Reuse of Biosolids from a Waste Water Treatment Plant

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Abstract

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Since the limit of resources has been realized, preventing from waste of resources became an important issue. Sludge is a source of nutrients and organic materials and has the capability of use as a fertilizer but unfortunately disposal of the sludge is the most current approach in WWTPs including Montreal WWTP. At the Jean. R. Marcotte waste water treatment plant, the sludge is incinerated and sent for disposal. In this study an attempt has been made to solve this issue by recycling the sludge.

The mentioned sludge has high concentrations of cadmium, copper, cobalt and selenium and therefore a treatment process is needed to pass Quebec regulations before use as fertilizer. Among all treatment methods, leaching was selected in this research. Leaching has high efficiency for heavy metal removal but nutrient loss is also its disadvantage. In this thesis, preserving nutrients and removing heavy metals are performed at the same time.

To meet the mentioned goals, a new leaching agent is proposed, K_2HPO_4, and its effects and removal efficiency on the sludge was investigated. The correlation of heavy metal removal and preserved nutrient concentration with time and pH is shown.

Based on the result, the removal efficiencies of cadmium, copper, cobalt and selenium are respectively 80%, 44%, 70% and 93%. Also the remaining concentrations of primary nutrients in the biosolids including nitrogen, phosphorus and potassium are respectively 17%, 17% and 25%.

To conclude, using dipotassium phosphate as a leaching agent is an effective method to remove heavy metals and increase primary macro nutrients at the same time. The efficiency of this method has indirect correlation with pH and direct correlation with time and considering the product properties, its price is acceptable.

Acknowledgments

I wish to express my gratitude and indebtedness to Dr. Catherine Mulligan for her support, generous consultation and giving me her precious time throughout this study. In this clear sighted way, she has always been inherently sympathetic and social in character, a perspective which I am now beginning to understand after three years of study at this university.

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To my parents

To my Love Mahtab

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List of Abbreviations

^{o}C	Degrees Celsius
µm	Micrometre
g	Gram
ml	Millilitre
M	Molar
WWTP	Waste Water Treatment Plant
DTPA	Diethylene Triamine Pentaacetic Acid
TEA	Triethanolamine
S, S-EDDS	S, S-Ethylenediamine-Disuccinate
[PR4][TS]	Trihexyl(Tetradecyl) Phosphonium Thiosalicylate
[PR4][MTBA]	Trihexyl(Tetradecyl) Phosphonium 2-(Methylthio)Benzoate
PESA	Polyepoxysuccinic Acid

1. Introduction

Sewage sludge is semi-solid residue of waste water treatment process. Sludge is usually disposed of in landfills after a dewatering process. Of course in some waste water treatment plants there are extra units for pollution treatment or volume reduction before disposal. These units can decrease the harmful effects of sludge disposal in the environment.

Disposal of sludge has many disadvantages. It is actually selected by WWTP designers only because of its easiness. But environmental concerns, resource depletion and increasing of sludge production due to growth of the world population, no longer let human societies to close their eyes on this problem.

By advancement of science, new methods for treating and recycling are found. These methods can prevent wasting the sources and damaging the environment while their production is cost effective and the products have acceptable quality so unlike general belief the processes are profitable too. Substituting old approaches with new ones is a necessity today and it is no longer acceptable to damage the environment and waste resources.

Sludge usually contains high concentrations of different nutrients and organic materials. These useful contents make sludge suitable for use as fertilizer in agriculture fields. Chemical fertilizers usually contain only one or two nutrients and they easily can be leached through the soil to below the plant roots where they are no longer available for plant usage. This problem can be solved by humus in the soil. Humus is stable organic matter of soil and can preserve nutrients for plants usage. Using sludge as fertilizer can increase organic matter. In comparison to chemical fertilizers, using sludge as fertilizer can add different nutrients to soil and increases soil fertility, while it can preserve added nutrients in the root area.

The third largest waste water treatment plant (WWTP) in the world is located in Montreal called Jean-R. Marcotte. This WWTP produces a large volume of sludge daily and it is one of those which send their sludge to landfill for disposal. To decrease the volume of sludge and to control biological pollutions the incineration facilities are built in the plant and its bottom ashes and fly ashes are gathered and disposed of instead of raw sludge.

As heavy metals have high concentrations in the influent flow of Montreal WWTP, the ashes are highly polluted by heavy metals too. Therefore disposing of these ashes has harmful effects on the Montreal environment which has been done for a long time. Also large amounts of useful resources have been wasted so far. In this thesis a solution is proposed for this problem to stop this procedure.

Instead of disposing of the ashes in the landfill, it is possible to use the biosolids as a fertilizer in an agriculture field. In our case heavy metal removal is a necessity for use as a fertilizer but nutrient protection also should be done.

Among all the treatment methods, leaching is selected in this thesis. This method is simple and it does not need any expensive or complex facilities. The leaching method usually shows a high removal percentage for heavy metals but nutrients are removed too. In this thesis an attempt is made to remove this weakness and convert the sludge of Montreal WWTP to a fertilizer by a leaching method to remove heavy metals and achieve an acceptable concentration of nutrients.

1.1 Objectives

The general objective of this thesis is solving a local environmental issue which is disposal of the ashes of Jean. R. Marcotte WWTP in a local landfill. To do so the sludge is to be changed to a high quality fertilizer by a leaching method.

The specific objectives are to:

- Evaluate the effects of the proposed leachant on the sludge
- Determine the correlation between pH and reaction time with concentrations of heavy metals and nutrients
- Compare the treated solids with similar ones to evaluate its quality.

1.2 Organization of Research Study

There are five chapters in this thesis. In chapter one, the introduction and purposes of the research are presented. Chapter two describes background information about sludge treatment methods and literature review on leaching. Chapter three includes materials, instruments, and methods which were used in the experiments. In chapter four, the results of different experiments are demonstrated and discussed. Chapter five summarizes the conclusions and contributions of this study and introduces the recommendations for future work. This thesis is completed by the list of references and appendices.

2. Background Information & Literature Review

2.1 Cadmium

Cadmium is a heavy metal with the chemical symbol of Cd. It is the second member in group 12 with atomic number of 48.Cadmium is a silver white colored metal with density of 8.65$g \cdot cm^{-3}$, and its stable form in the natural environment is Cd (+ 2).

Figure 2-1 : Cadmium (Wikipedia, 2013)

Three major sources has been known for cadmium since it discovered by Friedrich Stromeyer and Karl Samuel Leberecht Hermann in 1817 (Farnsworth, 1980). They discovered cadmium as an impurity in zinc carbonate during their research. Thereafter it was revealed that cadmium is found usually with zinc in carbonate and sulfide ores. Also more research was done and the results showed cadmium is produced during refining of other metals as a by-product, moreover it was found that during several centuries, copper, lead and zinc producers polluted environment by cadmium unknowingly. So metal refining, carbonate and sulfide ores containing zinc are the most important sources of cadmium (Moore & Ramamoorthy, 1984).

The major sources are not the only sources, cadmium can be found everywhere in nature like earth's crust, oceans and rainwater but in minor amounts. This amount depends on the source. For example in igneous and metamorphic rocks it is from 0.02 to 0.2 ppm, in sedimentary rocks from 0.1 to 25 ppm, In the raw materials for iron and steel production from 0.1 to 5 ppm (Cook & Morrow, 1995), in oceans the average amounts are reported varying from 5 to 110 ng/L. In surface water it highly depends on location and industrial activities in the place (Morrow, 2010). Therefore finding small amounts of cadmium are expected almost everywhere. Eight different cadmium-containing minerals are known (which are listed in Table 2-1) but Greenockite among them is the most common one and it is always associated with zinc ores (Morrow, 2010).

Table 2-1: Cadmium-Containing Minerals (Morrow, 2010)

Name	Formula	CAS Registry Num	Cadmium (%)
Sphalerite	ZnS	[1314-98-3]	0.02–1.4
Wurtzite	ZnS	[1314-98-3]	0.02–1.4
Galena	PbS	[1314-87-0]	500 ppm
Chalcopyrite	$CuFeS_2$	[1308-56-1]	500 ppm
Otavite	$Zn(Cd)CO_3$	[513-78-0]	<1.2
Greenockite	CdS	[1306-23-6]	77.8
Monteponite	CdO	[1306-19-0]	87.5
Cadmoselite	CdSe	[1306-24-7]	58.7

Cadmium producers can be found in all continents except Africa (Morrow, 2010) but the world's primary cadmium producers are in Asia. China, Japan and the Republic of Korea have the highest share of production (Tolcin et al., 2012). 75% of cadmium production is done by zinc producers and the rest 25% is from metal refining and mostly recycling of NiCd batteries. It is not known what their exact production amount is in different areas. The world primary cadmium production amount from 2000 to 2011 is shown in Fig. 2-2 and its gradual upward trend can be seen (the amounts are in metric tons).

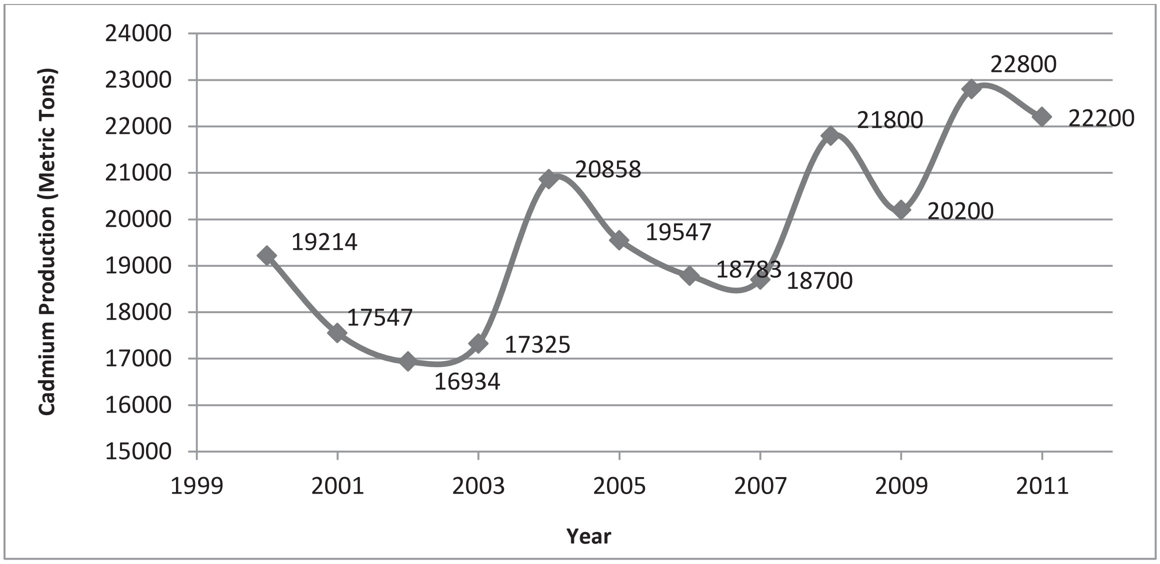

Figure 2-2: World Primary Cadmium Production (Morrow, 2010)

Cadmium has some similarities with zinc and mercury also it has lipid solubility, bioaccumulation and toxicity properties. It can accumulate in liver and kidney because of its strong binding with cysteine residues of metallothionein. As cadmium metabolism is similar to zinc metabolism, metallothionein binds and transports both cadmium and zinc therefore cadmium displaces zinc in many vital enzymatic reactions and disrupts their activities (Morrow, 2010).

2.2 Sludge Treatment Methods

Sludge, the residue of waste water after treatment, needs to be treated before disposal or reuse. High concentrations of pathogens and chemicals in the sludge can be harmful for environment and living organisms so that reducing the dangerous contents to the below the regulations limit before returning the sludge contents to the environment or reuse is necessary. The common methods for sludge treatment are aerobic digestion, anaerobic digestion, alkaline stabilization, composting, and incineration (Anon., 2004). The product of each method has different properties and therefore choosing the method is based on the determined goal.

2.2.1 Anaerobic Digestion

Using microorganisms for breaking down the biodegradable materials in absence of oxygen is called anaerobic digestion (Centre, 2011) this complex biochemical process is done in four stages. The first one is hydrolysis; in this stage insoluble organic polymers are broken in to soluble derivatives. The second is acidogenesis in which they are converted to organic acids. The third stage is acetogenesis wherein organic acids are changed to acetic acid along with carbon dioxide, hydrogen and ammonia. Finally in methanogenesis stage, methane and carbon dioxide are produced. In each stage there is a specific kind of bacteria responsible for each process. The final solid product is stable and odorless also, in comparison to the primary sludge and its volume, its mass and pathogenic microorganisms are reduced (Turovskiy & Mathai, 2006). Figure 2-3 shows process stages of anaerobic digestion.

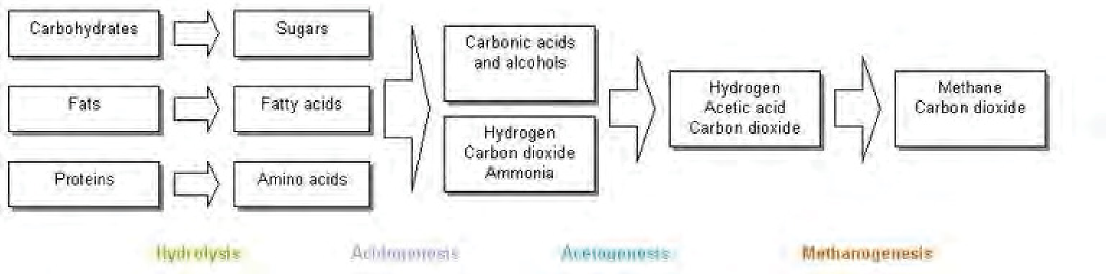

Figure 2-3: Process Stages of Anaerobic Digestion (Wikipedia, 2014)

Anaerobic digestion’s products are biogas, digestate and waste water and therefore it has products in all three phases of gas, liquid and solid. These products have different applications and each can be chosen based on the goal for further processes to form the final product of the plant. The gas products include methane, carbon dioxide and hydrogen. The liquid products comprise waste water and the only solid one is the digestate. Figure 2-4 shows a digester and its products.

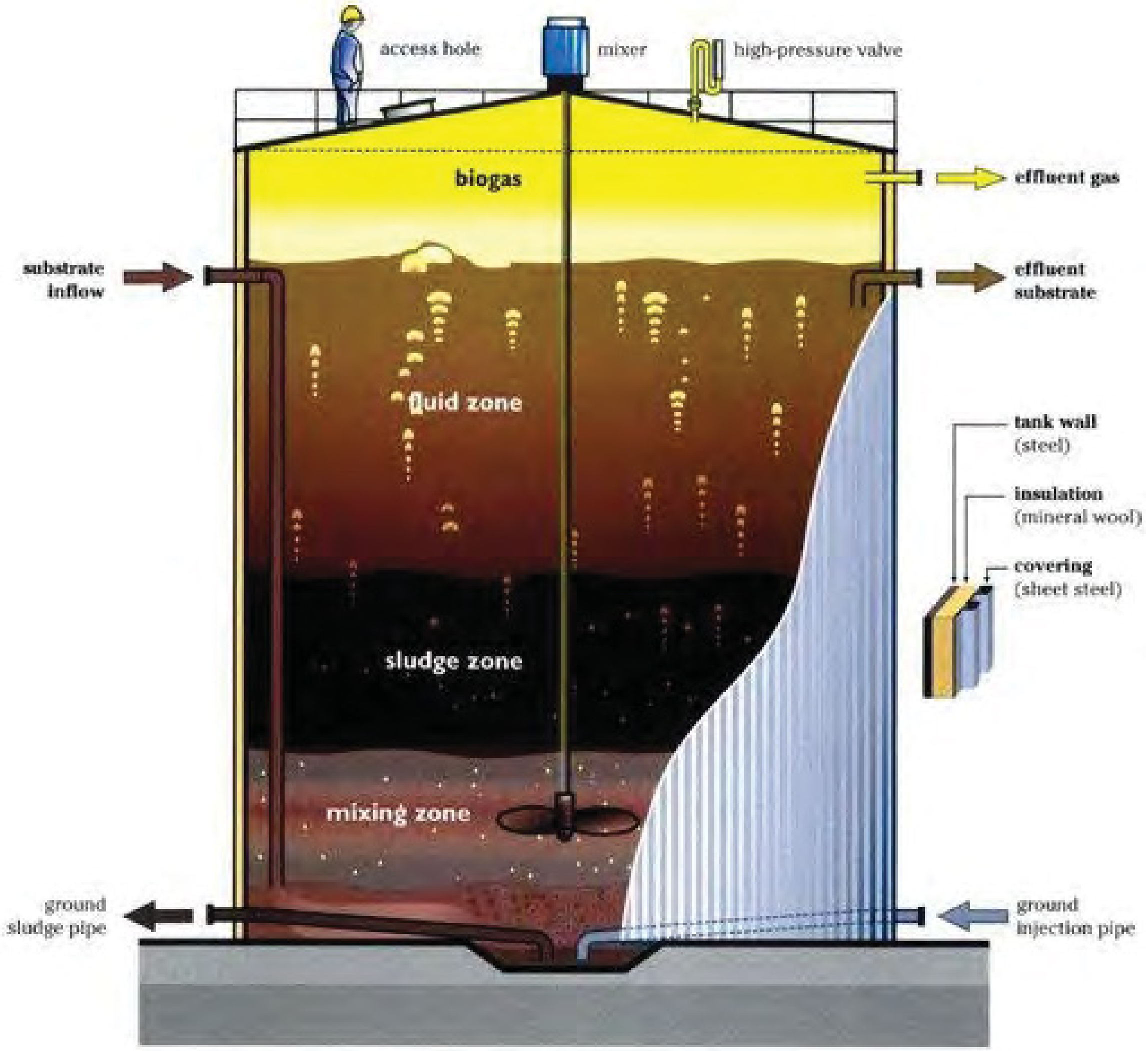

Figure 2-4: Anaerobic Digester (Encyclopedia-of-Alternative-Energy, n.d.)

Producing renewable energy is one of the most important applications of this method. As it is mentioned in the previous paragraph, during anaerobic digestion, methane, carbon dioxide and hydrogen are produced. The combination of these three gases is called biogas (Abdullah et al., 2007). The biogas can be used as fuel for gas engines to provide electricity or it can be burned to provide heat. Therefore anaerobic digestion can treat hazardous wastes while covering the energy needs (Ismail et al., 2012).

Making soil conditioners is another application of anaerobic digestion. In the second stage of digestion digestate is produced, this solid product includes lignin and cellulose and may also contain minerals and remnant bacteria. The moisture retention properties and including organic contents which are degradable aerobically make this product a good choice as a soil conditioner.

Fertilizer is the third important and possible production of anaerobic digestion. As total nitrogen and total phosphorus concentrations do not change during anaerobic digestion, it is also used as a fertilizer producing method. Of course there are some mineralization processes which change organic nitrogen to ammonia and organic phosphorus to phosphate (Dvorak & Frear, 2012) but these changes not only don't have harmful effects on plants but also facilitate the plant uptake. In normal situations organic nutrients must be mineralized by microorganisms in soil before plants could uptake them and it takes a long time. The nutrients of digested materials are present in the methanogenic digestate. This part is non-biodegradable for anaerobic bacteria and also it is in liquid form and can be used during irrigation operations in agriculture fields. So if the influent has acceptable nutrient concentrations, making fertilizer can gain some benefits or at least cover part of digestion expenses, although being a liquid is a negative point and can make some difficulties in transportation and storage.

