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## Phytostabilization potential of *Saccharum spontaneum* in chromium contaminated soil

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### Abstract

The Philippine archipelago is abundant in extractable metallic resources, which is being exported to other countries. But when global market prices of chromium go down, it is stockpiled temporarily. This study focused on metallophytes growing in a processing plant in Manticao, Misamis Oriental, which stockpiled ferrochromium for the past five years. Plant and associated soil samples in the area were collected, identified, and tested for the amount of Chromium (Cr). Among ten plant species found in the location of a ferrochromium stockpile, the grass commonly known as the wild sugarcane (*Saccharum spontaneum*) from the family Poaceae tolerated the high concentration of Chromium - a characteristic of a metallophyte better suited for phytostabilization. It contained 811.0 mg kg<sup>-1</sup> Chromium in its below ground biomass, and was found to have potential use in a phytostabilization strategy for chromium contaminated soil.

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## Introduction

Chromite and iron ore are among the largest mineral deposits and product of the Philippines (Nettleton *et al.*, 2004; Agub, 2013; NSCB-PEENRA, 2015).

The country produces most of its chromite for export as refractory grade (high-aluminum) chromite concentrate and metallurgical grade (high-chromium) chromite. Chemical grade or high-iron chromite is also produced, mainly for Cr metal production and Cr-based chemicals for paint pigments and leather tanning. Ferrochromium or ferrochrome (FeCr) is an alloy of iron (Fe) and chromium (Cr).

There are times however, that these minerals are stockpiled thereby exposing the ores to sunlight, rain, and wind, undergoing weathering and then consequently being eroded and leached, which may contaminate the soil and ground water.

The presence of excess metals in the soil and water may cause adverse effects to the ecosystem, to the assemblage of plants and animals, and to the health of the community in the surrounding areas. Bioavailable metals though may be taken up by the very few growing plant species called metallophytes.

Metallophytes are plants growing on metal-rich soils such as those found in mining sites and capable of tolerating relatively high concentrations of bioavailable metals in the soil, and are able to survive and reproduce in these types of soil. More specialized under this classification are the hyper accumulators, plants capable of accumulating relatively high concentrations of metals without suffering toxicity (Rascio and Izzo, 2011).

For a hyper accumulator plants, heavy metals and metalloids taken up from soils are deposited and concentrated in the above ground part, either in the stem or leaves or in the reproductive organs. Less than 0.2% of all plant species are known to be hyper accumulators, and around 25% of these are from the family Brassicaceae, tolerant to certain metals, and

tend to take up and translocate 100-1000 times more of one or more of these metals (Rascio and Izzo, 2011).

Several parts within the tropics which are characterized as being metalliferous have not been explored for the collection and analysis of these plants. Over the years, there has been increasing attention to identify indigenous plants which may be used in phytoremediation.

In 2014, Gotera *et al.* reported a new hyper accumulator of nickel, *Breynia cernua*. It is highly possible that similar plants which may take up large quantity of chromium, be it in the roots or in the shoots could be found in a stockpile of ferrochrome, an alloy of Fe and Cr, in Manticao, Misamis Oriental. The stockpile has been in the area, undisturbed, for the past five years and has been colonized by vegetation.

It is interesting to determine, whether or not these vegetation that colonized a long standing pile of ferrochrome, are capable of hyper accumulating chromium, and to which structure it is deposited.

