

TRENDS IN ELEMENTAL CONCENTRATIONS OF TREE RINGS FROM THE SIBERIAN ARCTIC

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ABSTRACT

The biogeochemistry and ecology of the Arctic environment have been heavily impacted by anthropogenic pollution and climate change. We used ICP-MS to measure concentrations of 26 elements in the AD 1300–2000 tree rings of larch from the Taymyr Peninsula in northern Siberia for studying the interaction between environmental change and wood chemistry. We applied a two-stage data reduction technique to identify trends in the noisy measurement data. Statistical assessment of variance of normalized time series reveals pronounced depletion of xylem Ca, Mg, Cl, Bi and Si concentrations and enrichment of P, K, Mn, Rb, Sr and Ba concentrations after *ca.* AD 1900. The trends are unprecedented in the 700-year records, but multiple mechanisms may be at work and difficult to attribute with certainty. The declining xylem Ca and Mg may be a response to soil acidification from air pollution, whereas increasing P, K, and Mn concentrations may signal changes in root efficiency and excess water-soluble minerals liberated by the permafrost thaw. The changes seem consistent with mounting stress on Arctic vegetation. This study supports the potential of tree rings for monitoring past and ongoing changes in biogeochemistry of Arctic ecosystems related to pollution and permafrost thaw.

Keywords: wood chemistry, dendrochemistry, *Larix decidua*, biogeochemical cycling, soil acidification, permafrost thawing, Arctic pollution, Norilsk Nickel smelting complex, ICP-MS.

INTRODUCTION

The landscape of the Siberian Arctic has been roiling in a cauldron of environmental change over the course of the 20th Century. Tree cover has increased as northern tree limit has expanded both northward and upward (Kharuk *et al.* 2006; Kirilyanov *et al.* 2012; Golubeva *et al.* 2013), but there have been concomitant adverse impacts on forest health and productivity from pollution loading (Nilsson *et al.* 1998; Kirilyanov *et al.* 2014) and climate change (Lloyd *et al.* 2011). Furthermore, permafrost thawing has influenced biogeochemical cycling with various environmental feedbacks

(Shur and Jorgenson 2007; Yarie and Van Cleve 2010; Keuper *et al.* 2012). Plant moisture stress from the deepening of the active melting layer of permafrost soils has contributed to unusual decline in forest growth in the high north (Barber *et al.* 2000; Girardin *et al.* 2014), with additional stress from acidification of the environment and soil (Shortle *et al.* 1997; Nilsson *et al.* 1998; Shur and Jorgenson 2007; Rice and Herman 2011). The global acceleration of nitrification, anthropogenic acidification, and deposition of contaminants has also greatly altered biogeochemistry of Arctic ecosystems (Galloway *et al.* 2003; Smith *et al.* 2011). Acid compounds induced by air pollution over the Arctic observed since the 1970s have been

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attributed to industrial pollution originating in mid-latitudes (AMAP Assessment 2006), but pollution over the Arctic has been present even earlier (Law and Stohl 2007).

The effect of these environmental changes cascades through plant-soil interactions. 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, *e.g.* SO_4^- and NO_3^- , affects tree uptake of important macronutrients, *e.g.* Ca, P, Mn and K (Agren *et al.* 2012). Acidity effects extend to leaching and transport of base cations Ca^{2+} , K^+ and Mg^{2+} within the soil profile and their depletion from the exchangeable pool available for tree uptake (Hogberg *et al.* 2006). Consequently, long-term (decadal) environmental alterations in Siberian boreal forests can influence exchange of elements between soil and trees.

Given these likely changes in the Siberian Arctic chemical environment, one approach to long retrospective monitoring of biogeochemistry changes is through elemental analysis of tree rings (*e.g.* Hall *et al.* 1975; Hughes *et al.* 1980; Baes and McLaughlin 1984; Guyette *et al.* 1992; Padilla and Anderson 2002; Kuang *et al.* 2008). Concentrations of elements in tree rings have been applied to reconstructing soil pH and atmospheric pollution, and in monitoring sulfur deposition and metal contamination (Cutter and Guyette 1993; Chen *et al.* 2010; Doucet *et al.* 2012), and sometimes molar ratios of elements (*e.g.* Ca/Mg, Mg/Mn or Ca/Al) have been found to be more diagnostic for environmental effects than xylem elemental concentrations alone (DeWalle *et al.* 1999; Kuang *et al.* 2008).

