Indian Journal of Plant Sciences ISSN: 2319–3824
Online, International Journal, Available at http://www.cibtech.org/jps.htm
2023 Vol.12, pp.41-60/Basuchaudhuri
Review Article (Open Access)

MOLYBDENUM NUTRITION IN PLANTS

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ABSTRACT
In plants, with time the requirement of trace element molybdenum, along with other trace elements are gaining importance, because of depletion of these nutrients in the crop fields as well as balanced combinations of the nutrients in the produce such as grains, vegetables and fruits. Molybdenum nutrition critically stimulates nitrate reduction, nitrogen metabolism, and enzymes associated with molybdenum cofactor (Moco). Analysis of ionimics suggested a close relationship amongst other ions and molybdate in plant system. Recently details of molybdenum transporters in cellular level and in plant systems had been identified and characterised in different environments. Mutants are elucidated and performances are being delineated for betterment and improvement in future.

Keywords*: Molybdenum, Nutrition, Plants, Nitrate reductase, Nitrogen metabolism, Mo-transporters*

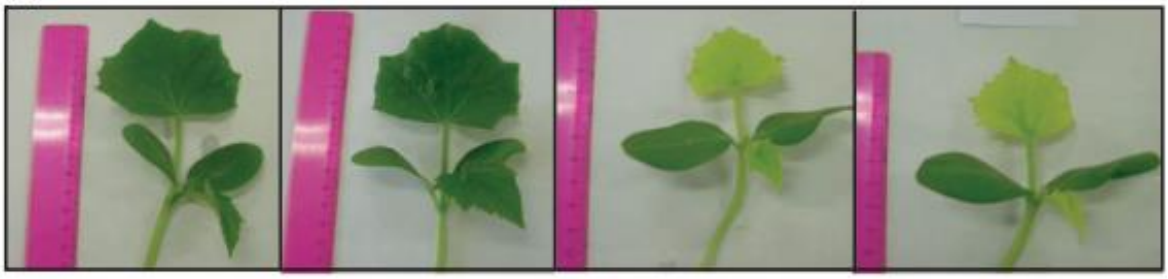
INTRODUCTION
Dissolved molybdenum available to plants is commonly found in the soluble MoO_4^{2-} anion form (Lindsay, 1979). Once in solution, the MoO_4^{2-} anion is subject to normal anion adsorption/desorption reactions, which are dependent on the specific chemistry of the soil solution. MoO_4^{2-} can adsorb onto positively charged metal oxides (Fe, Al, Mn), clay minerals, dissolved organic compounds and carbonates.

Molybdenum is a trace mineral that is essential for plants as a component of enzymes that regulate nitrogen, oxygen, and sulphur cycles. Plants need very small amounts of molybdenum, but the availability of the mineral depends on the soil pH, with alkaline soils having more molybdenum than acidic soils. Different plant species have different molybdenum requirements, with legumes needing more than grass or corn. Molybdenum deficiency or toxicity can affect plant growth and development. Molybdenum availability in soil strongly pH dependent with maximum adsorption occurring between pH 4 and 5 (Smith *et al.,* 1997b). As the soil solution becomes more alkaline MoO_4^{2-} availability increases. Every unit increase above pH 3, MoO_4^{2-} solubility increases approx. 100-fold primarily through decreased adsorption of metal oxides (Lindsay, 1979). Consequently, the application of lime to agricultural soils has been an important tool to adjust soil pH and increase soluble molybdate.

The patterns of molybdenum (MoO42-) absorption and transport were investigated in intact bean (Phaseolus vulgaris L.) and rice (Oryza sativa L. cv. I.R.8) plants. The mobility of MoO42- absorbed by roots and by leaves was compared with that of a freely mobile element, Rb+. Although MoO42- absorption by bean roots was nearly as high as that of Rb+ transport to the shoot was considerably less. When MoO42- was fed to one of the primary leaves, most of it was transported to the stem and root. Evidence obtained here showed that MoO42- was mobile. Experiments with intact rice seedlings revealed large differences in the absorption and transport of MoO42- between the plants grown in CaSO4 and those in Hoagland solution. Molybdate uptake by excised rice roots was suggested to be an active process since it was greatly inhibited by a metabolic inhibitor. The presence of Mn2+, Zn2+, Cu2+, CI-, or SO42- in the absorption medium reduced MoO42- uptake which was markedly enhanced by the presence of Fe2+(Kannan and Ramani,1978).

For most plants, the molybdenum requirement is 0.1-2.0 ppm for optimal growth. However, some plants, especially legumes, cucurbits, and crucifers, require up to 5 ppm or more. On the other hand, analysis of plant tissue or leaves has shown that the normal concentration is 0.01-1.5 ppm, with some plants having more, some up to 80 ppm, without showing any signs of toxicity. Plants that require high molybdenum include lettuce, cabbage, cauliflower, brussels sprout, alfalfa, peas, clover, soybeans, tobacco, sugar beets, spinach, broccoli, and tomatoes. Others are grapes, citrus, table beets, duckweed,

poinsettia, primula, tobacco, and other legumes. Grasses, corn, apples, barley, carrots, celery, cotton, grapes, potatoes, peaches, raspberries, rice, sorghum, and other small grains tolerate low molybdenum amounts.



Cont. +Mo+Fe -Mo -Fe

Fig.1.Influences of Mo and Fe nutrition on seedling growth of cucumber.

Figure 2: Symptoms of whiptail in cole crop

Molybdate application at 2 lb per acre was capable of increasing lucerne yields approx. 3-fold over control plots (Anderson, 1942). Shortly thereafter, Davies (1945) and Mitchell (1945) demonstrated that the whiptail phenotype in cauliflower could be overcome with the addition of molybdenum to the soil. Walker (1948) observed that tomato grown in molybdenum-deficient serpentine soils could be rapidly rescued (return of green colour, loss of mottling) with application of sodium molybdate directly to the soil, or by leaf painting and leaf infiltration.

High yielding varieties of rice (*Oryza sativa*) cultivars were tested for their tolerance to different levels of molybdenum (Mo) (0.1 µM – control, 0.2, 0.4, 0.8 and 1.6 µM) in nutrient solution at pH 6.8. Seeds of rice were germinated and grown in presence of molybdenum under controlled environmental conditions. Standard growth parameters such as root length, shoot length, root/shoot dry biomass and root/shoot tolerance index were tested as markers of molybdenum toxicity. Measurements as early as 48 hours after the germination did not yield consistent results. However, root measurement on 3, 6 and 9 days after root emergence showed significant differences among cultivars of rice. Rice cultivars Annapurna, Kusuma, Deepa and Vaghari developed better root system while, Paridhan-1, Pusa-2-21 and Ratna showed poor growth of the roots in presence (0.8 µM) of molybdenum. The root tolerance index (RTI) and the shoot tolerance index (STI) in Annapurna, Kusuma and Deepa in rice were high indicating their tolerance to molybdenum; Paridhan-1 and Ratna, however, showed low RTI and STI. Based on the growth parameters, twenty cultivars of rice were ranked in respect
of their tolerance to molybdenum: Annapurrna > Deepa > Kusuma > Vaghari > Hamsa > Vikram > Bharati > Paridhan-2 >Aswathi > Subhadra > Sankar > Sakti > Nilgiri > Rudra > Hema > Pragati >

Pusa-2-21 > Ratna > Paridhan-1, respectively. Molybdenum toxicity was correlated with increased peroxidase and catalase activity in different cultivars of rice (Rout and Das, 2002).

NITRATE UTILIZATION

Nanoscale molybdenum oxide (nano-MoO_3) is widely used in industrial and environmental fields and its use to the environment is increasing. However, the potential effect of nano-MoO_3 on rice (*Oryza sativa* L.) seedling growth is unclear. Herein, the different impacts of varied concentrations (0, 50, 100, 200 and 300 μg Mo L^{-1}) of Na_2MoO_4 and nano-MoO_3 on the growth and nitrate (NO_3^-) utilisation of rice were investigated using hydroponics. The Mo concentration in roots and shoots, N metabolism enzyme activity, root morphology, root redox ability and root exudates were then analysed to understand the potential mechanisms of the impacts. Results showed that the Mo concentration in rice roots increased gradually as the amount of Mo application increased, whereas different Mo sources did not affect the Mo concentration in shoots. Both Na_2MoO_4 and nano-MoO_3 promoted the growth and NO_3^- utilisation of rice. The promotion effects of higher nano-MoO_3 levels were better than those of Na_2MoO_4. NanoMoO_3 application significantly affected the activity of nitrate reductase (NR), glutamine synthetase (GS) and glutamate synthase (NADH-GOGAT), which in turn promoted NO_3^- assimilation. Additionally, rice seedlings treated with nano-MoO_3 had a relatively high rice root volume, surface area, total absorption area, active absorption area, low-molecular-weight organic acids, root oxidation and reduction capacities. Based on these results, it is proposed that nano-MoO_3 facilitates rice growth and NO_3^- assimilation via the enhancement of nitrogen metabolism enzyme activity and the promotion of more and efficient root morphological and physiological characters with high root secretion concentration and redox ability. This provides insights regarding the further application of nano-MoO_3 in agriculture enhancing N use efficiency and rice productivity (Zhang *et al*., 2022).

