Université du Québec en Abitibi-Témiscamingue

ÉTUDE ÉCOTOXICOLOGIQUE DES ÉMISSIONS DE LA FONDERIE HORNE SUR LE BIOME DU SOL FORESTIER ET LES ARBRES BORÉAUX : APPROCHES SPATIO-TEMPORELLE ET EXPÉRIMENTALE COMBINANT DENDROGÉOCHIMIE ET GÉNOME DU MICROBIOME DES SOLS

Thèse par articles
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Par
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AVANT-PROPOS

Cette thèse par articles, réalisée dans le cadre du doctorat sur mesure en écologie forestière à l'Université du Québec en Abitibi-Témiscamingue (UQAT), présente le résultat de mes recherches sur l'impact de la pollution industrielle sur les écosystèmes boréaux en combinant l'analyse rétrospective de données environnementales issues des arbres avec des expérimentations en conditions contrôlées. Elle se compose d'une introduction, de trois chapitres en anglais sous forme d'articles scientifiques (Chapitres I, II et III), et d'une conclusion.

En tant que première auteure, j'ai rédigé les versions initiales des Chapitres I, II et III. Les co-auteurs ont contribué à leur révision et ont approuvé les versions finales destinées à la publication. Les travaux présentés dans les Chapitres I et II ont été réalisés en collaboration avec Joëlle Marion et Martine M Savard (Commission géologique du Canada), et avec Christine Martineau (Centre de Foresterie des Laurentides) pour les Chapitres II et III.

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Le Chapitre I, « *Spatiotemporal assessment of lead (Pb) and cadmium (Cd) contamination in urban tree rings near an industrial smelter: high intraspecific variability but limited spatial differentiation* », traite de la dispersion des métaux lourds issues de la fonderie Horne dans un milieu urbain. Il met en évidence l'accumulation de Pb et de Cd dans les cernes de croissance des arbres urbains, marquée par une forte variabilité intraspécifique mais une différenciation spatiale limitée. Une version de ce chapitre a été publié dans la revue Atmospheric Pollution Research en mai 2025 : Dejoie E, Lemay M-A, Fenton NJ, DesRochers A, Marion J, Savard MM, Porter TJ, Proulx D, Gennaretti F (2025) Spatiotemporal assessment of lead (Pb) and cadmium (Cd) contamination in urban tree rings near an industrial smelter: high intraspecific variability but limited spatial differentiation. Atmospheric Pollution Research 16: 102582. https://doi.org/10.1016/j.apr.2025.102582

Le Chapitre II, « *Impact of industrial pollution on nitrogen cycle and tree growth detected by $\delta^{15}N$ in tree rings* » examine l'effet de la pollution industrielle, testé en conditions contrôlées, sur le cycle de l'azote et la croissance des arbres, en s'appuyant sur les variations isotopiques du $\delta^{15}N$ enregistrées dans les cernes comme indicateur des perturbations biogéochimiques. Ces résultats sont ensuite comparés aux signatures isotopiques observées en milieu forestier et sur des périodes passées. L'article correspondant a été soumis dans la revue scientifique Environmental Pollution en novembre 2025 : Dejoie E, Lemay M-A, Fenton NJ, DesRochers A, Marion J, Savard MM, Martineau C, Gennaretti F (soumis en mars 2026) Impact of industrial pollution on nitrogen cycle and tree growth detected by tree-ring $\delta^{15}N$ series.

Le Chapitre III, « *Interactive effects of lead (Pb) contamination and soil acidification on microbial communities involved in nitrogen (N) cycle* » s'intéresse à la pollution en conditions contrôlées, mais se focalise spécifiquement sur le plomb. Il examine la manière dont la combinaison entre la contamination au plomb et l'acidification du sol influence la composition, la diversité et les fonctions métaboliques des communautés microbiennes impliquées dans le cycle de l'azote. L'article correspondant est en préparation pour soumission à une revue scientifique : Dejoie E, Thomas M, Fenton NJ, DesRochers A, Martineau C, Gennarett F (soumis en mars 2026) Interactive effects of lead (Pb) contamination and soil acidification on microbial communities involved in nitrogen (N) cycle.

Les résultats de la thèse ont été partagés avec les présentations scientifiques (posters et conférences) et articles de presse suivants :

Elsa Dejoie, Nicole J. Fenton, Annie DesRochers, Christine Martineau, Fabio Gennaretti. Impacts of lead pollution and soil acidification on plant growth and soil microbiome (présentation orale) Rhizosphere 6 - Rooting for Earth. University of Edinburgh, Edimbourg, Ecosse. (2025-06-18)

Elsa Dejoie, Marc-André Lemay, Nicole J. Fenton, Annie DesRochers, Joëlle Marion, Martine Savard, Fabio Gennaretti. Les cernes d’arbres comme bioindicateur de la pollution au plomb et au cadmium : le cas des arbres urbains de Rouyn-Noranda (présentation orale) 1er colloque de l'ONICSE. UQAT, Rouyn-Noranda, Québec. (2025-05-27)

Elsa Dejoie, Nicole J. Fenton, Annie DesRochers, Martine M Savard, Christine Martineau, Fabio Gennaretti. Impacts de la pollution au plomb et de l'acidification du sol sur la croissance des plantes - $\delta^{15}N$ comme témoin des impacts industriels (poster) 18e colloque annuel du CEF, Université du Québec à Rimouski (2025-05-07)

Elsa Dejoie, Nicole J. Fenton, Annie DesRochers, Fabio Gennaretti. Impacts de la pollution au plomb et de l'acidification du sol sur la croissance des plantes (présentation orale) 6e colloque de la Chaire sur la Biodiversité Nordique en Contexte Minier (BCM). UQAT, Rouyn-Noranda, Québec. (2025-04-17)

Elsa Dejoie, Marc-André Lemay, Nicole J. Fenton, Annie DesRochers, Joëlle Marion, Martine Savard, Fabio Gennaretti. Les cernes d’arbres comme bioindicateur de la pollution au plomb et au cadmium : le cas des arbres urbains de Rouyn-Noranda (présentation orale) 26e colloque de la Chaire AFD. Hôtel Forestel, Val-d'Or, Québec. (2024-11-20)

Elsa Dejoie, Fabio Gennaretti, Nicole J. Fenton, Annie DesRochers, Martine Savard, Trevor Porter. Les cernes d'arbres comme bioindicateur de la pollution au plomb et au cadmium : le cas des arbres urbains de Rouyn-Noranda (présentation orale) 17e colloque annuel du CEF, Université du Québec en Outaouais (2024-05-03)

Elsa Dejoie, Nicole J. Fenton, Annie DesRochers, Fabio Gennaretti. Étude spatio-temporelle du plomb et du cadmium dans les cernes d'arbres aux alentours de Rouyn-Noranda (poster) 25e colloque de la Chaire AFD. Université du Québec en Abitibi-Témiscamingue, Rouyn-Noranda, Québec. (2023-11-28)

Elsa Dejoie, Nicole J. Fenton, Annie DesRochers, Fabio Gennaretti. Exploration inédite : Est-ce que les arbres de Rouyn-Noranda peuvent dévoiler la pollution en métaux lourds dans la ville? (article de presse, Couvert Boréal - Automne 2023)

Elsa Dejoie. Étude spatio-temporelle du plomb et du cadmium dans les cernes d'arbres aux alentours de Rouyn-Noranda (poster). 2e colloque annuel du GREMA, Université du Québec en Abitibi-Témiscamingue (2023-06-06)

RÉSUMÉ

La pollution industrielle, notamment les émissions provenant des fonderies, est une source majeure d'émissions atmosphériques de métaux lourds et de gaz acidifiants. Ces polluants peuvent entraîner une contamination des sols et des perturbations écologiques, notamment en forêt boréale. Nous pouvons citer le cas de Rouyn-Noranda au Québec (Canada), où la fonderie Horne opère depuis près d'un siècle et a rejeté de nombreux polluants dans l'atmosphère, notamment de l'arsenic, du plomb, du cadmium et des oxydes de soufre et d'azote. Dans cette thèse nous avons décidé d'utiliser les cernes des arbres comme des archives environnementales pour retracer l'historique spatio-temporel des métaux dans l'environnement et les perturbations du cycle biogéochimique de l'azote dans la région de Rouyn-Noranda, tout en intégrant une amélioration de la compréhension des mécanismes en jeu grâce à des expériences en milieu contrôlé. Deux approches complémentaires ont été mises en œuvre. En premier lieu, un échantillonnage dans les arbres urbains et en forêt a été réalisé pour reconstituer la contamination métallique dans les cernes. Pour cela, nous avons fait des analyses dendrogéochimiques des cernes de conifères (pins, épinettes) situés aux alentours de la fonderie afin de quantifier les concentrations en plomb (Pb) et en cadmium (Cd). En deuxième lieu, nous avons réalisé des expérimentations en serre. Des graines d'épinette noire ont été exposées à des variations de la teneur en plomb et de pH dans le sol afin d'évaluer leurs effets sur la germination, la croissance, la composition isotopique de l'azote dans le xylème ($\delta^{15}N$) et la structure des communautés microbiennes du sol impliquées dans le cycle de l'azote. Nous avons montré que les arbres urbains à Rouyn-Noranda révèlent une accumulation significative de Pb et Cd dans les cernes, avec une forte variabilité intraspécifique mais une différenciation spatiale et temporelle limitée dans un rayon d'analyse de 5 km autour de la fonderie. D'autre part, les signatures isotopiques $\delta^{15}N$ dans le bois des plantules en serre indiquaient une perturbation du cycle de l'azote en milieu pollué, corrélée à l'acidification des sols mais qui contrastaient avec les valeurs de $\delta^{15}N$ des arbres en milieu naturel. De plus, nous avons démontré que la baisse du pH a eu un effet marqué sur la croissance des plantules et sur la composition microbienne du sol, réduisant la diversité des microorganismes impliqués dans le cycle de l'azote. La contamination au Pb a amplifié ces effets uniquement au niveau du microbiome, modifiant la structure des taxons microbiens liés au cycle de l'azote mais sans induire d'effet au niveau de la croissance des plantes. Ces résultats révèlent des interactions complexes entre la contamination des sols, la dynamique des communautés microbiennes et les réponses physiologiques des plantes, soulignant l'importance d'approches intégrées pour comprendre les impacts de la pollution industrielle sur les écosystèmes et évaluer l'efficacité des mesures d'atténuation de la pollution.

Mots-clés : Pollution industrielle, cernes des arbres, isotopes stables, cycle de l'azote, contamination des sols, microbiome du sol

Keywords: Industrial pollution, tree rings, stable isotopes, nitrogen cycle, soil contamination, soil microbiome

ABSTRACT

Industrial pollution, particularly emissions from smelters, is a major source of atmospheric releases of heavy metals and acidifying gases. These pollutants can lead to soil contamination and ecological disturbances, especially in boreal forests. A notable example is Rouyn-Noranda in Québec (Canada), where the Horne smelter has operated for nearly a century and released numerous atmospheric pollutants, including arsenic, lead, cadmium, as well as sulfur and nitrogen oxides. In this thesis, we used tree rings as environmental archives to reconstruct the spatio-temporal history of metal deposition and disruptions to the nitrogen biogeochemical cycle in the Rouyn-Noranda region, while improving our understanding of the underlying mechanisms through controlled experiments. Two complementary approaches were implemented. First, sampling in urban and forest trees was conducted to reconstruct metal contamination recorded in tree rings. We performed dendrogeochemical analyses on conifer growth rings (pine, spruce) located around the smelter to quantify concentrations of lead (Pb) and cadmium (Cd). Second, we carried out greenhouse experiments in which black spruce seeds were exposed to variations in soil lead concentrations and pH to assess their effects on germination, growth, nitrogen isotopic composition in the xylem ($\delta^{15}N$), and the structure of soil microbial communities involved in the nitrogen cycle. We showed that urban trees in Rouyn-Noranda exhibit significant accumulation of Pb and Cd in their rings, with strong intraspecific variability but limited spatial and temporal differentiation within a 5-km radius of the smelter. In addition, $\delta^{15}N$ isotopic signatures in the wood of seedlings grown in the greenhouse revealed disruptions to the nitrogen cycle under polluted conditions, associated with soil acidification but contrasting with $\delta^{15}N$ values of trees in natural environments. We also demonstrated that decreasing soil pH strongly affected seedling growth and soil microbial composition, reducing the diversity of microorganisms involved in nitrogen cycling. Lead contamination amplified these effects only at the microbiome level, altering the structure of nitrogen-cycle-related microbial taxa but not affecting plant growth. Overall, these results highlight the complex interactions between soil contamination, microbial community dynamics, and plant physiological responses, emphasizing the importance of integrated approaches to understand the impacts of industrial pollution on ecosystems and to evaluate the effectiveness of pollution-mitigation measures.

Keywords: Industrial pollution, tree rings, stable isotopes, nitrogen cycle, soil contamination, soil microbiome

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AIC	Critère d'information d'Akaike
ANCOM-BC2	Analyse de composition des microbiomes avec correction de biais
AND / DNA	Acide désoxyribonucléique / Desoxyribonucleic acid
ANOVA	Analyse de la variance
ARN / RNA	Acide ribonucléique : Ribonucleic acid
ASV	Variants de séquences d'amplicon
Cd	Cadmium
$\delta^{2}H$	Rapport isotopique de l'hydrogène
$\delta^{13}C$	Rapport isotopique du carbone
$\delta^{15}N$	Rapport isotopique de l'azote
$\delta^{18}O$	Rapport isotopique de l'oxygène
DBH	Diamètre à hauteur de poitrine
DON	Matière organique dissoute
EA-IRMS	Analyseur élémentaire – Spectrométrie de masse à rapport isotopique
GLM	Modèle linéaire généralisé
GS	Saison de croissance
ICP-MS	Spectrométrie de masse à plasma à couplage inductif
KCl	Chlorure de potassium
lmer	Modèles mixtes linéaires (package R)
LOESS	Lissage local (Locally Estimated Scatterplot Smoothing)
N	Azote
NH_4^+	Ammonium
NMDS	Mise à l'échelle multidimensionnelle non métrique
NO_3^-	Nitrate
NO_x	Oxydes d'azote
Pb	Plomb
PERMANOVA	Analyse de la variance multivariée par permutations
pH	Potentiel hydrogène
SO_2	Dioxyde de soufre

LISTE DES SYMBOLES ET DES UNITÉS

%	Pourcent
‰	Pour mille
µm	Micromètre
Gt	Gigatonne (de carbone)
km	Kilomètre
mg	Milligramme
mg/kg	Milligramme par kilogramme
ppm	Partie par million

INTRODUCTION

Mise en contexte. Ce doctorat s'insère dans la Chaire de recherche institutionnelle REGENERE, dont les travaux portent sur la renaturalisation des parcs à résidus miniers et visent la mise en commun de l'expertise des deux instituts de recherche de l'UQAT, soit l'Institut de recherche en mines et en environnement (IRME) et l'Institut de recherche sur les forêts (IRF). Sa programmation de recherche s'articule autour de trois volets complémentaires : (1) la caractérisation hydrogéologique et hydrochimique du site afin de mieux comprendre les conditions d'écoulement et la composition des eaux souterraines, (2) l'évaluation et l'optimisation des stratégies de restauration des aires d'entreposage par la valorisation de matériaux issus du traitement du minerai, et (3) la renaturalisation des sites dégradés par la reconstitution des sols et des communautés végétales, dans le but de rétablir des écosystèmes forestiers fonctionnels. Mon projet s'inscrit spécifiquement dans ce dernier volet, qui vise également à comprendre le fonctionnement écologique des milieux affectés par les activités industrielles, notamment celles liées à la fonderie de cuivre.

L'industrie minière au Canada. L'industrie minière constitue depuis plus d'un siècle l'un des piliers économiques du Canada et un moteur essentiel de son développement territorial (Ressources Naturelles Canada, 2019; Têtu et al., 2015). Le pays se classe parmi les principaux producteurs mondiaux de métaux et de minéraux, exploitant une grande variété de ressources, dont l'or, le cuivre, le nickel, le zinc, le fer, ainsi que des métaux critiques comme le lithium, le cobalt et les terres rares (Bridge, 2017; Carvalho, 2017). Les activités minières sont particulièrement concentrées dans les provinces de l'Ontario, du Québec, de la Colombie-Britannique et dans les territoires du Nord, où elles représentent une part importante du produit intérieur brut et des exportations canadiennes (Association Minière du Canada, 2020; Kingsbury et Wilkinson, 2023). Cette industrie soutient directement et indirectement des milliers d'emplois, favorise le développement d'infrastructures et contribue à la vitalité économique de nombreuses communautés rurales et autochtones (Horowitz et al., 2018; Caron et Asselin, 2020). Le territoire québécois, marqué par une géologie variée et riche en gisements, abrite une grande diversité de métaux et minéraux qui figurent parmi les plus exploités (Ludden et al., 1986; Veillette et al., 2005). Au Québec, le Plan stratégique du ministère des Ressources naturelles et des Forêts (2023-2027) estime que l'industrie minière génère plus de 7 milliards de dollars de PIB annuellement et soutient plus de 30.000 emplois directs et indirects. Représentant près de 21 % du PIB minier canadien et environ 0,4 % du PIB total du pays, l'industrie minière constitue un acteur majeur de l'économie nationale (Gouvernement du Québec, 2023; Institut national des mines, 2023).

Par ailleurs, les fonderies métallurgiques sont l'une des principales causes de la pollution industrielle régionale au Canada. Dès le début du XX[e] siècle, des complexes tels que ceux de Sudbury en Ontario (Gundermann et Hutchinson, 1995; Winterhalder, 1995) et de Rouyn-Noranda au Québec (Alpay et al., 2006; Bilodeau et al., 2020) ont figuré parmi les plus importantes sources d'émissions atmosphériques de métaux lourds et de dioxyde de soufre du pays. Leurs activités, centrées sur la fusion du cuivre, du nickel et du plomb (Dion et al., 2024), ont entraîné une contamination étendue des sols, de la végétation et des milieux aquatiques, accompagnée d'une acidification persistante des sols environnants (Haider et al., 2021; Sinha et al., 2015; Zulfiqar et al., 2019). À partir des années 1970, la mise en œuvre de réglementations environnementales plus strictes et l'adoption de technologies de dépollution (filtres, tours d'absorption, électrofiltres) ont entraîné une réduction progressive des émissions métalliques (MELCCFP, 2023; Rivard, 2021). Toutefois, cette activité s'accompagne de pressions sociales importantes, notamment en Abitibi-Témiscamingue (Québec, Canada), où la cohabitation entre exploitation minière, communautés locales et écosystèmes forestiers soulève des enjeux de durabilité et de gestion responsable des ressources (Vodouhe et Khasa, 2015; Kingsbury et Wilkinson, 2023).

Impacts environnementaux de l'activité industrielle. ***Dispersion et transport des métaux lourds dans l'environnement.*** Les panaches de fumée émis par les cheminées industrielles transportent dans l'atmosphère des particules et des gaz contenant des métaux lourds. Ces métaux lourds peuvent s'adsorber à la surface de particules fines en suspension, ce qui leur permet de rester dans l'atmosphère et d'être transportés sur de longues distances par les masses d'air (Khaniabadi et al., 2018). L'ampleur de leur dispersion dépend à la fois de la taille des particules, des conditions atmosphériques et des caractéristiques des sources d'émission (Daggupaty et al., 2006; Soriano et al., 2012). Les particules les plus grossières se déposent à proximité immédiate de la source, tandis que les plus fines (< 2,5 µm) peuvent parcourir plusieurs centaines de kilomètres avant de se déposer (Daggupaty et al., 2006; Hou et al., 2006; K. Zhang et al., 2018). La hauteur des cheminées industrielles influence fortement la dispersion des métaux lourds : plus elles sont élevées, plus les particules peuvent parcourir de longues distances avant de se déposer (Romeiro et al., 2020). Les métaux lourds comme le plomb se déposent rapidement, tandis que les particules fines restent plus longtemps en suspension et se transportent plus loin (Fergusson et Stewart, 1992; Daggupaty et al., 2006). La direction des vents joue également un rôle déterminant, les concentrations en particules retrouvées dans le sol étant généralement plus élevées sous le vent de la source de pollution (Žibret et Šajn, 2008; Khaniabadi et al., 2018). Les procédés des fonderies et la direction des vents modulent également la dispersion, expliquant, par exemple, les niveaux plus élevés de contamination observés à l'opposé des vent dominants à Rouyn-Noranda au Québec, car autrement les contaminants seraient plus abondant en ville sous les vents dominants (Bilodeau et al., 2020).

Une fois déposés dans le sol, les métaux peuvent interagir avec divers composants : ils se fixent à la surface, s'associent aux composés organiques, se dissolvent dans l'eau interstitielle ou sont assimilés par les plantes puis stockés dans leurs tissus (Evans, 1989). Ces mécanismes peuvent varier selon les espèces de plantes, les caractéristiques du sol et les métaux lourds impliqués. Plus précisément, les racines des plantes sécrètent des substances appelées chélateurs qui se lient aux ions métalliques pour former un complexe stable, ce qui permet aux ions métalliques de se déplacer plus facilement (More et al., 2019). Les métaux, sous forme d'ions hydratés ou de complexes métal-chélateur, sont ensuite absorbés par les cellules racinaires grâce à des transporteurs membranaires. Le transport vers les parties aériennes s'effectue principalement via le xylème, où les métaux circulent sous forme libre ou complexée. Ils peuvent se fixer dans le xylème en se liant à des sites spécifiques des protéines, tels que les groupes sulfhydryles, carboxyles et phosphates (Clemens et al., 2002; Lux et al., 2011; Matei et al., 2025).

Les métaux lourds affectent significativement les mécanismes physiologiques des plantes vasculaires (Zvereva et Kozlov, 2012; Perone et al., 2018). Ils provoquent une augmentation de la perméabilité racinaire qui entraîne une fuite des nutriments au niveau des racines et induisent un stress hydrique menant au flétrissement et à la chute précoce des feuilles (Bini et al., 2012; Fodor, 2002; M. N. V. Prasad, 1995). Ils sont responsables du rabougrissement des jeunes pousses et peuvent limiter l'élongation racinaire en lignifiant les parois. Ils perturbent ainsi la croissance (John et al., 2012) et le développement des plantes (Påhlsson, 1989; Kozlov et Zvereva, 2007; Khan et al., 2015). Le métabolisme est également touchés par la pollution aux métaux lourds (Baccouch et al., 2001; Boyd, 2020; Yadav, 2010). L'activité photosynthétique diminue (Prasad et Strzałka, 1999), à cause d'une réduction de la concentration en chlorophylle et en caroténoïdes dans les feuilles (Boyd, 2020; Fodor, 2002; John et al., 2012). Enfin, les métaux lourds peuvent perturber la translocation des assimilats photosynthétiques produits dans les feuilles vers les organes puits, notamment via des dépôts de callose dans les tubes criblés du phloème, limitant ainsi la circulation de la sève élaborée (Bini et al., 2012; Fodor, 2002; Påhlsson, 1989) et induisent également la production de dérivés réactifs de l'oxygène (Boyd, 2020; John et al., 2012; Jozefczak et al., 2012). A l'échelle des individus, la densité de peuplement des plantes vasculaires à proximité des fonderies est réduite, notamment celle des espèces constituant la canopée supérieure (Zvereva et Kozlov, 2012). Un gradient de perte spécifique peut être établi avec des pertes maximales à proximité de la fonderie, diminuant progressivement en s'éloignant de la fonderie et créant des espaces dénudés de végétation (Zvereva et al., 2008; Koroteeva et Veisberg, 2019).

Impacts environnementaux de l'activité industrielle. ***Mécanismes d'absorption des métaux lourds par les plantes.*** L'accumulation des métaux dans les plantes, en particulier dans les tissus ligneux, résulte de processus physiologiques complexes qui influencent à la fois leur incorporation et leur distribution dans les cernes. La principale voie d'entrée est généralement l'absorption racinaire, suivie du transport dans le xylème (Clemens et al., 2002; Z.-B. Luo et al., 2016). Une fois dans l'arbre, les métaux peuvent être immobilisés dans les parois cellulaires, stockés dans les vacuoles ou redistribués radialement entre les cernes dépendamment de l'élément considéré (Cutter et Guyette, 1993). De plus, la mobilité des éléments varie selon leurs propriétés chimiques et les conditions du sol, notamment le pH, qui influence leur biodisponibilité (de Matos et al., 2001; R. R. Martin et al., 2006). Dans ce contexte, l'interprétation des données dendrogéochimiques nécessite de considérer non seulement les gradients environnementaux, mais aussi les caractéristiques du milieu d'étude. Les environnements urbains se distinguent par la multiplicité des sources de contamination (trafic routier, émissions industrielles, dépôts atmosphériques) et par des conditions édaphiques souvent hétérogènes (Bi et al., 2020; Jadaa et Mohammed, 2023). Toutefois, cette complexité confère également une pertinence particulière à l'étude des arbres urbains, qui agissent comme des intégrateurs des expositions locales et reflètent des conditions directement liées aux milieux de vie humains. Ainsi, l'intégration d'arbres provenant de milieux urbains et périurbains, tels que des cours arrière et des parcs publics, s'inscrit dans une volonté de documenter la contamination dans des contextes réalistes et spatialement hétérogènes. Bien que ce choix implique certaines limites, notamment l'influence potentielle des pratiques de gestion des sols, des apports locaux ou des perturbations anthropiques, il permet de compléter les observations issues de milieux plus éloignés.

Acidification et impact sur les microorganismes du sol. Les émissions atmosphériques issues des fonderies ne se limitent pas au transport de métaux lourds : elles s'accompagnent également d'importantes quantités de gaz acides, principalement le dioxyde de soufre (SO_2) et les oxydes d'azote (NO_x) (L. Zhang et al., 2021). Les dépôts acides s'étendent bien au-delà de la zone immédiate d'émission, favorisant la dispersion régionale de l'acidification, suivant les vents dominants (Khaniabadi et al., 2018; Romeiro et al., 2020). Dans les sols des forêts boréales, cette acidification entraîne une diminution du pH (Gundermann et Hutchinson, 1995a), une mobilisation accrue des métaux toxiques (Kedziorek et Bourg, 1996) et une altération de la disponibilité des nutriments essentiels comme le calcium, le magnésium et le potassium (Haynes et Swift, 1986). L'acidification tend généralement à accroître la solubilité et la mobilité des métaux lourds, augmentant ainsi leur biodisponibilité et leur toxicité potentielle pour les organismes du sol, tandis qu'un pH plus élevé favorise au contraire la rétention des métaux lourds par des réactions d'hydrolyse (Harter, 1983; Bruemmer et al., 1986; Kedziorek et Bourg, 1996).

Le fonctionnement des communautés du sol est influencé par des paramètres externes comme le climat ou la qualité du substrat qui régulent l'activité métabolique des organismes du sol (Bradford et al., 2014, 2017). Nous savons que les émissions acidifiantes des fonderies peuvent avoir un effet sur le cycle de l'azote des forêts, car les communautés bactériennes et fongiques du sol qui influencent la disponibilité en azote sont sensibles aux changements de pH et à la déposition des polluants (Evans et Ehleringer, 1993; Pajares et Bohannan, 2016). Certaines espèces ou groupes fonctionnels présentent toutefois une remarquable résistance ou une capacité d'adaptation à ces conditions, formant ainsi des communautés distinctes de celles des sols non pollués (S. Li et al., 2021; X. Wang et al., 2025; Yin et al., 2023). Par exemple, l'abondance relative des *Acidobacteria* peut augmenter dans les environnements plus acides, tandis que plusieurs groupes de *Proteobacteria* sont plutôt associés à des pH plus élevés (Rousk et al., 2010). Cependant, les réponses au sein des *Proteobacteria* ne sont pas uniformes : certaines lignées, comme le genre *Burkholderia*, ont développé des adaptations spécifiques leur permettant de persister, voire de prospérer, dans des conditions de pH faible (Stopnisek et al., 2014). D'autres bactéries sont également reconnues pour leur tolérance aux métaux lourds, notamment au sein des phylums *Actinobacteria* et *Proteobacteria*, fréquemment détectés dans les sols contaminés (George et Wan, 2020a; Yin et al., 2023). Les mêmes observations ont été faites au sein des champignons, avec des espèces plus ou moins résistantes aux perturbations anthropiques (Krishnamoorthy et al., 2015). Ces changements dans la structure et la composition des communautés peuvent entraîner des modifications des voies du cycle de l'azote, altérer certaines associations symbiotiques (par exemple avec les mycorhizes), et affecter en conséquence la productivité des écosystèmes ainsi que leur capacité de résilience et de régénération après une contamination.

Dans l'environnement naturel, une diminution du pH du sol réduit directement la disponibilité des nutriments et des métaux, ainsi que l'activité enzymatique et microbienne (Neina, 2019; Puissant et al., 2019). Indirectement, l'acidification modifie la composition des communautés du sol, ce qui affecte l'ensemble des cycles biogéochimiques (Naz et al., 2022), provocant un lessivage des cations nutritifs essentiels (Ca^{2+}, Mg^{2+}, K^{+}) (Grant et al., 2019), et réduisant leur disponibilité pour les plantes, tout en augmentant la mobilité et la biodisponibilité de métaux toxiques. Ces déséquilibres chimiques perturbent l'absorption d'eau et de nutriments, limitent la croissance racinaire et réduisent l'efficacité des symbioses mycorhiziennes, essentielles à l'acquisition de phosphore et d'azote (Malhotra et al., 2018). À terme, ces contraintes entraînent une inhibition du développement racinaire, compromettant la stabilité, la nutrition et la productivité globale de la plante (C. Meng et al., 2019; Shi et al., 2021).

Les perturbations de l'absorption des nutriments et l'augmentation de la toxicité métallique au niveau racinaire s'expliquent notamment par un phénomène de « détournement » des transporteurs membranaires : des métaux toxiques tels que le cadmium, le plomb, l'arsenic ou le mercure empruntent les mêmes voies d'entrée que les nutriments essentiels (Qin et al., 2020). Cela entraîne à la fois une compétition directe pour l'absorption et des perturbations métaboliques en aval. Cela induit une réduction de la croissance globale des plantes (Menon et al., 2007). La diminution de la biomasse, du développement racinaire et de la capacité photosynthétique entraîne des performances réduites en termes de survie et de reproduction. À l'échelle des peuplements, ces contraintes physiologiques se répercutent sur la composition et la densité des espèces. La réduction de la biomasse et des capacités reproductives entraîne un appauvrissement progressif en individus, ce qui se traduit par une diminution de la densité des espèces sensibles aux sols acidifiés (Zinko et al., 2006).

Le cycle de l'azote. L'azote atmosphérique et la matière organique forestière représentent les sources principales d'azote dans les sols des forêts. En effet, même si la quantité d'azote dans le sol est élevée, elle se trouve sous une forme souvent inaccessible pour de nombreuses espèces (i.e. sous forme organique) (Knicker, 2004). L'azote fait partie des éléments chimiques indispensables pour la vie et la croissance des êtres vivants, et est souvent limitant en forêt boréale (Talbot, 2001). Dans le sol, l'azote est présent sous différentes formes et peut subir différentes transformations grâce aux organismes du sol, tels que la nitrification, la dénitrification ou les transferts mycorhiziens (Handley et Raven, 1992; Sponseller et al., 2016). La biodisponibilité des différentes formes de l'azote (N_2, NO_3^-, NO_2^-, NH_4^+, NH_3) (Fig. 1) et leur transfert d'un réservoir à un autre sont régulés majoritairement par les communautés microbiennes du sol (Tao et al., 2019).

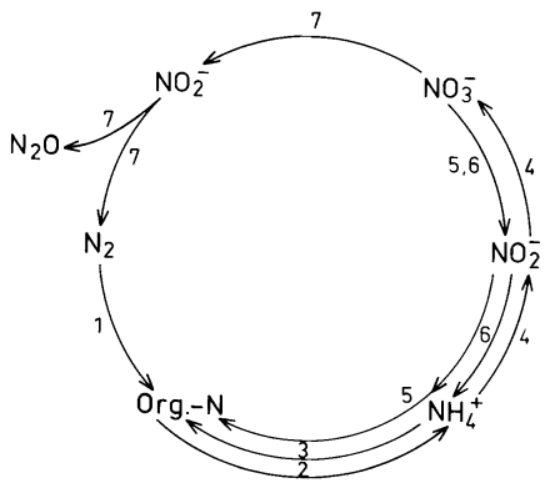

Figure 1
Vue schématique du cycle biogéochimique de l'azote forestier. 1) Fixation de l'azote. 2) Minéralisation. 3) Immobilisation. 4) Nitrification. 5) Assimilation de nitrate. 6) Réduction des nitrates 7) Dénitrification (Rosswall, 1982). Les microorganismes du sol régulent la majorité de ces processus.

Les bactéries représentent le deuxième composant majeur de la biomasse mondiale, avec environ 7 gigatonnes (Gt) de carbone, soit près de 15 % de la biomasse totale (Bar-On et al., 2018). Au-delà de leur abondance, elles jouent un rôle central dans les cycles biogéochimiques, notamment celui de l'azote. La première étape du cycle de l'azote est la transformation de l'azote en matière assimilable par les organismes. Des cyanobactéries sont capables de fixer efficacement le diazote atmosphérique et le transformer en NH_3 (Sprent et James, 2007). Une fois fixé, l'azote est transformé en azote organique, stocké dans la biomasse microbienne ou végétale et finit par se retrouver dans le réservoir de matière organique du sol (Fujita et Uesaka, 2022; Pajares et Bohannan, 2016). Il est ensuite décomposé en ammonium puis en nitrite et en nitrate au cours de la nitrification (Schimel et Bennett, 2004). Une dernière étape notable du cycle de l'azote est la dénitrification des nitrates, processus par lequel les nitrates sont réduits en gaz azotés retournant à l'atmosphère (Fang et al., 2015).

Les champignons jouent un rôle essentiel dans le cycle de l'azote en complément des bactéries. A l'échelle planétaire, les champignons sont les espèces dominantes des communautés du sol. Ils représentent une biomasse d'environ 12 Gt de carbone, tandis que les bactéries ne représentent que 7 Gt de carbone et les animaux 2 Gt (Bar-On et al., 2018). Ils participent à la dénitrification fongique, au cours duquel les champignons transforment les nitrates du sol en gaz azotés (Bollag et Tung, 1972; Shoun et Tanimoto, 1991; Aldossari et Ishii, 2021). Les champignons interviennent dans la fermentation de l'ammonium, transformant l'azote organique complexe en ammonium assimilable par les plantes et autres microorganismes, ce qui contribue à la minéralisation de la matière organique du sol (Aldossari et Ishii, 2021; Hayatsu et al., 2008). Les mycorhizes sont omniprésentes dans les sols et réalisent des symbioses avec de nombreuses racines fines (Read, 1991; Lindahl et Tunlid, 2015). Ces mycorhizes sont aussi capables d'absorber l'azote sous formes minérale et organique, et de transférer de l'azote sous forme assimilable à son symbionte, ce qui en fait des organes clés dans le cycle de l'azote forestier (Koch et Sessitsch, 2024; Phillips et al., 2013).

Le cycle de l'azote est perturbé par la contamination aux métaux lourds et l'acidification liées à l'activité industrielle. En effet, l'acidification du sol modifie la disponibilité des formes d'azote : la baisse du pH favorise l'accumulation de NH_4^+ et réduit la formation de NO_3^-, entraînant un déséquilibre des formes d'azote assimilables par les plantes. Une diminution de la nitrification est observée lorsque le pH du sol diminue, tandis qu'un lessivage accru du NO_3^- peut se produire (Gundersen et al., 2006; Gundersen et Rasmussen, 1990). L'altération des processus microbiens constitue un mécanisme majeur par lequel la contamination métallique et l'acidification perturbent le cycle de l'azote. Les métaux lourds, combinés à un pH faible, réduisent la diversité et inhibent l'activité des microorganismes impliqués dans la minéralisation, la nitrification et la fixation biologique, limitant la capacité du sol à transformer et recycler l'azote (Lenart-Boroń et al., 2014). Ainsi, la nitrification est significativement inhibée dans les sols contaminés (Yan et al., 2013), et la concentration élevée des métaux réduit l'abondance des gènes impliqués dans la nitrification (J. Li et al., 2024; L. Lu et al., 2022).

Les arbres comme archive pour retracer les impacts environnementaux. *La dendrochronologie.* Dans cette thèse j'ai choisi d'utiliser des approches qui dérivent de la dendrochronologie pour reconstituer les impacts de la contamination industrielle dans la région d'étude. La dendrochronologie est une méthode scientifique qui consiste à analyser et dater les cernes de croissance des arbres afin de reconstituer des événements et des conditions environnementales passées (Kuniholm, 2008). Les cernes de croissance, formés par le xylème, constituent des archives particulièrement pertinentes car ils permettent de collecter des informations tout au long de la période de croissance de l'arbre (pouvant dater de plusieurs dizaines d'années) (Pearl et al., 2020; Robinson et al., 1990). En effet, l'épaisseur et la structure de chaque cerne reflètent les conditions environnementales rencontrées au cours de la vie de l'arbre. Chaque cerne correspond à une année de croissance, offrant ainsi une résolution temporelle fine pour reconstituer les variations climatiques, les perturbations écologiques ou anthropiques. En fournissant une chronologie précise et continue, cette approche constitue la base de nombreuses disciplines dérivées, telles que la dendrogéochimie et la dendroisotopie, qui exploitent la même structure temporelle pour relier la croissance des arbres aux changements environnementaux passés (Aznar et al., 2008; Chen et al., 2021a).

Les arbres comme archive pour retracer les impacts environnementaux. *La dendrogéochimie.* La dendrogéochimie étudie la composition chimique des cernes de croissance des arbres afin de retracer les variations spatio-temporelles des éléments chimiques présents dans l'environnement (Vaganov et al., 2013; Watmough, 1997). La mobilité des métaux lourds dans le sol et les tissus végétaux constitue un paramètre déterminant pour l'utilisation des concentrations mesurées dans les cernes de croissance comme bioindicateurs de la pollution historique, car elle conditionne la fiabilité de la reconstruction des dépôts métalliques dans l'environnement (Ballikaya et al., 2022; Cook, 1987; Lepp, 1975; Perone et al., 2018). De nombreuses études ont montré que les concentrations en Pb et Cd mesurées dans les cernes constituaient des indicateurs efficaces pour reconstituer l'historique des dépôts métalliques (Chen et al., 2021a; Cutter et Guyette, 1993; Doucet et al., 2012; Savard et al., 2006), en raison notamment de leur mobilité radiale limitée, particulièrement chez les conifères qui présentent une structure ligneuse homogène d'un cerne à l'autre (Doucet et al., 2012; Watmough et al., 1999). Néanmoins, le potentiel de mobilité des métaux lourds dans les tissus du xylème varie selon les espèces d'arbres, qui possèdent des capacités différentielles d'absorption et d'accumulation dans leurs tissus (Alahabadi et al., 2017; Li-qiang et al., 2004).