Our project endeavored to produce long, highly-resolved and well-replicated records of concentrations of a broad suite of chemical elements in tree rings from the Taymyr Peninsula of Russia. These records not only provide early baseline information on chemical composition hundreds of years ago, but also serve as a bellwether for increasing impacts of the recent human-induced changes of the last century. This paper statistically analyzes the variance of the chemical record derived from larch tree rings extending back 700 years, far exceeding the length described in previous studies (Padilla

and Anderson 2002), and the results of Principal Component analysis form the basis for considering the contributions of various possible environmental influences.

MATERIALS AND METHODS

Site Settings and Tree Collection

Tree rings of larch (*Larix gmelinii* Rupr.) collected on the Kotuy River catchment of the Taymyr Peninsula were used for this study (Figure 1). Larch is an optimal choice for dendrochemistry in the region, consistent with the common ideals of a long-lived conifer tree species, wide range of geographical distribution, distinct heartwood, a small number of rings in sapwood, and low heartwood moisture content (Cutter and Guyette 1993). The site is a 36-km transect along the Kotuy River terraces between *ca.* 70°53'N 102°55' E (350 m a.s.l.) and 70°37'N 103°23' E (160–350 m a.s.l.). Wood cross-sections from vigorous-looking trees with full foliage and no evidence of anthropogenic injury or fire scars were originally collected for a dendroclimatic study (Naurzbaev and Vaganov 2000). We sub-sampled cross-sections of 16 trees from the collection of several hundred specimens gathered at the site.

The study area is located at the northernmost limit of tree growth in Eurasia and the world. The landscape encompasses sparse vegetation (less than 30% tree coverage) growing on polygonal tundra soils with permafrost and thermokarst topography. The constraints of regional topography and the prevailing surface winds (westerlies) result in open-air transport into the area from the west, north and south. The seasonal intensification of the Siberian High and the Siberian Low as well as the Arctic front play a key role in the atmospheric circulation of this region as for the entire Eurasian continent. The site is *ca.* 400 km northeast of the edge of an 85-km zone of direct contamination impact from the Norilsk Nickel smelting complex (Figure 1), the largest source of heavy metals and sulfate-S pollutants in the world since the 1940s (EPR 2010).

Tree-Ring Sampling

Our sampling selected individual wood specimens with large growth rings to provide sufficient

