Global NEST Journal, Vol 22, No 2, pp 147-152
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Molybdenum in forests - a short review

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Received: 18/03/2020, Accepted: 28/04/2020, Available online: 30/04/2020
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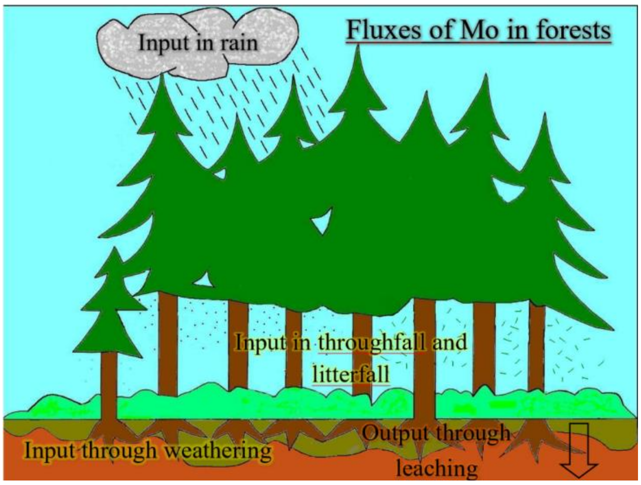
https://doi.org/10.30955/gnj.003309

Graphical abstract



Abstract

This review deals with the importance of molybdenum (Mo) in nitrogen fixation in forests as well as the distribution of Mo in the various components of a forest ecosystems and its cycling. With regard to nitrogen (N) fixation in tropical forests, the limiting factor is the availability of phosphorus in soils. For the temperate and boreal forests, the Mo availability is more crucial. The canopies of the tropical forests retain Mo from precipitation, which is used for N fixation by the microorganisms living there. There is also retention of Mo in throughfall deposition by the canopy of temperate forests but so far, there has been no information as to the biological processes taking place there. The contribution of Mo in bulk and throughfall deposition in the Mo cycling is more important than once thought. There is great variability in Mo concentrations in tree leaves either conifers or broadleaves and even within the same species. In soils, the organic matter, clay and the oxides of Al, Fe and Mn play a predominant role in preventing Mo from leaching.

Keywords: Molybdenum, nitrogen fixation, forest, Mo cycling.

1. Introduction

Although Mo is considered a rare trace element, its importance to the global N cycle is immense. Plants can assimilate nitrates only if the latter is converted to ammonia through its reduction by two separate enzymes: nitrate reductase, which reduces nitrate to nitrite and nitrite reductase, which reduces nitrite to ammonia. The nitrate reductase is a complex enzyme. It contains several prosthetic groups including cytochrome and Mo. It is assumed that during the reduction electrons are directly transferred from Mo to nitrates (Marschner, 1985).

Perhaps the most prominent role for Mo is as a cofactor in the nitrogenase enzyme in the N fixation process. Nitrogen fixation is a reaction used by some bacteria to obtain N from the atmosphere through its conversion to ammonia. The N_2 molecule is extremely stable. The industrial production of ammonia requires a temperature of 400 °C and a pressure of 200–350 atmospheres and a catalyst, usually Fe. Bacteria are able to carry out this reaction at normal temperature and pressure using the nitrogenase enzyme which consists of two proteins, a large one containing Fe and Mo and a small one containing Fe (Wood, 1989). Short supply of Mo can lead to limitation of biological N_2 fixation (Silvester, 1989; Jean *et al*., 2013).

For all these reasons agricultural research has long payed attention to the importance of Mo in the growth and health of both N-fixing and non-fixing crop plants, which has also contributed to the understanding of Mo chemistry in soils (Gupta, 1997; Kaiser *et al.*, 2005).

The important factors that determine Mo availability in soils are pH and sorption by clay minerals and Fe, Al and Mn oxides, a process, which is pH dependent. At low pH (3–5) Mo becomes strongly adsorbed (Xu *et al*., 2013). Recent evidence suggests that Mo can also bind to soil organic matter through ligand exchange and specific adsorption (Wichard, 2009). At high pH, Mo solubility increases with decreased adsorption to the solid soil constituents, which in turn increases Mo loss in leachates as soluble molybdate (MoO_4^{2-}). The molybdate is the predominant ion form in the soil solution.

