

Laser-ablation vs. bulk tissue ICP-MS for conifer tissue elemental analysis

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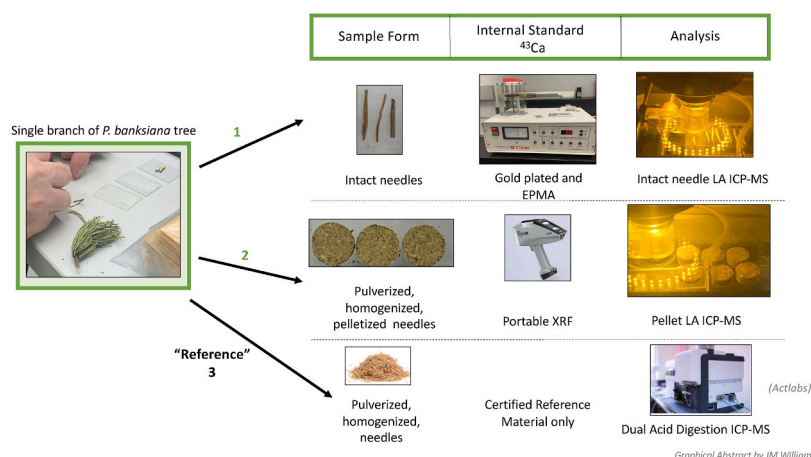
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HIGHLIGHTS

- LA ICP-MS on intact jack pine needles accurately measured most abundant elements in tree tissues.
- Grinding, sieving and pelletizing needles prior to LA ICP-MS did not yield more accurate analysis for most elements.
- LA ICP-MS values on intact needles were aligned with acid digestion ICP-MS values for nutrients and divergent for volatiles.

GRAPHICAL ABSTRACT



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ABSTRACT

Laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) has emerged as a robust tool for directly measuring trace elements in solid, intact samples. Laser ablation requires minimal sample preparation, whereas more conventional bulk sample analysis entails preliminary size reduction and acid digestion, and hence risks sample contamination and volatilization losses. LA ICP-MS may allow for rapid determination of elemental constitution in plants at low detection limits; however, application of LA ICP-MS on plant tissues is challenged by sample heterogeneity, as well as the lack of recognized standards for calibration and criteria for sample preparation. We analyzed needle samples from an adult jack pine (*Pinus banksiana* L.) tree through LA ICP-MS using a widely available NIST SRM 610 quartz calibration standard, with ^{43}Ca as an internal standard element measured by electron probe microanalysis. LA ICP-MS analyses were run on intact needle samples and on pulverized, homogenized and pelletized samples ($n = 21$), and compared to needles dried, ground, and analyzed in triplicate with aqua regia acid digestion and conventional ICP-MS. Overall, the LA ICP-MS measures on intact pine samples accurately predicted the chemical composition of pine needle tissue obtained by the bulk sample acid-digestion and ICP-MS method for most elements, while preliminary pulverizing and pelletizing did not result in greater accuracy or reduced bias. LA ICP-MS analysis of many plant nutrients (^{31}P , ^{24}Mg , ^{66}Zn) from both intact and

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pelletized tree needle samples matched the values obtained from acid-digestion ICP-MS most closely, while measures of less-stable metals (such as ^{140}Ce , ^{139}La , and ^{57}Fe) deviated more from acid-digested samples. Values of ^{39}K estimates varied between methods, as storage of ^{39}K is preferentially located in needle mesophyll layers beyond laser depths. Large deviations were found for volatile elements, with significantly lower ^{208}Pb concentrations measured by LA ICP-MS than acid-digested samples. We conclude that LA ICP-MS of intact tissues is a viable tool for accurate, non-destructive analysis for most elements and is particularly suitable for analysis of small samples and for volatile elements not amenable to conventional methods.

1. Introduction

Essential minerals and trace elements are fundamental to the survival and growth of plants, and a detailed understanding of both substrate and individual plant composition is necessary for optimizing yields and improving crop nutrition status (Kirkby, 2022). However, some elements can be phytotoxic even at trace levels and thus plant element uptake is also of interest in areas affected by soil, water, or atmospheric pollution. Trace contaminants stored in tree woody tissues, needles and leaves represent a concern for forest health and can also pose risks of food chain transfer to animals and humans (Gall et al., 2015). Methods of trace element detection must be sensitive to parts per billion or trillion levels for some contaminants, as allowable quantities in edible plants are commonly regulated by legally mandated thresholds (Briffa et al., 2020).

To date, most analyses of plant element uptake and storage have been based on harvesting and homogenization of ground plant specimens to allow for repeated, split-sample testing. The combination of pulverizing, sieving, and acid-digestion used by most commercial laboratories makes conventional inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectrometry (ICP-OES) necessarily destructive techniques requiring from a few hundred mg to several g of homogenized plant tissue per sample (Hansen et al., 2013; Pedrosa Diniz et al., 2019), and as such, the amount of raw sample material available can become a limiting factor. Studies into contaminant uptake and accumulation are impeded in the case of ongoing field trials with seedlings and saplings for which complete harvesting or extensive sampling is not possible. Sample processing, in particular mechanical grinding, can also introduce trace elements from ambient air or sample abrasion with mill parts (Hoffmann et al., 2000; Becker et al., 2008). In addition, certain elements, such as As, Cd, Pb, and Sb, show substantial losses via volatilization during acid digestion procedures (Da Silva et al., 2014; Somer, 2006), and may be greatly underestimated by conventional analyses (Lachas et al., 1999). Aqua regia acid digestion is among the most common digestions used, but also susceptible to atmospheric contamination and loss of volatile elements (Chen and Ma, 2001). As, Cd, and Pb can persist in soils and their ions may be toxic at trace amounts when accumulated by plants (Clemens and Ma, 2016), thus their accurate detection in plant tissues is relevant to ecotoxicology research.