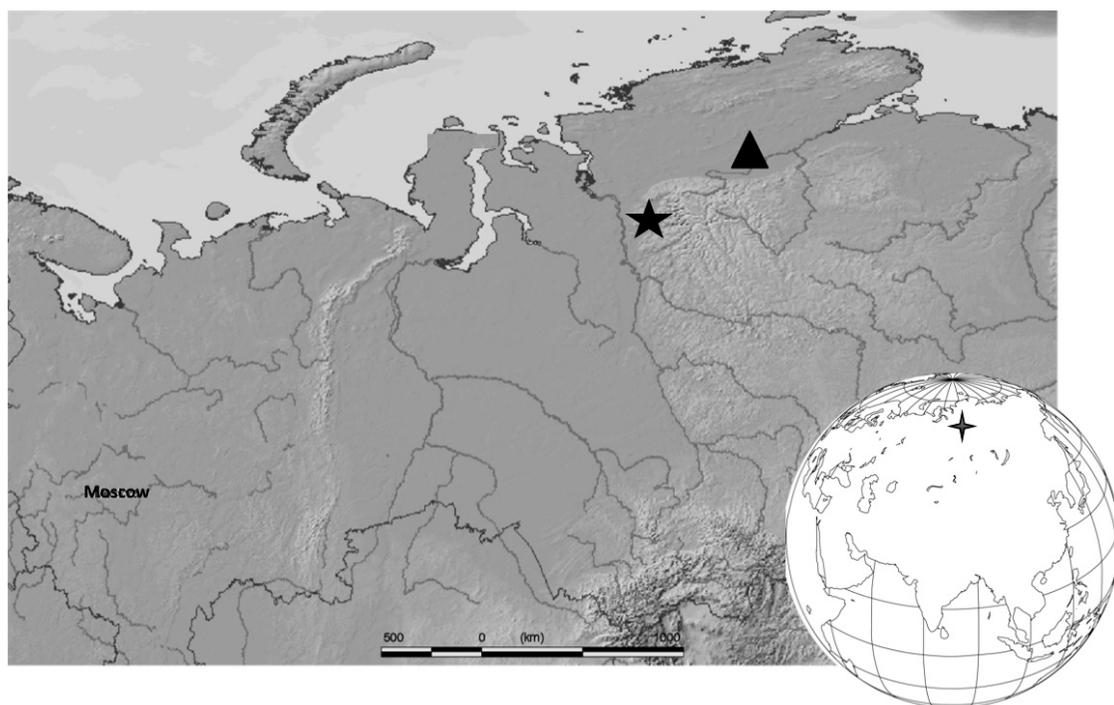


Figure 1. Location of the tree-ring site (triangle) in Siberian Arctic and the Norilsk Nickel mining and smelting complex (star). World map at lower right insert denotes the study region.

material per ring group for analysis. The age of sub-sampled tree rings was defined with crossdating against a well-replicated Taymyr tree-ring width chronology (Naurzbaev and Vaganov 2000). Small radial blocks *ca.* 1-cm wide by 1-cm thick were cut from 16 tree cross-sections, which provided replication of 5–6 trees over the outer 450 years of the 700-yr record and at least 3 trees for the remaining early years (Supplementary Figure S1A). The rings were separated into 5-year or 10-year groups with a mass of dry wood at least 100 mg (Figure S1B). Because of small mass of ring growth, we mostly isolated 10-year groups, which determined the decadal resolution of the resulting tree-ring records.

Analytical Analysis

Concentrations of 26 chemical elements were measured for each sub-sampled ring-group (Figure S1B). Chemical pre-treatment of wood and analytical measurements were done at the Limnological Institute SBRAS (Irkutsk, Russia). The sub-sampled wood was digested in nitric acid (HNO_3)

(Sheppard *et al.* 2008). The 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). Concentrations of nitrogen and sulfur were not measured because pretreatment of the wood samples utilizes nitrogen (HNO_3), and the carrier gas (argon) contains small amount of sulfur. Rigorous 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 dishware, regular calibration checks of ICP-MS operational parameters and replication of measurements (Dahlquist and Knoll 1978; Sheppard *et al.* 2008). To enhance the measuring accuracy of trace element detection, we measured each wood sub-sample 3 to 6 times.

ICP-MS measurements were calibrated with 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). A standard of Lake Baikal water was used for

other elements (Na, Mg, Si, S, Cl, K, Ca) (Suturin *et al.* 2008). We present here concentration of elements in ppb ($\mu\text{g}/\text{kg}$) with respect to the mass of dry wood sample prior to adding acid. Analytic uncertainty 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 less $\pm 30\%$, while analytic uncertainty of other elements (B, Si, P, Cl, Zr, Ag, Cd, Sn and I) was slightly higher than $\pm 30\%$. See more details on analytical methods applied in this study in Grachev *et al.* (2013).

Statistical Analysis of Time Series

To constrain high variance and differences of concentration measurements associated with chemical properties and biochemical cycling of studied elements, we normalized tree-ring time series to their mean and standard deviation (Z-scores) with the formula:

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

where Z_c = standardized value whose mean = 0 and standard deviation = 1; c = the measured concentration; \bar{c} = mean; σ_c = standard deviation. Z-scores were calculated for each series of element measurements per sampled tree then averaged into a tree-ring chronology of an element concentration (Figure S1C). Each tree-ring chronology (henceforth designated “element time series”) includes 3-5 trees for any given year from 1300 to 2000 (Figure S1A).

