Comparative Hydro-geochemistry: Distribution of Metal Ions in Groundwater, Surface Water, Soils and Plants in the South East of Ireland.

Institiúid Teicneolaíochta Cheatharlach

INSTITUTE *of* TECHNOLOGY CARLOW

At the heart of South Leinster

By

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A Thesis presented for the Degree of Doctor of Philosophy Submitted to the Institute of Technology, Carlow

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DECLARATION

I certify that this thesis, submitted in line with the requirements for the award of PhD, (Philosophiae doctor) is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text. This thesis was prepared according to the regulations for postgraduate study by research of the Institute of Technology Carlow and has not been submitted in whole or in part for an award in any other Institute or University. The work reported in this thesis conforms to the principles and requirements of the Institute's guidelines for ethics in research.

Signature _____**Date** _____

Dedication:

For my beautiful fiancée Sarah and my children Holly and Jacob.

"Remember life is what happens while you're busy"

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Structure of thesis

Chapters 1-4 in this thesis are written and formatted as journal manuscripts, i.e. each chapter has an abstract, introduction to the theme discussed in that specific chapter, the methodologies employed, the results and respective discussion and conclusions. Chapter 5 contains a brief conclusion and future recommendations, chapter 6 includes the dissemination of this thesis both nationally and internationally. Lastly, chapter 7 contains all references used throughout this thesis.

Safety protocol

Lithium is relatively non-toxic, nevertheless, care was taken when handling any lithium compounds. Several other compounds used in this work like heavy (cadmium, copper, iron, lead, manganese, nickel, zinc) alkali (potassium, sodium) metal salts and Ethylenediaminetetraacetic acid were treated the same way regardless of their toxicity. Material digestions were carried out using hydrochloric acid, hydrogen peroxide and nitric acid. Great care was exercised when using these compounds and adequate control measures put in place to manage risks before performing the methods described in this thesis. Additional the material safety data sheets of each chemical were readily available, and a risk analysis document was produced. A risk assessment was carried out and produced prior to any field or laboratory work. The external document is available from PI.

Key safety requirements; (1) the hygroscopic nature of lithium compounds means that they must be stored appropriately, so as to avoid errors in measurement. (2) All digestions should be carried out in a controlled manner in a fume hood. Specialised and appropriate personal protective equipment should also be used. (3) Solid waste materials should be autoclaved ($121°C$ for 15 minutes) prior to disposal. Liquid waste should be stored as per the risk analysis document and disposed of later by the relevant authority employed by the Institute. (4) All greenhouse work should be carried out in strict observance of the greenhouse rules and protocols.

Abbreviations

[S, R]	[Sinister, Rectus] [Left, Right]
AAS	Atomic Absorbance Spectroscopy
AG	Aktiengesellschaft (Corporation)
AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
Co.	County
Con	Control
CUD1	Clean Vehicle (EU Directive)
CRM	Critical Raw Material
df	Degrees of Freedom
D.R. Congo	Democratic Republic of Congo
EC	European Commission
EDDS	Ethylenediamine-N, N'-disuccinic acid
EDTA	Ethylenediaminetetraacetic acid
EED	Energy Efficiency (EU Directive)
EPA	Environmental Protection Agency
EU	European Union
EV	Electric Vehicle
FES	Flame Emission Spectroscopy
GL	Ganfeng Lithium
GW	Groundwater
Ha	Alternative Hypothesis
HAP	Hyperaccumulator Plant
HEV	Hybrid Electric Vehicle
Ho	Null Hypothesis
HREE	Heavy Rare Earth Elements
IBM	International Business Machines
ILC	International Lithium Corporation
LCT	Lithium, Caesium, Tantalum
Li_2O	Lithium Hydroxide

LIB	Lithium Ion Battery
LOD	Limit of Detection
LOQ	Limit of Quantification
LREE	Light Rare Earth Elements
ND	Not Determined
NYF	Niobium, Yttrium, Fluorine
PGM	Platinum Group Metals
PHEV	Plugin Hybrid Electric Vehicle
PI	Principal Investigator
P-value	Probability value
r	Correlation Coefficient
r^2	Coefficient of Determination
REE	Rare Earth Elements
RoHS	Restriction of Hazardous Substances (EU Directive)
SD	Standard Deviation
SPSS	Statistical Package for the Social Sciences
SW	Surface Water
UK	United Kingdom
USA	United States of America
USSR	United Soviet Socialist Republic
WEEE	Waste Electrical and Electronic Equipment (EU Directive)
WHO	World Health Organisation

Abstract

Until recently lithium has been an unpopular, often unthought of metal tucked away on the far left of the periodic table. You might recall a song or two of the same name, or that it is used to treat bipolar disorder, but that's about it. Today lithium is more popular than ever because it is the main component of rechargeable lithium ion batteries. Lithium batteries represent the best battery technology that is commercially available to date. These batteries are powering our portable electronics and are set to power the vast electric vehicle landscape of the future. The global electric vehicle market is growing rapidly, and along with it the demand for lithium resources.

In chapter one, the geological sources and industrial uses of lithium are discussed. This chapter focuses on the European Union's need to develop its own lithium resources and the potential future security of supply issue. Geographically small lithium mineralisations are distributed all over the world. One of these small mineralisation's is found in the South East of Ireland and is the main impetus for this work. Whether this mineralisation of lithium is economic or not is a question which an interested lithium mining corporation is currently trying to answer. This work establishes background concentrations of lithium and a suite of other metals in the environment surrounding the known lithium mineralisation's in Ireland, prior to any mining activity. In chapter two the baseline concentration of lithium in the surface and groundwater of the area are established (surface water at $\bar{X} = 0.020$ and groundwater at $\bar{X} = 0.023$mg/l). In chapter three lithium baseline concentrations are given for the topsoil and two endemic plant species in the area (i.e. topsoil at $\bar{X} = 57.8$, Ash at $\bar{X} = 43.7$ and Ivy at 52.3mg/kg). In chapter four we investigated the potential application of five plant species to agromine lithium. The concept of agromining involves the use of plants to sequester large amounts of metals from the soil with an aim of recovering those metals from the plant tissue. The work is the first of its kind and may set the groundwork for any future research in the subject. Highlights from the work include promising results from both cabbage and rapeseed plants with lithium plant concentrations approaching 3000 mg/kg dry weight.

General introduction

Lithium is a metal which is rapidly becoming a popular topic of conversation. Scientists, industrialists, and economists looking at renewable, clean sustainable energy storage, and the emergence of the fossil fuel free electric vehicle era, are all discussing lithium, more specifically lithium ion batteries. They are looking towards lithium battery technology as the protagonist in our looming energy crisis story. What we know today as a battery was first conceptualised in the 18th century. The story goes that in 1748, Benjamin Franklin described the similarities of an array of charged glass capacitors to that of an artillery battery. Then in 1800, when Alessandro Volta presented his famous voltaic pile, linking several electrochemical cells, capable of producing a continuous electrical current, the system became commonly known as a battery. Battery technology has come a long way since the 18th century, the culmination of which today is lithium battery technology. Lithium's ability to attract electron density to itself makes it an ideal battery component, and currently the top candidate to power the vast electric landscape of our immediate future. Already lithium batteries are powering the majority of our portable electronic devices. If you look in your pocket you will most likely find a phone powered by a lithium ion battery. There are already close to two million electric vehicles privately owned in the world today, the majority of which are powered by lithium batteries. In Ireland, the electric vehicle market is growing, and the government have ambitious plans, for example, that ten percent of all vehicles in Ireland will be electric by 2020, and a ban on the sale of fossil fuel powered vehicles by 2030. The Sustainable Energy Authority of Ireland is offering incentives to new electric vehicle owners. A lower rate of annual motor tax, lower toll fees, free public charging points, and grants worth thousands of Euro. These government incentives are not just in Ireland but are becoming a global phenomenon. Our dependence on oil is unsustainable. Fossil fuels contribute significantly to global warming, a problem which we face today. The proliferation of electric vehicles and renewable energy sources will reduce a large portion of our contribution of greenhouse gases to the environment. Lithium battery technology may well set us on a path towards a low carbon sustainable future. This drive for an electric vehicle-powered future and the storage of renewable energy from sources like solar, wave and wind, is creating demand for this previously unobtrusive metal, lithium. Lithium seldom accumulates into economic deposits, today it is mined from two main sources, mineral and brine deposits. Originally all lithium was extracted from mineral sources. However, in the 1980s the more cost-efficient production of lithium from mineral-rich brines drastically reduced the production of lithium from mineral sources. Lithium production

from brines took over the market. Brine deposits are confined to relatively few areas of the globe like the Andes of South America and the Tibetan plateau. The lack of infrastructure in some of these areas, a potential security of supply issue, and the steady demand for lithium over the years meant that some mineral deposits of lithium remained an important source of the metal. Currently, new demand is resulting in even marginal mineralisation's of lithium becoming a point of interest for mining companies. In the Leinster Granites of the South East of Ireland, one such lithium mineralisation exists as the lithium rich mineral spodumene. The impetus for this work stems from this fact and the circumstance of recent and ongoing prospecting in the area. This mineralisation of lithium has attracted recent international attention, along with several other sites across Europe. The potential for an active lithium mining operation in Ireland is a distinct possibility for the future. This work endeavours to provide information that will both protect the local environment and provide information to any prospective mining companies. Ireland's lithium resources represent an opportunity to demonstrate a modern, responsible, and sustainable mining venture, in a country with complicated land use issues in a relatively small area. We have provided information regarding the nature and occurrence of lithium in the environment, and its presence in the waters, soils, and plants of the south-east of Ireland.

Chapter 1

Global Lithium Sources-Industrial Use and Future in the Electric Vehicle Industry: A Review

Authors: Laurence Kavanagh, Jerome Keohane, Guiomar Garcia Cabellos, Andrew Lloyd and John Cleary.

1.1. Abstract

Lithium is a key component in green energy storage technologies and is rapidly becoming a metal of crucial importance to the European Union. The different industrial uses of lithium are discussed in this review along with an update of the locations of the main geological sources of lithium. An emphasis is placed on lithium's use in lithium ion batteries and their use in the electric vehicle industry. The electric vehicle market is driving new demand for lithium resources. This new demand will result in an industry-wide scaling up which could limit current lithium supply. The expected scale-up in this sector will put pressure on current lithium supplies. The European Union has a burgeoning demand for lithium and is the second largest consumer of lithium resources. Currently, only 1–2% of worldwide lithium is produced in the European Union (Portugal). There are several lithium mineralisation's scattered across Europe, the majority of which are currently undergoing mining feasibility studies. The increasing cost of lithium is driving a new global mining boom and should see many of Europe's mineralisation's becoming economic. The information given in this paper is a source of contextual information that can be used to support the European Union's drive towards a low carbon economy and to develop the field of research.

Keywords: lithium; electric vehicle; source; Industrial use

1.2. Introduction

Presented is a review of the available literature regarding the industrial uses and sources of lithium, with a focus on the European Union (EU) and electric vehicle (EV) market. The work organises the literature in order to review and evaluate the state of the art in this field of research. There is a trend in the literature showing an increasing amount of interest by both developed and developing countries in previously uneconomic mineralisation's of lithium globally. Here we present detailed information on historic and more recently discovered lithium mineralisation's. The industrial uses of lithium are varied and often go unreported in any great detail in publications relating to lithium. In this paper, the main industrial uses of lithium have been collated. This work is designed to highlight and summarise research findings regarding lithium's use, presence in the environment, mining and occurrence. The impetus for lithium's future recycling is also discussed as a requirement for a future sustainable circular lithium economy (Graedel *et al*., 2015).

The last century has seen an increase in the amount of all metals including lithium consumed globally. In the last twenty years, there has been an exponential increase in the amount of metals consumed. This rapid increase has been correlated with China's economic reforms and development. China's vast manufacturing capacity and ability to sell lithium products cheaply has led to the country dominating the lithium product manufacturing industry. Even though China has its own lithium resources it still imports massive amounts of the metal (Chen and Kang 2007). World leading Chinese lithium manufacturing companies like "Tianqi" and "Ganfeng Lithium" currently control almost half of the worlds lithium production. China has invested in lithium projects all around the world and has the power to distort the market. If China decided to limit the export of lithium to the EU a real supply security issue could take place. China has already limited its export quotas of Rare Earth Elements (REEs); If China decided to place a similar limit on the export of lithium to the EU, it could give rise to a real supply security issue. Within the EU, demand for lithium is growing increasingly fast quickly (Simon *et al.,* 2015). The United Nations (UN) Environment Programme launched an international resource panel in 2007, with an aim to gather and share information on global metal resources, the availability of critical raw materials (CRMs) and the concept of a circular economy (United Nations, 2018). The European Commission (EC) uses a CRM approach to describe materials which are essential to the EU's economy. The EC defines a CRM as a material which forms a strong industrial base, producing a broad range of goods and applications used in everyday life and modern technologies (United Nations, 2018).

CRMs are crucial to the EU's economy. The EC has created a list of CRMs which includes 27 materials (Table 1.1).

Table 1.1. CRMs listed by the EC in 2017. HREEs - heavy rare earth elements, LREEs - light rare earth elements, PGMs - platinum group metals (United Nations, 2018).

Antimony	Fluorspar	LREEs	Phosphorus
Baryte	Gallium	Magnesium	Scandium
Beryllium	Germanium	Natural graphite	Silicon metal
Bismuth	Hafnium	Natural rubber	Tantalum
Borate	Helium	Niobium	Tungsten
Cobalt	HREEs	PGMs	Vanadium
Coking coal	Indium	Phosphate rock	

The EC revises its CRM list every three years and the list was last updated in 2017 (United Nations, 2018). Lithium is not currently considered a CRM, rather a near critical material. Factors contributing to lithium not being classified as a CRM include its relative global abundance (although it rarely appears in large deposits) and because there are currently available suitable substitutes for some lithium technologies, for example, other battery technologies using manganese and nickel (Graedel *et al*., 2015). Nickel and manganese are globally abundant and not classified as CRMs (Simon *et al.,* 2015). Lithium is likely to be classified as a CRM in 2020 when the EC revises its CRM list, because of current and expected future demand. Lithium has a high economic importance and is essential to the growth of green technologies in the EU. The EU has the potential to become self-reliant for lithium supplies by developing its own domestic lithium resources reducing reliance on other suppliers (Table 1.2). In the EU hard rock mineralisation's of lithium offer the best potential to provide the EU with lithium in the future. New mining investment in the EU will strengthen the competitiveness of its lithium industry.

Table 1.2. Known EU lithium mineralisation's. Main mineral present, percentage lithium oxide and estimated lithium reserve. (Yaksic and Tilton 2009 [5]; Martin *et al*., 2017[6]; Novo Litio, 2017[7]; Mohr *et al*., 2012[8]; Kalevi *et al*., 2018[9]; Kavanagh *et al*., 2017[10]; Kozłowski, 2002[11]; Vikström *et al.,* 2013[12]; Sousa *et al*., 2018[13]; Vine, 1976[14]; Kunasz 2006[15])

Description	Mineral	%Li$_2$O	reserve (Mt)	Reference
EU, Austria, Wolfsberg,	Spodumene	1.0	0.1	[5]
EU, Czechia, Cinovec,	Zinnwaldite	0.39	-----	[6]
EU, Germany, Sadisdorf	Zinnwaldite	0.45	-----	[7]
EU, Finland, Hirvikallio	Spodumene	0.47	0.00047	[8]
EU, Finland, Kietyonmaki	Spodumene	0.7	0.007	[8]
EU, Finland, Länttä, Ullava	Spodumene	0.94	0.014	[8]
EU, Finland, Osterbotten	Spodumene	0.43	0.0019	[8]
EU, Finland, Syväjärvi	Spodumene	1.24	1.97	[9]
EU, Finland, Rapasaari	Spodumene	1.15	3.46	[9]
EU, Finland, Outovesi	Spodumene	1.43	0.28	[9]
EU, Finland, Emmes	Spodumene	1.43	0.82	[9]
EU, Finland, Leviäkangas	Spodumene	1.01	0.4	[9]
EU, Ireland, Leinster	Spodumene	2.3	0.5	[10]
EU, Norway, Helgeland	----	-----	-----	[8]
EU, Poland, Kostrzya	Zinnwaldite	-----	-----	[11]
EU, Portugal, Barroso-Alvao	Spodumene	0.57-1	0.0514	[12]
EU, Portugal, Gondiaes	petalite			[7]
EU, Portugal, Serra de Arga	-----	-----	-----	[7]
EU, Portugal, Barca de Alva	-----	-----	-----	[7]
EU, Portugal, Mangualde	-----	-----	-----	[7]
EU, Portugal, Guarda-Goncalo	Lepidolite	-----	-----	[13]
EU, Portugal, Segura	-----	-----	-----	[7]
EU, Serbia, Jadar valley	Jadarite	0.84	1.4	[12]
EU, Spain, Morille	Lepidolite	-----	0.2	[12]
EU, Spain, San Jose	Lepidolite	1	0.2	[12]
EU, Spain, Alberto	Lepidolite	-----	-----	[12]
EU, Sweden, Järkvissle,	Spodumene	0.45	0.003	[14]
EU, Sweden, Utö, Haninge	Petalite	-----	-----	[15]
EU, Sweden, Varuträsk	Spodumene	1.3 - 2	0.001	[14]

EU, Sweden, Spodumenberget	Spodumene	1.0	-----	[15]
EU, UK, Cornwall Camborne	Amblygonite	0.84	-----	[16]
EU, UK, Devon	Amblygonite	-----	-----	[16]

1.2.1. Methodology

There is an ever-increasing output of scientific publications concerning lithium resources driven by recent demand for this until now relatively unfamiliar metal. This paper provides an up to date overview of the literature in this specific area and brings together relevant material from various sources. Articles included in this review were accessed from journal databases, bibliographic databases and subject-specific professional websites. The inclusion criteria for articles comprised of only relevant peer-reviewed qualitative and quantitative articles related to both the uses and sources of lithium globally.

1.2.2. Lithium

Lithium is the 3rd element on the periodic table and the 1st element in the alkali metal group. It has an atomic mass of 6.94 g/mol, an atomic radius of 1.33 Å, a melting point of 180.5°C and a boiling point of 1342°C. With a density of just 0.534 g/cm^3, lithium metal floats in water even as it reacts. Lithium has a hardness of 0.6 on the Mohr scale, is softer than talc ($Mg_3Si_4O_{10}(OH)_2$), the softest mineral on the Mohr scale (talc hardness = 1). Lithium is harder than carbon = 0.5, caesium = 0.5, and sodium = 0.5 but softer than lead = 1.5 (Kunasz, 2006). Lithium has the highest specific heat capacity (at 25°C) of any solid element at 3.56 J/g K. Lithium is the most polarising of all the alkali metals and more electropositive than hydrogen so it can accumulate chemical energy very efficiently. At a pressure in excess of 40 gigapascals (400,000 atmospheres) lithium becomes a superconductor (Rumble, 2017). There are several radioisotopes of lithium (^{4}Li to ^{12}Li). Their half-lives range from 9 x10^{-23}s for ^{4}Li to 8 x 10^{-1} s for ^{8}Li. Naturally occurring lithium exists as the two stable isotopes ^{6}Li at (7% abundance) and ^{7}Li at (93% abundance).

Lithium has a single valence electron on its outer shell which is freely given up for reaction to form other a variety of compounds (Oliveira, 2015). The highly reactive nature of lithium (the least reactive of the alkali metals) towards oxygen, a trait it shares with other group one alkali metals, means that it never occurs as a pure metal in nature, instead, it occurs in as various salts and minerals. One property of lithium is its apparent cosmological discrepancy. Lithium follows in the periodic table after the two most

abundant elements in the universe hydrogen and helium. Despite lithium's positioning on the table, but it is far less abundant in the universe than it has been predicted to be, according to the standard cosmological model (SCM) (Fields, 2011; Garrett, 2004). During the first few minutes of the "Big Bang" H, He, and Li were created. The amounts of hydrogen and helium occurring in the universe agree with those figures proposed by the SCM, lithium (and beryllium and boron) estimates, however, are too low (Garett, 2004). This lithium discrepancy question has not been solved to date although some authors have attempted to provide explanations (Poulin and Serpico 2015). The leading theory is that the lithium is transmuted to other elements early in the life-cycle/formation of stars.

The chemical history of lithium began with the characterisation of the aluminosilicate minerals petalite ($LiAlSi_4O_{10}$) and spodumene ($LiAlSi_2O_6$). They were discovered at the start of the 18th century by the Brazilian statesman and naturalist José Bonifácio de Andrada e Silva on the island of Utö, near Stockholm, Sweden (Berzelius, 1964). In 1817 the Swedish chemist Johan August Arfwedson discovered a previously unknown element previously unknown in the new mineral petalite. Arfwedson was working at the time for another Swedish chemist, Baron Jöns Jacob Berzelius. Lithium, according to the author Berzelius (1964) (who coincidentally shares the same name as Jöns Jacob Berzelius) formed compounds similar to those of sodium and potassium (Berzelius, 1964). Although lithium's carbonate and hydroxide forms are less soluble in water and more alkaline (Weeks and Larson 1937). Together the two chemists named the mysterious element lithion/lithina from the Greek for stone. Arfwedson went on to discover lithium in lepidolite ($K(Li,Al)_3(Al,Si,Rb)_4O_{10}(F,OH)_2$). In 1818 Christian Gottlieb Gmelin a colleague of Arfwedson was the first to observe that lithium salts, when exposed to flames, gave off an intense red flame (Weeks, 2003). Although Arfwedson had discovered the element he never managed to isolate pure metallic lithium. In 1821, the English chemist William Thomas Brande, a colleague of Sir Humphry Davy, obtained lithium by the electrolysis of lithium oxide (Brande, 1841). In 1855, the German chemist Robert Wilhelm Eberhard Bunsen famous for the Bunsen burner and English chemists Augustus Matthiessen isolated lithium from lithium chloride by electrolysis (Weeks, 2003). Their production method was later commercialised by the German company Metallgesellschaft AG (1923), who produced metallic lithium electrolytically from a mixture of 55% lithium chloride and 45% potassium chloride at a temperature of 450 °C (Weeks, 2003).

1.3. Lithium in the Environment

1.3.1 Lithium in Water

Lithium occurs in trace amounts in fresh water, rivers, lakes, and surface waters. Its concentrations in fresh waters depend on numerous variables like local geology and topography. The range is from 0.001 to 0.020 mg/l lithium, (Lenntech, 2018; Ayotte *et al.,* 2011; Klimas and Mališauskas 2008; De Vos *et al.,* 2006; Huh *et al.,* 1998; Emery *et al.,* 1981). Groundwater concentrations are much more variable mainly due to geological factors and in places can reach concentrations >500 mg/l. (Kavanagh *et al*., 2017). Generally, a range between 0.5 and 19 mg/l lithium in groundwater is agreed upon (Shahzad *et al.,* 2016). Although there are exceptions, in Northern Chile where lithium is actively mined from brines, the water lithium concentrations are exceptionally high (Figueroa *et al.,* 2012). In Chile, the daily dietary intake of lithium may be as high as 10 mg/day (Schrauzer, 2002). Lithium intake this high has not shown any harmful effects to humans (Shahzad *et al.,* 2017). Lithium intake of adults has been calculated in several countries, and ranges from 0.35 mg/kg of body weight per day in Vienna Austria to 1.6 mg/kg/day in Xi'an China (Schrauzer, 2002). Lithium is the 14th most abundant element in seawater. Its concentration varies across different oceans, despite this it is largely accepted to occur in seawater at a concentration between 0.14 and 0.20 mg/l (Table 1.3). An average lithium concentration of 0.17 mg/l is often reported. Seawater is known to contain vast amounts of lithium between 230,000 megatons (Mt) and 250,000 Mt (WebElements, 2018; Meshram *et al.,* 2014; Han *et al.,* 2012; Aral and Vecchio-Sadus 2008; Chung *et al.,* 2008; Chitrakar *et al.,* 2001; Takeuchi, 1980). The low level of lithium in seawater makes it difficult to create a process to extract it efficiently or profitably (Tarascon, 2010). Despite this several attempts have been made to extract lithium economically from seawater using different techniques like electrodialysis and membrane filtration. (Hoshino, 2013; Han *et al.,* 2012; Chung *et al.,* 2008; Nishihama *et al.,* 2011; Umeno *et al.,* 2002; Chitrakar *et al.,* 2001; Miyai *et al.,* 1988; Abe and Chitrakar 1987). Aluminium salts are widely used to precipitate lithium from seawater (Kaneko and Takahashi 1990; Takeuchi, 1980; Kitamura and Wada 1978). Another common method of extracting lithium from seawater involves using a manganese-based absorbent (MnO_2) has a high selectivity for the lithium ion) followed by a precipitation process (Meshram *et al.,* 2014). In a 1986 Japanese study, manganese oxide was evaluated for its ability to sequester lithium from seawater (Ooi *et al.,* 1986). Some inorganic ion-exchangers exhibit high selectivity for the lithium ion. The majority of downstream seawater processing includes the following steps, flotation, sorption, ion exchange, membrane

filtration and solvent extraction (Meshram *et al.,* 2014). Tin antimonate ($Sn_3(SbO_4)_4$) has been used as a lithium ion absorber (Ooi *et al.,* 1986). A massive amount of seawater would have to be processed in order to extract economic amounts of lithium (Vikström *et al.,* 2013). Lithium will likely not ever have to be extracted from seawater and this approach may never become economically viable, the process is just too expensive compared to current mineral and brine mining (Grosjean *et al.,* 2012). The amount of lithium in the Dead Sea is 10 mg/l (Mg/Li ratio – 2000:1). The Great Salt Lake in Utah, USA contains on average 400 mg/l lithium (Mg/Li ratio – 250:1), in seawater the ratio of Mg/Li is – 7000:1 (Vikström *et al.,* 2013).

Table 1.3. Lithium concentrations in seawater given in the literature, units – mg/l.

(mg/l) Lithium	Reference	(mg/l) Lithium	Reference
0.2	(Gaitan, 1989)	0.17 - 0.2	(Vine, 1976)
0.18	(Mindat, 2018)	0.17	(Ryu *et al*., 2013)
0.18	(JeffersonLab, 2018)	0.17	(Peiró *et al.,* 2013)
0.18	(Rumble, 2017)	0.17	(Fasel and Tran 2005)
0.18	(WebElements, 2018)	0.17	(Lenntech, 2018)

1.3.2. Lithium in Soil

Lithium is found in trace amounts in all soils. Several figures are given in the literature for the abundance of lithium in the Earth's crust (Table 1.4). An average of 20 mg/kg of lithium is commonly cited. But an average value is minimally informative given 4 orders of magnitude of lithium concentrations recorded in different geological situations; skewed towards the lower end of the range. Lithium is slightly more abundant in the Earth's crust than Cu, Cr, Ni, and Zn and less abundant than Al, Mg, Mn, and Ti. Lithium does accumulate to economic levels in some areas like as aluminosilicate minerals, in some specialised clays, and in lake evaporate. Clay minerals are a group of hydrous aluminosilicates. These minerals are similar in chemical and structural composition to the primary minerals that originate from the Earth's crust (Yalamanchali, 2012). A range between 10 and 40 mg/kg is generally accepted as the "background" concentration of lithium in soil with an average value of 20 mg/kg in the soil, and 30 mg/kg in granites (Table 1.5 and 1.6). According to some authors, the lithium content of soils is determined more by the conditions of soil formation than by its initial content in parent rocks (Ammari *et al.,* 2011; Kabata-Pendias, 2010). Lithium has been reported to correlate strongly with aluminium in the clay fraction of soils (Cannon *et al.,* 1975). It has also

been shown to be positively correlated with calcium and magnesium in soils and negatively correlated with sodium. Yalamanchali (2012) reported correlations between lithium and Al, B, Fe, K, Mg, Mn and Zn in the soil of New Zealand.

Table 1.4. Lithium's average crustal abundance, units – mg/kg lithium.

(mg/kg)	Reference	(mg/kg)	Reference
65	(Naumov and Naumova 2010)	20	(Vine, 1976)
26	(Yalamanchali, 2012)	20	(Wilson and Long 1983)
24	(FOREGS, 2018)	18	(Greenwood and Earnshaw 1997)
20	(JeffersonLab, 2018)	17 - 20	(BGS, 2016)
20	(Mindat, 2018)	17	(WebElements, 2018)
20	(Kaye and Laby 2018)	16	(Linnen *et al.,* 2012)
20	(Rumble, 2017)	13.7	(Wänke *et al.,* 1984)
20	(Mason, 1952)	13	(Taylor and McClennan 1985)

Table 1.5. Lithium concentrations in various rocks, units – mg/kg, Sources, (Garrett, 2004[1]; Yalamanchali, 2012[2] ; Aral and Vecchio-Sadus 2008[3] ; Kabata-Pendias, 2010[4] ; Shahzad *et al.,* 2016[5] ; Kunasz, 2006[6]; Mason, 1952[7] ; Vine, 1976[8] ; Parker, 1969[9] ; Horstman, 1957[10] ; Patterson, 1952[11] ; Nockolds and Mitchell 1947[13] ; BGS, 2016 [14]; Strock, 1936[15]).

Rock	(mg/kg)	Rock	(mg/kg)	Rock	(mg/kg)
Granite	20[1]	Limestone	27[14]	Sedimentary	52[11]
Granite	13[2]	Limestone	28[1]	Sedimentary	53[6]
Granite	28[6]	Limestone	5 – 20[4]	Sedimentary	53[7]
Granite	24[7]	Limestone	5[11]	Sedimentary	56 – 60[10]
Granite	30[3]	Limestone	12[5]	Sedimentary	52[5]
Granite	30[8]	Sandstone	10 – 40[4]	Shale	50 – 75[4]
Granite	25 – 40[4]	Sandstone	15[14]	Shale	33 – 165[13]
Granite	40[11]	Sandstone	17[9]	Shale	20 – 100[5]
Granite	74[10]	Sandstone	62[13]	Shale	66[14]
Granite	20[9]	Sandstone	18[1]	Shale	44[5]

Table 1.6. Lithium concentration in different soils, units – mg/kg. Sources, (Davey and Wheeler 1980 [1]; (Magalhães and Wilcox 1990 [2]; Kabata-Pendias, 2010 [3]; Aral and Vecchio-Sadus 2008 [4]; Fay *et al*., 2007 [5]; Shahzad *et al.,* 2016 [6]; Yalamanchali, 2012 [7]; Cannon *et al.,* 1975 [8]; Anderson *et al.,* 1988 [9]; Shacklette and Boerngen 1984 [10]; Swaine, 1956 [11]; WebElements, 2018 [12]; Swain, 2017 [13]; Scott and Smith 1987 [14]; Steinkoenig, 1915 [15]; Schrauzer, 2002 [16]).

Soil Description	mg/kg	Soil Description	mg/kg
Australian soil [1]	6 - 28	New Zealand, soil [3]	60 - 105
Clay faction of soil [2]	0.002 - 63	U.S (meadows) [3]	10 - 57
Denmark (meadow) [3]	0.5 – 3.2	Various soil [12]	20 - 70
Jordan valley soils [6]	0.95 – 2.7	Great Britain soils [3]	25
Light organic soils [6]	1.3	Various soil [6]	25
New Zealand (clay soil) [3]	1.4 - 130	Russian (forest) [3]	25 – 26
New Zealand (meadows) [3]	0.01 – 2.8	U.S (clay) [6]	10 - 64
New Zealand soil [7]	0.08 - 92	U.S (clay) [6]	11.5 - 12
Papua New Guinea soil [1]	0.29 – 118.3	Ireland's soils [5]	20 - 30
Poland (clay soil) [3]	0.1 - 38	Russian (sandy soil) [3]	17 - 60
Poland (sandy soil) [3]	0.01 - 12	Various soil [15]	10 - 100
U.S (Nevada, California) [8]	8 - 400	Various soil [13]	70
U.S (siliceous soils) [6]	3.7 – 5.8	Calcareous soil [6]	56
U.S (Silty soils) [9]	3.7 – 59.9	Authigenic clays [6]	200 - 500
U.S (South East) [9]	3.74 – 59.93	Various soil [14]	26
U.S (various soils) [3]	0.7 – 1.6	U.S (various soils) [10]	20.4
Various soil [16]	7 - 200	U.S (calcareous soils) [3]	60 - 105
Various soil [11]	8 - 400	Detrital clays [4]	70 - 80
Various soils [4]	3 - 350	U.S (fine soils) [6]	25.4 – 33.3

1.3.3. Lithium Industrial Resources

Lithium is not a particularly rare metal, rather it is widely distributed globally. It is only found in suitably large concentrations in three types of material; silicate minerals and mineral-rich brines and rare sedimentary clays (Garrett *et al.,* 2004). Currently there are no mines producing lithium from a sedimentary clay deposit. Prior to the 1980s, all lithium was mined from hard rock mineral sources. The production of cheap lithium from mineral-rich brines like those found in the Andes, resulted in the closure of several lithium

mineral mines (Gruber *et al.,* 2011). The capital expenditure required for lithium production from a brine source is lower than that required for a mineral source. Mineral sources may have valuable accessory elements like Be, Cs, F, P, Sn, Ta, and Rb; brine sources tend to have a larger concentration of accessory minerals like B, K, Na, and Mg. Today Approximately 59% of the world's lithium resources are found in brines and 25% in minerals, the remainder is found in clays, geothermal waters, and oil field brines (Swain, 2017; Gruber *et al.,* 2011). In 2009, 13% of worldwide lithium reserves, expressed in terms of contained lithium, were reported to be within mineral deposits, and 87% within brine and mineral water deposits (Goonan, 2012). Gruber *et al*., (2011) state that 57% of the world's lithium resources are contained in just three locations, the Salar de Atacama, Chile, the Salar de Uyuni, Bolivia, and the Kings Mountain belt, USA (Salar is Spanish for Salt Lake) (Gruber *et al.,* 2011). Given the expense associated with lithium mineral mining, the majority of lithium on the market today is sourced from brines. Salt brines (dry saline lake beds) are the main source of lithium today (approximately 50%), but extraction from minerals is still significant (40%), the other (10%) is sourced from clay deposits and other sources (Mohr *et al.,* 2012).

Mineral deposits are viewed as a means of offsetting any deficit in lithium production from brines as well as mitigating some concerns about the security of lithium supply in the future (Linnen *et al*., 2012). The high concentration of lithium in mineral sources can often offset additional costs associated with the process. Despite the cost-effectiveness of extracting lithium from brines rather than minerals, the increased demand in lithium means that it is still being processed from mineral sources all over the world. Mineral deposits in countries like Afghanistan and Ireland are currently being prospected for lithium resources (ILC, 2018; Risen, 2010). In Ireland, lithium occurs in the south-east of the country and is associated with the Leinster granitic batholith (Kavanagh *et al*., 2017). Afghanistan has been identified as a major future potential lithium market supplier if its vast resources are utilised (Risen, 2010). Afghanistan's lithium deposits occur in dry lake beds located in the western provinces of Herat and Nimroz and in the central-eastern province of Ghazni. The geologic setting is similar to that found in the Andes. Lithium mineral deposits are also found in the north-eastern provinces of Badakhshan, Nangarhar, Nuristan, and Uruzgan (Risen, 2010). Afghani lakes such as Lake Namaksar-e-Herat, Dasht-e-Nawar and Godwe Zareh in the west of the country contain lithium at concentrations between 41 and 99 mg/l (Belt, 2014).

The language used to describe minerals identified in a deposit is divided into two major groups, resources and reserves. Resources refer to the amount of those minerals that are known to exist in a deposit that may be extracted economically and are reasonably well defined with regard to grade and quantity. Resources are further subdivided into three more categories (CRIRSCO, 2013). An inferred resource refers to reasonable estimates on the amounts of minerals present in a deposit, made given based on early limited information. Indicated resources refer to estimates given when more information about the deposit like grade and size are known. Measured resources refer to a resource estimate given after all the characteristics of a deposit are known. Reserves refer to the quantity of target mineral which can be feasibly/economically extracted from a resource. Factors which determine reserve figures include current mining technologies, environmental factors, and available infrastructure. Reserves may be subdivided into proven and probable reserves. Probable reserves have the potential to be economic while proven reserves are known to be economic (CRIRSCO, 2013; Meinert *et al.*, 2016). Estimates of global lithium reserves and resources have been published extensively in the literature, however, these estimates are often inaccurate. It is difficult to estimate the world's lithium reserves, because of the abundance of contradictory estimates which are typically made by investors and venture capitalists rather than specialist researchers in the field (Tarascon, 2010). In some cases, there is often simply a lack of data available from which predictions on reserves or resources may be made. As the price of a metal rises some resources may become economically feasible to recover and also become classified as reserves (Gruber *et al.,* 2011). Mohr *et al.,* (2012) provide an extensive list of the global lithium resources and reserves at different sites around the world (Mohr *et al.,* 2012). Some countries are known to contain lithium resources, but the little data is unavailable. All resource and reserve estimates are subject to change as new projects come online, others close, and some go unreported (BGS, 2018). Lithium resource and reserve estimates are expected to increase in the future as new deposits are discovered and technology advances. Lithium global resource estimates vary from author to author and have varied over the years (Tables 1.7 and 1.8).

Table 1.7. Total global lithium resource estimates, units – Mt (megatons).

Year	(Mt)	Reference	Year	(Mt)	Reference
1999	12	(Harben, 1999)	2011	38.68	(Gruber *et al.,* 2011)
2005	9.4 - 21	(Fasel and Tran 2005)	2011	25.5	(Wanger, 2011)
2007	35.5	(Tahil, 2007)	2012	30.9	(Kesler *et al.,* 2012)
2008	31.8	(Oliveira, 2015)	2012	50.2	(Mohr *et al.,* 2012)
2008	29.9	(Evans, 2008)	2012	56	(Ziemann *et al.,* 2012)
2009	39.4	(Clarke and Harben 2009)	2013	39	(Peiró *et al.,* 2013).
2009	44	(Yaksic and Tilton 2009)	2013	65	(Vikström *et al.,* 2013)
2010	74	(Grosjean *et al.,* 2012)	2014	64	(Meshram *et al.,* 2014)
2010	69	(Gruber and Medina 2010)	2016	73	(Sverdrup, 2016)
2010	34.5	(Evans, 2010)	2017	34	(Martin, 2017)
2011	39	(Wadia *et al.,* 2011)	2018	53	(Ober, 2018)

Table 1.8. Estimates of global lithium resources by country from the literature. Units – Mt (megatons), (D.R.Congo – Democratic Republic of Congo).

Country	(Mt)	Reference	Country	(Mt)	Reference
Afghanistan	2	(Tahil, 2007)	Chile	40	(Hao *et al.,* 2017)
Afghanistan	1.27	(Peiró *et al.,* 2013)	Chile	8.4	(Ober, 2018)
Argentina	10.6	(Hao *et al.,* 2017)	Chile	8	(Oliveira, 2015)
Argentina	9.8	(Ober, 2018).	Chile	7.5	(Yaksic and Tilton 2009)
Argentina	9	(Yaksic and Tilton 2009)	Chile	7.1	(BGS, 2016)
Argentina	6.52	(BGS, 2016)	Chile	6.3	(Gruber *et al.,* 2011)
Argentina	6	(Oliveira, 2015)	Chile	6.2	(Wright, 2010)
Argentina	2.6	(Meshram *et al.,* 2014)	Chile	3	(Tahil, 2007)
Australia	13	(Kesler *et al*., 2012)	China	17	(Hao *et al.,* 2017)
Australia	8	(Hao *et al.,* 2017)	China	7	(Yaksic and Tilton 2009)
Australia	5	(Ober, 2018)	China	7	(Ober, 2018)
Australia	2	(Yaksic and Tilton 2009)	China	2.7	(Tahil, 2007)
Austria	0.134	(BGS, 2016)	China	3.35	(BGS, 2016)
Austria	0.1	(Yaksic and Tilton 2009)	D.R.Congo	2.3	(BGS 2016)
Austria	0.05	(Ober, 2018)	D.R.Congo	1	(Yaksic and Tilton 2009)
Bolivia	10.2	(Gruber *et al.,* 2011)	Finland	.001	(BGS, 2016)
Bolivia	9	(Tahil, 2007)	Mali	0.2	(Ober, 2018).

Bolivia	9	(Meshram *et al.,* 2014)	Mexico	0.2	(Yaksic and Tilton 2009)
Bolivia	9	(Yaksic and Tilton 2009)	Mexico	0.18	(BGS, 2016)
Bolivia	9	(Evans, 2010)	Mexico	0.18	(Ober, 2018)
Bolivia	9	(Ober, 2018)	Portugal	0.3	(Hao *et al.,* 2017)
Bolivia	8.9	(BGS, 2016)	Portugal	0.1	(Ober, 2018)
Brazil	1	(Tahil, 2007)	Russia	1	(Yaksic and Tilton 2009)
Brazil	0.3	(Hao *et al.,* 2017)	Russia	1.68	(BGS, 2016)
Brazil	0.2	(Yaksic and Tilton 2009)	Spain	0.4	(Ober, 2018)
Brazil	0.185	(BGS, 2016)	Serbia	1.4	(Yaksic and Tilton 2009)
Brazil	0.18	(Ober, 2018)	USA	7	(BGS, 2016)
Canada	2	(Yaksic and Tilton 2009)	USA	6.9	(Yaksic and Tilton 2009)
Canada	1.9	(Ober, 2018)	USA	6.8	(Ober, 2018)
Canada	1	(BGS, 2016)	Zimbabwe	1	(Hao *et al.,* 2017)
Canada	1	(Tahil, 2007)	Zimbabwe	0.1	(Yaksic and Tilton 2009)

1.3.4. Lithium in Brines

Commercial quantities of lithium exist in brines (a high concentration salt solution). The main type of brine deposit mined for lithium is found in an interior saline desert basin, these basins in the past contained water before the rate of evaporation exceeded the rate of recharge, leaving behind a dry lake bed. The terminology used to describe these dry lake beds is varied. They are referred to as salt pans, salt flats, salt marsh, alkali flats Playas or most usually Salars. Sediments in salars are primarily lacustrine but some are derived from modern depositional processes. Many mineral rich and hot geothermal waters contain elevated concentrations of lithium, between 0.1 and 500 mg/l lithium (Swain, 2017; Vine, 1976). Geothermal waters become enriched in lithium because hot water is more effective than cold water at leaching lithium from rocks. The lithium in geothermal brines can come from volcanic activity, weathering of silicates, and leaching from lake sediments (Kunasz, 2006). In geologically active countries like Iceland (the Reykanes geothermal field), Japan (the Hatchobaru and Oguni geothermal fields) and New Zealand (Wairakei), the potential commercial extraction of lithium from geothermal waters has been studied (Epstein *et al.,* 1981; Hano *et al.,* 1992; Yanagase *et al.,* 1983; Fouillac and Michard 1981). Other potential lithium sources in geothermal waters are found in Cesana, Italy, and Alsace, France (Garrett, 2004). Recovery of lithium from geothermal sources often involve methods such as ion-exchange, precipitation often as a lithium aluminate, and membrane filtration (Swain, 2017; Vine, 1976). Efforts have also

been made to extract lithium from saline water bodies like the Dead Sea (Wilson and Long 1983).

Mineral-rich brines known as oilfield brines are produced as a waste product of certain oil extraction process. The brines can occur at a depth > 2 km. Oilfield brines in the USA contain 0.1 to 700 mg/l lithium (Meshram *et al.,* 2014; Vine, 1976). Oilfield brines such as the Smackover oilfields in southern Arkansas, USA, have been investigated for their potential as an economic source of lithium (Collins, 1975; Chan *et* al., 2002; Evans, 2008; Meshram *et al.,* 2014). The Smackover oilfield has been shown to contain lithium at concentrations between 100 and 500 mg/l (Dang and Steinberg 1978). Other oilfield brines being investigated, occur in areas such as the oilfield brines at Leduc, Alberta, Canada, the Heletz-Kokhav oilfields in Israel and the gas fields of Altmack, Germany (Garrett, 2004). The USA has several oilfield brine deposits including East Texas, the Devonian formation in North Dakota, Rock Springs Formation in Wyoming, Wilcox Formation in Oklahoma, Paradox Basin in Utah, and the Pennsylvanian Minnelusa formation (Collins, 1975; Evans, 2008; Garrett, 2004). Lithium is produced directly from oilfield brine and does not require evaporation ponds. Lithium extraction from oilfield brines can be an expensive process because of the need for pumping from such depths (Gruber *et al.,* 2011). Currently, there is enough lithium being produced from other sources, although geothermal waters and oil field brines may become an economic source of lithium in the future depending on demand (Vine, 1976).

The most abundant source of lithium-rich brine are the high altitude continental brine aquifers of the Andean mountain region in South America. The Andes is a major subduction zone, which has resulted in a series of endorheic basins (BGS, 2016). The brine deposits of South America occur at high altitude which promotes the evaporation process due to the inverse relationship between atmospheric pressure and altitude. Salars exist in three countries Argentina, Bolivia and Chile collectively known as the Lithium Triangle, where 50% of global lithium reserves are found Martin (2017). Argentina has several salars including the Salar de Muerto Hombre, the Salar de Olaroz, and the Salar de Marianna all of which contain substantial amounts of lithium. The Salar de Atacama in Chile is currently the largest producer of lithium from a brine source (Gruber *et al.,* 2011). By far the largest reserve base of lithium in the world is in the Salar de Uyuni in the southwest of Bolivia (Wright, 2010; Tahil, 2007). Bolivia alone may hold up to 25% of world lithium reserves. According to the Bolivian government, their resources add up to 100 Mt. Lithium reserve estimates for the Salar de Uyuni have been placed at 0.6 to 9 Mt (Meshram *et al.,* 2014; Yaksic and Tilton 2009; Tahil, 2007).

Lithium is extracted from brines as lithium carbonate or lithium chloride by solar evaporation. Broadly the process involves evaporation, precipitation, adsorption and/or ion exchange (Meshram *et al.,* 2014). Usually, the brine is pumped to open man-made ponds where solar evaporation is used to concentrate the lithium into a smaller volume of brine. The brine is transferred through a series of these ponds becoming progressively more concentrated by solar evaporation. The process from start to finish can take 18 to 24 months. Because the brine is open to the environment, the process may be slowed down by rain or flooding, sheet flooding of the South American salars is a common occurrence. After sufficient concentration of the brine, the lithium is eventually extracted by chemical means as lithium chloride or more commonly lithium carbonate. To extract magnesium from the brine calcium carbonate is added to precipitate out magnesium carbonate ($CaCO_3 + MgCl_2 \rightarrow CaCl_2 + MgCO_3$). This results in a brine that is between 5.5 and 6.5% lithium chloride. Finally, sodium carbonate is added (at 90°C) to precipitate out lithium carbonate at a ratio of 1.8:1 ($LiCl + Na_2CO_3 \rightarrow Li_2CO_3 + 2NaCl$) (BGS, 2016). Lithium and magnesium have similar chemistries and are difficult to separate in brine deposits. The higher the Mg/Li ratio the more expensive it is to separate the two in the production process. The Mg/Li ratio of seawater is 7000, the Mg/Li ratio of several salars are given in table 1.9. Swain (2017) discusses in detail the different techniques, mechanisms and chemistry by which lithium is extracted from brines (Swain, 2017).

Apart from the Lithium Triangle, there are numerous brine deposits around the world in countries like Canada, China, India, Israel, and the USA (Vikström *et al.,* 2013). China has numerous Salt Lake deposits in areas like the Qaidam basin (>30 lakes) and the Tibetan plateau (> 300 lakes). These deposits include the Taijinaier Salt Lake (Qinghai Province), and Lake Zabuye (Shigatse Prefecture). The Qaidam Basin, where Lake Taijinaier is located is the largest salt bed lithium reserve in China (Garrett, 2004). In the USA brine deposits include the Searles Lake, Nevada, the Salton Sea in California and Utah's Great Salt Lake (Gruber *et al.,* 2011; Evans, 2008; Kunasz, 2006; Gaitan, 1989).

Table 1.9. Location and parameters of some of the main lithium containing brines (Kunasz, 2006 [1]; Evans, 2008 [2]; Vine, 1976 [3]; Martin, 2017 [4]; Gaitan, 1989 [5]; Gruber *et al.,* 2011 [6]; ILC, 2018 [7]; Aral and Vecchio-Sadus 2008 [8]; Rodinia, 2018 [9]; LSClithium, 2018 [10]; Garrett, 2004 [11]).

