CHAPTER 3

CHEMICAL PROPERTIES AND POTENTIAL USE IN AGRICUILURE OF LEONARDITE FROM DIFFERENT SOURCES IN THAILAND

3.1 Introduction

Leonardite is a natural organic material through the decomposition process for more than 1,000 million years. This organic material is considered as an oxidized form of lignite that occur at shallow depths, overlying more compact coal in a coal mine (Stevenson, 1979). Leonardite cannot be used as fuel because of its low heating content. Although undesirable as fuel, its high content of humic acid (HA) (which ranges from 30 to 80%), may make it useful as a soil amendment and organic fertilizer. Humic and fulvic acids are usually used in agricultural production and are widely known as having agronomic potential (Ece et al., 2007). Humic substances (humic and fulvic acids), components of soil organic matter, are mostly used to eliminate adverse effects of chemical fertilizers that cause a decrease in soil pH (Chen and Aviad, 1990; Akıncı et al., 2009; Katkat et al., 2009). Humic substances (humics, HS) constitute an important fraction of soil organic matter, have a positive influence on soil fertility and the physical integrity of soil, and increase the availability of nutrients (Stevenson, 1979; Akinremi et al., 2000). There are economic deposits of humate-rich material in Arkansas, Florida, Louisiana, New York, North Dakota, Michigan, Minnesota, Texas, and Wyoming (Burdick, 1965). Humic substances are refractory, dark-colored heterogeneous organic compounds produced in the decay of the total biota in the environment (Stevenson, 1994). Their unique structure makes them a versatile material with applications in industry, medicine, environmental protection, and agriculture. It is becoming clearer, that the presence of humics in soil is necessary for sustainable agriculture, due to their ability to condition the soil, enhance its stability and increase its resistance to erosion (Laker et al., 1993; Spaccini et al., 2002), ensure enhanced biological activity (Canellas et al., 2002; Canellas et al., 2008; Nardi et al., 2000a, b; Zandonadi et al., 2007) and obtain higher crop yields (Antošová et al., 2007; Brownell

et al., 1987; Eyheraguibel *et al.*, 2008)., and may be used in soil remediation (Fava *et al.*, 2004; Stehlíčková *et al.*, 2009; von Wandruszka, 2000).

There are several sources of leonardite in Thailand occurring with lignite which is mined in northern Thailand, particularly Mae Moh mine, Lampang province, and might be a major source of loenardite mineral. The amount of lignite coal in this reserve area are about 1,139 million tons which represents highest volumes of both lignite and leonardite in Thailand. Leonardite was found at bench outcrops of the Mae Moh mine, and has humic acid content around 20 - 40% or more and economically used for humic acids extraction. There are other sources of leonardite in the new mining areas such those in Lamphun, Phayao and Krabi provinces. Quality and property of leonardite might vary widely from deposit to deposit. For appropriate use and application of leonardite, evaluation of its chemical properties is of importance. Therefore, this study aims to investigate the chemical properties of leonardite and evaluate its potential use in agriculture i.e. soil and crop yield improvement.

Recently, the use of leonardite in agriculture at the commercial scale is expanding. However, information related to its properties is quite limited. High plant nutrients and humic acid content in leonardite samples indicates its possible use to improve organic matter, humic acid and some plant nutrient levels in soil. However, the low pH level in leonardite should be raised to an optimum level for plant growth before soil application.

The information obtained from our study should be useful for appropriate use of leonardite in agriculture. In addition, the rate of leonardite and availability of nutrients in this high humus material, should be investigated for use in specific soil and plants before application to obtain maximum benefit from this natural organic material.