To detect common variance among time series of measured element concentrations, we applied a two-stage data reduction process of cluster analysis followed by principal components analysis (PCA). These data reduction processes are routinely applied to data mining of multivariate tree-ring data and climate series (*e.g.* LaMarche and Fritts 1971; Shishov and Vaganov 2010). We believe this is the first application of these techniques to dendrochemical series. First, we ran cluster analysis (Späth 1980) that agglomerated an optimum number of most-interrelated groups for 26 element time series (Figure S1D). The optimal distance between clusters was measured with Pearson correlation using Ward’s method (Ward 1963) that minimizes the sum of

squares of neighboring clusters. Second, we examined the clustered set of element time series with Principal Component analysis (Figure S1E). Factor loadings of principal components (PCs) were calculated with the Varimax (orthogonal) rotation method to maximize variance of loadings across a correlated assemblage of variables (Jolliffe 2002).

RESULTS

Trends in the Variance of Element Time Series

The raw decadal/pentadal concentration measurement series are quite variable across the range of elements analyzed (Figure S2; Vaganov *et al.* 2013). For example, some elements (*e.g.* Ca and Mg) show a long-term decline, others are generally low in concentration punctuated by abrupt high peaks (*e.g.* Fe and Cr), and yet others increase towards the end of their records (*e.g.* K and Rb). The mean of most measurement time series have a small standard error indicating a strong coherence among the individual-tree element records.

There was no consistent change in concentration coincident with the timing of the splices to form the 700-yr series. Some elements (*e.g.* Ba) showed no change coincident with the splices, while other elements did so at AD 1700 (Bi, Cd) and AD 1900 (Rb, Mn). Elements with abrupt changes coincident with the AD 1700 and 1900 splices did not show a similar change coincident with the AD 1600 splices.

The diagnostic statistical approach we used effectively classifies linear and non-linear interactions in the variance of the normalized element time series. The cluster analysis identified four classes within which element concentrations are most interrelated through last 700 years (Table 1). The number of element time series included in a single cluster varies from four to ten. The PCA implemented for the element time series of a single cluster quantifies a common domain of signals recorded across the elemental concentrations previously selected by clusters. The first two clusters (cluster #1 and #2) captured the variance patterns in concentrations of various metals and several biologically essential trace elements: the Fe-Zr-Cd-Sn-Pb assemblage and the Li-B-Na-Al-Cr-Ni-Cu-Zn-Ag-I assemblage, respectively. These assemblages show no significant changes of element concentrations

Table 1. Results of cluster and principal component (PC) analysis of 26 element time series for the period 1300–2000.

PC#	Eigenvalue	Total Variance %	Cumulative Eigenvalue	Cumulative Variance, %
Cluster #1: Fe, Zr, Cd, Sn, Pb				
1	1.43	28.54	1.43	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, 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

with time. The two other clusters (cluster #3 and #4) captured time-series of macro- and micronutrient elements whose concentrations have been considerably changing after *ca.* 1900.

The two principal components derived from the element time series assembled in the third cluster (#3, Si-P-Cl-Bi) share 56% and 26% of common variance (Table 1). The first principle component with significant loadings (PC1) pools Bi, Cl and Si series together and shows an accelerated decline after *ca.* 1900 (Table 2, Figure 2a). The second PC (PC2) presents a positive trend after *ca.* 1940 expressing the signal mainly associated with the loading of the phosphorous concentration variable (Table 2, Figure 2b).

Table 2. Factor loadings for PCs of cluster #3 and #4 with detected trend after *ca.* 1900. Each PC denotes a sign of the fitted trends shown in Figure 2. Bold font denotes significant correlation coefficients.

Cluster #3 Elements	PC1 Negative Trend	PC 2 Positive Trend	Cluster #4 Elements	PC 1 Negative Trend	PC 2 Positive Trend	PC3 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
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

The three PCs of the fourth cluster (#4, Mg-K-Ca-Mn-Rb-Sr-Ba) explain 45%, 27% and 12% of common variance in the contributing series (Table 1). The PC1 of this cluster links dominant variance between the Mg and Ca series and shows a negative trend over the last 200 years (Table 2, Figure 2c). In contrast, PC2 and the PC3 present positive trends after *ca.* 1800 and 1900, respectively, and their factor loadings are highest for Mn and Rb concentrations and for K, Sr, and Ba concentrations, respectively (Table 2, Figure 2d–e).

Significance of Detected Trends

ANOVA modeling applied to the PC variables for two separate intervals, 1305–1900 and 1900–1995, confirms statistically high significance of changes in the variance of element concentrations detected by the cluster analysis and PCA. A few element concentrations even follow the trends in the raw measurements.