Location	% Li_2O	Mg/Li ratio	Li reserve (Mt)
Chile, Salar de Atacama [1]	0.18	6.6	7.5 - 8
Chile, Salar de Maricunga [2]	0.092	8	0.4
USA, Smackover [3]	0.065	20	0.75
Bolivia, Salar de Uyuni [4]	0.0532	21.5	5.5
USA, Searles Lake [5]	0.047	4.1	-----
Argentina, Salar de Hombre Muerto [2]	0.043	1.37	0.85
Chile, Salar de Aguas Calientes [2]	0.025	0.5	-----
Canada, Fox Creek [1]	0.02	10	0.3 – 1.3
USA, Clayton Valley [1]	0.018	1.33	0.04 – 0.1
Argentina, Salar de Vida [6]	0.017	2.2	1.188
Argentina, Salar de Cauchari [2]	0.015	2.84	0.035
Argentina, Salar de Rincon [1]	0.013	8.61	0.14
USA, Salton Sea [3]	0.013	1.27	0.3 – 0.5
Chile, Aqua Amarga [2]	0.011	0.05	-----
Chile, Salar de Pedernales [2]	0.009	-----	-----
Chile, Tara [2]	0.009	0.97	-----
Chile, Gorbea [2]	0.009	0.01	-----
USA, Brawley [6]	0.009	-----	1.0
Chile, Quisquiro [2]	0.008	0.18	-----
Argentina, Salar de Mariana [7]	0.007	16	0.618
Chile, Pajonales [2]	0.005	0.03	-----
Israel, Dead Sea [8]	0.004	1700	0.9 – 1.9
USA, Bonneville Salt Flats [3]	0.004	100	-----
Chile, Punta Negra Salar [2]	0.003	-----	-----
Chile, El Laco [2]	0.003	0.06	-----
Argentina, Salar de Olaroz [6]	0.0015	2.8	0.156
Chile, La Isla [2]	0.001	0.22	-----
Chile, Pujsa [2]	0.001	0.26	-----
Argentina, Salar de Arizaro [7]	-----	-----	-----
Argentina, Salar de diablilos [9]	-----	-----	-----

Argentina, Salar de Grandes [10]	-----	-----	-----
Argentina, Salar de Los Angelas [2]	-----	-----	-----
Bolivia, Salar de Coipasa [4]	-----	-----	-----
Canada, Beaver hill Lake [1]	-----	-----	0.515
Chile, Aguilar [2]	-----	0.05	-----
Chile, Parinas [2]	-----	0.11	-----
China. East Taijaner Salt Lake [11]	-----	-----	-----
China, Lake Qarchan [11]	-----	-----	-----
China. Zabuye Salt Lake [11]	-----	-----	-----
China. Zhacang Kaca Salt Lake [11]	-----	-----	-----
China, Sichuan Abe [11]	-----	-----	-----
China, Jaijika [11]	-----	-----	-----
China, Maerkang [11]	-----	-----	-----
China, Ningdu [11]	-----	-----	-----
USA, Great Salt Lake [1]	-----	133.33	0.2 – 0.3

1.3.5. Lithium in Minerals

Lithium minerals fall into three general classes: complex aluminium silicates, phosphates, and micas (Aral and Vecchio-Sadus 2008; Colton, 1975). Micas are normally classified as aluminium silicates (Colton, 1975). There are 145 named lithium-bearing minerals (Table 1.10). Not all of these minerals are of commercial value. There are only a few lithium minerals like spodumene, petalite and lepidolite that are economically worthwhile to process for lithium if a large enough deposit is found (Meshram *et al.,* 2014). The aluminium silicate spodumene is the most commonly available and economic lithium bearing mineral. Its colour can be white when it is low in iron and dark green when rich in iron (Kunasz, 2006). Lithium minerals mainly occur as a subset of a type of rock called a pegmatite. Pegmatites are coarse-grained igneous rocks associated with the late crystallisation stage of postmagmatic fluids in intrusive granitic plutons (Kabata-Pendias 2010; Kunasz, 2006). The main constituents of pegmatite are feldspar, quartz and mica. Pegmatite rock is the last to solidify during the emplacement of a pluton and because it cools slowly pegmatite tends to become enriched with more diffuse elements like lithium.

When pegmatites are cooling the process is controlled by the presence of lithium and other volatile elements like fluorine and boron, resulting in fewer and larger crystals (BGS, 2016). These volatile elements remain in solution until late in the cooling process,

so they become concentrated in late-stage pegmatites. The distribution of lithium within minerals is controlled by the $(MgO + Fe)/Li_2O$ ratio (Kunasz, 2006; McDonough and Sun 1995). Lithium has similar chemical properties to magnesium and iron. Lithium has been shown to substitute for magnesium in many systems both inorganic and organic (WebElements, 2018). The Mg/Li ratio varies from 2900 in ultramafic rocks to 120 in granites (Horstman, 1957). Lithium substitutes for Mg, Fe, Al, and Ti in magmatic melts. In a magmatic melt when the ratio $(MgO + FeO)/LiO$ is large, crystals which precipitate out of the melt first contain little lithium (Horstman, 1957). In melts both magnesium and iron are removed by ferromagnesian minerals in preference to lithium this contributes towards the enrichment of lithium in pegmatite (Kunasz, 2006). There are two main types of pegmatites (Cerný and Ercit 2005). The NYF group which predominantly accumulate the elements niobium, yttrium and fluorine. The LCT groups accumulate lithium, caesium, and tantalum, and are typically associated with late tectonic peraluminous (S-type) granites. S-type granites are derived from sedimentary protoliths containing high amounts of Al_2O_3 and relatively low amounts of Na_2O. (Linnen et al 2012). The NYF pegmatites are typically associated with A and I-type granites (Linnen et $al.,$ 2012). I-type granites are derived from igneous protoliths plagioclase-rich and muscovite poor and A-type granites are characterised by low water and typically occur in rift zones and in the interiors of continental plates (Gao et $al.,$ 2016). There are two main types of pegmatites (Černý and Ercit 2005). The NYF group which predominantly accumulate the elements niobium, yttrium, and fluorine. The LCT groups accumulate lithium, caesium, and tantalum, and are typically associated with late tectonic peraluminous (S-type) granites (Linnen et al., 2012). The NYF pegmatites are typically associated with A and I-type granites (Linnen et al., 2012). Generally, S-type granites are derived from sedimentary rocks and I-type granites are derived from igneous rocks, usually plagioclase-rich and muscovite poor (Gao, 2016). A-type granites typically occur in rift zones and in the interiors of continental plates. Pegmatites are fairly common throughout the Earth's crust however lithium; bearing pegmatites make up only 1% of the world's pegmatite resources. LCT pegmatites typically contain 12 to 30% spodumene, 22 to 27% quartz, 30 to 50% feldspar, and 3 to 5% mica and accessory minerals such as cassiterite (SnO_2) and columbite $(Fe^{2+}Nb_2O_6)$ (Colton, 1975). Of the, two main economic lithium-bearing minerals, spodumene has a maximum theoretical percentage Li_2O of 8.03% (3.7% lithium), and petalite has a maximum percentage Li_2O of 4.88% (2.2% lithium). Other minerals with less lithium that are often mined when they occur in large enough quantities are lepidolite $(K(LiAl)_3(AlSi)_4O_{10}(FOH)_2)$ and amblygonite $((Li,Na)AlPO_4(F,OH))$

(Meshram *et al.,* 2014). There are two significant clay sources of lithium; hectorite ($Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$) a magnesium, lithium smectite clay mineral and jadarite ($Na_2OLi_2O(SiO_2)_2(B_2O_3)3H_2O$) a monoclinic silicate mineral (Meshram *et al.,* 2014). Hectorite occurs in the Kings Valley California, USA, where it has an estimated reserve of 2 Mt, Jadarite is found in the Jadar Valley, Serbia, with an estimated reserve of 1.4 Mt (Kesler *et al.*, 2012). Global lithium reserves as hectorite and jadarite have been estimated to be 9.9 Mt (Tahil, 2007). In hectorite, the lithium tends to replace magnesium. Jadarite is a boron, lithium and sodium-rich silicate hydroxide mineral (Gruber *et al.,* 2011). Vine (1976) provides a detailed description of clay like minerals.

Table 1.10. List of 145 named lithium minerals, Sources: (Mindat, 2018; Webmineral, 2018; Meshram *et al.,* 2014; Kunasz, 2006).

Lithium mineral	chemical formula
Aleksandrovite	$KCa_7Sn_2Li_3Si_{12}O_36F_2$
Alumino-ottoliniite	$NaLi(Mg_3Al_2)\ Si_8O_{22}(OH)_2$
Amblygonite	$(LiNa)AlPO_4(FOH)$
Balestraite	$KLi_2V^{5+}Si_4O_{12}$
Balipholite	$BaLiMg_2Al_3(Si_2O_6)_2(OH)_4$
Baratovite	$KCa_7(Ti,\ Zr)_2Li_3Si_{12}O_{36}F_2$
Berezanskite	$K_2Li_3(Ti,\ Zr,\ Sn)_2(Si_{12}O_{30})$
Bertossaite	$(Li,\ Na)_2(Ca,Fe^{2+},Mn^{2+})Al_4(PO_4)_4(OH,F)_4$
Bikitaite	$(LiAlSi_2)_6 \cdot H_2O)$
Bityite	$LiCaAl_2(AlBeSi_2O_{10})\ (OH)_2$
Borocookeite	$LiAl4(BSi_3O_{10})\ (OH)_8$
Brannockite	$(K,\ Na)2Li_3(Sn,\ Zr,\ Ti)_2(Si_{12}\ O_{30})$
Bulgakite	$Li_2(Ca,\ Na)\ Fe^{2+}Ti_2(Si_4O_{12})_2O_2(OH)_4(F,\ O)\ (H_2O)_2$
Ciprianiite	$Ca_4[(Th,\ U)\ (Li)_2(Al)_2(Si_4B_4O_{22})\ (OH,\ F)_2$
Clino-ferri-holmquistite	$Li_2(Mg_3Fe_2^{3+})\ (Si_8O_{22})\ (OH)_2$
Clino-ferro-ferri-holmquistite	$Li_2(Fe_3^{2+}Fe^{3+})\ (Si_8O_{22})\ (OH)_2$
Clinoferroholmquistite	$(Li_2Fe^{++}3Al_2)\ Si_8O_{22}(OH)_2$
Clinoholmquistite	$(Li_2Mg_3Al_2)\ Si_8O_{22}(OH)_2$
Colquiriite	$Ca\ Li(AlF_6)$
Cookeite	$LiAl14Si_3O_{10}(OH)_8$
Cryolithionite	$Na_3Li_3(AlF_6)_2$
Darapiosite	$K\ (Na,\ K)_2(Li,\ Zn,\ Fe)_3(Mn,\ Zr,\ Y)_2(Si_{12}O_{30})$
Darrellhenryite	$Na(LiAl_2)\ Al_6(BO_3)_3Si_6O_{18}(OH)_3O$
Dellaventuraite	$Na3(Mg_2,\ Mn,\ Li,\ Ti)\ Si_8O24$
Dilithium	Li_2Te
Diomignite	$Li_2B_4O_7$
Dusmatovite	$K\ (Na,\ O)_2(Zn,\ Li)_3(Mn^{2+},\ Y,\ Zr)_2(Si_{12}O_{30})$
Elbaite	$Na\ (Li\ Al)_3Al_6Si_6O_{18}(BO)_3(OH)_4$
Eliseevite	$LiNa_{1.5}Ti_2(H_{1.5}Si_4O_{12})\ O_2 \cdot 2H_2O$
Emeleusite	$Li_2Na_4Fe_2Si_{12}O_{30}$
Ephesite	$LiNaAl_2(Al_2Si_2O_{10})\ (OH)_2$

Eucryptite	$(LiAlSiO_4)$
Faizievite	$K_2Na(Ca_6Na) Ti_4Li_6Si_{24}O_{66}F_2$
Ferri-clinoferroholmquistitee	$Li_2(Fe^{2+}Fe^{3+}) Si_8O_{22}(OH)_2$
Ferri-fluoro-leakeite	$Na(Na_2) (Mg_2Fe_2^{3+}Li) (Si_8O_{22}) F_2$
Ferri-leakeite	$Na(Na_2) (Mg_2Fe_2^{3+}Li) Si_8O_{22}(OH)_2$
Ferri-ottoliniite	$(Na, Li) (Mg_3Fe^{3+}) Si_8O_{22}(OH)_2$
Ferripedizite	$NaLi_2(Fe^{3+}2Mg_2Li) Si_8O_{22}(OH)_2$
Ferrisicklerite	$Li_{1-x}(Fe_x^{3+}Fe^{2+}_{1-x}) PO_4$
Ferriwhittakerite	$Na(NaLi) (Mg_2Fe^{3+}Li) Si_8O_{22}(OH)_2$
Ferro-ferri-fluoro-leakeite	$Na(Na_2) (Fe_2^{2+}Fe^{3+}Li) (Si_8O_{22}) (F)_2$
Ferro-ferri-pedrizite	$Na) (Li_2) (Fe_2^{2+}Fe^{3+}Li) Si_8O_{22}(OH)_2$
'Ferro-fluoro-leakeite'	$NaNa_2(Fe_2^{2+}Al_2Li) (Si_8O_{22}) F_2$
Ferro-holmquistite	$Li_2(Fe_3^{2+}Al_2) (Si_8O_{22}) (OH)_2$
Ferroleakeite	$NaNa2(Fe^{2+})_3(Fe^{3+})_2Li(Si_8O_{22}) (OH)_2$
Ferro-pedrizite	$NaLi_2(Fe_2^{2+}Al_2Li) Si_8O_{22}(OH)_2$
Fluor-elbaite	$Na(Li_{1.5}Al_{1.5}) Al_6(Si_6O_{18}) (BO_3)_3(OH)_3F$
Fluor-liddicoatite	$Ca(Li_2Al) Al_6(Si_6O_{18}) (BO_3)_3(OH)_3F$
Fluoro-ferroleakeite	$NaNa_2(Fe^{2+}Fe^{3+}Li) Si_8O_{22}F_2$
Fluoro-leakeite	$NaNa_2(Mg_2Al_2Li) (Si_8O_{22}) F_2$
Fluoro-Liddicoatite	$Ca(Li_2Al) Al_6(BO_3)_3Si_6)_{18}(OH)_3F$
Fluoro-sodic-pedrizite	$NaLi_2(Mg_2Al_2Li) S_5Si_8O_{22}F_2$
Footemineite	$Ca_2Mn^{2+}Mn^{2+}2Mn^{2+}2Be_4(PO_4)_6(OH)_4•6H_2O$
Gainesite	$Na (Na, K) (Be, Li) Zr_2(PO_4)_4 \cdot 1.5\text{-}2H_2O$
Garmite	$CsLiMg_2(Si_4O_{10}) F_2$
Gorbunovite	$CsLi_2(Ti, Fe) Si_4O_{10}(F, OH, O)_2$
Griceite	LiF
Griphite	$Na_4Li_2Ca_6(Mn^{2+}, Fe^{2+}, Mg)_{19}Al_8(PO_4)_{24}(F, OH)_8$
Hectorite	$(Na_{0.3}(Mg, Li)_3Si_4O_{10}(OH)_2)$
Holmquistite	$Li_2(Mg_3Al_2) (Si_8O_{22}) (OH)_2$
Hsianghualite	$Ca_3Li_2(Be_3Si_3O_{12}) F_2$
Jadarite	$(Na_2OLi_2O(SiO_2)2(B_2O_3)3H_2O)$
Katayamalite	$KLi_3Ca_7Ti_2(SiO_3)_{12}(OH)_2$
Kupletskite-(Cs)	$(Cs, K)_2 Na (Mn, Fe^{2+}, Li)_7(Ti, Nb)_2Si_8O_{26}(OH)_4F$
Lavinskyite	$K (Li Cu) Cu_6(Si_4O_{11})_2(OH)_4$
Leakeite	$NaNa_2(Mg_2Fe^{3+}_2Li) Si_8O_{22}(OH)_2$
Lepidolite	$K (Li Al)_3(Al Si)_4O_{10}(FOH)_2$
Liberite	Li_2BeSiO_4
Liddicoatite	$Ca(Li_2Al) Al_6(Si_6O_{18}) (BO_3)_3(OH)_3(OH)$
Lintisite	$LiNa_3Ti_2(Si_2O_6)_2O_2 \cdot 2H_2O$
Lithiomagnesite	$Li_2Mg(CO_3)_2$
Lithiomarsturite	$LiCa_2Mn_2Si_5O_{14}(OH)$
Lithiophilite	$LiMnPO_3$
Lithiophorite	$(Al, Li) Mn O_2(OH)_2$
Lithiophosphate	Li_3PO_4
Lithiotantite	$Li (Ta, Nb)_3O_8$
Lithiowodginite	$LiTa_3O_8$
Luanshiweiite	$KLiAl_{1.5}(Si_{3.5}Al_{0.5}) O_{10}(OH, F)_2$

Lunijianlaite	$Li_{0.7}Al_{6.2}(AlSi_7O_{20}) (OH, O)_{10}$
Magnesioclinoholmquistite	$Li_2(Mg, Fe^{2+})_3Al_2Si_8O_{22}(OH)_2$
Magnesioholmquistite	$Li_2(Mg, Fe^{2+})_3Al_2Si_8O_{22}(OH)_2$
Magnesioneptunite	$KNa_2Li (Mg, Fe)_2Ti_2Si_8O_{24}$
Magnesiostaurolite	$Mg (Mg, Li)_3(Al, Mg)_{18}Si_8O_{44}(OH)_4$
Manandonite	$Li_2Al_4(Si_2AlB) O_{10}(OH)_8$
Mangani-dellaventuraite	$Na(Na_2) (MgMn_2^{3+}LiTi^{4+}) Si_8O_{22}O_2$
Manganoneptunite	$Na_2KLiMn_2^{2+}Ti_2Si_8O_{24}$
Masutomilite	$(K, Rb) (Li, Mn^{3+}, Al)_3(AlSi_3O_{10}) (F, OH)_2$
Mccrillisite	$Na Cs (Be, Li) Zr_2(PO_4)_4 \cdot 1\text{-}2H_2O$
Montebrasite	$(Li Al(PO_4) (OH$
Murakamiite	$Ca_2LiSi_3O_8(OH)$
Nalipoite	$NaLi_2PO_4$
Nalivkinite	$Li_2Na (Fe^{2+}, Mn^{2+})_7Ti_2Si_8O_{26}(OH)_4F$
Nambulite	$(LiNa)Mn_4Si_5O_{14}(OH)$
Nanlingite	$Na (Ca_5Li) Mg_{12}(AsO_3)_2[Fe(AsO_3)_6] F_{14}$
Nanpingite	$Cs (Al, Mg, Fe^{2+}, Li)_2(Si_3Al) O_{10}(OH, F)_2$
Natromontebrasite	$(Na, Li) Al(PO_4) (OH, F)$
Natronambulite	$(Na, Li) (Mn, Ca)_4Si_5O_{14}OH$
Neptunite	$Na_2KLiFe_2^{2+}Ti_2Si_8O_{24}$
Norrishite	$KLiMn_2^{3+}(Si_4O_{10}) O_2$
Olympite	$Na_5Li(PO_4)_2$
Orlovite	$KLi_2Ti(Si_4O_{10}) OF$
Oxo-mangani-leakeite	$NaNa_2(Mn_4^{3+}Li) Si_8O_{22}O_2$
Pahasapaite	$Li_8(Ca, Li, K)_{10.5}Be_{24}(PO_4)_{24} \cdot 38H_2O$
Palermoite	$(Li, Na)_2(Sr, Ca) Al_4(PO_4)_4(OH)_4$
Peatite-(beta)	$Li_4Na_{12}Y_{12}(PO_4)_{12}(CO_3)_4(F, OH)_8$
Petalite	$LiAlSi_4O_{10}$
Pezzottaite	$Cs(Be_2Li) Al_2Si_6O_{18}$
Piergoritee	$(Al_{0.5}, Fe^{3+}_{0.5}) (Li, Be)_2Si_6B_8O_{36}(OH, F)_2$
Polylithionite	$KLi_2Al(Si_4O_{10}) (F, OH)_2$
Potassiccarpholite	$K (Li, Mn^{2+})_2Al_4(Si_2O_6)_2(OH, F)_8$
Potassic-ferri-leakeite	$K(Na_2) (Mg_2Fe_2^{3+}Li) Si_8O_{22}(OH)_2$
Potassicleakeite	$KNa_2Mg_2Fe^{3+}_2LiSi_8O_{22}(OH)_2$
Potassic-mangani-leakeite	$(Na, K) (Na_2) (Mg_2Mn_2^{3+}Li) Si_8O_{22}(OH)_2$
Punkaruaivite	$LiTi_2(HSi_4O_{12}) (OH)_2 \cdot H_2O$
Ramikite-(beta)	$Li_4(Na, Ca)_{12}Y_6Zr_6(PO_4)_{12}(CO_3)_4O_4[(OH), F]_4$
Rankamaite	$(Na, K, Pb, Li)_3(Ta, Nb, Al)_{11}(O, OH)_{30}$
Rossmanite	$(LiAl_2) Al_6(Si_6O_{18}) (BO_3)_3(OH)_3(OH)$
Saliotite	$(Li, Na) Al_3(AlSi_3O_{10}) (OH)_5$
Sicklerite	$(Li (Mn, Fe) PO_4)$
Silinaite	$NaLiSi_2O_5 \cdot 2H_2O$
Simferite	$Li (Mg, Fe^{3+}, Mn^{3+})_2(PO_4)_2$
Simmonsite	Na_2LiAlF_6
Sodic-ferri-clinoferroholmquistite'	$Na_{0.5}(Li_2) (Fe_3^{2+}Fe^{3+}) (Si_8O_{22}) (OH)_2$
Sodic-ferripedrizite	$Na(LiNa) (Fe^{3+}2Mg_2Li) Si_8O_{22}(OH, F)_2$
Sogdianite	$K(Na)_2Li_3(Zr, Fe, Ti)_2[Si_{12}O_{30}]$
Sokolovaite	$CsLi_2Al(Si_4O_{10}) F_2$

Soliotite	$(LiNa)Al_3(AlSi_3O_{10})(OH_5)$
Spodumene	$Li\,Al\,(SiO_3)_2$
Sugilite	$KNa_2(Fe\,Mn\,Al)_2Li_3Si_{12}O_3$
Swinefordite	$Li\,(Al, Li, Mg)_4((Si, Al)_4O_{10})_2(OH, F)_4 \cdot nH_2O$
Tainiolite	$KLiMg_2(Si_4O_{10})\,F_2$
Tancoite	$LiNa_2Al\,(PO_4)\,(HPO_4)\,(OH)$
Tanohataite	$LiMn_2(HSi_3O_9)$
Tavorite	$(LiFe^{3+}(PO_4)\,(OH))$
Tiptopite	$K_2\,(Na, Ca)_2Li_3Be_6(PO_4)_6(OH)_2 \cdot H_2O$
Trilithionite	$K(Li_{1.5}Al_{1.5})\,(AlSi_3O_{10})\,(F, OH)_2$
Triphylite	$(LiFe^{2+}PO_4)$
Virgilite	$LiAlSi_2O_6$
Voloshinite	$Rb\,(LiAl_{1.5})\,(Al_{0.5}Si_{3.5})\,O_{10}F_2$
Walkerite	$Ca_{16}(Mg, Li)_2(B_{13}O_{17}(OH)_{12})_4Cl_6 \cdot 28H_2O$
Watatsumiite	$Na_2K\,Li\,(Mn^{2+}, Fe^{2+})_2V_2^{4+}(Si_8O_{24})$
Wilancookite	$(Ba, K, Na)_8(Ba, Li)_6Be_{24}P_{24}O_{96} \cdot 32H_2O$
Zabuyelite	(Li_2CO_3)
Zektzerite	$Li\,Na\,(Zr\,Ti\,H\,F)\,Si_6O_{15}$
Zinnwaldite	$K\,Li\,Fe\,Al\,(AlSi_3)\,O_{10}(OHF)_2$

Normally lithium is extracted from minerals as lithium carbonate which is a precursor for nearly all lithium commercial compounds. Initially, the process for the majority of minerals follows the same sequence. Crushing and grinding (comminution) is the first stage in the process, it liberates the lithium minerals from the rock matrix. Aluminosilicate minerals are hard and abrasive. As a consequence, comminution is energy intensive and accounts for up to 50% of the processing cost. The lithium ore is then separated using physical, electrical and magnetic processes. The next step involves chemical processing after which final processes like froth flotation and/or dense media separation are used to further concentrate the lithium (BGS, 2016).

Chemical processing is usually carried out by specialised companies. Spodumene in nature exists as α – spodumene a monoclinic alumosilicate that is very resistant to most chemical breakdown, although, hydrofluoric acid can dissolve the silicate matrix over time. A method for the extraction of lithium from β – Spodumene by leaching with hydrofluoric acid has been described as; $LiAl(SiO_3)_2 + 19HF \rightarrow LiF + H_3AlF_6 + 2H_2SiF_6 + 6H_2O$ (Rosales *et al.,* 2014). Often during processing α – spodumene is converted to β – spodumene by roasting at a temperature of 1100°C (calcination). The crystal structure is changed during roasting resulting in the β - spodumene becoming more reactive and susceptible to chemical breakdown.

Sulphuric acid is heated to different temperatures depending on the mineral being treated (e.g. spodumene at >1050 °C). Chen *et al.*, (2011) describe a method for the extraction of lithium from spodumene using a sodium carbonate autoclave process. β-spodumene is mixed with hot sulphuric acid, then water is used to leach out lithium as Li_2SO_4; $Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + H_2SO_4 \rightarrow Li_2SO_4 + Al_2O_3 \cdot 4SiO_2 + H_2O$. Finally, sodium carbonate is added to extract the lithium as Li_2CO_3, $Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3 + Na_2SO_4$. The sodium carbonate method has a low energy requirement compared to other extraction methods.

The separation of lithium from β – spodumene concentrates using the physical methods of froth flotation with oleic and naphthenic acids followed by heavy media separation processes has been described (Amarante *et al.,* 1999). Petalite is not as resistant to chemical attack as spodumene, it is still roasted prior to processing. Sitando and Crouse (2012) describe a method using sulphuric acid at 300°C to process lithium carbonate from petalite $LiAlSi_4O_{10} + H_2SO_4 \rightarrow Li_2SO_4 + Al_2O_3 \cdot 4SiO_2 + H_2O$. Sitando and Crouse (2012) also describe an alkali process where petalite is mixed with calcium carbonate heated to 1050°C and, lithium is extracted by hydrochloric acid as lithium chloride. A method for the separation of lithium from lepidolite called chlorination roasting (at 750°C), which uses sodium chloride and/or calcium chloride as reacting agents rather than hydrochloric acid (Sitando and Crouse 2012). This process is usually followed by a   followed by a water leaching technique which has been described (Yan *et al.*, 2012). More commonly used methods for extracting lithium from lepidolite are roasting in the presence of sodium sulphate or potassium sulphate at 860°C (Sitando and Crouse 2012). Barbosa *et al.,* (2014) demonstrated the extraction of lithium from β – spodumene using pure gaseous chlorine at temperatures > 1000°C (Barbosa *et al.*, 2014). Vu *et al.,* (2013) report on the extraction of lithium and rubidium from the mineral zinnwaldite $(KLiFeAl(AlSi_3)O_{10}(OHF)_2)$ using an alkali digestion method (Vu *et al.*, 2013). Their process heats the ore (825°C) in the presence of calcium carbonate followed by water leaching (90°C) to extract the lithium. Other valuable elements like caesium, tantalum and rubidium are often produced along with lithium from a mineral source.

The three main global suppliers of lithium from mineral sources today are Australia, Canada, and Zimbabwe (Kunasz, 2006). In Australia, the Greenbushes pegmatite mine in southwest Australia is currently the largest producer of lithium from a mineral source (Partington *et al.,* 1995). There are other locations in Australia that have substantial lithium pegmatite deposits at Broken Hill, New South Wales, at Mount Cattlin 2.2 km north of Ravensthorpe, Western Australia and at Mount Marion 40 km south-west of

Kalgoorlie, in the Goldfields region of Western Australia (Lithium Australia, 2016; Grosjean *et al.,* 2012; Evans, 2008). In Canada, there are numerous pegmatite mines such as LaCorne, Val d'Or Nemaska mines in Quebec, and Tanco pegmatite mine at Bernic Lake, Manitoba where lithium, caesium and tantalum are mined from (LCT) pegmatites (Meshram *et al.,* 2014; Evans, 2008; Kunasz, 2006). Sub Saharan Africa is exceptionally rich in minerals. The Bikita mine in the Masvingo province of Zimbabwe is one of the largest lithium mines in Africa and has been operating since the 1950s. Lithium mineralisations are also known to exist in the Bauberton, Benson, Fort Rincon, Harare, Kamativi, and Uredefort regions of Zimbabwe. Other locations in Sub Saharan Africa like Karibib in Namibia, the D.R.Congo, Rwanda, Mozambique, and the Noumas and Norrabees areas of South Africa also contain lithium pegmatite mineralisations. Lithium pegmatites also exist in Bougouni, Mali as the mineral amblygonite; in the Indian regions of Chhattisgarh, Jharkhand, Karnataka, Rajasthan as spodumene; and the pegmatites of the Republic of Suriname in South America (Martin, 2017; Vikström *et al.,* 2013; Mohr *et al.,* 2012; Evans, 2008; Kunasz, 2006). In the EU, old tin mines are receiving renewed interest as sources of lithium in places like Cornwall in England and the Czechia/German border town of Cinovec. Table 1.11 contains a listing of some of the more well-known lithium pegmatites deposits globally.

Table 1.11. Location and parameters of some lithium pegmatites mines globally. (Vikström *et al.,* 2013 [1]; Risen, 2010 [2]; Evans, 2008 [3]; Yaksic and Tilton 2009 [4]; Martin, 2017 [5]; Mohr *et al.,* 2012 [6]; Kavanagh *et al.,* 2017 [7]; Vine, 1976 [8]; Kunasz, 2006 [9]; Sheppard *et al.,* 1977 [10]; Gruber *et al.,* 2011 [11]; Meshram *et al.,* 2014 [12]; Sitando and Crouse 2012 [13]).

Description	Main Mineral	%Li$_2$O	Li reserve (Mt)
Afghanistan, Drumgal, Parun [1]	Spodumene	1.38	0.235
Afghanistan, Jamanak [2]	-----	1.83	0.45
Afghanistan, Lower Pasghusta [2]	-----	2.2	0.124
Afghanistan, Nilaw, Laghman [2]	Spodumene	3	1.5 – 2.5
Afghanistan, Parun, Badakhshan [2]	Spodumene	1.5	3
Afghanistan, Pasghusta [2]	-----	2.14	-----
Afghanistan, paskhi [2]	-----	1.46	0.127
Afghanistan, Tsamgal [2]	-----	1.5	0.1875
Afghanistan, Yaryhgul [2]	-----	1	0.124
Afghanistan, Yorigal [2]	-----	----	----

Australia, Broken Hill region [3]	Amblygonite	10	-----
Australia, Greenbushes [4]	Spodumene	1.2 – 3.9	0.3 – 0.7
Australia, Londonderry [3]	Petalite	5	-----
Australia, Mt Cattlin [1]	Spodumene	7 – 8.4	0.07
Australia, Mt Marion [3]	Spodumene	1.3	0.0198
Australia, Pilgangoora [3]	Spodumene	1.25	156.3
Brazil, Ceará [4]	Lepidolite	3.5-4.2	0.139
Brazil, Minas Gerais [4]	Spodumene	1.56	0.085
Canada, Big Bird / Curlew [1]	Spodumene	1.2 – 1.7	-----
Canada, English River Greenstone [1]	Spodumene	-----	-----
Canada, Gods Lake [1]	Spodumene	-----	-----
Canada, James Bay, Whabouchi [1]	Spodumene	1.54	0.18
Canada, La Motte [4]	Spodumene	0.5	0.023
Canada, Lac du Bonnet mine [1]	Spodumene	1.85	-----
Canada, LaCorne [1]	Spodumene	0.85	0.08
Canada, Manitoba, Bernic Lake [1]	Spodumene	1.28	0.2
Canada, McAvoy [1]	Spodumene	3.3 – 4.5	-----
Canada, Moblan [1]	Spodumene	1.7	0.04
Canada, Moose 2 [1]	Spodumene	----	0.016
Canada, Nama Creek [1]	Spodumene	1.1	2.4
Canada, Niemi Lake [1]	Spodumene	-----	0.001
Canada, Ontario, Nakima mine [1]	Eucryptite	-----	-----
Canada, Quebec, Barraute [4]	Spodumene	0.2 – 0.5	0.09 – 0.3
Canada, Quebec, Val d'Or [1]	Spodumene	1.02	10.2
Canada, Rose [1]	-----	-----	-----
Canada, Separation Rapids [4]	Petalite	0.7	0.056
Canada, Shawinigan, Quebec [1]	Spodumene	6	27.3
Canada, Sirmac Lake [1]	-----	-----	0.003
Canada, Sirmac Lake [1]	-----	-----	-----
Canada, Snow Lake [1]	-----	-----	0.026
Canada, Snow Lake [1]	-----	-----	-----
Canada, Thompson Brothers [4]	-----	-----	0.026
Canada, Wekusco [1]	Spodumene	0.79	0.028
Canada, Wekusko Lake [1]	Spodumene	0.79	0.028
Canada, Yellowknife [4]	Spodumene	0.66	0.1

Location	Mineral		
Chin, Sichuan Dexin's mine [3]	-----	0.05	0.05
China, Altai Mountains [3]	Spodumene	1.5	-----
China, Daoxian [3]	Lepidolite	0.552	0.125
China, Gajika [4]	Spodumene	0.3	0.591
China, Hunan, Lushi [3]	-----	0.47	0.009
China, Hupei [3]	Petalite	-----	0.042
China, Jiajika [4]	-----	0.59	0.204
China, Jinchuan [3]	Petalite	-----	-----
China, Lijiagou [3]	Petalite	-----	0.06
China, Maerkang [4]	Spodumene	0.125	0.225
China, Ningdu [3]	Petalite	-----	-----
China, Sichuan, Jaijika [3]	Spodumene	1.28	0.480
China, Yichun [3]	Lepidolite	2	0.325
D.R.Congo, Katanga [1]	-----	-----	-----
D.R.Congo, Kinshasa [1]	-----	-----	1
D.R.Congo, Kitotolo [1]	Spodumene	0.6	0.8
D.R.Congo, Manono [1]	Spodumene	0.6	2.3
EU, Czechia [5]	-----	-----	-----
EU, Finland, Haapaluoma [6]	Spodumene	-----	-----
EU, Finland, Hirvikallio [6]	Spodumene	0.47	0.00047
EU, Finland, Kietyonmaki [6]	Spodumene	0.7	0.007
EU, Finland, Länttä [6]	Spodumene	0.5	0.014
EU, Finland, Osterbotten [6]	Spodumene	0.43	0.0019
EU, Finland, Toro [6]	Spodumene	-----	-----
EU, France [6]	-----	-----	-----
EU, Ireland [7]	Spodumene	1.5 – 2.3	0.5
EU, Norway, Helgeland, Bramble [6]	----	-----	-----
EU, Portugal, Barroso [1]	Lepidolite	0.57	0.0514
EU, Portugal, Boticas [1]	Spodumene	1.1	0.05
EU, Serbia, Jadar valley [1]	Jadarite	0.84	1
EU, Spain, Morille [1]	Lepidolite	-----	0.2
EU, Spain, San Jose [1]	Lepidolite	1	0.2
EU, Sweden, Järkvissle, Medelpad [8]	Spodumene	0.45	0.003
EU, Sweden, Utö, Haninge [9]	Petalite	-----	-----
EU, Sweden, Varuträsk [8]	Spodumene	1.3 - 2	0.001

EU, UK, Cornwall Camborne [10]	Amblygonite	0.84	-----
EU, UK, Devon [10]	Amblygonite	-----	-----
EU. Austria, Koralpe [4]	Spodumene	-----	0.1
Mexico, Sonora [6]	-----	-----	-----
Russia, Achivansky / Uchastok [11]	-----	-----	0.05
Russia, Alti mountains [11]	Spodumene	0.8	1.74
Russia, Diturskoe [11]	-----	------	-----
Russia, Knyazheskoe [1]	-----	-----	-----
Russia, Kolmorzerskoe [1]	-----	-----	0.288
Russia, Ohmylk [1]	-----	-----	-----
Russia, Olondinskoe [1]	-----	-----	-----
Russia, Otboninoe [1]	-----	-----	-----
Russia, Pellapahik [1]	-----	-----	-----
Russia, Podgorskoe [1]	-----	-----	-----
Russia, Raduga [1]	-----	-----	-----
Russia, Suglugskoe [1]	Spodumene	-----	-----
Russia, Tala [1]	-----	-----	-----
Russia, Tuva Republic Tastyg [1]	Spodumene	1.86	0.05
Russia, Voznesenskoe [11]	-----	-----	0.14
Russia, Белоре́ченск [11]	Spodumene	-----	0.05
Russia, Белу-Tagninskoe [11]	-----	-----	-----
Russia, Большой Потчемварек [11]	-----	-----	-----
Russia, Забайкалье, Etykinskoe [1]	Lepidolite	0.23	0.046
Russia, Иркутская область [11]	-----	0.49	0.2
Russia, Иркутская область [1]	Spodumene	0.8	-----
Russia, Urikskoe [11]	Spodumene	-----	0.1 – 0.3
Russia, Vishnyakovskoe [11]	-----	0.49	0.21
Russia, Кривой Рог [11]	Spodumene	-----	0.130
Russia, Му́рманская о́бласть [1]	-----	-----	0.4
Russia, Олений Хребет [1]	-----	-----	-----
Russia, Орловское [1]	Lepidolite	-----	0.05
Russia, Пограничное [1]	-----	-----	0.05
Russia, Северный Vystup [1]	-----	-----	-----
Russia, Улуг-Tanzek [11]	-----	-----	0.3
Russia, Читинская область, [11]	-----	-----	0.14

USA, Arizona, Yavapai county [6]	Clay	0.01	-----
USA, Alabama, Bessemer [1]	-----	0.67	0.42
USA, South Dakota, Black Hills [9]	Spodumene	0.5-3 Li	-----
USA, California [1]	Lepidolite	0.2	-----
USA, California, Hector [6]	Hectorite	0.27	2
USA, California, Kramer [6]	Clay	0.19	-----
USA, California, Stewart mine [6]	-----	-----	-----
USA, Connecticut, Branchville [6]	Eucryptite	-----	-----
USA, Arkansas, Magnolia [6]	-----	-----	-----
USA, Nevada, Humboldt County [6]	Spodumene	0.69	-----
USA, Nevada, HYclaims [6]	-----	-----	----
USA, Nevada, Kings Valley [12]	Hectorite	0.04 - 0.7	0.015
USA, Nevada, Paymaster [6]	-----	-----	-----
USA, New Mexico, Harding mine [9]	Eucryptite	-----	-----
USA, North Carolina, Cherryville [4]	Spodumene	1.2	-----
USA, North Carolina, Foote [3]	Eucryptite	-----	0.15
USA, North Carolina, Kings Mt [4]	Spodumene	0.07 - 2	0.083
USA, Utah's Spor Mountain [12]	-----	0.11	-----
Zimbabwe, Barkam [1]	-----	-----	0.22
Zimbabwe, Bikita [13]	Spodumene	1.4 – 3.6	0.0567
Zimbabwe, Harare [13]	-----	-----	-----
Zimbabwe, Hwange [13]	-----	-----	-----
Zimbabwe, Insiza [13]	-----	-----	-----
Zimbabwe, Kamativi [1]	Spodumene	0.28	0.28
Zimbabwe, Masvingo [6]	Spodumene	1.4	0.057
Zimbabwe, Matobo [13]	-----	-----	-----
Zimbabwe, Mazoe [13]	-----	-----	-----

1.3.6. Lithium Mining and the Environment

A priority and legal necessity for all modern mining companies is the sustainable management and stewardship of the environment. Modern mining companies are responsible, practice low impact mineral extraction processes, and take stewardship of the environment seriously. In the past, however, and even today in some small-scale mining operations this has not been the case. Poorly managed mining operations have left a legacy of environmental problems, like the destruction of the local ecosystem and land

transformation. For example, in India, large-scale coal mining operations have affected local communities due to land transformation resulting in a loss of forestry and agricultural land, in one of the most densely populated countries in the world (Jamal et al., 2017). Other notable examples include small-scale gold mining operations in Africa and South America which have severely increased mercury concentrations in rivers. Mines are sometimes huge in scale, the ecosystem of a mined area is effectively destroyed during mining, although nowadays most mining companies are concerned with efforts to reclaim previously mined sites and rehabilitating the local ecosystem. Open pit mines associated with mineral lithium deposits are often small compared to other mines. Although not a phenomenon which has been related to lithium mining "conflict minerals" in countries like the Democratic Republic of Congo (D.R. Congo), which contains a vast mineral wealth, may also be considered a potential mining related impact. Lithium mining has a relatively low environmental mining impact compared to the mining of other metals like Platinum Group Metals (PGMs) and REEs.

Another legacy of poorly managed mining operations is acid mine drainage (AMD). The acidification of waters leached from mine tailings or old mines that have been left to fill with both surface and groundwater. These waters contain toxic metals, like copper and lead and have been shown to have a negative effect, at a reduced pH, on fresh waters (Sapsford *et al*., 2009). The negative effects associated with AMD often do not manifest until several years after mining has begun and can persist for centuries. Nowadays preventative measures which are normally compulsory in most countries are in place to mitigate AMD (Akcil and Koldas 2006). Treatments for AMD problems include alkaline neutralization, bioremediation and constructed wetlands and have been described elsewhere (Akcil and Koldas 2006; Johnson and Hallberg 2005). Mine tailings normally take the form of a slurry and are therefore easily stored in a pond/dam construction usually on the same site as the mine, preventing them from entering the wider environment. This technique is effective but there have been cases of dam failures. Tailings contain compounds like sulphides and typically a large number of heavy metals which are normally only found deep underground. These heavy metals, using a pathway which usually involves water, can find their way into the surrounding environment with potential toxic effects on both flora and fauna. It is estimated that globally total volume of mine tailings generation is about 18 billion m^3/year and is expected to double in the next few decades (Sheoran *et al.,* 2013). Mining of ores increases the presence of metals in environments and physically rearranges land formations which can interfere with groundwater carrying soil layers. Metals originating from mining activities have been

found in a wide variety of environmental media, including soil, plants (including food products), air and fresh waters. The extraction of lithium from brines requires a large amount of fresh water in the process. In the areas where the salars of South America occur fresh water supplies are relatively scarce. This has led to some "water conflicts" in the area between the brine mineral extraction industry and traditional farming (Figueroa *et al.*, 2012). Lithium brine production may have negative effects on the local environment. One source of potential pollution is from the large PVC lined ponds used to evaporate the brine, which could leak substances like lime to the environment (Sadiki and Williams 1999). The PVC itself may also leach harmful substance to waters that find their way back into the local environment. Volatile organics and substances like organotin albeit at very low concentrations have been described as leaching from PVC pipes (Sadiki and Williams 1999; Skjevrak *et al.,* 2003). Wanger (2011) describes how a reduction in the flamingo population may result in an increase of harmful cyanobacteria (Wanger 2011) Flamingos have a variety of habitats including mangrove swamps, tidal flats, and salars. Flamingos eat cyanobacteria (blue-green bacteria) in these salars and naturally keep their number in check. The extraction of lithium can have significant environmental and social impacts if not properly regulated and controlled. Water pollution, toxic chemical releases through leaching, and air emissions are the main concerns. The inhalation of siliceous dust associated with hard rock mining is known to be harmful. The mining of lithium, just like any other mining process, can have an effect on the environment if poorly managed. However, it is important to state that mining is an important part of our global economy. For decades mining has provided millions of people with employment and helped developing nations with economic security (Hilson, 2002). Mined metals are also indispensable for the production of technology that reduces environmental impacts, technologies like wind generators and solar panels would not be possible without metals. Metals are invaluable to our society and it is not an option to just not use them.

1.4. Lithium Uses

Lithium is a versatile metal, with a wide range of uses. Its applications vary from its use as a medication to treat mental illness in the form lithium carbonate to its use in the manufacture of lightweight alloys for the aeronautics industry. In this section, we have compiled the information given in the literature concerning the main industrial uses of lithium.

1.4.1. Glass and Ceramics

For a long time, the principal use of lithium ore was in glasses, glass ceramics, porcelain enamels, fritted glazes, raw glazes, and refractories (Vine, 1976). The glass and ceramics industries are still major consumers of lithium. In these industries, lithium ores like spodumene are used as a fluxing agent (chemical cleaning, flowing or purifying agent) (Kunasz, 2006). Spodumene concentrate is often used, rather than lithium, in combination with other lithium-bearing minerals like amblygonite, lepidolite, and petalite. Lithium is used to reduce the viscosity and lower the production temperatures of glass and ceramic manufacturing processes, thereby reducing costs. Due to lithium's small ionic radius, it has a low coefficient of thermal expansion ($46\ \mu m \cdot m^{-1} \cdot K^{-1}$) (Rumble, 2017). When added to molten glass it reduces the thermal expansion and fluidities (elasticity) of the mix. Adding 0.17% Li_2O to glass lowers the melting temperature by 25°C and reduces energy consumption by 5 to 10%. When used in ceramic production it lowers the firing temperatures and increases the strength of ceramic bodies. The addition of lithium provides additional durability, particularly in heatproof ceramic and glass cookware. The addition of lithium produces pyroceramic products with prolonged furnace refractory lifespans, greater surface tension, resistance to thermal shock, and increased mechanical strength. Lithium also improves the colour fastness of glazes and decreases shrinkage during production and increases resistance to corrosion.

Lithium fluoride crystals are used in specialised optics. Lithium fluoride forms a simple ionic crystal lattice structure, which is useful in the ultraviolet and infrared optics. The lithium fluoride crystals are transparent to short wavelength ultraviolet radiation, more so than any other material. The lithium fluoride crystal has one of the lowest refractive indexes and the farthest transmission range in the deep ultraviolet of most common materials. Due to these properties, lithium fluoride is commonly used in the manufacture of prisms, and lenses in monochromators as well as the focal lenses in large telescopes. Double glazed windows (using heat-reflective glass) are coated with a thin layer of metallic chemicals which includes lithium to improve the insulating properties of the glass. The glass for the Californian Institute of technology's 5.1m telescope (Hale telescope) at the Mount Palomar Observatory in Pasadena California, USA contains lithium as a minor ingredient (Rumble, 2017). The addition of lithium to the telescopic mirror helps the glass withstand prolonged heating and slow cooling annealing manufacturing processes (Vine, 1976). Lithium niobate and lithium tantalate also have specialised applications in optics in the production of electronic grade crystals for use in

electronic oscillators. Lithium has been found effective in assisting silicon nano-welds in electronic components for electric batteries and other devices. Glass lenses such as those in car headlights which are exposed to rapid temperature changes contain lithium to reduce thermal shock (Vine, 1976). The production of high barium, containing monochromatic television tubes in the past required lithium as a melting aid (Vine, 1976). Lithium is also used in the production of monochromatic computer monitors (Ebensperger *et al.,* 2005). It is used in the production of glass foam as an alternative to other more polluting ingredients, glass foam is an insulating building material (Vine, 1976). A blue glaze is acquired when lithium is combined with copper, a pink glaze results from the combination of lithium and cobalt (BGS, 2016).

1.4.2. Lithium as a Desiccant

Lithium chloride and lithium bromide are extremely hygroscopic and used as desiccants for gas streams. Lithium chloride is one of the most hygroscopic compounds and is commonly used in sophisticated air conditioning systems. Lithium bromide solutions at 55% are used in the air conditioning systems of large buildings. Lithium chloride is used in industrial dehumidification and drying. Lithium bromide and lithium chloride have low vapour pressures and have been used in adsorption refrigeration (Kunasz, 2006). Anhydrous lithium hydroxide and lithium peroxide are used in submarines and the international space station as chlorofluorocarbon-free, carbon dioxide removers (scrubbers). The lithium hydroxide takes carbon dioxide from the air and converts it to lithium carbonate. Lithium peroxide reacts in the same way but also releases oxygen. When lithium is burned in the air it will produce lithium oxide and lithium peroxide. Lithium chromate has also been used in air conditioning systems. Lithium perchlorate is used in the manufacturing of candles that provide oxygen. Lithium hydroxide was used as a desiccant in the rebreather systems used in the Apollo space missions.

1.4.3. Organolithium Chemistry

Due to the high electropositive nature of lithium, organolithium compounds are extremely powerful bases and nucleophiles. Organolithium compounds are sold as bases commercially and used in the production of high-grade pure chemicals. Butyllithium is used in both polymer and pharmaceutical industries as an intermediate. Lithium and its compounds are used to catalyse the polymerization of conjugated dienes and the copolymerisation of alkenes (Fenton *et al,* 1957). Butyllithium is used as a catalyst in the polymerisation of Butadiene, isoprene, styrene, and to produce styrene butadiene and polybutadiene synthetic rubber (Kunasz, 2006). It is used to catalyse polymer reactions

with thermoplastic properties (Martin, 2017). Organolithium reagents are used as exceptionally powerful and selective reducing agents in organic synthesis. Lithium aluminium hydride is the most common lithium compound used as a reducing agent. It is used in reactions such as in the Birch reduction, Grignard-type reactions and in the synthesis of vitamin A (Parker *et al.,* 2016). Unlike the other alkali metals lithium is soluble in organic solvents like pyridine, diethyl ether and 1-pentanol (Colton, 1975). This property is often exploited in the lab as a means of separating lithium from a solution using a liquid/liquid extraction process. Lithium's solubility in diethyl ether is also used to create an organolithium compound in a Wurtz-type coupling reaction, where two alkyl halides are reacted with sodium in a diethyl ether solution to form higher alkanes ($RX + 2Li \rightarrow RLi + LiX$) (Fenton *et al.,* 1957). This reaction is used to produce many organic compounds. Organolithium compounds will bond to an alkene (Fenton *et al.,* 1957). The alkylation (transfer of an alkyl group from one molecule to another) of organolithium compounds is a common and useful reaction in organic chemistry, for example, an organolithium compounds reaction with a ketone produces a tertiary alcohol ($R_2 C=O + R'Li \rightarrow RsR'COLi$) (Fenton *et al.,* 1957).

