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Process Technology

Life Cycle Assessment of an NPK Fertilizer Production with the Focus on Principal Harmful Substances

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Summary:

The management of fertilizers is important to produce food, but it also has an influence on the environment since it may have negative impacts on the quality of the air, soil, and water. Heavy metals are naturally present in soils and in the raw materials used to make fertilizers. Heavy metal emissions during production or in final fertilizer product can have adverse effects on biodiversity, impacting various organisms and ecological systems. The thesis investigates the environmental impacts of heavy metal emissions in the production of NPK fertilizers. Supported by Yara-Norway, the study addresses regulations surrounding heavy metal emissions at both the production and product level. It lists various techniques for mitigating heavy metal contamination. The different production methods for NPK fertilizers are explained, and the Nitrophosphate route is examined in detail. The thesis calculates the required raw materials based on established principles and collects conventional emissions data from Yara's monitoring system. The methodology provided by Yara is utilized to calculate heavy metal emissions during production. Conducting a Life Cycle Assessment up to the factory gate, the thesis explores the goal, scope, and inventory analysis. It compares different scenarios, taking into account different phosphate rocks and the presence or absence of heavy metal emissions. While heavy metal emissions during production may not be significant in terms of quantity, it is acknowledged that they may accumulate over time and still hold importance. The study finds that heavy metal emissions have notable impacts on Terrestrial, Marine, and Freshwater ecotoxicities, as well as Human carcinogenic and non-carcinogenic toxicities. The thesis emphasizes the importance of raw material sources and their compositions, as well as the potential long-term consequences of heavy metal emissions, despite their relatively small immediate impact.

Preface

This report was written on the topic of "Life Cycle Assessment of an NPK Fertilizer Production with the Focus on Principal Harmful Substances" to fulfill the partial requirement for the Master's study program in Process Technology at the University of South-Eastern Norway, Faculty of Technology, Natural Science and Maritime Sciences, Department of Process, Energy and Environmental Technology.

The goal of the work was to model the NPK production process and calculate the life cycle footprint at the factory gate of a typical NPK grade.

I would like to take this opportunity to express my deep appreciation and gratitude to my supervisor professor Marianne Sørflaten Eikeland, for her invaluable support, guidance, and expertise throughout the completion of this thesis.

I am particularly grateful for Dr. Stéphane Bungener’s patient guidance and unwavering support in navigating the challenges and complexities encountered during this research endeavor. As my external supervisor, his insightful suggestions, meticulous attention to detail, and constructive feedback have been instrumental in shaping my understanding of the subject matter and refining my analytical skills.

I would also like to thank all my colleagues at Yara International for their comments and support during this work. This could not be done without their help.

In addition, I would like to thank my beloved wife Ladan and my wonderful family for their continuous support and motivation throughout my new endeavor in Norway.

And finally, to YOU …!

Porsgrunn, 15.05.2023

Mohammad Hesan

Contents

Nomenclature

Abbreviation	Description
AEL	Associated Emission Level
AN	Ammonium Nitrate
AP	Acidification Potential
BAT	Best Available Techniques or Technology
BLW	Bundesamt für Landwirtschaft (Switzerland Federal Office for Agriculture)
BOM	Bill of Material
BREF	Best Available Techniques Reference Documents
CAN	Calcium Ammonium Nitrate
CAP	Common Agricultural Policy
CML	Center for Environmental Studies
CN	Calcium Nitrate
COC	Contaminants or Compounds of Concern
CSTEE	The Scientific Committee on Toxicity, Ecotoxicity and the Environment
CWW	Common Waste Water
DAP	Di-Ammonium Phosphate
DCB	Dichlorobenzene
DCP	Di-Calcium Phosphate
E	Egalitarian
EP	Eutrophication Potential
EPA	USA's Environment Protection Agency
EPD	Environmental Product Declaration
EPS	Environmental Priority Strategies
ErP	Energy-related Products
EU	European Union
GLO	Global

GWP	Global Warming Potentials
H	Hierarchist
HM	Heavy Metal
I	Individualist
ILCD	International Reference Life Cycle Data System (ILCD) Handbook
IMPACT	Integrated Methodology for Impact Assessment of Chemicals
IPCC	Integrated Pollution Prevention and Control bureau
ISO	The International Organization for Standardization
kgCO2e	kilogram Equivalent Carbon Dioxide
LCA	Life Cycle Assessment
LCI	Life Cycle Inventories
LCIA	Life Cycle Impact Assessment
LVIC	Large Volume Inorganic Chemicals
MAP	Mono-Ammonium Phosphate
MOP	Muriate of Potash or Potassium Chloride
NPK	Nitrogen, phosphorus, and potassium
PAF	Potentially Affected Fraction
PED	Primary Energy Demand
pH	potential of Hydrogen a measure of the acidity or alkalinity (basicity) of a solution
PIMS	Process Information Management System
POCP	Photochemical Ozone Creation Potential
Pt	Point or single score
REACH	Registration, Evaluation, Authorization, and restriction of Chemicals
ReCiPe	Resource Use, Emissions, and Health Impacts
RER	Rest of Europe exclude Swiss
RoHS	Restriction of Hazardous Substances directive

RoW	Rest of the world exclude Europe
SACHT	Swiss Centre for Applied Human Toxicology
SMR	Steam Methane Reforming
SOP	Sulfate of Potash
SSP	Single Super Phosphate
TRACI	Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts
TSP	Triple Super Phosphate
USEtox	Unified System for the Evaluation of Toxicity

1 Introduction

Fertilizers are compounds that are added to crops to boost their yield. Fertilizers may contain impurities, contaminants, or intentionally introduced compounds of concern that could harm both human health and the environment.

Losses of ammonia to the air and nitrate and phosphate to water in response to increased nitrogen (N) and phosphorus (P) inputs have an impact on air and water quality and eutrophicate terrestrial and aquatic ecosystems. However, the primary source of effects on soil quality is the addition of heavy metals, which can also have negative effects on soil biodiversity and, in the case of cadmium, food quality [1].

Harmful substances, in other words heavy metals concentrations in fertilizers, agricultural minerals, and agricultural amendments have been a major concern for researchers, policymakers and international organizations to bring in preventive regulations.

This regulation's goal is to safeguard human health and natural resources from the toxicity of certain heavy metals. Standards has been adopted during 2002 for heavy metals like arsenic, cadmium, lead, mercury, etc. concentrations in the fertilizers. Because the use of fertilizers and associated materials is a recurring activity, cumulative changes over decades of application must be considered [2].

Moreover, heavy metals (and other dangerous elements) are found in goods because of fertilizer blending with recovered industrial waste (e.g., steel mill flue dust, mine tailings). US federal statutes permit the use of reclassified industrial wastes in the production of fertilizers, provided that such usage represents "beneficial recycling" and that the quantities of hazardous elements in the resultant fertilizers do not exceed the waste treatment limits [3].

According to risk evaluations undertaken by the US Environmental Protection Agency and others, the hazardous components included in inorganic fertilizers don't often cause threats to the environment or public health. Just a small proportion of the numerous fertilizer products examined were found to have pollutants at levels high enough to be thought of as a possible health risk (i.e., arsenic or dioxins in some micronutrient and liming materials) [4].

Calculations of soil metal concentrations after years of product application determine human health risk [2]. Estimates of heavy metals distribution coefficients dominate forecasts of soil metal accumulation through time, and these estimates are very imprecise.

There are few studies about heavy metals distribution during fertilizers production process. Fertilizers producers like Yara International have run their own experimental tests and measurements during the years and estimate heavy metal emissions to the environment [5].

1.1 Yara Porsgrunn

Yara, founded in Norway in 1905 as Norsk Hydro — the world's first producer of mineral nitrogen fertilizers — and de-merged as Yara International ASA on March 25, 2004. Yara has a global presence with sales to 150 countries.

Yara provides solutions for sustainable agriculture and environmental protection. Yara's mineral fertilizers and crop nutrition programs aid in the production of food for the world's rising population.

Industrial goods and solutions from Yara minimize emissions, enhance air quality, and promote safe and efficient operations.

The Porsgrunn plant is located 14 miles southwest of Oslo on Herøya by Porsgrunn. The production area is 1.5 square kilometers in size and is Norway's largest industrial region.

Figure 1.1: Yara’s industrial complex in Herøya Industripark.

Yara, Porsgrunn has one ammonia plant, three nitric acid plants, two NPK plants (Nitrogen, phosphorus, and potassium) and one calcium nitrate (CN) plant. Yara's factory in Herøya is an integrated production system for nitrogen-based products and has Europe's and Yara's largest production capacity for NPK complex fertilizer based on the nitrophosphate process.

The ammonia, nitric acid and fertilizer factories also produce a wide range of gases and chemicals for industrial use. Around half of the production on Herøya goes to overseas markets, mainly in Asia. The rest is sold to various European markets.

Herøya has large warehouses and an efficient port for loading and unloading bulk goods. Three bagging facilities enable the bagging of large bags (NPK and CN) and small bags on pallets (CN). The bagged products are loaded onto boats, trucks or in containers.

1.2 Aim and Assumptions

The thesis aims to understand what must be in place to document the effects of contaminant emissions throughout the fertilizer value chain up to the factory gate. Integrating the knowledge of the Life Cycle Assessment, inorganic fertilizer production process, harmful substances coming from the raw material, and current regulations are needed.

The Life Cycle of a representative NPK fertilizer is evaluated in this study, and emissions of selected heavy metals (Hg, Cu, As, Cr, Ni, Zn, Cd, Pb) to water, air, and sand deposits are calculated.

Ammonia, nitric acid, phosphate rock, and potash are principal inputs for producing an NPK product. At highly integrated plants like Yara Porsgrunn, all reactors along the nitrogen value chain are interconnected. Starting from natural gas ammonia is produced, and converted to nitric acid and further processed to give final products like NPK fertilizers, calcium nitrate (CN), calcium ammonium nitrate (CAN), melamine or urea products [6].

Since no raw materials or sources with contaminants or heavy metals are utilized in the production of ammonia or nitric acid these processes are not elaborated. However, Phosphate rock and potash are provided from mines and contain contaminants.

The fundamental assumption in this work was based on previous research demonstrating that heavy metals in raw materials primarily follow phosphorus in NPK formation [5].

1.2.1 Objectives

To comply with the aim, the thesis has the following objectives:

- Literature review of harmful substances stemming from the fertilizer industry, and relevant regulations
- Analyze and describe the LCA standards ISO14040 and ISO14044
- Identification of "Cradle-to-factory gate" impact of harmful substances for an NPK product
- Break down the value chain of NPK and review of the emissions associated with every step from feedstock to final product.
- LCA modelling of NPK production process and consequential upstream processes.
- Identification of mitigation techniques to reduce harmful substance use and the impact.
- Discussion on the next steps for Yara and the systemization of methodologies and calculations to other products and plants

1.3 Report outline

The thesis is built up of 8 chapters, where Chapter 1 covers the introduction. Chapter 2 is a collection of information about NPK fertilizers, contaminants from the raw material, the relevant regulations and heavy metals mitigation techniques. In Chapter 3 fundamentals of the life cycle assessment with a breakdown of the standards ISO 14040 and ISO14044 are explained. To be easily followed in the next chapters, capabilities of the SimaPro (an LCA software), ReCiPe model (an impact assessment method) and ecoinvent database (for life cycle inventory) are also discussed.

In Chapter 4, NPK production processes with a lot of details on ODDA process are presented. Thereafter, in Chapter 5, “Guidance on performing an LCA”, the necessary steps that must be taken to complete an LCA to determine emissions of NPK will be explained.

Chapter6, shows how the raw material amounts and emissions are monitored, quantified, and used for the modeling. Much information at this point is confidential so plant data are given in the Appendixes. In Chapter 7, a discussion of the findings is made before a conclusion and further work is given in the final chapter, Chapter 8.

1.4 Method

Throughout the work of the thesis, a large part of the time has been spent doing thorough research on the following topics.

- Importance of NPK fertilizers
- Inorganic NPK production processes
- Harmful substances from NPK production
- Principle of the Life Cycle Assessment (LCA), databases and the impact assessment methodologies
- Modeling LCA in SimaPro software.

The literature search includes all relevant topics to achieve a high grade of completeness in the thesis, and most of the information and data is collected from reports, standards, and previous scientific articles. Most of the scientific articles and reports are found through Elsevier’s ScienceDirect and Google Scholar, which both include a large database of revised scientific publications and eBooks, which ultimately increases the credibility of the thesis. Otherwise, Google's search function has been widely used, where you may also have access to publications that include relevant and valuable information.

It took some time to grasp the workings of SimaPro, the LCA software, due to the distinct emissions, inputs, outputs, and flows associated with each process.

The challenging part of the thesis was the lack of sources of information to help better understanding and comparison of the NPK production LCA modelling and emissions calculation. Thus, some Yara internal reports and presentations were used. It is worth mentioning that conducting several interviews with the NPK experts laid the groundwork for modeling and emissions quantifications.

2 Introduction to the NPK Fertilizers

Nitrogen, phosphorus, and potassium (NPK) are three nutrients required for plant growth and development. In this chapter, I will provide an introduction to NPK fertilizers, discussing their composition, properties, and benefits.

2.1 Plant Nutrients

To grow properly each plant needs 18 essential elements each with their own functions, levels of requirement, and characteristics [7]. Hydrogen, carbon, and oxygen are obtained from water and air through photosynthesis and the others should be obtained from the soil.

Elements used in large quantities by the plant are termed macronutrients. The primary and secondary (intermediate) macronutrients include nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur.

The final essential elements are used in small quantities by the plant, but nevertheless are necessary for plant survival. These micronutrients include iron, boron, copper, chlorine, manganese, molybdenum, zinc, cobalt, and nickel. Figure 2.1 and Figure 2.2 show the classification and hierarchy coherently.