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3.2 Materials and Methods

3.2.1 Locations and Leonardite Sampling

Leonardite mines in variuos locations were surveyed and selected for this experiment. Three selected locations regarded as different sources of leonardite were;

- Mae Moh, located in Lampang province,

- Chiang Muan, located in Phayao province and
- Lee, located in Lamphun province

Three spots of each location mentioned above were chosen for leonardite sampling except for Lee area where only two spots could be sampled. In each spot, 3 samples were collected for further analysis. Leonardite samples were collected in all selected areas (expected by diverse sources on site), 18 samples were obtained from Mae Moh (9 samples) and Chiang Muan (9 samples), and only 6 samples from Lee mines. Therefore, a total of 24 samples were obtained and used for further analysis. Analysis was performed with 3 replications of each samples (72 analyzed samples).

3.2.2 Chemical Analysis of Leonardite Samples

All leonardite samples were analyzed for nutrient contents; nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), zinc (Zn) and manganese (Mn) (DOA, 2005) (Table 3.1).

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List	Analytical methods	Unit	Reference
Total Nitrogen	Kjedalh	%	Department of
Total Millogen	Kjeuain	70	Agriculture, 2541
Total Phosphorus	Molybdovanadate reagent	m a /l.a	Department of
(P_2O_5)	(Barton's solution)	mg/kg	Agriculture, 2541
Catal Datagaium (V. O)	Acid digestion method	%	Department of
Cotal Potassium (K ₂ O)	(HNO3 + HClO4); AAS	70	Agriculture, 2541
Calcium, Ca	Acid digestion method	0/	Department of
	(HNO3 + HClO4); AAS	70	Agriculture, 2541
Magnesium ,Mg	Acid digestion method	%	Department of
Wagnesium, wig	(HNO3 + HClO4); AAS	/0	Agriculture, 2541
Iron, Fe	Acid digestion method	%	Department of
non, re	(HNO3 + HClO4); AAS	/0	Agriculture, 2541
Zinc, Zn	Acid digestion method	ma/ka	Department of
Zinc, Zii	(HNO3 + HClO4); AAS	mg/kg	Agriculture, 2541
Manganasa Mr	Acid digestion method	ma/ka	Department of
Manganese, Mn	(HNO3 + HClO4); AAS	mg/kg	Agriculture, 2541

Tabel 3.1 Methods of leonardite analysis for plant nutrients

Some selected samples of leonardite were also analyzed for other characteristics; organic matter content (%OM), C/N ratio, and humic acid (%HA) (Nunan et al., 1998; Deborah and Burba, 1999; DOA, 2005) (Table 3.2).

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List	Analytical method	Unit	Reference
	Measurement of pH in water ratio		Department of
pН	soil: water. = 1:10 (w/w)		Agriculture, 2541
	Measuring the pH of the soil solution	-	
	as well. pH meter		
Organic matter	Walkley Black modified acid-dichromate	%	Walkley and Black,
	digestion, FeSO4 titration method		1934
Total sulfur (TS)	Calculation of carbon and nitrogen	%	
Total sulfur (TS),	analysis.	30	_
C/N ratio	Calculation of carbon and nitrogen		
C/IN Tatio	analysis.	1.2	31
Humic acid	0.5 M NaOH/0.15 M Na ₄ P ₂ O ₇	%	Adapted from Deborah
			and Burba, 1999

Tabel 3.2 Methods of leonardite analysis for chemical and organic properties

3.3 Results

3.3.1 Leonardite Sampling Areas

Leonardite properties might vary from place to place, therefore, we collected the samples from three different spots in Mae Moh and Chiang Muan mines. However in Lee mine, we could obtain the sample only from two spots since the mine was closed during our sampling. The Mae Moh basin located in Lampang province is the largest lignite mine in Thailand with the reserves of 1.46 million tons. Several million tons of leonardite occur near-surface deposits and mix with lignite. We also suggested that this area is the largest reserve of leonardite because an expansion of the commercial use of leonardite was started in this area. However, other new mining areas such as those in Chiang Muan (Phayao province) and Lee (Lamphun province) were found to be good sources of leonardite. Physical appearance of leonardite in Mae Moh and Lee areas was dark brown or black. However, at Chiang Muan area we obtain the sample in the collected piles near the mine's office, not that in the pit mine. In each spot, we randomly collected three samples of leonardite: therefore, a total of 24 leonardite samples were obtained for further investigations (Table 3.3).