1.4.4. Lithium as a Lubricant

Lithium grease is waterproof; capable of maintaining its viscosity for a long time; has an extremely low melting point; high mechanical strength, and high thermal resistance. Since lithium grease first came onto the market in the early 1940s it has practically replaced sodium-based greases (Yalamanchali, 2012). Essentially lithium grease is an oil mixed with an emulsifying agent like soap. Lithium stearate and lithium 12-hydroxystearate are often used in the saponification of triglycerides (lipids) to manufacture high-temperature resistant greases (Delgado *et al.,* 2006). These greases are commonly used as a lubricant in metal on metal mechanisms, both indoor and outdoor and are commonly used in automotive applications. Lithium hypochlorite is used as a disinfectant in swimming pools and as a reagent for some chemical reactions. Lithium hydride is used in the synthesis of hydrides of certain metalloids like silane (compounds with four substituents on a silicon atom) in the Sundermeyer process ($4LiH + SiCl_4 \rightarrow 4LiCl + SiH_4$) (Rittmeyer and Wietelmann 2000). Lithium-based chemicals have other applications such as in hydrogen and oxygen generation, in flavours, colourings and fragrances (Kunasz, 2006). Lithium burns bright red, because of this property lithium compounds are often used in fireworks and flares as pyrotechnic colourants. When lithium oxide is extracted from spodumene by roasting the gangue is used as an additive to cement, where it reduces cement kiln operating expenses and increases setting time

(Colton, 1975). Lithium is also used as a tracer in soil and water contamination studies because it mimics the movement of metals in the soil solution and water body closely and can be used to accurately predict residence times.

1.4.5. Lithium in Medicine

Lithium's beneficial neurological effects have been exploited since the height of the Roman Empire. Perhaps the first recorded use of lithium as a therapeutic agent was between the years 98 and 138. The Roman physician Soranus of Ephesus (modern-day Turkey) discovered that patients suffering from mania who repeatedly bathed and drank the alkaline waters of the area showed improved conditions (Thompson, 2007). Mania or manic behaviours are a symptom of type one bipolar disorder, characterised by unusually heightened moods and hyperactivity. These waters contained high levels of lithium salts. Without knowing it Soranus had discovered the therapeutic effects of lithium on people suffering from mania. Lithium was first used to treat gout in 1845. The reasoning for this was that a lithium solution was observed to dissolve uric acid crystals in urine, the formation of which is a symptom of gout (Schrauzer 2002; Kaill 1999). At the time "urate imbalances" were proposed to be responsible for a number of medical ailments like gout. Uric acid was also known to be a psychoactive substance, so it was postulated that treatment with lithium would reduce uric levels in patients suffering from mania (Oruch *et al.,* 2014). Lithium was seen as a miracle neuroprotective agent and was added to tonics to boost mental fitness. Its growing popularity even saw it been added to products like "Bib-Label Lithiated Lemon-Lime Soda" the precursor to 7-up (where lithium was the original "up" ingredient) and "Lithia water" in the 1920s (Davis, 1987). Lithium chloride was also used as a replacement for common table salt for people requiring low sodium diets. The widespread use of lithium eventually led to several cases of lithium toxicity, resulting in it been banned in soft drinks (Kaill, 1999).

Some groups suggest there are beneficial effects to be had from taking lithium supplements such as lithium orotate. Claimed benefits include enhancing mental development, the protection from use of psychoactive medications such as serotonin reuptake inhibitors, and protection to the brain from alcohol abuse (Mauer *et al.,* 2014; Watase *et al.,* 2007; Nonaka and Chuang 1998). In the 1880s it was noted that lithium had a beneficial therapeutic effect on patients suffering from mania, and also reduced suicidal tendencies in patients (Kaill, 1999). Credit for rediscovering the therapeutic properties of lithium goes to the Australian psychiatrist Dr John Cade in the 1940s (Colp, 2000; Rush, 1988; Shorter and Healy 1997; Schou *et al.,* 1954; Cade, 1949). Cade treated

patients suffering from mental ailments successfully using lithium carbonate (Kaill, 1990). He determined that lithium carbonate had a calming effect. Cade's findings went unnoticed for some time: *"Made by an unknown psychiatrist with no research training, working in a small chronic hospital with primitive techniques and negligible equipment, was not likely to command attention"* (Cade, 1949). Lithium carbonate, as well as lithium acetate, lithium aspartate, lithium citrate, lithium borate, lithium orotate and lithium sulphate, has been used since then to treat people with bipolar disorder (manic depression) and to alleviate suicidal thoughts in patients (Oruch *et al.,* 2014). It has also seen some use in the treatment of schizophrenia and addiction. Lithium is known to interact with neurotransmitters and receptors in the human brain, increasing serotonin levels and reducing brain production of norepinephrine a hormone and neurotransmitter. Lithium's interactions in human biochemistry are complex and the topic of much research (Schrauzer, 2002). The exact mechanisms by which lithium acts neurologically are not fully understood, however, at least nine theories having been put forward (Oruch *et al.,* 2014).

Lithium has been used to treat headaches, hypertension, diabetes, epilepsy and even dental caries (Timmer and Sands 1999; Magalhães and Wilcox 1990). Lithium bromide was used as a sedative/hypnotic in the past, but its use was discontinued due to some complications caused to patients with pre-existing heart conditions (Oruch *et al.,* 2014). Lithium is also used in the chemotherapeutic treatment of inflammation in joints. It accumulates preferentially in the thyroid gland where it can cause problems like hypothyroidism and thyrotoxicosis, this has only been observed in patients receiving lithium treatments (Timmer and Sands 1999). Autopsies have shown that lithium also accumulates in the cerebellum, cerebrum, and kidneys (Schrauzer, 2002). Lithium has been investigated as a possible preventative/treatment for Alzheimer's disease. One symptom of Alzheimer's is a "tangling" of microtubules in cells. Lithium's presence reduces the amount of "tangles" by limiting the amount of a protein produced which propagates these "tangles" (Forlenza *et al.,* 2012; Kaill 1990). Lithium may have a preventative effect on dementia in mice (Terao *et al.,* 2006). There are also studies investigating whether lithium in humans can prevent dementia (Kessing *et al.,* 2010). There are no cases in the literature relating a natural source of lithium to any acute or chronic toxicities. Ingestion of approximately 5g of lithium chloride is enough to cause fatal toxicity in humans (Shahzad *et* al., 2017; Aral and Vecchio-Sadus 2008). Shahzad *et al.,* (2017) provide an extensive list of the symptoms associated with lithium acute and chronic toxicity in humans associated with people receiving lithium treatments. Lithium

has been reported to reduce reproduction in some fish and crustaceans (Aral and Vecchio-Sadus 2008; Kszos *et al.,* 2003). Lithium is an important micronutrient that has a function in metabolism, cell proliferation and neural communication (Shahzad *et al.,* 2017)

There is evidence to suggest that lithium at low concentrations in the human diet has a beneficial effect on human behaviour. Lithium's beneficial effect on risk factors associated with atherosclerotic heart disease like hypertension and serum lipid levels have been described in detail (Voors, 1969). Voors, (1969) work showed a negative correlation to exist between atherosclerotic heart disease and lithium in drinking water (r = – 0.426 at α = 0.05) in white males (Voors, 1969). A sustained increase in the amount of lithium in the human diet can result in its accumulation in the body where it could potentially have undesired effects. Lithium easily enters human cells but finds it more difficult to leave (Dehpour *et al.,* 1995; Schou, 1958). Schou, (1958) reported on the distribution of lithium in mammalian bodies (Schou, 1958). Physiological symptoms in humans due to a lithium deficient diet have not been observed.

Evidence linking low lithium levels with behavioural abnormalities has been shown. In 1990 a study carried out in Texas, USA over 10 years found lower rates of suicide, homicide, and rape in areas with relatively higher concentrations of lithium in the public drinking water (0.07 – 0.160 mg/l) (Blüml *et al.,* 2013). Their work suggested that lithium has moderating effects on suicidal and violent criminal behaviours at levels that may be encountered in municipal water supplies (Schrauzer and Shrestha 1990). It has been suggested that putting minuscule amounts of lithium into public drinking water supplies would have a beneficial effect on the general population by improving the mood of people and lowering suicide rates. In a Japanese study, the lithium levels in the drinking water of eighteen municipalities in Oita prefecture were measured and used to investigate if there were any associations between suicide rates and lithium levels. It was found that suicide rates were significantly and negatively associated with lithium concentrations (Ohgami *et al.,* 2009). A study which involved > 6000 drinking water samples taken across ninety-nine Austrian, districts, was carried out to evaluate any correlation between local lithium concentrations and suicide mortality rates. The study showed that there was strong evidence that Austrian regions with higher lithium drinking water levels were associated with lower suicide mortality rates (Kapusta *et al.,* 2011). A similar study was carried out in the east of England, the study found that the lithium drinking water concentration in forty-seven subdivisions of the east of England was significantly and negatively associated with suicide rates (Kabacs, 2011). Another observational study in Japan involving eighteen neighbouring Japanese municipalities with a total of 1,206,174

individuals, suggested that naturally occurring lithium in drinking water increased human lifespan (Zarse *et al.,* 2011). In the Aomori prefecture of Japan which has the highest suicide mortality rates in Japan, findings from a similar study indicated that the natural concentrations of lithium in drinking water reduce the risk of suicide among females (Sugawara *et al.,* 2013). The Ministry of Health, Labour and Welfare who are the authority in charge of water supply for domestic use in Japan has recommended that lithium could be added to the drinking water at a level of 2 mg a day per adult to promote mental health and lower suicide rates (Wright, 2012).

These studies provide strong evidence that regions with high concentrations of lithium in the drinking water are associated with lower suicide mortality rates. In some of these studies confounding variables to do with physiological and economic factors were not taken into account, so it is difficult to say the results are conclusive (Schrauzer and Shrestha 2010). Several authors suggest that these associations do not establish a causal relationship, their argument generally being that the parameters measured are too variable and subject to many other societal issues. Despite this, there are numerous studies which suggest that lithium in the drinking water can modulate behaviour. (König *et al.,* 2017; Ishii *et al.,* 2015; Lewitzka *et al.,* 2015; Pompili *et al.,* 2015; Giotakos *et al.,* 2013; Helbich *et al.,* 2012; Schrauzer and Shrestha 2010; Desai *et al.,* 2009; Terao *et al.,* 2009; Schrauzer, 2002; Dawson *et al.,* 1972; Pokorny; *et al.,* 1972; Dawson *et al.,* 1970).

1.4.6. Lithium in Warfare

Both stable isotopes of lithium ^{6}Li and ^{7}Li are used in the production of nuclear weapons. The first man-made nuclear fusion reaction using ^{7}Li was achieved by Mark Oliphant in 1932 (Holden 2018). On July 16th, 1945 in the Jornada del Muerto desert of New Mexico, the USA carried out their first successful nuclear weapon test (The Trinity test) (Parekh *et al*., 2006). Only a matter of weeks later on August 6th and 9th the USA dropped nuclear weapons on the Japanese cities of Hiroshima and Nagasaki effectively ending the Second World War in the Pacific. In January 1946 the United Nations called for the elimination of nuclear weapons. However, in August 1949 the United Soviet Socialist Republic (USSR) test fired its first nuclear weapon, a major contributing factor to the already ongoing Cold War between the two world superpowers, the USA and the USSR. The demand for lithium increased significantly during the Cold War along with the proliferation of thousands of nuclear fusion weapons. Lithium produces net energy through nuclear fusion. ^{6}Li acts as a neutron absorber and ^{7}Li is used as an enriched lithium fluoride coolant in the nuclear power industry. Both isotopes, when exposed to a

stream of neutrons in an exothermic (^{6}Li) and endothermic (^{7}Li) reaction, produce the radioactive hydrogen isotope tritium, an important component in nuclear weapons. In the 1950s the USA military required vast amounts of lithium as lithium hydroxide from which they harvested ^{6}Li to produce staged thermonuclear weapons (Saeidnia and Abdollahi 2013). Tritium is also important for the future production of thermonuclear fusion reactors, a technology which has the potential to cleanly meet the future energy needs of the world (Kunasz, 2006; Vine, 1976). The estimated future requirement of lithium to meet the demand of a mass production of thermonuclear fusion reactors is 200 to 1000 t / 1 GW electric power (Vikström *et al.,* 2013).

Lithium hydride was used to store hydrogen for warships in World War Two and as a means of rapidly producing hydrogen to inflate lifting balloons, emergency signalling, and barrage balloons used as a means of protection from enemy plane attacks (Kunasz, 2006; Vine, 1976). Lithium hydride and lithium aluminium hydride are used as a high energy additive to liquid and solid rocket fuel propellants (Saeidnia and Abdollahi 2013). The propellants Li, F_2 and H_2 together produced the highest specific impulse ever test-fired in a rocket engine (5,320 m/s) (Gordon and Huff 1951). Sulphur hexafluoride reacted with metallic lithium is also used as a propellant fuel in military applications. The advent of rocketry also necessitated the need for high-temperature resistant materials. The properties of lithium make it an ideal candidate to produce these materials like the composite ceramic (Pyroceram®) which expands very little and resists cracking at high temperatures and is used as a heat shield in rocketry (Kunasz, 2006). Pyroceram® is manufactured by Corning incorporated, New York, USA. Lithium ion batteries (LIBs) are used extensively by military around the world, favoured because of their lightweight, efficiency and ability to conform to almost any required shape.

1.4.7. Metallurgy

Similar to the glass and ceramics industries, lithium is primarily used in metallurgy as a flux to reduce energy costs. It promotes the fusing of metals when soldering or welding. In continuous steel casting, it reduces the melt viscosity, improving flow rates and assisting in thermal insulation. It has a lubricating effect on the surface of the steel making the continuous casting process more efficient by reducing friction. In the production of high conductivity copper and the copper-tin alloy bronze, lithium is used as a degasifier; in very low amounts lithium metal scavenges available oxygen and other gases from molten metals. When casting iron, lithium reduces defects in the process by reducing the incidence of veining (a sheet-like casting defect). Lithium fluoride is used to adjust the

melting points during the smelting and refining of aluminium in the Hall–Héroult process. Lithium is used in the electrolysis of aluminium oxide to lower the temperature of the reaction, increases electrical conductivity, decrease viscosity, and reduce the amount of the mineral cryolite (Na_3AlF_6) used. Cryolite is also used as a flux to reduce reaction temperatures and dissolve oxide minerals from ores allowing the easy extraction of the aluminium by electrolysis. Lithium is the lightest of the all the solid elements, because of this property it is ideal for making high strength to weight ratio alloys, and several of its alloys are produced on an industrial scale. Lithium alloys of Al, Cd, Cu and Mn are used in the aeronautical industry to make lightweight parts. Other lithium alloys are common and include alloys with metals such as Ag, Au, Mg, and Pb. Mg/Li alloys have a low density which makes them an attractive material for several industries including engineering and armour-plating (Chakravorty, 1994). Cu/Li alloys are used in the copper casting industry. Lithium is used in the degasification of copper castings because of its affinity for oxygen, it is added prior to pouring as a means of creating denser casting free of pinhole porosity, which is a common problem (Fenton *et al.,* 1957). Al/Li alloys are used in the aerospace and aeronautics industries, where their strength and weight reduction properties allow better fuel consumption. Lightweight lithium alloys used in the manufacture of aircraft have the potential to reduce weight by as much as 10%. Li/Al alloys contain up to 7.5% lithium and Li/Mg alloys can contain up to 13% lithium, most other lithium alloys contain 2 to 3% lithium (Garrett, 2004). These alloys are quite expensive, consequently plastics are often used in their place. In 1918, Germany, an Al, Zn, Cu, Mn, and Li alloy containing 0.1% lithium called Scleron was manufactured as one of the first commercial lithium alloys (Prasad *et al.,* 2013). Another such alloy created in Frankfurt am Main, Germany during World War One was Bahnmetall (bearing metal) an alloy of Li, Ca, Na, and Pb. Bahnmetall is still used today in the manufacturing of specialised (anti-friction) railroad car bearings (Emsley, 2011).

1.4.8. Lithium Batteries

In 1912, Gilbert Newton Lewis investigated the electrochemical properties of the lightest and one of the most electropositive stable elements lithium (Raghavan, 2013). Early lithium batteries used lithium metal as the cathode and could not be recharged. A common problem with these batteries was the build-up of dendrites (microscopic fibres of lithium) on the lithium electrodes, caused by the repeated removal and addition of lithium ions. If the dendrites bridged the gap between the two electrodes the battery would short circuit often resulting in a fire. In 1972 while working for the company Exxon, Michael Stanley

Whittingham developed the first rechargeable lithium battery. This advance in battery technology was based on a lithium disulphide cathode and a lithium metal anode with lithium perchlorate in dioxolane as the electrolyte. The technology was still susceptible to dendrite formation often resulting in thermal runaway. Credit for developing the modern LIB goes to John Bannister Goodenough. The presence of lithium in its ionic rather than metallic form in the Goodenough design effectively solved the dendrite problem (Tarascon and Armand 2011). According to Goodenough (2018), Professor Akira Yoshino, a fellow at the Asahi Kasei Corporation, Japan manufactured the first commercial LIB by combining a lithium cobalt oxide cathode with a graphitic-carbon anode (Goodenough, 2018). Sony and Asahi Kasei commercialised the technology in 1991. The battery was used by the Sony Corporation to power the very first portable phone, and since then the demand for LIBs has consistently grown (Goodenough, 2018). Tarascon and Armand (2011) provide a detailed account of the development of the modern LIB. Today LIBs are used in most of our everyday portable electronic devices from pacemakers to smartphones. In recent years the consumer electronics and energy storage industries have driven the demand for LIBs.

Primary lithium batteries use metallic lithium with compounds like manganese dioxide and sulphur dioxide as the cathode (Peiró *et al.,* 2013). Primary batteries are not rechargeable. Secondary batteries are rechargeable (LIBs) and use a lithium metal oxide as the cathode and often lithium-based compounds such as lithium perchlorate as an electrolyte (Peiró *et al.,* 2013). A modern LIB contains a graphite anode, a lithium metal oxide cathode and the electrolyte solution doped with a lithium solution such as lithium hexafluorophosphate in a mixed organic solvent (often ethylene carbonate or dimethyl carbonate. (Scrosati and Garche 2010). The design of electric vehicle (EV) LIBs consists of a number of battery cells arranged in sequence in a module, a group of modules becomes a battery pack and a group of packs is referred to as the battery system (Väyrynen and Salminen 2012). The terms battery and battery cell are often used interchangeably in the literature, a battery is made from a number of cells (e.g. a 12 V lead-acid battery contains 6 cells) (Väyrynen and Salminen 2012). According to Tahil (2007), a 30 kWh LIB system for an EV cost €7,500 in 2007. The price of Li/kWh has steadily decreased since then, from €800/kWh in 2010 to just over €200/kWh in 2018 and is expected to fall to €100/kWh by 2025 (Inside EVs 2018; Clean technical 2018).

LIB advantages include high energy density, low self-discharge rate, long life cycle (1000 cycles), no memory effect, low maintenance, fast charging, and low weight (40 to 60% less than lead-acid batteries). Some of the disadvantages of LIBs include the need for a

protection circuit and travel restrictions (e.g. air travel) in order to prevent thermal runaway. Current LIBs, operate best at a temperature between 20°C to 60°C (Väyrynen and Salminen 2012). Nickel metal hydride batteries are still used in some HEVs (hybrid Electric Vehicle) and nickel-cadmium based batteries are also used in some EVs. These batteries, despite not being as powerful as LIBs, are still vying for a share of the EV market. However, any future technology using these metals is not expected to impact significantly on lithium's dominance of the market. LIB production is the largest consumer of lithium resources today. LIBs are replacing known nickel metal hydride and nickel-cadmium batteries as the battery of choice for new EVs (Tarascon and Armand 2011). LIB batteries provide more voltage than previous battery technologies (Table 1.12). The amount of electrical energy in a battery is best given by the specific energy (Wh/kg), the nominal battery energy per unit mass.

Table 1.12. Comparison between current LIB technologies and previous battery technology. (Tahil 2007; Wright 2010; Väyrynen and Salminen 2012).

Lithium ion Technology	Voltage	Specific Energy
Lithium Cobalt Oxide ($LiCoO_2$)	3.65 V	150–200 Wh/kg
Lithium Manganese Oxide ($LiMn_2O_4$)	3.8 V	100–150 Wh/kg
Lithium Nickel Manganese Cobalt Oxide	3.7 V	150–220 Wh/kg.
Lithium Iron Phosphate ($LiFePO_4$)	3.2 V	90–120 Wh/kg
Lithium Nickel Cobalt Aluminium Oxide	3.67 V	200-260 Wh/kg
Lithium Titanate ($Li_4Ti_5O_{12}$)	2.4 V	50–80 Wh/kg
Other Battery Technology	**Voltage**	**Specific Energy**
Nickel Metal Hydride Battery	1.2 V	60–120 Wh/kg
Sodium Nickel Chloride Battery	2.58 V	100–120 Wh/kg
Zinc – Air Battery	1.35 – 1.4 V	430 Wh/kg
Lead Acid Battery	2.1 V	33–42 Wh/kg
Nickel Cadmium	1.2 V	40–60 Wh/kg
Nickel-zinc battery	1.65 V	100 Wh/kg
Nickel-iron battery	1.2 V	19–25 Wh/kg

In 2007 to manufacture a 5 kWh LIB for each of the estimated 1 billion cars in the world today, would require 20% of current lithium reserves (Tahil, 2007). However, a 5-kWh battery is a conservative estimate for the size of a standard EV battery, the capacity of EV LIBs will undoubtedly increase as technology advances (Tahil, 2007). According to Tahil (2007), 60 kWh LIB in every car would use up 50% of world lithium reserves (Tahil,

2007). These figures do not take into account heavy and light goods vehicles which would require a battery at least 10 times larger than a generic EV LIB (Tahil, 2007). According to Speirs *et al.,* (2014) usually an EV battery requires 0.165kg of lithium carbonate for each kW/h, a PHEV (Plug-in Hybrid Electric Vehicle) battery requires 0.176 kg/kWh and a HEV requires 0.375 kg/kW/h (Speirs *et al.,* 2014). A lithium carbonate-based LIB requires 0.18 kg of lithium carbonate per kW/h (Speirs *et al.,* 2014). The Tesla Model S Performance EV contains an 85 kWh LIB pack with approximately 50.8kg of lithium carbonate. The Tesla Model S, LIB can fully recharge in 20 to 40 minutes and has an electric range of 539 km, higher than any other EV (Patry *et al.,* 2015). A battery of 8 kWh capacity would give 50 km range (Tahil, 2007). Lithium carbonate is one of the lowest-cost components in a LIB (Linnen *et al.,* 2012). Different LIBs require different amounts of lithium carbonate depending on their application. A smartphone requires at least 3g, a laptop computer 10 to 30g and a power tool 40 to 60g (Vikström *et al.,* 2013). EV batteries depending on their capacity may require anything from 8 to 100kg of lithium carbonate.

There is a race to develop the next big thing in battery technology. LIBs may not continue to dominate the EV battery market, other battery technologies currently at the research stage like metal-air, bio-electric, foam, graphene, and gold nanowire batteries may be more efficient that LIBs. Solid state lithium batteries are making a comeback as well. The development of solid electrolytes which allow the passage of ions and prevent the formation of dendrites are currently being developed. These solid electrolytes can be made from plastic or even glass, the batteries also have the advantage of being able to work at low temperatures (-20°C). Goodenough (2018) describes a dielectric amorphous-oxide solid electrolyte (developed by Maria Helena Braga of the University of Porto, Portugal). The battery is comparable to modern-day LIBs. Goodenough (2018) has used this electrolyte material to develop all-solid-state rechargeable batteries that are dendrite free, have a long-life cycle and has acceptable charge and discharge rates. Figure 1.1 shows the increasing use and production of lithium from 2003 to 2020. Figure 1.2 (A-D) shows the percentage of lithium use in each main industry since 2005.

Figure 1.1. Annual use of lithium in tonnes in each of the primary lithium usage industries from 2002 to 2020. Sources, (Metalary, 2018; Ober, 2018; Martin, 2017; Swain, 2017; Sverdrup, 2016; Barbosa *et al.,* 2014; Meshram *et al.,* 2014; Vu *et al.,* 2013; Goonan, 2012; Yaksic and Tilton 2009; Tahil, 2007; Kunasz, 2006 Ebensperger *et al.,* 2005).
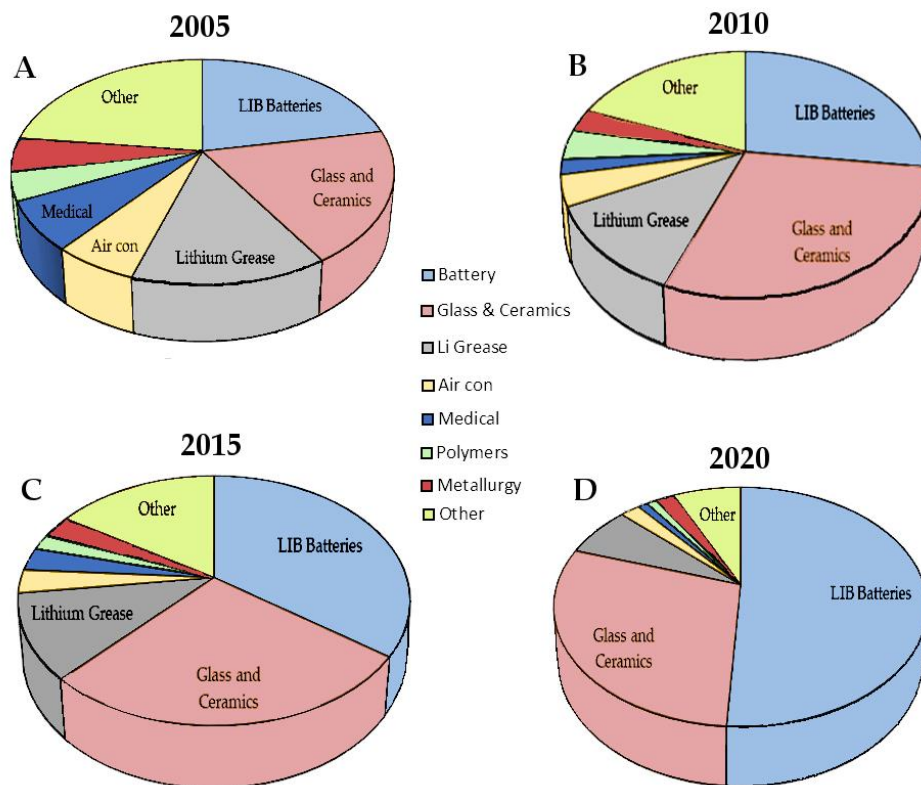
Figure 1.2. **(A)** Percentage lithium use in each of the main lithium using industries in 2005. **(B)** Lithium use in 2010, **(C)** lithium use in 2015, and **(D)** lithium projected use in 2020. Sources, (Ober, 2018; Swain, 2017; Sverdrup, 2016; Meshram *et al.,* 2014; Goonan, 2012; Tahil, 2007; Ebensperger *et al.,* 2005).

1.4.9. Lithium Recycling

Less than 1% of lithium is currently recycled. There is currently no great incentive to recover lithium from waste streams because of its relative abundance. The majority of mined lithium is still in use in our society, for example as LIBs. There is not a large enough lithium waste stream yet to justify the development of a lithium recycling industry. If demand increases for lithium resources, there will be a future imperative to recapture lithium before it is lost in waste streams. One such waste stream is old mobile phones. Over a billion mobile phones are produced globally every year. These phones contain approximately 30 to 40 g of lithium. These phones also contain on average metals like gold at approximately 9 mg, palladium at 24 mg and silver at 250 mg (Graedel *et al*., 2015). The amount of metal present is largely dependent on the model of phone. Gold, palladium, and silver are currently recycled from old mobile phones. In the future it should make economic sense to also recover lithium from old mobile phones and other waste streams. Unlike oil, lithium is easily recyclable, its low melting point (180 °C) and the low solubility of its fluoride, carbonate and phosphate salts make its recovery quite easy (Tarascon, 2010). The recovery of valuable metals from spent batteries is a common procedure which can be easily applied to LIBs. LIBs usually contain aluminium, copper, and cobalt which are often recovered during recycling (Nan *et al.,* 2005). Lithium recycling has not yet taken off as an industry (Martin, 2017). The recycling of LIBs will require an already well-established EV market functioning for several years. Any large-scale recycling of lithium will come online in a few years, the demand for lithium should fuel strong investment in its recycling in the future.

Lithium can be recycled from LIBs using the following methods, leaching, precipitation, ion exchange or solvent extraction (Meshram *et al.,* 2014). Meshram *et al.,* (2014) estimate that 250 t of ore or 750 t of brine or 28 t of LIBs are needed to produce 1 t of metallic lithium. Large EV LIBs will be easier to recycle than smaller batteries (Vikström *et al.,* 2013) also the economies of scale for the LIB recycling industry should emerge when the use for LIBs in EVs increases (Vikström *et al.,* 2013). Swain (2017) describes 3 methods by which lithium is recovered from batteries, (1) Hydrometallurgy (dissolution, leaching, solvent extraction, precipitation and electrochemical methods), (2) Pyro-metallurgy (mechanical shredding, thermal, calcination, roasting, reduction and chlorine metallurgy); and (3) Biological processes (Bio-leaching and phytomining). Peiró *et al.,* (2013) describe a cryogenization process (freezing, shredding, leaching, and precipitation). According to Swain (2017) as of 2017, only 3% of LIBs were recycled and < 1% of lithium globally was recovered. The recycling of LIBs in the EU is regulated

under the Waste Electrical and Electronic Equipment Directive (Directive 2012/19/EU) (collection, recycling and recovery) WEEE Directive, and the RoHS Directive, which sets restrictions on European manufacturers as to the material content of new electronic equipment placed on the market (Directive 2012/18/EU). The recycling of LIBs is an important factor and should facilitate any future shortfalls in lithium resources (Wanger, 2011). Environmental pollution from battery materials is a concern for the future (Saeidnia and Abdollahi 2013). Lithium's newfound popularity means that it is now considered to be an emerging environmental contaminant. Improper LIB disposal is one way in which lithium can infiltrate the environment, where it can be absorbed by plants, enter the food chain and potentially accumulate in humans.

1.5. Discussion

Demand for lithium today is largely driven by the applications of LIBs in EVs. It has been predicted that there will be between 3.8 and 4.5 million EVs in use by 2020, (Peiró *et al.,* 2013). Lithium demand is expected to increase by 8 to 11% every year from 2017 (Martin, 2017; Yalamanchali, 2012). LIB production in the USA nearly doubled between 2005 and 2010 (Vikström *et al.,* 2013). Currently, 35% – 39% of global lithium production is used for LIBs (Swain, 2017). The LIB market is estimated to grow to €180 billion by 2024 and require at least 66% of all lithium produced (Swain, 2017). The European Union (EU) has put in place directives to encourage the spread of EVs. These include the Clean Vehicle Directive (CVD1) and the Energy Efficiency Directive (EED) (Directive 2006/32/EC; Directive 2009/33/EC; Peiró *et al.,* 2013). Also, individual countries offer incentives like free road tax and free charging points to encourage people to buy EVs (Peiró *et al.,* 2013). Most major vehicle companies are actively pursuing the development and production of EVs using LIBs (Richa *et al.,* 2017). EV companies include Nissan, Tesla, General Motors, Ford, and Toyota. Fossil fuels currently account for 95% of the total energy used for global transport (Vikström *et al., 2013)*. Predicting the future demand for lithium resources is a complicated issue which requires predicting the future growth of the various industries that use lithium rather than just the LIB industry (Vine, 1976). Most of the data regarding the price and demand of lithium are found in commercial reports rather than in scientific journals, (Martin, 2017). Gruber *et al.,* (2011) report on global lithium resources and demand in 2011 and list 103 lithium-containing sites. Drivers for the lithium market include targets for carbon dioxide emissions, lowering LIB costs, and extended EV ranges (Tarascon, 2010). Some predict that there will be a shortfall in the amount of lithium produced in the future (Speirs *et al.,* 2014; Wanger, 2011), but this argument has been going on since the 1970s (Vine, 1976).

Sverdrup (2016) believes that there will be enough lithium to meet demand until 2050, after which the price of lithium will rise although lithium recycling by then should help offset some of the cost. Financial market analysts at the Macquarie Group noted that lithium prices have increased 50% since the start of 2015 and are continuing to increase rapidly (Macquarie, 2016).

The EV market is on the verge of large-scale commercialisation and implementation. However, there are some doubts as to whether or not infrastructure like charging points will be in place to ensure a seamless transition from fossil fuel to electric power. The perceived limited range of EVs also creates uncertainties among customers: Sverdrup (2016) points out that for an EV to be comparable to the performance of a fossil-fuelled car it should have a range of at least 300 km, this corresponds to a battery pack that would contain approximately 10kg of lithium. LIBs are still very expensive which could explain the persistence of nickel metal hydride battery technology in PHEVs. The obvious incentive for consumers to buy an EV is that they are cheaper to run than fossil fuel vehicles. Wright (2010) worked out that the cost of running an EV is €0.012/km while fossil fuel vehicles cost €0.155/km to run. The EV global market is experiencing a rapid market evolution. In 2016 the number of EVs worldwide was greater than 2 million. New registrations of EVs hit a new record in 2016, with over 750 thousand sales worldwide. Tens of thousands of EVs are already on our roads in countries like Norway where they have a market share of 29% and the Netherlands with a 6.4% EV market share (IEH, 2016). Tesla Incorporated's, new Giga-factory in Nevada, USA, is projected to supply > 30% of the world's LIBs by 2020 and have an annual output of the production of 500,000 EVs (Zubi *et al.,* 2018). Tesla's energy storage home Powerwall battery pack has also received $800 million worth of presale orders. The UK and France have stated that there will be a ban on the sales of all of petrol and diesel cars by 2040. China represents one of the largest and fastest growing markets in the world, the Chinese government is working on a timetable to end the production and sales of traditional energy vehicles and are developing several new EV models for production. In 2016, China was by far the largest electric car market, accounting for more than 40% of the electric cars sold in the world and more than double the amount sold in the USA (IEH, 2017). Several major car manufacturers including Volvo, Toyota, and Volkswagen have set dates by which they plan to phase out vehicles powered solely by the internal combustion engine.

1.6. Conclusion

Film directors Andreas Pichler (Italian) and Julio Weiss (Bolivian) first coined the term "The Lithium Revolution" in their documentary of the same name (The Lithium Revolution 2012). That title effectively paints an optimistic vision for the future of lithium. Their documentary illustrates our unsustainable dependence on oil and the search for an alternative energy source. If the alternative energy source is renewable green energy produced from technologies like solar and wind, then storing that energy in LIBs is an important element in the equation. The propagation of EVs globally and a reduction in the number of fossil fuel burning vehicles would effectively reduce greenhouse gasses and perpetuate the green energy economy. The responsible mining of lithium resources could very well be the key that sets us on a path toward a low carbon energy future. The EU needs lithium in order to meet its commitments to the green economy.

Lithium demand is growing along with the lithium revolution. The distribution of lithium deposits both brine and mineral around the world should be sufficient to meet future demand and to ensure a security of supply for the EU (Mohr *et al.,* 2012; Gruber *et al.,* 2011). Resource estimates should increase as new deposits are discovered and mining and recycling technology advances. This also means that previously uneconomical to mine sites, such as that in Ireland, are perhaps becoming commercially valuable (Kavanagh *et al.,* 2017). Some authors predict that there will not be enough lithium to meet future demands and that we are just switching one diminishing resource, oil, for another, lithium (Swain, 2017; Vikström *et al.,* 2013; Wanger, 2011). According to some the demand for lithium may also overtake production in the future unless at least 90% of lithium is recovered by recycling (Swain 2017). Some of the largest deposits of lithium exist in countries that lack the infrastructure to mine it, thus the supply of cheap lithium in the future is not guaranteed. An enormous resource of lithium exists unmined in Bolivia. The Bolivians are understandably reluctant to allow their valuable resource to be taken from them having experienced the "resource curse" first hand in their past (Bebbington, 2015). Afghanistan also contains a massive lithium resource. Countries like Bolivia and Afghanistan have the potential to become as many authors have suggested: "The New Saudi Arabia of Lithium" (Risen, 2010; Wright, 2010).

It is likely that demand for future lithium resources will be dominated by the battery industry, especially in the EV market. Other applications of lithium-based battery technology that should come online in the coming years including grid electrical storage,

as well as applications in the nuclear power industry, will undoubtedly increase demand on lithium resources. With the vast resource of lithium in the world, albeit in as many different locations as deposits, there still should be enough to meet demand. If the industry passes a certain threshold then it will likely boom like the smartphone market at the start of the century. Our fossil fuel resources are depleting and becoming more difficult to extract. On top of that, there is constant and growing concern over the security of future oil supplies. There is an urgent need to find new sources of energy and industrialised nations are looking towards lithium. As more nations develop and their people need transport, lithium technology can ensure that this need for transport will not come at the cost of our environment. Because of the efficiency and environmental cleanliness of lithium technology, worldwide financial and political support for its development is increasing. It is in our interest to advance the production of EVs. The world lithium market is rapidly growing, although it is essentially still in its infancy prior to the mass production of EVs. The EU should have enough lithium deposits to ensure a future security of supply.

Chapter 2

Lithium in the Natural Waters of the

South East of Ireland.

An Investigation into the Concentration of Lithium in the Surface and Groundwater of
the South East of Ireland.

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2.1. Abstract

The South East of Ireland (County Carlow) contains a mineralisation of the valuable lithium-bearing mineral spodumene ($LiAl(SiO_3)_2$). This resource has recently attracted interest and abstractive mining in the area is a possibility for the future. The open cast mining of this resource could represent a potential hazard in the form of metalliferous pollution to local water. The population of County Carlow is just under 60,000. The local authority reports that approximately 75.7% of the population is supplied public drinking water (which is abstracted from surface water) and 11.6% from groundwater. In total, 12.7% of the population abstract their water from private groundwater wells. Any potential entry of extraneous metals into the area's natural waters will have implications for people in County Carlow. It is the goal of this paper to establish background concentrations of lithium and other metals in the natural waters prior to any mining activity. Our sampling protocol totalled 115 sites along five sampling transects, sampled through 2015. From this dataset, we report a background concentration of dissolved lithium in the natural waters of County Carlow, surface water at $\bar{x}$ = 0.02, Standard deviation = 0.02 ranging from 0 to 0.091 mg/l and groundwater at $\bar{x}$ = 0.023, Standard deviation = 0.02 mg/l ranging from 0 to 0.097 mg/l.

Keywords: *lithium; groundwater; surface water; mining.*

2.2. Introduction

Lithium is an uncommon parameter in routine drinking water analysis. Its spatial and temporal distributions are not commonly studied and are often overlooked because it appears at very low concentrations. Its concentration in natural waters varies depending on geology, topography, hydrogeology and other variables. Despite this, there are some generally referred to ranges of lithium concentrations in waters. In seawater, where it is the fourteenth most abundant element, it occurs at 0.14 to 0.20 mg/l (Angino *et al.,* 1966; Lenntech, 2017; Riley *et al.,* 1965) and in fresh waters it occurs at 0.001 to 0.020 mg/l (Ayotte *et al*., 2011; Bingham *et al*., 1964; Emery *et al*., 1981; Hawrylak *et al*., 2012; Hue *et al*., 1998; Kilmas and Malisauskas, 2008; Kszos *et al*., 2003; Lenntech, 2017; Salminen, 2017). Shand *et al*., (2007) report medium levels of lithium in groundwater, associated with different bedrock geologies in England: Chalk at 0.0008 mg/l and Permian-Triassic Sandstone at 0.001 mg/l (Shand *et al*., 2007). There is no legislative requirement for lithium to be monitored in Irish drinking water, therefore it has no safety standard. This does not mean that concentrations cannot reach dangerous levels. The high altitude continental brine aquifers of Argentina, Chile and Bolivia contain most of the world's accessible lithium; Bolivia alone is said to have jurisdiction over approximately one-third of the world's recoverable lithium (Gonzales *et al*., 2013). The lithium levels in the natural waters in these areas are very high: ≥5 mg/l. Northern Chile has recorded the highest concentrations of lithium in surface waters in the world, at concentrations between 2 and 20 mg/l, 2–3 orders of magnitude higher than most rivers. Because of this, there has been some work in the area concerning the high exposure of lithium in these populations (Bingham *et al*., 1964; Cannon *et al*., 1975; Evans, 1978).

Lithium has recently come into public awareness because of its use in lithium-ion batteries (LIBs). LIBs are already powering most of the electronic devices we use every day, such as our phones and laptops, a market that did not exist 20 years ago. The fact that lithium is set to power the electric vehicles (EV) of the future makes it a key resource for both the industrialized world and emerging economies. Other uses of lithium include as lithium carbonate, a medication to treat mental disorders; as lithium stearate an all-purpose high-temperature lubricant; as a fluxing agent in the ceramics industry; as a light-weight alloy; and as lithium chloride a hygroscopic agent in air conditioning systems. The emerging EV market is pushing this ordinary alkali metal to become the new "white petroleum" of the 21st century. It is the objective of this work to establish a background

level of lithium in the waters of County (Co) Carlow, prior to any future commercial abstraction.

Lithium has been used as a mood-stabilizing drug in people with mood disorders such as bipolar and major depression for over 150 years. It has also been used successfully to treat people with suicidal tendencies. There are several studies which suggest a negative association between lithium levels in drinking water and suicide rates in populations (Figueroa et al., 2013; Schrauzer and de Vroey 1994). Large doses of lithium (10 mg/l in serum) are used in patients to treat these disorders. Lithium has a narrow therapeutic index: at 10 mg/l of blood, a person is considered mildly lithium poisoned; at 15 mg/l, they experience confusion and speech impairment; at 20 mg/l, there is a risk of death (Bingham et al., 1964). The lithium ion displays chronic toxicity on the human central nervous system (Bingham et al., 1964; Kabacs, 2011; Ohgami, 2009). A lethal dose of lithium chloride in rats has been measured at 526–840 mg/kg body weight. The amount of lithium in the human body is about 7 mg; a dose of approximately 5 g of lithium chloride can result in fatal poisoning (Bingham et al., 1964). On the other hand, lithium from drinking water has a very low environmental toxicity. The lithium requirement in humans is low; available experimental evidence appears to suggest that a provisional recommended daily allowance for a 70 kg adult is 1 mg/day. This same evidence also states that the average daily intake of lithium of a 70 kg adult is around 0.65 to 3.1 mg/day from foods such as grains and vegetables (Dolara, 2014; Neves et al., 2014).

Geochemically, lithium is a rare metal with average crustal abundances rarely exceeding 10–20 mg/kg. Lithium levels in granite (which makes up about two-thirds of Carlow's bedrock geology) are higher at around 22 to 65 mg/kg. Lithium tends to be tightly bound in the crystal structure of the rock, therefore it alone does not pose an ecological problem (Bingham et al., 1964; ICPS, 2017; Mason and Moore 1982; Neves et al., 2014; Schrauzer, 2002; Timmer and Sands 1999). Lithium does not appear in its pure form in nature due to its highly reactive properties. The metal occurs predominantly in the silicate matrices of pegmatites; some clay minerals such as hectorite $Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$ (Taylor, 1964), geothermal brines; oilfield brines; and in solution in naturally occurring continental alkaline brine aquifers. The two major exploitable sources are pegmatite minerals such as spodumene and continental brine deposits. Brine deposits are easy to explore, fast to put into production and require less initial capital. Although lithium is easily extracted from brine sources, mineral deposits can contain much greater amounts of lithium. Lithium concentrations in subsurface brine range from 20 to 1500 mg/l

(Bingham *et al*., 1964; Teng *et al*., 2004) while mineral deposits may contain 530 to 55,100 mg/kg (Taehoon *et al*., 2011). Hard rock mineral mining is a more involved process and usually takes the form of open pit mining depending on the depth at which the pegmatites occur. The processing of lithium-containing minerals involves crushing, wet grinding in a ball mill, sizing, gravity concentration followed by flotation using a fatty acid as a collector (Bingham *et al*., 1964).

The geology of the South East of Ireland is dominated by the Caledonian Leinster Batholith: a massive felsic intrusion of granite which occurred during the Caledonian orogeny about 419.2 ± 3.2 Mya. It is within this batholith that the lithium-rich pegmatites are found. First discovered in the late 1970s, the lithium mineralisation at that time was deemed to be of low economic value. Today, however, the growth of the LIB market means that mining this once marginal occurrence of lithium is a distinct possibility. These spodumene-bearing pegmatites represent one of the largest potential resources of lithium in Western Europe (Taehoon *et al*., 2011). There are six known sites along the batholith associated with lithium bearing pegmatites: Aclare, Snowy Vale, Seskinnamadra, Stranakelly, Monaughrim and Moylisha. The largest discovered pegmatite occurrence is at Aclare House, Myshall, Co. Carlow. There are no natural outcrops of the pegmatite occurrence at Aclare; its presence was confirmed by drilling and the existence of pegmatite boulders in the area. Pegmatite deposits are extracted in one of two ways: either by open pit mining or underground mining. Both of these methods produce mine tailings, the disposal and treatment of which is an important environmental issue for most mining projects. These tailings contain elements and compounds which are not naturally exposed to the ecological system and therefore have the potential to adversely affect the surrounding environment. The levels of lithium found in the waters of such tailings ponds have been measured at levels approaching 13 mg/l (Bingham *et al*., 1964). The post-disturbance pathway that these exposed metals take is likely to involve the natural waters of the locality. As well as being found in natural waters, metals and metalloids released during mining activities have been found in soil and plants. Farming is the dominant land use and industry in the study area (Figure 2.1). Carlow's economy relies heavily on its agronomic sector, so any potential intrusion of lithium to the land is an important issue for the population. Lithium is readily absorbed by plants, and high levels of lithium have been shown to have harmful effects on plants. In some plants, lithium has been shown to stimulate growth. It has also been shown to cause growth depression in some citrus plants, causing drastic reductions in crop yields. Bradford (1963) described toxic symptoms in citrus plants when irrigated with water containing lithium concentrations of 0.05 mg/l

lithium. Information on lithium hazard to other economic plants is limited (Gonzales *et al*., 2013; Figueroa *et al*., 2013; Schrauzer and de Vroey 1994; Mason and Moore 1982).
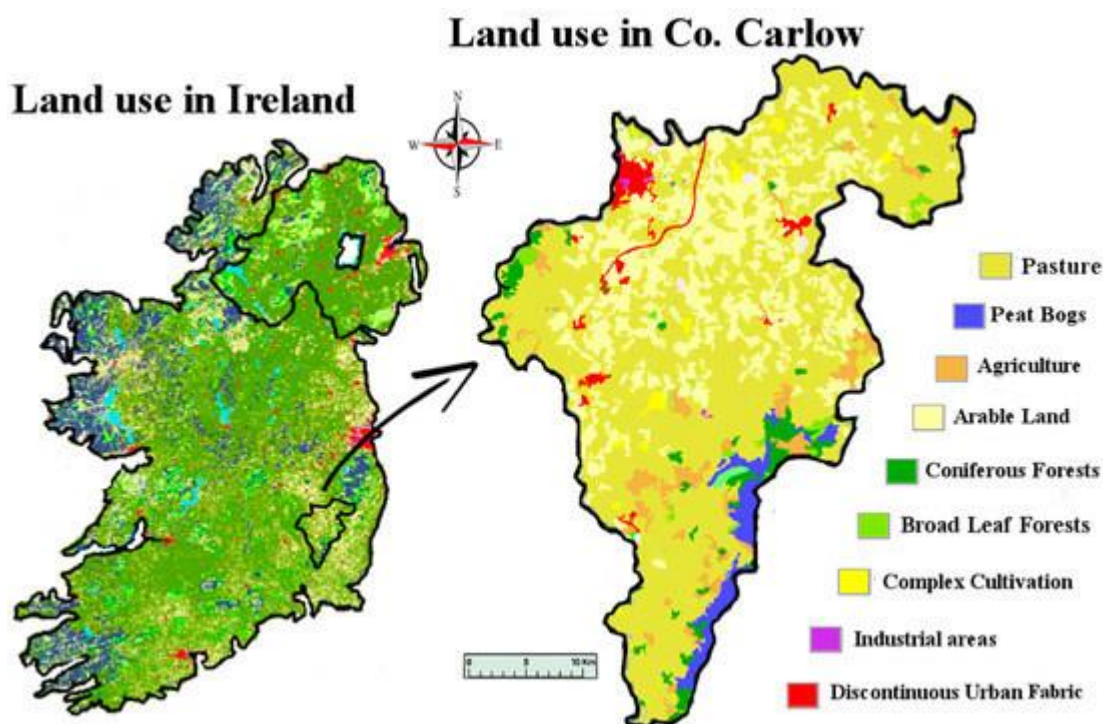
Figure 2.1. Map of Co. Carlow, showing land use. Image modified from (IRL EPA, 2017; GSI, 2016).