Les arbres comme archive pour retracer les impacts environnementaux. *La dendroisotopie*. La dendroisotopie, une branche de la dendrogéochimie, consiste à mesurer les rapports isotopiques stables (par exemple $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$ ou les isotopes du plomb $^{206}Pb/^{207}Pb$ et $^{208}Pb/^{206}Pb$) dans les cernes de croissance des arbres afin d'inférer les conditions environnementales et physiologiques ayant prévalu au cours du temps. Les isotopes stables du carbone ($\delta^{13}C$), de l'oxygène ($\delta^{18}O$) et de l'hydrogène ($\delta^{2}H$) permettent d'évaluer les conditions climatiques et la disponibilité en eau auxquelles l'arbre a été soumis, reflétant son stress hydrique et les variations environnementales au fil du temps (Managave et Ramesh, 2012; Shestakova et Martínez-Sancho, 2021). Les isotopes stables de l'azote ($\delta^{15}N$) renseigne sur les sources et le cycle de l'azote, révélant l'influence de la pollution industrielle ou des processus microbiens sur la nutrition de l'arbre (Robinson, 2001; Savard et Siegwolf, 2022). Enfin, les isotopes du plomb offrent un outil pour tracer l'origine et l'évolution historique des dépôts métalliques, permettant de distinguer les apports naturels des émissions industrielles (Arteau et al., 2020; Hou et al., 2006; Savard et al., 2006; Widory et al., 2018).

Les arbres comme archive pour retracer les impacts environnementaux. *Les isotopes de l'azote dans les cernes.* Les isotopes sont des atomes d'un même élément chimique qui possèdent le même nombre de protons mais un nombre différent de neutrons et ayant une masse atomique distincte (O'Neil, 1986; Schauble, 2004). Dans le cas de l'azote, il existe deux isotopes stables : l'isotope léger ^{14}N, majoritaire (≈ 99,6 %), et l'isotope lourd ^{15}N (≈ 0,4 %) (Craine et al., 2015; Evans, 2007; Handley et Raven, 1992). Le fractionnement isotopique correspond à la modification du rapport entre isotopes d'un même élément au cours d'un processus chimique, physique ou biologique (O'Neil, 1986; Schauble, 2004). Le fractionnement se produit lorsque certains processus métaboliques ou biogéochimiques vont discriminer les isotopes en raison de leur différence de masse, par exemple lors de la volatilisation, de la nitrification, de la dénitrification ou de l'assimilation par les plantes (Adl et al., 2020; P. Högberg et al., 1999; Mariotti et al., 1982). Cette discrimination entraîne des variations mesurables du rapport isotopique $^{15}N/^{14}N$. Le calcul du rapport isotopique se fait par comparaison avec une référence internationale (valeur du rapport isotopique de l'azote atmosphérique) selon la formule :

$$\delta^{15}\mathrm{N}\ (‰) = \frac{(^{15}N/^{14}N)_{éch} - (^{15}N/^{14}N)_{std}}{(^{15}N/^{14}N)_{std}} \times 1000$$

où $(^{15}N/^{14}N)_{éch}$ et $(^{15}N/^{14}N)_{std}$ sont respectivement les rapports isotopiques de l'échantillon à mesurer et de l'échantillon de référence.

Au cours des processus microbiens tels que la minéralisation, la nitrification et la dénitrification, les microorganismes utilisent préférentiellement l'isotope léger ^{14}N, ce qui conduit à la formation de nitrate appauvri en ^{15}N et laisse le réservoir d'ammonium résiduel relativement enrichi en ^{15}N (Pardo et Nadelhoffer, 2010; Hobbie et Högberg, 2012; Savard et Siegwolf, 2022). Par conséquent, le NH_4^+ du sol présente généralement des valeurs de $\delta^{15}N$ plus élevées que le NO_3^-. Les champignons ectomycorhiziens incorporent préférentiellement le ^{15}N dans leurs tissus, tout en fournissant le ^{14}N aux plantes symbiotiques (Hobbie et Högberg, 2012; P. Högberg, 1997).

Le rapport $\delta^{15}N$ constitue un outil particulièrement adapté pour étudier la nutrition des arbres et les cycles de l'azote dans les sols forestiers (Robinson, 2001; Doucet et al., 2012a; Savard et Siegwolf, 2022), et permet de suivre les transformations et les sources de l'azote dans l'écosystème (Savard et al., 2023). Contrairement aux mesures directes de la concentration en azote, qui varient selon les compartiments de l'arbre (aubier ou duramen) en raison de la mobilité du N (Sheppard et Thompson, 2000), le rapport $\delta^{15}N$ reste stable lors du transport de l'azote dans le tissu ligneux, fournissant ainsi une signature fiable des processus biogéochimiques (Tomlinson et al., 2014).

L'aire d'étude : Rouyn-Noranda et la fonderie Horne. La région d'étude qui a été choisie pour les analyses de cette thèse est la région autour de la ville de Rouyn-Noranda en Abitibi-Témiscamingue (Québec, Canada). La découverte des gisements de cuivre et d'or dans les années 1910-1920 a marqué le début du développement minier dans la région de Rouyn-Noranda. Cette découverte a conduit à la fondation de la fonderie Horne en 1927 par Noranda Mines Ltd, aujourd'hui exploitée par Glencore (Berthiaume, 1981; Glencore, 2025b). La fonderie de Rouyn-Noranda est spécialisée dans le traitement de concentrés de cuivre provenant de mines du monde entier (Glencore, 2025a). Dans les années 1970, la fonderie a progressivement intégré le recyclage de déchets métalliques à ses opérations, en complément du traitement du minerai, qui incluent désormais des matériaux issus du recyclage industriel et électronique (Glencore, 2025b; Rivard, 2021). La fonderie est rapidement devenue un moteur central de l'économie locale (Aviseo, 2019), jouant un rôle clé dans le développement et l'essor de Rouyn-Noranda. Aujourd'hui, elle demeure la seule fonderie de cuivre au Canada, traitant à la fois des minerais locaux et internationaux, ce qui souligne sa position unique dans le secteur minier national (Glencore, 2025a).

L’exploitation minière et la fonderie Horne ont produits des émissions atmosphériques massives, incluant notamment le dioxyde de soufre et divers métaux lourds et métalloïdes tels que le plomb, l’arsenic, le cadmium, le cuivre et le zinc (Bonham-Carter, 2005; Canada Government, 2021; Dinis et al., 2021). L’Inventaire national des rejets de polluants évalue à près de 55 000 kg de plomb, plus de 870 kg de cadmium et plus de 36 500 kg d’arsenic et plus de 14 000 tonnes de dioxyde de soufre et de 250 tonnes d’oxydes d’azote ont été rejetés dans l’atmosphère en 2021 par la fonderie Horne (Bonham-Carter, 2005; Canada Government, 2021). Ces émissions ont entraîné des conséquences visibles sur l’environnement, notamment le dépérissement forestier, la contamination des sols et l’accumulation de dépôts sur les bâtiments et les infrastructures (Alpay et al., 2006; Bilodeau et al., 2020; Bonham-Carter et al., 2006; Gagné et Létourneau, 1993). Par ailleurs, l’exposition chronique des populations urbaines à des contaminants tels que l’arsenic et le plomb a posé d’importants problèmes de santé publique, documentés dès les années 1970-1980 (Gagné, 1994; Gagnon et al., 2016). La situation de Rouyn-Noranda illustre ainsi un conflit emblématique entre développement industriel et protection de la santé et de l’environnement, similaire à d’autres contextes industriels où la croissance économique a eu des impacts environnementaux et sanitaires majeurs (Pérez et al., 2021; Phillips et al., 1998; Tilt, 2013).

À partir des années 1970-1980, des pressions sociales et politiques croissantes ont émergé à Rouyn-Noranda, portées en grande partie par des études citoyennes visant à documenter la contamination des terrains privés. Cette mobilisation s’inscrivait dans un contexte de transition de la fonderie vers le traitement de concentrés importés (Rivard, 2021). C’est également durant cette période qu’a été mis en place le Programme de biosurveillance de l’arsenic, qui constitue une étape clé dans la reconnaissance et le suivi des enjeux environnementaux et sanitaires liés aux activités métallurgiques dans la région (Glencore, 2025c). Pour répondre à ces préoccupations, des technologies de dépollution ont été progressivement implantées, incluant des filtres, des électrofiltres et des fours plus efficaces. Parallèlement, le gouvernement du Québec a mis en place des plans spécifiques visant la fonderie, incluant des normes environnementales et sanitaires ainsi qu'un suivi régulier (Glencore, 2022; MELCCFP, 2023). Ces mesures ont permis une réduction progressive des émissions de SO_2 et d'arsenic : les concentrations atmosphériques d'arsenic sont passées de plus de 1 000 ng/m³ dans les années 1970 à environ 100 ng/m^3 dans les années 2000, bien qu'elles restent largement supérieures aux normes actuelles de 3 ng/m^3 (Bonham-Carter, 2005). En 2024, la moyenne annuelle de la concentration atmosphérique en arsenic est passé sous la barre des 45 ng/m^3 (norme de la nouvelle autorisation ministérielle 2023-2028), avec une valeur annuelle de 39,1 ng/m^3 (Communiqué de la fonderie Horne, avril 2025).

Problématique. Des études antérieures ont permis de démontrer que les métaux lourds autour de la fonderie de Rouyn-Noranda s'étendent sur plusieurs dizaines de kilomètres (Hou et al., 2006; Savard et al., 2006; Zdanowicz et al., 2006). Toutefois, l'étendue actuelle et la distribution historique de cette contamination dans la zone urbaine de Rouyn-Noranda (<5km de la fonderie) demeurent mal connues. Il est donc difficile de quantifier précisément la dispersion spatiale et temporelle de la pollution. Des études sur les sols urbains ont montré que les concentrations en métaux lourds ne suivent pas toujours un gradient clair avec la distance, et présentent parfois des hotspots ponctuels (Gagné et Létourneau, 1993; Bilodeau et al., 2020). Sur le plan temporel, la majorité des travaux se concentrent sur les forêts naturelles, où les arbres ont souvent plus de 70 ans (Dinis et al., 2021; Savard et al., 2023), alors que les arbres urbains ont généralement entre 20 et 40 ans et sont donc rarement antérieurs à l'implantation de la fonderie Horne.

D'autre part, les effets de la pollution industrielle sur la composition et la dynamique des communautés microbiennes du sol demeurent largement méconnus. Bien que les impacts séparés de l'acidification et des métaux sur la croissance végétale (Shi et al., 2021), le cycle de l'azote (Savard et al., 2021) ou la biodiversité microbienne (Fajardo et al., 2019) soient relativement bien documentés, on dispose de peu de connaissances sur l'interaction de ces deux facteurs. Cette combinaison pourrait avoir des effets synergiques ou antagonistes non prévisibles à partir des études portant sur chaque facteur isolé, laissant un vide important dans notre compréhension des écosystèmes contaminés. Étant donné que les modifications des communautés du sol entraînent des perturbations du cycle biogéochimique de l'azote (Denk et al., 2017), il apparaît essentiel de comprendre comment ces changements se reflètent dans les signatures isotopiques ($\delta^{15}N$) des cernes d'arbres, afin d'établir un lien entre pollution, fonctionnement microbien et indicateurs dendroisotopiques. Cependant, l'utilisation du $\delta^{15}N$ comporte certaines limites. Bien que l'utilisation des isotopes de l'azote comme traceurs des processus écologiques et biogéochimiques ait déjà été utilisée (Savard et al., 2020; Savard et Siegwolf, 2022), il y a peu d'études expérimentales en environnements contrôlés permettant d'interpréter les variations isotopiques observées. À ce jour, il est difficile de dissocier les effets de la pollution, des propriétés du sol et de la physiologie des plantes sur la composition isotopique de l'azote. L'absence de telles études limite la capacité à utiliser le $\delta^{15}N$ comme outil diagnostique dans des écosystèmes naturels complexes.

Structure et objectifs spécifiques de la thèse. Cette thèse vise à mieux comprendre l'impact de la pollution industrielle sur les écosystèmes boréaux en combinant l'analyse rétrospective de données environnementales issues d'arbres urbains avec des expérimentations en conditions contrôlées. L'approche repose sur l'étude conjointe des sols, des communautés microbiennes et des arbres, permettant ainsi d'intégrer différents niveaux d'organisation biologique et temporelle et d'établir des liens de cause-effet. L'hypothèse de travail unificatrice est que la contamination atmosphérique entraîne des répercussions à cascade sur l'écosystème boréal visibles sur les fonctionnements microbiens et la composition des cernes des arbres. Trois objectifs principaux guident ce travail :

Chapitre I : Reconstituer l'historique de la contamination métallique dans les arbres : En analysant la bioaccumulation du plomb et du cadmium dans les cernes de croissance de conifères urbains (notamment pins et épinettes), nous visons à retracer les conditions de pollution passées (années 1990) et actuelles (années 2020). Ce volet permettra d'évaluer l'empreinte des émissions de la fonderie dans un contexte urbain, en caractérisant la dynamique spatio-temporelle de la contamination métallique enregistrée dans les arbres. Nous nous attendions à ce que les concentrations en métaux diminuent avec la distance à la fonderie et en suivant l'axe des vents dominants vers le sud-est. Nous supposions que les cernes de croissance plus anciens présenteraient des concentrations plus élevées que les cernes récents en raison des mesures de réduction de la pollution. Nous anticipions également des différences de concentrations entre les espèces étudiées. Enfin, nous prévoyions que les ratios isotopiques du Pb reflètent clairement la signature des émissions de la fonderie.

Chapitre II : Évaluer l'impact de la pollution sur le cycle de l'azote et la croissance des arbres : Ce volet combine une expérimentation en serre et l'observation d'arbres en milieu naturel. En conditions contrôlées, nous souhaitons évaluer l'effet simple et conjoint du plomb et de l'acidification sur la croissance et la composition isotopique de l'azote dans le xylème de plantules d'épinette noire, et appliquer ces informations pour interpréter les données de $\delta^{15}N$ dans les cernes d'arbres matures collectées en forêt. Cette approche devrait permettre de distinguer les effets de la chimie du sol de ceux liés à la physiologie de l'arbre en comparant des arbres de la même espèce dans des conditions contrôlées. Elle constitue aussi un cadre pour confronter les réponses expérimentales aux observations réalisées en milieu naturel exposé à la pollution. Elle offre ainsi la possibilité de tester la pertinence du $\delta^{15}N$ comme indicateur des perturbations environnementales. Nous nous attendions à ce que la baisse du pH réduise la concentration en nitrate et augmente la concentration en ammonium, tandis que le Pb seul n'affecterait pas directement ces formes d'azote. Nous prévoyions que l'acidification augmenterait les valeurs de $\delta^{15}N$ du pool azoté du sol. Nous anticipions également que des concentrations élevées en Pb et un pH faible réduiraient la germination et la croissance des plants. A l'instar des sols, nous supposions que les arbres présenteraient des valeurs de $\delta^{15}N$ plus élevées en conditions acides. Enfin, dans les forêts polluées, nous nous attendions à une hausse du $\delta^{15}N$ des cernes proches de la source de pollution, en raison du pH plus faible et de la contamination accrue en métaux.

Chapitre III : Explorer le lien entre la pollution des sols et les communautés microbiennes : Enfin, nous examinerons comment la pollution affecte la structure et la composition des communautés microbiennes du sol. Ce chapitre repose également sur un dispositif expérimental en serre, permettant de tester directement les effets de la pollution du sol sur la biodiversité microbienne. Nous anticipions que la contamination au Pb réduirait la diversité et l'abondance microbiennes. Nous nous attendions cependant à ce que l'acidité du sol ait un effet encore plus marqué que le Pb, diminuant fortement la biodiversité microbienne. Nous supposions que la combinaison acidité + Pb amplifierait les effets négatifs de chaque pollution prise isolément. Finalement, nous prévoyions que l'acidité et/ou le Pb modifierait la composition des taxons liés au cycle de l'azote et perturberait les processus clés de transformation de l'azote.

Ces trois volets devraient permettre d'apporter des perspectives complémentaires sur les impacts de la pollution industrielle. Le premier chapitre établit le contexte historique et spatial de la contamination métallique dans les arbres urbains. Les deuxième et troisième chapitres, innovants en conditions expérimentales, permettent de tester de manière contrôlée les mécanismes sous-jacents reliant la pollution du sol, la physiologie végétale et la dynamique microbienne. Ensemble, ces approches offrent une compréhension intégrée de la manière dont la pollution industrielle affecte les sols et ses processus, les communautés vivantes et la mémoire environnementale inscrite dans les cernes des arbres.

1. SPATIOTEMPORAL ASSESSMENT OF LEAD (PB) AND CADMIUM (CD) CONTAMINATION IN URBAN TREE RINGS NEAR AN INDUSTRIAL SMELTER: HIGH INTRASPECIFIC VARIABILITY BUT LIMITED SPATIAL DIFFERENTIATION.

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Résumé

L'évaluation des concentrations de plomb (Pb) et de cadmium (Cd) dans les cernes de croissance des arbres peut fournir des archives historiques de la contamination environnementale, en retraçant les variations temporelles et la distribution spatiale des polluants. Cette étude a examiné la bioaccumulation de métaux lourds (ML) dans les cernes d'arbres afin d'évaluer l'impact des activités de fusion à l'aide d'arbres urbains. Des cernes d'arbres de conifères urbains ont été échantillonnés dans un rayon de 5 km autour de la fonderie pour estimer les tendances spatio-temporelles des concentrations de Pb et de Cd, en évaluant les effets des mesures de réduction de la contamination et les différences interspécifiques de bioaccumulation. Les rapports isotopiques du plomb ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$) ont également été mesurés afin d'identifier l'origine du Pb. Les résultats n'ont révélé aucun patron spatial clair en fonction de la distance à la fonderie, ce qui pourrait s'expliquer par la faible superficie d'échantillonnage. Toutefois, la bioaccumulation de Cd chez les pins urbains était de 4 à 7 fois plus élevée que dans le site éloigné, situé à 80 km, indiquant un impact local de la contamination industrielle dans la zone urbaine. L'analyse temporelle chez le pin a montré une diminution de 0,27 mg/kg de Cd (47 %) entre 1990 et 2020, reflétant l'influence potentielle des mesures de réduction de la pollution, tandis que les concentrations de Pb dans le pin étaient 2,7 fois plus élevées (augmentation de 0,06 mg/kg) sur la même période. Le pin a accumulé davantage de Cd que l'épinette, alors que cette dernière présentait des concentrations plus élevées de Pb que le pin. Les mesures isotopiques ont confirmé que la fonderie de cuivre constitue la principale source de Pb. Ces résultats soulignent la complexité des mécanismes d'absorption des métaux lourds chez les arbres urbains et suggèrent que des recherches supplémentaires sont nécessaires afin de mieux comprendre les effets spatio-temporels sur les patrons de bioaccumulation des ML et d'identifier les espèces les plus adaptées à la phytoremédiation.

Mots-clés : Métaux lourds, contamination, cernes de croissance, fonderie, arbres urbains

Abstract

Assessing lead (Pb) and cadmium (Cd) concentration in tree rings may provide historical records of environmental contamination, capturing temporal changes and spatial distribution. This study examined heavy metal (HM) bioaccumulation in tree rings to assess the impact of smelting activities using urban trees. Tree rings from urban conifers were collected within a 5 km radius of the smelter to estimate spatiotemporal trends of Pb and Cd concentrations, evaluating the outcomes of contamination reduction measures and interspecies bioaccumulation patterns. Pb isotopic ratios ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$) were also measured to evaluate the Pb origin. Results showed no clear spatial pattern in relation to distance to the smelter, which may be due to the small sampling area. However, Cd bioaccumulation in urban pine was 4 to 7 times higher than in the distant site, 80 km away, indicating a local impact of industrial contamination in the urban area. Temporal analysis for pine showed a decrease of 0.27 mg/kg Cd (47%) between 1990 and 2020, reflecting the potential influence of contamination-reducing measures, while Pb concentrations in pine were 2.7 times higher (increased by 0.06 mg/kg) for the same period. Pine bioaccumulated more Cd than spruce, while spruce accumulated higher levels of Pb compared to pine. Isotope measurement confirmed that the copper smelter is the primary source of Pb. These findings underscore the complex nature of HM uptake in urban trees and suggest that further research is needed to understand the spatiotemporal effects on HM bioaccumulation patterns and which species are best suited for phytoremediation.

Keywords: Heavy metals, contamination, tree rings, smelter, urban trees

1.1 Introduction

Urban environments are affected by airborne heavy metal (HM) contamination, primarily from anthropogenic sources (Kumar et al., 2017). HM are found in particularly high concentrations in industrial cities associated with metallurgy, mining operations, and waste incineration facilities (Bi et al., 2020; Briffa et al., 2020; De Silva et al., 2016; Perone et al., 2018). The presence of HM in urban environments poses risks to human health and ecological systems, as soil, water, and vegetation have the ability to accumulate these metals (Binner et al., 2023; X. Li et al., 2001), leading to chronic exposure and potential toxicity for both residents and wildlife (Devi, 2024; Edo et al., 2024; Jadaa & Mohammed, 2023). Lead (Pb) and cadmium (Cd) are toxic heavy metals with serious health and environmental impacts. Pb affects the nervous system, especially in children (Q. Wang et al., 2009) and is linked to cardiovascular and kidney diseases. Cd is a known carcinogen that accumulates in the kidneys and weakens bones (Järup et al., 1998). In plants, HM can cause disruptions in nutrient uptake, oxidative stress, transcriptomic and enzymatic damage, impaired photosynthesis, and a reduction in biomass and overall development (Haider et al., 2021; Matei et al., 2025; Zulfiqar et al., 2019).

Heavy metals can adhere to fine particulate matter (PM), allowing them to remain suspended in the air and be transported over long distances by wind. The extent of their dispersion depends on particle size, atmospheric conditions, and emission sources (Daggupaty et al., 2006; Soriano et al., 2012), as well as the wind direction in which PM are often more concentrated in the downwind direction from the emission source (Khaniabadi et al., 2018; Žibret & Šajn, 2008). Larger particles tend to settle closer to the source, while smaller ones (< 2.5 μm) can travel hundreds of kilometers before deposition (Daggupaty et al., 2006; Hou et al., 2006; K. Zhang et al., 2018). PM can carry HM directly onto leaves and stems, but only smaller ones can enter (< 0.1μm). Heavy metals in soil dissolve into bioavailable forms influenced by pH and organic matter, then enter roots via passive diffusion or active transport. Once absorbed, they move through the xylem to stems and leaves or are sequestered in root tissues limiting toxicity (Clemens et al., 2002; Matei et al., 2025).

To assess HM dispersion patterns in the environment, airborne pollution monitoring networks are needed, which can include sensors that integrate average exposure conditions. In this context, analyzing tree rings as indicators of environmental contamination offers several advantages, including the ability to reveal pollutant spatial distribution and temporal changes in contamination levels through the absorption of HM by root water uptake (Kiss et al., 2019; Martinelli, 2004; Nabais et al., 1999; Savard et al., 2006). HM are then translocated from the roots to the trunk and shoots, where they can be retained (Sumiahadi & Acar, 2018). HM are primarily stored in stem woody tissues of tree species (H. Li et al., 2020). The mobility of HM in the soil and plant tissues is a key factor to be considered for using tree rings to monitor historical pollution, as it determines the reliability of these indicators for reconstructing metal deposition in the environment (Lepp, 1975). Numerous studies have highlighted the potential of tree ring Pb and Cd concentrations as effective indicators to reconstruct historic metal deposition (Chen et al., 2021a; Cutter & Guyette, 1993; Doucet et al., 2012; Savard et al., 2006) as they exhibit limited radial mobility, particularly in conifers, which have an even wood structure across rings (Doucet et al., 2012; Watmough et al., 1999). Pine and spruce are effective biomonitors for HM due to their long lifespan and ability to accumulate pollutants in both needles and wood over time, providing a reliable record of contamination (Godek et al., 2015; Sawidis et al., 2011). However, the potential mobility of HM in xylem tissue varies between tree species, which may have distinct abilities to uptake and accumulate metals in their tissues (Alahabadi et al., 2017; Li-qiang et al., 2004).

In addition, contamination sources can be identified and confirmed using environmental indicators such as Pb isotopes ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$), which help distinguish between natural, industrial, and other anthropogenic emissions such as mining (Novak et al., 2010; Savard et al., 2006). For example, Savard et al. used Pb isotopes to trace pollution sources in forest trees located outside the city of Rouyn-Noranda, which differ from urban trees in terms of environmental exposure (Savard et al., 2006). Acute levels of emissions from complex, heterogeneous contamination sources, including local traffic, construction activities, and multiple industrial processes, can be found in urban areas, leading to specific HM concentrations and isotopic ratios (Widory et al., 2018; Yu et al., 2016).

The use of tree rings in the context of smelter emissions can provide valuable insights for evaluating the evolution of emissions over the years. In this paper, we aim to assess the spatial and temporal patterns of HM contamination in Rouyn-Noranda by quantifying metals bioaccumulated in the tree rings of urban trees. Rouyn-Noranda, located in western Québec, Canada, has a history closely tied to the in-town Horne copper smelter that initiated its activity in 1927 (Glencore, 2025b). We hypothesized that (1) HM concentrations in tree rings would decrease with distance from the smelter and (2) will vary across the tree species considered (spruce and pine). Additionally, we hypothesized that (3) HM concentrations would be higher in earlier tree rings compared to recent rings due to the implementation of pollution-reducing regulations affecting smelter operations. Finally, we expected that (4) the Pb isotopic ratios in the analyzed tree rings would clearly fingerprint smelter emissions.

1.2 Methods

1.2.1 Study area

The Horne smelter has been a significant source of HM emissions in the region of Rouyn-Noranda (RN) since its beginning. Operating since 1927, the smelter has released various pollutants into the surrounding environment, including HM and metalloids such as cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and arsenic (As) (Bonham-Carter, 2005; Canada Government, 2021). In the Rouyn-Noranda area, tree rings have shown high concentrations of heavy metals beginning in the 1940s, with a significant rise after 1960 (Savard et al., 2005). Additionally, isotopic analysis of lead identified the smelter as the primary source of contamination in the nearby natural forest ecosystems (Savard et al., 2006). The dispersion of these pollutants is also influenced by the prevailing winds. These winds carry the emitted particles across the region, leading to higher concentrations of pollutants in soils and trees in downwind areas (Hou et al., 2006).

1.2.2 Tree selection and wood sampling

Trees were selected after a public call for participative science on social media. A total of 63 residents from Rouyn-Noranda expressed interest, alongside participation from the municipal administration. 53 coniferous trees were selected within the urban area limit, including 32 trees from private yards and 21 trees from public parks. The sampled tree species includes 21 white spruce (*Picea glauca* (Moench) Voss), 19 red pines (*Pinus resinosa* Aiton), 4 white pines (*Pinus strobus* L.), 5 larch (*Larix laricina* (Du Roi) K. Koch), and 4 cedars (*Thuja occidentalis* L.) (Fig. 2, Table A1). White and red pines were considered together for the analyses because they belong to the same genus and share similar functional traits related to nutrient uptake, wood formation, and physiological responses to environmental stressors (Motley, 1949; Wetzel & Burgess, 1994). We chose to focus our analysis on the two most extensively sampled species (Spruce and Pine) to ensure consistency in sampling structure and enhance the robustness and comparability of our results. The other species had too few samples, making meaningful comparisons impossible and rendering the data difficult to interpret. However, the complete data are available in Supplementary materials (Appendix A).

All 53 trees were located within a 5 km radius of the Horne smelter, but only four trees were located north of the smelter because of limited urban development in this direction. For comparison purposes, ten additional “distant” trees (5 white spruce and 5 red pines) were chosen in Amos, Québec, Canada, a city located roughly 80 km northeast of Rouyn-Noranda, where the influence of the smelter should be low (Henderson & Knight, 2005) but not nonexistent since the fingerprint of the Horne smelter is measured in the air more than 100 km (Daggupaty et al., 2006). This choice was supported by the low industrial influence in Amos and the absence of a major source of metal contamination comparable to the Horne smelter. Despite some differences in urban structure or population density, Amos shares similar regional characteristics with Rouyn-Noranda (climate, geology, forest cover), allowing for a relevant comparison of background levels.

Metadata on the maintenance practices of private yards was collected through a survey proposed to the owners to know if additional factors could explain HM concentrations (ex. soil restructuration around the tree, major renovation work of the house or use of pesticides in the garden); however, none of the management variables was significant in our analysis (Appendix A).

For each tree, a 1.2 cm diameter wood core was extracted at breast height (around 1.3 m) with an increment borer. A single core was sampled from each tree to minimize damage, particularly because many trees were located on private properties. This approach was the only feasible option that provided enough wood material while remaining acceptable to the property owners. Tree cores were selected for sampling because the trunk, as the largest and most stable organ of the tree, offers a reliable and continuous archive of metal accumulation over time (Aznar et al., 2008; Sevik et al., 2019). Unlike needles, which are responsive to short-term environmental fluctuations, wood tissue allows for reconstruction of long-term contamination patterns (Chen et al., 2021b; Turkyilmaz et al., 2018). In the lab, each wood core was processed to obtain two flat, polished faces using a sliding microtome (WSL Core-Microtome, Gärtner and Nievergelt, 2010). This method facilitated tree ring measurement and counting while preventing contamination by wood dust. Cores then underwent oven-drying at 60°C for 3 hours before being stored at room temperature. Manual counting of growth rings was performed under a binocular microscope. Using a steel blade, the last five complete growth rings of each core (44 trees in Rouyn-Noranda and 10 trees in Amos), corresponding to the years 2018-2022, were dissected under a binocular microscope. In addition, the oldest trees from Rouyn-Noranda (5 white spruce and 5 red pines) were also sampled for growth rings corresponding to two other time frames: 1998-2002 and 1989-1993 (Fig. A1). Subsequently, around 200 mg of material from each dissected period (2020s, 2000s and 1990s) was obtained with equal weight for each tree ring, and the samples were stored in Eppendorf tubes waiting for metal analysis. In our study, when we refer to 2020, we are specifically considering the tree rings from that year and have not accounted for the temporal lag in pollutant uptake. When interpreting the results, readers should consider that the metals found in the 2020 ring may have originated from emissions occurring over the previous 10-15 years.

In addition, 5 white spruce trees from various directions around the smelter among the 21 sampled were selected for a preliminary lead isotope analysis to assess the feasibility of source attribution (Table A2). The distinct isotopic ratios of lead can help trace its origin, whether it is from natural, industrial, or other anthropogenic emissions (Savard et al., 2006).

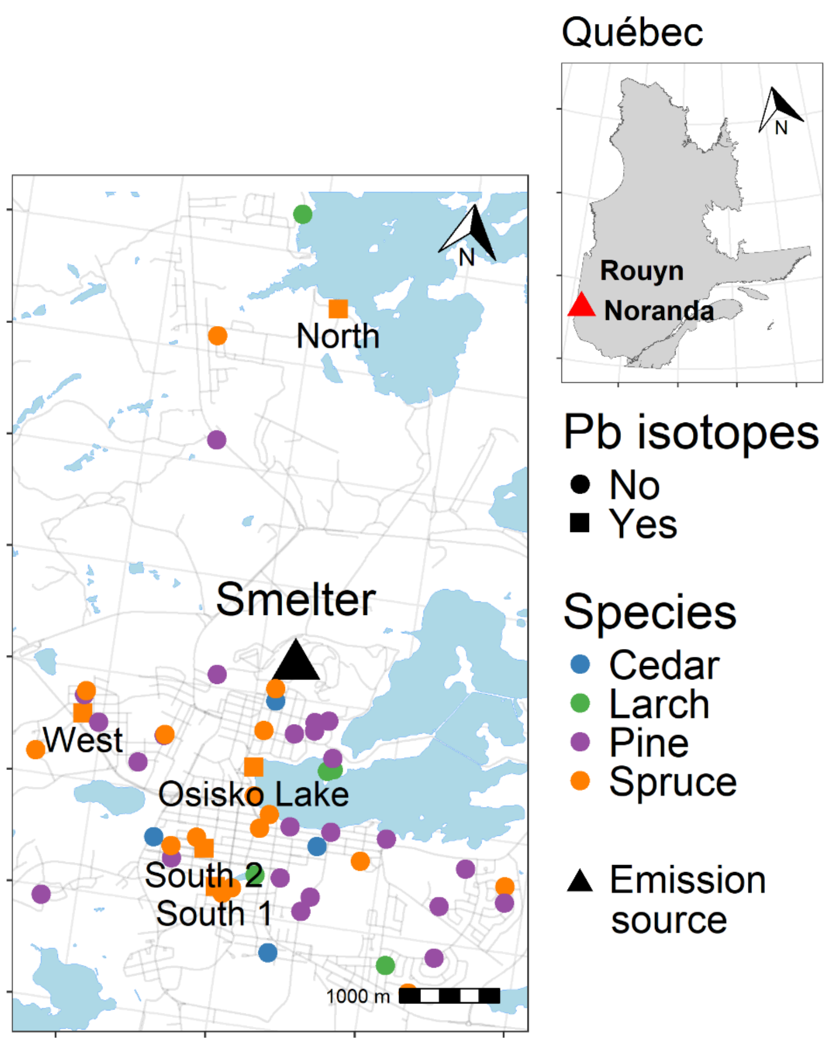

Figure 2
Species and spatial distribution of the selected trees in the urban area limit of the Horne smelter, Rouyn-Noranda (Québec, Canada). Heavy metal concentration was measured from all trees, and only some trees analyzed for lead isotopes (refer to legend). Streets (represented with black lines) and lakes (shaded polygons with blue lines) are displayed as background features to provide geographical context.

1.2.3 Pb and Cd analyses

All analyses, including metal concentrations and lead isotopes, were conducted at the INRS-ETE Geochemistry Laboratory, Québec, Canada. The composite wood samples underwent a digestion process using nitric and hydrofluoric acid within polytetrafluoroethylene containers, followed by gentle heating to concentrate metals. Subsequently, digested samples were treated with ultrapure water and nitric acid. Pb and Cd concentrations within tree rings were determined using Inductively Coupled Plasma Mass Spectrometer (ICP-MS Therma XSeries) (Poupon, 2021; U.S. E.P.A, 1994). Quality assessment of the heavy metal concentration analyses was ensured by incorporating blank solutions (ultrapure water) and certified reference materials (pine needles 1575a, Mackey et al., 2004 ; and citrus leaves 1572, (Alvarez, 1982)) in each batch of samples analyzed. The detection limits were 0.002 and 0.004 mg/kg for Cd and Pb respectively, and the analytical precision for metal concentration measurements varied depending on the tree species and metal analyzed. For Cd, the precision was 3.0% in pine and 10.3% in spruce. For Pb, the precision was 20.4% for pine and 15.2% spruce (10% replicates). The precision for certified reference materials ranged from 3 to 8%.

The isotopic ratios of Pb ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$) were analyzed using a Thermo iCAP Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Samples were filtered in a solution of 0.2% HNO3. Correction for mass bias during the determination of the isotopic ratios was performed using analyses of SRM 981 (Common lead NIST, USA) after every two samples.

1.2.4 Prevailing wind direction

The direction of the prevailing winds was integrated as a key parameter for studying the dispersion of HM. This factor was considered in the interpretation of our data, even though no samples were collected from the northeastern zone, a non-urban area directly influenced by the prevailing winds. Wind direction and speed from a meteorological station located in Rouyn-Noranda (Environment Canada ROUYN station, ID number: 10849, latitude: 48°14'45" N ; longitude: 79°02'03" W), were acquired from Environment and Natural Resources Canada's historical data covering the period from 1994 to 2023 (Environment Canada, 2023). The wind direction was measured in tens of degrees and represents the direction from which the wind is blowing. This value represents the average direction at the time of observation aggregated to an hourly interval. To extract the prevailing wind directions from the data, “polarFreq” function from “openair” package (Carslaw & Ropkins, 2012) was used in RStudio environment. This function is designed to generate a polar diagram illustrating the frequency of winds in various directions and speeds.

To create a variable indicating the relative exposure of the sampled trees to the prevailing winds, the Beers’ transformation (Eq. 1) was used (Beers et al., 1966).

$$\text{Aspect} = \cos(\theta_{max} - \theta) + 1 \qquad \text{(Eq. 1)}$$

Here, θ is the angle between the smelter and a tree and θ_{max} is the angle which is to be assigned the highest numerical value on the transform scale corresponding to the prevailing wind axis (20°, angle obtained from x-axis in the counterclockwise (trigonometric) direction). This approach yields a value between 0 and 2. The closer the value is to 2, the closer the tree is to the prevailing wind axis relative to the smelter; conversely, the closer the value is to 0, the farther the point is. In theory, higher values therefore indicate a higher likelihood of receiving contamination from the smelter.

1.2.5 Statistical analysis

All statistical analyses and computations were performed using the R software (R Core Team, 2025).

Linear models were used to evaluate how the (log-transformed) metal concentration in the wood of the sampled trees over the period 2018-2022 was affected by exposure to the prevailing winds (Aspect; winds passing over the smelter), by the distance to the smelter (km), by their interaction and by tree species identity. All possible combinations of variables, ranging from the simplest (one variable) to the most complete, including (Eq. 2) and excluding interaction terms, were systematically tested, with models ranked according to the lowest Akaike Information Criterion (AIC corrected for small samples: AICc). We used model averaging to evaluate the relative support for each model. When no single model has an Akaike weight above 0.9, model averaging provides more robust parameter estimates (Burnham & Anderson, 2002; Grueber et al., 2011).

$$\log_{10}[\text{Metal}] = \beta_0 + \text{Species} + \text{Aspect} * \text{Distance} \qquad \text{(Eq. 2)}$$

where Metal could be either Pb or Cd. β_0 represents the baseline value of the log-transformed metal concentration when all other variables are at their reference levels.

Additionally, the Kruskal-Wallis test was used to further assess significant differences in log-transformed metal concentrations between the studied tree species. The test is adapted to small sample sizes and heterogeneous variance between groups. Subsequently, Dunn's post-hoc test was applied to identify the specific species showing significant differences in metal concentrations.

A Wilcoxon rank-sum test was performed for both spruce and pine to compare metal concentrations between samples from Rouyn-Noranda and the distant group in Amos. This non-parametric method is appropriate for comparing two groups from small and heterogeneous samples.

To analyze the temporal evolution of pollutant concentrations (Pb and Cd) in tree rings, linear mixed-effects models were fitted using the lme4 package in R. Year was considered as a fixed effect to assess the general trend in metal concentrations over time, and individual tree identity was included as a random effect since measurements were repeated on the same trees. The model structure was specified as: metal concentration ~ Year + (1 | Tree ID). Model fit was evaluated using marginal and conditional R^2 values, and residual diagnostics were performed to verify model assumptions (normality and homoscedasticity)

1.3 Results

1.3.1 Spatial distribution of sampled trees

All trees were located between 0.3 and 4.5 km from the smelter, with the majority located in the southwest direction (Fig. 2). This spatial distribution is due to the location of the city of Rouyn-Noranda relative to the smelter, as well as the presence of Osisko Lake to the east of the smelter and tailings ponds to the north. Prevailing winds in the city also originate from the southwest and northwest. However, for the following analyses, the prevailing winds with the highest frequency were selected, which come from the southwest (Figs. A2 and A3). This aligns with the dominant summer winds, which is also the main growing season for trees. Due to the location of the sampled trees and the direction of the prevailing wind, most of the trees had mid to low exposure to wind passing over the smelter (Fig. A4).

