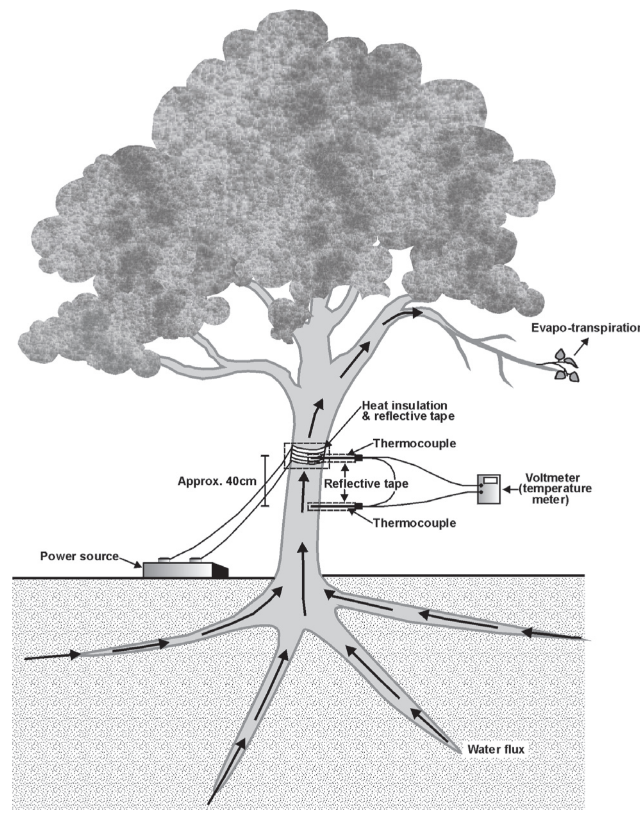
OF2000-4

Geochemical Flux in Black Spruce (*Picea mariana*) Crowns and the Correlation With Root Water Uptake: Effects of Sample Site Drainage and Tree and Crown Morphology on Crown Twig and Outer Bark Metal Concentrations



By
E. Sailerova

OPEN FILE REPORT

Manitoba
Industry, Trade
and Mines

Cover:
Schematic diagram of the experimental design of water flow rate measurements apparatus.

Georeference:
NTS area(s): 63J/9

Keywords:
bark
biogeochemical methods
black spruce
Cross Lake
drainage
Jenpeg
Manitoba
mineral exploration
mineralization
morphology
roots
sampling
trace metals
trees
vegetation

Suggested reference:
Sailerova, E. 2001: Geochemical flux in black spruce (*Picea mariana*) crowns and the correlation with root water uptake: effects of sample site drainage and tree and crown morphology on crown twig and outer bark metal concentrations; Manitoba Industry, Trade and Mines, Geological Survey, Open File Report OF2000-4, 25 p.

Manitoba
Industry, Trade
and Mines
Geological Survey

Open File Report OF2000-4

Geochemical Flux in Black Spruce (*Picea mariana*) Crowns and the Correlation With Root Water Uptake: Effects of Sample Site Drainage and Tree and Crown Morphology on Crown Twig and Outer Bark Metal Concentrations

by E. Sailerova
Winnipeg, 2000

This publication is available in large print, audiotape or braille on request.

TABLE OF CONTENTS

FIGURES

TABLES

APPENDICES

Appendix 1: Essential elements (Ca, K, Mg, Fe, Mn, P, Zn, Cu) – group A
Elemental content measured in twig ashes and elemental content calculated per one gram of dry weight in twigs and crowns in trees of WS, WB, DS, DB and HB groups. Measurements for individual sampling dates are shown as well as standard deviations for multiple and double samplings. Average values for elemental content, median and seasonal variation (seasonal SD) are also shown.

Appendix 2: Essential elements (Ca, K, Mg, Fe, Mn, P, Zn, Cu) – group A
Correlation between the rate of root water uptake and elemental concentration in twig ashes and tree crown (twig). Sampling dates were four to five days apart and the amount of water uptake (liters) per period was measured. The sampling of three crowns was done at the end of the sampling period. Individual charts for an element and each experimental group (WS, WB, DS, DB and HB) are shown.
- ■ Changes in water uptake during the sampling period
- ● Changes in elemental content in one gram of crown DW during the sampling period
- ○ Changes in elemental content in twig ashes during the sampling period

Appendix 3: Nonessential elements (Ag, Co, Ni, Rb) – group B
Elemental content measured in twig ashes and elemental content calculated per one gram of dry weight in twigs and crowns in trees of WS, WB, DS, DB and HB groups. Measurements for individual sampling dates are shown as well as standard deviations for multiple and double samplings. Average values for elemental content, median and seasonal variation (seasonal SD) are also shown.

Appendix 4: Nonessential elements (Ag, Co, Ni, Rb) – group B
Correlation between the rate of root water uptake and elemental concentration in twig ashes and tree crown (twig). Sampling dates were four to five days apart and the amount of water uptake (liters) per period was measured. The sampling of three crowns was done at the end of the sampling period. Individual charts for an element and each experimental group (WS, WB, DS, DB and HB) are shown.
- ■ Changes in water uptake during the sampling period
- ● Changes in elemental content in one gram of crown DW during the sampling period
- ○ Changes in elemental content in twig ashes during the sampling period

Appendix 5: Nonessential elements (Al, As, Au, Ba, Br, Cd, Cr, Cs, Hf, Na, Pb, Sb, Sc, Sr, Th, V, W) – group B
Elemental content measured in twig ashes and elemental content calculated per one gram of dry weight in twigs and crowns in trees of WS, WB, DS, DB and HB groups. Measurements for individual sampling dates are shown as well as standard deviations for multiple and double samplings. Average values for elemental content, median and seasonal variation (seasonal SD) are also shown.

Appendix 6: Nonessential elements (Al, As, Au, Ba, Br, Cd, Cr, Cs, Hf, Na, Pb, Sb, Sc, Sr, Th, V, W) – group B
Correlation between the rate of root water uptake and elemental concentration in twig ashes and tree crown (twig). Sampling dates were four to five days apart and the amount of water uptake (liters) per period was measured. The sampling of three crowns was done at the end of the sampling period. Individual charts for an element and each experimental group (WS, WB, DS, DB and HB) are shown.
- ■ Changes in water uptake during the sampling period
- ● Changes in elemental content in one gram of crown DW during the sampling period
- ○ Changes in elemental content in twig ashes during the sampling period

Appendix 7: Rare-earth elements (REEs) (Ce, La, Sm, Yb) – group C
Elemental content measured in twig ashes and elemental content calculated per one gram of dry weight in twigs and crowns in trees of WS, WB, DS, DB and HB groups. Measurements for individual sampling dates are shown as well as standard deviations for multiple and double samplings. Average values for elemental content, median and seasonal variation (seasonal SD) are also shown.

Appendix 8: Rare-earth elements (REEs) (Ce, La, Sm, Yb) – group C
Correlation between the rate of root water uptake and elemental concentration in twig ashes and tree crown (twig). Sampling dates were four to five days apart and the amount of water uptake (liters) per period was measured. The sampling of three crowns was done at the end of the sampling period. Individual charts for an element and each experimental group (WS, WB, DS, DB and HB) are shown.

- ■ Changes in water uptake during the sampling period
- ● Changes in elemental content in one gram of crown DW during the sampling period
- ○ Changes in elemental content in twig ashes during the sampling period

Appendix 9: Tree description. Each sampled tree was described according the appearance of the crown, length of the leader, differences in the number of branches, bark quality and tree location (sunny, semi-sunny, shade). Tables are organized according to experimental groups (WS, WB, DS, DB and HB).

Appendix 10: Contains the original analytical data (INAA and ICP-AES analysis) for ashed bark and ashed twigs.

INTRODUCTION

Plants have the ability to select and store metals derived from the growth substrate and distribute them to tissues according to metabolic requirements and tolerances. This ability is being used in biogeochemical exploration. Biogeochemical techniques have been developed and improved for decades. Studies have been undertaken to examine species specific barriers to metal uptake (Kovalevskiy, 1990), partitioning studies to determine the relative abundance of metals in various plant tissues (Fedikow and Dunn, 1996), and laboratory studies of the effect of pH and redox potential on metal utilization in plant tissues (e.g. Redy and Patrick, 1977). This study was designed to improve biogeochemical techniques applied to mineral exploration by: (1) assessing site-specific criteria with potential to seriously affect metal uptake and (2) determining optimum sampling criteria for biogeochemical exploration based on tree morphology and sampling site characteristics.

The absence of a good soil-plant geochemical correlation may be the result of seasonal changes of metal concentrations in the living plant tissue. Seasonal changes are problematic when samples are collected over a prolonged time period. A second concern is tree morphology (size, number of branches, crown type, bark type) and site quality (i.e. drainage, tree density). This study was designed to address these problems. Water flux in trees was measured throughout the period of study to distinguish between seasonal metal flux attributable to changes in the tree physiology and geochemical flux induced by differences in root water uptake.

Black spruce (*Picea mariana* (Mill.) BSP) is the most common tree species in the study area. Crown tissues and outer bark were selected as the principle sample types because of ease of collection and acropetal tendency for metals to concentrate in crown tissues.

EXPERIMENTAL GROUPS AND SAMPLE COLLECTION

One hundred black spruce (*Picea mariana*) crowns and outer bark samples were collected from three different sites. Trees growing on two of these three sites were separated into two sub-groups according to the number of transpiring branches. This provides five different experimental groups from which twenty crown and bark samples were collected. Samples were collected between June 6 and July 31, 1996 in four to seven day intervals resulting in eleven sampling dates for each experimental group. Duplicate and replicate (five samples) sampling was undertaken during the season for each experimental group in ten to twelve day intervals. Sampling was restricted to trees with a circumference of 34-39 cm (measured at chest height). Tree crowns were cut at a constant 45 cm distance measured from the leader base. Crowns were characterized according to whether they were: (1) packed or loose, (2) wide or narrow and (3) by the length of the leader. Outer bark was collected from chest height and characterized as coarse, semi-coarse or fine. The location of each tree was noted according to the availability of direct sunshine (sunny, semi-sunny or shade). The age of each tree was determined by tree ring counts in wafers cut from the tree at 20-30 cm above the ground.

All three experimental sites were located close to the Manitoba Hydro damsite near Jenpeg (Fig. 1). The distance between experimental sites was up to 700 meters. Black spruce was the predominant vegetation type on each site with sporadic tamarack (*Larix laricina*). Site W, the first experimental site, was swampy, remaining wet throughout the measuring season and contained variably decomposed forest litter. The second experimental site (site D) was well drained and remained dry during the season. The third site (site H) was only partly drained reflecting most typical conditions of those encountered during the measuring season. Black spruce trees growing on site H were shorter with a relatively high number of transpiring branches. The density of trees growing on site H was about three times higher than either sites D or W. The transpiration rate from bottom branches was expected to be limited by solar radiation and lowered by the higher surface layer diffusion resistance.

Trees growing on sites D and W were separated into two experimental groups. The first group (group S) contained trees with small transpiring surfaces representing seven to twenty transpiring branches. Trees from the second group (group B) had twenty to forty transpiring branches, which were approximately fifty percent longer than those belonging to S group. Accordingly, group B trees had approximately three times the transpiring surface as compared to trees from group S. The transpiring surface of trees growing on site H was similar to the trees from group B (twenty to forty branches) and as such was labeled as group B as well. The designations and site characteristics of the experimental groups are provided in Table 1.

The age of the sampled tree, as estimated by tree ring counts, was similar for all experimental groups. The WS trees averaged 96.1 years (SD=2.3), DS trees were 97 years old (SD=2.4), WB trees were 92.3 years old (SD=4.4), DB trees were 96 years old (SD=3.9) and HB trees were 93.9 years old (SD=4.5). The range of all tree ages was 84 to 104 years.

SAMPLE PREPARATION AND ANALYSIS

Black spruce crown and outer bark samples were air-dried and the crown separated into twig, needle and cone portions. One third of the twig samples in each experimental group, collected in the beginning, in the middle and at the end of the season, were separated into thin and thick twigs and the element content analyzed separately. Volumetrically, thin twigs had 1 to 3 times more bark compared to the woody part with maximal radial diameter of 4 mm. Thick twigs with diameters >4 mm contained a higher portion of wood compared to bark. One third of all the cone samples were separated into closed cone and open cone samples and analyzed separately. Remaining cone samples were characterized

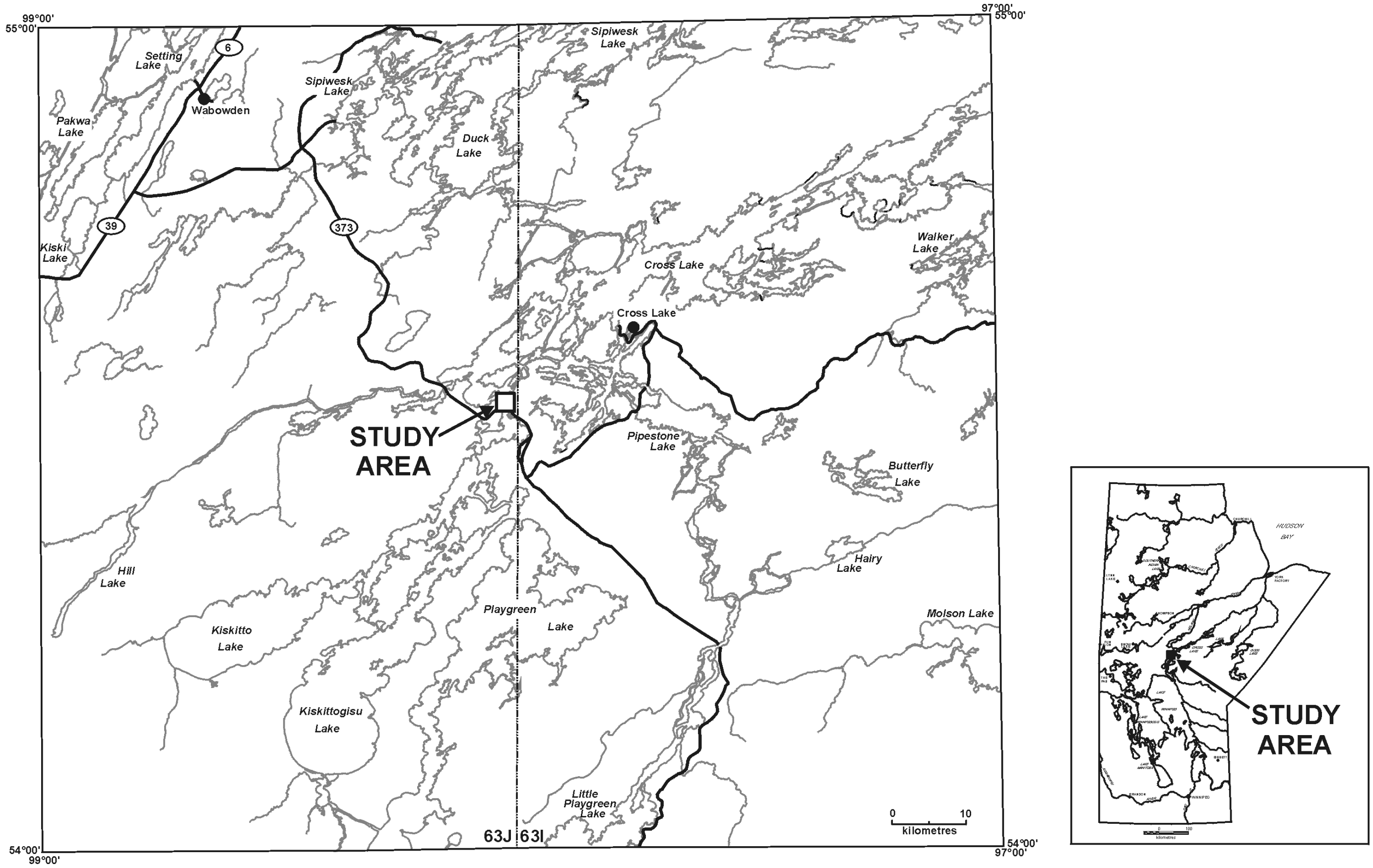


Figure 1: Location map of the study area.