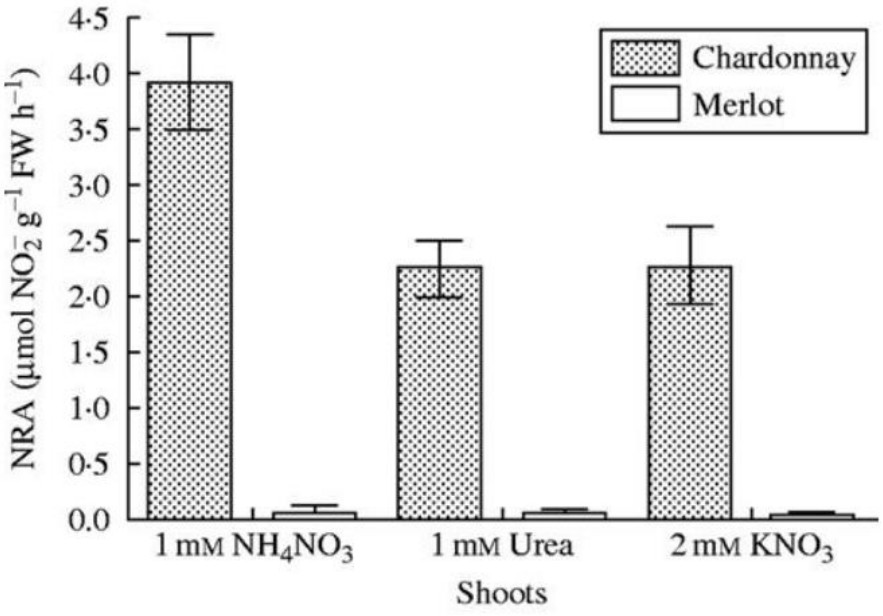


Figure 3: *In vitro* nitrate reductase activity in grapevine shoots grown in sand culture.

Rice (*Oryza sativa* L.) cv. IR8 was grown in sand culture with nutrient solutions of normal (40 ppm) nitrogen (N), and 3 times the normal nitrogen (3N) applied in the form of ammonium nitrate in combination with molybdenum as foliar spray at the rates of 0, 15. 30, and 45 μg per plant. In both the nitrogen concentration the foliar application of molybdenum increased the mean crop growth rates. Molybdenum application also increased nitrate reductase activity leading to higher concentration of reduced nitrogen in the tissue and thereby creating a concentration gradient for the uptake and assimilation of applied nitrogen (DasGupta and Basuchaudhuri, 1974 & 1977).

Table 1: Effect of molybdenum on total nitrogen content in leaves and stem, and chlorophyll content, nitrate reductase activity in the leaves of the rice plant (cv. IR8) grown under N and 3N levels of nitrogen on the 15th day after treatment with molybdenum.

Levels of molybdenum (µg/plant)	Leaf Nitrogen content (mg/plant)		Stem Nitrogen content (mg/plant)		Chlorophyll content (mg g fw^{-1})		Nitrate reductase activity (µmoles NO_2^- $gfw^{-1}h^{-1}$)	
	N	3N	N	3N	N	3N	N	3N
0	71.4	123.3	72.8	126.5	1.92	2,20	0.16	0.55
15	103.8	173.9	87.0	169.4	2.54	2.59	0.65	0.98
30	142.0	216.9	95.7	198.9	2.05	3.04	0.71	0.71
45	84.9	152.1	55.0	153.3	1.85	2.77	0.71	0.65
S.Em±	15.3	19.7	8.9	15.1	0.15	0.11	0.13	0.09

The first experiment was conducted to investigate the effects of ammonium nitrate (AN) on nitrate (NO_3^-) accumulation rates as well as some other vegetative traits in spinach in four treatments and three replicates and the second experiment was done to investigate the effects of elemental Mo and green synthesized Mo NPs on NO_3^- accumulation, nitrate reductase (NR) activity and some morphological parameters in seven treatments with three replicates. The results of the first experiment indicated that the greatest accumulation of NO_3^- in the aerial parts of the plants was observed in the 3 M AN treatment. That is why the same concentration was utilized in the second experiment to study the effects of elemental Mo and green synthesized Mo NPs on the NR activity, NO_3^- accumulation and the other traits. The results of the second experiment indicated that various concentrations of elemental Mo and green synthesized Mo NPs have significant effects on all measured traits including the fresh and dry weights of the plant, NO_3^- concentration, NR activity, chlorophyll *a* (Chl *a*) and chlorophyll *b* (Chl *b*) rates, total chlorophyll (Chl *a* + *b*) and the plant height. Moreover, it was found that the green synthesized Mo NPs, as compared to elemental Mo, have a greater effect on the increase of NR activity and, consequently, significant reduction of NO_3^- accumulation (Zhang *et al*.2022).

The induction of nitrate reductase in plants requires both nitrate and molybdenum: if either nutrient is deficient, the enzyme is either non-existent or less active. In deficient plants, the induction of enzyme activity by molybdenum has been found to be much faster than the induction of nitrate reductase activity by nitrate (Hamlin, 2007).

In fact, many studies have shown that application of Mo improves the absorption of Mo, the transformation of NO_3^-–N to NH_4^+–N as well as free nitrogen to albuminous nitrogen in seeds, and it increases the nitrate reductase (Li-Ping *et al.,* 2007).

Liu and Yang (1999) investigated the relationship between molybdenum and the nitrogen metabolism of three soybean varieties in each stage of growth. Five levels of molybdenum were studied. An increase in both nitrate reductase activity and total N content were found in leaves and a reduction of NO_3–N content was found with molybdenum application. In addition to this, according to Vieira *et al.* (1998) experiment, molybdenum foliar spray (40 g ha^{-1} of Mo) at 25 days after plant emergence significantly enhanced nitrate reductase activities, producing an increase of the total nitrogen accumulated in the plant shoots of common beans.

In contrast, molybdenum toxicity in plants under most agricultural conditions is rare. In tomato and cauliflower, plants grown on high concentrations of molybdenum will have leaves that accumulate anthocyanins and turn purple, whereas, in legumes, leaves have been shown to turn yellow (Bergmann, 1992; Gupta, 1997b). The greatest concern associated with high plant molybdenum levels is with crops used for grazing or silage production.

Mo is an essential element that is indispensable for plant growth and development. All plants require Mo for the biosynthesis of molybdenum cofactor (Moco), which has vital roles in nitrate assimilation, abscisic acid biosynthesis, purine degradation, and sulphite detoxification (Bittner, 2014). In addition, root and shoot histology, leaf ultrastructure, leaf chlorophyll content, and the morphology and physiological function of the root system were investigated to better understand why leaf yellowing and poor root growth occur under Mo deficient conditions. Strawberry seedlings grown under standard Mo conditions showed a well-developed microstructure and ultrastructure, a large number of chloroplasts,

and a higher chlorophyll content. Enhanced root activity and well-developed root systems were observed when seedlings were cultivated on a standard Mo medium. Improved root system traits included enhanced root length and surface area, larger numbers of tips, forks, and crossings, and increased. Yet, recent evidence indicates that intracellular molybdate levels are tightly controlled by molybdate transporters, in particular, during plant development. Moreover, a tight connection between molybdenum and iron metabolisms is presumed because (i) uptake mechanisms for molybdate and iron affect each other, (ii) most molybdo-enzymes do also require iron-containing redox groups such as iron-sulphur clusters or heme, (iii) molybdenum metabolism has recruited mechanisms typical for iron-sulphur cluster synthesis, and (iv) both molybdenum cofactor synthesis and extramitochondrial iron-sulphur proteins involve the function of a specific mitochondrial ABC-type transporter.

