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School of Chemical
Technology

School of Chemical Technology
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Tea Miller

COMPARATIVE ENVIRONMENTAL ASSESSMENT OF ORGANIC AND MINERAL FERTILIZERS – CASE STUDY OF BIOA FERTILIZER PRODUCED FROM INDUSTRIAL WASTE

Master’s thesis for the degree of Master of Science in Technology submitted for inspection, Santiago de Chile, 12 November, 2013.

Supervisor	Professor Katrina Nordström
Instructor	D.Sc. Elina Kähkönen D.Sc. Mari Tuomaala

Aalto University
School of Chemical
Technology

Aalto University, P.O. BOX 11000, 00076
AALTO
www.aalto.fi

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Author Tea Miller

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Abstract

Mineral fertilizers are a powerful tool in guaranteeing world's food supply but their production and use also cause a significant environmental burden. A possible substitute for mineral fertilizers are organic fertilizers, the production of which does not consume virgin, non-renewable raw materials. This master's thesis studies an organic fertilizer which is produced by reusing industrial waste originating from a factory site of which the main activity is pulp and paper production. This fertilizer is named as the BioA fertilizer.

The study had two objectives. The first objective was to determine the composition of the BioA fertilizer. The second objective was to conduct an environmental assessment which compares the environmental impacts that arise during the life cycle of the two research targets: the BioA fertilizer and the reference mineral fertilizer. A Life Cycle Assessment (LCA) was selected for the assessment method and the analyzed environmental impacts were calculated in proportion to the quantity of fertilizer required to obtain a crop yield of 3000 kg of barley per hectare.

The NPK rating for the BioA fertilizer was calculated to be 5-1-1, which is quite similar compared to the organic fertilizers on the Finnish market. In addition, the composition of the fertilizer did not exceed the maximum permitted limit for heavy metals in cadmium. Thus, according to the design criteria used in the present study, the BioA fertilizer is a technically feasible product.

The environmental assessment studied the environmental impacts of the following five modules: 1) raw material consumption, 2) energy consumption, 3) emission generation, 4) waste generation, and 5) usage and nutrient release. In the present study, no single value representing the total environmental impact balance could be provided, rather environmental impacts were compared according to the above modules. It can be stated that from an environmental perspective, in terms of nitrogen content, energy consumption and required quantity, the reference mineral fertilizer appeared to be superior. On the other hand, the BioA fertilizer proved to be superior in raw material consumption, limiting of waste generation and probably in emission generation.

Keywords Organic fertilizers, mineral fertilizers, Life Cycle Assessment (LCA), Life Cycle Inventory Analysis (LCI), biorefinery

Aalto-yliopisto
Kemian tekniikan korkeakoulu

Aalto-yliopisto, PL 11000, 00076
AALTO
www.aalto.fi

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Maailman ruokatuotanto pohjautuu mineraali- eli väkilannoitteiden tehokkaaseen käyttöön. Kasvintuotannon tehostamisen lisäksi mineraalilannoitteet aiheuttavat kuitenkin myös ympäristöhaittoja. Vaihtoehtona mineraalilannoitteille ovat orgaaniset lannoitteet. Tämä diplomityö tarkastelee tapaustutkimuksena orgaanisen BioA-lannoitteen tuottamista paperi- ja selluteollisuuden jätevirroista.

Tämän työn tavoitteet oli jaettu kahteen osaan. Ensimmäisenä tavoitteena oli määrittää BioA-lannoitteen koostumus ja toisena tavoitteena oli suorittaa vertaileva ympäristöarviointi elinkaaren aikaisista ympäristövaikutuksista BioA-lannoitteen ja vertailuun valitun mineraalilannoitteen välillä. Ympäristöarviointimenetelmänä käytettiin elinkaariarviointia (eng. *Life Cycle Assessment*, LCA). Analysoidut ympäristövaikutukset suhteutettiin lannoitekohtaiseen satovasteeseen, joka kuvaa tarvittavaa lannoitteen määrää, jotta pellon tuotto on 3000 kg ohraa hehtaarilta.

BioA-lannoitteen NPK-arvoksi saatiin 5-1-1, joka on samantasoinen verrattuna Suomessa markkinoilla oleviin orgaanisiin lannoitteisiin. BioA-lannoitteen koostumus ei myös ylittänyt kadmiumin ylintä sallittua pitoisuutta. Täten BioA-lannoite on teknisesti toteuttamiskelpoinen tuote tässä diplomityössä käytettyjen tuotekoostumuksen suunnittelukriteereiden mukaan.

Ympäristöarviointi keskittyi viiden eri moduulin ympäristövaikutusten arviointiin. Moduulit olivat 1) raaka-aineen kulutus, 2) energian kulutus, 3) päästöt, 4) jätteiden synty ja 5) käyttö ja ravinteiden vapautuminen. Tämän tutkimuksen perusteella ei pystytty arvioimaan lannoitteiden kokonaisympäristövaikutusta, vaan ympäristövaikutuksia vertailtiin moduulikohtaisesti. Tulosten perusteella voidaan todeta, että ympäristön kannalta vertailuun valitun mineraalilannoitteen typpipitoisuus, energian kulutus ja tarvittava määrä olivat parempia kuin BioA-lannoitteen vastaavat arvot. Toisaalta BioA-lannoite oli ympäristön kannalta parempi raaka-aineen kulutuksessa ja jätteiden synnyssä sekä todennäköisesti myös päästöjen suhteen.

Avainsanat Orgaaniset lannoitteet, mineraalilannoitteet, elinkaariarviointi (LCA), elinkaari-inventaario (LCI), biojalostamo

Preface

This master's thesis was conducted between February and October 2013 at Aalto University Department of Energy Technology as a part of the Bio Refine Tech research project. Bio Refine Tech is a joint project the other members of which are Cursor Ltd. and University of Turku.

I wish to thank my instructors D.Sc. Elina Kähkönen and D.Sc. Mari Tuomaala for their ideas and input throughout the process. Their guidance was essential in order to keep the work structured and analytical. I also dedicate thanks to my thesis supervisor prof. Katrina Nordström who presented encouraging comments on the thesis draft. I am also thankful to M.Sc. Mikko Kouhia who participated in this very same project. He was always one step ahead and thus provided valuable information and opinions on my thesis. Thanks are also extended to other members of the Bio Refine Tech project group at Aalto University. Our meetings played an important role in understanding the perspective of the project. M.Sc. Jukka Kivelä from the University of Helsinki provided me with essential information about organic fertilizers and helped me to understand this branch of science previously unfamiliar to me. Thanks also to all of my proof-readers; this work is definitely better due to the comments, suggestions and corrections they so kindly gave me.

Beyond the workplace, I want to thank Julia Wiikeri who just finished her master's thesis when I started writing my own. Thus, she has been an excellent help, a sort of mentor, and has given me valuable advices such as "Relax whenever it's possible because well planned or not, you'll find yourself in a hurry at the end of the project". I also wish to thank Saara Lehtinen who has helped me understand the fundamentals of both, inorganic chemistry and life. Finally, I thank my family and friends for making life great, outside the office.

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Tea Miller

CONTENTS

1 INTRODUCTION

Between 1950 and 2010 the world population grew by 170% (UN, 2013). A salient factor enabling the steep population growth has been the intensive use of mineral fertilizers, which positively correlates with population growth (Dawson and Hilton, 2011). Fertilizers provide essential nutrients for plants and thus promote plant growth in terms of both, quality and quantity (Finck, 1982). Albeit the mineral fertilizers are a powerful tool to improve the global food security, they also cause an environmental burden and thus alternatives to them are required (Dawson and Hilton, 2011; Lukehurst et al., 2010). The Bio Refine Tech project provides one solution to alleviate dependency on mineral fertilizers by affording a novel approach to produce an organic fertilizer – the BioA fertilizer.

Bio Refine Tech is a research project which objective is to integrate a biorefinery into an existing factory site of which the main activity is pulp and paper mill operations – this concept is named as BioA. The term biorefinery has been established to denote a facility which utilizes biomass for production of both, energy and bioproducts (Naika et al., 2010; Kahiluoto et al., 2011). In the BioA case, the purpose of the biorefinery is to exploit energy and nutrients bound to the organic waste streams originating from the existing factory site. The biorefinery activities that are maintained by the energy and nutrients recovered from the waste streams are algae cultivation, biogas production, and organic fertilizer production. The core idea of the BioA concept is to capture and refine energy and nutrients embedded in the non-product output into profitable forms, and simultaneously reduce the amount of industrial waste.

The BioA concept addresses to the current structural change in Finnish pulp and paper industry and also to political issues at a national and international level. The changing role of the Finnish pulp and paper industry forces companies to innovate new business strategies as the economic importance of forest products is decreasing. At an international level, the climate and energy policy of Finland is guided by a set of binding legislation by the European Union. The targets of the European Union Climate and Energy Package are often referred as "20-20-20" targets due to the three objectives by 2020: a 20% reduction in EU greenhouse gas emissions from 1990 levels, a 20% improvement in the EU's energy efficiency, and increasing the proportion of the energy produced from renewable sources to 20% of the total energy production (EC, 2013a). The BioA concept is in line with these targets with the key objective being the improved energy efficiency and the increased production of renewable energy. In addition to the "20-20-20" targets, the BioA concept also complies with the EU Waste Framework Directive (EC, 2013b) and the Finnish Waste Tax Act (Ministry of the Environment, 2011) both of which restrict waste disposal and enforce the utilization of exploitable waste streams. As a consequence of the structural change in Finnish industry and politics, there is a need for BioA concept type of solutions.

Accordingly, the present study concentrates on one of the three end products of the BioA concept, the organic fertilizer.

In addition to the political issues, another motivation to study organic fertilizers is the strong reliance of the world food security on mineral fertilizers. The fertilizer markets of today are dominated by mineral fertilizers the production of which is generally based on the utilization of non-renewable natural resources and intensive use of fossil fuels (Roy et al., 2006; Heffer and Prud'homme, 2012). Due to the accelerating depletion of non-renewable nutrient resources, the prices of mineral fertilizers are increasing (Vaneeckhaute et al., 2013). In addition, the residues of mineral fertilizers in nature are pollutants degrading the ecosystem (Gilliam et al., 1985). On the other hand, the nutrient concentration is remarkably higher in the mineral fertilizer than in organic fertilizers due to the differences in their manufacturing methods and mobility of nutrient compounds. Contrary to the synthetized mineral fertilizers, production of organic fertilizers mainly consists of minor processing of organic waste streams. Consequently, the nutrient concentration of organic fertilizers is dependent on the raw material streams locally available. Thus, despite the potential environmental advantages of organic fertilizers over mineral fertilizers, there are some doubts as to whether organic fertilizers can provide enough nutrients to guarantee the world food security. (Finck, 1982; Roy et al., 2006)

This master's thesis studies the production of the organic BioA fertilizer from industrial waste in the BioA concept. First, the manufacturing processes and composition of the BioA fertilizer are examined and secondly, a comparative environmental assessment of the organic BioA and the reference mineral fertilizer is conducted. The analysis of the composition of the BioA fertilizer aims to determine, if a technically feasible organic fertilizer product can be produced in the BioA concept. The objective of the comparative environmental assessment between the BioA fertilizer and the reference mineral fertilizer is to analyze how the environmental impacts differ between the BioA fertilizer and the reference mineral fertilizer and, whether the environmental impacts of the BioA fertilizer are smaller compared with those of the reference mineral fertilizer. A streamlined version of the Life Cycle Assessment (LCA) was selected for the method for the environmental assessment. The LCA method was selected because it recognizes the different environmental impacts of a product during its complete life cycle. This is essential as the environmental impacts of organic and mineral fertilizers are assumed to ensue during different phases of their life cycles. In addition, being an established method, the LCA provides a structured framework which facilitated its adaption for the present case study.

The topic of the master's thesis is approached first by the literature survey, followed by the case study. Different types of fertilizers and options for their production and application need to be studied in order to assess both positive and negative environmental impacts that ensue during the life-cycle of a fertilizer product. This data is used to suggest ways in which production and use of fertilizers could be optimized from an environmental perspective.

2 BIOA CONCEPT

The BioA concept is a part of the Bio Refine Tech project which was initially developed by Cursor Ltd. The BioA concept aims at the utilization of industrial residual streams in order to capture and refine valuable nutrients and energy embedded in these streams and to reduce the quantity of industrial waste. The BioA concept consists of two parts: an existing factory site and a plan for a future biorefinery. The aim is to reuse the residual streams of the original factory site in the future biorefinery. (Bio Refine Tech, 2012a)

The existing factory site located in Finland is a pilot project of the design phase of the BioA concept with a view to possibly expand the concept to other similar factory areas. Currently, the main end products from the factory site are the pulp and paper products and in addition heat and power. Integration of the biorefinery next to the existing factory site would allow for the production of three new end products, namely microalgae extracts, biogas and organic fertilizer. The schematic illustration of the BioA concept is presented in Figure 2-1.

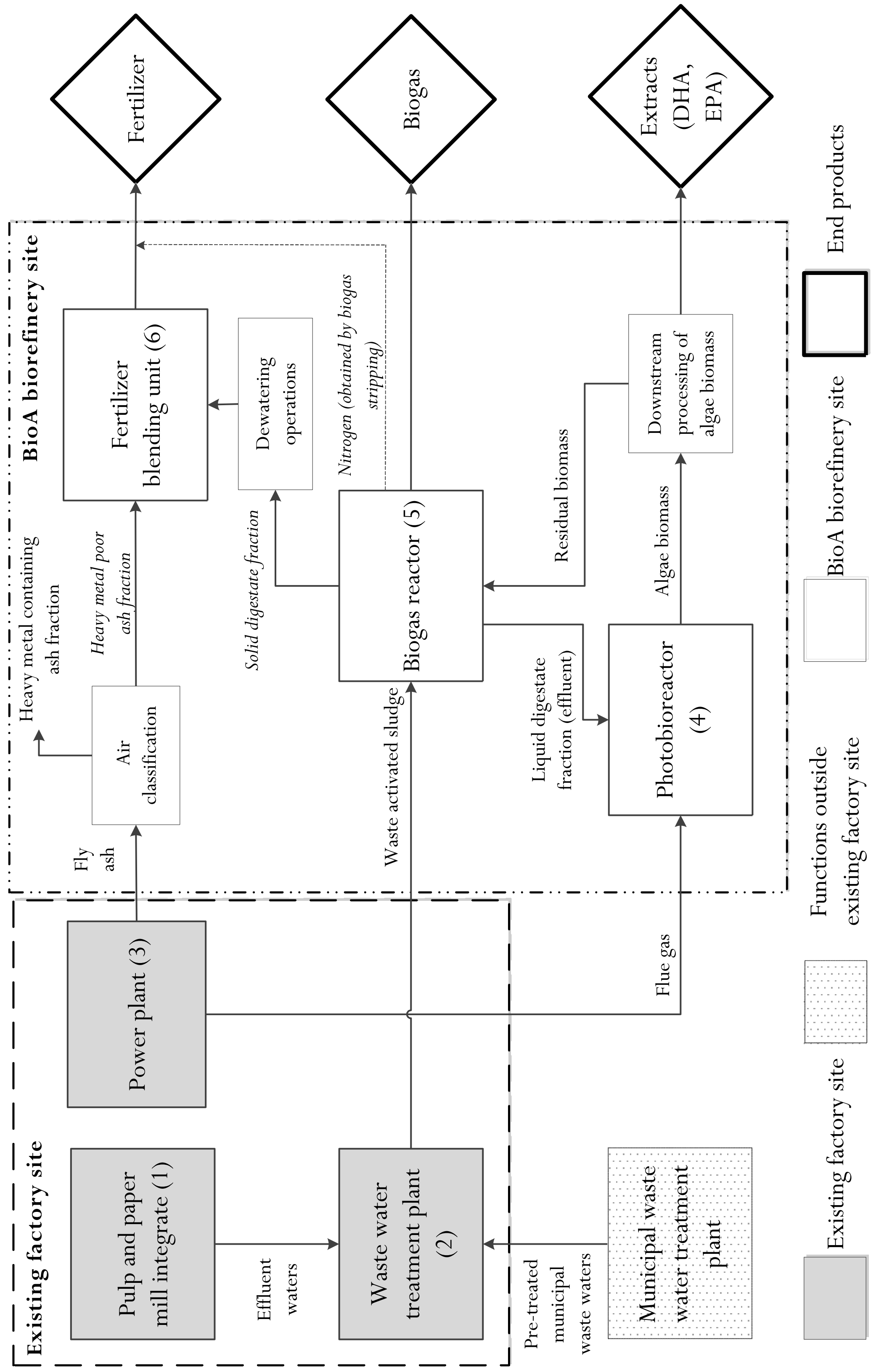


Figure 2-1. Process description of the BioA concept. The manufacturing facilities in the existing factory site are numbered from 1 to 3 and the biorefinery facilities from 4 to 6. Raw material streams for the fertilizer production are italicized.

As shown in Figure 2-1, the existing factory site consists of three facilities, 1) a pulp and paper mill integrate, 2) a waste water treatment plant and, 3) a power plant. Similarly, the future biorefinery site will also include three facilities, namely 4) a photobioreactor, 5) a biogas reactor and, 6) a fertilizer blending unit. The existing factory site also includes some other infrastructure, which, however, is not related to the BioA concept. (Bio Refine Tech, 2012a)

In the biorefinery, waste materials are utilized from all three existing factory facilities, as identified above. Effluent waters from the pulp and paper mills as well as municipal waste waters from the nearby town are redirected to the waste water treatment plant. In addition to effluent waters and municipal waste waters, the waste water treatment plant also processes effluent waters from a nearby tall oil distillery and a flue gas condensate from the power plant. In the waste water treatment plant, waste activated sludge is separated and redirected to the biogas reactor. The end products from the anaerobic digestion in the biogas reactor are biogas, which is mostly methane (CH_4), and digestate. (Bio Refine Tech, 2012a) Ammonia is removed during anaerobic digestion by biogas stripping and the recovered nitrogen is utilized in the fertilizer production (Järvinen, 2013). Heat from the filtrate waters of the pulp and paper mill is directly led to the photobioreactor. Possible surplus heat can be utilized in the drying operations in the fertilizer production. (Bio Refine Tech, 2012a)

Subsequent to anaerobic digestion in the biogas reactor, raw biogas is recovered and digestate is separated into liquid and solid fractions, and nutrients are spread over both fractions. The liquid fraction is directed to the photobioreactor whereas the solid fraction is directed to the fertilizer blending unit. The liquid fraction of the digestate and flue gases from the power plant both serve as nutrient sources for algae and the latter also contributes as a carbon dioxide source for the algae. Subsequent to algal cultivation, high-value algal extracts are separated and the remaining algal biomass is again redirected to the biogas reactor for digestion. (Bio Refine Tech, 2012a) The liquid fraction of the digestate and algal biomass circulate in the closed loop structure, as shown in Figure 2-1.

In addition to the flue gases, also fly ash from the power plant is utilized for fertilizer production. The operation of the power plant produces a substantial amount of ash which is classified and used for fertilizer production. Ash is separated into a heavy metal containing a light fraction and a heavy fraction with lower heavy metal concentrations and then mixed with the solid fraction of the digestate in order to produce organic fertilizer. Currently, the disposal of ash occurs in the form of landfilling substance without any earnings or costs. As licensed by the Environmental Administration of Southern Finland, the landfilling option is available about ten years more. (Bio Refine Tech, 2012a)

3 MICROALGAL BIOTECHNOLOGY

The studied biorefinery in the BioA concept is based on the cultivation of microalgae. Microalgae are among the most abundant organisms and the earliest life forms on earth. They form a rich assemblage of organisms where variation among the group is high as regards appearance, distribution or cell organelles. (John et al., 2011; Falkowski et al., 2004) Utilization of microalgae for human consumption dates back 2000 years but concerted efforts for development of microalgal biotechnology started only in the mid-20th century. At present, algal products comprise a vast array of applications. In addition to direct consumption as food, microalgae have applications in areas of supplementary nutrients, cosmetics, fertilizer industry, animal feed, metabolic engineering and biofuels. (McHugh, 2003; Spolaore et al., 2006)

The advantages of microalgal based biomass over other biomass options are high growth rates and productivity. In addition, microalgal species can be adapted to live in diverse environmental conditions with reference to temperature ranges and feedstock options. Consequently, their cultivation requires less arable land than cultivation of other current biomass options and cultivation of algae does not compete with terrestrial crop production for human consumption. (Mata et al., 2010)

3.1 ALGAE CLASSIFICATION

A precise taxonomic definition of the diverse polyphyletic group of algae is controversial. Commonly algae are divided into macroalgae and microalgae, the former ranging from few centimeters to 20 meters and the latter being microscopically small (McHugh, 2003; John et al., 2011). Another categorization divides algae into bacteria-type prokaryotes, which do not have a nucleus and plant-like eukaryotes, which do have a nucleus. However, for example Barsanti and Gualtieri (2006) classify prokaryotic cyanobacteria and prochlorophytes as algae whereas Madigan and Martinko (2006) do not consider them as algae at all. Either way, eukaryotic algae are more dominant by the number of the species. Due to the uncertainties of what to be called alga and abundance of these organisms in all existing earth ecosystems, estimations of the number of algal species have great variations, mostly ranging between 30,000 to one million. According to the estimation based on the on-line taxonomic database AlgaeBase (Guiry and Guiry, 2013), the number of algal species is likely to be about 72,000, most of the species being microalgae. (Guiry, 2012) A taxonomic classification of algae based on Barsanti and Gualtieri (2006) and Guiry and Guiry (2013) is presented in Table 3-1.

Table 3-1. Classification of algae (modified from Barsanti and Gualtieri (2006) and Guiry and Guiry (2013)).The most potential microalgae alternatives for the BioA concept are made bold.

Empire	Phylum	Class	Common name
Prokaryota	Cyanophyta	Cyanophyceae	Blue-green algae
	Prochlorophyta	Prochlorophyceae	n.a.
Eukaryota	Glaucophyta	Glaucophyceae	n.a.
	Rhodophyta	v.a.	Red algae
	Heterokontophyta	Chrysophyceae	Golden algae
		Xantophyceae	Yellow-green algae
		Bacillariophyceae	**Diatoms**
		Phaeophyceae	Brown algae
		Eustigmatophyceae	n.a.
		Dictyochophyceae	n.a.
		Raphidophyceae	n.a.
	Haptophyta	Haptophyceae	Coccolithophorids
	Cryptophyta	Cryptohyceae	Cryptomonads
	Dinophyta	Dinophyceae	Dinoflagellates
	Euglenophyta	Euglenophyceae	**Euglenoids**
	Chlorarachniophyta	Chlorarachniophyceae	n.a.
	Chlorophyta	v.a.	Green algae

n.a. not available, v.a. various available

According to the information received between April and September 2013 from the University of Turku (BioA research group), the most potential microalgae for the cultivation are *Euglena gracilis*, *Pheodactylum tricirnutum, Nannochloropsis oculata* and *Monodopsis subterranea* of which the first is an Euglenoid, the second a Diatom and the third and fourth represent the class Eustigmatophyceae (Tyystjärvi, 2013, Guiry and Guiry, 2013). These four potential eukaryotic microalgae are made bold in Table 3-1.

3.2 CHARACTERISTICS OF MICROALGAE

Microalgae form a heterophyletic group and consequently their characteristics are diverse. The principal common factor among organisms is oxygenic photosynthesis. (Barsanti and Gualtieri, 2006) It is the capability to the effective photosynthesis which drives the microalgae into the center of the biotechnology solutions for energy and climate questions. Microalgae are capable of synthetizing large quantities of carbohydrates, proteins and lipids over a relatively short period when compared with terrestrial plants. This is possible because algae have a high photon conversion efficiency which expedites the utilization of light energy in photosynthesis, which consequently expedites the accumulation of biomass. In addition, many microalgal species are unicellular and do not have to spend energy on distribution and transportation of storage molecules between tissues. (John et al., 2011)

The cell structure of prokaryotic and eukaryotic microalgae varies greatly and there is also variation among these subgroups. Typical cell organelles of eukaryotic microalgae are the nucleus, chlorophyll-rich chloroplasts, mitochondria, Golgi bodies, an endoplasmic reticulum, and membrane-bound vacuoles. (Barsanti and Gualtieri, 2006; Andersen, 2013) In addition to the green chlorophyll α pigment, which all photosynthetic microalgae contain, many microalgae appear as brown or red due to other pigments such as xanthophylls and carotenoids which mask the green color (Madigan and Martinko, 2006).

Microalgae commonly grow in aquatic environments, where they can exploit nutrients and water, also such which are unsuitable for human consumption, and tolerate a wide range of pH and temperatures. Their vital requirements are only light, CO_2 and H_2O, which are the starting materials for oxygenic photosynthesis – a common feature of nearly all algae. During photosynthesis light energy is converted into chemical energy which fuels the activities of the organisms. In addition, the high energy algal compounds provide a feedstock option for example for biofuel and food production. Photosynthesis is essential for ecosystems as it maintains atmospheric CO_2 and O_2 levels and supplies organic compounds. Algae are responsible for approximately half of the photosynthetic productivity on earth, most of the production occurring in the oceans. (Masojídek et al., 2013) A simplified process of photosynthesis is presented in Equation 3.1 (Barsanti and Gualtieri, 2006):

$$\mathrm{nCO_2 + nH_2O + light \xrightarrow{Chlorophyll\ \alpha} (CH_2O)_n + nO_2}, \qquad (3.1)$$

where $(CH_2O)_n$ represents carbohydrates. Microalgae which carry out photosynthesis obtaining their energy from light and fixing CO_2 into organic materials such as carbohydrates, are called phototrophs. Some algae are chemoorganotrophs, which means that they obtain energy by catabolizing simple sugars, organic acids or even carbon from CO_2 without the requirement of light. (Madigan and Martinko, 2006; Masojídek et al., 2013) Certain algal species can be either phototrophic or chemoorganotrophic, depending on the availability of light for energy metabolism, and are thus called mixotrophs (John et al., 2011; Mata et al., 2010).