Despite these shortcomings, acid digestion combined with ICP-MS (or ICP-OES) is in ubiquitous use for trace element analysis of plant tissues with such data informing toxicological assessments and environmental remediation practices. Research into optimizing sample preparation is increasing. For example, Zhang et al. (2018) proposed a double-layer tube for sample ashing with an attached cooling area to trap volatile elements, while Potocnik et al. (2021) and others suggest microwave digestion for reduced contamination and loss of volatile elements. Nevertheless, it is widely accepted that existing sample preparation techniques generally remain the largest source of error during analytical element measurement (Welna et al., 2011).

Laser ablation combined with ICP-MS is an alternative analysis technique that can directly measure intact plant components. In brief, a laser beam is fired at the plant surface which creates ablated material to be directly analyzed in the plasma torch of an attached ICP device (Su et al., 2012). LA ICP-MS allows for quantitative elemental analysis of a

range of materials due to its high sensitivity (Pozebon et al., 2017). It also has capacity for the spatial analysis of elements within biological samples, and can be used to test small, whole tissue samples directly (Hoffmann et al., 2000). Moreover, LA ICP-MS may detect heavy metals and minerals in distinct plant parts with minimal sample preparation (Kaiser et al., 2009) and may fill a testing gap between destructive, bulk analysis and nano-scale techniques.

In spite of these advantages, application of LA ICP-MS to plants remains uncommon (Amais et al., 2021). Hoffmann et al. (2000) used leaf samples of *Quercus robur* to test application of LA ICP-MS for measuring the spatial distribution of element concentrations in leaves. Punshon et al. (2004) successfully applied LA ICP-MS to measure Ni and U residues on *Andropogon elliptii* leaf surfaces. Kaiser et al. (2009) reported on the feasibility of LA ICP-MS for measuring Pb, Mg, and Cu in leaves of *Helianthus annuus* L. Shi et al. (2009) measured patterns of Cu and Zn in roots of *Cucumis sativus* L. with LA ICP-MS data. These trials have all applied LA ICP-MS to intact samples of angiosperms. LA ICP-MS has also been used to measure mercury concentrations and for tissue localization in fungi (Debeljak et al., 2018; Kavčič et al., 2019). To our knowledge, no prior study has applied LA ICP-MS to measure elements in conifer needle samples. There are also no published comparisons of LA ICP-MS on both intact and ground plant samples, nor any direct comparisons to traditional acid-digestion ICP-MS.

External calibration is fundamental to ensuring accuracy of element quantification in LA ICP-MS, regardless of sample type (Pan et al., 2022). Matrix effects in LA ICP-MS analysis refer to a discrepancy between plasma loads introduced to the ICP-MS device and are caused by variations in sample surfaces ablated per laser pulse. These effects reduce precision of measurements for most sample types (Günther et al., 2000), and as such, accurate adjustment to a matrix-matched standard is imperative (Miliszewicz et al., 2015).

Elemental fractionation has been observed to some extent in all laser ablation applications (Günther et al., 2000); the use of certified reference materials with known concentrations for elements of interest ensures more accurate calibration and reduced error from both elemental fractionation and matrix effects (Su et al., 2012). Nevertheless, there is a deficit of laser ablation-compatible standards and appropriate reference materials (Pozebon et al., 2017), specifically for organic plant and soil samples (Hoffmann et al., 2000). Certified reference materials exist for needles of select pine species (e.g., SRM 1575a for *Pinus taeda*) but are not available as intact specimens - the form best suited for LA ICP-MS analysis as per the National Institute of Standards and Technology (NIST) (NIST, 2012; Pan et al., 2022). Analyses of conifer needles present unique challenges in comparison to other reference materials due to a distinct needle matrix and the location of elements within samples. To date, mass fractions of B, Ca, K, Fe and Mn from limited trials have been particularly divergent from other agricultural and plant Standard Reference Materials (Mackey et al., 2004).

Pairing the use of a known internal standard element in tandem with an external Standard Reference Material should enhance accuracy of LA ICP-MS measurements. Selection of an internal standard element with adequate and homogeneous distribution throughout given samples is crucial to ensure accurate and precise measures using laser ablation techniques (Limbeck et al., 2015). Most commonly, internal standardization of organic samples has been performed with ^{13}C , however its high ionization potential and the risk of diffusion losses during the transfer

from laser to ICP equipment reduces effectiveness of ^{13}C calibration (Pan et al., 2022).

Here we test the application of LA ICP-MS for non-destructive element analysis of intact *Pinus banksiana* L. tissues and compare results to measures of pelletized, laser-ablated samples with those analyzed by conventional acid digestion followed by ICP-MS. Samples from a mature jack pine tree were used to conduct tissue elemental analyses with three distinct methods and calibration techniques. We tested the following hypotheses: 1) Laser-ablation ICP-MS analysis of both intact and homogenized samples will yield comparable element measurements to conventional acid-digestion ICP-MS analysis with the exception of known volatile elements (As, Cd, Sb, Pb), which we predict to have higher LA ICP-MS values given the reduced risk of volatilization losses; 2) Sample homogenization prior to LA ICP-MS will provide a closer match to conventional acid digestion combined with ICP-MS analysis for non-volatile elements.