sampling location	sampling spot	sample code (number of samples)
1. Mae Moh (Lampang)	1.Mae Moh 1	LD1 (3) (LD1-1 to LD1-3)*
	2.Mae Moh 2	LD2 (3) (LD2-1 to LD2-3)*
	3.Mae Moh 3	LD3 (3) (LD3-1 to LD3-3)*
2. Chiang Muan (Phayao)	4.Chiang Muan 1	LD4 (3) (LD4-1 to LD4-3)*
	5.Chiang Muan 2	LD5 (3) (LD5-1 to LD5-3)*
	6. Chiang Muan 3	LD6 (3) (LD6-1 to LD6-3)*
3.Lee (Lamphun)	7. Lee 1	LD7 (3) (LD7-1 to LD7-3)*
	8. Lee 2	LD8 (3) (LD8-1 to LD8-3)*

 Table 3.3 Location, spot and sample code of leonardite sampling

*Randomly collected 3 samples

3.3.2. Concentration of Plant Nutrients in Leonardite Samples

Leonardite samples from Mae Moh, Lampang province

The leonardite samples from Lampang province were LD1-1 to LD1-3 from Mae Moh spot 1, LD2-1 to LD2-3 from Mae Moh spot 2 and LD3-1 to LD3-3 from Mae Moh spot 3. On the average, all the samples form Mae Moh mine had a very low pH (acidity-alkalinity) with values ranged from 2.38 to 2.55 (Table 3.4). It was considered as strongly acid. The leonardite sample with highest acidity was the LD2 samples (pH = 2.38). Total nitrogen (N; %) ranged between 0.48 to 0.60 %. The leonardite sample with the highest total nitrogen was LD1-3 (0.60 %N). In contrast to nitrogen (N), the concentration of phosphorus (P₂O₅: ppm) in all leonardite samples was quite low. Total phosphorus ranged from 330 to 480 mg/kg. The leonardite sample with highest total phosphorus was LD3-2 and LD3-3 (480 mg/kg). Total potassium (K₂O; %) of the samples ranged from 1.40 to 1.68%. The leonardite sample with the highest total K₂O was LD1-3 (1.68 %K).

Available calcium (avail. Ca; %) ranged from 1.81 to 3.36 %. The leonardite sample with highest avail Ca was LD2-1 to LD2-3 (3.30 to 3.36%). Available magnesium (avail Mg; %) ranged from 0.39 to 0.57 %. Available iron (avail. Fe; %) ranged from 3.11 to 5.33%. The leonardite sample with highest avail Fe was LD2-3

(5.33 %). Available Zinc (avail. Zn; ppm) ranged from 56 to 77 ppm. The leonardite sample with highest avail. Zn was LD1-2 (77 mg/kg). Available manganese (avail. Mn; ppm) ranged from 85 to 126 mg/kg. The leonardite sample with highest avail. Mn was LD3-3 (126 mg/kg) (Table 3.4).

 Table 3.4 Total concentrations of selected plant nutrients contained in leonardite of

 Mae Moh; Lampang

Leonardite	sampling	рН	Total N	Total P_2O_5	Total K ₂ O	Ca	Mg	Fe	Zn	Mn
sample	spot		(%)	(mg/kg)	(%)	(%)	(%)	(%)	(mg/kg)	(mg/kg)
LD1-1	Mae Moh1	2.51	0.48	340	1.61	1.88	0.57	3.25	75	110
LD1-2	Mae Moh1	2.54	0.55	380	1.68	2.00	0.55	3.11	77	109
LD1-3	Mae Moh1	2.48	0.60	340	1.68	2.22	0.54	3.22	54	102
LD2-1	Mae Moh2	2.38	0.51	330	1.50	3.03	0.39	5.33	58	86
LD2-2	Mae Moh2	2.38	0.51	380	1.40	3.05	0.43	5.24	56	86
LD2-3	Mae Moh2	2.38	0.49	370	1.43	3.36	0.42	5.10	67	85
LD3-1	Mae Moh3	2.49	0.54	460	1.44	1.98	0.50	3.21	69	112
LD3-2	Mae Moh3	2.44	0.55	480	1.58	1.81	0.52	3.24	61	123
LD3-3	Mae Moh3	2.55	0.57	480	1.51	2.10	0.51	3.35	63	126
	Mean	2.46	0.53	395.56	1.54	2.38	0.49	3.89	64.44	104.33
	±SD	0.06	0.04	57.76	0.10	0.56	0.06	0.94	7.69	14.84