Table 2: Components of molybdenum metabolism in higher plants (*Arabidopsis thaliana*). After Bittner, 2014

Protein names	Agi code	Known / proposed function
MOT1/SULTR 5;2	AT2G25680	Molybdate transport
MOT2/SULTR5;1	AT1G80310	Molybdate transport/export from the vacuole
CNX1	AT5G20990	Moco biosynthesis step 3
CNX2	AT2G31955	Moco biosynthesis step 1
CNX3	AT1G01290	Moco biosynthesis step 1
CNX5	AT5G55130	Moco biosynthesis step 2
CNX6	AT2G43760	Moco biosynthesis step 2
CNX7	AT4G10100	Moco biosynthesis step 2
Nia1/NR1	AT1G77760	Nitrate reductase (Minor form)
Nia2/NR2	AT1G37130	Nitrate reductase (Main form)
SO	AT3G01910	Oxidation/elimination of cytotoxic sulphite
mARC1/MOSC1	AT4G44720	Unknown
mARC2/MOSC2	AT1G30910	Unknown
AAO1	AT5G20960	Unknown
AAO2	AT3G43600	Unknown
AAO3	AT2G27150	ABA biosynthesis
AAO4	AT1G04580	Synthesis of benzoic acid
AtXDH1	AT4G34890	Purine degradation
AtXDH2	AT4G34900	Unknown
ABA3/LOS5	AT1GI6540	Moco sulphuration and activation of AO and XDH proteins
ATM3/ABCB25	AT5G58270	Transporter involved in cytosolic Fe-S assembly and Moco synthesis

COMPONENTS OF MOLYBDENUM METABOLISM

The main components of molybdenum metabolism in plants are shown including the Moco biosynthetic pathway (CNX proteins) in mitochondria and cytosol, the Moco user enzymes and their respective main

functions in nitrogen assimilation (NR), ABA synthesis (AAO3), purine catabolism (XDH1), and sulphite detoxification (SO). mARC enzymes are proposed to function in reduction of certain N-hydroxylated substrates, which have not yet been identified. While one of the two mARC isoforms (mARC2) contains an NH_2-terminal mitochondrial targeting sequence, such targeting sequence is absent at the second isoform, which therefore is assumed to act in the cytosol. In contrast to the molybdate transporter MOT2, which functions at the vacuolar membrane as a molybdate exporter, MOT1 might localize to the endomembrane system, possibly to the endoplasmic reticulum. A mitochondrial localization of MOT1 has also been reported but appears less likely as no obvious reason exists for import or export of molybdate into or out of the mitochondria, respectively. The plant homolog (MFS-MOT) of the major facilitator superfamily molybdate transporter MOT2 from *Chlamydomonas* might be required for molybdate import across the plasma membrane. The function of the Moco sulfurase ABA3 in activation of AO and XDH is indicated, just as the functions of the mitochondrial ABC transporter ATM3 in export of cPMP from mitochondria and in cytosolic iron-sulphur cluster ([Fe-S]) assembly for AO and XDH (and other extra-mitochondrial proteins). Further details are given by Bittner and Mendel(2010) and Mendel (2013). Molybdo-enzymes are indicated by blue letters, other components of molybdenum metabolism by orange letters; dotted arrows indicate requirement for Moco by molybdo-enzymes.

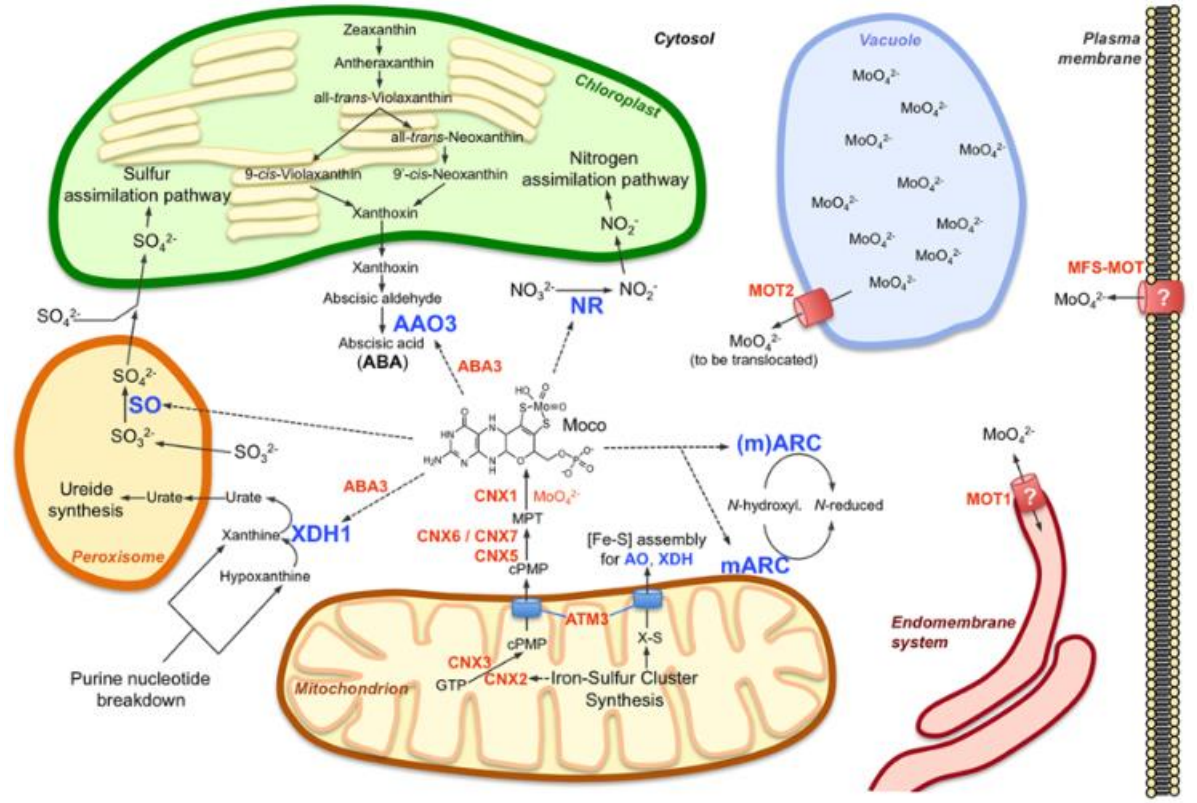


Figure 4: Molybdenum metabolism in plant cells. After Bittner (2014).

Significantly larger variations were found for the concentration of the second group consisting of the three essential micronutrients B, Co and Mo and Na (Na is a functional but nonessential element). It is likely that the elements in the second group were under less pressure to regulate their concentrations (unless they approach toxicity levels), thus having more relaxed control mechanisms. The differences in these control mechanisms exist not only among genotypes, but can also vary temporally and spatially within a given plant. Because this regulatory variability exists, it would appear that enhancing the micronutrient density of edible plant components through the manipulation of physiological processes is an achievable goal.

Table 3: Precision and accuracy of detection and heritability (H^2) of 20 root and 18 shoot ionomic phenotypes measured on the Rice Diversity Panel 1 (n=373)

Abbrev.	Ion	Lower limit of Detection (ppm)	Bayesian RSD* Roots	Shoots	Heritability(H^2) Roots	Shoots
As	Arsenic	0.038	16.89	34.03	0.14	0.13
B	Boron	0.146	36.18	9.97	0.17	0.18
Ca	Calcium	0.291	10.32	11.54	0.18	0.31
Cd	Cadmium	0.004	17.20	22.72	0.28	0.33
Co	Cobalt	0.003	15.15	26.01	0.22	0.12
Cr	Chromium	0.022	18.34	6.11	0.14	0.15
Cu	Copper	0.005	24.28	18.85	0.30	0.14
Fe	Iron	0.240	15.99	16.96	0.16	0.25
K	Potassium	6.684	13.71	NA	0.24	NA
Mg	Magnesium	1.219	13.81	10.43	0.30	0.38
Mn	Manganese	0.001	24.23	21.34	0.20	0.25
Mo	Molybdenum	0.003	68.87	13.76	0.43	0.56
Na	Sodium	0.788	15.86	18.00	0.16	0.21
P	Phosphorus	2.794	9,73	8.15	0.29	0.40
Pb	Lead	0.008	22.16	NA	0.10	NA
S	Sulphur	0.509	9.79	9.71	0.46	0.37
Se	Selenium	0.014	11.92	10.43	0.32	0.28
Si	Silicon	0.089	22.89	14.30	0.11	0.22
Sr	Strontium	0.001	14.32	10.86	0.18	0.34
Zn	Zinc	0.065	18.31	18.63	0.24	0.11

Heritability estimates represent Bayesian approximations of broad sense heritability (H^2=Var (among lines)/Var (among lines)+Var (among replicates) 0f shoot and root phenotypes.NA not included in GWAS due to high Bayesian RSD and/or low H^2.RSD=Bayesian relative standard deviation

A hydroponic trial was carried out to determine the effect of molybdenum (Mo) on utilization and uptake of macro and micronutrients in different rice cultivars. The experiment was conducted using a randomized complete-block design, with a split-plot arrangement of treatments and three replications. Four rates of Mo (0, 0.01,0.1 and 1mg L^{-1}) and five cultivars (MR219, HASHEMI, MR232, FAJRE and MR253) provided the main and sub-plots, respectively. The results showed that the enhancement of Mo levels (from 0.01 to 0.1 and 0.1 to l mg L^{-1}) led to increase of root Mo uptake by 81.7 and 61.6% and shoot Mo uptake by 43 and 87%, respectively. Also, Mo application significantly affected shoot Phosphorus uptake so that highest shoot Phosphorus (P) uptake (0.43% $plant^{-1}$) was achieved at l mg Mo L^{-1} but there was no significant influence on root P uptake. Shoot Iron (Fe) uptake was inversely proportional to increment of Mo rates therefore, the highest rate of shoot Fe (59.05 µgplant-^{1}) was obtained in treatments with least amount of applied Mo. Also, increase in Mo application enhanced manganese (Mn) uptake of shoot but there was no significant effect on Mn root uptake (Zakikhani *et al.,* 2014).