2. Materials and methods

2.1. Sample preparation and referencing

One branch measuring approximately 1 m in length was harvested at a height of 1.5 m from a live *P. banksiana* tree, oven dried unwashed at 60 °C for 36 h, and all needles were subsequently removed and retained. Triplicate split-samples of dried needles were macerated in a Retsch cutting mill with internal 1 mm sieve (SM400 Cutting Mill with internal 1 mm sieve, Verder Scientific Companies, U.S.A.) then acid-digested with a mixture of hydrochloric and nitric acids at 95 °C for 2 h prior to dilution and elemental analysis with ICP-MS. Acid digestion ICP-MS analysis of needle tissue was conducted at Activation Laboratories Ltd. (Ancaster, Ontario). Quality control and recovery reporting was performed by Activation Laboratories Ltd. Through comparison of measured and certified values of CLV-1 and CLV-2 Certified Reference Materials (milled, ground spruce twigs and needles, respectively) obtained from the Canadian Certified Reference Materials Project (CanmetMINING Canadian Certified Reference Materials Project, 2023), in addition to conducting analysis on duplicate samples to obtain lower limit precision reporting. Duplicate analyses were conducted on identical split samples of ground, unwashed internal woody tissue from the harvested *P. banksiana* branch supplied to Activation Laboratories Ltd. Due to limitations on the element concentrations certified for CLV-2, recovery rates for most elements were determined based on CLV-1 (milled, ground spruce twigs). Recovery reporting for thirteen elements was provided by Activation Laboratories Ltd. With values defined in Table S2. Results from the third-party ICP-MS guided selection of an appropriate common element for the internal standardization of succeeding LA ICP-MS procedures. Calcium (^{43}Ca) was chosen for this based on its relative abundance across the needle tissue samples. Calcium isotopes have been used as an internal standard for analyses on geological and biological samples (e.g., Bellotto and Miekeley, 2000; Hanc et al., 2013) with the signal intensity of the ^{43}Ca isotope demonstrating a particularly strong match to those from elements of interest measured using LA ICP-MS (Miliszewicz et al., 2015).

2.2. Intact tree specimens

Three dried unwashed jack pine needles were randomly selected and mounted on transparent glass slides overlaid with clear, two-sided tape using sterilized tweezers (multiple random sample points per needle selected for each subsequent procedure). Two-sided tape placed atop glass slides served to affix samples with equal spacing and reduce movement during testing. Intact needle samples were first analyzed using an electron microprobe analyzer (EMPA) (JEOL JXA8230 5-WDS, JEOL, Tokyo, Japan) at the University of Toronto to non-destructively obtain independent values for ^{43}Ca composition. Slide-mounted samples were gold-coated using a sputter coater (Cressington 108auto,

Cressington Scientific Instruments, United Kingdom) at a uniform distance of 1 cm and current setting of 20 mA for 30 s/slide to reduce resistance and probability of electric charge accumulation on surfaces of the samples. A strip of conductive carbon tape over carbon paint was also applied across the slide on the extremities of each needle to further minimize surface electric charge. Three unique points on uniform surface sections of each needle were analyzed with the probe and triplicate measurements were averaged. Mean data from the EPMA were corrected by eliminating Au_2O_3 measures and recalibrating elemental composition under the assumption that Au_2O_3 stemmed entirely from the gold coating process. Carbon mass percent for jack pine needles was estimated based on current literature as 47.6% and used to adjust EPMA measurements (Thomas and Martin, 2012). Averages of triplicate measurements for ^{43}Ca were then applied as an internal standard (IS) for intact sample LA ICP-MS data interpretation. Samples were removed from gold-plated slides with sterilized tweezers and mounted onto unused, otherwise identical glass slides prior to laser ablation and analysis.

2.3. Pelletized tree specimens

Triplicate split-samples of the dried, pulverized and sieved needles prepared by Activation Laboratories were also used to generate compressed pellets (2.5 cm diameter, 1 cm height, particle size <100 μm) with a hydraulic pellet press and without binding agents. A representative measure for the internal reference element (^{43}Ca) was obtained by first analyzing the three pellets with a Bruker tracer 5 g portable XRF device (Bruker Corporation, U.S.A.) in soil-sample mode and using three beam wavelengths operated for 60 s each.

2.4. LA ICP-MS analysis

LA ICP-MS analyses were accomplished with a ESL193 excimer-based laser ablation system (Elemental Scientific Lasers, U.S.A.) paired with an Agilent 7900 quadrupole mass spectrometer (Agilent Technologies Inc., U.S.A.); settings and parameters are detailed in Table 1. An initial set of 12 analyses were conducted on three intact tree needles (2–6 analyses/needle depending on sample surface uniformity). External calibration was conducted using a unique NIST610 with glass matrix; the NIST sample was ablated and analyzed across four distinct linear trajectories with two sweeps mapped prior to and following each intact needle sample analysis. Intact tree needle samples were kept on distinct slides, whereas all six pellets were positioned onto one glass slide without two-sided tape. Similarly, two NIST610 sweeps were run prior to and following each group of analyses on sample pellets (four NIST610 sweeps + three pellet trajectories per pellet sample).

Table 1
LA ICP-MS measurement parameters.

Laser Conditions	
Wavelength	193 nm
Laser Ablation Intensity	70%
Frequency (Repetition Rate)	10 Hz
Spot Size	25 μm (samples), 100 μm (NIST610)
Average fluence	4.53 J/cm ²
Laser Line Length	600 μm
Pre-Ablation time	1 sweep at 60 μm /s.
Data Collection	
Sweeps	2
Dwell Time	0.1 ms (intact), 0.002–0.005 ms (pellet)
Isotopes	^7Li ^{24}Mg ^{27}Al ^{31}P ^{39}K ^{43}Ca ^{44}Ca ^{47}Ti ^{51}V ^{52}Cr ^{55}Mn ^{57}Fe ^{59}Co ^{60}Ni ^{63}Cu ^{66}Zn ^{75}As ^{88}Sr ^{95}Mo ^{107}Ag ^{111}Cd ^{118}Sn ^{121}Sb ^{137}Ba ^{139}La ^{140}Ce ^{197}Au ^{208}Pb

2.5. Data analysis

Data were analyzed with the R statistical programming environment (R Core Team, 2020). Data from LA ICP-MS and the internal standard values for ^{43}Ca were reduced using the MATLAB-based SILLS computer software (Signal Integration for Laboratory Laser Systems, The MathWorks Inc., 2021). The relationships among elemental concentration values determined by alternative methods were assessed using the linear regression of log-transformed values, based on mean element composition values. Pairs of analysis methods were fit using linear regression models for elements by group (major mineral nutrients, elements prone to volatilization, other potentially phytotoxic elements, and other elements). Regression r^2 values were used as an indicator of the overall consistency of values within element groups. Deviations of the relationship from 1:1 (slope = 1 and intercept = 0) were tested to detect consistent biases. Values for each element measured by the three methods were also compared for bias using a one-way analysis of variance (ANOVA) with significant response ($p < 0.05$) further assessed using Tukey's honest significant difference (HSD) post-hoc test to determine differences among the three methods. Prior to conducting ANOVA tests, data were verified for homogeneity of variance using the Bartlett test, and residuals were assessed for normality with Q-Q plots.