It is important to understand the possible environmental impacts of extracting lithium in Ireland. The pegmatite in the south-east of Ireland exists as elongated tabular dykes and sheets. Mining of these pegmatites will probably take the form of open pit mining one of the most common forms of strategic mineral mining. A good example of hard rock open pit pegmatite mining is the Talison Greenbushes and Wodgina mines in Western Australia which are the world's leading producer of lithium from hard rock deposits. A good example of an underground pegmatite mine is the Tanco mine at Bernic Lake Manitoba, Canada, where the lithium exists as several minerals in LCT (lithium, caesium, and tantalum) pegmatite. Lithium mining requires that pegmatite ores which have lain unexposed since deposition are brought to the surface for treatment. The ores are crushed and milled and then separated. The crushing creates silicate dust which if absorbed into lung tissue over a prolonged time, can cause problems such as pneumoconiosis and silicosis. Prolonged exposure to silicate dust can cause fluid to build up in the lungs, leading to pulmonary oedema, it must be said that this is not a common problem in modern mining ventures. The separation process produces tailings (pulverized rock and liquids) from which toxic elements can leach into the bedrock and nearby water sources if not stored safely. The use of enormous amounts of water in the lithium extraction

process is also an issue both for hard rock mining and brine deposits. Lithium brine mining operations in South America have seen several "water conflicts" arise due to the large amounts of water required by the lithium extraction industry (Larrain, 2012). The extraction of lithium in Ireland could potentially have harmful effects on the local environment through leaching, spills or air emissions. There are no other active mining operations near the known lithium mineralisation in Ireland. Any mining operation inevitably comes with a lengthy list of environmental concerns and potential issues. Public opinion and activism such as resistance to mining play an important role in deciding whether a mineral occurrence is recoverable. It is possible that public opposition may hinder any lithium mining operation in Ireland (White, 1992). There is a need to measure baseline levels of lithium in the natural waters of the Carlow area prior to any mining operation. The purpose of this research was to establish those baseline levels of dissolved lithium and other metals in the natural waters of Carlow, namely the ground and surface water of the area; the rationale being that if mining were to take place in the region, the data produced here could be used as a benchmark to determine whether disturbed lithium, and by extension other metals we have analysed, have been leached into the South East's natural waters.

2.3. Materials and Methods

2.3.1. Sampling

Natural waters refer to both surface water (SW) and groundwater (GW). This study aimed to sample Carlow's GW and SW. Carlow's land area covers approximately 897 km^2. GW and SW samples were taken along five transect sampling lines (Figure 2.2) crossing Carlow from East to West. These specific transect lines did not represent any significant geological features but were rather a numerical split of the area taking into account existing road access. This sampling method was chosen to sample the whole county in a cost-efficient way. This method also allowed us to address the question: has the lithium from the pegmatites located in the East part of the county permeated towards the river Barrow in the West of the county.
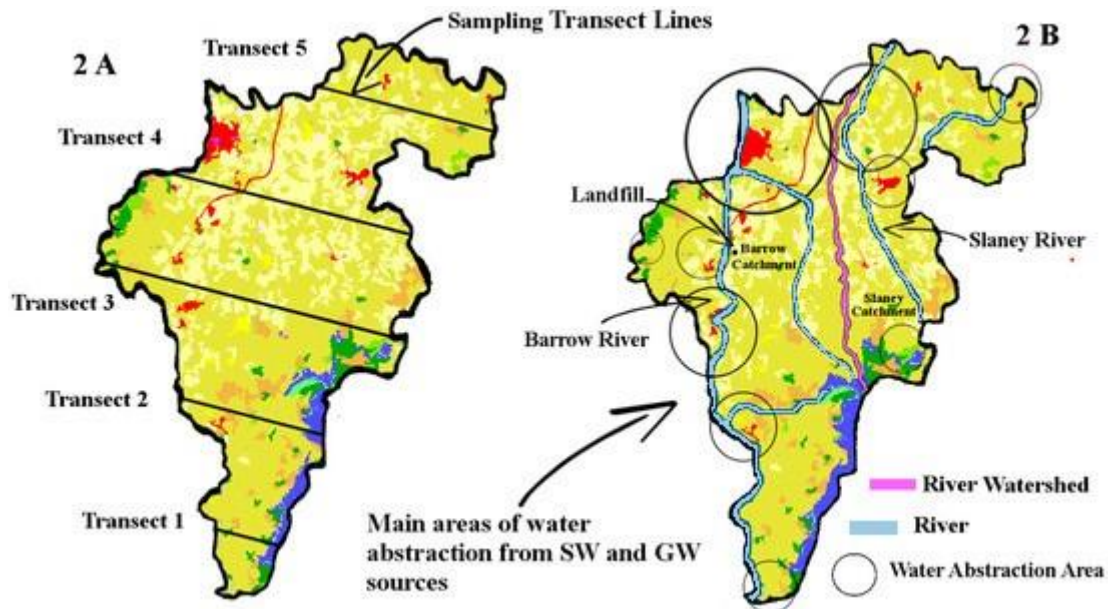
Figure 2.2. Map of Co. Carlow, showing locations of transect sampling lines (2A) and main rivers, catchment and drinking water abstraction areas (2B). Image modified from (IRL EPA, 2017; GSI, 2016).

The study was conducted over a period of seven months during 2015, from March to September. Water samples were collected every two months (four sampling events) from a total of 115 sampling sites, 80 of which were GW and 35 SW, giving a total of 460 water samples (Figure 2.3). GW samples were taken directly from household taps that were connected to private boreholes. SW samples were taken from streams and rivers along and adjacent to transect sampling lines. Water samples were collected in acid-washed High-Density Polyethylene sampling bottles. All bottles were acid washed with dilute nitric acid, then filled with the dilute acid and allowed to sit for approximately one day. Bottles were then rinsed several times with deionized water and placed in sealable bags to prevent any contamination. Parts per billion measurements require rigorous cleaning and sampling methods; because of this, only ultra-pure analytical grade acids were used in this study. Samples collected in the field were filled to the brim leaving very little air space at the top of the bottle. Physico-chemical measurements (pH, Temperature and Conductivity) were taken in the field prior to filtering or acidification. Samples were filtered within 24 h of collection and then acidified. The samples were acidified to arrest any biological activity; dissolve any precipitates present; and discourage the adsorption of lithium onto the walls of the bottles. Trace metals are particularly prone to adsorption. Samples were stored at 4 °C ± 1 °C for the duration of the study.
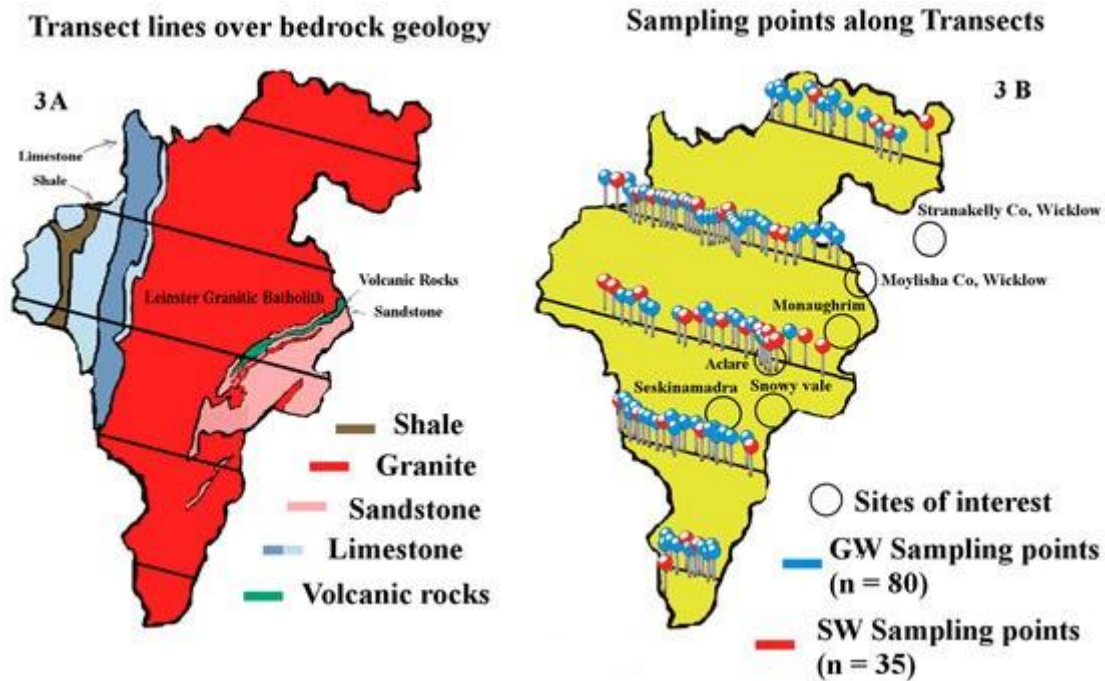
Figure 2.3. Map of Co. Carlow, showing bedrock geology, transect sampling lines (3A) areas of interest and approximate sampling point locations (3B) Image modified from (IRL EPA, 2017; GSI, 2016).

2.3.2. Surface Water Sampling

SW samples (Number of samples (n) = 140) were taken from rivers and streams where they intersected the sampling transect lines. Sample bottles were rinsed three times with the water being sampled. To avoid non-representative samples caused by surface films and the entrainment of river sediments, a grab sampling method was used. Samples were taken from the centre of rivers below the surface of the water while the sampler stood downstream of the sampling point. In some cases, (i.e., shallow streams), several small samples were amalgamated into a sufficiently large sample from which a final sample was taken.

2.3.3. Groundwater Sampling

GW samples (n = 320) were collected directly from homeowners' plumbing systems (i.e., domestic taps). Only sites which had their own GW well system installed were selected for the study. Care was also taken to avoid any water softening system or other treatment between the GW source and the tap. Prior to sampling from taps, the water was left to flow for two minutes before a sample was taken. When collecting GW samples, the container was rinsed three times with the water to be sampled before taking the final sample. Samples were also taken as close as possible to the source of the supply to minimize any potential influence from the plumbing system.

2.3.4. Sample Preparation

All water samples and blanks underwent the same preparatory procedures. Firstly, the samples were concentrated by a factor of 10 by evaporation, 200 ml samples were concentrated down to 20 ml before being analysed (lithium has a boiling point of 1330°C, thus was not volatilised during this step). This ensured that the naturally low lithium levels in our samples would be measured at an order of magnitude greater than they appear naturally and therefore be more easily detected by our instrumentation. Samples were then filtered, using a slow filtration rate filter paper with particle retention at 2–3 µm to remove coarse and gelatinous precipitates from the solution. Further to this, samples were filtered using 0.45 µm pore size cellulose-based membrane syringe filters. These filters trap particles both on the surface of the filter and within the filter; consequently, the retention of small particles increased as the filter became more loaded. Samples were filtered avoiding excessive pressure. Algal cells are known to concentrate trace metals, so rupture of an algal cell could cause inaccurately high results; rupture may also introduce natural chelating agents into the water.

2.3.5. Reagents

Lithium Standard for Atomic Absorbance Spectroscopy (certified reference material), TraceCERT®, 1000 mg/l Li in nitric acid was used to prepare all working standards. Potassium solution as an ionization suppressant, at 2000 mg/l was made up in double deionized water from Potassium hydroxide pellets for analysis (EMSURE®) and acidified using nitric acid. All working solutions and working standards were acidified using nitric acid, $\geq 69.0\%$, for analysis (EMSURE®) to the same percentage as collected samples (i.e., 1%). Glassware was thoroughly soaked in dilute nitric acid and rinsed several times with deionized water before use. No other metals in the analysis required an ionization suppressant. All reagents used were commercially available from Sigma Aldrich Ireland Ltd. Vale Road, Arklow, Wicklow, Ireland.

2.3.6. Analysis

All water samples were analysed for lithium, as well as cadmium, copper, iron, manganese, nickel, lead and zinc using an Agilent (Tech 200 AA series) flame atomic absorption spectrometer (AAS) in an air-acetylene flame (FES, 2016). Potassium and sodium were analysed using a Flame Emission Spectrophotometer (FES) (Sherwood Model 410 Flame photometer). These instruments provided sufficient sensitivity, short analysis time and a level of accuracy required for the study. Limit of Detection (LOD)

for FES analysis was 0.13 mg/l while the limit of quantification (LOQ) was 0.44 mg/l. LOD for all AAS analyses was 0.005 mg/l while LOQ was placed at 0.018 mg/l. The working range for lithium was up to 5 mg/l; working ranges for all the other metals were up to 10 mg/l. Samples were concentrated by a factor of 10 prior to any instrumental analysis, therefore a concentration factor of 10 was applied to all data before reporting the result. Processed samples were drawn at random before being read on the AAS to minimize procedural bias. After every 50 samples, the instrument was recalibrated using blank samples and working standards. Validation of procedures was carried out as stated by Agilent (Tech 200 AA series). Matrix modifications were validated, and spiked sample recovery rates were > 60%. Typical readings obtained from blank samples were 0.0001 to 0.0003 mg/l of lithium. Speciation of the lithium and the other metals analysed in the water was not a factor in this study; only total dissolved metal content was measured.

2.3.7. Interferences

Alkali metals are very susceptible to ionization. In an air-acetylene flame, lithium ionization is appreciable. To control this ionization, all solutions were made to contain 2000 mg/l of the easily ionized potassium cation (ionization potential of 4.3 eV vs. 5.39 eV for lithium). At 2000 mg/l, minor changes in the potassium concentration had little or no effect on lithium's absorbance readings.

2.3.8. Data Analysis

Statistical analysis was carried out using International Business Machines (IBM®) statistical package, Statistical Package for the Social Sciences (SPSS®) version 23.0, IBM® Corp, Armonk, New York, USA, and Microsoft Excel® (2016 MSO 16.0.8625.2121). The lithium data were not normally distributed and when graphed showed considerable left skewness (GW skew = 3.89, kurtosis = 18.36; SW skew = 3.25, kurtosis = 12.11). To adjust the data to normality and allow the use of parametric tests, all data underwent a logarithmic transformation (Figure 2.4). When comparing lithium means among transects and geographical areas, a one-way ANOVA was used. Where significant differences were found, a post-hoc t-test was used to identify significant differences between sample means. A probability-value of 0.05 was considered significant. Bonferroni corrections were used as appropriate.
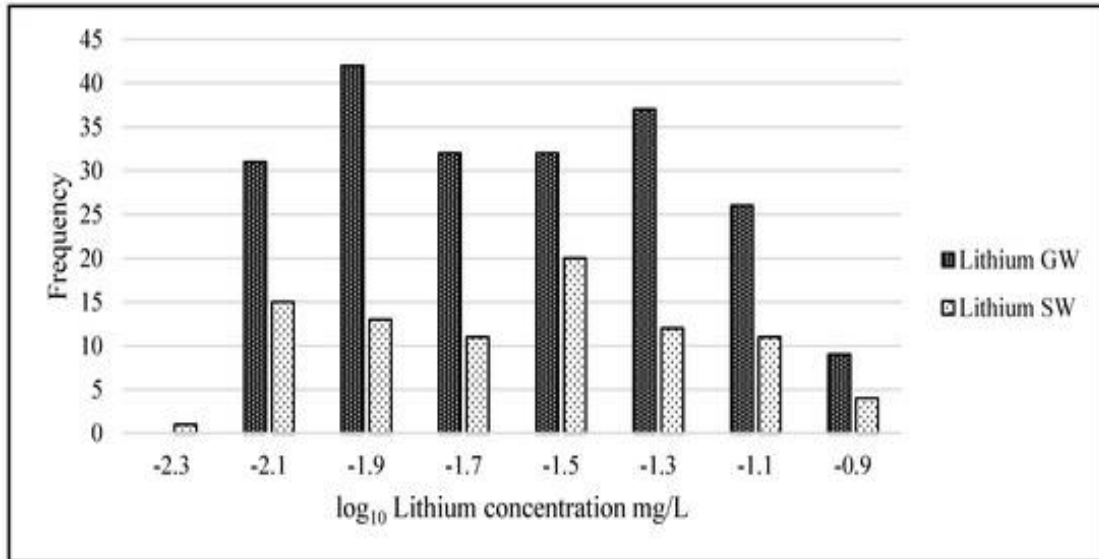
Figure 2.4. Histogram of SW and GW lithium concentration data. X-axis units are the logarithmic transformed mg/l data and Y-axis units are frequency. (n = 460 samples).

2.4. Results

2.4.1 Statistical Analysis

The majority of water samples (n = 460) contained detectable amounts of lithium apart from 21 SW and 39 GW samples. In the case of GW sampling from people's homes, we wanted to determine whether there was a difference when sampling from a pipe system that was unused overnight versus a system that had been used by a household all day, the null hypothesis was that there was no significant difference between the mean lithium levels measured in the morning and evening. One sampling point was selected from which 20 water samples were taken: 10 in the morning and 10 in the evening, then analysed for lithium content. In total, 80 GW sites located along each of the five transect sampling lines were sampled four times giving a total of 320 observations. In total, 35 SW sites located along each of the five transect sampling lines were sampled four times from which a total of 140 observations were made. Surface water at $\bar{x} = 0.02$, Standard deviation (SD) = 0.02 ranging from 0 to 0.091 mg/l and groundwater at $\bar{x} = 0.023$, SD = 0.02 mg/l ranging from 0 to 0.097 mg/l (Figure 2.5).
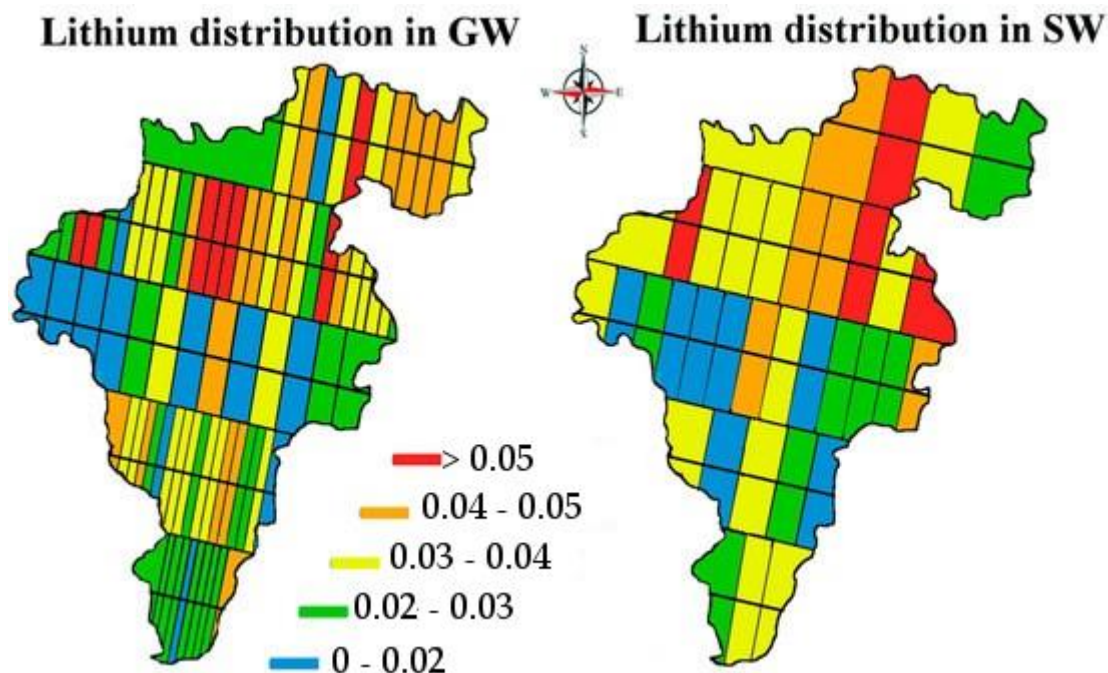
Figure 2.5. Map of Co. Carlow, showing lithium distribution levels in GW and SW, units - mg/l. Image modified from (IRL EPA, 2017; GSI, 2016).

A correlation analysis was carried out to assess whether there was any association between lithium and the physicochemical variables (pH, Conductivity and Temperature). No significant correlations were observed with the variability explained, (r^2) ranging from 0 to 6%. The mean lithium concentration in SW and GW appeared similar. A t-test (two-sample assuming equal variance) was carried out to test a null hypothesis that there was no significant difference between GW and SW mean lithium levels obtained from the entire data set, n = 460 observations (Ho: $\mu gw - \mu sw = 0$, vs. Alternative hypothesis: Ha: $\mu gw - \mu sw \neq 0$). The test (t = 1.96, df = 458, p-value = 0.66) failed to reject the null hypothesis. There was no statistical difference between lithium levels in SW and GW.

2.4.2. Bimonthly Data

Bimonthly sampling took place during 2015 with four different sampling events (March, May, July and September). One peculiar observation in the data can be seen in (Figure 2.6). The variation in lithium levels in March and July appears similar to the data in May and September. An ANOVA conducted on our logarithmic transformed monthly lithium data, with a null hypothesis that there was no heterogeneity among months for lithium concentrations, ($F_{(7, 288)} = 34.67$, $p = 6.5 \times 10^{-35}$) showed a significant heterogeneity among the months.

Initially, we suspected that this relationship could be explained by procedural bias. Before any analysis began, all 460 SW and GW samples were mixed together. During the analysis, samples were selected randomly from this mix. Selecting samples using this method should have effectively negated the possibility of any procedural bias. Rainfall data for the area at the time of sampling did not correlate with the measured lithium concentrations; the above pattern was not present (March 53.5 mm, May 89.4 mm, July 79.4 mm, September 27.6 mm total rainfall in the sampling area) in the data (MetÉireann, 2016). To mitigate any diluting influence, sampling only took place two to three days after significant precipitation. We also considered that agricultural activities could have been responsible for the pattern. Land spreading of organic and chemical fertilizers is prohibited in Ireland during the times when the ground is likely to be frozen (September to January) under the European Union's Nitrates Directive (Directive 91/676/EEC). In the South-East, fertilizer application is prohibited from 15 September to 12 January (DAFM Ireland, 2017). In Ireland, farmers tend to apply fertilizer in the spring (February to April). Some fertilisers have been shown to contain lithium at concentrations between 0.1 and 5.3 mg/kg (Anderson et al., 1988). Lithium addition from fertilisers can potentially build up in the soil affecting the natural trace concentrations of lithium already there. Senesi *et al.,* (1979) showed that after three applications of lithium containing fertiliser, between 0.02 and 1.17 g/ha lithium was present in the soil (Senesi *et al.,* 1979). The project's sampling began in mid-March and ended in mid-September. At any time during our sampling, fertilizer spreading may have taken place. It is impossible to know when farmers spread fertilizer during our sampling, but we cannot ignore the possibility that agricultural activities may be responsible for the pattern. Ireland's farmers rely heavily on nitrogen, phosphorous and potassium fertilizers. There is also one landfill site located within Co. Carlow (Powerstown Landfill and Recycling Centre) approximately 8 km South of Carlow town. This is almost exactly midway between transects 3 and 4 and is thus unlikely to directly impinge on our measurements.
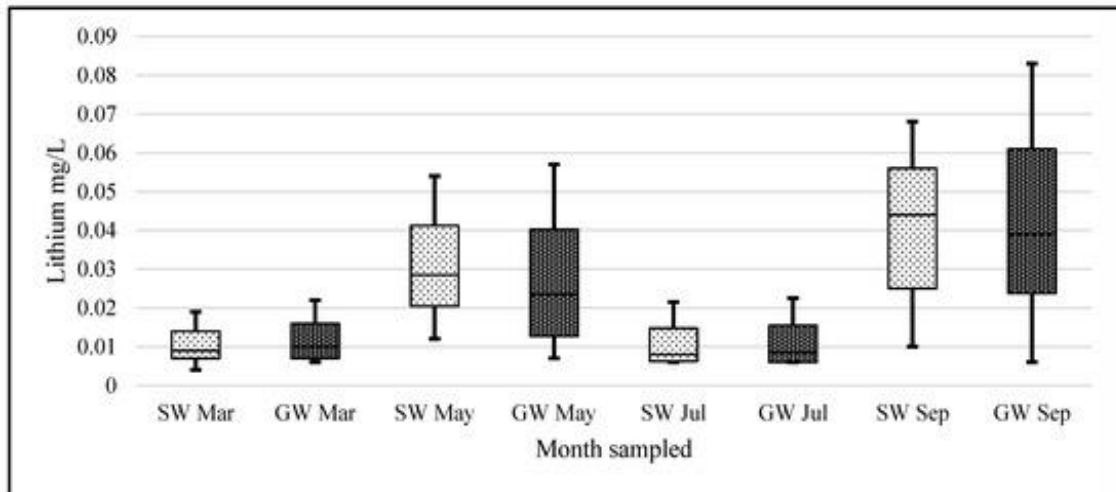
Figure 2.6. Boxplots of SW and GW lithium concentration data for each month. X-axis units represent months sampled and Y-axis units are mg/l lithium (n = 35 SW and n = 80 GW samples for each month).

Data that we have collected for other alkali metals analysed during the same time do not display the same pattern. For example, when an ANOVA was conducted on our logarithmic transformed monthly potassium data, with a null hypothesis that there was no heterogeneity among months for potassium concentrations, the following was observed $(F_{(6, 418)} = 5.80, p = 8.08 \times 10^{-6})$ rejecting the Ho. We do not observe the same pattern in our potassium data (Figure 2.7 and Figure 2.8). An ANOVA using the same hypothesis was conducted on the logarithmic transformed monthly sodium data, showing the following $(F_{(7, 452)} = 6.17, p = 6.46 \times 10^{-7})$ also rejected the Ho (Figure 2.9 and Figure 2.10). There is heterogeneity in the potassium and sodium data, but it is a different pattern than in the lithium data. This pattern may be attributable to normal variation in the data.
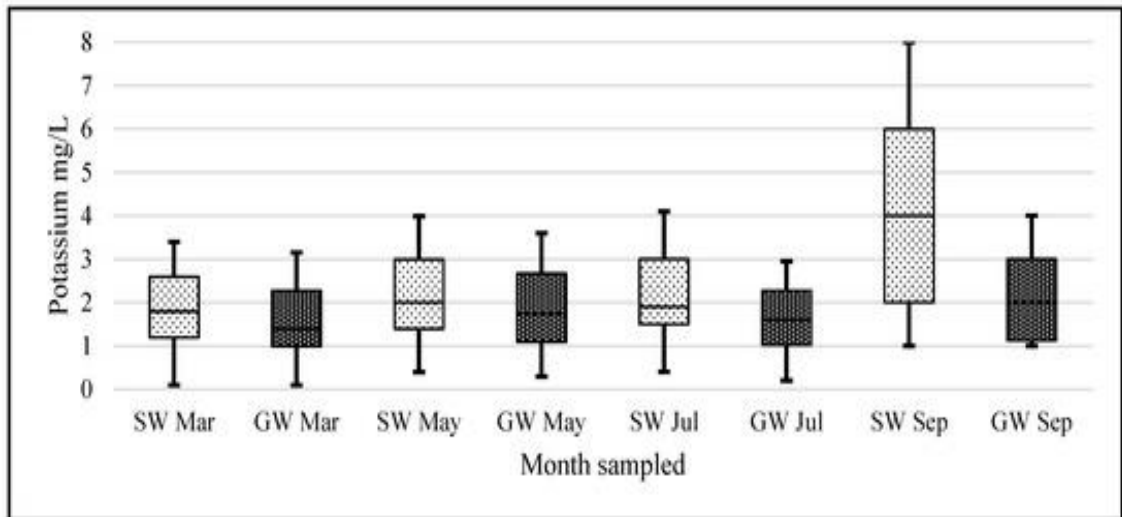
Figure 2.7. Boxplots of SW and GW K concentration data for each month. X-axis units represent months sampled and Y-axis units are mg/l potassium (n = 35 SW and n = 80 GW samples for each month).
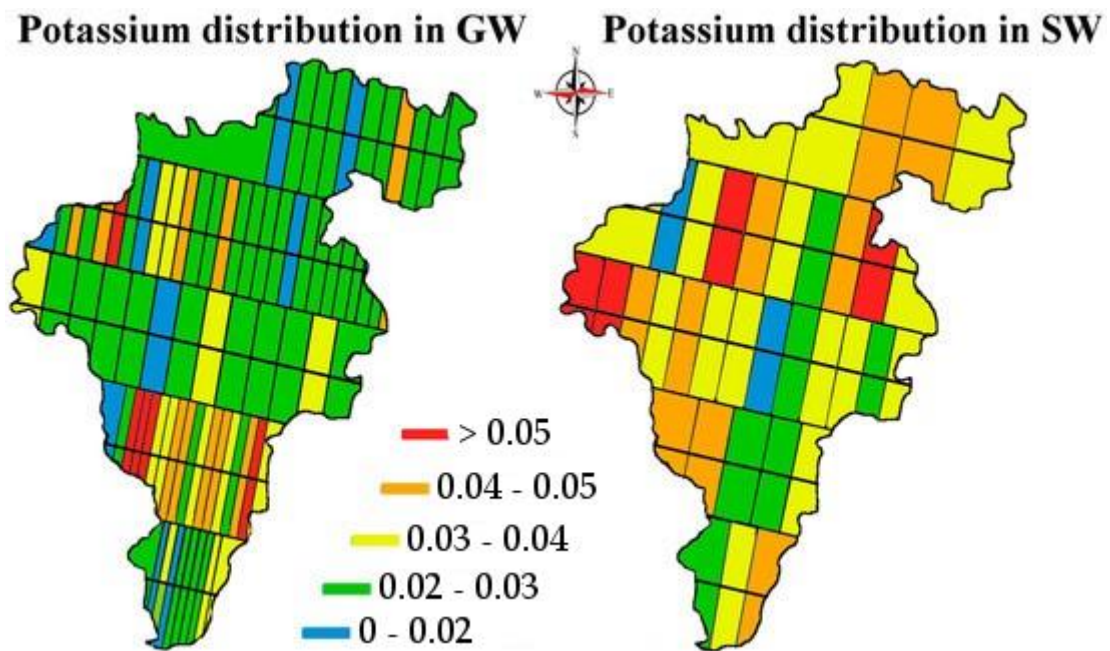
Figure 2.8. Map of Co. Carlow, showing potassium distribution levels in mg/l. Image modified from (IRL EPA, 2017; GSI, 2016).
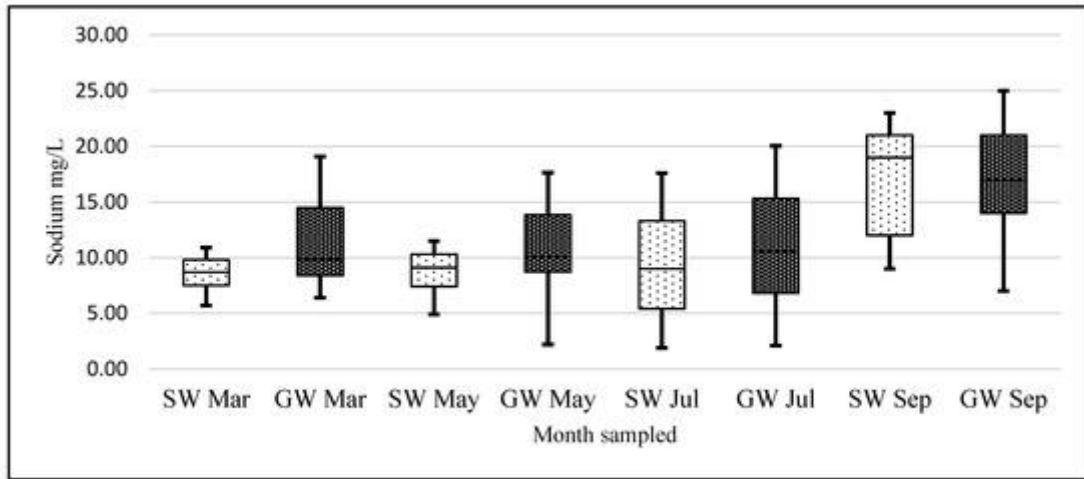
Figure 2.9. Boxplots of SW and GW sodium concentration data for each month. X-axis represents months sampled and Y-axis units are mg/l sodium (n = 35 SW and n = 80 GW samples for each month).
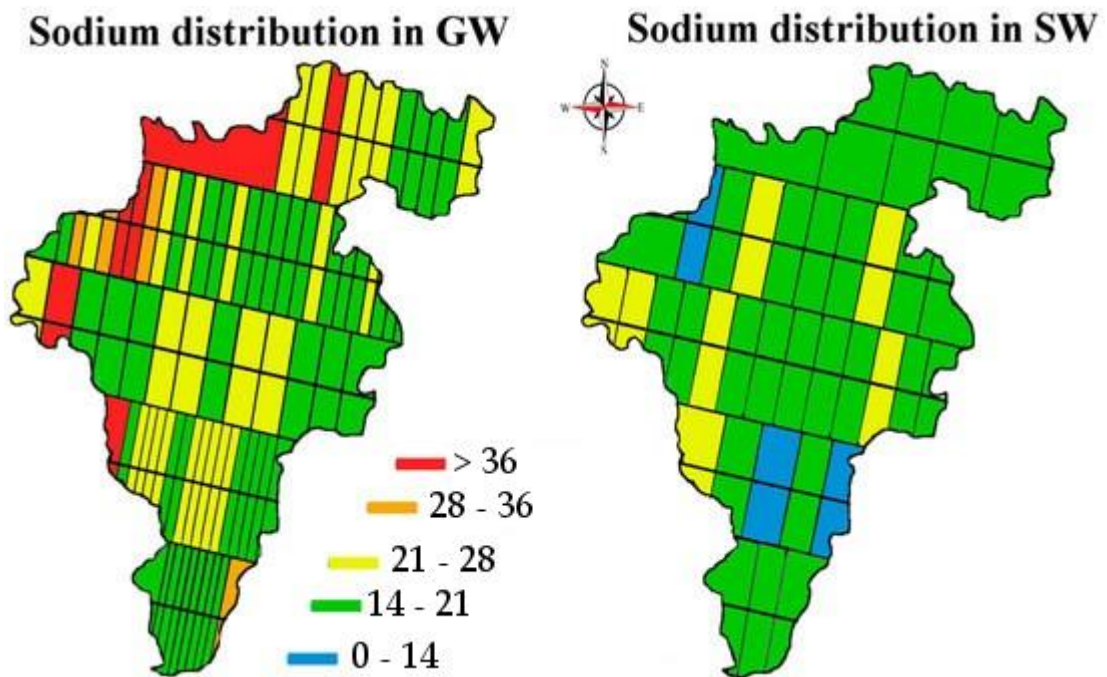
Figure 2.10. Map of Co. Carlow, showing sodium distribution levels in mg/l. Image modified from (IRL EPA, 2017; GSI, 2016).

Nevertheless, the pattern of variation among months is different for the three elements, so we conclude that the heterogeneity is not due to procedural bias. We are currently unable to propose a mechanism to explain the observed pattern in the lithium data. Lithium enrichment is often expressed by the lithium to sodium ratio which is used as an indicator of residence time within an aquifer. The sodium to lithium ratio in the GW and SW of Co. Carlow is illustrated in Figure 2.11. (Taylor, 1964).
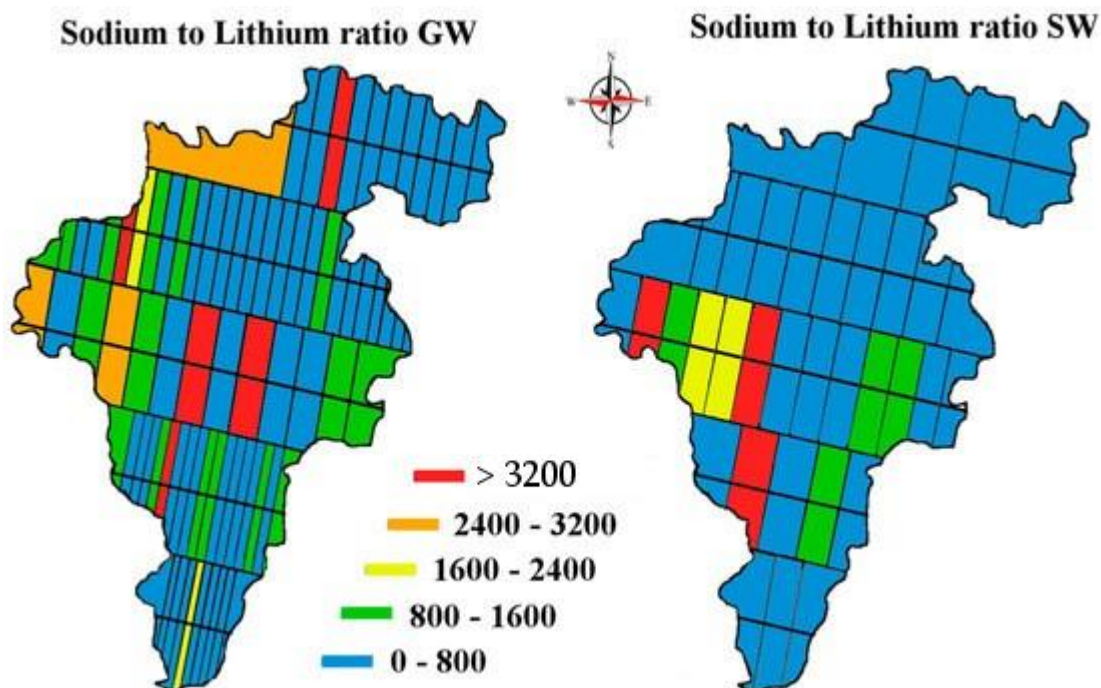
Figure 2.11. Map of Co. Carlow, showing the sodium to lithium distribution ratio in GW and SW, units mg/l. Image modified from (IRL EPA, 2017; GSI, 2016).

An ANOVA analysis was performed on the logarithmically transformed transect lithium data (Figure 2.12). The null hypothesis stated that there was no statistical difference between each transect mean lithium concentration. In the case of both SW, $(F_{(4, 82)} = 1.88, p = 0.12)$ and GW $(F_{(4, 204)} = 2.44, p = 0.084)$, we failed to reject the null hypothesis when a Bonferroni correction for multiple testing was applied. This contrasts with the comparisons among months.
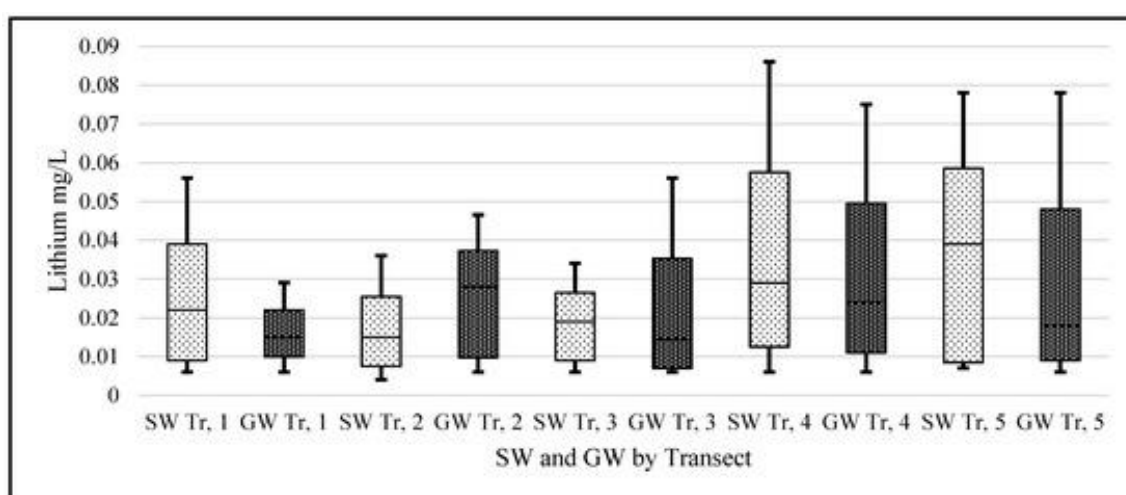
Figure 2.12. Boxplots of SW and GW lithium concentration data for each transect. The x-axis represents the sampling transects and Y-axis units are mg/l Lithium (n = 35 SW and n = 80 GW samples for each month).

The lithium-bearing pegmatites are located along the Eastern border of the County; the Western border of the County is marked by the river Barrow valley. The river Barrow's watershed boundary includes some of the areas of known pegmatite occurrences (Figure 2.13). One of the questions we sought to answer was whether the levels of lithium are higher in the East than in the West. This hypothesis was based on the known highly mobile nature of the lithium ion and the weathering over time of the lithium-bearing pegmatites. Dividing our data into West, Central and East data bins (the lithium bearing pegmatites being in the East of the County) and then conducting a t-test on the logarithmic transformed data—with the null hypothesis that there was no difference between East and West lithium means—the following observations were made: for SW at ($t = 1.98$, df = 85, $p = 0.24$), we failed to reject the Ho and for GW at ($t = 1.97$, df = 207, $p = 0.062$), we also failed to reject the Ho.
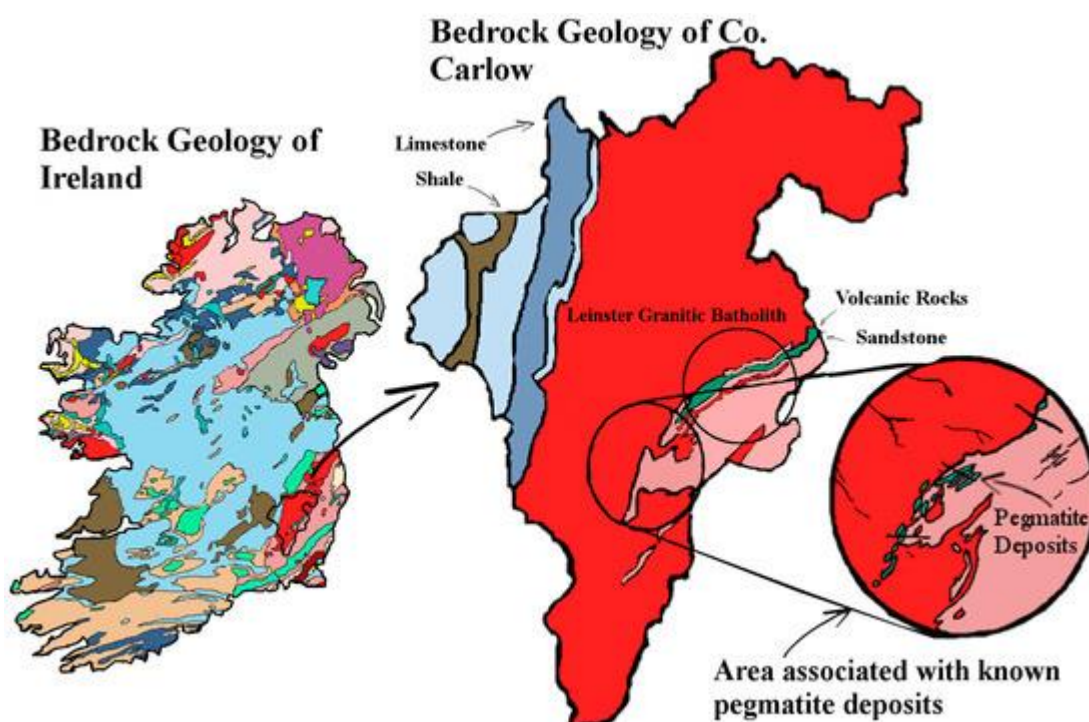
Figure 2.13. Bedrock geology map of Ireland and county Co. Carlow showing the general location of lithium bearing pegmatites. Image modified from (GSI, 2016).

2.4.3. Additional Metals

Along with lithium, potassium and sodium, seven other metals (Cd, Cu, Fe, Mn, Ni, Pb and Zn) were analysed both in SW and GW. The results are listed in (Table 2.1). The measured levels of each of these metals were within the safe range of threshold levels for drinking water monitored by the Irish Environmental Protection Agency (IRL EPA) and the World Health Organization (WHO) and are of no immediate concern. Further, these

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levels did not exceed any maximum thresholds set for GW and SW by the Irish EPA (IRL EPA, 2017; WHO, 2011). The Irish EPA carries out routine water quality analyses all over Ireland, the data from which are publicly available (IRL EPA, 2017). These metals were chosen because they represent a common set of metals associated with water quality and to determine whether there were any significant correlations between lithium and the other metals. When a correlation analysis was carried out to assess this, no significant correlations were observed.

Table 2.1. Concentrations of analysed metals in SW and GW given in mg/l (SD = Standard deviation, ND = Not Detected).

Metal	SW Mean	SW SD	GW Mean	GW SD
Cd	ND	-----	ND	-----
Cu	0.08	0.43	0.12	0.28
Fe	0.1	0.21	0.05	0.19
K	2.7	1.7	2.2	2.1
Li	0.02	0.02	0.02	0.02
Mn	0.04	0.08	0.04	0.15
Na	11.1	5.2	15.5	14.2
Ni	0.01	0.01	0.01	0.04
Pb	0.04	0.05	0.04	0.07
Zn	0.08	0.19	0.14	0.23

2.5. Discussion

The mean values obtained for lithium levels in Co. Carlow's SW at $\bar{x} = 0.02$, SD = 0.02 mg/l and GW at $\bar{x} = 0.02$, SD = 0.02 mg/l are compatible with published figures for lithium concentrations in drinking waters; for example, drinking water in Texas 0.003 to 0.16 mg/l; in Oita, Japan 0.0007 to 0.059 mg/l; in England 0.001 to 0.021 mg/l; and in Portugal 0.001 to 0.19 mg/l (Figueroa *et al*., 2012; Figueroa *et al*., 2013; Larrain, 2012; Schrauzer and de Vroey 1994). It is worth noting that these figures are associated with studies investigating an inverse association between lithium levels in drinking water and suicide rates in the local population. Some of these studies also claim a positive correlation among lithium levels, longevity and general mental health. The theory is that lithium in trace amounts enhances the connectivity among neurons and exposure over a lifetime enhances happiness (Kapusta and König 2015). However, data for Ireland, let alone Co. Carlow, in relation to suicide, are not currently available at sufficient

geographical granularity to allow an investigation of potential associations between suicide rates and lithium levels in drinking water.

Lithium's small ionic radius (0.68 Å) means that it has a high ionic potential and therefore has a strong affinity for water molecules. If the lithium from the known pegmatite sources is being slowly eroded and making its way down into the Barrow Valley, we should have measured an elevated amount of lithium in our samples. Our data suggest that the lithium concentrations, although quite variable in the natural waters of Carlow, are within the range of normal 'background' levels reported in the literature and not elevated. The passage of water through the pegmatites is low (O'Connor *et al.*, 1991). They are situated at an altitude above the level of the local water table and are unsaturated. The pegmatites also occur within a poor aquifer. The low concentrations found appear to be consistent with limited dissolution of the pegmatites.

When a one-sample t-test assuming unequal variances was carried out on our data the null hypothesis that the population mean was 0.010 mg/l; the alternative hypothesis that our samples were greater than this level, the following was observed, ($t = 1.96$, $df = 459$, $p = 3.1 \times 10^{-13}$) rejecting the Ho. This should serve to focus some critical attention away from mean/median values to the range of levels for 'lithium in natural waters' when the literature and our data suggest variation through 3 orders of magnitude (0.0007 to 0.19 mg/l).

Finding bedrock outcrops of Ireland's granitic batholith is quite rare. This is especially the case with the South East's pegmatites. Neither recent nor historic prospecting have uncovered any cases of exposed pegmatite-bearing bedrock in the area. Pegmatites are very similar in composition to granite in that they both are susceptible to weathering. However, spodumene $LiAl(SiO_3)_2$ is an aluminosilicate mineral, thus the leaching from its lattice structure is very slow. This fact, the lack of exposed bedrock outcrops in the area and the fact that the pegmatites are unsaturated may account for the low levels of lithium in our samples. Some of the compounds that lithium forms in nature such as its fluoride, carbonate and phosphate compounds also have a very low solubility in water (Luecke, 1981; Moore, 2011; Starkey, 1982; Vikström *et al.*, 2013).

2.6. Conclusion

Lithium occurs at very low concentrations in water, and this elusiveness means that it is also an inherently difficult element to quantify. This research offers a snapshot of the lithium levels within the natural waters of the County Carlow area in the South East of Ireland. As with other studies, we have found low levels of dissolved lithium in natural waters but with significant heterogeneity through the year. This emphasizes the importance of repeated sampling to establish a true measure of lithium at a given site. From our work, we suggest that the following mean lithium values be used to establish baseline concentrations of lithium levels in the natural waters of the region: for surface water at $\bar{x} = 0.02$, SD = 0.02 ranging from 0 to 0.091 mg/l and for groundwater at $\bar{x} = 0.023$, SD = 0.02 mg/l ranging from 0 to 0.097 mg/l. These data establish a reference concentration for lithium in the natural waters of the area prior to any mining activity. The study may also be useful for other purposes: to assist in establishing a threshold value for lithium in natural waters, as a protocol of future baseline studies, to inform local water authorities and as a record for mining companies of the environmental conditions before ground is broken. Our analysis indicates that undisturbed, the lithium-rich pegmatites of the Blackstairs have a negligible effect on lithium concentration in the local watershed.

Lithium in the Soils and Plants of the

South East of Ireland

A Study Examining the Concentration of Lithium in the Soils and Plants of the South East of Ireland.