The interaction of molybdenum and variety on Mo uptake in shoots and roots were significant ($p<0.01$) so that highest molybdenum uptake in shoots (0.708 µg $plant^{-1}$) and roots (0.669 µg $plant^{-1}$) were observed in MoV3 treatment. This might account for the high efficiency of cultivar V3. Also, binding sites of Mo might be controlled genetically. Mandal *et al.* (1998) stated that application of Mo increased uptake of Mo in lentil plants grown in soil. Moore and Patrick (1991) reported that Mo contents of the rice were positively correlated with activities of the molybdate ions. Other results revealed that concentration of Mo in clover tissues enhanced when application of Mo increased at different cutting stages (Nayyar *et al.*1980). In contrast, Weng *et al.* (2009) noted that an ascending trend in Mo content in round leaf *cassia* plants was with increasing the Mo application of Mo (up to 2mg kg^{-1}) but plant Mo content at 4mg kg^{-1}Mo were lower than that 2mg kg^{-1} which may be due to active adsorption of Mo.

Stout et al. (1951) reported that phosphorus accounts for Mo release from the root cells into system of translocation.

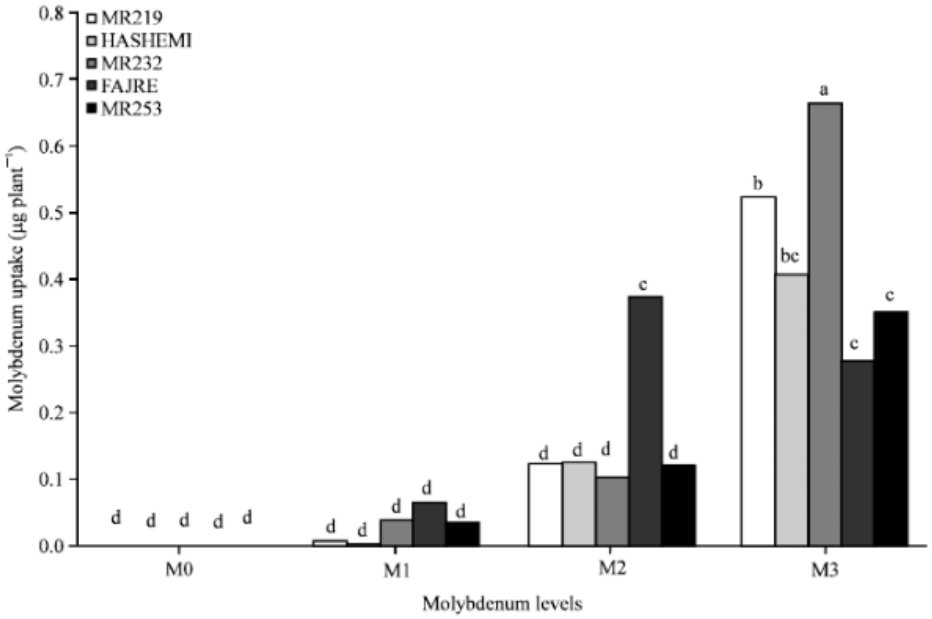


Figure 5: Root molybdenum uptake by rice varieties grown hydroponically under different levels of molybdenum. After Zakikhani *et al.*, 2014

Table 4. Descriptive statistics of agronomic and grain element traits in the PRAY panel grown in four environments (IR12: IRRI 2012, IR13: IRRI 2013, PR12: PhilRice 2012, PR13: PhilRice 2013). After Cu *et al.* 2021

Trait	IR12	IR13	PR12	PR13	H^2
B	6.4 ± 1.5^{b}	13.1 ± 3.5^{a}	2.5 ± 1.0^{d}	4.2 ± 2.1^{c}	0.26
Ca	96.8 ± 14.7^{b}	106.1 ± 16.2^{a}	99.3 ± 12.7^{b}	104.4 ± 15.7^{a}	0.90
Co	0.043 ± 0.017^{c}	0.052 ± 0.025^{a}	0.048 ± 0.016^{b}	0.055 ± 0.18^{a}	0.79
Cu	4.6 ± 1.7^{b}	5.9 ± 1.1^{a}	3.3 ± 0.6^{c}	3.2 ± 0.6^{c}	0.55
Fe	11.9 ± 2.0^{b}	12.6 ± 1.5^{a}	10.6 ± 1.6^{c}	11.7 ± 1.5^{b}	0.76
K	3287 ± 343.7^{b}	3521 ± 343^{a}	2862 ± 266.2^{c}	3471 ± 294^{a}	0.82
Mg	1455 ± 123.8^{c}	1485 ± 122.4^{b}	1268 ± 124.4^{d}	1516 ± 96.1^{a}	0.70
Mn	28.3 ± 4.6^{b}	33.3 ± 6.4^{a}	23.7 ± 3.9^{d}	25.1 ± 4.7^{c}	0.83
Mo	1.03 ± 0.35^{b}	1.56 ± 0.45^{a}	0.40 ± 0.098^{c}	0.36 ± 0.099^{c}	0.73
Na	13.8 ± 4.0^{b}	19.8 ± 10.1^{a}	10.3 ± 2.6^{c}	10.0 ± 3.6^{c}	0.47
P	3882 ± 374^{b}	4014 ± 383^{a}	3445 ± 317^{c}	3994 ± 320^{a}	0.79
Zn	25.2 ± 4.9^{a}	23.3 ± 3.8^{b}	21.0 ± 2.7^{d}	22.1 ± 3.3^{c}	0.85
DF	93.3 ± 17.5^{a}	77.6 ± 10.7^{c}	74.8 ± 11.3^{c}	81.0 ± 9.7^{b}	0.76
GY	274.0 ± 136.6^{d}	417.4 ± 141.8^{c}	1003 ± 281.3^{a}	616.5 ± 152.8^{b}	0.38
PH	151.7 ± 34.1^{a}	139.5 ± 29.6^{b}	129.4 ± 18.9^{c}	131.9 ± 24.9^{c}	0.89
TGW	–	17.0 ± 2.5^{b}	–	17.7 ± 2.5^{a}	–

