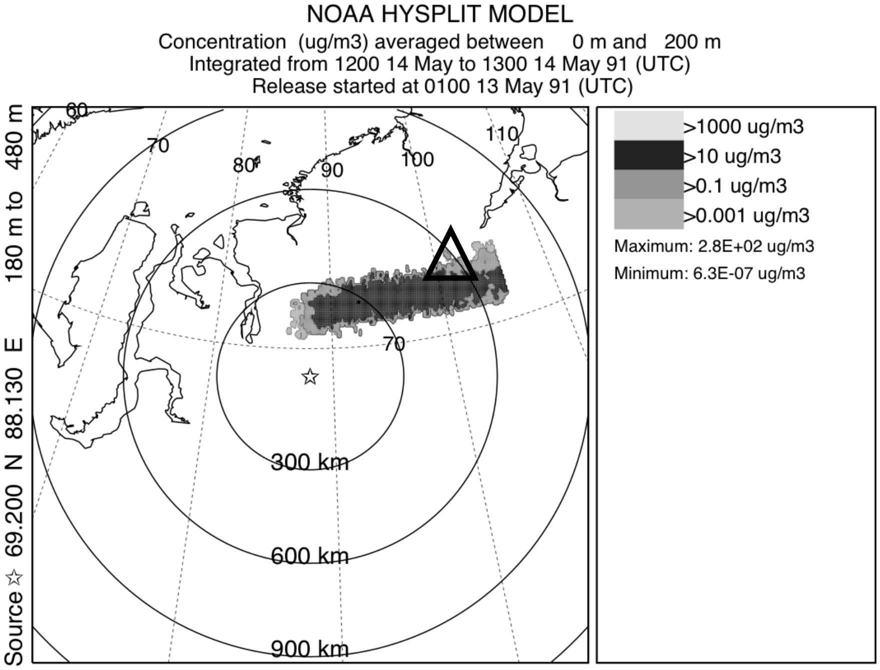
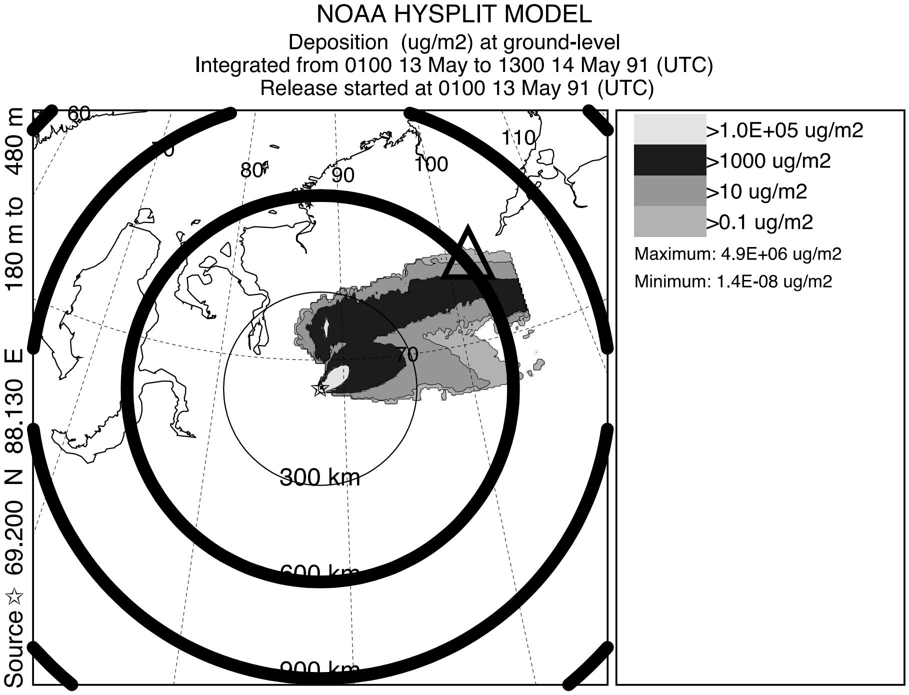


Figure S2. Simulation results of SO_2 transport from the Norilsk Nickel complex (star) into the studied area (triangle) using Dispersal HYSPLIT 4.8 model (Draxler and Rolph 2013). Downloaded from http://ready.arl.noaa.gov/HYSPLIT.php Example of concentration (a) and deposition (b) of daily sulfur dioxide emission along a 48-hour dispersal pathway as calculated for May 13, 1991. Annual value of SO_2 emission in 1991 was 2397 thousand tons, which is ca. 6 million kg day^{-1} on average (Doklad 2010). The tallest smelting smokestack in 1991was 300 m. Norilsk elevation is about 180 m a.s.l. Note that the background concentration of SO_2 in the Russian Arctic is on average 1 μg m^{-3} (AMAP 2006). The modeled daily concentration of sulfur suggests its 10-fold enrichment over the tree sampling region compared to the background concentration in the Russian Arctic. The modeling indicates a 12-hour transport of emissions to the tree-ring site, on average.

a)


NOAA HYSPLIT MODEL
Concentration (ug/m3) averaged between 0 m and 200 m
Integrated from 1200 14 May to 1300 14 May 91 (UTC)
Release started at 0100 13 May 91 (UTC)
>1000 ug/m3
>10 ug/m3
>0.1 ug/m3
>0.001 ug/m3
Maximum: 2.8E+02 ug/m3
Minimum: 6.3E-07 ug/m3
60
70
80
90
100
110
70
300 km
600 km
900 km
Source ☆ 69.200 N 88.130 E 180 m to 480 m

b)


NOAA HYSPLIT MODEL
Deposition (ug/m2) at ground-level
Integrated from 0100 13 May to 1300 14 May 91 (UTC)
Release started at 0100 13 May 91 (UTC)
>1.0E+05 ug/m2
>1000 ug/m2
>10 ug/m2
>0.1 ug/m2
Maximum: 4.9E+06 ug/m2
Minimum: 1.4E-08 ug/m2
60
70
80
90
100
110
70
300 km
600 km
900 km
Source ☆ 69.200 N 88.130 E 180 m to 480 m