Authors: Laurence Kavanagh, Jerome Keohane, Guiomar Garcia Cabellos, Andrew Lloyd and John Cleary.

3.1. Abstract

There is an extensive belt of lithium mineralization in the southeast of Ireland. The lithium occurs primarily as the mineral spodumene ($LiAl(SiO_3)_2$) within pegmatites of the lithium-caesium-tantalum class. Pegmatites are often associated with a granitic pluton such as the Tullow Pluton of the Leinster Batholith, which dominates the geology of the area. Spodumene (stoichiometrically containing 8% Li_2O) is an important commercial source for the metal. The potential of Irish lithium has recently attracted international interest in mineral exploration and mining in the area is a distinct possibility for the future. This presents an opportunity to establish criteria for responsible lithium mining for Ireland and elsewhere benefiting from a study area rich in data and easily accessible for sample collection and study. The goal of this study was to determine the concentration of lithium and eight other metals in the soil and plants of the southeast of Ireland prior to any mining activity. We also examined whether or not there is any association between metal concentrations in soils and plants. In this study, 118 sites were sampled three times for soil and two plant species resulting in > 1,000 individual samples. The samples were acid digested and analysed using Flame Emission and Atomic Absorption Spectrophotometry. From the data, we determine average lithium soil concentrations in the area at 57.8 ± SD 18.6 mg/kg. Plant samples, for Ash (*Fraxinus excelsior)* at 43.7 ± SD 12.2 mg/kg and Ivy (*Hedera hibernica)* at 52.3 ± SD 14.6 mg/kg. There are no significant correlations in concentration between soil and plant species or among plant species.

Keywords: *Lithium; Plant; Soil; Mining*

3.2 Introduction

Lithium has until recently played a modest role in society. It exists in nature as a monovalent cation and does not naturally occur in its elemental form due to its reactivity. Lithium is a versatile metal, it is marketed in several industries and has a wide range of applications. Lithium is the most polarising of all the alkali metals and more electronegative than hydrogen making it the ideal candidate for battery technology (WebElements, 2018). The battery industry is currently the biggest consumer of lithium globally (Yaksic and Tilton 2009). The economic value of lithium has increased in recent years because of its increasing use in lithium-ion batteries (LIBs), in particular, those batteries being used to power modern electric vehicles (EVs) and portable consumer electronics. Lithium is a pervasive metal with a concentration range of 10 to 40 mg/kg in continental crusts and 10 to 30 mg/kg in plants. It occurs only at low concentrations in humans at 0.1 to 0.5 mg/kg. (Taylor *et al*., 2005).

The lithium used in LIBs is highly pure lithium carbonate. Meshram *et al.,* (2014) reported that 22% of lithium production went to the LIB industry in 2014 and predicted that this figure should rise to 40% by 2020 (Meshram *et al*., 2014). Meshram's figures agree closely with the majority of estimates given by other authors. With the growth of the EV market and increasing demand in the consumer electronics market, lithium demand is expected to increase significantly in the coming decades. As demand for lithium increases then the exploitation of more dilute mineralisation of lithium will become economic, undoubtedly leading to more lithium mining operations possibly including the lithium occurrence in the southeast of Ireland. The mobilisation of lithium in the future will result in it being more exposed in the environment thus potentially becoming an emerging environmental contaminant. Any type of mining in any part of the world triggers concern about the environmental impact of the process. The mobilisation of lithium in the environment may also affect crop production and undoubtedly find its way into the human food chain (Shahzad *et al*., 201). The aim of this work is to report data which can be used to set baselines for the concentration of lithium and other metals within the soils and selected plants of the area. The plant species ash and ivy were chosen for this work because of their pervasiveness throughout the study area. At each of the 118 sampling sites, both plant species were present. The different root systems of the plants (i.e. relatively deep in Ash and shallow in Ivy*)* also allowed us to measure the amount of analysed metals absorbed by the plants from two levels of the topsoil horizon.

3.2.1. Lithium

The price of lithium metal has increased steadily since the turn of the century apart from a slight fall during the global recession of 2008 and 2010, from. €1,600/tonne in 1999 to €16,100/tonne in 2018 (Figure 3.1). Increasing demand for lithium is creating a new "gold rush" for lithium deposits around the world. During the 1970s the lithium occurrence in the southeast of Ireland was deemed to be uneconomical to extract by the now dissolved Irish Base Metals Company. Today demand for the metal means that marginal lithium occurrences like the one in the southeast of Ireland are becoming worthwhile to extract (ILC, 2018). While the price of LIBs for EVs is decreasing, the price of metallic lithium is rising. Lithium is not currently produced in Ireland, however, the International Lithium Corporation, Canada, and its financial partners Jiangxi Gangfeng Co. Ltd hold prospecting licences for the Avalonia Lithium project which includes prospecting licences covering 294 km^2 overlapping the study area (ILC, 12018).
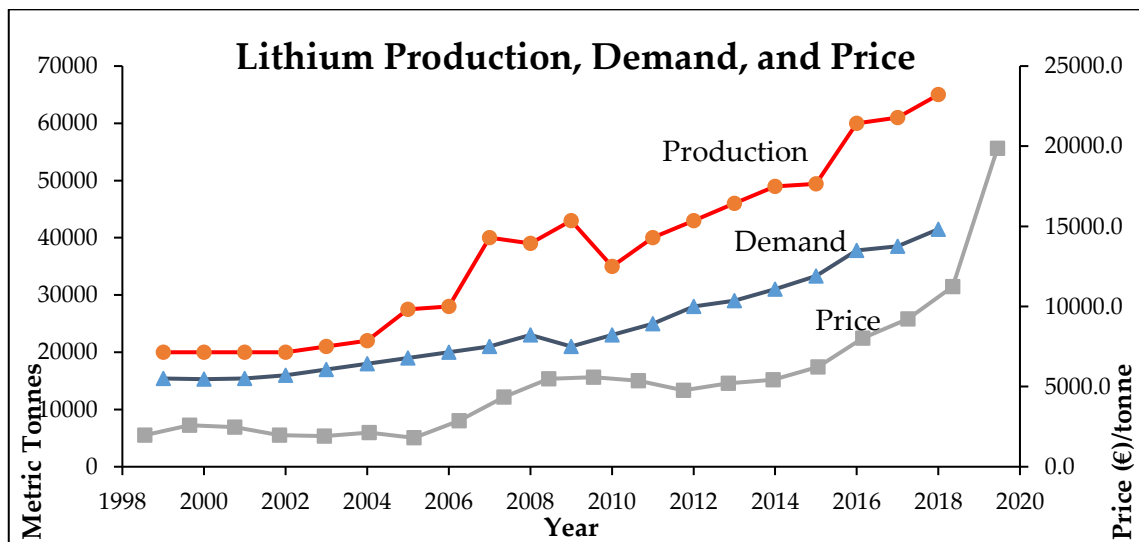
Figure 3.1. The price of lithium/tonne in Euro by year and the demand and production for lithium in tonnes/year. Data Sources (Metalary, 2018; Tahil, 2007; WebElements, 2018; Yaksic and Tilton 2009).

There are three main commercial sources of lithium. Mineral deposits like spodumene, clays associated with volcanism like hectorite ($Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$) and mineral-rich brine like the brines found in the Salars of the Andes. Lithium occurs in 145 minerals, but there are relatively few minerals that have enough lithium to justify the capital to extract it. Lithium-rich minerals include spodumene ($LiAl(SiO_3)_2$), Lepodite ($K(Li,Al,Rb)_2(Al,Si)_4O_{10}(F,OH)_2$), petalite ($LiAlSi_4O_{10}$) and Amblygonite (($Li,Na)AlPO_4(F,OH)$). Other less lithium-rich minerals that are often mined include

zinnwaldite (K, Li, Fe, Al (AlSi$_3$) O$_{10}$ (OH,F)$_2$). The lithium which exists in the southeast of Ireland is in the form of the lithium-rich mineral spodumene (LiAl (SiO$_3$)$_2$) within a pegmatite rock associated with an intrusive granitic pluton which dominates the geology of the area (the Leinster granite). Spodumene is a pyroxene mineral often found in granite pegmatite. A pegmatite is an intrusive igneous rock of coarse grain, composed mainly of quartz, feldspar, and muscovite. It often occurs in dykes, veins, bands and sills, geological formations associated with granitic plutons. Less than 1% of pegmatite globally are lithium bearing. The pegmatite in Ireland has been classified as a lithium, caesium and tantalum bearing or LCT pegmatite. These pegmatites often contain commercial amounts of caesium and tantalum (Barros, 2017). The Leinster granites and the LCT pegmatite have been extensively studied in the literature, providing detailed descriptions of the petrogenesis and makeup of the Leinster granites and associated minerals (O'Connor *et al*., 1991; Elsdon, 1975; Luecke, 1981; Mohr, 1991; McArdle and Kennan 1988; Roycroft, 1989; Sweetman, 1987; Whitworth, 1992).

3.2.2. Lithium Globally

Normally lithium is extracted from minerals as lithium carbonate which is a precursor for nearly all commercial lithium compounds. Lithium pegmatite mines exist all over the world ensuring a good security of supply for the future. Mines exist in countries like Australia, Brazil, Madagascar, Pakistan, Canada, China, USA and several central African countries. 66% of world lithium resources are in brines, 26% in minerals and just 8% in sedimentary rocks. Although lithium from brines is cheaper to extract than lithium from minerals, these mineral sources are still an important source of lithium because of demand. Of all the world's currently known lithium reserves, approximately two-thirds are thought to exist in the salars of three Andean countries Argentina, Bolivia, and Chile. The area has collectively become known as the Lithium Triangle because of its vast lithium resources. Mineral sources of lithium have been exploited for years and have well-established extraction and purification technologies. Brine operations can take several months to produce lithium and are dependent on the weather while production of lithium from mineral sources potentially only takes a few days. The Greenbushes pegmatite mine in the southwest of Australia is currently the largest producer of lithium from a mineral source (Partington *et al*., 1995).

3.2.3. Lithium in the Southeast of Ireland

The Avalonia Lithium project is the name given to a current prospecting survey for lithium in the southeast of Ireland. The partners that have invested in the project are the International Lithium Corporation (ILC), Canada and Ganfeng Lithium (GL), Jiangxi province, China, GL owns a majority share in the project at 51%. Historic prospecting in the area revealed 10 significant lithium pegmatite occurrences in the area, the largest of which was at Aclare House, Myshall, Co. Carlow. According to the historical survey, the pegmatites at Aclare were 20m wide with lithium reserves estimated at 570,000t grading 1.5% Li_2O as spodumene. ILC (2018) recently described the pegmatite at Aclare as 23.3m wide with a grading of 2.23% Li_2O. The survey also discovered a previously unknown pegmatite occurrence at Orchard, County Carlow, described as 5.06m wide with a grading of 1.5% Li_2O. According to ILC (2018) extraction of lithium from the area in the future is a distinct possibility (ILC, 2018).

3.2.4. Lithium in soil

Lithium is widely distributed in the Earth's crust but generally only gathers in suitably economic deposits in two main forms, in silicate minerals and in mineral-rich brines. The average concentration of lithium in the Earth's crust has been estimated at various values in the 10 to 40 mg/kg range. Commonly quoted values are 20 mg/kg for the concentration of lithium in the Earth's crust, and 30 mg/kg in granites (Aral and Vecchio-Sadus 2008; Ronov and Yaroshevsky 1969; Taylor, 1964; Turekian and Wedepohl 1961). Lithium is found in trace amounts in all soils and originates from the weathering of parent lithium-containing rocks. There are several factors which determine the distribution and concentration of lithium in soil. Those factors are; the type of parent rock/mineral; soil formation processes (erosion, water, wind, temperature, gravity, chemical interaction, living organisms and pressure differences); physicochemical factors like pH and conductivity; moisture and organic matter content and anthropological factors (Ammari *et al*., 2011; Kabata-Pendias, 2010; Rogóż, 2010). This results in wide variations in the concentrations of lithium in different soils around the world from 0.5 mg/kg lithium in meadow soils from Denmark to 500 mg/kg in various autogenic soils (Kabata-Pendias, 2010; Shahzad *et al*., 2016). Lithium exists naturally at high concentrations in soils with a high salt content and at low levels in the organic layer of soils. Of the ten main great soil groups that occur in Ireland, seven of them occur in Co. Carlow. Grey-Brown Podzolics (21.6%), Brown Earth (24.4%), Brown Podzolics (9.6%). Podzolics (3.5%), Lithosol (1.5%), Gleys (24.8%), and Regosols (14.6%). The soils are defined as being

coarse loamy drift with igneous, metamorphic shale and siliceous stones. The bedrock geology of Co. Carlow is dominated by the Leinster granites. In the east of the County the granites encounter local country rocks from the Ordovician, this contact is where the majority of lithium-rich pegmatites occur. In the west of the County, the granites meet the Lower Carboniferous limestone of the Barrow valley. There are anthropogenic routes by which lithium can enter the soil apart from natural sources i.e. mining activities (Rogóż, 2010). The various industries which use lithium like the glass/ceramics and metallurgy industries, both of which are major consumers of lithium resources, are potential sources of industrially emitted lithium. Lithium-based grease can be found in almost all current fossil fuel vehicles from which it can easily be mobilised into soils. There are other more obscure sources of lithium in soils like the spreading of natural fertilisers (Yalamanchali, 2012). Other anthropogenic sources of lithium in soils include pesticides, solid wastes, and other soil amendments. Aerial deposition of lithium can come from aerosols, particulate matter, and silicate dust. Although currently at low levels the disposal of LIBs is also a source of extraneous lithium in soils, a source that will potentially increase along with the expected global proliferation of EVs. Physico-chemical factors like climate, pH, organic matter and moisture content also determine the lithium content of soil (Kabata-Pendias, 2004). Lithium exists predominantly in the clay fraction of soils, clay minerals occur in that part of the soil comprising the smallest inorganic particles (Schrauzer, 2002). Clay minerals fix lithium normally in tetrahedral and octahedral sheets (Yalamanchali, 2012). The clay fraction of most soils can be anywhere from 7 to 200 mg/kg (Schrauzer, 2002). Lithium has been reported to correlate strongly with aluminium in the clay fraction of soils (Schrauzer, 2002). It has also been shown to be positively correlated with calcium and magnesium in soils and negatively correlated with sodium (Davey and Wheeler 1980). The lithium ion is small, it has an ionic radius of 0.6 Å, a hydrated radius of 3.40 Å and a charge/hydrated radius ratio of 0.29. Metals affinity for exchange sites on soil particles are proportional to this ratio. Lithium does not have as strong an affinity to bind to soil particles as calcium which has a charge/hydrated radius ratio of 0.62, potassium at 0.43, magnesium at 0.43, and sodium at 0.36, meaning that it remains more available in the soil than other common metals (Rogóż *et al*., 2010). Lithium is highly mobile in the soil/water solution, consequently, it is very bioavailable to plants. Lithium is absorbed by plants easily because of the similarities between the lithium ion and other common ions. Figure 3.2. shows the position of Co. Carlow in Ireland, a land map use of the area, which is predominantly

arable agriculture with some pasture and a description of the soils and bedrock geology of the area.
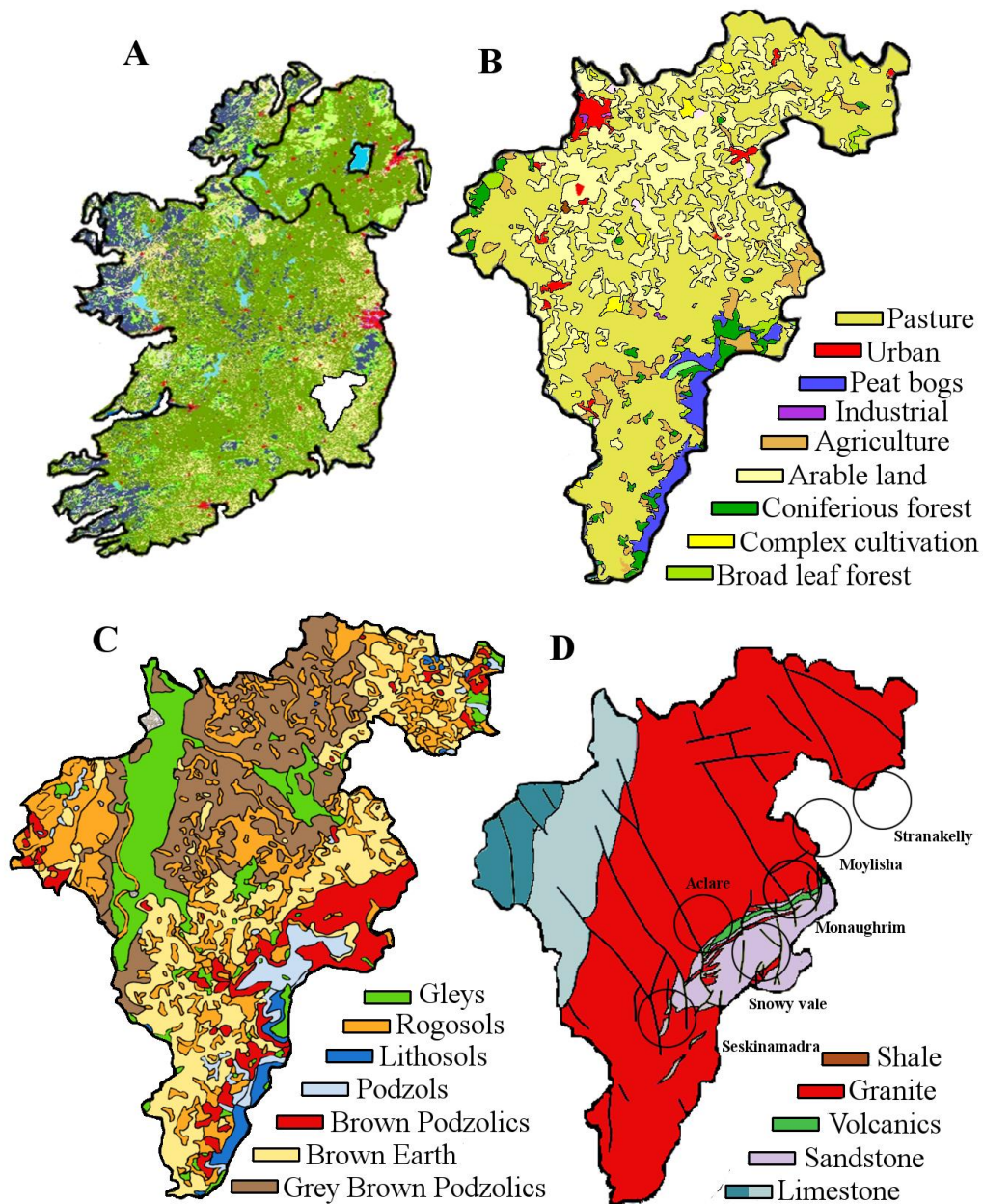
Figure 3.2. (A) Ireland, Co. Carlow area in white**. (B)** Land use in Co. Carlow. **(C)** Major soil groups Co. Carlow. **(D)** Bedrock geology of Co. Carlow (GSI, 2018; IRL EPA, 2018).

Lithium is stored in the leaves of plants and at high concentrations can have toxic effects (i.e. > 100 mg/kg lithium dry matter) (Figueroa *et al.,* 2012; Rogóż *et al.,* 2010; Shahzad *et al.,* 2016). In citrus plants concentrations as low as 10 mg/l used in irrigation waters has been shown to have toxic effects (Kavanagh *et al*., 2018). Toxic symptoms include a

reduction in crop yield and necrosis of leaves. Lithium toxicity and the availability of lithium to plants has been discussed in the literature (Davey and Wheeler 1980; GSI, 2018; Kavanagh *et al*., 2018; Schrauzer, 2002; Shahzad *et al*., 2016; Wallace *et al*., 1977). Citrus fruits are particularly sensitive to lithium levels (Wallace *et al*., 1977). The mining of lithium in the area could result in lithium and other previously unexposed metals finding their way into the soils and water of the area. Agriculture makes up the bulk of land use in Co. Carlow so the influx of any novel metal is an important issue for the people in the area. The agricultural economy of Co. Carlow is based largely on tillage cropping and animal husbandry. Farms also grow cash crops like wheat, barley, and potatoes (Yalamanchali, 2012). Ultimately high lithium levels in soil have the potential to harm some crops. The risk to human health from lithium is determined by its availability to plants. Lithium's mobility in the soil/water phase makes it highly available to plants thus it can easily enter the food chain.

3.2.5. Lithium in Plants

The lithium in the soils of the southeast of Ireland is directly accessible to the majority of plants in the area. Almost all plant species absorb lithium passively from soils because of its similarities to other common alkaline ions like Ca^+, K^+, Na^+, and Mg^+. Lithium easily replaces other alkali ions in plants because of its small ionic size and polarising strength, it has been shown to substitute for up to 50% of potassium in plants and is easily transported throughout plants via the sodium and potassium transport systems (Shahzad *et al.,* 2016). The presence of calcium has been reported to inhibit lithium uptake by plants supposedly because they share the same absorption sites in plant roots (Shahzad *et al.,* 2016). The concentration of lithium in plants is variable and can be anywhere from 0 to thousands of mg/kg (Bingham *et al.,* 1968). Lithium has been measured at a maximum level of > 5000 mg/kg in the *Beta vulgaris* (Common beet) plant and > 3000 mg/kg in the *Helianthus annuus* (Sunflower) plant (Kavanagh *et al*., 2018). Aral and Vecchio-Sadus (2008) report a conservative estimate of 0.2 to 30 mg/kg lithium in the ash of most plants, Saeidnia and Abdollahi (2013) report a lower range of 0.15 to 0.42 mg/kg lithium (Aral and Vecchio-Sadus 2008; Magalhães and Wilcox 1990). Figueroa *et al* (2012) measured the concentrations of lithium in plants in an area in north Chile naturally high in soil lithium levels and reported a lithium range between 1.0 and > 200 mg/kg (Saeidnia and Abdollahi 2013). Lithium is stored in plant leaves. Lithium's role in plant biochemistry is only partially understood; it is not believed to be essential for plant life, growth and development. Despite this, it does have a measurable effect on plants, at low levels (0.05 to 10 mg/kg) lithium stimulates growth in plants, increases crop yields, speeds up

maturation times and even increases resistance to disease. This concentration of lithium in natural waters is almost never observed, very few locations may have elevated lithium concentrations (Figueroa *et al.,* 2013). Lithium toxicity in plants usually manifests as interveinal chlorosis, leaf curling, necrotic lesions and leaf abscission (Figueroa *et al.,* 2012; Shahzad *et al.,* 2016). Bradford (1963) described toxic symptoms in citrus plants when irrigated with water containing lithium concentrations of 0.05 mg/l lithium (Figueroa *et al.,* 2012). Lithium has also been observed to affect the following in plants: photosynthesis, transportation, nitrogen metabolism, circadian rhythms and several enzymatic processes among others (Bingham *et al.,* 1968; Shahzad *et al*., 2016). When *Zea mays* (Maize) plants were treated with water containing 5 mg/l lithium, plant yield increased by 15% and when treated with 50 mg/l a 32% reduction in plant yield was observed (Bradford, 1963; Shahzad *et al.,* 2016). In *Helianthus annuus* 5 mg/l of lithium increased plant yield by 10% and 50 mg/l lithium reduced plant yield by 27% (Bradford, 1963; Shahzad *et al.,* 2016). Other effects lithium has on plants include affecting root growth and gravitational responses, inhibition of inositol production, rhythmic movements and disrupted pollen development (Shahzad *et al.,* 2016). Certain plants are known to be very tolerant and even hyperaccumulators of lithium (Davey and Wheeler 1980). Halophytic plants are exceptionally tolerant to high concentrations of lithium. Yalamanchali (2012) calculated the amount lithium in common plants growing on non-lithium contaminated soil (0.031 – 1.792 mg/kg) which would need to be consumed to approach toxic lithium blood serum concentrations in the body of a 70kg adult human, 30.9kg of the *Beta vulgaris* plant and 24.7kg of the *Lactuca sativa* (Lettuce) plant (Yalamanchali 2012). Yalamanchali (2012) also worked out the amount of the same plants required to be eaten to manifest lithium toxicity symptoms on soil contaminated with lithium at 1000 mg/kg, 0.06kg of Common beet and 0.03kg of Lettuce (Yalamanchali 2012). Acute lithium toxicity from eating plants is unlikely, more likely are chronic toxicity symptoms in people with a consistently elevated amount of lithium in their diet. Lithium toxicity and the availability of lithium to plants has been discussed in the literature (Davey and Wheeler 1980; GSI, 2018; Kavanagh *et al*., 2018; Schrauzer, 2002; Shahzad *et al*., 2016; Wallace *et al*., 1977).

3.3. Materials and Methods

3.3.1. Reagents

Nitric acid (225711 Sigma-Aldrich), hydrochloric acid (435570 Sigma-Aldrich) and hydrogen peroxide (95321 Sigma-Aldrich) were used for soil and plant digestions, acid washing glassware and as sample matrix modifiers. Lithium (59916 Sigma-Aldrich), potassium (96665 Sigma-Aldrich) and sodium (02397 Sigma-Aldrich), standards (certified reference material), TraceCERT®, 1000 mg/l in nitric acid were used to prepare all working standards for Flame Emission Spectroscopy (FES) determinations. Copper (38996 Sigma-Aldrich), iron (16596 Sigma-Aldrich), manganese (77036 Sigma-Aldrich), nickel (42242 Sigma-Aldrich), lead (16595 Sigma-Aldrich), zinc (18827 Sigma-Aldrich), TraceCERT®, 1000 mg/l in nitric acid were used to prepare all working standards for Atomic Absorbance Spectroscopy (AAS) determinations. All reagents used were commercially available, Sigma-Aldrich, Vale Rd, Ballyraine Lower, Arklow, Co. Wicklow, Ireland.

3.3.2. Sampling

Sampling took place along 5 previously established sampling transect lines (Kavanagh *et al*., 2017). Transect sampling lines were chosen not because of a specific topographical feature but rather as a means of sampling as large an area as possible given access and resources. A network of 118 sampling points was established, where samples of soil, ash and ivy were collected. Three sampling events took place during 2015 (triplicate sampling), resulting in > 1,000 samples. Composite soil samples of approximately 200 g were taken from the topsoil at a depth of 10 to 30 cm at each sampling point. When sampling plants, leaves were collected from each species at the same sampling points that soil samples were taken (excess metals are almost always sequestered in the leaves of plants). Approximately 5 to 10 leaves were collected from each plant. Samples were collected in acid-washed High-Density Polyethylene containers and stored at $4° ± 1°$ for the duration of the study.

3.3.3. Sample Preparation

Soil samples were dried in a forced air oven (WiseVen®) at $60 ± 1°C$ to a constant weight overnight. Soil samples were then sieved (2mm) to a fine powder. Leaf samples were washed with deionised water and then dried in a forced air oven (WiseVen®) at $60 ± 1°C$ to a constant weight overnight. Dried leaf samples were then crushed to a fine powder using a pestle and mortar. 1g of leaf material from each plant was acid digested in an open

vessel using a hot plate (WiseStir ®) in a mix of nitric acid and hydrogen peroxide at a ratio of 4:1 for 30 minutes. Samples were gently heated until the plant material was brought into solution. 1g of soil from each sample was also acid digested in an open vessel using a hot plate (WiseStir ®) in a mix of nitric acid and hydrochloric acid (4:1) for 30 minutes. These digestions cannot be considered as total digestions. The digests from each sample (soil, plant) were filtered using Whatman® (800 Centennial Avenue, Building 1, Piscataway, New Jersey 08854-3911, USA) grade 1 filter paper and then using a 0.45 µm cellulose-based membrane syringe filter. The filtrates were brought to a constant volume of 100ml in a volumetric flask with deionised water i.e. giving a dilution factor of 1/100 when analysed.

3.3.4. Analysis

Lithium, potassium, and sodium were analysed using a Sherwood 410 FES using a mixture of natural gas and air, operating at a temperature of 1,700 to 1,800°C (Limit of Detection LOD = 0.13 mg/l and Limit of Quantitation LOQ = 0.44 mg/l). The instrument was recalibrated after every 20 samples. All other metals (Cu, Fe, Mn, Ni, Pb and Zn) were measured using an Agilent (Tech 200 AA series) flame AAS in an air-acetylene flame (AAS, LOD = 0.005 mg/l and LOQ = 0.018 mg/l). After every 50 samples, the instrument was recalibrated. Physico-chemical measurements were taken from soil samples, 10g of soil was placed in a sample container along with 50ml of deionised water. The samples were then agitated for 3 hours. After mixing samples were centrifuged using a Hettich Rotanta 460RF® centrifuge. Conductivity measurements were taken from the supernatant using a Mettler Toledo FiveEasy® FE30 conductivity meter and pH measurements were taken using a Hanna® pH20 pH meter.

3.4. Discussion and Results

3.4.1. Lithium, pH and conductivity in soil (Figure 3.3) (Table 3.1).
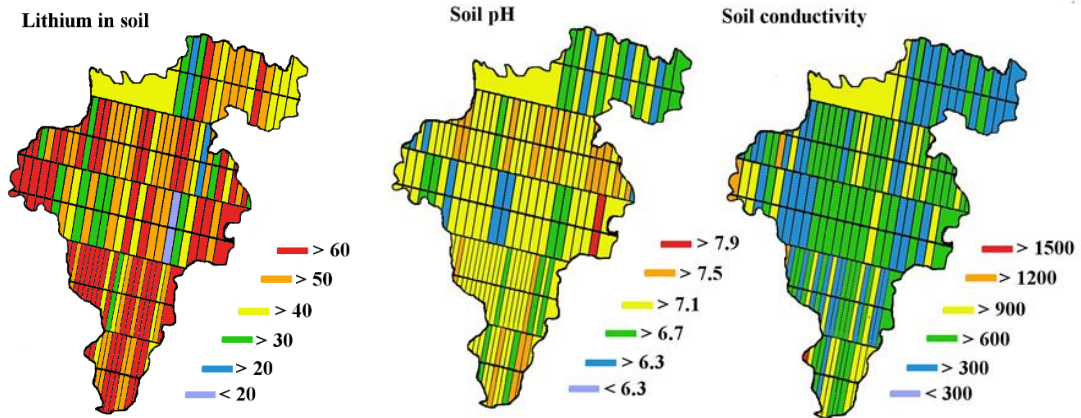
Figure 3.3. Lithium concentration (mg/kg) in the soil, pH measurements, and conductivity measurements in the soil.

Table 3.1. Lithium in soil, pH of soil and conductivity of soil data (soil lithium units = mg/kg) (soil conductivity units = µS/cm), SD = Standard deviation.

Parameter	Mean	SD	Range
Lithium in soil	57.8	18.6	0.2 - 190
pH	7.2	0.36	5.9 – 8.1
Conductivity	736.6	530.2	54 - 3201

3.4.2. Lithium in Ash and Ivy (Figure 3.4) (Table 3.2).
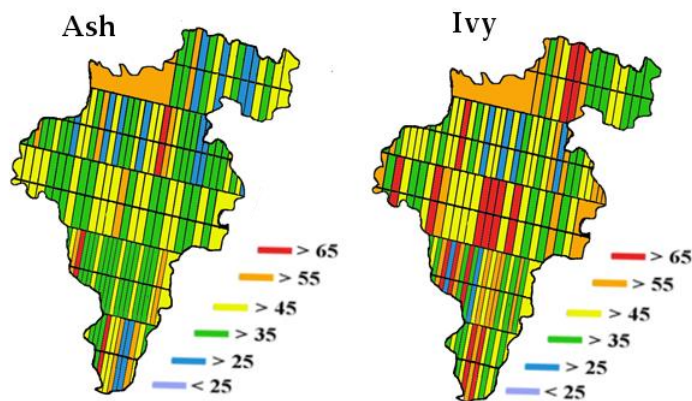
Figure 3.4. Lithium concentration (mg/kg) in Ash and Ivy plants.

Table 3.2. Lithium in Ash and Ivy plants (units = mg/kg), SD = Standard deviation.

Plant species	Mean	SD	Range
Ash	43.7	12.2	0.0 – >160
Ivy	52.3	14.6	0.0 - >180

3.4.3. Recorded accessory metals concentration in measured soils and plants (Tables 3.3. – 3.5).

Table 3.3. Metals concentrations in soil (units = mg/kg), SD = Standard deviation.

Metal	Mean	SD	Range
Cu	24.9	16.5	4.4 – 159.9
Fe	2161.4	4266.1	7.2 – 50200
K	863	553	80 – 6700
Mn	501.4	329.2	21.8 – 2566.8
Na	251.9	145.7	50 – 1230
Ni	22.6	9.5	0.0 – 79.6
Pb	49.3	21.3	1 – 150
Zn	159.8	256.8	18.3 – 4107.7

Table 3.4. Metals concentrations in Ash (units = mg/kg), SD = Standard deviation.

Metal	Mean	SD	Range
Cu	6.9	6.1	0 – 30.8
Fe	57.8	91.8	0 – 616.2
K	2120.8	2128.2	40 – 9260
Mn	19.8	32.9	0 – 412.1
Na	191.9	149.2	40 – 1250
Ni	4.4	4.2	0 – 40.4
Pb	14.1	8.5	0 – 39.8
Zn	34.2	25.5	5.6 – 179.2

Table 3.5. Metals concentrations in Ivy (units = mg/kg), SD = Standard deviation.

Metal	Mean	SD	Range
Cu	7.7	9.6	0 – 72.5
Fe	41.5	52.9	0 – 512.2
K	2780.8	1742.4	2.7 – 10340
Mn	26.4	33.8	0 – 226.9
Na	191.4	163.1	10 – 1630
Ni	2.5	3.2	0 – 13.8
Pb	11.5	8.8	0 – 37.9
Zn	46.6	43.8	3 – 377.5

3.4.4. Data Analysis

Statistical analysis was carried out using Statistical Package for the Social Sciences (SPSS®) version 23.0, International Business Machines (IBM®) Corp, Armonk, New York, USA) and Microsoft Excel® (2016 MSO 16.0.8625.2121). A p-value of 0.05 was considered significant. Bonferroni corrections were used as appropriate. Correlation analysis was used to test the hypothesis of an association between the metals across each medium. No significant correlations were observed in the lithium data among the sampled mediums (Table 3.6). There were n = 354 samples in each group (N = 1,062).

Table 3.6. Correlation matrix of lithium r^2 values in each sample medium.

Lithium	Soil	Ash	Ivy
Soil	1		
Ash	0.0007	1	
Ivy	0.0004	0.0014	1

An Analysis of Variance (ANOVA) was used to measure the variance in the lithium data within the group from each medium. Soil lithium concentration variance was ($F_{(2, 351)}$ = 44.1, p = 8.24x10^{-18}) Ash variance was ($F_{(2, 351)}$ = 83.7, p = 1.9x10^{-30}) and Ivy variance was ($F_{(2, 351)}$ = 60.8, p = 2.04x10^{-23}) in each case the p-values were < α, (i.e. the variance was significant). No significant correlations were observed in the data. A correlation matrix (r^2 values) among soil lithium concentration, measured physicochemical parameters and other metal concentrations in soil contained no significant r^2 values ranging from 0 to 0.1707. A correlation matrix (r^2 values) among Ash lithium concentrations and other metals measured in the plants produced no significant r^2 values, r^2 ranging from 0 to 0.0638. The same was observed for Ivy data. When a correlation analysis was performed on all of the metals in all three mediums (soil, Ash and Ivy) no statistically significant associations were noted, apart from 4 weak correlations, (1), (Soil lead – Soil nickel at r^2 = 0.17), (2), (Ivy manganese – Ivy sodium at r^2 = 0.15), (3), (Ash manganese – Ivy copper at r^2 = 0.15), and (4), (Soil lithium – Soil potassium at r^2 = 0.14) which are likely due to multiple testing issues. No consistent relationship between lithium and any other element was demonstrated in the three media. Perhaps if the sample size were increased more consistent associations would be observed. McGrath *et al.,* (2008) note that because of the complex nature of Irish soils extensive field trial data are often necessary in order to achieve acceptable levels of correlation (Kavanagh *et al.,* 2017). Figure 3.5 illustrates the distribution of the data.
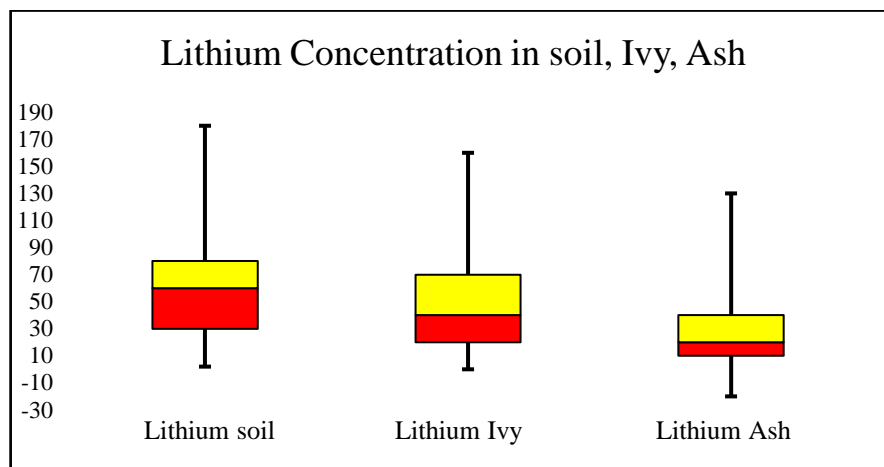
Figure 3.5. Distribution of Lithium Data in Three Mediums (Soil, Ivy, and Ash). Y vertical-axis units, mg/kg of lithium.

We report an average concentration of 57.8 ± SD 18.6 mg/kg ranging from 0.2 to 190 mg/kg lithium in the soil (n = 354 samples) as a measurement of lithium soil concentrations for the area sampled in Co. Carlow, southeast Ireland. This figure is larger than that reported as the generally accepted "background concentration" of 20 mg/kg lithium in the Earth's crust a finding which is not unexpected given the known presence of the granitic bedrock geology and theoretically the lithium mineralisation in the east of the sampling area. Lithium is known to occur at higher than background concentrations in areas which are predominantly granitic, which is the case in the study area (Hawrylak-Nowak *et al.,* 2012). Granites tend to commonly have lithium concentrations > 30 mg/kg (Aral and Vecchio-Sadus 2008; Kabata-Pendias, 2010). A t-test carried out on our lithium soil data with a null Ho that our data was not statistically different than the generally accepted background concentration of lithium in the Earth's crust. Given a p-value of = 2.08×10^{-18} the Ho was rejected, showing that lithium soil concentrations are elevated in the area compared to background lithium concentrations. Our data are similar to data published by a study which was mapping available metal concentrations in the soils of Ireland in 2007 (McGrath *et al.*, 2008). Fay *et al.,* (2007) reported on available metals in soil, whereas our study reported on pseudo-total metals (i.e. pseudo-total, in the absence of the complete acid digestion of silicates using hydrofluoric acid). Although the data is not directly comparable, we present it here as a comparison in the absence of any other such data. The methods used by Fay *et al.,* (2007) were not identical to the methods used in this study. According to Fay *et al.,* (2007), the normal range of lithium expected to occur in Irish soils is between 20 and 30 mg/kg (McGrath *et al.*, 2008). They reported the following for lithium concentrations in the soils of Ireland taken from n = 1310 samples, a minimum value of < 2 mg/kg, a maximum value of 165.7 mg/kg, and a median value

of 19.3 mg/kg. Fay *et al.,* (2007) sampled 24 sites in the Co. Carlow area and provided images with their work that we have adapted and presented here for comparison (Figure 3.6). The data and ranges from each study compare favourably but are not the same. We report a higher concentration of lithium in the soils of the area than Fay *et al.,* (2007), for the Co. Carlow area of Ireland we report from n = 118 sampling sites sampled in triplicate, a minimum value of 0.2 mg/kg, a maximum value of 190 mg/kg, and a median value of 60 mg/kg.
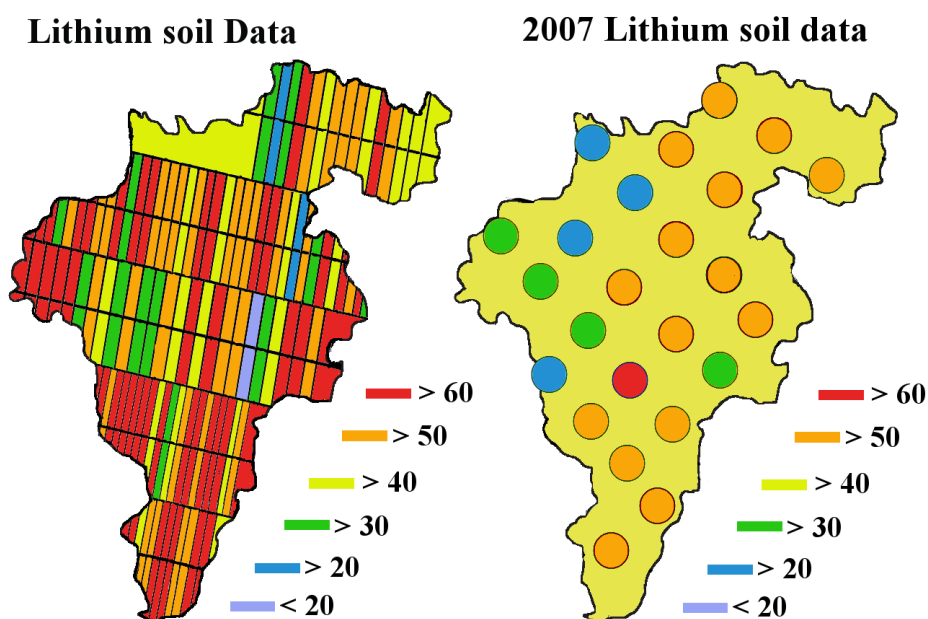
Figure 3.6. Lithium soil concentrations measured in this study and lithium soil concentrations measured in the Fay *et al.,* (2007) study, units are in mg/kg lithium (McGrath *et al*., 2008).

The 2007 map showed generally higher concentrations of lithium to be prevalent in the east of Co. Carlow corresponding to the presence of the Leinster granite and known locations of lithium mineralisations. Twenty-four soil samples were taken from the Co. Carlow area. The authors state that in the southeast of Ireland lithium soil concentrations may reach levels between 40 and 50 mg/kg while in the northeast and southwest of the country lithium occurs at an average concentration of 20 mg/kg (McGrath *et al*., 2008). Bradford *et al* (1996) measured the concentrations of lithium and several other trace metals in the soils of the entire state of California, USA. They reported the following figures for lithium, average lithium concentration = 23 mg/kg, SD = 17 mg/kg and range from 4 to 90 mg/kg (Fay *et al*., 2007).

Lithium is taken up by plants through the root epidermis and then via the apoplast or symplast pathway travels to the cortex of the root and the vascular system of the plant eventually ending up in the plant leaves. They are sequestered by either metal-ligand complexation or removal to inactive compartments such as vacuoles and cell walls (Davey and Wheeler 1980). Lithium tolerant species include *Solanum lycopersicum* (Tomatoes) *Chloris gayana* (Rhodes grass) and *Hordeum vulgare* (Barley) (Bingham *et al.,* 1964). Highly lithium-sensitive species include *Persea americana* (Avocado), *Glycine max* (Soybean) *Citrus sinensis* (Oranges) and *Vitis vinifera* (Grape) each of these species have shown lithium toxicity symptoms at levels >100 mg/kg lithium dry matter (Bingham *et al.,* 1964). In 2013 a new lithium accumulator plant was discovered in China (*Apocynum Venetum)* and could potentially be used for Geobotanical prospecting for lithium deposits (Bradford *et al*., 1996). Regarding plant lithium levels, we report an average concentration of $43.7 \pm$ SD 12.2 mg/kg lithium measured in the leaves of Ash (*Fraxinus excelsior)* plants in the study area and an average concentration of $52.3 \pm$ SD 14.6 mg/kg in the leaves of Ivy (*Hedera hibernica)* plants. Given the large variation in the quoted figures for lithium content in plants from the literature (i.e. 0.01 to 6,000 mg/kg reported by Magalhães and Wilcox (1990) our data appears on the low end of this range (Bingham *et al*., 1968). Although when compared to figures quoted by Aral and Vecchio-Sadus (2008) who reported a range of 0.2 to 30 mg/kg lithium in plants and Figueroa *et al.,* (2013) who reported a lithium range between 1.0 and > 200 mg/kg our data seems to fit the norm (Aral and Vecchio-Sadus 2008; Jiang *et al*., 2014). A t-test between the two plant lithium data sets with a Ho that there was no difference between the lithium concentrations in the two plants was performed. Given a p-value of $= 8.6 \times 10^{-07}$ the Ho was rejected, which can be interpreted as there being statistically more lithium present in the leaves of Ivy plants. Which is contrary to what was expected given the fact that there is less lithium available in the organic topsoil layer where Ivy roots exist than in the deeper topsoil where Ash plant roots are present. The significant difference in the amount of lithium absorbed by Ash and Ivy indicates that the amounts of lithium absorbed by each of these plant species were not predominantly determined by their root structures. Both of the average lithium concentrations recorded in the plants (Ash at 43.7 and Ivy at 52.3 mg/kg) were slightly below the average recorded soil lithium concentration of (57.8 m/kg) suggesting that neither plant species is a hyperaccumulator of lithium (Davey and Wheeler 1980). The data may also imply that both plants have in place lithium excluding/limiting mechanisms as part of their makeup.

3.5. Conclusion

Lithium concentrations in *Fraxinus excelsior* and *Hedera hibernica* did not correlate well with lithium levels in the soil. There was no statistically significant association observed in the lithium data among the three mediums. According to Schrauzer (2002), the amount of lithium in the majority of plants is usually correlated with Ni, Co, Cu, Fe, Ni, and Mn and to a lesser extent Al, Cd, and Pb (Kabata-Pendias, 2004). According to Cannon *et al.,* (1975) the amount of lithium in plants correlates well with the amount of lithium in the soils of southern California and Nevada North America, but only at average lithium levels above 100 mg/kg present in soils (Schrauzer, 2002). In this work, there were no observed relationships between lithium concentrations in plants and the other measured metals. Our data also indicates neither plant would be suitable for indicating the amount of lithium present in the local soils. For some plants, the presence and concentration of metal in their tissues are used to indicate the presence of a specific metal in the soil. The technology is commonly referred to as Geobotanical prospecting (Figueroa *et al*., 2013). The presence of *Equisetum arvense* (Horsetail) has been interpreted as an indication of gold, *Eriogonum ovalifolium* (Buckwheat) may indicate silver, *Eschscholtzia mexicana* (Mexican poppy) copper, and *Viola calaminaria* (Violet) zinc (Figueroa *et al*., 2013). The geographic distribution of the lithium in the soil of the area appears to be random. Certainly, it is not at a higher concentration near the known sources of lithium in the bedrock. Which may be due to the fact that the known lithium mineralisations are situated at an altitude above the level of the local water table in a poor aquifer and are unsaturated, limiting dissolution of the lithium (McGrath *et al*., 2008). No consistent relationship between lithium and any other measured metal could be demonstrated to occur between the plants and soil. Davey and Wheeler (1980) also found no correlations between lithium concentrations in selected plants and lithium concentrations in the soil of Papua New Guinea (Cannon *et al*., 1975).

Lithium's current and future role in our economy means that it is now being classified as an emerging environmental contaminant. Despite its relatively low toxicity; it has the potential to threaten crop production and enter the food chain easily where it may affect human health. The responsibilities of mining companies toward the environment, awareness of their impact and stewardship have never been better in the history of the industry. Despite this, accidents still, happen. The risk of a lithium metal influx to the environment of Ireland from a mining-related accident is low but not impossible. The slow release and gradual accumulation of lithium in the flora and fauna of the area is far

more likely to occur if and when the lithium deposits are exposed. The data presented here should act as a benchmark of lithium concentrations in the soils and plants of the area prior to any mining.

Chapter 4

Induced Plant Accumulation of Lithium

The potential for Plants to Hyperaccumulate Lithium as an alternative Mining Technology.

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4.1. Abstract

Lithium's value has grown exponentially since the development of lithium-ion batteries. It is usually accessed in one of two ways: hard rock mineral mining or extraction from mineral-rich brines. Both methods are expensive and require a rich source of lithium. This paper examines the potential of agro-mining as an environmentally friendly, economically viable process for extracting lithium from low-grade ore. Agro-mining exploits an ability found in few plant species, to accumulate substantial amounts of metals in the above ground parts of the plant. Phyto-mined metals are then retrieved from the incinerated plants. Although the actual amount of metal collected from a crop may be low, the process has been shown to be profitable. We have investigated the suitability of several plant species including *Brassica napus* and *Helianthus annuus*, as lithium accumulators under controlled conditions. Large plant trials were carried out with/without chelating agents to encourage lithium accumulation. The question we sought to answer was, can any of the plant species investigated accumulate lithium at levels high enough to justify using them to agro-mine lithium resources. Results show maximum accumulated levels of >4000 mg/kg lithium in some species. Our data suggest that agro-mining of lithium is a potentially viable process.