Relationships among elemental concentration values are presented with log-log axes in Figs. 1 and 2 (Figs. S1 and S2 in the Supplemental Information present this data on x-y axes scale).

3. Results

A linear model could accurately describe the relationship between LA ICP-MS measurements on both intact and homogenized, pelletized needle samples and the associated acid-digestion ICP-MS values ($r^2_{\text{intact}} = 0.916$, $r^2_{\text{pellet}} = 0.932$, Table S1). The crushing and pelletizing of needle samples prior to laser ablation resulted in more values with significant differences from associated acid digestion and ICP-MS measurements; however, this remained a minority of the total elements tested. LA ICP-MS elemental results from pellets and intact tissues remained within one standard deviation from one another for ^{24}Mg ($p = 0.6470$), ^{31}P ($p = 0.3160$), ^{52}Cr ($p = 0.3443$), ^{66}Zn ($p = 0.143$), ^{55}Mn ($p = 0.9989$), ^{55}Mo ($p = 0.1388$), and ^{47}Ti ($p = 0.0821$).

3.1. Plant mineral nutrients

Considering both intact and pellet samples, the analyses conducted by laser ablation ICP-MS corresponded most closely to conventional

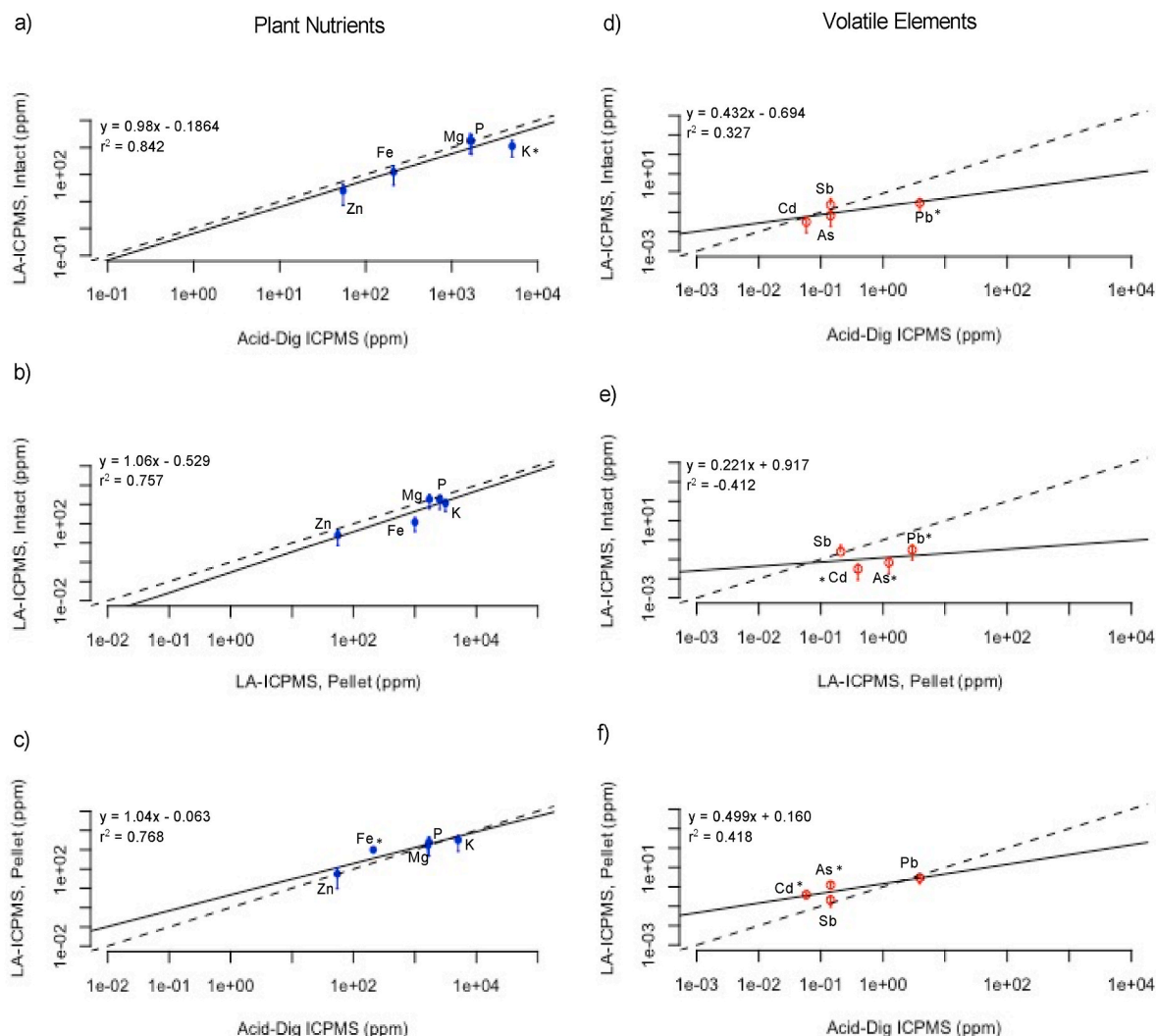


Fig. 1. Relationships for (a,b,c) major plant nutrients and (d,e,f) volatile elements between intact sample LA ICP-MS, pellet LA ICP-MS, and acid digestion ICP-MS for pine needles with values representing elemental composition. Element labels with * indicate deviation from a 1:1 relationship with significance at $p < 0.05$. Solid lines represent linear regression model fits significant at $p < 0.05$ and error bars represent $\pm 95\%$ confidence interval. Dashed lines represent 1:1 relationship. Axes are displayed on a log-log scale.