1.3.2 Lead and cadmium concentration in present tree rings (2018-2022)

Model averaging based on Akaike weights indicated that species identity was the only significant variable explaining metal accumulation patterns in tree rings, suggesting that tree species accumulated metals differently. White spruce had higher Pb concentrations and lower Cd concentrations than pine (Table 1, Fig. 3 and A5). Other factors, such as wind and distance, did not significantly affect Cd or Pb concentrations in tree rings (Table 1, Table A3 and A5). The Kruskal-Wallis test confirmed these differences between species in metal accumulation, with p-values < 0.0001 for both Pb and Cd (chi-squared = 14.951 and 24.699 for Pb and Cd respectively).

Table 1
Model-averaged parameter estimates with their 95% confidence intervals for the models for Pb and Cd concentrations (log-transformed) in relation to environmental variables and species identity. These results apply only to trees sampled in Rouyn-Noranda. Each row presents the estimates for each independent variable in the sets of candidate models retained by model averaging. The 95% CI estimates in bold do not include 0 and are considered statistically significant.

Metal	Parameter	Estimate	Upper CI	Lower CI
Pb	Wind	0.05	-0.23	0.33
	Distance	0.02	-0.13	0.17
	Wind:Distance	-0.16	-0.49	0.18
	Species_Pine	**-0.59**	**-0.84**	**-0.34**
	Species_Spruce	0.59	-0.34	0.84
Cd	Wind	0.00	-0.23	0.24
	Distance	-0.06	-0.18	0.06
	Wind:Distance	-0.02	-0.30	0.26
	Species_Pine	**0.76**	**0.55**	**0.97**
	Species_Spruce	**-0.76**	**-0.97**	**-0.55**

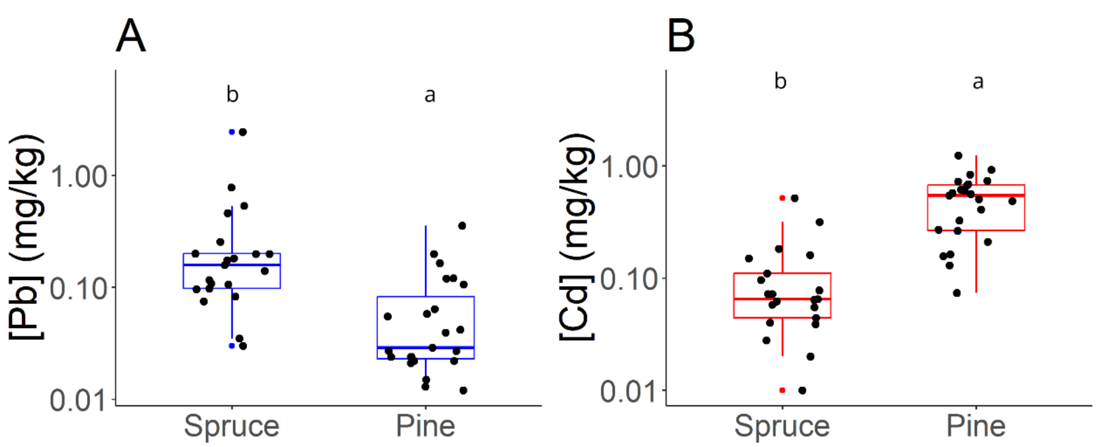

Figure 3
Concentration of (A) lead and (B) cadmium by species in Rouyn-Noranda samples. Boxes represent the interquartile range (Q1 to Q3), horizontal middle line are the median, and bars extend to the most distant data points that are not considered as outliers (values exceeding 1.5 times the interquartile range from the quartiles). Y-axes are all mg/kg but use a log10 scale. Letters show the results of Dunn's post-hoc test to identify which species exhibited

significant differences in their medians (Table A6). Boxes sharing the same letters are not significantly different from each other.

A Wilcoxon rank-sum test indicated that Pb concentrations were similar between trees from Rouyn-Noranda and the distant sites, with p-values of 0.093 for pine and 0.398 for spruce (Fig. 4A, Table A5). In contrast, Cd concentrations in distant pines had levels 4 to 7 times lower than pines from Rouyn-Noranda (Fig. 4B, Table A5). This suggests that while Pb contamination may not differ markedly between the two cities, Cd levels remained significantly elevated in Rouyn-Noranda compared to Amos.

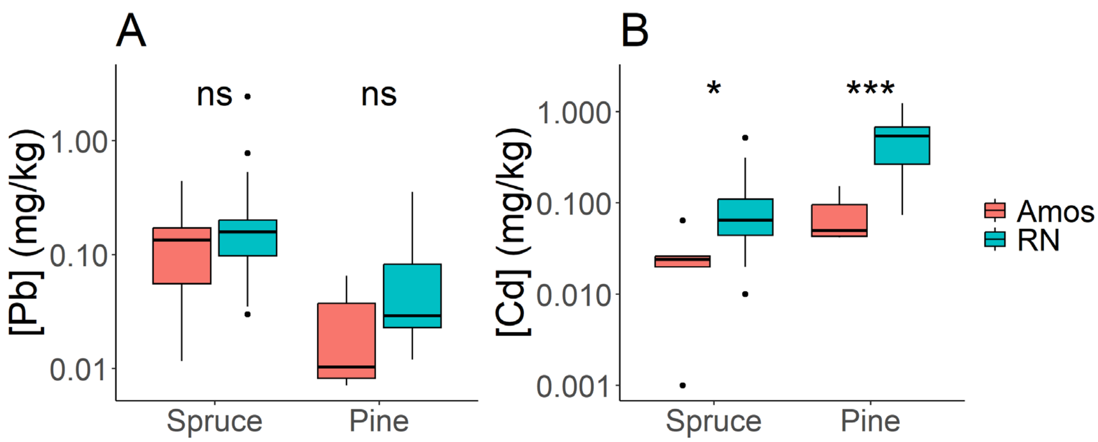

Figure 4
Concentrations of (A) Pb and (B) Cd by species and location (distant (Amos) vs. Rouyn-Noranda (RN)). Y-axes are all mg/kg but use a log10 scale. Statistical significance determined by Wilcoxon test is indicated as follows: ns = not significant, *** = p-value < 0.001, * = p-value < 0.05.

1.3.3 Lead and cadmium concentration in past tree rings

There was a significant decrease in Cd concentrations in pine between 1990 and 2020 (p-value = 0.02) while Cd concentrations between 1990 and 2000 were similar (p = 0.688). Cd concentrations in 2020 were 0.27 mg/kg lower than in 1990, representing a 47% decrease. In spruce, no significant change in Cd concentrations was observed between 1990 and 2020 and between 1990 and 2000 (p = 0.129 and 0.68 respectively). However, the analysis suggests a slight downward trend in metal accumulation over this period (Fig. A6). The Pb concentrations in pine trees were higher in 2020 and 2000 compared to 1990 (p = 0.026 and 0.005 respectively). There was an increase of 0.04 mg/kg in 2000 and 0.06 mg/kg in 2020 compared to 1990, representing concentrations 2 to 2.7 times higher than those in 1990. No significant change in Pb concentrations was observed in spruce trees compared to the reference level (Table 2).

Table 2
Temporal variations in Pb and Cd concentrations in Rouyn-Noranda tree rings using linear mixed-effect models: log10(Metal)=Year+(1|tree). "Year" is included as factor and "tree" is specified as a random effect, which accounts for individual differences among the sampled trees (n = 5). The estimate column reports the estimates of the periods in the original unit (mg/kg) obtained as 10^(Y). p-values indicate difference between a specific period and Year 1990 (* = p-value < 0.001, ** = p-value < 0.01, * = p-value < 0.05).**

			Estimate (mg/kg)
Pb	Spruce	Year 1990	0.13 (***)
		Year 2000	0.11
		Year 2020	0.14
	Pine	Year 1990	0.03 (**)
		Year 2000	0.10 (**)
		Year 2020	0.07 (*)
Cd	Spruce	Year 1990	0.15 (**)
		Year 2000	0.14
		Year 2020	0.06
	Pine	Year 1990	0.59
		Year 2000	0.65
		Year 2020	0.32 (*)

1.3.4 Lead origin

Three of the five analyzed trees fall within the isotopic ranges of the smelter origin for both the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios. For the South 1 and Osisko Lake sites, the $^{206}Pb/^{207}Pb$ ratio was approximately 1.1 and the $^{208}Pb/^{206}Pb$ ratio was around 2.15 (Table 3). These values are in between the smelter signature and the normal Canadian urban air signature (Sturges & Barrie, 1987). Finally, the $^{206}Pb/^{207}Pb$ isotopic ratios recorded for all specimens were remarkably consistent, ranging from 0.99 to 1.10.

Table 3
Measurements of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in the last tree rings of the five selected white spruce trees, in Rouyn-Noranda. The reported signatures from different Pb sources are also indicated for Horne (Hou et al., 2006; Savard et al., 2006; Widory et al., 2018) and Sudbury (Widory et al., 2018) smelters, along with Canadian (Carignan & Gariépy, 1995) and American (Simonetti et al., 2000) urban air signature.

Tree	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
West	1.01	2.30
North	1.03	2.29
Osisko Lake	1.10	2.17
South 1	1.10	2.18
South 2	1.02	2.33
Horne smelter signature	0.92 to 1.03	2.20 to 2.50
Sudbury smelter signature	1.15	2.15
Canadian urban air signature	1.15 to 1.17	2.05 to 2.10
American urban air signature	1.17 to 1.23	2.00 to 2.07

1.4 Discussion

1.4.1 Metal contamination in the city of Rouyn-Noranda

Higher Cd concentration was detected in studied trees in Rouyn-Noranda in comparison to those in Amos. Values in Amos were comparable but higher than those at unpolluted sites located 800 km north of the Horne smelter, which showed Pb and Cd concentrations ranging from 0.01 to 0.03 mg/kg (Savard et al., 2005). The values from these unpolluted sites are three times lower than the median Pb concentrations and nine times lower than Cd levels found in this study near the Horne smelter, with more than 73% of Pb data and 94% of Cd data exceeding 0.03 mg/kg (Fig. 3). Historical data measured in past tree rings in Rouyn-Noranda region before 1930 indicated that average concentrations of Pb were below 0.1 mg/kg and Cd below 0.2 mg/kg (Savard et al., 2005). Such values are similar to those of natural reserves or parks, where anthropogenic impact is minimal and Pb concentrations are typically below 0.1 mg/kg (Bindler et al., 2004). In our case, 53% of our Pb data and 70% of our Cd data exceeded these levels of past concentrations (Savard et al., 2005, Fig.

3). These comparisons strongly suggest that emissions from the Horne smelter could have contributed to heavy metal accumulation on the trees of Rouyn-Noranda. These elevated values show that urban areas, particularly sites close to the smelter and other industrial sources, experience significantly higher levels of metal contamination compared to forested regions. However, typical concentrations of heavy metals in plants are not well documented, particularly for urban trees. There could be considerable variation due to differences in study conditions such as soil characteristics, plant species, and analytical methods. All these aspects can impact reported thresholds for normal and toxic heavy metal concentrations (Table 4).

The isotopic values of Pb, when compared with established ranges in the literature (Komárek et al., 2008; Savard et al., 2006; Widory et al., 2018), confirm the smelter as the primary source of this HM concentrations.

Table 4
Summary of reported Pb levels in tree rings across various contexts found in the literature, documented in mining areas, regions near copper smelters, and natural reserves. It summarizes both background or historical concentrations and the maximum levels recorded.

Context	Location	Past/Background	Maximum concentration	References
Mining	Duparquet, Québec, Canada	Past: 0.05 mg/kg	0.25 mg/kg	(Arteau et al., 2020)
Mining	Murdochville, Gaspé, Canada	Past: 0.05 mg/kg	0.55 mg/kg	(Aznar et al., 2008)
Copper smelter	San Luis Potosi, Mexico	Background: 0.35 mg/kg	Up to 1.4 mg/kg	(Beramendi-Orosco et al., 2013)
Copper smelter	Příbram, Czech Republic	0.02 mg/kg	Up to 0.8 mg/kg	(Mihaljevič et al., 2008)
Copper smelter	Rouyn-Noranda, Québec, Canada	Background: 0.03 mg/kg Past: <0.1 mg/kg	Up to 1 mg/kg	(Savard et al., 2006)
Reserves and parks	Sweden	< 0.1 mg/kg	-	(Bindler et al., 2004)

According to Savard et al. (2004), the highest concentrations of Pb and Cd found in forest ecosystems near the Horne smelter were 1 mg/kg and 0.6 mg/kg, respectively, for sites that were more than 9 km away from the smelter. Arteau et al. (2020) reported a maximum value of [Pb] of 0.25 mg/kg in Abitibi region, while Aznar et al. (2008) indicated that concentrations remained below 0.55 mg/kg in Eastern Canada contaminated sites. Regarding Cd, few studies have specifically focused on this metal. In our study, the maximum concentrations observed in the urban environment of Rouyn Noranda were notably higher, reaching 2.29 mg/kg for Pb and 1.24 mg/kg for Cd (Table A6). Urban areas might experience additional sources of HM contamination such as road dust or past leaded gasoline (Duzgoren-Aydin, 2007; Yang et al., 2024). While the smelter is a significant source of pollution, it is important to consider that these other urban background sources may also contribute to the elevated Pb and Cd levels observed in the urban trees (Savard et al., 2006). Road traffic can generate significant Pb contamination through the resuspension of historically deposited Pb from gasoline, while construction activities and deteriorating infrastructure (e.g., Pb-based paints, corroding pipes) may also release other metals into the environment (Thornton, 1992; Yang et al., 2024; Zwolak et al., 2019). Urban soils might accumulate pollutants over time, and apparent decreases in contamination are generally only observed following explicit remediation or soil management interventions, which could further complicate the interpretation of our results. In the 1990s, a large-scale soil decontamination effort took place in the Notre-Dame neighbourhood of Rouyn-Noranda, the nearest to the Horne smelter. This intervention involved the removal of 6 inches of soil across more than 580 affected properties. After 1990, soil decontamination was carried out if the owners accepted the decontamination offer (Bilodeau et al., 2020; Gagné, 2007). A survey conducted on decontamination processes did not allow us to establish a link between these practices and any potential impact on our samples (Appendix B). Indeed, none of our respondents reported having carried out soil decontamination, which may be due to their recent residence in the house and their lack of awareness regarding the property's history. Additionally, 7 respondents (30%) indicated that they had performed soil addition when planting the sampled tree (Appendix B).

1.4.2 Metal concentration in relation to distance from the smelter within the urban perimeter

Our study reveals that distance from the HM source was not a relevant parameter in our analysis, despite our initial hypothesis that increasing distance from the pollution source would lead to a corresponding decrease in these concentrations. One plausible explanation for this outcome is the proximity of all sampled sites to the smelter, which may have constrained our ability to detect distance-related effects. Studies have shown that soil contamination originating from the Horne smelter can extend up to 100 km (Daggupaty et al., 2006; Hou et al., 2006). In addition, other studies have also demonstrated that metal concentrations often follow a clear gradient within a 5 km radius, similar to our study area, with urban sites closer to the smelter exhibiting significantly higher soil metal concentrations (Bilodeau et al., 2020; Gagné, 2007). These results suggest that distance-related patterns might still be expected in the range of our study. Additionally, the height of the chimneys plays a critical role in determining the distance over which heavy metals can be dispersed. Higher chimneys release pollutants at greater altitudes, allowing the particles to travel longer distances before settling (Romeiro et al., 2020). For certain heavy pollutants like Pb, faster deposition is expected, while finer and lighter particles have longer atmospheric lifetimes and can be transported over greater distances (Daggupaty et al., 2006; Fergusson & Stewart, 1992). The deposition of Cd particles occurs within 10-20 km from the emission source, which means that the 5 km perimeter of this study may not allow for precise understanding of Cd attenuation with distance (Fergusson & Stewart, 1992). Additionally, the smelter's operational practices determine the optimal time for emission by considering the direction of wind and its potential impact on dispersion. Consequently, it has been shown that Mount Powell, in the northwest of the city center of Rouyn-Noranda, had higher contamination levels compared to the urban area (Bilodeau et al., 2020). In addition, along the same lines, the absence of a clear distance and wind signature in the results may also reflect fine-scale climatic variability, including local shifts in wind direction and speed that are not captured by regional meteorological data (Duran Sala et al., 2025). Such microclimatic heterogeneity can influence the dispersion and deposition of airborne contaminants, potentially obscuring expected spatial patterns, and may reduce the detectability of directional gradients and complicate the interpretation of pollutant distributions in relation to prevailing winds.

As shown in Figure 2, the sampling distribution was uneven, with only four trees located north of the smelter and a small number of trees sampled windward from the smelter, an area where Osisko Lake creates a natural barrier. This spatial imbalance may have affected our ability to detect directional pollution trends. Future studies with a broader and more evenly distributed sampling design would improve this directional evaluation and provide a clearer understanding of pollution dispersion patterns. However, such studies should focus on natural forests rather than urban environments, in order not to be constrained by specific urban geography. In addition, the direction from which the wood sample is taken could be important, as some metals, such as Nickel and Cobalt, tend to accumulate more in the direction of pollution (Key et al., 2023), although this has not been observed for Chromium (Pulatoglu et al., 2025). To date, no such evidence exists for Pb and Cd. In our study, we were unable to assess this aspect because only one core sample per tree was collected, in order to minimize damage to trees located in private yards and to encourage owner participation.

1.4.3 Temporal variation of heavy metal in tree rings

The temporal differences observed in metal concentrations in pines, particularly the decrease in concentration of Cd between 1990 and 2020, provide insights into the evolution of environmental contamination in urban areas. The increase in Pb concentrations indicates that Pb contamination remains a persistent issue despite regulatory efforts aimed at reducing emissions. Several factors can contribute to this trend. First, historical industrial activities and leaded gasoline have left significant lead deposits in urban soils, which can continue to affect vegetation (Duzgoren-Aydin, 2007; Nazari Heris et al., 2020; Wade et al., 2021). Unlike Pb, Cd has fewer prominent sources in urban environments. Its primary sources include industrial activities such as mining and battery production (Thornton, 1992). The observed decrease in Cd concentrations in recently formed growth rings, in contrast to the persistent levels of

Pb, can also be explained by the differences in emission patterns and regulatory measures over time. The smelter emitted Pb at levels reaching thousands of tons until 1995, followed by hundreds of tons, thereafter. In contrast, Cd emissions were significantly lower, amounting to only tens of tons after 1995 (Fig. 5) (Bonham-Carter, 2005; Savard et al., 2006). This suggests that, unlike Cd, whose levels have shown a more marked decrease due to fewer residual sources, Pb contamination remains persistent in the urban environment. The analyzed tree rings do not seem to effectively reflect the historical reduction trends in emissions from the Horne smelter, at least for Pb. This pattern may reflect the relatively short time span considered, but also the persistence of metals in soils, which can buffer the response of trees to reductions in atmospheric emissions (Kahle, 1993). Although plants tend to absorb more metals under higher contamination levels, decreases in emissions do not necessarily translate into immediate declines in metal uptake , as legacy contamination in soils can remain available for root uptake over extended periods (Peijnenburg, 2025). As a result, tree-ring concentrations may not clearly reflect recent emission reductions from the Horne Smelter, particularly if soil pools continue to act as a sustained source of metals.

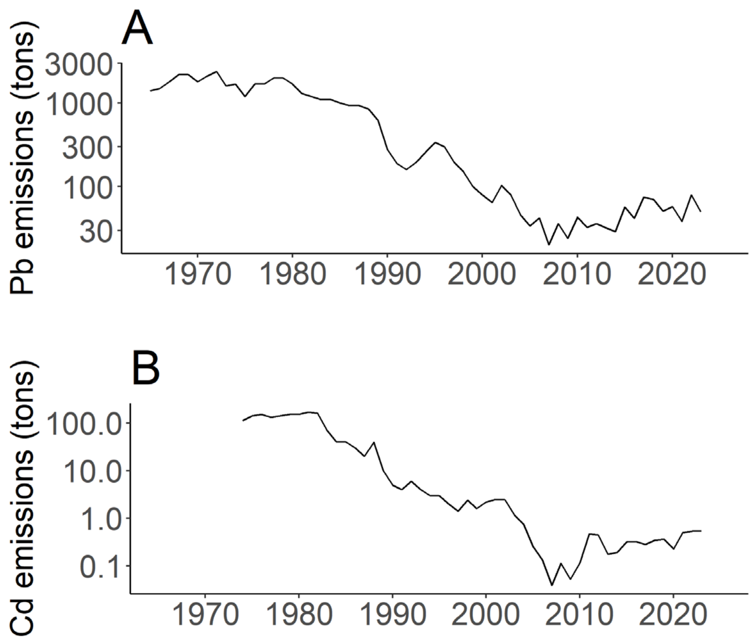

Figure 5
Data on atmospheric emissions processed by the Horne Smelter per year from (A) 1965 to 2023 for Pb and from (B) 1975 to 2023 for Cd. The data from 1965 or 1975 to 2001 originate from the GSC MITE Point Sources Project of the Geological Survey of Canada (Bonham-Carter, 2005). The data from 2002 to 2023 come from the National Pollutant Release Inventory, which compiles pollutant emissions and transfers reported by industrial facilities across Canada.

It is important to highlight that the limited number of samples for the temporal analysis (only five individuals per species) may have affected the robustness of the results, which increases the risk of Type II errors, where actual trends in heavy metal accumulation may go undetected due to limited statistical power. This small sample size is partly due to the relatively young age of trees in urban areas (under 40 years old), which limits the amount of growth rings available for analysis. In forests, trees can provide a longer historical record of metal accumulation, allowing for a more comprehensive study of temporal trends. Expanding the study to include more trees or spanning a greater range of years would likely improve the ability to detect finer trends in both Cd and Pb concentrations.

Interestingly, past studies have found a temporal lag of approximately 13 to 15 years between the emission of pollutants and their possible absorption into tree rings (Arteau et al., 2020; Aznar et al., 2008; Savard et al., 2006), due to the time required for HM to migrate in the soil-root-trunk continuum (Sumiahadi & Acar, 2018). However, it could present a challenge if we want to compare our tree ring data to emission records from the smelter, as it is difficult to account for the temporal lag between metal emissions and absorption in the trees. In our case, this means that tree rings from 1990 may contain metals emitted over the previous 10–15 years rather than 1990 conditions (Fig. 5). Therefore, when interpreting the data and assessing the timeline of contamination events, this lag must be carefully accounted for to accurately evaluate the impact of the smelter and the effectiveness of environmental regulations.

1.4.4 Species differences

In this study, we observed that pine trees accumulated more Cd than spruce, while spruce showed higher concentrations of Pb compared to pine. Heavy metals can enter plants through multiple pathways, including root uptake from soil, foliar absorption via stomatal gas exchange, and direct deposition of airborne particles on leaves or bark (Clemens et al., 2002). Disentangling the relative contribution of each mechanism to metal uptake in our trees remains challenging. One hypothesis is that root uptake dominates in the absorption of HM in our study. Indeed, foliar absorption through stomatal gas exchange could play a role in metal absorption in urban environments, but it is mainly relevant for ultrafine particles (< 0.1µm). Heavy metal bioaccumulation varies by species due to differences in metal uptake, storage, and detoxification mechanisms according to the tree anatomical structure (Koç et al., 2024; Pulatoglu et al., 2025). Some species accumulate more metals due to their tissue affinity for certain metal ions and their ability to store them in specific compartments, such as vacuoles or cell walls, thereby reducing their toxicity (Peng & Gong, 2014). Currently, the specific differences in metal bioaccumulation between pine and spruce species have not been examined in depth. These differences in bioaccumulation may be related to each species' unique characteristics and their distinct metal uptake mechanisms (Li-qiang et al., 2004).

Spruce, with a slower growth rate and a superficial root system, may differ in its metal uptake capacity compared to pine, which has a faster growth rate and deeper taproots (Puhe, 2003). These differences in root architecture could influence the efficiency with which each species absorbs metals from the soil (H. Li et al., 2020; Lilles & Astrup, 2012; Swidrak et al., 2013). Conversely, bark properties do not appear to influence the accumulation of Pb and Cd, as these metals are primarily absorbed through the cambium and fixed to the cell walls during growth (Catinon et al., 2008). Furthermore, each species may have developed unique adaptations to cope with environmental stress, such as the production of intracellular chelators or the storage of metals in root vacuoles, which limits their translocation to aerial parts (Clemens et al., 2002) and could explain the observed differences between pine and spruce (Pajević et al., 2016; Saladin, 2015). For example, pine trees have shown greater resistance to Pb compared to spruce (Seiler & Paganelli, 1987), which may explain the relatively low Pb accumulation observed in the sampled tissue of pine, likely due to more efficient detoxification mechanisms, such as metal sequestration in cell walls or vacuoles, reduced translocation to aboveground tissues, and enhanced antioxidant responses that limit metal-induced oxidative stress (Clemens et al., 2002; Peng & Gong, 2014).

The variability in analytical precision for Pb and Cd concentrations may affect the interpretation of the data. We report a maximum precision variability of 20.4% for Pb and 10.3% for Cd. With [Pb] mean values of 0.07 and 0.31 mg/kg for both pine and spruce, a difference lower than 0.01 and 0.06 mg/kg may just be due to analytical precision. With [Cd] mean values of 0.50 and 0.11 mg/kg for both pine and spruce, a difference lower than 0.05 and 0.01 mg/kg may just be due to analytical precision. However, the standards used in our analyses underwent a much more rigorous homogenization process compared to our wood samples, and the variability range was from 3% to 8%. As a result, this number represents both intra-sample variability and analytical error.

Tree species capable of accumulating heavy metals in their wood are particularly important for phytoremediation studies, as they can help assess long-term pollution trends and contribute to environmental remediation efforts (Tangahu et al., 2011).

Wood, as the largest organ of the tree, offers substantial storage capacity for contaminants over time. However, it generally accumulates lower concentrations of heavy metals compared to needles or bark (Koç et al., 2024, 2025). Our results indicate that pine accumulates higher Cd concentrations, whereas spruce accumulates higher Pb concentrations in tree rings, highlighting species-specific differences in metal uptake and incorporation into woody tissues. These differences suggest that the two species may provide complementary information for biomonitoring purposes. However, it is important to note that metal concentrations in tree rings are generally lower than in more metabolically active tissues such as needles or bark, which may accumulate higher levels due to more direct exposure and faster turnover (Clemens et al., 2002; El-Khatib et al., 2020). They can help stabilize contaminants and reduce their bioavailability in soil.

Tree ring analysis presents several methodological challenges, particularly regarding the uptake of heavy metals by trees. However, the relative importance of these pathways can vary depending on species and local conditions (Lepp, 1975). While the uptake of heavy metals through roots is generally considered the most significant route (Ali et al., 2013; Padmavathiamma & Li, 2007; Sumiahadi & Acar, 2018), variability in metal absorption and accumulation is influenced by factors such as root exposure, selective uptake, and fixation mechanisms, which differ among species, contamination types, and soil conditions (Balouet et al., 2007; Beramendi-Orosco et al., 2013). Ideally, each tree species should be assessed individually as species-specific traits, such as root architecture, xylem structure, and metal detoxification mechanisms, can influence metal uptake and distribution in tree tissues. These differences affect the concentrations recorded in tree rings. While our study did not target species-level analyses, accounting for these traits is important for interpreting interspecific variation and improving biomonitoring accuracy.

1.5 Conclusion

The analysis of urban tree rings provided insights into HM bioaccumulation, showing that pine trees accumulated more Cd than spruce, while spruce trees contained higher concentrations of Pb in their tree rings compared to pine. The results highlight the importance of considering species-specific traits when analyzing environmental contaminants. The study highlights that species differ in their capacity to accumulate heavy metals, indicating that only certain genus may be suitable candidates for phytoremediation purposes. Contrary to expectations, no clear reduction in HM concentrations within the 5 km distance from the smelter was observed in our study. However, it was established that Cd bioaccumulation in Rouyn-Noranda was 4 to 7 times higher than in Amos, suggesting a localized impact of Horne smelter contamination in the urban area. Additionally, a decrease in Cd bioaccumulation over time was observed in pine, likely reflecting the effects of pollution-reducing measures implemented by the smelter. In contrast, Pb bioaccumulation in pine increased across the years, indicating a more persistent presence of Pb in the environment despite regulatory changes. Nevertheless, the smelter isotopic signature of the Pb in tree rings was confirmed by the measured $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ values. Future research is needed, particularly over different time scales, to better understand temporal patterns of heavy metal bioaccumulation in the study area. Additionally, given the ability of certain tree species to accumulate heavy metals in their wood, further studies should explore their potential role in phytoremediation. Understanding species-specific accumulation capacities could provide valuable insights for developing nature-based solutions to mitigate soil and atmospheric contamination.

1.6 Conflict of Interest

The authors declare that the Horne smelter contributed in part to the financing of the study but did not interfere in any phase of the analyses or interpretation of results.

1.7 Funding

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1.8 Author Statement

Elsa Dejoie: Writing – review & editing, Writing – original draft, Conceptualization, Methodology, Formal analysis, Visualization. Marc-André Lemay: Writing – review & editing, Formal analysis. Annie DesRochers: Writing – review & editing, Conceptualization, Supervision, Funding acquisition. Nicole J. Fenton: Writing – review & editing, Conceptualization, Supervision, Funding acquisition. Joëlle Marion: Writing – review & editing, Methodology. Martine M. Savard: Writing – review & editing. Trevor J. Porter: Writing – review & editing. Daniel Proulx: Writing – review & editing, Methodology. Fabio Gennaretti: Writing – review & editing, Writing – original draft, Conceptualization, Supervision, Project administration, Funding acquisition.

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2. IMPACT OF INDUSTRIAL POLLUTION ON NITROGEN CYCLE AND TREE GROWTH DETECTED BY TREE-RING $\delta^{15}N$ SERIES

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Résumé

Les activités industrielles telles que la fonte des métaux libèrent des polluants qui peuvent acidifier les sols et augmenter leur teneur en métaux, ce qui peut entraîner des conséquences sur le cycle de l'azote (N) et le développement des plantes. Dans le cadre d'une expérience en serre, nous avons isolé les effets de l'acidification des sols et de la contamination au plomb (Pb) sur la germination, la croissance des plantes et le $\delta^{15}N$ dans les tissus végétaux de semis d'épinettes noires poussant dans des sols acidifiés avec ou sans ajout de plomb. Nous avons également étudié les effets de l'acidification sur les concentrations de NH_4^+ et de NO_3^- dans le sol. De plus, nous avons mesuré les séries $\delta^{15}N$ des cernes annuels d'épinettes noires matures dans des peuplements forestiers exposés à la pollution des fonderies afin d'étudier les variations temporelles du cycle de l'azote et de la nutrition des plantes en relation avec les émissions industrielles. Nous avons constaté que les sols acidifiés présentaient des concentrations de NH_4^+ et des valeurs $\delta^{15}N$ plus élevées, associées à une concentration réduite de NO_3^-, ce qui suggère une réduction de la nitrification microbienne. La croissance des semis a été considérablement réduite dans le traitement d'acidification, indiquant une modification de l'absorption des nutriments. Les semis cultivés dans des sols acidifiés ont également présenté des valeurs $\delta^{15}N$ plus faibles dans le xylème par rapport au traitement non acidifié, reflétant des changements dans les sources d'azote ou le fractionnement isotopique pendant l'absorption et l'assimilation. Dans les peuplements forestiers, les séries $\delta^{15}N$ des cernes des arbres ont révélé un schéma temporel caractérisé par un pic de $\delta^{15}N$ vers 1980. Notre expérience en serre offre une occasion précieuse de clarifier comment l'acidification des sols affecte l'absorption d'azote et la croissance précoce des arbres. Cependant, l'échantillonnage dans des environnements naturels suggère que les résultats tirés d'expériences contrôlées ne peuvent pas être directement extrapolés à l'utilisation d'isotopes d'azote comme indicateurs de processus ou outils de reconstruction pour la contamination des sites sur le terrain.

Mots clés : Azote, Acidification des sols, Métaux lourds, Nutrition des arbres, Isotopes azotés, $\delta^{15}N$

Abstract

Industrial activities such as metal smelting release pollutants that can acidify soils and increase their metals content, with potential consequences for nitrogen (N) cycling and plant development. In a greenhouse experiment, we isolated the effects of soil acidification and lead (Pb) contamination on germination, plant growth, and $\delta^{15}N$ in plant tissues of black spruce seedlings growing in acidified soils with or without lead addition. We also investigated the effects of acidification on soil NH_4^+ and NO_3^- concentrations. In addition, we measured tree-ring $\delta^{15}N$ series on mature spruce trees in forest stands exposed to smelter pollution to investigate temporal variations in N cycling and plant nutrition in relation to industrial emissions. We found that acidified soils showed higher NH_4^+ concentrations and $\delta^{15}N$ soil values, coupled with reduced NO_3^- concentration, suggesting a reduction in microbial nitrification. Growth of seedlings was significantly reduced in the acidification treatment, indicating an altered nutrient uptake. Seedlings grown in acidified soils also exhibited lower $\delta^{15}N$ values in xylem compared with the non-acid treatment, reflecting changes in N sources or isotopic fractionation during uptake and assimilation. In forest stands, tree-ring $\delta^{15}N$ series revealed a temporal pattern characterized by a $\delta^{15}N$ peak around 1980. Our greenhouse experiment provides a valuable opportunity to clarify how soil acidification affects nitrogen uptake and early growth in trees. However, sampling in natural environments suggests that results inferred from controlled experiments cannot be directly extrapolated to the use of nitrogen isotopes as process indicators or reconstruction tools for contamination of field sites.

Keywords: Nitrogen, Soil acidification, Heavy metals, Tree nutrition, Nitrogen isotopes, $\delta^{15}N$

2.1 Introduction

Metals and acidifying compounds such as nitrogen oxides (NO_x) and sulfur dioxide (SO_2) may be introduced into the environment through various anthropogenic activities, including mining, smelting, and metallurgical and chemical industries (Devi, 2024; Dinis et al., 2021; Savard et al., 2006; Savard & Siegwolf, 2022). These compounds can be transported over varying distances from the industrial source depending on the prevailing wind pattern (Daggupaty et al., 2006; Hou et al., 2006). Their dispersion depends on particle size, atmospheric conditions, and wind direction, with higher concentrations often found downwind emission sources (Khaniabadi et al., 2018). Consequently, soils near industrial sites may be strongly acidified and contain elevated concentrations of metals such as nickel, lead, cadmium and copper (Gagné, 2007; Gundermann & Hutchinson, 1995). At low concentrations, certain metals can exert beneficial effects, particularly for enzymatic processes (Andreini et al., 2008), however, these same elements can become toxic at elevated concentrations and tend to accumulate in soils and vegetation, raising significant ecological concerns (Adnan et al., 2022; Solgi et al., 2012). Metal accumulation and soil acidification can disrupt essential nutrient cycles, particularly nitrogen (N) cycling, by hindering soil biological activity and reducing nitrogen mineralization and nitrification (Hahn et al., 2019; Kabata-Pendias, 2010; C. Meng et al., 2023).

The nitrogen cycle is largely driven by soil microbial communities, whose composition and activities may be influenced by soil chemistry. These microbial communities control nutrient transformation, directly affecting nitrogen availability, soil fertility and plant nutrition (H. Li et al., 2023). Specifically, the nitrogen isotopic ratio ($\delta^{15}N$) may reflect the dynamics of N cycle in soils (Legge et al., 1984; Robinson, 2001). During microbial processes such as mineralization, nitrification, and denitrification, lighter isotopes (^{14}N) are preferentially transformed, leaving the remaining NH_4^+ pool enriched in ^{15}N and the resulting nitrate (NO_3^-) relatively depleted in ^{15}N (Hobbie & Högberg, 2012; Pardo & Nadelhoffer, 2010; Savard & Siegwolf, 2022). Consequently, the NH_4^+ pool in soils typically shows $\delta^{15}N$ values higher than those of the NO_3^- pool. In addition, the biomass of ectomycorrhizal fungi is often enriched in ^{15}N and the fungi transfer a higher proportion of ^{14}N to their host plants (Hobbie & Högberg, 2012; Michelsen et al., 1998).

The N cycle can be disrupted by heavy metal contamination and soil acidification linked to industrial activity. Soil acidification alters the availability of N forms: decreasing pH promotes the accumulation of NH_4^+ and reduces the formation of NO_3^-, leading to an imbalance in plant-available nitrogen (Savard et al., 2021). Nitrification declines as pH decreases and increased NO_3^- leaching may occur (Gundermann & Hutchinson, 1995; Gundersen et al., 2006). In addition, heavy metals combined with low pH reduce microbial diversity and inhibit key microbial processes involved in mineralization, nitrification, and biological nitrogen fixation (J. Li et al., 2024; L. Lu et al., 2022), limiting the soil ability to recycle nitrogen (Lenart-Boroń et al., 2014; Yan et al., 2013). Such changes in microbial communities can influence plant growth by modifying nitrogen availability and the efficiency of nutrient uptake, ultimately affecting ecosystem productivity, recovery, and resilience (Habiyaremye et al., 2020).

In industrial polluted environments, trees are directly influenced by alterations in the physicochemical properties of the soil (Clemens et al., 2002; Matei et al., 2025). In acidic soils, where nitrification is inhibited and nitrate availability is low, dissolved organic nitrogen becomes a relatively more important nitrogen source for trees (Näsholm et al., 2009), and significantly increase $\delta^{15}N$ in tree-rings (Savard et al., 2021). Once absorbed, nitrogen is incorporated into plant tissues without altering its isotopic composition (Adl et al., 2020). Therefore, the $\delta^{15}N$ signal fixed in the tree-rings reflects the isotopic signature of the available nitrogen at the time of uptake, allowing tree-rings to serve as archives of past soil nitrogen conditions (Gačnik & Gustin, 2023), recording these variations in their xylem chemical composition (Savard et al., 2021).

To date, it remains challenging to disentangle the effects of pollution, soil properties and plant physiology on N stable isotopes in forest pools (Savard et al., 2020; Savard & Siegwolf, 2022). The absence of studies limits our ability to use $\delta^{15}N$ as a diagnostic tool in complex natural ecosystems. To fill this knowledge gap, we used a greenhouse experiment to study the links between soil contamination, tree growth, and $\delta^{15}N$

variations, using black spruce as a model species. In a second phase, we extended our observations to the natural environment to assess whether the $\delta^{15}N$ trends detected in the greenhouse were coherent with those observed in the vegetation at proximity with a smelter. We first hypothesized that (H1) a decrease in soil pH would lower nitrate (NO_3^-) concentrations and increase ammonium (NH_4^+) accumulation, whereas elevated Pb concentrations alone would not directly affect NO_3^- and NH_4^+ concentrations. Consequently, (H2) acidification was expected to increase soil $\delta^{15}N$ values of N pool in soils. We further hypothesized (H3) that elevated Pb concentrations and low soil pH would reduce germination and inhibit plant growth. We therefore hypothesized (H4) that trees would have higher $\delta^{15}N$ values under acidified conditions. In forests affected by pollution (H5), we anticipated an increase in $\delta^{15}N$ values in tree-rings closer to the pollution source, essentially due to the combined effects of lower soil pH and increased heavy metal contamination (Fig. 6).