3.3 COMMERCIAL APPLICATIONS OF MICROALGAE

Microalgae provide a rich source of potential chemical compounds for a wide range of industries, such as, food, feed, nutritional, cosmetics, pharmaceutical, bioengineering and biofuels. On the other hand, despite the great potential of microalgal applications, commercial achievements have been modest due to the fact that from a biotechnological point of view microalgae are not a well-studied group (Spolaore et al., 2006; Olaizola, 2003). This has hindered the development of microalgal based compounds to marketable products (Olaizola, 2003). Apt and Behrens (1999) and Spolaore *et al.* (2006) both emphasize that important developments have taken place in recent years in microalgal biotechnology. Currently, the predominant microalgal product is the biomass of microalgae sold as pastilles or powder in the human health food market (Pulz and Gross, 2004).

Pulz and Gross (2004) have divided microalgal products into four groups which are biomass, coloring substances, antioxidants and special products (Table 3-2). Olaizola (2003), Spolaore *et al.* (2005) and Apt and Behrens (1999) highlight the same promising microalgal products in their studies. In Table 3-2, soil conditioner product is the closest reference to the fertilizers.

Table 3-2. Potential commercial microalgal products (Pulz and Gross, 2004).

Product group	**Product**	**Retail value (US \$ x 10^6)**	**Development**
Biomass	Health food	1,250-2,500	Growing
	Functional food	800	Growing
	Feed additive	300	Fast-growing
	Aquaculture	700	Fast-growing
	Soil conditioner	n.a.	Promising
Coloring substances	Astaxanthin	<150	Starting
	Phycocyanin	>10	Stagnant
	Phycoerythrin	>2	Stagnant
Antioxidants	β-Carotene	>280	Promising
	Tocopherol	n.a.	Stagnant
	Antioxidant extract	100-150	n.a.
	ARA	20	Growing
	DHA	1,500	Fast-growing
	PUFA extracts	10	n.a.
Special products	Toxins	1-3	n.a.
	Isotopes	>5	n.a.

n.a. not available

3.4 POTENTIAL MICROALGAL PRODUCTS IN THE BIOA CONCEPT

All three end products from the BioA biorefinery site; microalgal extracts, biogas and organic fertilizer, are partly or entirely based on microalgal biomass (see Figure 2-1). High value microalgae extracts play a pivotal role in the BioA concept because it is estimated that algal cultivation is not commercially lucrative for biogas and fertilizer production alone as they are products of low profit margin (FAO, 2006; Suominen et al., 2013). To improve the cost-effectiveness of the BioA concept, the algal species, which will be selected for the cultivation, must also produce some high-value components. According to current understanding, polyunsaturated fatty acids (PUFA) would be the most potential microalgal extracts suitable for the BioA concept (Tyystjärvi, 2013). According to the literature survey and personal communication (Tyystjärvi, 2013), commercial potential is also offered by extractable natural pigments of algae.

3.4.1 Polyunsaturated fatty acids

The most studied and prominent algae-derived polyunsaturated fatty acids (PUFAs) are docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA). DHA is composed of 22 carbon atoms with 6 double bonds (22:6) and EPA is composed of 20 carbon atoms with 5 double bonds (20:5). (Apt and Behrens, 1999; Sijtsma and de Swaaf, 2004) They are both omega-3 fatty acids, which signifies that the first double bound in a molecule chain is located at the third carbon-carbon bond calculated from the distal carbon atom at the methyl group end of the molecule (Berg et al., 2007). The human body cannot synthetize PUFAs in excess of chain lengths of 18 carbons, and thus, these fatty acids must be obtained from dietary sources. The best dietary sources of DHA and EPA are mainly fish and fish oils. However, fish do not synthetize DHA or EPA, rather the accumulated DHA and EPA in fish originate from the consumption of algae. The advantages of algal oils over fish oils are 1) reduced risk of accumulated contaminants (e.g. heavy metals and lipid-soluble environmental pollutants which accumulate in fish), 2) a higher purification potential and, 3) a tendency of algae to accumulate one specific PUFA rather than a mixture of various PUFAs, which is beneficial for further use. (Pulz and Gross, 2004; Apt and Behrens, 1999; Sijtsma and de Swaaf, 2004)

DHA is essential for infants as it is a major structural fatty acid in the grey matter of the brain and in the retina of the eye, and also a key component of the heart muscle tissue. The primary nutrient source of DHA for a human infant is breast milk. If breast milk is not available, infant formulas containing the highly purified DHA are important substitutes. For adults, DHA maintains cardiovascular health. EPA is harmful for infants affecting growth rates and causing other developmental difficulties. For adults, EPA affects positively on the coronary vascular status due to its metabolic products, such as eicosanoids, which have antithrombotic and antiaggretory effects. (Apt and Behrens, 1999; Spolaore et al., 2006; Sijtsma and de Swaaf, 2004)

When selecting the algal species for PUFA production, it is important to know whether the algal fatty acids occur as components of triacylglycerol in intracellular fluids or as components of membrane lipids (e.g. phospholipids). It is preferable to have a high lipid content in triacylglycerols than in membrane lipids as the PUFA content in triacylglycerols can be modified by optimizing the nutrient levels and environmental conditions during cultivation, whereas the quantity of membrane lipids is more stable. (Sijtsma and de Swaaf, 2004; Tyystjärvi, 2013) The location of fatty acids in cell structure also affects the processes selected for downstream processing (Sijtsma and de Swaaf, 2004). As DHA and EPA affect adults and infants in different ways, it is necessary to be able to purify DHA and EPA separately (Apt and Behrens, 1999; Spolaore et al., 2006).

3.4.2 Natural pigments

Natural pigments, such as carotenoids and phycobiliproteins, are the second best high-value microalgal extracts to be produced in the BioA concept. They are light-gathering accessory pigments which help algae to capture light across a broader spectrum in comparison to the narrower spectrum of chlorophylls. Carotenoids are mainly used as food coloring agents and phycobiliproteins as molecular probes. (Madigan and Martinko, 2006; Spolaore et al., 2006; Apt and Behrens, 1999)

A typical example of a carotenoid is astaxanthin, which is an extended polyene: a chain of conjugated double bonds where single and double bonds alternate. In nature, astaxanthin normally occurs either as conjugated to proteins or esterified with one or two fatty acids, which stabilizes the molecule. The human body and mammalian cells on general cannot synthetize astaxanthin. (Madigan and Martinko, 2006; Spolaore et al., 2006) The main consumer of astaxanthin is the salmon industry where it is fed to fish to enhance the color of the flesh. In addition to being a strong coloring agent, astaxanthin has antioxidant, UV-light protection and anti-inflammatory properties, and thus it has important applications in the nutraceutical, cosmetics and food industries. (Spolaore et al., 2006; Guerin et al., 2003)

Similar to microalgae-derived fatty acids, microalgal carotenoids are also competing with corresponding synthetic forms. Thus far it has not been possible to stabilize the market share of microalgae-derived astaxanthin over the synthetized version in the salmon industry due to the much higher production costs. However, there are some applications in the animal feed industry where natural astaxanthin is preferred due to its' enhanced deposition in tissues, regulatory requirements and consumer demand for natural products. (Spolaore et al., 2006) As a rule, synthetic forms are generally more commercially profitable whereas microalgal derived forms are superior in terms of purity, and in some cases in terms of natural chemical composition, which can be hard to achieve via synthetic chemistry (Olaizola, 2003).

Another pigment product studied in the BioA concept are phycobiliproteins which are light-harvesting red or blue pigment molecules which function as components of the photosynthetic apparatus in the microalgae. Phycobiliproteins consists of a chain of tetrapyrroles which are coupled to the proteins. (Madigan and Martinko, 2006) Phycobiliproteins are used as natural dyes (e.g. phycocyanin), in pharmaceutical applications and in the immunological industry. From an immunological perspective, the advantages of phycobiliproteins are their capability to create stable conjugates with antibodies, receptors and other biomolecules and thus function as fluorescent tags for highly specific probes. Some other significant applications in immunology are in flow cytometry and fluorescence-activated cell sorting. (Spolaore et al., 2006; Apt and Behrens, 1999)

4 FERTILIZERS

The present study examines fertilizer production in the BioA concept and compares environmental impacts of organic and mineral fertilizers. Due to the central role of fertilizers in the present study, these products are dealt in detail in the following.

A fertilizer can be defined as any natural or synthetized material which contains at least 5% in total one or more of the three primary nutrients which are nitrogen (element symbol N), phosphorus (P) and potassium (K) (FAO and IFA, 2000).The purpose of fertilizers is to enhance or replenish the nutrient supply of plants by providing essential nutrients, which consequently results in higher yields and quality of crops. The application of fertilizers aims at maintaining the nutrient balance in soil since nutrients are constantly depleted from the soil as crops are harvested. (Ludwick et al., 1990; Roy et al., 2006; Finck, 1982) As Dawson and Hilton (2011) have stated "fertilizers do not make plants grow but the lack of the nutrients can prevent the plant from expressing its full productive potential". The crop production scale can be improved in two manners: by increasing the area cultivated and by increasing the crop yield per area, where the latter contributes relatively more. The quantity and quality of crop yield per area can be improved by accelerating the movement of requisite nutrients through the ecosystem, and this can be done with the aid of fertilizers. (Byrnes and Bumb, 1998; Finck, 1982)

4.1 FERTILIZER TYPES

Fertilizers can be divided into two types, 1) mineral fertilizers and 2) organic fertilizers. In addition, there are also biofertilizers which do not contain nutrients per se but are microbial inoculants affecting soil structure and the mobility of nutrients. (Roy et al., 2006) The present study encompasses mineral and organic fertilizers but biofertilizers are excluded from the inspection.

Mineral fertilizers are also called inorganic, synthetic or chemical fertilizers and are defined as a product which is synthetized from inorganic natural compounds. They contain inorganic compounds. (Roy et al., 2006; Finck, 1982) As a rule, inorganic fertilizer compounds do not contain carbon and they are mainly derived from non-biological mineral sources (Finck, 1982). Common inorganic fertilizer compounds are mineral salts, oxides and sulfides which readily yield charged ions when dissolved in water (Finck, 1982; FAO and IFA, 2000). Some inorganic fertilizer compounds exist in nature (e.g. urea and crude phosphates) but for fertilizer purposes they are mainly produced or modified synthetically (FAO and IFA, 2000).

Contrary to artificially manufactured mineral fertilizers, organic fertilizer is defined as a substance of a biological nature which is used in the form in which it is formed in nature or with minor processing. Organic fertilizers can also contain mineral materials, thus they must be unprocessed. (Finck, 1982; Roy et al., 2006) Thus with reference to fertilizers, the word organic does not strictly refer to organic compounds albeit organic fertilizers are mostly composed of them, rather the reference pertains to the organic raw materials. In organic fertilizers, nutrients are bound to relatively large and complex organic molecules, which contrary to inorganic compounds, do contain carbon. During the decomposition of organic matter by microorganisms in the soil, properties of the organic substances change and the nutrients bound to organic matter are slowly released as inorganic compounds. (Roy et al., 2006; Palojärvi et al., 2002; Madigan and Martinko, 2006) Common examples of organic fertilizers are such as crop or food residues, manure, animal waste slurry, sewage sludge, peat, ash and their processed forms (Roy et al., 2006; Finck, 1982). Both, the concentration and release rate of nutrients, are significantly lower in organic fertilizers than in mineral fertilizers (Roy et al., 2006; Ludwick et al., 1990; Palojärvi et al., 2002).

The borderline between mineral and organic fertilizers is not always a clear-cut, partly because both mineral and organic fertilizers can be naturally occurring or synthetically manufactured substances. A good example of this is the nitrogen compound urea ($CO(NH_2)_2$). Urea is a naturally occurring substance but it can also be manufactured by a chemical synthesis from inorganic starting materials: ammonia and carbon dioxide. In most cases, the synthetized urea is categorized as mineral fertilizer, albeit according to its chemistry, it is an organic compound. (Finck, 1982; Roy et al., 2006; Parnes, 1990)

4.2 NUTRIENTS

The number of essential nutrients for successful plant growth is 16. Three of them, oxygen (O), carbon (C) and hydrogen (H), are obtained from water and carbon dioxide, and the other 13 from soil, animal manure and/or fertilizers. (FAO and IFA, 2000; Ludwick et al., 1990) Although oxygen, carbon and hydrogen collectively compose from 90 to 95% of the dry matter of the plant and are in constant abundant supply, organisms cannot remain viable without the rest of the 13 nutrients (Dawson and Hilton, 2011).

4.2.1 Macro and micronutrients

The 13 nutrients obtained from soil, animal manure and/or fertilizers are divided into macro and micronutrients. Macronutrients are further subdivided into primary and secondary nutrients. The primary nutrients are nitrogen (N), phosphorus (P) and potassium (K) and they are all needed in large amounts for adequate plant growth. They are also in the dominant position from the fertilizer industry's point of view. The secondary nutrients are magnesium (Mg), sulfur (S) and calcium (Ca) and as primary nutrients, plants also take up these in considerable amounts. The micronutrients, which are also called the trace elements, are iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), chlorine (Cl) and boron (B). Also the micronutrients are equally important substances for plant growth, even though they are only needed in minute amounts. Although there are significant differences in required quantities of different nutrients, none of the macronutrients or micronutrients can be substituted for another without negative impact on plant growth. (FAO and IFA, 2000; Ludwick et al., 1990; Dawson and Hilton, 2011)

Ionic forms of the macro and the micronutrients as well as their typical concentrations in plant dry matter are presented in Table 4-1. Since 1984 also selenium (Se) has been added to Finnish NPK-fertilizers due to the low selenium content in Finnish soils (Riistama et al., 2005). In addition to the 13 essential nutrients, fertilizer products contain inert additives, the most common ones being dolomite and limestone (Kongshaug, 1998).

Table 4-1. Typical ionic forms of macro and micronutrients in soil solution (Roy et al., 2006).

Nutrient	Ionic form	Concentration in plant dry matter
Macronutrients		
Primary nutrients		
Nitrogen (N)	NH_4^+, NO_3^-	1.50 %
Phosphorus (P, P_2O_5)	$H_2PO_4^-$, HPO_4^{2-}	0.1-0.4%
Potassium (K, K_2O)	K^+	1-5%
Secondary nutrients		
Sulfur (S)	SO_4^{2-}	0.1-0.4%
Calcium (Ca)	Ca^{2+}	0.2-1.0%
Magnesium (Mg)	Mg^{2+}	0.1-0.4%
Micronutrients		
Boron (B)	H_3BO_3, $H_2BO_3^-$	6-60 µg/g (ppm[2])
Iron (Fe)	Fe^{2+}	50-250 µg/g (ppm)
Manganese (Mn)	Mn^{2+}	20-500 µg/g (ppm)
Copper (Cu)	Cu^+, Cu^{2+}	5-20 µg/g (ppm)
Zinc (Zn)	Zn^{2+}	21-150 µg/g (ppm)
Molybdenum (Mo)	MoO_4^{2-}	< 1 µg/g (ppm)
Chlorine (Cl)	Cl^-	0.2-2%

Three primary nutrients, nitrogen (N), phosphorus (P) and potassium (K), have different effects on plants. Nitrogen is one constituent of chlorophyll ($C_{33}H_{72}O_5N_4Mg$) and hence responsible for a dark green leaf color and lush vegetative growth. It is also vital for fruit and seed formation and promotes aerial vegetative growth and improves the top/root ratio. Nitrogen is also essential for protein synthesis, which cannot proceed in the absence of nitrogen. (Boswell et al., 1985) Phosphorus stimulates early plant growth and it is essential for proper root development (Parnes, 1990; Ludwick et al., 1990). Lack of phosphorus leads to delayed maturity which can cause a significant visual disorder affecting crop market quality (Young et al., 1985). At the molecular level, phosphorus affects the formation of nucleic acids (DNA and RNA). Phosphorus also plays a pivotal role in the function of ATP molecules and hence the energy metabolism of cells. (Ludwick et al., 1990; Parnes, 1990) Potassium is vital for the translocation of photosynthesis and hence promotes starch formation. Potassium is also required for adequate water intake of plants. In addition, it hastens root growth, increases plant resistance to disease, improves winter hardiness and increases size and quality of fruits and vegetables. (Ludwick et al., 1990; Parnes, 1990; Barber et al., 1985)

4.2.2 Nutrient release in soil

Mineral and organic fertilizer compounds have different release modes and distribution rates in the soil solution due to the different chemical nature of inorganic and organic compounds. Eventually, all nutrients, whether derived from inorganic or organic sources, must be converted into inorganic ionic forms because this is the only form in which they are usable by plant roots (Roy et al., 2006).

Common inorganic compounds in mineral fertilizer products are such as salts and oxides which are formed by ionic bonding which can readily dissolve in water. After the dissolution of inorganic compounds, the nutrients are in soil solution as positively or negatively charged ions in which form they are available for plants. (Zumdahl and Zumdahl, 2003; Roy et al., 2006) In addition to plants, also soil microbes utilize inorganic compounds converting them into organic compounds – this process is called immobilization and it prevents nutrients being accessible to the plants. Due to the water solubility of inorganic compounds, they can be washed away lakes, rivers and other water bodies and consequently contribute eutrophication. (Roy et al., 2006)

In organic matter, nutrients are mainly bound with covalent bonds to relatively large carbon containing molecules. In addition to the strong covalent bonds, there are also weak bonds, such as hydrogen bonds, van der Waals forces and hydrophobic interactions. It is the chemical nature of covalent bonds which makes organic compounds rather stable. Contrary to the water solubility of inorganic compounds, the main breakdown route of organic compounds is decomposition by microorganisms. (Madigan and Martinko, 2006) Decomposition of organic compounds to inorganic compounds is called mineralization, and it is the opposite process to immobilization. Degradation of organic compounds by microorganisms, often by oxidation-reduction reactions, leads to a vast array of more simple compounds. Hereby complex organic compounds are converted into more simple inorganic ones which can then further be broken down into ions. (Palojärvi et al., 2002) Some organic molecules, such as amino acids or metal chelates, can be taken up by plants as entire molecules (Roy et al., 2006). Figure 4-1 presents a simplified illustration of the release modes of inorganic and organic compounds in soil.

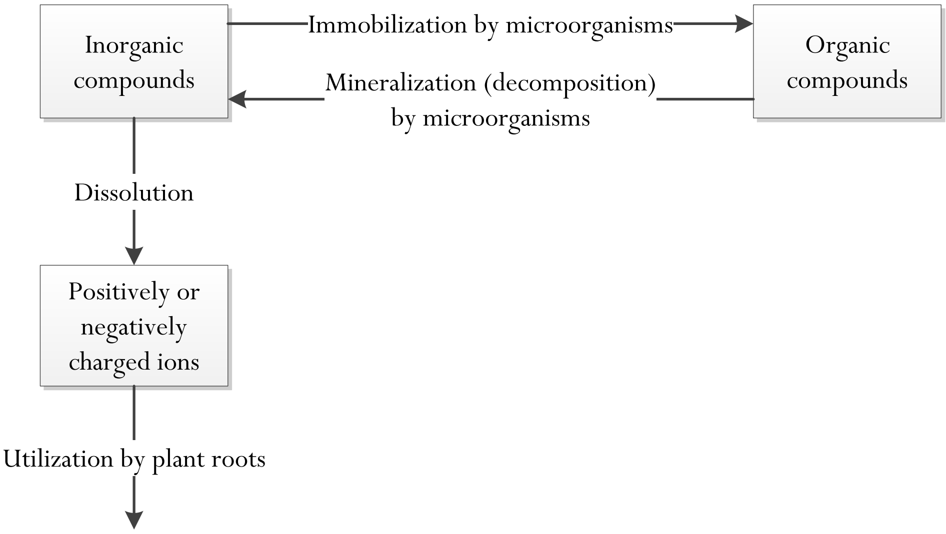


Figure 4-1. Simplified illustration of the release modes of inorganic and organic compounds in soil. The illustration is based on the information provided in Palojärvi *et al.* (2002) and Roy *et al.* (2006).

In the case of organic fertilizer compounds, the ratio of carbon to nitrogen (C:N ratio) can expedite or hinder the release of organic compounds. The C:N ratio of both, of an organic fertilizer and of soil, affect the decomposition rate of the organic compounds. If the organic fertilizer has too high a C:N ratio in comparison with the soil, there is not enough nitrogen for microbes and instead of decomposing fertilizer compounds, microorganisms will utilize more easily available nitrogen sources from soil which leads to immobilization instead to the desired mineralization. While C:N ratio of the organic fertilizer is low, organic matter is easier to decompose and nitrogen is released more than microbes require, and surplus nitrogen is utilized by plants. An optimum C:N ratio of arable land is from 10 to 16. (Palojärvi et al., 2002) In addition to degrading the organic compounds into more usable forms, microbial activity also nourishes the soil. Decomposition of organic matter improves the soil structure and aeration, increases soil water holding capacity, assists in regulation of soil temperature and protects against erosion. (Roy et al., 2006; FAO and IFA, 2000)

To summarize, crops can utilize mineral fertilizer compounds faster than organic fertilizer compounds because the ionic bond dissolves readily in water and thus nutrients are quickly released in charged ionic form. The breaking down of organic compounds is a much slower process and hence nutrition release occurs during a longer period and concentration of nutrients remains moderate. Crops can also utilize some organic complexes as such, but their rate of absorption is relatively slow. (Roy et al., 2006; Madigan and Martinko, 2006; Palojärvi et al., 2002) The differences between mineral and organic fertilizers are recapitulated in Table 4-2.

Table 4-2. Differences between mineral and organic fertilizers. Compiled from data in Zumdahl and Zumdahl (2003), Roy *et al*. (2006), Madigan and Martinko (2006), Palojärvi *et al.*(2002) and FAO and IFA (2000).

	Mineral fertilizer	**Organic fertilizer**
Chemical bond	Ionic bond	Covalent bond
Release mode	Dissolution	Decomposition by microorganisms, dissolution
Release rate	Fast	Slow
Leaching probability	High	Low
Required quantity	Small	High
Nutritional value	High	Moderate
Quantity of organic matter	Zero	High
Improvement of soil	No	Yes

4.2.3 NPK rating

The quantity of primary nutrients in the fertilizer product is expressed by NPK rating where the letters stand for the percentage by weight of N, P and K in the fertilizer product. The N value is always a percentage of elemental nitrogen (N) whereas P and K values can be expressed as percentages of elemental compounds (P and K) or oxidized compounds phosphate (P_2O_5) and potash (K_2O), respectively. Either way, the primary nutrients do not exist in fertilizer products in the above mentioned elemental or oxidized forms. Such forms are only a convenient calculation basis which allows the comparison between different fertilizer products. The NPK rating plays a salient role in fertilizer industry as its definition is consistent in all regions which consequently enables the comparison between different fertilizer products. (FAO and IFA, 2000; Ludwick et al., 1990; Finck, 1982) In this thesis, all NPK ratings are expressed on an elemental basis unless otherwise stated.

4.3 MANUFACTURING

Although the use of simple organic fertilizers has long historical roots, it was the development of the mineral fertilizers manufacturing processes which enabled a rapid population growth and development of society during the 20th century. The production scale of mineral fertilizers has increased in line with population growth since 1960s, and both are expected to continue to increase. (Byrnes and Bumb, 1998; FAO, 2006) On the contrary to established mineral fertilizer production processes, a vast array of different methods as well as raw materials exists for organic fertilizer production (Roy et al., 2006). Production of organic fertilizers is mainly based on recycling of nutrients whereas production of mineral fertilizers relies on utilization of virgin raw materials (Roy et al., 2006; Windridge, 1996).

4.3.1 Mineral fertilizers

Industrial scale manufacturing of the main components of mineral fertilizers dates back to the early 20th century. Naturally, the processes have improved substantially during the years, but for example the breakthrough of the Haber-Bosch process for ammonia production was achieved in 1909 and a wet process for phosphoric acid production was developed in 1920s. (Dawson and Hilton, 2011; Schrödter et al., 2013; Kongshaug et al., 2013) According to the International Fertilizer Association (IFA) (2013), the world major producing countries of mineral fertilizers and their raw materials are China, Russia, India, Morocco, US, Canada, Indonesia and Belarus. The demand for the mineral fertilizers is growing at an annual rate of 2.1% estimated to grow from the current 177 million tonnes to 193 million tonnes by 2016 (Heffer and Prud′homme, 2012; Dawson and Hilton, 2011). In 2010-2011, the global fertilizer consumption of three primary nutrients was 104.1 Mt (60.5%) nitrogen, 40.5 Mt (23.5%) phosphate and 27.6 Mt (16.0%) potash nutrients (Heffer and Prud′homme, 2012).

The global production of mineral fertilizers consumes approximately 1.2% of the world's total annual energy produced and fertilizer production is responsible for approximately the same proportion of the global greenhouse gas emissions (Kongshaug, 1998). Albeit production processes of mineral fertilizers are today in Europe energy efficient as they operate close to a theoretical thermodynamic limit, they can still be considered energy intensive (Dawson and Hilton, 2011; Kongshaug, 1998). According to Ramírez and Worrell (2006), the energy embedded in the global fertilizer industry in 2001 was about 3660 PJ. As a comparison, the total energy consumption in Finland in 2001 was 1389 PJ (Motiva Ltd, 2013). Fertilizer production processes presented below serve as examples of typical mineral fertilizer production processes of three primary nutrients.

4.3.1.1 Nitrogen fertilizers

Although almost 80% of the atmosphere consists of nitrogen, most of plants cannot convert the highly stable nitrogen atom (N_2) into utilizable form. Nitrogen fertilizers contain nitrogen in absorbable form for plants, the most important compounds being those which yield ammonium (NH_4^+) or nitrate (NO_3^-) ions. (Finck, 1982) In Finland, the most common compounds in nitrogen fertilizers are ammonia (NH_3) and nitric acid (HNO_3) and also occasionally urea ($CO(NH_2)_2$) (Riistama et al., 2005). Other common nitrogen fertilizer compounds are urea-ammonium nitrate (UAN), ammonium nitrate (AN), calcium ammonium nitrate (CAN) and ammonium sulfate (Windridge, 1996; Kivelä, 2013). Below, a method for ammonia synthesis is presented as it is the most salient nitrogen compound in the fertilizer industry.