Anaerobic digestion is a biological process therefore influent characteristics and toxicity of its contents have effects on the efficiency of digestion. In some situations like our case study because of high heavy metal concentration, the sludge or on other hand the living environment of microorganisms is toxic. This toxicity can disturb the growth of microorganisms and thereupon the efficiency of process and the quality of product will be decreased (Eckenfelder & Santhanam, 1981).

2.2.2 Aerobic Digestion

Using microorganisms for breaking down the biodegradable materials and microbial cells in the presence of oxygen is called aerobic digestion (McFarland, 2001). First of all in this process biodegradable organic matter converts to biodegradable soluble organic matter. In the next step, water, carbon dioxide and active biomass are produced from soluble organic matter. At the end, additional carbon dioxide and water are generated during decay of the produced biomass. (Gredy et al., 1999) An aerobic digester is shown in Figure 2-5. This method has some restriction in average inflow and only can be used in industrial and small municipal applications (Adams & Wesley Eckenfelder, 1981).

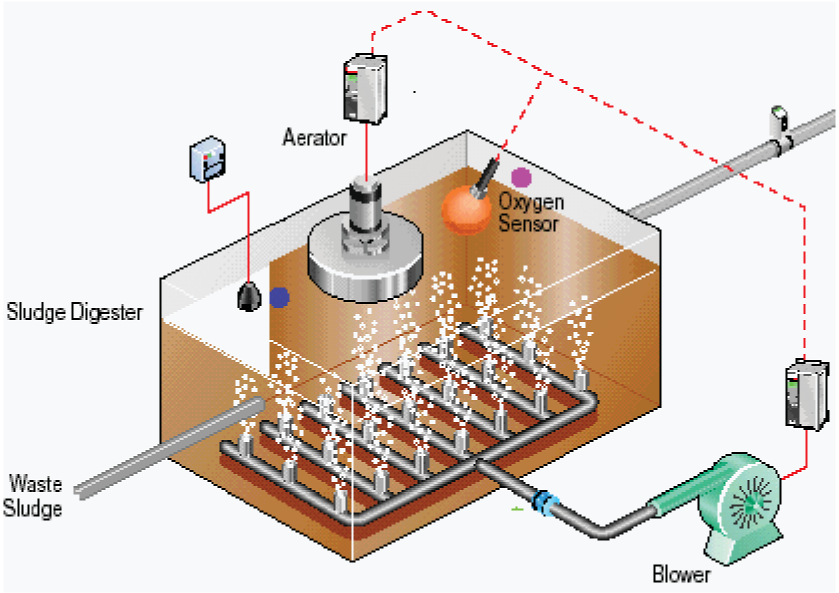

Figure 2-5: Aerobic Digester (Electrical-Engineering-Portal, 2012)

2.2.3 Alkaline Stabilization

Alkaline stabilization is usually done by adding lime to the sludge. The added lime increases the pH of sludge which is inhibitory to biological activities. Lime stabilization can significantly reduce pathogens and the other microorganism concentrations in the sludge and as the odor of sludge is the result of anaerobic decomposition of organic matter, this method also can decrease odor (Turovskiy & Mathai, 2006).

This method has some advantages in comparison to the other sludge stabilization processes. The capital cost in this method is low and the process is easy to operate. Also pathogen reduction in this method is more effective than digestion processes. As it is mentioned before pH elevation is occurred during the process so that metal ions will be immobilized in the sludge and therefore possible uptake of plants will be restricted (Turovskiy & Mathai, 2006). Immobility of metals is not considered by regulations which are designed based on total concentration of metals in sludge.

This method has some disadvantages too. For instance, phosphorus and nitrogen concentrations are lower than products of digestion methods so only the presence of organic matter in the biosolid for improving soil texture and water holding capacity is important in this method. Also during the process, ammonia and the other odorous gases are produced and they need to be treated before being exhausted (EPA, 2000; Turovskiy & Mathai, 2006).

2.2.4 Composting

Composting is a bio-thermal process which decomposes organic matter in the sludge. This process can be done in aerobic or anaerobic conditions but the aerobic is faster and releases more heat and also its product is stable humus-like material (Turovskiy & Mathai, 2006).

Composting is done in three phases. The first phase is mesophilic; in this phase temperature increases to around $40^{o}C$ and acid producing bacteria metabolize carbohydrates, sugars and proteins. After that the thermophilic phase starts and temperature increases from $40^{o}C$ to $70^{o}C$ and thermophilic bacteria in this phase metabolize proteins, lipids and fats. In the final phase which is called the maturation phase, the cooling occurs and microbial activities reduces and composting becomes completed (Turovskiy & Mathai, 2006). Figure 2-6 shows composting phases.

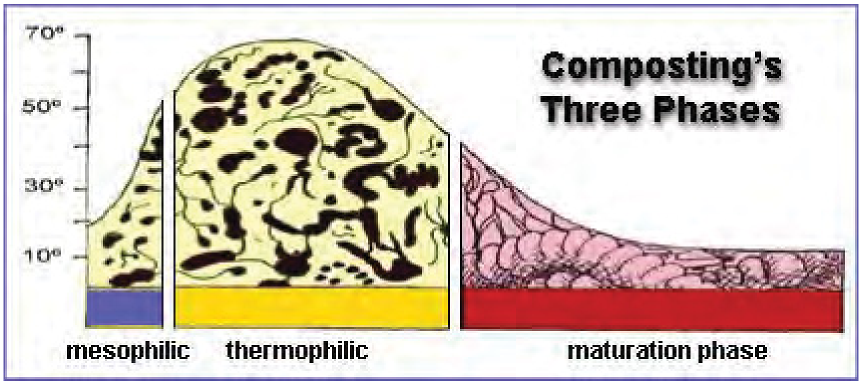

Figure 2-6: Composting phases (Organic-Soil-Technology, n.d.)

Compost has an abundance of nutrients especially about nitrogen, because nitrogen is released as ammonia gas during the process it can be class “A” biosolid if the sludge becomes well composted as it includes humus materials that increases the water contents of soil (Turovskiy & Mathai, 2006).

2.2.5 Incineration

The rapid exothermic oxidation of combustible elements in sludge is called incineration. Incineration produces carbon dioxide, water vapor and ash from the organic solids of sludge. For complete combustion of organic matter, temperatures of 760 to 820^{o}C are needed. The application of incineration is when the sludge utilization is impossible or it is not cost effective (Turovskiy & Mathai, 2006).

Incineration can completely destroy the pathogens and reduce toxins but it is an expensive process. Also the ashes and the emissions need to be treated before entering to the environment (Turovskiy & Mathai, 2006).

2.3 Literature review

In this section, we review the literature in several areas. First the heavy metal removal is reviewed and then nutrient loss during heavy metal removal.

2.3.1 Heavy metal extraction from sludge

As cadmium (Cd) and copper (Cu) are the only metals in the reviewed papers related to research this section is divided in to two subsections for showing the removal percentages and some other information about the experiments separately.

Extracting Cu from sludge

Different extractants have been used for Cu extraction from sludge. The extraction efficiency is not only dependent on extractant type and its concentration but also it is dependent on shaking speed, pH, time, solid/liquid ratio and temperature. As it is shown in Table 2-2, the best removal was reached by Kuan et al. (2010). It was shown that using 0.5M sulfuric acid for two hours in 103^{o}C can remove 99% Cu from sludge. Also using ionic liquids as shown by Fuerhacker et al. (2012) enabled 91% removal but with a smaller S/L ratio and longer time. Generally it seems using acids are more common although their efficiencies are variable according to sludge contents and experimental conditions.

Table 2-2: Copper Extraction Experiments

Extractant	*Best Removal (%)*	*Conditions*	*Reference*
DTPA	15%	4 g sample 2 h shaking 40 ml of 0.05 M DTPA, 0.01 M CaCl2, 0.1 M TEA pH 7.3	(Fuentes et al., 2003)
S,S-EDDS	55%	5g sample 60^{o} C Temp pH 10	(Ullmanna et al., 2013)
S,S-EDDS	72%	0.5g sample 24 h 25 ml EDDS :Metal=10:1 pH 7	(Lihua et al., 2007)
H_2SO_4	99%	S/L=5 g/L 2 h 0.5M Temp=103^{o}C Speed=250rpm	(Kuan et al., 2010)

H_2SO_4	86%	S/L= 0.25 g/L 30 min 20% H_2SO_4 Temp= 80^{o}C	(Stylianou et al., 2006)
H_3PO_4	61%	S/L = 0.02 24 h 5%H_3PO_4 Speed=200 rpm	(ZHANG et al., 2010)
HCl	56%	10 g sample 30 ml 1N HCl 1 h	(Yoshizaki & Tomida, 2000)
H_2SO_4	20%	10 g sample 30 ml 1N H_2SO_4 1 h	(Yoshizaki & Tomida, 2000)
HNO_3	24%	10 g sample 30 ml 1N HNO_3 1 h	(Yoshizaki & Tomida, 2000)
HNO_3	81%	S/L = 0.17 48 h 1N HNO_3	(Kuo et al., 2005)

H_2SO_4	74%	S/L = 0.17 48 h 1N H_2SO_4	(Kuo et al., 2005)
Ionic liquid: [PR4][MTBA]	91%	S/L = 14 g/L 1 night 1g IL	(Fuerhacker et al., 2012)
Ionic liquid: [PR4][TS]	91%	S/L = 14 g/L 1 night 1g IL	(Fuerhacker et al., 2012)

Extracting Cd from sludge:

Based on Table 2-3, the best cadmium removal between reviewed papers is 99% by Kuan et al. (2010). This removal is reached by using 0.5M sulfuric acid for two hours in 103°C. Also chelating agents were used (Fuentes et al., 2003) (Ullmanna et al., 2013) but their best removal percentages are 15.27% and 36% respectively. These removals are the lowest in comparison to the other extractants.

Table 2-3: Cadmium Extraction Experiments

Extractant	***Best Removal (%)***	***Conditions***	***Reference***
DTPA	15.27%	4 g sample 2 h shaking 40 ml of 0.05 M DTPA, 0.01 M $CaCl_2$, 0.1 M TEA at pH 7.3	(Fuentes et al., 2003)
S,S-EDDS	36%	5g sample 60 C Temp pH 10	(Ullmanna et al., 2013)
H_2SO_4	99%	S/L=5 g/L 2 h 0.5M Temp=103°C Speed=250rpm	(Kuan et al., 2010)
H_3PO_4	71%	S/L = 0.02 24 h 5%H_3PO_4 Speed=200 rpm	(ZHANG et al., 2010)

HCl	60%	10 g sample 30 ml 1N HCl 1 h	(Yoshizaki & Tomida, 2000)
H_2SO_4	57%	10 g sample 30 ml 1N H_2SO_4 1 h	(Yoshizaki & Tomida, 2000)
HNO_3	52%	10 g sample 30 ml 1N HNO_3 1 h	(Yoshizaki & Tomida, 2000)
Ionic liquid: [PR4][MTBA]	90%	S/L = 14 g/L 1 night 1g IL	(Fuerhacker et al., 2012)
Ionic liquid: [PR4][TS]	89%	S/L = 14 g/L 1 night 1g IL	(Fuerhacker et al., 2012)
PESA	78%	Acid: Metal = 10:1 24 h pH 4	(ZHU et al., 2009)

2.3.2 Nutrient loss during heavy metal extraction

In Ullmann et al. (2013), the removal efficiencies of S,S-EDDS and one of its derivative C24-EDDS as leachants were investigated. The experiment was done with 5 grams of sludge at a temperature of 60°C and pH 10. The removal percentages of leachants are shown in Table 2-4.

Table 2-4: Nutrients loss in Ullmanna et al. (2013) Experiments

Nutrients	***S, S-EDDS***	***C24-EDDS***
Calcium	18%	14%
Magnesium	8%	9%
Phosphorus	1%	1%
Iron	9%	6%

The nutrient loss was very low for both leachants and especially for phosphorus which is the most important one. C24-EDDS has only 4% cadmium removal and 35% copper removal and its best result is related to zinc with 68% removal and therefore its efficiency in heavy metal removal is not high.

3. Materials and Methods

3.1 Materials

Dipotassium Phosphate, 70% (K_2HPO_4):

This salt was used as a main factor in the leaching solution and it was provided by Fisher Scientific Co.

Nitric Acid Trace Metal (70%):

The acid was used for pH adjustment in the leachant solution. It was also used during acid digestion based on 3050B EPA protocol and for diluting samples before putting them into ICP-MS. Nitric acid was obtained from Fisher Scientific Co.

Hydrogen Peroxide (30%):

It was purchased from Fisher Scientific Co and used during acid digestion based on 3050B EPA protocol.

Hydrochloric Acid (Trace Metal (70%)):

This acid was used for diluting samples before analysis with ICP-MS.

3.2 Instruments

3.2.1 Inductively coupled plasma mass spectrometry (ICP-MS)

An Agilent Technology 7700 X ICP-MS was used for metal analysis in the liquid phase. It can analyze some non-metals with a limit of detection as low as 0.001ppb.

The ICP-MS has an auto sampler device for taking samples from tubes. The liquid samples are sent to the nebulizer. There is also a peristaltic pump to make this process faster. This device has a low flow nebulizer which mixes argon gas with the taken sample to form fine aerosol. The aerosol passes through peltier-cooled spray chamber which removes larger droplets and improves plasma’s robustness. The rest of the droplets pass through transfer tube and enter to the plasma. ICP-MS is shown in Figures 3-1 and 3-2.

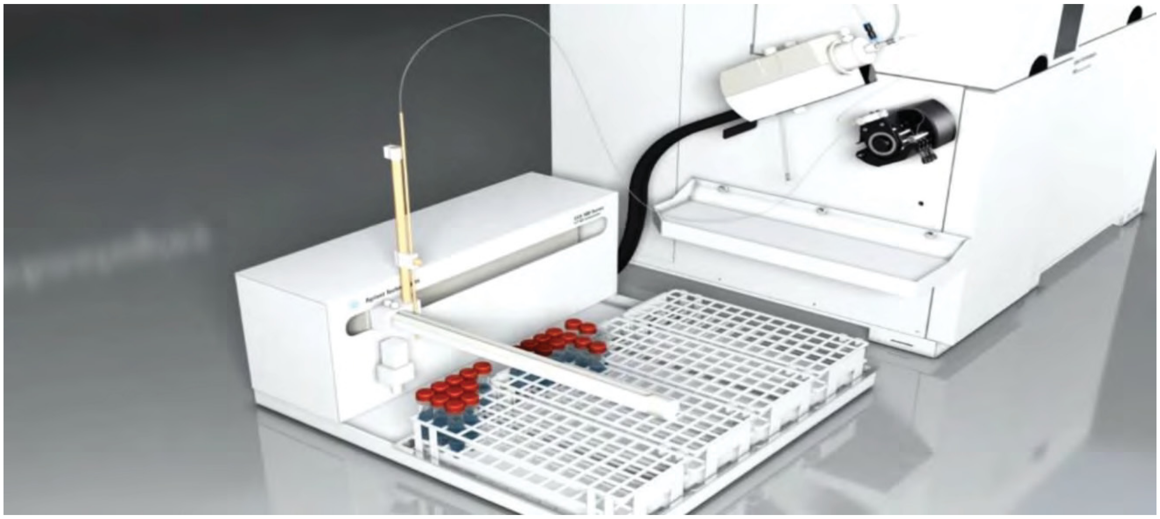

Figure 3-1: Auto Sampler and ICP-MS (7700 Series ICP-MS animation, n.d.)

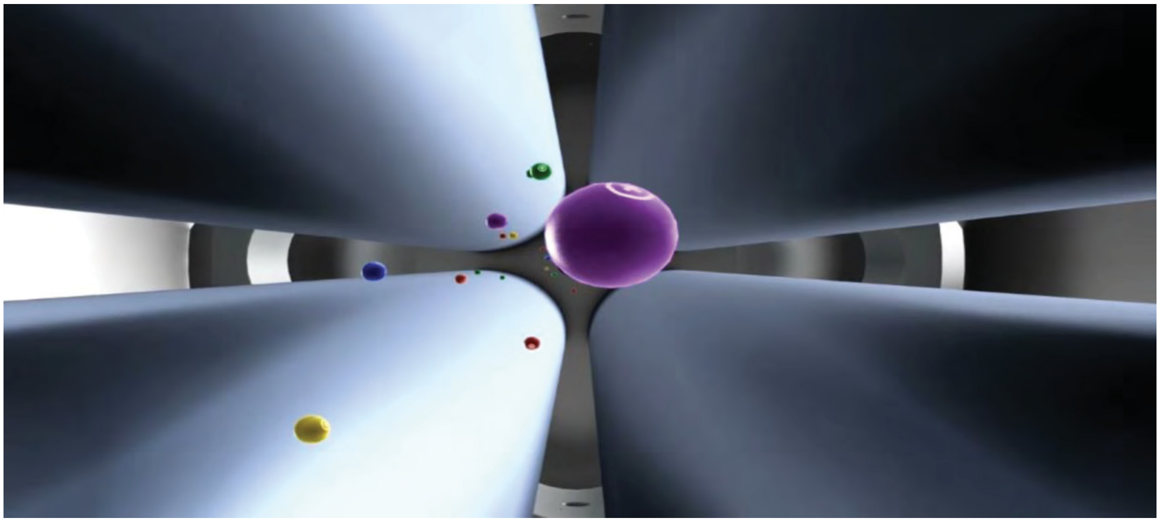

Figure 3-2: Quadrupole Mass Analyzer (7700 Series ICP-MS animation, n.d.)

3.2.2 TNT Kits

The High Range Total Nitrogen Reagent Set from Hach Company was used for nitrogen analysis. These kits can measure 10 to 150 mg/L nitrogen. (Hach, n.d.)

Figure 3-3: Total Nitrogen Reagent Set, HR (Hach, n.d.)

Persulfate digestion was necessary before nitrogen analysis. Persulfate digestion oxidizes dissolved organic nitrogen to nitrate. It has been developed for soil and fresh water (Cabrera & Beare, 1993).

Persulfate digestion was performed by adding persulfate reagent powder and sample to the HR total nitrogen hydroxide digestion reagent vial and heating it for 30 minutes in 105^{o} C. This process was done based on Hach Company instructions by DBR200 device. Total nitrogen hack kits and DBR200 are shown in Figures 3-3 and 3-4.

Figure 3-4: Digital Reactor Block (DRB200) (Hach, n.d.)

Nitrogen concentrations in the samples were read by the DR2800 product of Hach Company, a portable spectrophotometer with a lithium-ion battery that can be used for more than 240 analytical methods (Hach, n.d.). A DR2800 spectrophotometer is shown in Figure 3-5.

Figure 3-5: Portable Spectrophotometer (DR2800) (Hach, n.d.)