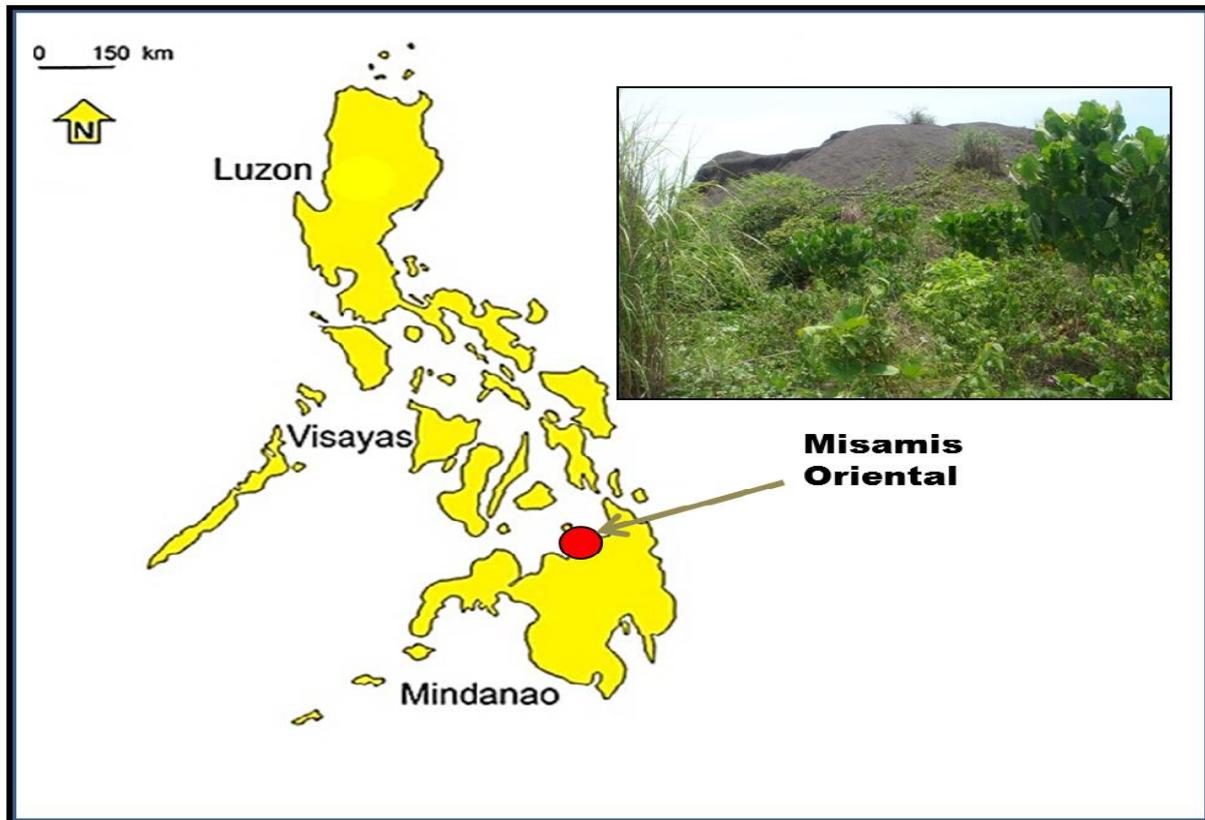
This paper describes results of the survey of metallophytes in the Philippine Minerals and Alloy Corporation (PMAC) in Manticao, Misamis Oriental, Philippines, including its potential use for phytoremediation and phytostabilization of a chromite contaminated soil.

## Materials and methods

### Sampling site

The ferrochromium processing site of the Philippine Minerals and Alloys Corporation (PMAC) in Manticao, Misamis Oriental was chosen for sampling.

The area contains stockpiled ferrochromium which has been left undisturbed for more than five years that allowed the natural colonization by plants. The area is marked as the yellow star in the map shown in Fig. 1.



**Fig. 1.** Geographic location of study site (Manitcao, Misamis Oriental). Inset is a photograph of the ferrochromium stockpile with notable natural colonization by plants. Philippine map modified after Dela Torre *et al.*, 2014.

#### *Sample collection and processing*

Two 100-m transects were set up arbitrarily in the stockpile, where plant samples were collected along the transect lines. Associated soil samples were also collected by taking 10 to 20cm-deep topsoil from the area and placing them in sealed bags.

Plants with reproductive structures were pressed in between newspaper and wooden frames and tied firmly.

These samples were then taken to the University of the Philippines, Institute of Biology Herbarium for taxonomic identification.

Another set of collected plants were placed in plastic bags for processing. The above ground structures were separated from the below ground structures. The roots were cleaned with tap water to remove the soil and other debris.