The timing of the concentration rise and enrichment trends correlates between some of the elements. A sharp peak in the concentrations of several PCs emerges during the second half of the 20th Century (1950–2000), the last 50 years of the element time series. Evidence suggests these end-of-record shifts cannot be explained by higher cation mobility in sapwood (living outer xylem tissue where upward water conduction in the tree trunk takes place), as has been observed in many studies with shorter element time series (Helmisaari and Siltala 1989; Smith *et al.* 2009). For example, although some elements, *e.g.* P and K, have a propensity to accumulate in sapwood through the function of protoplasts (Smith and Shortle 1994),

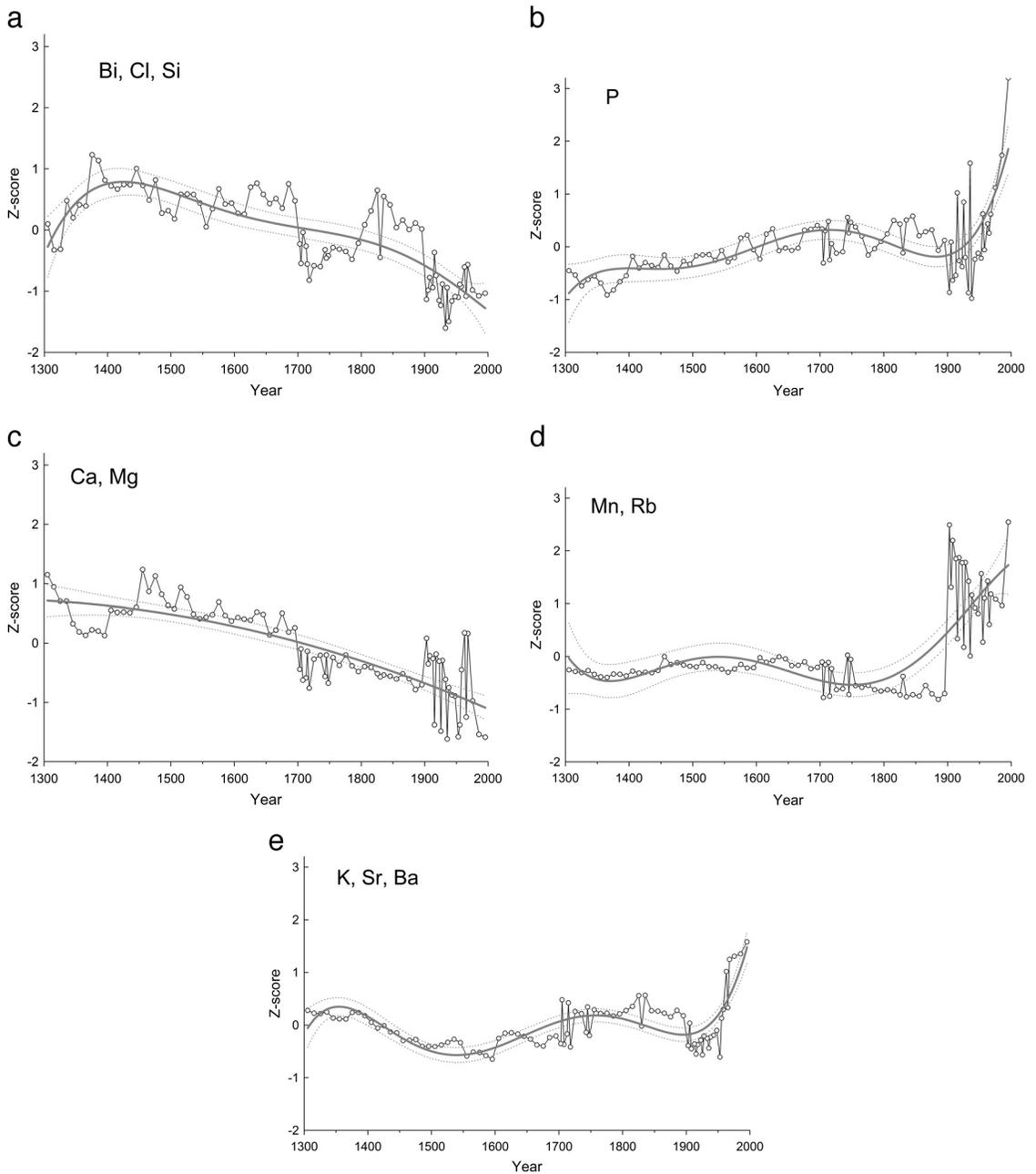


Figure 2. Results of principal component analysis of normalized element concentrations from 1300 to 2000 for cluster #3: PC1 (a) and PC2 (b), and cluster #4: PC1 (c), PC2 (d) and PC3 (e). Table 2 shows the factor loadings of PCs from the cluster #3 and #4. Elements of major contribution to the PC variance are denoted on the plots. Thick line shows trend estimated with distance-weighted least squares fitting, and thin dashed lines are 95%-confidence intervals calculated with linear regression.

sapwood of larch in our study accounts for only 20–25 outer rings so sapwood accumulation cannot explain post-1900 trends. Furthermore, in our study the sub-sampled tree-ring specimens contain

two segments of sapwood, *i.e.* ca. 1875–1900 and 1975–2000 (Figure S1A). For the most part, trends in raw tree-ring element concentrations in sapwood of the wood from the end of the 19th Century are

different from those in the 20th Century sapwood (Figure S2), so we must reject the prospect that the elemental trends at the end of the 20th Century are simply an artifact of sapwood processes.

Pearson correlation analysis between monthly precipitation and temperature from the nearby Khatanga weather station and the normalized 26–element tree-ring series for the interval 1936–2000 shows no significant correlations, indicating the variance of tree-ring element series is not strongly influenced by weather. The chemical signature of declining Ca-Mg and Bi-Cl-Si, and rising P-Mn-Rb-K-Sr-Br in the PCs of the studied tree rings over 700 years seems therefore most likely a response to alteration of soil chemistry affecting the availability of these exchangeable minerals in soil. Competing environmental factors may be at play to produce these long-term changes in soil and larch chemistry.

DISCUSSION