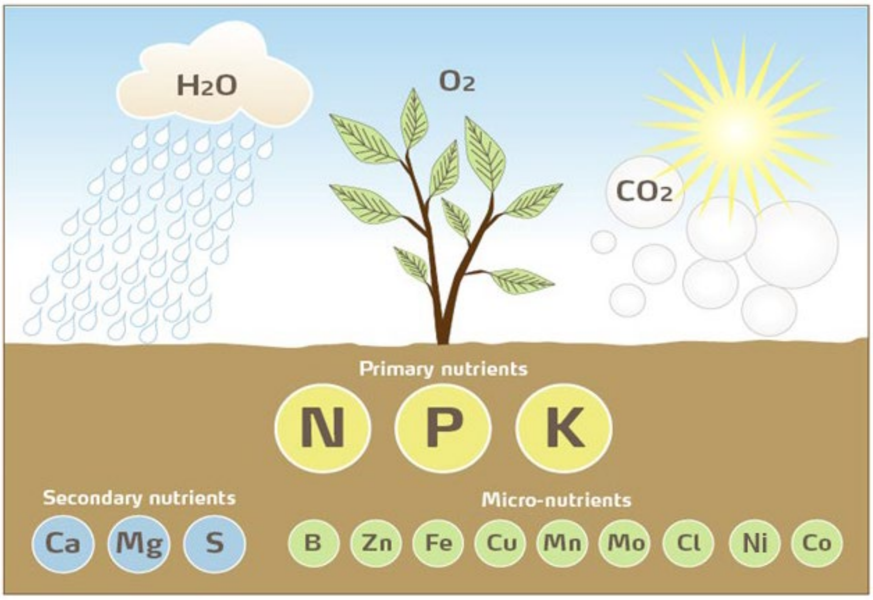

Figure 2.1: Eighteen essential elements for plant nutrition (from [8] with some modifications)

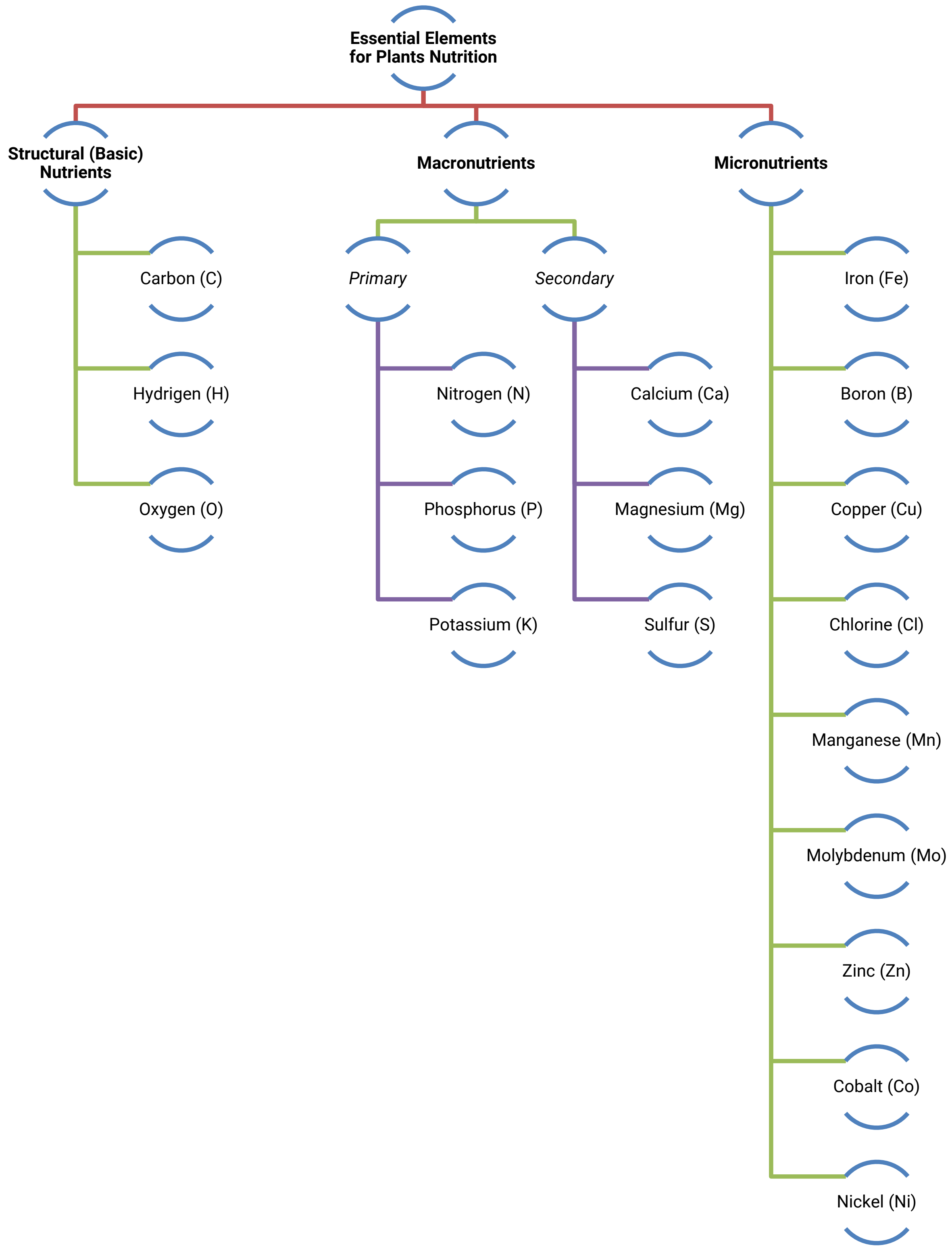

Figure 2.2: Classification of essential elements for plants nutrition.

2.2 Fertilizers

In nature, the nutrients appear often as a powder, a crystal, a gas, or a rock and cannot be used as such by farmers. They need to be put in the form that they can be used and handled.

Therefore, if the soil is not adequately rich in nutrients for the successful plant growth and development, fertilizers can be used for the soil enrichment.

Fertilizer is any substance, whether natural or synthetic, that is applied to soil or plant tissues in order to provide nutrients for the plants. They belong to three categories [9]:

- Mineral/inorganic/synthetic/chemical fertilizer: a fertilizer that contains the declared nutrients in the form of mineral compounds that were obtained through industrial physical and chemical processes or extraction.
- Organic fertilizer: a fertilizer made from organic materials that are either of animal or plant origin and is composed of organic compounds to which the key components of fertility are chemically linked in organic form, or in any case, are an essential component of the matrix.
- Organo-mineral fertilizer: the mixture of organic residues and mineral fertilizer results in a new category of farm input called organo-mineral fertilizers and combines the best features from mineral fertilizers and organic components [10].

The three most crucial elements delivered by fertilizers are the primary macronutrients (N, P, and K) because their deficiency results in decreased plant growth, health, and productivity.

Nitrogen helps plants produce the proteins needed for strong leaf development. A surplus result in quick growth but poor blooming, whereas a deficit results in stunted development.

Phosphorus aids in strong root growth as well as flower development and larger seeds. Excess causes poor growth and bleaching, deficiency causes leaf death.

Potassium supports the growth and general health of the crop. Deficits can result in illness and generally poor health while excesses can prevent N and P absorption.

The wide range of N/P/K ratios and the many techniques used in their manufacturing must be considered when describing compound fertilizers. Product types are PK, NP, NK and NPK. In this study the main focus will be on a full form of the fertilizer or an NPK.

If a particular formulation of major nutrients or N, P, and K is desired (from now on called NPK), a blend can conveniently meet the needs of the farmer or gardener, while reducing the costs associated with buying and applying multiple fertilizers.

Three NPK values are provided as the analysis, which represent the overall weight fraction of N, P, and K in the fertilizer. These numbers are usually in large print on the front of the container or bag. Figure 2.3 and Figure 2.4 show fertilizers produced by Yara company (established in 1905 as Norsk Hydro) that has NPK values print on the bags. NPK values are discussed in section 2.2.2.

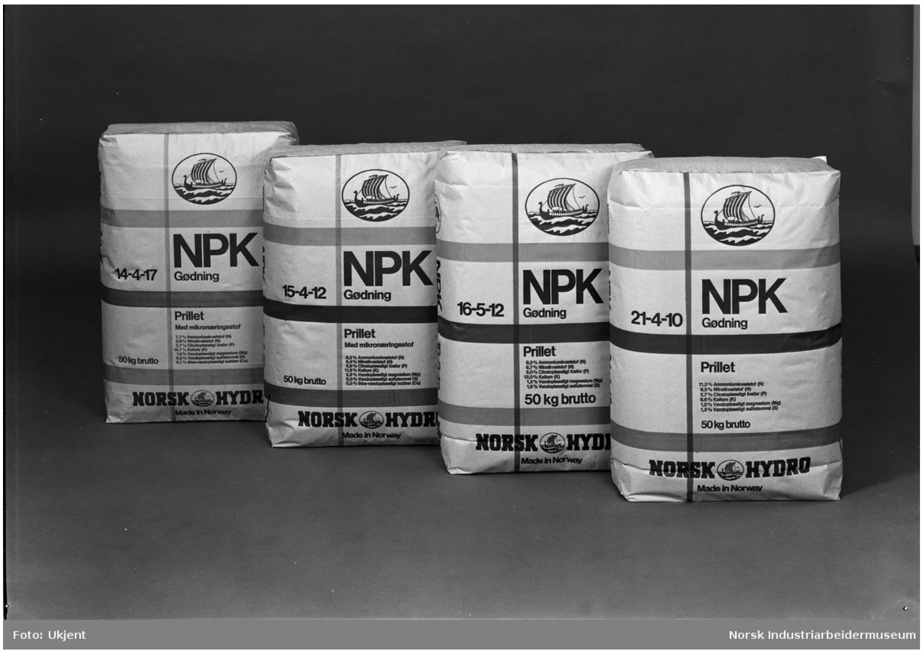

Figure 2.3: NPK fertilizer bags from Norsk Hydro (now Yara international)

Figure 2.4: Fertilizers with different N, P, and K nutrients contents [11].

2.2.1 Value/Supply Chain

The value chain is a term used to describe the full spectrum of operations that companies carry out to bring a product from its conception to its ultimate usage and beyond. This covers the following: design, raw material extraction, manufacturing, marketing, distribution, final use and customer service [12].

A value chain's components may be spread across several companies or may be confined within a single one. Value chain activities can create products or services, and they can be confined to a specific region or dispersed across a larger one.

As shown in Figure 2.5 there might be some similarities between supply chain and value chain. However, the value chain is more of an abstract idea that involves giving items positive attributes than the supply chain, which is more focused on physical products and processes.

The most simplified supply chain of the NPK is shown in Figure 2.6. The components themselves come first. Mining is used to extract minerals like potash and potassium. These components are prepared at production facilities before being transported to different storage sites and reaching the fertilizer retailers who blend the materials in exact quantities.

A plant might be more integrated. In other words, it combines multiple processes or operations within a single location. More detailed information regarding NPK production is available in further sections.

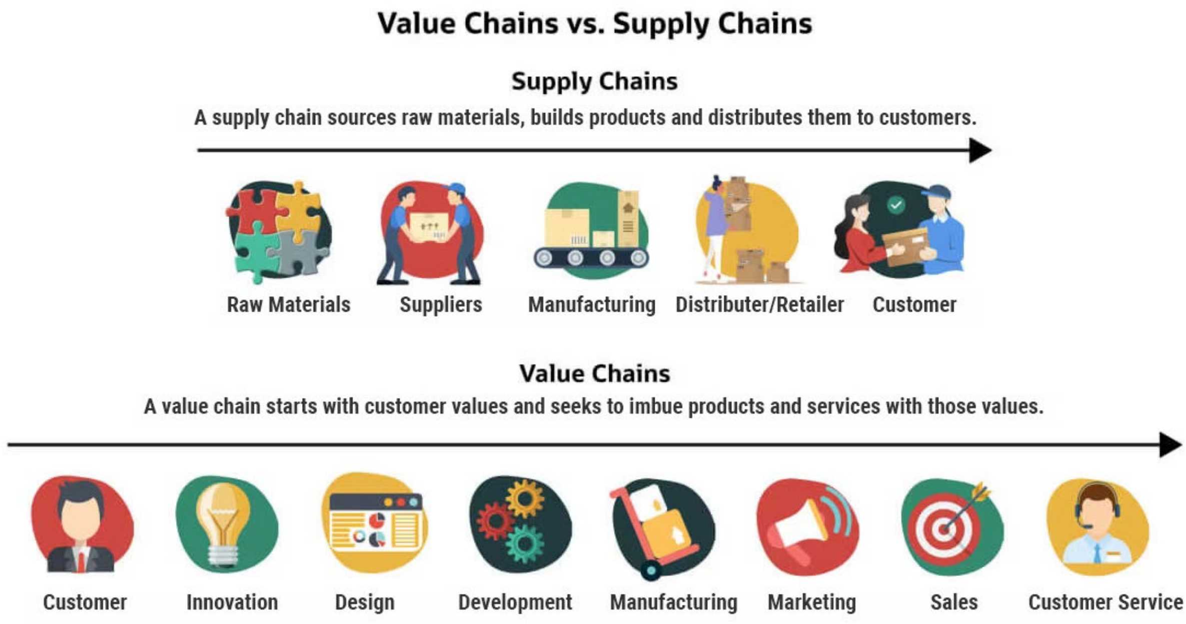

Figure 2.5: Supply chain and value chain comparison [13].

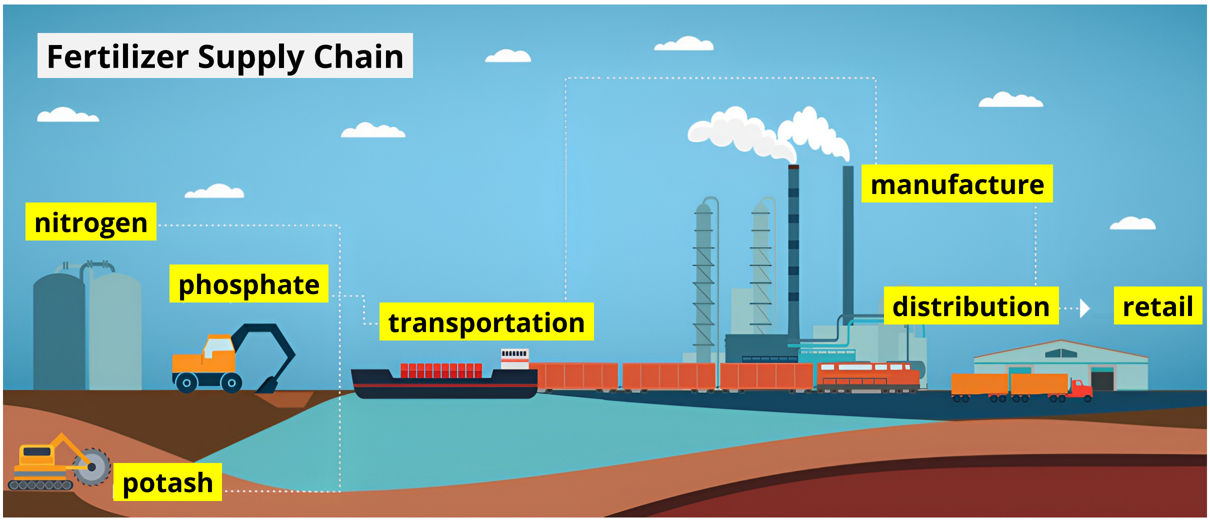

Figure 2.6: Fertilizer production supply chain [14].