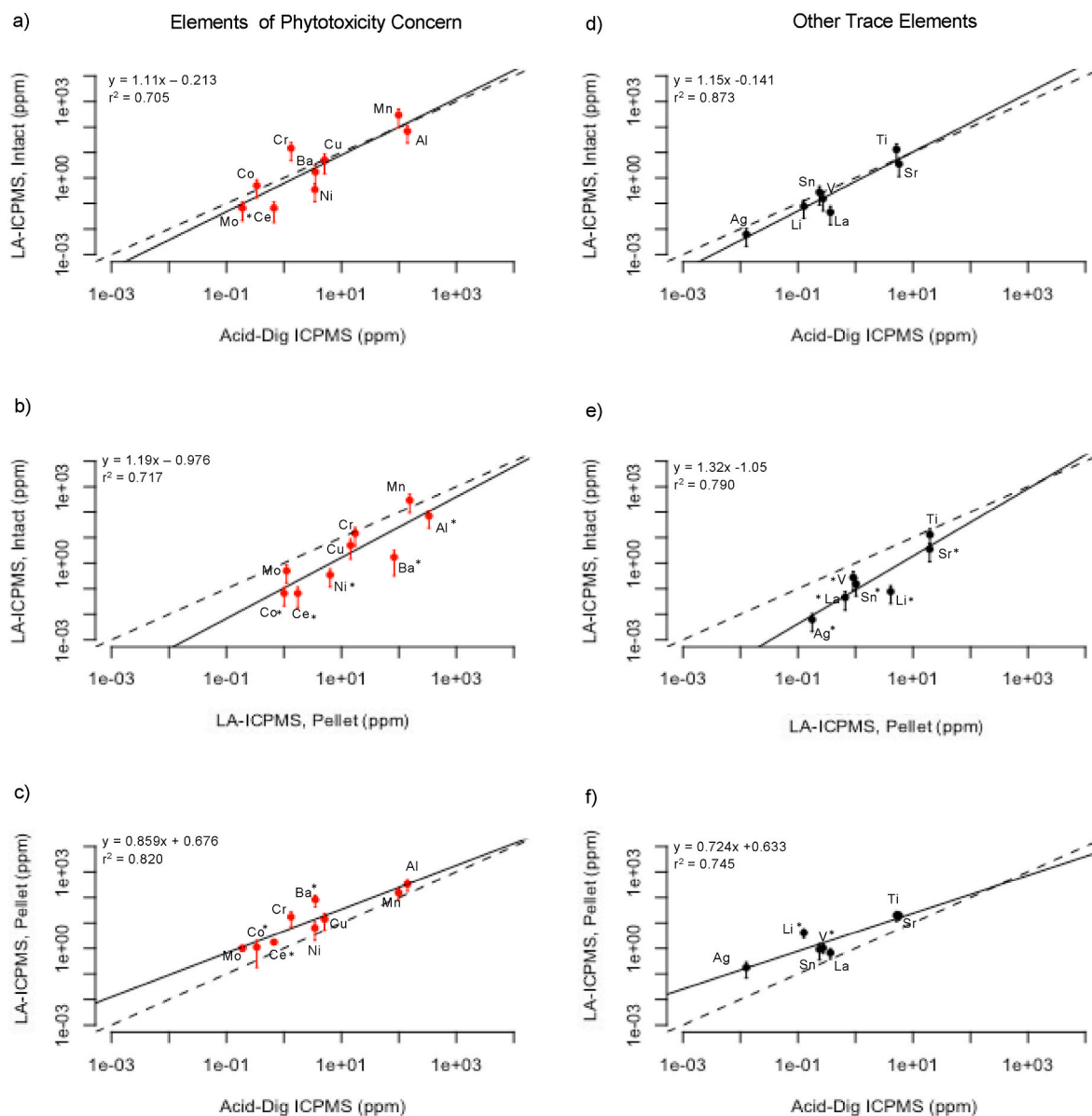


Fig. 2. Relationships for (a,b,c) elements of phytotoxicity concern and (d,e,f) other lower priority (trace) elements between intact sample LA ICP-MS, pellet LA ICP-MS, and acid digestion ICP-MS for pine needles with values representing elemental composition. Element labels with * indicate deviation from a 1:1 relationship with significance at $p < 0.05$. Solid lines represent linear regression model fits significant at $p < 0.05$ and error bars represent $\pm 95\%$ confidence interval. Dashed lines represent 1:1 relationship. Axes are displayed on a log-log scale.

acid-digestion and ICP-MS analysis for major plant nutrients measured (^{39}K , ^{31}P , ^{24}Mg , ^{66}Zn , ^{57}Fe) with $r_{\text{intact}}^2 = 0.842$, $r_{\text{pellet}}^2 = 0.768$. Though measured values closely matched a direct 1:1 relationship in the case of ^{24}Mg , ^{31}P , and ^{66}Zn (Fig. 1a–c), results for ^{39}K ($F_{(2,21)} = 5.63$, $p = 0.011$) and ^{57}Fe ($F_{(2,21)} = 27.2$, $p = 1.48 \times 10^{-6}$) were significantly different amongst the three methods. Results for ^{39}K from intact needle LA ICP-MS deviated most from other test methods, whereas pelletized sample LA ICP-MS results were within one SD from associated acid-digestion ICP-MS measurements (Fig. 1c). Conversely, LA ICP-MS analysis on intact needles yielded ^{57}Fe values that closely matched those from conventional acid digestion ICP-MS, but values from pelletized sample LA ICP-MS were significantly higher ($p = 0.00169$) (Fig. 1c).