In general, the total Mo concentration in mineral soils reflects the nature of parent material. The exception is the organic soil horizons, which can be enriched by Mo in deposition derived from industrial activities and sea sprays. Measuring a core from an ombrotrophic Swiss bog representing 12 370 ^{14}C years of peat accumulation, Krachler and Shotyk (2004) showed that Mo in atmospheric aerosols today was derived mainly from anthropogenic emissions. Nygård *et al.,* (2012) argued that both local point sources and long-range atmospheric transport of pollutants contribute to the enrichment of soil organic horizons with Mo. The sea sprays also contribute to soils enrichment, as Mo is the most abundant transition metal in open seawater (approximately 10 mg L^{-1}) (Smedley and Kinniburgh, 2017).

As expected, far fewer works have dealt with Mo in forests than in agricultural lands. The aim of this work is to review the importance of Mo in N fixation in forests as well as the distribution and cycling of Mo in forest ecosystems.

2. The role of Mo in N fixation in forests

When studying the role of Mo in N fixation in natural forests (symbiotic or asymbiotic), researchers usually divide the forest types into temperate, tropical and boreal ones. The reason for this is the energy cost. Nitrogen fixation needs energy in the form of ATP (adenosine triphosphate) and an environment free of oxygen (Gutschick, 1981). To fulfill these conditions the N fixing organisms use large amounts of phosphorus (P). This can be a problem in tropical ecosystems where highly weathered soils are depleted in rock-derived nutrients (like P). In tropical forests of lowland Panama, Wurzburger *et al*. (2012) showed that Mo limits fixation in P-rich soils while Mo and P co-limit the process in P poor soils. In a tropical forest in Costa Rica, Reed *et al.* (2013) found that Mo affected the N fixation only in the tree canopies (where the Mo content is very low) but not in the leaf litter or soil where the P content was the most influential factor. The importance of canopy with regard to N fixation in tropical forests was stressed by Stanton *et al.* (2019). These authors found that fixation of N by cyanobacteria in tree canopies in a tropical forest in Panama can contribute to significant N fluxes at the ecosystem level, especially if the atmospheric inputs of nutrient-rich dust provide phosphorus and Mo to N fixers.

In temperate forests, the role of Mo in N fixation is probably more crucial than that in the tropical forests as available P is not so limited in soils. Dynarski and Houlton (2018) reviewed all forms of N fixation that did not involve a plant symbiotic partner. They found that in temperate forests fertilization with Mo significantly stimulated N fixation, whereas in tropical forests the combination of Mo x P was the crucial factor. Silvester (1989) found that a variety of forest species {Douglas fir (*Pseudotsuga menziesii* Mirbell, Franco), red cedar (family *Cupressaceae*, Bartlett), pines, alder (*Alnus* species, Mill.)}, etc. in Pacific Northwest forests in USA produce litter, which supports nitrogen fixation during the decay process. He also found that the quantity of nitrogenase of bacteria increased significantly with Mo additions in a litter substrate when the latter had very low Mo concentrations. Jean *et al*. (2013) found that seasonality played a significant role with regard to the importance of Mo in N fixation in Canadian cold coniferous forests {black spruce (*Picea mariana* Mill., Britton, Sterns & Poggenburg) and pines}. In contrast to tropical forest where litter is continuously produced and degraded, the litterfall and nutrient cycling in these forests are strongly dependent on seasons. The above-mentioned authors argued that Mo was important (for N fixation in litter) in the mid growing season but not in the early or late season. In temperate forests, an association was found between symbiotic and heterotrophic N fixation. Working in 24 forests in the Oregon Coast Range dominated by Douglas fir, Perakis *et al*. (2017) reached the conclusion that legacies of symbiotic N-fixing trees can increase the abundance of multiple elements (including Mo) important to heterotrophic N-fixation. The same authors suggested the relationship of C/Mo in organic soils to predict the Mo limitation of N fixation.

In a boreal forest dominated by black spruce in north Sweden, Rousk *et al*. (2017) found that biological N fixation by moss-associated cyanobacteria was up to four-fold higher shortly after the addition of Mo, in both the laboratory and field experiment. These findings show that N fixation activity as well as cyanobacterial biomass in dominant feather mosses from boreal forests are limited by Mo availability. Sometimes cryptogamic species and their associated cyanobacteria in areas of Mo limited (like boreal forests) resort to alternative nitrogenases, which use vanadium (V) or iron (Fe) in place of Mo at their active site. This was found in specimens of the green dog lichen (*Peltigera aphthosa* L., Willd.), a symbiotic association between a fungus, a green alga and a N-fixing cyanobacterium derived from Alaska, Alberta, Sweden and Russia and Canada. In any case, the acquisition of V was strongly regulated by the abundance of Mo (Darnajou *et al*., 2017).