#### *Sample processing and laboratory analysis*

In the laboratory, the above and below ground structures were further washed with a final rinse of distilled water and later oven-dried. The plants were cut into smaller pieces and stored in sealed and labeled plastic bags.

The processed above ground structures as well as the below ground structures were sent to the Philippine Institute of Pure and Applied Chemistry (PIPAC) for total Fe and Cr content analysis.

The soils samples were measured for pH. These were then placed in clean aluminum trays, oven-dried and stored in sealed plastic bags. A fraction of the soil samples along with the plant samples were sent to the Philippine Institute of Pure and Applied Chemistry (PIPAC) for total Fe and Cr content analysis. Bulk of the remaining soil samples were used for determining soil texture.

**Results and discussion**

The results of chemical analysis revealed that from among the ten plant species collected (Table 1), the species *Saccharum spontaneum* belonging to the family Poaceae was able to take up large amounts of Chromium (811.0 mg kg<sup>-1</sup>) followed by *Euphorbia hirta* from Euphorbiaceae family (130.0 mg kg<sup>-1</sup>) as shown in Fig. 2. The rest of the species also took up the metalloids to a lesser degree, such as the two species of family Fabaceae, another one species of Euphorbiaceae family, and the species of Asteraceae, Commelinaceae, Malvaceae, and Lamiaceae family.

This result is similar to that obtained by Ghosh and Singh (2005) for plants such as *Brassica juncea*, *Datura innoxia*, and *Ipomoeae carnea*. These plant species may have developed mechanism such as the one described by Baker (2010), at which changes happened at the genetic level leading to the development of ecotypes – a plant assemblage called metallophytes because of its ability to survive in a very restrictive environment with high metal content specially chromium; this metalloid is known to cause toxicity in plants (Gomez *et al.*, 2017; Oleveira, 2012; Zayed and Terry, 2003 and McGrath, 1982).

**Table 1.** List of all plants collected along the ferrochromium stockpile in Manticao, Misamis Oriental.

Plant Species	Family
<i>Imperata cylindrica</i>	Poaceae
<i>Macroptilium lathyroides</i>	Fabaceae/Leguminosae
<i>Chromolaena odorata</i>	Asteraceae
<i>Commelina</i> sp.	Commelinaceae
<i>Macaranga tanarius</i>	Euphorbiaceae
<i>Saccharum spontaneum</i>	Poaceae
<i>Sida</i> sp.	Malvaceae
<i>Calopogonium mucunoides</i>	Fabaceae
<i>Euphorbia hirta</i>	Euphorbiaceae
<i>Vitex parviflora</i>	Lamiaceae

In a metalliferous soil with chromium as high as 2,230 mg kg<sup>-1</sup> in Manticao, Misamis Oriental, compared to non-metalliferous soils with chromium with only about 10-25ppm (Fageria *et al.*, 1990; Shanker *et al.*, 2005), plants that were collected were observed to grow and survive in such high concentrations of chromium and the associated Fe (10,620 mg kg<sup>-1</sup> to 34,000 mg kg<sup>-1</sup>) therefore qualifies these collection as metallophytes.

The soil pH at which the metallophytes grew while taking up the metalloids ranges from 6.5 to 7.6.

Soil textural analysis showed a loamy texture between sandy and silty loam with an occasional sandy clay loam (Table 2).

It was also observed that chromium in the above ground (AG) biomass and below ground (BG) biomass were less than 100 mg kg<sup>-1</sup> for all the metallophytes except for the BG biomasses of *Saccharum spontaneum* (811.0 mg kg<sup>-1</sup>) and *Euphorbia hirta* (130.0 mg kg<sup>-1</sup>) in Fig. 2; and the Bioaccumulation Factor (BAF) of all these metallophytes ranges from 0.03 to 1.35 (table 3). This suggests that translocation of chromium to above ground part of plant is difficult, and is confined only in the roots of the collected plant species such as the *S. spontaneum* and *E. hirta*. The translocation factor in table 3 shows this difficulty – all of the plants have low translocation factor values. This is in contrast to what was observed by Zhang *et al.* (2007) in a plant *Leersia hexandra* Swartz.