2.2.2 N, P, and K Sources

As discussed before, the three letters, N, P, and K, correlate to three figures that represent the proportion of each nutrient in that specific product. The nutrient content of fertilizers can be declared as either oxide or elemental. There are converters that allow conversions between the two units [15]. In this thesis, although N shows nitrogen amount in the NPK, P and K stand for P_2O_5 and K_2O respectively since pure elements of the P, and K, are never found in nature[1] [16].

A product labeled 10-10-10, for example, has 10% nitrogen (as N), 10% phosphorus (P_2O_5), and 10% potassium (K_2O). A bag labeled 20-20-20 had double the amount of each mineral. The rest material in the bag is filler or inert components that is used to bulk up the fertilizer and facilitate its application and have no significant effect on the plant.

In the following three headings the main sources of these nutrients and relevant calculation for a 25 kg bag of 8-11-20 NPK is presented.

2.2.2.1 Nitrogen (N)

Nitrogen nutrient in an NPK product is not from a single input, so it is reported as total N and may take different chemical forms such as nitrate or NO_3-N, ammonium or NH_4-N[2], etc. The majority of fertilizers combine a couple of N types. Thus, it can be concluded that a 25 kg bag of 8-11-20 contains 2 kg of total-N, which accounts for 8% of the bag.

The main reason for having different nitrogen sources is to control pH or acidity of the final product. However, there are some other reasons as well. A comparison of ammonical nitrogen and nitrate nitrogen is explained below.

[1] The reason could also have to do with the way that these elements were quantified in the past when doing chemical analysis. So, it is simple to convert today while still maintaining consistency with all our prior reports on fertilizer compositions.

[2] Derived from nitric acid (HNO_3) and ammonia (NH_3) respectively.

1. Ammonical Nitrogen ($NH4+$):
   - Advantages:
     - Efficient uptake: ammonium ions are readily taken up by plant roots, making nitrogen quickly available to plants.
     - Reduced leaching: ammonium ions are less prone to leaching compared to nitrate ions.
   - Considerations:
     - Limited mobility: ammonium ions do not move easily within the soil, so they may not reach plant roots in deeper soil layers.
     - Potential toxicity: high levels of ammonium ions can be toxic to plants.
2. Nitrate Nitrogen ($NO3-$):
   - Advantages:
     - High mobility: nitrate ions are highly soluble and mobile in soil, allowing them to reach plant roots in different soil depths.
     - Efficient utilization: many crops prefer nitrate as their primary nitrogen source and can efficiently uptake and utilize it for growth.
     - Reduced ammonia volatilization: nitrate-based fertilizers generally have lower ammonia volatilization potential compared to ammonium-based fertilizers.
   - Considerations:
     - Leaching potential: nitrate ions are more susceptible to leaching, especially in soils with high drainage or excessive rainfall.

2.2.2.2 Phosphorus (P)

Pure elemental phosphorus is never found in nature. Instead, phosphorus pentoxide, often known as P_2O_5, is the chemical component P in fertilizers which can be found in the phosphate rock[1]. The percentage of P_2O_5 in a complete fertilizer is represented by the second of the three analysis numbers. Therefore, a 25 kg bag of 8-11-20 contains 2.75 kg of P_2O_5. To calculate elemental P, we must determine the percent by weight of P in P_2O_5, which is 44%. So, this bag contains 2.75 kg of P_2O_5 and 1.21 kg elemental P.

2.2.2.3 Potassium (K)

Potassium is also never present as pure elemental K, but is reported as its oxide form of K_2O, commonly called potash[2].

83% of K_2O is elemental K. Consequently, a 25 kg bag of 8-11-20 contains 5 kg K_2O and 4.15 kg elemental K.

In this study talking about secondary macro nutrients, microelements and other elements is avoided since they are not the focus of this thesis.

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[1] Phosphoric acid can also be another source of P directly or indirectly as MAP (mono-ammonium phosphate with 11% N and 52% P_2O_5) or DAP (di-ammonium phosphate with 18% N and 46% P_2O_5). Since phosphoric acid is typically produced through the treatment of phosphate rock with sulfuric acid, only phosphate rock is considered as the main source of P_2O_5 in this work.

[2] To be more accurate K is coming from MOP (muriate of potash or potassium chloride with 60~62% as K_2O), or from SOP (sulfate of potash with 50% as K_2O).

2.3 Contaminants in the Raw Material

A contaminant is a biological, chemical, physical, or radioactive material that is unintentionally or on purpose added to the air, water, soil, or food and endangers humans or other living things. According to the USA's Environment Protection Agency (EPA), contaminants of concern (COC) are chemicals that pose an excessive or unacceptable harm to the environment or to human health [17].

A fertilizer product may include impurities, contaminants, or deliberately introduced compounds of concern. However, in this study the main purpose is to consider heavy-metal contaminants getting into the production process of fertilizers due to the raw material and being emitted to the environment. This might have an adverse effect on both human health and the environment. In the context of chemistry and environmental science, heavy metals refer to metallic elements that have high atomic weights and densities. These elements typically have a density greater than 5 g/cm^3.

As described in previous chapter to produce an NPK product based on the nitrophosphate process[1], the main raw materials are ammonia and nitric acid (source of N), P-rock (source of P_2O_5), and potash (source of K_2O).

2.3.1 Ammonia and Nitric Acid

Ammonia is most commonly made from methane, water and air, using steam methane reforming (SMR) (to produce the hydrogen) and then the Haber-Bosch process to produce ammonia from hydrogen and nitrogen [18][2]. Due to the production process and feedstock needed for ammonia production no heavy metals are expected to be emitted or to exist in the final ammonia product.

The Ostwald method, in which ammonia is oxidized with air to yield nitric monoxide, is used to produce nitric acid. NO is then oxidized further to make nitrogen dioxide (NO_2), which is then absorbed in water to produce HNO_3 [6]. So, the main component in producing nitric acid is ammonia which does not contain any heavy metals.

Thus, heavy metals trace in nitric acid production is negligible. Some producers report the heavy metal (as Pb) amount in their nitric product maximum 100 parts per billion (ppb) [19].

2.3.2 Potash and Fillers

MOP (Muriate of potash or potassium chloride) and SOP (sulfate of potash) are the main source of potassium. Dolomite can be used as the filler[3] for the NPK. All of them are extracted from the mine and reports show that they contain heavy metals to a detectable limit [20]. Thus, they

[1] Fertilizer production processes will be discussed in detail in chapter 4.

[2] In future the production of the sustainable ammonia will increase. The most widely adopted technology for sustainable hydrogen production used for ammonia synthesis is water electrolysis coupled with renewable technologies such as wind and solar.

[3] Fertilizer fillers are inert components that have no effect on the plant. However, they also make the mixture easier to spread, reduce the concentration of the nutrients and keep them from clumping and drying.

can be sources of heavy metal emissions. However, compared to phosphate rock their amount is much lower.

2.3.3 Phosphate Rocks

Rocks are the building blocks of the Earth's crust. There are three main types of rocks:

- Igneous: igneous rocks originate at extremely high temperatures or from molten materials. They are derived from magma.
- Sedimentary: wind, water, snow, and creatures all contribute to the formation of sedimentary rocks. They make up almost three-quarters of the Earth's surface. The majority are formed as sediments on the bottoms of rivers, lakes, and oceans.
- Metamorphic: Metamorphic rocks are those that have been altered from their original state by heat, pressure, or chemical activity [21].

Commercial mineral phosphates or beneficiation products of apatite ores, sometimes referred to as phosphate rock, are generally found and exploitable in two forms in nature: igneous intrusions and sedimentary deposits.

Apatite, as a group of phosphate minerals, usually refers to hydroxylapatite, fluorapatite and chlorapatite[1]. Igneous rock phosphate is predominantly composed of fluoro apatite, which is strikingly similar to the enamel of human teeth. It is a byproduct of volcanic eruptions that took place many millennia ago and contributes to around 15% of the production of phosphate rock worldwide[2]. It is mostly mined in Kola, Russia; Phalaborwa, South Africa; Araxa and Jacupiranga, Brazil; and Siilinjärvi, Finland. Fluoro apatites are for all practical purposes insoluble in weak organic acids.

On the other hand, sedimentary rock phosphate was created by the decay of animal life in shallow lakes and oceans between 50 and 70 million years ago. Around 85% of the world's production of commercial mineral phosphates comes from this form of phosphate. In contrast to igneous phosphates, sedimentary rock phosphates include a large quantity of magnesium and sodium in place of calcium, and up to 25% of phosphorus in the form of carbonates[3]. These "soft" rock phosphates are appropriate for direct application in some situations because they are substantially more soluble in mild organic acids. Important deposits of this type of phosphate occur in North Africa (Senegal, Togo, Morocco, Algeria and Tunisia), the Middle East (Jordan, Palestine and Egypt), Australia (Queensland) and the USA (Florida, North Carolina and Idaho) [21].

In comparison to igneous phosphates, sedimentary phosphates typically include substantially greater quantities of hazardous substances like arsenic (As) and heavy metals like cadmium

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[1] They are named for high concentrations of OH^-, F^-, or Cl^- ions, in the crystal $Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_3(F)$, and $Ca_5(PO_4)_3(Cl)$ respectively. It can be generalized as $Ca_{10}(PO_4)_6(OH, F, Cl)_2$, however, $Ca_{10}(PO_4)_6F_2$ is the most well-known form.

[2] Magmatic ore deposits are primarily associated with igneous rock.

[3] In some references it is called francolite (carbonate fluorapatite). It can be generalized as $Ca_{10}(NaMg)(PO_4)_6((CO_3)(CO_3F)(SO_4))F_2$

(Cd) [22]. As an example, Cadmium level in sample rocks is given in Table 2.1. As discussed above, sedimentary rocks contain more heavy metals like Cd.

To summarize, fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks. And for an NPK product the bigger the minerals amount (mostly P), the higher heavy metals emissions possibility. While producing NPK fertilizers, it is preferable to use a single source of phosphate rock, except when only a small amount of one type remains or when we need to control heavy metal contamination in a particular rock by blending it with another type that has fewer contaminants.

For easier understanding, constituents in francolite and apatite can be presented like what is shown in Figure 2.7. This color-coded Periodic table shows the elements that can be detected in rocks.

Table 2.1: Cadmium level in different rocks [23].

Rock		Country	%P	ppm Cd	mg Cd/kg P
Igneous rocks	Palfos	South Africa	17.4	0.15	0.9
	Kola	Russia	17	0.1	0.6
	Graenges	Sweden	16.8	0.15	0.9
	LKAB	Sweden	15.4	0.15	1.0
Semi-calcined	Texas Gulf	USA	14.6	40	275
	Youssoufia	Morocco	14.6	46	315
	Zin	Palestine	14.4	24	170
Sedimentary	Taiba	Senegal	16.0	80	500
	Togo	Togo	15.8	57	360
	Boucraa	Morocco	15.8	35	220
	Jordan	Jordan	14.6	8	50
	Florida	USA	14.4	7	50
	Khourigba 20	Morocco	14.4	20	140
	Khourigba 10	Morocco	13.8	10	70
	Gafsa	Tunis	13.2	55	420

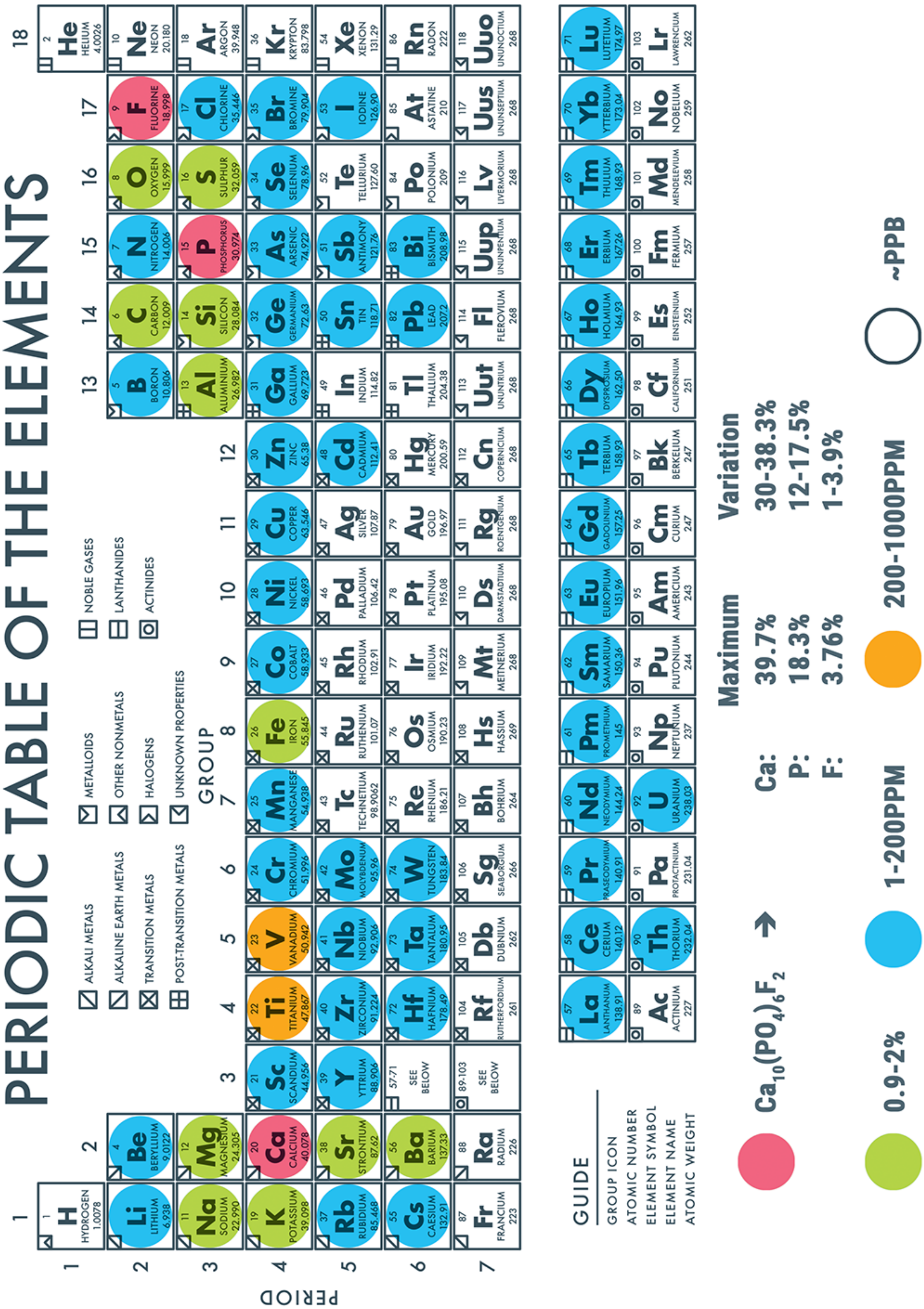

Figure 2.7: chemical elements present in some rock types (inspired by [23]).