3. Molybdenum cycling and distribution

3.1. Hydrological cycle

The concentrations of Mo in precipitation are low measured in ng L^{-1}. There is also great variability. Agusa *et al.* (2006) found a mean value 100 ng L^{-1} of Mo in suburban areas of Hanoi, Vietnam. Michopoulos *et al*. (2020) found a range of 70–182 ng L^{-1} in a mountainous fir forest in Greece. In an older work, Shijo *et al*. (1996) found a range of 13–62 ng L^{-1} in rainwater in Japan. Marks *et al.* (2015) found lower values of Mo concentration in open precipitation in the Oregon Coast Range in USA (range: 2–20 ng L^{-1}). Despite the low concentrations of Mo in rain, the fluxes of this element in deposition should not be underestimated. They have been found higher than those in litterfall (Marks *et al.*, 2015; Michopoulos *et al.*, 2020). In addition, Mo in throughfall can enrich soil organic layers appreciably. Brun *et al*. (2008) found that during litter decomposition on the forest floor, Mo concentrations increased dramatically. Michopoulos *et al*. (2020) in a fir forest and Tyler (2005) in a beach forest found that the FH horizon in the forest floor had higher concentrations of Mo than those in foliar litterfall, leading to the conclusions that the FH layer is enriched by the Mo content in the throuhgfall deposition. Marks *et al*. (2015) reached the same conclusions dealing with the above-mentioned forest (Douglas fir) in the Oregon Coast Range in USA.

The difference between Mo fluxes in throughfall and bulk precipitation entails retention or not in forest canopies (higher bulk deposition than throughfall fluxes is retention). Retention of Mo by forest canopies was found by Campbell *et al*. (2010) in conifer forests and one deciduous paper birch one in British Columbia and Michopoulos *et al*. (2020) in a fir forest in Greece. It is not known if forest species can utilize Mo from precipitation just like in the case of nitrogen. This hypothesis should be a subject for further research. There is some evidence from agricultural plants as incubation of deficient (in Mo) wheat leaf segments in solutions containing Mo markedly increased the activity the nitrate reductase (Randal, 1969). Lichens existing in canopies and tree branches can also retain Mo to use it for N fixation. In Pacific Northwest forests in USA Horstmann *et al*. (1982) found that the lettuce lichen (*Lobaria oregana* Tuck. Müll. Arg.) was deficient in Mo and attributed that fact to the low concentrations of Mo in throughfall under Douglas fir canopies.

There has been not much information with regard to Mo concentration in soil solutions in open field. In a glasshouse experiment, Riley *et al*. (1987) found negligible amounts of Mo in leachates from acidic sandy soils when Mo was added as Na-molybdate. Rutkowska *et al*. (2017) found an average of 282 ng L^{-1} in the most common agricultural soils in Poland using a vacuum pump. Applying zero tension lysimeters at 65 cm in the soil of a fir forest Michopoulos *et al*. (2020) found a range of 100–137 ng L^{-1} in the soil solution.

The budget of the hydrochemical fluxes of Mo (throughfall minus soil solution fluxes) were found positive in the fir forest mentioned by Michopoulos *et al*. (2020) entailing Mo retention from soils. It is not known which part of soils retained the most of Mo. Both organic matter and Fe, Al and Mn oxides have this capacity. Well-drained sandy soils have been shown to leach significant amounts of Mo unless the pH is low (Jones and Belling, 1967). As the C content becomes lower further down a soil profile, the responsible soil components for Mo absorption are mainly the clay content and the mineral oxides.