Leonardite samples from Chiang Muan, Phayao Province

In contrast to leonardite of Mae Moh, the pH values of leonardite samples from Chiang Muan were only slightly acidic with the values ranged from 5.61 to 6.20. It could be considered as moderately acid (Table 3.5). The leonardite sample with highest acidity was LD6-3 (pH 6.20). On the average, the nitrogen content of leonardite samples from Chiang Muan was about half of leonardite from Mae Moh. Total nitrogen ranged from 0.25 to 0.36 %. The leonardite sample with highest N was LD4-2 with the value of 0.36 %N. The P concentration of leonardite from Chiang Muan was also quite low as compared with those from Mae Moh. Total P of the samples ranged from 65 to 95 mg/kg. The leonardite sample with highest total P was LD4-1 with the value of 95 mg/kg. Total K ranged from 1.02 to 1.22 % and the highest total K₂O was obtained with LD 6-1 (1.22 %). Available Ca ranged from 0.55 to 0.71 % and available Mg ranged

from 0.70 to 0.74 %. Available Fe ranged from 1.62 to 1.83 % which were about half to Fe concentration in leonardite from Mae Moh. Available Zinc ranged from 49 to 81 mg/kg and available Mn ranged from 50 to 62 mg/kg. The leonardite sample with highest Mn was LD5-2 with the value of 62 mg/kg (Table 3.5).

 Table 3.5 Total concentrations of selected plant nutrients contained in leonardite of

 Chiang Muan; Phayao

Leonardite sampling sample spot		pН	Total N	Total P ₂ O ₅	Total K ₂ O	Ca	Mg	Fe	Zn	Mn
sample	spot		(%)	(mg/kg)	(%)	(%)	(%)	(%)	(mg/kg)	(mg/kg
LD4-1	Chiang Muan 1	5.61	0.34	95	1.09	0.71	0.70	1.73	80	50
LD4-2	Chiang Muan 1	5.63	0.36	71	1.02	0.71	0.70	1.63	63	60
LD4-3	Chiang Muan 1	5.86	0.31	65	1.12	0.64	0.72	1.69	67	52
LD5-1	Chiang Muan 2	6.18	0.33	87	1.13	0.66	0.72	1.78	63	57
LD5-2	Chiang Muan 2	6.18	0.27	85	1.20	0.56	0.74	1.83	81	62
LD5-3	Chiang Muan 2	6.11	0.28	88	1.14	0.57	0.73	1.79	80	55
LD6-1	Chiang Muan 3	6.15	0.25	73	1.22	0.55	0.74	1.70	49	52
LD6-2	Chiang Muan 3	6.11	0.28	66	1.16	0.55	0.73	1.62	64	56
LD6-3	Chiang Muan 3	6.20	0.26	69	1.20	0.56	0.72	1.64	78	58
	Mean	6.00	0.30	77.67	1.14	0.61	0.72	1.71	69.44	55.78
	±SD	0.23	0.04	10.47	0.06	0.06	0.01	0.07	10.36	3.74

