RESEARCH ARTICLE

ICP-MS Analysis of Elemental Composition in Soil and Forage Plant Irrigated with Sewage water and Bore Well Water

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ABSTRACT

Ensuring sufficient nutrition for livestock is crucial for maximizing livestock productivity besides bridging the widening gaps between demand and supply of green fodder. The cumbu napier hybrid grass, known for its high biomass yield per unit area and wider adaptability has played a vital role in managing the green fodder requirement to a substantial extent is the focus of the current study. Present research aims to explore the impact of sewage wastewater on the growth of *Cumbu Napier hybrid grass.* The findings revealed that elevated levels of heavy metals *viz*., 37.77 ppm (parts per million) of lead and 10.46 ppm of tin accumulation in Cumbu Napier hybrid grass grown in soil irrigated with sewage water was recorded as compared to those irrigated with borewell water where 7.73 ppm of lead and 1.92 ppm of tin were registered. Hence, the results indicated that recycling the sewage water for high water demanding forage crops such as cumbu napier hybrid grass found to accumulate more heavy metals than bore well water. The order of mean concentrations of heavy metals in the soil obtained was Sn>Sb>As>Pb>Cd.

Keywords: *Sewage water; Borewell water; Elemental analysis; ICPMS; Microwave Digestion Technique, Cumbu Napier hybrid grass.*

INTRODUCTION

In India, fodder is cultivated in approximately 9.13 million hectares, representing about 4% of the nation's total cultivable land. Freshwater is vital for sustaining agriculture, industry, and human life (Abdul *et al.,* 2012). Yet, when it comes to producing cattle feed and fodder, the practical and effective solution would be utilizing sewage water or domestic wastewater that dosed without proper utility although water scarcity is alarming in many part of our country. However, a notable challenge in utilization of wastewater arises due to the presence of heavy metal contamination. Current research work endeavors to explore and address a crucial nexus within the agricultural landscape - the intricate relationship between water scarcity, fodder cultivation, and livestock sustenance. Focusing on India, a country recognized for hosting the world's largest livestock population and serving as a vital hub for the rural economy, that study delves into the implications of water scarcity on the availability of irrigated fodder crops crucial for sustaining livestock productivity. To meet the current level of livestock production and its annual growth in cultivation of perennial fodder varieties, which can yield higher biomass per unit area, is the immediate solution (Babu *et al.,* 2014). By unravelling the complexities of this dynamic interplay, the research aims to contribute valuable insights into the sustainable management of water resources, fodder cultivation practices, and the overall productivity of livestock systems in the context of evolving global challenges.

However, the burgeoning demand for water in agriculture, intensified by a high population, has resulted in a scarcity of water for irrigation. In response to this pressing issue, a sustainable solution involves harnessing alternative water sources, such as sewage water or domestic wastewater for soil

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irrigation, particularly in the cultivation of fodder crops. This practice not only alleviates water shortages but also aligns with principles of water conservation and responsible resource management, offering a potential avenue for sustainable agriculture in regions grappling with water constraints due to burgeoning populations.

The current research focuses on assessing the nutritional composition of sewage water and bore well water, aiming to understand how these distinct water sources influence the soil properties, subsequently, the nutritional composition of the fodder crops cultivated in that soil. Inductively Coupled Plasma Mass Spectrometry (ICPMS) stands out as the most potent technique among atomic spectrometry methods for identifying trace and ultra-trace elements at levels ranging from parts per billion (ppb) to parts per million (ppm). This attributed to its exceptional sensitivity, low detection limits, and the ability to detect multiple elements simultaneously (Hill, 2007 &Hansen and Pergantis, 2007). Through a meticulous comparative study, the research extends beyond nutrient analysis to include an examination of heavy metal levels, providing a comprehensive understanding of the potential environmental and agricultural implications associated with using these water sources for irrigation. This multifaceted approach contributes valuable insights into sustainable water management practices and the overall safety of fodder production and feeding to livestock.