The foremost method for ammonia (NH_3) synthesis is the Haber-Bosch process which is based on combining atmospheric nitrogen with hydrogen commonly originating from natural gas, oil or coal. The previously mentioned hydrogen sources also serve as an energy sources, the natural gas option being the dominant route with about 77% share of world ammonia production. (EFMA, 2000a) The best available technique (BAT) for hydrogen separation from hydrocarbon source is steam reforming of natural gas or other light hydrocarbons. The process air used in steam reforming also functions as a nitrogen source. Nitrogen is acquired from air through a liquid air distillation or an oxidative process. The end product of steam reforming is ammonia synthesis gas: a purified gas containing only hydrogen and nitrogen. (EFMA, 2000a; Harnisch et al., 2006) Ammonia synthesis is conducted in the presence of ammonia synthesis gas and an iron catalyst under high pressure ranging from 100 to 250 bars and temperature ranging from 350° to 550°C. The yield of reacted pass is rather low, 20-30%, and thus ammonia synthesis gas is recycled numerous times. To accomplish the synthesis, ammonia vapors are liquefied in the refrigeration compressor. The simplified reaction of ammonia synthesis is presented in Equation 4.1. (Boswell et al., 1985; EFMA, 2000a)

$$\mathrm{N_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{NH_3} \qquad (4.1)$$

Two key factors for successful process are a) an iron-based catalyst which makes it possible to perform the process at lower temperatures, and b) the removal of ammonia from batch as soon as it has formed: both factors favoring a reaction equilibrium where ammonia formation is maintained. A newly developed alternative catalyst for iron is ruthenium on-a-graphite which has higher activity per unit of volume. Furthermore, an efficient heat exchanger is required due to the exothermic nature of the reaction and the wide temperature range applied in the process. (EFMA, 2000a)

4.3.1.2 Phosphate fertilizers

Phosphate fertilizers contain compounds which yield phosphate anions (PO_4^{3-}) when dissolved (Young et al., 1985). Common phosphate fertilizer compounds are phosphoric acid (H_3PO_4) and Single and Triple Superphosphates (SSP and TSP), of which the two latter ones are upgraded from the former (Windridge, 1996; Kongshaug, 1998). Phosphate raw materials for fertilizer production are commonly derived from apatite containing phosphate rocks, phosphate containing ores and other P-compounds in nature (Finck, 1982). Apatite minerals have been formed in volcanic processes and therefore do not contain heavy metals (Riistama et al., 2005). North America, Russia, Morocco, Jordan, South-Africa and China are known to have rich apatite deposits (Young et al., 1985; Dawson and Hilton, 2011). Non-renewable and hence finite resources of rock phosphate scattered only in few countries can cause political and commercial issues already in the foreseeable future due to depletion of reserves at an accelerating rate (Dawson and Hilton, 2011).

Phosphate compounds are obtained from raw materials by fine grinding or chemical treatment such as wet process or thermic process (Finck, 1982; Young et al., 1985; Riistama et al., 2005). In Finland, only the wet process is used which is the only economically feasible way to produce phosphoric acid (Riistama et al., 2005). In the wet process, phosphate mineral is decomposed with nitric, hydrochloric or sulfuric acid, the sulfuric acid route being the dominant in Europe. The sulfuric acid wet process can still be divided into three subcategories upon the condition of the calcium sulfate produced in the process. These subcategories are anhydrite, hemihydrate and dehydrate process where name of the subcategory refers to the condition of calcium sulfate produced. The hemihydrate process is considered as the best available technology for phosphoric acid production. (Kongshaug, 1998; EFMA, 2000d; Riistama et al., 2005)

The wet process starts by dissolving apatite mineral derived calcium phosphate in the sulfuric acid (H_2SO_4). The reaction releases phosphoric acid (H_3PO_4) and calcium sulfate ($CaSO_4$) from which calcium sulfate is filtered out. The concentration of phosphoric acid lies between 39 and 41% H_3PO_4. (EFMA, 2000d; Riistama et al., 2005) The simplified reaction of the wet process is presented in Equation 4.2. Phosphoric acid can be utilized as such or it is used as a phosphate raw material for other upgraded phosphate compounds. (EFMA, 2000d)

$$\mathrm{Ca_3(PO_4)_2} + \mathrm{3H_2SO_4} \rightarrow \mathrm{2H_3PO_4} + \mathrm{3CaSO_4} \tag{4.2}$$

A challenge for the phosphate fertilizer industry is the great variety in the quality of raw materials. Phosphate ores mined from different geographical locations differ both in content of minerals and impurities. The irregularities of raw materials force phosphoric acid producers to constantly readapt technologies. (EFMA, 2000d) Another reason for the irregularities of raw materials is their increasingly extensive use. Decreases in deposits of phosphate rock and, on the other hand, a constant increase in demand, has created a situation in which lower grade phosphate rock is utilized by improved technology of mining and beneficiation. However, despite the adaption of new technologies, phosphate rock costs may arise in future. (Dawson and Hilton, 2011)

4.3.1.3 Potash fertilizers

Potash fertilizers contain compounds which yield potassium cations (K^+) when dissolved (Barber et al., 1985). Common potash fertilizer compounds are potassium chloride (KCl, trade name MOP) and potassium sulfate (K_2SO_4, trade name SOP) (Riistama et al., 2005; Kongshaug, 1998). Ores and brines are the most important sources of potassium minerals for fertilizer production. Contrary to phosphate rock deposits, potassium reserves are abundant and it is anticipated that supply is guaranteed for many hundreds of years. The largest deposits are found in Canada and in the countries of the former Soviet Union. (Schultz et al., 2013; Barber et al., 1985)

Basically, the recovery of potassium chloride from underground ores consists of shaft mining followed by physical separation operations such as flotation techniques, or by precipitation in the case of brine sources (Finck, 1982; Schultz et al., 2013). Potassium chloride is the most popular of potash fertilizers but it can also be upgraded by the Mannheim process in which potassium chloride (KCl) reacts with sulfuric acid (H_2SO_4) yielding potassium sulfate (K_2SO_4) and hydrochloric acid (HCl) (Freilich and Petersen, 1996). Potassium chloride is imported to Finland mostly from Germany and Russia (Riistama et al., 2005). The reaction equilibrium of the Mannheim process is presented in Equation 4.3.

$$2\,\mathrm{KCl} + \mathrm{H_2SO_4} \rightarrow \mathrm{K_2SO_4} + 2\,\mathrm{HCl} \tag{4.3}$$

The advantage of the potassium sulfate over the potassium chloride is a low concentration of chloride, which is essential for some plants, such as tomato and root vegetables. (Riistama et al., 2005) However, potassium sulfate has slightly lower potassium content than potassium chloride: 41.5% K and 49.8% K, respectively (Barber et al., 1985; Schultz et al., 2013).

4.3.2 Organic fertilizers

Examples of production processes of typical organic fertilizers are not available in contrast to those described for mineral fertilizer production. This is due to the fact that manufacturing processes of organic fertilizers are not uniform, as they rely on the use of a high variety of raw materials and their processing technologies. In addition, the raw materials for organic fertilizers are also often country-specific, depending on which kind of biomass streams are locally available. Organic fertilizers are also not nutrient specific but they contain various nutrients depending on the raw materials. (Roy et al., 2006; Finck, 1982) The International Fertilizer Industry Association (IFA) only reports official statistics on the use of mineral fertilizers and thus the total global production of organic fertilizers per annum is unknown. However, it is evident that the global food supply strongly relies on use of mineral fertilizers, and not organic fertilizers (Roy et al., 2006; Dawson and Hilton, 2011).

Treatment of organic material in order to produce organic fertilizers can be divided into three approaches. First, the organic matter, such as crop residues or farmyard manure, can be used as such, secondly, it can be aerobically composted or third, it can undergo anaerobic digestion. Other processing methods are drying, shredding, mixing, granulating, odor removal and/or pH modification. Many of these are associated with aerobic composting or anaerobic digestion. (Roy et al., 2006) In developing regions manure and crop residues are used as such as organic fertilizers, but processing of organic matter is preferable as processing alters nutrient compounds thus that they will be better utilized by plants (Roy et al., 2006). In addition to organic material, a common compound in organic fertilizers is ash. Ash is not organic material per se, but inorganic residues remaining after the combustion of organic material. Thus, ash is obtained by minor processing of organic material formed in nature and therefore recognized as a suitable substance for organic fertilizers. (Roy et al., 2006; Parnes, 1990)

In the following, processing methods which are essential from the perspective of the BioA concept are presented. The present study focuses on the anaerobic digestion of organic matter because organic raw material for the BioA fertilizer is digestate which is the by-product of the biogas production. The other raw material for the BioA fertilizer is ash and therefore common techniques for ash processing are dealt. From this point onwards this thesis will refer to the organic fertilizer produced in the BioA concept as the BioA fertilizer.

4.3.2.1 Anaerobic digestion

Anaerobic digestion is a series of biochemical processes in which microorganisms decompose organic matter and its intermediate products in the absence of oxygen under anaerobic conditions. There are two types of anaerobic digestion: dry fermentation which is used when the dry matter content of biomass is between 20 and 50% and wet fermentation which refers to biomass of which dry matter content is between 5 and 15%. Of these two options, the latter one is employed in the BioA concept. Anaerobic digestion can also be performed in two different temperature ranges: mesophilic (35-37°C) or thermophilic (50-55°C), of which the mesophilic conditions are used in the BioA concept. (Latvala, 2009)

The main end products from anaerobic digestion are methane (i.e. biogas) and carbon dioxide. In addition, digestate, which is residues of unvolatilized organic matter, is formed as by-product. Prior to obtaining these end products, four process steps are needed: hydrolysis, acidification, acetogenesis and methanogenesis. Anaerobic digestion starts with hydrolysis during which carbohydrates, lipids and proteins are broken down into sugars, amino acids and long chain fatty acids. From the fertilizer point of view, particular interest lies in the degradation of amino acids because nitrogen bound to them is converted into inorganic ammonia. During the second step, acidification, hydrolyzed products are converted into more simple molecules, for instance volatile fatty acids such as propionic and butyric acid, alcohols and aldehydes. During the third step, acetogenesis, the products formed during the acidification step are converted into acetic acid and hydrogen. Finally, in the last methanogenesis step, methane-producing bacteria utilize acetic acid and hydrogen to produce final products, methane (CH_4) and carbon dioxide (CO_2). (Latvala, 2009)

In the BioA concept, the by-product of the anaerobic digestion, digestate, is used for the fertilizer production. Although the total quantity of nutrients remains same prior and subsequent to anaerobic digestion, digestion alters structures of organic compounds and enhances their availability to crops (Iivonen et al., 2013; Marttinen et al., 2013). During anaerobic digestion some of organic compounds are mineralized into inorganic ones which is important as the nutritional value of digestate depends on the nutrients present in digestate and plants can better utilize nutrients in their inorganic form. Digestate can be utilized in fertilizer production as such, or it can be separated into solid and liquid fractions of which one or both can be used in fertilizer production (Marttinen et al., 2013). As a rule, inorganic compounds are dissolved in the liquid fraction whereas organic compounds are found in the solid fraction (Iivonen et al., 2013; Lukehurst et al., 2010). A typical nutritional composition of the digestate cannot be given as it depends on the raw materials fed to the anaerobic digestion.

4.3.2.2 Ash processing

In addition to the digestate, another key substance of the BioA fertilizer is fly ash from the power plant. Ash is inorganic residues which is the result of combustion and hence the composition of ash is always fuel-specific. In addition to fuel type, also combustion temperature, type of boiler and fly ash capturing mechanisms all modify the fly ash composition. (Dahl et al., 2009) In energy production, fuels combusted are rather mixtures than one single fuel only, common bio-combustibles in Finland being for example peat, woodchips and bark (Hynönen et al., 2008). Ash which is the result of combustion of fuel combinations should not be assumed to represent a sum of the properties of each fuel, rather, it is always combination-specific (Steenari and Lindqvist, 1999). It is worth acknowledging, that the composition of ashes also varies greatly among bio-combustibles, for instance the nutrient concentrations are significantly lower in peat-fired ash than wood-fired ash (Hynönen et al., 2008).

Stenaari and Lindqvist (1997) measured the content of major elements of wood ashes in various Finnish and Swedish combustion facilities and according to their survey, the principal elemental components are calcium (17%), potassium (4.2%) and silicon (7.6%). Other key elements are magnesium (1.9%), sodium (0.7%), aluminum (1.4%), iron (1.0%), manganese (1.2%), phosphorus (0.9%) and sulfur (0.5%). Thus, the nutritional value of ash is mainly based on the primary nutrients phosphorus (P) and potassium (K) and on the liming effect of calcium (Ca) which raises the pH of the soil. In ashes, macronutrients Ca and K exist as oxides, carbonates, chlorides and sulfates, which are mostly bound by ionic binding and thus have a good mobility in soil solution. Contrary to Ca and K, solubility of P, which is tightly bound to apatite type compounds, is rather low. Low release of P is partly explained by the high alkalinity of wood ash: at high pH P is bound to calcium phosphate compounds which have low solubility. However, when pH decreases below 8, phosphates are released and become available for plants. (Steenari and Lindqvist, 1997; Steenari and Lindqvist, 1999; Dahl et al., 2008) Alkalinity of wood ash can be explained by the high concentration of calcium, which exists mainly as calcium oxide – a strong alkaline compound. In soil solution, alkaline ash acts as soil conditioners as Scandinavian soils are recognized to have relatively acidic pH, which can hinder availability of nutrients for crops and thus decrease soil fertility. (Hynönen et al., 2008; Nurmesniemi et al., 2008; Steenari and Lindqvist, 1999)

Prior to use ash as a fertilizing substance, at the minimum two processing steps are required: classification and stabilization (Steenari and Lindqvist, 1997; Dahl et al., 2008).

Due to the heavy metal compounds found in ash, ash must be classified into a heavy metal containing fraction and a heavy metal free fraction of which the latter can be used in fertilizer production (Dahl et al., 2008). One method for the ash classification is an air classification which is the method used in the BioA concept. In the air classification the separation of ash particles into fractions is based on the size of ash particles (Korpijärvi et al., 2009). Heavy metals are accumulated into the small particles during the combustion. During combustion heavy metals are first vaporized and then cooled. When cooling occurs, the vaporized heavy metals are condensed and they adsorb on the surface of ash particles. As smaller particles have greater surface area to volume ratio, heavy metal concentration is highest in the smallest particles. (Korpijärvi et al., 2009; Dahl et al., 2009)

Another important processing step is stabilization of ash which facilitates handling of dust-like ash material, and establishes some reactive compounds which can cause undesirable effects in soil solution (Steenari and Lindqvist, 1999). As most simplified, stabilization can be carried out by adding water in ashes as wood ash materials have ability to solidify when combined with water (Hynönen et al., 2008). One of the most important reactions occurring during the stabilization is the conversion of calcium oxide and calcium hydroxide into calcium carbonate, of which solubility is more moderate compared with its precursors. Lower solubility extends the liming effect and prevents the pH shock. (Steenari and Lindqvist, 1999) The hydrated ash can be left as it is to self-harden without further processing, or it can be granulized or pelletized according to the purpose of the final application. Granulation or pelletization accelerates the hardening process and the water content of a final product is lower compared to self-hardened ash. Alternatively, the self-hardening process is cheaper hence it requires less processing steps. Stabilization carried out by hydration and solidification reduce the accessible surface area of ash particles and produce a pore fluid with a high pH – both effects encouraging low leachability which can be desirable from a heavy metal point of view, but a hindering effect from a nutrient point of view. (Steenari and Lindqvist, 1997; Hynönen et al., 2008)

5 BIOA CASE STUDY

The BioA case study had two objectives and thus the case study was dealt with two parts. The first objective was to determine the composition of the BioA fertilizer. The second objective was to conduct an environmental assessment which compares the environmental impacts of the BioA fertilizer with one reference mineral fertilizer. The assessment method was a Life Cycle Assessment (LCA), with particular focus placed on a Life Cycle Inventory Analysis (LCI). The ambition of the comparative environmental assessment was to evaluate how the environmental impacts that ensue during the life cycle of the BioA fertilizer differ from those of the reference mineral fertilizer.

Research questions

According to the evaluation report on the emission reduction potential of the BioA concept, the BioA fertilizer has the potential of causing less environmental impacts during its life cycle than conventional mineral fertilizers (Bio Refine Tech, 2012d). The author has predicted that the production and use of the BioA fertilizer could have advantages over mineral fertilizers in the following four sectors: 1) recycling of nutrients embedded in industrial waste streams instead of utilizing virgin raw materials, 2) utilization of the surplus heat energy from the existing factory site in the fertilizer production processes instead of utilizing imported energy alone, 3) utilization of digestate and fly ash as raw materials for the fertilizer production instead of their disposal and, 4) low nutrient leaching potential of the organic nutrient compounds in soil solution compared to the high leaching potential of mineral fertilizer compounds. On the other hand, mineral fertilizers have remarkably higher nutritional value per volume than organic fertilizers due to which mineral fertilizers need to be produced and applied in less volume than organic fertilizers (Roy et al., 2006). Smaller volume of production and application is an advantage to the mineral fertilizers from an environmental perspective. Nevertheless, production processes of mineral fertilizers are considered energy intensive (Dawson and Hilton, 2011; Kongshaug, 1998).

The aim of the present case study was to determine accuracy of the above arguments. To fulfill the objective, following two research questions were set:

1) What is the composition of the organic BioA fertilizer and is it a technically feasible product?

2) How do the environmental impacts that ensue during the life cycle of the BioA fertilizer differ from those of the reference mineral fertilizer?

The first question addresses the first part of the case study which is the definition of the composition of the BioA fertilizer (Section 5.1) and the second question is linked to the second part of the case study which is the environmental assessment (Section 5.2). The two research questions are also linked together as possibly smaller environmental impacts during a life cycle of the BioA fertilizer compared to the reference mineral fertilizer are not worthwhile, if the BioA fertilizer is technically not feasible product. The production of the BioA fertilizer is also assumed to improve the cost-effectiveness of the whole BioA concept. This economic perspective is recognized, but not examined in the present thesis.

5.1 COMPOSITION OF BIOA FERTILIZER

Assessment of the composition of the BioA fertilizer was based on assumptions and estimations in addition to the experimental data. This is due to the fact that at the time of writing this thesis, the BioA concept was at the design phase and not much process-specific data was available. However, it is essential to estimate the product composition at the present design phase in order to adjust the design criteria and consequently production processes so, that the BioA fertilizer will be a technically feasible product. The adjustment of the design criteria at the early stage of the project is important as it affects further process planning of the BioA concept.

The BioA fertilizer is composed of two raw materials which are the solid digestate fraction from the biogas plant and the heavy metal poor ash fraction from the power plant. In addition, ammonia is removed in anaerobic digestion in the biogas plant by biogas stripping and a part of this surplus nitrogen is added to the fertilizer product in order to balance its nutrient composition (see Figure 2-1) (Järvinen, 2013). However, from this point onwards in the present thesis only digestate and ash will be referred as raw materials and the stripped nitrogen flow is dealt separately.

5.1.1 Data collection

The data used for the definition of the composition of the BioA fertilizer was obtained from the BioA concept related experiments (Bio Refine Tech, 2012b, 2012c), Kouhia's (2013) master's thesis studying the BioA concept, and the prefeasibility report of the BioA concept (Bio Refine Tech, 2012a). In addition, Järvinen (2013) provided essential information. The documents used in the data analysis for the definition of the composition of the BioA fertilizer are listed in Table 5-1.

Table 5-1. Summary of data collection.

Document	Type	Information	Reference
Fly ash analysis	Experiment	Nutrient content of the fly ash	Bio Refine Tech 2012c
Anaerobic digestion analysis	Experiment	Composition of the output flow of the anaerobic digestion, nitrogen stripping	Bio Refine Tech 2012b
Personal communication	Personal communication	Composition of the output flow of the anaerobic digestion, nitrogen stripping	Järvinen 2013
BioA prefeasibility report	Report	Quantities of the material flows, design criteria	Bio Refine Tech 2012a
Integration of a microalgae-utilizing biorefinery to a pulp and paper mill	Master's thesis	Nutrient contents of the raw material flows, design criteria	Kouhia 2013

[1] Kouhia's Master's thesis (2013) is partly based on the other documents listed in Table 5-1.

Key results of the fly ash analysis are presented in Table 5-2. According to the analysis, the coarse fraction, which is the ash accept used in the fertilizer production, contains 1.17% P and 1.21% K. Fly ashes do not contain N.

Table 5-2. Results of the fly ash analysis (Bio Refine Tech, 2012c).

	Nutrients (mg/kg)		Heavy metals (mg/kg)			Moisture
Fly ash	**P**	**K**	**Cd**	**Pb**	**Ni**	**(%)**
Fly ash total	9000	14300	4.1	45.6	52.7	0.3
Light fraction (reject)	12100	19800	8.5	76.9	62.0	0.7
Coarse fraction (accept)	11700	12100	2.7	49.7	46.0	0.4

According to Kouhia (2013), the solid digestate fraction, which is used for fertilizer production, contains 6.8% N and 0.64% P. However, it is doubted that there might have occurred nitrogen leaching in the form of volatilization during the anaerobic digestion experiment because the nitrogen concentration in digestate remained significantly lower than expected (Bio Refine Tech, 2012b). For the present, the reason for the low nitrogen concentration is not verified and thus the question remains unsolved. A new digestion experiment is being performed but results were not as yet available at the time of writing the thesis. Due to the uncertainty of the results of the anaerobic digestion experiment, an estimate received from Järvinen (2013) is used for the nitrogen content of the digestate. According to this estimate, digestate and stripped ammonia flow from the biogas reactor together contain 10% N. Due to the early stage of the project, the exact quantities of nitrogen in both flows, digestate and stripped ammonia, were not known. Thus, to facilitate the process calculations, in the following data analysis it has been presented that the nitrogen concentration of the digestate is 10% albeit in practice a part of the 10% originates from the stripped ammonia flow.

5.1.2 Design criteria and limiting factors

On the basis of the information provided by Järvinen (2013) and Kouhia (2013), three design criteria for the composition of the BioA fertilizer were chosen. The first design criterion is that the BioA fertilizer is composed of 50% digestate and 50% ash on a dry matter basis. The second design criterion is that the BioA fertilizer does not contain any synthetized fertilizer compounds. However, the ammonia which is recovered from the anaerobic digestion by stripping can be added to the fertilizer product in order to balance the nutrient composition. This is possible because stripped nitrogen flow does not represent synthetized compound rather organic fertilizer compound obtained within the BioA concept. Due to the absence of synthetized fertilizer compounds, the fertilizer type of the BioA fertilizer is organic, not mineral. In terms of marketability, it is essential that the fertilizer type of the BioA fertilizer is organic because the nitrogen content of the BioA fertilizer cannot compete with nitrogen contents of mineral fertilizers and thus, the BioA fertilizer would not have a market value as a mineral fertilizer. According to the third design criterion, the total solids content of the final fertilizer product is 80%.

In addition to the design criteria, the product composition of the BioA fertilizer was controlled by two limiting factors. The first limiting factor is the minimum quantity of nitrogen (N) in a fertilizer product. According to Kivelä (2013), the lowest commercially feasible NPK rating for fertilizer is 4-X-X. If the nitrogen content of a fertilizer remains below 4%, the required quantity of fertilizer per hectare is so large that the labor expenditures exceed positive impacts of fertilizer use on crop yield. The second limiting factor is the cadmium (Cd) concentration which maximum permitted limit is 1.5kg Cd/ t fertilizer (Ministry of Agriculture and Forestry, 2011).

Thus, the design criteria are adjustable whereas the limiting factors are set by the legislation (Cd concentration) or by the commercial feasibility of the product (N content). The design criteria and the limiting factors for the BioA fertilizer are illustrated in Figure 5-1. It is also depicted how both raw material streams contribute to the nutrient and heavy metal content of the fertilizer product.

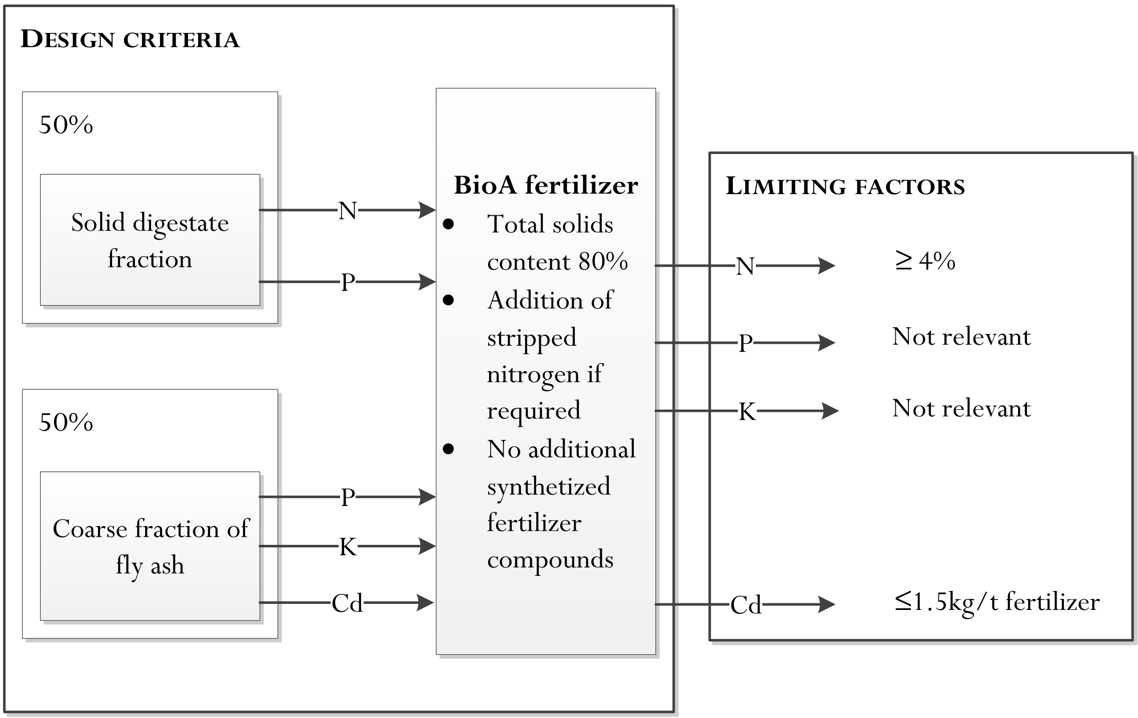


Figure 5-1. Design criteria and limiting factors for the composition of the BioA fertilizer.