Leonardite samples from Lee, Lamphun province

As compare to the pH values of Mae Moh and Chiang Muan leonardite, the pH of leonardite form Lee was the lowest. The pH values of leonardite samples collected from Lee ranged from 1.84 to 2.55 (strongly acid) (Table 3.6). Total nitrogen ranged from 0.42 to 0.57 %. The leonardite sample with highest total nitrogen was LD8-3 with the value of 0.57 %. Total P ranged from 151.9 to 397.2 mg/kg which was higher than those of Chiang Muan. The highest P value was found with LD7-1, 392.7 mg/kg. Total K ranged from 1.90 to 2.71%. The leonardite sample with highest total K₂O was LD 7-2, 2.71%. Available Ca ranged from 0.70 to 1.92 % and available Mg ranged from 0.30 to 0.78%. Available iron ranged from 1.75 to 2.67%. Available Zinc ranged from 19 to 149 mg/kg and available Mn ranged from 83 to 212 mg/kg (Table 3.6)

Lauradita			Total	Total	Total					
Leonardite sample	sampling spot	pН	Ν	P_2O_5	K_2O	Ca	Mg	Fe	Zn	Mn
sample	spor		(%)	(mg/kg)	(%)	(%)	(%)	(%)	(mg/kg)	(mg/kg)
LD7-1	Lee 1	2.40	0.45	392.7	2.61	0.72	0.63	2.18	139	197
LD7-2	Lee 1	2.55	0.42	339.9	2.71	0.70	0.78	2.02	147	202
LD7-3	Lee 1	2.52	0.43	309.3	2.57	1.92	0.40	1.89	149	212
LD8-1	Lee 2	1.99	0.45	221.8	1.94	1.82	0.39	1.75	30	83
LD8-2	Lee 2	1.96	0.48	151.9	2.19	1.54	0.47	2.67	25	86
LD8-3	Lee 2	1.84	0.57	280.9	1.90	1.73	0.30	2.31	19	88
	Mean	2.21	0.47	282.75	2.32	1.41	0.50	2.14	84.83	144.67
	±SD	0.29	0.05	78.42	0.33	0.50	0.16	0.30	60.33	59.18

 Table 3.6 Total concentrations of selected plant nutrients contained in leonardite of Lee; Lamphun

3.3.3 Organic Properties of Leonardite

We also analyzed some organic properties of leonardite i.e. percentages of organic matter (%OM), total carbon (%TC), total sulfur (%TS) and humic acid (%HA). The ratio of carbon-to-nitrogen (C/N ratio) was also calculated.

Organic properties of Leonardite samples from Mae Moh, Lampang province

The leonardite sample with highest organic matter were LD1-1, LD1-2 and LD1-3 with values of 30.45 to 31.27%. Organic matter contained in the rest of the samples was lower than 30% (Table 3.7). It was found that, the sulfur content in leonardite samples were quite high. Total sulfure (TS; %) of leonardite form Mae Moh ranged from 4.22 to 6.36 %. The leonardite sample with highest TS were LD 2-1 with value of 6.36%. The ratio of carbon to nitrogen (C/N ratio) ranged from 25.40 to 37.17. Our results showed that leonardite from Mae Moh ranged from 34.73 to 61.58 %. The leonardite sample with highest humic acid were LD3-2 with the OM of 61.58% (Table 3.7).

Sample	Location	ОМ	TS	C/N	Humic acid
Sample	Location	(%)	(%)	ratio	(%)
LD1-1	Mae Moh1	30.76	5.18	37.17	58.55
LD1-2	Mae Moh2	30.45	5.25	32.02	59.53
LD1-3	Mae Moh3	31.27	5.14	30.48	55.8
LD2-1	Chanyut1	22.30	6.36	25.40	36.65
LD2-2	Chanyut2	22.87	5.50	26.08	34.73
LD2-3	Chanyut3	22.45	5.11	26.13	44.32
LD3-1	BOONSOM1	28.00	4.22	29.93	56.15
LD3-2	BOONSOM2	27.84	4.61	29.17	61.58
LD3-3	BOONSOM3	29.83	4.75	30.22	57.25
5	Mean	27.31	5.12	29.62	51.62
	±SD	3.54	0.57	3.44	9.67
	dards Organic [°] ertilizers ¹	>30% /W	K	≤20 : 1	305