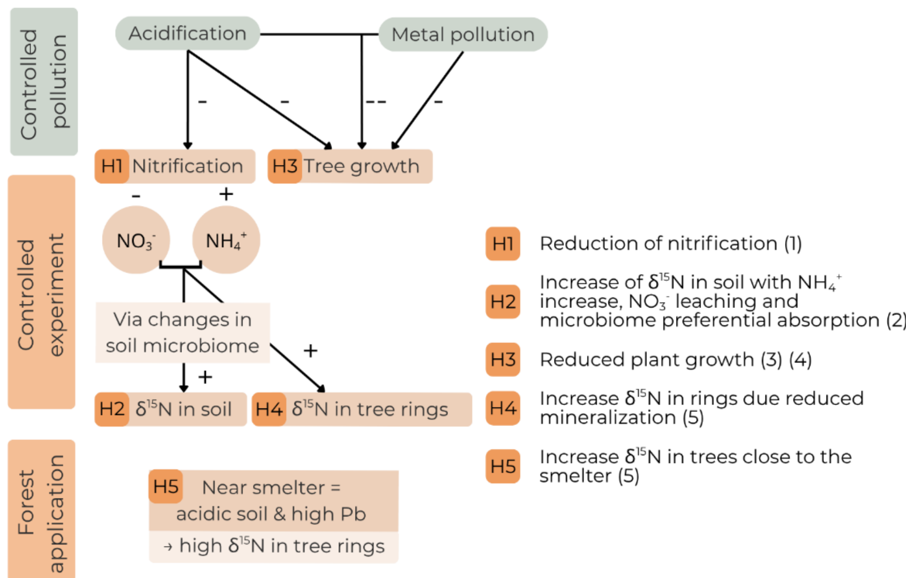

Figure 6
Diagram summarizing the tested hypotheses explaining $\delta^{15}N$ variations in contaminated environments. Hypotheses were tested with data from both controlled (greenhouse) and natural settings in forest around the Horne smelter, Abitibi region, Quebec, Canada. The hypotheses depict how low soil pH and high metal concentration should impact tree growth and nutrition. Arrows represent expected effects. Hypotheses are based on literature review: (1) Yan et al. (2013), (2) Handley et al. (1999), (3) John et al. (2012), (4) Günthardt-Goerg et al. (2019), (5) Savard et al. (2021).

2.2 Methods

2.2.1 Controlled environment experiment

Soil provenance and preparation. The experiment in the controlled environment was conducted in a greenhouse at the Laurentian Forestry Centre (Québec, Canada). The soil used for the experiment was sampled near Amos (QC, Canada, 48° 38' 52" N, 78° 18' 13" W), in a natural, mature (60 years), black spruce forest. The litter and mosses were removed from the soil surface, and the organic fraction and the upper mineral soil were collected to a depth of 20 cm. We collected approximately 100 liters of soil for the experiment. We carefully sieved (5 mm grid) and homogenized the soil to ensure a uniform and consistent texture. Sieving helped remove large particles and unwanted debris, creating a finer, more regular substrate. Next, 30% perlite was added to the mixture to improve soil aeration and drainage. Plastic pots (2.7 x 5″) were filled with the prepared soil mixture, previously adjusted for pH and lead concentration (see below). Silica was added to the surface of each pot to stabilize seeds on the substrate, retain moisture, and inhibit the growth of mosses and other unwanted plants.

Treatments. The natural soil had an initial pH around 4.2. We added 50 ml of a sulfuric acid solution (2 ml/L) to a volume of 500 ml of soil mixture to create the "acid treatment" (ACD) resulting in a pH decrease of ~1 unit. These two levels of pH were applied in factorial combinations with three levels of Pb (natural concentration, low Pb concentration and high Pb concentration) for a total of six treatments (Table 5, Fig. C1). Lead treatments were applied by mixing lead chloride ($PbCl_2$) into 500 mL of soil per pot, at approximately 20 mg for the low Pb treatment (30 ppm) and 400 mg for the high Pb treatment (600 ppm). In total, each treatment was replicated 10 times, resulting in a total of 60 sample pots. After each treatment was applied, the pots were randomized within one block.

Table 5
Experimental treatments. Lead chloride was added at concentrations of 30 ppm relative to soil volume (low Pb concentration) and 600 ppm (high Pb concentration). Sulfuric acid was added at a concentration of 50 mL/L to achieve a decrease of one pH unit. Final concentration of Pb and pH are displayed in Table C1.

Treatment	Lead (Pb) concentration	Acidification (ACD)
Control	Natural content	No acidification
LowPb only	Natural content + 30 ppm	No acidification
HighPb only	Natural content + 600 ppm	No acidification
ACD only	Natural content	Acidification
LowPb_ACD	Natural content + 30 ppm	Acidification
HighPb_ACD	Natural content + 600 ppm	Acidification

Germination, seedling establishment, and seasonal manipulation. Three stratified black spruce seeds were sown in each pot. Six weeks after the start of the experiment, we recorded the number of emerged seedlings. Germination rate was calculated by counting the total number of seeds that germinated in each pot over the total number of seeds per pot (3 seeds). As the seedlings emerged, some pots contained multiple seedlings while others had none. To ensure one seedling per pot, we transplanted seedlings from pots where multiple seeds had germinated into pots where no germination had occurred, keeping them within the same treatment. Any additional seedlings were removed, leaving only one seedling per pot. The first growing season lasted 3 months, followed by 6 weeks of cold hardening, during which temperature and photoperiod were gradually reduced from 20/18 °C (day/night) with a 10 h photoperiod, to 16/14 °C without artificial lighting. After this, the seedlings underwent a dormancy period for another 6 weeks (10°C day/10°C night, without artificial lighting), allowing them to acclimate and prepare for the second growing season (Fig. C2). During the growing season, plants grew with a daytime temperature of 24 °C and a nighttime temperature of 18 °C, under a 12-hour light photoperiod.

Growth analysis. Height of each seedling was measured at the end of the first growing season. At the end of the second growing season, immediately before harvesting, we measured seedling height and root collar diameter, along with the number of branches. Aerial tissues including stem, branches, and needles were harvested by cutting seedlings at the base of the stem. The main stem was further separated from the bark, branches, and needles. The stem xylem was carefully isolated, dried at 60°C to a constant weight, and weighed. Wood samples from the dry stems were processed for measuring xylem $\delta^{15}N$ (see section 3.4.3). The list of all measurements is provided in Table 6.

Soil analyses. Soil samples were oven-dried and finely sieved through a 2 mm mesh to remove coarse fragments such as stones, roots, and debris, providing a homogeneous fine fraction for further analyses. Sieved samples were analyzed at the Pacific Forestry Centre (Victoria, BC, Canada) of Natural Resources Canada. Samples were mixed with 2 mol/L KCl to extract inorganic nitrogen (NH_4^+-N and NO_3^--N) and analyzed using a segmented flow analyzer (Kalra & Maynard, 1991). This allows to quantify the two main forms of inorganic nitrogen available in the soil, NH_4 and NO_3. Sieved soil samples were also analyzed for total carbon (C), total nitrogen (N), and $\delta^{13}C$ to assess potential differences in soil organic matter quality and composition between treatments. However, these variables did not show significant variation across conditions and were therefore excluded from further analysis (Table C2). Isotopic nitrogen analyses were also performed on the samples; detailed methodology is provided in section 3.4.3.

Metal concentrations in the soil were determined by digesting 0.5 g of dried soil with concentrated nitric acid (HNO_3) following the EPA Method 3051A, using concentrated nitric acid (HNO3). The resulting solutions were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7900, Agilent Technologies, Santa Clara, USA). Analytical precision was higher than 0.1 mg/kg. Soil pH was measured in a 1:2 soil-to-water ratio using sieved soil and deionized water and measured using a calibrated pH meter. Soil pH values at the end of the experiment stabilized to 3.9 in the non-acid treatment and 3.6 in the acid treatment (Table C1), compared with initial values of 4.2 and 3.2, respectively. Pb concentrations at the end of the experiment were consistent with the intended levels (Fig. C1).

Table 6
Variables measured in the controlled environment experiment. All measurements were done on 10 replicate pots of each treatment (n=60).

Measurement (unit)	**Compartment**	**Time**	**Method**
Germination	Seeds	6 weeks after seeding	Counting
Height (cm)	Aerial parts	End of first and second GS*	Measuring tape
Collar diameter (mm)	Aerial parts	End of second GS	Vernier caliper
Number of branches	Aerial parts	End of second GS	Counting
Xylem stem dry mass	Stem	End of second GS	Sample weighing
Xylem $\delta^{15}N$ (‰)	Stem	End of second GS	Isotope Ratio Mass Spectrometer (EA-IRMS)
$\delta^{15}N$ (‰)	Soil	End of second GS	Isotope Ratio Mass Spectrometer (EA-IRMS)
NH_4-N (ppm), NO_3-N (ppm)	Soil	End of second GS	Extraction with 2 mol/L KCl followed by colorimetric determination
Lead concentration (ppm)	Soil	End of second GS	Microwave Digestion & ICP-MS
pH	Soil	End of second GS	pH-meter

*GS is the growing season

2.2.2 Natural forests experiment

Site selection. The Horne smelter (Rouyn-Noranda, Quebec) has been a major pollution source since 1927. In the 1970s, it released up to 600,000 metric tons of SO_2 and 1,400 metric tons of Pb annually (Bonham-Carter, 2005). Emissions declined following new regulations, reaching about 90,000 tons of SO2 and 80 tons of Pb per year in the 2000s, though legacy and ongoing contamination persist (Fig. C3). Pollutants have dispersed over more than 100 km along the prevailing NNW-SSE winds (Fig. 7), as shown by tree, peat, soil, and snow analyses (Dumontet et al., 1990; Hou et al., 2006; Zdanowicz et al., 2006).

Seven mature spruce forest stands located at various distances from the Horne smelter were selected for sampling to capture the spatial aspect of contamination (Fig. 7). To minimize potential biases related to soil heterogeneity, we standardized our site selection as much as possible. All sites were located on glaciolacustrine deposits with thin organic layers (<30 cm) (Drobyshev et al., 2010). We excluded sites with signs of silvicultural activities, recent fire, windthrow, thick organic layers or recent insect epidemics damage. The seven selected sites consisted of mature black spruce stands (>70 years old) with a relative abundance of spruce trees greater than 75%. Five sites were located within a 65 km radius of the Horne smelter: four in the dominant wind direction (Dejoie et al., 2025) and one on the opposite side. The two other forest sites were distant sites: T2 was located 175 km north of the smelter in the Nord-du-Québec region and T1 was located 195 km to the east, in the direction of the prevailing winds (Fig. 7). While site T1 near Forsythe can be considered as a control site for our experiment, site T2 is considered as a less polluted site as it is close to another mining operation (Selbaie gold mine) (Fig. 7). Selecting ideal control sites was difficult due to the historically high density of metal mining operations in the Abitibi region.

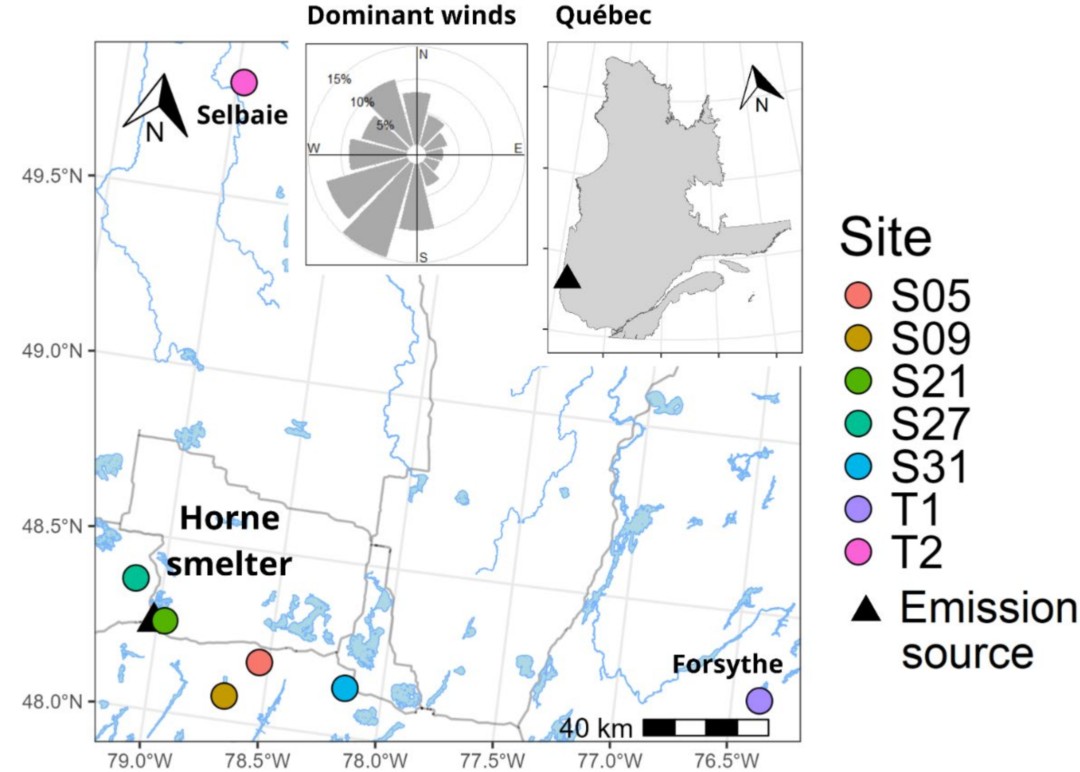

Figure 7
Location of the selected sites in the region of the Horne smelter (emission source) in Rouyn-Noranda (Québec, Canada). Main roads (represented with black lines) and lakes (shaded blue areas) are displayed as background features to provide geographical context. The wind rose illustrates the direction from which the prevailing summer winds originate. Wind data (June-August, 2000-202) were from the Rouyn-Noranda airport station (Environment Canada, 2023).

Tree and soil sampling in natural forests. At each site, 5 mature trees were sampled (Table C3). The selected sites were located at least 50 m from any road to minimize the risk of contamination from airborne dust, and the sampled trees were spaced at least 5 m apart from each other to avoid collecting closely related individuals or those potentially sharing root grafts. Trees were selected based on good overall health, upright form, and the absence of visible damage, disease, or major deformities, to ensure consistent growth patterns for dendrochemical analysis. For each tree, two 1.2-cm diameter wood cores were collected at breast height (approximately 1.3 m) using an increment borer. In the lab, cores were sectioned with a microtome to allow accurate ring counting while avoiding contamination (Dejoie et al., 2025). Tree-rings were subsampled at a biennial resolution, with one ring analyzed for every two-year period, which allowed us to reduce the number of measurements while documenting trends over a longer period. With the five sampled trees, approximately 20 mg of material was extracted per selected year and tree (10 mg from each core) and pooled to create a composite sample of approximately 100 mg per selected year and site. The composite samples were processed for xylem $\delta^{15}N$ ratios analyses (see section 3.4.3) to construct site series covering the period from 1960 onward.

For each site, we collected nine soil profiles using an auger, targeting an approximate volume of 500 mL per sample. Prior to sampling, only the moss and litter were removed, so the organic layer remained included in the soil samples, and samples were taken from three depth intervals within each profile: 0-20 cm, 20-40 cm, and 40-60 cm. Soil samples were air-dried for one week, then sieved through a 2 mm mesh to remove coarse fragments. Similarly to the controlled experiment, soil pH was measured in a 1:2 soil-to-deionized water solution using a calibrated pH meter.

2.2.3 Isotope analysis

Soil and dry xylem samples were finely ground with a Retsch MM400 steel ball mill and encapsulated in tin capsules. Soil $\delta^{15}N$ was measured at the Pacific Forestry Centre using an Elemental Analyzer in continuous flow coupled to a Thermo Delta Advantage IRMS (Thermo Fisher Scientific, Bremen, Germany). Xylem $\delta^{15}N$ was analyzed at the Delta Lab (Geological Survey of Canada, Québec) using an EA-IRMS system (ECS 4010, Costech, Valencia, CA, USA) coupled to a Delta V instrument via a Conflo IV interface (Thermo Fisher Scientific, Bremen, Germany). Soil samples were calibrated with B2159, B2205, and USGS-40; xylem samples with IAEA-N-2 and USGS-25, and validated with IAEA-N-1, USGS-26, USGS-40, and an internal xylem standard (Savard et al., 2023). Final values are expressed in ‰ AIR, with analytical precision < 0.2 ‰.

2.2.4 Statistical analysis

All statistical analyses and computations were performed in R version 4.5.0 (R Core Team, 2025).

Greenhouse experiment. Linear models were fitted using pH and Pb treatments as categorical predictors, with each soil, $\delta^{15}N$, and plant growth variable as the response. Germination was analyzed with a binomial Generalized Linear Model (GLM), and branch counts with a Poisson GLM. For each response, all model combinations, from single predictors to full models with interactions, were tested and ranked using Akaike Information Criterion (AIC). Model assumptions were verified using residual and Q–Q plots. Only NH_4^+ and NO_3^- required log10 transformation to meet assumptions.

Natural forest experiment. Correlations between soil pH at different depths (0-20, 20-40, and 40-60 cm) were assessed using Pearson's product-moment correlation, and the resulting correlation coefficients were used to evaluate the consistency of pH variation across the soil profile.

To assess the effect of distance from the smelter on soil pH we used linear models. Control sites were excluded because they are not influenced by the smelter and do not reflect the spatial gradient of contamination, while site S27, located upwind, was removed because it could bias the linear regression intended to capture downwind trends.

Tree-ring $\delta^{15}N$ series generally show high-frequency variations that do not match across individual trees from the same site (Savard et al., 2020), which complicates the detection of coherent temporal patterns. To address this, we used a LOESS (locally estimated scatterplot smoothing) regression. LOESS is a non-parametric method that fits local regressions across the dataset, generating a smooth curve that follows the overall trajectory without assuming a predefined functional form. This approach reduces the influence of short-term noise and highlights the underlying long-term trends in $\delta^{15}N$ values. Long term temporal trends in $\delta^{15}N$ ratio were then compared across sites by visual inspection of the smoothed series.

To assess the influence of pH on recent xylem $\delta^{15}N$ values, we fitted linear mixed-effects models. $\delta^{15}N$ values of the past 20 years were included as the response variable, while pH was tested as fixed effects. Soil pH was not expected to vary significantly over these timescales (Falkengren-Grerup, 1987; Jansone et al., 2020). Because samples were collected across multiple sites, site identity was included as a random effect to account for potential non-independence of observations within sites.

2.3 Results

2.3.1 Controlled environment experiment

Effects of acidification and Pb treatments on soil properties. The model with Acid as the only predictor had the lowest AIC value and was therefore the best-supported model, whereas the model including the interaction term with Pb was poorly supported (AICwt < 0.25, for all soil parameters). As a result, we selected the Acid-only model for further analyses (Table C4). Soil NO_3^- and NH_4^+ concentrations, as well as $\delta^{15}N$ in soil, were similar in the high, low, and no Pb treated pots. In contrast, NO_3^- concentrations decreased in the acidification treatment while NH_4^+ concentration and $\delta^{15}N$ ratios increased in the acid treatment (Fig. 8). NO_3^- was approximately 15 times higher in the non-acid treatment compared to the acid treatment. Conversely, NH_4^+ was about 1.75 times lower in the no acidification treatment. In addition, the acidification treatment resulted in an increase of 0.3 ‰ in soil $\delta^{15}N$ values (Fig. 8, Table C5).

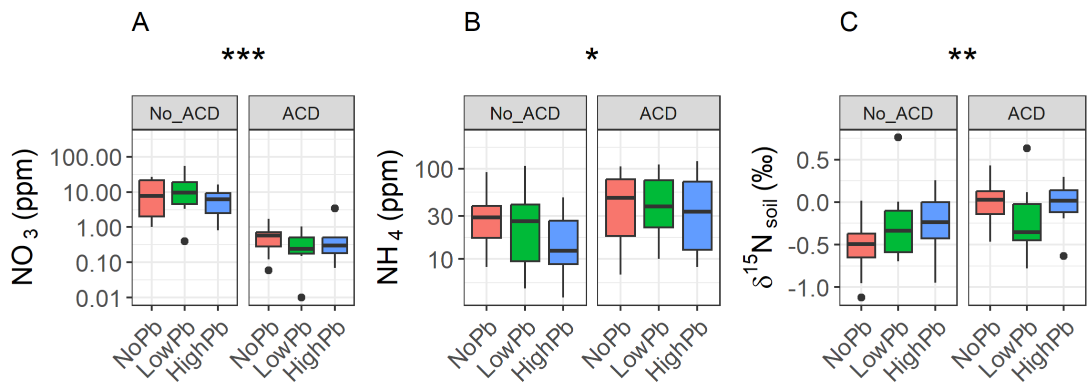

Figure 8
Soil concentration of (A) NO_3, (B) NH_4 and (C) $\delta^{15}N$ ratio of total N between combination of treatment. Asterisks indicate the statistical significance of the difference between acid (ACD) and non-acid (No_ACD) treatments for each parameter, determined by a linear model (*=p-value < 0.001; **=p-value < 0.01; *=p-value < 0.05). Y-axes of (A) and (B) use a log10 scale. Boxplots show the interquartile range (Q1-Q3) with the median indicated by the central line. Whiskers extend to 1.5 x IQR, and points represent outliers.**

Effects of acidification and Pb treatments on seedling development. The pH was consistently the most significant explanatory variable for growth parameters (Tables C6, C7 and C8). Acid treatment led to reduced germination, seedling height, collar diameter, number of branches, and xylem dry mass (Fig. 9). The inclusion of Pb treatments improved the model fit only for seedling height after the second growing season and for collar diameter (Table C8).

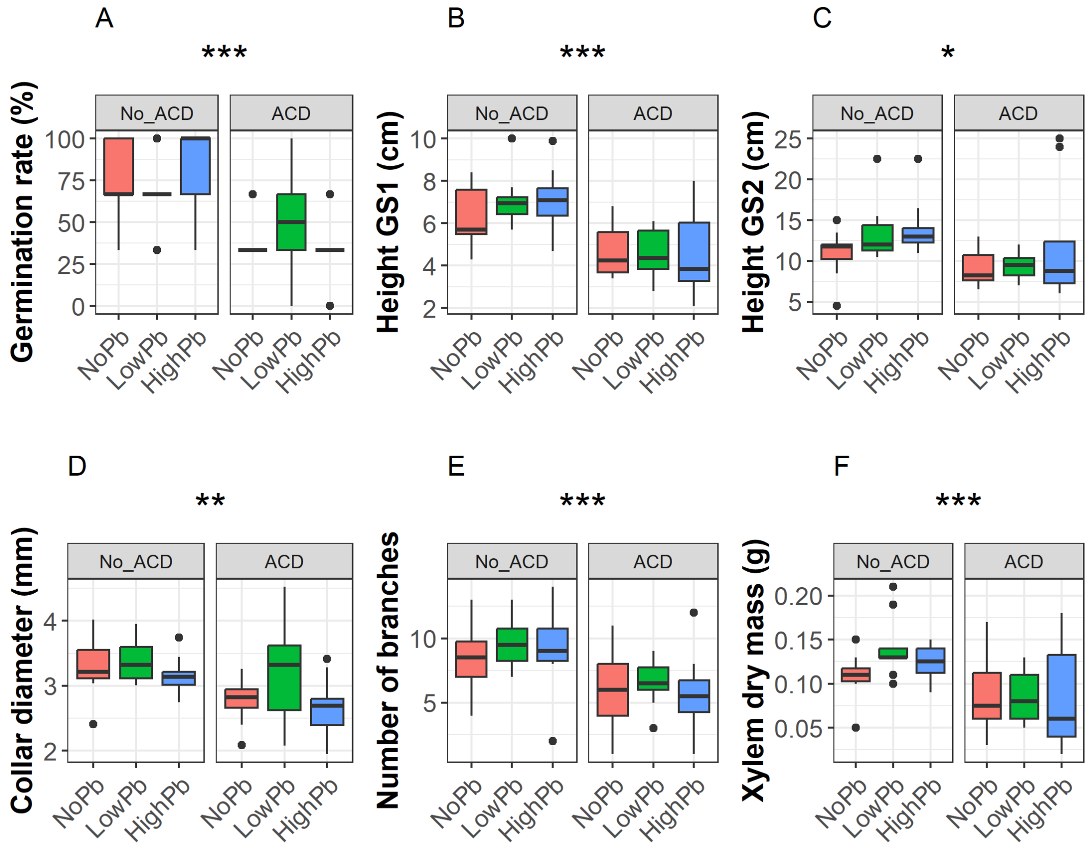

Figure 9
Comparison of acid (ACD) and non-acid (No_ACD) treatment, and lead (No Pb, low and high Pb concentration) treatments on growth parameters. (A) Germination, the height of plants measured after (B) the first and (C) the second growing season (GS), (D) collar diameter, (E) number of branches, and (F) xylem dry mass. Linear models were used for all traits except for the germination and number of branches, which were analyzed respectively using Binomial and Poisson Generalized Linear Models. Asterisks indicate the statistical significance of the difference between acid (ACD) and non-acid (No_ACD) treatments for each parameter (*=p-value < 0.001; **=p-value < 0.01; *=p-value < 0.05). Boxplots show the interquartile range (Q1-Q3) with the median indicated by the central line. Whiskers extend to 1.5 x IQR, and points represent outliers.**

$\delta^{15}N$ values in seedlings xylem. $\delta^{15}N$ values were similar between no Pb, high, and low Pb treatments (Fig. 10, Table C9). Conversely, $\delta^{15}N$ values in the stem wood were significantly lower in acid treatments compared to the no-acidification treatments (1.5 ‰ mean difference) (Fig. 10, Table C10).

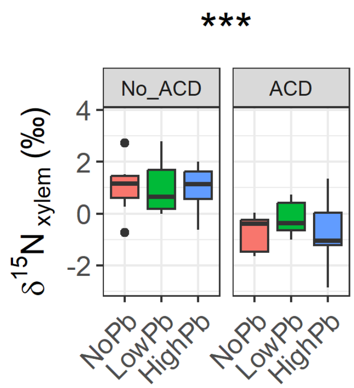

Figure 10
Variation of $\delta^{15}N$ in wood between non-acid (No_ACD) and acid (ACD) treatments and lead (No lead, low and high concentration) treatments. Asterisks indicate the statistical significance of the difference between acid (ACD) and non-acid (No_ACD) treatments, determined by a linear model (*=p-value < 0.001). Boxplots show the interquartile range (Q1-Q3) with the median indicated by the central line. Whiskers extend to 1.5 x IQR, and points represent outliers.**

2.3.2 Natural forest experiment

pH in soil. Preliminary correlation analyses indicated strong positive correlations between pH values of different depths ($p < 0.001$), suggesting that pH variations were largely consistent across the soil profile (Table C11). Soil pH at 0-20 cm depth decreased significantly with distance from the smelter ($p=0.002$) (Fig. C4). Similar patterns were observed at deeper layers (20–40 cm and 40–60 cm; see Fig. C4).

$\delta^{15}N$ values in tree-rings. Two types of temporal trends were observed across sites. Some sites exhibited roughly parabolic trends (S27, S05, S31, and T1), with a maximum around 1980, while others showed more sinusoidal fluctuations (S09 and T2) (Fig. 11). Site S21 was more complex to interpret, as the trees selected were younger than those at the other sites (Table C3). Variation in $\delta^{15}N$ values across the sites was not explained by soil pH or distance from the smelter. Neither soil pH (estimate=2.52±3.54, p=0.480) nor distance (estimate=0.0099 ± 0.0210, p=0.640) had a significant effect on $\delta^{15}N$ values (Table C13).

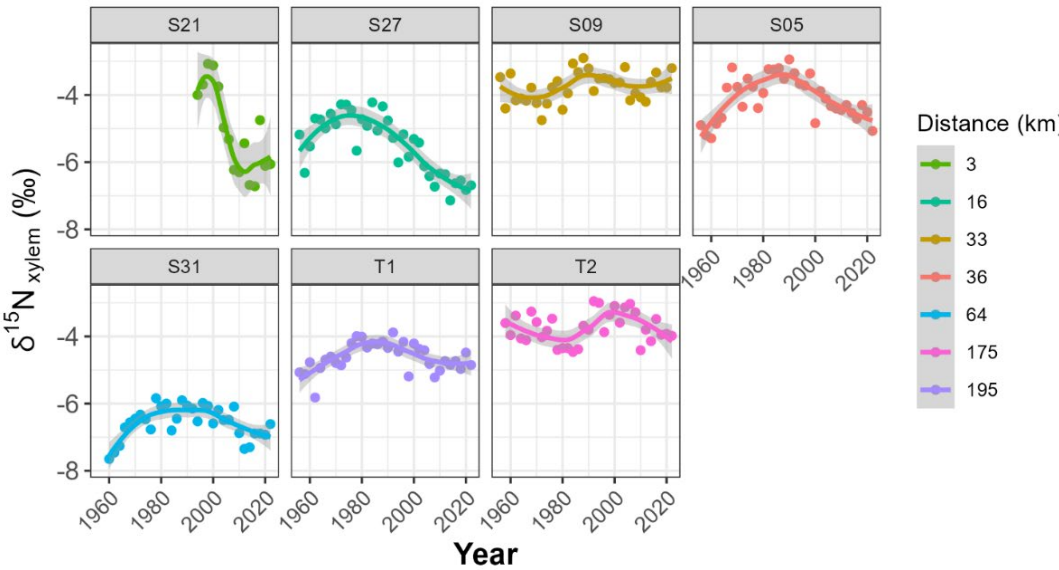

Figure 11
Temporal $\delta^{15}N$ trends across forest sites. Each point represents the $\delta^{15}N$ value for a given year and site. The solid line corresponds to the smoothed trend estimated with a LOESS (Locally Estimated Scatterplot Smoothing) regression, while the shaded area around the line indicates the 95% confidence interval of the fitted curve. We used LOESS smoothing to visualize flexible temporal trends without assuming a linear relationship.

2.4 Discussion

2.4.1 Pollution effects on N cycling in the soil-plant continuum

Our greenhouse study showed that Pb addition did not affect NO_3^- and NH_4^+ concentrations and $\delta^{15}N$ values in soils (Fig. 8). Other studies showed that higher concentration of Pb (up to 2,000 ppm) induced negative impact on microbial biomass and mineralization processes (George & Wan, 2020; Muhammad et al., 2005), suggesting that our Pb concentration, similar to polluted sites around the Horne smelter, may be too low to detect changes in N cycle. Nevertheless, even low concentrations of Pb have been shown to affect microbial communities. For instance, Sobolev and Begonia (2008) reported a decrease in microbial diversity following exposure to Pb at only 1 ppm (Sobolev & Begonia, 2008). These contrasting results suggest that soil functions can be less affected than microbial diversity in responses to Pb or that they may be context-dependent and influenced by site-specific soil properties.

As expected, $\delta^{15}N$ values in soils were higher under the most acidic conditions validating our H2. This pattern is consistent with reduced N transformation processes in acidified soils and amplified NO_3^- leaching (Gundermann & Hutchinson, 1995; Gundersen et al., 2006). Lower NO_3^- concentrations and higher NH_4^+ concentrations in the acid treatment suggest that nitrification was inhibited in accordance with our H1. Because nitrifying microorganisms preferentially use ^{14}N, limiting nitrification reduces isotopic fractionation and leads to the retention of ^{15}N in the remaining soil N pool (Adl et al., 2020; Dijkstra et al., 2008; Doucet et al., 2012; P. Högberg, 1997). Thus, the increase in soil $\delta^{15}N$ likely reflects a slowdown of N cycling processes, consistent with previous experimental studies (Little, 1997; Rochester et al., 1992).

Despite higher $\delta^{15}N$ values in soil of acid treatment, we observed lower $\delta^{15}N$ in plant tissues. These results contrast with those reported by Savard et al. (2021) and with our initial hypothesis (H4), who observed higher $\delta^{15}N$ values in tree rings under acidic conditions. However, our experiment was conducted at substantially lower pH levels than those reported by Savard et al. (2021), where nitrogen transformations are strongly suppressed. Interestingly, in Savard et al. (2021), $\delta^{15}N$ values showed no clear trend at pH levels around 3-4, although only a few data points were available in that range, suggesting that similar processes might occur under more extreme acidification conditions. At such low pH, the accumulation of ammonium and potentially dissolved organic nitrogen (DON) (S. J. Zheng, 2010), resulting from reduced plant N uptake, likely contributes to ^{15}N enrichment in the soil and lower $\delta^{15}N$ in plant tissues (Dijkstra et al., 2008; Doucet et al., 2012). Acidification can also reduce or modify the activities and communities of mycorrhizal fungi, which play a key role in nitrogen acquisition, especially for forms like NH_4^+ that dominate in low pH soils (Hawkins & Robbins, 2010). Therefore, a modification in mycorrhizal abundance and diversity under acid soil conditions could alter nitrogen acquisition pathways and potentially lead to shifts in plant $\delta^{15}N$ values (Danielson & Visser, 1989).

2.4.2 Pollution effects on growth

In contrast to our H3, Pb did not strongly influence plant growth (germination, first growing season, branching, or stem biomass). This result was unexpected, as Pb is known to reduce seed germination, reduce plant growth, and lower biomass accumulation in many species (Kabir et al., 2018; Selonen & Setälä, 2015; Zerkout et al., 2018). Pb is a relatively immobile heavy metal in soil and may not have been readily taken up by the seedlings during their early developmental stages (Liu et al., 2023; Vaněk et al., 2005). It is also possible that any Pb that was absorbed was sequestered in root tissues (Clemens et al., 2002; Jia et al., 2022), bound to cell walls (Clemens et al., 2002; Rolfe, 1974), or that seedlings were protected through associations with fungi (Colpaert et al., 2011a; Likar & Regvar, 2013), limiting its physiological impact. These results suggest that, under the treatments tested, Pb alone was not a major stressor for early seedling performance compared to acidification. It is worth noting that high lead concentration treatment (600 ppm) reflects levels that can commonly be found near smelters, and that lead toxicity in black spruce seedlings may become more significant only at higher concentrations (>1000 ppm) (Bilodeau et al., 2020; Chappelka et al., 1991; Davis & Barnes, 1973; Gagné, 2007).

The reduced germination and lower biomass observed in acid treatments (Fig. 9) indicate that soil acidity affects early seedling development consistently to our H3. Acid treatments may interfere with water uptake, enzyme activation, or cellular membrane stability. Indeed, Meng et al. (2016) found that low pH reduced both ammonium and nitrate uptake, decreased H^+-ATPase activity, and downregulated nitrogen transporter gene expression (S. Meng et al., 2016), suggesting that soil acidity impairs both nitrogen uptake and assimilation in conifer species. Low pH environments often reduce the accessibility of essential nutrients such as calcium, magnesium, and phosphorus (Läuchli & Grattan, 2012, 2017), while simultaneously increasing the toxicity of certain elements (S. J. Zheng, 2010). This may result in a lower photosynthetic capacity, impaired nutrient assimilation, or an increased allocation of resources to maintenance or stress-response mechanisms rather than biomass production. The apparent reduction in branching under acid treatments may also reflect a compensatory response by the seedlings. Plants that experienced delayed growth might have prioritized vertical development to catch up in height, potentially reallocating energy away from lateral growth and branching (Heppell et al., 2015).

2.4.3 $\delta^{15}N$ values in tree-rings of mature trees in natural forests

Our analysis of natural stands showed an unexpected trend, with soil pH decreasing with distance from the smelter (Fig. C4). This appears surprising, since sites closer to the source should theoretically be more acidic due to higher deposition of acidifying compounds (Daggupaty et al., 2006; Dumontet et al., 1990). However, this pattern is uncertain because pH values overlapped strongly among sites and showed high within-site variability (Table C12, Fig. C4). Nykvist and Skyllberg (1989) reported that differences of up to 0.6 pH units can be observed in a 2-m^2 plot, reflecting local variation in soil texture, organic matter, or drainage, which affect buffering capacity (Nykvist & Skyllberg, 1989; Wei et al., 2022; J. Zheng et al., 2022). Thus, while pH tends to decrease with distance, this result should be interpreted cautiously, as it may reflect natural heterogeneity in soil properties, including variations in texture, organic matter content, moisture, or local vegetation, rather than consistent ecological conditions related to pollution gradients (Y. Jiang et al., 2025).

In our study, $\delta^{15}N$ values in tree-rings showed different patterns when compared to our greenhouse experiment and to a previous study. In the controlled greenhouse experiment, $\delta^{15}N$ decreased under acidic treatments. Savard et al. (2021) reported a positive correlation between pH and $\delta^{15}N$ in tree rings. However, in our field survey, no consistent $\delta^{15}N$ trends over the past 20 years were observed across sites and pH levels. These contrasting results emphasize that factors other than pH may be influencing the $\delta^{15}N$. Alternatively, these differences could be linked to the variations in pH ranges among the various studies, ranging from 3.2-4.2 in our greenhouse experiment, 4.3-4.7 in our field survey, and 4-7 in Savard et al. (2021). In the greenhouse, acidity may have limited plant N uptake, leading to higher soil $\delta^{15}N$ and lower plant $\delta^{15}N$, whereas in the field, higher and more variable pH allows more active N transformations and uptake (Buzek et al., 2017; Ma et al., 2012; Reinhold-Hurek et al., 2015). Given that seedlings and mature trees differ in growth, root-to-shoot ratio, and nitrogen metabolism, absolute $\delta^{15}N$ values are not directly comparable. A stronger comparison could focus on relative patterns or trends within each group, rather than expecting the same $\delta^{15}N$ in both tissues.

Although no clear overall $\delta^{15}N$ trend emerged across the trees of the sampled forest sites, we observed that sites exhibited similar temporal patterns over the years (Fig. 11). Several sites exhibited a $\delta^{15}N$ peak in the early 1980s. This synchronization was observed even at site T1 (control), which is located far from the smelter but downwind to the smelter, suggesting a possible link with the smelter operations and the progressive decrease of smelter SO_2 acid emissions (Fig. C3). This temporal pattern contrasts with our greenhouse results, which highlight the link between lower acidity and higher xylem $\delta^{15}N$.

In fact, in our greenhouse experiment, the $\delta^{15}N$ values in plants can only reflect soil nitrogen and biochemical changes, as no additional N inputs were provided. In natural environments, additional atmospheric N sources, such as nitrogen oxides (NO_x) from industrial emissions, could also influence soil dynamics which may modify the $\delta^{15}N$ values in plants (e.g., Savard et al., 2023). Microclimatic conditions, such as temperature, humidity, and light availability can further modify nitrogen cycling processes and the isotopic composition of nitrogen in plants (Brookshire et al., 2011; Shaw & Harte, 2001). Similarly, stand characteristics, including species composition, tree density, and age structure (Menyailo et al., 2022) can shape mycorrhizal associations and affect plant $\delta^{15}N$ values. Different fungal partners preferentially assimilate distinct nitrogen forms (e.g., NH_4^+, DON), leaving varying proportions of ^{14}N available to the host. As a result, changes in soil biochemical processes can drive $\delta^{15}N$ values either up or down, depending on the fungal community composition and nutrient dynamics (Hobbie & Högberg, 2012; Lilleskov et al., 2002; Savard et al., 2021). Handley et al. (1999) emphasized that interpreting plant $\delta^{15}N$ results ideally requires considering the contribution of each mycorrhizal type to the observed range in foliar values. Therefore, caution is needed when extrapolating our greenhouse results to field conditions, as additional N sources and historical industrial inputs could modify the $\delta^{15}N$ ratios observed in natural soils and vegetation.