3.2. Volatile toxic elements

Conventional acid digestion ICP-MS values corresponded to values obtained via intact needle LA ICP-MS in the case of most volatile

elements considered, namely ^{75}As ($F_{(2,21)} = 23.98$, $p = 0.912$), ^{111}Cd ($F_{(2,21)} = 43.46$, $p = 0.770$), and ^{121}Sb ($F_{(2,21)} = 0.204$, $p = 0.9945$). While the ^{121}Sb results obtained from both intact needle and pellet LA ICP-MS analyses corresponded closely to values from conventional ICP-MS, both ^{75}As and ^{111}Cd measures from pelletized LA ICP-MS were significantly higher than those from conventional acid digestion analysis (Fig. 1f). Laser-ablation ICP-MS on the intact needle samples resulted in measurements of ^{208}Pb that were significantly lower than those obtained through acid digestion ICP-MS ($F_{(2,21)} = 13.56$, $p = 0.0018$), though results from pelletized tissue samples aligned closely to those from acid-digestion ICP-MS (Fig. 1f). Overall, volatile element composition obtained from conventional acid-digestion ICP-MS did not correspond to LA ICP-MS measurements on either intact or pellet samples, with the deviation mostly attributable to ^{208}Pb results ($r_{\text{intact}}^2 = 0.327$; $r_{\text{pellet}}^2 = 0.418$; Fig. 1d–f).

3.3. Other elements

LA ICP-MS measurements on intact needles corresponded closely to those from conventional acid-digestion ICP-MS for most elements of phytotoxicity concern (^{95}Mo , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{55}Mn , ^{27}Al , ^{137}Ba), with the relationship between methods also fitting a linear regression model ($r^2_{\text{intact}} = 0.705$, Fig. 2a). Similarly, these elements measured through LA ICP-MS on homogenized pellets also fit a linear regression model with the conventional acid-digestion ICP-MS values. Among all other elements measured with laser ablation ICP-MS, only ^{140}Ce ($F_{(2,21)} = 23.0$, $p = 5.7 \times 10^{-6}$) results were significantly different between intact LA ICP-MS and conventional acid-digestion ICP-MS methods, whereas laser ablation ICP-MS measures of pellet samples deviated significantly from acid-digestion ICP-MS results for ^{137}Ba ($F_{(2,21)} = 13.38$, $p = 0.0119$), ^{59}Co ($F_{(2,21)} = 50.86$, $p = 0.0000530$), ^{88}Sr ($F_{(2,21)} = 17.66$, $p = 0.0172$), ^{51}V ($F_{(2,21)} = 16.05$, $p = 0.0207$), and ^7Li ($F_{(2,21)} = 24.66$, $p = 0.000763$); all values from LA ICP-MS analysis on pellets are significantly higher than corresponding acid-digestion ICP-MS values (Fig. 2c–f). The average La^{139} measures from intact needle LA ICP-MS was below acid-digested ICP-MS results, however the divergence was not statistically significant (Fig. 2b). Results from intact needle LA ICP-MS fit a linear regression model with corresponding acid digestion and ICP-MS measures for elements of phytotoxicity concern ($r^2 = 0.706$, Fig. 2a.) as well as for the group of elements considered with lower plant priority ($r^2 = 0.873$, Fig. 2d). A linear model could also describe relationships between measurements on pelletized samples analyzed with LA ICP-MS and values from conventional acid-digestion ICP-MS for phytotoxic elements ($r^2 = 0.820$, Fig. 2c) and the group of elements with lower plant priority considered ($r^2 = 0.745$, Fig. 2f). Pelletized samples measured with LA ICP-MS yielded significantly lower La^{139} values relative to the associated intact needle LA ICP-MS results ($F_{(2,21)} = 14.05$, $p = 0.0000880$, Fig. 2d).

4. Discussion

Of the 25 elements measured through intact needle LA ICP-MS, only three deviated significantly from the corresponding results obtained by conventional grinding, acid digestion and ICP-MS analysis: specifically, ^{39}K , ^{140}Ce , and ^{208}Pb . In contrast, LA ICP-MS conducted on pellets of crushed, homogenized, and compressed jack pine tissue yielded a higher number of measures with significant deviations from the acid digestion ICP-MS values (9/25, 36% of elements considered). These results suggest that LA ICP-MS conducted on intact conifer samples, rather than on ground, pelletized samples, may yield more comparable results to conventional acid digestion and ICP-MS. The strong agreement between intact sample LA ICP-MS and acid digestion ICP-MS also supports our hypothesis that the use of a NIST610 glass as an external, matrix-matched standard and ^{43}Ca as a common element determined via EPMA is a suitable calibration technique when applied to intact *Pinus banksiana* L. needle samples.

LA ICP-MS results from pellet samples exhibited exclusively positive deviations from the associated acid digestion ICP-MS determined elemental values for all 25 elements, indicating that for pelletized sample, LA ICP-MS may yield a positive bias compared to both intact sample LA ICP-MS and acid digestion ICP-MS procedures. Jiménez et al. (2007) studied the effects of several parameters on precision of LA ICP-MS multi-element analysis of compost pellets and found that material grinding time and variable particle sizes within the pellet were primary factors of error, with material heterogeneity contributing most to inaccuracy for measures of ^{59}Co , ^{111}Cd , and ^{170}Hg . Our results align with Jiménez et al.'s (2007) observations and suggest that the significant deviations we observed in pellet LA ICP-MS measures of ^{59}Co and ^{111}Cd concentrations may be due to heterogeneity of the ground needle material within each pressed pellet. Results thus suggest that pelletizing samples for LA ICP-MS analysis is counter-productive.

4.1. Plant mineral nutrients

Major plant nutrients (^{39}K , ^{57}Fe , ^{66}Zn , ^{31}P , ^{24}Mg) were measured in the highest concentrations and yielded results with the lowest bias across all three analysis methods relative to other element groups considered. Nutrient composition of intact needles and pellets measured through LA ICP-MS also fit linear regression models with corresponding acid-digestion ICP-MS values. The relatively high concentration of nutrients in *P. banksiana* needle tissue likely contributed to reduced variability across repeated samples and analysis techniques. The consistency of measurements we observed across analysis methods for plant nutrients aligns with our hypothesis that deviations would be primarily found in elements prone to volatilization during grinding and acid digestion. However, an exception is potassium: although ^{39}K measured on pellet samples closely matched the acid digestion ICP-MS results, ^{39}K composition of intact needles from LA ICP-MS analysis was significantly lower. The concentration of many essential and non-essential elements differs in individual needle layers of gymnosperms (Giertych et al., 1997; Pongrac et al., 2018). Kötschau et al. (2013) applied LA ICP-MS in order to map the location of various elements within leaves of *Helianthus annuus* and reported that, unlike other major plant nutrients, ^{39}K was enriched preferentially in leaf mesophyll layers, a finding also supported by the tissue-specific element profiles conducted on *Pinus sylvestris* L. samples by Pongrac et al. (2018), who described lowest ^{39}K in the epidermal needle layer. Our analysis of intact *P. banksiana* needle samples through LA ICP-MS may have predominantly captured needle epidermis composition, whereas analysis of ground, homogenized samples measured through pellet LA ICP-MS and via acid digestion and ICP-MS likely captured an integrated leaf profile, possibly resulting in the negative LA ICP-MS deviation for ^{39}K . Results from our preliminary study motivate additional follow-up assessments with larger sample sizes of both intact and ground, digested conifer needles in order to verify contrasts between ^{39}K measurements.