2.3.4 Consequences of Main Heavy Metals Available in NPK

Heavy metals are present in the environment naturally and are necessary for living, but when they build up inside organisms, they can become dangerous. Because of their toxicity, protracted atmospheric persistence, and capacity to bioaccumulate in the human body, they are well-known environmental contaminants. Figure 2.8 simplifies how these heavy metals end in human body.

In Europe and Eurasia, soil pollution is the third most relevant environmental threat and copper and cadmium are the most common and widespread contaminants in European agricultural soils [24].

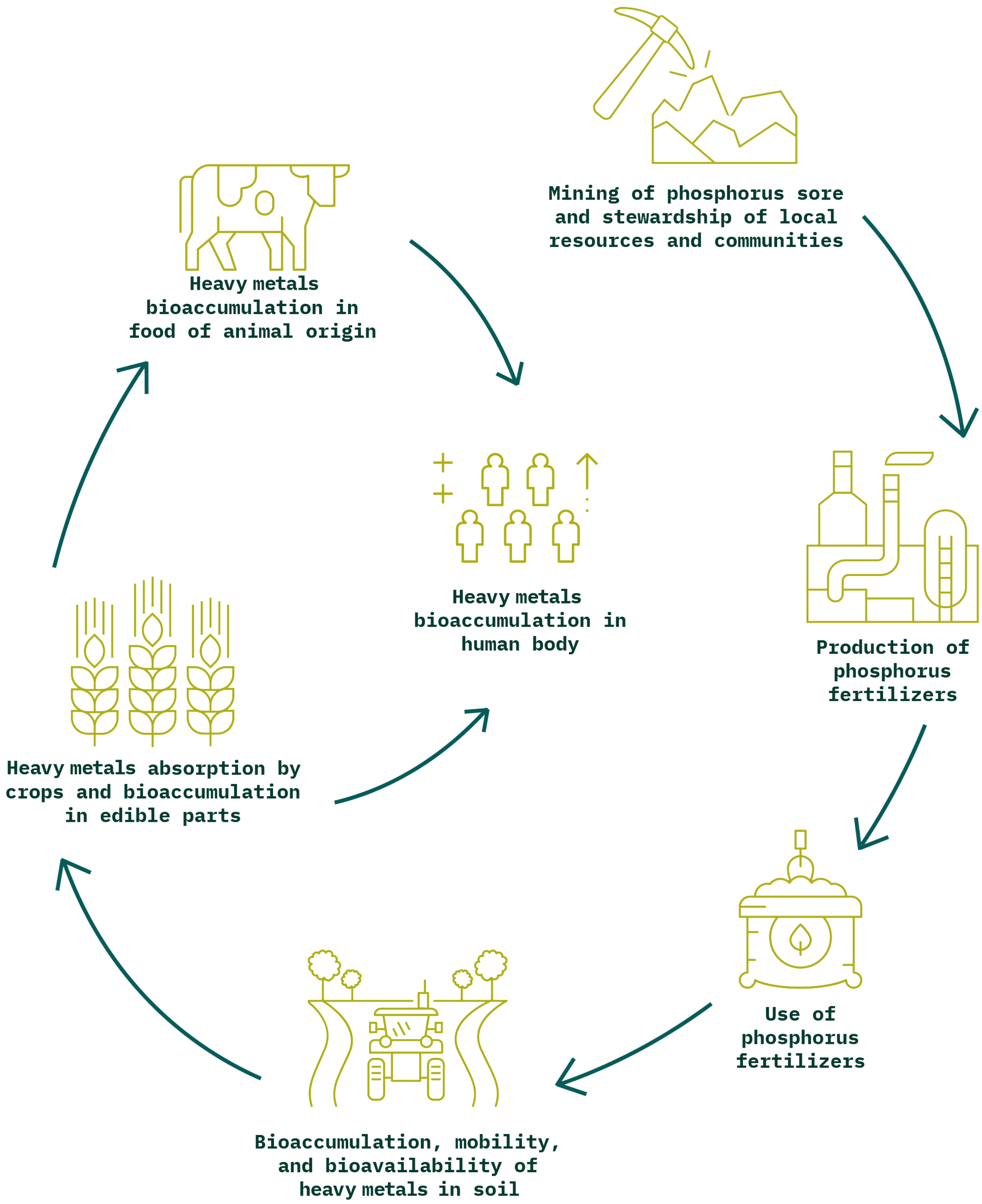

Figure 2.8: Life cycle of heavy metals in fertilizers ([24] with some modifications).

2.3.4.1 Mercury (Hg)

Mercury is a highly toxic heavy metal that may be found in the biosphere. It has also become a ubiquitous pollutant and is rising in the atmosphere because of human activities. When mercury comes into touch with aquatic sediments, it transforms to the very poisonous methylmercury [25]. Methylmercury enters the human body via the food chain via contaminated fish, shellfish, and animals that have been polluted by poisonous microorganisms After being absorbed into the human body, it enters the circulation and causes a range of neurological disorders [26]. Exposure may cause negative health effects such as kidney failure, cognitive impairment, and injury to the central nervous system [27].

2.3.4.2 Copper (Cu)

Copper is widely recognized as an essential micronutrient for all living organisms. It participates in normal physiological functions of plants such as chlorophyll formation, photosynthesis, carbohydrate and protein metabolism. Copper deficiency alters critical metabolic processes, and excessive exposure is toxic [28].

2.3.4.3 Arsenic (As)

Arsenic is one of the most significant heavy metals causing concern in terms of both ecological and individual health. Long-term arsenic exposure from drinking water and food can result in cancer and skin lesions. It's also linked to cardiovascular disease and diabetes. In utero and early childhood exposure has been linked to poor cognitive development and an increase in young adult mortality [29].

2.3.4.4 Chromium (Cr)

Chromium is a carcinogenic and toxic metal. It exists in two stable oxidation states in the environment: chromium (III) and chromium (VI). Chromium (III) is a less dangerous form of chromium (VI) [30]. During industrial activities, they can interconvert with one other. Conversion of chromium (VI) to chromium (III) on the other hand is less detrimental to the environment since the latter is less poisonous. Chromium(IV) is a reactive intermediate in most systems involving reduction of chromium (VI) to chromium(III) [31]. Chromium is employed in a variety of businesses that endanger regional climates. Bioaccumulation may cause lung cancers and DNA damage, as well as skin, renal, reproductive and neurological disorders [27].

2.3.4.5 Nickel (Ni)

Nickel is a naturally abundant element with numerous industrial applications. It is emitted into the atmosphere by both natural and anthropogenic sources [32]. It has numerous negative effects on humans and causes allergies, nasal and lung cancer, kidney and cardiovascular disease as a result of inhaling contaminated air [33].

2.3.4.6 Zinc (Zn)

Zinc is a fundamental and ubiquitous metal. It is involved in a variety of enzymatic reactions by acting as a cofactor. Zinc toxicity is determined by the method and amount of exposure. Zinc is primarily obtained through smelting and mining. Mineral processing activities emit a large amount of zinc into the environment, which has an impact on ecosystems as well as living organisms [34]. Zinc enters the human body through three major routes: inhalation, skin absorption, and ingestion. Each type of exposure affects different parts of the body and allows for different amounts of zinc to be absorbed [35].

2.3.4.7 Cadmium (Cd)

Cadmium is emitted into the atmosphere because of natural or man-made activity, and it affects both animals and people differently. Cadmium contamination of the aquatic environment arises because of absorption, industrial waste, and surface runoff into soil and sediments. Cadmium poisoning can occur by the consumption of cadmium-contaminated food, air, or water. Cadmium has no properties that are beneficial to plant growth or metabolic activities [36] but is predominantly found in fruits and vegetables due to its high rate of soil-to-plant transfer Figure 2.9 shows life cycle of the cadmium in fertilizer. The mechanism of cadmium toxicity is not understood clearly but its effects on cells are known. Exposure may impair kidneys function, cause bones demineralization, and affect liver and lungs, as well as renal dysfunction and cancers of the breast and prostate [27].

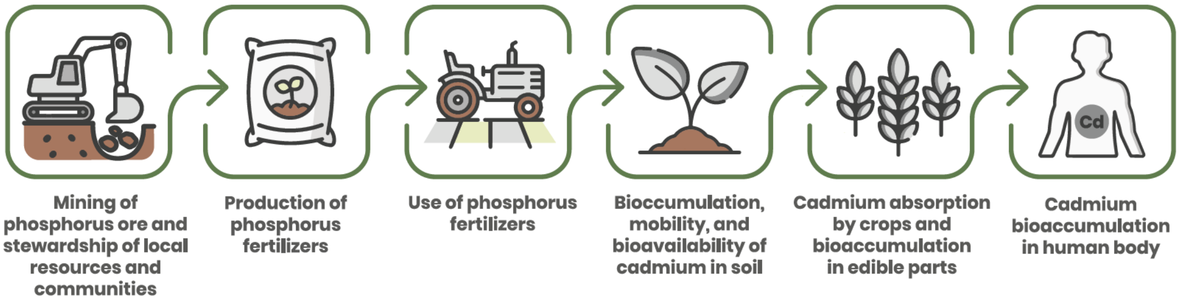

Figure 2.9: Life cycle of cadmium in fertilizers [24].

2.3.4.8 Lead (Pb)

Lead is a non-biodegradable metal that comes in nature in relatively small levels. Because of human activities such as manufacturing, mining, and the use of fossil fuels, atmospheric lead levels are steadily rising. When exposed to levels higher than the ideal, lead is hazardous to the human body. Children are more vulnerable to lead poisoning; when they come into touch with lead-contaminated dust, the severity of the poisoning rises [37]. Long-term exposure may cause developmental and neurobehavioral problems in fetuses, young infants, and children [27].

2.4 Regulations

The Norwegian Pollution Control Act of March 13, 1981, states that measures must be taken to avoid the incidence or growth of pollution, as well as to restrict any pollution that does occur [5]. Likewise, efforts must be made to avoid waste concerns. The Act is used to attain a desirable level of environmental quality based on an overall assessment of human health and welfare, the natural environment, the costs of any interventions adopted, and economic concerns. Efforts to avoid and minimize pollution and waste problems must be based on the technology that will produce the greatest outcomes in the context of a holistic assessment of current and future environmental use as well as economic factors. The Norwegian Environment Agency gave a discharge permission to Yara Norge AS, Porsgrunn, in accordance with the Norwegian Pollution Control Act.

BAT (Best Available Techniques) refers to the most effective and advanced methods, technologies, and practices that are considered economically viable and technically feasible for minimizing environmental impacts and achieving high levels of environmental performance. List of Best Available Techniques Reference Documents (BREF) by sectors and activities can be found online [38]. These documents are developed by the European IPPC Bureau (European Integrated Pollution Prevention and Control Bureau).

In EU the Best Available Techniques review work for inorganic chemical industry is just ongoing, and the old 2007 LVIC BAT [39][1] reference document did not contain much of this type of limit values for emissions. There is a newer BAT reference for common wastewater (CWW) heavy metals limit in the chemicals sector, but its applicability for fertilizers will be clarified in the LVIC review process in the future. In this document, BAT-Associated Emission Level (AEL) for Copper and Nickel is 5.0-50 μg/l and for Chromium and Zinc are 5.0-25 μg/l and 20-300 μg/l respectively [40].

Although there are limitations for the emissions during production, many regulations mention contaminant limits in final products. Heavy metals may be found in final products ranging from jewelry and watch casings to electrical components and toy paints. Because of their toxicity, the European Union rigorously controls and, in certain situations, forbids the use of these substances [27].

Commercial phosphate fertilizers (inorganic fertilizers), as previously noted, include trace levels of heavy-metal pollutants that were minor elements in the phosphate rock. The major organic fertilizers are animal manures and sewage sludges (biosolids), the latter of which may include heavy metal pollutants. Heavy metals in biosolids may be inorganic or organically complex, which may impact their chemical interactions in soil. Anyhow, by using organic or inorganic fertilizers repeatedly, these heavy metals may accumulate gradually.

The EU enacted several regulations and directives that restrict or ban certain heavy metals in consumer products, including:

- REACH
- RoHS Directive

[1] Integrated Pollution Prevention and Control - Reference Document on Best Available Techniques (BAT) for the Manufacture of Large Volume Inorganic Chemicals (LVIC)

- Toy Safety Directive
- Cosmetics Products Regulation
- Food Contact Materials Regulations

The REACH Regulation (Registration, Evaluation, Authorization, and restriction of Chemicals) limits the import and manufacturing of chemical compounds such as heavy metals in the EU. REACH also governs items that may contain these compounds if they are harmful to the consumer or the environment [27].