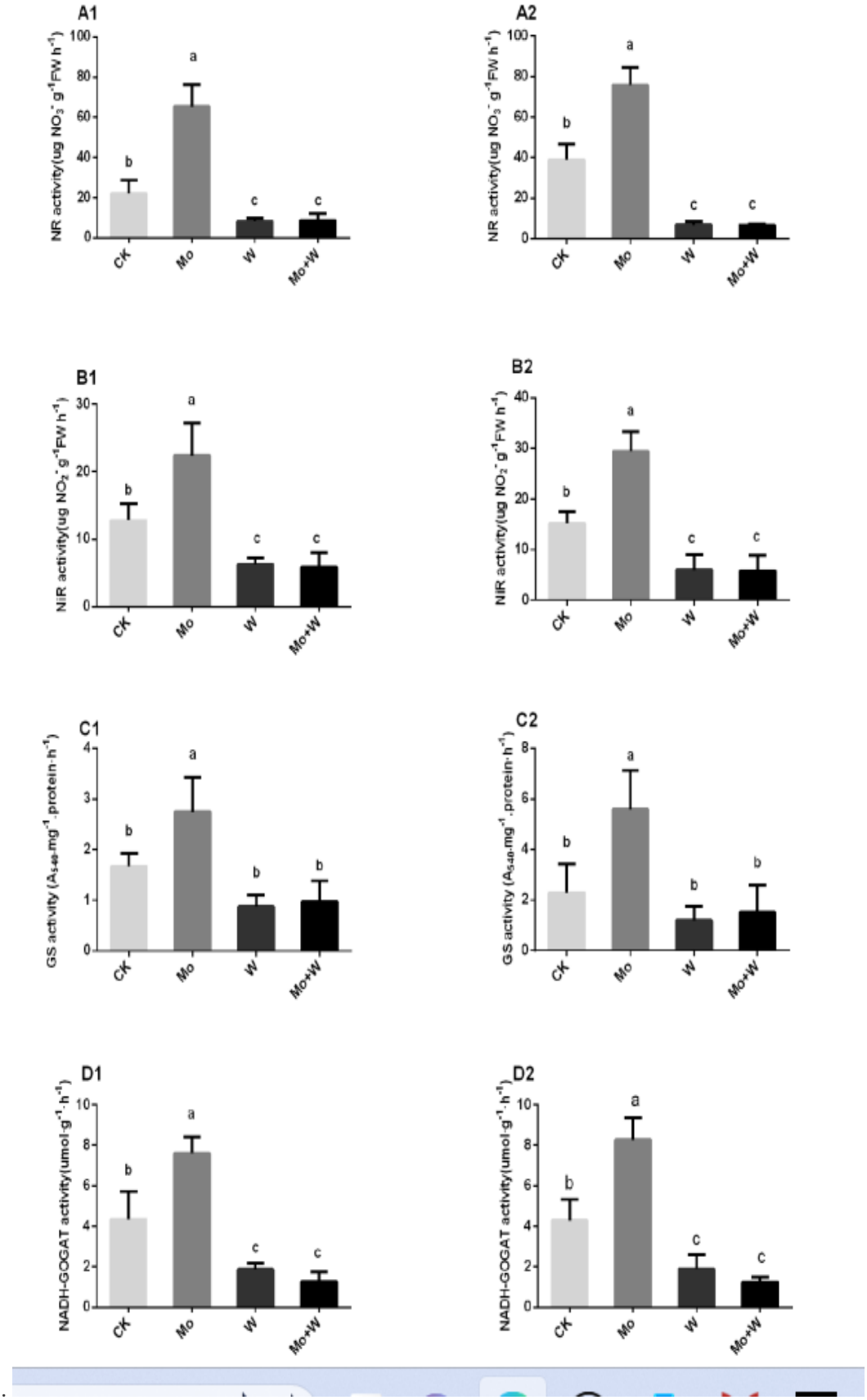


Figure 6: Influence of molybdenum on enzymes of nitrogen metabolism in rice. After Liu *et al.*, 2020.

Molybdenum (Mo) and iron (Fe) are essential micronutrients required for crucial enzyme activities in plant metabolism. It was investigated the existence of a mutual control of Mo and Fe homeostasis in cucumber (*Cucumis sativus*).

Plants were grown under single or combined Mo and Fe starvation. Physiological parameters were measured, the ionomes of tissues and the ionomes and proteomes of root mitochondria were profiled, and the activities of molybdo-enzymes and the synthesis of molybdenum cofactor (Moco) were evaluated. Fe and Mo were found to affect each other's total uptake and distribution within tissues and at the mitochondrial level, with Fe nutritional status dominating over Mo homeostasis and affecting Mo availability for molybdo-enzymes in the form of Moco. Fe starvation triggered Moco biosynthesis and affected the molybdo-enzymes, with its main impact on nitrate reductase and xanthine dehydrogenase, both being involved in nitrogen assimilation and mobilization, and on the mitochondrial amidoxime reducing component. These results, together with the identification of > 100 proteins differentially expressed in root mitochondria, highlight the central role of mitochondria in the coordination of Fe and Mo homeostasis and allow us to propose the first model of the molecular interactions connecting Mo and Fe homeostasis (Vigani *et al.,* 2017).

Table 5: Total molybdenum (Mo) and iron (Fe) contents in whole cucumber plants grown for 10 d under single or combined Mo and Fe starvation.

µg Mo g^{-1} DW	µg Fe g^{-1} DW	
Control	13.839 ± 2.430	656.696 ± 61.143
-Mo	0.282 ± 0.036 **	435.903 ± 22.352 *
-Fe	29.606 ±3.592 *	111.96 ±14.645 **
-Mo-Fe	0.520 ±0.205 **	124.012 ±7.611 **

Mo and Fe contents are shown in plants grown for 10 d in control hydroponic medium (+Mo+Fe), in medium devoid of Mo (-Mo), devoid of Fe (-Fe), or devoid of both micronutrients (-Mo-Fe). Each value is the mean SE of three independent samples, each containing a single whole plant. Significant differences with respect to controls in the same experimental conditions: **, $P < 0.01$; *, $P < 0.05$, according to Student's t-test.

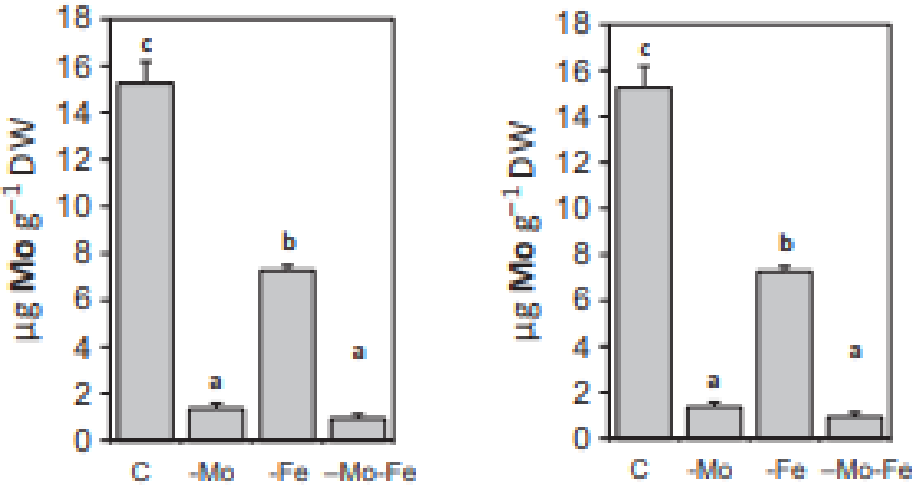


Figure 7: Root and Leaf molybdenum content of cucumber seedlings when grown under control and Mo and Fe starvation.

Ionomics revealed that changes in the Fe nutritional status of a plant are associated with changes in a given subset of elements, including molybdenum (Mo) (Baxter *et al*., 2008a; Baxter, 2009; Murgia and Vigani, 2015). The transition metal Mo is an essential micronutrient (in traces), taken up in the form of molybdate, for nearly all organisms including plants (Bittner and Mendel, 2010; Shinmachi *et al.,* 2010; Llamas *et al.,* 2011; Bittner, 2014). In higher plants, a few molybdate transporters have been identified belonging to the family of sulphate transporters, namely molybdate transporter (MOT1) (Tomatsu *et al.,* 2007; Baxter *et al.,* 2008b; Ide *et al.,* 2011) and MOT2 (Gasber *et al.,* 2011) in *Arabidopsis*, and sulphate transporter in *Stylosanthes hamata* (Fitzpatrick *et al.,* 2008). MOT1 is localized either in mitochondria

or in endomembranes, as reported by Baxter *et al.* (2008b) and Tomatsu *et al.* (2007), respectively, whereas MOT2 exports the stored molybdate from vacuoles to provide it to maturing seeds in senescing plants (Gasber *et al.,* 2011). Molybdate itself is biologically inactive and needs to be complexed by a Mo-binding pterin to form the biologically functional Mo cofactor (Moco). Moco biosynthesis starts in the mitochondrion, with circularization of GTP by Cnx2 and Cnx3 (cyclic pyranopterin monophosphate synthase) enzymes to produce cyclic pyranopterin monophosphate (cPMP). The cPMP intermediate is then exported out of the mitochondrion into the cytosol, where the biosynthesis of Moco is completed in three steps (Bittner & Mendel, 2010). Moco is inserted into the molybdo-enzymes nitrate reductase (NR), sulphite oxidase (SO), xanthine dehydrogenase (XDH) and aldehyde oxidase (AO) which have key roles in either essential or important metabolic processes such as nitrogen assimilation, detoxification of sulphite, purine catabolism and synthesis of abscisic acid (ABA), respectively. A fifth group of molybdo-enzymes, whose members are homologues of the human molybdo-enzyme mitochondrial amidoxime reducing component (mARC), which catalyses the reduction of a variety of N-hydroxylated substrates, exists in the genomes of algae, monocots and dicots (Ott *et al.,* 2015). Nearly all eukaryotic genomes with Mo metabolism encode two mARC proteins and all mammalian mARC proteins are characterized by the presence of an N-terminal extension, which targets the mARC protein either to the outer (e.g. pig) or the inner (e.g. mouse) mitochondrial membrane (Ott *et al.,* 2015). In *Arabidopsis*, mARC-2 carries a mitochondrial presequence whereas mARC-1 is lacking such an N-terminal extension, suggesting that these proteins are differentially localized.
In addition to the mineral elements described above, transporters for calcium, molybdenum, copper, chloride, and nickel (Ca, Mo, Cu, Cl, and Ni) are also required for the growth in rice. However, transporters for the uptake of these mineral elements have not been identified in rice, although some of them have been identified in *Arabidopsis*. For example, a transporter (MOT1) for Mo has been identified in *Arabidopsis* (Tomatsu *et al.,* 2007).