3.2. Vegetation

Information on concentrations of Mo in plant leaves from forests is not abundant. Most studies have focused on conifers (Lang and Kaupenjohann, 1999; Lang and Kaupenjohann, 2000; Michopoulos *et al*., 2020; Weidner *et al*., 1996). Two studies refer to deciduous trees, one for beech (*Fagus sylvatica* L.) (Tyler *et al*., 2005) and one for sugar maple (*Acer saccharum*, Marshall) (Richardson *et al*., 2018). Finally, there is one work for evergreen broadleaves in the Mediterranean zone (Sardans *et al*., 2008) and one for an evergreen laurel (*Laurus novocanariensis* Rivas Mart, Lousâ, Fern. Prieto, E. Diaz, J. C. Cost & C. Aguiar) forest in Tenerife (Heidak *et al*., 2014). A question that arises from those studies is if there is a deficiency level for Mo concentrations in tree leaves. Deficiency levels in Norway spruce trees are reported to be the 40 μg kg $^{-1}$ (Lang and Kaupenjohann, 2000) but the uncertainty is high because the tree age plays a significant role in Mo concentrations. Weidner *et al*. (1996) found 150 μg kg^{-1} Mo in current year needles of a 12 year Norway spruce (*Picea abies,* L., H. Karst) stand supposed to suffer from Mo deficiency. Lang and Kaupenjohann (1999) found 100 μg kg^{-1} in the current year needles of a 20 year old Norway spruce stand. Michopoulos *et al*., 2020 found 46–47 μg kg^{-1} of Mo in current and second year needles of a mature (100 years of age) Bulgarian fir (*Abies borisii-regis* Mattf.) in Greece. It seems that young trees have a higher uptake of Mo and when comparing Mo concentrations, one has to take into account the tree age. That stands true at least for conifers. Such conclusions have not been drawn for broadleaves. Tyler *et al*. (2005) found an average of 40 μg kg $^{-1}$ concentration of Mo in beech leaves but not a significant difference between leaves of different senescence. Richardson *et al*. (2018) measured higher concentrations (average 90 μg kg $^{-1}$) of Mo in sugar maple leaves in forests of the New York state. Even higher concentrations (126–159 μg kg^{-1}) were found in the leaves of evergreen broadleaved species, such as strawberries trees (*Arbutus unedo* L.), green olive trees (*Phillyrea latifolia* L.) and holm oak (*Quercus ilex* L.) in NE Spain (Sardans *et al*., 2008). Heidak *et al*. (2014) found a high variability in the leaves of laurel species in Tenerife mentioned above (range 0.30–500 μg kg $^{-1}$). We can conclude that all these various concentrations are the result of soils, deposition, species, age and/or the existence of efficient rooting systems connected with mycorrhiza.

The concentrations of Mo in tree trunks presents interest because trunk wood accumulates elements mainly from the soil and its metal concentrations do not reflect the atmospheric deposition (Rossini Oliva and Mingorance, 2006). In the trunk wood of the above mentioned species in Spain (Sardans *et al*., 2008) the Mo concentrations were in the range of 33 to 77 μg kg^{-1}, whereas Michopoulos *et al*. (2020) found 27 μg kg^{-1} in the trunk wood of a Bulgarian fir. For the same trees, other metals such as As were not detectable (Michopoulos *et al*., 2018). It can be concluded that, however high the Mo deposition is, there is uptake of Mo from the soil by trees.

With regard to forest ground vegetation, interestingly enough, there is data from two types of fern: one for bracken (*Pteridium aquilinum* L., Kuhn) a deciduous fern common in the northern hemisphere (Michopoulos *et al*., 2020) and the other one from the Christmas fern (*Polystichum acrostichoides* Michx., Schott), a perennial one native to Eastern-north America (Richardson *et al*., 2018). In the first species**,** the average concentration was found 114 μg kg $^{-1}$) whereas in the second the average Mo concentration was lower, about 0.70 μg kg^{-1}. One would expect that the perennial fern would be a better Mo scavenger than the deciduous one. However, the difference in species mean difference in the uptake. So assessments on the retention of Mo in dry deposition by canopies should be made within the same plant species.

3.3. Litterfall

The concentrations of Mo in foliar litterfall have been found higher than those in standing leaves either conifer needles (Michopoulos *et al.,* 2020) or beech leaves (Tyler *et al*., 2005). Higher concentrations of Mo (than in standing leaves) were also found in litter of *Arbutus unedo and Quercus ilex* (Sardans *et al*., 2008). As the foliar litterfall (or litter on soil surface) mainly consists of older needles and leaves, the dry deposition of Mo plays a significant role in the enrichment as mentioned above. Another interesting piece of information is that the non-foliar litterfall was found to have a higher concentration of Mo than the foliar one (Michopoulos *et al.*, 2020). This is due to the plenty exchange sites in that kind of litterfall consisting of twigs, lichens, mosses and insect frass.