2.5 Conclusion

Our results support that soil acidity is a major driver of tree growth and confirms the strong influence of pH on nitrogen uptake and isotopic discrimination in controlled conditions. We found that soil acidification had a much stronger impact than lead contamination on both nitrogen cycling and plant growth, altering soil N forms, isotopic signatures, and reducing all growth parameters, whereas lead addition showed no significant effects. However, patterns observed in forest settings were less consistent, suggesting that $\delta^{15}N$ values in tree-rings integrates multiple, potentially confounding environmental factors. Differences in soil composition, microbial communities, climatic fluctuations, and long-term ecological interactions may all influence the observed patterns, making direct comparisons between the two contexts challenging. While $\delta^{15}N$ series can be a useful indicator of nitrogen-related processes, their interpretation in natural forest systems remains complex and context dependent. To improve our understanding of N cycling and isotopic variations, additional sampling efforts are required. Investigating a broader range of soil pH under controlled greenhouse conditions could provide a clearer understanding of the role of pH in influencing $\delta^{15}N$ dynamics. In addition, expanding the number of study sites in natural stands would offer a more comprehensive spatial perspective, allowing for a finer characterization of local variability. Analyzing a greater number of tree-ring series would also enhance the ability to interpret temporal processes and environmental changes that have occurred across the region. Additionally, the influence of root- and soil-specific microbial communities on nitrogen cycling and isotopic values should be further investigated.

2.6 Conflict of Interest

The authors declare that this research was funded by the Horne Smelter, but it was conducted independently and without any potential conflict of interest.

2.7 Author Contributions

Elsa Dejoie: Writing – review & editing, Writing – original draft, Conceptualization, Methodology, Formal analysis, Visualization. Marc-André Lemay: Writing – review & editing, Formal analysis. Annie DesRochers: Writing – review & editing, Conceptualization, Supervision, Funding acquisition. Nicole J. Fenton: Writing – review & editing, Conceptualization, Supervision, Funding acquisition. Joëlle Marion: Writing – review & editing, Methodology. Martine M. Savard: Writing – review & editing. Christine Martineau: Writing – review & editing, Methodology, Conceptualization, Supervision, Funding acquisition. Fabio Gennaretti: Writing – review & editing, Writing – original draft, Conceptualization, Supervision, Project administration, Funding acquisition.

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3. INTERACTIVE EFFECTS OF LEAD (PB) CONTAMINATION AND SOIL ACIDIFICATION ON MICROBIAL COMMUNITIES INVOLVED IN NITROGEN (N) CYCLE

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Résumé

La pollution industrielle entraîne souvent une contamination des sols par des métaux lourds et des composés acidifiants, pouvant perturber les communautés microbiennes essentielles au cycle des nutriments. Cette étude examine les effets combinés de la contamination au plomb (Pb) et de l'acidification du sol sur la diversité microbienne et les communautés impliquées dans le cycle de l'azote dans des sols de forêt boréale. Une expérience en serre a été réalisée en cultivant des semis d'épinette noire (*Picea mariana*) dans un sol forestier naturel soumis à six traitements : témoin, Pb faible (30 ppm), Pb élevé (600 ppm), acidification, et combinaisons de Pb avec acidification. Les communautés microbiennes ont été caractérisées par séquençage Illumina des régions 16S rRNA bactériennes et ITS2 fongiques. L'acidification du sol s'est révélée être le facteur dominant structurant les communautés bactériennes, réduisant significativement la diversité de Shannon et la richesse, tandis que le Pb exerçait des effets plus faibles. Des interactions acidité × Pb ont amplifié certaines réponses, notamment la structuration des communautés bactériennes du sol. Plusieurs bactéries impliquées dans le cycle de l'azote étaient moins abondantes dans le traitement acide, tandis que des champignons tolérants au Pb étaient plus abondants dans les traitements au Pb. Les communautés associées aux racines ont montré une forte résilience, probablement grâce à la sélection exercée par l'hôte et à la présence de champignons tolérants aux métaux. Les communautés fongiques sont restées largement inchangées, sans modifications significatives de la diversité ou de la composition entre les traitements. Ces résultats soulignent que le pH du sol est un facteur clé de sensibilité microbienne dans les écosystèmes boréaux exposés aux polluants industriels.

Mots-clés : Microbiome du sol, Rhizosphère, Métaux lourds, Acidification du sol, Diversité bactérienne et fongique

Abstract

Industrial pollution often leads to soil contamination by heavy metals and acidifying compounds, which can disrupt microbial communities critical for nutrient cycling. This study investigates the combined effects of lead (Pb) contamination and soil acidification on microbial diversity and nitrogen-related communities in boreal forest soils. A greenhouse experiment was conducted using black spruce (*Picea mariana*) seedlings grown in natural forest soil under six treatments: control, low Pb (30 ppm), high Pb (600 ppm), acidification, and combinations of Pb with acidification. Microbial communities were characterized through Illumina sequencing bacterial 16S rRNA and fungal ITS2 regions. Soil acidification emerged as the dominant factor shaping bacterial communities, significantly reducing Shannon diversity and richness, while Pb exerted weaker effects. Acid × Pb interactions amplified some responses, including shaping soil bacterial communities. We detected several bacteria involved in N cycling that were less abundant in acid treatment, while fungi tolerant to Pb were more abundant in Pb treatments. Root-associated communities showed strong resilience, likely due to host selection and metal-tolerant fungi. Fungal communities remained largely unaffected, with no significant changes in diversity or composition across treatments. These findings underscore soil pH as a key driver of microbial sensitivity in boreal ecosystems exposed to industrial pollutants.

Keywords: Soil microbiome, Rhizosphere, Heavy metals, Soil acidification, Bacterial and fungal diversity

3.1 Introduction

Soil is a key component in the study of industrial pollution, as it acts both as a reservoir and a potential pathway for contaminants that can impact ecosystems and human health (Khan et al., 2015). Industrial emissions, particularly those related to metallurgy and mining, are a major source of soil pollution. Deposition of pollutants from these emissions increase soil metals or metalloids (e.g. lead (Pb), cadmium and arsenic) and acid compounds (e.g. sulfur dioxide and nitrogen oxides) concentrations, which are a concern due to their persistence in the environment (Alloway, 2013; El-Khatib et al., 2020) and their toxicity for plants, animals and humans (Ettler, 2016; Gagné, 1994; C. Meng et al., 2023).

Soil nutrient cycling, driven by microorganisms (bacteria and fungi) responsible for processes such as mineralization, nitrification, and biological nitrogen fixation, support organic matter decomposition and maintain ecosystem resilience in the face of abiotic stressors (J. Li et al., 2024; L. Lu et al., 2022). Pollution reduces microbial diversity and inhibits key microbial processes, such as nitrogen (N) cycling and enzymatic activities (H. Li et al., 2023). Acidification generally increases the solubility and mobility of heavy metals, thereby enhancing their bioavailability and potential toxicity to soil organisms, whereas higher pH conditions promote the retention of heavy metals through hydrolysis reactions (Bruemmer et al., 1986; Harter, 1983; Kedziorek & Bourg, 1996). Acidifying emissions from smelters can also affect the nitrogen cycle in forests, as soil bacterial and fungal communities that regulate nitrogen availability are sensitive to pH changes and pollutant deposition (Evans & Ehleringer, 1993; Pajares & Bohannan, 2016). Pb contamination also affects N cycling both by disrupting microbial communities and metabolism (George & Wan, 2020) and by interfering with root absorption processes (Bini et al., 2012; Fodor, 2002; M. N. V. Prasad, 1995). However, some microbial species or functional groups exhibit remarkable resistance or adaptability to soil pollution (S. Li et al., 2021; Yin et al., 2023). For instance, certain subgroups of Acidobacteria have been shown to be more adapted to acidic conditions (Rousk et al., 2010). In contrast, several proteobacterial groups tend to be positively associated with higher pH levels (Rousk et al., 2010). Some microorganisms are also known for their resistance to heavy metals, such as bacteria of Actinobacteria, and

Proteobacteria phyla, commonly detected in contaminated environments (Jarosławiecka & Piotrowska-Seget, 2014; Yin et al., 2023).

Although the independent effects of Pb and acidification are relatively well documented, their interaction remains poorly studied. Yet, this interaction is particularly important to investigate because industrial emissions are often both acidifying and metal-rich, exposing soils to simultaneous stressors. Acidification generally increases Pb solubility and mobility, enhancing its bioavailability and potential toxicity to soil organisms, whereas higher soil pH promotes Pb retention through hydrolysis reactions (Bruemmer et al., 1986; Harter, 1983; Kedziorek & Bourg, 1996). In natural soils, this effect is reinforced by the increased negative surface charge of organic matter, which reduces the solubility and bioavailability of Pb (Kedziorek & Bourg, 1996). However, this immobilization is reversible, since a decrease in pH can remobilize Pb and expose microbial communities, leading to suppressed metabolism, reduced biomass production, and shifts in diversity and abundance (George & Wan, 2020). Conversely, certain microbial processes influenced by pH can modulate the speciation and immobilization of metals. Microorganisms employ extracellular strategies or Pb precipitation to limit metal entry into the cell. When Pb enter the cell under high exposure, intracellular resistance mechanisms are activated, including sequestration in vacuoles, enzymatic transformation, or efflux systems that reduce Pb toxicity (George & Wan, 2020).

The aim of this study was to evaluate the effects of Pb contamination in interaction with soil acidification on nitrogen cycling and soil microbial communities. We conducted a greenhouse experiment to investigate the individual or combined effects of Pb contamination and acidification on soil biodiversity and nitrogen cycling, using black spruce (*Picea mariana* (Mill) B.S.P)) seedlings from Eastern Canada growing in natural forest soil as a biological model. Pb pollution and acidification levels were carefully selected to reflect the typical environmental conditions found near industrial sites in natural boreal forests of Eastern Canada. We seeked to understand the specific impacts of industrial contamination on critical ecosystem functions and soil health, which are essential for the long-term resilience of boreal forests. We hypothesized that Pb contamination and soil acidification would interactively affect soil microbial communities. Specifically, we expected that (i) both Pb and acidification would reduce microbial diversity and abundance, with acidification exerting a stronger overall effect, and (ii) these stressors would alter community composition, leading to shifts in the relative abundance of taxa associated with each treatment.

3.2 Methods

3.2.1 Experimental design

The experiment followed a factorial randomized complete block design. Two factors were tested: acidification (acid vs. non-acid) and Pb contamination (0, 30 and 600 ppm Pb), resulting in six treatment combinations. Each treatment was replicated ten times for a total of 60 experimental units. The experiment took place in the greenhouse of the Laurentian Forestry Centre (Québec, Canada). Black spruce seeds were sown after stratification in pots filled with organic soil collected in a natural black spruce forest, near Amos (Abitibi region, Québec, Canada). The full methodology of experimental design can be found in Chapter II. To simulate acidification, we added 50 mL of a sulfuric acid solution (2 mL/L), which lowered the soil pH by one unit. Lead was added by mixing $PbCl_2$ into 500 mL of soil per pot: about 20 mg of Pb for the low treatment (30 ppm) and 400 mg of Pb for the high treatment (600 ppm). The control treatment corresponds to no acidification and no Pb addition in the soil (Table D1). Three seeds were sown per pot and then thinned to only one per pot. Two growing seasons were performed as explained in Fig. D1 and soil sampling for microbiome characterization was conducted at the end of the second growing season (Fig. D1).

3.2.2 Microbiome sample collection

After the second growing period, we collected three types of samples for microbiome analysis: bulk soil, rhizosphere and roots. Bulk soil was collected by pulling the plants from the pot and gently shaking the root system to dislodge any loosely attached soil. This soil was then sieved through a 6 mm mesh to homogenize it and remove roots and larger debris. To collect the soil tightly attached to the roots (i.e. the rhizosphere), ¼ of the root system was cut and placed in a 50 ml tube containing 25 ml of PBST (Phosphate Buffered Saline with Tween). The tube was shaken by inversion 10 times.

The roots were transferred to another tube containing 25 ml of PBS (Phosphate Buffered Saline) for further cleaning while the rhizosphere soil was recovered by centrifugation. Additionally, the tube containing only the roots was sonicated 3 times for 30 seconds in a sonication bath to ensure thorough cleaning. Once cleaned, the roots were cut into approximately 1cm-segments, and a subsample of 0.1 g was taken for molecular analyses. This root subsample was frozen in a liquid nitrogen bath followed by mechanical grinding to homogenize the sample. Then, tissue lysis was accomplished using a TissueLyser with a sterile 5 mm tungsten bead. The roots were subjected to two 45-second cycles at a frequency of 26 Hz.

3.2.3 DNA extraction and microbiome analyses

For each sample, a total of 0.1 g of material was transferred into a PowerBead tube and a DNeasy PowerSoil DNA extraction kit was used within a QIAcube system (Qiagen, Germany). A negative control (i.e. no sample added) was included in each batch of 24 samples. DNA concentration was assessed using the Qubit dsDNA broad range (BR) assay and the Qubit Fluorometer (Thermo Fisher Scientific, Wilmington, DE, USA).

The library preparation for Illumina sequencing was performed according to the manufacturer's protocol (16S Metagenomic Sequencing Library Preparation, Part 15044223 Rev. B) with user defined primers with some modifications, as previously described (Nagati et al., 2024). Bacterial communities were amplified using primers 515F-Y and 926R targeting the V4–V5 regions of the 16S rRNA gene of bacteria and archaea (Parada et al., 2016). The ITS2 region of the fungal DNA was amplified using the primer set ITS9F and ITS4R (Ihrmark et al., 2012; White et al., 1990). The 16S rRNA and ITS amplicon pools were sequenced on an Illumina MiSeq instrument (Illumina, San Diego, CA) at the Centre de recherche du CHU de Québec-Université Laval using MiSeq Reagent Kit v3 (2x300 bp).

3.2.4 Processing of 16S and IST gene data (bioinformatic)

Bioinformatic analyses were conducted using the RStudio software 4.5.0 (R Core Team, 2025). We used the DADA2 pipeline for 16S rRNA gene and ITS2 region to process the Illumina-sequenced paired-end fastq files and to generate a table of amplicon sequence variants (ASVs), which are higher-resolution analogs of the traditional OTUs (B. J. Callahan et al., 2016). First, the primers were removed using an implementation of CutAdapt (M. Martin, 2011) for the ITS2 sequences and by position trimming in DADA2 for the 16S sequences. This step also served to trim low-quality bases from the end of the sequence. Resulting forward and reverse reads were merged, and then low-quality sequences, chimeras and rare ASV (frequency < 0.05 % of mean ASV frequency) were removed (Table D2). We used the Silva 138 database to assign taxonomy for bacteria (B. Callahan, 2024) and the UNITE database (version 10) for fungi (Abarenkov et al., 2025).

Fungal trophic modes were assigned using *FUNGuild* (Nguyen et al., 2016). To avoid over-interpretation, only assignments with a confidence ranking of “probable” or “highly probable” were retained for further analyses. Taxa that could not be assigned to a category of guild or those classified under multiple guilds were removed from the analysis. Relative abundances of each guild were then calculated per sample by summing the abundances of the corresponding ASVs.Fungal trophic modes were assigned using *FUNGuild* (Nguyen et al., 2016). To avoid over-interpretation, only assignments with a confidence ranking of “probable” or “highly probable” were retained for further analyses. Taxa that could not be assigned to a category of guild or those classified under multiple guilds were removed from the analysis. Relative abundances of each guild were then calculated per sample by summing the abundances of the corresponding ASVs.

3.2.5 Statistical analysis

To characterize microbial diversity, we calculated alpha- and beta-diversity metrics using the phyloseq package in RStudio, R version 4.5.0 (McMurdie & Holmes, 2013). For alpha-diversity, samples were rarefied to a sequencing depth of 20,000, 14,000 and 5,000 for bacteria in soil, rhizosphere and roots samples respectively, and 6,000, 2,700 and 6,000 for fungi in soil, rhizosphere and roots samples respectively (Table D2). We then computed observed richness, Shannon diversity, and Pielou’s evenness that were analyzed using two-way ANOVA to assess the effects of acidification (Acid), Pb contamination (Lead), and interaction (Acid × Lead). These linear models were checked to ensure that all assumptions were met, including homoscedasticity, independence of errors, and normality of residuals.

To visualize community composition, Bray-Curtis dissimilarities were computed from rarefied ASV relative abundances and used in a non-metric multidimensional scaling (NMDS) analysis with the *metaMDS* function of the vegan package in R (Oksanen et al., 2025). We used PERMANOVA (Permutational Multivariate Analysis of Variance) on rarefied data to test for differences in microbial community composition across treatments, based on Bray-Curtis dissimilarity matrices. The models were fitted with 999 permutations using the *adonis2* function from the vegan package (Oksanen et al., 2025). The relative influence of environmental factors on microbial community composition was assessed using partial R^2 from PERMANOVA.

To identify taxa that were differentially abundant across treatments at the genus level for both bacteria and fungi, and at the guild level for fungi, we used ANCOM-BC2 (Analysis of Composition of Microbiomes with Bias Correction, version 2) on unrarefied datasets, implemented in the ANCOMBC package (Lin & Peddada, 2024; Nearing et al., 2022). Only the top 20 most abundant genera were tested. ANCOM-BC2 method accounts for compositional constraints, unequal sampling depths, and overdispersion, and it provides bias-corrected estimates of differential abundance. It also handles structural zeros and controls the false discovery rate. Pairwise comparisons were corrected for multiple testing using the false discovery rate (FDR), and significant taxa were identified based on adjusted p-values. The model included Acid (two levels: NoACD, ACD) and Pb (three levels: NoPb, LowPb, HighPb) as fixed factors, as well as their interaction (Acid × Pb). Subsequently, we tested targeted pairwise comparisons to isolate the effects of Pb contamination under both normal and acidic conditions, as well as their potential interactions (Table 7).

Table 7
Pairwise comparisons used to assess the effects of Pb contamination and soil acidification on microbial relative abundance of specific taxa and fungal guilds, using ANCOM-BC2 (Analysis of Composition of Microbiomes with Bias Correction, version 2).

Condition	Pairwise comparison	Interpretation
Pb vs Control	LowPb vs Control	Effect of low Pb concentration at normal pH
	HighPb vs Control	Effect of high Pb concentration at normal pH
Acid vs Control	ACD vs Control	Effect of acidification
Pb vs Acid (ACD)	LowPb_ACD vs ACD	Effect of low Pb under acidic conditions
	HighPb_ACD vs ACD	Effect of high Pb under acidic conditions

3.3 Results

3.3.1 Effect of acidification and Pb treatments on alpha diversity

All alpha diversity indices (Shannon, richness, and evenness) of bacterial and fungal communities were affected by the acidic treatment in soil, while in the rhizosphere, bacterial diversity was influenced by the interaction between factors, and in roots, alpha diversity remained stable across treatments. Bacterial diversity decreased under acidic conditions, whereas fungal diversity increased. Pb contamination also exerted a negative influence on the Shannon index and on evenness but not on richness, reducing diversity for both bacteria and fungi. A significant interaction between acidification and Pb was additionally detected for bacteria Shannon index in the rhizosphere (Table 8, Figs. D2 and D3).

Table 8
Results of two-way ANOVA testing the effects of acidification (Acid), Pb contamination (Lead), and their interaction (Acid:Lead) on soil alpha diversity indices, including Shannon diversity, richness, and evenness. F value: F-statistic testing the significance of each factor. Pr(>F): p-value associated with the F-test. Significant p-values are indicated with standard notation (* p < 0.05, ** p < 0.01, *** p < 0.001).

Index	Compartment		F value	Pr(>F)			F value	Pr(>F)	
		Bacteria				Fungi			
Shannon	Soil	Acid	37.148	<0.001	***	Acid	6.024	0,02	*
		Lead	5.469	0,01	**	Lead	3.704	0,03	*
		Acid:Lead	0.158	0,85		Acid:Lead	0.794	0,46	
	Rhizosphere	Acid	6.100	0,02	*	Acid	4.904	0,03	*
		Lead	1.327	0,27		Lead	3.162	0,05	
		Acid:Lead	4.508	0,02	*	Acid:Lead	0.818	0,45	
	Roots	Acid	1.259	0,27		Acid	0.389	0,54	
		Lead	1.173	0,32		Lead	1.307	0,28	
		Acid:Lead	0.040	0,96		Acid:Lead	0.340	0,71	
Richness	Soil	Acid	22.670	<0.001	***	Acid	4.493	0,04	*
		Lead	2.735	0,07		Lead	2.295	0,11	
		Acid:Lead	1.508	0,23		Acid:Lead	1.598	0,21	
	Rhizosphere	Acid	5.424	0,02	*	Acid	1.463	0,23	
		Lead	0.555	0,58		Lead	1.283	0,29	
		Acid:Lead	2.345	0,11		Acid:Lead	1.004	0,37	
	Roots	Acid	0.007	0,94		Acid	0.775	0,38	
		Lead	2.123	0,13		Lead	2.159	0,13	
		Acid:Lead	0.111	0,90		Acid:Lead	1.019	0,37	
Evenness	Soil	Acid	13.952	0,00	***	Acid	5.509	0,02	*
		Lead	7.367	0,00	**	Lead	3.868	0,03	*
		Acid:Lead	2.732	0,07		Acid:Lead	0.492	0,61	
	Rhizosphere	Acid	0.006	0,94		Acid	4.924	0,03	*
		Lead	2.891	0,06		Lead	3.041	0,06	
		Acid:Lead	1.196	0,31		Acid:Lead	0.459	0,63	
	Roots	Acid	3.830	0,06		Acid	1.087	0,30	
		Lead	2.988	0,06		Lead	1.669	0,20	
		Acid:Lead	0.275	0,76		Acid:Lead	0.099	0,91	

3.3.2 Effect of acidification and Pb treatments on microbial community composition

Soil bacterial community composition was shaped by the interaction between Pb and soil acidity (Table 9). The ordination plot (Fig. 12A) showed a clear separation between acid and non-acid treatment on the first axis, whereas the distinction between Pb treatments was not clear. In the rhizosphere, the effect of acid alone was significant (Table 9). Clusters based on acidity in the ordination plot were less distinct in this compartment compared to soil (Fig. 12B) but still showed two significant clusters between acid and non-acid treatments. In the root compartment, the effects of the acidification and Pb treatments were significant, while the interaction between the two factors was not significant (Table 9). Although the effect of acidification on root communities was less evident than in the other compartments, the NMDS highlights an effect of soil acidity, with a noticeable separation between acidity levels (Fig. 12C), but no distinction between Pb treatments. In contrast, fungal community composition was stable across treatments, while we detected marked differences in bacterial community composition in all compartments: soil, rhizosphere and roots (Fig 12). There was no significant effect of acid or Pb treatments on fungal communities (Table 9), except for significant interaction in the soil compartment. In the ordination, samples were largely intermixed, and no clear clustering by treatment was observed (Figs. 12D, E and F).

The variance in bacterial community composition attributable to treatments (R^2 values, Table 9) differed among compartments. pH consistently accounted for the largest proportion of the variation, with decreasing importance from the soil (44%) to the rhizosphere (26%) and the roots (15%) (Table 9). Contribution of the interaction acid × Pb was modest, accounting for less than 5% of the variation in bacterial community structure in all compartments. For fungal communities, partial R^2 showed that all explanatory variables explained less than 5% of the total variation in community structure ($R^2 < 0.05$, Table 9).

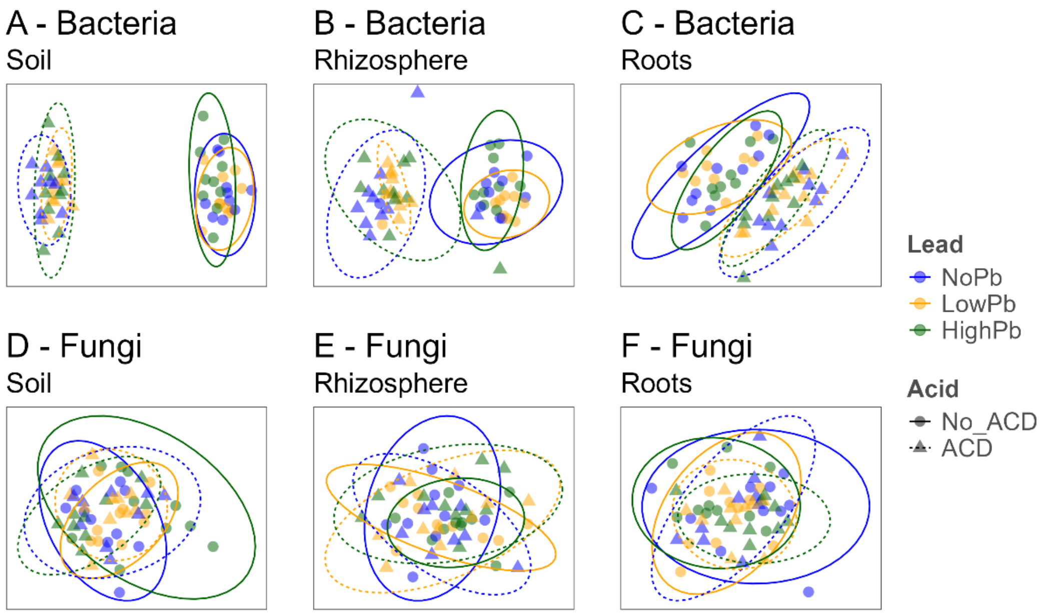

Figure 12
Two-dimensional non-metric multidimensional scaling (NMDS) of the bacterial communities in (A) soil, (B) rhizosphere, and (C) roots, and fungi communities in (D) soil, (E) rhizosphere, and (F) roots. Ellipses correspond to standard deviation of ordination scores for samples according to the Treatment (Acid x Lead). Ordination based on Bray-Curtis dissimilarities of the rarefied amplicon sequence variants (ASV) relative abundances.

Table 9
Permutational multivariate analysis of variance (PERMANOVA, displayed by terms) showing the significant effects of ACD and/or lead treatments and interaction on bacterial and fungi communities across soil compartments. Df indicates the degrees of freedom, SumOfSqs the sum of squares, R^2 the proportion of variance explained by the factor, F the F-statistic, and Pr(>F) the p-value testing the significance of the factor. Significance codes: '*' p < 0.001; '**' p < 0.01; '*' p < 0.05.**

			Df	SumOfSqs	R^2	F	Pr(>F)	
Bacteria	Sol	Acid	1	3.6941	0.44129	50.855	0.0001	***
		Lead	2	0.4735	0.05657	3.2595	0.0029	**
		Acid:Lead	2	0.3537	0.04225	2.4345	0.0186	*
	Rhizosphere	Acid	1	2.2480	0.25960	20.9554	0.0001	***
		Lead	2	0.3659	0.04225	1.7054	0.0571	
		Acid:Lead	2	0.3601	0.04158	1.6784	0.0605	
	Roots	Acid	1	1.3049	0.14672	9.8185	0.0001	***
		Lead	2	0.3955	0.04446	1.4878	0.0428	*
		Acid:Lead	2	0.2827	0.03179	1.0636	0.3398	
Fungi	Soil	Acid	1	0.1850	0.01885	1.1090	0.2726	
		Lead	2	0.2881	0.02935	0.8633	0.7641	
		Acid:Lead	2	0.5004	0.05097	1.4994	0.0159	*
	Rhizosphere	Acid	1	0.1526	0.01328	0.7845	0.7847	
		Lead	2	0.4979	0.04334	1.2798	0.0900	
		Acid:Lead	2	0.5275	0.04591	1.3557	0.0529	
	Roots	Acid	1	0.1673	0.01480	0.8610	0.5894	
		Lead	2	0.2838	0.02511	0.7304	0.8462	
		Acid:Lead	2	0.5541	0.04902	1.4260	0.0738	

3.3.3 Relative abundance

In Table 7, we identified sets of important pairwise comparisons to assess the effects of Pb contamination and soil acidification on abundance of specific taxa. For bacterial taxa, significant shifts were observed in the pairwise comparison Acid vs Control in the soil and the rhizosphere. In soils, some genera had higher relative abundances in the acid treatment compared to control treatment, including *Occallatibacter*, *Singulisphaera* and *Acidibacter*. Conversely, other genera had lower relative abundances under ACD treatment compared to Control treatment, such as *Burkholderia-Caballeronia-Paraburkholderia* and *Bradyrhizobium* (Fig. 13A and D6). In the rhizosphere, only *Occallatibacter* had higher relative abundances and *Bradyrhizobium* a lower abundance in ACD treatment vs Control treatment (Fig. 13B and D6). The taxa *Robbsia* was also often variable in the roots and sensitive to acidic and Pb treatments (Fig. 13C and D6). Although several taxa exhibited large absolute

LFC, however, these differences were not statistically significant, likely due to high variability among replicates. Despite, *Robbsia* tended to have higher relative abundance under acidic conditions compared to the control, and an opposite trend of reduced abundance under Pb exposure in both control and acidic conditions.

For fungal communities, none of the taxa showed significant differences in any of the pairwise comparisons identified in Table 7 (Figs. 13D, E and F). However, *Thelephora* consistently exhibited higher relative abundance in Pb treatments compared to the control in all compartments. In soils *Thelephora* is also more abundant in acid soil than in control but, in the rhizosphere and in roots, it seemed to be particularly associated with Pb-enriched treatments. Although *Cunninghamella* tended to increase in polluted soils (Acid, LowPb and HighPb vs control), its abundance declined when Pb was combined with acidification. In both soil and rhizosphere compartments, *Cunninghamella* was less abundant under HighPb_ACD and LowPb_ACD treatments than under acidification alone (Figs. 13D, E and D6).

The abundance of all guilds of fungi was similar among treatments in the soil, rhizosphere, and root compartments (Fig. D5). However, in both the rhizosphere and roots compartments, undefined saprotrophs tended to be more abundant under acid and Pb treatments alone compared to the control, but their abundance decreased under LowPb_ACD and HighPb_ACD treatment relative to ACD alone. In the rhizosphere, wood saprotrophs similarly showed higher abundance in acid and LowPb and HighPb treatments than in the control and appeared reduced in the HighPb_Acid treatment compared with acid alone. In contrast, in the roots, wood saprotrophs exhibited an opposite pattern, with lower abundance in Low and HighPb compared to control, and lower abundance in LowPb_ACD and HighPb_ACD than in ACD treatments (Fig. D5 and D8).

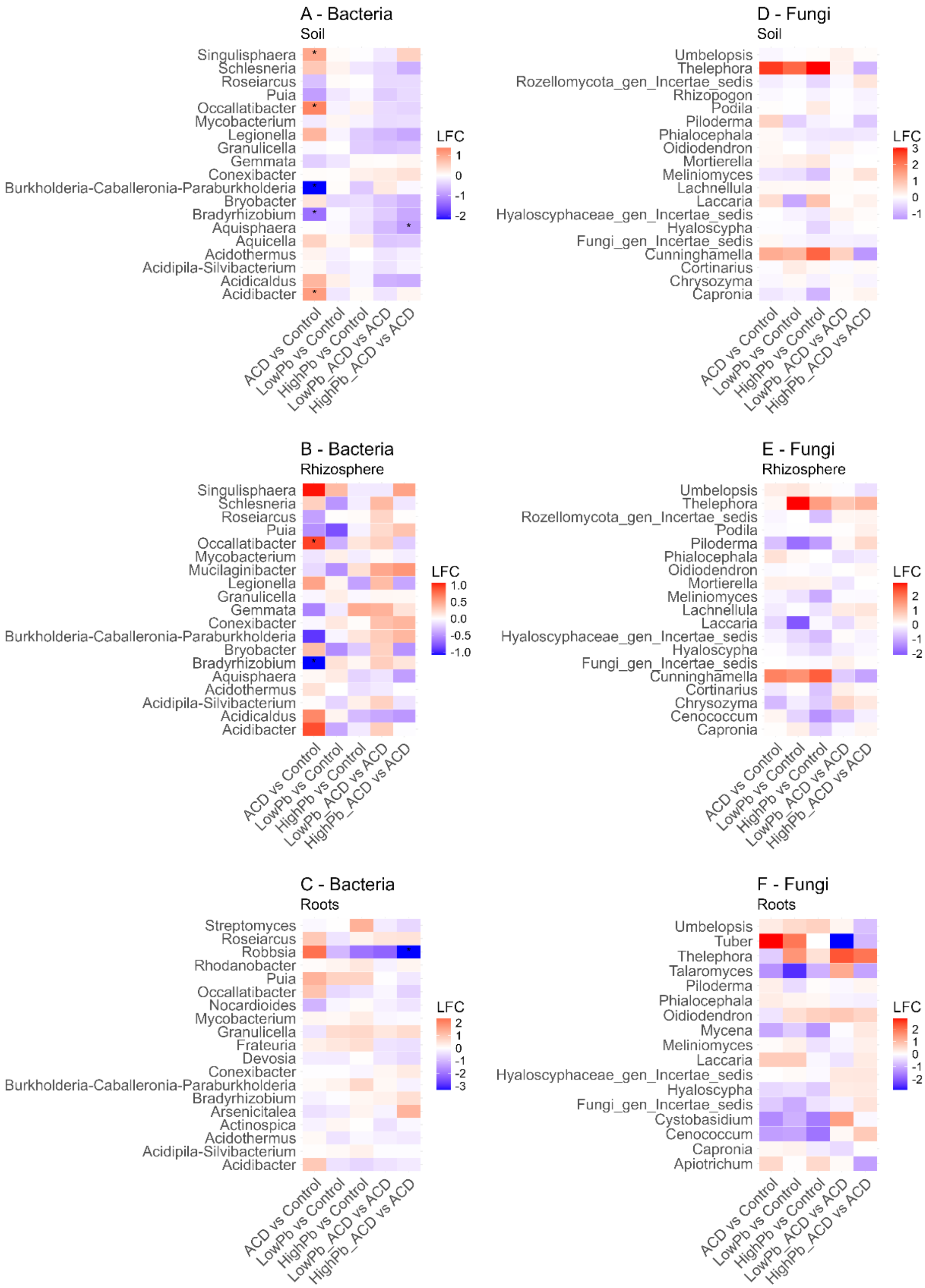
A - Bacteria
Soil
Singulisphaera
Schlesneria
Roseiarcus
Puia
Occallatibacter
Mycobacterium
Legionella
Granulicella
Gemmata
Conexibacter
Burkholderia-Caballeronia-Paraburkholderia
Bryobacter
Bradyrhizobium
Aquisphaera
Aquicella
Acidothermus
Acidipila-Silvibacterium
Acidicaldus
Acidibacter
LFC
1
0
-1
-2
ACD vs Control
LowPb vs Control
HighPb vs Control
LowPb_ACD vs ACD
HighPb_ACD vs ACD
D - Fungi
Soil
Umbelopsis
Thelephora
Rozellomycota_gen_Incertae_sedis
Rhizopogon
Podila
Piloderma
Phialocephala
Oidiodendron
Mortierella
Meliniomyces
Lachnellula
Laccaria
Hyaloscyphaceae_gen_Incertae_sedis
Hyaloscypha
Fungi_gen_Incertae_sedis
Cunninghamella
Cortinarius
Chrysozyma
Capronia
LFC
3
2
1
0
-1
ACD vs Control
LowPb vs Control
HighPb vs Control
LowPb_ACD vs ACD
HighPb_ACD vs ACD
B - Bacteria
Rhizosphere
Singulisphaera
Schlesneria
Roseiarcus
Puia
Occallatibacter
Mycobacterium
Mucilaginibacter
Legionella
Granulicella
Gemmata
Conexibacter
Burkholderia-Caballeronia-Paraburkholderia
Bryobacter
Bradyrhizobium
Aquisphaera
Acidothermus
Acidipila-Silvibacterium
Acidicaldus
Acidibacter
LFC
1.0
0.5
0.0
-0.5
-1.0
ACD vs Control
LowPb vs Control
HighPb vs Control
LowPb_ACD vs ACD
HighPb_ACD vs ACD
E - Fungi
Rhizosphere
Umbelopsis
Thelephora
Rozellomycota_gen_Incertae_sedis
Podila
Piloderma
Phialocephala
Oidiodendron
Mortierella
Meliniomyces
Lachnellula
Laccaria
Hyaloscyphaceae_gen_Incertae_sedis
Hyaloscypha
Fungi_gen_Incertae_sedis
Cunninghamella
Cortinarius
Chrysozyma
Cenococcum
Capronia
LFC
2
1
0
-1
-2
ACD vs Control
LowPb vs Control
HighPb vs Control
LowPb_ACD vs ACD
HighPb_ACD vs ACD
C - Bacteria
Roots
Streptomyces
Roseiarcus
Robbsia
Rhodanobacter
Puia
Occallatibacter
Nocardioides
Mycobacterium
Granulicella
Frateuria
Devosia
Conexibacter
Burkholderia-Caballeronia-Paraburkholderia
Bradyrhizobium
Arsenicitalea
Actinospica
Acidothermus
Acidipila-Silvibacterium
Acidibacter
LFC
2
1
0
-1
-2
-3
ACD vs Control
LowPb vs Control
HighPb vs Control
LowPb_ACD vs ACD
HighPb_ACD vs ACD
F - Fungi
Roots
Umbelopsis
Tuber
Thelephora
Talaromyces
Piloderma
Phialocephala
Oidiodendron
Mycena
Meliniomyces
Laccaria
Hyaloscyphaceae_gen_Incertae_sedis
Hyaloscypha
Fungi_gen_Incertae_sedis
Cystobasidium
Cenococcum
Capronia
Apiotrichum
LFC
2
1
0
-1
-2
ACD vs Control
LowPb vs Control
HighPb vs Control
LowPb_ACD vs ACD
HighPb_ACD vs ACD

Figure 13
Pairwise log fold changes (LFC) in Genus abundance across treatments. Only comparisons shown in Table 7 are presented (see Fig. D3 for all comparisons). Heatmap of log fold changes for bacteria in (A) soil, (B) rhizosphere and (C) roots, and for fungi in (D) soil, (E) rhizosphere and (F) roots. Bacteria and fungi were displayed from the Top20 most abundant Genus; no taxa in this set were statistically significant. Colors represent LFC values, with blue indicating negative values (LFC < 0) and red indicating positive values (LFC > 0). Stars showed taxa with significant differences according to adjusted p-values (FDR-adjusted p-values). Significance code: '*' p < 0.05.

3.4 Discussion

3.4.1 Acidification as the primary driver of microbial community in soils

Our results showed a decline in bacterial diversity and a shift in community composition under acid treatment in soil, rhizosphere and roots (Table 8 and Fig. 12). This result highlights the central role of pH as a major driver of bacterial communities and suggests that acidification acts as a strong environmental filter, narrowing the range of microorganisms that can persist under low pH. In our experiment, acid treatment likely imposed physiological constraints that only acid-tolerant taxa could withstand. As a result, these tolerant groups became more dominant and structured the community, while other taxa with narrower pH optima declined or disappeared. Indeed, soil pH is widely recognized as a primary determinant of bacterial diversity and composition across ecosystems (Fierer & Jackson, 2006; Wu et al., 2017; Zhalnina et al., 2015). Microbial metabolism and enzyme activity are highly pH-dependent, as most microorganisms exhibit optimal growth within a narrow pH range. Acidic conditions (pH of 4.7 and below) can disrupt enzymatic functioning and cellular homeostasis, leading to the decline of sensitive taxa (Mitsuta et al., 2025; Naz et al., 2022). The observed increase in fungal diversity is partly surprising considering the very acidic soil conditions. However, this pattern is also consistent with the ecology of coniferous forest ecosystems (M. N. Högberg et al., 2007), where fungi act as the dominant decomposers under naturally acidic conditions (J. Li et al., 2019; Lindahl & Clemmensen, 2016). The increase in fungal diversity observed under acidic conditions suggests that soil acidification may create ecological niches that favor fungi over bacteria. Fungi are generally more tolerant to low pH environments (Johansson et al., 2008). Acidification may therefore reduce competitive pressure from bacteria while simultaneously selecting for fungi capable of thriving under acidic conditions, resulting in higher fungal diversity (C. Wang & Kuzyakov, 2024).