Table 1: Designations and characteristics of experimental groups	
WS	trees growing on poorly drained site covered with pond water during the whole season; trees had small number of branches (7 to 20) and thus small transpiring surface; density of the trees growing on this site was low
DS	trees growing on well drained site; trees had small number of branches (7 to 20) and thus small transpiring surface; density of the trees growing on this site was low
WB	trees growing on poorly drained site covered with pond water during the whole season; trees had large number of branches (20 to 40) and thus large transpiring surface; density of the trees growing on this site was low
DB	trees growing on well drained site; trees had large number of branches (20 to 40) and thus large transpiring surface; density of the trees growing on this site was low
HB	trees growing on partially drained site, where the pond water remained up to 5 days after rainy period; trees had large number of branches (20-45) and thus large transpiring surface; higher density of trees on this site resulted in lower evapotranspiration rates from the lower branches attributable to limited irradiation

by the ratio of open and closed cones on a volume basis. The dry weight of each twig, cone and needle sample was recorded prior to ashing. Care was taken to collect all the twigs, needles and cones, so that the dry weight ratios would represent the true crown organ ratios for each crown sample.

Analysis of element content in all crown organs (i.e. thin and thick twigs, open and closed cones and needles), along with the description of crown appearance (twig, cones and needles ratio) in samples collected during the season was undertaken to analyze the seasonal element redistribution in the crown. We anticipated that this data might also show the effect of crown appearance on the twig element concentration (i.e. dependency of the element distribution factor between needles and twigs based on their relative amount). The same data set enables an accurate calculation of crown element content, which should correlate more strongly to root water uptake than twig element content. Unfortunately, only the data from twig analysis were available at the time of completion of this study. To minimize the differences in elemental twig content due to morphological differences in the crown collected during the field season and to demonstrate the correlation of element concentration in the crown with the root water uptake, a projected crown element concentration was calculated as shown in the Data Analysis section. A time-independent ratio between twig, cones and needles was assumed. The needle and cone elemental content was calculated separately for each crown using the organ dry weight and published element distribution ratios for twigs/needles, twigs/cones, closed cones/open cones and ash content ratios in actual and analyzed samples. The elemental crown organ distribution ratios originate from a single comprehensive data set for black spruce crowns collected by Fedikow and Dunn (1996).

Analytical results for only five of twenty bark samples collected from each experimental group were available at the time this report was prepared.

Twig and bark samples were ashed in a pottery kiln in the laboratories of the Geological Survey of Canada (Ottawa) under the supervision of Dr. Colin Dunn. Ashes were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and instrumental neutron activation analysis (INAA). Results from ICP-AES analysis for Ag, Cd, Cu, Mn, Ni, Pb, Zn, Al, Mg, P, Sn, Sr, Ti, V, Y, W, Zr and from INAA for Au, As, Ba, Br, Ca, Co, Cr, Cs, Hf, Fe, K, Na, Rb, Sb, Sc, Th, U, Zn, Eu, La, Lu, Nd, Ce, Sm, and Yb were used for this study. Elements Tb, Ta, Se, Mo, Ir, Sn, Se, Bi, Be and Hg were below the limits of determination for this study and are not discussed further. Analyses were undertaken by Activation Laboratories Ltd. (Ancaster, Ontario).

ROOT WATER FLOW RATE MEASUREMENTS

Water and solutes are absorbed by tree roots and transported through the tree xylem to the transpiring surfaces. This water flow rate was measured at the tree trunk level approximately 0.5 m above the ground. Two trees for each experimental group were monitored with water flux measured over a period of three to five days in one to two hour intervals, between 7:00 a.m. and 12:00 p.m. Weather conditions were monitored simultaneously and later compared to and supplemented by the official weather report from the Environment Canada weather station located in Norway House (about 80 km from the experimental sites). Daily water flow rate curves were calculated for two basic weather conditions: (i) for a clear sky or partly overcast and moderate to strong wind conditions and (ii) for overcast or partly overcast without wind.

Method

Principle

A known amount of heat is applied to the tree trunk xylem. Part of the applied heat is carried away by the water flowing through the xylem. The higher the water flow rates, the lower the resulting temperature in the heated spot. The temperature changes are measured differentially against the reference temperature in an unheated part of the trunk xylem.

Experimental design

The outer bark and phloem tissue were carefully cut and exposed in an approximately 7 cm wide strip partly separated from the xylem tissue (trunk wood, Fig. 2). This part of the trunk was tightly circled by heating wire with known resistance that was connected to a portable power source. The heated part of the tree trunk was isolated by several layers of insulating material covered by reflective tape to prevent any heat loss or temperature increase due to sunshine. A heavy duty copper/constant thermocouple, inserted in a 15 cm long protective metal coat, was placed in the center of the heated spot, with the temperature sensitive connection located in the center of the trunk. A second thermocouple, monitoring the reference temperature, was placed 40 cm below the first thermocouple with the temperature sensitive connection also in the middle of the trunk. Both thermocouples were protected from the direct sunshine by reflective tape. The temperature difference was measured by a specially calibrated voltmeter that enabled direct temperature readings. The voltage of the power source was monitored as well as the temperature measurements. An equilibration period of 12 hours was required. The design of the apparatus is shown in Figure 2.

Trees were cut and the crowns sampled 10-30 days after the measurements. During this time period the phloem pathway to the roots was disconnected, while the xylem pathway remained intact. Trees thus continued to receive nutrients and metals but the transport back to the roots was eliminated. The resulting increase in the element crown content was termed “element phloem buildup”.

DATA ANALYSIS

Element Concentration in Different Crown Organs

The elemental concentration in crown twigs (TW), needles (N), cones (C) and crown (CR) was calculated using the measured parameters as well as “model black spruce tree” parameters as determined by Fedikow and Dunn (1996):

Measured parameters:
element concentration in twig ash.........................E(ash)
twig ash content..A
open cones/closed cones ratio.......................................k
twig weight..Wt
needles weight...Wn
cones weight..Wc

Parameters analyzed for a “model black spruce tree” - L76N, 25W (Fedikow and Dunn, 1996):
needles ash content/twig ash content..........................Kn
cones ash content/twig ash content............................Kc
open cones ash content/closed cones ash content...Koc
elemental concentration in needles ash/element
concentration in twig ash.......................................Cn
elemental concentration in cones ash/element
concentration in twig ash.......................................Cc

Equations utilized for this study assuming negligible element losses during ashing (Dunn, 1995):
elemental concentration in twigs: TW=E(ash)*A/100
elemental concentration in needles: N=TW*Cn*Kn
elemental concentration in cones:
C=TW*(Cc*Kc*k*Wc*Koc/(k+1) + Cc*Kc*Wc*Koc/(k+1))/Wc

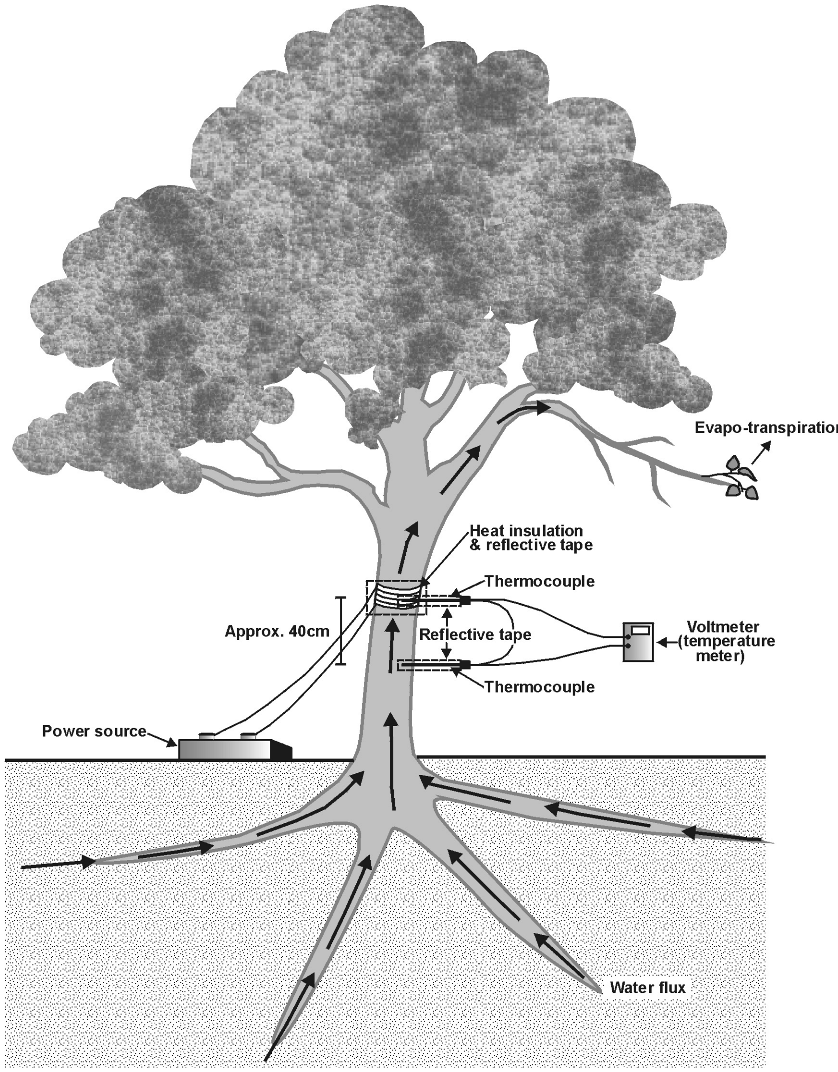


Figure 2: Schematic diagram of the experimental design of water flow rate measurements apparatus.

elemental concentration in crown:

CR=(TW*Wt+N*Wn+C*Wc)/(Wt+Wn+Wc)

elemental concentration in twigs and cones:

TW+C=(TW*Wt+C*Wc)/(Wt+Wc)

elemental concentration in twigs and needles:

TW+N=(TW*Wt+N*Wn)/(Wt+Wn)

elemental concentration in cones and needles:

C+N=(C*Wc+N*Wn)/(Wc+Wn)

The standard deviation (SD) was calculated for four multiple samplings on one sampling date per each experimental group. The average SD was calculated for these three SD values and thus does not reflect seasonal changes. The seasonal SD (n=11) reflects the variation of the specific parameter during the season.

Calculation of the root water flow rate (Fw):

Heat supply to the tree trunk xylem: $Q_1=U*I*t=U^2*t/R$

Heat carried away by water flux: $Q_2=m*c*(T_1-T_2)= V*d*c*(T_1-T_2)$

At equilibrium when $T_1-T_2=$ constant , $Q_1=Q_2$ and

Water flow rate through the tree trunk (F) F=V/t $[m^3*s^{-1}]$

then $F=U^2/(R*c*(T_1-T_2))$

$Fw=F-F_0$

F_0 (const) was calculated as the F value measured at conditions when water flow rate assumed to be zero (dark night, after rain conditions) and represents the heat losses and cuticular transpiration, assumed to be negligible in conifers.

where:

U......voltage on the power supply
I........electric current
R......resistance of the heating wire (29.5 ohm)
c.......specific heat of water
T_1.....temperature measured at the spot heated by the heating wire
T_2.....temperature measured at the reference spot
t........time
d.......water density
V.......volume

Root water flow rate was measured at one hour intervals for each tree and the water flux per day calculated for two weather conditions as described above. Water flux per sampling period varies according the number of sunny and rainy (overcast) days.

Phloem Buildup

Water and solutes are transported to the crown and transpiring branches through the xylem tissue. From transpiring and photosynthesizing tree organs, a stream of solutes is transported back to the roots through the phloem tissue, providing the roots with necessary energy. Along with a variety of energy-rich products, elements that were not utilized or redistributed in the tree shoot are transported to the roots as well. High phloem buildup values indicate that higher element concentrations have been transported either to the roots or to the rest of the tree shoot, branches or trunk. The phloem solute transport route was disconnected for 10 - 30 days in trees where water flow measurements took place. Changes in the crown (twig) element concentration was calculated as a difference between crown (twig) element concentration and crown (twig) element concentration in trees sampled the same day with the phloem pathway intact.

RESULTS

Root Water Flow Rate

Trees with low numbers of of transpiring branches (WS and DS) and thus small transpiring leaf (needle) areas growing on wet and well drained sites showed little difference in daily flow rate profile (Figs. 3, 4). Differences in water flow rates on sunny and overcast days (Figs. 3 to 8), confirm the stomatal response as a determining factor in water flow rate regulation. About 2.5 times more water was flowing through the xylem of trees with a higher number of branches (WB, DB) compared to WS and DS trees (Figs. 5, 6, 8), which corresponds with the ratio of transpiration area in these trees. Smaller differences in the water flow rate on sunny and overcast days was measured in trees of the WB group (66.6 and 42.7 liters per day, respectively) compared to trees of the DB group (71.4 and 27.5 liter per day, respectively). This indicates a more significant role of the stomatal regulatory system in trees growing on well drained sites. Lower daily water flux along with a lower difference on sunny and overcast days in trees of the HB group (53.6 and 41.2 liter per day, respectively, Fig. 7) is most probably a result of high tree density on site H and thus limited irradiation of lower branches. Saturation irradiance levels in black spruce are relatively low and shaded branches will respond to different weather conditions only on the basis of air humidity and wind strength changes.

Element Concentration in Black Spruce Crown and Outer Bark

Analyzed elements were separated into four basic groups. The first group (group A) contains essential elements and group B contains pH sensitive elements. Group C contains the rest of analyzed elements including the rare-earth elements (REEs). Group D represents Ti, U, Y and Zr. Designations and characteristics of experimental groups are summarized in Table 1. Summaries for all elements (essential and nonessential A,B,C and D) are given in Tables 2, 3, 4 and 5. These tables give the average element content in twig ashes for thin and thick twigs, average values and ranges for ash, twig and crown element concentration measured during the season, and average values of estimated phloem daily buildup shown as a change in % or ppm in crown or twig content per day. For a quick evaluation of the extent of seasonal changes, a “seasonal category” is included. This evaluation is based on the relative value of seasonal SD and average SD measured in multiple same-day samplings. For seasonal category 1 seasonal SD is less than or equal to the SD of multiple samplings. Seasonal category 2 indicates the seasonal SD is greater than the SD of multiple samplings. Seasonal category 3 indicates the seasonal SD is greater than 2xSD of multiple samplings. The quality of correlation between the root water uptake with the element content in the crown twigs and the whole crown is labeled as 0 (poor), 1 (satisfactory) and 2 (excellent). Finally, the average, median and SD values of element content in outer bark ashes are given in Tables 6, 7 and 8. Tables 9, 10, 11 and 12 demonstrate the differences in elemental concentrations between twigs and bark.