Our project has produced novel and provocative records of tree-ring chemistry that may be related to recent and ancient changes in chemical environment experienced in the Taymyr area, perhaps in part amplified by climatic warming. Although very remote, it turns out that multiple conditions and anthropogenic processes may contribute to the observations, particularly those of the last century. Even though our field data set is not sufficient to precisely identify primary cause (s), this section considers possible mechanisms influencing the tree-ring elemental data, which could promote exploration with data from disparate existing studies and help focus further investigations (Vaganov *et al.* 2013).

Changes in Soil Nutrient Bioavailability and Tree Uptake

The trends in elemental composition in tree rings can be influenced by various factors that affect their concentration and availability in soils. The overall bulk quantity of elements in soils, contributed from various sources and processes can influence the element concentrations 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 (Johnson *et al.* 2008; Chen *et al.* 2010).

Furthermore, processes affecting availability and uptake of nutrients by trees can also determine the trends in elemental composition of tree rings. 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 (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 (Hirschuk 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).

Connection to Soil Acidification and Pollution

In the Taymyr region, polygonal tundra soil generally has low organic matter content, gleying and acidity (Goryachkin 2010). Soils in wet settings of the Kotuy are near neutral (pH 7.3) on average but soils from dry microenvironments are slightly acidic (pH 5.3) (Schmidt 1999). The study site had dry soil conditions with maximum thaw depth up to 60 cm (field observation of authors). The estimated negative trend in the xylem Ca and Mg concentrations at the site (cluster #3 PC1) may signal soil acidification effects on base-cation loss. Similarly, the detected negative trend in xylem chlorine concentrations

(cluster #4 PC1) may suggest low Cl availability in the soil and possible decrease of soil salinity caused by excess of water or fluctuations of water table. Tree uptake and transport of Cl is highly sensitive to soil salinity and more saline condition of soil boosts Cl-uptake by roots and *vice versa* (Broadley and White 2001). The observed increase of xylem Mn concentration can indicate ongoing soil acidification. Studies on reconstructions of soil pH with tree rings suggest that xylem concentration of Mn correlates negatively with soil pH (Kogelmann and Sharpe 2006). The acidity may be mobilizing Mn that might otherwise be locked up in mineral oxides. Like Mn, Ba concentration in trees also has a negative relationship with soil pH (Broadley and White 2001) and has been used to monitor sulfur transport and deposition into soils (Cutter and Guyette 1993).