3.3 Methods

The experiments were divided into two parts, one for determining initial concentrations of elements, and the other one for leaching experiments to determine final concentrations at different pHs and reaction times.

3.3.1 Scheme of Experiments

A. Primary Sludge Analysis

1. Sampling from WWTP
2. Sample preparation = 1 g dewatered sludge
3. Digestion:
    - Acid digestion for heavy metals and nutrients
    - Per-sulfate digestion for nitrogen
4. Analysis:
    - Heavy metals and nutrients analyzing by ICP-MS
    - Nitrogen analyzing by Hach Kits

B. Leaching Experiments And Analysis

1. Preparation of 3 leaching solutions (pH 1 , 2 and 3) :
    - 1 Molar di-potassium phosphate (K_2HPO_4) solution
    - DI Water
    - HNO_3 (for pH adjustment)

2. Sample Preparation = 1 g dewatered sludge + 50 ml leachant in 50 ml tube
3. Putting samples on a shaker with 150 rpm
4. Each sample has a different reaction time on shaker (1 or 2 or 4 hours)
5. Centrifuging samples with 3000 RPM for 15 minutes
6. Separating sludge from leachate
7. Digestion:
    - Acid digestion for heavy metals and nutrients
    - Per-sulfate digestion for nitrogen

8. Analysis:
    - Heavy metals and nutrients analysis by ICP-MS
    - Nitrogen analysis by Hach Kits.

3.3.2 Heavy Metal Analysis

All heavy metal analysis was done by ICP-MS. As ICP-MS can only analyze liquid samples, all samples should be digested and to do so EPA 3050B method was used. ICP-MS is a very accurate and sensitive device and the sample concentration should not be more than 200 ppb so dilution of the samples was needed before analysis by the ICP-MS.

For digestion based on 3050B, 1 gram dewatered sludge (cake) was separated and after adding 10 ml of 1:1 HNO_3 and water, it was heated to 95^{o} ^{o}C by a hotplate for 15 min. After cooling the sample, 5 ml HNO_3 was added and heating was continued for 2 hours. Again the sample was cooled and 2ml DI water and 3ml H_2O_2 was added and it was heated while adding 1 ml H_2O_2 was continued until general appearance of sample is unchanged. The final step of digestion was heating the sample by hotplate for two hours. After this step the sample was cooled and diluted by DI water 100 times before filtering.

To prepare a sample for ICP-MS analysis, first filtration was needed by a 0.7 micrometer filter paper. The filtering takes a long time because of the filter size therefore using a vacuum pump is recommended. The filtered sample should be diluted by 2% HNO_3 and 1% HCl, the final concentration should be less than 200 ppb. The reason of filtering and diluting by acid is to protect the device against suspended and dissolved solids. In this case, all samples were diluted 500 times by 2% HNO_3 and 1% HCl.

To prepare ICP-MS for analysis calibration is necessary. The concentrations of all the analyzed samples were calculated based on the drawn calibration curve. In our case five calibration samples with 0.1, 1, 10, 100 and 300 ppb were prepared to have an accurate curve.

3.3.3 Nutrient Analysis

ICP-MS is unable to analyze nitrogen and therefore nitrogen analysis was performed by Hach Kits and the other nutrients were analyzed by ICP-MS.

3.3.3.1 Nitrogen Analysis

Persulfate digestion is needed before nitrogen analysis. The digestion was done based on the Hach instructions. The sample and persulfate powder was added to the HR total nitrogen hydroxide digestion vial and after 30 seconds of mixing it was heated to 105^{o}C for 30 minutes by the Hach Digital Reactor Block 200. The digested sample needed to be cooled before using for nitrogen analyses.

The nitrogen analysis was also followed based on the Hach instructions. It included adding two different powders called A and B to the digested sample and taking 2 ml from the produced solution for mixing with a new solution called C. At the end nitrogen analysis results were shown by the DR 2800 Hach device.

3.3.3.2 Other Nutrient Analysis

Analyzing all the nutrients except nitrogen was done by ICP-MS. The only difference for this analysis with heavy metal analyses is the dilution of samples.

As the nutrient concentration range was higher than the heavy metal more dilution was also needed, of course the dilution solution was the same, it was DI water with 2% nitric acid and 1% hydrochloric acid but 50000 times dilution was used for calcium, magnesium and iron and 1000000 times dilution was used for potassium and phosphorus. Generally ICP-MS has some difficulties for phosphorus analysis and its results for phosphorus are not as accurate as the other elements.

3.3.4 Leaching Experiment

Leaching is the selected method for treating the sludge. In these experiments, the proposed leachant efficiency and effect of some important factors on the final product were investigated.

The samples were obtained from Montreal WWTP called Jean.R.Marcotte. This WWTP is the third largest plant in the world. As it is shown in Figure 3-6 after pumping water, the pre-treatment is started with screening units to remove large solids and continued with grit removal to be sure that nothing can disturb the treatment process. The main treatment unit in this WWTP is primary treatment, a coagulant, ferric chloride or alum, is added before screening units. Also an additional flocculation aid, a long string polymer, is added after grit chamber units. Coagulation and flocculation occur in the primary clarifiers. The total solid in the primary sludge is around 3%. This sludge is sent to be homogenized, conditioned and dewatered. Also there are mechanical traversing bridges to remove the scum from the surface of the water. The treated water is discharged to the regional river. Figure 3-7 shows that there are four reservoirs after the primary clarifier to help managing the biosolid treatment. Sludge is pumped from these reservoirs to a homogenization unit. Also it is shown in Figure 3-7 that the polymer is added before dewatering to increase efficiency of filter presses. After producing cake, it is sent to incineration and the ashes are sent for disposal.

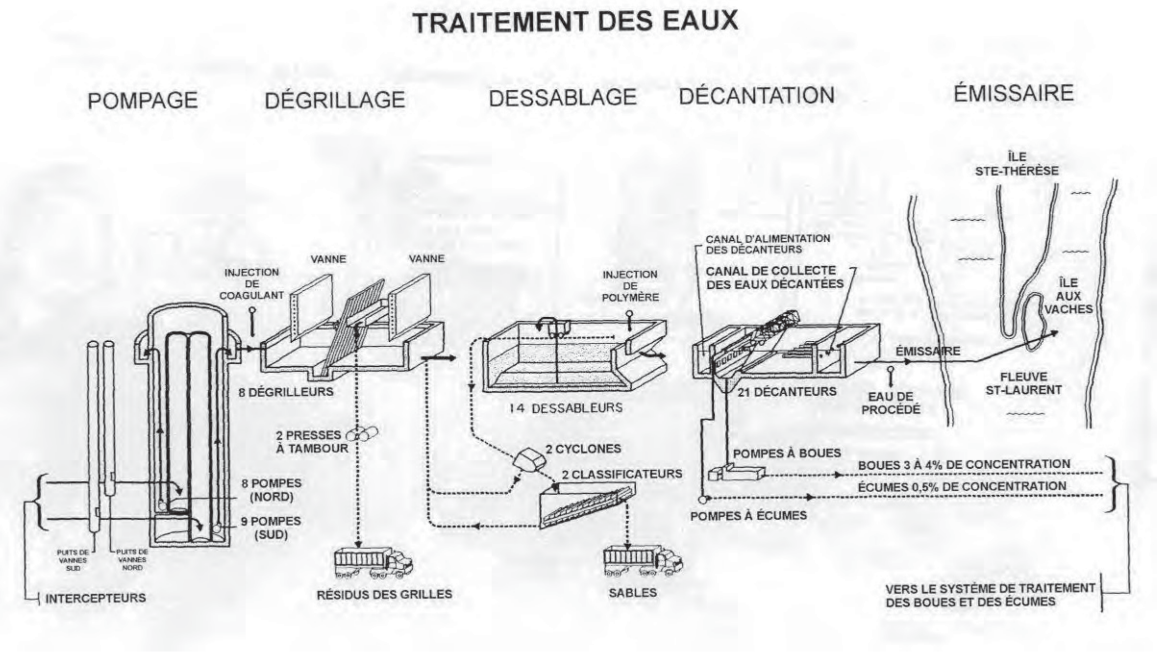

Figure 3-6: Water Treatment Units (Pilote, 2010)

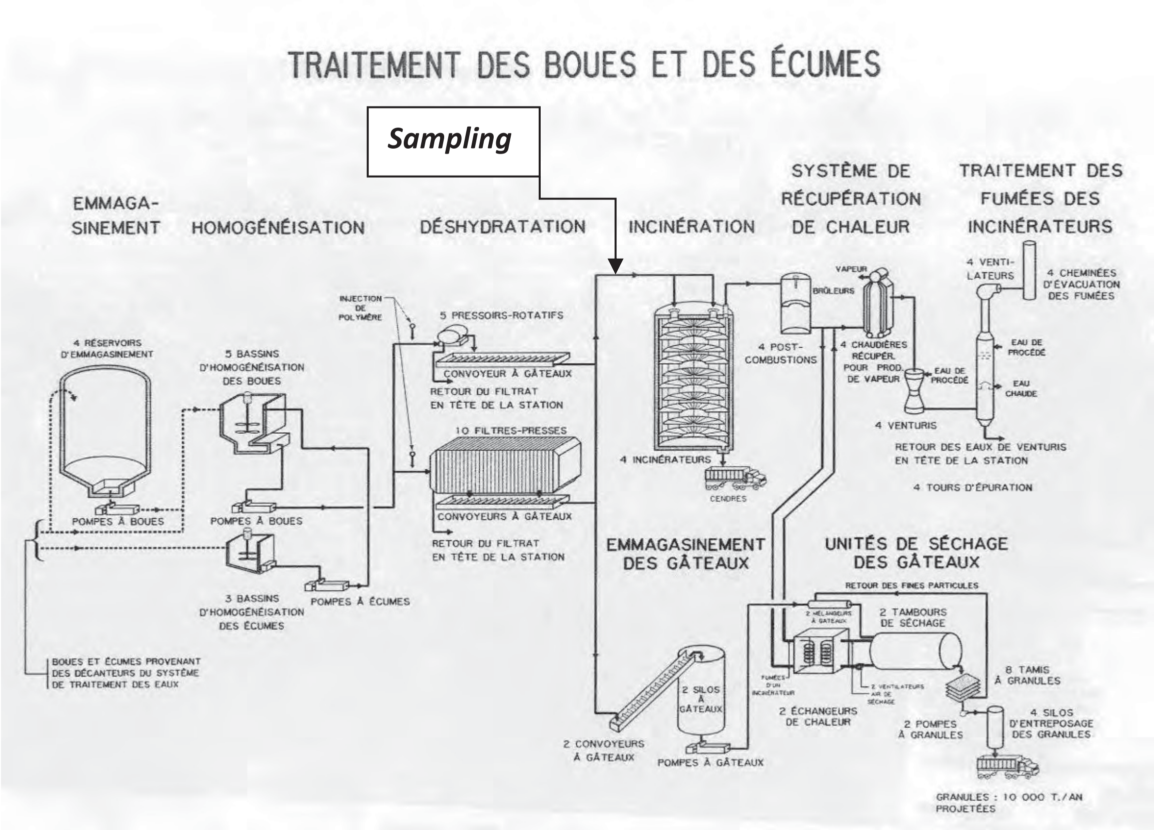

Figure 3-7: Sludge Treatment Units (Pilote, 2010)

Samplings were done on 23/08/2012, 9/11/2012 and 22/5/2013. The samples were obtained from primary sludge after dewatering and before sending the cake to the incinerator. Also the samples have been kept in plastic containers inside the refrigerator in 4 ^{o}C temperature.

The leaching experiments were done in the same tubes and solid/liquid ratio but each sample has different reaction times and pH. Also the proposed leachant in this thesis is a dissolved salt in DI water with adjusted pH by acid.

For preparing a sample, 1 gram of dewatered sludge was taken and put in 50ml tube. Leaching solution was also prepared by dissolving dipotassium phosphate in DI water; this solution was a molar solution. After dissolving the salt, the leachant was divided into three beakers for pH adjustment by nitric acid. The adjusted pH was 1, 2 and 3. At the end 50ml of leaching agent were added to each tube.

To start the leaching process, all the tubes were put on a horizontal shaker and the shaking speed was adjusted to 150 rpm. After 1, 2 and 4 hours tubes were removed and put in a centrifuge for 15 minutes with 3000 rpm after removal from the shaker. This can help to separate the solid part from the leachate. The samples were then analysed. For more accurate results, the leaching experiment was repeated three times and the final result was the average of these three experiments.

4. Results and Discussion

4.1 Historical Data

In this part we study the historical data statistically. The data is compared with Quebec regulations to show the capability of sludge to use as fertilizer and importance of heavy metal removal in sludge. Also the trend of concentrations during these two years will be investigated. These data are derived from annual reports of 2010 and 2011 from Montreal waste water treatment plant. The concentrations are an average of 28 samples; seven samples were taken each three month period over seven consecutive days. The samplings were done on February, May, August and November. A copy of the data sheets is provided in Appendix I.

4.1.1 Nutrients

The most important nutrients for plants are nitrogen, phosphorus and potassium which are called primary nutrients. These three are usually shown as NPK in fertilizer descriptions. The average concentrations of these nutrients in 2010 and 2011 are shown.

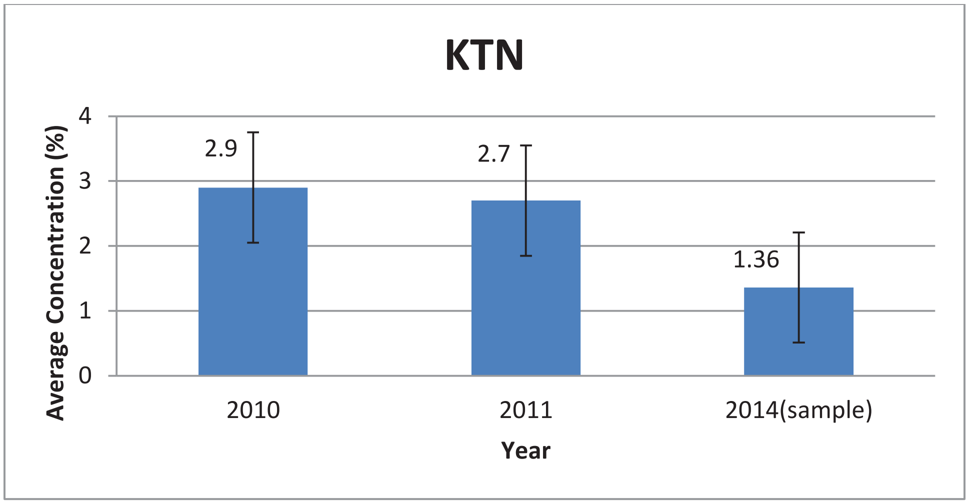

Figure 4-1: Total Calcium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

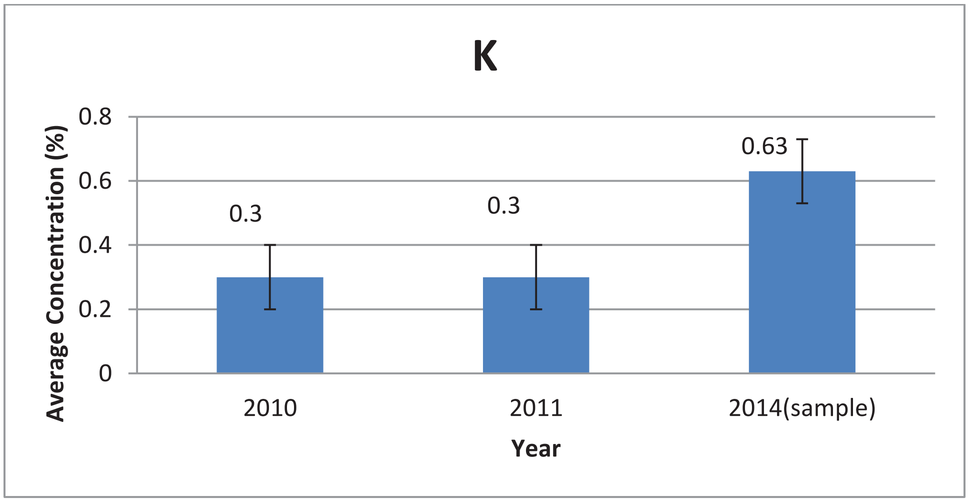

Figure 4-2: Total Calcium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

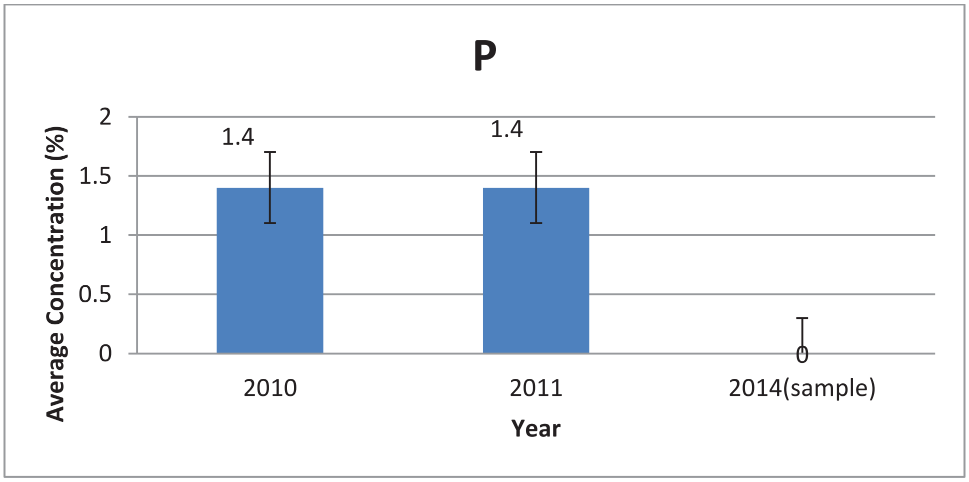

Figure 4-3: Total Calcium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

It is seen in Figures 4-1, 4-2 and 4-3 that the concentrations are approximately constant and although the concentrations in comparison to chemical fertilizers are low but unlike the chemical fertilizers the sludge can provide all three nutrients for plants. Of course these numbers are initial concentrations and the effect of proposed method on nutrients will be investigated to show the final concentrations of each nutrient in the product.