Some countries have set tolerance limits on heavy-metal additions to soil because their long-term effects are unknown. These limits usually are set for the tillage layer (surface 20-30 cm) of soil where most root activity occurs [41].

The EU Member States are specifically encouraged to take action as part of CAP (Common Agricultural Policy) Strategic Plans to minimize soil pollutants, according to the interinstitutional agreement on the new EU Common Agricultural Policy signed between the EU Council and European Parliament [42].

In addition to national laws, a number of pertinent EU Directives that are based on permitted levels of crops, soil amendments, or water levels have been put in place or are being changed to safeguard soil (and crops) and water against metal contamination. In Table 2.2 several relevant directives are listed.

Table 2.2: Overview of selected legal frameworks at EU level and targets addressed.
Unless specified otherwise the Directives listed refer to As, Cd, Cr, Cu, Hg, Ni, Pb and Zn [1].

EU Directive	Addressing	Regulating principle
Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture	Levels of heavy metals in sewage sludge used on arable land	Setting maximum concentration in sludge, the total annual load of metals to be applied to soil and allowed increase in total metal content relative to background values to avoid unwanted accumulation of metals in soil
Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers. As of 2021 this regulation is replaced by FPR (EU2019/1009)	Acceptable upper limits for metals in inorganic and organic fertilizers as well as a selected types of components thereof	Setting maximum allowed levels for metals in inorganic and organic fertilizers as well as soil improvers to have the product listed as EC Fertilizer.
Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. For Cd and Pb this Regulation has been replaced by commission regulation (EU) 2021/1323	Quality of food to protect human intake of metals via food	Setting maximum levels for Cd, Pb and Hg in products for human consumption to avoid excess intake of metals
Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on	Quality of fodder for animals	Setting maximum levels for Pb, Cd, As and Hg in fodder and food products for animals to

EU Directive	Addressing	Regulating principle
undesirable substances in animal feed		reduce intake and transfer into food products for human consumption
Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy	Quality of surface waters to protect ecosystem health	Setting maximum levels for metals in surface waters based on ecological thresholds for aquatic organisms
DIRECTIVE 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration	Quality of groundwater	Obligation to set standards for priority elements (Cd, Pb, As, Hg as well as some other non-metallic contaminants) to protect the general quality of water. Part of the WFD.
COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption	Quality of drinking water intended for human consumption	Setting maximum levels for contaminants including metals (note: Zn not included)

Cadmium (Cd) is the heavy metal of most concern because it may affect human health seriously. The designation of Cd as a human carcinogen, dates to the 1990s. Regulation EU2019/1009 (replaces the former regulation EU2003/2003) was passed by the European Union, capping the amount of Cd in phosphate/inorganic fertilizers at 60 mg/kgP_2O_5 [43]. On July 16, 2022, the sale of phosphate fertilizers with a composition of more than 60 mg/kg P_2O_5 was prohibited.

The Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) states that in most soils, fertilizers containing 20 mg Cd/kg P_2O_5 or less are not anticipated to cause long-term accumulation in the soil [44].

In comparison to the Cd threshold values in several EU nations, 60 mg/kgP_2O_5 level appears insufficient: 12 member states have a Cd threshold between 20 and 50 mg Cd/kg P_2O_5, 8 of those states have the same threshold as that suggested in the rule, and 2 of them have a higher threshold[1] [24, 45]. This can be due to the new scientific evidence from SACHT (Swiss Centre for Applied Human Toxicology) report for Federal Office for Agriculture (BLW). They concluded that lower limit is needed to most likely have a Cd trend decreasing rather than increasing in soil over the next 100 years [46].

Other metals regulated in EU2019/1009 are arsenic (As), chromium (Cr, measured as Cr(VI)), mercury (Hg), nickel (Ni) and, not included previously in EU2003/2003 also for Cu and Zn. In Table 2.3 all limit values for principal contaminants in fertilizers are summarized.

[1] Member States with Cd limit values ≤ 50 mgCd/kgP_2O_5: CZ, DK, FI, DE, PL, HU, IT, SK, BG, SE, NL, NO. MS with Cd limit values of 60 mgCd/kgP_2O_5: FR, CY, LT, S, RO, SI, GR, LU. Two MS with higher Cd limit values: Austria and Belgium.

Table 2.3: Contaminants limit in fertilizers. Data extracted from EU2019/1009; for more detail information and some remarks refer to this regulation [43].

Contaminants	Organic fertilizer	Organo-mineral fertilizer	Inorganic fertilizer
Cadmium (Cd)	1.5 mg/kg dry matter	3 mg/kg dry matter, if P_2O_5 < 5%	3 mg/kg dry matter, if P_2O_5 < 5%
		60 mg/kgP_2O_5, if P_2O_5 > 5%	60 mg/kgP_2O_5, if P_2O_5 > 5%
Hexavalent chromium (Cr VI)	2 mg/kg dry matter	2 mg/kg dry matter	2 mg/kg dry matter
Mercury (Hg)	1 mg/kg dry matter	1 mg/kg dry matter	1 mg/kg dry matter
Nickel (Ni)	50 mg/kg dry matter	50 mg/kg dry matter	100 mg/kg dry matter
Lead (Pb)	120 mg/kg dry matter	120 mg/kg dry matter	120 mg/kg dry matter
Inorganic arsenic (As)	40 mg/kg dry matter	40 mg/kg dry matter	40 mg/kg dry matter
Biuret ($C_2H_5N_3O_2$)	0 mg/kg dry matter	12 g/kg dry matter	12 g/kg dry matter
Copper (Cu)[1]	300 mg/kg dry matter	600 mg/kg dry matter	600 mg/kg dry matter
Zinc (Zn)[1]	800 mg/kg dry matter	1500 mg/kg dry matter	1500 mg/kg dry matter

2.5 Heavy Metals Mitigation Techniques

End-of-pipe techniques, also known as pollution control or pollution abatement techniques, refer to strategies that aim to mitigate or remove pollutants from industrial processes at the final stage before their release into the environment. On the other hand, cleaner production or pollution prevention techniques focus on preventing or reducing the generation of pollutants at the source, thereby minimizing, or eliminating the need for end-of-pipe measures[2].

Here are some common heavy metals mitigation techniques:

- Source control: ensuring that the raw materials used in fertilizer production are low in heavy metal content is crucial. Implementing strict quality control measures and sourcing materials from reliable suppliers who comply with regulatory standards can help minimize heavy metal contamination.
- Material selection, blending and dilution: choosing raw materials that have lower concentrations of heavy metals can help reduce their presence in the final fertilizer product. Blending different materials with varying heavy metal levels can also help dilute and balance their concentrations.

[1] These limit values shall not apply where copper (Cu) or zinc (Zn) has been intentionally added to an organo-mineral fertilizer for the purpose of correcting a soil micronutrient deficiency and is declared in accordance with Annex III of EU2019/1009.

[2] Yara is actively engaged in a cadmium removal research project within its nitrophosphate process, aiming to develop innovative solutions that minimize cadmium content and enhance the environmental sustainability of their fertilizer production.

- Ore beneficiation: phosphate rock beneficiation processes can help reduce the concentration of heavy metals in the final product. Beneficiation techniques such as flotation, washing, and gravity separation can selectively remove impurities, including heavy metals, from the ore [47].
- Screening and separation: employing screening and separation techniques during the manufacturing process can help remove larger particles or impurities that may contain higher concentrations of heavy metals. This step can help improve the overall quality and purity of the fertilizer.
- Washing and leaching: treating raw materials or the final product with water can aid in leaching out water-soluble heavy metals. Acid washing or acid leaching can be employed to remove heavy metal contaminants from phosphate rock. This process involves treating the rock with acid solutions to dissolve the heavy metals, followed by separation and purification steps. This process can help reduce the heavy metal content in the fertilizer [48].
- Chemical treatments: certain chemicals, such as chelating agents or complexing agents, can be used to bind with heavy metals and make them less available or less likely to be absorbed by plants. These chemicals can be applied during the manufacturing process or incorporated into the fertilizer formulation [49, 50].
- Phosphoric acid purification: If the phosphate rock is used for the production of phosphoric acid, purification steps in the acid production process can help remove heavy metals. Techniques like solvent extraction, precipitation, or ion exchange can be employed to selectively remove heavy metals from the acid stream [51, 52].
- Thermal treatment: high-temperature processes, such as calcination or roasting, can be used to thermally treat phosphate rock. This can aid in the volatilization or decomposition of certain heavy metals, resulting in their removal or conversion to less mobile forms [53].
- Quality control and testing: implementing rigorous quality control measures, including regular testing of the final fertilizer product, is crucial for ensuring compliance with heavy metal regulations. Testing can help identify and address any deviations from the acceptable limits.
- Recycling and waste management: proper disposal or recycling of waste generated during fertilizer production can help prevent heavy metal contamination in the environment. Implementing effective waste management practices reduces the risk of heavy metals leaching into soil or water sources.
- Research and innovation: continuous research and development efforts are essential for improving mitigation techniques. This includes exploring innovative technologies, such as nanotechnology or bioremediation, that can help remove or immobilize heavy metals more effectively [54, 55].

It's important to note that the selection and effectiveness of these mitigation techniques may depend on factors such as the specific heavy metal contaminants present, the geological characteristics of the phosphate rock deposit, and the desired quality standards for the final product. Therefore, a comprehensive evaluation of the specific situation is necessary to determine the most appropriate mitigation strategies.

3 Life Cycle Assessment (LCA)

Life cycles are consecutive and interlinked stages of a product system, from raw material acquisition or generation from natural resources to final disposal (Figure 3.1). Life cycle assessment originated in the 1960s in the United States. Originally, the emphasis was on energy efficiency, raw material usage, and, to a lesser extent, waste disposal [56]. A life cycle assessment (LCA) is the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle [57].

The life cycle assessment can be applied in a variety of cases, and can assist in [57]:

- identifying opportunities to improve the environmental performance of products at various points in their life cycle,
- informing decision-makers in industry, government, or non-government organizations,
- the selection of relevant indicators of environmental performance, including measurement techniques, and
- marketing

The assessment takes into account every phase of a product's life cycle and is founded on the idea that every stage, from the acquisition of raw materials through manufacturing, use, and non-use phases, can have an impact on the environment in different ways.

Figure 3.1: Different stages of a product's life cycle (from [58] with some modifications).

3.1 LCA Perspectives

The acquisition and consumption of resources and components are referred to as the (raw material) extraction phase. The modalities of transportation should be described because this phase involves the extraction of materials and the delivery of raw materials to production facilities. In this stage, the materials, parts, and components that are required might be termed material usage. Moreover, the energy required for obtaining the raw materials, treating the materials, and transporting the resources should be taken into account. At this point, it is essential to consider the harmful emissions, effluent, and waste produced during the obtainment and transformation of the resources.

The manufacturing procedures, auxiliary materials utilized in industrial production, and material transformation are all included in the production/manufacturing phase. It is important to include all auxiliary materials (such as screws, electronic components, and electrical items) and substances utilized during production. According to this idea, the procedures that were not included in the previous stage, such as those involving welding, painting, and molding, should be. In addition, the factory's waste materials (such as offcuts, rejects, and byproducts), hazardous waste production and energy consumption in all processes are considered.

The packaging and the means of transportation from factories to retailers and end users are all included in the distribution phase. As a result, storage times and transport distances between production facilities or warehouses and retailers or distributors are required. All components of repackaging needed for transportation and distribution are included in the materials used for packaging in addition to the basic product packing (i.e., secondary and tertiary packaging). The amount of energy used during packaging, packing, and distribution should also be taken into account.

The use phase takes into account the amount of energy and consumable materials used when a product is being used, as well as the expected spare components needed for maintenance. The overall amount of energy used by energy-related products (ErPs) throughout the course of their anticipated useful lifetime is crucial. In order for the product to execute as planned, it is important to consider how end customers may access and utilize it. This step should also include and evaluate waste from consumables and replacement components.

The end-of-life phase can be thought of as a step of final disposal that includes waste management, material recovery, and energy recovery (e.g., landfilling, incineration, dismantling, recycling, municipal waste, and household waste). Energy usage in any end-of-life system of goods or components is one of the activities in this stage, along with the consumption of raw and auxiliary materials for the end-of-life treatment. Energy use for moving wastes to end-of-life systems is typically taken into account. Emissions from this stage include all harmful waste produced by the product, recycled materials, and wastes from end-of-life systems.

An LCA (Life Cycle Analysis) is the basis for developing an EPD. EPD (Environmental Product Declaration) is a document based on specific standards, endorsed usually by and independent third party that incorporates life-cycle inventory data and offers a clear summary of a product's environmental effect. EPDs are an essential validation tool that allows producers to give clear data on the environmental sustainability of their goods while also allowing specifiers to make wise purchase decisions.

As discussed, the product life cycle consists of five crucial phases, namely, extraction, production, distribution, use, and end-of-life phases. The assessment method is often used from cradle-to-grave standpoint, but it may also be applied from cradle-to-gate, cradle-to-cradle, gate to gate, cradle-to-customer, or gate-to-grave, depending on the analysis's purpose and system boundaries. Figure 3.2 illustrates the different perspectives.

