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The use of humic substances - Leonardite as a soil amendment

By

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MERG is a cooperative working group made up of the Federal and Yukon Governments, Yukon First Nations, mining companies, and non-government organizations for the promotion of research into mining and environmental issues in Yukon.

Executive Summary

Humus is dark, organic well-decomposed soil material that helps plants grow. The positive influence of humic substances on plant growth was first discovered in the 19^{th} century.[1] Leonardite is a humic substance—a type of oxidized immature coal widely used as raw material for commercial production of various soil additives in the agricultural sector. The characteristics of Leonardite offer unique properties, such as the ability to bind with heavy metals and to retain water, that suggest it may be a useful amendment in northern re-vegetation efforts.

The Yukon has a long history of mining and has many disturbed sites in need of re-vegetation. The range of soil amendments normally considered in re-vegetation would include topsoil, lime (to reduce acidity), mulch and organic sludge. There is little research about using Leonardite as a soil amendment in mine re-vegetation efforts. This paper reviews literature related to the topic and suggests some next steps for research efforts.

Acknowledgements

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Methodology

Work on this project was comprised primarily of a literature review. Journal articles, magazine articles, conference proceedings, and workshop presentations were examined both in hard copy and in electronic formats, via the Internet. Promising and project specific leads, beyond the theoretical, were followed up with emails and by telephone correspondence. Common terms and definitions are included in Appendix 1.

[1] O.S. Iakimenko **"**Commercial Humates from Coal and their Influence on soil properties and initial plant development" *NATO Science Series: IV: Earth and Environmental Sciences,* 2005, p.365.

Table of Contents

1. Nature of humic substances

Humic substances contain completely decomposed organic matter -- dead plants (and animals). They exist in soils, groundwater, wetlands, and in geological deposits. They are ubiquitous post-mortal organic materials in the environment, abundant in nature and comprise the most abundant pool of non-living matter. Humic substances consist of a complex inseparable mixture of molecules that makes their study difficult. Generally, humic substances contain:

a) Humic acid – the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. The process by which humic acid is formed is called humification—it involves numerous biochemical reactions, connected with the organic and nitrogen cycles in the environment;
b) Fulvic acid-the fraction of humic substances that is soluble in water under all pH conditions;
c) Humin-the fraction of humic substances that is not soluble in water at any pH value.[2]

The International Humic Substances Society (IHSS) has established a suite of standard humic substances including soil, peat, Leonardite and surface water. "Humic substances are involved in many processes in soils and natural waters: e.g., soil weathering, plant nutrition, pH buffering, trace metal mobility and toxicity, bioavailability, degradation and transport of hydrophobic organic chemicals, formation of disinfection by-products during water treatment, and heterotrophic production in blackwater ecosystems." [3] Humic substances are highly chemically reactive yet recalcitrant with respect to biodegradation.[4] The mean residence time (MRT) varies from 250 to 1900 years and shows a stability of humic substances to microbial attack. [5]

2. Importance of humic substances

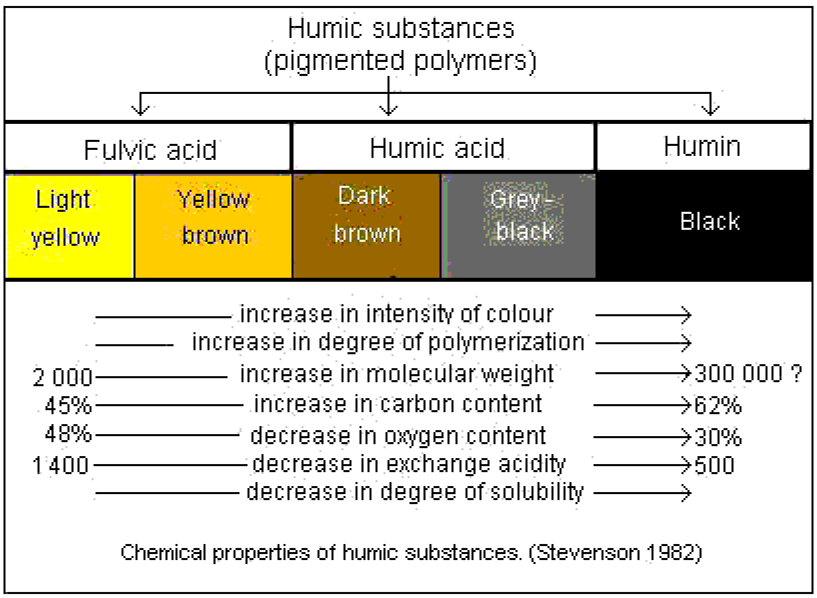
Humic substances play an important role in weathering and accelerating the decomposition of primary minerals, such as silicates. The interaction of humic acid with metal ions is an important factor in the creation of stable soil structures. [6] They are believed to be highly degradation-resistant materials formed during decomposition of organic matter. Humic substances allow microbial life to thrive. Some reasons that humic substances are important include:

- Research has shown that "…stored carbon remains a formidable energy source for many microorganisms". [7]
- By way of enzymatic decomposition, humic substances are broken down into H_2O and CO_2 which completes the organic cycle. Degradation of soils starts with destruction of humic matter ….".[8]
- Humic matter is vital to biochemical activities in the soil. Deforestation is most noteworthy by the reduction in soil organic matter.