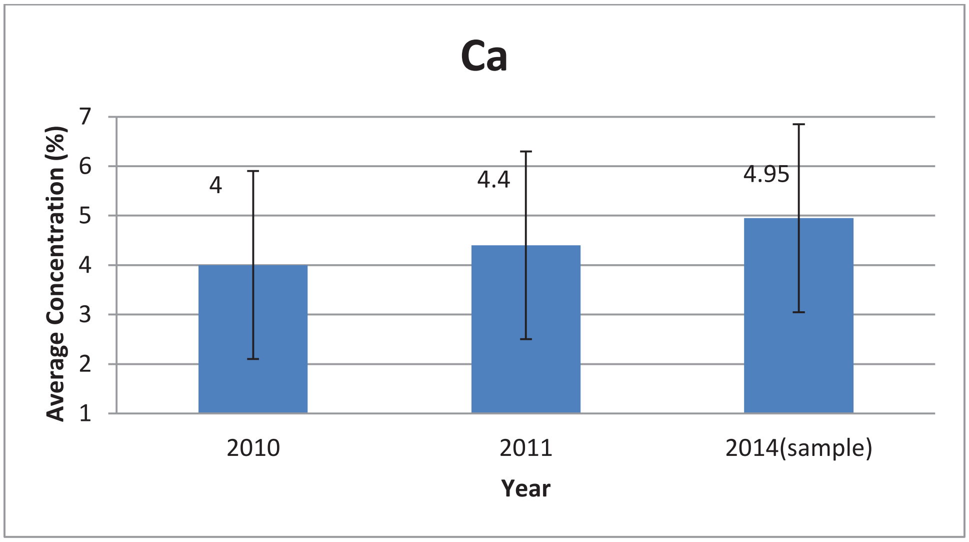

Figure 4-4: Total Calcium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

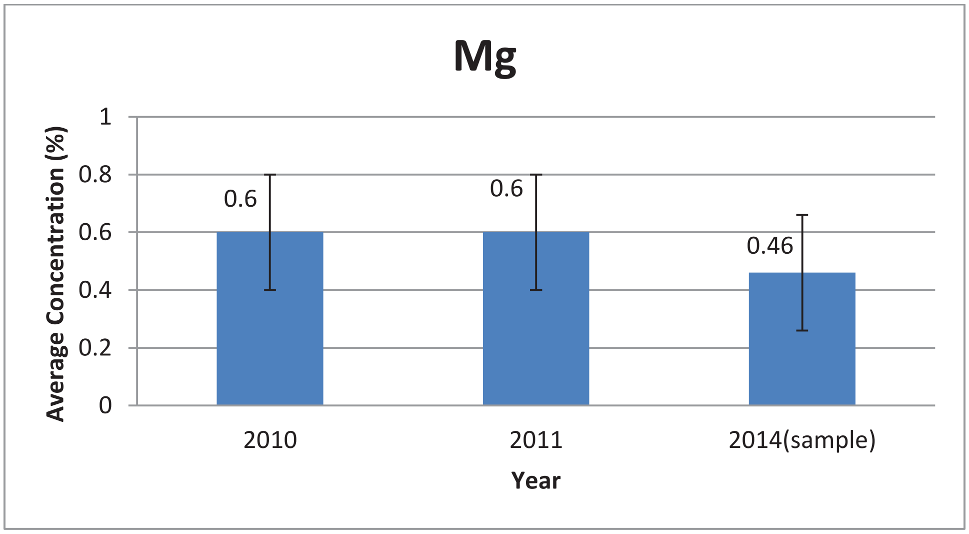

Figure 4-5: Total Magnesium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

Calcium and magnesium are in the secondary macro nutrient group. This group includes sulfur too but there is no information about this element in the annual reports. As it can be seen in Figures 4-4 and 4-5, like primary macronutrients, the concentration in this group is also constant during 2 years and existence of these two nutrients is one of this sludge advantages.

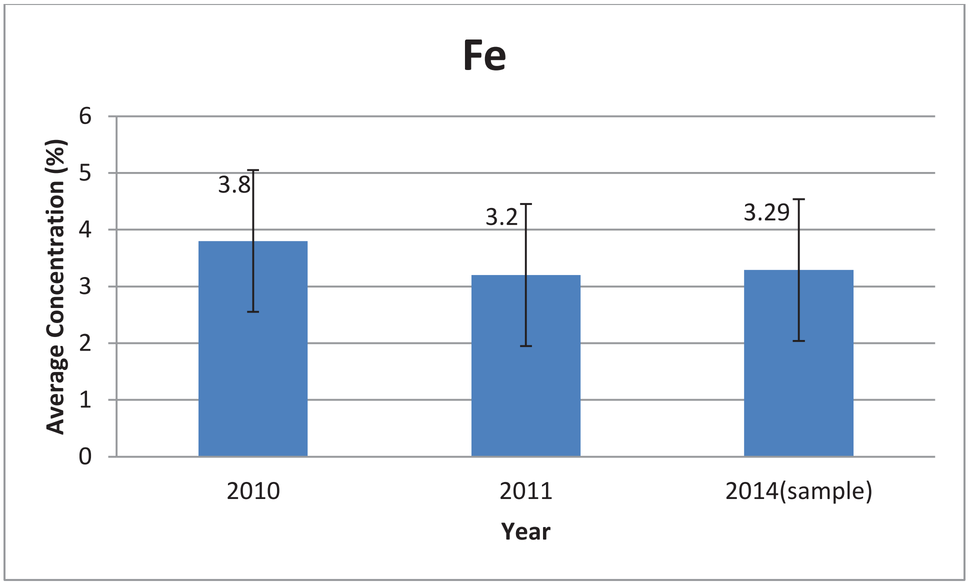

Figure 4-6: Total Iron in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

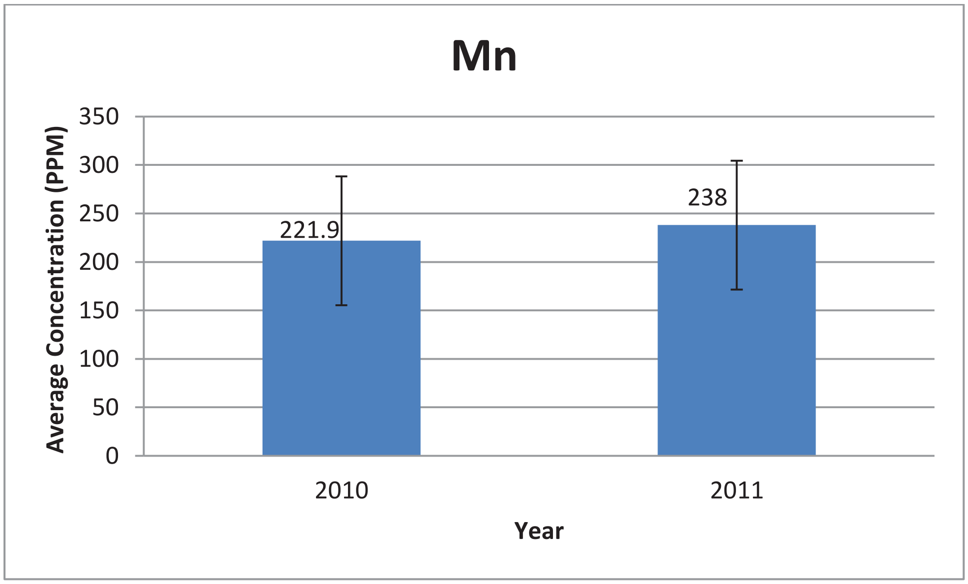

Figure 4-7: Total Manganese in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

The third group is micronutrients, this group includes 8 different elements and 6 of them can be found in the sludge based on the historical data. Based on Figures 4-1 to 4-7 it seems iron and manganese and the rest of the nutrients are stable. To summarize there are 11 out of 14 nutrients in this sludge that are stable during the two year study.

4.1.2 Metals and Heavy Metals

The average concentration of metals and heavy metals reported in 2010 and 2011 is shown as follows.

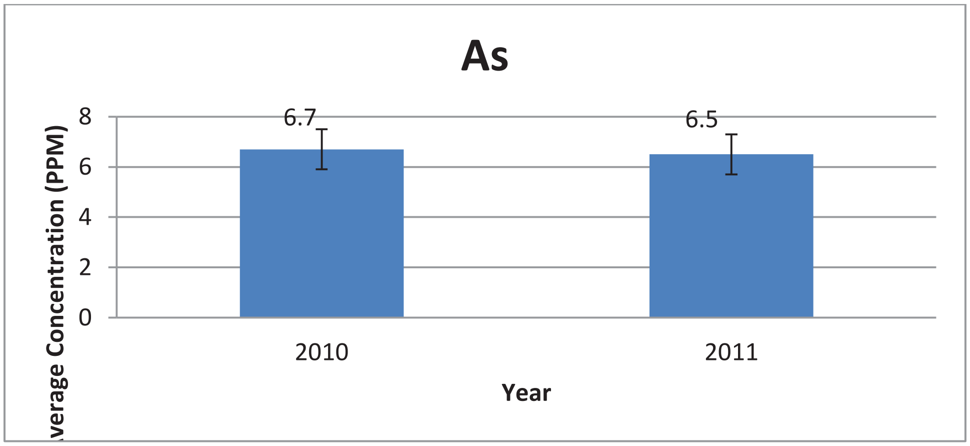

Figure 4-8: Total Arsenic in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

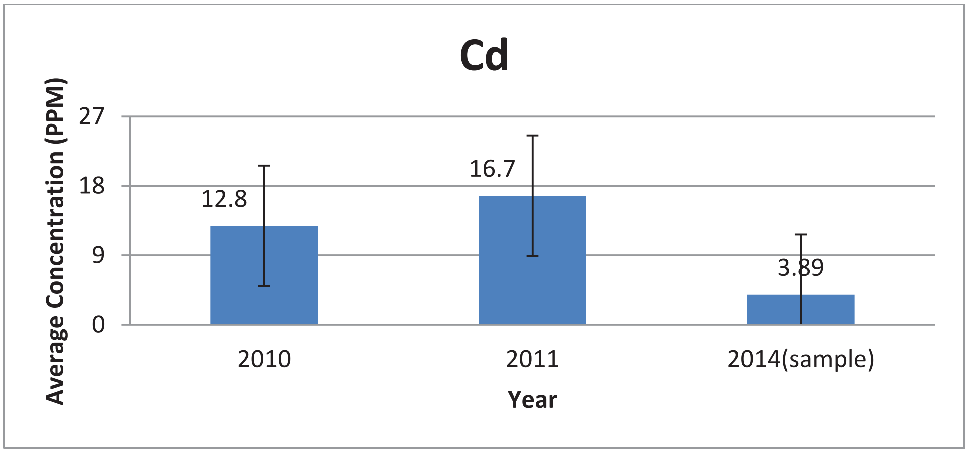

Figure 4-9: Total Cadmium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

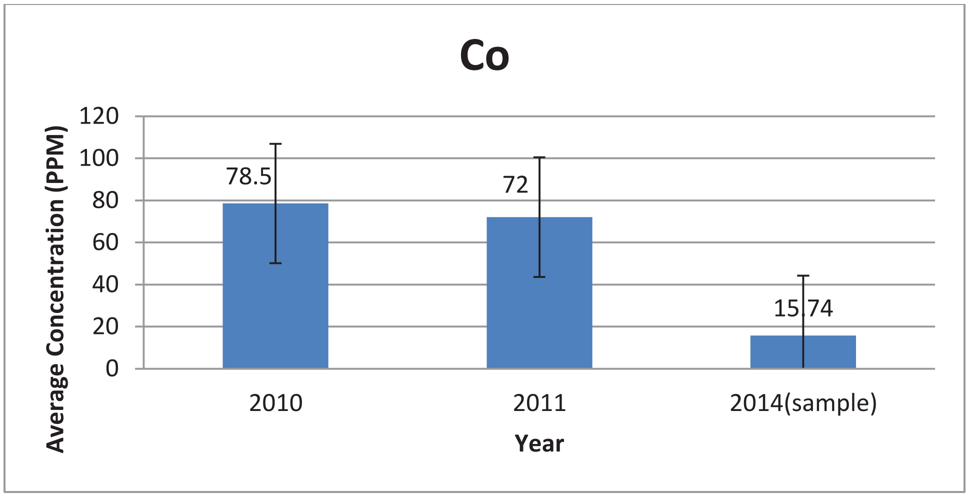

Figure 4-10: Total Cobalt in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

Figure 4-11: Total Chromium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

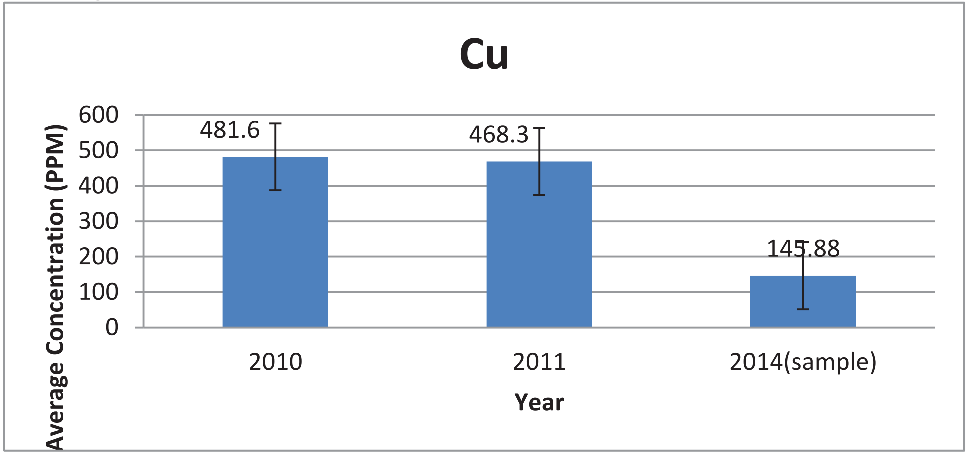

Figure 4-12: Total Copper in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

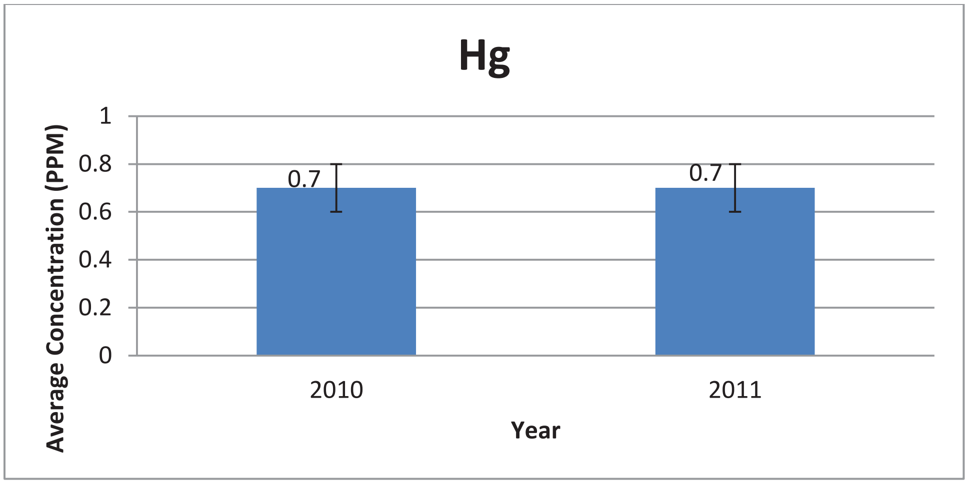

Figure 4-13: Total Mercury in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

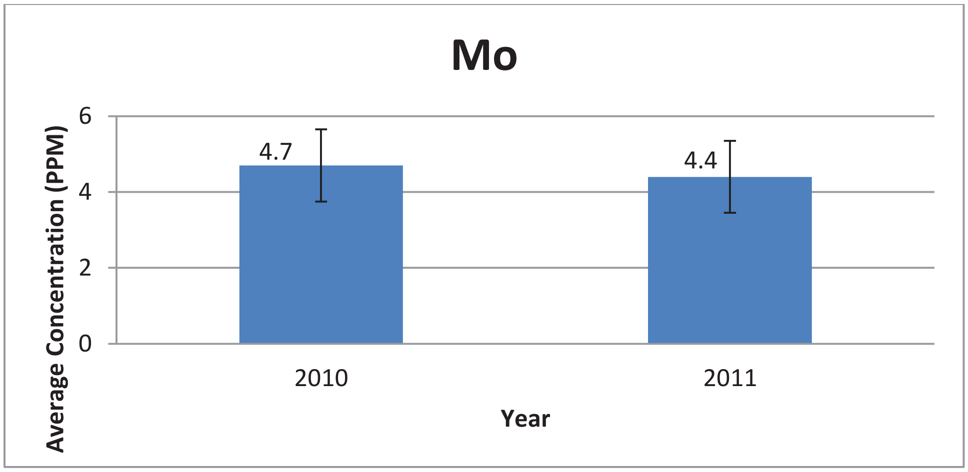

Figure 4-14: Total Molybdenum in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

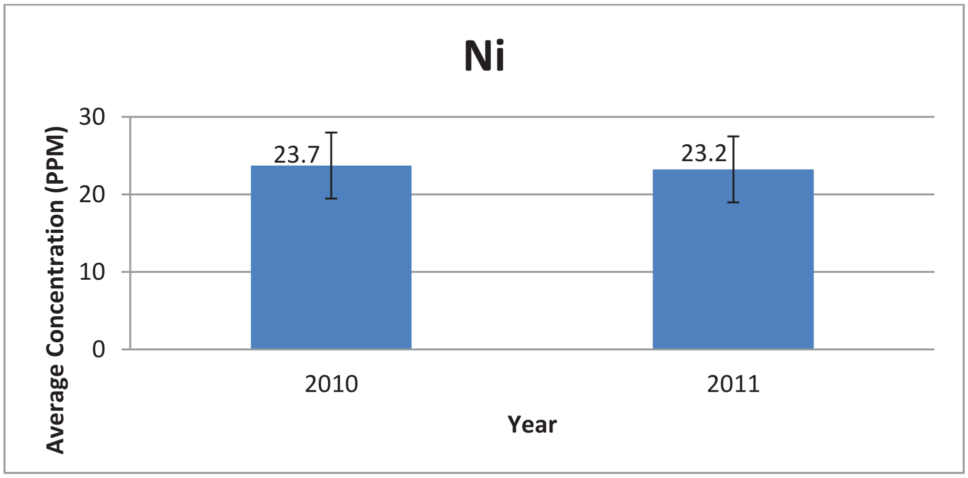

Figure 4-15: Total Nickel in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