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 60 years and presently reaches *ca.* 85 km from Norilsk (Ivshin and Shiyatov 1996; Voronin and Ziganshin 1999; Kirilyanov *et al.* 2014). There is no direct evidence of detrimental effects of the Norilsk pollution on the Taymyr forest (Golubeva *et al.* 2013) although modeled trajectories indicate active transport of airborne sulfur to the site at times (Figure S3). Historically, the smelting complex has been operating since the 1940s, and the metal production tripled between the 1960s and 1980s. In 1983 the emissions of sulfur dioxide and mineral dust from the Norilsk metal production reached a maximum of 2483 thousand tons and 73.7 thousand tons, respectively (EPR 2010). More recently, air pollution in 1990–1999 remained high, as the 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 (EPR 2010). Our tree-ring observations of post-1950 chemical concentrations at the study site may signal soil pH changes, perhaps linked to consequences of both local and global sources of Arctic acidification after the 1940s.

Possible Connection to Permafrost Thaw

The trend of increased xylem K, P, Rb and Sr concentrations in the tree-ring records over the last century is puzzling. The K⁺ activity in soils with low pH should decline (as occurs for Ca²⁺ and Mg²⁺) when presence of H⁺ and Al³⁺ cations increases and the base ions are leached away. 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.* 2001). It therefore seems likely that the interrelated concentrations of these elements are driven by a mechanism distinct from soil acidification. Acquisition of phosphorous by trees mainly occurs through diffusion (Barber 1984). We hypothesize that changes in larch root morphology and absorption efficiency would be the primary mechanisms for increased uptake. Root-induced increase of soluble P, K and Rb in alkaline or slightly acid soils has been reported as a function of both decreasing soil pH (acidification) and warming air temperature (Burton *et al.* 2001; Hinsinger 2001; Ruess *et al.* 2006). Considering the fact that climate of the Taymyr Peninsula and soil temperature have been warming steadily since 1880 and 1920, respectively (Figure S4; Naurzbaev and Vaganov 2000; Park *et al.* 2014), 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). Mineralization of soluble elements during the decomposition of organic matter may alter their concentration in the soil solution and on adsorption sites. Even so, the rate of release of base cations from the permafrost thaw is controversial (Keuper *et al.* 2012), and the thawing and associated nutrient release are coupled with tree nutrient uptake (Hobbie *et al.* 2002; Herzschuh *et al.* 2013). Furthermore, 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 (Kreuzwieser and Gessler 2010).

CONCLUSIONS

The 700-year tree-ring records of elemental concentrations from the Taymyr Peninsula indicate dramatic changes in tree-ring concentrations of P, Ca, Mg, Bi, Cl, Si, Mn, K, Rb, Sr and Ba in larch after ca. 1900. However, many possible influences on soil and plant chemistry (e.g. local pollution and regional pollution inputs, acidity, permafrost thawing) operate in the Taymyr area and the record of elemental concentrations in the tree rings is not sufficient by itself to identify the cause(s) with certainty.

The negative trend in tree uptake of soluble Ca^{2+} - Mg^{2+} and Bi^{3+} - Cl^- - Si^{4+} , and the positive trends in soluble P, Mn^{2+} - Rb^+ and K^+ - Sr^{2+} - Ba^{2+} suggest ecologically important changes in biogeochemical cycling of major nutrients available to the trees, which could be identified through the historical patterns of elemental composition of tree rings. The signal of low Ca-Mg-Cl and high P-Mn-K exposes a possible diagnostic relationship between concentrations of these elements, and supports the potential of tree rings in addressing how the concentrations of nutrient elements in soils have changed with time.

We propose that our tree-ring records of wood chemistry relate to changes in soil chemistry driven by both climate changes and Arctic pollution. Although no soil chemistry measurements were available at the site, 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 impact of permafrost thawing water on soil. The geographical scale of the estimated long-term changes in wood chemistry of larch needs further investigation.

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