MATERIAL AND METHODS

The present study was carried out at the Department of Forage crops, Tamil Nadu Agricultural University, Coimbatore. This study aims to analyse heavy metals in soils and cumbu napier grass grown under sewage water and bore well water. The present study is focused on analyzing the suitability of sewage water for fodder production. Thus, six different kinds of samples were taken for analysis, viz., sewage water, bore well water, soil irrigated with sewage water, soil irrigated with bore well water, fodder plants grown under sewage water, and fodder plants grown under bore well water. After the pre-processing of samples and proper microwave digestion, the samples have been analyzed for elements. The fodder crop used in the present study is the cumbu napier or bajra napier hybrid grass (CO(BN)5) which is of interspecific origin. Although this fodder crop yields highest biomass (365 t/ha) among available various fodder resources, it demands high water (1800 – 1900 mm) throughout the year for its cultivation.

Chemicals and Reagents

Multi element Aqueous CRM which is a mixture of 30 elements i.e., Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Ti, Tl, V, Zn 100 µg/ml in 5% HNO3was procured from VHG Labs, Manchester, NH , USA. Nitric acid (HNO3), 67-70%, for trace metal analysis procured from Fisher Chemicals, India. HPLC grade water used for the preparation of all samples and standards. All lab accessories used were of “A” grade and duly calibrated. Calibrated micropipettes used with the range of two µl to 1000 µl.

Instrumentation

Inductively Coupled Plasma-Mass Spectrometry [ICPMS], Thermo Scientific™ iCAP™ RQ, equipped with micro mist borosilicate glass nebulizer; quartz cyclonic spray chamber; ICP torch, nickel sampler cone and skimmer cone, Quadrapole mass analyser and mass spectrometry detector. All the samples were analyzed in Kinetic Energy Discrimination (He KED) mode using pure He as the collision gas in the collision/reaction cell (CRC) under optimized auto-tune conditions of the equipment directly from Quality control with Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. To automate the sampling process, an ASX 560Auto sampler (Omaha, NE, USA) used. Sample digestion performed through a closed-vessel microwave digestion system – Multiwave GO (Anton Paar) with a multi wave pro rotor, temperature, and pressure sensor, provided with an auto pressure vent PTFE vessels.

Preparation of Calibration Standard solutions

Accurately 1 ml of mixed standard reference solution pipetted into a 100 ml volumetric flask diluted to the volume to 100 ml using HPLC grade water. This taken as the stock solution used for the preparation of calibration standard solutions and was stored under suitable conditions. Appropriate aliquots taken and further diluted with 5% nitric acid in HPLC grade water to give a series of calibration standard solutions having the concentration range of 1.0, 20.0, 50.0 and 100.0 µg/l.

Preparation of sample solutions

Approximately 0.20 ±0.01 g, accurately weighed, dried homogenized powder samples (already milled with Teflon mortar to avoid metal contamination) of each soil and plant leaf samples were taken in 6.0 ml of concentrated ultra-pure HNO_3 in a tightly closed PTFE vessel and digested in a microwave digester separately. The digestion was carried out in three steps with a constant microwave power, the program was set to increase the temperature 160°C in 10 minutes and held at that for 5 minutes and cooled down the digester at room temperature and diluted the digested samples with HPLC grade water up to 50 ml. Three replicate samples were prepared for each sample for analysis

ICP-MS operating conditions

RF power (W)	1500
Nebuliser pump (rpm)	40
Plasma gas flow rate (L min−1)	14
Extract lens (V)	1.5
Auxiliary gas flow rate (L min−1)	0.8
Pirani pressure (mbar)	1.81
Carrier gas flow rate (L min−1)	1
Penning pressure (mbar)	3.05x10-7
Spray chamber T (∘C)	2
Plasma exhaust (mbar)	0.45-0.56
Sample depth (mm)	8.6
Number of replicates	3