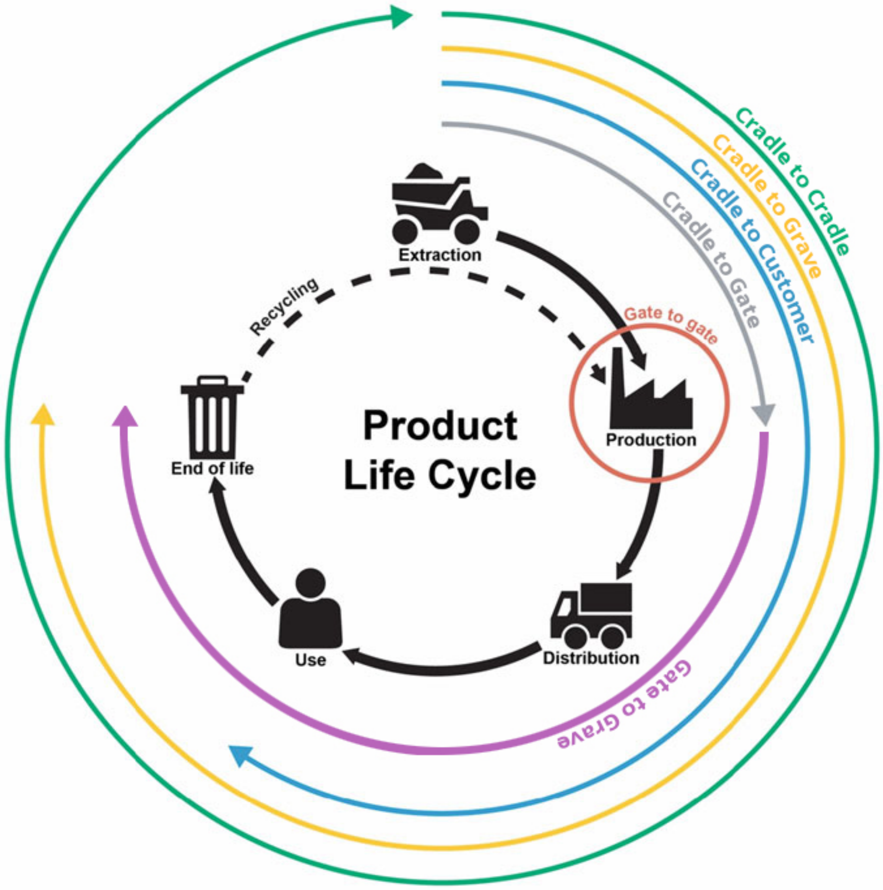

Figure 3.2: Product life cycle and six approaches of defining a system boundary (from [59] with some modifications).

The cradle-to-grave perspective is defined as a full LCA, from the resource extraction, “cradle”, to the use phase and eventually the disposal phase, “grave”. As for a boundary limit of an NPK plant, the “cradle”-phase would be the phosphate rock or other raw materials extraction from the mine or other sources. The “grave”-phase would then be defined as the consumption of NPK as the fertilizer for agro industry.

An alternative cradle-to-grave approach that takes recycling into consideration is a cradle-to-cradle evaluation. The recycling is here done as the end-of-life disposal step of a product or service, and the method is commonly used to minimize the environmental impact of the product, in addition to ensuring a sustainable production, operation, and disposal.

Cradle-to-gate is a technique for assessing the life cycle of a product from the extraction of raw materials (cradle) to the factory gate or before it is delivered to the consumer. The phases of product usage and disposal are commonly disregarded. Sometimes cradle-to-gate assessments are used as the foundation for environmental product declarations (EPD).

Gate-to-gate is an assessment of a partial product life cycle from the starting point of the manufacturing processes (production) to the factory gate. All inputs and outputs are considered for each production process in the factory [59]. Thus, a gate-to-gate LCA only accounts for one value-added process in the entire production chain.

The environmental effects of the procurement of raw materials, production, trading, and delivery of consumer goods and services to the end-users are assessed using the Cradle-to-Customer methodology. The routes of transportation and the kind of energy used must be mentioned in this method.

3.2 LCA Phases

The International Organization for Standardization (ISO) provides principles and framework through ISO 14040 and guidelines and requirements through ISO 14044.

No matter how the LCA is carried out or which approach is employed, the evaluation should always comprise the four phases depicted in Figure 3.3:

- Goal and scope definition
- Life cycle inventory analysis (LCI) phase
- Life cycle impact assessment (LCIA) phase
- Interpretation

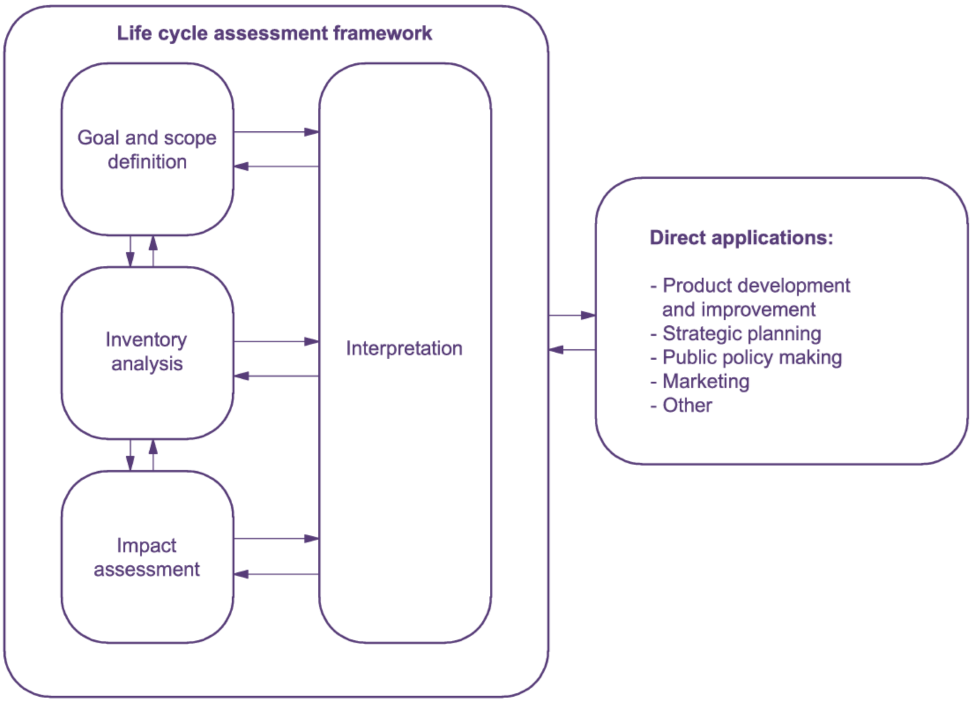

Figure 3.3: Four phases of an LCA framework [57].

3.2.1 Goal and scope definition

Goal and scope definition is the first phase in LCA approach and is considered the most significant process since it defines the context of the research, creates requirements for the conducted modeling, and plans the project. Thanks to the phase that defines your goals and scope, your LCA will be carried out consistently. This is the initial phase of LCA research, and it is referred to as the planning phase. As a result, the goals of LCA applications are to study the contribution of the life cycle stages to the overall environmental burden, to prioritize product or process changes, and to compare goods for internal use.

As a result, for design practitioners, choosing the proper step at the start of integrating LCA in the product design and development processes is critical. Generally, design practitioners must identify four critical activities throughout the goal and scope defining stage: (1) designate a functional unit, (2) establish a clearly delineated system boundary, (3) choose the sort of environmental impacts to be evaluated, and (4) scope the study's degree of complexity and data needs.

The functional unit and system boundary are important modelling specifications that need to be determined through the scope. Every other product or service data in the system whose influence is being evaluated is compared to the functional unit. To perform the desired purpose, the reference flow in each product system must be determined, with the system boundary constituting all the unit processes contained in the assessed system. The scope section must also include any assumptions, limits, and restrictions across the system. Figure 3.4 shows an example of a product system that applies to the entire product life cycle including manufacturing and all downstream and upstream activities. So, it includes a wide boundary, however, due to the need of the company and limitations this boundary could be smaller and result in assumptions.

The system boundaries define what is included in the evaluation and what is excluded. Little amounts of substances, for example, that contribute little to the total footprint might be excluded from the scope of the analysis. As a result, the system boundaries exclude this [58]. This is famous as a cut-off criterion. LCA practitioners can use cut-off criteria to do LCA without having to model the entire product system.

The cut-off criteria, according to the ILCD Handbook[1], pertain to the elimination of irrelevant life cycle phases, activity kinds, particular processes and products, and elementary flows from the system model [60].

Product systems are subdivided into a set of unit processes like what we see in Figure 3.5. The smallest element considered in the analysis is a unit process. Each unit process has inputs flowing in and outputs flowing out, after the process has been undergone. Inputs can come from nature such as resources from the ground, water and air or from technosphere, i.e. human altered environment, such as products from other unit processes [61].

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[1] The ILCD Handbook refers to the "International Reference Life Cycle Data System (ILCD) Handbook," which is a comprehensive guidance document for conducting LCA studies. This Handbook provides standardized methodologies, guidelines, and best practices for collecting, analyzing, and interpreting life cycle data.

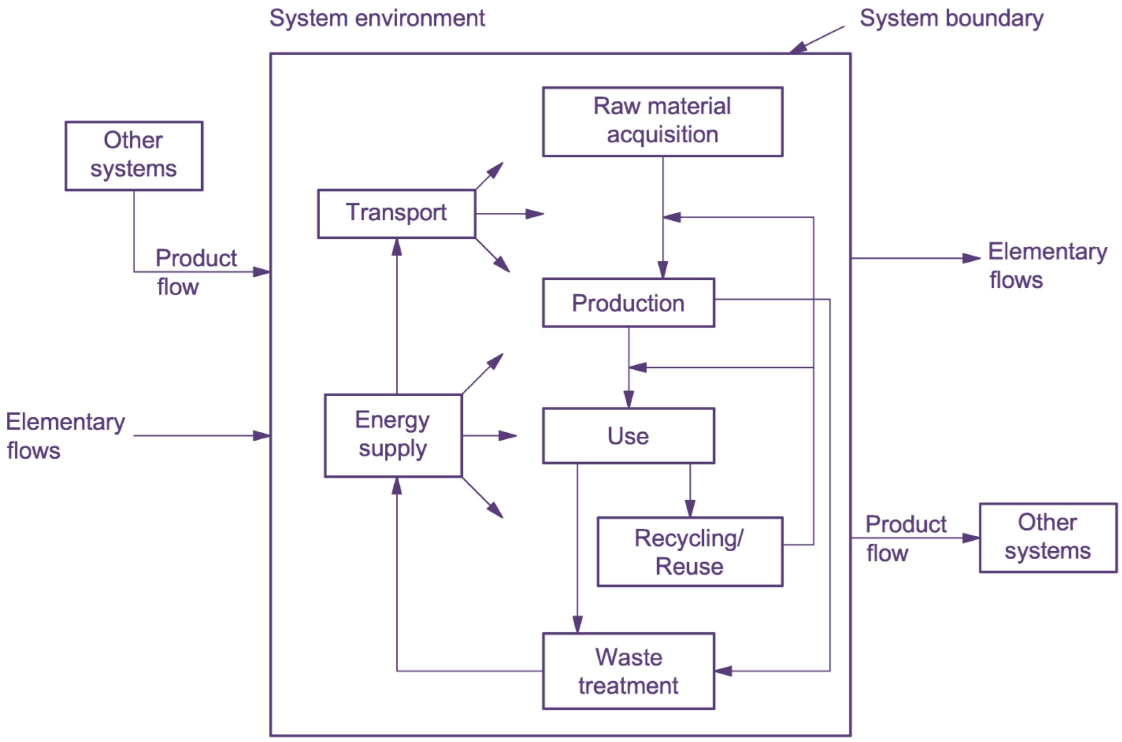

Figure 3.4: Example of a product system for LCA [57].

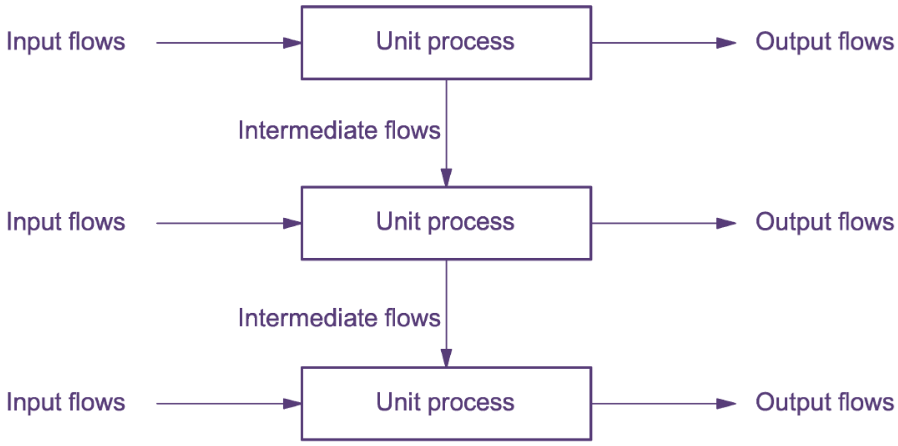

Figure 3.5: Example of a set of unit processes within a product system [57].

3.2.2 Life cycle inventory analysis (LCI)

The second part of an LCA is the life cycle inventory analysis, which entails obtaining, identifying, and quantifying all the data in a product system as inputs and outputs. The inputs will comprise all resources needed, such as energy, power, and raw materials, and the outputs will include the system's products, by-products, and different emissions, products and co-products, wastes, and other environmental issues throughout the system. Figure 3.6 depicts the numerous inputs and outputs, as well as the processes in between.

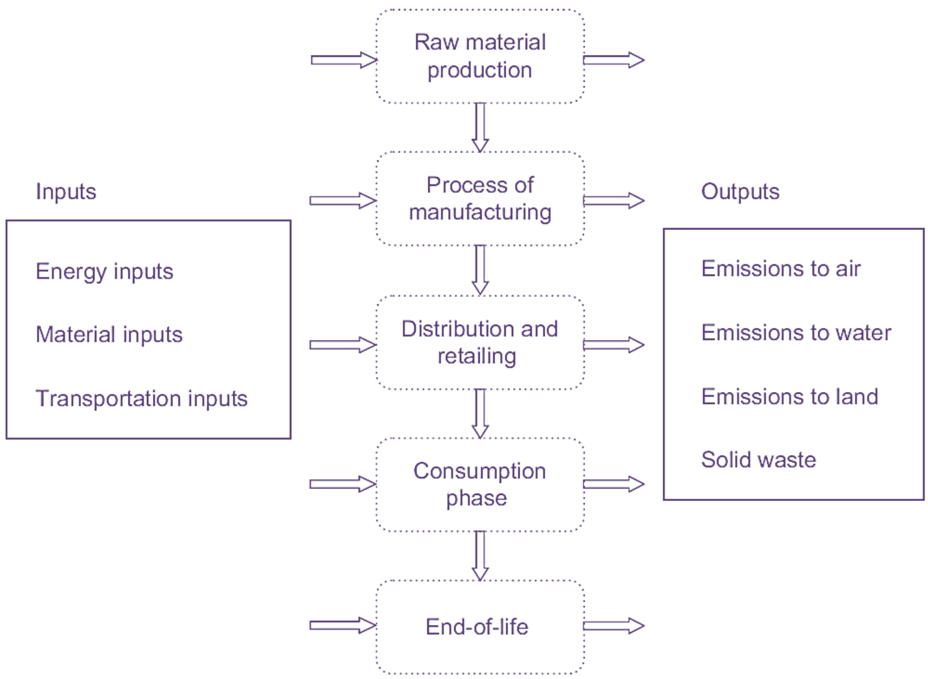

Figure 3.6: Generalized unit process flow diagram with inputs and outputs from LCI [56].

