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SOME ESSENTIAL TRACE ELEMENTS IN *Salsola vermiculata* (AMARANTHACEAE) USING ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

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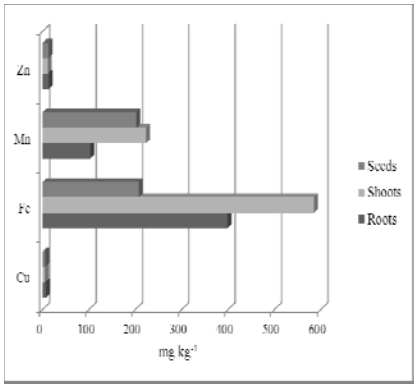
We have used energy dispersive X-ray fluorescence (EDXRF) to determine some essential trace elements (Cu, Fe, Mn, Zn) in *Salsola vermiculata* L. (Amaranthaceae) that is used for ruminant gazing in Algerian arid steppes, in order to gain information on the deficiency and/or excess of some chemical elements for ruminants grazing therein, fed mainly with this species. The precision of the results was assessed by analyzing the certified reference material CRM - IAEA-336 (Lichen). Results show that pasture *S. vermiculata* had substantial levels of Fe and Mn to meet requirements of ruminants. However, it seems that this shrub had insufficient amounts of Cu and Zn than the critical levels established by National Research Council (NRC).



INTRODUCTION

Energy dispersive X-ray fluorescence (EDXRF) occupies a prominent position among the various analytical methods due to its advantages of low detection limit, multi-elemental capability, a non-destructive samples.[1] This analytical technique was often applied to determine chemical composition of multiples matrices such as geological and biological materials.[2]

Animal feeds were usually divided into various nutriments sources such as grassland species, forages, concentrates and mineral supplements. However, efforts to minimize the cost of mineral supplementation in livestock production require a detailed knowledge of the quantity and availability of mineral in feed and forages.[3]

Salsola vermiculata L. (Amaranthaceae) commonly known as Mediterranean saltwort and *rotha* in Arabic, is a perennial native shrub widespread throughout arid and semi-arid regions of the North Africa, southern Europe and Middle East where it is used as a fodder plant for livestock.[4,5] To our knowledge, there are no published studies focusing on the trace elements composition of *S. vermiculata* despite its forage value and importance in North African steppes. Therefore, this study was aimed to evaluate the chemical composition of *S. vermiculata* in natural pasture in relation to mineral requirement of livestock. This information on forage nutritive values would be useful for Algerian steppe as well as for other Mediterranean countries with similar climate and ecological conditions.

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EXPERIMENTAL

Study area

S. vermiculata samples (shoots, roots and seeds) were collected from the area of *Mesrane* in the province of Djelfa (3°03'E longitude, 34°36'N latitude and 830 m elevation) covered by a plant community including *Atriplex halimus,* and *Suaeda fruticosa* found in the Northern steppe of Algeria. The climate is typically Mediterranean, characterized by wet winters and hot dry summers with a mean annual rainfall of 250 mm year^{-1}. The average minimum winter and maximum summer temperatures are 5°C in January and 26°C in July respectively. According to Halitim[6] the principal type of soils in *Mesrane* zone are the calci-magnesic solontchak and isohumic soils.

Plant collection and sample preparation

Three transects of 100 m were laid across the population of *S. vermiculata*. These transects were further divided into three random blocks. Ten plants from each block were randomly harvested to measure element contents. The samples were brought to the laboratory and were washed with distilled de-ionized water to remove any surface contamination and dried for 48 h in an oven at 60 °C. The dried samples were ground to fine powder (particle size fraction of <200μm).

X-ray fluorescence (EDXRF)

Plant samples (about 100 mg for each sample) were analyzed using energy dispersive X-Ray Fluorescence (EDXRF) analysis. The powdered plant sample was pressed to a pellet of 10 mm diameter and 50 mg mass using a 15 ton hydraulic press. EDXRF analysis of the pellets was performed using PAN analytical-Epsilon 3.xl spectrometer. The X ray system consisted of source of excitation ^{109}Cd and a Si(Li) type detector with a resolution of 135 keV for the line Kα (5.9 keV) of Mn with active surface of 30 mm². Spectra X was collected during a time of 2100 seconds for each sample. Triplicate experiments were performed for each plant sample. The system's software (Epsilon 3 software) automatically analyzed the sample spectrum and determined the net intensities of element peaks as soon as the measurement was completed (Fig. 1).