RESULTS AND DISCUSSION

Ensuring the proper levels of essential elements is important for the health of the livestock. The elements are integral part of an animal's diet and are commonly included in feed production. A deficiency in crucial elements such as magnesium, phosphorus, potassium, boron, sodium, cobalt, copper, iron, manganese, zinc and calcium can lead to severe adverse physical effects and, in some cases, even result in death (Georgievskii *et al.,* 1992 & Suttle, 2010). The results obtained by the He collision method in ICPMS with MDS tabulated in Table 1. It provides detailed information on micro and macronutrients derived from water to soil to plants and the results are presented in parts per million. Bore well water recorded 69.02 ppm of sodium, 25.17 ppm of magnesium, 2.441 ppm of potassium, 34.68 ppm of calcium. Additionally, there are trace amounts of 0.01-0.1 ppm for boron, phosphorus, manganese, iron, copper, zinc, and molybdenum, while cobalt is not detected, registering at zero levels.

In sewage water, all these essential nutrients were in elevated quantities with percentages varying from 10% (Magnesium) to 90% (Zinc) than the bore well water due to contamination from different sources. In soil, the nutrients in the soil irrigated with sewage water are high (4% to 35%) except phosphorus, copper and zinc. In soil, the nutrients in the soil irrigated with sewage water were noted high percentages except phosphorus, copper and zinc. The soil irrigated with sewage water exhibits comparatively high levels of major toxic heavy metals, including tin, chromium, nickel, and lead. Fodder plants irrigated with sewage water also show a higher accumulation of heavy metals, as indicated by concentrations such as 10.46 ppm of tin and 37.77 ppm of lead in the samples depicted in Figure 1.

It is understood from the present study that elemental composition of the sewage water-irrigated soil influences the nutrient composition of fodder plants grown in that particular soil. The contamination of soil with toxic trace metals and their accumulation is a major concern for fodder production, which exerts adverse effects on crop growth (Nagajyothi *et al.,* 2010). This might be due to the accumulation of heavy metals in soil including vanadium, chromium, nickel, mercury, cadmium, lead, and arsenic and none of which serve any beneficial nutrition to the crops and are toxic even at low concentrations. Livestock is especially vulnerable to the dangers posed by these toxic elements, leading to extensive research to establish the levels at which toxic symptoms manifest in different animal species (Bampidis *et al.,* 2013). The order of mean concentrations of heavy metals in the soil so obtained was Sn>Sb>As>Pb>Cd. In the comparison between soil irrigated with sewage water and soil irrigated with bore well water, an increase of 13-16% observed for vanadium, chromium, nickel, arsenic, and silver concentration in the sewage water-irrigated soil. However, Tin and lead exhibited even higher percentages when compared to all the other heavy metals, attributable to contamination from various surfaces exhibited in Figure 2.

Among soil pollutant, lead (Pb) is one of the toxic metal pollutants (Shahid *et al.,* 2011). Lead negatively affects various aspects of plant growth, seed germination, seedling development, root elongation, transpiration, chlorophyll production, fodder plants take up lamellar organization in chloroplasts, and cell division (Gupta *et al.,* 2010) .However, the heavy metals as they grow in the soil. Alternate approach of recycling of sewage water, crop rotation and interchange of sewage and bore well water irrigation at certain period will augment the utility of sewage water during crucial condition of water scarcity.

Impact of nutrients on crop growth

It includes the two categories of macro and micro nutrients. We have analysed the levels of macronutrients (Ca, Mg. P and K) and micronutrients (B, Na, Mn, Fe, Co, Cu, Zn, and Mo) in the different categories of water, soil, and fodder plants. The results obtained in the present study and their impacts were well discussed below for comprehensive understanding. These macro and micro nutrients are highly essential for plants to survive, grow, develop and reproduce. Among macro nutrients, nitrogen, phosphorus and potassium are required in large quantities while rest of the macro nutrients are required in moderate quantities to the plants. Micro nutrients are required in small quantities.