[2] MacCarthy, et.al."An introduction to soil humic substances", *Humic Substances in Soil and Crop Sciences* Chicago: International Humic Substances Society, 1990, p.6.
[3] International Humic Substance Society, retrieved on 7-Jul-2012 from http://www.humicsubstances.org/
[4] Ibid.
[5] Kim H. Tan, *Humic Matter in the Soil and the Environment* (New York, Marcel Dekker,2003), p.269. The MRT represents the average age of humic substances, not the absolute age.
[6] Tan, p.255.
[7] Tan, p.271.
[8] Tan, p.292.

- Humic matter in most soil varies from 0 to 10%. [9] Humic substances have a high content of free radicals that play an important role in polymerization and oxidation-reduction reactions.
- Humic substances vary greatly in sources and characteristics, including pH, molecular weight, cation exchange capability and chemical composition.

Researchers note the complexity of research due to the inability to determine enzymes in the soils. While dissolved organic matter plays an important part in the mobility and translocation of many soil elements, the physical and chemical properties of dissolved organic matter are difficult to define precisely because of the complexity of their structure and components. [10] "Humic substances in soils are the dark brown, fully decomposed (humified) remains of plant or animal organic matter. They are the most chemically active compounds in soils, with cation and anion exchange capacities far exceeding those of clays." [11]



Chemical properties of humic substances. (Stevenson 1982)

The chemical properties depicted above, show the carbon and oxygen contents, acidity and degree of polymerization all change systematically with increasing molecular weight. The low - molecular - weight fulvic acids have higher oxygen but lower carbon contents than the high - molecular - weight humic acids. Fulvic acids contain more functional groups of an acidic nature, particularly COOH. The total acidities of fulvic acids (900 - 1400 meq/100g) are considerably higher than for humic acids (400 - 870 meq/100g). [12]

[9] Gaffney, Jeffrey S., Marley, Nancy A., and Clark Sue. B. eds. *Humic and Fulvic Acids: Isolation, Structure and Environmental Role* Washington, D.C. : American Chemical Society, 1996, p.2.

[10] Lixiang X. Zhou and J.W.C. Wong, "Behavior of Heavy Metals in Soil: Effect of Dissolved Organic Matter", *Geochemical and Hydrological Reactivity of Heavy Metals in Soils, eds.* Selim Magdi and William L. Kingery (Boca Raton, Florida: CRC Press, 2003) p.246.

[11] Lawrence Meyhew "Humic Substances in biological agriculture" *Acres USA- A Voice for Eco-Agriculture*, Jan-Feb, 2004. Retrieved on 31-Aug-2012 from http://www.nexgenagro.com/uploads/Acres_Mayhew_Humic_Substances.pdf, p1.

[12] F.J.Stevenson *Humus Chemistry.* New York: John Wiley and Sons Inc., 1982. Retrieved from http: // karnet.up.wroc.pl /~weber/kwasy2.htm on 20-Aug-2012.

3. Humic acid

Humic acid is a principal component of all humic substances. The important role of humic acid in plant growth is widely acknowledged in scientific literature. It improves the physical, chemical and biological properties of the soil and helps plants grow. It increases the permeability of plant membranes, so promoting the uptake of nutrients. In fact, humic acid is an essential part of the soil that helps fix nitrogen, aids in nutrients availability to plants, and improves the chemical structure of the soil.[13]

There are three main characteristics of humic acid, noted below, that are of prime interest in re-vegetation:

1. Humic acid has a positive effect on plant growth due to the important roles of phenols and carbonyl structures in metabolic processes—humic materials promote respiration and photosynthesis. [14]
2. Humic acids have large cation exchange capacities and are useful in chelating with waste metal molecules aiding in absorption by suitable flora.
3. Humic acid complexes decrease loss of moisture from the soil and increase its workability.

4. Humic Matter in Geological deposits

The transformation process whereby bog, peat and organic materials are transformed into coal is called diagenisis (geo-chemistry) or metamorphosis (soil science). It is thought that the humic acid content is gradually converted to humin in a polymerization process. The coalification theory suggests that humin gradually increases through the coalification process, ie. humic acid is coverted in the long run to humin. Peat is transformed into lignite (brown coal) then to sub-bituminous coal, then to bituminous coal, anthracite and finally graphite.

The humus of forest soils is characterized by a high content of fulvic acids while the humus of peat and grassland soils is high in humic acids. The humic acid / fulvic acid ratio usually, but not always, decreases with increasing depth. [15] Humic acid can be found in concentrated forms in certain lignite deposits (brown coals). Generally, the most immature coals contain the highest portion of humic acid and are the most organic in nature.