Appendices contain data illustrating the seasonal changes in element concentration in twig ashes (ash), twigs (TW) and crown (CR) in trees of the WS, DS, WB, WB and HB group. Tables for individual elements along with sampling dates standard deviation values for multiple samplings and seasonal and analytical method SD were calculated for each experimental group and each element. For trees with double crowns the SD values are also shown. These data are presented in Appendix 1 (group A), Appendix 3 (group B), Appendix 5 (group B) and Appendix 7 (group C). Due to a lack of available data in our “model tree” for some elements, the crown element concentration could not be calculated. The SD related to the analytical method reproducibility was 2 to 30 times lower than average SD for multiple samplings. The element content differences measured for a double crown (found mostly in DB trees) were similar to the differences within multiple samplings.

Figures illustrating the correlation between the amount of water uptake during the sampling period and corresponding changes in the element concentration in crown and twig ashes during the measuring season are located in Appendix 2 (group A), Appendix 4 (group B), Appendix 6 (group B) and Appendix 8 (group C). The crown element concentration was replaced by twig element concentration when missing data for the “model tree” made the calculation impossible. A substantially better correlation between root water uptake and crown element content compared to twig ash element content was found for the majority of studied metals.

In general, no differences were found in crown element content between trees with a high and low number of transpiring branches, although the difference in the amount of water accepted by those trees was substantial (Fig. 7). Differences between selected experimental groups were all attributable to the differences in site drainage and some to the site tree density. Elements

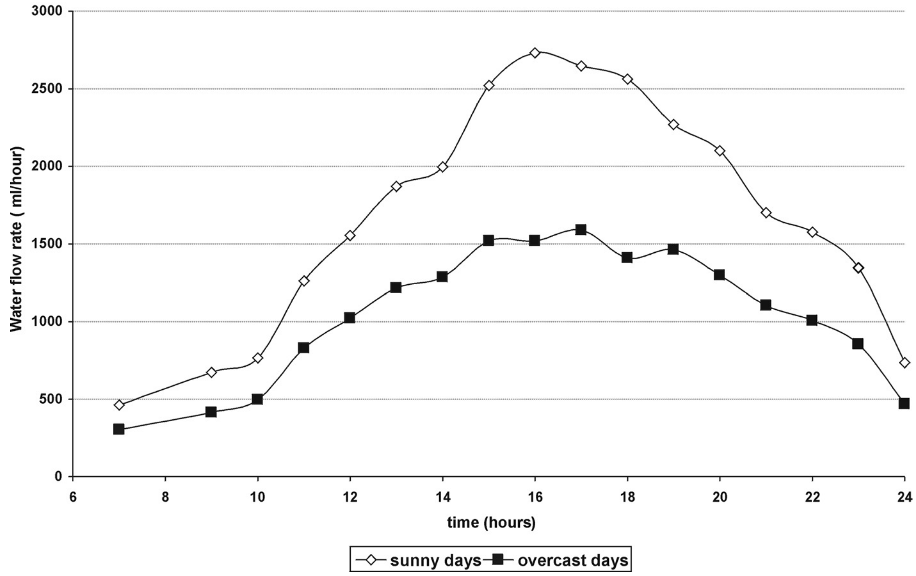


Figure 3: Daily root water flow rate profile - WS.

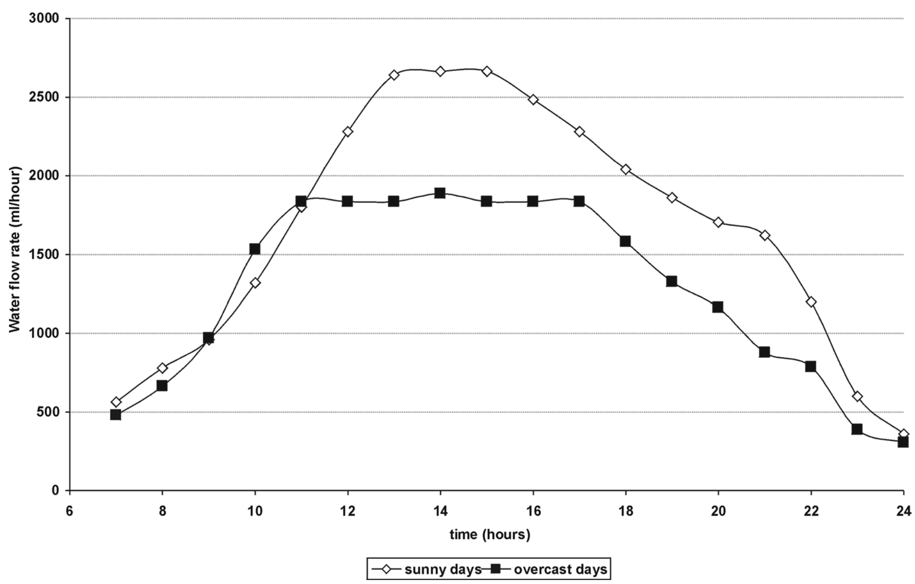


Figure 4: Daily root water flow rate profile - DS.

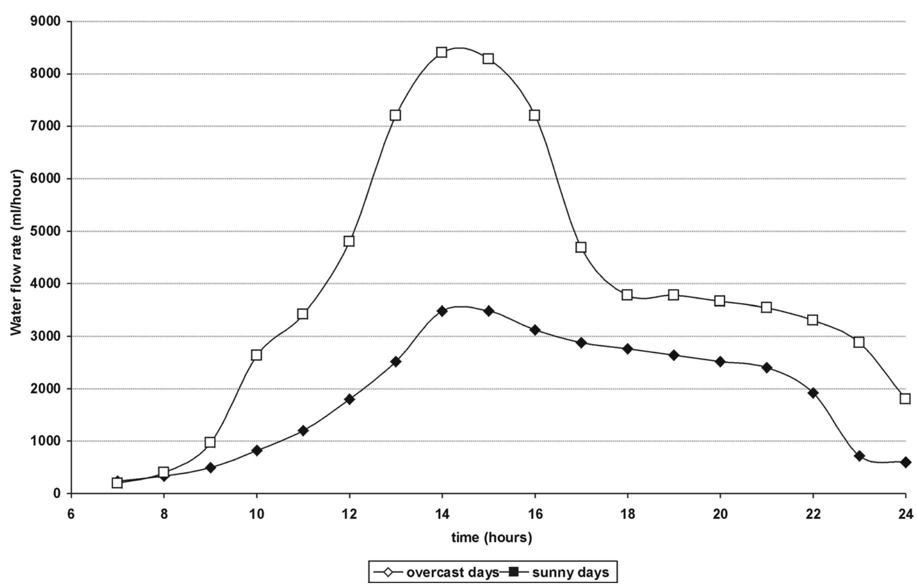


Figure 5: Daily root water flow rate profile - WB.

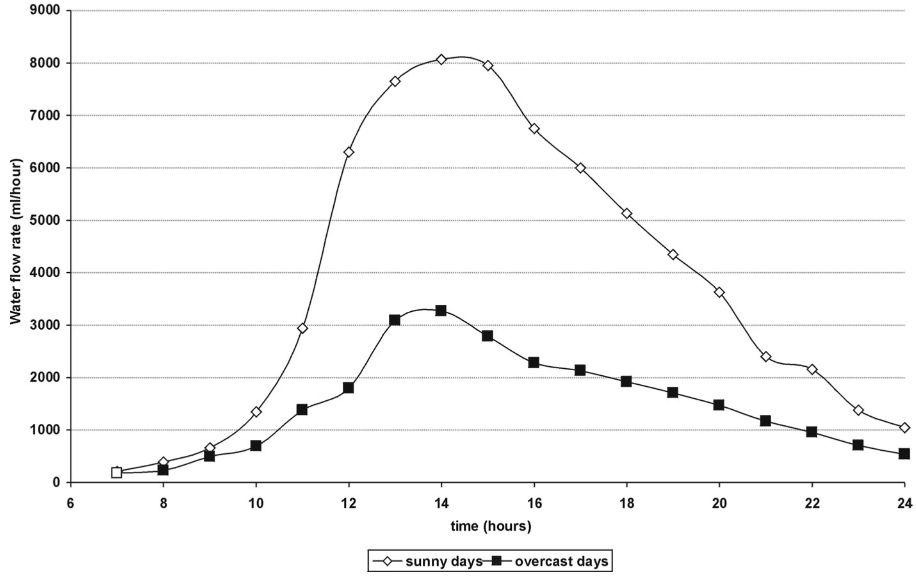


Figure 6: Daily root water flow rate profile - DB.

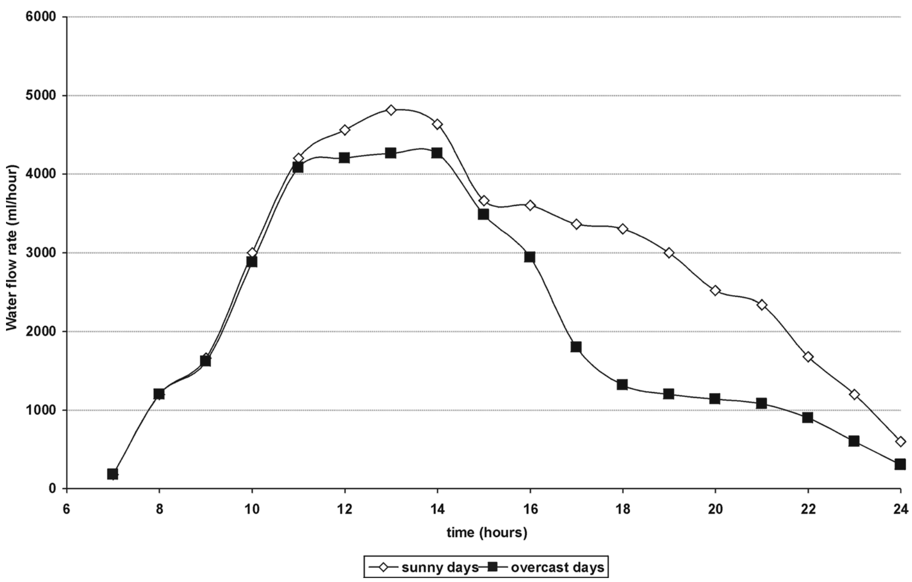


Figure 7: Daily root water flow rate profile - HB.

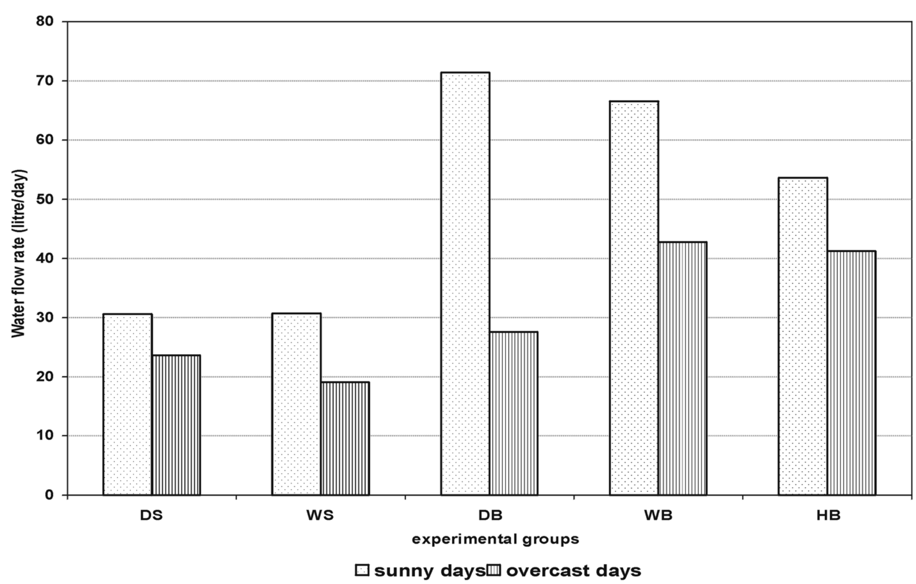


Figure 8: Average daily root water flow rate.

Table 2: Group A elements in black spruce crowns in WS, DS, WB, DB and HB trees. Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs) and evaluation of the correlation between the crown element content and root water uptake.

element content in twig ash				*seasonal average*			*element content range*			*seasonal category*			*phloem build-up*	*correlation with the root water uptake*	
		thin (%)	thick (%)	ash (twig) (%)	twigs (%/DW)	crown (%/DW)	ash (twig) (%)	twigs (%/DW)	crown (%/DW)	ash (twig)	twigs	crown	CR (TW) (%of CR conc./day)	ash	CR (TW)
Ca	WS	16.8	20	17.32	0.357	0.211	14.9-22.1	0.32-0.44	0.162-0.273	1	2	3	-1.32E-01	0	2
	DS	16.6	19.2	16.39	0.352	0.239	13.0-19.2	0.29-0.42	0.183-0.340	2	2	1	-1.87E+00	0	0
	WB	18.2	20	17.94	0.415	0.27	15.5-19.6	0.152-0.334	0.152-0.465	1	1	1	-7.49E+00	1	2
	DB	16.5	19.6	17.75	0.382	0.279	13.6-19.9	0.276-0.462	0.169-0.390	1	2	1	-2.13E+00	0	0
	HB	15.8	17.8	16.64	0.361	0.232	14.3-19.6	0.285-0.470	0.139-0.351	1	2	2	-9.13E+00	0	1
K	WS	18.9	19.5	19.23	0.397	0.344	14.37-23.76	0.267-0.585	0.264-0.484	2	1	2	-2.12E+00	0	1
	DS	20.8	20.4	19.34	0.418	0.434	14.3-26.7	0.328-0.595	0.182-0.562	3	2	3	1.11E+00	1	2
	WB	16.8	17.3	18.16	0.426	0.405	13.2-25.4	0.329-0.772	0.231-0.872	2	2	2	9.30E-01	0	1
	DB	13.5	18	16.89	0.365	0.414	13.2-20.0	0.302-0.471	0.278-0.659	1	2	2	-9.35E-01	0	0
	HB	18.9	18.5	18.68	0.404	0.372	13.85-23.93	0.301-0.536	0.210-0.513	2	2	2	-3.80E+00	0	2
Mg	WS	5.7	6.2	5.33	0.108		2.98-7.64	0.063-0.147		3	2		2.25E+00	1	1
	DS	4.08	4.08	4.28	0.092		3.08-5.68	0.069-0.127		1	2		3.92E+00	0	0
	WB	4.77	5.04	5	0.118		2.86-7.62	0.078-0.177		1	1		4.98E+00	1	1
	DB	6.5	5.7	4.59	0.098		2.78-5.53	0.057-0.130		1	2		2.19E+00	0	0
	HB	5.6	6.3	5.27	0.114		3.52-7.6	0.084-0.133		2	1		1.64E+00	1	1
Fe	WS	0.45	0.35	0.36	0.00769	0.00337	0.27-0.43	0.0066-0.0097	0.00223-0.00686	2	1	3	5.57E+00	0	0
	DS	0.45	0.4	0.396	0.00848	0.00366	0.24-0.71	0.0053-0.0149	0.0022-0.00625	1	1	1	1.16E+01	0	0
	WB	0.41	0.27	0.286	0.00673	0.00264	0.18-0.355	0.0052-0.0083	0.00175-0.00398	1	1	1	-9.98E-01	1	2
	DB	0.38	0.32	0.33	0.00727	0.00312	0.21-0.5	0.0055-0.0096	0.0021-0.0044	3	2	3	1.70E+00	0	2
	HB	0.49	0.31	0.389	0.00847	0.00197	0.28-0.54	0.0059-0.0112	0.0021-0.0051	1	1	1	2.27E+01	0	2
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)				(%of CR conc./day)		
Mn	WS	4749	4733	4785	98.8		3410-5715	72.3-131.4		2	2		2.15E+00	0	0
	DS	11656	11248	10712	233.1		8375-17100	154.8-415.5		2	2		3.37E-01	1	1
	WB	4831	5739	5531	124.6		1470-7310	44.7-174		2	2		-9.66E-01	1	1
	DB	12608	12100	11373	250.9		4897-13448	135.5-326		3	3		1.18E+00	0	0
	HB	5592	5702	5029	113.6		2985-8400	67.2-169.6		3	2		-6.80E+00	1	1
P	WS	44275	32528	38021	803		21501-23500	570-1139		2	3		2.48E+00	0	0
	DS	46320	32080	37418	816		21974-50100	608-1117		2	2		2.60E+00	1	1
	WB	43375	33600	35799	838		22775-46100	491-1025		2	1		3.96E+00	0	0
	DB	44130	30060	33374	741		25072-38919	498-949		2	2		2.89E+00	1	1
	HB	33303	29217	34334	757		21108-44000	417-1086		2	2		6.06E+00	0	0
Zn	WS	2238	2075	2056	42.98	19.38	1368-2900	31.8-61.2	13.98-38.98	2	2	3	6.35E+00	0	0
	DS	2020	1900	1734	37.5	17.6	1242-2100	23-42.37	12.17-22.93	2	2	2	4.52E+00	1	2
	WB	2212	1988	1795	41.8	18.8	1544-2200	32.5-51.7	10.34-30.20	2	2	2	5.75E-01	0	0
	DB	1700	1580	1610	34.6	16.9	1242-2200	25.4-47.2	12.46-23.58	2	2	2	5.09E-01	1	2
	HB	2316	1850	1859	41.9	19.3	1400-2400	18-58.6	7.92-27.05	2	2	3	1.72E+00	0	0