Measured ^{57}Fe was closely aligned between acid-digestion ICP-MS and intact needle LA ICP-MS analysis, but was significantly higher when measured through LA ICP-MS analysis conducted on the homogenized pellet samples. The localized concentration of ^{57}Fe in pine needles may be affected by variations in chlorophyll content from needle tip to base (Giertych et al., 1997), and this could result in increased variability in measures from intact sample LA ICP-MS, however the alignment detected here between intact sample estimates and acid-digestion ICP-MS measures suggest that conducting laser sweeps across a needle length and averaging multiple laser ablation measures per needle reduced effects of within-sample heterogeneity. The detection of ^{57}Fe from both acid-digestion ICP-MS and LA ICP-MS analysis may be imprecise for several reasons. ^{57}Fe is the preferred isotope for measurement with LA ICP-MS analysis, however it remains subject to chemical interferences, for example from $^{40}\text{Ca}^{16}\text{O}^1\text{H}$, and this may lead to inconsistent measures particularly when paired with a NIST610 silicate standard that contains relatively low levels of Fe (Danyushevsky et al., 2011). Moreover, in conventional acid-digestion, solution-based ICP-MS, lighter metals such as Fe typically show lower precision (Gallo and Almiralli, 2009). Nonetheless, considering both the strong Fe recovery rate reported through conventional ICP-MS analysis (98.5%; Table S2) and the close alignment between estimates of ^{57}Fe from acid digestion ICP-MS and intact needle LA ICP-MS methods, we can assume that pellet preparation produces inflated ^{57}Fe estimates relative to the other testing and preparation techniques.

4.2. Volatile toxic elements

The elements ^{75}As , ^{111}Cd , ^{121}Sb , and ^{208}Pb are volatile at relatively low temperatures and conventional methods using acid digestion can thus underestimate their concentrations (Hoening, 2001; Totland et al., 1992). LA ICP-MS analysis may offer a method of measurement whereby loss of volatiles from sample heating and acid digestion is prevented.

Results from intact needle LA ICP-MS closely matched those from acid digested samples measured with ICP-MS for ^{75}As , ^{111}Cd , and ^{121}Sb , which disagrees with our hypothesis and suggests volatilization was minimal in the grinding and acid digestion stages of sample preparation. Our results thus suggest that LA ICP-MS on intact pine needle samples represents a viable analysis method for ^{75}As , ^{111}Cd , and ^{121}Sb quantification, and may serve as a particularly important technique in scenarios when study sample size limits more conventional preparation techniques. The results from our preliminary comparative study motivates follow-up corroborative experiments using larger intact sample sizes in order to ascertain the consistency of volatile element measures using LA ICP-MS. The use of dual-acid digestion prior to ICP-MS may have contributed to a close value match for ^{75}As and ^{121}Sb , as determination of these volatile elements tends to remain accurate with this technique, most notably compared to the more vigorous, four-acid “total” digestion options also offered at most commercial laboratories. In contrast, significant deviations between methods were observed for ^{208}Pb , with intact tissue LA ICP-MS yielding lower values relative to those from conventional acid-digestion ICP-MS analysis. Measurements for ^{208}Pb from LA ICP-MS on intact samples were also significantly lower than values from pellet LA ICP-MS analysis, indicating that intact tissue ablation may underestimate ^{208}Pb amounts or, alternatively, that crushing and homogenization of needle tissues inflates ^{208}Pb estimates. Considering LA ICP-MS measurements of ^{208}Pb in ground, pelletized samples closely match values obtained from acid digestion and ICP-MS, the NIST610 reference material may represent a more accurate matrix-match to these sample forms than to the intact needle sample. Jochum et al. (2012) applied LA ICP-MS to trace element measures in calcium carbonates and reported on the crucial significance of closely matrix-matched standards for accurate determination of select trace elements with low boiling points. Large discrepancies in ^{208}Pb were reported when using three distinct reference materials and various laser spot sizes, more so than other volatile elements considered. Jochum et al. (2012) suggested that LA ICP-MS measurements for chalcophile elements with low boiling points, such as ^{208}Pb , may require matrix-matched calibration using a carbonate reference material rather than the more conventional glass NIST610 applied in our study. The use of LA ICP-MS on plant materials is thus not recommended for ^{208}Pb ; however, this might be rectified by development of plant standards with both a matched matrix and element composition profile (Hanc et al., 2010; Pedrosa Diniz et al., 2019).

Results comparing total and surficial foliar element concentrations has also revealed that distinct analysis techniques may be required for accurate detection of ^{208}Pb (Rautio and Huttunen, 2003). Pine needles in particular have been studied as biomonitors of atmospheric element loads through analysis of both washed and unwashed needle samples (Bertolotti and Gialanella, 2014) and Pb is among the elements most prone to airborne transport and surface needle deposition (Steinnes and Friedland, 2006). Other researchers (e.g., Watmough et al., 1996) have suggested that Pb particles in atmospheric pollution will eventually penetrate tissue surfaces and be incorporated into xylem of leaves and needles. The ^{208}Pb concentration values we obtained from intact needle LA ICP-MS were lower than from either analysis technique carried out on homogenized samples, suggesting Pb was likely located within inner needle structures. Future research expansions into the use of LA ICP-MS for elemental depth profiling on pine needles, through manipulation of laser penetration and trajectory, may reveal a viable alternative to conventional sample washing and homogenization techniques.