 Table 3.7 Total concentrations of selected chemical properties of leonardite from Mae

 Moh, Lampang

¹Standards Organic Fertilizers, 2548 By Department of Agriculture

Organic properties of leonardite samples from Chiang Muan

The quantity of organic matter (OM; %) ranged from 14.48 to 25.16%. The leonardite sample with highest organic matter was LD4-2 with the value of 25.16%. (Table 3.8). Leonardite from Chiang Muan might be contaminated with soils in the sampling piles resulted in higher pH values (≈ 6.0) than the rest of leonardite samples from Mae Moh and Lee (pH < 3.0). The organic matter of leonardite from Chiang Maun, therefore, was quite low and was the lowest among all the samples (14.48 to 25.1%). Total sulfur (TS; %) ranged from 0.11 to 0.73 %. The leonardite sample with highest TS was LD4-2 (0.73 %). The carbon to nitrogen (C/N ratio) ranged from 32.36 to 41.41. Our results showed that leonardite from Chiang Muan contained humic acid with values ranged from 22.72 to 33.18 %. The leonardite sample with highest humic acid was LD4-1 (33.18 %) (Table 3.8).

Table 3.8 Total concentrations of selected chemical properties of leonardite from Chiang Muan, Phayao.

Sample	Location	ОМ	TS	C/N	Humic acid	
Sample	Location	(%)	(%)	ratio	(%)	
LD4-1	Chiang Muan1	24.00	0.66	41.41	33.18	
LD4-2	Chiang Muan1	25.16	0.73	40.71	31.97	
LD4-3	Chiang Muan1	21.11	0.62	39.36	29.32	
LD5-1	Chiang Muan2	21.03	0.40	37.43	31.63	
LD5-2	Chiang Muan2	15.41	0.50	33.69	23.03	
LD5-3	Chiang Muan2	17.29	0.11	35.61	24.86	
LD6-1	Chiang Muan3	16.08	0.47	36.98	22.72	
LD6-2	Chiang Muan3	18.18	0.46	37.72	25.82	
LD6-3	Chiang Muan3	14.48	0.68	32.36	24.11	
	Mean	19.19	0.51	37.25	27.40	
±SD		3.60	0.18	2.85	3.90	
Stan	dards Organic	>30%	mon -	<20:1	-202-1	
F	Fertilizers ¹	/W	N - V	≥20∶1	202	

¹ Standards Organic Fertilizers, 2548 By Department of Agriculture

Organic properties of Leonardite from Lee

Among leonardite samples from the three locations, leonardite samples from Lee, Lamphun contained the highest amount of organic matter 48.66 to 61.02%. At Lee mine, LD8-3 contained the highest amount of organic matter (61.02%) (Table 3.9). Total sulfur (TS; %) ranged from 1.87 to 5.12 %. The ratio of carbon to nitrogen (C/N ratio) ranged from 62.32 to 69.66. Our results showed that humic acid contained in leonardite from Lee ranged from 39.19 to 85.05 %. The leonardite sample with highest humic acid was LD8-3(85.05%) followed by LD8-2 (77.86%).

a 1		ОМ	TS	C/N	Humic acid
Sample	Location	(%)	(%)	ratio	(%)
LD7-1	Lee 1	53.78	2.96	69.49	44.22
LD7-2	Lee 1	48.66	1.87	66.64	41.85
LD7-3	Lee 1	48.78	2.33	66.09	39.19
LD8-1	Lee 2	53.96	5.12	69.66	72.44
LD8-2	Lee 2	54.75	3.27	66.94	77.86
LD8-3	Lee 2	61.02	5.01	62.32	85.05
1	Mean	53.49	3.43	66.86	60.10
	±SD	4.17	1.24	2.45	18.76
	ards Organic ertilizers ¹	>30% /W	-	≤20 : 1	31

 Table 3.9 Total concentrations of selected chemical properties of leonardite from Lee,

 Lamphun.