**Table 2: Group A elements in black spruce crowns in WS, DS, WB, DB and HB trees.
Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs)
and evaluation of the correlation between the crown element content and root water uptake. (continued)**

		element content in twig ash		***seasonal average***			***element content range***			***seasonal category***			***phoem build-up***	***correlation with the root water uptake***	
		thin (%)	thick (%)	ash (twig) (%)	twigs (%/DW)	crown (%/DW)	ash (twig) (%)	twigs (%/DW)	crown (%/DW)	ash (twig)	twigs	crown	CR (TW) (%of CR conc./day)	ash	CR (TW)
Cu	WS	152	142	137.6	2.87		99.8-166	2.05-3.55		1	1		2.37E+00	0	0
	DS	225	205	211.2	4.54		172-366	3.479-7.32		2	2		2.48E+00	0	0
	WB	154	155	154	3.56		92.7-220	2.307-4.87		1	2		3.84E+00	1	1
	DB	203	201	191.3	4.18		148-208	3.145-5.96		3	3		6.50E+00	2	2
	HB	145	130	123.8	2.74		74.6-158	1.476-3.79		3	2		1.85E+00	1	1

Arithmetic mean (n=11) of metal content in ashes of thin (up to 4 mm diameter) and thick twigs; metal content in twigs and crowns based on the twig, crown dry weight.
The range for metal concentrations measured in twig ashes, twigs (DW) and crowns (DW) is shown.
Seasonal category 1 indicated that SD for multiple samplings is higher than seasonal SD; category 2 indicated that seasonal SD is higher than SD for multiple sampling, but does not exceed twice the value.
Category 3 indicates very high seasonal variations, where seasonal SD exceed more than twice the SD of multiple sampling.
The rate of phloem build-up is shown as a percentage of the crown element concentration per day.
The quality of element concentration in twig ashes and in the crown with the root water uptake is qualified as poor (0), good (1) and excellent (3).

Table 3: Group B elements in black spruce crowns in WS, DS, WB, DB and HB trees. Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs) and evaluation of the correlation between crown element contents and root water uptake.

		element content in twig ash		*seasonal average*			*element content range*			*seasonal category*			*phloem build-up*	*correlation with the root water uptake*	
		thin (ppm)	thick (ppm)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig)	twigs	crown	CR (TW) (%of CR conc./day)	ash	CR (TW)
Ag	WS	1.2	1.54	0.761	0.0155	0.0045	0.6-1.021	0.0116-0.0156	0.0031-0.0049	1	2	2	-3.38E+00	0	1
	DS	0.733	0.877	1.278	0.0274	0.00252	0.884-2.2	0.0204-0.044	0.0062-0.0164	3	2	2	-9.94E+00	0	0
	WB	0.775	1.05	0.837	0.0191	0.00141	0.4-1.2	0.0087-0.0286	0.002-0.0097	1	1	1	-1.29E+01	0	1
	DB	1.42	1.74	1.403	0.0303	0.0098	0.85-2.4	0.0197-0.0493	0.0041-0.0198	2	2	3	-5.95E-01	0	1
	HB	0.73	1.11	0.706	0.016	0.00141	0.4-0.851	0.0098-0.0208	0.00097-0.0087	2	2	2	-8.87E-01	0	1
Co	WS	4.6	5.1	4.278	0.0872	0.0386	3.222-5.169	0.0736-0.1118	0.031-0.0651	1	1	3	3.24E-01	1	1
	DS	15	16.4	13.7	0.2956	0.1322	10.0-18.0	0.0226-0.4374	0.0705-0.1744	1	1	1	4.04E-01	0	0
	WB	3.5	3.5	3.826	0.0876	0.039	2.669-9	0.0576-0.207	0.0234-0.1074	2	2	3	4.61E+00	0	1
	DB	11.2	11.8	10.74	0.2312	0.1099	5.103-22	0.1142-0.4598	0.0463-0.2242	3	3	3	9.22E-01	0	0
	HB	3.8	3.1	3.907	0.0853	0.0384	2.698-5	0.054-0.1075	0.0205-0.0518	1	2	2	4.56E-01	1	1
Ni	WS	41	27	29.36	0.629		14-48	0.297-1.085		1	1		6.50E+00	1	1
	DS	114.8	98	109.3	2.359		79.14-176	1.758-3.52		1	1		1.88E+00	0	0
	WB	34.5	22	30.67	0.704		12.46-78	0.269-1.794		2	3		4.06E+00	1	1
	DB	120	112.6	99.81	2.188		66.26-154.8	1.369-3.461		3	3		1.14E+00	0	0
	HB	53	32	43.07	0.948		21.84-56	0.432-1.383		2	2		1.52E+01	0	0
Rb	WS	62.1	59.5	54.28	1.1196	0.662	33-71.29	0.6996-1.4214	0.4338-0.9541	1	1	1	1.54E+00	1	1
	DS	212	212	188	4.0207	2.8032	51-363.8	1.2393-8.028	0.5282-5.3318	2	2	2	-9.83E+00	0	0
	WB	56.9	62.3	59.27	1.3565	0.9095	42-110	0.9744-2.53	0.3785-2.0753	2	2	2	2.63E+00	1	1
	DB	163	161	151.6	3.2355	2.3106	62.68-259.4	1.295-5.415	1.2812-3.7519	2	2	2	-2.83E+00	0	0
	HB	157	150	152.9	3.3153	2.0544	95-210	2.0425-5.187	1.1888-3.198	2	2	3	2.73E+00	0	0

Arithmetic mean (n=11) of metal content in ashes of thin (up to 4 mm diameter) and thick twigs; metal content in twigs and crowns based on the twig, crown dry weight.
The range for metal concentrations measured in twig ashes, twigs (DW) and crowns (DW) is shown.
Seasonal category 1 indicated that SD for multiple samplings is higher than seasonal SD; category 2 indicated that seasonal SD is higher than SD for multiple sampling, but does not exceed twice the value.
Category 3 indicates very high seasonal variations, where seasonal SD exceed more than twice the SD of multiple sampling.
The rate of phloem build-up is shown as a percentage of the crown element concentration per day.
The quality of element concentration in twig ashes and in the crown with the root water uptake is qualified as poor (0), good (1) and excellent (3).

Table 4: Group B elements in black spruce crowns in WS, DS, WB, DB and HB trees. Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs) and evaluation of the correlation between the crown element content and root water uptake.

		element content in twig ash		*seasonal average*			*element content range*			*seasonal category*			*phloem build-up*	*correlation with the root water uptake*	
		thin (ppm)	thick (ppm)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig)	twigs	crown	CR (TW) (%of CR conc./day)	ash	CR (TW)
Al	WS	0.27	0.18	0.207	0.0044		0.133-0.26	0.0021-0.0059		1	1		-1.66E+00	0	0
%	DS	0.35	0.32	0.31	0.0066		0.16-0.52	0.0039-0.0109		1	1		1.04E+01	0	0
	WB	0.25	0.16	0.193	0.0045		0.107-0.24	0.0023-0.0057		1	1		-2.94E+00	1	1
	DB	0.27	0.22	0.223	0.005		0.143-0.335	0.003-0.0079		2	2		5.90E+00	0	0
	HB	0.3	0.18	0.255	0.0056		0.182-0.36	0.0036-0.0077		1	1		2.10E+01	1	1
As	WS	2.6	3	2.214	0.0464	0.0193	0.12-0.337	0.025-0.070	0.0113-0.0403	1	1	2	2.12E+00	0	0
	DS	2.06	1.68	1.803	0.039	0.0167	0.65-2.8	0.013-0.059	0.006-0.025	1	1	1	1.11E+01	0	1
	WB	1.35	0.8	1.924	0.0439	0.018	0-5.3	0-0.1219	0-0.0223	2	2	2	8.60E-02	0	0
	DB	1.38	1.5	1.554	0.0343	0.0149	0.8-2.569	0.019-0.0498	0.0082-0.0221	1	1	1	7.72E-01	0	1
	HB	2.21	0.95	1.613	0.0379	0.0153	0-2.6	0-0.0642	0-0.029	2	2	2	1.01E+01	0	0
Au	WS	44.9	25.5	32.96	0.714	0.292	10-92.0	0.21-1.95	0.081-0.703	2	2	2	8.66E+00	0	1
ppb	DS	30.8	15.8	32.54	0.7092	0.318	17.75-50	0.33-1.13	0.168-0.510	2	2	2	9.19E+00	1	2
	WB	37.3	19.4	29.74	0.7	0.294	13.97-55.5	0.41-1.16	0.144-0.694	2	2	2	2.68E+00	0	1
	DB	43.2	23.5	31.39	0.689	0.311	9.85-44.61	0.204-1.108	0.116-0.556	1	1	1	1.08E+01	0	1
	HB	24.8	22.17	28.34	0.599	0.25	10.92-48	0.216-0.926	0.082-0.341	1	1	1	9.33E+00	0	1
Ba	WS	860	973	890.3	18.28	7.62	520-1190	11.02-24.86	3.76-16.79	2	2	2	-6.88E+00	0	1
	DS	1144	1416	1258	27.28	12.648	757.7-1900	16.83-46.17	6.83-17.34	1	1	1	-5.32E+00	1	0
	WB	886	992	811	18.61	8.6377	520-1250	11.554-28.11	3.86-14.41	1	1	1	-6.36E+00	0	2
	DB	1266	1265	1287	27.66	14.096	719.2-2600	13.94-54.34	7.04-29.12	2	2	2	-6.42E-01	0	2
	HB	935	988	768	16.9	7.5873	510-1100	12.42-26.4	3.68-15.47	2	2	2	-9.20E+00	0	0
Br	WS	34.7	37	33.1	0.672	0.6893	24-52	0.422-1.102	0.49-1.01	1	1	1	-8.89E+00	0	1
	DS	26.2	19.8	23.6	0.515	0.5723	12.42-36.5	0.23-0.766	0.31-0.82	1	1	1	1.20E+01	0	1
	WB	20.8	20.4	22.8	0.526	0.5411	'11-44	0.338-1.002	0.381-0.706	3	2	1	-2.01E+00	2	1
	DB	20.8	20.1	19.3	0.423	0.5246	14.91-24.5	0.303-0.576	0.387-0.813	2	2	2	-1.21E+00	1	0
	HB	19.3	19.7	22.5	0.476	0.522	16.19-29	0.324-0.683	0.326-0.738	1	1	1	-1.49E+01	0	2
Cd	WS	1.67	1.7	1.32	0.0279		0.6-1.705	0.0128-0.0509		2	1		-7.31E+00	2	0
	DS	1.88	1.6	1.53	0.0335		1.061-2.2	0.0236-0.0535		1	1		2.69E+00	0	0
	WB	1.2	0.6	1.21	0.0279		0-2.6	0-0.0567		2	2		-6.99E+00	1	0
	DB	1.08	0.92	1.47	0.0323		0-2.676	0-0.0629		2	2		3.35E-01	0	2
	HB	1.3	0.3	1.22	0.0269		0-2.2	0-0.0543		1	2		1.18E+01	0	0
Cr	WS	14.4	13.6	12.5	0.263	0.1057	8.104-16	0.124-0.338	0.079-0.225	1	1	3	2.07E-01	0	1
	DS	14.8	15	14.5	0.311	0.1284	9.0-23	0.201-0.483	0.098-0.196	1	1	1	8.96E+00	0	1
	WB	13.9	8.4	10	0.235	0.0905	6.23-15	0.134-0.345	0.0534-0.166	1	1	2	-2.04E+00	0	2
	DB	15.4	16.9	16.1	0.345	0.1448	9.15-21.41	0.206-0.435	0.112-0.181	2	2	1	6.32E-01	2	1
	HB	18.3	15	16.1	0.351	0.1433	12.59-25	0.252-0.538	0.107-0.22	1	1	1	2.69E+00	0	2