3.4. Soils

The average total concentration of Mo in the earth crust is 1500 µg kg^{-1} (Das *et al.*, 2007) whereas in soils, it is somewhat higher (2300 µg kg^{-1}, Fortescue, 1992). This is probably due to the creation of absorption sites in soils as a result of weathering and the existence of organic matter. Marks *et al*. (2015) found an average 1200 µg kg^{-1} of total Mo in the 0–10 cm soil layer overlying sedimentary rock. In subalpine forests soils with metamorphic rocks as parent material Wang *et al*. (2009) found an increasing concentration with depth 1550–1760 µg kg^{-1} in the mineral layers (maximum depth 30 cm) of Alpine forests in China. In Greece, Michopoulos *et al*. (2020) found also the same increasing gradient for Mo concentration (916–1470 µg kg^{-1}) with depth (maximum depth 80 cm) in the mineral soil layers of a mountainous fir forest overlying flysch, a sedimentary rock. A useful piece of information is that carbonate material, like limestone, contain about 400 µg kg^{-1} which is of course much less than the average Mo concentrations (Smedley and Kinniburgh, 2017). Very important forest ecosystems are situated on soils the parent material of which is limestone. Of course, the pH of such soils is relatively high and available Mo should not be a problem. However, if weathering rates are low, such as in mountainous forests, when temperatures are close to zero, the low concentrations of Mo in limestone rock may not be enough to replenish the Mo quantities needed by trees.

With regard to Mo weathering the works of Burghelea *et al*. (2018) and Gardner *et al*. (2017) are the most representative. The first work deals with (in a controlled experiment) the release of Mo from four rock types in the presence and absence of an arbuscular mycorrhizal fungi. The results showed that Mo was easily released and the mycorrhiza contributed to the Mo enrichment in the plant biomass of buffalo grass (*Bouteloua dactyloides* Nutt., Columbus). Gardner *et al*. (2017) argued that unlike large river systems in which dissolved Mo had been attributed predominantly to pyrite weathering, Mo concentration in small mountainous rivers was higher and did not correlate with sulfates and other chemical process are the agents of weathering like the nature of clay minerals, pH and biological weathering mentioned above.

The organic matter plays a crucial role in retaining Mo in forest soils. Wichard *et al.* (2009) found that the leaf litter in forests from Arizona and New Jersey formed strong complexes with Mo through plant derived tannins. Nitrogen fixing bacteria can remove Mo from these complexes and incorporate it to nitrogenase in their own bodies. In forested areas of the Czech Republic, due to industrial activities and through atmospheric deposition Mo has been accumulated in forest floor humus mainly in central and southwestern Bohemia reaching 1750 µg kg^{-1} (Suchara *et al*., 2002), whereas in remote forest areas the Mo content in the humus layer reaches 711 µg kg^{-1} (Michopoulos *et al*., 2020). The maximum Mo concentration in the O horizon (together L and FH horizon so somewhat diluted) was 147 µg kg^{-1} in forest soils in Oregon Coast Range (Marks *et al*. (2015). The latter authors concluded that the organic matter regulated long-term Mo retention and loss from forest soils. Similar results were found by Richardson *et al*. (2018) in a different concept. Examining the decomposition of organic matter by earthworms in forest soils under deciduous trees in the New York state they observed enrichment of the A soil horizon with Mo because of the dissolution of the above organic Mo sink. As the organic C content becomes lower with depth, the concentration gradients of total Mo follow that of clay. Lombin (1985) found a significant correlation between oxalate extractable Mo and clay content in soils low in organic matter in Nigeria. The clay fraction includes clay minerals as well as Fe, Al and Mn oxides. It can be inferred that under climate change increased temperatures will bring about decomposition of the surface organic matter in forest soils (especially in countries of high latitude) and Mo will start migrating and finally will be held by mineral oxides. If, however, the soils are sandy it is highly probable that Mo will be leached out of the ecosystem.

There is some controversy over the best extractant to determine available Mo in soils. The use of ammonium oxalate (still widely used) to extract available Mo has been criticized by some researchers (Griggs, 1960; Burmester *et al*., 1988) on the grounds that it extracts some Mo unavailable to plants. In any case, Lombin (1985) found a significant correlation between Mo concentrations in legumes and ammonium oxalate extractable Mo when the soil organic matter was also taken into account as independent variable. For forest soils, Lang and Kaupenjohann (1998) proposed the use of anion exchange resins as they found good correlation between the Mo extracted and the Mo content in spruce needles. With regard to the percentage of available Mo, (in relation to the total Mo) the results vary. Duval *et al*. (2015) found low percentages (0.32–0.42%), of the oxalate extractable Mo in coastal Florida podzol soils, whereas Michopoulos *et al.* (2020) found a range of 3.4% in the FH layer to 14.4% in the 20–40 cm mineral layer in a Humic alisol (FAO, 1988) forest soil. There is one possible explanation for this discrepancy. The labile Mo probably depends on plant uptake, which in turn depends on the plants rooting system structure. The latter is not uniform in space and therefore the available Mo content is affected. This conclusion is close to the one reached by Lang and Kaupenjohann (2000) who stated that Mo turnover within forest ecosystems was governed by Mo plant availability of mineral soils as well as by plant uptake.