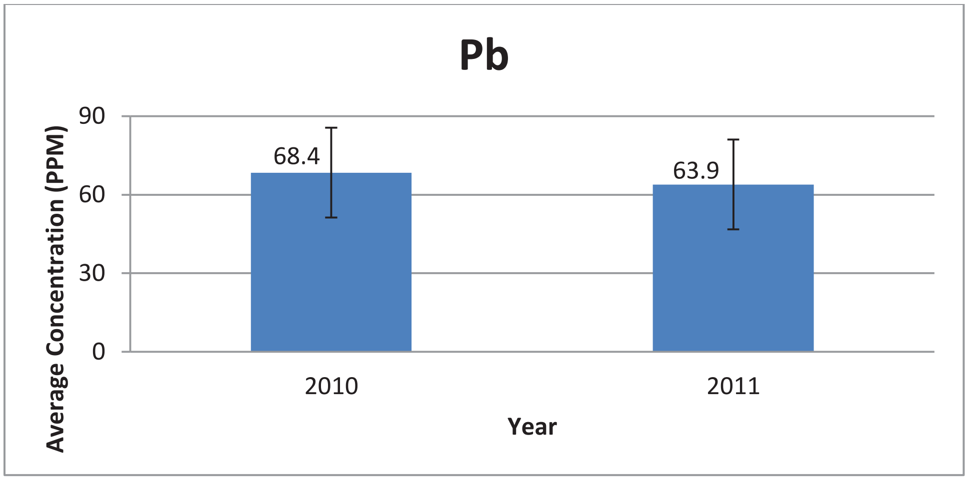

Figure 4-16: Total Lead in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

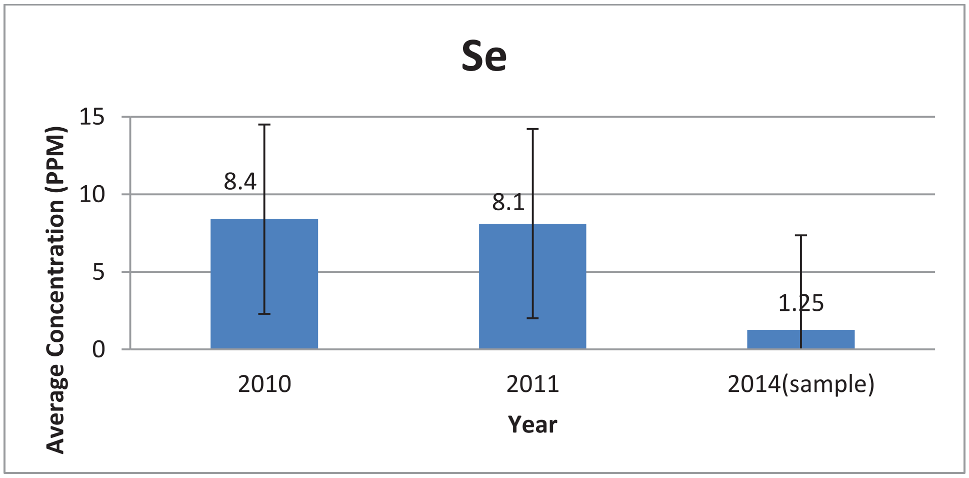

Figure 4-17: Total Selenium in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

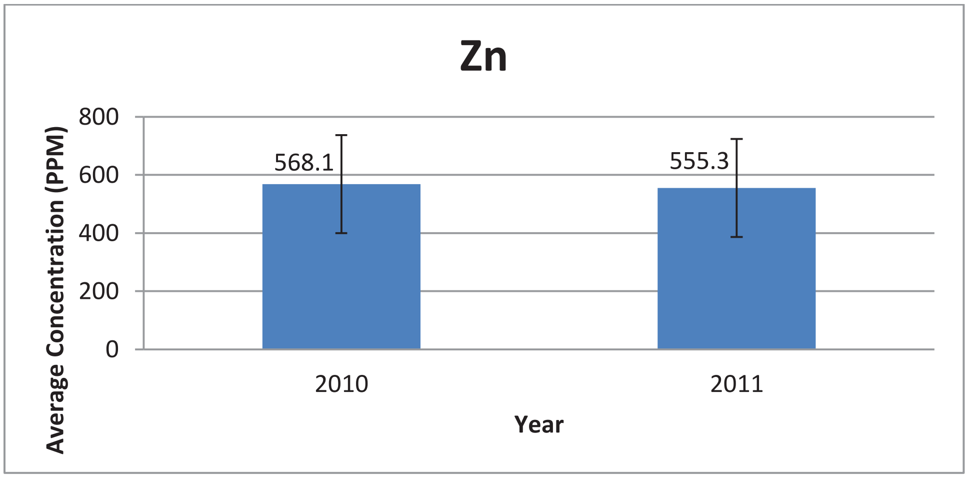

Figure 4-18: Total Zinc in 2010 and 2011 (Pilote, 2010), (Pilote, 2011)

Heavy metals usually have toxic effects on plants except for zinc (Zn), copper (Cu), molybdenum (Mo) and nickel (Ni) at low concentrations. These four elements are in micro nutrients group. At higher concentrations, these four heavy metals will be harmful for plants.

Based on Figures 4-8 to 4-18, the average concentrations of all heavy metals between 2010 and 2011 are approximately constant except for cadmium and chromium. Cadmium increases 30 percent and chromium decreases 14 percent. Decreasing chromium is a positive change although chromium was under the C1 limit before this change. It will be explained that high concentrations of cadmium is a main problem even in 2010 and it seems this problem is intensified during 2011.

Table □-1: Comparison of sludge sample contents in 2011 to Quebec Regulations

Elements	C1	C2
As	*Yes*	*Yes*
Cr	*Yes*	*Yes*
Hg	*Yes*	*Yes*
Mo	*Yes*	*Yes*
Ni	*Yes*	*Yes*
Pb	*Yes*	*Yes*
Zn	*Yes*	*Yes*
Co	*No*	*Yes*
Cu	*No*	*Yes*
Se	*No*	*Yes*
Cd	*No*	*No*

As it can be seen in Table 4-1, by comparison between Quebec regulations and the average concentrations in 2011, heavy metals can be divided into three groups. The first group including As, Cr, Hg, Mo, Ni, Pb and Zn can pass both regulations without any treatment. The second group includes Co, Cu and Se that can pass C2 so and thus the prepared sludge is acceptable but improving the quality of biosolid is needed to decrease their concentration to the C1 limit. As Canada agriculture regulations for heavy metals is defined in the unit of kilograms metal per each hectare during 45 years ($\frac{kg}{ha \times 45\ Year}$), this removal will let the farmer to use more of the biosolid as fertilizer if it is needed. The third group includes Cd; this element cannot even pass C2 regulations and has a high concentration in the biosolid. Its concentration in historical data shows however it cannot pass C2 in 2010; it even has a 30% increase in 2011. Therefore Cd can be defined as the major problem here for using the sludge as a fertilizer. Also based on the average concentration in 2011, it is necessary to reach 82% cadmium removal percentage to pass C1. To conclude cadmium can be defined as a major problem and copper, cobalt and selenium as minor problems and solving these problems before using the produced biosolid is mandatory.

4.2 Leaching Experiment Results

In this part the decrease of metal concentrations in the sludge will be investigated. The mandatory condition for the produced biosolid is to have an acceptable cadmium removal for passing C1 Quebec regulations. An attempt was made to decrease copper, cobalt and selenium concentrations and preserve or increase the nutrient concentrations of the biosolids.

This is necessary to mention that for increasing the accuracy and decreasing the error in results, all results are based on average of three different experiments. It will be shown that pH and time are two important factors in this method. As a result in this experiment, elemental concentration is a function of two variables, time and pH.

4.2.1 Heavy metals

The main mechanism in this method is using a potassium leaching solution for removing heavy metals from sludge by ion exchange process, it means potassium goes in the sludge during the leaching experiment and fills the place of heavy metals and heavy metal ions are removed from the sludge into the leachate solution. Therefore the treated sludge has potassium instead of heavy metals. The existence of the ion exchange process between potassium and several heavy metals cations was studied and shown by Sparks (1989) in soil previously and this research can exhibit a new application for that.

Potassium is an important nutrient for plant too during the removal of heavy metals the fertility of sludge is increased by adding potassium to it. On other hand the quality of biosolid is increased by two ways at the same time, first by removal of harmful heavy metals and second, by adding a useful nutrient.

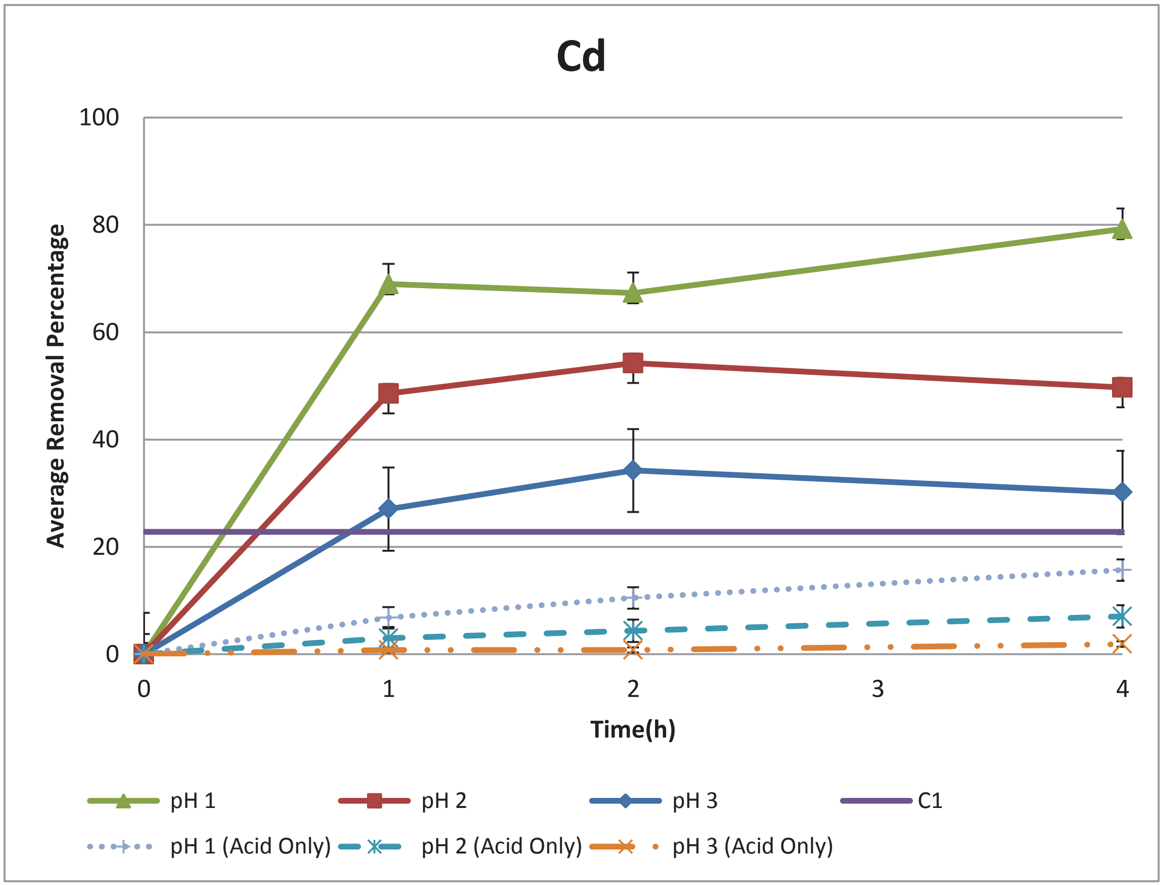

Figure 4-19: Cadmium Removal at Different pHs

Fig. 4-19 shows the average removal percentage for cadmium at different pHs during 4 hours. As it is seen, this method needs a short time period for reaction and most of the removal occurred during first hour. Also there is an indirect correlation between removal percentage and pHs, by decreasing the pH, removal percentage increases. The experiments show that the acceptable range for pH is less than 3. Otherwise the biosolid cannot pass C1 regulation and so that the mandatory condition will be not satisfied. Moreover the removal percentage by this method for cadmium reaches its maximum removal percentage, around 80%, after four hours reaction at pH 1. Also the difference between using a salt and using only acid is shown in Figure 4-19 to prove efficiency of the method. Salt can increase the removal percentage from 18% to 80% at pH 1 after four hours.

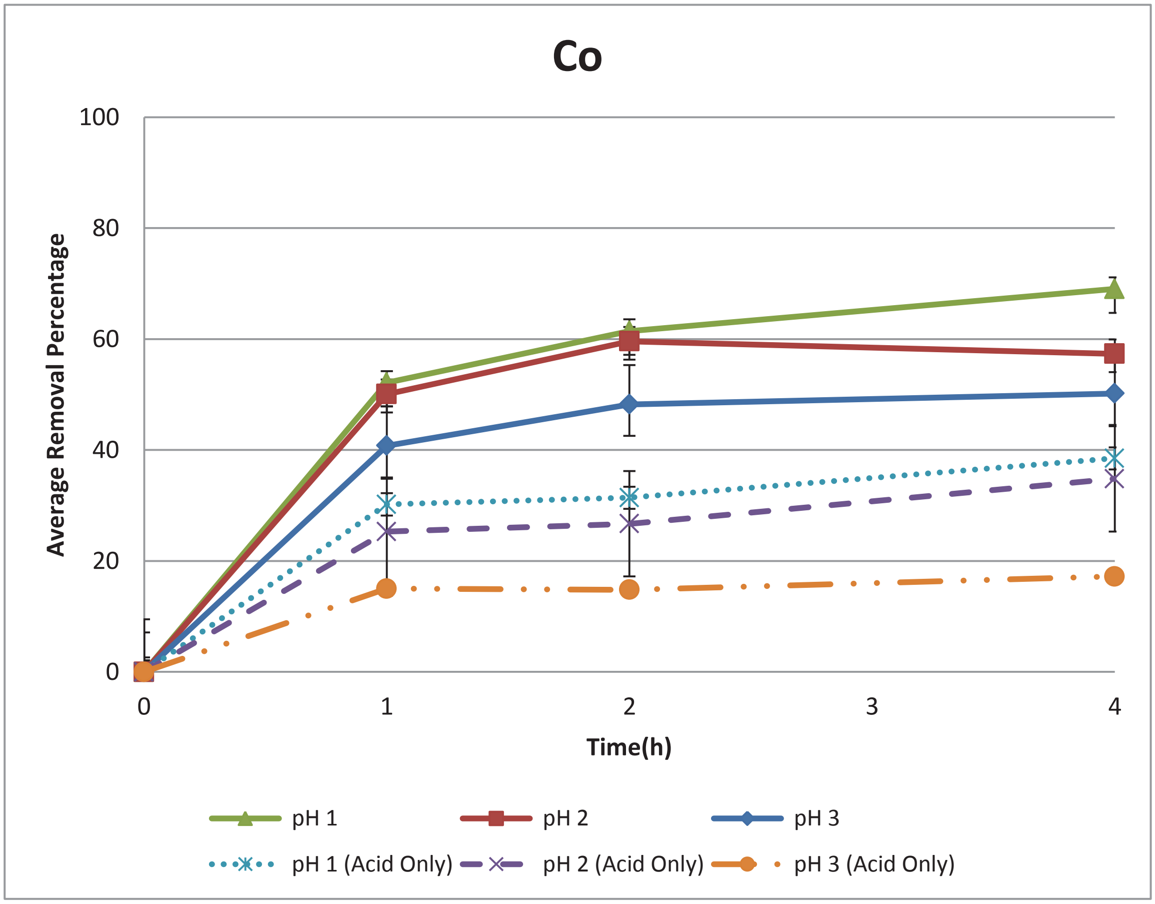

Figure 4-20: Cobalt Removal at Different pHs

After satisfying the mandatory condition, it is time to investigate the impacts of method on the minor problem group. The first element is cobalt with a range of removal percentage from 40% to 70% (shown in Figure 4-20). This range of removal percentage shows acceptable capability for ion exchange between cobalt and potassium. This capability has an indirect correlation with pH and the small difference between pH 1 and 2 shows that the removal percentage is around its maximum and decreasing the pH to less than 1 probably cannot change the result a lot. This conclusion has more reliability for less than 2 hours reaction. It can be seen that the most of the cobalt removal also is done in first hour and only at pH 1 there is a change of around 7% after 2 hours. Also as it is shown not using salt can decrease removal efficiency 50% from around 70% to 35% at pH 1 after four hours.

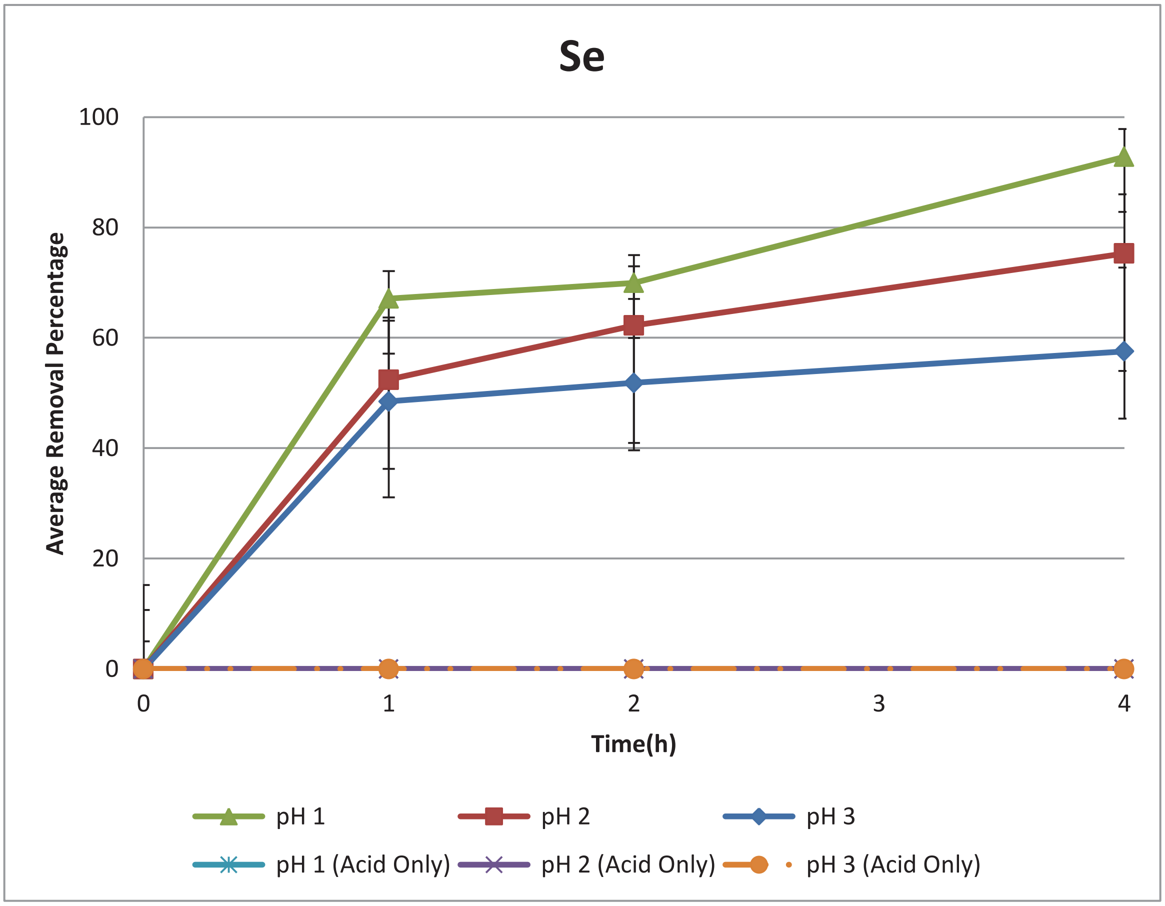

Figure 4-21: Selenium Removal at Different pHs

The second element in the minor problem group is selenium. As it is shown in Fig. 4-21 the best removal percentage between the studied heavy metals belonged to selenium which has the maximum of 93% removal after 4 hours in pH 1. The continued increase of removal before 4 hours shows that there is the possibility of improving removal by continuing the reaction for more than 4 hours. There are two points here that should be mentioned. First, this is not needed to continue the reaction even after one hour because the goals are reached in that time. Secondly, the major part of removal with the highest slope is at first hour which means a fast and effective removal process happened in that time. Also it is shown that without using salt selenium removal is 0% after four hours at all pHs.