Keywords: *lithium; induced accumulation; agro-mining*

4.2. Introduction

Agro-mining describes a process that uses plants to abstract metals from soils (Chaney, 1983). The process ideally harvests metals from high biomass crops which are grown in metal-rich soils, particularly those associated with sub-economic mineralization (Sheoran, 2009). The crop is harvested, and incineration of the biomass generates a high metal concentration grade bio-ore. In some cases, energy is recovered during the incineration process (Van Der Ent *et al*., 2009). Agro-mining offers the possibility of exploiting metal-rich soil substrates that are otherwise uneconomic to mine, its impact on the environment is minimal compared to conventional mining methods (opencast, underground) (Garbisu and Alkorta 2009). Agro-mining can be thought of as an extension of the same process as growing fuel (alcohol) from crops (Brooks and Robinson 1998). The goal is to extract viable amounts of metals from substrates with profit (Robinson *et al*., 2015). The agro-mined metal is virtually sulphur free unlike metals extracted from ore bodies, so the smelting process requires less energy and does not contribute significantly to acid rain (Sheoran *et al*., 2013). The metal concentration of a bio-ore is often higher than conventional ores, therefore requires less storage space. Agro-mining offers an environmentally friendly alternative to energy-intensive conventional mining practices (Sheoran, 2009). Although agro-mining will not replace conventional mining processes the technology is appealing both economically and socially (Robinson, 1999)

Moreover, agro-mining can be an environmentally responsible approach to site remediation (Renault *et al*., 2000). It can also help like any other plant-based reclamation process to restore landscapes damaged by mining and industrial activities. Restoration of such landscapes is one of the most pressing issues of the modern age (Timofeeva, *et al*., 2017). Probably the first record of metal accumulation in a plant was reported in 1855 by the German botanist Alexander Carl Heinrich Braun, who reported elevated levels of zinc in the *Viola calaminaria* plant (Reeves and Baker 2000). In 1865 the German botanist, Julius von Sachs, in his book 'Experimental Physiology of Plants', referred to *Thlaspi caerulescens,* a plant in the *Brassicaceae* family to contain over 17% Zn in its ash (Assunção, *et al*., 2003; Sachs, 1865) In 1885 another German botanist Albert Bernhard Frank reported *Thlaspi caerulescens* and *Viola calaminaria* to contain over 10% Zn in plants ash (Sheoran, 2009). In the 1930s elevated levels of selenium in *Astragalus* plants was reported (Jaffré *et al*., 1976). In 1948 Italy, Minguzzi and Vergnano reported a concentration of 7.9% Nickel in the dry weight the *Alyssum bertollonii* plant, a species of the low-growing flowering plant also from the *Brassicaceae* family (Assunção, *et al*.,

2003; Verbruggen *et al.,* 2009). The most recent rejuvenation of plant metal accumulation technology began in 1976 in the French territory of New Caledonia in the Southwest Pacific where researchers discovered the *Pycnandra acuminata* tree from the *Sapotaceae* family that perfectly fitted the title of nickel hyperaccumulator plant (Brooks *et al*., 1998). They were the first group of researchers to use the term hyperaccumulator plant (HAP). HAP plants absorb extraordinary high levels of metals in their tissues, 100 to 1000 times higher than levels in the substrate in which they grow, they are also very tolerant to high metal soil conditions. They achieve this without apparent harm while growing in their natural habitat (Van Der Ent *et al*., 2009). Non-HAP plants do not display this trait and when grown on the same substrate will not accumulate metals at an elevated concentration and may perish. The word HAP has been used extensively ever since the New Caledonian researchers developed the theory, in countless publications. The nickel content within the latex of the *Sebertia acuminate* tree was recorded at a mean level of 26% and 12% in leaves in its dry mass (Brooks *et al*., 1998). Since then a lot of research emphasis has been placed on the evaluation of the metal hyperaccumulating capacity of high biomass plants that can be easily and quickly cultivated using established agronomic practices (Brooks and Robinson 1998).

Metal HAPs are relatively rare, and often growing on metalliferous soils in remote areas geographically (Baker *et al*., 1994a). It has been found that over 90% of known HAPs occur only on serpentine (ultrabasic) mineralized soils around the world (Pollard *et al*., 2014). Metals are regularly stored in plant leaves, especially in the epidermis and the cuticle. They are sequestered by either metal-ligand complexation or removal to inactive compartments such as vacuoles and cell walls (Rascio and Navari-Izzo 2011). Some plants sequester certain toxic metals around the roots while other plants store metals in their stems. The prevailing theory as to why plants accumulate metals in their tissues is protection from insect and animal herbivory as well as protection from disease. In this study, only the leaves were considered when reporting on the metal content of each plant. The principal distinguishing feature between a HAP and a non-HAP is that a HAP can reach metal concentrations of 100 to 1000 times higher than those in non-HAP species when grown on the same soil (Assunção, *et al*., 2003; Garbisu and Alkorta 2009; Rascio and Navari-Izzo 2011). Many plant species have been discovered which have very high concentrations of metals in their tissue. A list of some metal levels recorded in HAP plants is included in (Table 4.1). Metal accumulating plants are observed in over 500 species across several families, orders and genera of vascular plants and in approximately 0.2%

of angiosperms (Sarma, 2011). Plants from the *Brassicaceae* family feature extensively in the HAP group (Baker *et al*., 1994b).

Table 4.1. Concentrations of some metals recorded in known HAP plants from the literature.

Metal	Plant Species	(mg/kg)	Reference
As	*Pteris vittata*	23,630	(Wang *et al*., 2007)
Cd	*Thlaspi caerulescens*	14,000	(Assunção, *et al*., 2003)
Co	*Haumaniastrum robertii*	10,200	(Dodson *et al*., 2012)
Cu	*Aeolanthus biformifolius*	9,000	(Morrison *et al*., 1979)
Mn	*Macadamia neurophylla*	55,000	(Brooks *et al*., 1998)
Ni	*Thlaspi caerulescens*	4,700	(Assunção, *et al*., 2003)
Pb	*Brassica juncea*	15,000	(Blaylock *et al.,* 1997)
Se	*Astragalus bisulcatus*	10,000	(Freeman *et al.,* 2006)
Tl	*Biscutella laevigate*	14,000	(Anderson *et al.,* 1999)
U	*Brassica juncea*	5,000	(Huang *et al.,* 1998)
V	*Brassica juncea*	10,111	(Elektorowicz and Keropian 2015)
Zn	*Arabis paniculate*	20,800	(Tang *et al.,* 2009)

HAP traits include higher metal content in the leaves of the plant than non-HAP's, high metal tolerance, low growth rates and low biomass yields (Ernst, 2006; Krämer, 2010). Some of these traits like slow growth and low biomass make it somewhat impractical to use these plants for agro-mining; for this reason, more recent research has focused on high biomass crop species and the technology of induced metal accumulation in plants. Induced metal accumulation uses non-HAPs with a large biomass to accumulate significant amounts of metals. One form of induced metal accumulation in plants uses chelating agents. These chelating agents are applied to the soil where they form water-soluble metal organic complexes through the dissolution of precipitated compounds and desorption of sorbed elements, making metals more available for plant uptake (Norvell, 1984; Salt, 1995). These chelating agents are added to the soil near the end of the plant-growth phase, the plants are then harvested within several days or a week (Manitoba Mine, 2018). The solubilised metals are taken into the plant via the apoplast pathway rather than the symplast pathway (Nowack *et al*., 2006). There are numerous studies discussing the efficacy of using chelating agents to induce metal accumulation in plants (Nowack *et al*., 2006; Peters, 1999). Probably the best known and most successful chelating agent is ethylenediaminetetraacetic acid (EDTA), first synthesized in 1935 by

the Interessen-Gemeinschaft Farbenindustrie AG company in Frankfurt am Main, Germany (Kołodyńska, 2011). EDTA is one of the cheapest and most suitable complexing agents for many technical purposes and has the best cost/performance ratio of all chelates (Nörtemann, 2005). EDTA is not readily biodegradable, although it experiences some photodegradation at a very slow rate in the environment. Its biodegradation has been demonstrated using specialized bacterial cultures (Kołodyńska, 2011; Nörtemann, 2011; Satroutdinov *et al.,* 2005). The use of EDTA in phytoremediation/phytoextraction has been banned in most countries because of the dangers associated with complexed metals been leached into the environment. The problem with EDTA is that it is persistent in the environment and can easily leach into and accumulate in natural waters, its environmental toxicity has been discussed (Bucheli-Witschel and Egli 2001; Nowack, 2002). EDTAs exceptional ability to bind metals into a complex can contribute to heavy metal bioavailability and remobilization processes in the environment, EDTA can also solubilize radioactive metals and increase their environmental mobility (Oviedo and Rodríguez 2003). Concentrations of 2.2 mg/l EDTA or greater in natural waters can cause eutrophication problems, but this level is rarely observed (Nowack *et al.*, 2006).

Thousands of tonnes of EDTA are used every year in industries such as detergent and paper production (Kołodyńska, 2011). EDTA has a low toxicity profile for humans and is commonly used in cosmetics and pharmaceuticals. Its environmental toxicity is also low and limited to point source emissions to natural waters. Environmental risk levels for EDTA in the environment are available (Van Herwijnen and Van Fleuren 2009). Ethylenediamine-N, N'-disuccinic acid (EDDS) is a biodegradable alternative of EDTA and is its closest performing counterpart. EDDS is readily degraded and one of the more widely studied biodegradable chelating agents. It has seen some commercial application in the detergent industry as a replacement for EDTA (Hyvönen, 2008; Schowanek *et al.*, 1997; Tandy *et al.*, 2004). EDDS has three stereoisomers [SS], [RR], and [SR] / [RS] of which only the [SS]-isomer is 100% biodegradable (Meers *et al.*, 2008; Takahashi *et al.,* 1997). All works discussed in this paper consider only the [SS]-isomer when referring to EDDS. The biodegradability of several chelating agents in activated sludge has been studied (Metsärinne *et al.*, 2001). The authors of this study found that the EDTA molecule remained intact for up to 100 days, whereas EDDS was biodegraded rapidly in the activated sludge. The biodegradation of EDDS has been shown to be effective even in polluted soils (Turan and Esringu 2007). Some metal complexes of EDTA and EDDS are susceptible to photodegradation (Kos *et al.*, 2003; Meers *et al.*, 2008; Nowack, 2001). In

general, chelating agents which form complexes with relatively low stability constants are readily degradable whereas those forming stronger complexes (i.e., higher stability constants) are more resistant to biodegradation (Hyvönen, 2008). Crown ethers (Monocyclic polyethers) such as 12-crown-4 have a marked selectivity for alkali metals and are normally used to complex alkali cations like lithium. These compounds and similar compounds like cryptands and lariat ethers which have equivalent properties to crown ethers are generally very expensive. The complexation constants for lithium are very weak compared to other metals but multidentate ligands do form complexes with lithium. The Li-EDTA complex has a stability constant of 2.79 while the Li-EDDS complex has a very small stability constant. The stability of an EDDS metal complex is relatively low when compared to an EDTA complex, for example, a Ca-EDTA complex has a stability constant of 10.65 while the Ca-EDDS complex is around 4.6. This is especially true for lead, because of the high stability constant of the Pb-EDTA complex at 18.0 versus the Pb-EDDS complex at 12.7 (Huang *et al*., 1998). Several studies show that chelating agents such as EDTA and EDDS can be used to increase metal mobility in soils making them more available to plants (Blaylock *et al*., 1997; Huang *et al.,* 1998; Hyvönen, 2008; Nowack *et al.,* 2006; Pereira *et al.,* 2010; Seth *et al*., 2011).

EDTA has been used in several induced metal accumulation studies. The addition of EDTA to lead spiked soil has been shown to increase the lead content in *Canavalia ensiformis* (Jack bean) and *Helianthus annuus* plants significantly (Luo and Shen 2005; Pinto *et al*., 2014). Alternatively, a weak extraction of lead using EDDS has been noted several times (Nowack *et al.,* 2006). In some rare cases, EDDS outperforms EDTA for metal uptake in plants, dependent on species and the target metal (Tandy *et al*., 2006). The effects of the application of EDTA, EDDS and citric acid on the uptake of Cu, Cd, Pb, and Zn by the *Zea mays* and *Phaseolus vulgaris* (Common bean) plants have been studied. Results showed that EDDS was more efficient at solubilizing copper and zinc than EDTA and that EDTA was better at solubilising lead and cadmium than EDDS (Hauser *et al.,* 2006). In a study of EDDS chelate induced metal accumulation from soil using the *Helianthus annuus* plant, results showed levels >4000 mg/kg copper and >300 mg/kg lead in the plant tissues (Grčman *et al.,* 2003). The same group of researchers also reported that EDDS outperformed EDTA solubilising copper and zinc in solution (Fine *et al*., 2014). Several studies comparing the effectiveness of EDTA and EDDS to induce metal accumulation in plants have been performed (Cao *et al*., 2007; Lenntech, 2017; Nowack *et al.,* 2006; Schrauzer, 2002; Shilev *et al*., 2007). Cao *et al.,* (2007) used EDDS successfully (4 and 8 mmol/kg of soil) to phytoremediate lead and zinc using the *Mirabilis*

jalapa plant (Marvel of Peru) (Cao *et al*., 2007). Nowack et al., (2006) showed significant increases in plant metal uptake using EDDS as a chelating agent (Nowack *et al.,* 2006). Shilev *et al*., (2007) introduced EDDS into the rhizosphere of *Zea mays* (Maize) and *Helianthus Hibernica* (Sunflower) to enhance the accumulated concentrations of cadmium, lead and zinc (Shilev *et al*., 2007).

Lithium is taken up easily by most plants but is not thought to be an essential element for plant health (Wallace *et al.,* 1977). The question of whether plants need lithium is still debated (Kabata-Pendias and Pendias 1984). It has not been shown to act as a cofactor in any enzyme or enzymatic transportation system within plants. The concentration of lithium in plants is highly variable (Shahzad *et al*., 2016). The amount of lithium in plants is a function of the amount of lithium in the soil substrate in which the plants are growing because of this it has been suggested that the concentration of lithium in plants is a good guide to the amount present in the soil (Ammari *et al*., 2011). One study reports that lithium occurs in plants at levels of 0.15 to 0.3 mg/kg (Aral and Vecchio-Sadus 2008). Others report that the amount of lithium in plants lies somewhere between 0.2 and 6000 mg/kg (Kent, 1994; Magalhaes *et al.,* 1990; Hawrylak-Nowak *et al.,* 2012). The amount of lithium in plants is dependent on the plant species and the amount of available lithium in the soil. Lithium is translocated to the leaves of plants where it is immobilized (McStay *et al*., 1980). Lithium is known to act upon plants in three ways: at low concentrations, it increases resistance to disease and stimulates growth. At high concentrations it inhibits growth and can become toxic to plants with a low tolerance for lithium like citrus plants (McStay *et al*., 1980). There are numerous studies showing that at low lithium levels, plant growth stimulation has been observed (Aral and Vecchio-Sadus 2008; Bingham *et al.,* 1964; Cannon *et al*., 1975; Elektorowicz and Keropian 2015; Jiang *et al*., 2014; Kabata-Pendias and Pendias 1984; Kent, 1994; Li *et al*., 2009; Saeidnia and Abdollahi 2013; Tölgyesi, 1983; Wallace *et al.,* 1977).

Species of plants tolerant to lithium are found mainly in the *Solanaceae* and *Asteraceae* families and are also said to include the *Ranunculacae* and *Rosaceae* families (Anderson, 1990; Ammari *et al*., 2011; Magalhaes *et al.,* 1990; McStay *et al*., 1980). In 2013 a new lithium accumulator plant was discovered in China *Apocynum venetum*. This species could potentially be used to geobotanically prospect for lithium deposits (Schwertfeger and Hendershot 2013). *Cirsium arvense* (Creeping Thistle) and *Solanum dulcamera* (bittersweet nightshade) have been shown to accumulate lithium at 3 to 6 times more than other plants (Wuana *et al.,* 2010). A study of *Brassica juncea'*s (Indian mustard) ability

to accumulate lithium, vanadium and chromium from lithium mine tailings has shown concentrations of lithium > 300 mg/kg in the plant (Elektorowicz and Keropian 2015). Elevated concentrations of lithium have been recorded in many plant species across many fields of research, (Table 4.2.) lists some of these species.

Table 4.2. Some recorded levels of lithium in plants from several lithium plant tolerance studies.

Metal	Plant Species	(mg/kg)	References
Li	*Allenrolfea occidentalis*	3,000	(Tölgyesi, 1983)
Li	*Apocynum venetum*	1,800	(Saeidnia and Abdollahi 2013)
Li	*Beta vulgaris*	5,500	(Cannon *et al*., 1975)
Li	*Brassica cartinata*	8,000	(Jiang *et al*., 2014)
Li	*Chloris gayana*	2,400	(Cannon *et al*., 1975)
Li	*Distichlis spicate*	1,000	(Tölgyesi, 1983)
Li	*Gossypium hirsutum*	1,947	(Wuana *et al*., 2010)
Li	*Gossypium hirsutum*	2,385	(Shahzad *et al.,* 2016)
Li	*Gossypium malvaceae*	1,100	(Cannon *et al*., 1975)
Li	*Helianthus annuus*	3,292	(Bingham *et al.,* 1964)
Li	*Hordeum vulgare*	1,131	(Wuana *et al*., 2010)
Li	*Hordeum vulgare*	2,058	(Shahzad *et al.,* 2016)
Li	*Juncus cooperi*	3,000	(Tölgyesi, 1983)
Li	*Lycium barbarum*	1,120	(Tölgyesi, 1983)
Li	*Nasturtium officinale*	1,216	(Hawrylak-Nowak *et al.,* 2012)
Li	*Raphanus raphanistrum*	1,008	(McStay *et al.,* 1980)

4.3 Materials and Methods

4.3.1. Reagents

Sodium salt-based chelators were used in this work and were of analytical grade. Disodium ethylenediaminetetraacetate dihydrate, EDTA disodium salt ($C_{10}H_{14}N_2Na_2O_8$ · $2H_2O$) (E6635 Sigma Aldrich Ireland Ltd., Vale Road, Arklow, Wicklow, Ireland) was used to prepare all EDTA solutions at 0.05 M. This salt is only partially soluble in water at room temperature, the gradual addition of a concentrated sodium hydroxide solution (100ml of 10% NaOH in H_2O) was used to solubilise the salt. All EDDS solutions were made from an [SS]-EDDS trisodium salt solution in at 0.05M ($C_{10}H_{13}N_2Na_3O_8$) (92698 Sigma Aldrich Ireland Ltd., Vale Road, Arklow, Wicklow, Ireland). Lithium solutions for soil spiking were prepared from lithium chloride salt (203637 Aldrich), ≥99.99% trace metals basis. Lithium (59916 Sigma Aldrich Ireland Ltd., Vale Road, Arklow, Wicklow, Ireland), potassium (96665 Sigma-Aldrich) and sodium (02397 Sigma-Aldrich),

standards (certified reference material), TraceCERT®, 1000 mg/l in nitric acid were used to prepare all working standards for FES determinations. Plants were fertilised using the commercially available fertiliser Miracle-Gro® (Scotts Miracle-grow, Marysville, Ohio, USA) water soluble all-purpose plant food, Total nitrogen-24%, 3.5% ammoniacal nitrogen, 20.5% urea nitrogen, available phosphate-8%, soluble potash-16%, boron-0.02%, copper-0.07%, iron-0.15%, manganese-0.05%, molybdenum-0.0005%, zinc-0.06%. Plant and soil digestions were carried out using, nitric acid (225711 Aldrich), 70%, purified by redistillation, ≥99.999% trace metals basis, hydrogen peroxide solution (95321 Sigma-Aldrich), ≥30%, for trace analysis and hydrochloric acid (435570 Sigma-Aldrich), reagent grade, 37%. Glassware was thoroughly soaked in dilute nitric acid and rinsed several times with deionized water before use. Nitric and hydrogen peroxide were used as matrix modifiers in all plant working standards. All reagents used were commercially available from Sigma Aldrich Ireland Ltd., Vale Road, Arklow, Wicklow, Ireland apart from Miracle-Gro® which is widely available. Soil used in these experiments was obtained from Westland Horticulture Ltd., 14 Granville Industrial Estate Granville Road Dungannon Co. Tyrone BT70 1NJ.

4.3.2. Germination Trials

Seed germination trials were carried out to assess the total germination percentage of 34 plant species in the presence of lithium and selected chelating agents. Most plants show tolerances to lithium because of the similarity of the element to potassium and sodium which are ubiquitous in all plants. Lithium also has comparable effects on the metabolic processes of plants to potassium and sodium. Taking this into account the information obtained from these germination trials can only be viewed as general. The trials were conducted this way to narrow down the number of initial plant species to carry on to plant trials. The trials were carried out over 21 days at a temperature of 19 ± 1 °C. Test groups contained 10 replicates of 4 seeds, for each concentration of lithium tested (n = 400 seeds per plant tested). Seeds were placed on cotton wool in a petri dish along with 4 ml of a specific concentration of lithium solution. The lithium solutions ranged from 20 mg/l to 1000 mg/l with controls. Thirty-four species of plants were selected for germination trials, firstly in the presence of lithium and then in the presence of lithium and EDTA and lithium and EDDS. The plants used were: *Brassica napus, Brassica oleracea var. capitata, Helianthus annuus, Solanum lycopersicum, Nicotiana tabacum, Lolium perenne, Pisum sativum, Vicia faba, Phaseolus coccineus, Hordeum vulgare, Avena sativa, Beta vulgaris, Daucus carota, Allium ampeloprasum, Mentha spicate, Cucumis*

melo, Spinacia oleracea, Brassica oleracea var. italica, Brassica oleracea var. gemmifera, Brassica oleracea gongylodes group, Brassica hirta, Brassica oleracea var. botrytis, Brassica rapa subsp. rapa, Brassica rapa subsp. chinensis, Salvia splendens, Brassica hirta, Raphanus raphanistrum, Brassica oleracea var. sabellica, Brassica oleracea borecole, Cardamine hirsuta, Nasturtium officinale, Eruca sativa, Lepidium sativum and *Cardamine hirsuta.*

4.3.3. Soil Preparation

Lithium occurs in most soils in small quantities and was present in the soils used in these experiments. All soil used in these experiments was a commercially obtained top soil, consisting of a sieved dark brown/black rich clay loam soil with a high humus content. The soil used in this work (Top soil) available commercially in Ireland, sourced from Westland Horticulture Ltd, Alconbury Hill, Huntingdon, Cambridgeshire PE28 4HY, United Kingdom. Ten 1g soil samples from our bulk soil supply were characterised for lithium content. Soil samples were thermally acid digested in hydrochloric and nitric acid at a ratio of 1:1 for 2 hours, filtered and then analysed for their lithium content using FES. The $\bar{x}$ lithium concentration measured in soil samples was 20.9 mg/kg SD = 8.2 mg/kg ranging from 9 to 34 mg/kg. Soil was dried and then sieved (4 mm) for pot experiments. Approximately 2 kg of soil was transferred to polyethylene pots (15 cm diameter and 15 cm depth). All plants in these trials were grown in a large greenhouse maintained at a relative humidity of 69.5% (day/night) and an air temperature of 26 ± 3 °C. Soils used in these experiments was artificially spiked with lithium. Lithium as lithium chloride was made up in deionised water at each concentration of lithium required (i.e., of 0, 20, 50, 100, 150, 200, 300, 400, 500 and 1000 mg/kg). Each plant species tested required 100 pots (i.e., 10 pots at each concentration). 10 pots required around 20 kg of soil. Groups of 20 kg of soil were saturated with a specific lithium solution, mixed allowed to dry and then the process repeated until testing of the soil for lithium concentration showed that the soil was ± 5 mg/kg the desired concentration. These soils were then transferred to pots. All pots for each trial were treated this way. This method of 'spiking' the soil with lithium was adapted from other works (Strange, 1953).

4.3.4. Plant Trials

Initial plant trials consisted of 100 plants of each of the five species (*Brassica napus, Brassica oleracea var. capitata, Helianthus annuus, Solanum lycopersicum* and *Cardamine hirsuta*) planted in lithium amended soils. Plants were grown in soils amended

with lithium at levels of 20, 50, 100, 150, 200, 300, 400, 500 and 1000 mg/kg with 10 control plants grown in untreated soil. Ten plants were grown (one plant per pot) at each concentration, totalling ten groups of ten plants for each of the five species (N = 500 initial plants, N = 500 pots). Plants were grown for approximately four months to maturity and then harvested. The plants were watered on alternate days and fertilised once a week with nutrients in the form of Miracle grow® a commercially available water soluble all-purpose plant food. The study was conducted in a screened greenhouse at the Institute of Technology Carlow, Ireland. TomtechHC80 environmentally controlled research greenhouse facility, available from TOMTECH, Lincolnshire, England. Screens provided thermal protection at night and shading during the day. Plants were grown with a cycle of 16 hours light and 8 hours dark each day, with a constant light phase temperature of 26 °C (±3 °C) and dark phase temperature of 24 °C (±3 °C). The lighting system consisted of 18,400-watt lighting luminaries which supplemented natural daylight if insufficient. Light intensity threshold was set to 10 KL. Three of the original species progressed to chelator-induced accumulation trials *Brassica napus, Brassica oleracea var. capitate* (referred to herein after as *Brassica oleracea*) and *Helianthus annuus*. One hundred plants of each of the three species (N = 300) were planted in lithium amended soil as before with ten plants (one plant per pot) in each group. The plants were grown to maturity (circa, four months) then treated with EDTA in trial 1 and EDDS in trial 2 on alternate days for one week prior to harvesting. In most induced metal accumulation experiments chelating agents are generally added to the soil at concentrations between 0.001 M and 0.02 M (Nowack *et al*., 2006). In these experiments EDTA and EDDS were added to the soil at a concentration of 0.05 M in aliquots of 100 ml during regular watering times (Robinson *et al*., 2003). The chelate concentration used was large to offset the co-complexation of other metals present in the soil with stronger chelating stability constants than lithium. For example, the stability constant for Li-EDTA is 2.79 while the constant for Fe-EDTA is 25.1 and Ca-EDTA is 10.65, both of which typically have high concentrations in soil and compete for EDTA. At this high level of chelate addition the co-complexation of other more toxic elements from the soil used to the plants such as lead is a real danger and was also considered as a contributing factor to plant mortality in this study. Another possible contributing factor to plant mortality included the toxic effect of salinity caused by the addition of large amounts of lithium chloride to the plants at high concentrations. A trend of plant mortality was observed in all plants receiving large doses of lithium (i.e. the higher the lithium concentration the more likely plant mortality). The chosen chelate

concentration also served to maintain the pH of the soil solution low enough for the lithium to exist as ions.

4.3.5. Sample Preparation and Analysis

Plants were harvested and washed with deionised water. The leaves from each plant were separated from the rest of the plant, and then dried in a forced air oven (WiseVen® Am Bildacker 16, 97877 Wertheim, Germany) at 60 ± 1 °C to a constant weight overnight. One gram of leaf material from each plant was grinded and then acid digested. All plant samples were digested using the same method. The method involved the pre-digestion of samples (overnight) in a mixture of nitric acid and hydrogen peroxide at a ratio of 4:1. Further digestion took place in an open vessel, heated on a hot plate (WiseStir® Am Bildacker 16, 97877 Wertheim, Germany) in the same mix at the same ratio for approximately 30 to 40 minutes until the majority of plant material was brought into solution. This method cannot be said to constitute a complete digestion of materials but was internally consistent being replicated with all samples in the study. The digestion method used here was insufficient to digest any silica-based compounds in the plants. The digest was then filtered first using Whatman® (800 Centennial Avenue, building 1, Piscataway, New Jersey 08854-3911, USA) grade 1 filter paper and then using a 0.45 µm syringe filter. The filtrate was brought to a constant volume of 100 ml in a volumetric flask with deionised water i.e., giving a dilution factor of 1/100 when analysed. The FES (Flame Emission Spectroscopy) instrument used was a Sherwood 410 Flame Photometer using a mixture of natural gas and air, operating at a temperature of 1700 to 1800 °C, suitable for lithium, potassium and sodium analysis. Lithium is routinely analysed by FES. Limit of Detection (LOD) for FES analysis was 0.13 mg/l while limit of quantification (LOQ) was 0.44 mg/l. After every 20 samples, the instrument was recalibrated using blank samples and working standards. Typical readings obtained from blank samples were 0.0001 to 0.0003 mg/l of lithium. Lithium in plants and animals interacts with potassium and sodium (Kent, 1994). In this study we determined the potassium and sodium content in all plants both as internal consistency standards and to investigate their intrinsic concentration. The accuracy of lithium determinations using FES (670.8 nm) are not affected by the presence of potassium and sodium which have intense spectrum lines at 589 and 767 nm respectively (Keeling *et al.,* 2003).

4.3.6. Data Analysis

Statistical analysis was carried out using Statistical Package for the Social Sciences (SPSS®) version 23.0, International Business Machines (IBM®) Corp, Armonk, New York, USA) and Microsoft Excel® (2016 MSO 16.0.8625.2121). Where significant differences were found, a post-hoc t-test was used to identify significant differences between sample means. A p-value of 0.05 was considered significant. Bonferroni corrections were used as appropriate.

4.4. Discussion and Results

4.4.1. Germination Trial Data

The results from the general germination trials were used as a means of selecting suitable plant species for the plant trials. In all cases, as the concentration of lithium increased the germination rate decreased. Of the original thirty-four species, nine had total germination rates above 90%, germinating in deionised water along with increasing lithium concentrations. These nine species were selected to continue to further germination trials, *Brassica napus, Brassica oleracea var. capitate, Helianthus annuus, Solanum lycopersicum, Brassica hirta, Brassica rapa subsp. chinensis, Raphanus raphanistrum, Lepidium sativum* and *Cardamine hirsuta*. These germination trials were carried out as before but included the addition of EDTA and EDDS along with lithium. In the presence of EDTA germination was poor with only three species showing germination rates above 10%. In the presence of EDDS four species had germination rates above 90% and the other five above 55%. Based on the results of these trials, five species were selected to continue to plant trials, *Brassica napus, Brassica oleracea var. capitate, Helianthus annuus, Solanum lycopersicum,* and *Cardamine hirsuta.*

4.4.2. Plant Pot Trials

Three main pot trials were carried out using the selected plant species. In each trial the soil of each group was amended with increasing concentrations of lithium, to identify any potential natural lithium accumulators among the five species. Trial 2 was carried out to assess the effect EDTA doping on the amounts of lithium taken into the plants. Trial 3 was used to assess the effect doping the soil with EDDS on the uptake of lithium into the plants, using the same parameters as in trial 2.

4.4.3. Trial 1, lithium Amended Soil

The purpose of this trial was to determine if there were any natural lithium accumulator plants among our five-selected species, *Brassica napus, Brassica oleracea, Helianthus annuus, Solanum lycopersicum,* and *Cardamine hirsuta.* N = 100 plants of each of the five species were planted in individual pots at the start of trial 1 e.g., ten plants as a control in untreated soil, ten plants in soil at 20 mg/kg lithium, ten plants in soil at 50 mg/kg lithium and so on to 1000 mg/kg lithium. (Table 4.3). Figure 4.1 lists the $\bar{x}$ amounts of lithium recorded in the leaves of ten plants from each species at each of the nine-different lithium soil amendment levels and at control level. Figure 4.2 shows the distribution of levels of the concentration of lithium in leaves for the five species.
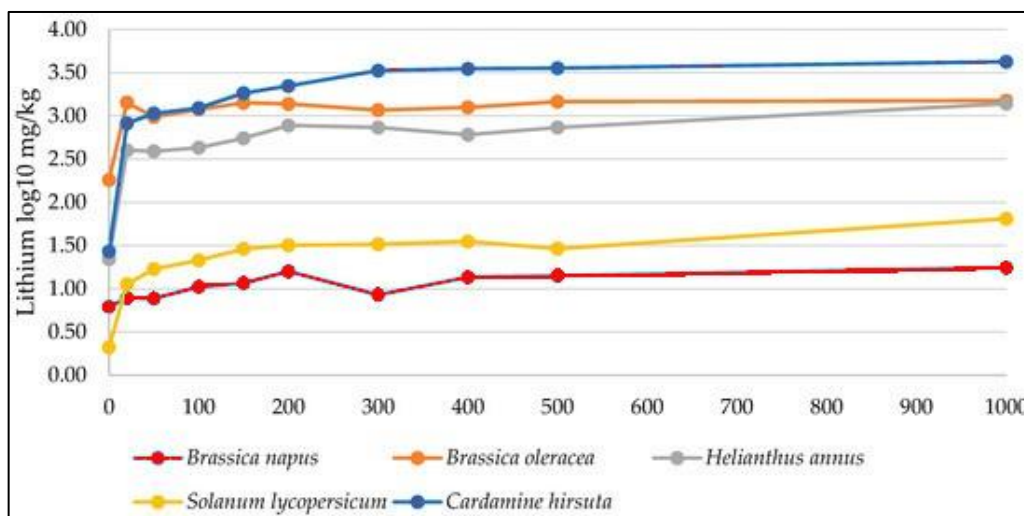
Figure 4.1. $\bar{x}$ Lithium concentrations in leaves of five species (*Brassica napus, Brassica oleracea, Helianthus annuus, Solanum lycopersicum,* and *Cardamine hirsuta*). Y-axis, logarithmic transformed mg/kg lithium data. X-axis, lithium soil amendments, (N = 468 plants) (Units = mg/kg).
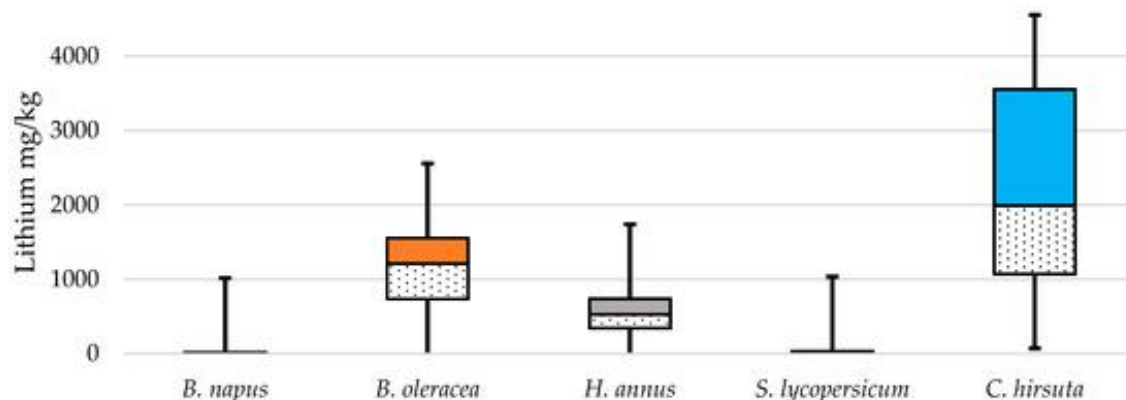
Figure 4.2. $\bar{x}$ Lithium concentration in leaves of the five species (*Brassica napus, Brassica oleracea, Helianthus annuus, Solanum lycopersicum,* and *Cardamine hirsuta.*) (Units = mg/kg).

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Table 4.3. x̄ Lithium concentrations in leaves (mg/kg) of five plant species at each level of only lithium added to the soil (i.e. no chelates in trial 1) x̄ plant dry biomass in grams. (Con = Control group) (Starting, n = ten plants per group) (Total number of plants at end of trial 1 = 468).

Plant Species	Con	20	50	100	150	200	300	400	500	1000
Brassica napus (mg)	6.2	7.8	7.7	10.5	11.6	15.9	8.5	13.6	14.1	17.5
Biomass (g)	5.6	7.6	8.5	7.5	12.5	12.8	10.2	11.2	11.5	11.7
Brassica oleracea (mg)	181	1423	971	1184	1416	1372	1161	1252	1456	1496
Biomass (g)	27.9	31.9	31.7	26.1	20.1	20.4	20.9	14.9	16.1	11.9
Helianthus annuus (mg)	22	400	388	428	551	773	732	604	733	1385
Biomass (g)	187.7	169.1	186.3	165.3	460.9	129.6	119.2	201.8	332	146.3
Solanum lycopersicum (mg)	2.1	11.3	16.9	21.3	28.9	31.8	32.6	35.2	29	64.5
Biomass (g)	19.2	18.3	16.8	13.6	14.1	15.7	17.3	13.7	13.9	10.5
Cardamine hirsute (mg)	27	819	1066	1229	1831	2216	3340	3500	3559	4221
Biomass (g)	1.9	1.3	1.9	1.5	1.4	1.67	1.73	1.29	0.8	1

Brassica oleracea, Helianthus annuus and *Cardamine hirsuta* showed a considerable increase in their lithium content from the control group up to the 1000 mg/kg lithium doped soil group. *Brassica oleracea* and *Helianthus annuus* showed variable lithium levels and x̄ maximum levels of 1496, SD = 691 and 1385, SD = 354 mg/kg respectively. The data from these two-species suggested that they were natural lithium accumulators, which could absorb lithium from soil and accumulate the metal in substantial amounts in their tissues. This accumulation also seems to have had a negligible effect on the health of the plants which had a mortality rate of just 5% in *Brassica oleracea* and *Helianthus annuus* (five plants of each). A strong linear association between the lithium content in the plants and lithium content amended to the soil was evident, *Brassica oleracea* at a coefficient of determination $(r^2) = 0.927$ and *Helianthus annuus* at $r^2 = 0.953$. These two

species were selected to progress to further trials. There was a x̄ increase of around 150 mg/kg lithium from group to group in *Brassica oleracea* and *Helianthus annuus*. *Cardamine hirsuta* showed increases of around 460 mg/kg lithium between treatments, with x̄ maximum level of 4997, SD = 339 mg/kg. Even though *Cardamine hirsuta* accumulated the highest concentrations of lithium among the five-species tested, the size of the plant (i.e., it is a low yielding crop) means that the species could never be used successfully in any agro-mining project which requires substantial amounts of biomass to justify the process economically. Although the exceptionally high growth rate of this species could potentially make it a viable venture, this is unlikely as the harvesting frequencies would need to be increased thereby increasing costs. *Cardamine hirsuta* also displayed the highest level of plant mortality among the five-species tested i.e., >20% in trial 1 (i.e., 22 plants), because of these facts *Cardamine hirsuta* did not progress to further trials. *Brassica napus* and *Solanum lycopersicum* showed Li x̄ maximum levels of x̄ = 11.3, SD = 3.9 and x̄ = 120, SD = 32.4 mg/kg respectively. Both species had a strong positive linear association between lithium in the plant and lithium amended to the soil, *Brassica napus* at r = 0.68 and *Solanum lycopersicum* at r = 0.85. There were no plant mortalities observed in trial 1 for *Brassica napus* and *Solanum lycopersicum* the plants appeared to have a high tolerance to lithium. The low concentrations of lithium present in the leaves of both species should have determined that they did not progress to further trials. However, because of the possibilities provided by *Brassica napus* such as oil and biodiesel production the plant was selected to continue to further trials. *Solanum lycopersicum* did not progress to further trials.
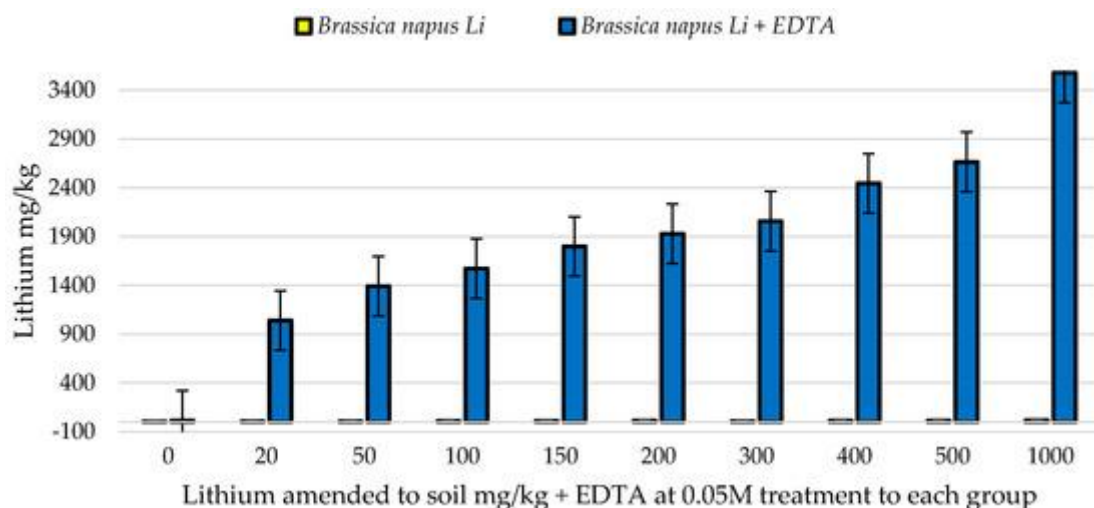
Figure 4.3. x̄ Lithium concentration in leaves of *Brassica napus* from trial 1 (no chelator) and *Brassica napus* from trial 2 (EDTA treatments at 0.05 M). X-axis, the concentration of lithium amended to the soil. (Units = mg/kg).

4.4.4. Trial 2, Li Amended Soil, EDTA Treatment

These trials were carried out using the plants *Brassica napus, Brassica oleracea* and *Helianthus annuus* (N = 300 new plants). The purpose of trial 2 was to assess the effect EDTA doping had on the amounts of lithium taken into the plants. Trials were carried out as before using the same lithium soil amendment protocol and the same number of plants in each group. The only difference between the trials was that one week prior to harvesting (i.e., around 3.5 months) EDTA at 0.05M was added to the soil along with their normal watering (i.e., approximately 100 ml of 0.05M EDTA solution in deionised water). Giving approximately 2.5 mmol EDTA/kg. Figure 4.3, Figure 4.4 and Figure 4.5 illustrate the differences in the amount of lithium absorbed by *Brassica napus, Brassica oleracea* and *Helianthus annuus,* respectively in trial 1 (i.e., only lithium amendments) and trial 2 (Lithium and EDTA amendments).
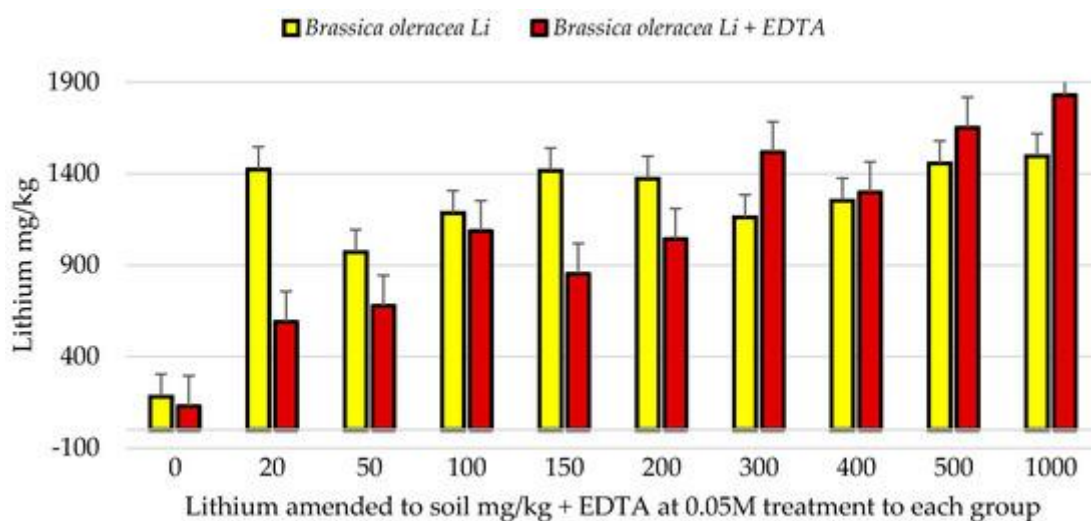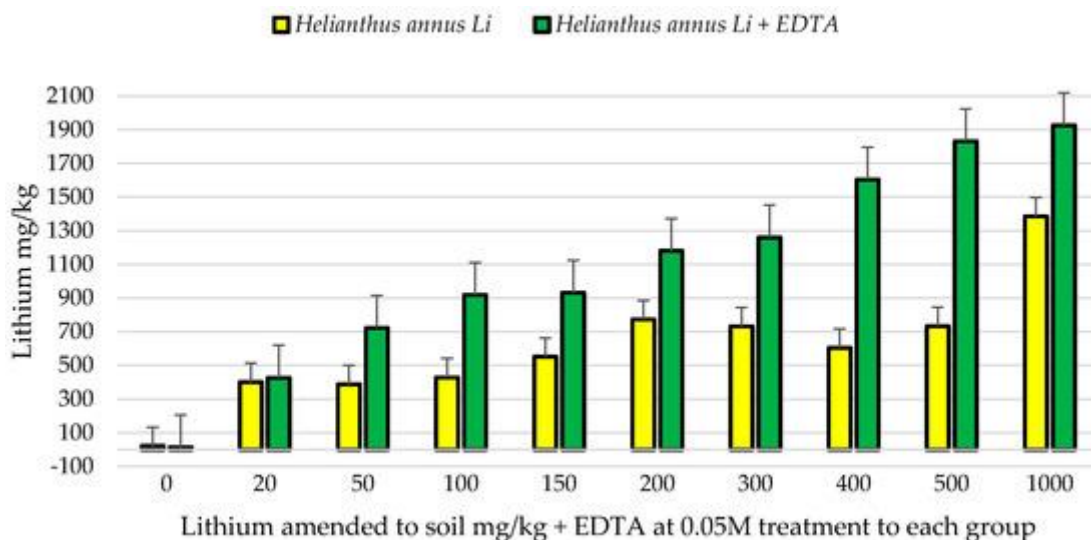

Figure 4.4. $\bar{x}$ Lithium concentration in leaves of *Brassica oleracea* from trial 1 (no chelator) and *Brassica oleracea* from trial 2 (EDTA treatments at 0.05M). X-axis, the concentration of lithium amended to the soil. (Units = mg/kg).
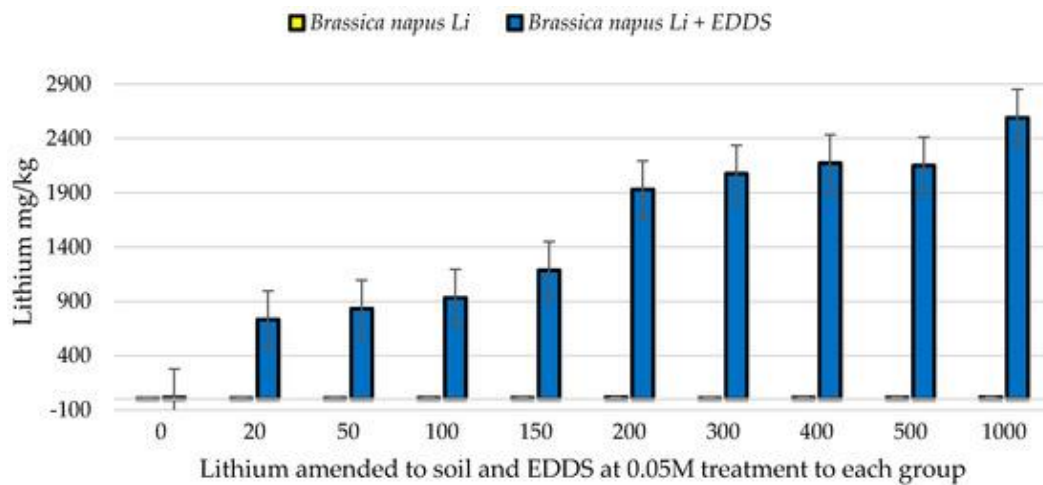
Figure 4.5. x̄ Lithium concentration in leaves of *Helianthus annuus* from trial 1 (no chelator) and *Helianthus annuus* from trial 2 (EDTA treatments at 0.05M). X-axis, the concentration of lithium amended to the soil. (Units in mg/kg).

There was an increase in the amount of lithium found in the EDTA treated *Brassica napus* plants in trial 2 compared to trial 1. No plant mortalities were observed in trial 2 for *Brassica napus*. There was an x̄ increase in the amount of lithium in *Brassica napus* by around 300 mg/kg, from group to group *Brassica oleracea* by around 180 mg/kg from one soil treatment to the next and *Helianthus annuus* by around 210 mg/kg. These figures for *Brassica oleracea* and *Helianthus annuus* were only slightly larger than the previous figures reached in trial 1 (i.e., *Brassica oleracea* trial 1 = 150 mg/kg, *Helianthus annuus* trial 1 = 150 mg/kg) while *Brassica napus* at an x̄ increase of 1.3 mg/kg in trial 1 from group to group showed a considerable increase. *Brassica napus* reached a x̄ maximum lithium level of 1849, SD = 914 mg/kg in trial 2, comparable to the same figures in trial 1 at 11.3, SD = 3.9 mg/kg. *Brassica oleracea* reached a x̄ maximum lithium level of 1830, SD = 625 mg/kg in trial 2. When compared to the same figures from trial 1 of 1496, SD = 691 mg/kg there was a slight x̄ increase of around 300 mg/kg. Plant mortalities in *Brassica oleracea* were >25% (26 plants) after the addition of EDTA. *Helianthus annuus* reached a maximum lithium level of 1081, SD = 609 mg/kg in trial 2. When compared to the same figures from trial 1 of 601, SD = 354 mg/kg there was a slight x̄ increase of around 300 to 400 mg/kg. Plant mortalities for *Helianthus annuus* were also close to 25% (24 plants) after the addition of EDTA. A positive linear association between lithium content in the plants and lithium content amended to the soil was observed in all three species in trial 2, *Brassica napus* at $r^2 = 0.80$, *Brassica oleracea* at $r^2 = 0.71$ and *Helianthus annuus* at $r^2 = 0.73$.