QUANTITATIVE TRAIT LOCI

A biparental population consisting of 145 recombinant inbred lines (RILs) derived from a cross between IR64 *(indica*) x Azucena (tropical *japonica*) and previously genotyped with 30,982 SNP markers (Spindel *et al.* 2013) was phenotyped following the same hydroponic protocol used with RDP1. A set of 106 QTLs associated with 19 elements were detected in root and shoot tissue of the RILs. QTLs were distributed on all chromosomes except for chromosome 10, and the average interval size of a biparental QTL was 3.66 Mb (18×the size of the average GWA peak). Six (5.7%) of the biparental QTLs overlapped with GWA peaks for the same element, and four had additional support from POCRE SNPs. As with the GWA peaks, overlapping QTLs associated with the same element in different tissues (roots and shoots) were also rare in the RIL population, with Mo and P being the only ex

Table 6: QTLs associated with molybdenum detected in root and shoot tissue of the RILs. After Cu *et al.*, 2021

QTL	Env.	Chr	StartMb	EndMb	$-\log_{10}P$	PVE%	Add.effect	High all Freq
qMo3.3	1	3	26.76	26.83	6.4	7.2	0.67	0.05
qMo3.3	3	3	26.70	26.78	6.0	6.3	0.17	0.06
qMo8.1	3	8	0.0	0.25	9.2	10.1	0.12	0.85
qMo8.1	4	8	0.0	0.33	8.0	9.9	0.07	0.38
qMo10.2	2	10	5.17	5.28	5.4	4.4	0.10	0.09
qMo10.2	3	10	5.17	5.36	7.1	7.5	0.59	0.09

Mo, as molybdate, enters plant cells through specific transporters belonging to the MOT1 (Molybdate Transporter type 1) or MOT2 (Molybdate Transporter type 2) families. MOT1 family molybdate transporters were first discovered in *C. reinhardtii* and *Arabidopsis* (Tejada-Jiménez *et al.,* 2007; Tomatsu *et al.,* 2007). Knocking out AtMOT1;1 resulted in decreased accumulation of Mo in roots and shoots, and the atmot1;1 mutant exhibited Mo deficiency symptom when grown under limited Mo supply, indicating an essential role for AtMOT1;1 in the uptake of Mo from the soil (Tomatsu *et al.,* 2007; Baxter *et al.,* 2008). Huang *et al.* (2018) demonstrated that the rice Mo transporter OsMOT1;1

transported and controlled Mo concentrations in grain. Until now, the role of MOT1 proteins from small fruit in molybdate uptake, transport, and homeostasis has not been investigated. In this study, a putative Mo transporter with conserved characteristics of the MOT1 family, FaMOT1, was isolated from *Fragaria* × *ananassa* Duch. A phylogenetic tree showed that FaMOT1 was closely related to MdMOT1 from Malus domestica and PpMOT1 from Prunus persica, both of which are also members of the *Rosaceae* family. In addition, the conserved domains analysis shows that the functional domain of FaMOT1 is MFS_MOT1, which is a family of molybdate transporters. The above results suggest that FaMOT1 belongs to the MOT1 family and may be responsible for molybdate uptake and transport in strawberry. However, a characterization of FaMOT1 requires much more work in the future. FaMOT1 expression was higher under Mo-sufficient conditions than under Mo-limited conditions, suggesting that more MoO_4^{2-} was taken up and translocated from roots to shoots. Researchers had cloned and analysed a putative molybdate transporter, FaMOT1, which may encode a molybdate transporter involved in the uptake and translocation of molybdate. Interestingly, the addition of the molybdate analog tungstate led to lower tissue Mo concentrations, reduced the translocation of Mo from roots to shoots, and increased the plants' sensitivity to Mo deficiency. Seedlings cultivated with MoO_4^{2-} altered expression of genes in Moco biosynthesis. As expected, NR activity was higher under sufficient MoO_4^{2-} levels.

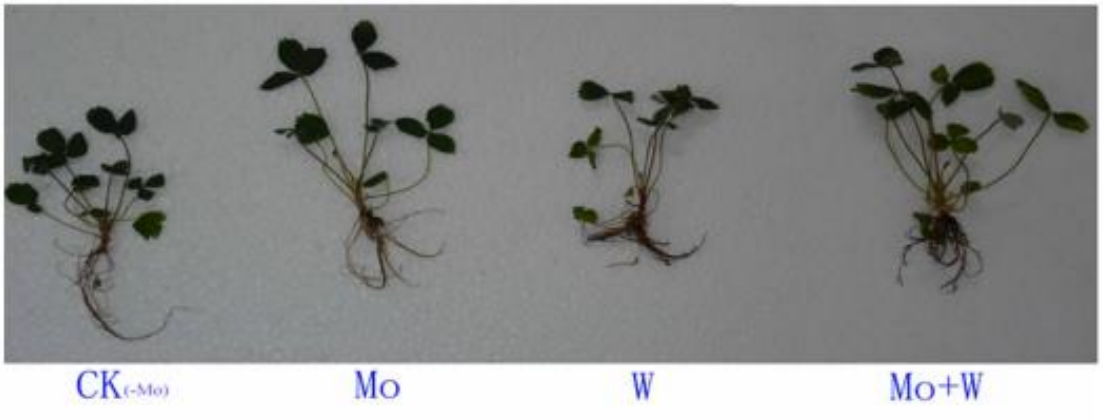


Figure 8: Effects of molybdenum on growth of strawberry seedlings.

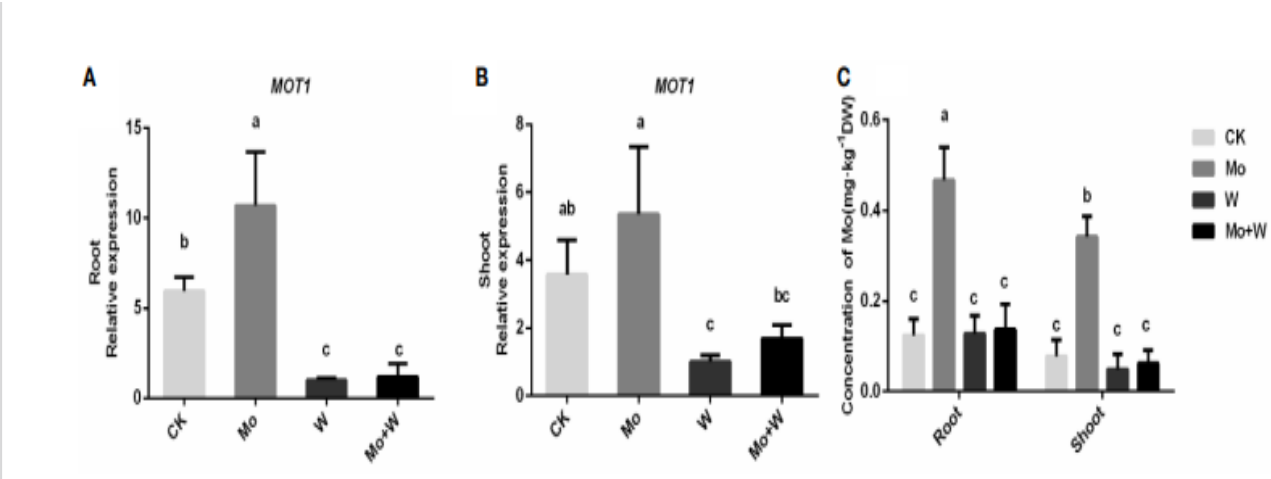


Figure 9: Relative expression of MOT1 in root and shoot under molybdenum nutrition and the corresponding molybdenum concentrations. After Liu *et al.*, 2020

In eukaryotes, two types of Mo transporters have been found in the green alga *Chlamydomonas reinhardtii:* one with high affinity and low capacity, and the other with low affinity and high capacity (Tejada-Jiménez *et al.,* 2007; Tejada-Jiménez *et al.,* 2011). In *Arabidopsis thaliana*, the sulphur transporter (SULTR) family members SULTR5.1 and SULTR5.2 were shown to be Mo specific transporters and named AtMOT1;2 and AtMOT1;1 (Tomatsu *et al.,* 2007; Gasber *et al.,* 2011; Tejada-Jiménez *et al.,* 2013). In *Lotus japonicas*, LjMOT1 has been shown to be an essential high affinity molybdate transporter (Duan *et al*., 2017), and in *Oryza sativa*, quantitative trait locus (QTL) analysis has shown that OsMOT1;1 is a molybdate transporter (Huang *et al.,* 2018). The *C. reinhardtii* antisensemutantmot1 exhibitedlowerMOT1 expression and reduced MoO_4^{2-} transport (Tejada-Jiménez *et al.,* 2007). NR activity was also lower in mot1, presumably as a result of Mo deficiency. Likewise, atmot1;2 mutant seedlings showed reduced nitrate levels and slightly lower NR activity compared with the wild-type plants (Gasber *et al.,* 2011). However, in the absence of MoO_4^{2-}, the atmot1;2 mutant showed substantially higher nitrate levels and significantly lower NR activity (Gasber *et al.,* 2011). In Lotus japonicas, changes in NR activity coincided with changes in Mo concentration, which strongly suggested that Mo is an essential part of NR and plays a vital role in NR catalysis. In Cucumis sativus, the model of the molecular interactions connecting Mo and Fe homeostasis was firstly proposed by Vigani *et al.* (2016).