Phosphorus is essential for root development, production of flowering, fruiting, transportation of energy and resistant to diseases. Calcium is mainly involved in the cell division and regulates hormonal activity. Potassium involves in the maintenance of osmotic potential of the cell, transfer of sugar and starch and act as an iron carrier in oxidation-reduction process. Magnesium is a vital component of chlorophyll which produces green colour leaves, involves in the production of carbohydrates, oil, fats and vitamins and regulates the uptake of nutrients. Iron involves in the protein synthesis, absorption of other nutrients in plants and oxygen carrier during respiration. Zinc influences the production of growth hormone like auxin and promotes the reproduction process. Manganese is essential for movement of iron, photosynthesis and carbohydrate production. Cobalt plays a vital role in plant metabolism. Copper can neutralize the soil which is at harmful conditions, formation of essential compounds derived from protein and amino acids. Molybdenum is involved in the fixation of atmospheric nitrogen by increasing the efficiency of legume crops and synthesis of vitamin C. Boron increases the absorption rate of nitrogen in plants, regulates potassium/calcium ratio and essential for formation of root nodules (Agritech Portal, 2021). These elements are considered as essential nutrients if it is at the optimum level and as toxic if it get accumulates beyond the optimum level.

Impact of heavy metals on plants

The heavy metals include copper, vanadium, chromium, nickel, arsenic, silver, cadmium, tin, antimony and lead. Copper is also produces toxic effect of plant growth retardation, leaf chlorosis and production of reactive oxygen species (Stadtman and Oliver, 1991). Cadmium reduces the absorption rate of nitrate by inhibiting the nitrate reductase activity and also reduces the activity of enzymes involved in CO2 fixation (Filippis and Ziegler, 1993). Chromium affects photosynthesis in plants by creating snag in the CO2 fixation, transport of electrons and activity of enzymes (Clijsters and Van Assche, 1985). Lead is the most abundant toxic elements available in soil (Asati *et al.,* 2016). It creates negative effects on plant growth, morphology and photosynthesis (Juwarkar and Shende, 1986). Excess nickel produces necrosis, chlorosis and affects calvin cycle in plants (Sheoran *et al.,* 1990). Arsenic reduces fruit yield and leaf weight in tomato (Barrachina *et al.,* 1995). In the present investigation, the mean percentages were determined for Tin, Lead, Cadmium, Antimony, Copper, Chromium, Nickel, Vanadium and Arsenic in cumbu napier grass irrigated with sewage water, with the order being Tin > Lead > Cadmium > Antimony > Arsenic.

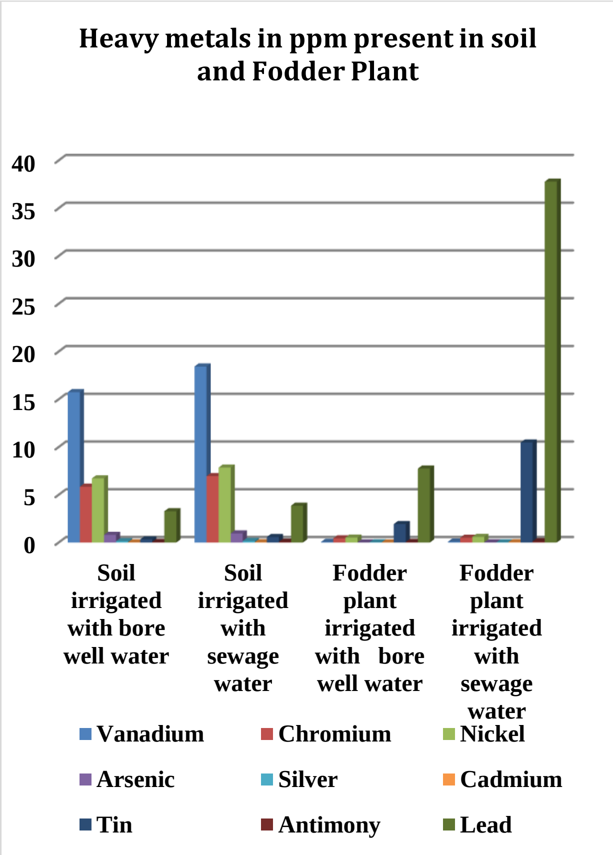

Figure1 Comparative analysis of heavy metal levels in soil and fodder plants irrigated with sewage water and bore well water