In a similar manner pellets were also prepared from the certified reference materials (CRM) viz. Lichen (IAEA-336) obtained from the International Atomic Energy Agency (IAEA), Vienna, Austria. Prior to irradiation of the sample, pellets of CRM were irradiated as standard for calibration, quantification and verification of results.

The elemental concentrations were determined using the equation:

$$Cx = Cs\ (Ix\ .\ Mx\ /\ Is\ .\ Ms)$$

where Cx is the element concentration present in the sample, Cs is the element concentration present in the standard, Ix is the net intensity of element in the sample, Is is the net intensity of element in the standard, Mx is the mass of the sample and Ms is the mass of the standard.

To estimate the precision of the analytical method, we have determined the |Z-score| as:

$$|Z\text{-score}| = x_{lab} - x_{ref} \,/\, \sigma_{ref}$$

where: x_{lab} is the laboratory measured value,
x_{ref} is the certified value and
σ_{ref} is the standard uncertainty of the certified value.
When the Z-score ≤ 2, the result is in agreement with the certified value;
when 2 < Z-score ≤3, the performance is questionable; and
when the Z-score >3, the result is not in agreement with the certified value.[7]

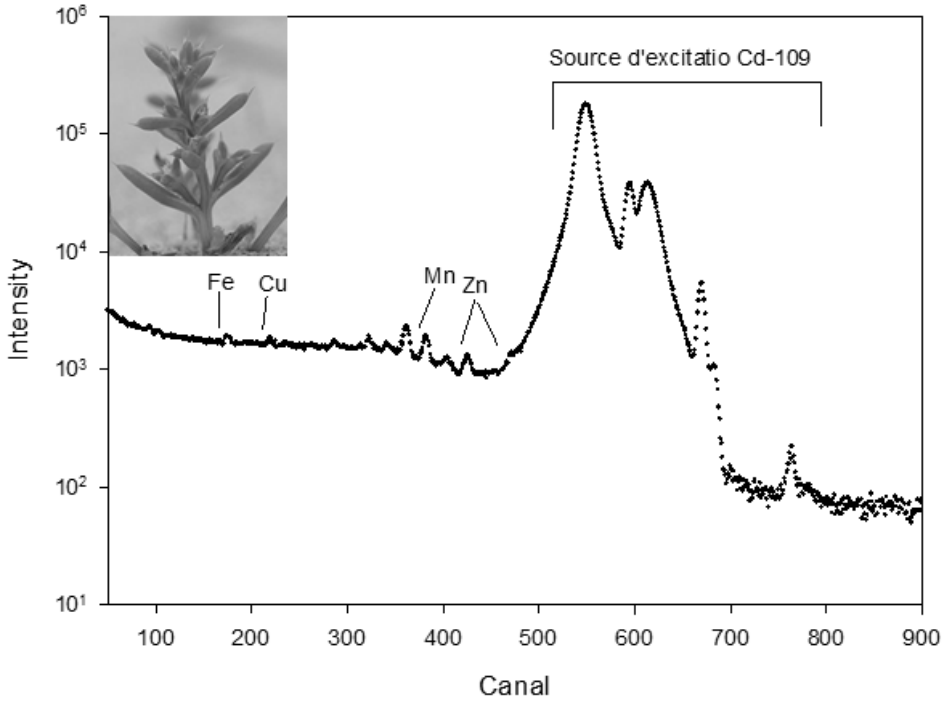

Fig. 1 – Typical EDXRF spectrum of *S. vermiculata* shoot sample.

RESULTS AND DISCUSSION

Chemical element contents

The elemental concentrations were determined using calibration-curve method by comparing the peak areas and heights of the sample with that of certified reference material CRM (standard).

Detection Limits (DLs) were calculated using three times the square root of the background (3σ). The results are presented in Table 1.

$$DLs = Np/\sqrt{Nb} \geq 3$$

Where Np is the number of counts measured on the peak and Nb the number of counts measured on the background. Due to the low DLs obtained, it is possible to determine the analytes usually presented in very low concentrations.

Four essential trace elements were characterized in *S. vermiculata* using EDXRF. The certified reference material IAEA-336 (Lichen) was used for quality control and validation of results. Table 1 represents comparison of our results for the reference material to their certified values. For all elements no significant discrepancy was observed between the measured and reference values (Table 1).

The results are presented in Table 2 where all mass fractions are reported on dry weight basis as the averages of three independent determinations with standard errors. Four essential trace elements quantified in different organs of *S. vermiculata* follow the trend in the descending order; Fe > Mn > Zn > Cu.