Maximum permitted concentrations of heavy metals in Finnish fertilizer products are provided in Table 5-3. It can be seen that according to the results of the fly ash analysis (see Table 5-2) the concentration of cadmium in coarse fraction exceeds the limit value 1.5mg/kg set for fertilizer products.

Table 5-3. Maximum permitted concentration of heavy metals in fertilizer products (Ministry of Agriculture and Forestry, 2011).

Heavy metal	Maximum permitted concentration (mg/kg)
Cadmium (Cd)	1.5
Lead (Pb)	100
Nickel (Ni)	100
Arsenic (As)	25
Mercury (Hg)	1
Chromium (Cr)	300
Copper (Cu)	600
Zinc (Zn)	1500

5.1.3 Data analysis

The aim of the data analysis was to determine the NPK rating for the BioA fertilizer. NPK rating expresses the percentages by weight of N, P and K in a fertilizer product and it is a critical parameter in defining the composition of a fertilizer (FAO and IFA, 2000; Ludwick et al., 1990). In addition to the NPK rating, also the heavy metal concentration of the BioA fertilizer was studied. The analysis of the heavy metal concentration was limited to the cadmium (Cd) as it is the only heavy metal which concentration exceeds the maximum permitted limit according to the fly ash analysis (see Table 5-2 and Table 5-3). If not otherwise stated, all the following values are reported on a dry matter basis.

The nutrient contents of the raw material streams and the final fertilizer product on a tonne basis are presented in Table 5-4. The nutrient content of the final fertilizer product is obtained by multiplying the nutrient content of the digestate or ash by the proportion of that raw material in the final product (see Figure 5-1). P is the only nutrient of the three primary nutrients which is found in both raw material streams. P and K content of the ash accept were obtained from Table 5-2. P content of the digestate was obtained from Kouhia (2013) and N content of the digestate from Järvinen (2013). Distribution of nutrients between the ash accept and solid digestate is presented in Table 5-5. Distribution factors were calculated on the basis of the information provided in Table 5-4. According to the information presented in Table 5-4, the NPK rating for the BioA fertilizer is 5.0-0.9-0.6, which is rounded up to be 5-1-1.

Table 5-4. Concentrations of the primary nutrients in the raw material streams and in the fertilizer on a tonne basis (Kouhia, 2013; Bio Refine Tech, 2012c; Järvinen, 2013).

		Nutrient (kg/t material flow)		
Material flow	**t**	**N total**	**P total**	**K total**
Ash accept	1	–	11.7	12.1
Solid digestate	1	100.0	6.4	–
Fertilizer	1	50.0	9.1	6.1

[1] N content of the solid digestate also includes the nitrogen obtained by biogas stripping

Table 5-5. Distribution of the primary nutrients between the ash accept and solid digestate.

	Share of nutrient (%)		
Material flow	**N**	**P**	**K**
Ash accept	–	65	100
Solid digestate	100	35	–

Cadmium (Cd) is accumulated to the fertilizer product from the coarse fraction of the fly ash. According to the fly ash analysis (Bio Refine Tech, 2012c), the coarse fraction contains 2.7 mg Cd/kg. As it is known that the BioA fertilizer is composed of 50% ash, the Cd concentration in the final fertilizer product is 1.35 kg Cd/ t fertilizer.

5.2 ENVIRONMENTAL ASSESSMENT

Improved sustainability is the overall goal of the BioA concept fertilizer production. In the BioA case study, the environmental impacts of the BioA fertilizer and the reference mineral fertilizer were analyzed and compared. The objective was to find key differences in the environmental impacts between the two fertilizer types in order to facilitate the optimization of the manufacturing and use of the BioA fertilizer.

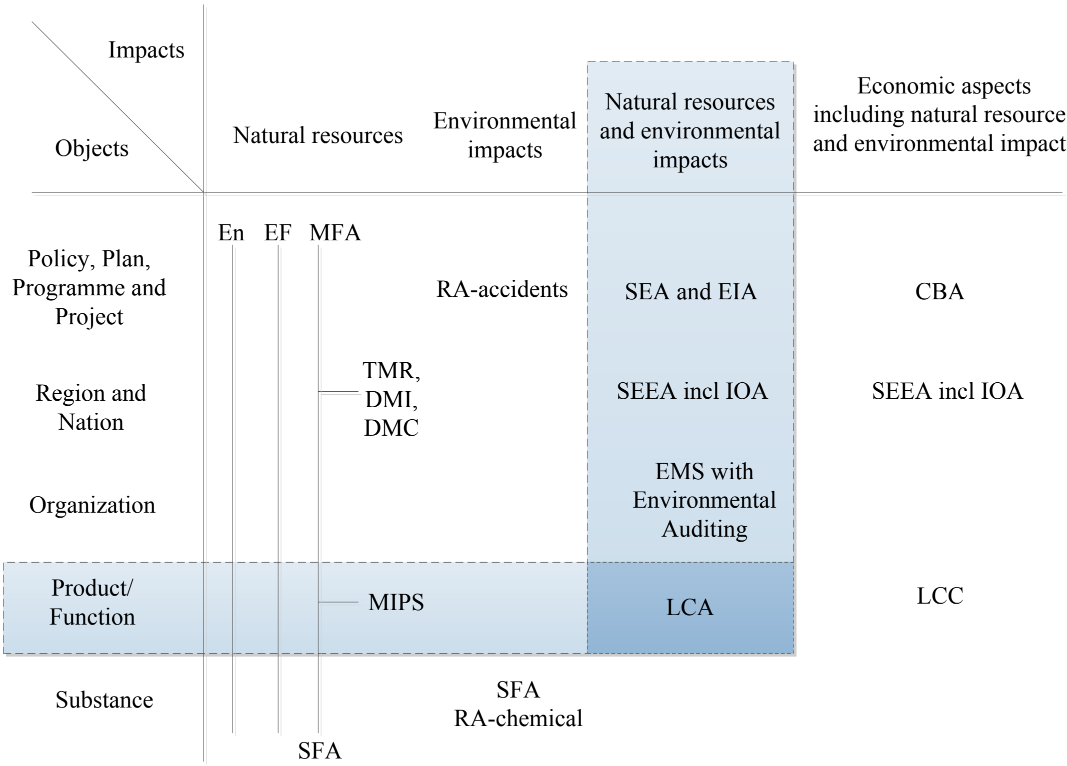
5.2.1 Method

There are a wide array of methods for environmental assessment, which have been applied at many levels of society to assist decision making and to track comprehensive performance. Examples of the environmental assessment methods include Life Cycle Assessment (LCA), Environmental Impact Assessment (EIA), Energy analysis (En), Ecological Footprint (EF), and Material Flow Accounting (MFA). The fundamental purpose of the assessment tools is to direct performance towards sustainability. The focus of assessment tools can vary from a whole nation to something more specific, such as a business, a service, a project or a product. The environmental assessment tools aim at to evaluate the impacts of complex interactions between environmental, social and economic issues related to a phenomenon under scrutiny. Despite the aim to bring all three perspectives – the environment, society and economics – under scrutiny simultaneously, many of the analysis methods focus more on one of the aspects rather than on the others. As some of the assessments tools are more procedural and other analytical, whereas some retrospective and others prospective, it is sometimes necessary to complete the coverage of the selected tool with the aid of another tool. (Finnveden and Moberg, 2005; Ness et al., 2007)

5.2.1.1 Selection criteria

On the basis of the objective and research targets of the present environmental assessment study, two selection criteria were emphasized in the selection of the environmental assessment method for the case study. According to the first design criterion, the main focus of the environmental assessment method used in the BioA case must be on environmental impacts and on the use of natural resources. According to the second design criterion, the target or object of the assessment method must be a product, such as a fertilizer. In addition, it was preferred that the assessment method is well established. The assessment method was not required to cover the socio-economic dimension.

Finnveden and Moberg (2005) have classified different environmental system analysis tools according to two variables: the object or scope of a tool (e.g. policy, nation, organization, product) and which types of impacts are measured (e.g. natural resources, environmental impacts, economics aspects, or different kinds of combinations of the previous mentioned). The selection of the environmental assessment method for the BioA case was founded on this classification provided by Finnveden and Moberg (2002) which is presented in Figure 5-2. According to the selection criteria and the options provided in Figure 5-2, the most suitable environmental assessment tool in the BioA case is a Life Cycle Assessment (LCA).



CBA	Cost-Benefit Analysis
DMC	Direct Material Consumption
DMI	Direct Material Input
EF	Ecological Footprint
EIA	Environmental Impact Assessment
EMS	Environmental Management System
En	Energy Analysis
IOA	Input-Output Analysis
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
MFA	Material Flow Accounting
MIPS	Material Intensity Per Unit Service
RA	Risk Analysis
SEEA	System of Economic and Environmental Accounts
SEA	Strategic Environmental Assessment
SFA	Substance Flow Analysis
TMR	Total Material Requirement

Figure 5-2. Different environmental system analysis tools in relation to their objects and impacts measured (modified from Finnveden and Moberg, 2005). The LCA is highlighted as it is the environmental assessment method used in the present case study.

Life Cycle Assessment (LCA) is a product-related, iterative assessment tool which allows both retrospective and prospective inspection. It is the most established and well-known tool to evaluate natural resource use and environmental impacts during the life cycle of a product. However, the LCA underemphasizes socio-economic issues despite its strong focus on environmental issues. (Ness et al., 2007) Nevertheless, of all the sustainability assessments methods presented extensively by Finnveden and Moberg (2005), the LCA is the most suitable for the BioA case due to this strong focus on environmental impacts, its comprehensive vision of the life cycle of a product, and the possibility to use it for comparing similar products (Finnveden and Moberg, 2005; Pennington et al., 2004). An ISO standard, ISO 14040:2006, has been developed for the LCA methodology (ISO, 2013).

5.2.1.2 Life Cycle Assessment (LCA)

The core idea of the LCA is to aggregate natural resources used and environmental impacts caused throughout the life cycle of a product. This life cycle perspective is also called the cradle to grave approach. LCA is comprised of four phases which are 1) Goal and Scope Definition, 2) Life Cycle Inventory Analysis (LCI), 3) Life Cycle Impact Assessment (LCIA) and 4) Interpretation. An LCA is a continuous iterative process and hence more accurate results can be obtained when the loop of four phases is repeated. (Koskela et al., 2010; Finnveden et al., 2009; Rebitzer et al., 2004) The four phases and their interactions and interdependencies are presented in Figure 5-3. In the following, the phases will be introduced in more detail.

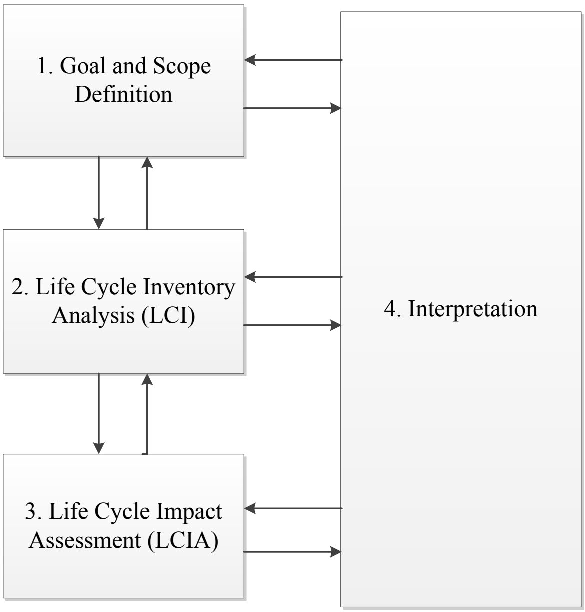


Figure 5-3. Four phases of LCA (Rebitzer et al., 2004).

Goal and Scope Definition

In the first phase of an LCA, the goal and scope of a study are defined and the system boundaries are selected. It is also defined who will be informed about the results and in which form they will be delivered. A complete product system includes all material and energy flows associated to a life cycle of a product. It is also possible not to include all material and energy flows to the system boundaries but to select those inputs and outputs which best cover the scope of a study. Definition of system boundaries is a subjective choice and can strongly affect results obtained. (Finnveden et al., 2009)

The first phase also covers definition of the functional unit. A functional unit is a measurable unit for the output of a product system. A representative functional unit describes both the physical properties and function and efficiency of the product. To illustrate this with an example, a functional unit emphasizing physical properties can be defined as quantity of end product delivered (e.g. t fertilizer) whereas a functional unit which also describes the functions of the product can be defined as quantity of fertilizer applied per hectare (e.g. t fertilizer/ha). The purpose of a functional unit is to serve as a reference to which input and output flows of a system are related and thus to allow goods or services under scrutiny to be comparable. Comparativeness among similar products or services facilitates to distinguish differences between them. (Grönroos and Voutilainen, 2001; Finnveden et al., 2009; Rebitzer et al., 2004)

Life Cycle Inventory Analysis (LCI)

The second phase of an LCA is a Life Cycle Inventory Analysis (LCI) which compiles the inputs (e.g. consumption of resources, required energy) and the outputs (e.g. products, emissions, waste flows) related to a life cycle of one functional unit of a product. To organize the data gathered about the inputs and the outputs, it can be divided into modules of which each represent one unit operation or group of similar unit operations. The quantity of each input and output flow is measured or estimated and presented in a flow chart: this is called an inventory data. A flow chart can further be divided into specific unit processes. Thus, each material, energy and emission flow can be addressed to a specific unit process, at least theoretically. (Koskela et al., 2010; Grönroos and Voutilainen, 2001)

Common characteristics of input and output flows are that they are likely to occur at multiple sites and regions, at different times and over different time periods. This complicates both data gathering and addressing it to a correct module. LCI is a challenging phase in an LCA and it normally demands co-operation and communication across several organizational levels involved in a project. (Rebitzer et al., 2004; Finnveden et al., 2009; Grönroos and Voutilainen, 2001)

Life Cycle Impact Assessment (LCIA)

The objective of the third phase, a Life Cycle Impact Assessment (LCIA), is to evaluate importance of LCI data. Importance is defined by allocating and weighting LCI data according to three key elements of an LCIA: 1) impact categories, 2) category indicators and 3) characterization factors. Impact categories represent sites or phenomena affected due to the environmental impacts related a product. Generally recognized impact categories are, for instance, climate change, stratospheric ozone depletion, photochemical ozone formation, acidification, nutrient enrichment (or eutrophication), human toxicity, and ecotoxicity. Selected impact categories should encompass aspects of three broad areas of protection which are resource use, human health consequences and ecological consequences. (Stranddorf et al., 2005; Pennington et al., 2004; EC, 2010) Impact categories and their association with the areas of protection are illustrated in Figure 5-4.

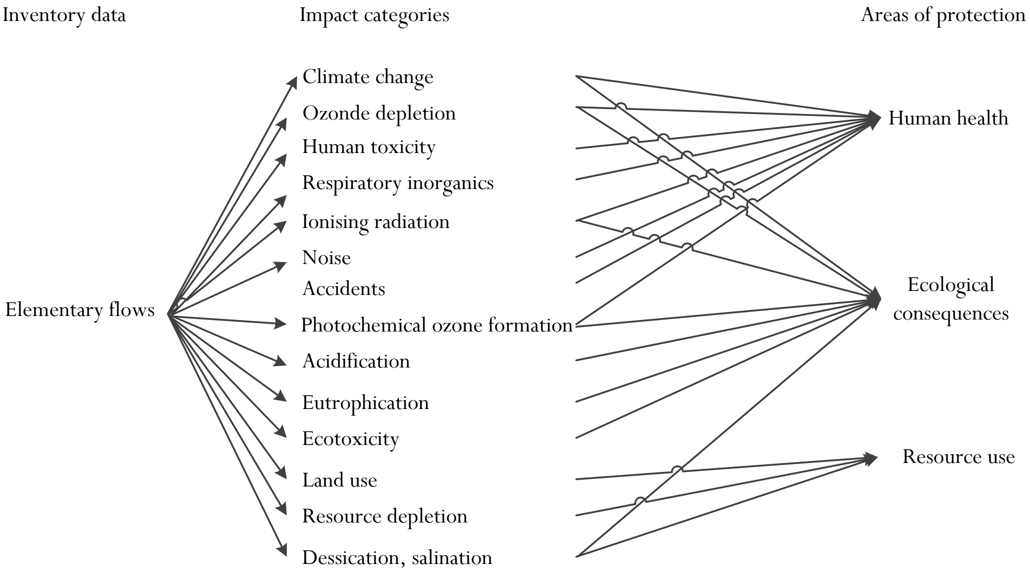


Figure 5-4. Overall scheme of the LCI data linked via the impact categories to the areas of protection (EC, 2010).

When impact categories are defined, one or several category indicators for each impact category are selected. The category indicators represent substances which negatively contribute to the phenomena of which impact categories represent. For example, category indicators related to the impact category which represent climate change are greenhouse gases such as CO_2, CH_4 and N_2O. Finally, the characterization factors for category indicators are calculated or obtained from the literature. The idea of the characterization factors is to weight importance of each category indicator. (Pennington et al., 2004) For instance, the category indicators CO_2, CH_4 and N_2O can all be converted into carbon dioxide equivalents (CO_2-e) by multiplying each of the category indicators by a compound specific characterization factor (Wood and Cowie, 2004).There is no agreement about universal impact categories, category indicators or characterization factors and a large number of supportive methodologies exist for their evaluation (Pennington et al., 2004). Table 5-6 gives an example of one impact category and its possible category indicators and characterization factors.

Table 5-6. Category indicators and characterization factors for the climate change impact category (compiled from data in Norris (2003) and Solomon *et al.* (2007)).

Impact category	Equivalent type	Category indicator	Characterization factor
Climate change	CO_2	CO_2	1
		CH_4	21
		N_2O	310

In addition to the mandatory elements of an LCIA, which are impact categories, category indicators and characterization factors, optional elements can be employed. Optional elements of an LCIA are for instance calculation of the category indicator results relative to the reference values (normalization), grouping and weighting of the category indicator results, and data quality analysis. (Pennington et al., 2004)

The last phase of an LCA is interpretation of the results which concentrates on evaluation of the results with relation to the goal and scope defined on the first phase (Rebitzer et al., 2004).

5.2.1.3 Methodological limitations

The LCA which was conducted in the present case study is a streamlined version for three reasons. First, the LCA deliberately excludes some phases of a life cycle and consequently those input and output flows which are located outside of the selected system boundaries were not examined. Thus, the LCA performed in the present case study do not cover the complete product system. Secondly, the LCA was not applied for all the possible activities occurring inside the selected system boundaries, but for the central ones from the research questions perspective. The third limitation is that the LCA performed in the present case study do not cover the third phase of an LCA which is the Life Cycle Impact Assessment (LCIA). A preliminary framework for the LCIA is provided but the phase was not examined in detail. The performance of the complete LCIA was excluded from the study as it requires both, a substantial amount of additional case-specific information, and professional knowledge on the LCA method. Consequently, the importance of each environmental impact could not be evaluated and one single environmental impact indicator representing all measured environmental impacts cannot be provided. Instead of the total environmental impact indicator, impact-specific results are given.

5.2.2 Research targets

The present BioA case study had two research targets: the organic BioA fertilizer and the reference mineral fertilizer. The composition of the BioA fertilizer was defined in Section 5.1 and the reference mineral fertilizer was selected on the basis of the characteristics of the BioA fertilizer. In the following, the composition and the manufacturing processes of the both research targets are presented. In addition, the selection criteria for the reference mineral fertilizer are presented.

5.2.2.1 BioA fertilizer

Composition used in the environmental assessment

The NPK rating for the BioA fertilizer was calculated to be 5-1-1 (see Section 5.1.3) and this NPK rating was used in the present case study for the composition of the BioA fertilizer. The composition of the BioA fertilizer is in line with reference organic fertilizers on the market in which the nitrogen content is between 4 and 8% (Elosato Ltd., 2013; Novarbo Ltd., 2013).

Manufacturing process

The manufacturing of the BioA fertilizer is rather straightforward and no technically demanding process steps are needed. Simplified, the main processing steps are dewatering of digestate and separation of fly ash by air classification. Finally, these two streams, processed digestate and ash, are blended together and the product is granulated. If the N content of the fertilizer remains below 5%, ammonia obtained by biogas stripping is added to the granulated fertilizer product in order to reach N content 5% (see Figure 2-1). According to the design criteria for the composition of the BioA fertilizer, the total solids content of the final fertilizer product is 80% and the fertilizer is composed of 50% ash accept and 50% solid digestate.

The digestate originates from the anaerobic digestion in which a mixture of waste activated sludge originating from the waste water treatment plant and algal biomass originating from the algae cultivation site are co-digested in the biogas reactor. The total solids content of the outflowing digestate from the biogas reactor is assumed to be 8%. (Kouhia, 2013) After anaerobic digestion, the digestate undergoes two process steps which prepare the mass to be blended with ash. The two steps are hygienization and mechanical dewatering. In the hygienization step, the digestate is led to a hygienization tank where it is kept for a period of one hour at a temperature above 70°C. After hygienization, the hot digestate is taken to a heat recovery exchanger and after cooling the stream is redirected to a buffer tank. Next, the digestate is separated into a solid and a liquid fraction by mechanical dewatering which is conducted using a screw press. (Bio Refine Tech, 2012a; Järvinen, 2013) According to the literature, a degree of up to 60% total solids can be achieved with this dewatering technique (Lohiniva et al., 2001). In the BioA case, the objective is to increase the total solids content of the solid digestate up to 50% (Järvinen, 2013). After mechanical dewatering, the liquid fraction of the digestate is redirected to the algal cultivation and the solid fraction is used in the fertilizer production (Järvinen, 2013).

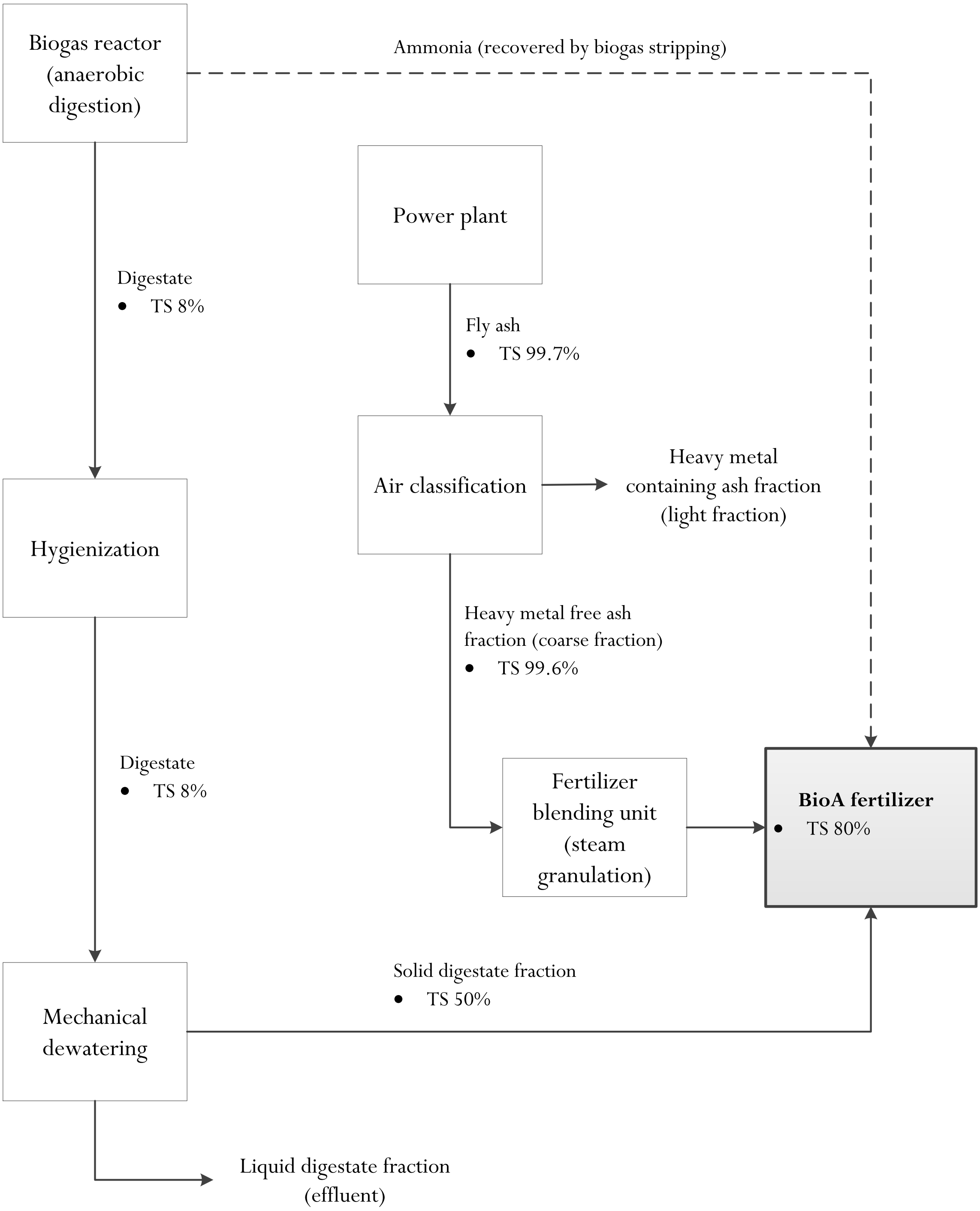
In addition to the digestate, another raw material of the BioA fertilizer is ash. Power plant ashes are divided into bottom ash and fly ash (also called flue ash) of which the latter is partly used for fertilizer production. Utilization of bottom ash from the power plant has not studied. The main combustibles in the power plant located in the existing factory site are bark, bio sludge, logging residues and recycled fuels (Bio Refine Tech, 2012a). As the fly ash coming from the power plant exceeds some limit values for heavy metals (see Table 5-2 and Table 5-3), it cannot be used for fertilizing purposes per se. The fly ash must be separated into a nearly heavy metal free coarse fraction (accept) and a heavy metal containing light fraction (reject). In the BioA concept, ash separation is carried out with an air classification method in which ash particles are separated into two or more fractions according to their size (Bio Refine Tech, 2012a; Korpijärvi et al., 2009). It is estimated that ash accept will be 75% and ash reject about 25% of the total quantity of the fly ash (Kouhia, 2013). The coarse fraction is used in fertilizer production and the light fraction goes to landfilling. A possibility to use ash reject in cement production is studied by one of the project partners (Bio Refine Tech, 2012a). In addition to the air classification, another required processing step is the stabilization of ash. In the present study the decision was made that no particular stabilization unit is required as the stabilization occurs when the solid digestate is blended with the coarse fraction of the fly ash.