**Table 1.** Texture and pH of soil associated with each plant sample.

Plants collected	Soil pH	Soil texture
<i>Imperata cylindrica</i>	6.59 @ 23.6°C	Silty loam
<i>Macroptilium lathyroides</i>	6.81 @ 23.9°C	Silty loam
<i>Chromolaena odorata</i>	6.92 @ 24.1°C	Medium loam
<i>Commelina sp.</i>	7.16 @ 24.6°C	Silty loam
<i>Macaranga tanarius</i>	7.29 @ 26.4°C	Sandy loam
<i>Saccharum spontaneum</i>	6.85 @ 26.3°C	Sandy clay loam
<i>Sida sp.</i>	7.52 @ 26.3°C	Sandy loam
<i>Calopogonium mucunoides</i>	7.58 @ 26.3°C	Sandy loam
<i>Euphorbia hirta</i>	7.60 @ 26.5°C	Sandy loam
<i>Vitex parviflora</i>	7.43 @ 27.2°C	Sandy clay loam

The plant absorbs more than 1000 mg kg<sup>-1</sup> of chromium and deposited large quantity of it in the leaves than the stem. Though there was no mentioned of translocation factor, but it can be deduced from the results presented by Zhang *et al.* (2007). In other plants like the *Allium cepa*, chromium is stuck in the vacuoles of roots cells as determined in a study of Nematshahi *et al.* (2002). Liu and coworkers (2008)

reported that hexavalent chromium was primarily deposited in the roots of a hydroponically grown *Amaranthus viridis*. There are studies as well which suggest that accumulation of chromium in different plant organs is following in this order: roots > stem > leaves > seed (Oliveira, 2012; Tiwari *et al.*, 2009 and Gomez *et al.*, 2006).

**Table 2.** The Bioaccumulation and translocation factor of chromium in plants.

Plant Species	Cr content In soil (mg/Kg)	Chromium content		Cr Conc. in Plant (mg/Kg)	BF <sup>1</sup>	TF <sup>2</sup>
		above ground	below ground			
<i>Imperata cylindrica</i>	59.7	3.7	1.3	5	0.0837	2.8461
<i>Macroptilium lathyroides</i>	57.8	8.1	3.3	11.4	0.1972	2.4545
<i>Chromolaena odorata</i>	30.8	25.6	10.7	36.3	1.1785	2.3925
<i>Commelina sp.</i>	75.5	13.8	12.5	26.3	0.3483	1.104
<i>Macaranga tanarius</i>	455	5.3	24.7	30	0.0659	0.2145
<i>Saccharum spontaneum</i>	603	3.3	811	814.3	1.3504	0.0040
<i>Sida sp.</i>	1852	60.3	49.4	109.7	0.0592	1.2206
<i>Calopogonium mucunoides</i>	2,227	22.3	46.5	68.8	0.0308	0.4795
<i>Euphorbia hirta</i>	785	37	130	167	0.2127	0.2846
<i>Vitex parviflora</i>	619	3.6	58.2	61.8	0.0998	0.0618

<sup>1</sup> BF–Bioaccumulation Factor

<sup>2</sup> TF–Translocation Factor.

It then appears that all of these collected metallophytes could not meet the standard for a hyper accumulator described by Baker and Whiting (2002), Prasad and Freitas (2003), and Lorestani *et al.* (2011). Baker and Brooks (1989) as cited by Zhang

*et al.* (2007) declared that chromium hyper accumulator plants pick up at least 1000 mg kg<sup>-1</sup> of chromium.

Mobility and uptake of chromium may have been affected by soil texture. This could be due to adsorption of chromium to surfaces of silts. The silt particles have large surface area than sand, and since most chromium are positively charged, such as Cr(III) and Cr(VI), the metalloid tend to adhere closely to negative sites of the surface, rendering

chromium immobile and reducing bioavailability (Malik *et al.*, 2010). There are other factors influencing solubility, mobility and bioavailability such as the presence of chelating agents specially soil organic matter, redox potential and potential of hydrogen (pH).