4.3. Other elements

LA ICP-MS on intact needles generally produced comparable results to those from acid digestion and ICP-MS among other elements posing plant toxicity risks (^{27}Al , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{95}Mo , ^{137}Ba). However, the mean values for ^{140}Ce measured by LA ICP-MS on intact needles deviated significantly below the corresponding measures from acid

digestion ICP-MS. Though most rare earth elements (REEs) are not considered essential for plant life, their presence in soils is ubiquitous and the effects of REEs on plants is an emerging topic of research (Tyler, 2004; Wiseman et al., 2016). Cerium is the most abundant REE in soils and may diminish plant and tree uptake of essential elements (Diatloff et al., 2008), though its phytoavailability has also been linked to both growth enhancements and beneficial physiological effects in certain crops (Ramírez-Olvera et al., 2022). The divergent values obtained for Ce through intact specimen LA ICP-MS may be the result of sample heterogeneity. The influence of laser-induced element fractionation in LA ICP-MS analysis is typically lowest for lithophile refractory elements, such as REEs; thus, the deviation of intact needle LA ICP-MS Ce measurements likely stems instead from irregular Ce distribution within the needles analyzed. Studies into REE uptake within plants report the tendency for Ce to be preferentially stored in plant leaf veins, leading to uneven composition results in analyses of intact samples (Gong and Dong, 2021), though we are not aware of Ce mapping having been performed on coniferous tree needles to date. We observed among-sample variation in Ce measures from intact pine needle LA ICP-MS to be much higher than the corresponding values from ground, pellet LA ICP-MS measures (Fig. 2a–c), which suggests that an accurate measure of intact needle Ce may require higher sample size or homogenized tissue samples. Similar to Ce results, LA ICP-MS measures of ^{139}La in intact needles were measured below corresponding ^{139}La values from acid-digestion ICP-MS and significant deviations were observed between ^{139}La measures from pellet and intact sample LA ICP-MS. Very few applications of LA ICP-MS to quantitative measures of trace elements, such as ^{139}La , have been reported to date (Shimma et al., 2020).

Measures of ^{52}Cr from intact needle LA ICP-MS were slightly, but not significantly, higher than values obtained from acid digestion ICP-MS analyses. Challenges in the accurate measurement of ^{52}Cr by ICP-MS are well-documented and stem from interference between Ar gas, plasma ions, and reference matrix ions (Riss et al., 2017). Moreover, although a multi-acid digestion method for sample preparation is among the most vigorous used for ICP-MS, select stable mineral compounds including chromite commonly remain undissolved. Duodu et al. (2015) reported high deviation in ^{52}Cr results from laser-ablated wet-milled, pelletized sediment samples compared to acid digested samples and similarly, Zayed et al. (1998)'s investigation of Cr accumulation in crops described low reliability in analytical Cr measures due to species transformation risks during sampling, pretreatment, and analysis.

4.4. Sample preparation effects and recommendations

Arroyo et al. (2009) reported that fine-grinding, sieving ($d_{50} < 10\ \mu\text{m}$), and pressing soil and sediment material into tablets allowed for homogenous data acquisition of sixteen elements via LA ICP-MS with ablation spot size of $200\ \mu\text{m}$. Although pressing pellets formed from sieved, pulverized tree segments increases homogeneity, our application of LA ICP-MS on pulverized, pelletized samples yielded more element values deviating from conventional acid digestion measures. This result suggests that microanalysis of intact plant tissue will achieve adequate spatial resolution without the need for grinding and pelletizing if LA spot size is low ($25\ \mu\text{m}$). Intact sample LA ICP-MS analysis with low ablation spot size has been tested for accuracy through microanalysis of rock and mineral samples (Garbe-Schönberg and Müller, 2014). Indeed, our results suggest that most deviations between laser ablation and acid digestion ICP-MS analyses arise from digestion rather than mechanical grinding or pelletizing procedures. One exception, LA ICP-MS on intact tissue and pulverized tissue pellets yielded significantly different measures for ^{107}Ag with the intact tissue analysis aligning very closely with measurements from conventional acid digestion ICP-MS analysis; further studies into accurate, non-destructive quantification of ^{107}Ag in plant tissues are thus required.

5. Conclusions

A procedure for applying LA ICP-MS to the accurate elemental analysis of intact *Pinus banksiana* L. needles has been proposed and compared to alternative procedures. Lack of appropriate type and form of standard reference materials for the use of LA ICP-MS on plant tissue samples has been a barrier to its more widespread application. Here we used an internal standard common element (^{43}Ca) determined by electron probe microanalysis of gold-plated intact samples, and a conventional glass NIST610 pellet for external calibration. LA ICP-MS was also applied to the measurement of elemental composition in ground, pelletized pine needle samples with common element quantification achieved through XRF. Results from LA ICP-MS for both sample preparation techniques were compared to one another and also to third-party ICP-MS analysis measurements on crushed, dual-acid digested samples. Our results suggest application of LA ICP-MS on intact plant samples, referenced with NIST610 and an internal standard of ^{43}Ca , is a viable tool for accurate, non-destructive analysis of pine tissue composition for most elements of interest – though problematic in the cases of ^{39}K , ^{52}Cr , ^{107}Ag , ^{140}Ce , and ^{208}Pb . Use of LA ICP-MS on intact plant samples may prove particularly useful for analysis of individual plant components or on sample sizes too small for digestion techniques, as well as when measuring certain elements (such as ^{75}As , ^{111}Cd , and ^{121}Sb) subject to volatilization losses during mechanical and chemical sample preparation.

CRedit authorship contribution statement

Jasmine M. Williams: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Sean C. Thomas:** Writing – review & editing, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: JM Williams reports financial support was provided by Natural Sciences and Engineering Research Council of Canada (NSERC). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2025.144200>.

Data availability

Data will be made available on request.

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