GENE EXPRESSION

To investigate whether the expression of the FaMOT1 gene was regulated by Mo availability, we performed quantitative RT-PCR to quantify FaMOT1 mRNA in tissue culture seedlings grown under Mo sufficient or deficient conditions. Under standard Mo conditions, FaMOT1 expression in shoots and roots was approximately 50% higher than that of seedlings cultivated under Mo-free conditions.

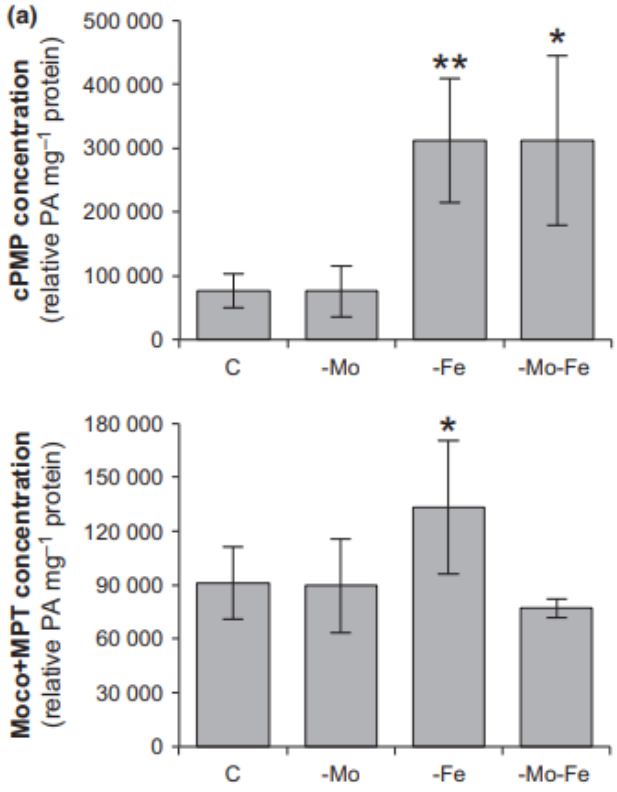


Figure 10: cPMP concentration and Moco+PMT concentration in strawberry under molybdenum nutrition. After Vigani *et al.*, 2017

The first step in Moco synthesis is the formation of cyclic pyranopterin monophosphate (cPMP) by guanosine triphosphate (GTP) under the action of cofactor for nitrate reductase and xanthine dehydrogenase 2 (CNX2) and nitrate reductase and xanthine dehydrogenase 3 (CNX3). The expression

of CNX2 and CNX3 genes was higher in the roots of seedlings grown on Mo sufficient medium than in the roots of seedlings grown on medium with a Mo inhibitor. A similar trend was observed in the shoots . The second step in Moco synthesis is the conversion of cPMP to MPT, catalyzed by CNX5, CNX6, and CNX7. Both the shoots and roots of seedlings cultured under standard condition.

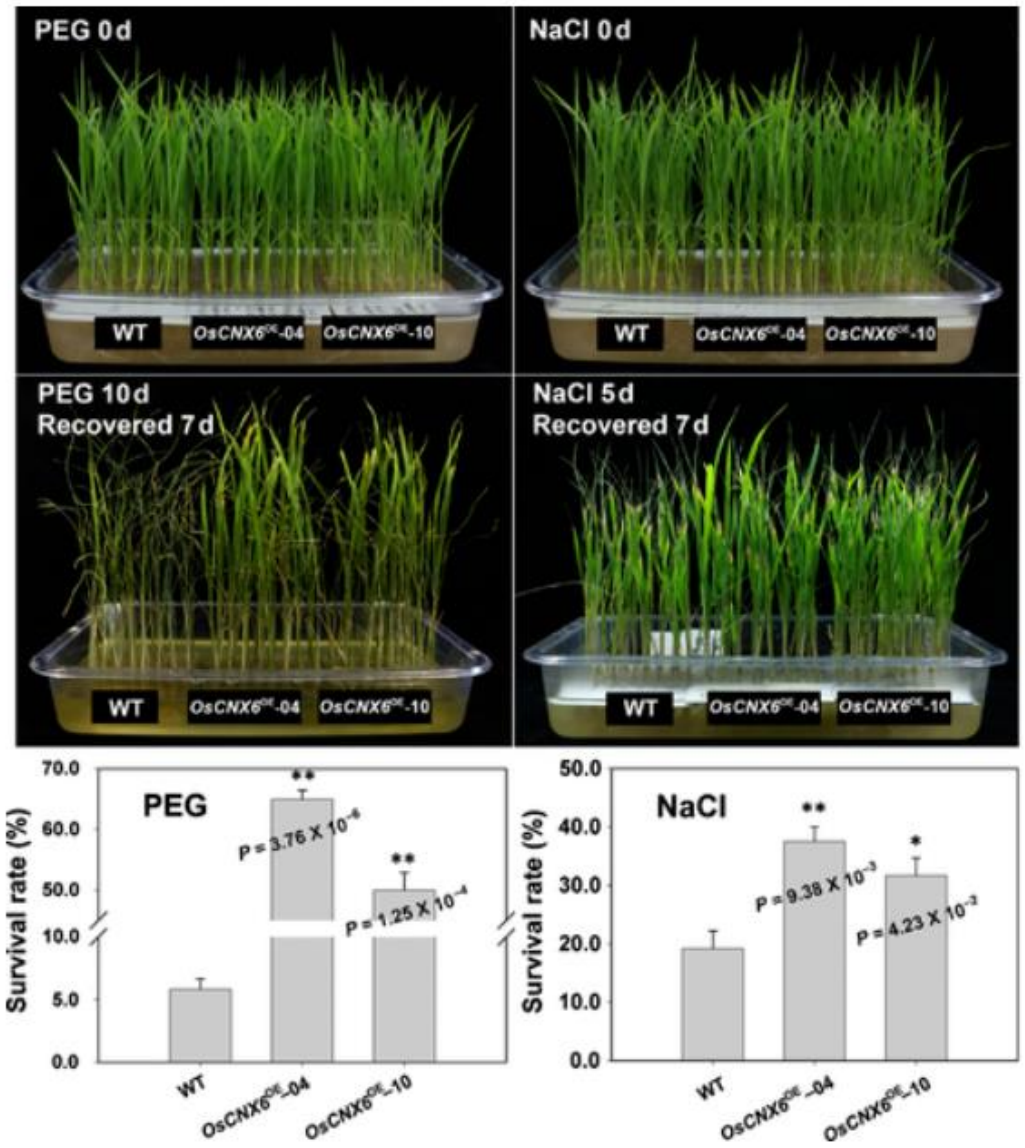


Figure 11: *OsCNX6* overexpression plants can significantly enhance the MoCo-dependent enzyme activities and improved the osmotic and salt stress tolerance without unfavourable phenotypes. After Liu *et al.*, 2020.

The MoCo-biosynthesis pathway in *E. coli* has been well studied, and gene mutants of the MoCo-biosynthesis pathway were shown to decrease NR activity (Hoff *et al*., 1995; Schwarz and Mendel, 2006). To further determine whether CNX6 has biochemical activities, we constructed an *moaE* mutant in *E. coli*, which was highly orthologous to *OsCNX6*, and then transformed the complete coding sequence of *OsCNX6* into an *E. coli* mutant to verify the hypothesis. The results showed that NR activity in the *E. coli* mutant carrying the empty plasmid produced only background levels of NO_2^-, but the level of NO_2^- produced by the *moaE* mutant with *OsCNX6* was 54% of the wild-type, significantly higher than the *moaE* mutant carrying the empty plasmid. The result indicated that the *OsCNX6* could partially complement the *moaE* mutant, and probably had similar biochemical activities to MoaE in *E. coli*.