4.4.5. Trial 3, Lithium Amended Soil, EDDS Treatment

Lithium was amended to the soil in trial 3 in the same manner as in trial 1 and 2 (i.e., 20, 50, 100, 150, 200, 300, 400, 500, 1000 mg/kg lithium with a control group). In trial, 3 EDDS was used as the chelating agent the exact same way as EDTA was used in trial 2 (i.e., EDDS at 0.05M added to the mature plants one week prior to harvesting). Figure 4.6, Figure 4.7 and Figure 4.8 illustrate the differences in the amount of lithium absorbed by *Brassica napus, Brassica oleracea* and *Helianthus annuus,* respectively in trial 1 (i.e., only lithium amendments) and trial 3 (Lithium and EDDS amendments).

Figure 4.6. x̄ Lithium concentration in leaves of *Brassica napus* from trial 1 (No chelator) and *Brassica napus* from trial 3 (EDDS treatments at 0.05M) X-axis, the concentration of lithium amended to the soil. (Units in mg/kg).

Figure 4.7. x̄ Lithium concentration in leaves of *Brassica oleracea* from trial 1 (No chelator) and *Brassica oleracea* from trial 3 (EDDS treatments at 0.05M) X-axis, the concentration of lithium amended to the soil. (Units in mg/kg).

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Figure 4.8. x̄ Lithium concentration in leaves of *Helianthus annuus* from trial 1 (no chelator) and *Helianthus annuus* from trial 3 (EDDS treatments at 0.05M) X-axis, the concentration of lithium amended to the soil (Units in mg/kg).
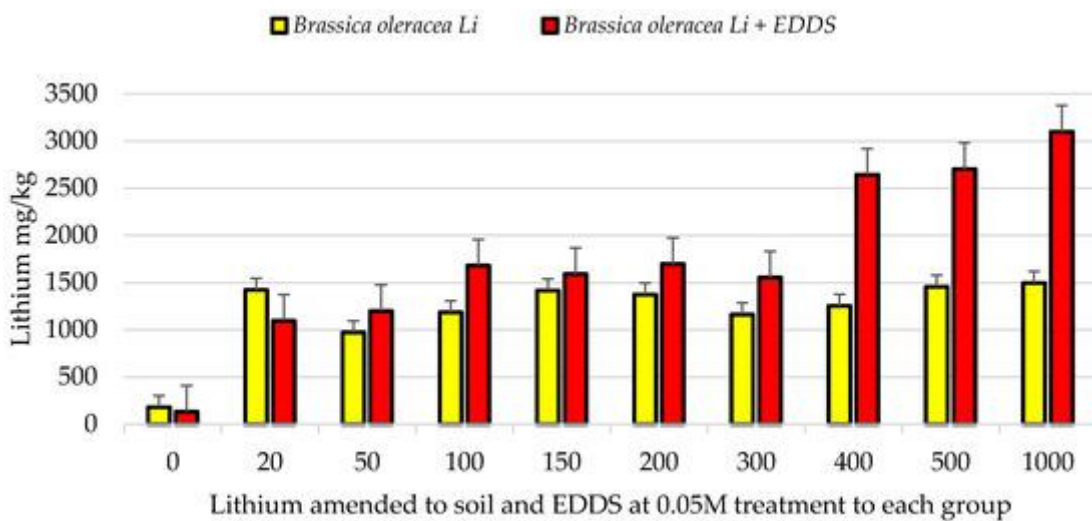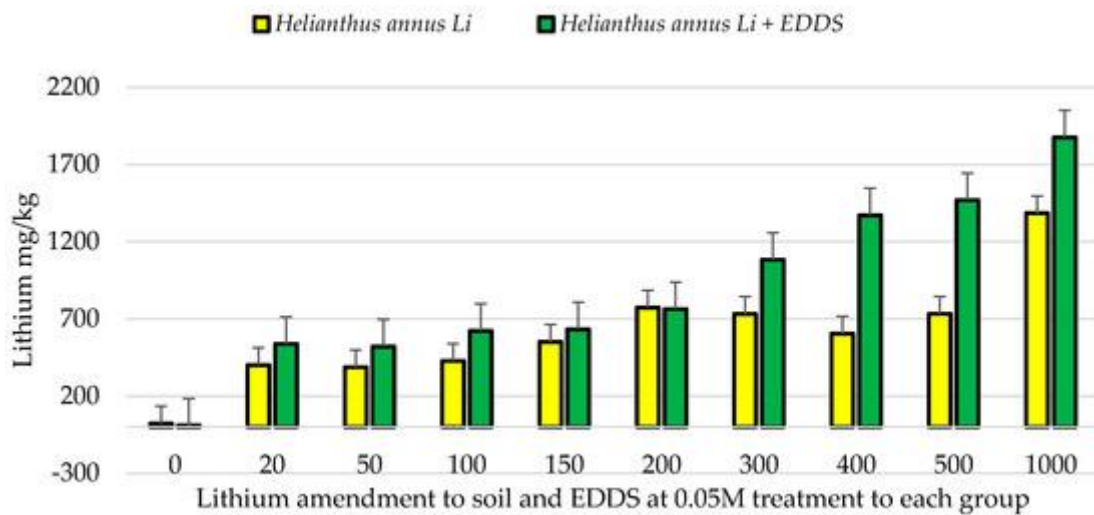
Brassica napus showed x̄ maximum lithium levels of x̄ = 1461, SD = 301. There was an x̄ increase in the amount of lithium in the *Brassica napus* plants in trial 3 (EDDS) by around 300 mg/k from group to group compared to data from trial 1 of 1.3 mg/kg. *Brassica oleracea* showed x̄ maximum lithium levels of x̄ = 1739, SD = 878 and a x̄ increase of around 330 between groups compared to trial 1 at 150 mg/kg. *Helianthus annuus* showed x̄ maximum lithium levels x̄ of = 889, SD = 554 and a x̄ increase of around 210 between groups compared to trial 1 data at 150 mg/kg. Plant mortalities in trial 3 were low >5% for each species (i.e., *Brassica napus* = 1, *Brassica oleracea* = 6 and *Helianthus annuus* = 4). Table 4.4 lists the x̄ and maximum lithium levels measured in the leaves of each plant species in trial 1, 2 and 3 at the highest lithium amendment. A positive linear association between lithium content in the plants and lithium content amended to the soil was observed in all 3 species in trial 3, *Brassica napus,* r^2 = 0.73 at *Brassica oleracea*, at r^2 = 0.73 from and *Helianthus annuus* at r^2 = 0.86.

Table 4.4. x̄ Maximum lithium levels, standard deviations (SD) and maximum levels of lithium in plants from all 3 trials (units in mg/kg).

Plant Species and Trial No.	x̄ Concentration	SD	Max Li
Trial 1, Brassica napus and Li	11.3	3.8	17.5
Trial 2, Brassica napus Li and EDTA	1849	914	3524
Trial 3, Brassica napus Li and EDDS	1461	301	3240
Trial 1, Brassica oleracea and Li	1191.2	390.6	1496
Trial 2, Brassica oleracea Li and EDTA	1830	625	2780
Trial 3, Brassica oleracea Li and EDDS	1739	878	2660
Trial 1, Helianthus annuus and Li	601.6	354.7	1385
Trial 1, Helianthus annuus Li and EDTA	1081	609	1820
Trial 1, Helianthus annuus Li and EDDS	889	554	1870

An analysis of variance (ANOVA) was conducted on the lithium values from each plant species to test the null hypothesis that there was no significant difference between all lithium data within the groups of each plant. *Brassica napus* at ($F_{(2, 27)}$ = 17.36, p = 1.42^{-5}) rejected the null hypothesis. Post hoc t-tests showed at (t = −8.08, *df* = 9, p-value = 2.02×10^{-5}) a significant difference between trial 1 and 2 and at (t = −5.5, *DF* = 9, p-value = 0.00018) a significant difference between trial 1 and 3. An ANOVA analysis performed on *Brassica oleracea* data at ($F_{(2, 27)}$ = 3.19, p = 3.35) failed to reject the null hypothesis. Post hoc testing revealed at (t = 1.01, *df* = 9, p-value = 0.169) there was no statistical difference between trial 1 and 2 and at (t = −2.68, *df* = 9, p-value = 0.012) showed only a marginally significant difference between trial 1 and trial 3 data. The same ANOVA analysis and null hypothesis were carried out on the *Helianthus annuus* lithium data from each trial. At ($F_{(2, 27)}$ = 2.17, p = 0.133) it also failed to reject the null hypothesis. Subsequent t-tests at (t = −4.26, *df* = 9, p-value = 0.001) between trial 1 and 2 data and at (t = −3.14, *df* = 9, p-value = 0.005) between trial 1 and 3 showed that there was only a marginally significant difference between the groups. *Brassica napus* despite not been a natural lithium accumulator performed significantly better when it came to lithium accumulation when both chelating agents were applied, EDTA treated plants showing a marginally higher level that EDDS treated plants. Although *Brassica oleracea* and *Helianthus annuus* accumulated large amounts of lithium in trial 1, the addition of chelating agents did not increase the amount of lithium accumulated by any significant difference. As part of this work, both potassium and sodium were measured along with lithium in all samples taken from all plant species. A multiple regression analysis was carried out to assess whether there was any association between lithium, potassium and sodium levels. The following was observed in trial 1: *Brassica napus*, Lithium/Sodium,

$r^2 = 0.58$, Lithium/Potassium, $r^2 = -0.1$, *Brassica oleracea,* Lithium/Sodium, $r^2 = -0.15$, Lithium/Potassium, $r^2 = 0.23$, *Helianthus annuus,* Lithium/Sodium, $r^2 = -0.70$, Lithium/Potassium, $r^2 = -0.25$, *Cardamine hirsuta,* Lithium/Sodium, $r^2 = 0.53$, Lithium/Potassium, $r^2 = 0.33$. No significant correlations were observed, only weak negative and positive associations were present. An analysis was also performed on data from trials 2 and 3, no significant correlations were observed.

4.5. Conclusion

Agro-mining as a mining technology has not yet been widely implemented. The process takes time compared to conventional mining which produces more immediate results. Mining companies are not yet eager to invest in any commercial-scale application of the technology. The main economic considerations of any agro-mining project include; global metal prices, energy recovery and agronomic costs. These factors can determine whether a project is feasible or not (Robinson, 1999). Other considerations such as plant biomass, climate, growth rates and whether the process is introducing an invasive species to an area are also important. In general, hyperaccumulators have a lower biomass than regular plants and are mostly endemic to ultrabasic soils. Induced plant metal accumulation uses endemic crops that have a high biomass. The key value for agro-mining is the amount of metal extracted per hectare multiplied by the value of the metal (Bani *et al.,* 2015). Studies have been carried out on hundreds of plant species and their suitability for agro-mining different metals (Brooks *et al*., 1998; Saeidnia and Abdollahi 2013). The data from some of these studies are listed below in Table 4.5.

Table 4.5. List of metal yields reached during agro-mining research.

Metal	Plant Species	kg/ha	Reference
Au	*Daucus carota*	1.4	(Sheoran *et al*., 2013)
Co.	*Berkheya coddii*	12.6	(Metallary, 2017)
Ni	*Streptanthus polygaloids*	100	(Robinson *et al*., 2015)
Ni	*Alyssum murale*	105	(Van Der Ent *et al.,* 2013)
Ni	*Berkheya coddii*	100	(Brooks *et al*., 1998)
Ni	*Streptanthus polygaloids*	100	(Van Der Ent *et al.,* 2009)
Ni	*Berkheya coddii*	121	(Sheoran *et al*., 2009)
Pb	*Cannabis sativa*	26.3	(Seth *et al*., 2011)
Tl	*Iberis intermedia*	40	(Dodson *et al*., 2012)
Zn	*Thlaspi caerulescens*	30.1	(Baker *et al*., 1994b)
Zn	*Cardaminopsis halleri*	10.3	(Baker *et al*., 1994a)

The experiments presented here are the first examining lithium accumulation in plants with the intention of agro-mining lithium. The data shows that EDDS performed as well

as EDTA at inducing lithium accumulation in these trials. EDDS' biodegradability in comparison to EDTA's persistence and performance in these trials make it an ideal candidate for chelate induced agro-mining of lithium. The highest concentrations of lithium recorded in this study using EDDS as a chelating agent was observed in the plants *Brassica napus* (2590 mg/kg) and *Brassica oleracea* (3091 mg/kg). Lithium prices are at an all-time high and the price is expected to increase in the coming years, has increased massively since the early 21st century from $1590 per tonne in 2002 to $9100 in 2017 (Metallary 2017). *Brassica napus* crops have a yield of around 1.3 tonnes per hectare fresh weight. The moisture content of fresh cut *Brassica napus* is around 13%, so 1.3 tonnes yields around 1.1 tonnes dry plant matter and 1.1 tonnes of plant matter should contain approximately 0.26 kg of lithium worth around $23.7/ha. A conservative estimate of a crop yield of *Brassica oleracea* is approximately 50 tonnes/ha fresh weight. The moisture content of cabbage is commonly >90% so a crop of 50 tonnes should produce around five tonnes of dry plant matter. Grown under the conditions set out in this work, five tonnes of dry plant matter should contain approximately 1.55 kg of lithium worth around $141.05/ha. When dried, the leaves of these two *Brassica* plants are prone to crumbling resulting in a loss of plant matter before transportation. Instead, the fresh plant matter could be transported (increasing costs) and used to recover energy (fermentation) before being processed for lithium. The true potential of agro-mining is still unknown, the technology, despite been around for the last four decades still needs to prove its economic significance. Large-scale agro-mining operations are needed to work through real world challenges and provide "real-life" evidence of profitability (Van Der Ent *et al.,* 2009). If agro-mining could be combined with other technologies such as forestry, there could be more of an economic incentive for companies to invest in the technology (Van Der Ent *et al.,* 2013). Genetic modification could also be the future of the technology (Dodson *et al*., 2012). The optimising of agronomic practices, such as irrigation and fertilization will increase the efficiency of the agro-mining process (Van Der Ent *et al.,* 2009). A lithium metal agro-mining industry may be wishful thinking right now. However, as suitable rich ore deposits become scarcer in the future, agro-mining may become a more feasible approach and industry may be willing to adopt the technology.

Chapter 5

Synopsis and future perspectives

5.1 Conclusion

The main aim of this thesis was to draw attention to the often unthought-of alkali metal lithium. Underlying the main aim of the thesis, is a narrative concerning any potential environmental implications for a future lithium mining venture in the country. The global distribution of the metal, its geopolitical circumstance, its current and future applications, and importantly its presence in Ireland are discussed. Lithium is not a rare metal, rather it is widely dispersed in the Earth's crust. Economic mineralisations of lithium are also widely dispersed across the globe and generally occur as relatively small deposits. The existence and distribution of known lithium mineral deposits suggest that there may be a large mineralisation of lithium in Ireland to justify a mining operation. To date, the mother lode of lithium has not yet been discovered, despite a spate of historic and recent prospecting. The long-term environmental benefits of mining lithium in Ireland and its use in clean energy storage technologies should outweigh any potential negative environmental and social effects of a small-scale mining operation in Ireland. However, possible environmental issues associated with any mining operation still warrant investigation.

Chapter one begins by focusing attention on the main industrial uses of lithium and its growing importance as a strategic metal for developed and developing nations. We have discussed the future of lithium and its use in the LIB industry, which is already becoming the main consumer of global lithium resources. Lithium battery technology, as the current most efficient battery technology, is set to power the new age of electric vehicles and energy storage systems. Today, there is a global race to secure lithium mineralisations around the world, the new demand driven primarily by the LIB industry. An Internet search for almost any country in the world along with the word lithium will likely yield an article related to that country's endeavours to access lithium. Demand for LIBs is fuelling a modern gold rush for lithium. The salars of South America, the salt lakes of the Middle East, China and Africa, lithium minerals, geothermal waters, volcanic clays, oilfield brines and even seawater are all being looked at as potential sources of lithium to meet future demand. Any negative effects of wholesale lithium exploitation can be ameliorated with fundamental scientific research such as described in this thesis. Nobody wants to, repeat the mining mistakes of the past.

Chapter two draws attention to Ireland's lithium mineralisation in the South East of the country, and the potential health implications associated with elevated lithium water concentrations. We have quantified the background concentrations of lithium and several

other metals in the SW and GW of Co. Carlow. Carlow contains the largest identified known lithium mineralisation sites in the South East of the country. The Co. Carlow area is also the location that has experienced both historical and modern prospecting. The concentrations of lithium in the waters across the county were, as expected, very low. Surface water at $\bar{x}$ = 0.02 mg/l, SD = 0.02 mg/l ranging from 0 to 0.091 mg/l and groundwater at $\bar{x}$ = 0.023 mg/l, SD = 0.02 mg/l ranging from 0 to 0.097 mg/l. The results of this study suggest that in their present condition the lithium mineralisation in Co. Carlow has a negligible effect on the local watersheds. These mean lithium values are given as the baseline concentration of lithium in the SW and GW of the region.

The main goal of chapter three was to establish lithium baseline levels in the topsoil and plants of the Co. Carlow area. The introduction includes lithium's future as an emerging environmental contaminant, its interactions in plants and soils, and the potential agricultural implications of an extraneous influx of lithium into the local environment. The already established sampling network from our previous work was used to gather over a thousand samples of topsoil, and the ubiquitous plant's *Fraxinus excelsior* (Ash) and *Hedera hibernica* (Ivy). The null hypothesis was that a relationship existed between lithium and a suite of other quantified metals among the different sampled mediums. The results of the analysis did not support that theory, however, the data from the study was comparable to the literature and is given as baseline concentrations of lithium in the topsoil and plants of the region. From the dataset, we reported baseline concentrations in topsoil at 57.8 ± SD 18.6 mg/kg lithium, plant samples, for Ash at 43.7 ± SD 12.2 mg/kg and Ivy at 52.3 ± SD 14.6 mg/kg. We determined the geographical distribution of lithium concentrations in the topsoil of the area. Taking into account the sampling density of this study, data appeared to be random and was not of a higher concentration adjacent to the known lithium mineralisation sites in the East of the county.

Chapter four described an agro-mining study. This chapter began with an introduction to the concept of agro-mining, and an outlook on the future potential of an economic agro-mining industry. Agromining, in general, has been described as the recovery of valuable metals from soils with high metal concentrations, using hyperaccumulator plants. The technology is presented as an environmentally sustainable supplementary source of income from sites of highly mineralised soils or sites of metal soil contamination not suitable for regular food crops. The technology also offers mining companies a potentially profitable means of restoring old mine sites by improving the soil fertility and resistance to erosion. Agromining was introduced in the 1970s, but the technology has not yet been widely implemented on a commercial scale. In this work, we selected four plants capable

of growing in an Irish climate with different biomass yields and investigated their ability to agromine lithium from soils with and without the use of chelating agents. The outcome of the study suggested that the plants *Brassica napus* (rapeseed) at a maximum lithium plant ash concentration of 2590 mg/kg, and *Brassica oleracea (cabbage)* at 3091 mg/kg using a biodegradable chelating agent, have potential as the starting point for a profitable agro-mining process in Ireland. However, the study was performed only at a relatively small greenhouse scale. In many cases, successful outcomes in the greenhouse are not translated into success at field trial level. The study may represent the beginning of a lithium agro-mining technology in Ireland but requires more solid evidence to validate the potential to commercialise the process.

The work presented here should go some way toward protecting our environment and informing a responsible and sustainable mining operation. Without mining, modern civilisation could never have progressed to the level it is today. However, the price that we have paid for benefits comes in some cases at the expense of the environment. Some old mine sites still have an environmental legacy, the repercussions of which we are still dealing with today. As civilisation has progressed so too have mining technologies. In most developed nations like Ireland, there is legislation in place that ensures the protection of our environment, which mining operations must accept and act accordingly. Ireland has an opportunity to develop an environmentally aware lithium mining model that involves the local community and local authorities as well as remote shareholders. Such a model could then be showcased to the rest of Europe.

5.2 Future Perspectives

Lithium is an important commodity for both current and future energy storage technologies. Research related to its applications, economics, and sources will undoubtedly evolve and increase in the coming years. In Ireland, there is an opportunity to supply a resource of relevant environmental data prior to, during, and after any potential lithium mining operation. There is a need to continuously monitor the concentrations of lithium and other appropriate metals in the plants, soils and waters of the Carlow area. The environmental concentrations of these metals should be measured periodically during the lift time and for several years after any mining venture in the area. There is also scope to expand the sampling density of the study and include several other plant species, ideally common endemic agricultural crops. A larger scale study should also involve the relevant local authorities, mining interests and communities. Research in the area will also offer an accessible means of disseminating important information to the

parties involved, an option that is all too often missing in such circumstances. Such a study would also provide valuable information regarding specific stressors placed on the environment by an active lithium mine. The gathered data may also be used as a benchmark for other similar lithium mineralisations across Europe.

With regard to agro-mining, the initial data presented here may represent the beginning of a potentially profitable lithium agro-mining process. The methods presented here would benefit from a more rigorous plant screening procedure. With close to 400,000 known plant species, there is room to expand the number of plant species selected to agromine lithium. The method needs to be trialled on a larger scale (field trials) in order to determine whether or not the process is profitable. The lithium ion is chemically similar to the potassium and sodium ions which are readily taken up by all plants. This means that the majority of plants will take up lithium indiscriminately. Some exotic lithium hyperaccumulator plants have been described (*Apocynum venetum*). Plant species which are exceptionally tolerant to lithium concentrations have also been described (Halophyte plants). Plants tolerant to sodium are ordinarily tolerant to lithium. There are other methods apart from chelation to aid the transport of lithium into plants such as soil acidification and hydroponics, these methods should be investigated. The potential of agro-mining to restore old mining and industrial sites should also be researched alongside any future works.

Chapter 6

Dissemination of Thesis

6.1 Scientific journal publications

- **Kavanagh, L.**; Keohane, J.; Cleary, J.; Garcia Cabellos, G.; Lloyd, A. Lithium in the Natural Waters of the South East of Ireland. International Journal of Environmental Research and Public Health 2017, 14, 561.

- **Kavanagh, L.;** Keohane, J.; Cabellos, G.G.; Lloyd, A.; Cleary, J. Induced Plant Accumulation of Lithium. Geosciences 2018, 8, 56.

- **Kavanagh, L.;** Keohane, J.; Cabellos, G.G.; Lloyd, A.; Cleary, J. Lithium in the Soils and Plants of the South East of Ireland. Journal of Environmental Monitoring, in review.

- **Kavanagh, L**.; Keohane, J.; Cabellos, G.G.; Lloyd, A.; Cleary, J. Global Lithium Sources, Industrial Use and Future in the Electric Vehicle Industry: A review. Resources 2018.

6.2 Conference Presentations

- Ireland's Lithium Resources.
  The 25th Irish Environmental Researchers Colloquium (ENVIRON 2015). 2015-04-08 | conference-poster.

- The Quantitative Analysis of Lithium in Ground and Surface Water of Co. Carlow Ireland.
  The 26th Irish Environmental Researchers' Colloquium, (ENVIRON 2016). 2016-03-22 conference-paper.

- Lithium in the Natural Waters of the South East of Ireland.
  ISEH 2016, ISEG 2016 and Geoinformatics 2016, NUIG Galway, Ireland. 2016-08-14 | *Conference-poster awarded the best poster in the conference.*

- Colourimetric determination of Lithium in natural water using the AZO Compound Thorin ($C_{16}H_{11}AsN_2O_{10}S_2$).
  The 15th Workshop on Progress in Trace Metal Speciation for Environmental Analytical Chemistry, Gdansk, Poland (2016).

- An Investigation into a Sustainable Eco-friendly Practice for the Mining of Lithium.
  The 27th Irish Environmental Researchers Colloquium (ENVIRON 2017) 2017-04-10 conference paper.

- The Viability of a Phytomining Protocol for Extracting Lithium from Low-Grade Ore.
  ICOEST International Conference on Environmental Science and Technology 2017, 19th – 23rd October 2017, Budapest, Hungary. Conference paper and poster.

- Geobotanical Prospecting for Lithium.
  The 28th Irish Environmental Researchers' Colloquium, (ENVIRON 2018). 2018-03-26 *Conference poster awarded the best poster at the conference.*
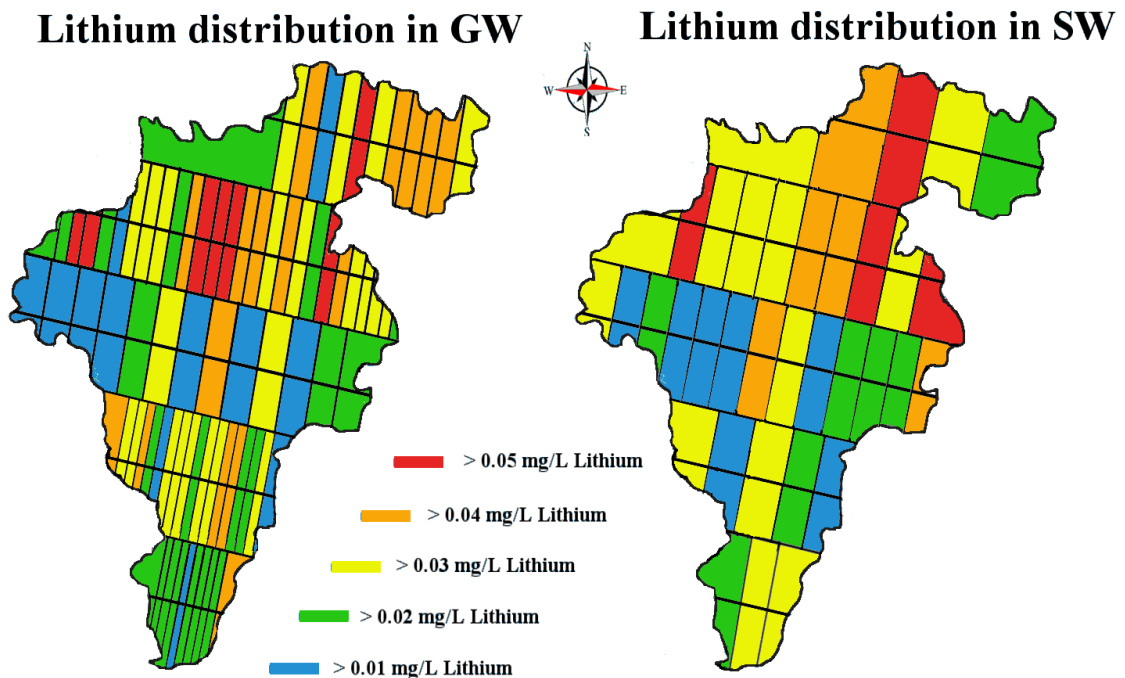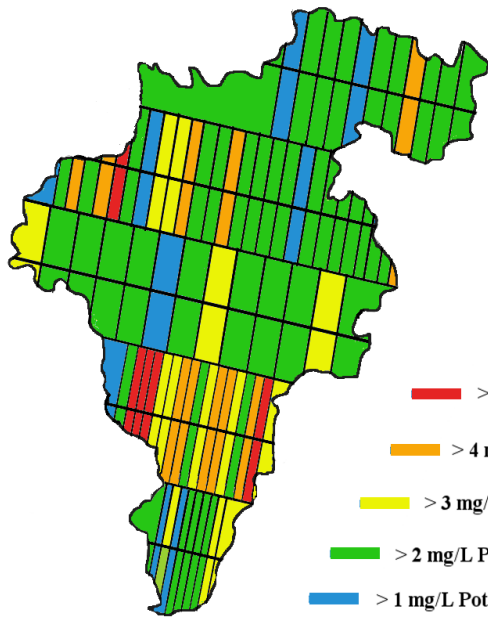
Appendix

7.1 Sampling point GPS data

Sample Identification	GPS LOCATION		Sample Identification	GPS LOCATION	
	Latitude	Longitude		Latitude	Longitude
GW-1001-07MAR15-R1	52° 30' 22.0"N	6° 55'42.0"W	GW-3023-10MAR15-R1	52°41'15.2"N	6°44'7.0"W
GW-1002-07MAR15-R1	52° 30' 30.8"N	6° 55'22.5"W	SW-3024-10MAR15-R1	52°41'4.5"N	6°42'51.5"W
GW-1003-07MAR15-R1	52° 30' 30.9"N	6° 55'37.1"W	SW-3025-10MAR15-R1	52°41'1.7"N	6°41'41.0"W
GW-1011-05MAR15-R1	52°30'18.6"N	6°54'51.8"W	GW-3026-MAR15-R1	52°41'45.4"N	6°49'59.5"W
SW-1004-07MAR15-R1	52° 30' 20.4"N	6° 54'16.0"W	GW-4001-18MAR15-R1	52°47'52.9"N	7°2'35.6"W
GW-1012-05MAR15-R1	52°30'20.2"N	6°54'12.6"W	SW-4002-18MAR15-R1	52°47'53.5"N	7°2'28.6"W
SW-1013-05MAR15-R1	52°30'26.6"N	6°53'31.3"W	GW-4003-18MAR15-R1	52°48'4.4"N	7°2'2.8"W
GW-1005-07MAR15-R1	52° 30' 24.7"N	6° 55'53.0"W	SW-4004-18MAR15-R1	52°47'55.5"N	7°1'59.1"W
GW-1006-07MAR15-R1	52° 30' 22.4"N	6° 55'25.8"W	GW-4005-18MAR15-R1	52°47'41.2"N	7°1'23.8"W
GW-1007-07MAR15-R1	52° 30' 26.7"N	6° 55'16.9"W	GW-4006-18MAR15-R1	52°47'26.1"N	7°0'26.2"W
GW-1008-07MAR15-R1	52° 30' 27.8"N	6° 55'21.5"W	SW-4007-18MAR15-R1	52°47'25.0"N	7°0'24.4"W
SW-1009-07MAR15-R1	52°29'18.6"N	6°55'38.9"W	GW-4008-18MAR15-R1	52°47'25.5"N	7°0'5.1"W
GW-1010-05MAR15-R1	52°29'14.2"N	6°55'39.2"W	SW-4009-18MAR15-R1	52°46'51.6"N	6°57'53.2"W
SW-2001-09MAR15-R1	52°37'48.6"N	6°59'24.9"W	GW-4010-18MAR15-R1	52°46'57.2"N	6°57'39.0"W
GW-2002-09MAR15-R1	52°37'26.0"N	6°58'19.6"W	GW-4011-18MAR15-R1	52°46'57.3"N	6°57'28.4"W
GW-2003-09MAR15-R1	52°37'21.3"N	6°58'17.9"W	GW-4012-18MAR15-R1	52°46'56.9"N	6°56'58.2"W
GW-2004-09MAR15-R1	52°37'1.1"N	6°58'8.8"W	GW-4013-18MAR15-R1	52°46'59.5"N	6°56'42.9"W
GW-2005-09MAR15-R1	52°36'55.5"N	6°57'57.7"W	GW-4014-18MAR15-R1	52°46'38.6"N	6°55'11.2"W
SW-2006-09MAR15-R1	52°36'54.5"N	6°57'56.3"W	GW-4015-18MAR15-R1	52°46'42.6"N	6°54'46.2"W
GW-2007-09MAR15-R1	52°36'33.0"N	6°57'8.3"W	SW-4016-18MAR15-R1	52°46'42.3"N	6°54'46.8"W
GW-2008-09MAR15-R1	52°36'22.7"N	6°56'38.1"W	GW-4017-18MAR15-R1	52°46'42.6"N	6°54'9.9"W
GW-2009-09MAR15-R1	52°35'32.2"N	6°55'16.9"W	GW-4018-18MAR15-R1	52°46'31.2"N	6°52'47.5"W
SW-2010-09MAR15-R1	52°35'43.5"N	6°55'2.7"W	GW-4019-18MAR15-R1	52°46'16.4"N	6°51'26.3"W
GW-2011-09MAR15-R1	52°35'37.9"N	6°54'38.9"W	GW-4020-18MAR15-R1	52°46'18.7"N	6°51'11.7"W
GW-2012-09MAR15-R1	52°35'30.2"N	6°54'28.9"W	GW-4021-18MAR15-R1	52°46'16.5"N	6°50'57.4"W
GW-2013-09MAR15-R1	52°35'32.0"N	6°54'5.8"W	SW-4022-18MAR15-R1	52°46'32.7"N	6°49'38.5"W
GW-2014-09MAR16-R1	52°35'30.7"N	6°53'40.7"W	SW-4023-18MAR15-R1	52°46'34.5"N	6°49'16.6"W
GW-2015-09MAR15-R1	52°35'10.1"N	6°52'47.0"W	GW-4024-18MAR15-R1	52°46'17.4"N	6°48'43.4"W
GW-2016-09MAR15-R1	52°34'41.4"N	6°47'11.1"W	GW-4025-18MAR15-R1	52°46'5.4"N	6°48'38.0"W
GW-2017-09MAR15-R1	52°34'53.5"N	6°51'20.0"W	GW-4026-18MAR15-R1	52°46'38.6"N	6°48'32.4"W
GW-2018-09MAR15-R1	52°34'44.0"N	6°50'41.4"W	GW-4027-18MAR15-R1	52°45'30.6"N	6°47'31.8"W
GW-2019-09MAR15-R1	52°34'24.1"N	6°50'55.5"W	GW-4028-18MAR15-R1	52°46'5.5"N	6°46'28.5"W
GW-2020-09MAR15-R1	52°34'9.0"N	6°50'0.9"W	GW-4029-18MAR15-R1	52°46'1.3"N	6°46'16.7"W
SW-2021-09MAR15-R1	52°33'47.8"N	6°49'38.9"W	SW-4030-18MAR15-R1	52°46'12.6"N	6°45'12.6"W
GW-2022-09MAR15-R1	52°33'42.1"N	6°49'33.9"W	SW-4031-18MAR15-R1	52°45'29.3"N	6°44'44.8"W
SW-2023-09MAR15-R1	52°33'33.7"N	6°49'53.0"W	SW-4032-18MAR15-R1	52°45'29.3"N	6°44'44.8"W
SW-3001-10MAR15-R1	52°42'27.4'N	6°57'15.8"W	GW-4033-18MAR15-R1	52°45'40.4"N	6°43'33.4"W

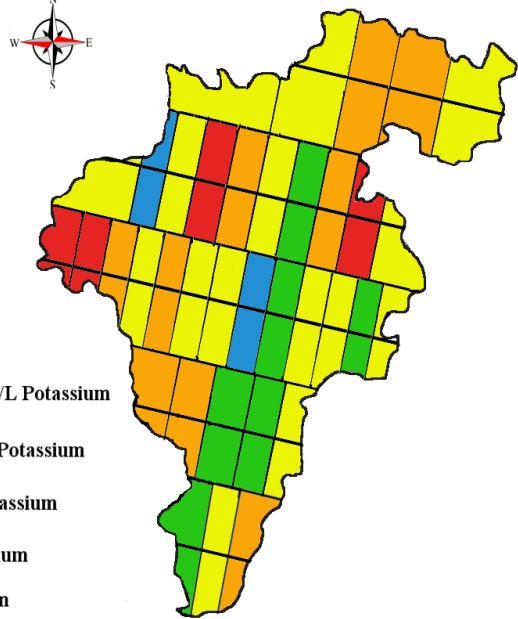| SW-3002-10MAR15-R1	52°42'11.5"N	6°56'11.7"W	GW-4034-18MAR15-R1	52°45'53.4"N	6°43'6.8"W
GW-3003-10MAR15-R1	52°41'55.3"N	6°55'50.8"W	GW-4035-18MAR15-R1	52°46'2.0"N	6°43'10.6"W
GW-3004-10MAR15-R1	52°42'0.6"N	6°55'27.2"W	GW-4036-18MAR15-R1	52°46'8.1"N	6°43'3.7"W
GW-3005-10MAR15-R1	52°41'37.7"N	6°54'28.2"W	GW-4037-18MAR15-R1	52°46'26.0"N	6°40'51.0"W
GW-3006-10MAR15-R1	52°41'24.1"N	6°54'9.3"W	GW-5001-19MAR15-R1	52°53'21.8"N	6°45'12.9"W
GW-3007-10MAR15-R1	52°41'1.5"N	6°52'9.2"W	GW-5002-19MAR15-R1	52°53'21.5"N	6°44'42.9"W
GW-3008-10MAR15-R1	52°40'54.0"N	6°51'21.1"W	GW-5003-19MAR15-R1	52°53'11.0"N	6°44'16.5"W
SW-3009-10MAR15-R1	52°40'31.8"N	6°50'46.1"W	GW-5004-19MAR15-R1	52°53'22.7"N	6°43'1.1"W
SW-3010-10MAR15-R1	52°40'55.3"N	6°50'44.8"W	GW-5005-19MAR15-R1	52°53'56.2"N	6°41'51.7"W
GW-3011-10MAR15-R1	52°41'34.0"N	6°50'20.2"W	SW-5006-19MAR15-R1	52°53'1.3"N	6°41'50.5"W
GW-3012-10MAR15-R1	52°41'34.3"N	6°50'4.6"W	GW-5007-19MAR15-R1	52°52'46.4"N	6°41'18.9"W
SW-3013-10MAR15-R1	52°41'31.7"N	6°49'3.2"W	GW-5008-19MAR15-R1	52°53'22.6"N	6°40'6.8"W
GW-3014-10MAR15-R1	52°41'45.4"N	6°47'32.5"W	GW-5009-19MAR15-R1	52°52'50.8"N	6°40'30.6"W
SW-3015-10MAR15-R1	52°41'33.2"N	6°47'7.5"W	GW-5010-19MAR15-R1	52°52'52.1"N	6°40'10.6"W
SW-3016-10MAR15-R1	52°41'6.4"N	6°46'50.5"W	GW-5011-19MAR15-R1	52°52'51.19"N	6°38'19.3"W
GW-3017-10MAR15-R1	52°41'12.4"N	6°46'5.4"W	GW-5012-19MAR15-R1	52°52'46.4"N	6°37'53.1"W
SW-3018-10MAR15-R1	52°41'7.2"N	6°44'50.3"W	SW-5013-19MAR15-R1	52°52'41.2"N	6°37'23.6"W
GW-3019-10MAR15-R1	52°41'7.2"N	6°44'50.3"W	SW-5014-19MAR15-R1	51°52'55.3"N	6°35'55.8"W
SW-3020-10MAR15-R1	52°41'7.2"N	6°44'50.3"W	GW-5015-19MAR15-R1	51°51'40.6"N	6°34'52.5"W
SW-3021-10MAR15-R1	52°41'7.2"N	6°44'50.3"W	SW-5016-19MAR15-R1	51°52'7.3"N	6°32,29.0"W
SW-3022-10MAR15-R1	52°41'7.2"N	6°44'50.3"W			

7.2 Water heat data maps

Lithium distribution in GW

Lithium distribution in SW

> 0.05 mg/L Lithium

> 0.04 mg/L Lithium

> 0.03 mg/L Lithium

> 0.02 mg/L Lithium
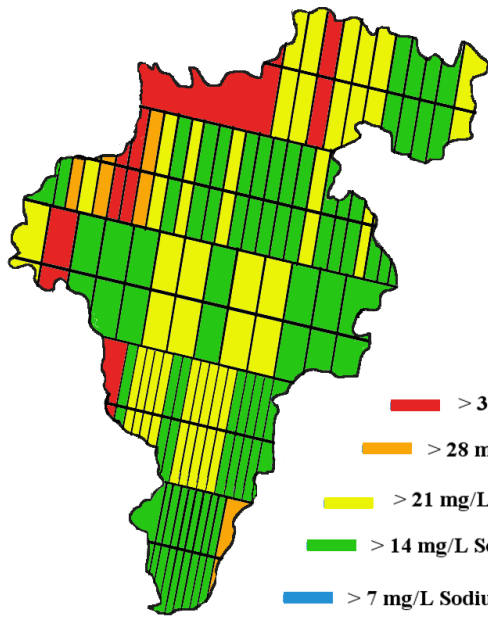
> 0.01 mg/L Lithium

129

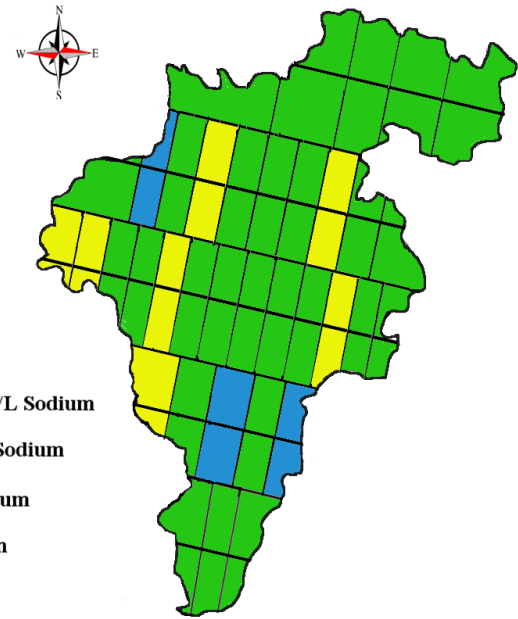# Potassium distribution in GW

Potassium distribution in SW

- > 5 mg/L Potassium
- > 4 mg/L Potassium
- > 3 mg/L Potassium
- > 2 mg/L Potassium
- > 1 mg/L Potassium

Sodium distribution in GW

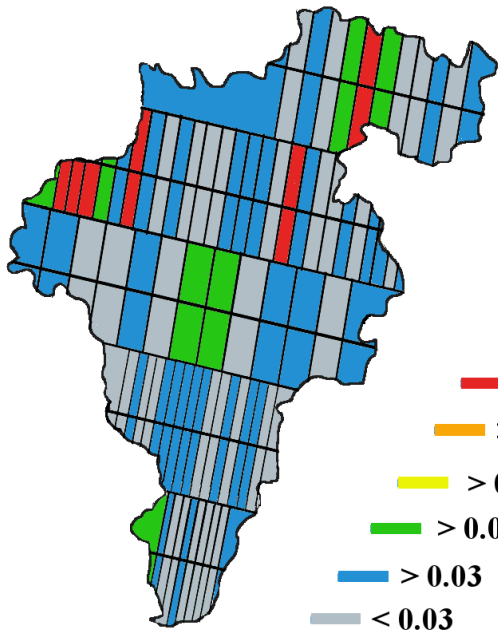# Sodium distribution in SW
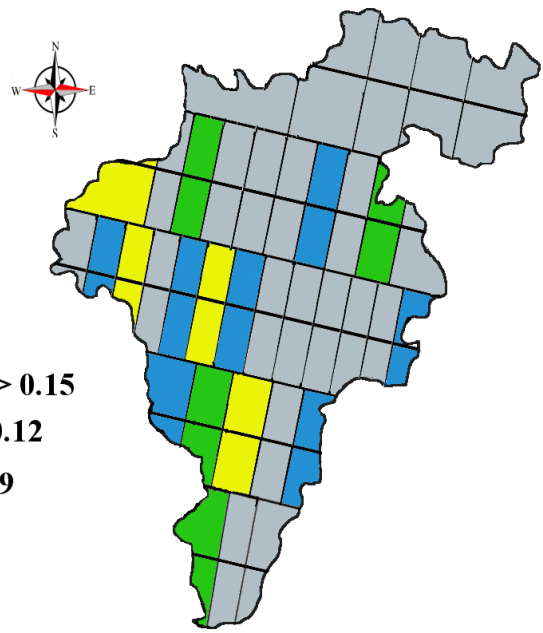
- > 37 mg/L Sodium
- > 28 mg/L Sodium
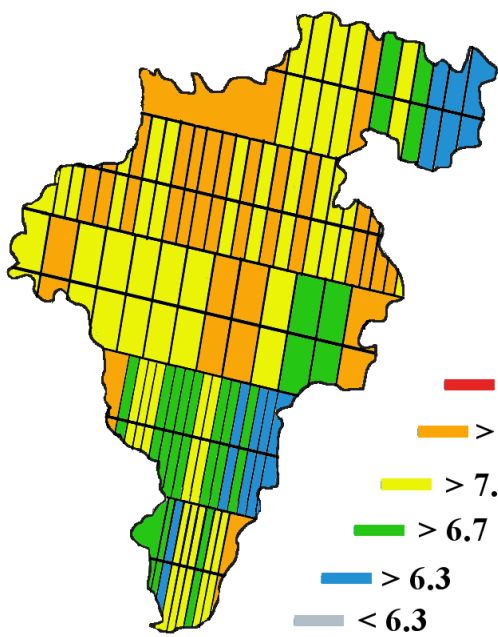- > 21 mg/L Sodium
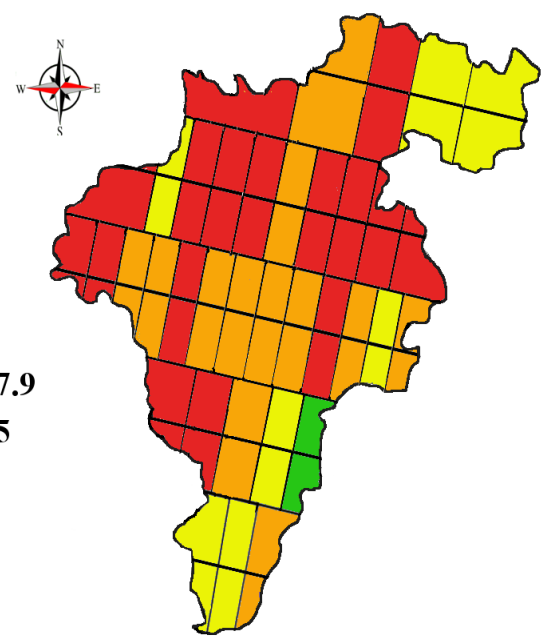- > 14 mg/L Sodium
- > 7 mg/L Sodium

Manganesse distribution in GW

Manganese distribution in SW

> 0.15
> 0.12
> 0.09
> 0.06
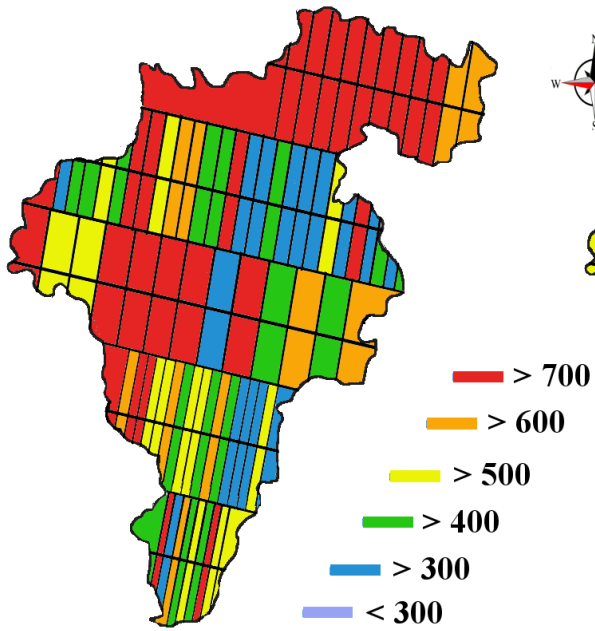> 0.03
< 0.03

pH distribution in GW

pH distribution in SW

> 7.9
> 7.5
> 7.1
> 6.7
> 6.3
< 6.3
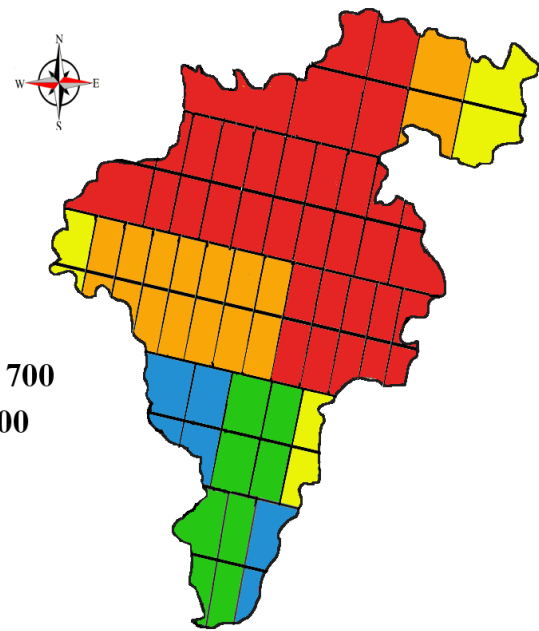
Conductivity distribution in GW