Finally, separately processed digestate and ash are blended together in order to yield the final fertilizer product. According to the author's decision, the blending method used in the present case study is steam granulation. Subsequent to the steam granulation, the nutrient content of the fertilizer is analyzed and stripped ammonia is added if the nitrogen content is below 5%. The adjustment of the nitrogen content with the aid of the stripped ammonia is important in order to maintain a uniform product quality.

Subsequent to the blending of the solid digestate (TS 50%) and the coarse fraction of the ash (TS 99.6%), the total solids content of the final product is 67%. Total solids content of the final product was calculated using Equation 5.1 when the total solids content of the digestate and ash and their proportional quantities in the final fertilizer product were known.

$$TS(\%)_{fertilizer} = \frac{m_{DW\ digestate} + m_{DW\ ash}}{m_{WW\ digestate} + m_{WW\ ash}} \qquad (5.1)$$

In the Equation 5.1 *TS* is the total solids percentage, m is the mass and *DW* refers to the dry weight and *WW* to the wet weight. However, according to the design criteria, the total solids content of the final product was set at 80%. The increase of the total solids content from 67% to 80% is assumed to occur in the form of vaporization of water as the temperature of the ash is about 150°C when it is blended with the digestate (Järvinen, 2013). In summary, Figure 5-5 illustrates a general view of the BioA fertilizer production processes used in the present case study.



TS = total solids, DW = dry weight, WW = wet weight

Figure 5-5. Flow chart of the manufacturing process of the BioA fertilizer.Initial data for process calculations obtained from Kouhia (2013) and Järvinen (2013).

5.2.2.2 Reference mineral fertilizer

Selection criteria

Successful selection of the reference mineral fertilizer is an essential part of the study as when the two research targets, the BioA fertilizer and the reference mineral fertilizer, are as equivalents as possible, an accurate comparison between these two fertilizers can be performed. The selection of the reference mineral fertilizer for the case study was based on the three criteria. The first criterion is that a reference mineral fertilizer is used for the same purpose and under the same conditions as the BioA fertilizer. Secondly, the NPK rating of a reference mineral fertilizer should correspond to the typical NPK ratings of commercial mineral fertilizers available on the market. Finally, the third criterion is that the ratio of N to P of a reference mineral fertilizer should correspond to the ratio of N to P of the BioA fertilizer.

The reference mineral fertilizer used in the present case study was selected from fertilizer manufacturers operating in Finland for products destined for professional use. Of this selection, a fertilizer having a NPK rating 24-4-4 was chosen for the case study. The NPK rating of the selected reference mineral fertilizer is in line with the selection criteria as the ratio of N to P is close to that of the BioA fertilizer: 24-4 vs. 5-1. The selected reference mineral fertilizer is also used under the same environmental conditions and for the same purpose as the BioA fertilizer: cultivation of cereal crops. Henceforth, in this thesis, the selected reference mineral fertilizer is referred to as mineral fertilizer.

Composition used in the environmental assessment

At the time of writing this thesis, there was no specific information available on the composition of the reference mineral fertilizer. It was assumed, that in the mineral fertilizer the N compound is ammonium nitrate (AN, NH_4NO_3) and the P compound is single superphosphate (SSP, $Ca(H_2PO_4)_2 + 2CaSO_4$).

Due to the NPK rating (24-4-4), it was known that the mineral fertilizer contains 24% N and 4% P. To calculate the required quantity of AN and SSP in fertilizer, the percentage by mass of N in AN and the percentage by mass of P in SSP were calculated according to Equation 5.2:

$$x_{e\ in\ c}(\%) = \frac{n_e \cdot M_e}{n_c M_c} \cdot 100\%, \qquad (5.2)$$

where x is the nutrient content in fertilizer expressed in percentage, n number of atoms and M molar mass. The lower index e refers to a element (N or P) and c to a compound (AN or SSP). The percentage by mass of N in AN is 35% and the percentage by mass of P in SSP is 12%. Consequently, to contain 24% N and 4% P, the mineral fertilizer must contain 69% AN and 33% SSP. In the present case, the total amount of AN and SSP exceeds 100% which is not possible. Thus, the author has decided to set the amount of SSP to 31%, which together with 69% of AN yield exactly 100%. The decrease of SSP content from 33% to 31% does not have a significant impact on the NPK rating.

Fertilizer manufacturers do not provide specific information which N and P compounds are the basis of their products. It could be assumed that N and P compounds used in industrial scale are more concentrated than AN and SSP used in the present study. In the present study, the quantities of N and P compounds are based on their stoichiometric quantities. For example, the mineral fertilizer also contains K compounds, some other macro and micronutrients and inert additives. However, the required amounts of AN and SSP already compose 100% of the fertilizer product and no other substances can be added without decrease in N and P contents. This strongly indicates that N and P compounds used in industrial scale differ from those used in the present study.

Manufacturing process

There was no specific information available on the manufacturing process of the reference mineral fertilizer at the time of writing the thesis. Thus, below described manufacturing processes are based on the literature.

AN is produced by an exothermic reaction in which nitric acid (HNO_3) is neutralized by ammonia (NH_3) (Kongshaug, 1998). In ammonia synthesis, atmospheric nitrogen is combined with hydrogen commonly originating from natural gas, oil, or coal (EFMA, 2000a). HNO_3 is produced by catalytic oxidation of NH_3 with air at high pressure and temperature (EFMA, 2000b). The overall reaction equations to produce NH_3 (5.3), HNO_3 (5.4) and finally AN (5.5) are presented below.

$$\mathrm{N_2 + 3H_2 \rightarrow 2NH_3} \qquad (5.3)$$

$$\mathrm{12NH_3 + 21O_2 \rightarrow 8HNO_3 + 4NO + 14H_2O} \qquad (5.4)$$

$$\mathrm{NH_3 + HNO_3 \rightarrow NH_4NO_3} \qquad (5.5)$$

In addition to AN, another nutrient compound under scrutiny is SSP. SSP is produced by reacting powdered apatite mineral ($Ca_3(PO_4)$) with sulfuric acid (H_2SO_4). Sulfur raw material for H_2SO_4 production can be obtained either by mining or as a co-product recovered from oil and gas production. Of these two options, the latter is the main route for sulfuric raw material acquisition and thus employed in this case study. Apatite mineral is obtained from phosphate rock which is acquired by mining activities. (Dawson and Hilton, 2011; Kongshaug, 1998; Windridge, 1996) A simplified reaction equation of SSP production (Equation 5.6) is presented below. SSP product includes both end products of the reaction: monocalcium phosphate ($Ca(H_2PO_4)_2$) and calcium sulfate ($CaSO_4$). (Finck,1982) There exist variations of chemical formula of SSP in the literature. This might be due to the heterogeneous nature of phosphate rock which affects the final composition of the end product.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4 \qquad (5.6)$$

Finally, AN and SSP are blended together to yield the mineral fertilizer. In this case study, it was assumed, that the mineral fertilizer does not contain any other substances in addition to AN and SSP. In summary, Figure 5-6 illustrates a general view of the mineral fertilizer production processes used in the present case study.

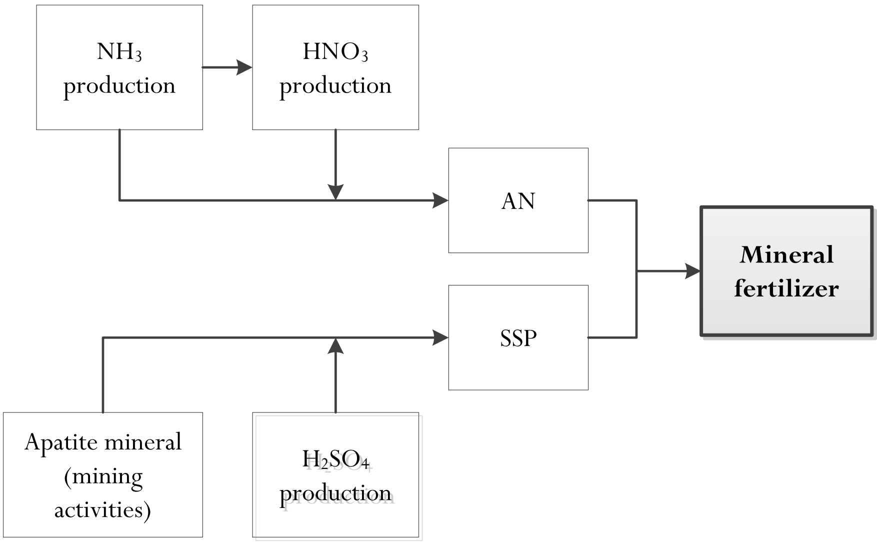


Figure 5-6. Flow chart of the manufacturing process of the mineral fertilizer.

5.2.3 Evaluation boundaries

Definition of the evaluation boundaries includes definition of the system boundaries and definition of the functional unit. The evaluation boundaries in conjunction with the selection of the assessment method and definition of the research targets provide a framework for the performance of the Life Cycle Inventory Analysis (LCI).

5.2.3.1 System boundaries

A complete product system of a fertilizer covers its life cycle from cradle to grave, more specifically articulated from raw material acquisition and processing to the fertilizer application on field and till inspection of impacts caused by mobility of nutrients in the soil solution phase, such as leakage to water bodies. However, within the timeframe of the present thesis, it was not possible to conduct an environmental assessment to full extent and only limited parts of a life cycle of a fertilizer were therefore examined. It is recognized, that limited system boundaries can misrepresent environmental impacts caused during a life cycle of a fertilizer and this limitation should always be taken into account when comparing the differences between the BioA and reference mineral fertilizers that may emerge as a result of the present examination. A complete life cycle of a fertilizer product and the two selected system boundaries for the present case study, named as 1 and 2, are presented in flow diagram in Figure 5-7.

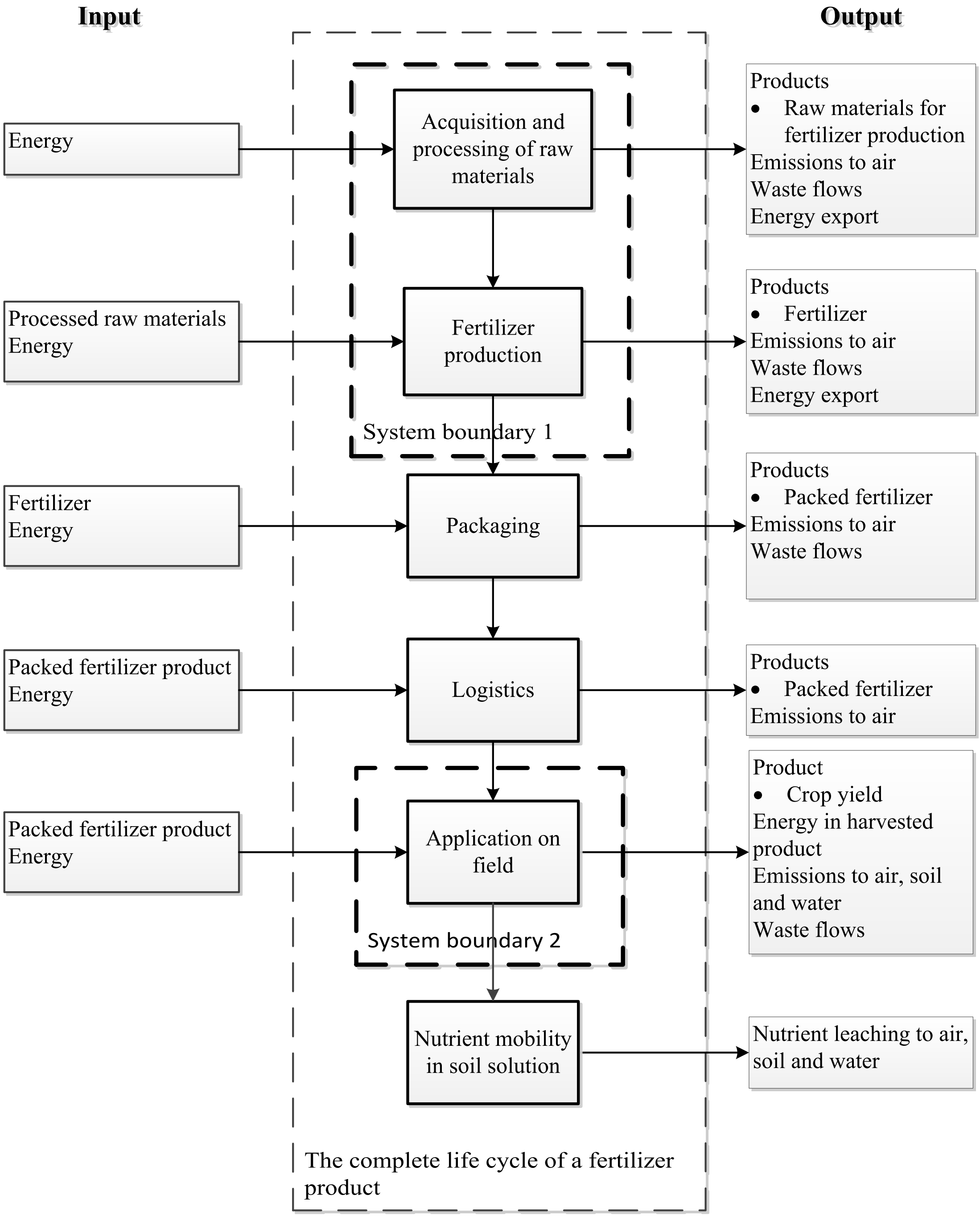


Figure 5-7. The complete life cycle of a fertilizer product and the selected system boundaries 1 and 2 for the case study.

There are two major reasons for the selection of the two system boundaries 1 and 2 for the case study. The first reason is that the system boundaries 1 and 2 represent the phases of a life cycle during which the foremost differences between the mineral and the organic fertilizer products occur. The second reason is that for these selected phases data was available.

The packaging phase was not accounted for, because of its impact on a unit base is considered to be similar in both cases but dependent on the required quantity of a fertilizer. Similarly, the logistics phase was not taken into consideration for the same reason. However, the difference in the required quantities of the BioA and the reference mineral fertilizer was acknowledged in other phases due to the selection of the functional unit. Thus, the requisite information to evaluate packaging and logistics related impacts is readily obtainable for possible further studies. Nutrient mobility in soil solution was not mathematically evaluated, but the principles of nutrient mobility and factors influencing mobility are presented in the literature part.

In addition to the process system boundaries 1 and 2, the present case study had other limitations too. Of the three primary nutrients N, P and K, the study only covers N and P. K was excluded due to its lesser nutritional importance when compared with N and P (Kivelä, 2013). Because the main interest of the fertilizer production is to recycle N and P, K is not the limiting factor in fertilizer composition. Production of inert additives of fertilizer product, such as filling agents and anticaking agents, was also excluded from the study. Thus, of all of compounds which a fertilizer product includes, this case study was limited to examine only N and P.

5.2.3.2 Functional unit

A functional unit is a quantitative measure of the functions that the product under scrutiny provides (for a more detailed definition, see Section 5.2.1.2). The quantitative measure, to which environmental impacts are allocated in LCA studies, is the functional unit. (Rebitzer et al., 2004)

Many important features of a functional unit are case specific. The scope that the functional unit should cover in the present BioA case is divided into four topics. Firstly, the differences emerging from the raw material acquisition should be acknowledged. Raw material acquisition is one of the key points, because in mineral fertilizer production virgin, non-renewable raw materials are used whereas organic fertilizer production utilizes recycled waste streams. Secondly, the functional unit must take into account nutrient concentration of a fertilizer product. The ratio of nutritional value to volume of a product has a major significance, because mineral fertilizers are much more concentrated in nutrients than organic ones. Thirdly, the nutrient concentration also determines production and application volume which are interdependent: a fertilizer low in nutrients needs to be produced and applied more frequently and in more volume than a fertilizer which is high in nutrients. Fourthly, the functional unit should cover the differences which occur during release mode and distribution rate between mineral and organic compounds in soil solution.

According to these four criteria, the suitable functional unit options in the BioA case are for instance one tonne of fertilizer product (t fertilizer), nitrogen content per tonne of fertilizer product (kg N/ t fertilizer), quantity of fertilizer applied per hectare (t fertilizer/ ha) or crop response which demonstrates the crop yield harvested per hectare (t crop/ha). Definition of crop response can be altered to fit better for the purpose of the case. Adding fertilizer use to the crop response, the term converts to: fixed level of crop yield achieved by the use of known quantity of fertilizer ((t crop/ha)/ t fertilizer)). Of these options, it is the modified crop response which best matches the criteria and hence it was selected to be the functional unit in the BioA case. Matching of different functional unit options to the selected criteria is presented in Table 5-7.

Table 5-7. Different function unit options and their capability to response to the set criteria in the present case study. Matching to the criteria is marked grey.

Criterion **Functional unit**	Raw material acquisition for production	Nutrient concentration	Production and application volume	Nutrient release mode and rate
One tonne of fertilizer product (t fertilizer)	▨			
Nitrogen content per tonne of fertilizer product (kg N/ t fertilizer)	▨	▨		
Quantity of fertilizer applied per hectare (t fertilizer/ ha)	▨	▨	▨	
Crop response ((t crop/ha)/ t fertilizer)	▨	▨	▨	▨

Crop response was set equal for both, mineral and organic, cases and the required quantity of fertilizer to obtain this set level of crop response was calculated. Fertilizer manufacturers provide information of expected crop responses at a given application quantity of certain fertilizer or nutrient. Due to the early development stage of the BioA concept, real case-specific data of the crop response of the BioA organic fertilizer was not available. The cereal, for which a crop response was calculated, is barley. Barley was selected due to its popularity in Finnish agriculture and because information about barley crop responses was readily available.

Based on the information obtained from the manufacturer of the selected mineral fertilizer for comparison and from the network organization of Finnish agriculture professionals (Farmit), the target crop response was selected to be 3000 kg barley per hectare (Farmit Website Oy, 2013; Yara Suomi Ltd., 2012). It was assumed that crop response is directly proportional to the quantity of fertilizer applied. According to the information published on a website of Farmit (2013), to obtain crop response 3000 kg barley per hectare, 69 kg N and 13 kg P are needed per hectare. The required quantities of the BioA and mineral fertilizers to fulfill the N or P requirement were calculated by using Equation 5.7. Results are presented in Table 5-8.

$$q_f = \frac{x_n}{m_n}, \qquad (5.7)$$

where q is the required quantity of fertilizer per hectare to achieve set crop response level, x is the required quantity of nutrient per hectare to achieve set crop response level and m is the quantity of nutrient in a fertilizer on a tonne basis; all expressed in kilograms. The lower index f refers to a fertilizer and n to a nutrient (N or P). For the both fertilizer types, m was obtained from their NPK ratings.

Table 5-8. Required quantity of the BioA fertilizer and the reference mineral fertilizer per hectare on a functional unit basis.

	Fertilizer type	
	BioA	**Mineral**
NPK rating	5-1-1	24-4-4
Target crop reponse	3000 kg/ha	3000 kg/ha
Quantity of fertilizer needed		
Limiting factor N (69 kg N/ha)	1380 kg/ha	288 kg/ha
Limiting factor P (13 kg P/ha)	1300 kg/ha	325 kg/ha

Values are reported on a dry matter basis.

According to the limiting nutrient factor, the required quantity of the BioA fertilizer is 1.38 t/ha and the same figure for the mineral fertilizer is 0.33 t/ha, both on a dry matter basis. The required quantity of the BioA fertilizer is already 1.73 t/ha if the total solids content of the product is calculated to be 80% instead of 100%. In the case study, dry weight values were employed. To summarize, the functional unit for the BioA fertilizer is 1.38 t fertilizer/ha and for the reference mineral fertilizer it is 0.33 t fertilizer/ha.

5.2.4 Life Cycle Inventory Analysis (LCI)

The focus of the environmental assessment study was on the second phase of an LCA: a Life Cycle Inventory Analysis (LCI). The idea of an LCI is to study the environmental impacts by aggregating resources used and products and by-products generated during a life cycle of a product, or in this case within the selected system boundaries. In the BioA case, the following five modules were selected for the LCI study:

Input modules

- Raw material consumption
- Energy consumption
- Usage and nutrient release

Output modules

- Atmospheric emissions
- Waste generation

Data related to the selected inputs and outputs was gathered and divided under input and output modules. The selected modules have been modified from the generally recognized modules applied in LCA studies (Grönroos and Voutilainen, 2001). The input and output modules in relation to the system boundaries 1 and 2 are illustrated in Figure 5-8. Figure 5-8 also indicates nutrient, energy and material flows which were analyzed in the present case study. The nutrient, energy and material flows occurring outside the system boundaries are not depicted.

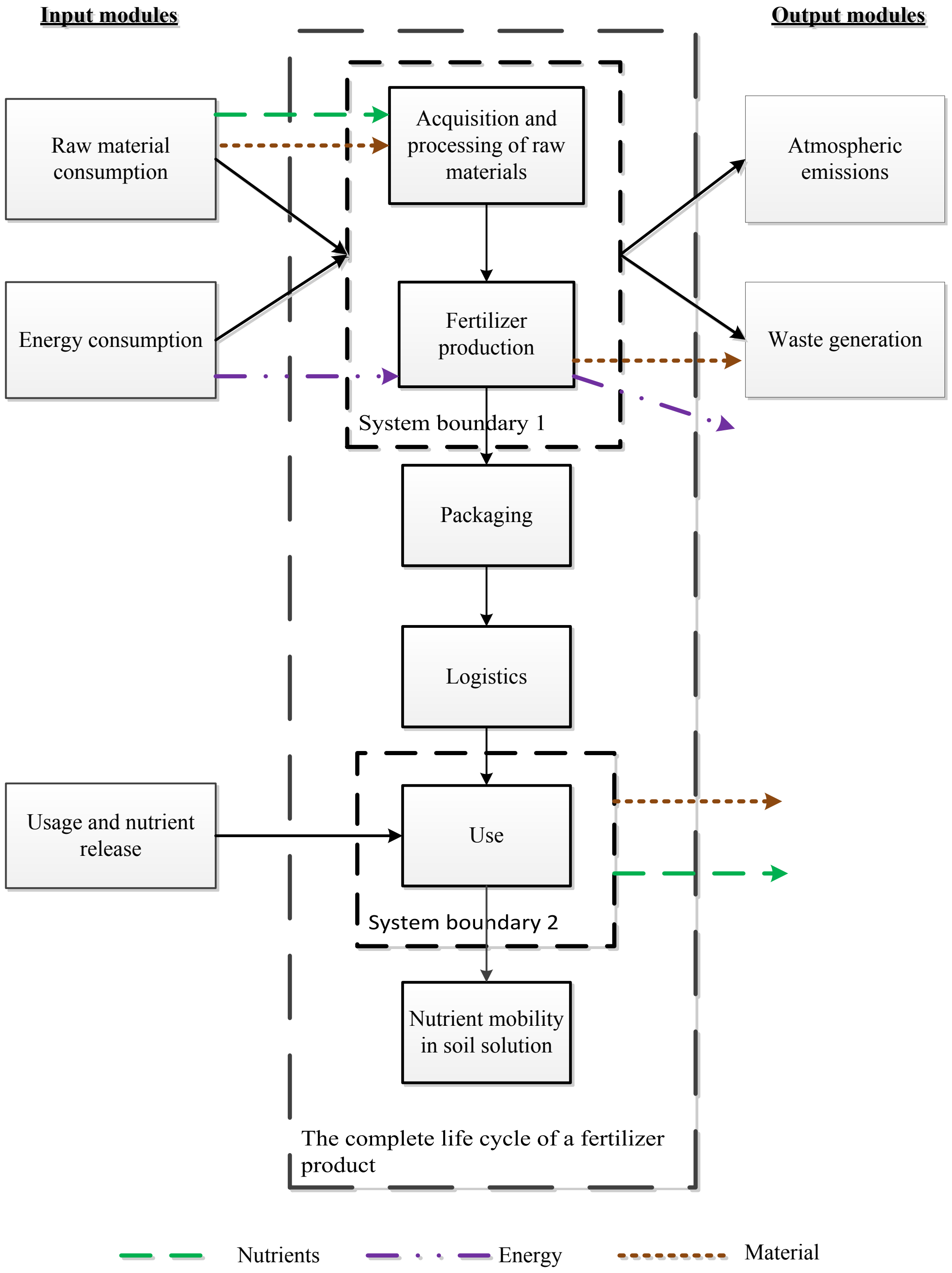


Figure 5-8. The relation between the input and output modules, system boundaries 1 and 2 and nutrient, energy and material flows.

The information to evaluate the environmental impacts was obtained from the literature and from the experimental data, of which the latter was available only in the case of the BioA fertilizer. Two factors which were emphasized in information retrieved from the literature were location of data sampling point (preferred Europe) and modernity of technology (preferred best available technology, BAT). All five studied modules were divided into two subcategories, the BioA fertilizer and the reference mineral fertilizer, and the same inspection was performed for both subcategories. Fertilizer manufacturing processes which were utilized in the LCI study are illustrated in Figure 5-5 for the BioA fertilizer and in Figure 5-6 for the mineral fertilizer. All environmental impacts were calculated in proportion to the required quantity of a fertilizer by functional unit. According to the functional unit, the required quantity of the BioA fertilizer was 1.38 t and the same figure for the mineral fertilizer was 0.33 t.

5.2.4.1 Raw material consumption

The production processes of the mineral fertilizer are mainly based on non-renewable energy and raw material sources whereas production of the BioA fertilizer can simplified to be seen as utilization of waste streams, which are generated regardless of fertilizer production. Hereby, in the case of the mineral fertilizer, environmental impacts arising from acquisition and processing of raw material were taken into account while in the case of the BioA fertilizer it was assumed that digestate and ash exist regardless of fertilizer production. It is axiomatic, that this illustration is partly biased, but on the other hand it emphasizes the phases of a life cycle in which mineral and organic fertilizers differ, which was one objective of the study.