Expression pattern showed that *OsCNX6* was richly expressed in seed during embryo maturation by quantitative reverse transcriptase PCR and RNA *in situ* hybridization. Furthermore, the *OsCNX6* overexpression plants can significantly enhance the MoCo-dependent enzyme activities and improved the osmotic and salt stress tolerance without unfavorable phenotypes.
Collectively, these data indicated that *OsCNX6* participated in MoCo biosynthesis, and is essential for rice development, especially for seed dormancy and germination, and *OsCNX6* could be an effective target for improving abiotic stress tolerance in rice.
Molybdenum is an essential micronutrient for most living organisms, including humans. Cereals such as rice (*Oryza sativa*) are the major dietary source of molybdenum. However, little is known about the genetic basis of the variation in molybdenum content in rice grain. A study mapped a quantitative trait locus (QTL) qGMo8 that controls molybdenum accumulation in rice. Legumes are also rich sources of molybdenum.
In summary, we have identified *OsMOT1;1* as the causal gene underlying the QTL for Mo accumulation in rice shoots and grains. OsMOT1;1 exhibits molybdate transport activity. The identification of *OsMOT1;1* provides an important insight into the regulation of Mo homeostasis in rice and a useful gene to breed rice varieties resistant to Mo deficiency in soils. Given the importance of cereals as a source of Mo in the human diet, the identification of natural variation at the *OsMOT1;1* locus provides an efficient way to breed rice varieties with Mo enrichment in the grain, which could improve the nutrient quality of grains.

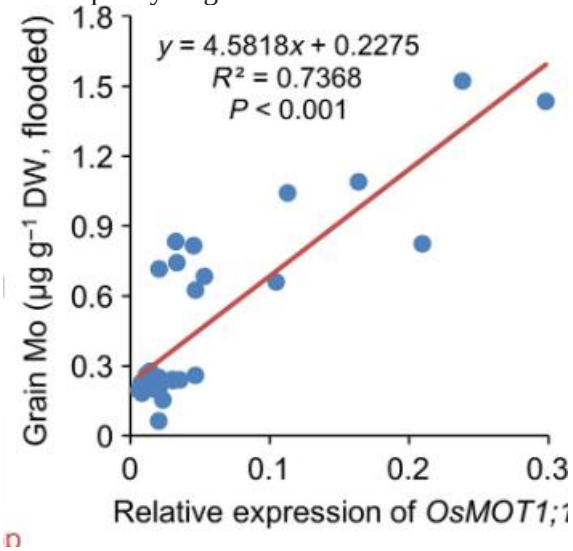


Figure 12: Relationship between rice grain Mo and relative expression of OsMOT1;1

Molybdenum (Mo) is an essential micronutrient for almost all living organisms. The Mo uptake process in plants has been well investigated. However, the mechanisms controlling Mo translocation and remobilization among different plant tissues are largely unknown, especially the allocation of Mo to rice grains that are the major dietary source of Mo for humans. In this study, we characterized the functions of a molybdate transporter, OsMOT1;2, in the interorgan allocation of Mo in rice. Heterologous expression in yeast established the molybdate transport activity of OsMOT1;2. OsMOT1;2 was highly expressed in the blades of the flag leaf and the second leaf during the grain filling stage. Subcellular localization revealed that OsMOT1;2 localizes to the tonoplast. Knockout of OsMOT1;2 led to more Mo accumulation in roots and less Mo translocation to shoots at the seedling stage and to grains at the maturity stage. The remobilization of Mo from older leaves to young leaves under molybdate depleted condition was also decreased in the osmot1;2 knockout mutant. In contrast, overexpression of OsMOT1;2 enhanced the translocation of Mo from roots to shoots at the seedling stage. The remobilization of Mo from upper leaves to grains was also enhanced in the overexpression lines during grain filling. Our results suggest that OsMOT1;2 may function as a vacuolar molybdate exporter facilitating the efflux of Mo from the vacuole into the cytoplasm, and thus, it plays an important role in the root-to-shoot translocation of Mo and the remobilization of Mo from leaves to grains.

For molybdenum there are four known transporter genes in plants (Mendel *et al.*2011), MOT1 and its homologue MOT2 in *A. thaliana*, plus SHST1 in *Stylosanthes hamata* and MOT2 (not a homologue of *A. thaliana* MOT1) from *Chlamydomonas reinhardti*i (Baxter *et al.*2008; Fitzpatrick *et al.*2008; Gasber *et al.*2011; Tejada-Jiménez *et al.*2011). The closest rice orthologue(s) for these four known transporter genes were identified using BLASTp analysis against the RGAP as describe in the methods section. For a number of these orthologues there are significant SNPs within 200 kb of the candidate genes as described in the paragraph below. For the MOT1 orthologue on chromosome 8 (LOC_Os08g01120) there were significant SNPs for grain molybdenum detected at the Texas field site within the "all" accessions analysis. Also of note, a QTL in this region was identified in a Bala x Azucena mapping population (Norton *et al.,* 2012) as well as within two Lemont x TeQing progeny populations (Zhang *et al.,* 2013). For the highest BLASTp hit of the SHST1 gene on rice chromosome 3 (LOC_Os03g09970), there were significant SNPs associated with grain molybdenum concentration within 200 kb of the orthologue. The SNPs that were significant at this location were detected within the "all" accessions analysis at the Faridpur field site and within the "all" accessions analysis and temperate japonicas subpopulation analysis at the Arkansas field site in 2006. The other two SHST1 orthologues in rice were not near significant SNPs. For the *A. thaliana* MOT2 orthologue on rice chromosome 1 (LOC_Os01g45830) there were significant SNPs detected within 200 kb for the Texas "all" accessions analysis, while for MOT2 from *C. reinhardtii* there were no SNPs significantly associated with grain molybdenum for either of the two rice orthologues. The location of significant SNPs associated with grain molybdenum at three of the four known plant molybdenum transporters suggests these genes are likely rice molybdenum transporters.

The protein sequence of the four known transporter genes of molybdenum in plants were obtained from the National Centre for Biotechnology Information (NCBI) database. The closest rice orthologue(s) for these four known transporter genes were identified using BLASTp analysis against the RGAP. The closest rice orthologue to the *A. thaliana* MOT1 gene (NP_180139) (Mather et al.2007) is located on chromosome 8 at 86335–88510 bp (LOC_Os08g01120) (E-value 1.8e2142). There are at least three rice orthologues for SHST1 from *S. hamata* (CAA57710) (Fitzpatrick et al.2008); one is located on chromosome 3 at 4984577–4992411 bp (LOC_Os03g09970) (E-value 2.5e2239), another on chromosome 8 at 19427423–19432708 bp (LOC_Os08g31410) (E-value 2.7e2233), and the third is located on chromosome 3 at 4996773–5002177 bp (LOC_Os03g09980) (E-value 3.1e2218). For MOT2 from *A. thaliana* (NP_178147) (Gasber et al.2011) there is a single rice orthologue on chromosome 1 at 26034930-26033145 bp (LOC_Os01g45830) (E-value 7.3e2146). For MOT2 from *C. reinhardtii* (AEY68285) (Tejada-Jiménez et al.2011) there are two possible rice orthologues: one on chromosome 10 at 20091716–20095059 bp (LOC_Os10g37520) (E-value 6.9e2128) and the other on chromosome 3 at 842386–846445 bp (LOC_Os03g02380) (E-value 3.4e2126).

YIELD IMPROVEMENT

Molybdenum is a micronutrient that is directly involved in the metabolic functions of nitrogen in the plant. The transition metal molybdenum, in molybdate form, is essential for plants as a number of enzymes use it to catalyse most important reactions in the nitrogen acclimatization, the synthesis of the phytohormone, degradation of the purine and the detoxification of the sulphite. There are more than known 50 different enzymes that need Mo, whether direct or indirect impacts on plant growth and development, primarily phytohormones and the N-metabolism involving processes. On the other hand, in the synthesis of ABA uniquely Moco is involved, there on the level of ABA Moco effect is highly vital and ultimately by the response in the stress and the stomatal control, it has a very important role in the rate of transpiration and water relations. The practices that are involved in the fertilization of Mo optimization in crops, has a very important scope in discovering primary source of available N. The deficiency of Mo and to enhance the molybdoenzymes activity, it may be very effective and vital important to use the spray of Mo as foliar application through the soil. The most recent understanding that from the soil how the plant gets access Mo or how they redistribute it is not still clear. However, in the system of prokaryotes, it has been found that in plants it has likewise physiological Mo transport phenotypes. So, the mechanism of transport of Mo in the prokaryotes is needed as well as the reconsideration of anion transport mechanism that is in plants, will provide a help to solve that how this is accumulated. In this review, the discussion covers about the vital importance of Mo to enhance the

productivity for optimizing the yield concentrating on metabolism, uptake, transport, storage, Mo cofactors, application, focusing on some other recent constrains in the recent situation of agriculture, where the yield and development in agriculture may be aided by increasing the Mo nutrition (Rana *et al.*2020).

CONCLUSION

In molybdenum nutrition of legumes and non-legumes emphasis is necessary to find out suitable plant types to perform efficiently under low nutrient content by efficient utilization of mutants and ionomics of environment keeping in mind that both yield and balanced dietary nutrients are made available in the produce of the crop on a pathway for fortification of the element in the dietary part to support human health.

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