**Table 4: Group B elements in black spruce crowns in WS, DS, WB, DB and HB trees.
Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs)
and evaluation of the correlation between the crown element content and root water uptake. (continued)**

		element content in twig ash		*seasonal average*			*element content range*			*seasonal category*			*phloem build-up*	*correlation with the root water uptake*	
		thin (ppm)	thick (ppm)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig)	twigs	crown	CR (TW) (%of CR conc./day)	ash	CR (TW)
Cs	WS	0.63	0.29	0.534	0.0108	0.0082	0-1.65	0-0.0327	0-0.0245	1	1	1	7.62E+00	0	0
	DS	1.7	1.46	1.506	0.0324	0.0268	1.1-1.75	0.022-0.394	0.0209-0.0325	1	1	1	-1.80E+00	0	1
	WB	0.83	0.64	0.711	0.0165	0.0133	0-1.6	0-0.0368	0-0.0095	1	1	1	-2.90E+00	1	0
	DB	0.86	0.92	1.077	0.0226	0.0214	0.627-1.5	0.0123-0.0348	0.0155-0.0373	1	1	2	3.70E+00	0	0
	HB	1.17	0.97	1.084	0.0235	0.0192	0.819-1.7	0.0155-0.042	0.00541-0.012	2	2	2	1.27E+00	1	2
Hf	WS	2.16	1.82	0.526	0.0111	0.004	0-0.9	0-0.019	0-0.0056	1	1	2	1.76E+01	0	0
	DS	2.25	1.72	0.554	0.0127	0.0042	0-1.5	0-0.0315	0-0.0111	1	1	1	2.14E+01	1	1
	WB	2.37	1.91	0.377	0.0088	0.0031	0-0.9	0-0.0209	0-0.0059	1	1	2	8.06E-01	0	2
	DB	2.21	1.89	0.359	0.0076	0.0026	0-0.942	0-0.0183	0-0.0064	1	1	1	4.49E+00	0	0
	HB	2.22	1.76	0.637	0.0139	0.0048	0-1.2	0-0.0232	0-0.0078	1	1	2	1.17E+01	2	0
Na	WS	2365	2043	1841	38.76	15.1	1350-2232	28.62-47.45	9.47-33.19	1	1	3	8.15E+00	0	0
	DS	2468	2218	2189	46.83	19.05	1400-3800	31.82-79.8	12.17-31.71	1	1	1	9.98E+00	0	0
	WB	2248	1336	1579	36.9	14.023	1180-2140	26.11-49.22	10.43-23.71	1	1	1	7.31E-01	1	2
	DB	1905	1809	1815	39.96	16.114	1316-2748	24.5-58.16	9.65-21.65	2	2	2	1.40E+00	0	1
	HB	2630	1709	2236	48.72	19.311	1437-3300	28.44-70.95	12.28-28.9	1	1	2	1.17E+01	0	2
Pb	WS	11.9	7	7.87	0.17		4.86-12	0.074-0.266		1	1		5.72E+00	0	0
	DS	17.9	11.8	12.51	0.272		4.0-22	0.089-0.462		1	1		9.86E+00	0	0
	WB	12.5	6.25	10.41	0.242		6.0-14.0	0.135-0.365		1	1		-4.16E+00	0	0
	DB	10.8	7.4	8.92	0.199		3.58-13.38	0.074-0.314		1	1		1.34E+00	0	0
	HB	13	6.7	10.12	0.221		5.4-20	0.108-0.43		1	1		3.23E+01	0	0
Sb	WS	0.22	0.23	0.206	0.0042	0.00179	0.1-0.298	0.00195-0.00633	0.00084-0.00323	1	1	1	2.60E+00	0	0
	DS	0.26	0.18	0.161	0.00346	0.00151	0-0.3	0-0.0063	0-0.0027	1	1	1	3.63E+01	0	0
	WB	0.21	0.1	0.188	0.00451	0.00186	0-0.3	0-0.00714	0-0.00352	2	2	2	-1.34E+00	0	2
	DB	0.2	0.17	0.163	0.0036	0.00161	0-0.25	0-0.00563	0-0.00321	1	1	1	4.16E+00	2	2
	HB	0.23	0.15	0.22	0.00481	0.00206	0.091-0.4	0.0018-0.00772	0.00075-0.00316	2	2	2	3.03E+00	0	0
Sc	WS	1.29	1.05	1.055	0.0223	0.0086	0.805-1.21	0.0149-0.0271	0.006-0.0191	1	1	3	5.40E+00	0	0
	DS	1.24	1.12	1.138	0.0244	0.0098	0.7-2.1	0.0156-0.0441	0.007-0.0174	1	1	1	1.15E+01	0	0
	WB	1.37	0.9	0.825	0.0191	0.0072	0.5-1	0.0134-0.0238	0.0053-0.0109	1	1	1	-7.44E-01	0	2
	DB	0.98	0.9	0.911	0.0201	0.008	0.582-1.284	0.0136-0.0288	0.0055-0.0106	2	2	2	2.21E+00	0	2
	HB	1.1	0.7	1.138	0.0249	0.0098	0.728-1.7	0.0144-0.0366	0.0054-0.0146	1	1	1	9.63E+00	0	1
Sr	WS	935	845	812	17.3	7.8441	0-1185	0-26.78	0-12.77	2	2	2	-6.96E+00	0	0
	DS	530	432	552	12.38	6.7845	0-1155	0-25.34	0-14.60	3	2	2	-1.24E+01	0	0
	WB	1087	1080	819	19.61	11.325	0-1400	0-42.56	0-31.731	3	2	2	-4.05E+00	1	1
	DB	676	629	628	13.21	8.4086	0-880	0-22.79	0-9.93	3	3	2	-6.47E-01	1	1
	HB	1268	1117	1130	24.24	12.451	846.1-1550	16.74-35.64	4.74-18.30	2	2	2	-1.46E+01	0	1

Table 4: Group B elements in black spruce crowns in WS, DS, WB, DB and HB trees. Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs) and evaluation of the correlation between the crown element content and root water uptake. (continued)

		element content in twig ash		*seasonal average*			*element content range*			*seasonal category*			*phloem build-up*	*correlation with the root water uptake*	
		thin (ppm)	thick (ppm)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig)	twigs	crown	CR (TW) (%of CR conc./day)	ash	CR (TW)
Th	WS	1.15	0.59	0.796	0.0176	0.0064	0.3-1.15	0.0097-0.0249	0.0022-0.0173	1	1	1	6.41E+00	0	0
	DS	1.24	0.8	0.989	0.0212	0.0083	0.7-1.6	0.0156-0.0336	0.0056-0.0143	1	1	1	1.98E+01	0	0
	WB	1.08	0.51	0.666	0.0157	0.0056	0-1.0	0-0.021	0-0.0072	1	2	1	-1.08E+00	0	0
	DB	0.83	0.8	0.861	0.0187	0.0073	0.58-1.37	0.011-0.0288	0.0052-0.0109	2	2	2	2.35E+00	0	0
	HB	1.2	0.8	1.067	0.0231	0.0088	0.819-1.4	0.0162-0.0342	0.0056-0.0136	1	1	2	1.36E+01	2	2
V	WS	6.25	4.25	4.9	0.105		3.241-6	0.050-0.1356		2	1		-3.00E+00	0	0
	DS	5.75	3.25	5.52	0.118		2-12.0	0.045-0.252		1	1		1.63E+01	0	0
	WB	5.75	3.25	4.21	0.097		1.78-6.0	0.038-0.143		1	1		-3.43E+00	1	1
	DB	4.8	4	4.06	0.09		3.31-6.69	0.074-0.157		2	2		7.00E+00	0	0
	HB	7	4.3	5.95	0.131		3.64-8.0	0.072-0.198		1	1		2.14E+01	1	1
W	WS	37.9	28	30.9	0.649		0-40.0	0-0.904		2	2		2.26E+00	0	0
	DS	36	24.4	25.8	0.567		10-40.0	0.232-0.972		2	2		6.95E+00	2	2
	WB	40	32	29.7	0.69		0-40.0	0-0.89		3	2		1.31E+00	0	0
	DB	38	8.4	28	0.61		16.6-44.6	0.37-1.048		2	2		4.67E-01	2	2
	HB	40	33.5	35	0.8		18.2-60.0	0.36-1.48		3	3		6.30E-01	0	0

Arithmetic mean (n=11) of metal content in ashes of thin (up to 4 mm diameter) and thick twigs; metal content in twigs and crowns based on the twig, crown dry weight.
The range for metal concentrations measured in twig ashes, twigs (DW) and crowns (DW) is shown.
Seasonal category 1 indicated that SD for multiple samplings is higher than seasonal SD; category 2 indicated that seasonal SD is higher than SD for multiple sampling, but does not exceed twice the value.
Category 3 indicates very high seasonal variations, where seasonal SD exceed more than twice the SD of multiple sampling.
The rate of phloem build-up is shown as a percentage of the crown element concentration per day.
The quality of element concentration in twig ashes and in the crown with the root water uptake is qualified as poor (0), good (1) and excellent (3).

**Table 5: Group C elements in black spruce crowns in WS, DS, WB, DB and HB trees.
Element content in thin and thick twigs, seasonal averages, phloem buildup values in crown (twigs) and evaluation of the correlation between the crown element content and root water uptake.**

		element content in twig ash			*seasonal average*		*element content range*			*seasonal category*			*phloem build-up*	*correlation with the root water uptake*	
		thin (ppm)	thick (ppm)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash (twig) (ppm)	twigs (ppm/DW)	crown (ppm/DW)	ash	twigs	crown	crown or twig (%of CR conc./day)	ash	crown
Ce	WS	8.75	3.9	5.87	0.1297	0.0482	0-9	0-0.203	0-0.659	2	2	3	3.84E+00	0	1
	DS	9.4	8	8.21	0.1769	0.0689	5.324-15	0.098-0.315	0.0423-0.121	1	1	1	1.41E+01	0	0
	WB	8.4	2.4	5.33	0.1267	0.0456	0-7.5	0-0.167	0-0.0759	1	1	1	1.04E+00	0	2
	DB	6.8	6.2	6.30	0.139	0.0541	3.744-9.418	0.095-0.202	0.0295-0.0826	3	2	2	2.58E+00	0	0
	HB	9.2	4.7	7.38	0.1613	0.0618	5.46-10	0.108-0.215	0.0355-0.0958	1	1	2	2.09E+01	0	2
La	WS	4.81	3.3	3.57	0.0764	0.0285	2.674-4.5	0.041-0.087	0.0189-0.0284	1	1	3	6.11E+00	0	1
	DS	4.96	3.76	4.30	0.0922	0.00363	2.6-8.1	0.058-0.171	0.0219-0.0655	1	1	1	1.33E+02	0	0
	WB	4.3	2.5	3.11	0.072	0.0265	2.046-3.5	0.044-0.093	0.0172-0.0403	1	1	1	-1.80E-02	1	1
	DB	3.71	3	3.20	0.071	0.0273	1.75-4.8	0.043-0.099	0.0167-0.0376	3	2	2	2.35E+00	0	0
	HB	5.25	2.98	4.20	0.0916	0.0351	2.46-5.8	0.049-0.125	0.0167-0.0495	1	1	1	1.29E+01	0	1
Sm	WS	0.56	0.39	0.43	0.0092	0.00341	0.322-0.55	0.0076-0.0116	0.00231-0.00789	1	1	2	5.05E+00	0	1
	DS	0.6	0.46	0.50	0.0108	0.00427	0.3-1	0.0066-0.0115	0.00248-0.00811	1	1	1	1.44E+01	0	0
	WB	0.53	0.29	0.38	0.0089	0.00326	0.267-0.5	0.0058-0.012	0.00224-0.00481	1	1	1	-2.41E-01	0	2
	DB	0.41	0.36	0.38	0.0085	0.00327	0.25-0.558	0.0052-0.013	0.00199-0.00472	2	2	2	2.26E+00	0	1
	HB	0.62	0.35	0.51	0.011	0.00418	0.273-0.8	0.0054-0.0172	0.0019-0.00679	1	1	2	1.41E+01	0	2
Yb	WS	0.22	0.12	0.13	0.0029	0.0012	0-0.27	0-0.0054	0-0.0041	2	2	3	1.86E+01	0	2
	DS	0.29	0.18	0.26	0.0058	0.0023	0-0.43	0-0.009	0-0.0037	1	1	1	1.62E+01	0	1
	WB	0.23	0.13	0.18	0.0041	0.0017	0-0.32	0-0.0063	0-0.0028	1	1	1	-4.97E+00	0	2
	DB	0.19	0.17	0.16	0.0036	0.0015	0-0.25	0-0.059	0-0.0026	2	2	2	7.78E-01	0	0
	HB	0.29	0.08	0.16	0.0038	0.0016	0-0.34	0-0.0084	0-0.0036	1	1	1	2.73E+01	1	2

Arithmetic mean (n=11) of metal content in ashes of thin (up to 4 mm diameter) and thick twigs; metal content in twigs and crowns based on the twig, crown dry weight.
The range for metal concentrations measured in twig ashes, twigs (DW) and crowns (DW) is shown.
Seasonal category 1 indicated that SD for multiple samplings is higher than seasonal SD; category 2 indicated that seasonal SD is higher than SD for multiple sampling, but does not exceed twice the value.
Category 3 indicates very high seasonal variations, where seasonal SD exceed more than twice the SD of multiple sampling.
The rate of phloem build-up is shown as a percentage of the crown element concentration per day.
The quality of element concentration in twig ashes and in the crown with the root water uptake is qualified as poor (0), good (1) and excellent (3).

Table 6: Group A elements in black spruce outer bark.

		ASH %	Ca %	K %	Fe %	Mg %	P ppm	Mn ppm	Zn ppm	Cu ppm
WS	arithmetic mean	4.23	17.32	2.6	1.38	0.86	4423	1620	1260	56.7
	SD	0.66	2.914	0.29	0.13	0.1	644	344.3	438	6.28
	median	4.435	15.85	2.6	1.41	0.88	4320	1680	1150	57
DS	arithmetic mean	7.162	17.58	2.47	1.6	0.71	2824	2242	762	45.2
	SD	1.079	3.834	0.26	0.25	0.08	216	646.2	242	6.1
	median	7.441	17.69	2.53	1.62	0.71	2827	2316	756	44.6
WB	arithmetic mean	5.19	18.8	2.39	1.33	0.84	3514	1538	1038	46.4
	SD	0.811	2.404	0.25	0.19	0.15	646	419.5	265	6.54
	median	5.11	18.9	2.42	1.28	0.78	3120	1640	960	44
DB	arithmetic mean	6.153	19.03	2.45	1.38	0.74	2461	1766	745	43.4
	SD	0.992	2.581	0.49	0.17	0.07	337	626.8	115	6.31
	median	6.385	17.85	2.54	1.47	0.73	2430	1725	710	43
HB	arithmetic mean	8.194	13.4	2.92	1.71	1.06	1990	1350	808	34.4
	SD	0.881	1.987	0.59	0.23	0.25	500	283.5	231	7.8
	median	8.11	12.7	3.05	1.77	0.94	1990	1250	730	34

Essential elements (group A) in bark ashes (n=5)

Table 7: Group B elements in black spruce outer bark.

		ASH %	Ag ppm	Co ppm	Cs ppm	Ni ppm	Rb ppm
WS	arithmetic mean	4.23	0.4	7.667	1.42	50.2	51.3
	SD	0.66	5.27	0.516	0.18	5.76	13.9
	median	4.44	0.4	8	1.45	52	53
DS	arithmetic mean	7.16	0	10.6	1.54	52.4	62.6
	SD	1.08	0	0.894	0.36	6.07	14.5
	median	7.44	0	10	1.5	56	69
WB	arithmetic mean	5.19	0.4	8.4	1.34	44	50.6
	SD	0.81	5.27	0.548	0.36	8.72	11.5
	median	5.11	0.4	8	1.4	46	48
DB	arithmetic mean	6.15	0.333	9.333	1.3	48	57.5
	SD	0.99	0.163	0.516	0.33	9.12	10.3
	median	6.39	0.4	9	1.3	45	57
HB	arithmetic mean	8.19	0.08	9.2	1.3	42.8	68.2
	SD	0.88	0.179	1.095	1.03	7.16	11.3
	median	8.11	0	10	1.6	42	68

Nonessential elements (group B) in bark ashes (n=5)

most affected by the soil drainage were: Mn (5158, 11043 ppm in ash in W and D trees, respectively), Cu (148, 203 ppm in ash in W and D trees, respectively), Ag (0.8, 1.34 ppm in ash in W and D trees, respectively), Co (4.05,14.4 ppm in ash in W and D trees, respectively), Ni (29.9, 105 ppm in ash in W and D trees, respectively) and Rb (56.8,169.8 ppm in ash in W and D trees, respectively). These elements are pH sensitive. Differences between element content in thin and thick crown twigs also display the effects of site drainage (Table 4, 5). Seasonal changes were highest for essential elements and pH sensitive elements depending on the experimental group (Table 2, 3), including Au (range 9.85-92.0 ppb in ash), Sr (0-1550 ppm in ash) and W (0-60 ppm in ash, Table 4). A steady increase or decrease in metal twig concentration during the two month measuring season was not observed.

Essential elements: group A

Nine essential elements were analyzed in twig ashes of black spruce crowns and outer bark (Ca, K, Fe, Mg, P, Mn, Zn, Cu and Mo). The Mo concentrations in twigs and outer bark were below the detection limit and are not shown.

Essential elements are necessary for plant metabolism. These elements are generally not expected to be enriched in extremities (outer bark) due to physiological functions. The essential elements would be elevated in crown organs or lower branches. This assumption was found correct for most of the essential elements in that twig element concentration of essential elements exceeded the bark concentration by factors of two to eight (Table 9). Similar values of twig and bark metal concentration were found for Ca and P; Fe was more concentrated in bark than in twigs.