5. Leonardite

Leonardite was named after a former state geologist of North Dakota, Dr. A. G. Leonard, in recognition of his pioneering work on this resource during the early 1900's. Leonardite is a naturally occurring type of oxidized lignite. It is a type of "immature" coal (ie.a brown coal in the early stages of the coalification process). Leonardite takes millions of years to form. Deposits occur at shallow depths (1 to 10 metres deep), usually beneath permeable overburden. The presence of alkaline groundwater over long periods of time seems to be essential to their formation. Deposits occur, most commonly in North America in

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[13] Roger W. Youngs, and Clyde M. Frost, "Humic acid from Leonardite—a soil conditioner and organic fertilizer." Grand Forks, N.D.:U.S.Dept.of the Interior, 1963. Retrieved from http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/07_1_CINCINNATI_01-63_0012.pdf on 31-Aug-2012, p.12.

[14] Paul L. Boughton, "Humic Acid Complexes from Naturally Oxidized Lignite: Their Genesis, Chemistry and Utilization." *Proceedings , Eighth Forum on Geology of Industrial Minerals, (*Iowa City: 1972) p.153.

[15] F.J.Stevenson *Humus Chemistry.* New York: John Wiley and Sons Inc., 1982. Retrieved from http://karnet.up.wroc.pl/~weber/kwasy2.htm on 20-Aug-2012

Saskatchewan, Alberta, and North Dakota. The lignite oxidizes through sub-surface air penetration or from ground water action. [16] Leonardite zones are usually irregular and gradational in character due to the variable rates of oxidation. [17] Leonardite is a complex mixture of humic and fulvic acids with a high content of humic acid. "The richest source of HS (Humic substances) is Leonardite - a soft brown coal like deposit usually found in conjunction with lignite". [18] While agricultural applications of Leonardite represent the greatest potential use for low rank coals[19], few academic studies have been done on the potential use of Leonardite for re-vegetation.

Leonardite has low water solubility and normally does not contain significant amounts of N, P or K, the common nutritional elements. Due to its high ion exchange capacity it has been found to be beneficial in removing heavy metals, including Pb, Zn, Ni, Cu and Ag from polluted groundwater.[20] It might be added that research by Akinremi (1999) and Smirl (1999) showed that Leonardite material is recalcitrant and not actively used as an energy source by microorganisms, thus ensuring its longevity in soil.[21]

Leonardite may be used in its original form "mine material" but is typically crushed and pulverized when it is mined for commercial use. One study found the powdered form of Leonardite significantly increased wheat yield compared to mine material. [22] Leonardite solutions are more dilute in the active ingredients, and more expensive. Little research exists on the differing cation/anion exchange capacity of Leonardite in its different forms.

Numerous companies market lignite products in liquid and solid forms in the agricultural sector for a variety of purposes the most important of which is increasing crop yields. [23] In many cases, the lignite, such as Leonardite, is combined with nutrient additions (P,K,S,N) to form the final product. The commercial products range from powdered Leonardite, K-humates, Na-humates, liquid concentrates. [24] Humates are salts of humic acids, most often derived from Leonardite. The humic acids in Leonardite tend to be bound to the ash content (normally around 18%) as calcium salts, a chemical process is used to extract more of the humic acid in the form of humates. For example, a typical potassium humate product would contain 85% humic acid and 12% potassium.[25]

5.1 Humic acid content of Leonardite

Leonardite contains a high proportion of humic matter. For example, North Dakota Leonardite may contain 80-90% humic matter. [26] Most importantly, Leonardite possesses a high humic substance

[16] Paul L. Boughton, "Humic Acid Complexes from Naturally Oxidized Lignite: Their Genesis, Chemistry and Utilization." *Proceedings , Eighth Forum on Geology of Industrial Minerals, (*Iowa City: 1972) p.135
[17] Broughton. p.136.
[18] I.V.Perminova, and K.Hatfield "Remediation chemistry of humic substances: Theory and implications for technology", *Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice* Zvenigorod, Russia: Springer, 2002, p.4.
[19] Broughton p.154.
[20] Ray Von Wandruszka "Humic acids: Their detergent qualities and potential uses in pollution remediation" *Geochemical Transactions* American Chemical Society, April, 2000, p.5.
[21] Sean Dilk. *Agronomic Evaluation of Leonardite on yield and chemical composition of canola and wheat.* Masters thesis. Winnipeg: University of Manitoba, 2002, p.57.
[22] Dilk. p.44.
[23] Just two examples see http://www.shac.ca/products/index.htm and http://www.alphaagri.com/Research.htm
[24] See, for example, New AG International "Humic and Fulvic acids-the black gold of agriculture?" Retrieved on 13-Oct-2012 from http://www.humintech.com/pdf/humicfulvicacids.pdf
[25] See http://www.canadaoceanic.com/Fertilizers/HumicTotal.shtml retrieved on 15-Oct-2012.
[26] Youngs and Frost state 86% humic acid.

content: at 40 to 85 percent humic and fulvic acids, a much higher humic/fulvic acid content than other sources, such as black peat at 10 to 40 percent, sapropel peat at 10 to 20 percent, manure at 5 to 15 percent, and compost at 2 to 5 percent. [27] Natural soil typically has 1 to 5 percent humic and fulvic acids. Lab testing is normally required to ascertain the chemical composition of the Leonardite to be used.