3.5. Uptake of Mo by trees

Trees have to replenish the amounts nutrients lost in litterfall, both above and belowground (Cole and Rapp, 1981). The same process takes place for Mo especially in trees that use nitrates to make up their N compounds. Michopoulos *et al*. (2020) found an aboveground litterfall flux of approximately 0.8 g ha^{-1} yr^{-1} in a fir forest. The same authors found about 2 g ha^{-1} of available Mo (ammonium oxalate extractable) and 45 g ha^{-1} yr^{-1} in the FH horizon and the upper 10 cm of mineral soil respectively. If the belowground litterfall is taken into account, the total litterfall amount of Mo that has to be replenished may approach an amount of 2 g ha^{-1} yr^{-1}. The available amount of Mo in the FH layer may not be enough for the plant needs. It can be concluded therefore, that the mineral soil, in terms of quantity, is more important in supplying Mo to forest trees than the FH horizon. This finding agrees with Joslin *et al*. (1992) who argued that the upper part of the mineral soil was more important as a nutrient pool for trees than the organic layer.

4. Concluding remarks

In a period of climate change the rise of temperature, can enhance decomposition of the soil organic matter in temperate and colder forested areas causing downward movement of Mo. Leaching prevention then depends entirely on the existence of mineral oxides and clay. Considering that Mo in precipitation can be an appreciable source of Mo in the forest floor, any lowering of rain height (due to climate change) will have far reaching consequences on the Mo cycling. As the trunk wood and litter have significant quantities of Mo, care should be taken, especially in forests overlying acidic and sandy soils that the remnants of logging should stay in the forests. Fertilization of forests is not common, but we know the soils that are likely to be Mo deficient or problematic with regard to nitrogen fixation. Old weathered or sandy soils fertilized with phosphorus will have a response to nitrogen fixation through the utilization of Mo. Soils of the temperate region having sufficient available phosphorus but not Mo will also benefit from Mo fertilization.

References

Agusa T., Kunito T., Fujihara J., Kubota R., Minh T.B., Kim Trang P.T., Iwata H., Subramanian A., Viet P.H. and Tanabe S. (2006), Contamination by arsenic and other trace elements in tube-well water and its risk assessment to humans in Hanoi, Vietnam, *Environmental Pollution*, **139**, 95–106.

Brun C.B., Astrom M.E., Peltola P. and Johansson M.J. (2008), Trends in major and trace elements in decomposing needle litters during a long-term experiment in Swedish forests, *Plant and Soil*, **306**, 199–210.

Burghelea C.I., Dontsova K., Zaharescu D.G., Maier RM, Huxman T., Amistadi M.K., Hunt E., Chorover J (2018), Trace element mobilization during incipient bioweathering of four rock types, *Geochimica et Cosmochimica Acta*, **234**, 98–114.

Burmester C.H., Adams J.F. and Odom J.W. (1988), Response of soybean to lime and molybdenum on ultisols in northern Alabama, *Soil Science Society American Journal*, **52**, 1391–1394.

Campbell J., Bradfield G.E., Prescott C.E. and Fredeen L. (2010), The influence of overstorey *Populus* on epiphytic lichens in sub boreal spruce forests of British Columbia, *Canadian Journal of Forest Research*, **40**, 143–154.

Cole D.W. and Rapp M. (1981), Elemental cycling in forest ecosystems, In: *Dynamic properties of forest ecosystems*, Reichle D.E. (eds.), London: Cambridge University Press.

Darnajoux R., Zhang X., McRose D.L., Miadlikowska J., Lutzoni F., Kraepiel A.M.L. and Belenger J.P. (2017), Biological nitrogen fixation by alternative nitrogenases in boreal cyanolichens: importance of molybdenum availability and implications for current biological nitrogen fixation estimates, *New Phytologist*, **213**, 680–689.

Das A.K., Charaborty R., Cervera M.L. and Guardia M. (2007), A review on molybdenum determination in solid geological samples, *Talanta*, **71**, 987–1000.

Duval B.D., Natali S.M. and Hungate B.A. (2015), What constitutes plant-available molybdenum in sandy acidic soils? *Communications in Soil Science and Plant Analysis*, **46**, 318–326.

Dynarski K.A. and Houlton B.Z. (2018), Nutrient limitation of terrestrial free-living nitrogen fixation, *New Phytologist*, **217**, 1050–1061.

FAO-Unesco (1988), Soil map of the world, Rome, Italy: FAO-Unesco.