BioA fertilizer

The BioA fertilizer contains 50% ash accept and 50% solid digestate on a dry weight basis (see Figure 5-1). Thus, 1.38 t fertilizer consists of 0.69 t ash accept and 0.69 t solid digestate. In air classification, 75% of the ash is classified as ash accepted and 25% as ash rejected. Consequently, 0.92 t ash must be classified in order to have 0.69 t ash accept. Raw material requirements are illustrated in Figure 5-9.

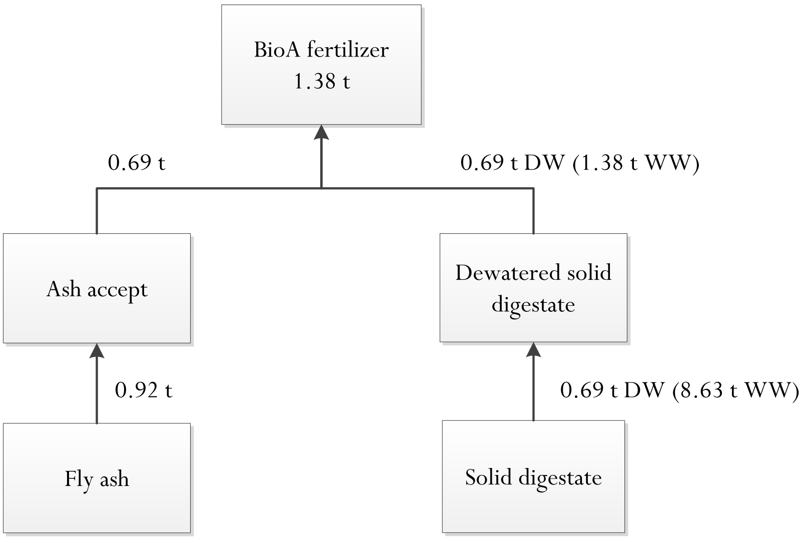


Figure 5-9. Raw material consumption of the BioA fertilizer.

Mineral fertilizer

The raw material requirements of the mineral fertilizer are based on the mass fractions of starting materials to yield 0.33t of the end product, which is the required amount of the mineral fertilizer according to the functional unit. Mass fraction is defined in Equation 5.8 as:

$$w_{\mathrm{a}} = \frac{m_{\mathrm{a}}}{m_a + m_b}, \qquad (5.8)$$

where w is mass fraction, m is mass and the lower indices a and b refer to compounds which compose the total mass of starting material of the reaction in question. Mass is defined as (5.9):

$$m_a = n_a \cdot M_a, \qquad (5.9)$$

where M is molar mass and n moles of component a in reaction.

AN and SSP requirements are based on Equation 5.2 and NH_3 and HNO_3 requirements in AN production are based on mass fractions: w_{NH_3} is 0.21 and w_{HNO_3} is 0.79. Similarly, H_2SO_4 and phosphate rock requirements in SSP production are based on mass fractions: $w_{H_2SO_4}$ is 0.39 and $w_{phosphate\ rock}$ is 0.61. Phosphate ore requirement is based on assumption that 5 tonnes of phosphate ore must be mined and beneficiated to produce one tonne of phosphate rock (Kongshaug, 1998). NH_3 requirement in HNO_3 production is based on literature value 0.28 t NH_3/t HNO_3 (Wiesenberger, 2002). Requirements of natural gas, nitrogen, air and by-products of oil and gas industry were not known at the present time. Raw material requirements of the mineral fertilizer are depicted in Figure 5-10.

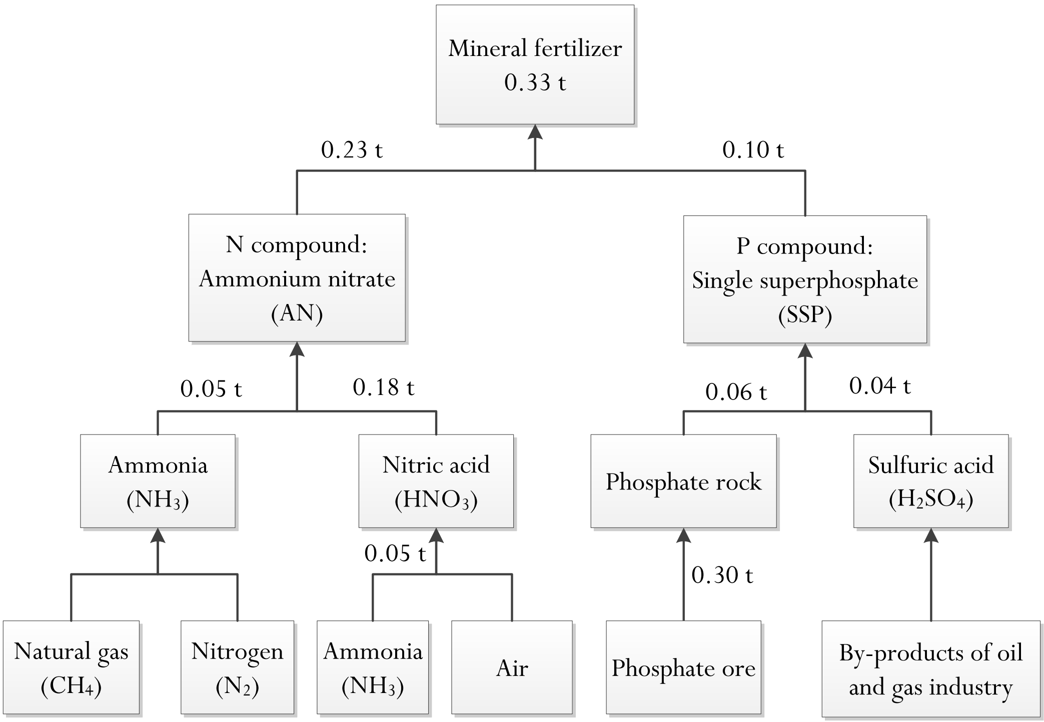


Figure 5-10. Raw material consumption of the reference mineral fertilizer.

5.2.4.2 Energy consumption

The energy consumption can be expressed as two different units: joules (J) or watt-hours (Wh), both of which are energy units. It was decided that in the present study only one unit is used, the joule. The energy consumption presented as watt-hours in the studied literature was thus converted to joules according to the conversion factor 1 Ws = 1 J (1 kWh = 3.6 MJ).

BioA fertilizer

Energy consumption in the production of the BioA fertilizer origins from downstream processing of its two raw materials: digestate and ash. The processing steps for the digestate are hygienization and mechanical dewatering, whereas fly ash has only one downstream processing step: air classification. Both raw material streams are first processed separately, and then blended together by steam granulation to yield the final fertilizer product. In the present case study, the hygienization step was excluded from the energy consumption calculations as at the time of writing this thesis it was being studied whether the hygienization could be conducted simultaneously with the anaerobic digestion. (Bio Refine Tech, 2012a; Kivelä, 2013)

The outflowing digestate from the biogas reactor have total solids content 8%. In the mechanical drying step, digestate is dried from total solids content 8% to total solids content 50%. Wet weights (WW) of the digestate in each processing step were calculated by using Equation 5.10 as the total solids percentages in each processing step were known and the mass of total solids was assumed to be stable. Calculations were performed on a basis to obtain one tonne of fertilizer.

$$m_{WW} = \frac{m_{TS}}{X_{TS}\left(\frac{\%}{100}\right)}, \qquad (5.10)$$

where m_{WW} is a mass expressed on a wet weight basis, m_{TS} is a mass of total solids and X_{TS} is a total solids percentage. The quantity of reduced water in each drying step was calculated by using Equation 5.11:

$$m_{H_2O} = m_{ww\,in} - m_{ww\,out}, \qquad (5.11)$$

where m_{H_2O} is a mass of reduced water and in refers to the inflowing digestate and out to the outflowing digestate prior and subsequent to a drying step, respectively. In Table 5-9, the compositions of digestate, ash and fertilizer subsequent to each processing step are presented.

Table 5-9. Mass flows and total solids content (%) of the digestate, ash and BioA fertilizer during the manufacturing processes.

Flow	**Total solids (%)**	**Total solids (t flow/t fertilizer)**	**Wet weight (t flow/ t fertilizer)**
Digestate subsequent to:			
Anaerobic digestion	8	0.5	6.25
Hygienization	8	0.5	6.25
Mechanical dewatering	50	0.5	1
Ash prior to:			
Air classification	99.7	0.67	0.67
Ash subsequent to:			
Air classification	99.6	0.5	0.5
Fertilizer subsequent to:			
Steam granulation	80	1	1.25

According to Lohiniva *et al.* (2001), the heat energy requirement for mechanical dewatering techniques is about 0.1-0.2 GJ/t for removed water. In the present case study, the average value of the above mentioned energy consumption figure was employed. At the time of writing this thesis, there was no extensive information available on energy consumption of air classification. According to one survey conducted by The Technical Research Centre of Finland (VTT), energy consumption in air classification was about 26.3 kWh/t classified ashes, corresponding to 0.1 GJ/ t classified ashes (Korpijärvi et al., 2009). Finally, processed digestate and ash accept are blended by steam granulation to yield

BioA fertilizer. According to Kongshaug (1998), energy requirement of steam granulation is 1.1 GJ/t product. Energy consumptions in each processing step are collected in Table 5-10.

Table 5-10. Energy consumption in each processing step of the raw materials of the BioA fertilizer.

Processing step	**Quantity**	**Heat energy (GJ/t removed H_2O)**	**Energy (GJ/t ash)**	**Energy (GJ/t product)**
Processing of digestate	$E_{digestate}$			
Mechanical dewatering	E_{MD}	0.15	–	–
Processing of ash	E_{ash}			
Air classification	E_{AC}	–	0.10	–
Processing of fertilizer	$E_{blending}$			
Steam granulation	E_{SG}	–	–	1.10

Total energy consumption in the production of the BioA fertilizer is illustrated in Equation 5.12. All energy consumption values were calculated on a tonne basis (GJ/t fertilizer).

$$E_{BioA} = E_{digestate} + E_{ash} + E_{blending} \tag{5.12}$$

Energy consumption in digestate processing consists of energy consumption in mechanical drying. Equations 5.13 and 5.14 present this energy consumption.

$$E_{digestate} = E_{MD} \tag{5.13}$$

$$E_{MD} = E_{heat\ MD} \cdot m_{{H_2O}_{MD}} \tag{5.14}$$

Energy consumption in ash processing only includes energy consumption in air classification, which was calculated according Equation 5.15:

$$E_{ash} = E_{AC} \cdot m_{{ww}_{ash\ (prior\ to\ AC)}} \tag{5.15}$$

Energy consumed in fertilizer blending is presented in Equation 5.16:

$$E_{blending} = E_{SG} \cdot m_{{ww}_{fertilizer}}, \tag{5.16}$$

Thus, energy consumption in the production of the BioA fertilizer on a tonne basis was obtained as follows (5.12):

$$E_{BioA} = E_{digestate} + E_{ash} + E_{blending}$$

$$E_{BioA} = E_{heat\ MD} \cdot m_{{H_2O}_{MD}} + E_{AC} \cdot m_{{ww}_{ash\ (prior\ to\ AC)}} + E_{SG} \cdot m_{{ww}_{fertilizer}} \tag{5.12}$$

Energy consumption in the production of the BioA fertilizer on a functional unit basis was obtained by multiplying the energy consumption in each step by 1.38 which is the required quantity of the fertilizer according to the functional unit. To summarize, energy consumption in production of 1.38 t BioA fertilizer is 3.08 GJ. Energy consumptions on a tonne basis and on a functional unit basis are presented in Table 5-11.

Table 5-11. Total energy consumption in the production of the BioA fertilizer.

Processing step	Energy consumption On a tonne basis (GJ/t fertilizer)	 On a functional unit basis (GJ/1.38 t fertilizer)
Digestate		
Mechanical dewatering	0.79	1.09
Ash		
Air classification	0.07	0.09
Fertilizer		
Steam granulation	1.38	1.90
Total	2.23	3.08

Mineral fertilizer

The energy consumption in the mineral fertilizer production consists of production of N and P compounds, a strong emphasis being on the production of the former. It has been decided that in the present case study the N compound is ammonium nitrate (AN, NH_4NO_3) and the P compound is single superphosphate (SSP, $Ca(H_2PO_4)_2 + 2CaSO_4$). If not stated otherwise, all energy consumption values including those obtained from the literature as well as those based on process calculations refer to energy which is consumed to produce one tonne of 100% substance (GJ/t substance (100%)). The process calculations are based on 100% conversion efficiency. Required quantities of compounds in reactions are based on either stoichiometric mass fractions, or literature references. Total energy consumption figures further presented describe total fuel requirements, including energy content of both fuel and feed.

AN is produced from ammonia (NH_3) and nitric acid (HNO_3). Thus, to calculate total energy consumption in AN production, energy consumption in NH_3 and HNO_3 production must also be calculated. The energy consumption values concerning NH_3 production cover both, fuel and feed requirements to yield one tonne of NH_3. According to IFA (2009), who surveyed 93 ammonia plants worldwide in 2008, the average energy consumption in ammonia plants was 36.6 GJ/t NH_3, ranging from 27.0 to 58.2 GJ/t NH_3. According to EFMA (2000a), energy consumption in a reforming ammonia plant employing BAT is approximately between 28.8 and 31.5 GJ/t NH_3. Eggleston *et al.* (2006) conclude that energy consumption in NH_3 production in modern plant in Europe is about 30.2 GJ/t NH_3 whereas Kongshaug (1998) states that energy consumption in modern plant is 28.3 GJ/t NH_3. In conclusion, in the present case study it was assumed that energy consumption in NH_3 production is 31.3 GJ/t NH_3, which is the average of the above mentioned literature references.

Contrary to energy consumption values of NH_3 production, energy consumption values of HNO_3 production include only fuel requirement to produce one tonne of HNO_3. Thus, feed requirement for HNO_3 production must be added to fuel requirement to give total energy consumption. Due to the exothermic nature of the HNO_3 reaction chain, net energy balance of reaction is negative, i.e. reaction produces more energy than it consumes. In practice, net energy export of HNO_3 production is between 0 and 2.4 GJ/t HNO_3, the theoretical maximum being 6.3 GJ/t HNO_3. (Kongshaug, 1998; Wiesenberger, 2001) In this case, the state-of-the-art energy export level was applied and the net energy balance of HNO_3 production was set to be -2.4 GJ/t HNO_3, including only the fuel requirement. The feed requirement is 0.28-0.29 t NH_3/t HNO_3 depending on the process technology (Wiesenberger, 2001). The feed requirement 0.28 t NH_3/t HNO_3 was used in the present case study.

The fuel energy consumption in the AN reaction (Equation 5.17) is modest: 0.15 GJ/t AN (Kongshaug, 1998). Total energy consumption in AN production was calculated as follows (5.17 and 5.18):

$$E_{AN_{total}} = E_{AN_{fuel}} + E_{AN_{feed}} \tag{5.17}$$

$$E_{AN_{feed}} = w_{NH_3} \cdot E_{NH_{3total}} + w_{HNO_3} \cdot E_{HNO_{3total}} \tag{5.18}$$

In HNO_3 production, fuel and feed requirements were calculated separately (5.19 and 5.20):

$$E_{HNO_{3total}} = E_{HNO_{3\,fuel}} + E_{HNO_{3feed}} \tag{5.19}$$

$$E_{HNO_{3feed}} = 0.28 \cdot E_{NH_{3total}} \tag{5.20}$$

An extended version of Equation 5.17 is given below and it yields the total energy consumption of AN production: 11.9 GJ/t AN. Energy consumption figures of AN production are recapitulated in Table 5-12.

$$E_{AN_{total}} = E_{AN_{fuel}} + E_{AN_{feed}} \tag{5.17}$$

$$E_{AN_{total}} = E_{AN_{fuel}} + \left(\frac{M_{NH_3}}{M_{NH_3} + M_{HNO_3}}\right) \cdot E_{NH_{3total}} + \left(\frac{M_{HNO_3}}{M_{NH_3} + M_{HNO_3}}\right) \cdot \left(E_{HNO_{3\,fuel}} + 0.28 \cdot E_{NH_{3total}}\right)$$

Table 5-12. Fuel and feed requirements ofthe ANproduction.

Substance	Energy (GJ/t substance)		
	Fuel	Feed	Total (fuel + feed)
NH_3	–	–	31.3
HNO_3	-2.4	8.8	6.4
AN	0.15	11.7	11.9

It is worth acknowledging that the calculated total energy consumption is not completely realistic because it is based on theoretical reaction equation, not on plant-based data. However, calculated energy consumption is rather well in line with the literature values. According to Kongshaug (1998), the accumulated energy consumption of ammonium nitrate production is 10.7 GJ/t AN and Kuesters and Jenssen (1998) report energy consumption to be 12.6 GJ/t AN.

The P compound of the mineral fertilizer, SSP, is produced from sulfuric acid (H_2SO_4) and phosphate rock ($Ca_3(PO4)_2$). Sulfur raw material for H_2SO_4 production can be obtained either by mining or as a co-product recovered from oil and gas production, the latter option employed in the case study. (Dawson and Hilton, 2011) Because the sulfur raw material obtained by this manner is a co-product of another process, no energy consumption is linked to the sulfur feed, but only to the fuel consumed in H_2SO_4 production processes. Net energy balance of H_2SO_4 production is negative because production processes are exothermic and generate steam to be exported. In plants employing BAT technology, a net energy export is equivalent to 6.0 GJ/t H_2SO_4. (Kongshaug, 1998)

The energy consumption value of SPP production presented by Kongshaug (1998) includes fuel and feed energy consumption of phosphate rock mining activities and fuel energy requirement of SSP production, but not fuel and feed energy consumption of H_2SO_4 production. According to Kongshaug (1998), energy consumption in SSP production processes is 6.7 GJ/t P_2O_5 which according to the author of the reference corresponds to 1.4 GJ/t SSP. However, when applying the chemical formula of SSP presented in this thesis, 6.7 GJ/t P_2O_5 corresponds to 1.9 GJ/t SSP which is the value employed in further calculations. Conversion of energy units from GJ/t P_2O_5 to GJ/t SSP is based on following Equation 5.21:

$$\frac{E}{m_{P_2O_5}} \cdot m_{P_2O_5} = \frac{E}{m_{SSP}} \cdot m_{SSP} \leftrightarrow \frac{E}{m_{P_2O_5}} \cdot n_{P_2O_5} \cdot M_{P_2O_5} = \frac{E}{m_{SSP}} \cdot n_{SSP} \cdot M_{SSP} \qquad (5.21\ )$$

According to Kongshaug (1998), phosphate concentration of SSP is about 21% P_2O_5 which corresponds to 9.2% P. However, according to the chemical formula of SSP employed in the case study ($Ca(H_2PO_4)_2 + 2CaSO_4$), P_2O_5 concentration of SSP is 28% which corresponds to 12% P. This implicates that Konsghaug (1998) has utilized different chemical formula of SSP than has been employed in the present cases study. The literature reference (Kongshaug, 1998) do not provide specific information on the chemical formula of SSP applied in that study, but it was assumed that chemical formulas of SSP applied by Kongshaug (1998) and in the present case study are rather similar and thus data obtained from Kongshaug (1998) is reliable.

Calculations of the total energy consumption in SSP production consists of following Equations 5.22-5.24:

$$E_{SSP_{total}} = E_{SSP_{fuel}} + E_{SSP_{feed}} \tag{5.22}$$

$$E_{SSP_{feed}} = E_{miningactivities\ _{total}} + w_{H_2SO_4} \cdot E_{H_2SO_{4}{}_{fuel}} \tag{5.23}$$

$$E_{H_2SO_{4}{}_{total}} = E_{H_2SO_{4}{}_{fuel}} \tag{5.24}$$

The total energy consumption of SSP production is presented in Table 5-13. Fuel and feed requirements of SSP production are not reported separately because specific information of fuel and feed energy requirements was not available at the present time.

Table 5-13. Fuel and feed requirements of the SSP production.

Substance	Energy (GJ/t substance)		
	Fuel	Feed	Total (fuel + feed)
H_2SO_4	-6.0	–	-6.0
SSP	–	–	1.9
Total SSP	–	–	-0.4

[1] Energy consumption (GJ/t substance)) includes fuel and feed consumption of phosphate rock mining activities and fuel requirement of SSP production, but not fuel and feed consumption of H_2SO_4 production.

To conclude, the total energy consumption in SSP production is -0.4 GJ/t SSP. Applying the chemical formula of SSP presented in this thesis, it corresponds to -1.6 GJ/t P_2O_5. However, according to Kongshaug (1998), the total energy consumption would be -3.8 GJ/tP_2O_5. The difference between energy consumption figures is probably due to two issues. Firstly, an energy consumption 1.9 GJ/t SSP was used in the case study whereas Kongshaug (1998) used energy consumption equal to 1.4 GJ/t SSP. Secondly, in the present case study mass fraction of H_2SO_4 in the SSP reaction was calculated with reference to the reaction stoichiometry (0.39 t H_2SO_4/t SSP) whereas Kongshaug (1998) reports a H_2SO_4 consumption of 1.75 t H_2SO_4/t P_2O_5 which corresponds to 0.49 t H_2SO_4/t SSP.

The reference did not provide information on what the basis of the H_2SO_4 consumption is in the study by Kongshaug (1998).

It was assumed that AN and SSP are mixed together by a bulk blending method. Bulk blending was chosen because there was no accurate information on mixing process and bulk blending is a common method. Energy consumption in bulk blending is negligible and it was rounded to be 0 in the present study (Kongshaug, 1998).

The required quantity of the mineral fertilizer is 0.33 t/ha which consists of 0.23 t AN and 0.10 t SSP (see Figure 5-10). Thus, the total energy consumption in production of 0.33 t mineral fertilizer was obtained as follows (5.25):

$$E_{mineral}\ (0.33t) = 0.23 \cdot E_{AN_{total}} + 0.10 \cdot E_{SSP_{total}} \tag{5.25}$$

The total energy consumption and the sources of energy consumption are summarized in Table 5-14. In conclusion, energy consumption in production of 0.33 t mineral fertilizer is 2.7 GJ.

Table 5-14. Total energy consumption in the production of the reference mineral fertilizer.

Substance	**Energy consumption** **On a tonne basis (GJ/t fertilizer)**	**On a functional unit basis (GJ/0.33 t fertilizer)**
NH_3	4.60	1.518
HNO_3	3.48	1.148
Fuel	0.10	0.033
∑AN	**8.18**	**2.699**
Fuel + mining activities	0.59	0.195
H_2SO_4	-0.73	-0.241
∑SSP	**-0.14**	**-0.046**
∑Fertilizer	**8.04**	**2.653**

5.2.4.3 Atmospheric emissions

This module exclusively covers gaseous emissions generated in manufacturing processes but, for instance, not the emissions arising from use of the fertilizer and the application. The fertilizer use and application cause emissions through leakage of nutrient compounds into air and the surrounding water bodies. Nutrient leakage to water bodies contributes significantly to eutrophication (Roy et al., 2006). Despite the significance of use and application associated emissions, those emissions were excluded from the present study.

Also emissions emitted in the production and combustion of energy, which is utilized in fertilizer production, were excluded from the study.

Emissions are either output products of manufacturing processes, or waste gases released during processing. The three main greenhouse gases (GHG) arising from fertilizer production are carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) (Wood and Cowie, 2004). Other typical atmospheric pollutants are ammonia (NH_3), ammonium salt aerosols, nitric oxides (NO_x), fluorines (as SiF_4 and HF), oxides of sulfur (SO_x), fertilizer dust, acid mists, and radiation (Windridge, 1996). This study analyzed CO_2, CH_4, NO_x (including N_2O), SO_x and NH_3 emissions arising from fertilizer production.

BioA fertilizer

The potential emission sources in the production of the BioA fertilizer are the processing steps of the digestate and ash and final fertilizer product. Hygienization tanks are gas and waterproof and do not emit discharges. The drying steps of the digestate mostly emit water vapor. (Bio Refine Tech, 2012a) There was no information available concerning possible emissions related to the air classification method for ash separation and thus it was assumed that air classification does not have airborne emissions. It was not known that there would be emissions associated with the fertilizer blending unit (Kongshaug, 1998). In summary, according to the current state of knowledge of the BioA concept, the BioA fertilizer production does not cause atmospheric emissions.

Mineral fertilizer

The possible emission sources in the mineral fertilizer production are the production of AN and its raw materials HNO_3 and NH_3, of which the latter is also used as a raw material in HNO_3 production. Similarly, possible emission sources are the production of SSP and its raw materials H_2SO_4 and phosphate rock. Because there was no information about raw material consumption of natural gas, nitrogen, air and by-products of oil and gas industry, emissions related to them were not evaluated (see Figure 5-10).

Airborne emissions of AN production are NH_3 and AN (Wiesenberger, 2002). If BAT is employed, these emissions are 0.5 kg for AN particulates and 0.2 kg for NH_3 per tonne of AN (EFMA, 2000e). Major atmospheric emissions related to NH_3 production are CO_2 and NO_2. CO_2 is generated in two stages in NH_3 production: firstly, as a by-product of manufacturing, and secondly, it is released within the flue gas. (Windridge, 1996) Use of by-product CO_2 for other processes would give an emission credit for CO_2 emissions linked to NH_3 production. However, in this case no emission credit was given and no reuse of CO_2 was recognized. The most significant emissions of HNO_3 production are NO_x, particularly nitrous oxide (N_2O). However, N_2O emissions were here not studied separately but are included in NO_x emissions. Other emissions associated with HNO_3 production are negligible. (Windridge, 1996; Harnisch et al., 2006)

The production of SSP from phosphate rock and sulfuric acid generate dust and fluorides, mostly hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4) (Wiesenberger, 2002). H_2SO_4 production emits SO_2 and acid mist, other emissions are not significant (Windridge, 1996). Phosphate rock mining and beneficiation emit dust particles, but no other emissions are associated with the mining operations (Wiesenberger, 2002).

Emission levels obtained from the literature for the NH_3, HNO_3 and H_2SO_4 production are presented in Table 5-15. Variation among HNO_3 production related NO_x emission levels arise from different HNO_3 production technologies and emission abatement technologies depending on different literature sources. In the present case study, the averages values of those values presented in Table 5-15 were used: 1.69 t CO_2/t NH_3 and 0.95 kg NO_x/t NH_3 for NH_3 production, 4.8 kg NO_x/t HNO_3 for HNO_3 production and 2.7 kg SO_x/t H_2SO_4 for H_2SO_4 production.