Soluble humic acid in Leonardite content varies from 32.8% to 42.2% in North Dakota to 28% in Texas. Higher humic acid concentrations have been reported in Leornardite- up to 84% in a Saskatchewan sample. [28] Alberta samples range from 15-80% with the average being 60%. The samples used in experimentation by the Yukon Research Centre contain at least 50% humic acid. [29] Higher humic acid content is better for the purposes of soil amendment since it leads to higher yields.

5.2 Chelating agent

Humic substances tend to form chelate complexes with iron, aluminum copper and other poly-valent ions. Chelate complexes are compounds that consist of a central metal atom attached to a large molecule, called a ligand, in a ring structure. Chelates are more stable than non-chelated compounds of comparable composition. Heavy metals are deactivated by the chelation of humic acid. Lignites, for example, have approximately 120 times the absorptive capacity as bituminous coal for copper solutions.[30] "The process of metal absorption by lignites under laboratory conditions, elucidating the role that low rank humic coals can play in the retention and accumulation of heavy metal. Since the last century, many observations on retention and accumulation of metals in fossils organic sediments have been reported. "[31]

Humic acid can chelate heavy metals effectively and have potential to be used in wastewater treatment for heavy metal removal. "Humic matter with its huge cation exchange and chelation capacity can absorb and detoxify a number of toxic compounds." [32] Chelation of heavy metals may also reduce toxic hazards for humans and animals. The propensity of humic acid to remove contaminants from polluted water has been recognized in several studies. [33] Their advantages include low cost, combustibility and resistance to acids. The chelation of heavy metals is of importance if the metals are chemically bound in the soil allowing plants to grow better.

The cation exchange capacity (CEC) of Leonardite is significantly higher than various types of clay. The CEC for clay minerals, for example, as measured by milliequivalent per 100g of dry soil (meq+/100g), for kaolite 3-15; illite and chorite 10-40 compared to a measure of 95 for Leonardite.[34] The high cation

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[27] "Humic Acids", *USDA DRAFT Technical Evaluation Report* Jan 2006. retrieved from http:// www.ams.usda.gov /AMSv1.0/ getfile?dDocName=STELPRDC5057310 on 31-Aug-2012, p.2.
[28] G.L. Hoffman, D.J.Nikols, S.Stuhec and R.A.Wilson "Evaluation of Leonardite (Humalite) Resources of Alberta" Open File report 1993-18. Alberta Research Council, March, 1993. pp. 8-9.
[29] Discussion with Chris Webb 24-Aug-2012.
[30] Ling Ong and Vernon Swanson "Absorption of Copper by peat, lignite and bituminous coal." *Economic Geology* Vol.61, 1966, p.1227.
[31] Saied Sumayya, Siddique Azhar, Mumtaz Majid, and Ali Kazim "Study of the Heavy Metal Pollution treatment of the Coal Generated Humic Acid" *Journal of Basic and Applied Sciences,* Vol1, No.2, 2005. P.1.
[32] Tan. p.278.
[33] Ray Von Wandruszka "Humic acids: Their detergent qualities and potential uses in pollution remediation" *Geochemical Transactions* American Chemical Society, April, 2000, p.5.
[34] Pertuit citing International Humic Substances Society (IHSS) standard Leonardite cation-exchange capacity see also http://en.wikipedia.org/wiki/Cation-exchange_capacity retreived on 15-Oct-2012.

exchange capacity of Leonardite and humates increases the amount of nutrients held in the soil when they are added.

5.3 Effect on plant growth

A wide variety of research has been undertaken on the effects of humic substance amendments on plant growth. Humic or fulvic acids have been shown to improve plant growth, particularly the root's ability to absorb nutrients. Research has shown increased root growth in agricultural crops: corn, canola and tomatoes. [35] Lee and Bartlett found humic substances caused roots to proliferate and to become highly branched. Using Leonardite specifically Adani (et.al. 1998) found tomato roots and shoots increased significantly (8-9%) with the application of dry humic acid.[36] Pertuit (et. al.2001) found that tomato plants increased growth with 0-25% Leonardite, while 50% actually inhibited growth. Dudley (et. al. 2004) conducted experiments that showed positive results from Leonardite applications on marigold and zinnia seedlings, yet there was little effect on lettuce and bush beans. [37]

Not all research showed Leonardite had a positive effect on plant growth. Dilk (2002) found canola was not affected by the application of Leonardite, while wheat yields increased at low levels of Leonardite. He concluded that "Leonardite and its products that were tested had little or no effects on emergence and final grain yield of crops …". [38]

Very limited research has been conducted with Leonardite as a soil amendment for mine reclamation purposes. One study compared various organic amendments including Leonardite and found they reduced leaching of Cd, Cu and Zn between 40–70% in comparison to untreated soil. [39] The US government has used humates successfully in re-vegetating some uranium lease track areas of Colorado.[40] Another study found "As it occurred with trace element extractability, the largest trace element decrease due to repeated amendment addition was found in plants growing on Leonardite treated soils."[41]

5.4 Effect on germination

Humic substances are capable of increasing the rate of germination as well as percent germination.[42] Seed species also vary in optimal conditions for germination such as temperature, pH, moisture, and

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[35] Sean Dilk. *Agronomic Evaluation of Leonardite on yield and chemical composition of canola and wheat.* Masters thesis. Winnipeg: University of Manitoba, 2002, p2. Various studies were noted.