While employing the LCI, it is critical to validate the acquired data as well as the source. This is related to the correctness of the data as well as the assessment's general completeness and comprehensiveness. The data quality is also crucial to the individual or firm that obtains or wants the life cycle assessment results, particularly in terms of the report's strength [57].

Although few industrial processes generate a single output or are dependent on a linearity of raw material inputs and outputs, the allocation of flows and releases is critical in the LCI. In reality, most industrial processes produce more than one product, and intermediate or waste goods are sometimes recycled as raw materials [62].

Allocation in life cycle inventory (LCI) refers to the process of distributing the environmental burdens and benefits associated with a multi-output system or process. Main types of allocation methods used in LCI assessments are

- Physical allocation: this method allocates impacts based on the physical properties or quantities of the different products. For example, if a process yields 80% Product A and 20% Product B, the consequences will be distributed proportionally.

- Economic allocation: in this method the share of impacts is assigned according to the market value or prices of the products.
- System expansion: this is based on avoiding allocation by expanding the boundaries of the system to include alternative processes. For example, instead of treating a byproduct as waste and allocating the full environmental impact of its disposal, the system expansion method takes into account its potential for alternative uses.

Each allocation method comes with its own strengths and weaknesses. Physical allocation is favored for its simplicity and objectivity, as it is not influenced by external factors like market changes or policy interventions. However, it may not accurately reflect the environmental significance or the cause-and-effect relationship between inputs and outputs, as certain outputs may have greater impact or value than others.

Economic allocation is often preferred for its relevance and consistency since it considers market demand and the value added by the system. However, it may not always be reliable or available due to data quality and variability issues, and it can introduce problems like double counting or circularity.

System expansion is valued for its robustness and comprehensiveness as it avoids allocation by considering the entire life cycle of the system and its alternatives. However, it may not always be feasible or practical due to the need for more data and assumptions, and it can introduce uncertainties and complexities into the analysis [63].

3.2.3 Life cycle impact assessment (LCIA)

ISO defines LCIA as the phase of the process focused at identifying and assessing the extent and relevance of potential environmental consequences for a product system over the course of its life cycle. The elements of the LCIA phase are illustrated in Figure 3.7. This figure depicts the LCIA flow, which includes both mandatory and optional parts. The identification of impact categories, category indicators, and characterization models is the first step in LCIA and then classification and characterization of the results. Other possible features that can be used include normalization, grouping, weighting, and data quality analysis, depending on the purpose, scope, and corporate priorities.

These elements are often carried out and simplified using LCA software, which simply requires the selection of impact categories and category indicators.

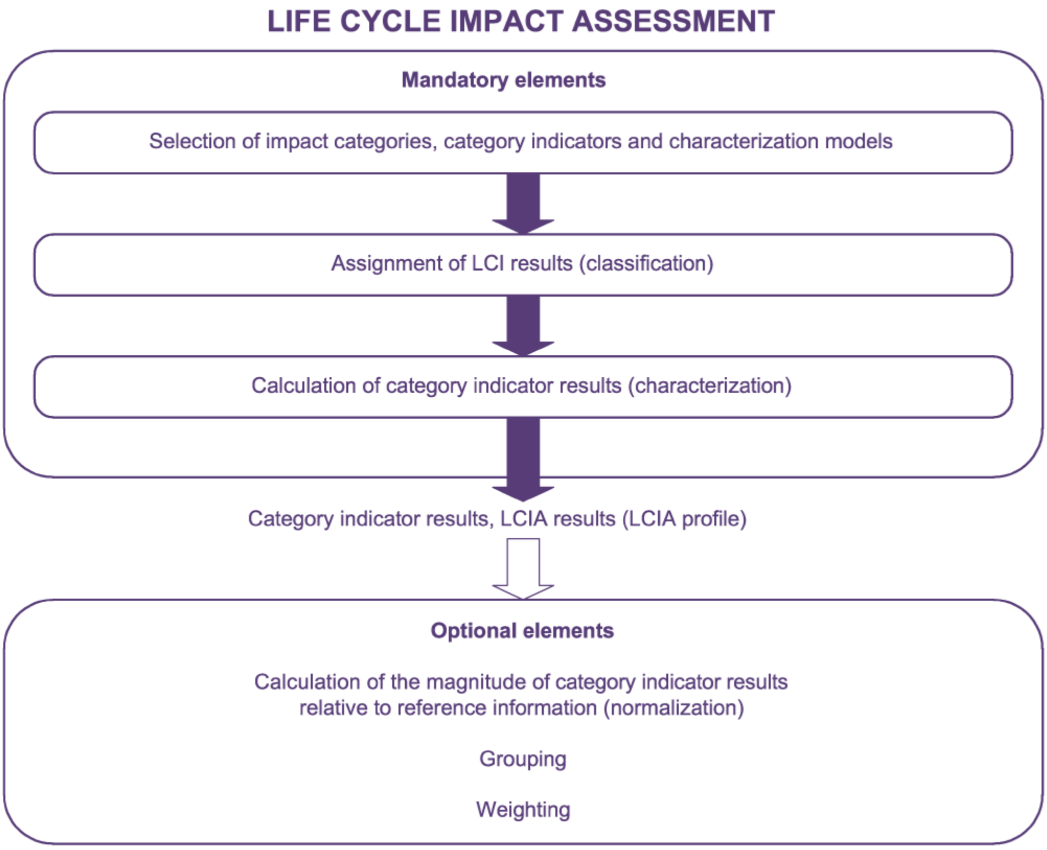

Figure 3.7: Elements of the LCIA phase [57].

Emissions take many forms and formats because emissions from raw material extraction differ greatly from emissions from energy generation.

This is when impact categories enter the picture. During an LCA's Life Cycle Impact Assessment (LCIA), we attempt to combine these various emissions into actionable values. That is, different emissions that have the same impact are combined into a single unit that corresponds to a single impact category.

Global Warming Potential or GWP is the most famous impact category. Greenhouse gas emissions other than carbon dioxide (CO2) drive climate change. For example, methane (CH_4) or laughing gas (N_2O).

By expressing these other GHG emissions in kg CO_2 equivalents ($kgCO_2e$) using other measurement units, a climate change effect category allows for the development of a single measure. Table 3.1 the 100-year time horizon global warming potentials relative to CO_2.

Table 3.1: Global warming potential (GWP) values relative to CO_2 [64].

Industrial designation or common name	Chemical formula	GWP values for 100-year time horizon			
		Second Assessment Report (SAR)	Fourth Assessment Report (AR4)	Fifth Assessment Report (AR5)	Sixth Assessment Report (AR6)[1]
Carbon dioxide	CO_2	1	1	1	1
Methane	CH_4	21	25	28	27.9
Nitrous oxide	N_2O	310	298	265	273
Sulfur hexafluoride	SF_6	23900	22,800	23,500	25,200
Nitrogen trifluoride	NF_3		17,200	16,100	17,400

There are several Life Cycle Impact Assessment (LCIA) models that have been developed and used to assess the environmental impacts of products and processes. Here are some commonly recognized LCIA models:

- ReCiPe (Resource Use, Emissions, and Health Impacts) - Developed by the European Commission's Joint Research Centre, ReCiPe is a widely used LCIA method that considers a broad range of impact categories, including climate change, human health, ecosystem quality, and resource depletion.
- IMPACT (Integrated Methodology for Impact Assessment of Chemicals) - The IMPACT model is specifically designed to assess the impacts of chemical emissions on human health and ecosystem quality, focusing on a range of toxicological and ecological impact categories.
- CML (Center for Environmental Studies) - Developed by the University of Leiden, the CML method is one of the earliest LCIA models and includes impact categories such as climate change, ozone depletion, acidification, and eutrophication.
- Eco-indicator - The Eco-indicator family of models, including Eco-indicator 99 and Eco-indicator 95, were developed by PRé Consultants and evaluate the potential impacts on human health, ecosystem quality, and resource depletion.
- EPS (Environmental Priority Strategies) - The EPS model, developed by the Swedish Environmental Research Institute, focuses on evaluating environmental impacts related to resource use, climate change, ozone depletion, acidification, and eutrophication.
- USEtox (Unified System for the Evaluation of Toxicity) - USEtox is a model that specifically addresses the characterization of human toxicity and freshwater ecotoxicity impacts of chemical substances.
- TRACI (Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts) - Developed by the U.S. Environmental Protection Agency (EPA), TRACI evaluates a broad range of environmental impact categories, including climate change, human health, ecosystem quality, and resource depletion.

[1] While collecting information for this thesis, AR6 report from IPCC (Intergovernmental Panel on Climate Change) were subject to final copy editing and layout.

These are just a few examples of the numerous LCIA models available. Each model has its own strengths, limitations, and specific focus areas. The choice of model depends on the specific research objectives, available data, and the context in which the assessment is being conducted.

LCA impact categories each have their own units. These units can be different in different models as compared in Figure 3.8 [65]. However, to allow for discussion / comparison these units can be normalized to a single score or point (Pt).

LCIA Methods	CML	EDIP	EF	EPD	ILCD	IMPACT	ReCiPe	TRACI
Region	Europe	Europe	Europe	Global	Europe	Europe	Global	North America
Version	IA-baseline	2003	2.0	2018	2001 Midpoint+	2002+	2016 Midpoint(H)	2.1
Approach	Mid	Mid	Mid/End	Mid	Mid	Mid/End	Mid	Mid
Global warming	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq
Acidification	kg SO_2 eq	m^2	mol H+ eq	kg SO_2 eq	mol H^+ eq	kg SO_2 eq	kg SO_2 eq	kg SO_2 eq
Ozone depletion	kg CFC-11 eq	kg CFC-11 eq	kg CFC-11 eq	kg CFC-11 eq	kg CFC-11 eq	kg CFC-11 eq	kg CFC-11 eq	kg CFC-11 eq
Eutrophication	kg PO_4 eq	kg P	kg P eq	kg PO_4 eq	kg P eq	kg PO_4 P-lim	kg P eq	kg N eq
Energy consumption	MJ		MJ	MJ		MJ primary	kg oil eq	MJ surplus
Resource	kg Sb eq	PR2004	kg Sb eq	kg Sb eq	kg Sb eq		kg Cu eq	
Smog	kg C_2H_4 eq	per.ppm.h	kg NMVOC eq	kg NMVOC	kg NMVOC eq	kg C_2H_4 eq	kg NO_x eq	kg O_3 eq
Water depletion			m^3 depriv.	m^3 eq	m^3 water eq		m^3	
Human toxicity (Cancer)	kg 1,4-DB eq	person	CTUh		CTUh	kg C_2H_3Cl eq	kg 1,4-DCB	CTUh
Human toxicity (Non-Cancer)	kg 1,4-DB eq	person	CTUh		CTUh	kg C_2H_3Cl eq	kg 1,4-DCB	CTUh
Particulate matter			disease inc.		kg PM2.5 eq	kg PM2.5 eq	kg PM2.5 eq	kg PM2.5 eq
Ecotoxicity (Freshwater)	kg 1,4-DB eq	m^3	CTUe		CTUe	kg TEG water	kg 1,4-DCB	CTUe
Land use			Pt		kg C deficit	m^2org.arable	m^2a crop eq	
Ionizing radiation			kBq U-235 eq		k Bq U235 eq	Bq C-14 eq	kBq Co-60 eq	

Figure 3.8: LCIA methods and impact categories [65].

BS EN15804 which is a standard for LCA's in the construction sector, lists fifteen categories and the parameters & indicators [66]. A summarized version is given in Table 3.2.

3.2.4 Interpretation

The interpretation of results is the final phase in the LCA process. The LCI and LCIA results shall be interpreted in accordance with the goal and scope of the study. Some critical factors must be examined in this case. According to ISO 14040 and ISO 14044, the interpretation phase should include: identifying significant issues based on the LCI and LCIA results, evaluation of the completeness, sensitivity and consistency, as well as reaching conclusions, defining limitations and provide recommendations or even asking for reevaluation after some corrections or having updated information or data [57, 62].

Table 3.2: fifteen famous impact categories [66].

Impact Category / Indicator	Unit	Description
Climate change – total, fossil, biogenic and land use	kg CO_2-eq	Indicator of potential global warming due to emissions of greenhouse gases to the air. Divided into 3 subcategories based on the emission source: (1) fossil resources, (2) bio-based resources and (3) land use change.
Ozone depletion	kg CFC-11-eq	Indicator of emissions to air that causes the destruction of the stratospheric ozone layer
Acidification	kg mol H+	Indicator of the potential acidification of soils and water due to the release of gases such as nitrogen oxides and sulphur oxides
Eutrophication – freshwater	kg PO_4-eq	Indicator of the enrichment of the freshwater ecosystem with nutritional elements, due to the emission of nitrogen or phosphor-containing compounds
Eutrophication – marine	Kg N-eq	Indicator of the enrichment of the marine ecosystem with nutritional elements, due to the emission of nitrogen-containing compounds.
Eutrophication – terrestrial	mol N-eq	Indicator of the enrichment of the terrestrial ecosystem with nutritional elements, due to the emission of nitrogen-containing compounds.
Photochemical ozone formation	kg NMVOC-eq	Indicators of emissions of gases that affect the creation of photochemical ozone in the lower atmosphere (smog) catalyzed by sunlight.
Depletion of abiotic resources – minerals and metals	kg Sb-eq	Indicator of the depletion of natural non-fossil resources.
Depletion of abiotic resources – fossil fuels	MJ, net calorific value	Indicator of the depletion of natural fossil fuel resources.
Human toxicity – cancer, non-cancer	CTUh	Impact on humans of toxic substances emitted to the environment. Divided into non-cancer and cancer-related toxic substances.
Eco-toxicity (freshwater)	CTUe	Impact on freshwater organisms of toxic substances emitted to the environment.
Water use	m3 world eq. deprived	Indicator of the relative amount of water used, based on regionalized water scarcity factors.
Land use	Dimensionless	Measure of the changes in soil quality (Biotic production, Erosion resistance, Mechanical filtration).
Ionizing radiation, human health	kBq U-235	Damage to human health and ecosystems linked to the emissions of radionuclides.
Particulate matter emissions	Disease incidence	Indicator of the potential incidence of disease due to particulate matter emissions

3.3 Software, Model, and Databases

The LCIA may be carried out using a number of well-established impact assessment methodologies. Through the assessment, each of these approaches frequently uses various impact categories, indicators, categorization, and characterization, which may contribute to differing LCA outcomes. Acidification, global warming, and human toxicity are common impact categories that are frequently evaluated [67].