¹Standards Organic Fertilizers, 2548 By Department of Agriculture

3.4 Discussion

The nutrients content in Leonardite

Although the pH values of leonardite was strongly acid, various nutrients necessary for plant growth were found to be in large quantities particularly trace elements. Therefore, leonardite could still be used to improved nutrient level in soils. In our study, major elements including total nitrogen (%N) and total potassium (%K₂O) ranged from 0.25 to 0.60 %, and 1.02 to 2.71 %, respectively. From the results of other studies, total N varied widely from 0.73 to 1.79 % (Arif *et al.*, 2013; Halil *et al.* 2011; Ali *et al.*, 2007; Alfredo *et al.*, 2005 and John *et al.*, 1998), and our results were somewhat in between these values (Table 3.10). On average, high value of K was found in the samples collected from Lee mine (1.90 to 2.71 % K₂O). Alfredo *et al.* (2005) and Halil *et al.* 2011 reported the analyzed concentration of K in leonardite to be 0.51 and 3.97 (%K), respectively.

The major nutrients (N and K) contained in leonardite were in the range of higher than the standard values of organic fertilizer (DOA, 2005). However, the total P values of all our leonardite samples were very low (65 to 480 mg/kg = 0.0065 to 0.0480%) and much lower than the organic fertilizer standard values (>0.5%). The results were in accordance with all the previous reports of P concentration in leonardite

(Arif *et al.*, 2013; Halil *et al.*, 2011; Ali *et al.*, 2007; Alfredo *et al.*, 2005 and John *et al.*,1998). Percentage of Ca and Mg of our samples ranged from 0.55 to 3.36 % and 0.30 to 0.78%, respectively. On average Ca and Mg contents in compost range from 1.2 to 4.5% and 0.30 to 0.57 %, respectively, depending on type of raw material use for composting (Shutsrirung, 2008). The analyzed values of trace elements were as follows; Fe, 1.62 to 5.33 %, Zn 19 to 149 mg/kg and Mn 50 to 202 mg/kg, which are consistent with these Arif *et al.* (2013), Halil *et al.* (2011), Ali *et al.* (2007), Alfredo *et al.* (2005) and John *et al.* (1998). Our results suggested that the P content of leonardite should be raised by applying high P materials such as rock phosphate before being developed as soil amendment and/or organic fertilizer. In addition, the pH values of the soil mixed with leonardite should be measured prior to crop cultivation since the Fe content in leonardite was quite high and might be toxic to the plant at low pH due to high solubility of all trace elements.

 Table 3.10 Comparison of nutrients levels contained in leonardite obtained from various experiments

Element	Arif <i>et al.</i> (2012)	Halil <i>et al.</i> (2011)	Ali <i>et al.</i> (2007)	Alfredo <i>et al.</i> (2005)	John <i>et al.</i> (1998)
N (%)	1.79	1.12	0.73	1.17	0.0012
P (%)	0.00024	0.09	0.00042	0.04	0.0013
K (%)	0.00135	0.51	0.014	3.97	0.002
S (%)	na	0.11	na	na	0.03
Ca (mg kg ⁻¹)	na	14,000	na	na	8,878.00
Mg (mg kg ⁻¹)	na	2,400	na	na	585.00
Na (mg kg ⁻¹)	na ch	960	na	na	636.00
$B (mg kg^{-1})$	na Chi	na	na na Ul	na	2.02
Fe (mg kg ⁻¹)	rignants	6,800	na		296.88
$Cu (mg kg^{-1})$	na	255	na	28.2	0.01
$Zn (mg kg^{-1})$	na	685	na	64.5	0.18
$Mn (mg kg^{-1})$	na	120	na	66.2	1.84
pH	6.80	6.70	4.24	na	na
Organic matter (%)	54.5	50.60	43.60	na	na
Humic + Fulvic acids (%)	50.5	41	na	na	na
Humidity (%)	16	na	na	na	na
Heavy metal content	Below threshold values	na	na	na	na