[36] Farrizio Adani, Pierluigi Genevini, Patrizia Zaccheo and Graziano Zocchi "The effect of Commercial Humic Acid on Tomato Plant Growth and mineral nutrition." *Journal of Plant Nutrition,* 1998 21(3), 561-575. and A.J. Pertuit, Jerry Dudley and Joe Toler "Leonardite and fertilizer levels influence tomatoe seedling growth", *HortScience* 36(5):913-915 2001, p.913.

[37] Jerry Dudley, Alton Pertuit Jr., and Joe Toler, "Leonardite Influences Zinnia and Marigold growth", *Hort Science* 39(2):251-255, 2004.

[38] Dilk. P.35 and p.128.

[39] Alfredo Pérez-de-Mora, Pilar Burgos, Francisco Cabrera and Engracia Madejón ""In Situ" Amendments and Revegetation Reduce Trace Element Leaching in a Contaminated Soil" *Water, Air, & Soil Pollution*
Volume 185, Numbers 1-4 (2007), 209-222 retreived at http://www.springerlink.com/content/v769756540426211/ on 15-Oct-2012.

[40] M. Kastens, E. Cotter, and D. Burns" Mined Land Reclamation on DOE's Uranium Lease Tracts, Southwestern Colorado" as retrieved from *www.lm.doe.gov/WorkArea/linkit.aspx?LinkIdentifier=id...305*

[41] Madejón, P., Pérez de Mora,A.,Burgos,P.Cabrera,F. and Madejón, E. "Amendments to enhance phytoremediation: Single or repetitive applications in time?" *10th International Conference on Biogeochemistry of Trace Elements*, Mexico: 2003 retreived from http: //digital.csic.es/bitstream/10261/28752/1/PaolaOCOBTEMexico.pdf on 16-Oct-2012. The trace elements tested were Cd, Cu and Zn.

[42] Dilk. p5. Citing Vaughn and Malcolm (1985)

nutrients. Hence, the reason for variation in germination due to application of humic substances is believed to be due to the large variation of humic substance characteristics and the conditions required for seed germination. Seed germination and top growth also are stimulated (Obreza et al 1989). In the presence of humic acid, both a larger percentage of seeds germinate and germination occurs at a faster rate. [43] One study showed increased wine grape yields by 25% and cotton (*Gossypium hirsutum* L.) yields by 11.2%; the greatest increase in yield was obtained when the extracts were added to the soil prior to application of a foliar fertilizer spray (Brownell et al.1987).[44]

5.5 Nutrient uptake

The addition of Leonardite or other humic substances could facilitate the uptake of nutrients by the plants and reduce or at least minimize the requirement for introduced fertilizers. Several studies have confirmed the ability of Leonardite to increase cation exchange and nutrient uptake. [45] The reason it has shown to increase nutrient uptake is because the nutrients are more available because they are being held in the rooting zone. Adani et.al. (1998) found that Leonardite increased the uptake of N and P content of tomato plants, while Wallace and Romney (1980) found an increased uptake in P and K concentration of bush bean plants. Akinremi (et. al. 2000) found that Leonardite increased nutrient uptake and yield on rape, wheat and green beans.[46]

Two key questions arise when dealing with soil amendments in soils contaminated by metals: is there a risk of mobility (ie. transport to water resources) and bio-availability (ie. uptake to plants)? Experimentation by Burgos (et.al. 2004) found that a Leonardite amendment increased the level of total organic carbon fourfold. The uptake of heavy metals was inconclusive, suggesting the need to monitor the soil amendments to ensure positive impacts outweigh risks.[47]

5.6 Water retention

Humic acid also acts in decreasing water evaporation from soils. This is essential in arid areas with sandy soils that retain little to no water. With water present, the compounds that were previously bound by humic acid are partially ionized (or given a charge). Coal derived humic substances can increase water retention and available water capacity in soils as well as improving the stability of structurally degraded soils. [48] "Because of their large surface area and internal electrical charges, humic substances function as water sponges. These sponge like substances have the ability to hold seven times their volume in water,

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[43] "Humic Acids", *USDA DRAFT Technical Evaluation Report* Jan 2006. Retrieved from http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5057310 on 31-Aug-2012, p.4.

[44] A.J. Pertuit, Jerry Dudley and Joe Toler "Leonardite and fertilizer levels influence tomatoe seedling growth", HortScience 36(5):913-915 2001, p.913.

[45] See for example Jerry Dudley, Alton Pertuit Jr., and Joe Toler, "Leonardite Influences Zinnia and Marigold growth", *Hort Science* 39(2):251-255, 2004, p.5.