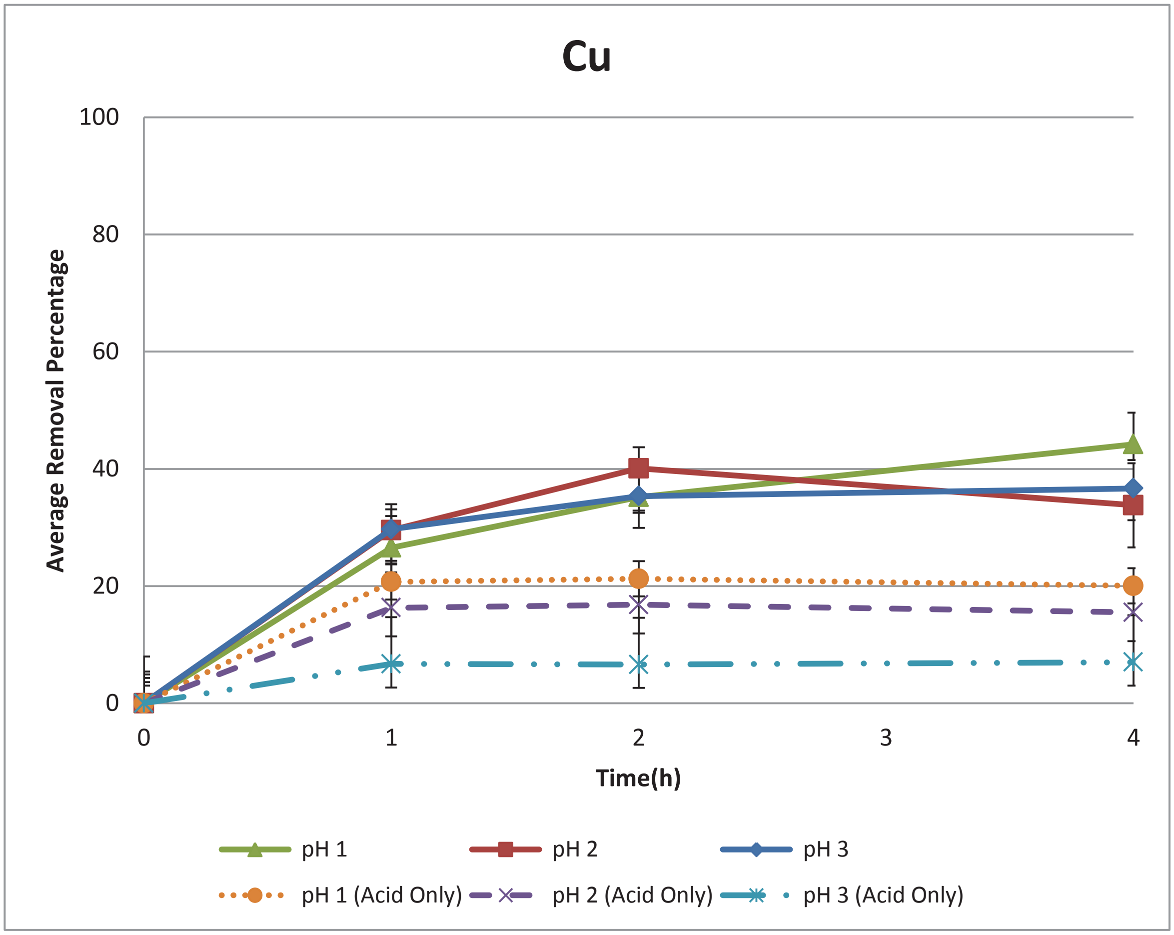

Figure 4-22: Copper Removal at Different pHs

Copper is the last element of the minor problem group and It has the lowest removal. Copper ions for potassium are not significantly changed by decreasing the pH to less than 3. Also the impacts of possible errors during the experiments are more visible here because of small differences between the experiments. But it can be concluded from Fig. 4-22 that there is not any correlation between pH and removal percentage for copper. Also it is shown that using salt can improve removal percentage from 20% to 44% at pH 1 after four hours.

4.2.2 Nutrients

After removing harmful heavy metals from the biosolids it is important to have sufficient nutrients in the biosolid, therefore preserving existing nutrients and even increasing their concentrations if it was possible is the second goal of this project. The most important nutrients are nitrogen, phosphorus and potassium so they are chosen to be involved in this treatment method. On the other hand, the selected acid and salt are chosen because of containing these three elements in their chemical composition. The effect of this leaching method on the concentration of six different nutrients was investigated.

Table □-2: Nutrient initial concentration in samples before leaching tests

Nutrient	Initial Concentration in samples
K	0.63%
N	1.36%
P	0%
Mg	0.23%
Ca	0.23%
Fe	1.58%

Table 4-2 shows the initial concentration of nutrients in the sample before treatment. The difference between the concentration of our samples and historical data will be analyzed at the end of this chapter.

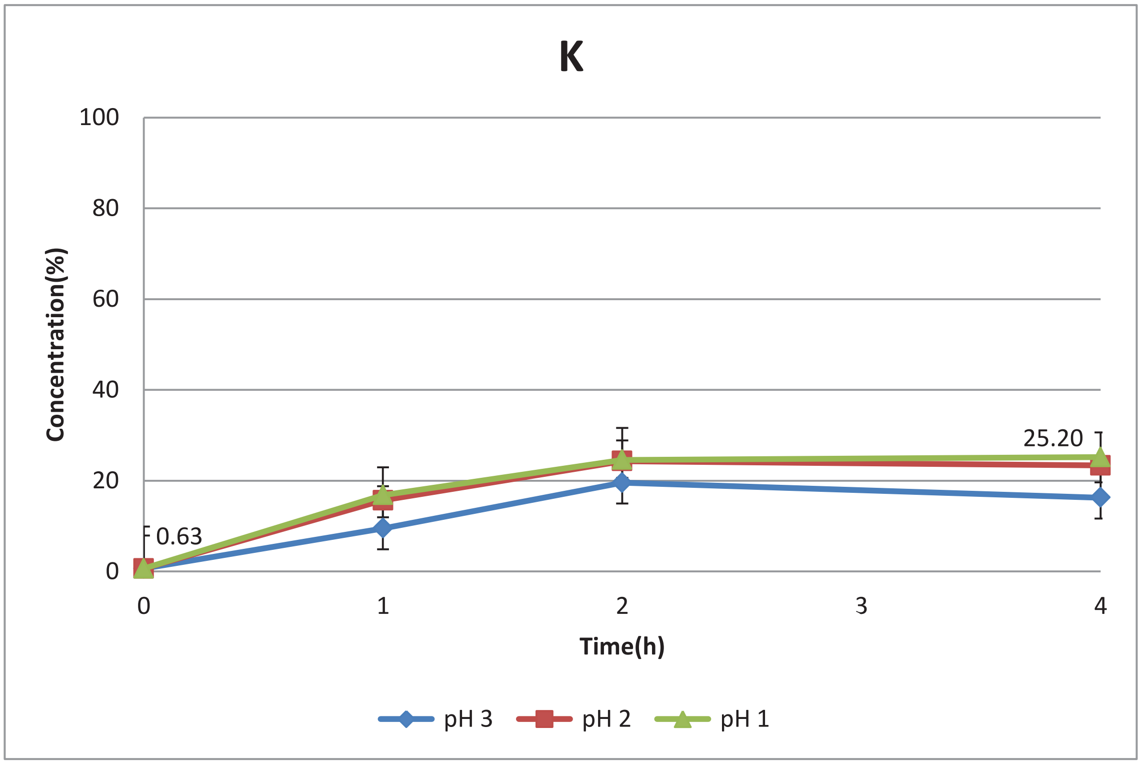

Figure 4-23: Remaining Potassium Concentration in Sludge after Leaching Experiment at Different pHs

Potassium exchange is the main mechanism for heavy metal removal. This mechanism increases the potassium concentration in the product. Also production of some salts with a lower solubility than dipotassium phosphate and precipitation of them can be a reason for the increase in concentration. For instance solubility of potassium nitrate is 330 $\frac{g}{l}$ while the solubility of dipotassium phosphate is 1500 $\frac{g}{l}$. The other possible combinations are potassium carbonate, potassium hydroxide and potassium hydrogen carbonate also their solubilities in order are 1110, 1120 and 337 $\frac{g}{l}$ (Zumdahl & Zumdahl, 2003).

As it is shown in Fig 4-23 there is an indirect correlation between pH of the leachant solution and potassium concentration in biosolid but for pH 2 and pH 3 the lines are close to each other. This shows that the maximum capacity for potassium is reached at pH 2 and a further decrease does not have effectively change the potassium concentration. Also in all pHs after 2 hours, the slope of the line is flat which means that 2 hours is sufficient to reach the maximum amount of potassium concentration at each pH.

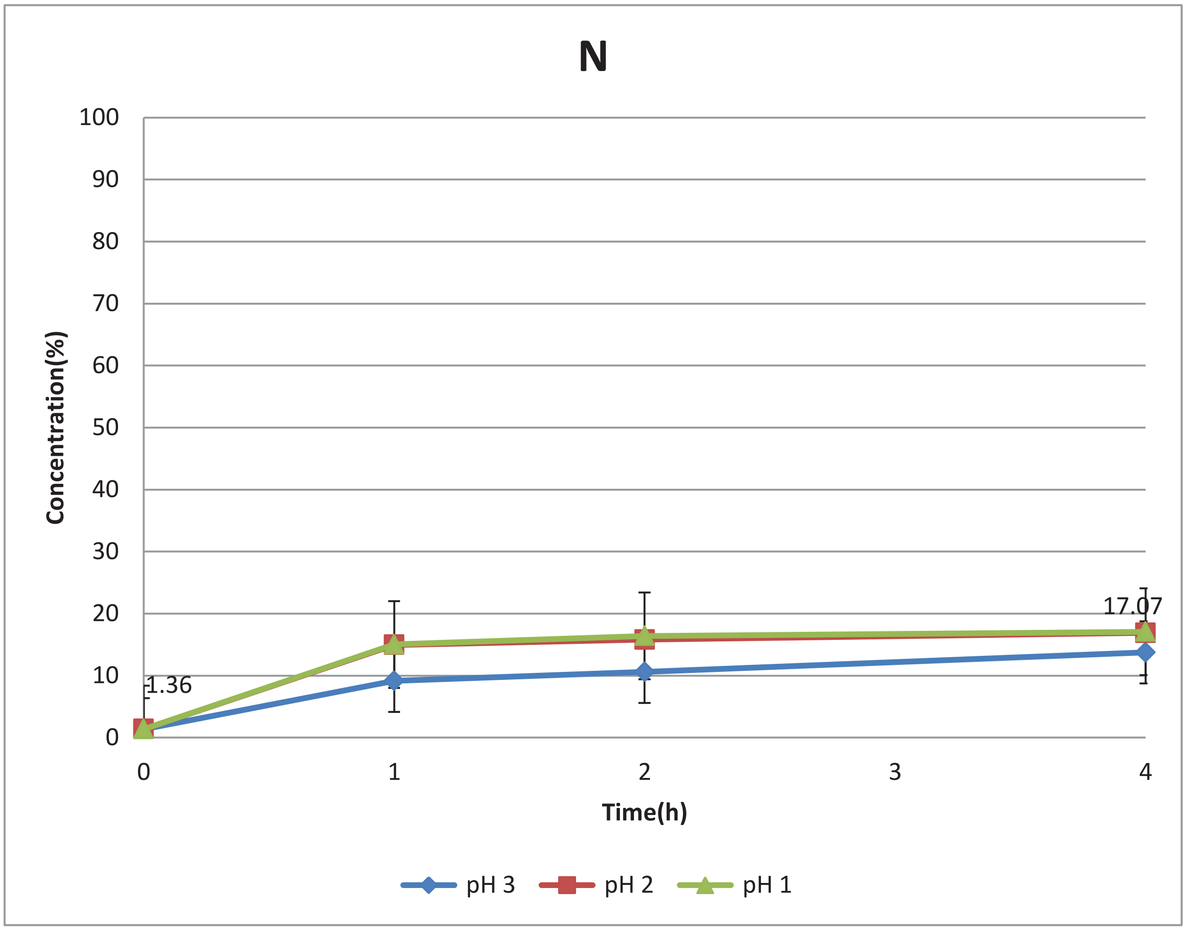

Figure 4-24: Remaining Nitrogen Concentration in Sludge after Leaching Experiment at Different pHs

Fig. 4-24 shows this method increases the nitrogen concentration in the biosolid. The reason is using nitric acid for adjusting pH during the experiments. Also it is seen that the initial amount of potassium is 1.36% and the highest amount is reached at pH 1 and pH 2 which is more than 17%. The pH and nitrogen concentration has an indirect correlation but the close amounts for pH 1 and pH 2 shows that the highest nitrogen capacity in biosolid is reachable at pH 2 and decreasing the pH is not necessary. Also this process is faster than potassium and the difference between the concentrations after one hour and two hour or even four hours of reaction time is not significant.

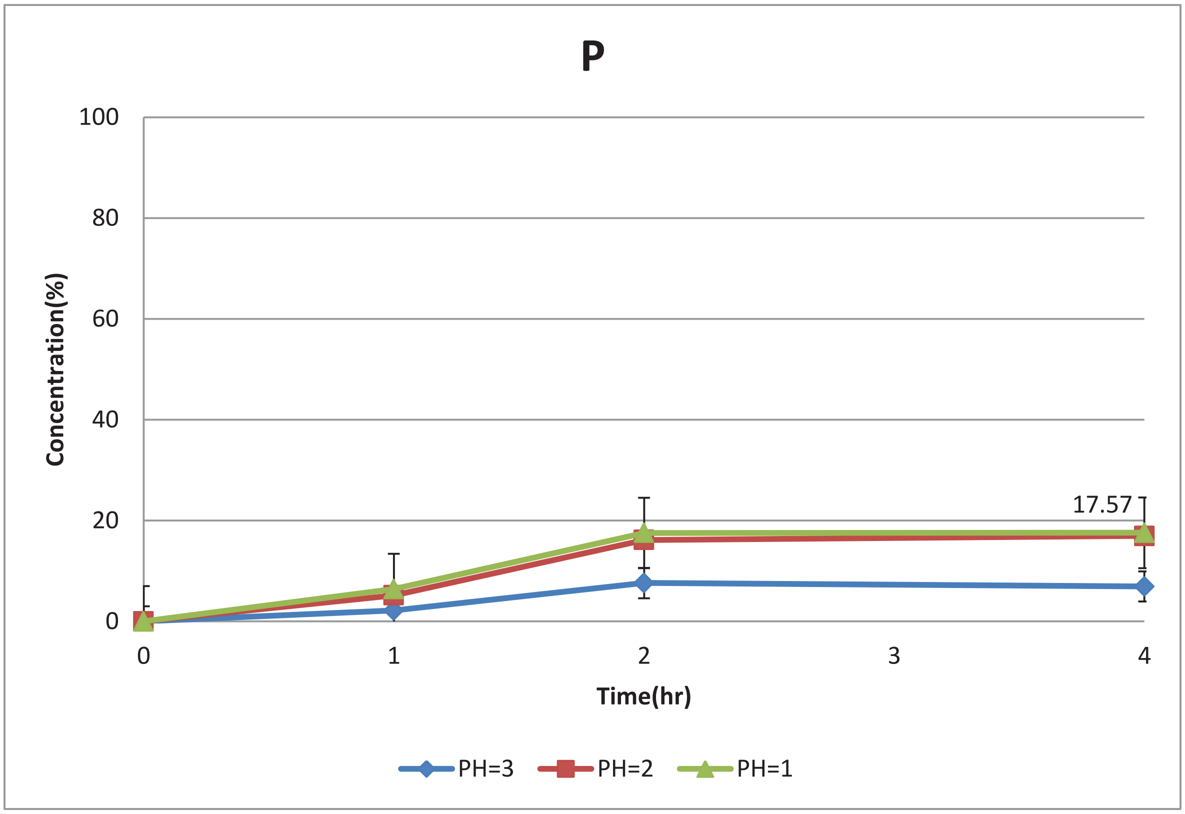

Figure 4-25: Remaining Phosphorus Concentration in Sludge after Leaching Experiment at Different pHs

Phosphorus has the lowest concentration between nutrients in the samples but it still shows significant change during this method and can be changed to more than 17% concentration after 2 hours when pH is two or less. As it is shown in Figure 4-25 phosphorus has an indirect correlation with pH therefore its concentration increases with decreasing pH but it reaches the highest concentration at pH 2 and therefore decreasing pH to less than two is not necessary.

The increase of phosphorus during the experiment is the result of producing some salts with lower solubilities than dipotassium phosphate such as magnesium phosphate, calcium phosphate and sodium phosphate with solubilities of 0.002, 0.02 and 121 $\frac{g}{l}$, respectively (Zumdahl & Zumdahl, 2003).

Of course the increasing slope is more at second hour of reaction in the graph which means this process is not as fast as the nitrogen increase and needs more time to be completed.

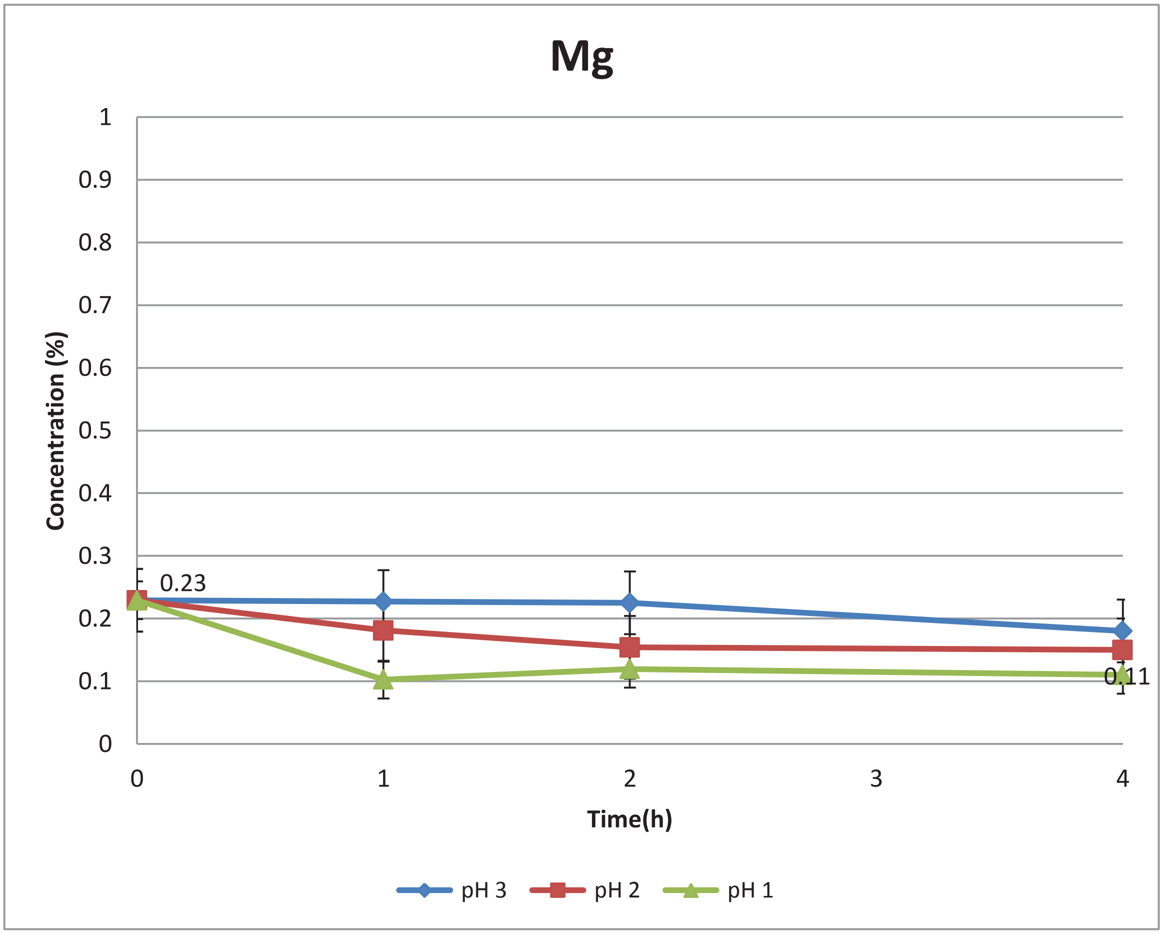

Figure 4-26: Remaining Magnesium Concentration in Sludge after Leaching Experiment at Different pHs

Decreasing pH can increase the leaching of magnesium as shown in Fig. 4-26. It takes more time for higher pH solutions to reach the maximum. For example it takes one hour when pH 1 and two hours when pH 2 and more than two hours when pH 3. The maximum loss of magnesium is also around 52% which occurs at pH 1 after four hours reaction time. The initial concentration of magnesium is not significant and therefore 52% removal at pH 1 is not important too.