Manganese and Cu were the only essential elements with a significant difference between experimental groups. Trees growing on dry sites accumulated approximately 100% more Mn and 25-50% more Cu compared to trees growing on wet or moderately drained sites (Tables 2, 9, Appendix 1). This difference was partly reflected by similar concentration differences in bark ashes for Mn; no difference was found in bark ashes for Cu (Table 9). Similar concentrations of Zn and P are present in crown twigs in all groups. Elevated Zn and P concentrations in bark was documented from trees growing on wet sites as compared to trees growing on dry or moderately drained sites (Tables 6, 9).

Ca

A good correlation between root water uptake

Table 8: Group B, C, and D elements in black spruce outer bark.

		ASH %	Al %	Au ppb	Au ppm	Ba ppm	Br ppm	Cd ppm	Ce ppm	Cr ppm	Cs ppm	Eu ppm	Hf ppm	La ppm	Lu ppm	Na ppm	Nd ppm	Pb ppm
WS	arithmetic mean	4.23	0.81	21.67	4.5	2183	27.5	3.46	38	36.33	1.417	0.593	3.817	21.67	0.155	10193	18	110.4
	SD	0.66	0.082	8.091	1.226	966.3	10.11	0.96	4.1	4.274	0.183	0.113	0.458	2.503	0.028	1675	3.633	10.14
	median	4.435	0.81	18.5	4.35	2050	29.5	3.3	38.5	36.5	12.95	0.625	3.8	22.5	0.16	10545	19	114
DS	arithmetic mean	7.162	0.968	1.6	2.84	1680	40.2	2.72	46.8	42.4	1.54	0.642	3.98	27.6	0.168	11326	21.4	145.6
	SD	1.079	0.103	3.578	0.723	249	12.17	0.63	8.23	6.427	0.365	0.125	0.576	5.03	0.029	2331	4.159	29.98
	median	7.441	0.98	0	2.8	1600	33	2.6	48	43	23.68	0.7	4.2	29	0.17	11500	23	156
WB	arithmetic mean	5.19	0.832	12.6	3.58	1840	35.6	2.4	37.4	36.8	1.34	0.572	3.68	21	0.142	10026	17.2	101.2
	SD	0.811	0.124	8.62	0.705	493	7.232	0.79	5.73	4.147	0.358	0.061	0.349	3.24	0.019	1948	2.28	9.338
	median	5.11	0.84	68.41	19.69	26.79	20.31	32.8	15.3	11.27	26.7	10.66	9.491	15.43	13.55	19.43	13.26	9.227
DB	arithmetic mean	6.153	0.9	8.333	2.6	1257	33.67	1.74	38.5	40.67	1.3	0.558	3.5	21.83	0.125	10483	17	104
	SD	0.992	0.113	5.574	0.447	345.6	8.165	0.31	6.66	4.457	0.335	0.062	0.374	2.787	0.03	1359	2.28	13.34
	median	6.385	0.87	8	2.6	1245	35	1.8	37	40.5	25.74	0.55	3.65	22.5	0.125	10800	17	101
HB	arithmetic mean	8.194	1.064	11.2	2.9	916	17.6	1.2	50.8	45.2	1.3	0.68	4.42	29.8	0.136	15580	19.8	135.6
	SD	0.881	0.18	6.686	1.102	68.77	5.814	1.26	6.42	4.604	1.032	0.096	0.54	3.633	0.026	1699	1.789	29.44
	median	8.11	1.12	15	2.6	930	16	1.6	53	46	79.38	0.75	4.6	31	0.14	16500	20	134

		Sb ppm	Sc ppm	Sm ppm	Sr ppm	Ti %	Th ppm	U ppm	V ppm	Yb ppm	Y ppm	Zr ppm
WS	arithmetic mean	0.917	3.833333	2.2	677	0.05	5.7	1.13	20.2	0.862	4.8	10.2
	SD	0.117	0.40332	0.21	227	0.01	0.94	0.24	1.48	0.095	1.095	1.483
	median	0.8	3.9	2.25	629	0.05	5.7	1.1	20	0.89	5	10
DS	arithmetic mean	0.88	4.18	2.6	296	0.068	7.8	1.32	22.8	0.93	5.6	12.4
	SD	0.217	0.657267	0.412	24.8	0.011	1.51	0.36	3.03	0.135	0.894	2.191
	median	0.9	4.2	2.7	308	0.06	7.7	1.4	24	0.93	6	12
WB	arithmetic mean	0.76	3.72	2.08	571	0.048	5.8	1.22	19.6	0.776	4.4	8.8
	SD	0.195	0.56745	0.286	219	0.011	1.21	0.2	2.61	0.08	0.894	2.28
	median	25.65	15.25404	13.77	38.4	22.82	20.9	16.8	13.3	10.33	20.33	25.91
DB	arithmetic mean	0.667	3.65	2.067	362	0.058	6.52	1.13	20.6	0.758	4.4	11.6
	SD	0.103	0.550454	0.301	101	0.004	0.95	0.19	2.97	0.104	0.894	1.673
	median	0.7	3.55	2.15	296	0.06	6.65	1.15	20	0.785	4	11
HB	arithmetic mean	0.56	4.28	2.56	391	0.096	9.88	1.7	23.6	0.772	4.4	16.4
	SD	0.134	0.589067	0.288	114	0.017	1.19	0.25	4.34	0.138	0.894	2.191
	median	0.5	4.6	2.7	356	0.1	10	1.8	26	0.74	4	18

Elements (group B, C and D) in bark ashes (n=5)

Table 9: Seasonal average of essential elements in group A twig ashes (TW) and average element concentration in outer bark (OB).

	Ca %	K %	Fe %	Mg %	P ppm	Mn ppm	Zn ppm	Cu ppm
WS-TW	17.32	19.23	0.36	5.33	38021	4785	2056	137.6
WS-OB	17.32	2.60	1.38	0.86	4423	1620	1260	56.67
DS-TW	16.39	19.34	0.40	4.28	37418	10712	1734	211
DS-OB	17.58	2.47	1.60	0.71	2824	2242	762	45.2
WB-TW	17.94	18.16	0.29	5.0	35799	5531	1795	154
WB-OB	18.8	2.39	1.33	0.84	3514	1538	1038	46.4
DB-TW	17.75	16.89	0.33	4.59	33374	11373	1610	191.3
DB-OB	19.03	2.45	1.38	0.74	2461	1766	745	43.4
HB-TW	16.64	18.5	0.39	5.27	34334	5029	1859	123.8
HB-OB	13.4	2.92	1.71	1.06	1990	1350	808	34.4

and Ca crown content was obtained for trees growing on well or partially drained sites (WS, WB and HB, Appendix 2). However, the seasonal SD did not substantially exceed the average SD of multiple samplings indicating that seasonal changes are of a similar magnitude to differences caused by variability in the plant material combined with the analytical error (Appendix 1). Phloem buildup was uniformly negative for all experimental groups. Higher Ca concentration in thick twigs compared to thin twigs suggests that Ca is being concentrated in the central woody part of the twig compared to the bark, confirming similar published findings (Dunn, 1981, 1992). Low phloem buildup values are indicative of high Ca redistribution from the crown, possibly to the woody parts of the tree. This is attributed to the role of Ca as a major component of the cells that comprise the wood tissue. No differences in Ca twig concentration were found in trees of different experimental groups. The concentration of Ca in bark and twigs was similar with the exception of HB trees (Table 9). Bark of HB trees had a lower Ca concentration compared to trees of the WB and DB group.

K

Potassium is the most abundant element in plant tissues, the major cation forming the osmotic balance.

Table 10: Seasonal average of pH sensitive elements in group B twig ashes (TW) and average element concentration in outer bark (OB), well drained sites. Nd=not detected.

	Ag ppm	Co ppm	Ni ppm	Rb ppm
WS-TW	0.76	4.28	29.4	54.3
WS-OB	0.40	7.67	50.2	51.3
DS-TW	1.28	13.7	109.3	188
DS-OB	nd	10.6	52.4	62.6
WB-TW	0.84	3.83	30.7	59.3
WB-OB	0.40	8.40	44.0	50.6
DB-TW	1.40	10.8	99.8	152
DB-OB	0.33	9.33	48.0	57.5
HB-TW	0.71	3.91	43.1	153
HB-OB	0.08	9.2	42.8	68.2

Table 11: Seasonal average of elements in group B twig ashes (TW) and average element concentration in outer bark (OB). Non-essential elements in crown twigs of group B, variable drainage. Nd=not detected.

	Al %	As ppm	Au ppb	Ba ppm	Br ppm	Cd ppm	Cr ppm	Cs ppm	Hf ppm	Na ppm	Pb ppm	Sb ppm	Sc ppm	Sr ppm	Th ppm	V ppm	W ppm
WS-TW	0.21	2.21	33.0	890	33.1	1.32	12.5	0.53	0.53	1841	7.87	0.21	1.06	812	0.80	4.90	30.9
WS-OB	0.81	4.50	21.7	2183	27.5	3.46	36.3	1.42	3.82	10193	110	0.92	3.80	677	5.70	20.2	nd
DS-TW	0.31	1.80	32.5	1258	23.6	1.53	14.5	1.51	0.55	2189	12.5	0.16	1.14	552	0.99	5.52	25.8
DS-OB	0.97	2.84	1.60	1680	40.2	2.72	42.4	1.54	3.98	11326	146	0.88	4.20	296	7.80	22.8	nd
WB-TW	0.19	1.92	29.7	811	22.8	1.21	10.0	0.71	0.38	1579	10.4	0.19	0.83	819	0.67	4.21	29.7
WB-OB	0.83	3.58	12.6	1840	35.6	2.40	36.8	1.34	3.68	10026	101	0.76	3.70	571	5.80	19.6	nd
DB-TW	0.22	1.55	31.4	1287	19.3	1.47	16.1	1.08	0.36	1815	8.92	0.16	0.91	628	0.86	4.06	28.0
DB-OB	0.90	2.60	8.33	1257	33.7	1.74	40.7	1.30	3.50	10483	104	0.67	3.70	362	6.52	20.6	nd
HB-TW	0.26	1.61	28.3	768	22.5	1.22	16.1	1.08	0.64	2236	10.1	0.22	1.14	1130	1.07	5.95	35.0
HB-OB	1.06	2.90	11.2	916	17.6	1.20	45.2	1.30	4.42	15580	136	0.56	4.30	391	9.88	23.6	nd

Table 12: Seasonal average of rare-earth elements (REEs) in group C twig ashes and average element concentration in outer bark (OB).

	Ce ppm	La ppm	Sm ppm	Yb ppm
WS-TW	5.87	3.57	0.43	0.13
WS-OB	38.0	21.7	2.20	0.86
DS-TW	8.21	4.30	0.50	0.26
DS-OB	46.8	27.6	2.60	0.93
WB-TW	5.33	3.11	0.38	0.18
WB-OB	37.4	21.0	2.10	0.78
DB-TW	6.30	3.20	0.38	0.16
DB-OB	38.5	21.8	2.10	0.76
HB-TW	7.38	4.20	0.51	0.16
HB-OB	50.8	29.8	2.6	0.77

There is twice as much K present in needles, compared to twigs according to published data (Fedikow and Dunn, 1996). No significant differences in trees of the various test groups were found in any of the crown organs and outer bark. Thin and thick twigs contained K in similar concentrations in all groups (Table 2). Twig ashes contain approximately 8 times less K compared to twigs and this is attributed to the role of K as a osmoticum in living tree organs. Good correlation exists between root water uptake and K crown concentration in DS and HB trees (Appendix 2). The seasonal changes exceed the average SD measured within multiple samplings in most experimental groups (Appendix 1).

Mg

Magnesium is an important element involved in many metabolic and plasma membrane transport processes. Magnesium is also a part of chlorophyll molecule thereby providing an explanation for the relatively high Mg concentrations in living plant tissues. No significant differences in Mg content was observed between different experimental groups including crown organs and outer bark concentrations. Twig Mg contents are greater than 6.5 times that of bark, reflecting the metabolic role of Mg in living tissues. Relatively high phloem buildup values coinciding with low Mg bark concentration (Table 2, 9) suggest substantial Mg redistribution to the main tree branches. Good correlation between root water uptake and Mg twig concentration was found in trees of the HB, DS and WS groups. Changes in Mg twig content with root water uptake were negligible in trees of DB and WB groups (Appendix 2).

Fe

Iron plays an important role in respiratory and secondary metabolism enhanced during plant growth. Nevertheless, no significant increase in twig Fe content was detected during the measurement period (Appendix 9). The standard deviation was lower for the crown Fe content compared to the twig ash Fe content in four out of five experimental groups indicating high Fe redistribution within the crown during the survey (Appendix 1). Iron concentration in thin twigs was higher than in thick twigs in trees growing on poorly drained sites (Table 2). Iron is approximately three times more abundant in bark than in twigs; no differences between experimental groups were observed (Table 9). A good correlation between root water uptake and Fe crown content was found in trees with higher numbers of transpiring branches (WB, DB and HB) and thus higher water flux values (Table 2, Appendix 2).

Mn

Significantly higher concentrations of manganese were found in crown twigs from trees growing on well drained sites (DS = 10 712 ppm in ash, DB = 11 373 ppm in ash) compared to those of trees growing on wet sites (WS = 4 785 ppm in ash, WB = 5 531 ppm in ash). Approximately twice as much Mn was measured in crown twigs in DS and DB trees compared to WS, WB and HB trees, respectively (Table 2, Appendix 2). Manganese is a pH sensitive element that is mobilized during rainy periods from the soil surface and as a result of ponded drainage is made accessible to tree roots. On poorly drained sites this does not occur and as a result roots of trees growing on these sites are not exposed to higher metal concentrations. Changes in Mn twig content correlate with root water uptake in DB, DS (except one measurement) and HB trees (Appendix 2). The seasonal SD was higher than SD of multiple sampling in all experimental groups indicating that this might be a concern when samples are collected during periods characterized by substantially different weather conditions (Appendix 1). Higher concentrations of Mn were found in the bark of DS and DB trees, similarly to that observed in twigs, but this difference was less pronounced than in twigs (Table 2, 6, 9). Generally, there was about 4-7 times less Mn in outer bark compared to twig Mn content (Table 9).

P

Phosphorus is an important element involved in all metabolic processes in living plant tissues. The highest concentration is usually found in needles. Phosphorus concentrations in thin twigs was higher than in thick twigs in all experimental groups. Higher P content was documented in bark of WS and WB trees (Table 6). P concentration in bark is comparable with P concentration in crown twigs (Table 9). Higher P bark concentration was measured in trees growing on wet sites compared to trees growing on well drained sites within groups with similar root water uptake (WS - DS, WB - DB). A good correlation between twig P content and the root water uptake was found in trees growing on well drained sites (Table 2, Appendix 2). The magnitude of changes in P twig content with water uptake was very small in WB trees.

Zn

Zinc is an important element involved in plant carbohydrate and protein metabolism. No significant differences between Zn concentrations in thin or thick twigs, and crowns from trees of different experimental groups were observed (Table 2). In trees growing on wet sites significantly higher Zn content in bark was measured (WS = 1260 ppm, WB = 1038 ppm) compared to trees growing on dry or semiwet sites (DS = 762 ppm, DB = 745 ppm, HB = 808 ppm). These differences were not found in twigs of trees of corresponding groups. There was about twice as much Zn found in twigs compared to outer bark (Table 9). The Zn content in crowns correlates with root water uptake in trees growing on dry sites (Table 2, Appendix 2). Higher values of the seasonal SD compared to the SD calculated for multiple samplings indicate the potential need for an evaluation of seasonal weather effects when black spruce crowns are sampled (Appendix 1).