[46] O. Akinremi, H.H.Janzen, R.L.Lemke and F.J.Larney, "Response of canola, wheat and greenbeans to Leonardite additions" *Canadian Journal of Soil Science* 2000 vol.80 No.3, pp.437-443 as retrieved at http://www.cabdirect.org/abstracts/20013091911.html;jsessionid=6200C694C0DEC952729A2F65A9FAA680 on 18-Oct-2012.

[47] P.Burgos, A. Perez, E.Madejon, and F.Cabrera "Assisted natural remediation of trace element polluted soils" *Waste Contaminant: Life Cycle and Entry into Food Chain* 2004 pp.65-68. Retreived from http://www.ramiran.net/doc04/Proceedings%2004/Burgos.pdf on 23-Oct-2012.

[48] A.Piccolo, G. Pietramellara, and J.S.C.Mbagwu, "Effects of coal derived humic substances on water retention and structural stability of Mediterranean soils", *Soil Use and Management*, 91996) 12, 209-213 retreived from http://www.johnandbobs.com/wp-content/uploads/2011/01/effects-humic.pdf on 5-Sep-2012.

a greater water holding capacity than soil clays. Water stored within the top-soil, when needed, provides a carrier medium for nutrients required by soil organisms and plant roots."[49]

5.7 Commercial products

A variety of commercial humic products exist for agricultural and other uses. Some of these products use lignites, some Leonardite, most often in conjunction with plant nutrients like fertilizers. Many commercial products are humates, essentially salts of humic or fulvic acids.[50] Typically commercial humates have high pH values 10-12. Many companies consider these to be fertilizers. However, by origin, humic acids do not carry the nutrient elements in the same amounts as fertilizers do. Small humic fractions can serve as a food source and the high cation exchange capacity of humates increases the amount of nutrients held in the soil when added. The nitrogen content of humic substances has been reported to increase the N-uptake in plants and to enhance plant utilization in nitrogen deficient environments.

Various humic substances are commercially sold of varying quality. Without laboratory testing it is difficult, for example, for individuals purchasing a humate- based fertilizer to tell the difference between a high quality humic substance and a low quality humic material. "The real test of any humic product is in the field. Growers interested in improving soil fertility and plant health need to set up field tests, with an open mind. Many growers have tried several different commercial humic substances before discovering one that improves crop yields and product quality on their soils." [51]

6. Disturbed mine sites in the Yukon

The Yukon has a number of disturbed and contaminated mine sites. Mine tailings, often decades old, have polluted the environment and resist natural re-vegetation in many cases. Mine tailings are not soil. They consist of finely ground rock (gangue) which remains after the target elements are removed in the milling process. [52] They are a source of water-borne toxic ions. Soils contain a mineral mass which provides nutrients to the soil; organic matter (humus) and micro-organisms.

Elevated metal content, lack of nutrients and acidity are major factors to be overcome. Most mine tailings are highly deficient in nitrogen. Phosphorus is typically limited in soils with low or very high pH. Mine tailings are typically acidic—they often have pH readings down to 2.0 or in some cases lower. While most agricultural soils have pH ranges from 4.5 to 7.5.[53] Acidity affects the solubility of metals and hence the toxicity to plants. Most soils have pH values from 4.5 to 8.0. Few plants can tolerate a pH < 4.0. [54]

Yukon tailings are rich in heavy metals and low in macro-nutrients. [55] The distribution of plants in

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[49] Robert E.Pettit "Organic matter, humus,humic acid, fulvic acid and humin: their importance in soil fertility and plant health.", 19 pages. Retrieved from http://www.alphaagri.com/Dr.%20Robert%20E.%20Pettit.pdf on 16-Aug-2012.
[50] Tan. p.305.
[51] Robert E. Pettit, "Organic matter, humus,humic acid, fulvic acid and humin: their importance in soil fertility and plant health.", p.17. Retrieved from http://www.alphaagri.com/Dr.%20Robert%20E.%20Pettit.pdf on 16-Aug-2012.
[52] Thomas Hutchinson and Allan Kuja, "The Use of Native and Agricultural Plant Species to re-vegetate Northern Mine tailings." Toronto: University of Toronto, December, 1981.
[53] Hutchinson, p.4.
[54] Hutchinson and Kuja, p.5.
[55] Alison Clark. "Enhancing natural succession on Yukon mine tailings sites: a low input management approach". (MSc Thesis) Peterborough, Ontario: Trent University, May-2005. p.17.

polluted environments is affected by soil type and rate of soil formation. "Competition for very limited nutrients plays an important role during primary succession and is a dominant factor in plant allocation and regenerative strategies." [56] Clark (2005) conducted experiments at three Yukon contaminated sites with amendments : compost, fertilizer and mixed. The study found that both compost and commercial fertilizer both greatly enhanced plant growth but her study concluded that ongoing use of commercial fertilizer was not a management solution.