Consistently, changes in pH were accompanied by marked shifts in the relative abundance of specific bacterial taxa. The abundance of several groups increased or decreased significantly in response to acid treatments only, indicating that acidification, rather than Pb exposure, was the main driver of community reorganization. Within the bacterial assemblages, *Occallatibacter* and *Acidibacter*, both belonging to the phylum Acidobacteria, were particularly enriched under acidic conditions, which is consistent with previous studies reporting that most Acidobacteria thrive in acid environments (Kalam et al., 2020; Zou et al., 2024). Conversely, several bacterial taxa showed reduced abundance under the acid treatments. Many of these taxa play important ecological roles: for instance, *Bradyrhizobium* is involved in nodulation and biological nitrogen fixation (Ormeño-Orrillo & Martínez-Romero, 2019), while *Burkholderia-Caballeronia-Paraburkholderia* contribute to nitrogen fixation and plant-microbe interactions, while others are involved in the decomposition of complex organic compounds or structuring microbial networks (K. Li et al., 2025; L. Zhang et al., 2023). Their decline suggests that combined acidification and acidic exposure can negatively affect key functional groups.

The experiment presented here was conducted in a controlled greenhouse environment, where pots containing black spruce seeds and seedlings were subjected to acidic and Pb treatments. Unpublished data from this experiment indicate that soil acidification was associated with higher NH_4^+ concentrations and elevated soil $\delta^{15}N$ values, alongside reduced NO_3^- availability. Acidification also negatively affected seedling growth and lower $\delta^{15}N$ values in xylem compared with those grown under non-acidic conditions, suggesting altered nitrogen uptake or assimilation pathways. No detectable effects of Pb were observed on these variables. Together these results are consistent with the strong impact of acidification on plant growth (Menon et al., 2007; Zinko et al., 2006) and the strong relationship between contamination (particularly soil pH), soil microbial communities, and plant performance (Aqeel et al., 2023; F. Jiang et al., 2024).

3.4.2 Impact of Pb on bacterial communities in soils

We showed that soil bacterial and fungal alpha-diversity declined under Pb treatments (Table 8), indicating that even moderate Pb concentrations can impact microbial communities. Nevertheless, these effects were much weaker than those of acidification. Ordination analyses (Fig. 12) revealed clear separation of bacterial communities by pH, but not by Pb levels, suggesting that moderate Pb exposure exerts diffuse stress that alters the relative abundance of taxa rather than causing strong taxonomic turnover (Akmal & Jianming, 2009). While Shannon diversity and evenness decreased under Pb, richness remained unchanged (Table 8), indicating that Pb does not uniformly affect all aspects of community diversity but instead imposes variable constraints depending on the index considered. Taken together, these patterns are consistent with functional redundancy in microbial communities, where multiple taxa can perform similar ecological roles, allowing overall composition to remain stable despite changes in diversity and evenness (Allison & Martiny, 2008; Louca et al., 2018).

The limited effect of Pb pollution on fungal communities may be partly explained by the presence of metal-tolerant fungi in the soil communities. Among the 20 most abundant fungi genera in our study, *Thelephora* (Borovička et al., 2022) and *Umbelopsis* (Janicki et al., 2018) are well-known to be metal-tolerant genera, as well as other taxa such as *Talaromyces* (X. Lu et al., 2024), and dark septate endophytes (Colpaert et al., 2011b) all of which have been documented to survive and even thrive in metal-contaminated soils. In a context of interaction with plants, these fungi can limit Pb uptake in roots, sequester metals within their structures, and maintain functional interactions with the plant host, thereby stabilizing the community under stress (Varjani & Patel, 2017), and then limit the toxic effects of Pb in plants as suggested by the homogeneous growth of the seedlings across Pb treatments (under review). Consequently, the prevalence of such tolerant taxa could buffer the microbial community against Pb toxicity, reducing detectable shifts in the diversity and composition of root-associated microbial communities (Berg & Smalla, 2009). In contrast, fungal communities, such as ectomycorrhizal guilds, remained largely unchanged across treatments, although a few Pb-resistant fungal taxa showed higher relative abundance under Pb treatments. The presence of Pb-resistant fungal taxa is consistent with our observation that black spruce seedlings showed no detectable impact of Pb contamination on their development or nitrogen uptake (under review).

3.4.3 Root-level sensitivity: limited impact of disturbances

We found that the impacts of pollution were stronger on soil and rhizosphere microbial community and much less pronounced at the root level, where neither alpha- nor beta-diversity metrics showed significant changes in acid or in Pb treatments and no differences in the relative abundance of individual taxa were detected. This limited response suggests that root-associated microbial communities may be more buffered against external disturbances than bulk soil or rhizosphere communities. Roots create a chemically and physically distinct microenvironment enriched in organic exudates, which can sustain a stable core microbiome even under stress. By releasing a variety of organic compounds (e.g., organic acids, sugars, amino acids, phenolics), roots can regulate pH, complex certain heavy metals, and stimulate specific microbial communities (Haichar et al., 2014; Steinauer et al., 2016). These processes contribute to the formation of a microenvironment distinct from the surrounding bulk soil, which can reduce the bioavailability and direct toxicity of contaminants (Montiel-Rozas et al., 2016). In addition, Pb-tolerant fungi (e.g. *Thelephora*) found in our Pb-treated soils, can promote the degradation of some organic pollutants and support mechanisms of metal tolerance or sequestration (Agarwal et al., 2024; Conlon et al., 2025). Consequently, the localized dynamics driven by roots may mitigate the broader effects of pollution observed in bulk soil, explaining why its impact appears less pronounced at the root level. The root microbiome appears to be definitely shaped by strong tree-microbiome interactions (Reinhold-Hurek et al., 2015).

3.4.4 Differential sensitivity of fungi and bacteria

Fungal communities appeared less sensitive to acid and Pb treatments than bacteria: community composition did not show significant shifts in all the analyzed compartments, i.e., soil, rhizosphere and roots (Fig. 12). In addition, acid and Pb explained only a very small proportion of the variability in fungal communities (less than 5% according to PERMANOVA results, Table 9). In the soil, the significance of the acid-Pb interaction suggests that fungi are generally resilient to single-factor disturbances but may become responsive when exposed to multiple stressors simultaneously (Johansson et al., 2008; Y. Luo et al., 2022). Ectomycorrhizal fungi form intimate symbiotic associations with plant roots, which provide them with a stable carbon source through root exudates and photosynthates (Bahram et al., 2014; Soares et al., 2024). This close connection likely buffers root fungi against fluctuations in the surrounding soil environment, making them less sensitive to changes in soil chemistry or contamination (Johansson et al., 2008). In contrast, bacteria rely more directly on soil nutrients and are therefore more strongly affected by factors such as pH shifts or heavy metal addition (Fajardo et al., 2019; C. Wang et al., 2020). These differences in ecological strategy and dependence on host plants may explain why bacterial communities exhibited greater variability in response to industrial pollution, while ectomycorrhizal fungi remained relatively stable.

3.4.5 Limitations

Pb concentrations in the humus of high polluted natural soils within 0–10 km of smelters in Gaspésie may range 400 to 800 ppm (Aznar et al., 2008), or 1,000 ppm, with extreme values around 3,000 ppm, in Rouyn-Noranda (Henderson & Knight, 2005; Hou et al., 2006). In contrast, the used soil, collected near Amos, had a natural Pb concentration of about 30 ppm, which is low but not negligible. Consequently, the relatively low Pb content in the control soil may have limited the magnitude of detectable differences, and larger effects might have been observed if a truly Pb-free soil had been used. The experiment introduced a single pulse 600 ppm Pb contamination, but the duration of exposure, approximately one year and two growing seasons, may have been too short to fully trigger long-term microbial responses. While microbial communities can respond more rapidly (e.g. 6–12 weeks under high Pb exposure (Nguyen-Viet et al., 2007)), short-term experiments may not capture the full range of effects that prolonged, low-dose exposure exerts on forest soil microbiomes.

3.5 Conclusion

Our study demonstrated that soil microbial diversity was negatively affected by acidification and Pb contamination. Acidification emerged as the dominant factor shaping bacterial communities, causing a marked reduction in bacterial alpha diversity and a clear restructuring of community composition. In contrast, Pb exposure had a more subtle effect, primarily affecting bacterial alpha diversity in the soil, without causing significant shifts in community composition. At the root level, microbial communities appeared largely resilient to both stressors, indicating a buffering role of the rhizosphere and highlighting the importance of microenvironments in mitigating environmental perturbations. Within bacterial communities, some taxa exhibited differential responses to acidic versus non-acidic conditions, whereas Pb treatments did not significantly alter the relative abundance of bacterial taxa. Fungal communities showed remarkable stability under both acid and Pb treatments, underscoring a differential sensitivity among microbial groups. Overall, these findings emphasize that soil bacteria and associated functions are more responsive to environmental stressors than fungi and that the effects of pollution can vary strongly depending on the microbial habitat and community composition.

3.6 Conflict of Interest

The authors declare that the Horne smelter contributed in part to the financing of the study but did not interfere in any phase of the analyses or interpretation of results.

3.7 Author Contributions

Elsa Dejoie: Writing – review & editing, Writing – original draft, Conceptualization, Methodology, Formal analysis, Visualization. Maxime Thomas: Writing – review & editing, Formal analysis. Annie DesRochers: Writing – review & editing, Conceptualization, Supervision, Funding acquisition. Nicole J. Fenton: Writing – review & editing, Conceptualization, Supervision, Funding acquisition. Christine Martineau: Writing – review & editing, Methodology, Conceptualization, Supervision. Fabio Gennaretti: Writing – review & editing, Writing – original draft, Conceptualization, Supervision, Project administration, Funding acquisition.

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CONCLUSION GÉNÉRALE

Cette thèse visait à mieux comprendre l'influence des émissions de la fonderie Horne sur les écosystèmes forestiers boréaux en combinant des approches dendrogéochimiques, expérimentales et microbiologiques. Elle avait pour objectifs (1) de caractériser la répartition spatio-temporelle des dépôts atmosphériques de métaux lourds autour de la fonderie en retraçant leur évolution dans les cernes d'arbres urbains, (2) d'évaluer les effets toxiques de cette pollution sur la croissance des plantes et sur le fonctionnement du microbiome du sol au moyen d'expérimentations contrôlées en serre, et (3) d'analyser comment ces émissions modifient les cycles biogéochimiques, notamment celui de l'azote afin de mieux comprendre les implications écophysiologiques associés à la contamination industrielle. Notre cas d'étude, la fonderie Horne, est idéal pour nos recherches en raison de son statut de dernière fonderie de cuivre encore en activité au Canada et de son rôle historique majeur dans l'émission de métaux lourds à Rouyn-Noranda depuis près d'un siècle. Son influence sur la qualité de l'air, des sols et des écosystèmes environnants en fait un site d'intérêt scientifique et sociétal important.

Bioaccumulation des métaux et cartographie de la pollution historique sur les arbres. Dans cette étude, nous avons observé que le pin accumulait davantage de Cd que l'épinette, tandis que l'épinette présentait des concentrations de Pb plus élevées. La bioaccumulation des métaux dans le tronc des arbres varie donc d'une espèce à l'autre en raison de différences dans les capacités d'absorption, de stockage et de détoxification, elles-mêmes liées à la structure anatomique des arbres (Koç et al., 2024; Pulatoglu et al., 2025). L'épinette, caractérisée par une croissance lente et un système racinaire superficiel, pourrait présenter une capacité d'absorption métallique différente de celle du pin, dont les racines pivotantes plus profondes et la croissance plus rapide favoriseraient une exploration plus efficace du sol (Puhe, 2003; Lilles et Astrup, 2012; Swidrak et al., 2013). À l'inverse, le pin présente une plus grande résistance au Pb que l'épinette (Seiler et Paganelli, 1987), probablement grâce à la séquestration des métaux dans les parois cellulaires ou les vacuoles, à la limitation de leur transport vers les tissus sensibles et à des réponses antioxydantes qui atténuent le stress oxydatif (Peng et Gong, 2014). Cela pourrait expliquer les concentrations relativement faibles mesurées dans les tissus analysés chez cette espèce. À ce jour, les différences spécifiques de bioaccumulation entre le pin et l'épinette demeurent peu explorées. Nos résultats suggèrent que ces divergences pourraient refléter les traits propres à chaque espèce et leurs mécanismes distincts d'acquisition des métaux (Li-qiang et al., 2004).

Nos résultats indiquent que, dans les arbres urbains de Rouyn-Noranda, la distribution spatiale du Pb et du Cd dans les cernes de croissance ne montre pas de gradient clairement décroissant avec la distance à la fonderie, ni de motif apparent aligné sur l'axe des vents dominants. Cette observation contraste avec certaines études réalisées sur des distances plus longues, mais elle pourrait refléter la variabilité locale des dépôts atmosphériques et des conditions édaphiques plutôt qu'une véritable absence de gradient de contamination (Daggupaty et al., 2006; Hou et al., 2006). Par ailleurs, nos résultats indiquent que les interventions de dépollution, réalisées de manière ponctuelle dans le quartier Notre-Dame et les quartiers avoisinants, pourraient avoir contribué à remodeler la distribution des métaux lourds dans les sols, comme le suggèrent les concentrations contrastées mesurées dans les arbres de parcelles voisines à celles ciblées par les interventions. Plus spécifiquement, l'enlèvement ou le remplacement partiel des horizons superficielles aurait pu réduire le pool de métaux présents dans certaines propriétés, atténuant ainsi la relation attendue entre proximité à la fonderie et concentration des métaux dans les arbres (Bilodeau et al., 2020; Gagné, 2007).

Nos résultats ont aussi montré que les concentrations de Cd dans les cernes de croissance étaient nettement plus élevées chez les arbres prélevés à Rouyn-Noranda que chez ceux d'Amos. Cette différence suggère une persistance plus marquée du Cd dans l'environnement urbain et industriel de Rouyn-Noranda, ce métal étant étroitement associé aux activités de fonderie (Hutton, 1983; Thornton, 1992). En revanche, les concentrations de Pb mesurées dans les deux villes étaient comparables malgré la centaine de kilomètres qui les sépare. Ce résultat indique que d'autres sources de pollution au Pb, notamment l'utilisation passée d'essence et peintures au plomb (Duzgoren-Aydin, 2007), ont pu contribuer aux concentrations observés à Amos, atténuant ainsi le contraste attendu entre un site industriel et un site considéré comme distant.

Sur le plan temporel, nos résultats ont montré une diminution marquée des concentrations en Cd dans les cernes des arbres au cours des trois dernières décennies, tendance cohérente avec les mesures réglementaires successives imposées à la fonderie visant à réduire ses émissions (MELCCFP, 2023). En revanche, les tendances pour le Pb demeurent plus ambigües : elles apparaissent globalement stables, voire légèrement croissantes selon les sites. Cette absence de décroissance suggère que le Pb constitue un contaminant particulièrement persistant dans l'environnement et dont la concentration est influencée par des sources multiples.

Pris ensemble, ces résultats démontrent que la dynamique spatio-temporelle des métaux lourds dans un contexte urbain industriel est complexe et n'est pas uniquement dictée par la proximité à la source d'émission comme pourraient l'être dans des forêts naturelles plus stables dans le temps. Ils soulignent l'importance de considérer l'historique industriel, les interventions variables de dépollution, la mobilité différenciée des éléments, ainsi que les autres sources de contamination pour comprendre la distribution du Pb et du Cd dans l'environnement. Au-delà du cas étudié, ces résultats suggèrent que les modèles simplifiés basés sur des gradients de distance pourraient être insuffisants pour caractériser la contamination dans les environnements urbains industrialisés. Ils soulignent ainsi la nécessité d'intégrer des approches multi-factorielles et historiques dans l'évaluation des risques environnementaux. En termes d'implications, cela pourrait affecter la manière dont les stratégies de suivi, de gestion et de restauration des sites contaminés sont conçues, notamment en mettant l'accent sur des diagnostics plus localisés et contextualisés.

Effets combinés de la pollution sur la croissance des plantes et le microbiome. D'un point de vue écotoxicologique, nos résultats en serre, reproduisant des niveaux de contamination proches de ceux observés à Rouyn-Noranda, ont montré que l'acidification limitait fortement la croissance des jeunes arbres, indépendamment de la présence de Pb. Cependant, la transférabilité de ces résultats au terrain reste limitée : la complexité des sols, les interactions microbiennes et la disponibilité en nutriments peuvent moduler la réponse des arbres. De plus, un biais de survivants peut survenir sur le terrain, seuls les individus les plus tolérants atteignant l'âge adulte, ce qui peut sous-estimer l'effet réel des conditions acides et polluées. En revanche, l'absence d'effet détectable du Pb sur la croissance des plants est plus surprenante. De nombreuses études ont démontré que lorsqu'il est présent à des concentrations suffisamment élevées, le Pb pouvait perturber la photosynthèse (Prasad et Strzałka, 1999), inhiber l'allongement cellulaire et réduire la biomasse végétale (John et al., 2012; Khan et al., 2015). Le fait que nous n'ayons pas détecté de réponse de la croissance dans les différents traitements de Pb, que ce soit seul ou en interaction avec le traitement acide, pourrait être lié à l'utilisation de concentrations proches de celles retrouvées en conditions naturelles mais non excessives, à la courte durée d'exposition des plantes à la pollution, ou encore à la tolérance de notre espèce modèle, l'épinette noire. L'acidité constitue donc le facteur de stress physiologique dominant, occultant potentiellement l'effet du Pb sur nos résultats de croissance de l'épinette noire.

Nos résultats montrent que l'acidification du sol a également profondément modifié le cycle de l'azote, dans le continuum sol-plante. L'acidification a entraîné une redistribution des formes minérales d'azote, se traduisant par une augmentation marquée des concentrations en NH_4^+ et une diminution des concentrations en NO_3^- dans les sols. Ce changement des formes de l'azote est cohérent avec ce que l'on sait des conditions acides, qui tendent à inhiber la nitrification et à favoriser l'accumulation d'ammonium. Parallèlement, les valeurs plus élevées de $\delta^{15}N$ mesurées dans le sol et plus faibles dans le xylème des plantules, indiquent une modification de la rapidité des processus biogéochimiques gouvernant le cycle de l'azote, possiblement liée à une réduction de la nitrification, à une dénitrification accrue ou à des pertes d'azote par lessivage. De manière cohérente, l'acidification s'est révélée être le principal déterminant de la structure et de la diversité des communautés microbiennes du sol. La diversité bactérienne est globalement réduite dans les sols acidifiés. En revanche, les champignons présentaient une réponse différente : leur diversité a augmenté en conditions acides, mais diminué en présence de Pb. Nos résultats montrent aussi que la structure des communautés bactériennes était fortement déterminée par l'acidification du sol, et a mis en évidence le rôle secondaire du Pb dans la réponse des bactéries. Nous avons mis en évidence la présence de taxons présentant une tolérance plus élevée aux stress chimiques, notamment adapté à des sols plus acides chez les bactéries : plusieurs groupes bactériens tels que *Bradyrhizobium*, bactéries impliquées dans le cycle de l'azote (VanInsberghe et al., 2015) ont vu leur abondance diminuer en conditions acides, tandis que d'autres, comme *Occallatibacter* et *Acidibacter*, (Kalam et al., 2020) sont devenues plus dominantes dans ce contexte.

D'autre part, la forte représentation dans les sols pollués au Pb de groupes fongiques connus pour leur résistance aux métaux ou leurs capacités de détoxification, comme *Thelephora* (Borovička et al., 2022), particulièrement abondant dans les traitements enrichis en Pb et presque absent ailleurs, pourrait expliquer les effets limités du plomb sur les plantules observés dans nos résultats. Elle pourrait également indiquer que la durée d'exposition de notre expérimentation était suffisante pour remarquer des effets sur le microbiome et pas suffisante pour remarquer des effets sur les végétaux. *Thelephora*, en tant que superaccumulateur de métaux, est susceptible de réduire la biodisponibilité du Pb en l'immobilisant dans ses structures fongiques, atténuant ainsi l'exposition réelle des communautés du sol et des racines. La présence dans tous les traitements des genres *Umbelopsis* (Janicki et al., 2018) et *Talaromyces* (X. Lu et al., 2024), résistant également aux métaux lourds pourrait aussi accentuer ces effets tampons des champignons du sol.

Dans l'ensemble, l'acidification du sol constitue le principal facteur structurant les communautés microbiennes, ce qui entraîne des répercussions directes sur les fonctions du sol, les processus biogéochimiques et, par ricochet, sur la croissance des plantes. Alors que le Pb a eu des effets limités sur les bactéries et presque aucun sur les champignons, la présence de taxons résistants ou capables d'accumuler et de détoxifier les métaux lourds ont probablement contribué à limiter les effets du Pb sur le sol et sur les plantes. Ainsi, la dynamique microbiome-sol-plante révèle que les interactions entre la chimie du sol et la structure microbienne sont essentielles pour comprendre la résilience des écosystèmes face à l'acidification et à la contamination métallique. Au-delà de ce système expérimental, ces résultats indiquent que les perturbations abiotiques majeures comme l'acidification peuvent dominer les effets des contaminants métalliques dans la structuration des microbiomes du sol. Ils soulignent également le rôle clé de la diversité fonctionnelle microbienne dans le maintien des fonctions écosystémiques en contexte de stress. Cela suggère que les stratégies de gestion et de restauration des sols contaminés pourraient prioriser la régulation du pH et la préservation (ou la restauration) des communautés microbiennes fonctionnelles, plutôt que de se concentrer uniquement sur la réduction des concentrations en métaux.

Limites. L'échantillonnage réalisé en milieu urbain, dans le premier travail de cette thèse (Chapitre II), présente certaines contraintes méthodologiques. Le nombre d'arbres disponibles était restreint, la diversité en termes d'espèces était plus élevée qu'en forêt, et les individus plus jeunes, donc rarement antérieurs au début des activités industrielles. Ces caractéristiques peuvent limiter la représentativité spatiale et temporelle des données dendrogéochimiques. De plus, le milieu urbain est marqué par une forte hétérogénéité environnementale : variations locales des sols, interventions anthropiques (ex. ajout de terre ou de paillis, travaux de construction ou de rénovation), et présence d'autres sources potentielles de pollution. Bien qu'il s'agisse d'un site éloigné du panache industriel de Rouyn-Noranda, la ville d'Amos choisie comme éloigné n'était peut-être pas un contrôle parfait, notamment en raison de la pollution urbaine et à d'autres sources locales. Un site témoin additionnel situé hors d'une zone urbaine aurait potentiellement offert un contraste plus net avec les sites exposés et permis d'affiner l'interprétation des patrons de contamination. Cependant, un tel choix aurait également introduit d'autres sources de biais difficiles à contrôler : les caractéristiques écologiques sont différentes entre un arbre isolé en milieu urbain et un peuplement forestier. Ainsi, déterminer quel témoin serait le plus approprié dans ce type d'étude demeure un compromis méthodologique, et le choix d'Amos, malgré ses limites, était cohérent avec les contraintes écologiques et logistiques du dispositif.

Les expérimentations de cette thèse, menées en conditions contrôlées, permettaient d'isoler l'effet de la pollution métallique et de l'acidification sur la croissance des semis et la dynamique du microbiome. Nous considérons que de telles études, bien que rares, permettent réellement d'établir des liens de cause à effet entre les processus en jeu. Cependant, les conditions en serre ne reflétaient pas toute la complexité des écosystèmes naturels. Les interactions biologiques, les variations microclimatiques, la compétition interspécifique, l'âge des plantes, la faune du sol ainsi que l'historique écologique d'un site ne pouvaient être reproduits intégralement en serre. Nous avons donc eu de la difficulté à transposer les résultats obtenus en serre aux observations faites en forêt en ce qui concernait les isotopes de l'azote dans le xylème. En outre, les tests réalisés sur de jeunes semis ne pouvaient complètement capturer les réponses à long terme observées chez des peuplements matures d'épinette noire, ce qui limitait la transposabilité directe des résultats au fonctionnement d'une forêt boréale adulte. En effet, nous avons observé que le $\delta^{15}N$ diminuait dans le xylème des plantules dans les traitements acides, alors qu'en forêt, aucun patron comparable n'a été détecté entre les variations de $\delta^{15}N$ des cernes de croissance et celles supposées du pH du sol. De plus, nous ne savions pas précisément comment le Pb se comportait dans les différents tissus des plantes. S'il était majoritairement retenu et complexé dans les racines, cela pourrait expliquer l'absence d'effet marqué sur la croissance aérienne, même en présence de concentrations élevées dans le sol. Dans ce scénario, le Pb pourrait rester piégé dans le système racinaire pendant une période prolongée et les effets physiologiques mesurables pourraient n'apparaître qu'au-delà de la durée de notre expérimentation. Des études en milieu naturel ont déjà montré qu'il y avait un délai d'environ 13-15 ans entre les émissions atmosphériques et les concentration que l'on retrouvait dans les cernes (Arteau et al., 2020; Aznar et al., 2008; Savard et al., 2006).

Implications. Un apport majeur de cette thèse réside dans l'analyse conjointe d'un milieu urbain fortement exposé à la pollution d'une fonderie de cuivre et d'un dispositif expérimental permettant de dissocier explicitement les effets du plomb de ceux du pH, offrant ainsi une compréhension plus fine des mécanismes écologiques sous-jacents. En combinant observations à long terme, analyses fines des tissus ligneux et approche expérimentale contrôlée, ce travail contribue à améliorer la compréhension des impacts écotoxicologiques chroniques en milieu boréal. Il offre une perspective intégrée permettant de mieux distinguer les effets du Pb et de l'acidification, un aspect rarement abordé conjointement dans la littérature, et apporte ainsi des éléments clés pour affiner les stratégies de biomonitoring dans les régions affectées par les émissions industrielles.

Le Chapitre II nous a montré que les différentes espèces d'arbres ne bioaccumulent pas les métaux lourds de la même manière dans leur bois et la concentration des métaux lourds dans les arbres urbains ne suit pas des gradients spatiaux facilement interprétables (dans le sens des vents et diminution avec l'éloignement). Ces résultats indiquent que les modèles traditionnels de déposition atmosphérique sont insuffisants pour prédire la contamination réelle dans les environnements urbains, notamment dans un rayon de 5 km autour d'une source de pollution. A l'intérieur de ce périmètre, des processus tels que la remobilisation des poussières, les travaux de terrain ou les apports de terre nouvelle modulent fortement la distribution des contaminants. La différence de bioaccumulation entre les différentes espèces complique l'interprétation des archives dendroécologiques et souligne la nécessité de combiner plusieurs métaux et d'utiliser seulement des espèces qui bioaccumulent fortement un certain métal pour reconstruire fidèlement l'historique de la pollution. De plus, nos résultats montrent qu'il n'y a ni décroissance nette du plomb dans les arbres urbains au cours du temps, ni différence marquée entre Rouyn-Noranda et Amos. Cela ne signifie pas que les arbres sont de mauvais indicateurs de pollution, ni que toute la région est uniformément saturée en plomb. Cela révèle plutôt que les arbres urbains enregistrent à la fois les retombées industrielles anciennes, la pollution résiduelle du sol, les poussières issues de rénovations et de peintures anciennes, ainsi que diverses perturbations propres aux milieux habités. Le plomb étant un contaminant très persistant, les stocks accumulés dans les sols urbains peuvent continuer d'être absorbés pendant des décennies, même si les émissions industrielles ont diminué. Ainsi, l'absence de gradient clair reflète une difficulté à isoler la contribution de la fonderie avec cette approche pour le plomb dans un environnement où de nombreuses sources s'additionnent et créent un bruit de fond important. La même approche appliquée au cadmium s'est révélée beaucoup plus facile à interpréter, l'effet spatial et temporel des émissions de la fonderie étant alors plus net.

Les résultats de l'expérience en serre avaient plusieurs implications importantes pour la compréhension des effets conjoints du plomb et de l'acidification. Dans les Chapitres III et IV, nos observations en serre montraient clairement que l'acidité est le facteur dominant : elle modifiait les formes d'azote dans le sol, réduisait les bactéries clés du cycle de l'azote et limitait la croissance des plantules, alors que le Pb n'avait d'effet détectable qu'au niveau de la composition microbienne fongique du sol. Cette absence d'effet du Pb sur la croissance des plantes suggère que les communautés microbiennes pourraient être tolérantes aux métaux, en particulier certains champignons observés en Chapitre IV, et pourraient agir comme tampon biologique, atténuant la toxicité du métal sur le temps de notre expérimentation. Autrement, l'épinette noire pourrait être particulièrement tolérant à la pollution au plomb. Cette observation soulève la question de la pertinence du Pb comme indicateur de stress environnemental, surtout comparé à d'autres métaux comme l'arsenic. Bien que l'arsenic soit un métal très toxique et dont le comportement environnemental est difficile à prédire, son utilisation comme indicateur serait problématique : il est très mobile, affecte différemment les plantes et le microbiome, et dans une approche dendrochronologique, il ne reflète pas de manière fiable les accumulations passées.

D'autre part, les analyses de $\delta^{15}N$ réalisées sur les cernes des arbres forestiers dans le Chapitre III ne reproduisaient pas des patrons comparables aux résultats observés en serre, ce qui indique que les réponses du cycle de l'azote en conditions naturelles sont façonnées par un ensemble de facteurs supplémentaires : hétérogénéité des sols, historique des dépôts, hydrologie, composition microbienne préexistante ou encore compétition entre espèces végétales. L'absence de similitudes entre serre et forêt souligne que les effets de l'acidité sur l'azote ne s'expriment pas de manière uniforme dans les écosystèmes et pourraient être masqués ou amplifiés par des processus de terrain plus complexes. Ces divergences entre milieux contrôlés et milieux naturels impliquent qu'il est nécessaire d'être prudent dans la transposition des résultats expérimentaux à l'écosystème réel. Elles rappellent surtout que la compréhension de la pollution ne peut pas reposer sur un seul compartiment : la chimie du sol, les communautés microbiennes et la physiologie des plantes interagissent étroitement, et leurs réponses peuvent diverger selon le contexte. Il est même probable que les résultats auraient différé si l'étude avait été réalisée dans un autre sol d'une autre partie de l'Abitibi, avec une composition préalable bactérienne et fongique différente au départ de l'expérimentation. En forêt, le microbiome n'est jamais uniforme : il varie fortement selon l'histoire locale, la nature du sol et les conditions environnementales, ce qui peut profondément modifier la manière dont les stress chimiques s'expriment dans les biocénoses.

Perspectives. Afin d'approfondir la compréhension des dynamiques spatio-temporelles de pollution et de leurs effets écosystémiques, plusieurs axes de recherche futurs peuvent être envisagés. Premièrement, l'intégration de bioindicateurs alternatifs, tels que les mousses, les lichens ou les espèces herbacées, constituerait un complément essentiel aux analyses dendrogéochimiques sur les arbres. Ces organismes, sensibles aux dépôts atmosphériques récents, contribueraient à améliorer l'évaluation de la pollution contemporaine et à valider les patrons observés dans les cernes des arbres (Balabanova et al., 2014). Cette approche multi proxy pourrait permettre de croiser les informations issues de différentes archives biologiques, offrant ainsi une vision plus complète et plus fine des dépôts atmosphériques récents et passés. Des études ont montré que différentes strates végétales pouvaient contenir des concentrations sensiblement différentes de métaux au sein d'un même écosystème (Gery et al., 2025).

Par ailleurs, l'évaluation des effets combinés du Pb et de l'acidification sur la physiologie des semis en conditions contrôlées pourrait être approfondie en quantifiant l'accumulation et la distribution des métaux dans les différents tissus de la plante (racines, tiges, branches, écorce, aiguilles). Cette approche permettrait de mieux comprendre les réponses physiologiques et biogéochimiques des jeunes arbres en conditions contrôlées, en mettant en évidence comment la croissance et l'assimilation des nutriments sont influencés par l'acidité et la présence de métaux. Elle permettrait également d'évaluer la capacité des arbres (notamment de l'épinette noire) à bioaccumuler et à compartimenter le Pb en comparant la quantité disponible dans le sol et celle retrouvé dans les tissus de la plante, offrant ainsi un aperçu précis de la séquestration potentielle des métaux mise en œuvre par les plantes face à une contamination métallique.

Une autre piste de recherche serait de transposer en milieu forestier les analyses de microbiome réalisées en serre dans le cadre de cette thèse, en procédant cette fois à des échantillonnages directement dans les sols forestiers. Ces analyses pourraient être couplées à une caractérisation complète des propriétés physicochimiques des sols, notamment les différentes formes d'azote et leurs rapports isotopiques, ainsi qu'aux mesures isotopiques effectuées dans les cernes de croissance. Une telle approche intégrée permettrait de comparer les réponses observées en conditions contrôlées avec celles mesurées en forêt boréale à proximité d'une source de pollution, afin d'évaluer la robustesse des patrons microbiens et biogéochimiques identifiés en serre et de mieux comprendre la dynamique des interactions sol-plante-microorganismes en contexte de pollution métallique.

ANNEXE A – MATÉRIEL SUPPLÉMENTAIRE DU CHAPITRE II

Table A1
Summary of descriptive statistics for tree species: age, DBH, and distance from the smelter.

Species	Age (year)				DBH (cm)				Distance (km)			
	Min	Max	Mean	Std	Min	Max	Mean	Std	Min	Max	Mean	Std
Cedar	18	37	25.7	10	15.8	21.5	19.1	2.51	0.406	2.89	1.84	1.05
Larch	14	35	25.8	9.03	15.5	28.2	232	4.96	1.11	4.53	2.4	1.46
Pine	9	48	24.9	9.7	15.1	53.2	34.5	10.1	0.601	3.43	1.92	0.872
Spruce	8	40	23.7	9.1	11.6	58.8	32.9	12	0.308	3.6	2.10	0.863

Table A2
Summary of descriptive statistics for properties of tree candidates for isotopic analyses

Site	Age	DBH	Distance
West	25	41.4	2.18
North	36	33	3.6
Osisko Lake	12	33.8	1.1
South 1	23	30.4	2.36
South 2	34	31.9	2.05

Table A3
Comparative outcomes of linear regression models assessing lead (Pb) and cadmium (Cd) concentration in the tree rings over the years 2018-2022. "Species" represents the four species studied, "Distance" is the distance from the smelter, "Aspect" is the winds passing over the smelter. "K" is the degree of freedom, "AICc" is the Corrected Akaike Information Criterion, "Delta_AICc" is the deviation in AICc relative to the best-performing model, "AICcWt" is the AICc weight, while "Cum.Wt" is the cumulative AICc weight. "LL" represents the Log-Likelihood of the model. The "Adjusted R-Square" column represents the proportion of variance in metal concentration explained by the model, adjusted for the number of predictors.

Metal	Model	K	AICc	Delta_AICc	AICcWt	Cum.Wt	LL	Adjusted R-square
Pb	Species	3	52.74	0.00	0.57	0.57	-23.07	0.33
	Species + Aspect	4	55.04	2.30	0.18	0.75	-23.01	0.31
	Species + Distance	4	55.06	2.32	0.18	0.93	-23.02	0.31
	Full no interaction	5	57.54	4.80	0.05	0.98	-22.98	0.30
	Full with interaction	6	59.29	6.55	0.02	1.00	-22.51	0.29
	Null	2	68.86	16.11	0.00	1.00	-32.28	0.00
	Distance	3	70.71	17.96	0.00	1.00	-32.05	-0.01
	Aspect	3	70.80	18.06	0.00	1.00	-32.10	-0.02

Metal	Model	K	AICc	Delta_AICc	AICcWt	Cum.Wt	LL	Adjusted R-square
	Aspect + Distance	4	72.42	19.68	0.00	1.00	-31.70	-0.02
Cd	Species	3	36.64	0.00	0.51	0.51	-15.02	0.55
	Species + Distance	4	38.06	1.42	0.25	0.76	-14.52	0.55
	Species + Aspect	4	39.05	2.42	0.15	0.91	-15.01	0.54
	Full no interaction	5	40.55	3.91	0.07	0.98	-14.48	0.54
	Full with interaction	6	43.22	6.59	0.02	1.00	-14.48	0.52
	Null	2	70.09	33.45	0.00	1.00	-32.90	0.00
	Distance	3	70.97	34.33	0.00	1.00	-32.18	0.01
	Aspect + Distance	4	71.08	34.45	0.00	1.00	-31.03	0.04
	Aspect	3	71.23	34.59	0.00	1.00	-32.31	0.00

Table A4
The estimated coefficients for all linear models analyzing the relationship between metal concentrations and various environmental variables. The "Metal" column indicates the specific metal being studied, lead (Pb) or cadmium (Cd), for which each model is fitted. The "Intercept" represents the predicted value of the metal concentration when all other variables are set to zero. "Aspect" is the effect of orientation to prevailing winds on metal concentration, while "Distance" represents the effect of distance from a pollution source. "SpeciesLarch," "SpeciesPine," and "SpeciesSpruce" show the impact of different tree species on metal concentration. "Aspect:Distance" indicates the interaction term. Significance is indicated into parentheses (* p < 0.001; ** p < 0.01, * p < 0.05).**

Metal	Model	Intercept	Aspect	Distance	SpeciesPine	Aspect:Distance
Pb	Null	-1.08 (***)	NA	NA	NA	NA
	Aspect	-1.02 (***)	-0.10	NA	NA	NA
	Distance	-1.20 (***)	NA	0.06	NA	NA
	Species	-0.77 (***)	NA	NA	-0.59 (***)	NA
	Aspect + Distance	-1.17 (***)	-0.14	0.08	NA	NA
	Species + Aspect	-0.80 (***)	0.05	NA	-0.60 (***)	NA
	Species + Distance	-0.82 (***)	NA	0.02	-0.59 (***)	NA
	Full no interaction	-0.83 (***)	0.04	0.02	-0.60 (***)	NA
	Full with interaction	-1.04 (**)	0.40	0.13	-0.63 (***)	-0.16
Cd	Null	-0.74 (***)	NA	NA	NA	NA
	Aspect	-0.85 (***)	0.18	NA	NA	NA
	Distance	-0.53 (*)	NA	-0.11	NA	NA

	Species	-1.14 (***)	NA	NA	0.76 (***)	NA
	Aspect + Distance	-0.60 (**)	0.26	-0.15	NA	NA
	Species + Aspect	-1.14 (***)	-0.01	NA	0.77 (***)	NA
	Species + Distance	-1.02 (***)	NA	-0.06	0.75 (***)	NA
	Full no interaction	-1.02 (***)	0.03	-0.07	0.75 (***)	NA
	Full with interaction	-1.04 (***)	0.07	-0.05	0.74 (***)	-0.02

Table A5
Pb and Cd concentration between Rouyn-Noranda and distant samples in Amos, by species. The columns present mean concentration values (mg/kg) and the ratio of mean concentrations in Rouyn-Noranda to those in the distant samples with significant values assessed using the Wilcoxon test (* indicates significant results p<0.05). No comparisons are made between different species.