na = not available

Organic properties of leonardite

We also analyzed some organic properties of leonardite i.e. percentages of organic matter (%OM), total carbon (%TC), total sulfur (%TS) and humic acid (%HA). The ratio of carbon-to-nitrogen (C/N ratio) was also calculated. The quantity of organic matter ranged from 14.48 to 61.02 %. As we discussed above that leonardite from Chiang Muan might be contaminated with soils in the sampling piles resulted in high pH values, the organic matter of leonardite from Chiang Maun, therefore, was quite low and was the lowest among all the samples (15.4-25.1%). All leonardite samples from Lee mine contained the highest amount of organic matter (48.66 - 61.02%). These amounts of OM determined were in accordance with the OM values in leonardite determined by Ali et al. (2007) and Sanli et al. (2013) (43.60 and 54.5%, respectively). On the average, the same trend was observed in the calculated values of TC and C/N ratio with value ranging from 8.61 to 34.30% and 25.40 to 69.66, respectively. The total sulfur ranged from 0.11 to 6.36%. On average, the sulfur content in leonardite were negatively correlated with the pH value i.e. the lower the pH value, the higher TS content in leonardite. The pH values of leonardite from Mae Moh and Lee mines (LD1, LD2, LD3, LD7 and LD8) were lower than 3 (1.84-2.55) with the TS ranging from 4.22-6.36% while the pH values of leonardite from Chiang Muan (LD7 and LD8) were higher than 5.5 with the TS range from 0.41-0.73%. Leonardite with high sulfur content has a high potential to produce more acidity by sulfur oxidation when incorporating into the soils. Soil acidity can reduce crop yield by directly affecting roots and increasing the availability of toxic elements. Most plants perform best at a soil with pH between >5.5to 6.8 (Shutsrirung, 2008b). Adjusting the pH of leonardite by lime or other materials which can raise its pH to the suitable range for crop production should be considered before soil application. Among organic matters, leonardite contains very high humic and fulvic acids (40-85%) compared to that of peat (10-20%) and compost (2-5%). Our results showed that leonardite from Mae Moh (LD1, LD2 and LD3) and Lee mine (LD7 and LD8) contained quite high amount of humic acid (34.73-61.58 and 39.19-85.05%, respectively). Humus (humic acid and fulvic acid) in organic material acts as a significant reserve of plant nutrients and improves soil structure and water holding capacity. However, organic matter content in most agricultural soil under modern agriculture is quite low (<1%) thus very low humus content (Shutsrirung, 2008a).

Organic matter depletion results in a decrease in crop productivity. Therefore, natural high humic acid material like leonardite could be used to improve organic matter, humic acid and some plant nutrient levels in the soils.

Conclusion

The pH values of leonardite samples ranged from 1.84-6.20. The leonardite samples from Mae Moh and Lee (LD1, LD2, LD3, LD7 and LD8) were considered as extremely acid with the pH values below 3 (pH 1.84 to 2.55). Pochadom et al. (2013) reported that the pH of leonardite from lignite mine was around 4, which is strongly acidic. In our study: however, the pH values of the three samples from Chiang Muan; LD4, LD5 and LD6 were only moderately or slightly acid (5.61 to 6.20). This might due to the fact that leonardite was already contaminated with ground soil in the collected area. Recently, the pH of most agricultural soil in Thailand is rather acidic due to excess input of agrochemicals. The beneficial effects of leonardite applied to those soils or to acid sulphate soils might not be expected if the pH of leonardite does not improve before application. In contrast, in alkali soils, leonardite might improve the fertility of the soils and help to lower the pH of alkali soil to a level suitable to plant growth. Leonardite from Mae Moh and Lee mine contained quite high major plant nutrients (except for P), low trace elements, and very high humic acid content. Most samples indicated high potential of leonardite to improve soil fertility and crop yield; however, some properties such as pH value and P content should be improved before application.

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