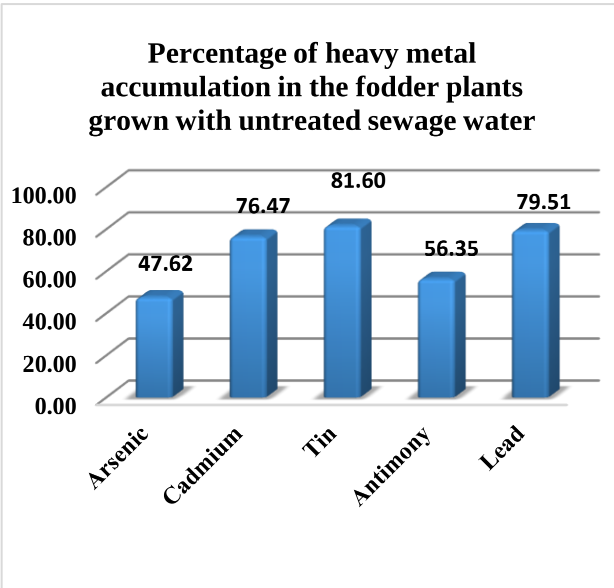

Figure 2. Percentage of heavy metal accumulation in the fodder plants grown with untreated sewage water

Table 1. Analysis of elements of water, soil and forage crop samples

Parameters	Borewell water (in ppm)	Sewage water (in ppm)	Soil irrigated with borewell water (in ppm)	Soil irrigated with sewage water (in ppm)	Fodder plant irrigated with borewell water (in ppm)	Fodder plant irrigated with sewage water (in ppm)
Boron	0.143	0.384	4.254	4.891	11.015	22.464
Sodium	69.02	171.15	85.559	132.95	11.433	24.598
Magnesium	25.178	28.099	2153.69	2340.02	1760.3	2390.25
Aluminium	0.184	1.39	4894.12	6402.58	13.607	17.271
Phosphorus	0.045	1.888	238.846	141.321	311.84	1291.18
Potassium	2.441	7.172	802.192	839.51	3305.79	6110.46
Calcium	34.68	45.982	3623.17	5080.21	1772.73	2485.53
Manganese	0.005	0.052	136.9	162.023	37.973	55.06
Iron	0.024	0.116	523.975	576.855	3.452	3.833
Cobalt	Nil	0.001	4.317	4.888	0.136	0.376
Copper	0.015	0.235	7.872	6.993	2.718	3.193
Zinc	0.008	0.085	17.76	14.169	10.072	21.671
Molybdenum	0.001	0.007	0.041	0.044	0.380	0.524
Titanium	0.142	0.211	223.965	242.33	5.363	7.872
Vanadium	0.027	0.06	15.741	18.421	0.066	0.089
Chromium	Nil	0.003	5.839	6.948	0.432	0.494
Nickel	0.001	0.006	6.713	7.846	0.512	0.589
Arsenic	Nil	0.001	0.796	0.95	0.011	0.021
Silver	Nil	0.002	0.130	0.151	0.016	0.016
Cadmium	Nil	Nil	0.025	0.029	0.008	0.034
Tin	Nil	0.003	0.321	0.574	1.925	10.463
Antimony	Nil	Nil	0.060	0.078	0.055	0.126
Cesium	Nil	Nil	0.409	0.336	0.005	0.003
Lead	0.003	0.016	3.271	3.851	7.739	37.778

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