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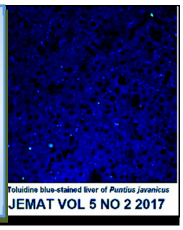

Elevated Molybdenum Concentrations in Soils Contaminated with Spent Oil Lubricant

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ABSTRACT

Molybdenum is an essential trace element of which its pollution due to excessive levels are increasingly reported worldwide. One of the most important usage of molybdenum is as an engine lubricant. Pollution of spent oil lubricant due to indiscriminate dumping of the waste is an important source of molybdenum pollution. In this study, soil samples from various locations in Malaysia were taken from sites which are visible with the dumping of spent oil lubricant and were tested for the presence of soluble and insoluble molybdenum content. The highest concentrations of Mo found for both of the aqua regia digested and ammonium extracted soil sample were at 35.27 and 17.86 mg/Kg soil, respectively. The percentage of ammonium acetate (soluble) extractable Mo to total Mo measured as the aqua regia digested sample was also the highest at 50.64%. The results indicated an excessive content of molybdenum on these soils which warrant remediation process.

INTRODUCTION

Mo is a trace element that is important for all organisms including the important nitrogen-fixing plant enzymes. It is required in trace amount but at elevated levels it is toxic, and ways to remove it from the environment is needed. Mo levels allowed in drinking water must not exceed 0.07 mg/L (WHO, 2011) while the general guidelines for water consumption for livestock are for Mo not to exceed 0.5 ppm [1]. This is because molybdenum is very toxic to the process of spermatogenesis in general and to ruminants specifically, and levels as low as several parts per million can lead to scouring and death at higher concentrations. Mo concentrations greater than 100 mg/L lead to negative effect on mice testes with changes observed to the enzymes superoxide dismutase (SOD), malondialdehyde (MDA), and glutathione peroxidase (GPx) [2] all of which are part of the complex testicular oxidative stress processes. This is probably the toxicity mechanism of molybdenum.

For ruminants, body weighs molybdenum concentration of 10 mg/kg leads to depletion of tissue copper that is exacerbated by dietary sulfate [3,4]. A symptom called hypocuprosis is a result of molybdenum toxicity [4–7]. One of the most serious issues of under the radar is that molybdenum pollution can come from spent oil lubricant especially those with 0.5 to 5% molybdenum content in a typical molybdenum sulphide-based oil lubricant [8]. Molybdenum disulphide in the oil lubricant is converted by oxidation to molybdenum trioxide (MoO_3), which subsequently dissolved in water forming the highly soluble molybdate anions. As spent lubricant oil contains significant Mo concentration, it is important that the concentration of soluble Mo, measured as an ammonium acetate extractable fraction is measured in areas where the soils show visible contamination of spent lubricant oil. This is the aim of this study.

MATERIALS AND METHODS

Molybdenum standard was prepared fresh from an atomic absorption spectrometry standard (Merck, Darmstadt, Germany) and diluted in 1 M ammonium acetate for the ammonium extractable experiment and in aqua regia for the aqua regia digestion experiment. Ammonium acetate (1 M) was prepared by mixing 4 M acetic acid and 4 M ammonia solution of 2.5 L each and the pH adjusted to 7.0 using 1 M ammonia solution or 1 M acetic acid. The whole solution was topped up to 10 L with distilled water. For aqua regia digestion, 1 volume of concentrated nitric acid (Fischer Scientific Sdn Bhd, Malaysia) was mixed with 3 volumes of 6 M HCl (Fischer Scientific Sdn Bhd, Malaysia) [9].

Sample Preparation

Ammonium-extractable Mo from soil was prepared by first air drying soil samples and then ground. The soil was then passed through 2 mm sieve. Extraction was carried out for 16 h using a ratio of 120 ml ammonium acetate for 7.5 g of soil. Then the slurry was centrifuged at 10,000 xg for 10 min, and Mo was measured from the supernatant.

Soil samples (5 g) were digested using aqua regia (16 ml) for 2 h via reflux boiling, and the solutions were made with distilled water to 100 ml. Suitable further dilutions were carried out by diluting the samples with 1 M ammonium acetate, and Mo was then determined directly in this solution [9] on a Perkin Elmer 5100 atomic absorption spectrophotometry (AAS).