Hutchinson and Kuja (1981) highlighted problems with using commercial fertilizers, use of sewage sludge and mulches. These included sudden declines in growth, the need for re-application and the expense. They suggested that a return to native flora is a better approach. "Metal tolerant grasses have shown tolerance to additional conditions typical of tailings such as low nutrient status (Jowett 1959), and drought and have been successfully grown in heavy metal laden tailings for several years without signs of regression (Gemmell and Goodman 1978)." [57] Kwiatkowski (2007) studied soil amendments and re-vegetation at NWT mines and examined issues related to establishing native plant cover. "Successful reclamation involves re-establishment of soil processes such as nutrient recycling and native plant communities, including a diversity of shrub, grass, forb and bryophyte species.[58]

Alternatives exist to re-vegetation such as covering the tailings with innocuous restraining material. This is what is planned for the main Cyprus-Anvil pit at Faro. Some mine tailings may also be re-processed: for example, a company has proposed to reprocess magnetite from tailings of the old Whitehorse Copper tailings site. However, if the goal is to establish and maintain self-sustaining plant cover at reclamation sites soil amendments may be required.

7. Use of Humic Substances

Humic substances are an important element in a soil amendment program since humus is a key building block for plant growth. Organic-rich material is the oft- stated means of aiding re-vegetation and re-establishing native colonization at disturbed mine sites. Topsoil is always the best source of organic material for mine reclamation, if it is available for salvage and use. In many cases in the north Mougeot and Withers (2001) suggested that importing topsoil is not always practicable as a reclamation measure because of the cost involved and the possibility of introducing undesirable plant species. [59] Sewage sludge is an organic amendment which can improve properties of disturbed sites (Reid and Naeth 2005).[60] There is some risk that sewage sludge may contain either pathogens or heavy metals, while Leonardite has the advantage of being an organic rich material, yet does not contain undesirable plant species. The application of commercial fertilizers is a simple way to boost nutrient levels.

Humic acids adsorb metal ions, producing a water-soluble complex. There is a concern that the plants absorb the toxic metals from the tailings. The dilemma is that re-vegetation requires plants be able to live with toxicity for growth yet these plants absorb toxins from the environment. Complexation of metals with humic acid is affected by pH. Humic acids compete more strongly for metal ions at acidic pH

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[56] Clark p.55.
[57] Hutchinson and Kuja, p.5.
[58] Bonnie L. Kwiatkowski "Diamond Mine Reclamation in the NWT: Substrates, Soil Amendments and native plant Community Development" (MSc thesis) Edmonton: University of Alberta, 2007, p.26.
[59] Mougeot, C. and Withers, S. "Assessment of Long Term Vegetation and Site Conditions at Reclaimed Yukon Mineral Exploration Sites". Proceedings of the Northern Latitudes Mining Reclamation Workshop, Whitehorse, Yukon, Canada. 2001. pp. 39-53
[60] Bonnie L. Kwiatkowski "Diamond Mine Reclamation in the NWT: Substrates, Soil Amendments and native plant Community Development" (MSc thesis) Edmonton: University of Alberta, 2007. p.16.

than at alkaline pH, whereas the clay particles of soil are competitive for metal adsorption at alkaline pH. The general selective adsorption of metals for humic acid is Cu > Cd> Zn> Ca. [61]

Soil acidity is an important variable to be considered in a soil amendment program. For example, "The optimum limit for absorption of copper in a natural environment lies between pH 3 and 8." [62]Absorption capacity of organic substances decreases as metamorphism increases, from peat to lignite to coal. Sumayya(et.al. 2005) "…found that humic acid-metal interaction is pH dependent, therefore, particular pH was set for each of the metal. The Cu^{2+}, Fe^{2+} and Zn^{2+} showed the maximum interaction at pH= 5.5 , whereas the other metals showed the high affinity at pH range 6.5 to 7.5…" .[63] Soil amendment trials can be carried out to test plant species and survival rates as well as the effectiveness of the amendment substances.

Extensive studies have already been undertaken in northern Canada on native species best suited to re-vegetation efforts. Northern researchers have emphasized the importance of using native species in re-vegetation efforts (Withers 2001, Clark 2005 and Kwiatkowski 2007). Factors to consider in selecting species for re-vegetation include growth form, nutritional requirements, drought resistance, soil conditions, reproduction characteristics, and climatic conditions. [64]

8. Leonardite in the Yukon Territory

Coal was mined in the Yukon Territory over 100 years ago near Dawson City, for a few years after the Klondike Gold Rush of 1898. Some limited coal mining occurred as late as 1992.[65] There are no known deposits of Leonardite in the Yukon Territory. Hence, any use of Leonardite, as a soil amendment, would require it to be imported.

9. Conclusions

Humic substances are ubiquitous in nature and are vitally important to consider in re-vegetation plans. A variety of humic substances exist including peat, compost, mulch, sludge, etc. Leonardite, a type of immature oxidized coal, is a humic substance, that is a concentrated source of humic acid. Humic acid, it is claimed; a) helps plants grow; b) activates nutrients; c) chelates metals and d) helps the soil retain water. The evidence suggests certain plants grow better than others when treated with Leonardite. It also suggests ability to facilitate the uptake of nutrients, to chelate metals in the soil and to retain water.