Cu

Copper is largely involved in respiratory and protein metabolism and essential to some photosynthetic processes. It is the second essential element identified that exhibits significant differences between the twigs from trees in different experimental groups. There was approximately 25-50% more Cu in crown twigs of trees growing on dry sites compared to trees growing on wet sites (Table 2). Copper as well as Mn is a pH sensitive element. Differences in element concentrations in twigs relating to site drainage characteristics were not observed in outer bark, probably due to relatively small Cu bark concentration (60-80 times lower compared to twig Cu concentration, Table 9). A good correlation between Cu twig content and the root water uptake was detected in trees with a higher number of branches and larger transpiration area (WB, DB and HB trees, Table 2, Appendix 2). Seasonal changes in Cu twig content exceeded differences obtained in multiple sampling suggesting some consideration of weather conditions might be prudent during geochemical surveys of this type (Appendix 1).

Nonessential elements: group B

Enriched elements — well drained sites

Four elements (Ag, Co, Ni and Rb) are enriched in twigs from trees growing on well drained sites compared to those growing on poorly drained sites (Table 3, Appendix 3). These elements are pH sensitive and may be concentrated in water saturated layers with better root-soil contact subsequent to mobilization by rain water. The seasonal variation in crown and twig concentration of these elements is relatively high (Appendix 3). The correlation of the root water uptake with the twig or crown element concentration in trees growing on well drained sites is poor compared to trees growing on poorly drained sites (Table 3, Appendix 4). All four elements were found in higher concentrations in crown twigs compared to outer bark in trees growing on well drained sites (Table 10).

Ag

Silver concentrations were approximately 80% higher in crown twigs from trees in the DS and DB groups compared to those from the WS, WB and HB groups (Table 3, 10). Silver is present in higher concentrations in thick compared to thin twigs (Table 3), reflecting high Ag accumulations reported for the woody part of twigs (Dunn, 1981). Similarly to Ca, negative phloem buildup values (Table 2, 3) indicate high redistribution from the crown, again, most probably to the trunk wood. A better correlation of Ag crown content (compared with the twig ash content) with the root water uptake (Table 3, Appendix 4) is the result of relatively high Ag concentrations in cones (Fedikow and Dunn, 1996). Silver concentrations in crowns correlates with root water uptake in trees of all experimental groups. Silver concentration in twigs is > twice as high as in outer bark (close to the detection limit), and as a result, observed differences are subject to large experimental error (Table 7, 10).

Co

Approximately three times more Co was measured in twigs of trees growing on well drained sites (DS = 1.28, DB = 1.40 ppm) compared to those from trees growing on poorly drained sites (WS = 0.76, WB = 0.84, HB = 0.71 ppm). Differences are not attributable to root water flux. Cobalt contents between thin and thick twigs are similar (Table 3). A good correlation between Co contents in crowns and root water uptake was documented for trees of WS, WB and HB groups (Table 3, Appendix 4). Seasonal changes were the highest for DB trees (Table 3, Appendix 3). Cobalt is commonly associated with Ni and platinum-group metals (PGM) and as such a careful evaluation of the geological characteristics of the sampling site should be done. Weather or seasonal changes in Co concentrations in bark are not anticipated since outer scaly bark is dead tissue. Accordingly, bark probably represents the preferred medium for biogeochemical surveys where Co is the element of major interest or as an indicator or pathfinder for platinum-group metals (Dunn et al., 1989).

Ni

Nickel was present in approximately 300% higher concentrations in crown twigs from trees growing on well drained sites (DS = 109.3, DB = 99.8) compared to trees growing on poorly drained or semi-wet sites (WS = 29.4 ppm, WB = 30.7 ppm, HB = 43.1 ppm). There was little difference in Ni content in thin and thick twigs from these trees (10-20%), about 80% higher Ni concentration occurs in thin twigs compared to thick twigs in trees growing on poorly drained or semi-wet sites (Table 3). This indicates higher relative Ni concentration in the woody part of twigs in DS and DB trees compared to WS, WB and HB trees. For the DS and DB trees low phloem buildup values were measured (Table 3) indicating higher Ni redistribution from the crown twigs. One might speculate on Ni “saturation” in twig bark possibly causing higher Ni concentration in the woody part (assuming relatively low Ni concentration in needles reported (cf. Fedikow and Dunn, 1996). The correlation between Ni content in twigs and root water uptake was poor for trees from the DS and DB groups in contrast to WS, WB and HB trees (Table 3, Appendix 4). Nickel concentration in the outer bark was similar to the twig Ni concentration in WS, WB and HB trees and no differences in bark Ni concentrations were detected between experimental groups (Table 10). The seasonal SD was higher than the average SD for multiple samplings in trees with high water flux (WB, DB and HB, Table 3, Appendix 3).

Rb

Approximately 300% more Rb was measured in crowns of trees growing on well drained and partially drained sites (DS = 188 ppm, DB = 152 ppm, HB = 153 ppm) compared to trees growing on poorly drained sites (WS = 54.3 ppm, WB = 59,3 ppm). These differences were not reflected in Rb contents of outer bark, that was of similar value as the Rb concentration in twigs from WB and WS trees (Table 10). There was no difference in Rb concentration in thin and thick twigs (Table 3). Low values for phloem buildup were measured in trees growing on well drained sites. For these trees, a poor correlation between root water uptake and Rb crown concentration was observed (Table 3, Appendix 4).

Elements with unchanged concentrations — well and poorly drained sites

For most of the elements of this group, higher concentrations were documented in outer bark compared to crown twigs (Table 11). The exception is Au, W and Sr. The bark and twig concentrations of Ba, Br, Cd and Cs were comparable.

Al

Approximately 80% more Al was measured in thin twigs compared to thick twigs from trees growing on wet or semi-wet sites (Table 4). For these trees a small phloem buildup was also measured, similar to that observed for Ni. The seasonal changes were comparable to differences in Al concentration in twigs measured for multiple samplings for most experimental groups. Good correlations between Al content of twig and the root water content was found for trees of WB and HB group (Table 4, Appendix 6). No differences were identified in the outer bark concentrations of Al between different experimental groups (Table 8). Aluminum concentration in outer bark was similar to the Al concentration in twigs (Table 11). Aluminum concentrations must be viewed with caution, however, as the twigs and bark samples were ashed in aluminum trays some contamination is possible.

As

Arsenic, sometimes considered an essential element (utilized for carbohydrate metabolism), was found in higher concentrations in the outer bark (average = 3.3 ppm) as compared to twigs (1.8 ppm). Arsenic concentrations in twigs were close to the detection limit and the differences in the As content between thin and thick twigs is not significant. Relatively high phloem buildup values were measured for trees of all experimental groups (Table 4). A good correlation of As content in crowns with the root water uptake was obtained for trees of the DS and DB groups (Table 4, Appendix 6). High SD values for multiple sampling indicate that seasonal changes might be negligible (Appendix 5). For higher As concentrations in soils (resulting possibly in higher As twig concentrations) the seasonal changes may be significant.

Au

Dunn and Scagel (1989) report the highest Au contents in black spruce twigs in the early spring. This observation could not be confirmed by results of this study, based on June and July measurements. There were no patterns other than a relatively good correlation between Au crown content and the root water uptake for all experimental groups (Table 4, Appendix 6). Similarly, a correlation was not observed for Au concentrations in twigs, indicating the importance of the crown morphology. This correlation might explain the good soil to plant correlation reported for Au (Dunn, 1992). The seasonal variations in Au concentrations in crowns are relatively high (lowest for DB = 9.9-44.6 ppb, highest for WS = 10-92 ppb, Table 4, Appendix 5) and correction for weather conditions (causing differences in water flux) should prove useful. Very high Au phloem buildup values suggest low redistribution of Au to other organs of the tree. Because approximately 100% more Au was found in thin (average 39.1 ppb in ash) twigs (with larger portions of bark) compared to thick twigs (21.1 ppb in ash), except for HB trees (Table 4), twig bark might be considered as the principal Au accumulation tissue. Additionally, crowns should be carefully evaluated according to the proportion of thick and thin twigs and values normalized with respect to the thin/thick twig ratio. Differences in twig Au content in trees of different experimental groups were not observed. However, more Au was measured in the outer bark of trees growing on poorly drained sites (Table 8). Gold contents in twigs approximated 30 ppb. This is more than three times background values reported for many plants in North America (Dunn, 1992).

Ba

A relatively high SD for multiple samplings was determined for Ba contents in twigs and crowns, making the differences between experimental groups and seasonal changes in the DS and WB groups insignificant (Appendix 6). Good correlation between Ba crown content and the root water uptake was determined for trees of the WS, WB and DB groups (Appendix 6). Lower Ba concentrations in the outer bark were measured for trees of the HB group (916 ppm) compared to other trees with high root water uptake rates (average of 1740 ppm). Similarly to Ag and Ca, phloem buildup values for all experimental groups were negative and high Ba redistribution might be expected (Table 4).

Br

Bromine in outer bark and twigs is present in similar concentrations (30.9 ppm and 24.3 ppm, respectively). Lower Br concentrations were measured in trees of the HB group (17.6 ppm) compared to trees of the DS, WB and DB groups (average = 34. 2 ppm). A good correlation between Br concentrations in crowns and root water uptake exists for trees growing on poorly drained or semi-wet sites (Appendix 6). Thin and thick twigs exhibited no difference in Br content.

Cd

Cadmium concentrations in crown twigs were close to the detection limit and therefore results are tenuous. There were no differences in Cd contents between thin and thick twigs (1.4 ppm and 1.0 ppm, respectively, Table 4). Seasonal analyses show good correlations between Cd concentrations in twigs and root water uptake singularly for trees of the DB group (Appendix 5). The projection of Cd content in twigs to the Cd crown content was not possible because of the lack of data above the detection limits (Fedikow and Dunn, 1996). Cadmium was measured in higher concentrations in the outer bark (average = 2.3 ppm) compared to twigs (1.3 ppm).

Cr

A high SD was measured for the INA analysis of Cr (Appendix 5); similar to the average SD for multiple samplings for the DS group (3.54 ppm and 4.12 ppm, respectively) and for the WB group (3.54 ppm and 4.71 ppm, respectively). A relatively high SD was noted for the rest of the experimental groups (approximately 60% of the average SD for multiple samplings, Appendix 5). High SD values suggest that the observed differences in experimental groups and seasonal variations are not significant. Nevertheless, Cr behaves similarly to Rb in terms of group behavior. Chromium in outer bark is approximately three times higher (40.3 ppm) than in twigs (13.8 ppm). No significant differences in the Cr content between thin and thick twigs were found (Table 4). A good correlation between Cr content in crowns and root water uptake was observed for all experimental groups.

Cs

The large SD in estimated Cs twig concentrations is attributable to numerous analyses at or below the lower limit of determination. Calculated differences between experimental groups were not significant, but Cs reflects similar patterns common for pH sensitive elements — a tendency towards higher element accumulation in trees growing on well drained sites (1.5 ppm in DS group, 1.08 ppm in DB group and 1.08 ppm in HB group compared to 0.53 ppm in WS and 0.71 in WB group). A good correlation for Cs crown concentration changes with the root water uptake was obtained only for trees of the DS and HB groups (Appendix 5). Cesium contents in outer bark are similar to those in twigs (Table 11). Seasonal variation was close to variations obtained for multiple samplings (Appendix 5).

Hf

Hafnium was detected in twigs and outer bark in low concentrations tending to accumulate in thin twigs compared to thick twigs (2.24 ppm vs. 1.82 ppm, respectively). No differences between experimental groups were identified for Hf concentrations in twigs or crowns (Table 4). The outer bark of trees of the HB group contained more Hf (4.42 ppm) compared to the trees of the WB and DB groups (3.68 and 3.50 ppm, respectively). High phloem buildup values for all tested groups were observed. A good water flux-Hf crown concentration correlation was obtained only for trees of the WB and DS groups (Table 4, Appendix 5).

Na

Sodium concentrations in crown twigs is approximately five times lower than in the outer bark (1932 and 11 522 ppm, respectively). There was 50% more Na in the outer bark of HB trees compared to the rest of the tested trees (Table 8). Higher Na concentrations were detected in thin twigs (WS = 2365 ppm, WB = 2248 ppm, HB = 2630 ppm) compared to thick twigs (WS = 2043 ppm, WB = 1336 ppm and HB = 1709 ppm) in trees growing on wet or semi-wet sites (Table 4). Sodium also displayed large differences between thin and thick twigs and in this regard is similar to Ni, Au, As and Hf. Phloem buildup values were high for all experimental groups (Table 4). A good correlation between root water uptake and Na concentrations in crowns was obtained for trees with large transpiring areas (WB, DB and HB groups; Table 4, Appendix 5). Seasonal variations compared favorably with variations in multiple samplings (Appendix 5).

Pb

Outer bark contains up to ten times the amount of Pb as crown twigs (119 ppm vs. 10 ppm, respectively). A substantial difference was also found in the Pb concentration in thin and thick twigs with up to 60% greater Pb contents in thin twigs (Table 4). Relatively high phloem buildup values were documented in three out of five experimental groups. The absence of a Pb concentration factor for cones made the projection from twig to crown Pb contents impossible. A poor correlation for twig Pb contents with the root water uptake was found for trees of all experimental groups. The poor correlation might be also caused by possible Pb release to the atmosphere (Luxmore et al., 1978). The seasonal Pb variations were comparable with the variations obtained for multiple samplings (Table 4, Appendix 5)).

Sb

Antimony was measured in outer bark at about five times higher concentration than in twigs (0.76 ppm and 0.19 ppm, respectively). Additionally, thin twigs contained more Sb than the thick twigs in trees of the WB (0.21 ppm and 0.1 ppm, respectively) and HB (0.23 ppm and 0.15 ppm, respectively) groups. Poor correlation between root water uptake and the Sb crown concentration was found for trees with lower water flux rates, including trees of HB groups (Table 4, Appendix 5). The standard deviation for Sb twig content estimated by multiple samplings was very high making any conclusions questionable. Seasonal variations were within the limits of average SD (Table 4, Appendix 5). Overall Sb contents were low and close to the lower limit of detection.

Sc

Scandium concentrations are higher in thin twigs than in thick twigs in trees of the WB group (1.37 ppm and 0.9 ppm, respectively) and the HB group (1.1 ppm and 0.7 ppm, respectively). No further differences in averaged values were found, either for twigs or for the outer bark in the experimental groups. The Sc content of outer bark was about four times higher than that for twigs (3.9 ppm and 1.0 ppm, respectively). A good correlation between root water uptake and Sc concentrations in crowns was documented for trees with a large number of branches and high water fluxes (Table 4, Appendix 5). This observation was not observed for Sc contents in twigs.

Sr

Strontium is the only element for which higher concentrations were found in thin and thick twigs from trees growing on wet or semi-wet sites (WS = 935 ppm and 845 ppm, WB = 1087 ppm and 1080 ppm, and HB = 1268 ppm and 1117 ppm, respectively). Trees growing on dry sites (DS = 530 ppm and 432 ppm, DB = 676 ppm and 629 ppm, respectively) contained lower Sr. No differences between thin and thick twig Strontium contents were detected. Strontium displayed high seasonal fluctuations which correlated with the root water uptake for trees of the WB, DB and HB groups (Table 4, Appendix 5). The outer bark Sr concentrations were similar to those found for twigs, with higher Sr content in bark of trees of WB and WS groups (571 and 677 ppm, respectively) compared to DB and DS groups (362 and 296 ppm, respectively). Phloem buildup values calculated for Sr crown content were all negative, similar to those calculated for Ba, Ag and Ca with similar or higher element content in thick twigs as compared to thin twigs (Table 4).