Fig. 4-27 shows that calcium loss occurred during this method also it shows the last concentration of all pHs are approximately equal but they reach to this point at different times. For pH 1, it takes 1 hour, for pH 2 it takes 2 hours and for pH 3 it takes 4 hours. Fig. 4-27 also shows that decreasing the reaction time and increasing the pH can help to retain more calcium in the produced biosolid.

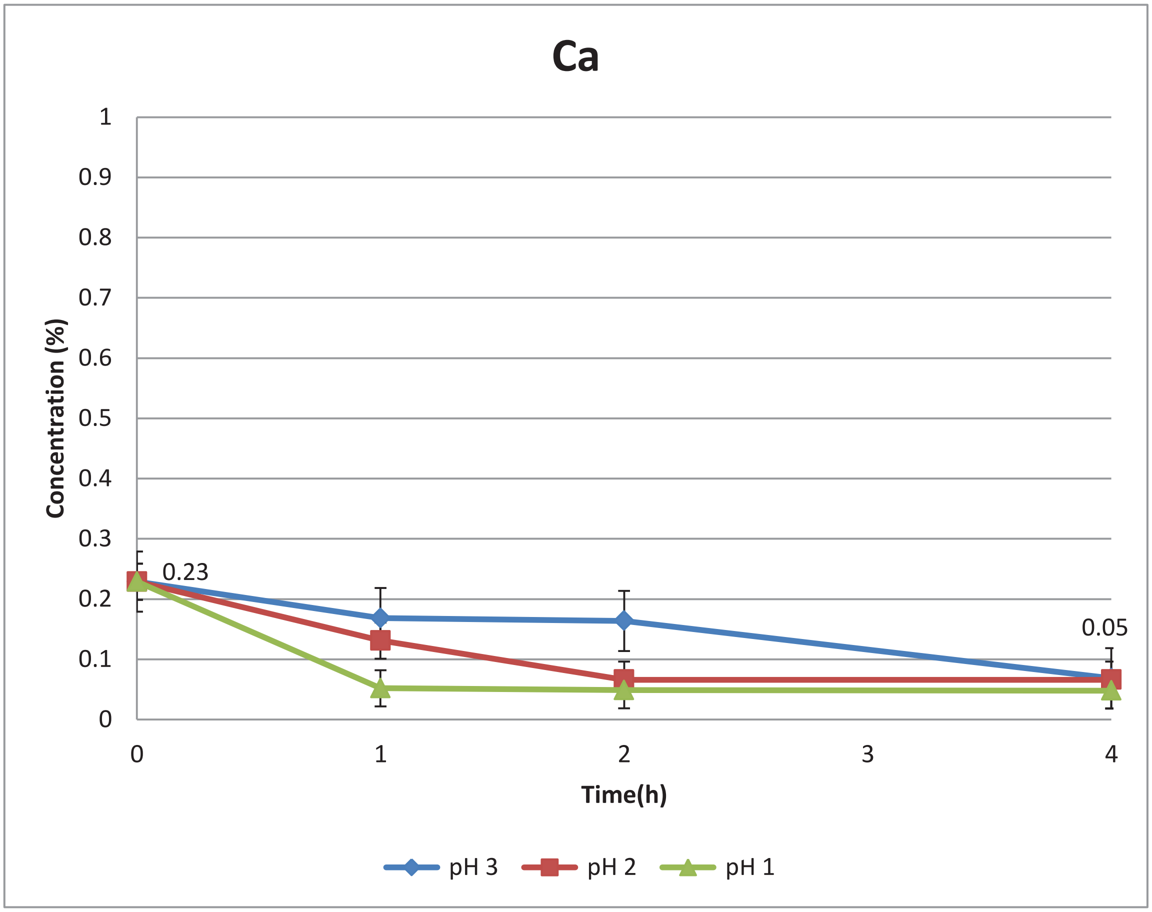

Figure 4- 27: Remaining Calcium Concentration in Sludge after Leaching Experiment at Different pHs

Fig 4-28 is very similar to Fig. 4-27 but it occurs at higher concentrations and also it shows 68% as the maximum iron removal in comparison to 78% calcium removal. Also the effect of a weaker solution i.e., a leachant with higher pH is obvious and therefore determining the lower pH and decreasing reaction time is also important here to have a better quality in the produced biosolid.

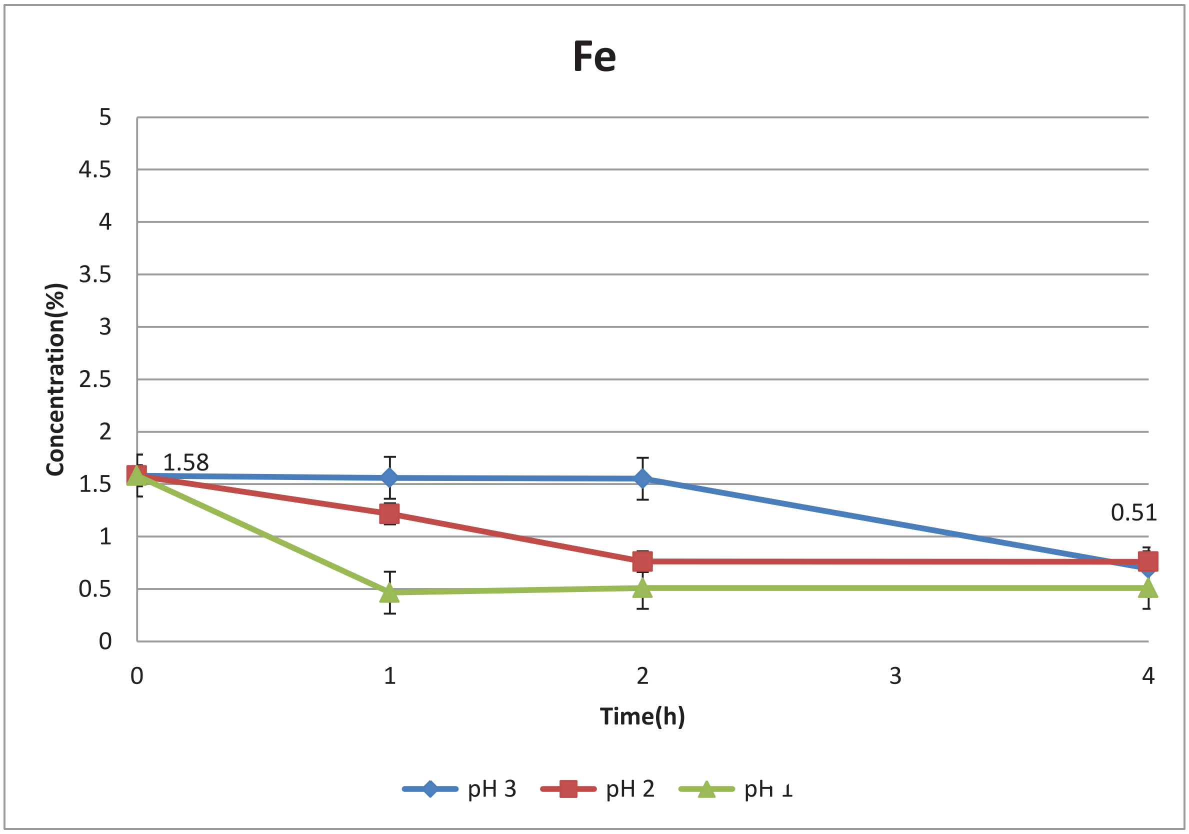

Figure 4-28: Remaining Iron Concentration in Sludge after Leaching Experiment at Different pHs

4.2.3 pH in the product

Before centrifuging the samples and separating the solid part, pHs of tubes were checked and all the pHs were between 8 to 10 based on initial pH in the leachants.

4.3 Comparison to produced biosolid in 2007

In 2007 in the Montreal wastewater treatment plant, a project for producing biosolid for beneficial purposes was done. The result of this project was not acceptable and it was stopped. The problems about this project were high concentration of some heavy metals in the biosolids which could not pass C1 Quebec regulation and low concentrations of nutrients. In Table 4-3, heavy metal concentrations are shown.

Table 4-3: Heavy Metals Concentration in Biosolid 2007 (Jean-R-Marcotte-WWTP, 2007)

Heavy Metals	Concentration (PPM)
As	6
Cd	9
Co	19
Cr	131
Cu	477
Hg	1
Mo	7
Ni	35
Pb	105
Se	9
Zn	596

As it is shown, cadmium, copper, mercury, molybdenum and selenium cannot pass the C1 level. The historical data about this project is compared to the results of this study in Table 4-4.

Table 4-4: Comparing Heavy Metal Content between Biosolid 2007 & This Study

Heavy Metal	Biosolid 2007 (ppm)	After using leachant at pH 1 for 4 h (ppm)
Cd	9	0.8
Co	19	4.87
Cu	477	81.41
Se	9	0.02

As it is shown in Table 4-4, the lower concentrations are obtained in this research and all heavy metals can pass C1 regulations and therefore the biosolid in this study is safer to be used in the environment.

Table □-5: Comparing Primary Macro Nutrient Content between Biosolid 2007 & This Study

Primary Macro Nutrients	Biosolid 2007 (%)	After using leachant at pH 1 for 4 h (%)
N	3	17.07
P	1.5	17.57
K	0.2	25.20

Also based on Table 4-5 there is a large difference between primary macro nutrients in these two projects and as it was mentioned before these three nutrients play the main roles in growing of plants. It is obvious that our biosolids have better fertility than the biosolid in 2007.

Table □-6: Comparing Secondary Macro and Micronutrient Content between Biosolid 2007 & This Study

Nutrients	Biosolid 2007 (%)	After using leachant at pH 1 for 4 h (%)
Mg	N/A	0.11
Ca	N/A	0.05
Fe	4	0.51

There is no information about magnesium and calcium, possibly because they don’t have significant concentrations or they were not analyzed. But as it is shown in Table 4-6 iron in biosolid 2007 is 4% which is higher in comparison to our results. It is important to mention that iron is a micro nutrient and plants use this element in very low concentration. If the iron concentration increases in the soil it can be toxic for plants although its limit is dependent on the type of plant.

To conclude, our product is lower in heavy metal contents and better in nutrient contents. If there is a change in the reaction time or pH, this comparison should be repeated but generally, better results will be reached in our study even if we change those two parameters.

4.4 Comparison to Milorganite biosolid

The Milorganite biosolid is a product of the Milwaukee metropolitan sewerage district in Wisconsin, USA. They have produced organic nitrogen fertilizers since 1926. They defined their main duty as water reclamation and flood management. They provide these services for 1.1 million residents. (Milwaukee-Metropolitan-Sewerage-District, 2013). Our results and the Milorganite biosolid are compared.

Table 4-7: Average Concentration of Heavy Metal Content in Milorganite (2012) (Milwaukee-Metropolitan-Sewerage-District, 2013)

Heavy Metals	2012 Milorganite Average (ppm)
As	1.4
Cd	0.81
Cr	330
Cu	240
Pb	50
Hg	0.51
Mo	11
Ni	37
Se	2.3
Zn	530

Based on Table 4-7, this biosolid cannot pass C1 regulation because the concentrations of chromium, molybdenum and selenium are higher than the permitted limit and also there is no information about cobalt concentration.

Table □-8: Comparing Heavy Metal Concentration between Milorganite and This Study

Heavy Metal	Milorganite Average (ppm)	After using leachant at pH 1 for 4 h (ppm)
Cd	0.81	0.8
Co	N/A	4.9
Cu	240	81.4
Se	2.3	0.02

As it is seen in Table 4-8 cadmium concentrations are approximately equal but selenium and copper has large difference and as it was mentioned before these two cannot pass C1 regulation in Milorganite biosolid. Also cobalt is an unknown problem in Milorganite biosolid. Therefore the heavy metal concentration in our results shows better condition than Milorganite biosolid and it is safer to use.

Table -9: Comparing Primary Macro Nutrient Concentration between Milorganite and This Study

Primary Macro Nutrients	**Milorganite Biosolid (%)**	**After using leachant at pH 1 for 4 h (%)**
N	5	17.1
P	2	17.6
K	0.32	25.2

Primary macro nutrients are compared in Table 4-9 and it is seen that the total concentration of primary macro nutrients in our produced biosolid is higher and the maximum difference is in the potassium concentration.

Table -10: Comparison of Secondary Macro and Micro Nutrient Concentration between Milorganite and This Study

Nutrients	**Milorganite Biosolid (%)**	**After.using leachant at pH 1 for 4 h (%)**
Mg	0.68	0.11
Ca	2.1	0.05
Fe	4.34	0.51

Table 4-10 shows that Milorganite biosolid has better fertility in secondary and micro nutrients. Also it should be mentioned again that as iron is a micro nutrient, the high concentration of this element in soil is not always advantageous, for all plants there is a limit for iron usage and passing from this limit have toxic effects on plants. (Hoyt, n.d.)

The cost of producing biosolid by our method is estimated to be compared with Milorganite biosolid price. First it is needed to estimate the price of our biosolid per kilogram. To do so the price of 1 liter leachant solution was calculated:

- pH 1 => 0.2 L HNO_3 in 1 L leachate => p1 = \$0.09 per liter (Taian-Jinye-Fertilizer-Co, 2014)
- Molar solution => 174.1 g/L K_2HPO_4 => p2 = \$0.15 per liter (Sichuan-Kindia-May-Science-And-Tech-Co, 2014)
- Total price of leachant solution = p1 + p2 = \$0.24 per liter

It is important here to mention that in this method the solid/liquid ratio is 20 which mean that 20 grams of sludge needs 1 liter leachant solution for producing biosolid. So the price can be estimated in \$/kg units.

- Solid / Liquid = 20 g/L => Price = \$12 per kg for pH 1
- Also the price for pH 2 and pH 3 are \$10.5 and \$9 per kg orderly

The price of 36 lb Milorganite fertilizer is \$15 which means the price is approximately \$1 per kilogram. In comparison to our produced biosolid Milorganite fertilizer is cheaper but has a higher heavy metal concentration also there is a large difference between primary macro nutrients concentration. The main nutrient of Milorganite biosolid is nitrogen which its concentration is 29% of nitrogen concentration in our biosolid and its phosphorus concentration is low and it doesn’t have potassium. In the other hand if someone decides to use

Milorganite fertilizer in the agriculture field for reaching 1% nitrogen concentration in soil, 20% of soil volume in root area should be Milorganite but only 5.8% of soil volume should be fertilizer if our product be used. Therefore the choice can be between 1kg Milorganite for 1$ and 0.28 kg of our product for 3.47$. Unlike our product Milorganite cannot provide phosphorous and potassium so another kinds of fertilizers are needed too if Milorganite is chosen. The conclusion can be drawn that the price of our produced biosolid is not more expensive.

4.5 - Results of preliminary tests

Some leaching experiments as preliminary tests were done. In these tests different leachant solutions were investigated. Reaction times were 4 hr but pHs were not adjusted.

Table 4-11: Removal percentages of heavy metals in preliminary tests

	Co	**Cu**	**Se**	**Cd**
H2SO4 (20%)	6.75%	20.58%	3.33%	22.95%
H2SO4 (10%)	4.19%	17.35%	2.94%	28.41%
HCL (20%)	3.25%	13.21%	1.36%	17.35%
HCL (10%)	3.03%	13.02%	2.13%	18.77%
HNO3 (20%)	6.27%	13.26%	2.44%	18.00%
HNO3 (10%)	4.90%	10.66%	1.37%	14.90%
CH3COOH (20%)	2.22%	6.36%	0.88%	12.88%
CH3COOH (10%)	1.65%	5.19%	0.00%	9.55%
NAOH (20%)	0.34%	1.09%	0.00%	0.07%
NAOH (10%)	0.40%	1.37%	0.00%	0.19%
FEO (4gr)	0.21%	1.40%	0.00%	0.13%

As above removal percentages were not satisfying, study on leaching was continued and during the tests, effect of sodium on removal of heavy metals was found. It is found that there is ion exchange process between sodium and heavy metals therefore as potassium is more important nutrient for plants and it is in the same group with sodium, some preliminary tests with sodium and potassium salts as leaching agents were done.

Table -12: Removal percentages of heavy metals in preliminary tests

	Co	Cu	Se	Cd
NaNO3	37.35%	18.20%	4.18%	3.41%
NaCl	45.05%	18.48%	0.00%	5.98%
K2HPO4	100.00%	15.18%	100.00%	100.00%
KOH	76.90%	61.40%	0.00%	82.06%

Since in the same conditions K2HPO4 has the best results and because potassium is more important than sodium this salt was chosen after preliminary tests for more accurate investigations.

5. Conclusions

5.1 Summary and Conclusions

The purpose of this research is to upgrade the sludge of Montreal waste water treatment plant to fertilizer. Reaching this purpose will help to stop incinerating sludge which wastes this source of nutrients and useful organic matter, also stops the requirement for ash disposal which can pollute the environment and make a large area unusable.

The produced biosolid should pass Quebec regulations to receive government approval for agricultural usage. To do so, the first four heavy metals with higher concentrations than C1 regulation should be removed from sludge. Second it is needed to preserve or increase nutrients concentration while heavy metals are removed to keep its value for being used as biosolid. Satisfying these two conditions can result in high quality biosolids.

The mentioned four heavy metals are cadmium, copper, cobalt and selenium but between them cadmium has higher concentration and based on historical data its concentration is increasing since 2010. Also the other three heavy metals can pass C2 regulations which are less strict than C1. Therefore they are divided into two groups, Cadmium cannot even pass C2 so it is in the major problem group but the others only cannot pass C1 so they are in the minor problem group.