Table 5-15. Emissions associated with the production of AN, NH_3, HNO_3 and H_2SO_4.

Production	Emission	Unit	Value	Reference
AN	NH_3	kg NH_3/ t AN	0.5	EFMA, 2000e
NH_3	CO_2	t CO_2 /t NH_3	1.65-1.80	Windridge, 1996; EFMA, 2000a
			1.65	Kongshaug, 1998
	NO_X	kg NO_X /t NH_3	0.6-1.3	Windridge, 1996; EFMA, 2000a
	SO_X	kg SO_X/t NH_3	0.01	Windridge, 1996
HNO_3	NO_X	kg NO_X/t HNO_3	6.7	Kongshaug, 1998
			1.4	EFMA, 2000b
			4.2	Windridge, 1996
			7	Eggleston et al., 2006
H_2SO_4	SO_X	kg SO_X/t H_2SO_4	2.15-3.15	Windridge, 1996
			1.6-4.0	EFMA, 2000c

Based on the mass fractions of the substances introduced in Equation 5.8 and 5.9 (see also Figure 5-10) and on the emission levels presented in Table 5-15, total emissions of CO_2, NO_x, SO_x and NH_3 were calculated. The results are summarized in Table 5-19.

Table 5-16. Total emissions associated to the production of 0.33 t mineral fertilizer.

Emission	Value	Unit
CO_2	0.17	t CO_2/0.33 t fertilizer
NO_X	0.96	kg NO_X/0.33 t fertilizer
SO_X	0.11	kg SO_X/0.33 t fertilizer
NH_3	0.05	kg NH_3/0.33 t fertilizer

5.2.4.4 Waste generation

Two types of waste generated in fertilizer production are solid waste and liquid waste waters, which both are co-products and by-products from fertilizer production. The present study does not class water or steam produced during fertilizer production as waste products. Also co-products or by-products which can be recovered and recycled back to the process were excluded from the study. The gaseous waste products are included in atmospheric emissions.

The major waste product of mineral fertilizer industry originates from the production of phosphoric acid which generates as by-products large quantities of phosphogypsum (calcium sulfate) (Windridge 1996). However, no phosphoric acid is needed in AN or SSP production and calcium sulfate generated in SSP production is part of the end product.

BioA fertilizer

The manufacturing of the BioA fertilizer has two possible sources of waste generation: processing of the fly ash and processing of the digestate. Fly ash is air classified into ash accept and ash reject of which only the former is used in fertilizer production and the latter is considered as solid waste. In the air classification fly ash is separated into accepted and rejected in the ratio of 75% to 25%, respectively. On the functional unit basis, the ash accept requirement in the fertilizer production is 0.69 t (see Figure 5-9), in which case 0.92 t ash must be classified. Thus, the ash reject is 0.23 t rejected ash/0.69 t accepted ash.

Not all the digestate is used in the fertilizer production, but it is separated into solid and liquid fraction of which the former is used in the fertilizer production and the latter is redirected to the algal cultivation (see Figure 2-1). Due to the recycling of the liquid fraction, it is not considered as waste. All solid digestate is planned to utilize in the fertilizer production (Kouhia, 2013). To summarize, waste generation in production of 1.38 t BioA fertilizer is limited to 0.23 t ash reject.

Mineral fertilizer

In the following, waste generation in AN and SSP production, and in production of their raw materials, NH_3, HNO_3, H_2SO_4 and rock phosphate, are studied. There are no significant solid or liquid waste products associated with AN, SSP, NH_3 and H_2SO_4 production. In these manufacturing processes negligible quantities of waste are generated, for example, as spent catalyst. There is no solid waste production in HNO_3 production either, but minor liquid waste waters containing dissolved salts and small amounts of ammonia exist. However, the recovery rate of liquid waste waters is high and environmental significance of waste waters is negligible. (Windridge, 1996) Phosphate rock is mined and beneficiated from phosphate ore: 5 t of the latter is needed to yield 1 t of the former. In the BioA case, phosphate rock requirement is 0.06 t (see Figure 5-10) and thus waste generation linked to phosphate rock is 0.30 t phosphate ore/0.06 t phosphate rock. Therefore, waste generation in production of 0.33 t mineral fertilizer is 0.24 t phosphate ore.

5.2.4.5 Usage and nutrient release

Environmental impacts related to the fertilizer usage and nutrient release were dealt with two parts. First, the impacts which originate from application were studied, and secondly, impact of nutrient release was examined. It was assumed that the same field application technique is used both for the BioA and the mineral fertilizer. The possibility to use the same application technique is important from the perspective of the end user as it facilitates the combined use of both fertilizer types if needed. In Finland, a general fertilizer package size intended for professional use is 650 kg and the maximum limit for spreading machines is in general 1200 kg/ha (Kivelä, 2013).

Nutrient compounds of organic and mineral fertilizer have different release modes and distribution rates (see Table 4-2). Detailed nutrient mobility in soil solution was not studied but release rates of nutrient compounds were evaluated based on the literature. Nutrient release rate describes the ratio of the quantity of a nutrient in a fertilizer which is easily released in soil solution to the total quantity of nutrient in a fertilizer, as presented in Equation 5.26:

$$X_i(\%) = \frac{m_{i_{released}}}{m_{i_{total}}}, \qquad (5.26)$$

Where X is release rate percentage, m is mass and the lower index i refers to a nutrient.

BioA fertilizer

The 1.38 t of BioA fertilizer needs to be applied per hectare to satisfy nutrient requirements of N and P which equals to 2.1 fertilizer packages. Particularly in the case of organic fertilizers, it is essential to define release rates of nutrients. Release rate is not always equal to solubility rate because organic compounds have two routes via which they may become available for plants: decomposition and dissolution, and release rate covers both of these. The release rates of four compounds were studied: P and K compounds found in the fly ash and N and P compounds found in the digestate. The release rate of the N obtained by biogas stripping was not studied because, in order to facilitate the process calculations, it was supposed that all N origins from the digestate.

Because ash is inorganic material, nutrients bound to ash compounds are released mainly by dissolution, not by decomposition. Thus in the case of ash, release rate equals solubility rate. In the present case study, solubility rate is defined as the ratio of the quantity of easily soluble nutrients to the total quantity of nutrients. Easily soluble plant nutrients in ash are commonly determined using ammonia acetate extraction (Dahl et al., 2009). Solubility rates of fly ash containing P and K compounds collected from the literature references are presented in Table 5-17. Based on the information provided in Table 5-17, the average solubility rate for P compounds is about 8% and for K compounds about 45%. These average values were used in the present case study.

Table 5-17. Solubility rates of the primary nutrients found in fly ash.

Fuel composition	**Solubility rate (%)**		**Reference**
	P	**K**	
Wood waste (43%) Peat (57%)	9.8	48.9	Nurmesniemi, Pöykiö et al. 2008
Wood (30-40%) Peat (60-70%)	n.a.	37.7	Steenari, Lindqvist 1999
Wood	n.a.	55	Ohno 1992
Wood	5.7	40	Ohno, Erich 1990
Average value	7.8	45.4	

n.a. not available

The primary nutrient compounds of organic digestate are N and P. The main release mode for digestate bound compounds is decomposition, or mineralization, but dissolution also occurs. Anaerobic digestion alters nitrogen compounds so that they are more readily available for plants. This is essential as the mineralization rate of insoluble organic nitrogen compounds is rather low. (Kapuinen, 2013) Lukehurst *et al.* (2010) have reported that N utilization percentage was on average 80% for 20 samples of digestate originating from a co-digestion of slurry and organic wastes from the food industry. The nutrient utilization percentage is defined as the relative quantity of mineral fertilizer nutrient necessary to obtain the equivalent crop yield as the total quantity of nutrients in the digestate (Lukehurst et al., 2010). Because in mineral fertilizers nutrients are 100% available for plants, the nutrient utilization percentage is equal to the release rate. Kivelä (2013) estimates that the general release rate of N in the digestate is between 80 and 90%.With reference to the information provided by Lukehurst *et al.* (2010) and Kivelä (2013), in the present case study it was assumed that 85% of total N in the digestate is usable for plants. According to the instructions administrated by Agricultural Environmental Aid, 40% of P originating from the waste water treatment plant sludge is considered to be released in soil solution and this valued was used in the present case study (Nummela and Tuononen, 2009).

Four studied release rates are recapitulated in Table 5-18. These release rates were employed in the present case study but they do not hold true universally, because nutrient release is also influenced, for instance, by downstream processing techniques of the raw material streams, soil microbial activity, and soil C:N composition (Roy et al, 2006; Palojärvi et al., 2002). The release rate of P in the BioA fertilizer was obtained by multiplying the total P mass flow in ash accept and in solid digestate by their flow specific release rates and then based on those values and to the fact that the fertilizer is composed of 50% of digestate and 50% of ash, release rate of P in final product was calculated according to Equation 5.26. The total P mass flows were obtained from Table 5.4.

Table 5-18. Release rates of N, P and K.

Flow	**Release rate (%)**		
	N	**P**	**K**
Ash accept	–	8	45
Solid digestate	85	40	–
Fertilizer	85	19	45

To illustrate the impact of the release rates on the nutrient content of the fertilizer, both the total quantities of nutrients and the released quantities of nutrients for the BioA fertilizer are presented in Table 5-19.

Table 5-19. Concentrations of the primary nutrients in the ash accept and solid digestate and in the final BioA fertilizer product. Concentrations of the nutrients are presented both on a total quantity basis and on a released quantity basis.

Material flow	**t**	**Nutrient (kg/t material flow)**					
		N total	**N released**	**P total**	**P released**	**K total**	**K released**
Ash accept	1	–		11.7	0.9	12.1	5.5
Solid digestate	1	100.0	85	6.4	2.6	–	–
Fertilizer	1	50.0	42.5	9.1	1.8	6.1	2.7

All values are reported on a dry matter basis.

Mineral fertilizer

The 0.33 t mineral fertilizer, which needs to be applied per hectare to satisfy the nutrient requirements of N and P, is equal to 0.5 fertilizer package, which spreading to fields presents no problem. Mineral fertilizers only contain inorganic nutrient compounds which are assumed to be completely available for plants; consequently, their release rates were assumed to be 100%. Thus, in the case of mineral fertilizer, the total quantity of a nutrient equals to the released quantity of a nutrient.

5.2.5 Framework for Life Cycle Impact Assessment (LCIA)

The third phase of an LCA, a Life Cycle Impact Assessment (LCIA), facilitates evaluation of the importance of the data gathered on the input and output modules in the previous LCI phase. In LCIA, the inventory analysis data is allocated to the impact categories for which category indicators and characterization factors are selected. Complete accomplishment of the LCIA includes definition of the impact categories, the category indicators and the characterization factors and their employment for the inventory data.

Within the present case study, only a preliminary LCIA study indicating the most relevant impact categories in the present case was outlined. In the preliminary LCIA, it was estimated to which impact categories the environmental impacts studied in the LCI are related to. Evaluation of the suitability of different category indicator options and methodologies to estimate characterization factors was not examined within this study. The BioA fertilizer and the reference mineral fertilizer were not studied separately because the LCIA framework is suitable for the both cases.

The interconnections between inventory data, impact categories and areas of protection are depicted in Figure 5-11. In the BioA case, the most significant impact categories appeared to be resource depletion, climate change and eutrophication. Significance of the impact categories was evaluated according to the amount of inventory data linked them. This preliminary outline can be utilized in possible further studies concerning the performance of the complete LCA of the fertilizer production.

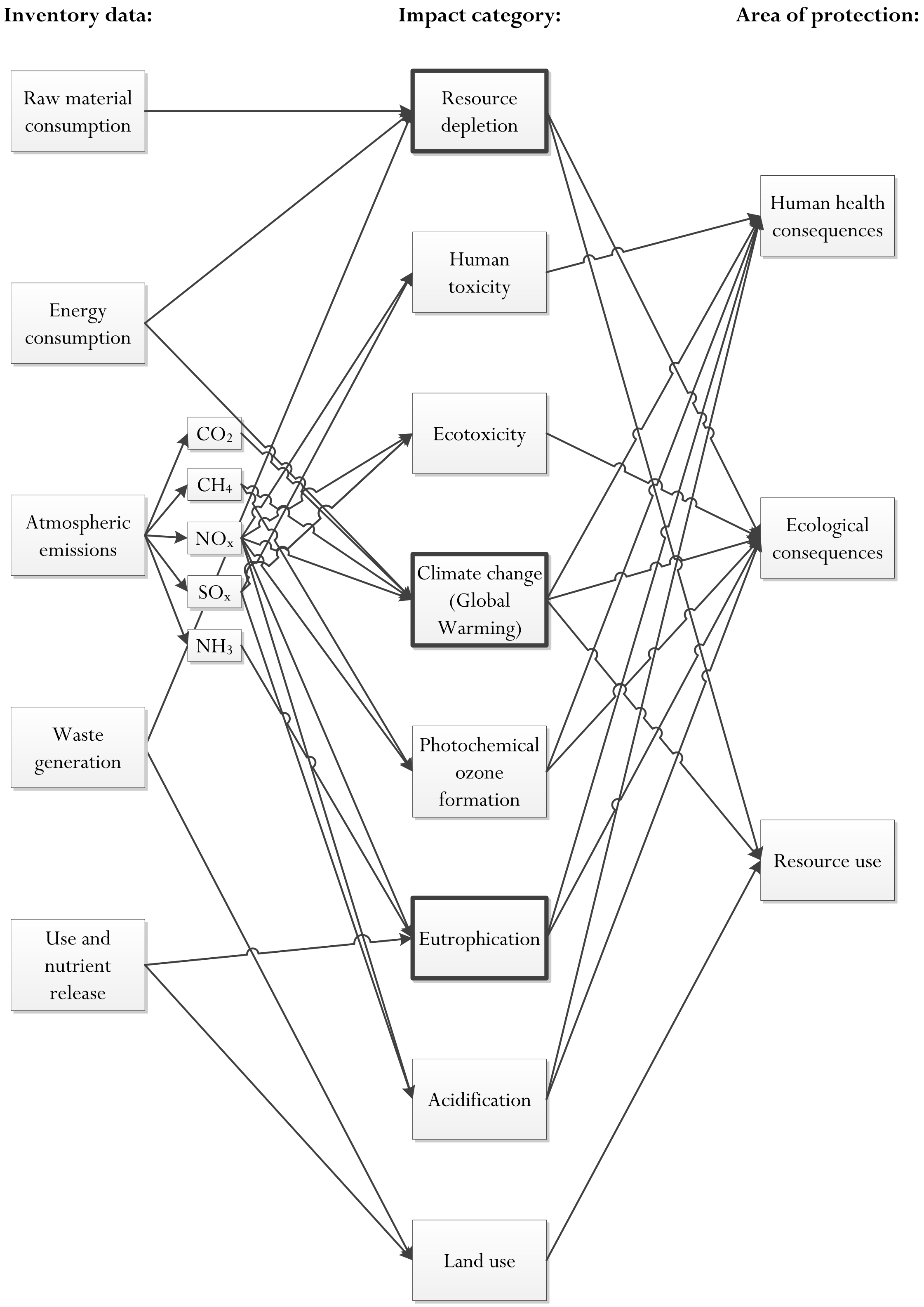


Figure 5-11. Preliminary outline of the LCIA study. The most significant impact categories in the present case study are made bold.

6 RESULTS AND DISCUSSION

Results and discussion of the BioA case study are dealt in two parts because the case study was also performed in two parts. As in the case study, the first part concentrates on the composition of the BioA fertilizer and the second part on the results of the environmental assessment.

6.1 COMPOSITION OF BIOA FERTILIZER

The first objective of the case study was to determine the nutrient content of the BioA fertilizer according to the design criteria applied to the present study and to evaluate if the calculated product composition meets the requirements set by the limiting factors (see Figure 5-1).

According to the process calculations, the NPK rating for the BioA fertilizer is 5-1-1 and the fertilizer product contains 1.35 kg Cd/t fertilizer. Consequently, the composition of the BioA fertilizer does comply with the requirements set by the two limiting factors according to which the nitrogen content of the fertilizer must be above 4% and the Cd concentration below 1.5 kg Cd/t fertilizer. Thus, according to the design criteria used in the present study, the BioA fertilizer is a technically feasible product.

The composition of the BioA fertilizer can be altered by changing the proportions of ash and digestate. According to the design criteria employed in the present study, the BioA fertilizer contains 50% ash accept and 50% solid digestate on a dry matter basis; values also respectively corresponding to the inorganic and organic matter of the fertilizer. On a wet weight basis both the inorganic and organic matter contents of the BioA fertilizer are 40% as the moisture content of the fertilizer is 80% (see Table 5-9). However, comparison of the BioA fertilizer with commercial organic fertilizers shows that the organic matter content of the BioA fertilizer is lower and the moisture content higher than those of the reference organic fertilizers (see Table 6-1). The N source of the BioA fertilizer is the digestate and stripped ammonia flow and consequently one explanation for the rather low N content of the BioA fertilizer is the low organic matter content, or the digestate content, and the high inorganic, or the ash, content.

Table 6-1. Comparison of the compositions between the BioA fertilizer and two commercial organic fertilizers Viljo and Arvo. Compositions of Viljo and Arvo are obtained from Elosato Ltd. (2013) and Novarbo Ltd. (2013), respectively.

	BioA (5-1-1)[1]	**Viljo (8-5-1)**[2]	**Arvo (4-1-2)**[2]
Primary nutrients			
Nitrogen (%)			
Total	5	8	4
Easily available	4.3	2.5	2
Phosphorus (%)			
Total	1	5	1.2
Easily available	0.19	0.15	1
Potassium (%)			
Total	1	1	2
Moisture content (%)	20	5	10
Organic matter content (%)	40	65	70

[1] Easily available defined by release rate (see Table 5-18)

[2] Easily available defined as water soluble

Figure 6-1 depicts the influence of the proportions of ash and digestate on the nutrient content of the BioA fertilizer. In order to have the nitrogen content above 4%, the BioA fertilizer can contain maximum 60% ash and consequently the digestate content must be minimum 40%. Figure 6-2 illustrates the dependence of Cd concentration of the fertilizer product on the proportion of ash accept. To maintain the Cd concentration below the maximum permitted limit 1.5 kg/t fertilizer, the BioA fertilizer can contain maximum 55% of ash accept. Thus, of the two limiting factors, the Cd concentration sets a more strict restriction for the proportion of ash accept and thus it is the dominating limiting factor.

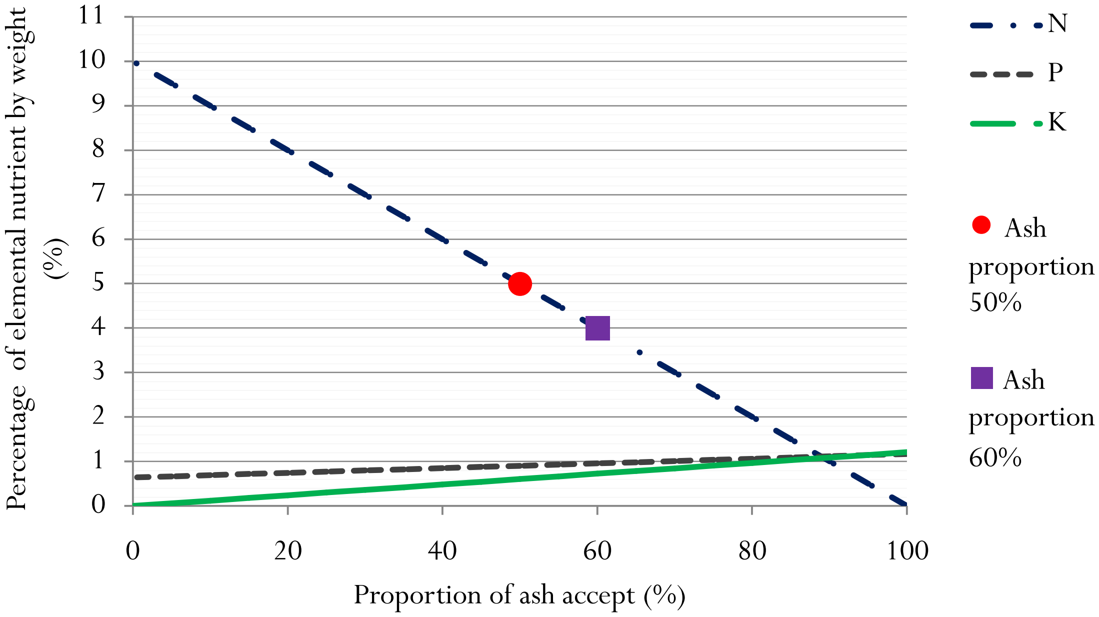


Figure 6-1. Effect of the proportion of ash on nutrient composition.

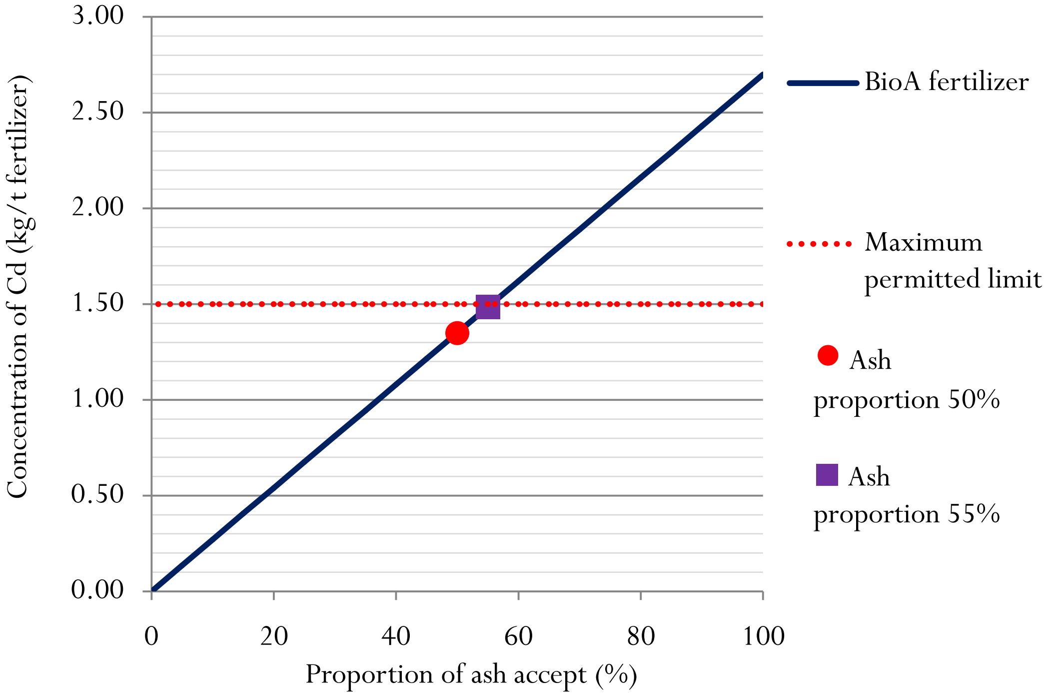


Figure 6-2. Effect of the proportion of ash on Cd concentration.

Beyond the current project plan, one scenario to increase nitrogen content of the digestate, and hence nitrogen content of the fertilizer, is to exploit nitrogen embedded in the digestate effluent (the liquid fraction of the digestate). Currently, the digestate is separated into a solid fraction and effluent in the mechanical dewatering and the effluent is redirected to the algal cultivation. The fertilizing value of nitrogen embedded in the digestate effluent corresponds to mineral nitrogen compounds as it is mostly in inorganic form (Marttinen et al., 2013). The employment of the digestate effluent for fertilizer production would increase nitrogen content of the fertilizer, but simultaneously preclude the algal cultivation option since no nutrients would be returned to the algae cultivation site. However, separation of nitrogen and phosphorus from the digestate effluent is a common practice in biogas plants which aim to utilize digestate for fertilizing purposes (Latvala, 2009).

6.2 ENVIRONMENTAL ASSESSMENT

In the environmental assessment, a Life Cycle Inventory Analysis (LCI) was performed. The LCI studied the environmental impacts of five modules which were raw material consumption, energy consumption, atmospheric emissions, waste generation and use and nutrient release. Results are presented by modules except raw material consumption and waste generation modules which are examined jointly. If not mentioned otherwise, results are given on a functional unit basis. Finally, a summary of the environmental assessment is provided.

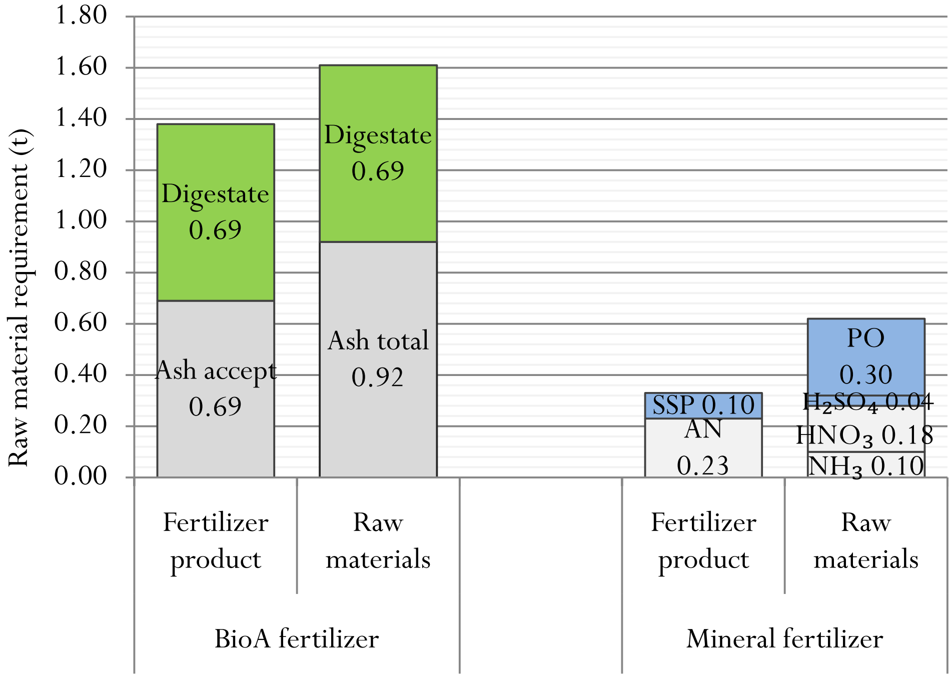
Raw material consumption and waste generation

The raw material consumption and waste generation are linked together due to the manufacturing method of the BioA fertilizer. In the case of the BioA fertilizer, ash and digestate can be considered both as raw materials for fertilizer production and as waste to be eliminated. From the LCI perspective, definition of the type of these streams is recommended as it facilitates allocation of material streams to one module and thus double calculation is avoided. Definition of the ash and digestate streams only as waste, instead of the current situation in which they are recognized both as raw materials and waste, would give an environmental credit for the BioA fertilizer production. The basis of the environmental credit would be that no raw materials would need to be produced and in addition waste would be eliminated.