Th

Thorium content in thin twigs from trees growing on wet sites (WS = 1.15 ppm, WB = 1.08 ppm and

HB = 1.2 ppm) was higher than in thick twigs (WS = 0.59 ppm, WB = 0.51 ppm and HB = 0.8 ppm). High phloem buildup values were calculated for four out of five experimental groups (Table 4). Thorium concentrations were much higher in outer bark compared to twigs (7.14 ppm and 0.88 ppm, respectively). Thorium content in crowns correlated with root water uptake only in trees of the HB group (Table 4, Appendix 5). Seasonal variations were similar to variations calculated for multiple samplings (Table 4, Appendix 5).

V

Vanadium is much higher in outer bark as compared to twigs (21.36 ppm vs. 4.93 ppm, respectively). No differences in twig or bark V concentrations within experimental groups were detected. Vanadium was more concentrated in thin twigs with higher proportion of bark than in thick twigs (5.9 ppm and 3.2 ppm, respectively). The correlation between water flux and V concentration in twigs was good in trees of WB and HB groups (Appendix 6). The SD values for multiple samplings were very high in WB. They were particularly high in the DS group, which also displayed the highest seasonal variations (Appendix 5).

W

Tungsten is present in concentrations 30 times greater than detection limit in crown twigs and below the lower limits of determination in the outer bark samples. Thin twigs contain slightly higher concentrations of tungsten than thick twigs (38.4 ppm and 25.3 ppm, respectively) along with moderate, positive, phloem buildup values in all experimental groups (Table 4). Very high seasonal fluctuations were detected for all experimental groups (Table 4, Appendix 5). The water flux- twig W content correlation was very good in trees growing on well-drained sites (Table 4, Appendix 5). As in the case of Sr, Mn, Zn or Rb, weather conditions should be monitored during the sampling season to correct for changing conditions.

Rare-earth elements (REEs): group C

The contents of the REEs Ce, La, Sm and Yb in crown twigs were higher (about 1.5 times) in thin twigs as compared to thick twigs (Table 5). The concentration of REEs in the crowns was the highest in trees of the DS group. The phloem buildup values were relatively high with the lowest value for WB trees. The outer bark concentrations were always about five times higher compared to twig concentrations (Table 12). An excellent correlation between REE contents in the crowns and the root water uptake was obtained for trees growing on poorly drained or semi-wet sites (Table 5, Appendix 8).

The REEs Eu, Lu and Nd were detected in the outer bark in measurable concentrations, whereas the twig concentration of these elements was < the detection limit. No differences were detected between experimental groups in the outer bark concentrations of these elements (Table 8).

Other elements: group D

Titanium, U, Y and Zr were present in measurable concentrations in outer bark but not detected in the twigs. Titanium, U and Zr were documented in higher concentrations in trees of the HB group; no differences between experimental groups were detected for Y (Table 8).

DISCUSSION

A number of different models of elemental uptake and incorporation into vegetation have been published (Luxmore et al., 1978; Dixon et al., 1978). Although the entire process is complex and affected by a number of parameters, including bulk water flow, a good correlation between element crown content and root water uptake should demonstrate the dominating role of bulk water flow in element accumulation in the crown. This is important because it demonstrates that element concentrations in soil and groundwater will be proportionally reflected in the crowns of black spruce. Although the correlation between crown element content and root water uptake will also be affected by analytical precision, a surprisingly good correlation was found for a majority of metals in more than one half of the experimental groups. Elemental concentrations of K, Mn, P and Zn in crown or twig samples correlate well with the root water uptake in trees growing on well drained sites. This was also observed for nonessential elements such as Ag, Co, As, Au, Cd and W. Silver, Co and Au displayed good correlation in all experimental groups, whereas no correlation for Pb was observed for any of the groups. The concentration of the remainder of the analyzed elements was highly correlated with the bulk water flux in trees growing on wet or semi-wet sites. The element concentration in the crowns was not measured directly, it was calculated from measured twig concentrations using season-independent parameters derived from a model tree (Fedikow and Dunn, 1996). It was assumed that the patterns of metal enrichment within the crown tissues are consistent and not necessarily dependent on the metal concentration in the soil (Fedikow and Dunn, 1996). The quality of this projection was very good, judging by the number of good correlations obtained. It was also demonstrated that root water uptake is correlated with the metal concentration in the crowns. For twigs, affected by metal redistribution in the crowns, this correlation was less well-developed (Appendices 2, 4, 6 and 8). It might be assumed that for those elements and experimental groups for which a poor correlation was obtained a significant season-dependent element crown redistribution occurs which could not be reflected using season-independent parameters.

Differences in average seasonal twig concentrations were found only in trees growing on sites which were well or poorly drained. No differences were detected between trees with a high number of branches (high water flow rates) and those with a low number of branches. It is clear that the element concentration in the soil allowed the equilibration of the crown concentration by the phloem transport to the roots and/or to other plant organs. Metals attached to the cell walls (Redy and

Patrick, 1977) and in equilibrium with xylem and phloem metal concentrations would satisfy the requirements for equilibrated phloem transport. The differences between metal concentration in crowns of trees growing on well or poorly drained sites was found only for pH-sensitive metals. These metals might have been mobilized from the soil surface, drained and concentrated in a layer directly accessible to tree roots. It is probable that this "concentrating" mechanism is generally applicable – with biogeochemical enrichment tending to occur down slope as has been reported by Dunn (1995). Similar experiments for trees growing on sites with multi-element soil enrichment is recommended.

High phloem buildup values were in most cases correlated with higher metal content in thin twigs relative to the metal content in thick twigs (i.e. Au) and at the same time low floem buildup values were calculated for trees where more metals were found in thick twigs (i.e. Ca, Ag) that are enriched in woody parts. This is in agreement with previously published results that indicate high accumulation of Ag and Ca in the trunk wood (Dunn, 1981) and high accumulation of Au in twigs with the most recent growth (Dunn and Scagel, 1989). It also suggests that twig bark retains some metals thereby serving as a temporary "storage place", before they are redistributed by the phloem. It also shows that for other metals (e.g. Ca, Ag) such binding potential is very low.

This relatively detailed analysis of the element concentration in thin and thick twigs may be very important in assisting the development of new biogeochemical exploration techniques. A normalization factor in respect to the twig type can be calculated and the ratio of thin and thick twigs in each sample is relatively easy to establish. Significant differences in element concentrations between thick and thin twigs were documented for a number of elements including Au.

Metal enrichment in outer bark compared to crown twigs was found for Co and Cs; in trees growing on wet or semi-wet sites (Tables 3, 4, 6 and 7). The concentration of these metals in twigs in these trees was about two times lower compared to the outer bark concentration in trees growing on dry sites (Tables 3, 4). No metal enrichment was detected in trees growing on dry sites (Tables 3, 4). Similar but somewhat lower differences were found for Ni (Table 3). Iron, As, Ba, Cd, Cr, Hf, Na, Pb, Sb, Sc, Th and V were found in higher concentrations in the outer bark in all experimental groups. Similar findings were reported previously (Fedikow and Dunn, 1996) with the exception that Pb, Cd, Cr and Hf were found in higher concentrations in twigs. However, the site quality, with regards to soil enrichment by metals, was different and black spruce trees in this study were not growing near a known mineral deposit. It could be speculated that multi-element soil enrichment might cause an increase of the relative Pb, Cd, Cr and Hf content in twigs compared to outer bark, and that phloem buildup values for these elements were relatively high (Table 4). One hundred bark samples were collected in this study with the intent of establishing the possible effect of the bark quality (fine, coarse, semi-coarse) on the accumulated metal content. Unfortunately only a quarter of the bark sample analyses were available at the time of writing this report which therefore precluded development of any final conclusions.

Outer bark formed by dead phloem cells will not accumulate metals in values that directly reflect the metal uptake by the roots and metal concentration in the xylem, but will reflect phloem metal flux through the tree trunk. Thus, higher element concentrations in the bark compared to the crown might indicate rich element transport from shoot to root. A large increase in element concentration for the youngest ring in the wood xylem was reported for Zn and Ca (Dilabio et al., 1982) indicating an element-rich phloem transport.

Conclusions drawn from this study could be generally applied only for similar element soil enrichment, considered as background concentrations. Trees growing in metal enriched soil might be exposed to concentrations inducing metal stress. Heavy metal stress reduces the root growth and transpiration rate, affecting the growth rate of the tree (Kahle, 1993). Higher metal concentrations will also affect the root absorption power (Kovalevskiy, 1990). Different defence mechanisms employed by trees to avoid metal stress (Kahle, 1993, Salt et al., 1998) can lead to different metal redistribution within the tree tissues in metal enriched soil. Important data offered by this study, including the effect of the site drainage and metal redistribution within thin and thick twigs for metals of high interest to mineral explorationists could be affected by significant soil enrichment in metals. Similar study on sites with metal soil enrichment is strongly recommended.

CONCLUSIONS

1. During the two-month sampling season no significant increase or decrease in crown metal content, other than those directly attributable to the water uptake changes, were observed. Vegetation samples are often sampled over a prolonged period of time. To date, no study has been undertaken to determine the extent or nature of changes in element concentration in metabolically active plant tissue, such as black spruce crowns. This uncertainty may be responsible for decreased confidence in the results of biogeochemical surveys based on such vegetation samples. Based on this study the seasonal changes identified for some elements are attributed to the root water uptake rate and thus to the weather conditions. Explorationists might use this data set for evaluation of the element of interest in terms of seasonal variations and impact of the weather conditions.
2. Maxima or minima in crown element content were not attributable to a particular seasonal period, as would be expected if they were dependent on the crown development stage. The leader length indicative of the metabolic activity of the crown was not correlated with metal concentration. The nature of seasonal changes of element concentrations was shown to be unrelated to the metabolic changes occurring in the black spruce crown during the growth season. This is

an important observation for explorationists when they compare results obtained from tree crowns growing in areas with different onset of crown growth or comparing data from different years sampling programs.

3. The element content in the crowns was correlated with the root water uptake for the majority of metals regardless of experimental groups and indicates good soil-crown correlation. Good soil-crown correlation is essential for the use of black spruce crowns as a reliable biogeochemical survey media. For those elements exhibiting large variations directly correlated with water uptake, a normalization based on weather conditions is recommended.
4. The crown morphology (wide, narrow, packed, loose crown) did not affect the crown metal concentration. Variation in the morpholoogy of black spruce crowns does not compromise the accuracy of the data and is therefore very important for biogeochemical exploration.
5. The crown concentration of important elements such as Ag, Co, Ni and Rb is directly related to the site drainage. Careful evaluation of the sampling site is strongly recommended with elemental concentration normalized to site drainage type. The demonstrated importance of sampling site drainage is a very important result of this study. If Ag, Co, Ni and Rb as well as the essential elements Mn and Cu are the elements of interest, vegetation samples must be collected from trees of similar drainage in order not to compromise the interpretation of the results.
6. For some elements high phloem buildup values were measured, reaching in some cases 10% of elemental crown content per day (i.e. Au, As). Thus, where possible, it might be useful to cut the phloem pathway and let the crown twigs concentrate the element of interest.
7. Nickel, Au, Pb, Th, W, Ce, Sm and Yb were found in significantly higher concentrations in thin twigs compared to thick twigs in the black spruce crown. Careful sampling is recommended when these are the metals of interest. From data obtained by this study it is possible to adjust the sampling technique according to the element of interest. If the element of interest is Au, the study recommends separating thin and thick twigs. If it is Rb, there is no need for it, because differences in thin and thick twigs were not detected.
8. Higher seasonal variability was measured for essential elements and pH sensitive elements compared to the rest of the heavy and REE metals. This result can be useful to explorationists when elements of interest fall into the non-pH sensitive or REEs category. Sampling can be undertaken during any weather conditions without compromising data reliability.

ACKNOWLEDGEMENTS

First I must thank the Manitoba Department of Industry, Trade and Mines for giving me the opportunity to do this project. My greatest thanks belong to Dr. Mark Fedikow. Without his support, enthusiasm and expertise this project would never have been realized; his valuable remarks and his help with the final text editing were greatly appreciated. Special thanks to Dr. Erik Nielsen for his moral support, time and expertise and for counting the tree rings on more than 100 samples. Thanks also to Samir Hathout, who assisted with the measurements when I was in the field and helped with late night measurements. The knowledgeable management of Red Devil Heating Ltd. made the field measurements a success. Without the help of the technical services staff in the Jenpeg Hydro station I would have been unable to complete the field measurements as a result of difficulties with our power source. In particular I would like to acknowledge the overall logistical assistance offered to me by Darrell McKay of Manitoba Hydro. The constructive criticism and editorial comments of Dr. Alan Bailes is greatfully acknowledged.

REFERENCES

Dilabio, R.N.W., Rencz, A.N., and Egginton, P.A. 1982: Biogeochemical expression of a classic dispersal train of metalliferous till near Hopetown, Ontario; Canadian Journal of Earth Sciences, v. 19, p. 2297-2305.

Dixon, K.R., Luxmore R.J., and Begovich, C.L. 1978: CERES-Model of Forest Stand Biomass Dynamics for Predicting Trace Contaminant, Nutrient and Water Effects; Ecological Modelling, v. 5, p. 17-38, 93-114.

Dunn, C.E. 1981: The biogeochemical expression of deeply buried uranium mineralization in Saskatchewan, Canada; Journal of Geochemical Exploration, v. 15, p. 437-452.

Dunn, C.E. 1992: Biochemical exploration for deposits of the noble metals; ***in*** Noble metals and Biological Systems, ed. R.R. Brooks, CRC Press, Boca Raton, FL.

Dunn, C.E. 1995: Mineral exploration beneath temperate forests: the information supplied by trees; Exploration and Mining Geology, v. 4, no. 3, p. 197-204.

Dunn, C.E., Hall, G.E.M., and Hoffman, E.L. 1989: Platinum group metals in common plants of northern forests: developments in analytical methods, and the application of biogeochemistry to exploration strategies; Journal of Geochemical Exploration, v. 32, no. 1-3, p. 211-222.

Dunn, C.E. and Scagel, R.K. 1989: Tree top sampling from a helicopter - a new approach to gold exploration; Journal of Geochemical Exploration, v. 34, p. 255-270.

Fedikow, M.A.F and Dunn, C.E. 1996: The geochemistry of vegetation growing over the deeply buried Chisel North Zn-rich massive sulphide deposit, Snow Lake area; ***in*** EXTECH I: A Multidisciplinary Approach to Massive Sulphide Research in the Rusty Lake-Snow Lake Greenstone Belts, Manitoba, (ed.) G.F. Bonham-Carter, A.G. Galley, and G.E.M Hall, Geological Survey of Canada Bulletin 426, p. 225-255.

Kahle, H. 1993: Response of roots of trees to heavy metals; Environmental and Experimental Botany, v. 33, no. 1, p. 99-119.

Kovalevskiy, A.L. 1990: Sampling-object choice in mercury biogeochemical prospecting for ore deposits; Scripta Technica, v. 27, p. 92-100.

Luxmore, R.J., Begovich, C.L., and Dixon, K.R. 1978: Modelling solute uptake and incorporation into vegetation and litter; Ecological Modelling, v. 5, p. 137-171.

Redy, C.N. and Patrick, W.H. 1977: Effect of redox potential and pH on the uptake of cadmium and lead by rice plants; Journal of Environmental Quality, v. 6, p. 256-262.

Salt, D.E., Smith, R.D., Raskin, I. 1998: Phytoremediation; Annual Review of Plant Physiology and Plant Molecular Biology, v. 49, p. 643-668.