The distributions of trace elements between plant parts revealed that both shoots and seeds had approximately the same contents of Mn. However, Fe concentrations in shoots were higher than those located in roots and seeds. For both Cu and Zn, the lowest concentrations were found in shoots.

S. vermiculata shoots (consumable plant parts) contained Fe levels in substantial amounts to meet adult range ruminant requirements (45 mg of Fe kg^{-1} of diet DM for sheep; NRC[8]). Similar findings were reported by Ogebe and McDowell,[9] and Khan *et al.*[10] who evaluated the Fe contained in native forages that grow respectively in semi-arid regions of Nigeria and Pakistan.

It has been suggested that forage crops containing more than 30 mg of Mn kg^{-1} of diet DM will protect livestock from Mn deficiency disorders[8]. In present investigation Mn mass fractions were sufficiently higher than the critical level for ruminant requirements. Other studies have found that *Salsola tomentosa* from central arid zone of Iran[11] and *Atriplex lampa* growing in arid region of Northeastern Patagonia[12] had sufficient amounts of Mn to meet requirements of adult range ruminants.

Table 1

Comparison of measured values of chemical element (mg kg^{-1} on dry mass basis) with certified values in CRM - IAEA-336 (Lichen). Values represent mean ± standard error of mean (n = 3)

Elements	CRM - IAEA-336 (Lichen)			
	Certified value	Measured value	*Z*-score	DLs
Cu	3.6 ± 0.55	3.18 ± 0.13	0.76	2
Fe	430 ± 23.17	423 ± 12.52	0.30	3
Mn	63 ± 2.33	61.98 ± 1.74	0.44	2
Zn	30.4 ± 1.47	30.18 ± 1.83	0.15	1.5

Table 2

Mean values of chemical element mass fractions on dry mass basis (mg kg^{-1}) determined in shoots, roots and seeds of *S. vermiculata* growing in Algerian arid steppe. Values represent mean ± standard error of mean (n = 3). Values with different letters are significantly different ($P < 0.01$, *Tukey's* test)

Elements	Shoots	Roots	Seeds
Cu	4.47 ± 0.98 (b)	6.91 ± 1.22 (a)	5.23 ± 1.77 (ab)
Fe	584.86 ± 12.89 (a)	398.15 ± 24.05 (b)	207.25 ± 21.88 (c)
Mn	222.53 ± 22.13 (a)	102.59 ± 3.11 (b)	202.10 ± 11.63 (a)
Zn	10.46 ± 0.71 (b)	12.31 ± 1.45 (a)	12.04 ± 2.22 (a)

Table 3

Potential chemical element intakes (mg kg^{-1}) by sheep from shoots of *S. vermiculata* growing in Algerian arid steppe. Values represent mean ± standard error of mean (n = 3)

Elements	Potential chemical element intakes per day [a]	NRC requirements [b]	Maximum tolerable limits
Cu	4.47	9	30
Fe	584.86	45	500
Mn	222.53	30	1000
Zn	10.46	27	500

[a] Assumed sheep body weight 50 kg; assumed daily DM intake 1.0 kg.
[b] Recommended average requirements by NRC (2007).

Cu requirement for ruminants is 9 mg of Cu kg^{-1} of diet DM.[8] Present results show that Cu mass fraction (4.47 mg kg^{-1}) was lower than this critical level. These results indicate that the problem of Cu deficiency was expected for ruminants grazing mainly this species. These results were in agreement with those found previously by Chelliah *et al.*[13] in shrubs growing in North Florida.

S. vermiculata was deficient in Zn contents to meet adult range ruminant requirements (27 mg of Zn kg^{-1} of diet DM for sheep; NRC[8]). These results were in agreement with those reported by Tiffany *et al.*[14] who found poor forage Zn concentrations in North Florida. However Abu-Zanat *et al.*[15] and Laudadio *et al.*[16] found high forage Zn concentrations (> 27 mg kg^{-1}) in Jordan and southern Tunisia respectively.

Potential of ruminant mineral intake

Table 3 shows the potential of chemical element intakes and daily chemical element requirements by ruminants from shoots of *S. vermiculata*. It seems that sheep weighing about 50 kg body weight consuming 1.0 kg per day DM of this species could meet its requirements in Fe and Mn. whereas those of Zn and Cu were lower.

CONCLUSION

It can be concluded that *S. vermiculata* shrub contain reasonable amount of Fe and Mn for livestock grazing in arid steppe of Algeria. However Zn and Cu were deficient in this shrub. Consequently, grazing animals need continued mineral supplementation of these elements to prevent diseases and to support optimum animal productivity.

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