	Species	Amos	RN	Ratio	Stats
Cd	Pine	0.0766	0.508	**6.64**	0.0001425*
	Spruce	0.027	0.107	**3.95**	0.01602*
Pb	Pine	0.0257	0.0690	2.68	0.09277
	Spruce	0.163	0.308	1.89	0.3976

Table A6
Summary of descriptive statistics for metal concentration in tree species.

Species	**Cd (mg/km)**				**Pb (mg/kg)**			
	Min	Max	Mean	Std	Min	Max	Mean	Std
Cedar	0.5	0.592	0.543	0.041	0.23	0.91	0.570	0.391
Larch	0.219	1.03	0.499	0.321	0.012	2.29	0.588	0.971
Pine	0.074	1.24	0.508	0.288	0.012	0.36	0.069	0.081
Spruce	0.01	0.516	0.107	0.116	0.03	2.44	0.308	0.521

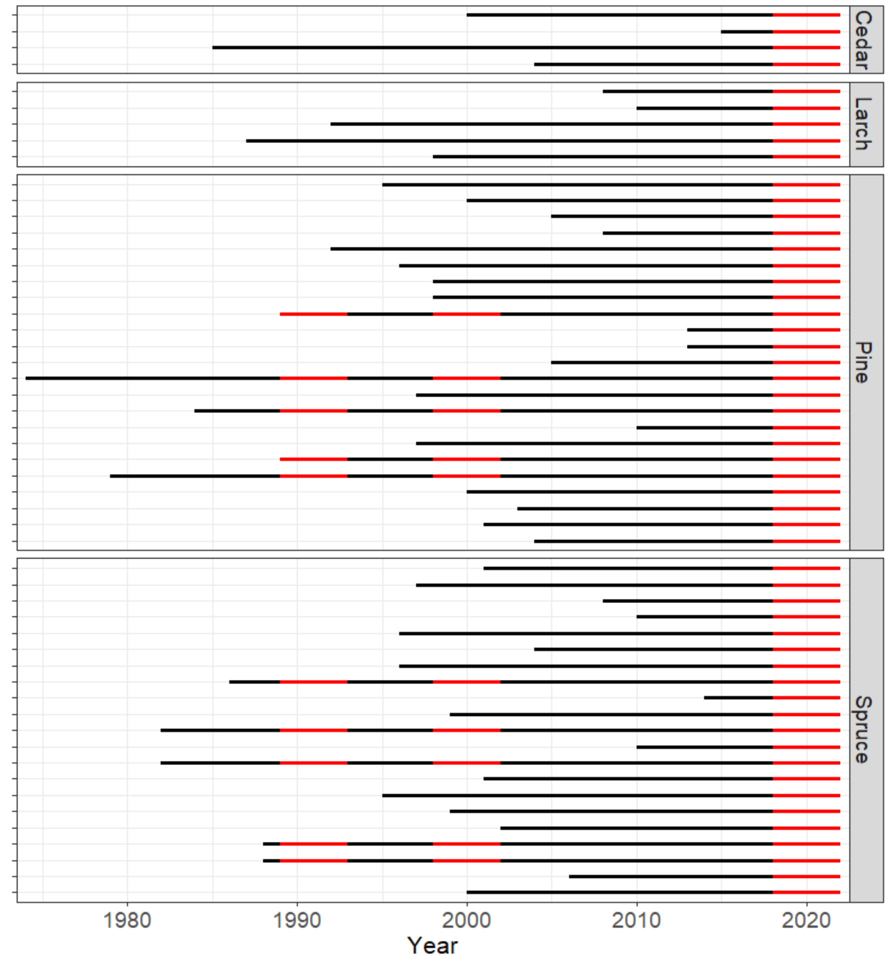


Figure A1
Graphical representation of sampled periods from tree cores collected in Rouyn-Noranda. Each black band represents the total measured tree-ring for a sample. The red bands indicate the specific period that was analyzed. The segments are organized by species.

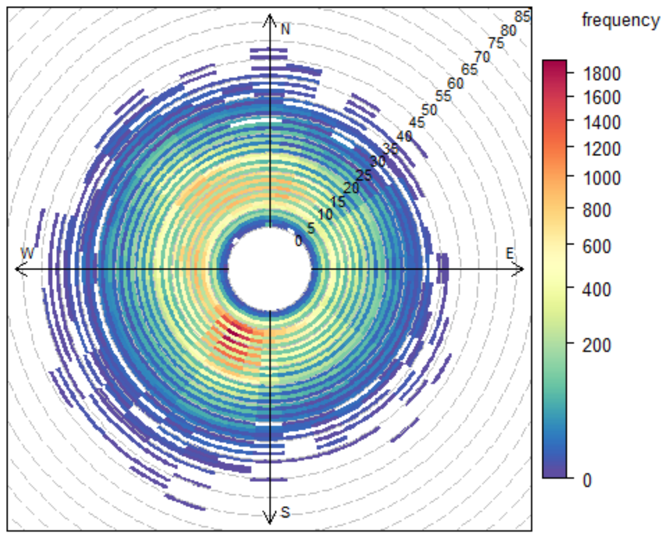


Figure A2
Wind speed-direction frequencies in ‘bins’ according to the data from the Rouyn station (Environment Canada, 2023) Wind direction was measured in tens of degrees and represents the direction from which the wind is blowing.

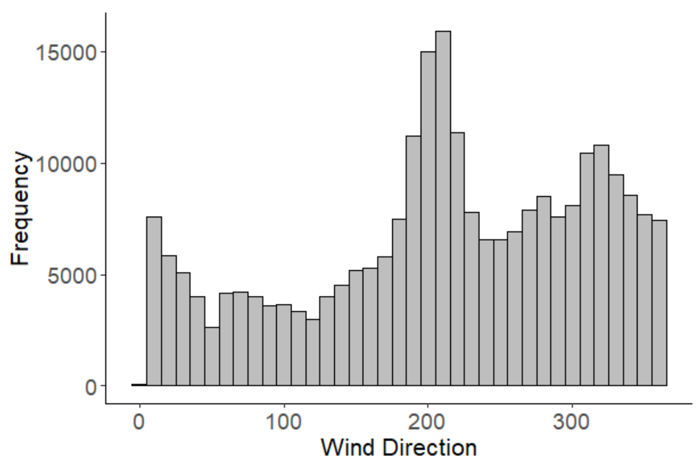


Figure A3
Frequency of wind direction according to the data from the Rouyn station (Environment Canada, 2023)**.**

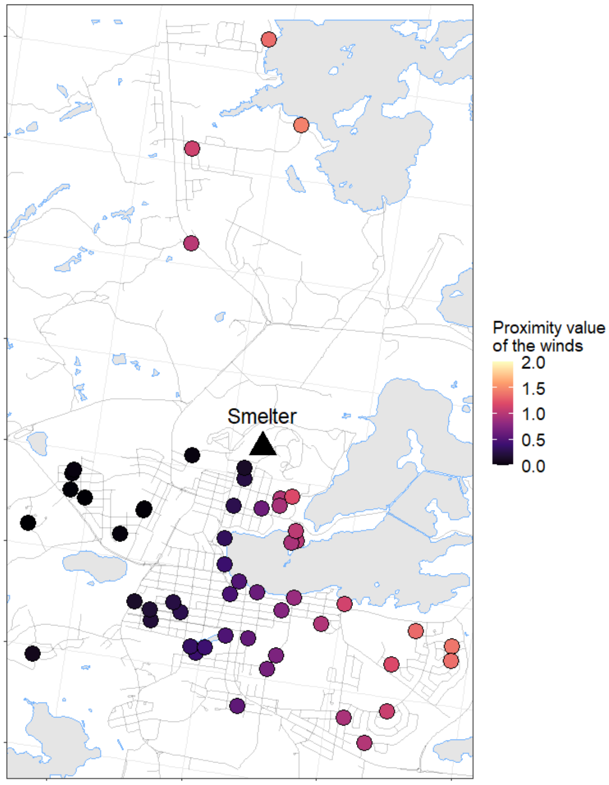


Figure A4
Downwind trees relative to the smelter encoded as an index from 0 to 2 (Beers et al., 1966)**. The smelter is marked by a black triangle. Streets and lakes are displayed as background features to provide geographical context.**

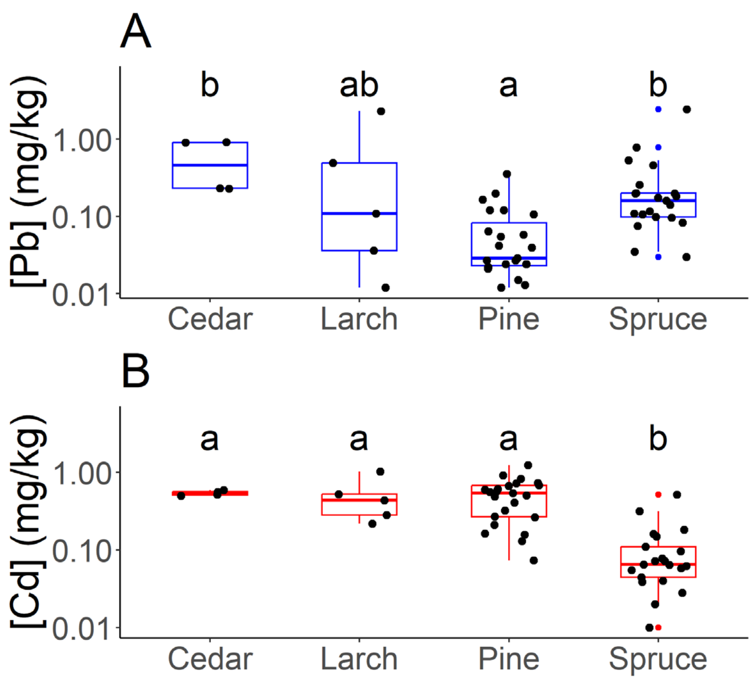


Figure A5
Concentration of (A) lead and (B) cadmium by species in Rouyn-Noranda samples. Boxes represent the interquartile range (Q1 to Q3), horizontal middle line are the median, and bars extend to the most distant data points that are not considered as outliers (values exceeding 1.5 times the interquartile range from the quartiles). Y-axes are all mg/kg but use a log10 scale. Letters show the results of Dunn's post-hoc test to identify which species exhibited significant differences in their medians (Table A6). Boxes sharing the same letters are not significantly different from each other.

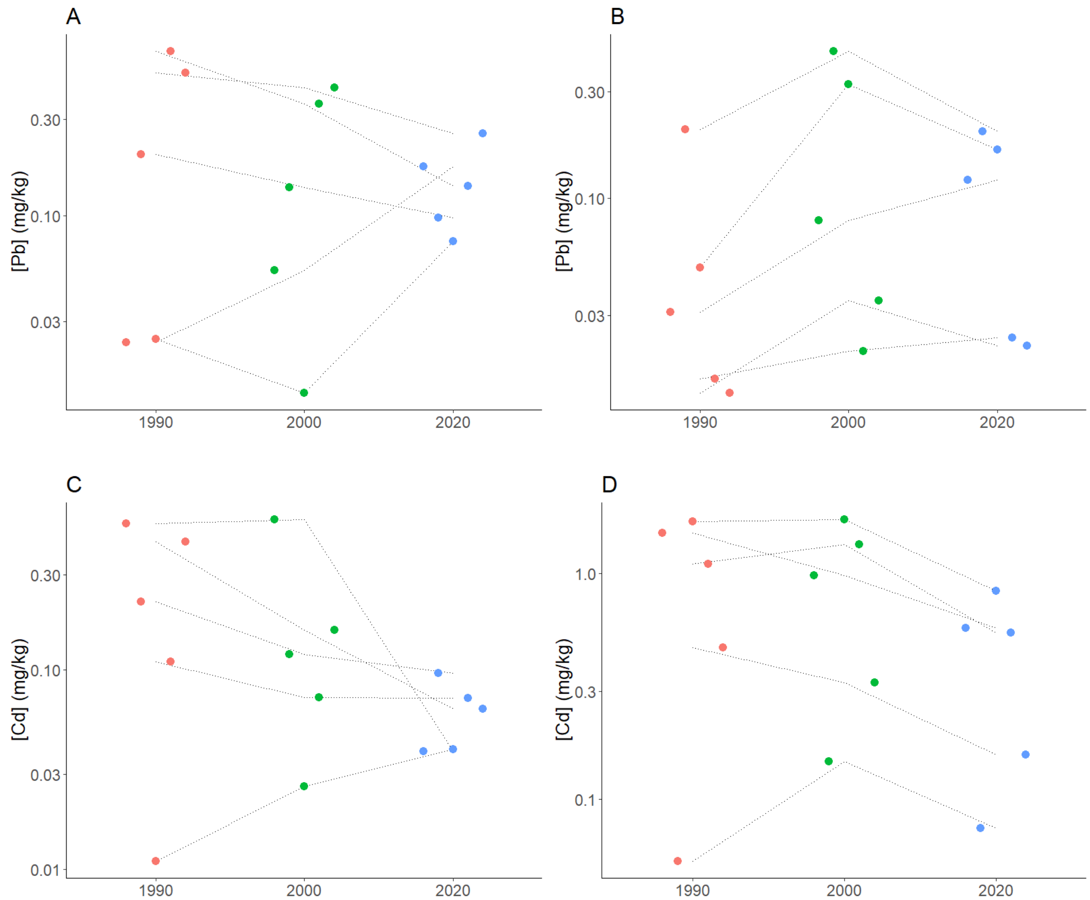


Figure A6
Pb concentrations for (A) spruce and (B) pine, and Cd concentrations for (C) spruce and (D) pine across different periods in Rouyn-Noranda sample. Dotted lines connecting the points indicate repeated measurements from the same individual.

ANNEXE B – PRATIQUES DE GESTION DES SOLS DES COURS PRIVEES / SOIL MANAGEMENT PRACTICES OF PRIVATE YARDS (CHAPITRE II)

Method: Owner survey

Data on land management practices were collected through a Yes/No survey distributed to residents whose properties had been sampled, with 22 responses obtained out of 32 surveys distributed. The survey gathered information on various practices, including soil decontamination, soil disturbance, the presence of paint flakes on walls, recent renovations, pesticide use, and the use of treated wood.

Statistics

The Wilcoxon rank-sum test was used to compare the "Yes" and "No" groups for each following variable: soil decontamination, soil restoration, presence of paint flakes on walls, pesticide use, and use of treated wood. Each variable was analyzed individually to identify significant influences on metal concentrations, providing insights into how specific practices may affect environmental contamination.

Results: Distinction between public and private trees/non environmental data

After the survey, none of the variables influence the concentrations of Pb and Cd in tree rings (p-value < 0.05).

Table B1
Summary of resident survey results on soil management practices in Rouyn-Noranda. The survey was sent to 32 individuals, from which 23 responses were received. Participants were asked yes/no questions regarding any renovation work, decontamination efforts, and maintenance practices, including the use of pesticides, and the use of treated wood.

Sources and mitigation of emissions	Number of "Yes" response
Soil restructuration around the tree	7
Peeling or flaking of painting in proximity of the tree	6
Major renovation work of the house	2
Use of pesticides in the garden	1
Treated wood in proximity of the tree	1
Soil decontamination	0

ANNEXE C – MATÉRIEL SUPPLÉMENTAIRE DU CHAPITRE III

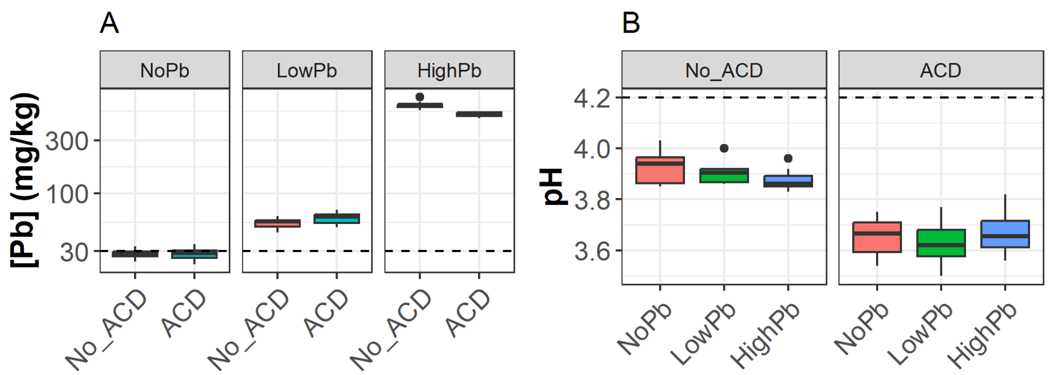


Figure C1
Distribution of (A) soil pH and (B) Pb concentrations by treatment. Y-axes of (A) and (B) are mg/kg but use a log10 scale. Initial soil pH (4.2) and Pb concentrations (30 ppm) prior to treatment are indicated as dashed lines. Boxplots show the interquartile range (Q1-Q3) with the median indicated by the central line. Whiskers extend to 1.5 x IQR, and points represent outliers.

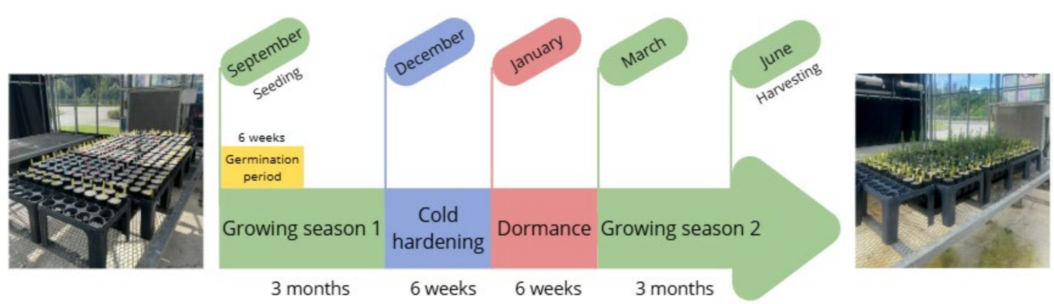


Figure C2
Diagram of growth periods for the greenhouse experiment

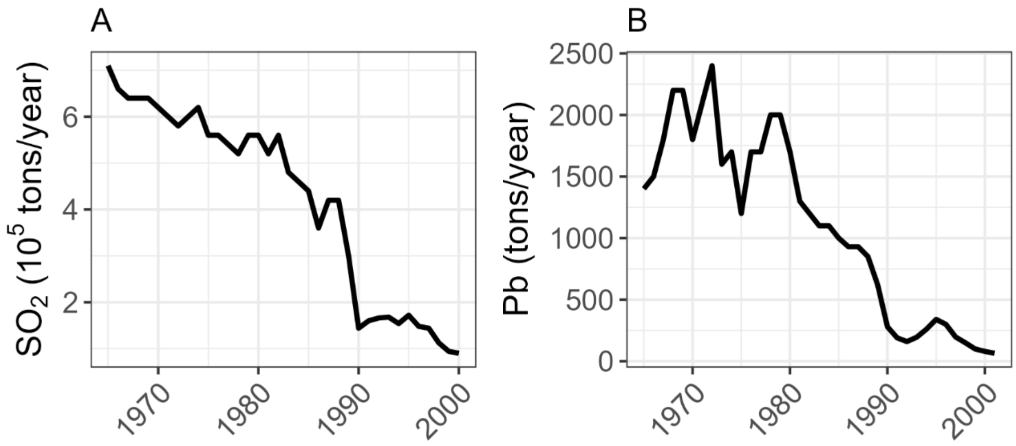


Figure C3
Data on atmospheric emissions processed by the Horne Smelter per year from 1965 to 2001 for (A) SO_2 and (B) Pb emissions. The data originate from the GSC MITE Point Sources Project of the Geological Survey of Canada (Bonham-Carter, 2005).

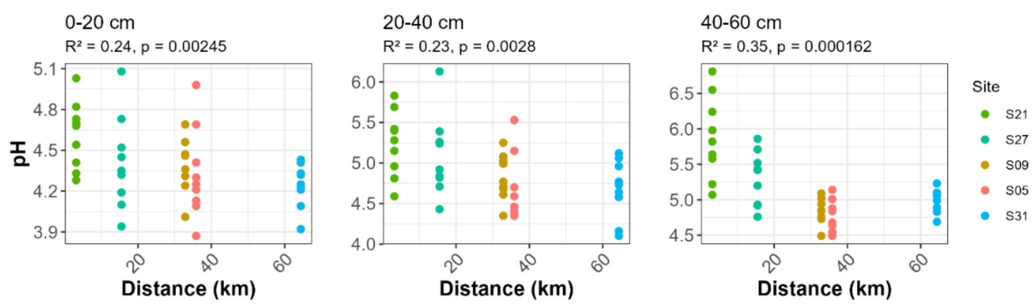


Figure C4
Soil pH as a linear function of distance from the smelter across the 5 nearest forest sites, fitted with a linear mixed-effects model (lmer) including site as a random intercept. Reported p-values were obtained using the lmerTest package. Distant sites (T1 and T2) were excluded from the plot. Note the substantial intra-site variability and overlap between samples. S27, located upwind of the smelter, was excluded from the linear regression analysis.

Table C1
Lead concentration and pH at the end of controlled experiment.

Treatment	Mean [Pb] ± SD* (ppm)	Mean pH ± SD
Control	30.1 ± 5.7	3.93 ± 0.06
LowPb only	50.1 ± 12.8	3.88 ± 0.09
HighPb only	613.0 ± 68.6	3.85 ± 0.09
ACD only	30.5 ± 6.2	3.68 ± 0.11
LowPb_ACD	59.8 ± 7.5	3.63 ± 0.09
HighPb_ACD	526.0 ± 31.5	3.69 ± 0.1

*SD is standard deviation

Table C2
Soil properties at the end of the second growing season, mean ± standard deviation

Treatment	NH4-N (ppm)	NO3-N (ppm)	$\delta^{13}C$ (‰)	C (%)	N (%)	$\delta\ ^{15}N$ (‰)
Control	35.31 ± 25.97	11.66 ± 10.75	-28.5 ± 0.47	14.4 ± 1.5	0.46 ± 0.058	-0.539 ± 0.325
LowPb	31.63 ± 30.63	16.91 ± 18.33	-28.46 ± 0.73	14.25 ± 1.22	0.459 ± 0.057	-0.26 ± 0.434
HighPb	18.13 ± 14.19	6.98 ± 5.28	-28.32 ± 0.59	14.1 ± 1.34	0.462 ± 0.045	-0.242 ± 0.349
Acid	49.25 ± 36.1	0.61 ± 0.47	-27.84 ± 0.67	14.94 ± 2.1	0.504 ± 0.075	0.003 ± 0.282
Acid + LowPb	51.38 ± 35.11	0.37 ± 0.31	-28.12 ± 0.83	13.82 ± 1.44	0.434 ± 0.051	-0.242 ± 0.418
Acid + HighPb	45.39 ± 37.91	0.62 ± 0.99	-28.61 ± 0.65	13.41 ± 0.73	0.427 ± 0.042	-0.019 ± 0.268

Table C3
Properties of the 5 sampled trees per site for tree-ring isotopic analyses.

Site	Distance (km)	DBH* (cm ± SD**)	Age (years ± SD)	Density (n ± SD)
S21	3.15	12.60 ± 1.42	52.86 ± 13.68	6.0 ± 2.12
S27	15.50	18.82 ± 1.48	79.80 ± 8.23	9.8 ± 3.63
S31	64.41	21.30 ± 1.78	76.89 ± 11.46	4.0 ± 1.87
S09	32.88	23.60 ± 1.48	90.88 ± 5.96	5.0 ± 1.87
S05	35.87	24.38 ± 2.08	84.08 ± 3.50	8.4 ± 3.36
T2	175.22	22.92 ± 1.72	122.18 ± 39.50	10.0 ± 2.92
T1	195.25	24.12 ± 1.98	86.65 ± 3.03	10.2 ± 2.49

Distance is the distance from the Horne smelter.
*DBH is the average diameter at breast height of the five sampled trees (cm).
Age corresponds to the mean number of tree-rings at breast height including pith offset.
Density is the mean number of trees with DBH greater than 9 cm within a 4 m radius from the sampled trees.
**SD is standard deviation

Table C4
Comparison of soil properties using different linear models, based on AIC values, to evaluate the effects of Acid and Lead as explanatory variables. "K" is the degree of freedom, "AICc" is the Corrected Akaike Information Criterion, "Delta_AICc" is the deviation in AICc relative to the best-performing model, "AICcWt" is the AICc weight, while "Cum.Wt" is the cumulative AICc weight. "LL" represents the Log-Likelihood of the model.

Parameter	Model	K	AICc	Delta_AICc	AICcWt	LL	Cum.Wt
(1) NO_3	Acid	3	93.77	0.00	0.86	-43.67	0.86
	Full no interaction	5	97.88	4.11	0.11	-43.39	0.97
	Full with interaction	7	100.73	6.96	0.03	-42.29	1.00
	Null	2	150.73	56.97	0.00	-73.26	1.00
	Lead	4	155.04	61.27	0.00	-73.16	1.00
(2) NH_4	Acid	3	60.58	0.00	0.62	-27.07	0.62
	Full no interaction	5	62.70	2.12	0.21	-25.79	0.83
	Null	2	64.15	3.57	0.10	-29.97	0.93
	Lead	4	66.34	5.77	0.03	-28.81	0.97
	Full with interaction	7	66.43	5.85	0.03	-25.14	1.00
(3) $\delta^{15}N$ in soil	Acid	3	52.70	0.00	0.59	-23.13	0.59
	Full with interaction	7	54.63	1.94	0.22	-19.24	0.81
	Full no interaction	5	55.56	2.87	0.14	-22.23	0.95
	Null	2	58.03	5.33	0.04	-26.91	0.99
	Lead	4	60.95	8.25	0.01	-26.11	1.00

Table C5
Estimated coefficients for soil parameters, using linear models. Only the best models selected based on AIC (see Table C4) are shown. The "Intercept" represents the predicted value of each growth parameter when all other variables are set to zero. Significant coefficients are indicated in bold.

Parameter	Variable	Estimate	Std. Error	t value	Pr(>|t|)
(1) NO_3	(Intercept)	0.80925	0.09304	8.698	**4.19e-12**
	AcidACD	-1.29941	0.13157	-9.876	**4.92e-14**
(2) NH_4	(Intercept)	1.30090	0.07056	18.438	**<2e-16**
	AcidACD	0.24190	0.09978	2.424	**0.0185**
(3) $\delta^{15}N$ in soil	(Intercept)	-0.34677	0.06607	-5.248	**2.27e-6**
	AcidACD	0.26063	0.09344	2.789	**0.00713**

Table C6
Germination by calculating the total number of seeds germinated in all the pots, divided by 30, corresponding to the total number of seeds for each treatment (3 seed for each 10 replicates). Germination per pot ranges from 0 to 3. Total germination ranges from 0 to 30.

Treatment	Total of germination	Germination (%)
Control	23	76.7
LowPb only	20	66.7
HighPb only	25	83.3
ACD only	12	40.0
LowPb_ACD	15	50.0
HighPb_ACD	10	33.3

Table C7
Model ranks based on AIC values for growth parameters using different statistical models (Binomial generalized linear model: 1, linear regression: 2-5, Poisson generalized linear model: 6). The models evaluate the effects of Acid and Lead as explanatory variables. "K" is the degree of freedom, "AICc" is the Corrected Akaike Information Criterion, "Delta_AICc" is the deviation in AICc relative to the best-performing model, "AICcWt" is the AICc weight, while "Cum.Wt" is the cumulative AICc weight. "LL" represents the Log-Likelihood of the model.

Parameter	Model	K	AICc	Delta_AICc	AICcWt	LL	Cum.Wt
(1) Germination	Acid	2	127.35	0.00	0.85	-61.57	0.85
	Full no interaction	4	131.87	4.52	0.09	-61.57	0.94
	Full with interaction	6	132.69	5.34	0.06	-59.55	1.00
	Null	1	147.70	20.35	0.00	-77.82	1.00
	Lead	3	152.06	24.71	0.00	-77.82	1.00
(2) Height GS1	Acid	3	217.83	0.00	0.87	-105.70	0.87
	Full no interaction	5	221.84	4.01	0.12	-105.36	0.98
	Full with interaction	7	225.54	7.71	0.02	-104.69	1.00
	Null	2	245.07	27.24	0.00	-120.43	1.00
	Lead	4	249.17	31.35	0.00	-120.22	1.00
(3) Height GS2	Full no interaction	5	338.44	0.00	0.50	-163.66	0.50
	Acid	3	339.22	0.78	0.34	-166.40	0.84
	Full with interaction	7	342.52	4.08	0.07	-163.18	0.91
	Lead	4	343.03	4.59	0.05	-167.15	0.96
	Null	2	343.41	4.97	0.04	-169.60	1.00

(4) Collar diameter	Full no interaction	5	83.64	0.00	0.66	-36.26	0.66
	Acid	3	86.36	2.73	0.17	-39.97	0.83
	Full with interaction	7	86.59	2.95	0.15	-35.22	0.99
	Lead	4	92.19	8.55	0.01	-41.73	1.00
	Null	2	93.91	10.27	0.00	-44.85	1.00
(5) Xylem dry mass	Acid	3	-217.08	0.00	0.76	111.76	0.76
	Full no interaction	5	-214.41	2.67	0.20	112.76	0.96
	Full with interaction	7	-211.17	5.91	0.04	113.66	1.00
	Null	2	-204.77	12.31	0.00	104.49	1.00
	Lead	4	-201.83	15.26	0.00	105.28	1.00
(6) Number of branches	Acid	2	291.49	0.00	0.83	-143.64	0.83
	Full no interaction	4	294.88	3.39	0.15	-143.08	0.98
	Full with interaction	6	299.24	7.75	0.02	-142.83	1.00
	Null	1	306.52	15.02	0.00	-152.22	1.00
	Lead	3	309.75	18.25	0.00	-151.66	1.00

Table C8
Estimated coefficients for plant growth parameters, using different statistical models (Binomial generalized linear model: 1, linear regression: 2-5, Poisson generalized linear model: 6). Only the best models selected based on AIC (see Table C7) are shown. The "Intercept" represents the predicted value of each growth parameter when all other variables are set to zero. Significant coefficients are indicated in bold.

Parameter	Variable	Estimate	Std. Error	t value	Pr(>|t|)
(1) Germination	(Intercept)	1.1285	0.2453	4.601	**4.21e-06**
	AcidACD	-1.4878	0.3257	-4.569	**4.91e-06**
(2) Height GS1	(Intercept)	0.82657	0.02129	38.824	**< 2e-16**
	AcidACD	-0.18573	0.03011	-6.169	**7.17e-08**
(3) Height GS2	(Intercept)	1.04400	0.03390	30.799	**< 2e-16**
	AcidACD	-0.11004	0.03390	-3.246	**0.00198**
	LeadLowPb	0.05655	0.04152	1.362	0.17858
	LeadHighPb	0.08802	0.04152	2.120	**0.03843**
(4) Collar diameter	(Intercept)	3.2325	0.1184	27.312	**< 2e-16**
	AcidACD	-0.3960	0.1184	-3.346	**0.00147**
	LeadLowPb	0.2560	0.1450	1.766	0.08283
	LeadHighPb	-0.1305	0.1450	-0.900	0.37183
(5) Xylem dry mass	(Intercept)	0.124667	0.006977	17.869	**< 2e-19**
	AcidACD	-0.039333	0.009867	-3.98	**0.0001**
(6) Number of branches	(Intercept)	2.20092	0.06075	36.232	**< 2e-16**
	AcidACD	-0.39263	0.09568	-4.104	**4.07e-05**

Table C9

Comparison of the effects of Acid and Lead on $\delta^{15}N$ in xylem tissues using Linear Models. "K" is the degree of freedom, "AICc" is the Corrected Akaike Information Criterion, "Delta_AICc" is the deviation in AICc relative to the best-performing model, "AICcWt" is the AICc weight, while "Cum.Wt" is the cumulative AICc weight. "LL" represents the Log-Likelihood of the model.

Model	K	AICc	Delta_AICc	AICcWt	LL	Cum.Wt
Acid	3	163.37	0.00	0.81	-78.47	0.81
Full no interaction	5	166.66	3.30	0.16	-77.78	0.97
Full with interaction	7	169.89	6.52	0.03	-76.87	1.00
Null	2	196.51	33.14	0.00	-96.15	1.00
Lead	4	200.26	36.89	0.00	-95.76	1.00

Table C10

Estimated coefficients for $\delta^{15}N$ in xylem tissues using Linear Models. Only the best model selected based on AIC (see Table C9) are shown. The "Intercept" represents the predicted value of each growth parameter when all other variables are set to zero. Significant coefficients are indicated in bold.

Parameter	Variable	Estimate	Std. Error	t value	Pr(>|t|)
$\delta^{15}N$ in xylem	(Intercept)	1.0151	0.1662	6.109	**9.02e-8**
	AcidACD	- 1.6034	0.2350	- 6.823	**5.80e-9**

Table C11

Correlation matrix of soil pH measured at three depths (0–20, 20–40, and 40–60 cm). Correlation coefficients were calculated using Pearson's product-moment correlation. Significance levels are indicated by asterisks (* = p < 0.001).**

	0-20	20-40	40-60
0-20	1,00	---	---
20-40	0,71 ***	1,00	---
40-60	0,60 ***	0,71 ***	1,00

Table C12
Mean and standard deviation (SD) of soil pH (0-20 cm depth) for each forest site, ordered by increasing distance. Nine soil samples were analyzed per site.

Site	Distance (km)	Mean pH ± SD*
S21	3.15	4.61 ± 0.24
S27	15.50	4.41 ± 0.34
S09	32.88	4.42 ± 0.22
S05	35.87	4.33 ± 0.33
S31	64.41	4.24 ± 0.16
T2	175.22	4.71 ± 0.52
T1	195.25	4.61 ± 0.49

*SD is standard deviation

Table C13
Fixed-effect estimates from the linear mixed-effects model of $\delta^{15}N$ as a function of soil pH and distance from the smelter with random intercepts for site. Columns show the estimate, standard error, t-value, and p-value for each predictor.

	Estimates	Std Error	t value	Pr(>|t|)
(Intercept)	-16.894	16.17	-1.045	0.302
Distance	0.001	0.02	0.713	0.640
pH	2.523	3.54	0.713	0.480

ANNEXE D – MARERIEL SUPPLÉMENTAIRE DU CHAPITRE IV

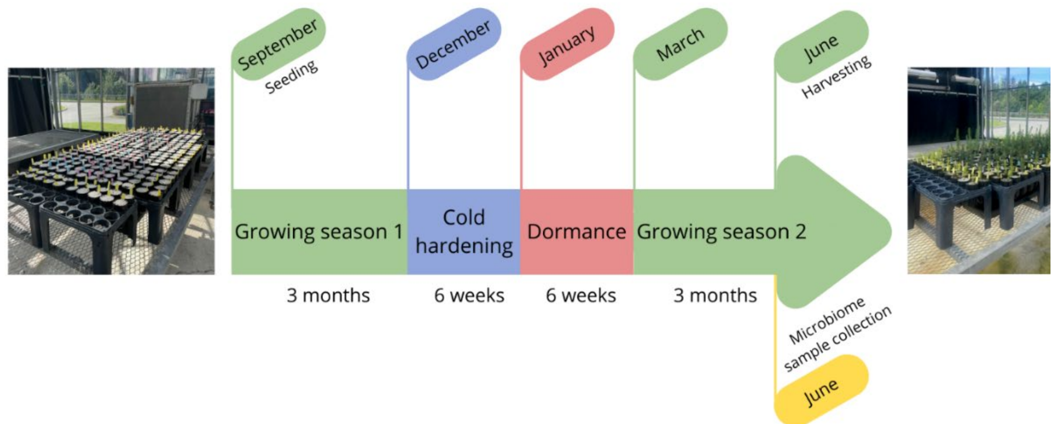


Figure D1
Diagram of growth periods for the greenhouse experiment

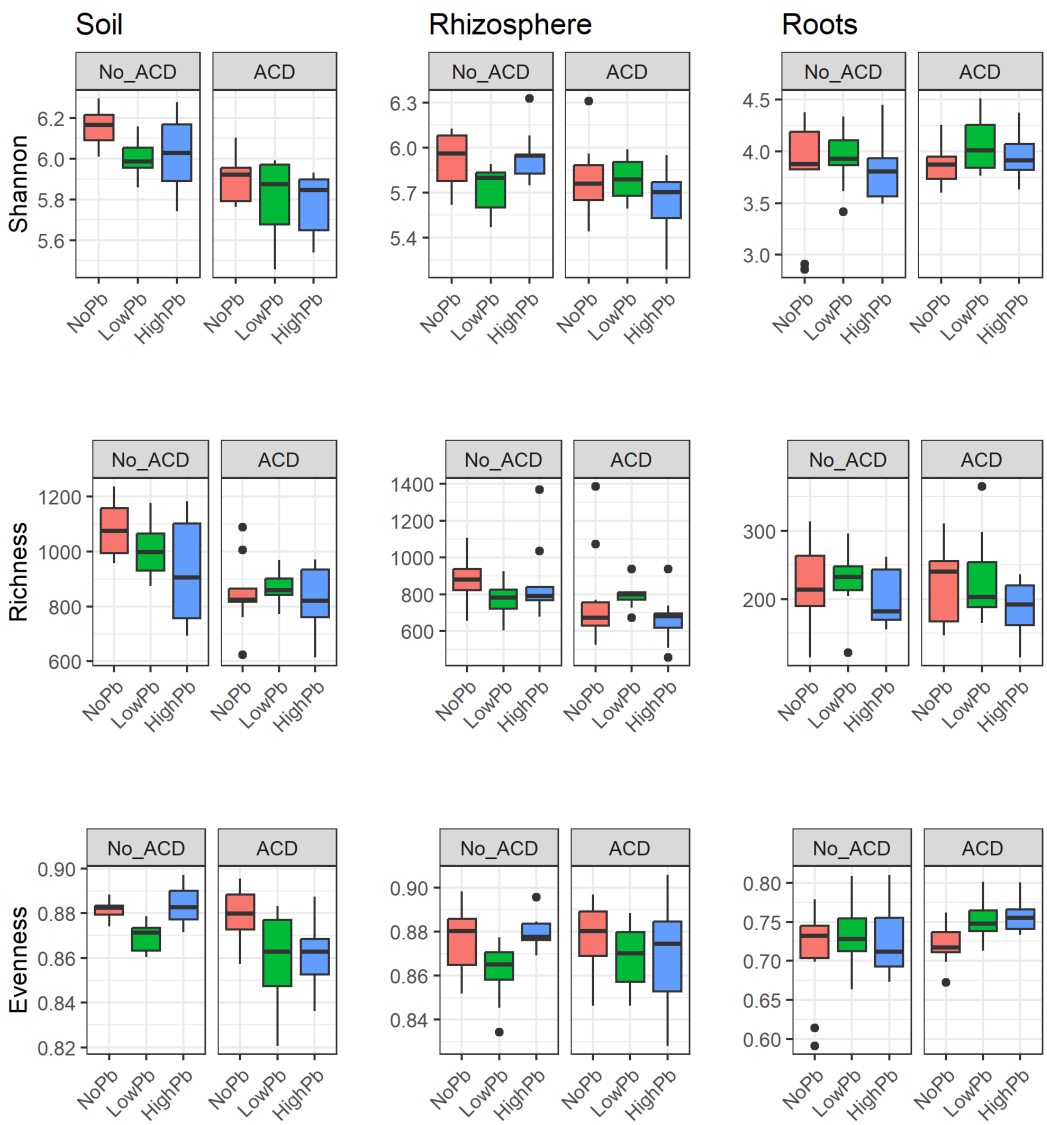


Figure D2
Alpha diversity indices (Shannon, Richness and Evenness) for bacterial communities in soil, rhizosphere, and roots. Boxplots show the interquartile range (Q1-Q3) with the median indicated by the central line. Whiskers extend to 1.5 x IQR, and points represent outliers.