Fortescue J.A.C. (1992), Landscape geochemistry: retrospect and prospect, *Applied Geochemistry*, **7**, 1–53.

Gardner C.B., Carey A.E., Lyons W.B., Goldsmith S.T., McAdams B.C. and Trierweiler A.M. (2017), Molybdenum, vanadium, and uranium weathering in small mountainous rivers draining high-standing islands, *Geochimica et Cosmochimica Acta*, **219**, 22–41.

Grigg J.L. (1960), The distribution of molybdenum in soils of New Zealand. I. Soils of the North Island, *New Zealand Journal of Agricultural Research*, **3**, 69–86.

Gupta U.C. (1997), Molybdenum in agriculture, New York: Cambridge University Press.

Gutschick V.P. (1981), Evolved strategies in nitrogen acquisition by plants, *American Naturalist*, **118**, 607–637.

Heidak M.O., Glasmacher U.A. and Schöler H.F. (2014), A comparison of micronutrients (Mn, Zn, Cu, Mo, Ni, Na) within rocks, soils, and leaves, from fallow agricultural lands and natural laurel forest areas (Tenerife, Canary Islands, Spain), *Journal of Geochemical Exploration*, **136**, 55–64.

Horstmann J.C., Dennison W.C. and Silvester W.B. (1982), $N^{15}{}_2$ fixation and molybdenum enhancement of acetylene reduction by *Labaria* spp, *New Phytologist*, **92**, 235–242.

Jean ME., Phayvong K., Forest-Drolet J. and Bellenger J.P. (2013), Molybdenum and phosphorus limitation of asymbiotic nitrogen fixation in forests of Eastern Canada: influence of vegetative cover and seasonal variability, *Soil Biology and Biochemistry*, **67**, 140–146.

Jones G.B. and Belling G.B. (1967), The movement of coper, molybdenum, and selenium in soils as indicated by radioactive isotopes, *Australian Journal of Agricultural Research*, **18**, 733–740.

Joslin J.D., Kelly J.M. and Van Miegroet H. (1992), Soil chemistry and nutrition of North American spruce fir stands: evidence of recent change, *Journal of Environmental Quality*, **21**, 12–30.

Kaiser B.N., Gridley K.L., Brady J.N., Phillips T. and Tyerman S.D. (2005), The role of molybdenum in agricultural plant production, *Annals of Botany*, **96**, 745–754.

Krachler M. and Shotyk W. (2004), Natural and anthropogenic enrichments of molybdenum, thorium, and uranium in a complete peat bog profile, Jura Mountains, Switzerland, *Journal of Environmental Monitoring*, **6**, 418–426.

Lang F. and Kaupenjohann M. (1999), Molybdenum fractions and mobilization kinetics in acid forest soils, *Journal of Plant Nutrition and Soil Science*, **162**, 309–314.

Lang F. and Kaupenjohann M. (2000), Molybdenum at German Norway spruce sites: contents and mobility, *Canadian Journal of Forest Research*, **30**, 1034–1040.

Lombin G. (1985), Evaluation of the Micronutrient Fertility of Nigeria's Semi-Arid Savannah Soils: Boron and Molybdenum, *Soil Science and Plant Nutrition*, **31**, 13–25.

Marks J.A., Perakis S.S., King E.K. and Pett-Ridge J. (2015), Soil organic matter regulates molybdenum storage and mobility in forests, *Biogeochemistry*, **125**, 167–183.

Marschner H. (1985), Mineral nutrition of higher plants, London: Academic Press.

Michopoulos P., Bourletsikas A., Kaoukis K., Daskalakou E., Karetsos G., Kostakis M., Thomaidis N.S., Pasias I.N., Kaberi H. and Iliakis S. (2018), The distribution and variability of heavy metals in a mountainous fir forest ecosystem in two hydrological years, *Global NEST Journal*, **20**, 188–197.

Michopoulos P., Kostakis M., Bourletsikas A., Kaoukis K., Karetsos G., Thomaidis N.S. and Nisianakis P. (2020), The fluxes and distribution of molybdenum in a mountainous fir forest in two hydrological years, *Global NEST Journal*, **22**, 15–21.

Nygård T., Steinnes E. and Røyset O. (2012), Distribution of 32 Elements in Organic Surface Soils: Contributions from Atmospheric Transport of Pollutants and Natural Source, *Water Air and Soil Pollution*, **223**, 699–713.

Perakis S.S., Pett-Ridge J.C. and Catricala C.E. (2017), Nutrient feedbacks to soil heterotrophic nitrogen fixation in forests, *Biogeochemistry*, **134**, 41–55.