Conductivity distribution in SW

> 700
> 600
> 500
> 400
> 300
< 300

Iron distribution in GW
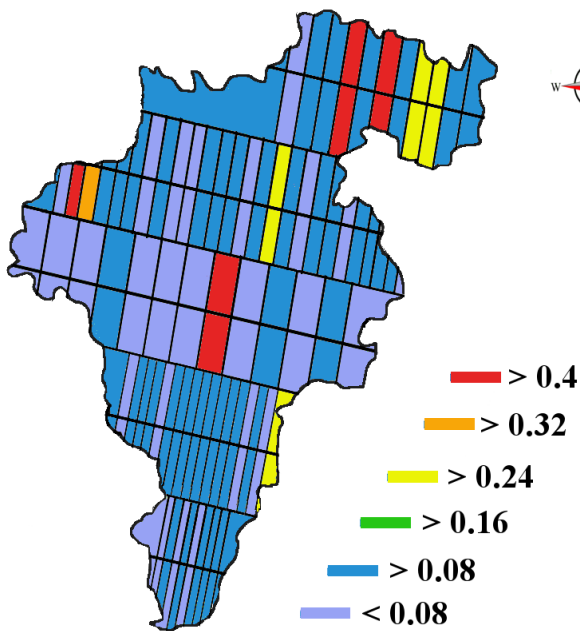
Iron distribution in SW

> 0.4
> 0.32
> 0.24
> 0.16
> 0.08
< 0.08
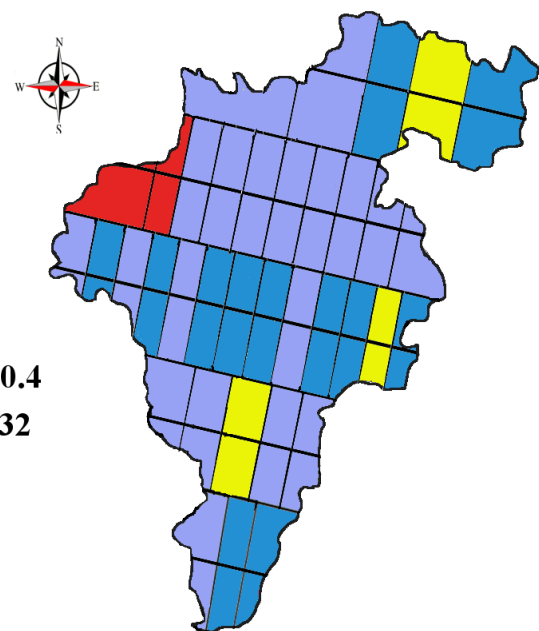
Zinc distribution in GW
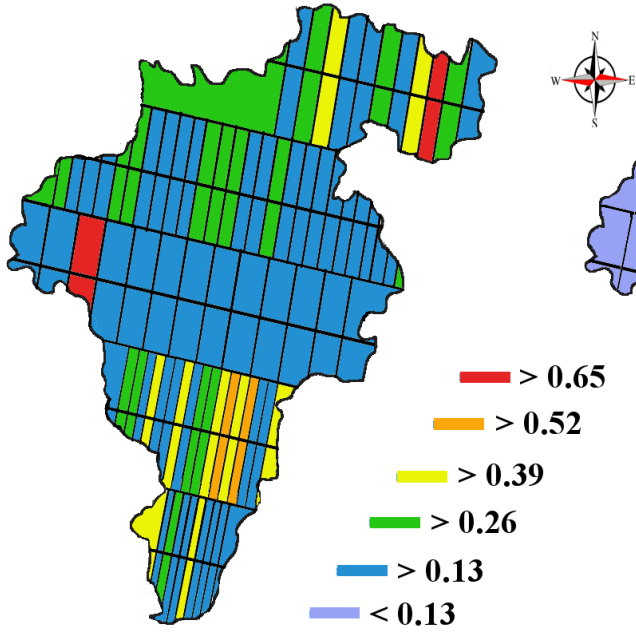
Zinc distribution in SW

> 0.65
> 0.52
> 0.39
> 0.26
> 0.13
< 0.13
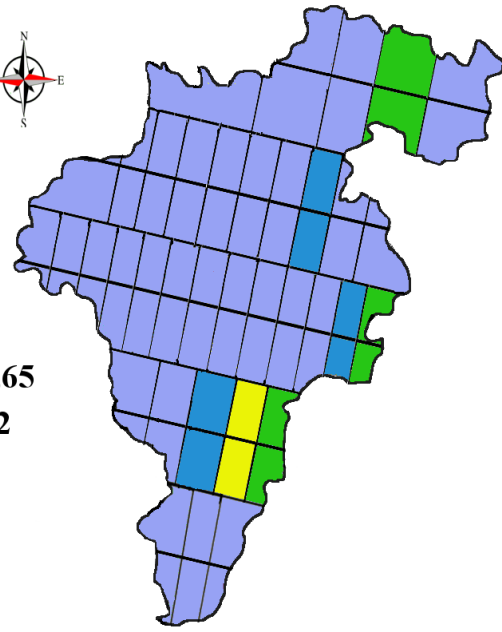
Copper distribution in GW
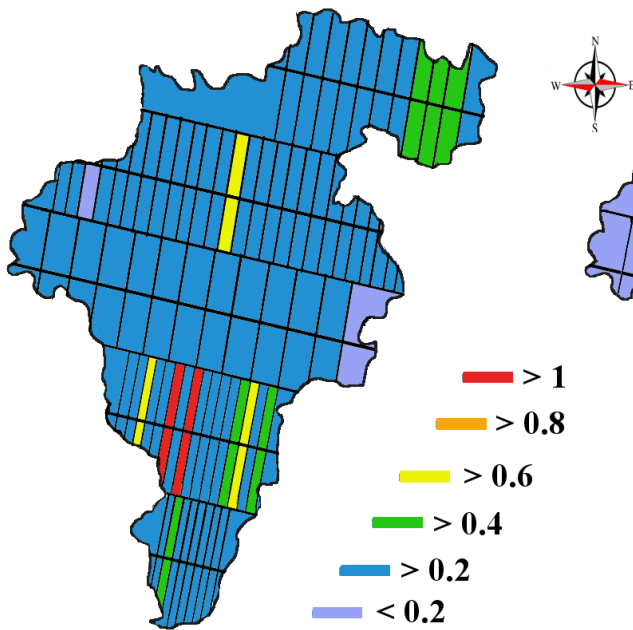
Copper distribution in SW

> 1
> 0.8
> 0.6
> 0.4
> 0.2
< 0.2
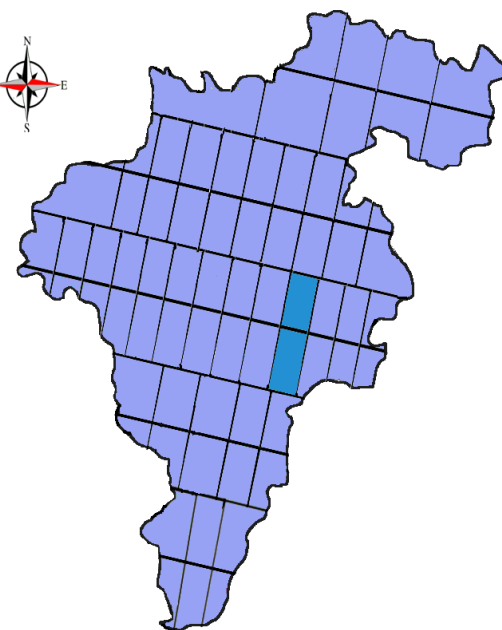
Nickel distribution in GW
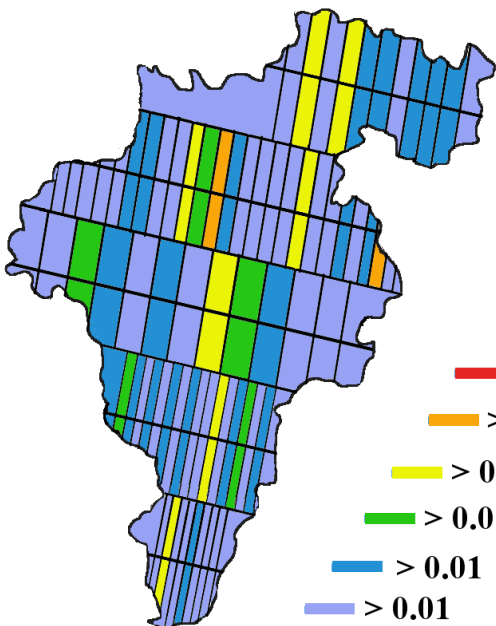
Nickel distribution in SW

> 0.03
> 0.025
> 0.02
> 0.015
> 0.01
> 0.01
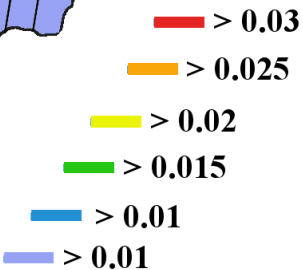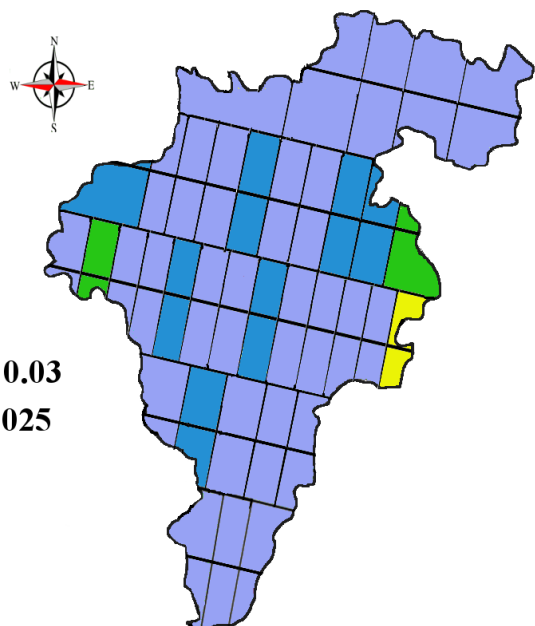
Lead distribution in GW

Lead distribution in SW

> 0.15
> 0.12
> 0.09
> 0.06
> 0.03
< 0.03

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Lithium to Sodium ratio GW

Lithium to Sodium ratio SW

- ■ 3200 - 4000+
- ■ 2400 - 3200
- ■ 1600 - 2400
- ■ 800 - 1600
- ■ 0 - 800

7.3 Soil heat data maps

Soil pH

Soil conductivity

- ■ > 7.9
- ■ > 7.5
- ■ > 7.1
- ■ > 6.7
- ■ > 6.3
- ■ < 6.3

- ■ > 1500
- ■ > 1200
- ■ > 900
- ■ > 600
- ■ > 300
- ■ < 300

Manganese in soil

🟥	> 1000
🟧	> 800
🟨	> 600
🟩	> 400
🟦	> 200
🟪	< 200

Iron in soil

🟥	> 1500
🟧	> 1200
🟨	> 900
🟩	> 600
🟦	> 300
🟪	< 300

Zinc in soil

🟥	> 410
🟧	> 320
🟨	> 230
🟩	> 140
🟦	> 50
🟪	< 50

Copper in soil

🟥	> 60
🟧	> 45
🟨	> 30
🟩	> 15
🟦	> 7.5
🟪	< 7.5
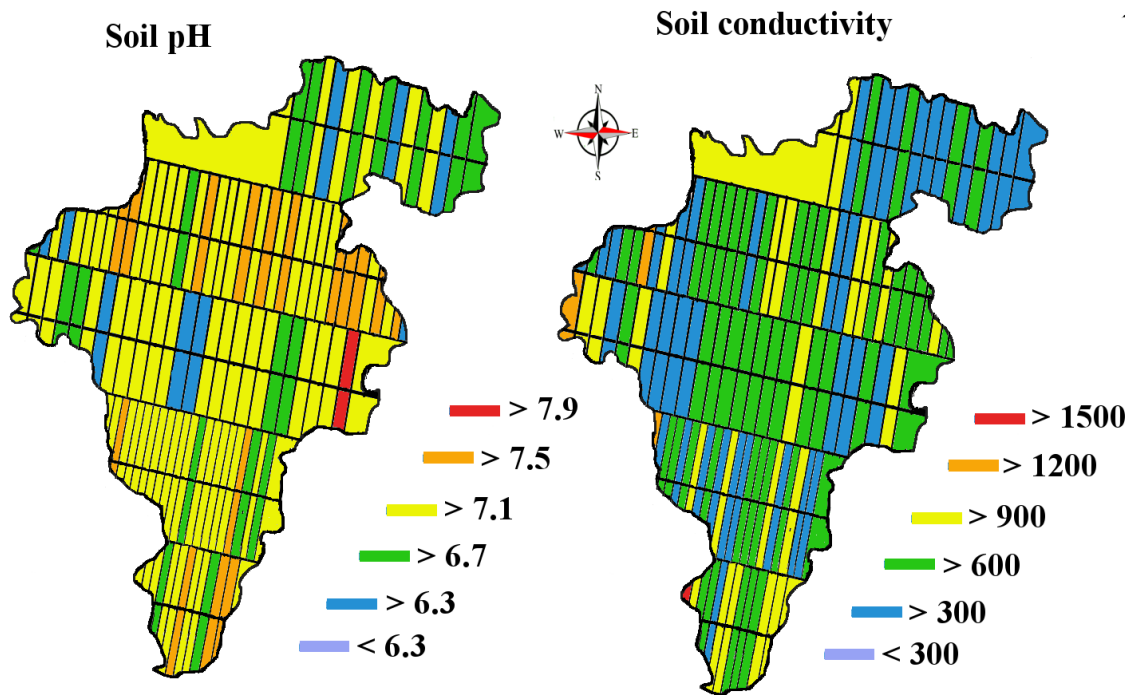
Nickel in soil

Lead in soil
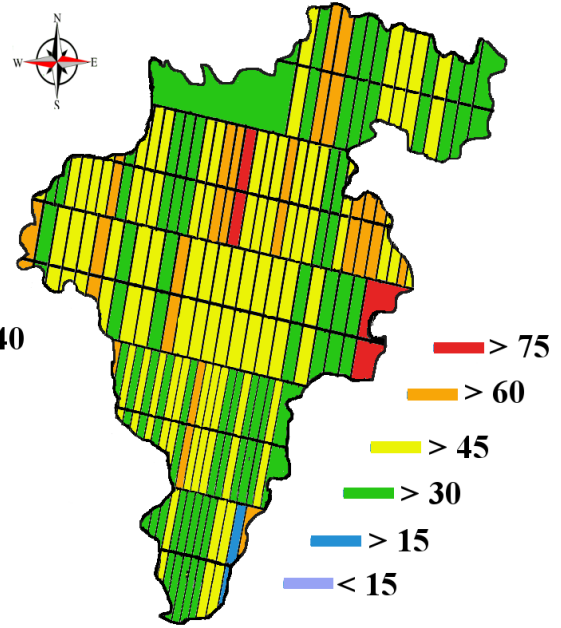
Potassium in soil

Sodium in soil

Lithium in soil

Lithium in soil

> 60
> 50
> 40
> 30
> 20
< 20

> 80
> 60
> 50
> 40
> 30
< 30
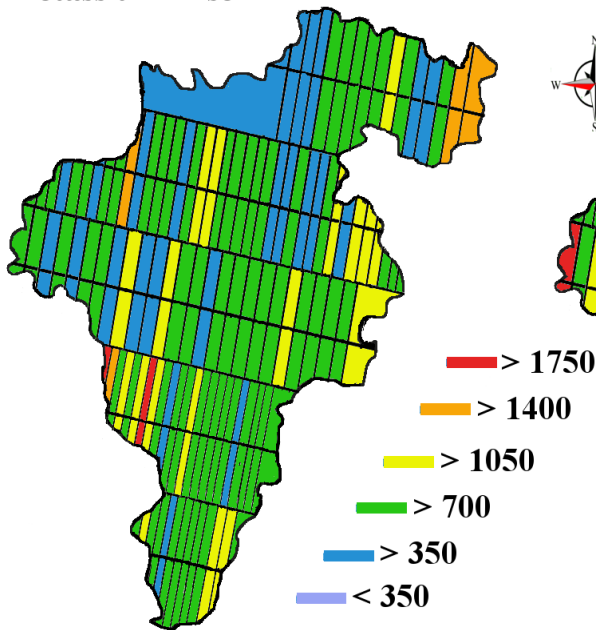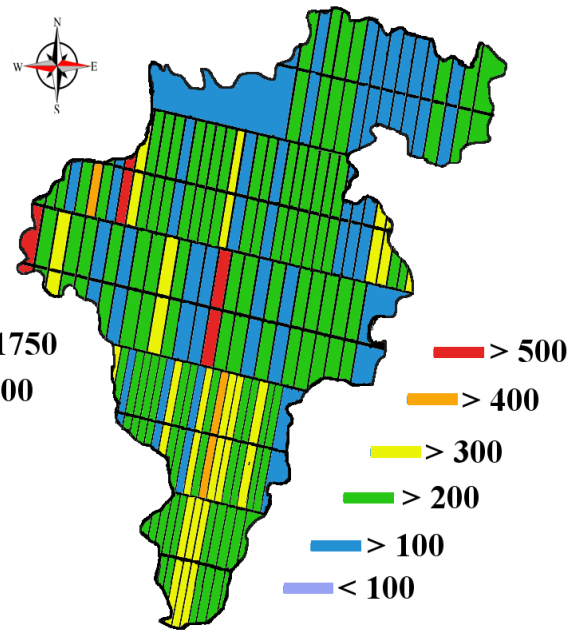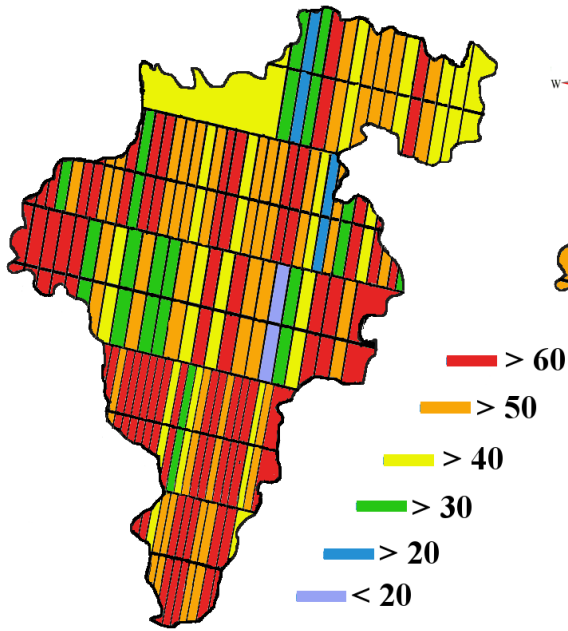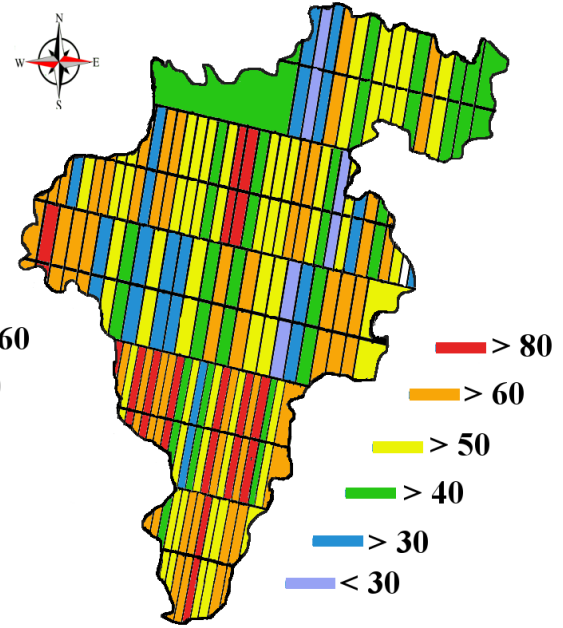
7.4 Plant heat data maps

Manganese distribution in Ash plant leaves
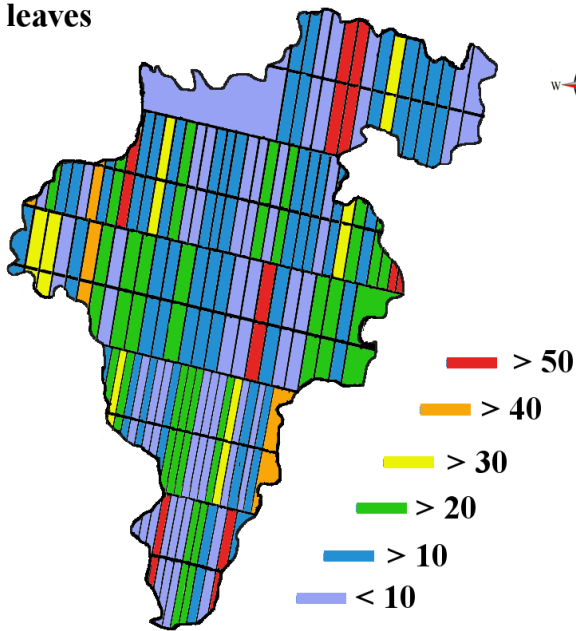
Manganese distribution in Ivy plant leaves

> 50
> 40
> 30
> 20
> 10
< 10

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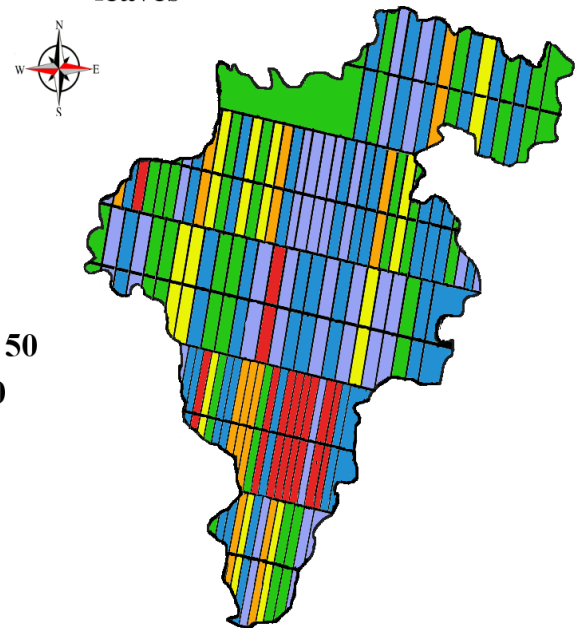
Iron distribution in Ash plant leaves
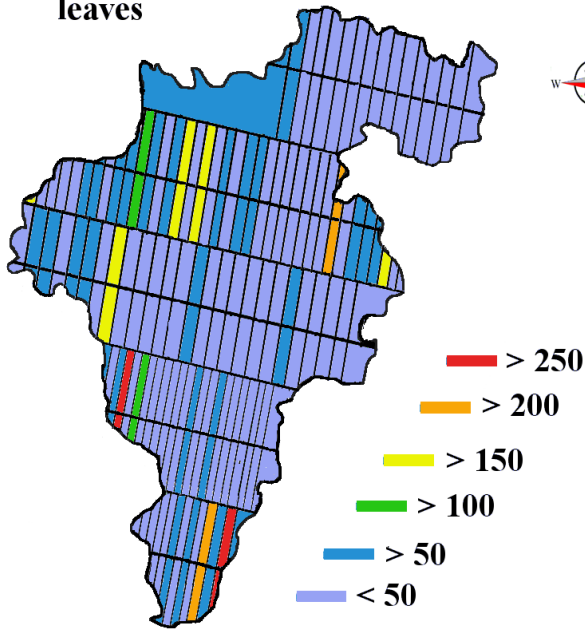
Iron distribution in Ivy plant leaves

> 250
> 200
> 150
> 100
> 50
< 50
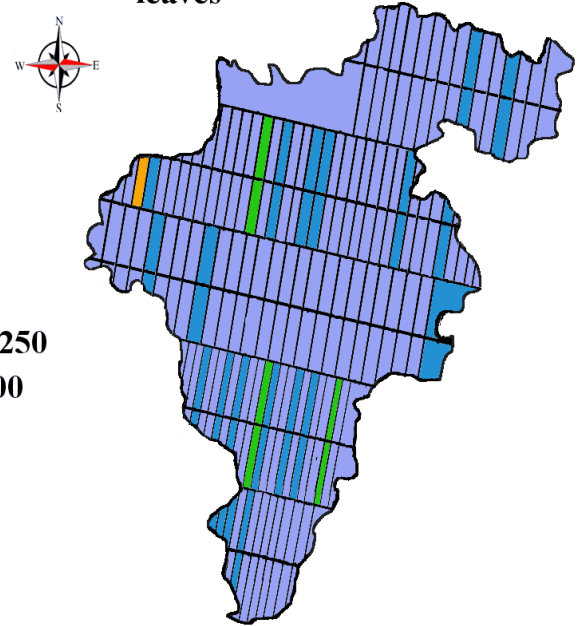
Zinc distribution in Ash plant leaves
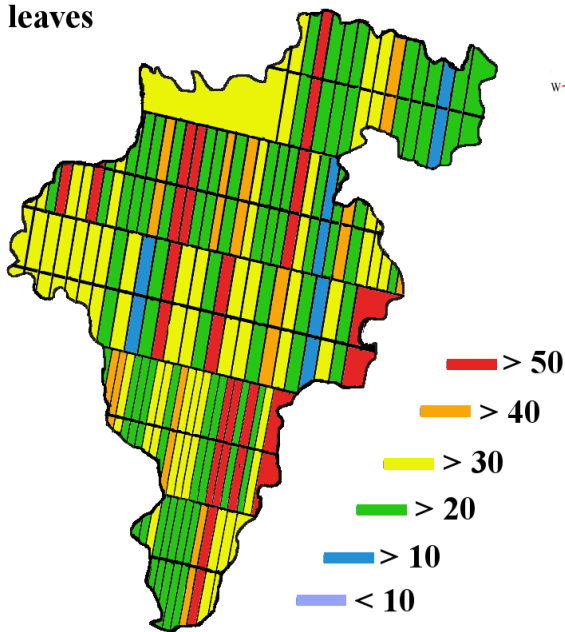
Zinc distribution in Ivy plant leaves

> 50
> 40
> 30
> 20
> 10
< 10
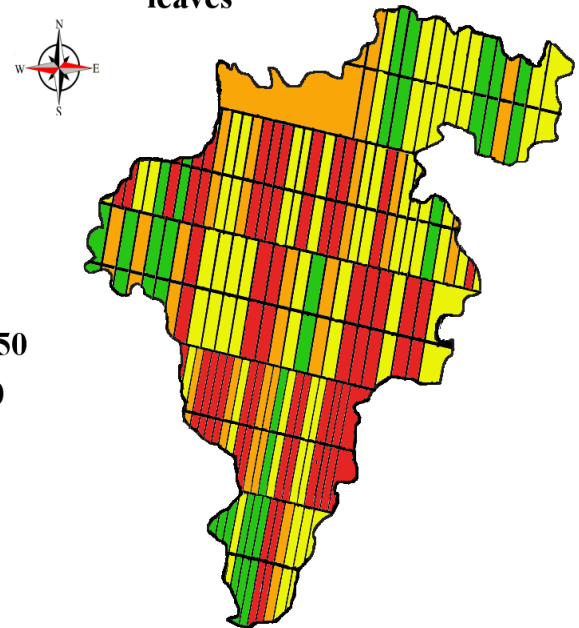
Copper distribution in Ash plant leaves
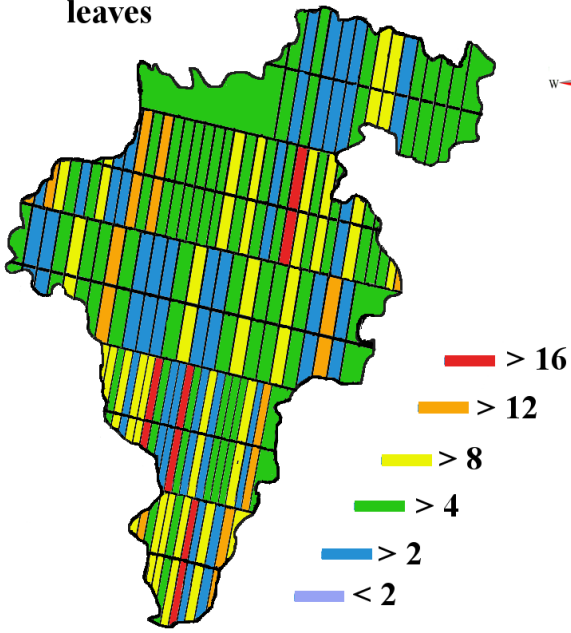
Copper distribution in Ivy plant leaves

> 16
> 12
> 8
> 4
> 2
< 2
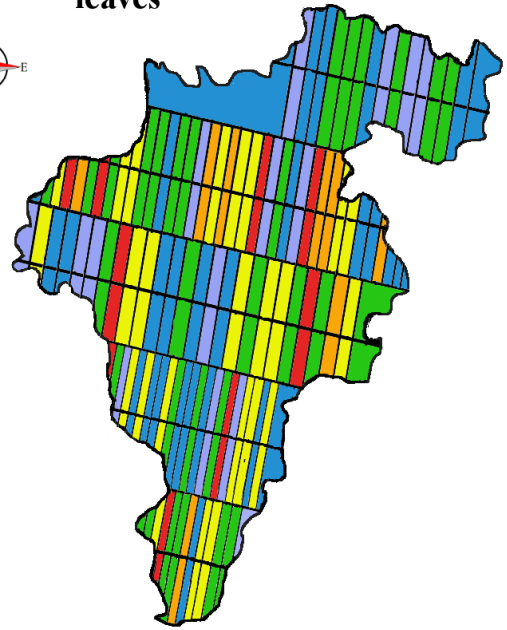
Nickel distribution in Ash plant leaves
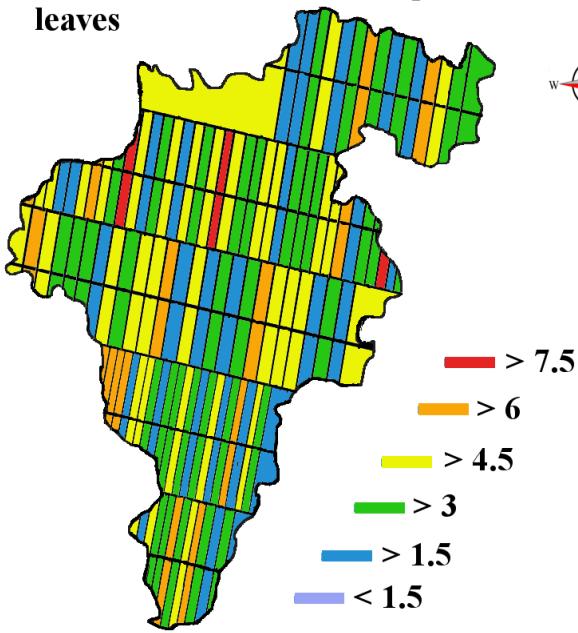
Nickel distribution in Ivy plant leaves

> 7.5
> 6
> 4.5
> 3
> 1.5
< 1.5
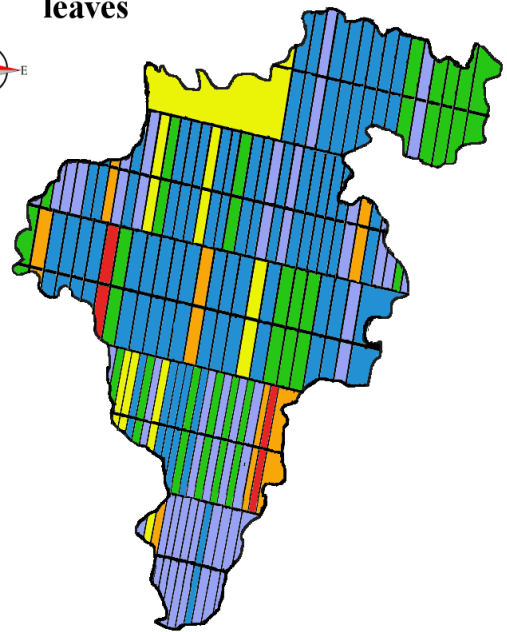
Lead distribution in Ash plant leaves
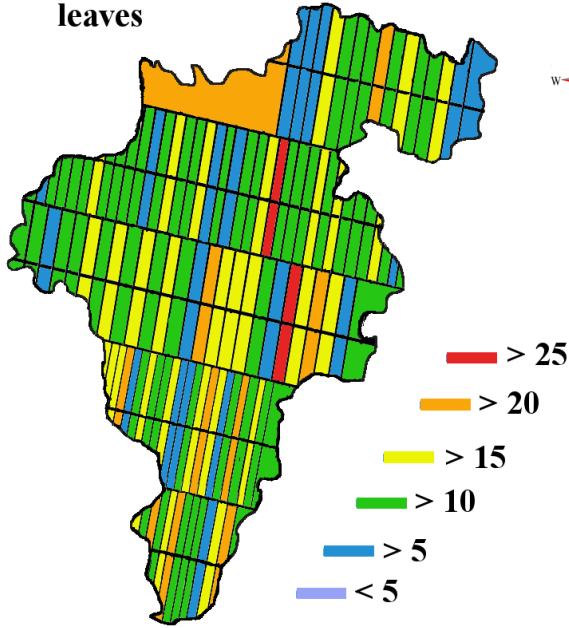
Lead distribution in Ivy plant leaves

> 25
> 20
> 15
> 10
> 5
< 5
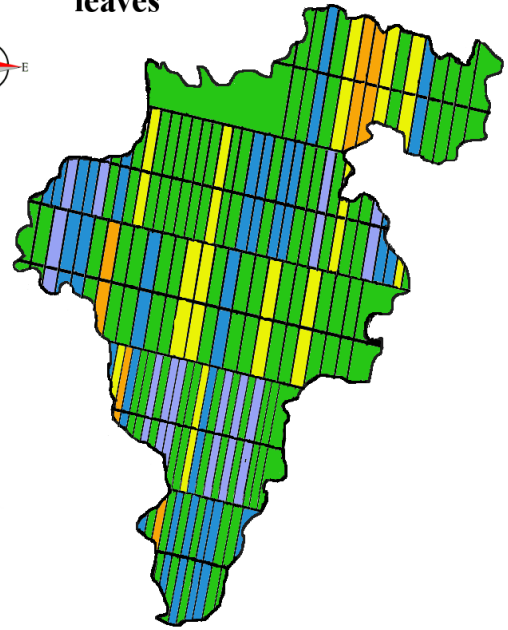
Lithium distribution in Ash plant leaves

Lithium distribution in Ivy plant leaves

> 65
> 55
> 45
> 35
> 25
< 25
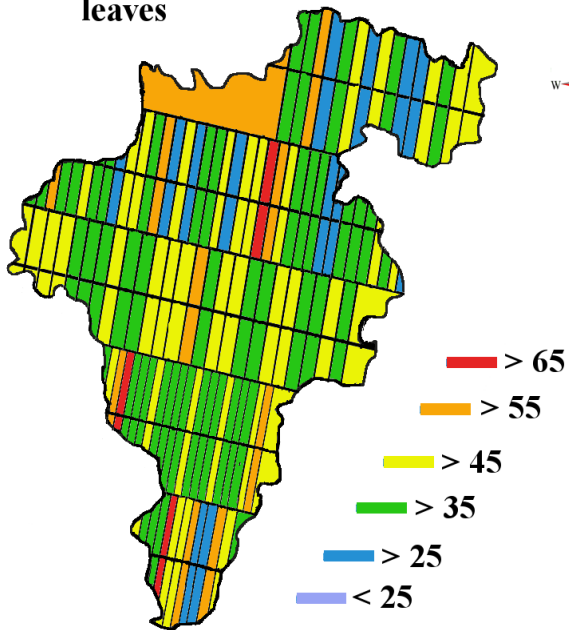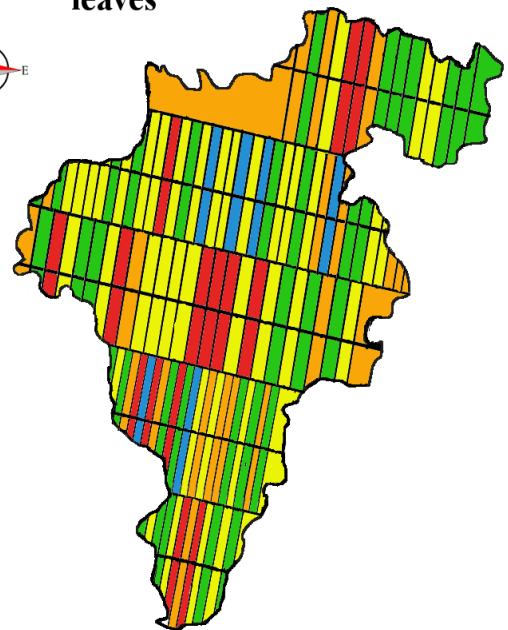
Potassium distribution in Ash plant leaves
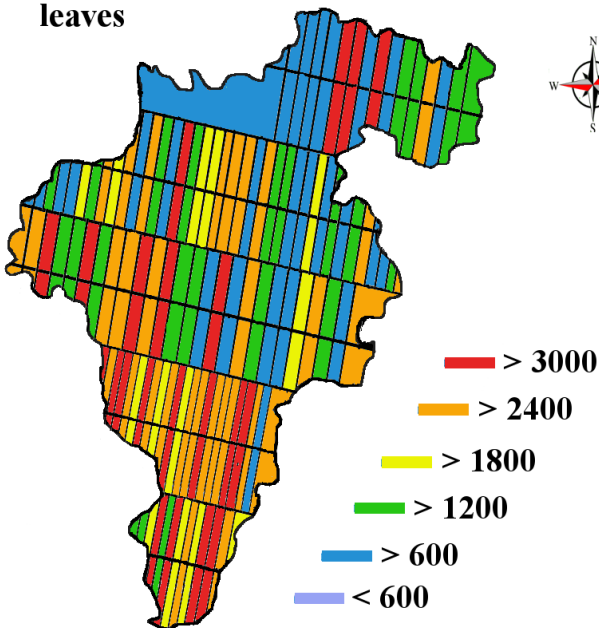
Potassium distribution in Ivy leaves

> 3000
> 2400
> 1800
> 1200
> 600
< 600
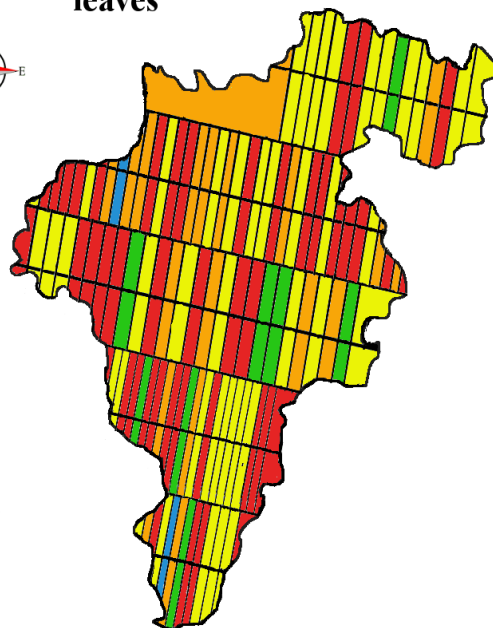
Sodium distribution in Ash plant leaves

Sodium distribution in Ivy plant leaves

> 300
> 250
> 200
> 150
> 100
< 100
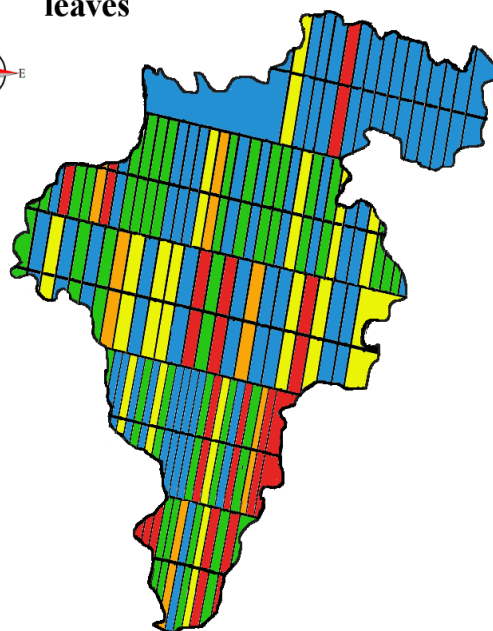
Zinc distribution in Grass plants

Nickel distribution in Grass plants
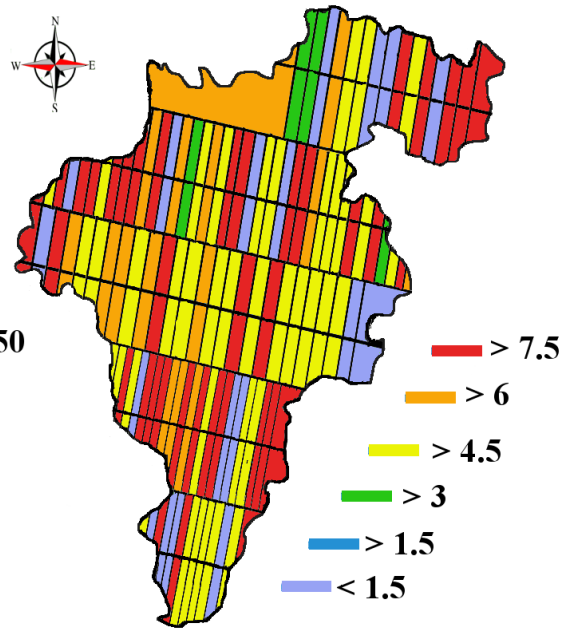
Lead distribution in Grass plants
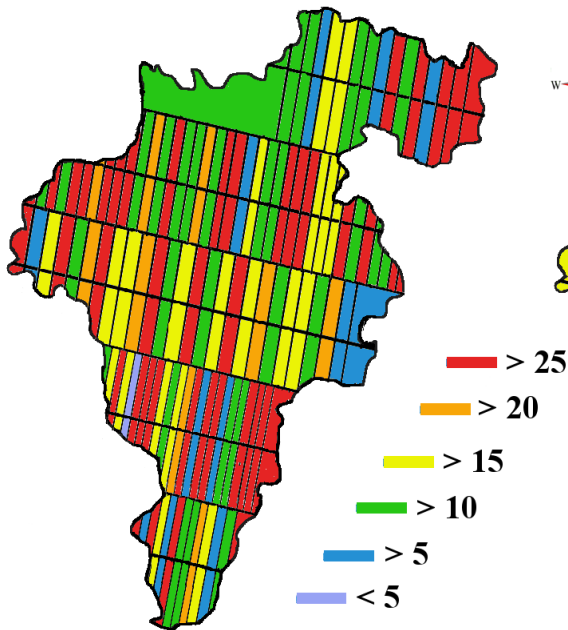
Lithium distribution in Grass plants
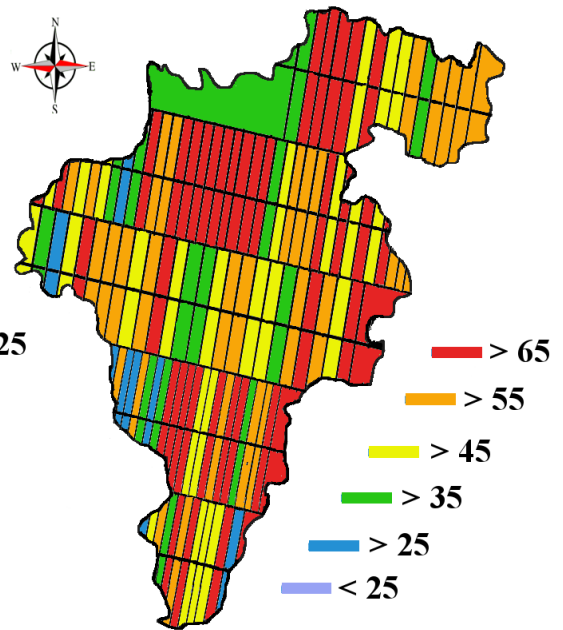
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Potassium distribution in Grass plants

■➤ > 4500	
■➤ > 4000	
■➤ > 3500	
■➤ > 3000	
■➤ > 2500	
■➤ < 2500	

Sodium distribution in Grass plants

■➤ > 1000	
■➤ > 800	
■➤ > 600	
■➤ > 400	
■➤ > 200	
■➤ < 200	
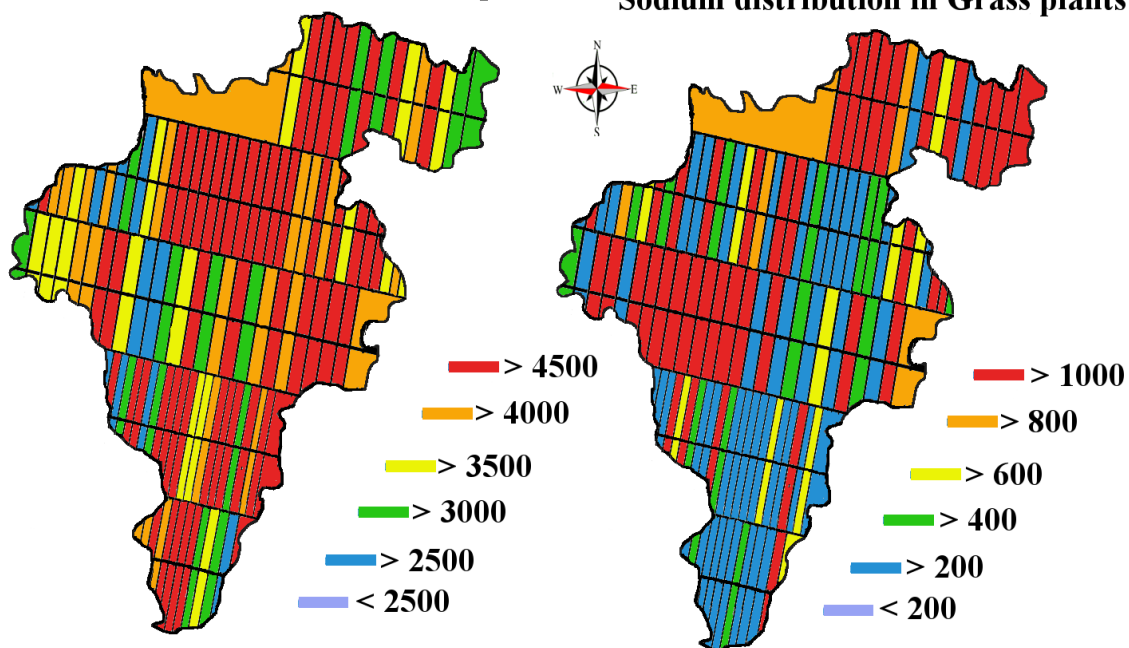
7.5 Germination trial data

	Lithium				Lithium and EDTA	Lithium and EDDS
Rapeseed	98.30%	Melon	15%	Rapeseed	12.50%	98%
Cabbage	90%	Spinach	39%	Cabbage	18.10%	98.70%
Sunflower	90.00%	Broccoli	51.25%	Sunflower	6.25%	100%
Tomato	92.20%	Sprouts	70.00%	Tomato	11%	83.70%
Nicotiana	50.30%	Kohl rabi	56.25%	Mustard	0%	57.90%
Rye grass	45%	Mustard	95.00%	Pok choi	0%	58.90%
Peas	83.75%	Cauliflower	53.75	Radish	0%	67.70%
Broad beans	76.25%	Turnip	71%	Cress W	0%	77%
Runner beans	70%	Pok choi	90%	Cress P	0%	100%
Barley	12%	Mustard	56.25%			
Oats	38.75%	Radish	92.50%			
Sugar beet	18%	Kale	60.00%			
Carrots	73.75%	Kale afro	87.50%			
Leeks	36.25%	Cress land	65%			
Mint	12%	Water cress	46.25%			
Grapes	0%	Rocket	77.50%			
Cress P	100%	Cress W	82%			

7.6 Supplementary Agro-mining data

		Lithium				Lithium	EDTA			Lithium	EDDS	
		Lithium	**Sodium**	**Potassium**		**Lithium**	**Sodium**	**Potassium**		**Lithium**	**Sodium**	**Potassium**
Cabbage	**Leaves**	1496.0	843.8	248.5	**Leaves**	1829.7	10010	9970	**Leaves**	3098.8	6070	7610
Cress	**Leaves**	4225.1	17180	8760	**Cress**	1973.5	1940	3800	**Cress**	2059.4	6220	10920
Sunflower	**Leaves**	1384.7	1256	24	**Leaves**	1925.8	14560	2930	**Leaves**	1875.1	12430	1450
	Stems	470	668	56	**Stems**	1430	19620	5050	**Stems**	780	9880	2730
	Roots	1586	940	540	**Roots**	760	10660	5250	**Roots**	70	6770	4510
	Seeds	230	718	36	**Seeds**	-----	-----	-----	**Seeds**	-----	-----	-----
Tomato	**Leaves**	64.5	385.8	53.2	**Leaves**	-----	-----	-----	**Leaves**	-----	-----	-----
	Stems	72.5	637.2	115.6	**Stems**	-----	-----	-----	**Stems**	-----	-----	-----
	Roots	57.5	250.7	173.5	**Roots**	-----	-----	-----	**Roots**	-----	-----	-----
	Fruit	9.6	514.7	28.1	**Fruit**	-----	-----	-----	**Fruit**	-----	-----	-----
Rapeseed	**Leaves**	17.52	4100	13100	**Leaves**	3577.1	1320	580	**Leaves**	2589.9	15710	4060
	Stems	21.9	3200	16100	**Stems**	900	1464	1104	**Stems**	1210	11970	6480
	Roots	13.4	9600	24500	**Roots**	1420	1352	1516	**Roots**	780	13320	3650
	Seeds	5.2	4100	3300	**Seeds**	2427	2347	433	**Seeds**	-----	-----	------

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