RESULTS AND DISCUSSION

The normal range of Mo in soils world-wide is between 0.1 and 7.35 mg/Kg with an average level of 2 mg/Kg [10]. The oxidation states of Mo in soils occur both as 3+ and 6+ (MoO_4^{2-}) but the latter is more dominant [11], and plant takes up Mo in this form through the phosphate pathway [11]. Mo is the cofactor for an enzyme involved in nitrogen fixation and nitrate reduction in plant and hence is an essential trace element [10]. Phytotoxicity as a result of elevated levels of Mo can occur at concentrations of between 10 and 50 ppm. However, concentrations as high as these are rare in agricultural soils [10]. Ruminants are particularly affected by Mo with a concentration of above 5 ppm Mo in forage lead to Cu deficiency induced by Mo leading to scouring and even deaths [7,12,13].

Two out of the eight soil samples visibly seen with contamination with spent oil lubricant showed elevated levels of soluble Mo far higher that the concentrations that can lead to disease in ruminants (**Table 1**). The highest concentration of Mo for both aqua regia digested, and ammonium extracted soil sample occurred from a soil taken very near a motorcycle repair workshop where spent oil lubricant in the soil accumulated to an extent where it colourized the soil black. The workshop is also very near cattle and goat grazing areas.

The percentage of ammonium acetate (soluble) extractable Mo to total Mo measured as the aqua regia digested sample was also the highest—nearly 50%. This probably indicates that the spent oil lubricant contaminated soil sample contained relatively high insoluble MoO_3 that has been weathered to form soluble molybdate ions. This high concentration is alarming and has not been reported before. It is likely that the high soluble Mo content leads from weathering of the molybdenum oxide from spent oil lubricant as reported previously [8,14].

Table 1. Molybdenum concentration in soils samples using aqua regia digestion and ammonium acetate extraction.

Location	GPS	Aqua regia (Total Mo) mg/Kg	Amm. Acetate (soluble Mo) mg/Kg	% soluble Mo
Taman Perindustrian Selaman, Bandar Baru Bangi, Selangor	2.976881 N, 101.747485 E	1.88±0.06	0.039±0.02	2.07
Tmn Sri Serdang, Seri Kembangan, Selangor	3.008749 N, 101.712885 E	5.848±0.96	1.061±0.36	18.14
Bangi Lama, Selangor	2.901538 N, 101.777329 E	5.573±0.92	1.987±0.97	35.65
Bandar Putra Permai, Seri Kembangan	2.986116 N, 101.664723 E	6.523±0.22	2.26±0.98	34.71
Desa Serdang, Seri Kembangan, Selangor	3.010818 N, 101.722534 E	6.75±0.77	0.639±0.13	9.46
Lestari Perdana Seri Kembangan	2.992470 N, 101.673239 E	20.94±0.87	12.912±0.13	61.66
Bandar Baru Bangi, Selangor	2.948245 N, 101.769316 E	35.27±0.41	17.86±0.54	50.64
Tmn Industri Selaman, Bandar baru Bangi, Selangor	2.980545N, 101.748755 E	1.35±0.064	0.204±0.081	14.8

Molybdenum at excess concentrations have been reported as the reason for death or cows and cattle globally but this issue is not being given enough attention since molybdenum is not important pollution for its levels to be monitored regularly [15–17]. Cases of deaths of cattle and ruminants as a result of ingesting plant contaminated with an elevated level of molybdenum from spent lubricant oil indiscriminate dumping has been reported, but the issue has not received enough limelight.

Places contaminated with elevated levels of molybdenum need remediation. Bioremediation of molybdenum in agricultural soils has been successfully attempted in Austria [18], and newer and much better bacterial molybdenum bioreducers have been isolated and characterized [19–29] and may be an important tool for bioremediation in these sites.

CONCLUSION

In the future, reference standard containing Mo from reputable sources will be used as benchmark sample for assessing the accuracy of the method utilized in this study. The method of standard addition is also needed to further asses the accuracy of the developed method. Despite these issues, the concentrations of Mo in the oil lubricant-contaminated soil is indeed very high and for all purpose is enough according to our aim to demonstrate and elevated concentration of Mo that warrants quick action by the relevant authority to monitor this issue. This is a novel reporting on the elevated concentration of Mo in soils in Malaysia. It has not escaped our attention that the use of Mo-reducing bacteria as bioremediation agents can be a tool to solve the toxicity issue.

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