Six different nutrients including all the primary macro nutrients (nitrogen, phosphorus and potassium) and two secondary macro nutrients (magnesium and calcium) and one micro nutrient with high concentration in sludge (iron) are studied. But it is obvious that primary macro nutrients are most important ones because of their high consumption by plants and their main roles in growth.

There are several methods for sludge treatment but the leaching method is selected. In this method properties of leachant solution like its kind, concentration and pH, and experiment conditions like temperature, reaction time and initial concentration of pollution are the main effective factors on the efficiency of method.

Our proposed leachant is one of our contributions. The current leachant for heavy metal removal is usually acid or base alone but a dissolved salt at low pH is proposed as leachant. It will be explained that removal efficiency will increase by decreasing pH so acid is used for adjusting pH in the leachant. But the main factor for removal is the salt not acid or base and the main mechanism is ion exchange not acid extraction.

The leaching experiment is done in 50 ml tubes which contain dipotassium phosphate (K_2HPO_4) and nitric acid (HNO_3) as leachant and 1 g sludge. The tubes are shaken with 150 RPM in different reaction times and different pHs. And after centrifuging with 3000 RPM for 15 minutes, the solid part is separated, extracted and analyzed for heavy metals and nutrient concentration.

Investigating effective factors on the efficiency of experiment is the next step. In this part the effect of pH and reaction time on changing of the mentioned element concentration is investigated to be sure that acceptable part of heavy metals is removed and still there are sufficient nutrients in the biosolid to use as fertilizer.

The produced biosolid showed good results in heavy metal removal. The best result (at pH 1 and time = 4 hours) for each heavy metal is removing 93% selenium, 80% cadmium, 70% cobalt and 44% copper. Although unlike the others, copper did not show correlation with pH but all of them have direct correlation with reaction time and also in all of graphs it can be seen that the main removal occurs in the first hour. The other important point here is unlike reviewed papers which show removal at very low pHs for instance 0.3 (Kuan et al., 2010), acceptable removal percentage at pH 3 is reached in this study. Therefore this method is effective and fast for heavy metal removal and safer for employees because of less acid usage.

As all three primary macro nutrients (nitrogen, phosphorus and potassium) are involved in removal process the concentrations of these three are higher than expected after the experiments. Although there is loss of the other nutrients during this method but as they will be used in low concentration by plants, still the results are acceptable.

Primary macro nutrients content determine the value of biosolid. It is demonstrated on the graphs that the concentrations of these three are increasing with this method and during two hours the maximum concentration is approximately reached. Also it is demonstrated that pH 2 and pH 1 have similar results. To conclude, macro primary nutrient concentration has direct and indirect correlation with time and pH but there is a maximum capacity for biosolid which can be reached after 2 hours and with pH 2, therefore increasing the time or decreasing pH is not effective after that point.

Non primary macro nutrient concentrations decreased with this method. But it can be seen that they are highly dependent on pH. Leachate with higher pH needs more time to decrease the concentration. Also it shows that after four hours in any pHs there are approximately the same results which means the maximum available amount of these elements in all the pHs are equal but it needed different times to reach that points with different pHs.

The comparison between our results and two actual projects was also investigated. One of the projects was done in our case study on 2007 and it was stopped because of unacceptable result. And the other one is Milorganite biosolid which is a famous organic nitrogen fertilizer in USA. The comparison shows in this study that a lower concentration of heavy metals and a higher concentration of primary macro nutrients were reached. Milorganite has a better concentration of secondary macro nutrients (calcium and magnesium) among all. Also both compared biosolids have 4% iron which is a micro nutrient and it is used in very low amounts by plants.

5.2 Contributions

- Proposing a new leachant solution:

  an ion exchange mechanism was used instead of acid or base extraction alone. Unlike reviewed papers, potassium salt was used as the main factor at low pH.

- Studying some properties of this new leachant:

  This study shows effects of using this leachant on the concentration of three heavy metals and seven nutrients. Also the correlation of concentration with time and with pH is investigated.

- First study on cobalt and selenium:

  This is the first study on removal of selenium and cobalt from sludge by leaching method. There are some studies about these two elements in soil but not in sludge.

- First study on nitrogen, potassium and calcium:

  This is the first study which investigated the effect of a leaching method on heavy metal removal in addition to the concentration of nitrogen, potassium and calcium in sludge.

The advantages of the method include:

- ✓ High removal percentages of heavy metals
- ✓ Increasing concentrations of primary macro nutrients
- ✓ Acceptable loss of studied secondary macro nutrients and micro nutrients
- ✓ Safer working environment for employees because of acceptable efficiency at higher pHs than reviewed work

The disadvantages include:

- o It needs heavy metal recovery from leachate at the end :

  There are some methods with high efficiency for heavy metal recovery. but these methods are not inexpensive but heavy metals are expensive too. Therefore if we do the recovery with high purity we can cover the expenses.
- o It needs nitrogen and phosphorus removal from leachate at the end :

  Eutrophication is the problem if we decide to send the leachate to the outlet. To do so we need nutrient removal facilities before outlet point. The better solution for this problem is designing a close system and sending back the leachate after heavy metal recovering to the batch again and using the remaining salts and nitric acid for producing new biosolids.

5.3 Future work

- Study on the other effective factors

  The effect of pH and reaction time was studied on element concentration but still there are more effective factors on the method efficiency:

  - ✓ Initial concentration of elements
  - ✓ Salt concentration in leachant
  - ✓ Temperature
  - ✓ Solid/liquid ratio.

- Study on the other heavy metals

  Cadmium, copper, cobalt and selenium were studied because they have high concentrations in our case study but different cases have different problems and therefore an investigation on the efficiency of this method on the other heavy metals is required.

- Study on the other nutrients

  7 different nutrients were studied that were the most important ones but there are totally 14 mentioned nutrients in agriculture references and therefore the study on the 7 remaining nutrients is required.

- Optimization of the conditions

  The price of product is function of experiment conditions for instance concentrations of chemicals, time or pH. Some of these optimizations are as follows:

  - Combination of acids

    Nitric acid is not an inexpensive acid and there is a capacity for nitrogen in the biosolid based on our study therefore maybe we can use an inexpensive acid and nitric acid together to decrease the price while we have the same results for nitrogen concentration in the produced biosolid such as acetic acid.

  - Optimum concentration of dipotassium phosphate

    Now potassium and phosphorus have high concentrations in the final product but lower concentrations are also acceptable therefore concentration of dipotassium phosphate can be less than 1 molar which can decreases the cost therefore the optimum concentration should be found.

  - Increasing solid/liquid ratio

    Increasing solid/liquid from 20 can decrease needed leachant solution amount therefore cost will be decreased.

- Study on microorganism concentration

  There are some regulations for microorganism concentration in biosolids. This subject was out of the scope of this thesis but it is important to be investigated. Although because of the low pH may be the produced biosolid can pass the regulations but it needs to be investigated.

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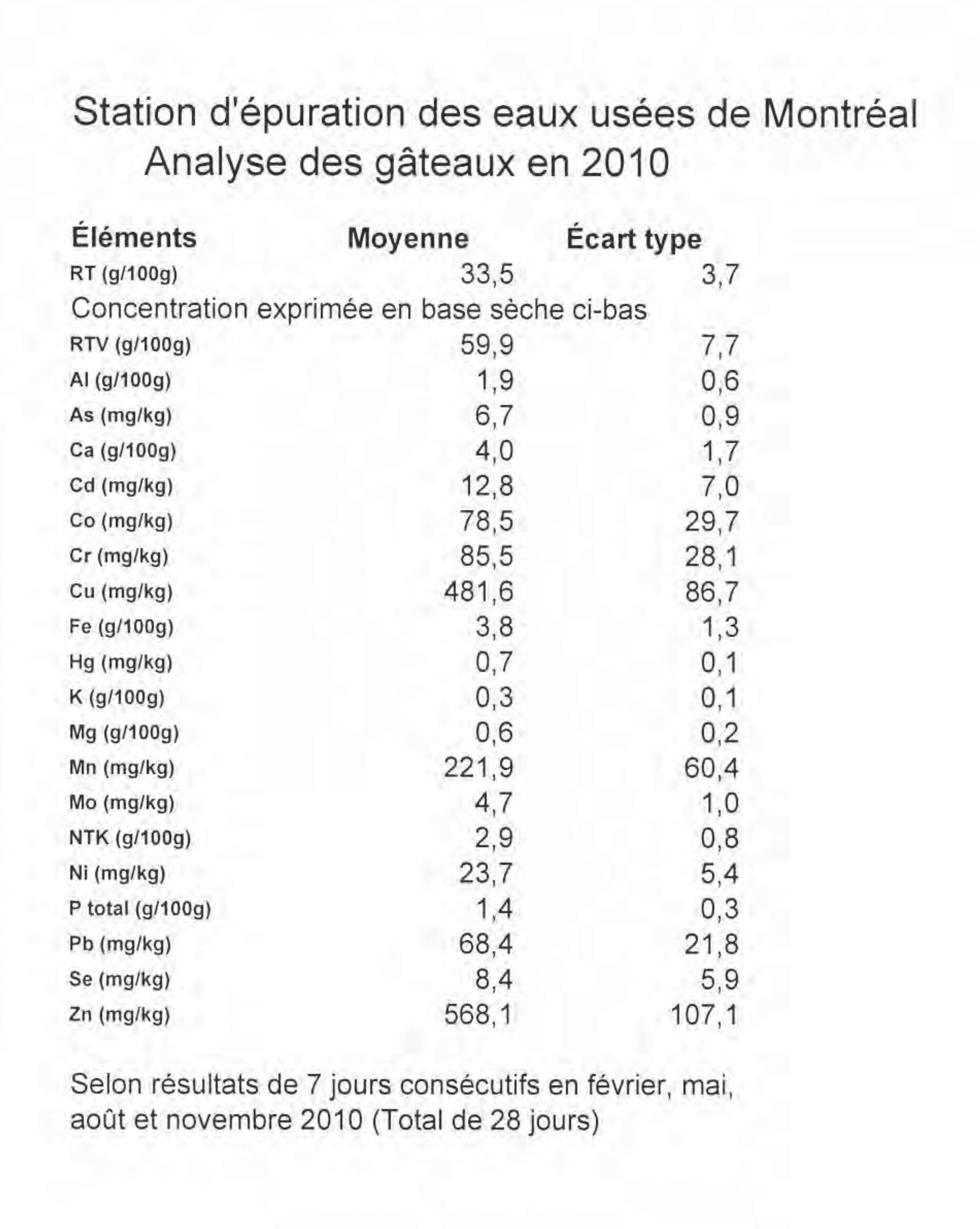
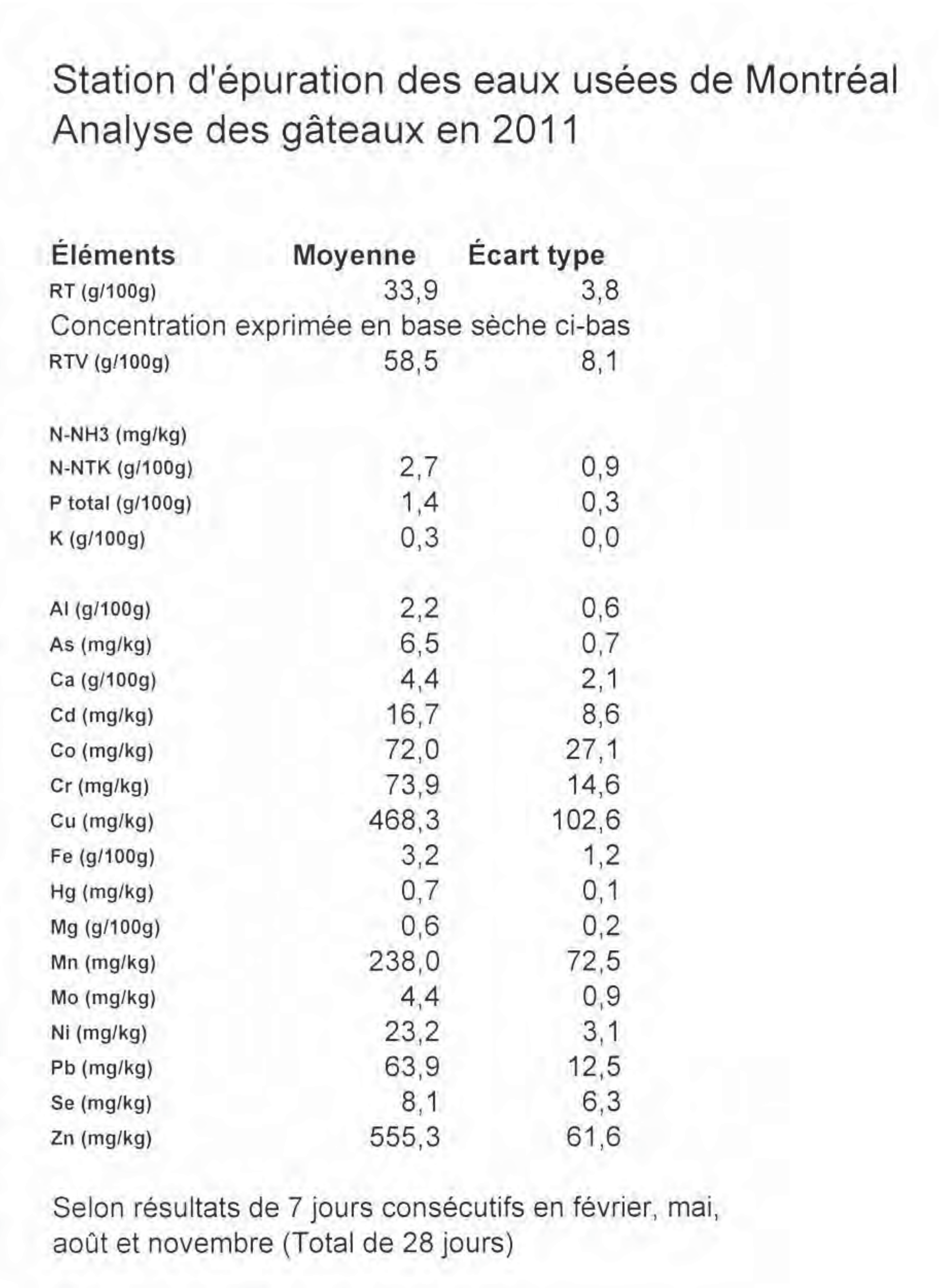
Appendix I (Historical Data)



Station d'épuration des eaux usées de Montréal
Analyse des gâteaux en 2010

Éléments	Moyenne	Écart type
RT (g/100g)	33,5	3,7
Concentration exprimée en base sèche ci-bas		
RTV (g/100g)	59,9	7,7
Al (g/100g)	1,9	0,6
As (mg/kg)	6,7	0,9
Ca (g/100g)	4,0	1,7
Cd (mg/kg)	12,8	7,0
Co (mg/kg)	78,5	29,7
Cr (mg/kg)	85,5	28,1
Cu (mg/kg)	481,6	86,7
Fe (g/100g)	3,8	1,3
Hg (mg/kg)	0,7	0,1
K (g/100g)	0,3	0,1
Mg (g/100g)	0,6	0,2
Mn (mg/kg)	221,9	60,4
Mo (mg/kg)	4,7	1,0
NTK (g/100g)	2,9	0,8
Ni (mg/kg)	23,7	5,4
P total (g/100g)	1,4	0,3
Pb (mg/kg)	68,4	21,8
Se (mg/kg)	8,4	5,9
Zn (mg/kg)	568,1	107,1

Selon résultats de 7 jours consécutifs en février, mai, août et novembre 2010 (Total de 28 jours)



Station d'épuration des eaux usées de Montréal
Analyse des gâteaux en 2011

Éléments	**Moyenne**	**Écart type**
RT (g/100g)	33,9	3,8
Concentration exprimée en base sèche ci-bas		
RTV (g/100g)	58,5	8,1
N-NH3 (mg/kg)		
N-NTK (g/100g)	2,7	0,9
P total (g/100g)	1,4	0,3
K (g/100g)	0,3	0,0
Al (g/100g)	2,2	0,6
As (mg/kg)	6,5	0,7
Ca (g/100g)	4,4	2,1
Cd (mg/kg)	16,7	8,6
Co (mg/kg)	72,0	27,1
Cr (mg/kg)	73,9	14,6
Cu (mg/kg)	468,3	102,6
Fe (g/100g)	3,2	1,2
Hg (mg/kg)	0,7	0,1
Mg (g/100g)	0,6	0,2
Mn (mg/kg)	238,0	72,5
Mo (mg/kg)	4,4	0,9
Ni (mg/kg)	23,2	3,1
Pb (mg/kg)	63,9	12,5
Se (mg/kg)	8,1	6,3
Zn (mg/kg)	555,3	61,6

Selon résultats de 7 jours consécutifs en février, mai, août et novembre (Total de 28 jours)

IDENTIFICATION DU PRODUIT

NOM	Granules ou biosolides granulés de la station d'épuration des eaux usées de Montréal
NOM ANGLAIS	Pellets or granulated biosolids from Montreal wastewater treatment plant

INGRÉDIENTS	N (azote)	3,0	% (b.s.)
	P (phosphore)	1,5	% (b.s.)
	K (potassium)	0,2	% (b.s.)
	COT (carbone organique total)	32	% (b.s.)
	Ca (calcium)	3,0	% (b.s.)
	As (arsenic)	6	mg/kg (b.s.)
	Cd (cadmium)	9	mg/kg (b.s.)
	Co (cobalt)	19	mg/kg (b.s.)
	Cr (chrome)	131	mg/kg (b.s.)
	Cu (cuivre)	477	mg/kg (b.s.)
	Hg (mercure)	1	mg/kg (b.s.)
	Mo (molybdène)	7	mg/kg (b.s.)
	Ni (nickel)	35	mg/kg (b.s.)
	Pb (plomb)	105	mg/kg (b.s.)
	Se (selenium)	9	mg/kg (b.s.)
	Zn (zinc)	596	mg/kg (b.s.)
	Al (aluminium)	21738	mg/kg (b.s.)
	Fe (fer)	40518	mg/kg (b.s.)
	Al + 0,5Fe	41997	mg/kg (b.s.)
	Dioxines et furannes	14	ng EQT/kg (b.s.)
	Escherichia coli	<2	NPP/g (b.s.)
	Salmonella	<1	NPP/4g (b.s.)

CARACTÉRISTIQUES PHYSIQUES			
	masse volumique	600 à 750	kg/m3
	granulométrie	1 à 4	mm diamètre
	pH	6,5	
	résidus totaux (RT)	95	g/100g
	matière organique	40 à 70	g/100g (b.s.)

UTILISATION
Engrais, amendement, combustible

CONSEILS
a) Couvrir le matériel en vrac afin d'éviter
- la contamination par les fientes d'oiseaux
- l'humectage par la pluie qui pourrait provoquer une fermentation et un feu

b) Incorporer au sol le plus rapidement afin de réduire les odeurs

11 juillet 2007

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Appendix II (Incineration Diagram)