Within the mineral fertilizer production, there is now overlap between raw material consumption and waste generation in the present study. According to the literature, waste generation in mineral fertilizer production is not a major issue and possible by-products are often redirected to other processes in which they are reused (Windridge, 1996; Wiesenberger, 2002).

Figure 6-3 presents the raw material consumption and Figure 6-4 the waste generation of the BioA and the reference mineral fertilizers on a functional unit basis. In the case of the waste generation of the BioA fertilizer, the ash accept and solid digestate used for the fertilizer production are defined as eliminated waste and thus indicated as negative flows.

Ash reject is the heavy metal containing fraction of the fly ash which is not used for the fertilizer production.



Abbreviations: SSP = single superphosphate, AN = ammonium nitrate, PO = phosphate ore, H_2SO_4 = sulfuric acid, HNO_3 = nitric acid and NH_3 = ammonia.

Figure 6-3. Raw material requirements to yield the required amount of the BioA and the reference mineral fertilizers on a functional unit basis.

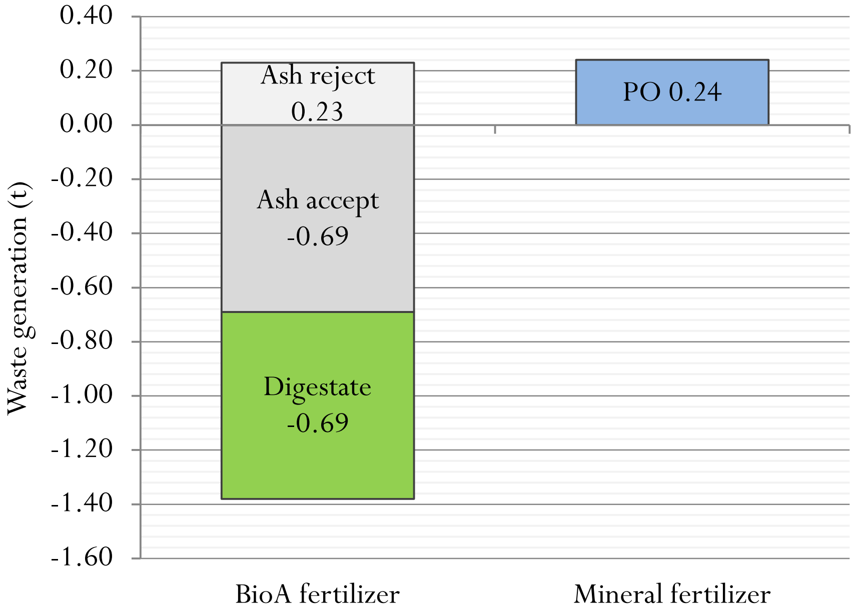


Figure 6-4. Waste generation in the production of the BioA and the reference mineral fertilizers on a functional unit basis.

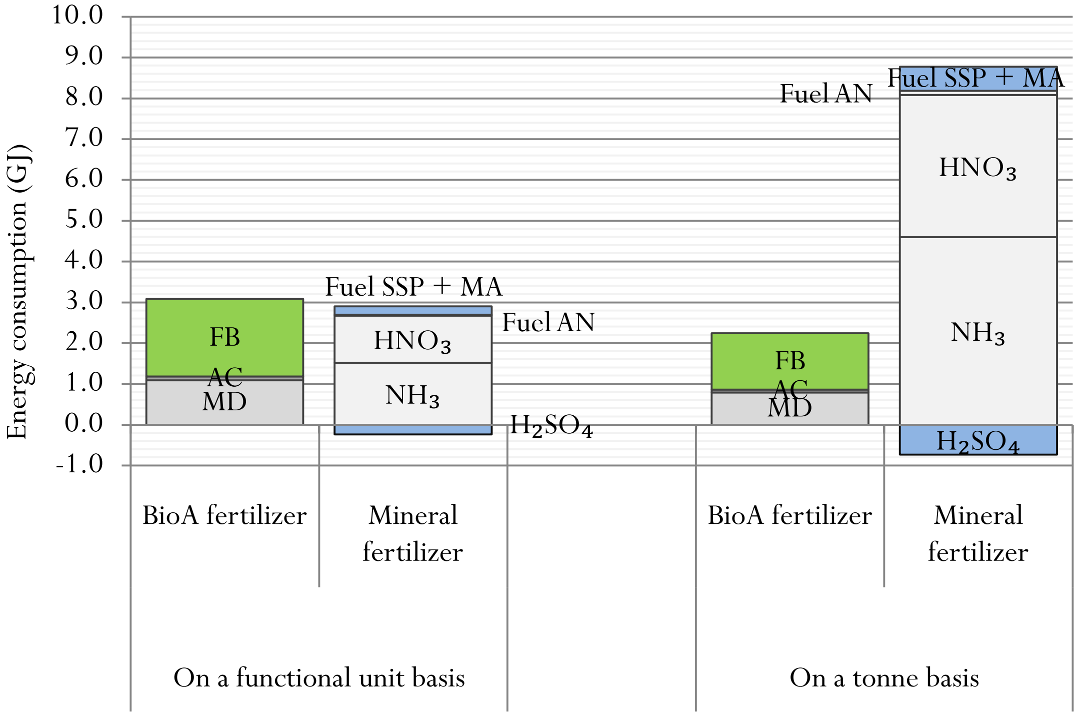
In the raw material consumption and waste generation the BioA fertilizer is superior to the mineral fertilizer as the production does not consume raw materials but eliminates waste. In addition, the raw materials for the BioA fertilizer are recycled renewable materials whereas the raw materials for the mineral fertilizer are mainly virgin, non-renewable materials. Consideration of ash and digestate in the BioA case as eliminated waste instead of consumed raw materials leads to a negative material balance. A negative material balance can be a significant contributor in the total environmental impact balance of the BioA fertilizer. However, the significance of the material balance in the total environmental impact balance remains unsolved within this study since its evaluation would require performance of a complete Life Cycle Impact Assessment (LCIA).

Energy consumption

The energy consumption consists of different type of activities in the BioA and mineral cases. In the BioA case, the energy consumption is related to the unit operations, such as mechanical processes, whereas in the mineral fertilizer case unit operations play a minor role and the most significant contributors to the energy consumption are feed and fuel requirements of chemical reactions.

Contrary to the expected result, on a functional unit basis production of the BioA fertilizer consumes more energy than production of the mineral fertilizer. On a tonne basis, energy consumption is to the contrary: production of the mineral fertilizer consumes more energy than production of the BioA fertilizer. The energy consumption on a functional unit basis is 3.1 GJ/1.38 t BioA fertilizer and 2.7 GJ/0.33 t mineral fertilizer but on a tonne basis same values are 2.2 GJ/t and 8.0 GJ/t, respectively. This confirms that production of the mineral fertilizer is energy intensive, but also efficient concerning the nutrient content of the product. The energy consumptions of the BioA and mineral fertilizers both on a functional unit and on a tonne basis are illustrated in Figure 6-5.

Total energy consumption in the production of the BioA fertilizer may still increase due to the hygienization step which was presently excluded from the calculations. On the other hand, it is estimated that the waste heat from the pulp and paper mill integrate could be utilized in the drying steps of the fertilizer production and consequently the total energy consumption in the production of the BioA fertilizer would be decreased.



Abbreviations: FB = fertilizer blending, AC = ash classification, MD = mechanical drying, SSP = single superphosphate, MA = mining activities, AN = ammonium nitrate, HNO_3 = nitric acid, NH_3 = ammonia, and H_2SO_4 = sulfuric acid.

Figure 6-5. Energy consumption on a functional unit basis and on a tonne basis.

In the case of the BioA fertilizer, the most significant energy consumption sources are mechanical drying and fertilizer blending whereas in the case of the mineral fertilizer production of NH_3 and HNO_3 composes the most part of energy consumption. As anticipated, the production of NH_3 alone consists the major part of the energy consumption in the case of the mineral fertilizer: 1.96 GJ/0.33 t fertilizer which corresponds to 73% of the total energy consumption. In global fertilizer production, the nitrogen fertilizer industry accounts for over 90% of the total energy demand (Dawson and Hilton, 2011).

Atmospheric emissions

The significance of the atmospheric emissions with regards to the total environmental impacts is difficult to evaluate as no data was available about the possible emissions of the BioA fertilizer. As it is not yet known if the BioA fertilizer would emit atmospheric discharges, emissions, for the purposes of the present study, were assumed to be zero. However, this matter should be studied in more detail in order to avoid granting an unintentional emission credit for the BioA fertilizer. Evaluation of the emissions originating from the production of the mineral fertilizer was based on the literature and thus it is clearly more reliable. However, as seen in Table 5-15, the values of the mineral fertilizer related emissions have a great variation. Many estimates of emission levels apply to specific processing techniques or to different regions, such as Europe or the World. In the present study, the averages of available values were employed. As a consequence, the margin of error in emission level values may be assumed to be rather large.

In the mineral fertilizer production, CO_2 (170 kg) is responsible for over 99% of the total emissions. Depending on the literature cited, the possibility to reuse CO_2 in other processes is recognized and thus the quantity of CO_2 emissions linked to the fertilizer production could be reduced. However, in the present study, the decision was made not to give an emission credit for reuse of CO_2 and therefore CO_2 emissions may have become exaggerated. In the mineral fertilizer production, CO_2 emissions exclusively originate from the NH_3 production. Other emissions are NO_x (0.96 kg), NH_3 (0.05 kg) and SO_x (0.11 kg) of which NO_x are linked to the NH_3 and HNO_3 productions, NH_3 to the AN production and SO_x to the H_2SO_4 production (see Table 5-19). The quantities of emissions in a compound level are depicted in Figure 6-6.

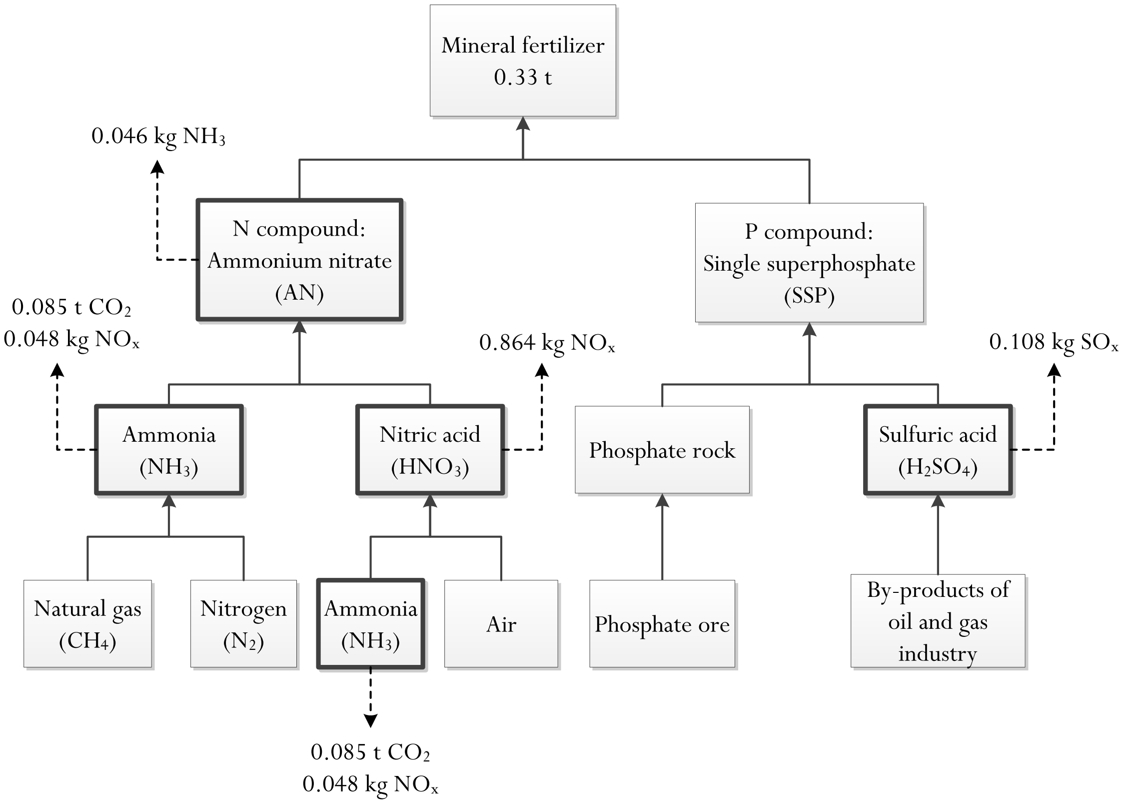


Figure 6-6. Sources of emission releases and quantities of emissions in a compound level associated with the production of the mineral fertilizer.

The CO_2 emissions compose over 99% of the total emissions when emissions are measured in kilograms. However, the use of kilograms as the basis of the calculations overestimates the role of the CO_2 emissions whereas the significance of other emission compounds is underestimated. This can be corrected by using emission equivalents which take into account both, the quantity and the quality of the emission. Emissions expressed in kilograms can be converted into emission equivalents by multiplying them by emission specific characterization factors. Emission equivalents were not calculated in the present study because the calculation requires more accurate information of emission compounds. In addition, the calculation of emission equivalents is part of the LCIA.

Use and nutrient release

The required quantity of the BioA fertilizer, 1.38 t/ha, exceeds the estimated maximum limit for fertilizer spreading machines which is 1.20 t/ha (Kivelä, 2013). However, the required quantities of the reference organic fertilizers are similar to that of the BioA fertilizer: Arvo 4-1-2 requires 1.5 - 2.7 t/ha (Novarbo Ltd., 2013) and Viljo 8-4-8 requires 0.75 - 1.25 t/ha (Elosato Ltd., 2013). This indicates that application volumes larger than 1.20 t/ha may not hamper use of fertilizer and the estimated maximum limit of fertilizer machines should be verified. However, due to the over fourfold required quantity of the BioA fertilizer (1.38 t/ha) compared to the required quantity of the mineral fertilizer (0.33 t/ha), environmental impacts related to the application of fertilizer are larger in the case of the BioA fertilizer.

Due to the complicated release mode of organic fertilizer compounds, actually fewer nutrients are available for plants than NPK rating indicates. Figure 6-7 illustrates the quantities of the primary nutrients in 1.38 t of the BioA fertilizer and in 0.33 t of the mineral fertilizer. In the case of the BioA fertilizer also the ratio of the released nutrients to the total nutrients is presented. The release rates of N, P and K in the case of the BioA fertilizer were obtained from Table 5-21.

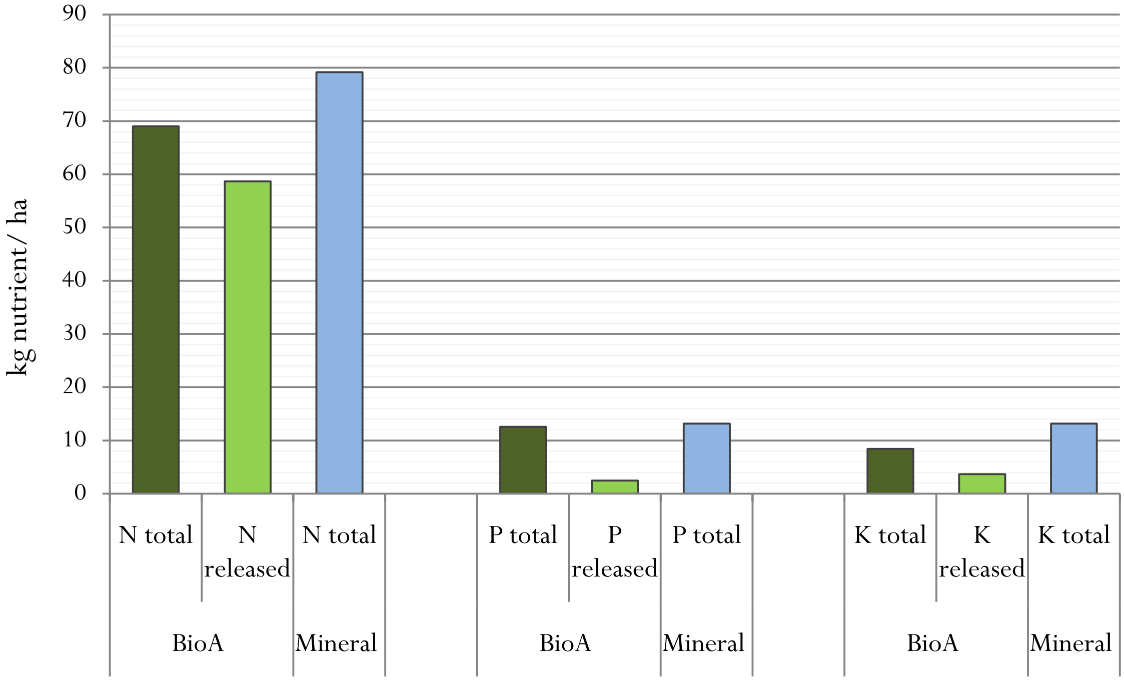


Figure 6-7. Quantities of N, P and K in the BioA and mineral fertilizers on a functional unit basis. In the case of the mineral fertilizer, the total quantity of a nutrient equals to the released quantity of a nutrient.

Although organic fertilizers cannot compete with mineral fertilizers in quantity of nutrients, they have other important characteristics. Organic fertilizers increase the amount of organic matter in soil and activate microbiological population; which both have various positive effects on soil structure which may be difficult to evaluate. Nevertheless, the capability of organic fertilizers to improve soil structure should be acknowledged and an environmental credit given as compared to mineral fertilizers, which nourish plants but not soil.

From an environmental life cycle perspective, mobility of fertilizer compounds in soil solution is an important factor which, however, was not studied. The slow release of organic compounds in soil solution diminishes nutrient leaching into water bodies. Contrary to the organic compounds, inorganic compounds are quickly released in soil solution. Due to their water solubility, some of inorganic compounds are washed away into water bodies and thus contribute eutrophication. To conclude, some salient characteristics of organic fertilizers are not readily measurable and thus evaluation of their importance is demanding. Notwithstanding these difficulties, their impacts on total environmental balance of the fertilizer should not be undervalued.

Summary of environmental assessment

According to the results obtained, the undeniable differences between the BioA and mineral fertilizers are in energy consumption and use and nutrient release. Raw material consumption and waste generation also pose a point of difference but the magnitude of this depends on whether the raw material streams of the BioA fertilizer are defined as waste streams which exist regardless of fertilizer production or as raw materials produced in order to produce fertilizer. The importance of atmospheric emissions is challenging to evaluate as there was no information about the possible emissions related to the BioA fertilizer production. However, emission-free production may pose a significant advantage to the BioA fertilizer. Figure 6-8 describes the BioA and mineral fertilizers in regard to nitrogen content, energy consumption and required quantity. In addition to the x and y values, three dimensional graph contains z value which is represented in the size of the bubble.

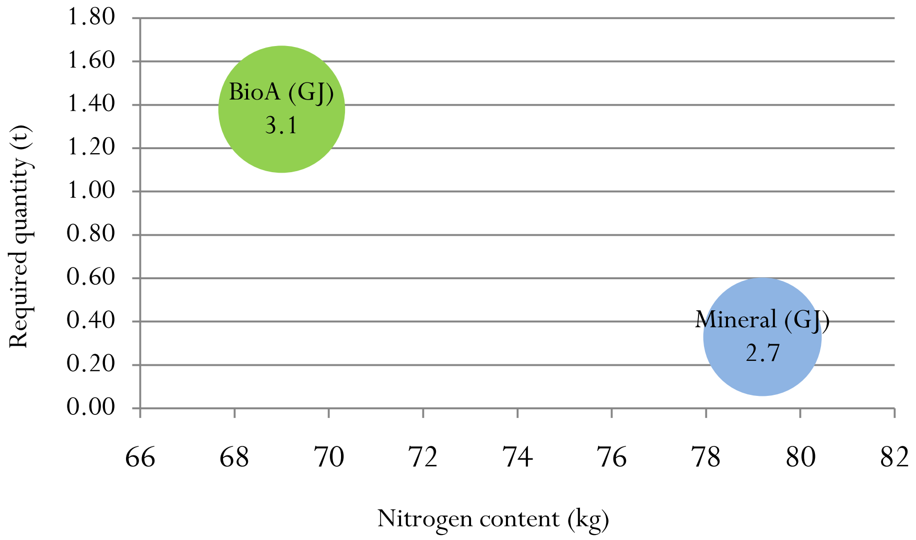


Figure 6-8. BioA and mineral fertilizers in regard to N content, energy consumption and use. The bubble size represents energy consumption. All values are presented on a functional unit basis.

7 CONCLUSIONS AND RECOMMENDATIONS

The aim of the thesis was to analyze organic fertilizer production in the BioA concept. Two research questions were set in order to determine the composition of the BioA fertilizer and to examine its environmental impacts compared to one reference mineral fertilizer. To summarize the results of the study, these research questions are now answered and recommendations for further actions are provided.

1) What is the composition of the organic BioA fertilizer and is it a technically feasible product?

The composition of the BioA fertilizer was calculated within the limits of the following design criteria. First, the BioA fertilizer was composed of 50% solid digestate and 50% fly ash, and no synthetized fertilizer compounds were added. However, additional nitrogen which is obtained by biogas stripping could be added to the fertilizer in order to balance the nutrient composition of the fertilizer. Secondly, the total solids content of the BioA fertilizer was set at 80%. In addition to the design criteria, the composition of the BioA fertilizer was restricted by the requirements of two limiting factors. According to the limiting factors, the lowest acceptable nitrogen content of the fertilizer was 4% and the cadmium concentration could not exceed 1.5 kg Cd/ t fertilizer. As a result of the study, it was calculated that the NPK rating for the BioA fertilizer is 5-1-1 and the fertilizer containes 1.35 kg Cd/t fertilizer. Thus, according to the design criteria used in the present study, the composition of the BioA fertilizer does comply with both of the requirements set by the limiting factors and thus the BioA fertilizer is technically feasible product.

The composition of the BioA fertilizer can be altered by adjusting the proportions of ash and digestate. To simultaneously maintain the nitrogen content above 4% and the cadmium concentration below 1.5 kg/t fertilizer, the proportion of the ash in the BioA fertilizer can be maximum 55%. Consequently, the proportion of the digestate is then 45%. However, if the nitrogen content of the BioA fertilizer is desired to be increased, it is recommended to modify the present design criteria for the BioA fertilizer so that the proportion of the digestate is increased and the proportion of the ash is decreased. The adjustment of the proportions of ash and digestate also affects the environmental impacts of the BioA fertilizer due to the varying quantities of the processed raw materials.

The objective of the second research question was to study the environmental impacts that ensue during the life cycle of a fertilizer and to conduct a comparison between the environmental impacts of the BioA fertilizer and the reference mineral fertilizer in order to determine their differences.

2) How do the environmental impacts that ensue during the life cycle of the BioA fertilizer differ from those of the reference mineral fertilizer?

The complete life cycles of the fertilizers were not undertaken. Instead, the assessment of the environmental impacts was limited to the following five modules: raw material consumption, energy consumption, emission generation, waste generation, and usage and nutrient release. The module selection was successful as all five modules contributed towards the environmental impacts of the BioA fertilizer and the reference mineral fertilizer. The analyzed environmental impacts were calculated in proportion to the quantity of fertilizer required to obtain a crop yield of 3000 kg of barley per hectare. Consequently, the required quantity of the BioA fertilizer was 1.38 t/ha whereas the same figure for the mineral fertilizer was 0.33 t/ha.

No unambiguous conclusion can be drawn about the results obtained as to whether the BioA or the reference mineral fertilizer is superior from an environmental perspective. However, it can be stated that concerning nutrient content, energy consumption and required quantity, the mineral fertilizer appeared to be superior, whereas, in terms of raw material consumption, waste generation and assumedly emission generation, the BioA was superior. It is worth acknowledging that the advantages of both fertilizers, the BioA fertilizer and the reference mineral fertilizer, appeared at different phases of their life cycles. The environmental impacts of the BioA fertilizer also depend on the definition of the purpose of the production: whether it is seen as the consumption of raw materials or as the elimination of waste.

Within the limitations of the present case study, the environmental impacts of the BioA and mineral fertilizers were compared only according to the five studied modules since no single value representing the total environmental impact balance can be provided. To calculate the total environmental impact balance of a fertilizer, a Life Cycle Impact Assessment (LCIA) should be conducted. Thus, it is recommended to continue the evaluation of environmental impacts of the BioA and mineral fertilizers by performing the LCIA based on the data provided in the present study.

In summary, it appears to be possible to produce a technically feasible organic fertilizer product within the BioA concept. According to the environmental assessment conducted in the present study, the BioA fertilizer has smaller environmental impacts compared to the reference mineral fertilizer in three of the five studied environmental impact modules. However, environmental impacts were studied by their quantity and the results were not weighted according to their significance. Thus, within the limitations of the present study, it cannot be concluded that the total environmental impact balance of the BioA fertilizer is smaller than that of the reference mineral fertilizer. However, it can be stated that the BioA fertilizer has the potential of having reduced environmental impacts when compared to the reference mineral fertilizer and the evaluation of the potential requires the performance of a more complete Life Cycle Assessment study.

Overall, compared to the mineral fertilizers currently dominating the markets, the production and use of the organic BioA fertilizer better complies with the tightening environmental politics which promote recycling of exploitable waste streams (EC, 2013b; Ministry of the Environment, 2011) and diminished reliance on non-renewable energy (EC, 2012a). Thus, it is recommended to continue the study of the BioA fertilizer and its environmental advantages over conventional mineral fertilizers.

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