Leonardite may be part of an optimal mix of a humic substance amendments that would allow successful re-vegetation at mine sites. The best soil amendments may involve combinations of:

- Lime to increase the pH (and lower acidity);
- Commercial fertilizer to provide nutrients;
- Leonardite to facilitate nutrient uptake, to chelate metals and to help retain water;
- Topsoil for humic content and ground cover.

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[61] Dilk, p.22 citing Hatton and Pickering 1985.
[62] Ling Ong and Vernon Swanson"Absorption of Copper by peat, lignite and bituminous coal." *Economic Geology* Vol.61, 1966, p.1228.
[63] Saeid Sumayya, Siddique Azhar, Mumtaz Majid and Ali Kazim "Study of the Heavy Metal Pollution treatment of the Coal Generated Humic Acid" *Journal of Basic and Applied Sciences,* Vol1, No.2, 2005.
[64] Kwiatkowski p.18.
[65] "Coal", a brochure by the Yukon Government, Department of Economic Development, 2008 retrieved from http://www.geology.gov.yk.ca/pdf/coal.pdf on 5-Sep-2012.

Further research work is required to assess the utility and effectiveness of Leonardite. The high levels of humic acid in Leonardite and solid evidence suggest beneficial results in re-vegetation efforts.

10. Next steps

The study of Leonardite has started in Yukon (by Yukon College); however, to date it has focused testing on use with agricultural species in a laboratory setting. Increasing knowledge of the benefits of use for mine re-vegetation would be a logical next step. The key would be to determine if there are significant benefits to the addition of Leonardite to native grass and shrub development for mine re-vegetation.

Two key questions and study concepts are listed below.

1. At sites where re-vegetation has been at least partially successful - does the addition of Leonardite provide any advantages (e.g., ground cover, growth rates, etc)?

2. At sites where re-vegetation efforts have not been successful, such as sites with low pH, does the addition of Leonardite make re-vegetation possible?

Testing could be completed in a laboratory setting and/or field trials. Field trials would be most appropriate at sites where reclamation is planned so Leonardite can be tested with other methods (e.g., fertilizer, site prep, etc.). For example, if re-vegetation trials are being considered at a mine site, Leonardite could be one of the many test factors tested.

Since the literature indicates benefits with metal deactivation, it would be beneficial to determine if application actually reduces metal levels in groundwater and native plant tissue. Other factors that should be measured include plant growth (e.g., height) and ground cover over a long period of time.

Appendix 1

Terms and Definitions [66]

Fulvic acids - the fraction of humic substances that is soluble in water under all pH conditions. They remains in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in color.

Humic substances – completely decomposed organic matter containing humic acid. Series of relatively high-molecular-weight, brown-to black substances formed by secondary synthesis reactions. The term is generic in a sense that it describes the colored material or its fractions obtained on the basis of solubility characteristics, such as humic acid or fulvic acid.

Humic acid - the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. They can be extracted from soil by various reagents and which is insoluble in dilute acid. Humic acids are the major extractable component of soil humic substances. They are dark brown to black in color.

Humalite - a naturally occurring humic acid material that has been derived from sub-bituminous coal deposits, rather than from lignite, as is the case for Leonardite.

Humate – Salts of humic acid.

Humification**-** Process whereby the carbon of organic residues is transformed and converted to humic substances through biochemical and chemical processes.

Humin – An alkali insoluable fraction of humate. Humins are black in color

Humus – Dark, organic well-decomposed soil material consisting of plant and animal residues and various organic elements. The term is often used synonymously with soil organic matter.

Leonardite - Oxidized (weathered) sub-bitumimous coal.

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[66] G.L. Hoffman, D.J.Nikols, S.Stuhec and R.A.Wilson "Evaluation of Leonardite (Humalite) Resources of Alberta" Open File Report 1993-18. Alberta Research Council, March, 1993. P.5 (from Roybal and Barker, 1987), also the Soil Glossary http://www.alphaagri.com/Soil%20Glossary.pdf retrieved on 28-Jul-2012 and http://karnet.up.wroc.pl/~weber/kwasy2.htm retreived on 20-Aug-2012 and http://retreadresources.com/ResourceHumalite.html retrieved on 20-Aug-2012.

Appendix 2 - Tailings Acidity at selected Yukon sites[67]

Mine	Residual Metal	pH range	Comment
Arctic Gold and Silver	Au,Ag	1.3-2.1	Highly acidic
Cyprus Anvil	Pb,Zn,Cu	1.8-4.0	Highly acidic
Canada Tungsten	Wo	7.1-7.2	
United Keno Hill Mines	Pb,Zn,Ag	5.8-6.1	
Whitehorse Copper	Cu,Au,Ag,Fe	8.9-9.1	Residual iron may be reprocessed.
Venus mine site	Au	7.0-7.1	

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[67] T.C. Hutchinson "Preliminary study on mine tailing re-vegetation in Northern Canada". Department of Indian and Northern Affairs, 1977., table 2. And T.C.Huthinson and A.Kuja "The use of agricultural plant species to re-vegetate northern mine tailings." Toronto:University of Toronto, 1981, table 13.

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