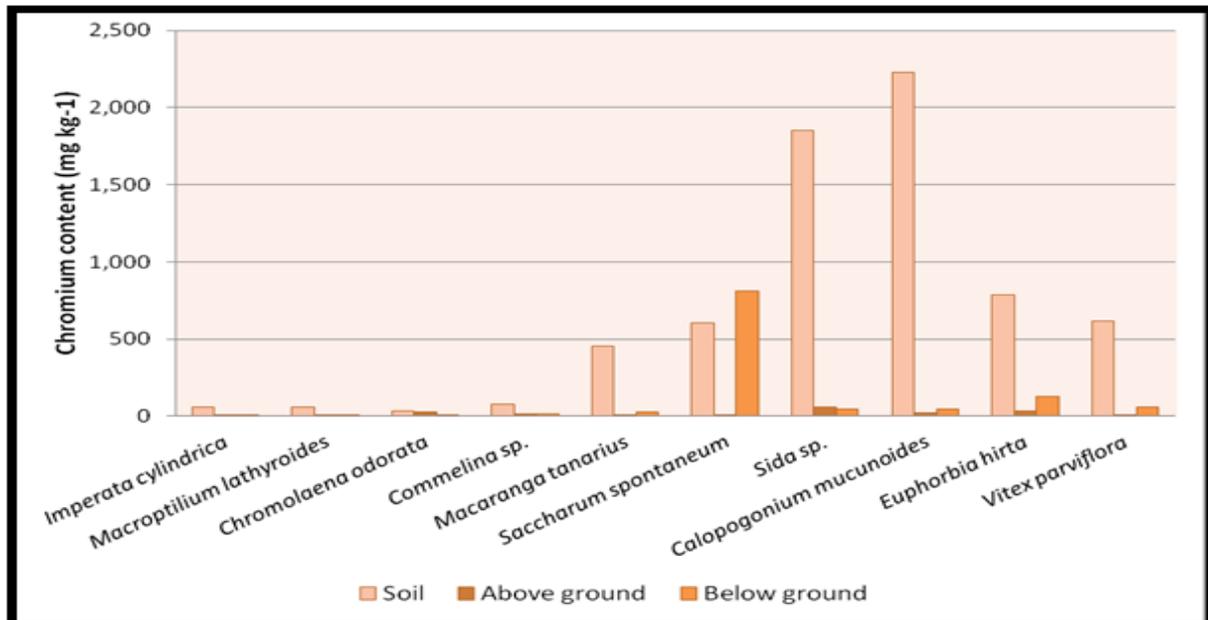


Fig. 2. Chromium content of plant and associated soil samples from Manticao, Misamis Oriental.

The range of pH in the stockpile of ferrochrome in Manticao, Misamis Oriental as shown in Table 2, may suggest that the collected metallophytes absorbed the Cr(VI) species; unlike Cr(III) which are readily available only at low pH. It could be that Cr(III) is present but unavailable. Chromium oxidative states ranges from -2 to +6, but the tri-valent chromium (Cr(III)) and hexa-valent chromium (Cr(VI)) are the most common forms (Oliveira, 2012). It is interesting to do further study to characterize chromium species in that site and its interaction with factors affecting solubility, mobility and bioavailability, including plant tissues where most of the chromium is deposited, to better understand the survival mechanism of the metallophytes.

The large amount of chromium deposited in the roots of *S. spontaneum* and *E. hirta* suggest its utility in phytostabilization project. Considering the effects of

chromium to human health, diversity of animals and growth performance of plants, phytostabilization somehow alleviate problems of contaminations of ground water and soil.

**Conclusion**

Out of the ten plant species studied from the site, *Saccharum spontaneum* demonstrated potential for alleviating problems of chromium contamination. It absorbs relatively high amount of chromium deposited in the roots, effectively restricting the movement of the metal that may contaminate ground water and soil. *S. spontaneum* may be used in the phytostabilization of Cr contaminated soils. In phytostabilization, it is a requirement that the plant is able to survive in soils with high metal concentrations.

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