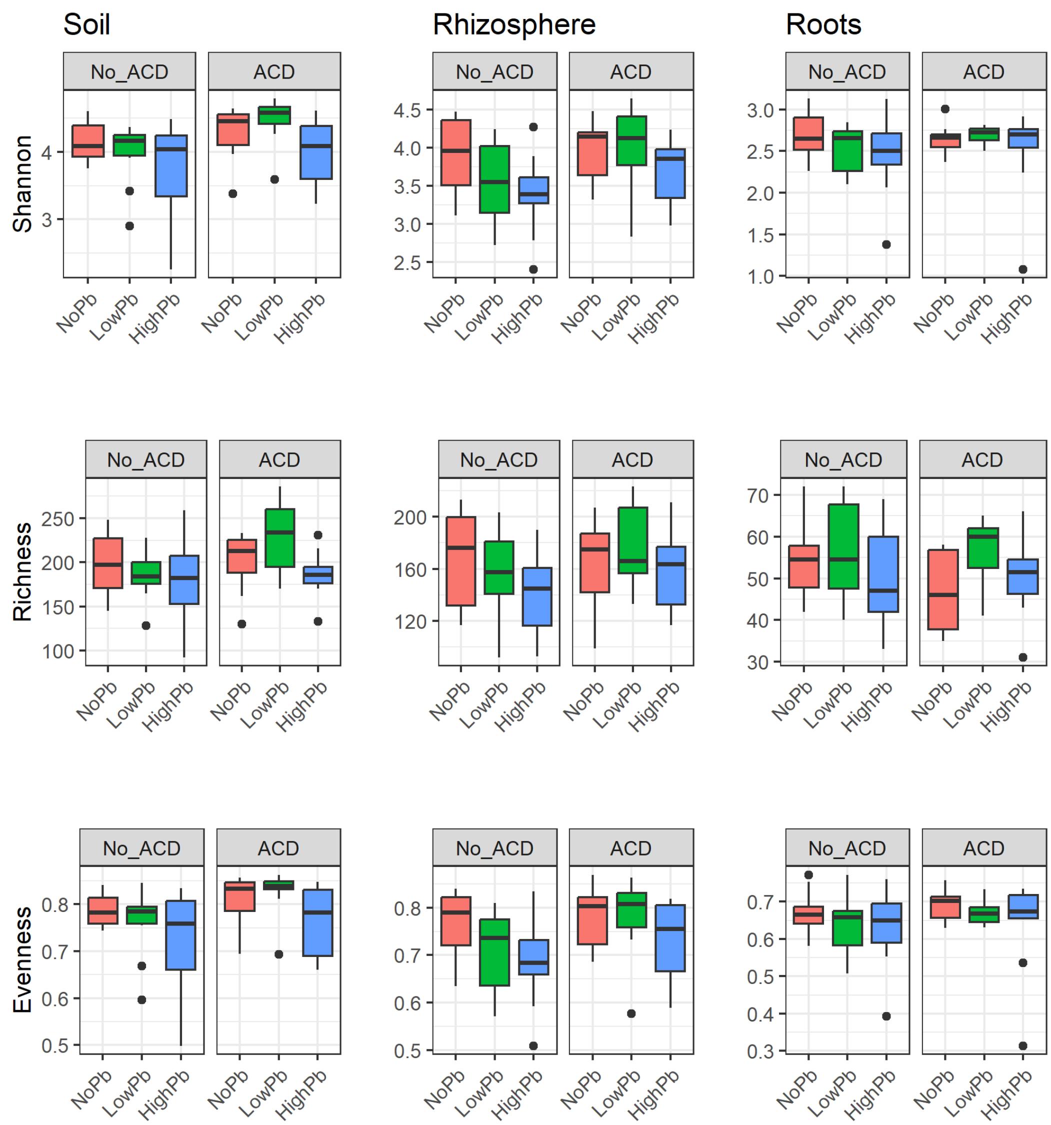
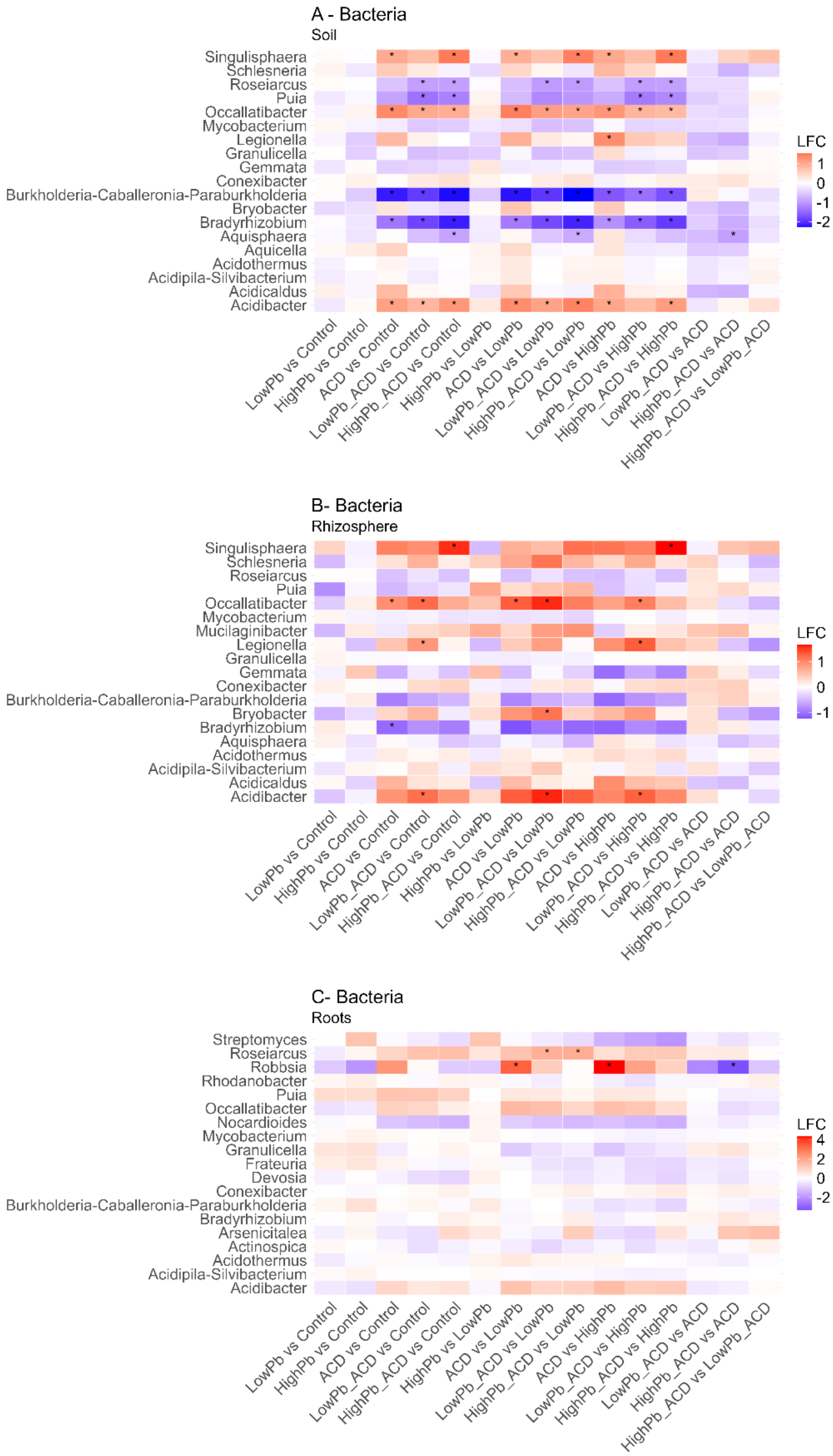


Figure D3
Alpha diversity indices (Shannon, Richness and Evenness) for fungal communities in soil, rhizosphere, and roots. Boxplots show the interquartile range (Q1-Q3) with the median indicated by the central line. Whiskers extend to 1.5 x IQR, and points represent outliers.



A - Bacteria
Soil
Singulisphaera
Schlesneria
Roseiarcus
Puia
Occallatibacter
Mycobacterium
Legionella
Granulicella
Gemmata
Conexibacter
Burkholderia-Caballeronia-Paraburkholderia
Bryobacter
Bradyrhizobium
Aquisphaera
Aquicella
Acidothermus
Acidipila-Silvibacterium
Acidicaldus
Acidibacter
LFC
1
0
-1
-2
LowPb vs Control
HighPb vs Control
ACD vs Control
LowPb_ACD vs Control
HighPb_ACD vs Control
HighPb vs LowPb
ACD vs LowPb
LowPb_ACD vs LowPb
HighPb_ACD vs LowPb
ACD vs HighPb
LowPb_ACD vs HighPb
HighPb_ACD vs HighPb
LowPb_ACD vs ACD
HighPb_ACD vs ACD
HighPb_ACD vs LowPb_ACD
B- Bacteria
Rhizosphere
Singulisphaera
Schlesneria
Roseiarcus
Puia
Occallatibacter
Mycobacterium
Mucilaginibacter
Legionella
Granulicella
Gemmata
Conexibacter
Burkholderia-Caballeronia-Paraburkholderia
Bryobacter
Bradyrhizobium
Aquisphaera
Acidothermus
Acidipila-Silvibacterium
Acidicaldus
Acidibacter
LFC
1
0
-1
LowPb vs Control
HighPb vs Control
ACD vs Control
LowPb_ACD vs Control
HighPb_ACD vs Control
HighPb vs LowPb
ACD vs LowPb
LowPb_ACD vs LowPb
HighPb_ACD vs LowPb
ACD vs HighPb
LowPb_ACD vs HighPb
HighPb_ACD vs HighPb
LowPb_ACD vs ACD
HighPb_ACD vs ACD
HighPb_ACD vs LowPb_ACD
C- Bacteria
Roots
Streptomyces
Roseiarcus
Robbsia
Rhodanobacter
Puia
Occallatibacter
Nocardioides
Mycobacterium
Granulicella
Frateuria
Devosia
Conexibacter
Burkholderia-Caballeronia-Paraburkholderia
Bradyrhizobium
Arsenicitalea
Actinospica
Acidothermus
Acidipila-Silvibacterium
Acidibacter
LFC
4
2
0
-2
LowPb vs Control
HighPb vs Control
ACD vs Control
LowPb_ACD vs Control
HighPb_ACD vs Control
HighPb vs LowPb
ACD vs LowPb
LowPb_ACD vs LowPb
HighPb_ACD vs LowPb
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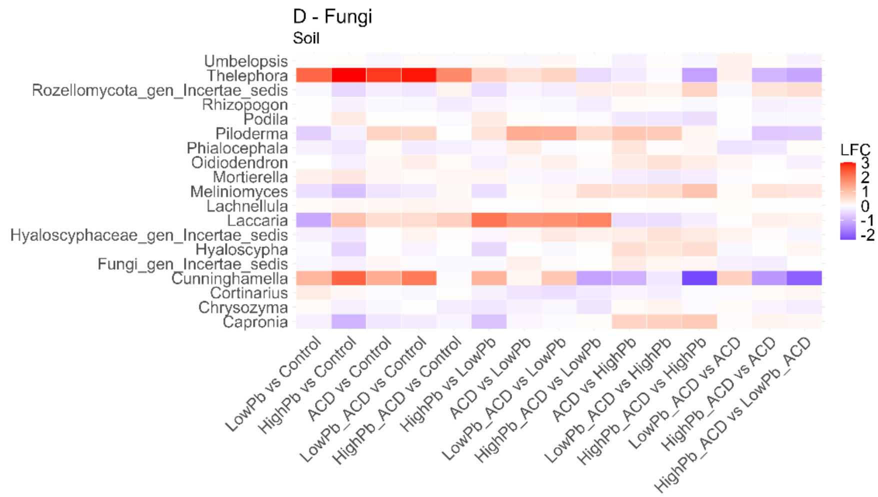
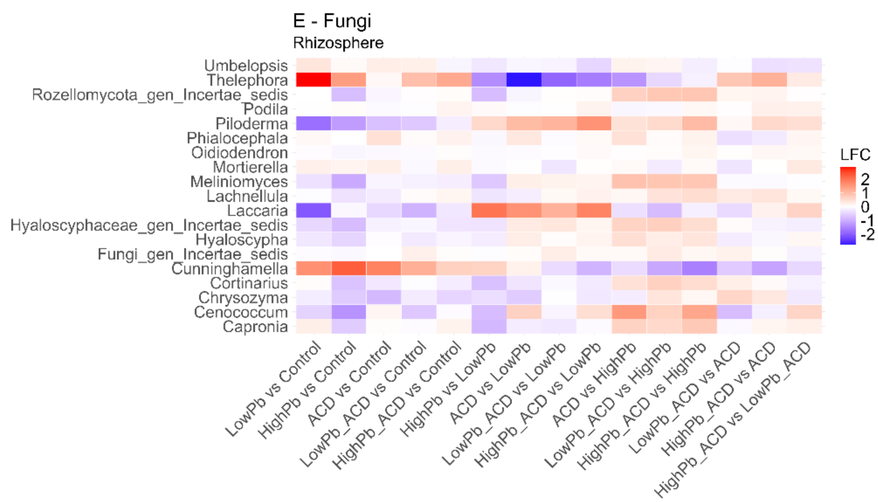
HighPb_ACD vs ACD
HighPb_ACD vs LowPb_ACD


D - Fungi
Soil
Umbelopsis
Thelephora
Rozellomycota_gen_Incertae_sedis
Rhizopogon
Podila
Piloderma
Phialocephala
Oidiodendron
Mortierella
Meliniomyces
Lachnellula
Laccaria
Hyaloscyphaceae_gen_Incertae_sedis
Hyaloscypha
Fungi_gen_Incertae_sedis
Cunninghamella
Cortinarius
Chrysozyma
Capronia
LowPb vs Control
HighPb vs Control
ACD vs Control
LowPb_ACD vs Control
HighPb_ACD vs Control
HighPb vs LowPb
ACD vs LowPb
LowPb_ACD vs LowPb
HighPb_ACD vs LowPb
ACD vs HighPb
LowPb_ACD vs HighPb
HighPb_ACD vs HighPb
LowPb_ACD vs ACD
HighPb_ACD vs ACD
HighPb_ACD vs LowPb_ACD
LFC
3
2
1
0
-1
-2


E - Fungi
Rhizosphere
Umbelopsis
Thelephora
Rozellomycota_gen_Incertae_sedis
Podila
Piloderma
Phialocephala
Oidiodendron
Mortierella
Meliniomyces
Lachnellula
Laccaria
Hyaloscyphaceae_gen_Incertae_sedis
Hyaloscypha
Fungi_gen_Incertae_sedis
Cunninghamella
Cortinarius
Chrysozyma
Cenococcum
Capronia
LowPb vs Control
HighPb vs Control
ACD vs Control
LowPb_ACD vs Control
HighPb_ACD vs Control
HighPb vs LowPb
ACD vs LowPb
LowPb_ACD vs LowPb
HighPb_ACD vs LowPb
ACD vs HighPb
LowPb_ACD vs HighPb
HighPb_ACD vs HighPb
LowPb_ACD vs ACD
HighPb_ACD vs ACD
HighPb_ACD vs LowPb_ACD
LFC
2
1
0
-1
-2

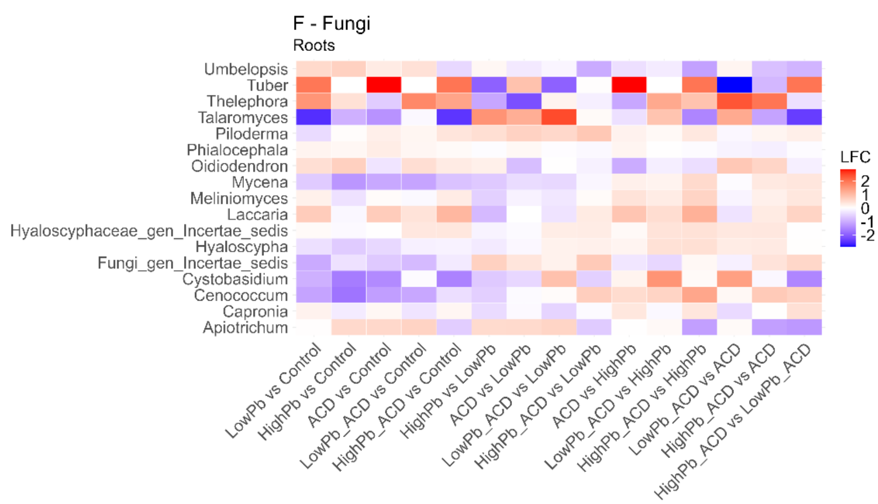

F - Fungi
Roots
Umbelopsis
Tuber
Thelephora
Talaromyces
Piloderma
Phialocephala
Oidiodendron
Mycena
Meliniomyces
Laccaria
Hyaloscyphaceae_gen_Incertae_sedis
Hyaloscypha
Fungi_gen_Incertae_sedis
Cystobasidium
Cenococcum
Capronia
Apiotrichum
LowPb vs Control
HighPb vs Control
ACD vs Control
LowPb_ACD vs Control
HighPb_ACD vs Control
HighPb vs LowPb
ACD vs LowPb
LowPb_ACD vs LowPb
HighPb_ACD vs LowPb
ACD vs HighPb
LowPb_ACD vs HighPb
HighPb_ACD vs HighPb
LowPb_ACD vs ACD
HighPb_ACD vs ACD
HighPb_ACD vs LowPb_ACD
LFC
2
1
0
-1
-2

Figure D4
Pairwise log fold changes (LFC) in Genus abundance across treatments. Heatmap of log fold changes for bacteria in (A) soil, (B) rhizosphere and (C) roots, and for fungi in (D) soil, (E) rhizosphere and (F) roots. Genus and fungi were displayed from the Top20 most abundant Genus; no taxa in this set were statistically significant. Colors represent LFC values, with blue indicating negative values (LFC < 0) and red indicating positive values (LFC > 0). Stars showed taxa with significant differences according to adjusted p-values (FDR-adjusted p-values). Significance code: '*' p < 0.05.

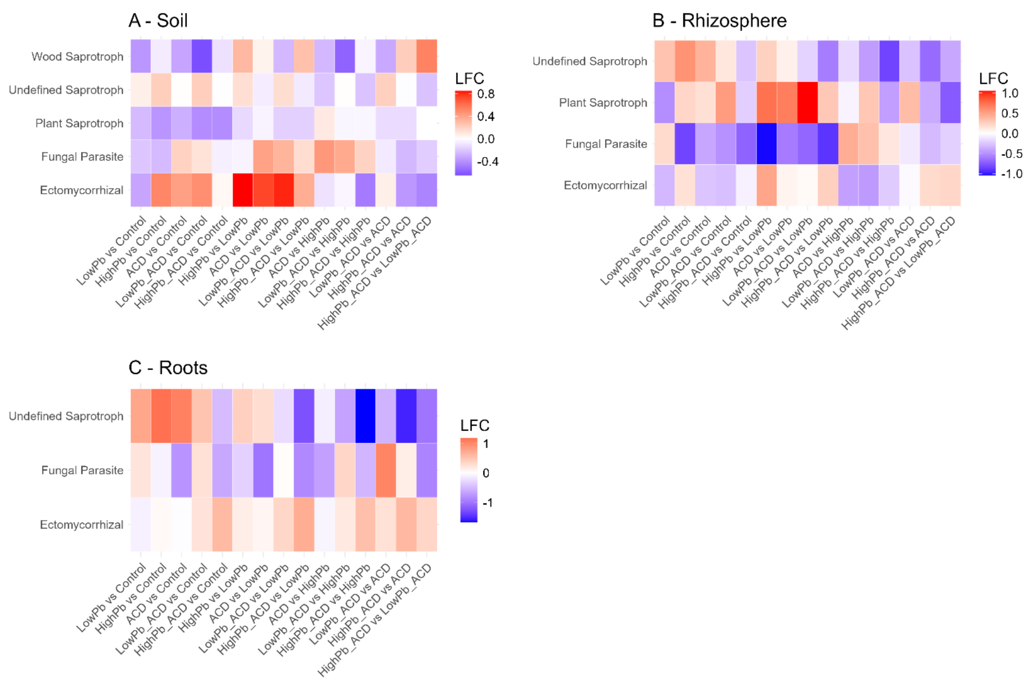


Figure D5
Pairwise log fold changes (LFC) in fungal guild abundance across treatments, for both (A) soil, (B) rhizosphere and (C) roots. Colors represent LFC values, with blue indicating negative values (LFC < 0) and red indicating positive values (LFC > 0). No taxa in this set were statistically significant.

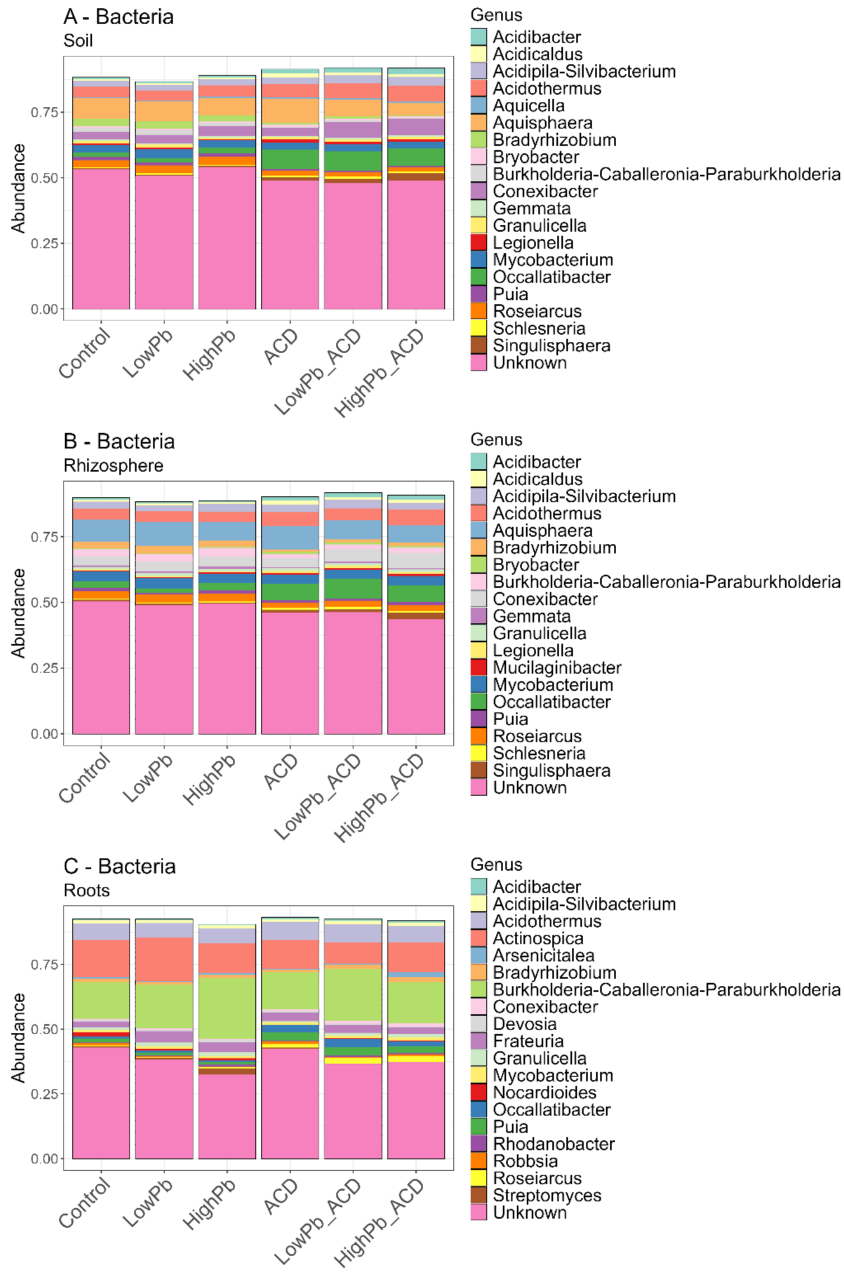


Figure D6
Barchart showing the relative abundance of the 20 most abundant bacteria genus across treatments.

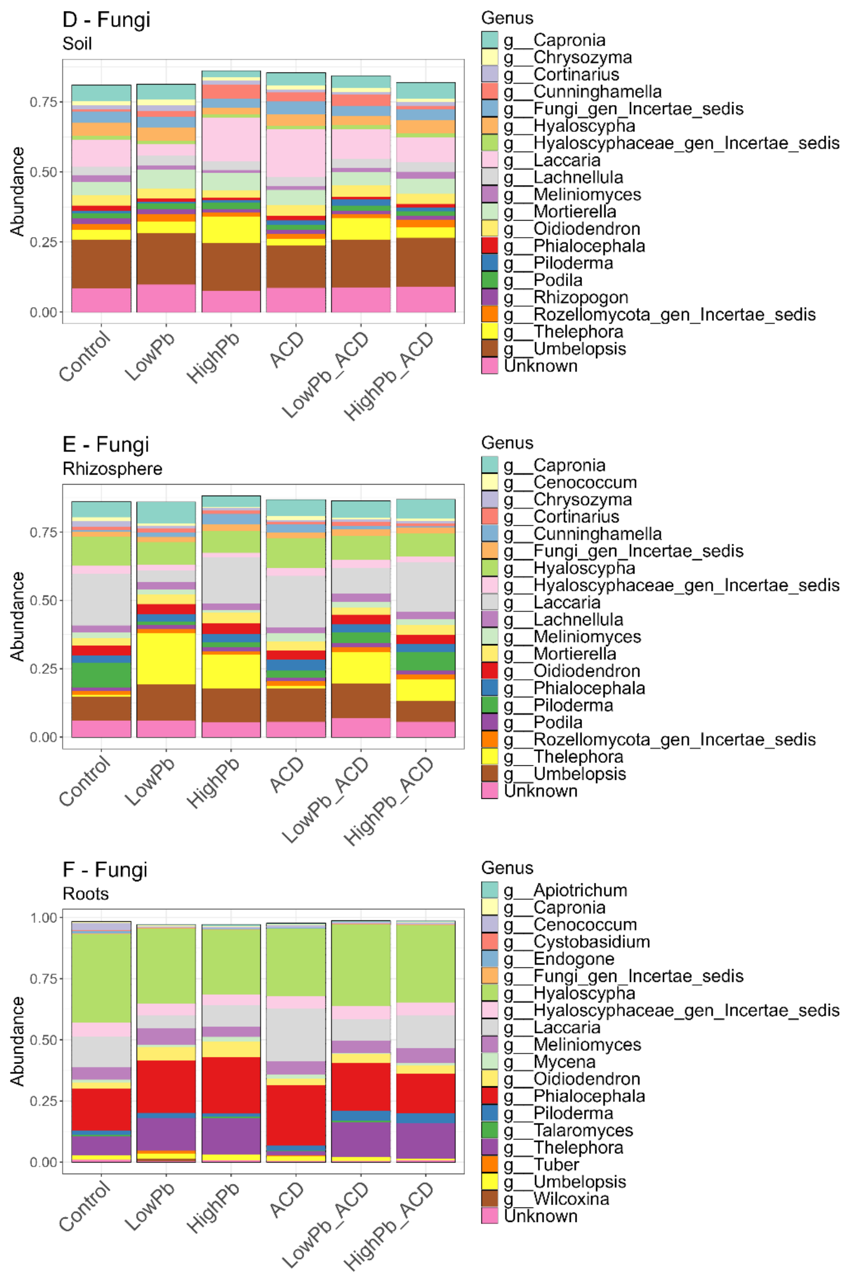


Figure D6 (continued)
Barchart showing the relative abundance of the 20 most abundant fungi genus across treatments.

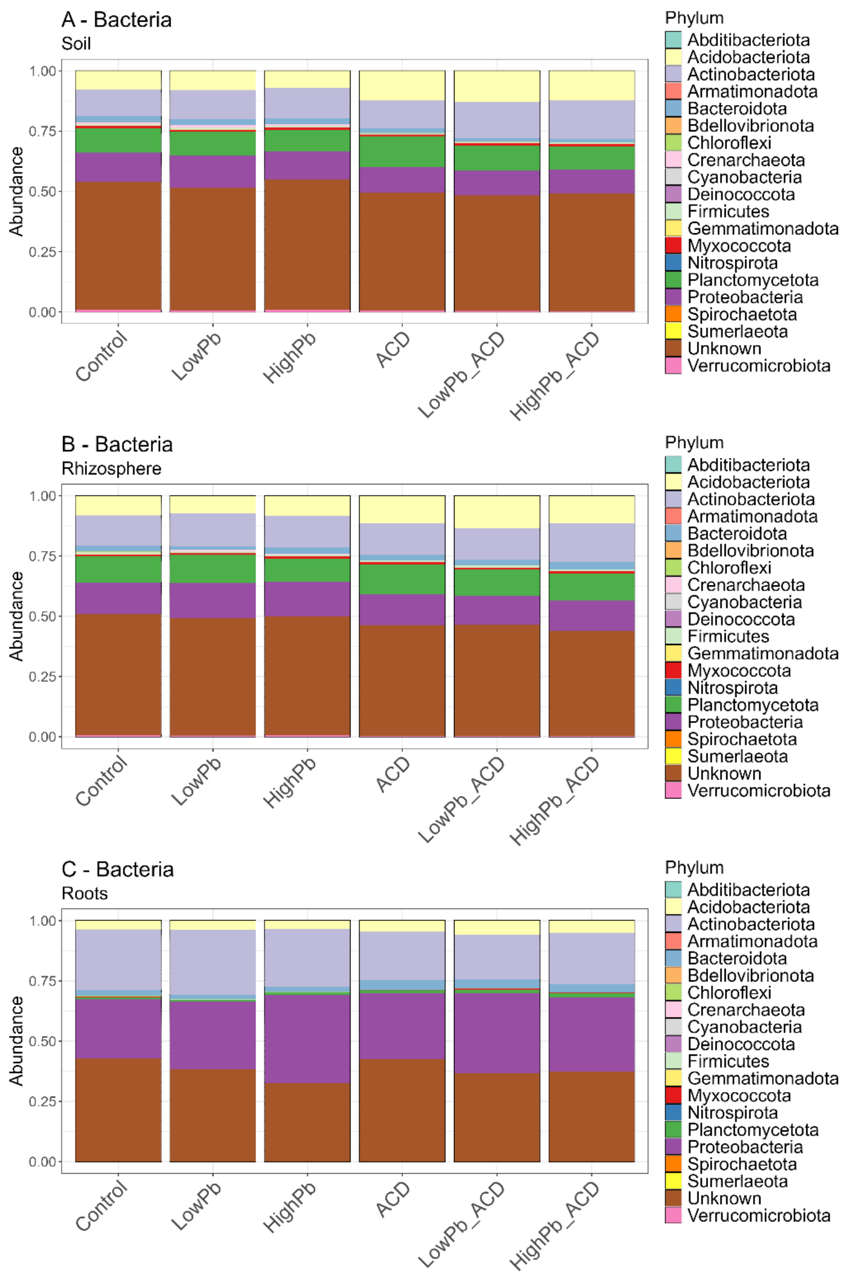


Figure D7
Barchart showing the relative abundance of the most abundant phylum across treatments.

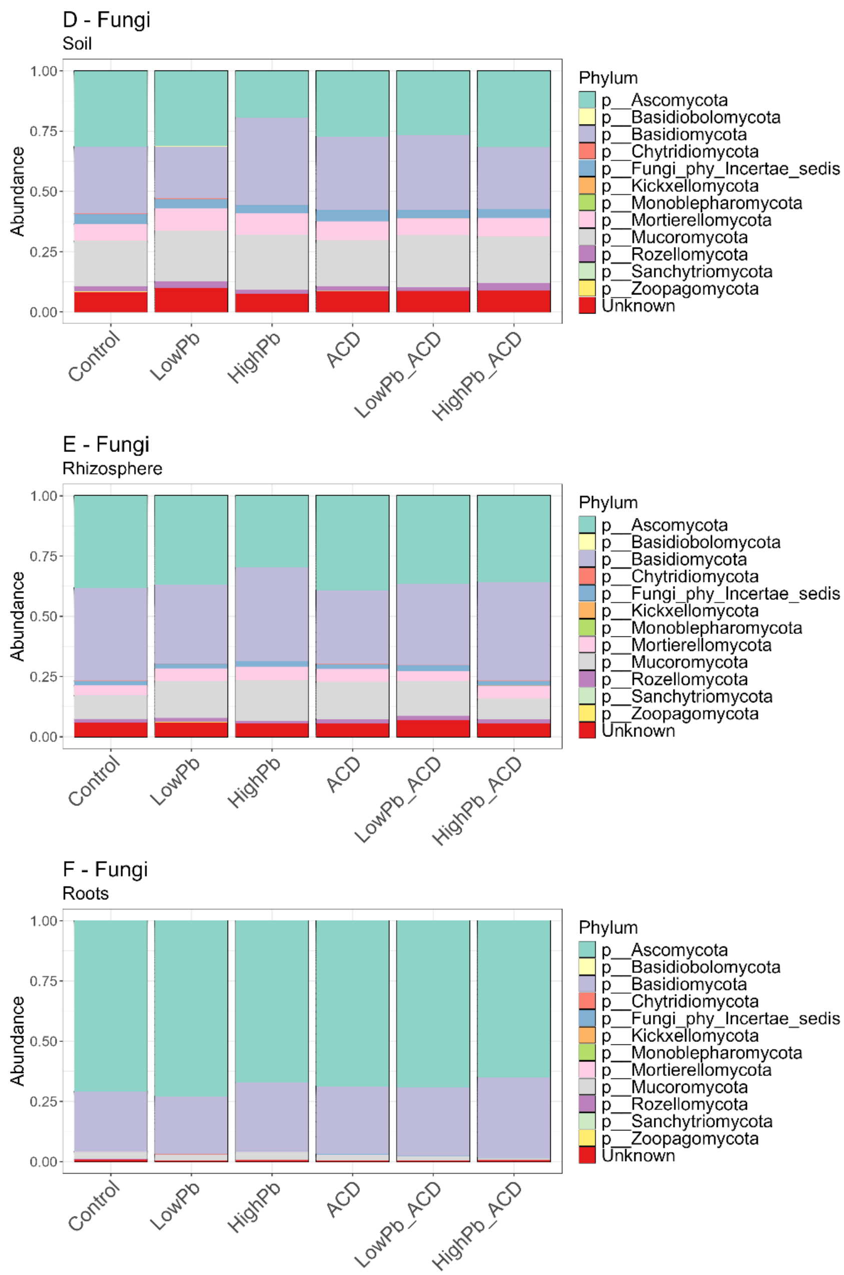


Figure D7 (continued)
Barchart showing the relative abundance of the most abundant phylum across treatments.

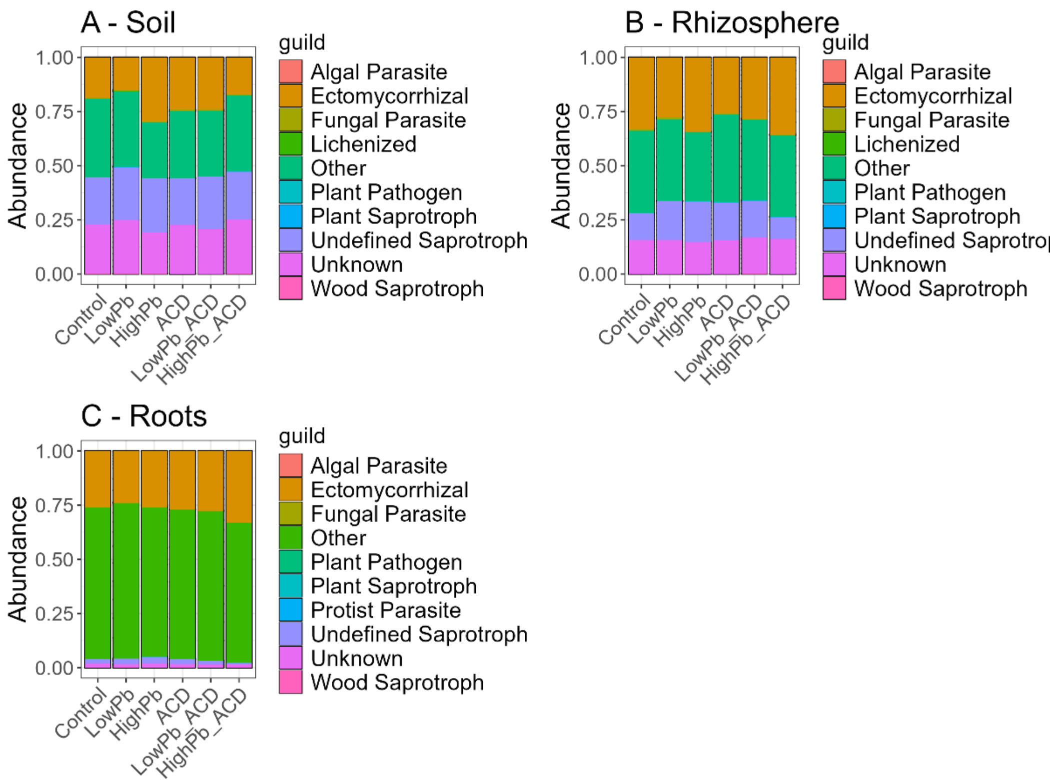


Figure D8
Compositions of main fungal functional trophic mode inferred by FUNGuild. ASVs assigned to a guild with the confidence ranking of “Highly probable” and “Probable” were retained for further use, whereas those with the “possible” confidence ranking were classified as ‘Others’.

Table D1
Experimental treatments. Lead chloride was added at concentrations of 30 ppm relative to soil volume (low Pb concentration) and 600 ppm (high Pb concentration). Sulfuric acid was added at a concentration of 50 mL/L to achieve a decrease of one pH unit.

Treatment	**Lead (Pb) concentration**	**Acidification (ACD)**
Control	Natural content	No acidification
LowPb only	Natural content + 30 ppm	No acidification
HighPb only	Natural content + 600 ppm	No acidification
ACD only	Natural content	Acidification
LowPb_ACD	Natural content + 30 ppm	Acidification
HighPb_ACD	Natural content + 600 ppm	Acidification

Table D2
Summary of the parameters used for rarefaction and the remaining ASVs for analysis. Rarefaction represents the number of reeds to normalize sequencing depth. ASV represents the total number of unique ASVs detected across all samples after rarefaction. The number in parentheses represents the number of samples under the threshold of rarefaction, which were not included in the analysis.

	Bacteria		Fungi	
	Rarefaction	Final ASV	Rarefaction	Final ASV
Soil	20,000 (1)	7,992	6,000 (1)	1,919
Rhizosphere	14,000 (1)	7,235	2,700 (1)	1,528
Root	5,000 (2)	3,174	6,000 (1)	667

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