Randal P.J. (1969), Changes in nitrate and nitrate reductase levels on restoration of molybdenum to molybdenum-deficient plants, *Australian Journal of Agricultural Research*, **20**, 635–642.

Reed S.C., Cleveland C.C. and Townsend A.R. (2013), Relationships among phosphorus, molybdenum and free-living nitrogen fixation in tropical rain forests: results from observational and experimental analyses, *Biogeochemistry*, **114**, 135–147.

Richardson J.B., Blossey B. and Dobson A.M. (2018), Earthworm impacts on trace metal (Al, Fe, Mo, Cu, Zn, Pb) exchangeability and uptake by young *Acer saccharum* and *Polystichum acrostichoides, Biogeochemistry*, **138**, 103–119.

Riley M.M., Robson A.D., Gartrell J.W. and Jeffrey R.C. (1987), The absence of leaching of molybdenum in acid soils from Western Australia, *Australian Journal of Soil Research*, **25**, 179–184.

Rosssini Oliva S. and Mingorance M.D. (2006), Assessment of airborne heavy metal pollution by aboveground pant parts, *Chemosphere*, **65**, 177–182.

Rousk K., Degboe J., Michelsen A., Bradley R. and Bellenger J.P. (2017), Molybdenum and phosphorus limitation of moss-associated nitrogen fixation in boreal ecosystems, *New Phytologist*, **214**, 97–107.

Rutkowska B., Szulc W., Spychaj-Fabisiak E. and Pior N. (2017), Prediction of molybdenum availability to plants in differentiated soil conditions, *Plant Soil and Environment*, **63**, 491–497.

Sardans J., Peuelas J. and Ogaya R. (2008), Drought's impact on Ca, Fe, Mg, Mo and S concentration and accumulation patterns in the plants and soil of a Mediterranean evergreen *Quercus ilex* forest, *Biogeochemistry*, **87**, 49–69.

Shijo Y., Suzuki M., Shimizu T. and Aratake S. (1996), Determination of trace amounts of molybdenum in rainwater and snow by graphite-furnace absorption spectrometry after solvent extraction and micro-volume back-extraction, *Analytical Sciences*, **12**, 953–957.

Silvester W.B. (1989), Molybdenum limitation of asymbiotic nitrogen fixation in forests of Pacific Northwest America, *Soil Biology and Biochemistry*, **21**, 283–289.

Smedley P.L. and Kinniburgh D.G. (2017), Molybdenum in natural waters: A review of occurrence, distributions and controls, *Applied Geochemistry*, **84**, 387–432.

Standon D.E., Batterman S.A., Von Fischer J.C., Lars O. and Hedin L.O. (2019), Rapid nitrogen fixation by canopy microbiome in tropical forest determined by both phosphorus and molybdenum, *Ecology*, **100**(9).

Suchara I. and Sucharova J. (2002), Distribution of Sulphur and heavy metals in forest floor humus of the Czech Republic, *Water Air and Soil Pollution*, **136**, 289–316.

Tyler G. (2005), Changes in the concentrations of major, minor and rare-earth elements during leaf senescence and decomposition in a *Fagus sylvatica* forest, *Forest Ecology and Management*, **206**, 167–177.

Wang X., Cheng G., Zhong X. and Li M.H. (2009), Trace elements in sub-alpine forest soils on the eastern edge of the Tibetan Plateau, China, *Environmental Geology*, **58**, 635–643.

Weidner M., Brückner H., Pajak E., Schmidt B. and Wichtmann H. (1996), Differential effects of potassium and molybdenum deficiency and fertilization on nitrogen metabolism in Norway spruce, *Zeitschrift Pflanzenernähr und Bodenkunde*, **159**, 199–206.

Wichard T., Mishra B., Myneni S.C.B., Bellenger J.P. and Kraepiel A.M.L. (2009), Storage and bioavailability Of Molybdenum in soils increased by organic matter complexation, *Nature Geoscience*, **2**, 625–629.

Wood M. (1989), Soil Biology, New York: Blackie.

Wurzburger N., Bellenger J.P., Kraepiel A.M., Hedin L.O. (2012), Molybdenum and phosphorus interact to constrain asymbiotic nitrogen fixation in tropical forests, *PLoS One*, **7**(3).

Xu N., Braida W., Christodoulatos C. and Chen J (2013), A review of molybdenum adsorption in soils/bed sediments: speciation, mechanism, and model applications, *Soil and Sediment Contamination*, **22**, 912–929.