3.3.1 SimaPro

SimaPro, developed by PRé Sustainability, has been among the leading LCA software solutions for over 30 years. The software may be used for a variety of purposes, including sustainability reporting, carbon and water footprinting, product design, environmental product declaration generation, and identifying key performance indicators. In this thesis SimaPro is used for the LCA modeling and assessment. With SimaPro you can [68]:

- Easily model and analyze complex life cycles in a systematic and transparent way.
- Measure the environmental impact of products and services across all life cycle stages.
- Identify emissions and the hotspots in every link of your supply chain, from extraction of raw materials to manufacturing, distribution, use, and disposal.

3.3.2 Life Cycle Impact Assessment (LCIA): the ReCiPe model

As discussed before many LCIA methods are available such as CML, EPD, EF, IMPACT, ReCiPe, and TRACI. ReCiPe is one of the most recent and updated impact assessment methods available to LCA practitioners. LCIA uses characterization factors to convert emissions and resource extractions into a few impact scores. For deriving characterization factors ReCiPe calculates two types of indicators: 18 Midpoint and 3 Endpoint indicators.

This method addresses a number of environmental concerns at the Midpoint level and then aggregates the Midpoints into a set of three Endpoint categories. As shown in Figure 3.9, Midpoint indicators concentrate on specific environmental issues, such as climate change or acidification. Endpoint indicators depict the environmental impact at higher levels of aggregation being the 1) effect on human health, 2) biodiversity and 3) resource scarcity. While midpoint methods measure an effect before the damage to one of the areas of protection occurred, endpoint methods follow the consequences of certain emission until it causes damage. Converting Midpoints to Endpoints simplifies the interpretation of the LCIA results. Three perspectives are included in ReCiPe for both midpoint and endpoint [69]:

- Individualist (I): is based on short-term interest, impact types that are undisputed, and technological optimism about human adaptation.
- Hierarchist (H): is based on scientific consensus regarding the time frame and plausibility of impact mechanisms.
- Egalitarian (E): is the most precautionary perspective, considering the longest time frame and all impact pathways for which data is available.

These three-time horizons are usually implemented: 20 years (Individualist), 100 years (Hierarchist) and infinite (Egalitarian). Table 3.3 provides an overview of how the perspectives were operationalized per impact category.

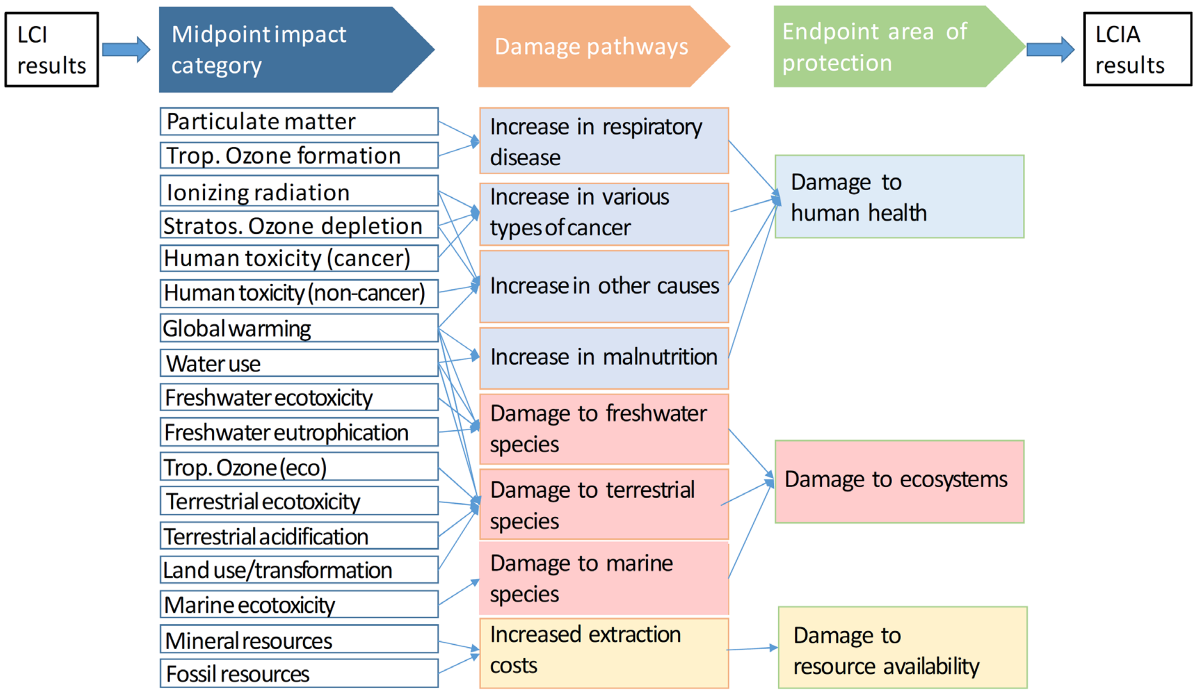

Figure 3.9: Overview of the impact categories that are covered in the ReCiPe2016 method and their relation to the areas of protection. Adapted from [69].

Table 3.3: Value choices in the derivation of characterization factors, as included in ReCiPe2016 v1.1 [69].

	Individualist (I)	**Hierarchist (H)**	**Egalitarian (E)**
Climate change			
Time horizon	20 years	100 years	1,000 years
Climate-carbon feedbacks non-CO_2	No	Yes	No
Future socioeconomic developments	Optimistic	Baseline	Pessimistic
Adaptation potential	Adaptive	Controlling	Comprehensive
Ozone depletion			
Time horizon	20 years	100 years	Infinite
Included effects	Skin cancer	Skin cancer	Skin cancer and cataract
Ionizing radiation			
Time horizon	20 years	100 years	100,000 years
Dose and dose rate effectiveness factor (DDREF)	10	6	2

Included effects	-Thyroid, bone marrow, lung and breast cancer -Hereditary disease	-Thyroid, bone marrow, lung, breast, bladder, colon, ovary, skin, liver, oesophagus and stomach cancer -Hereditary disease	-Thyroid, bone marrow, lung, breast, bladder, colon, ovary, skin, liver, oesophagus, stomach, bone surface and remaining cancer -Hereditary disease
Fine particulate matter formation			
Included effects	Primary aerosols	Primary aerosols, secondary aerosols from SO_2, NH_3 and NOx	Primary aerosols, secondary aerosols from SO_2, NH_3 and NOx
Toxicity			
Time horizon	20 years	100 years	Infinite
Exposure routes for human toxicity	Organics: all exposure routes. Metals: drinking water and air only	All exposure routes for all chemicals	All exposure routes for all chemicals
Environmental compartments for marine ecotoxicity	Sea + ocean for organics and non-essential metals. For essential metals, the sea compartment is included only, excluding the oceanic compartments.	Sea + ocean for all chemicals	Sea + ocean for all chemicals
Carcinogenicity	Only chemicals with carcinogenicity classified as 1, 2A, 2B by IARC	All chemicals with reported carcinogenic effects	All chemicals with reported carcinogenic effects
Minimum number of tested species for ecotoxicity	4	1	1
Water use			
Regulation of stream flow	High	Standard	Standard
Water requirement for food production	1000 m^3/year/capita	1350 m^3/year/capita	1350 m^3/year/capita
Impacts on terrestrial ecosystems considered	No	Yes	Yes
Mineral resource scarcity			
Future production	Reserves	Ultimate recoverable resource	Ultimate recoverable resource

3.3.3 ecoinvent Database

Access to the whole supply chain is necessary while conducting an LCA. It is nearly impossible to collect such data by hand, but databases like Ecoinvent enable LCA practitioners to focus on foreground data (the inputs and outputs of the system under investigation) while utilizing datasets for background data. (Supply-chain data). As a result, the LCA practitioner may concentrate on the primary hotspots in their system and its supply chain without having to spend substantial time discovering supply chain specifics [70].

The ecoinvent database comprises approximately 18000 valid life cycle inventory datasets from a variety of industries. These include, among other things, agriculture, and animal husbandry, building and construction, chemicals and plastics, energy, forestry and wood, metallurgy, textiles, transportation, touristic accommodation, waste treatment and recycling, and water supply.

The ecoinvent database assigns a geographic location to each activity. Geographic locations, often known as 'geographies,' are given as part of the dataset's name using globally standard acronyms[1]. As a backdrop database, the goal of the ecoinvent Database is to cover activity in the most relevant locations for the selected product or service. At the same time, geographic coverage is determined by the quality and availability of data. As a result, practically every action in the database includes a dataset describing the process worldwide, i.e. the average global output.

For each dataset in the ecoinvent database, Life Cycle Impact Assessment (LCIA) scores for several impact assessment methods (such as “IPCC 2021”, “EF v3.1”, or “ReCiPe”) and corresponding impact categories (such as “climate change”, “human toxicity”, “water use”, or “land use”) are available [71].

3.3.3.1 Unit and System Libraries

The ecoinvent libraries in SimaPro desktop contain both unit and system processes, which can be chosen by LCA practitioners without influencing the results.

Unit processes are the smallest element in the life cycle inventory analysis that describe a distinct part of a life cycle, and their scope can vary. On the other hand, system processes are an aggregated version of processes that represent the compilation and quantification of inputs and outputs for a product throughout its life cycle. System processes are calculated from unit processes and are not independent datasets. As shown in Figure 3.10, while unit processes contain emissions and resource inputs from one process step, a system process only contains inputs and outputs to and from the biosphere per reference product. The system process is experienced as a black box, as it is not easy to see which steps from previous processes are included, and it represents the result of an overall LCA.

[1] For instance (NO) stands for Norway. (RoW), (GLO), and (RER) are “rest of the world exclude Europe”, “Global” and “rest of Europe exclude Swiss” respectively. Knowing these acronyms help a lot while working with databases.

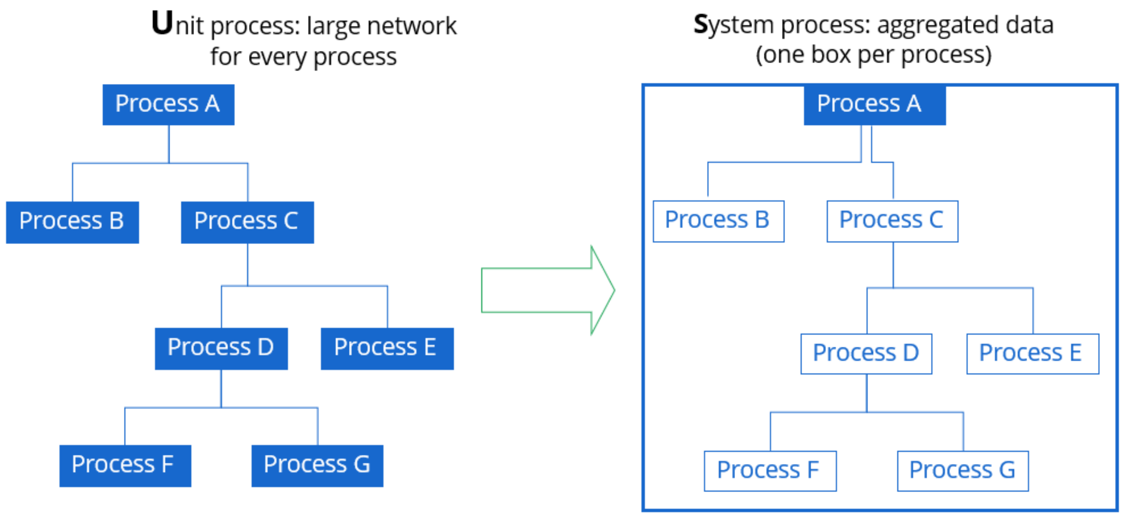

Figure 3.10: ecoinvent distinguishes unit and system processes [72].

For unit processes, the advantages are:

- It is easy to navigate the network and evaluate the supply chain since each unit operation is linked to other activities. You may, for example, utilize them to conduct an environmental hotspots study.
- Because they incorporate probability distributions (e.g., lognormal) of inventory data, unit processes may be utilized for uncertainty studies.

The advantages of using system processes are:

- System procedures enhance computation speed.
- A method for dealing with sensitive data. Datasets can be combined to generate a single system process. All underlying facts are erased in this manner, and no confidentiality concerns should occur.
- Furthermore, datasets may be provided as an average for a sector rather than as separate datasets for individual firms.

4 NPK Industrial Production Processes

The manufacturing of fertilizers often starts in liquid form. The final product is made into prills or granules which is the most typical appearance of solid fertilizers. Prilled and granular fertilizers are easy to handle in logistics chain and apply to crops. NPK production stages are described in this chapter generally and then a lot of details regarding NPK production processes at NPK plant in Porsgrunn are presented.

4.1 NPK Production Primary Stages

There are two primary stages to the NPK production process: the wet and the dry section. The "wet section" of this process is where reactions and the production of fertilizer slurry or melt take place. It may also include certain separation phases.

The process of granulating, prilling, drying, and coating sully or melt is known as the "dry section," which may also involve combining and adding certain dry raw ingredients.

In section “2.2.2 N, P, and K Sources” inputs for a typical NPK production have been discussed. Based on the recipe some secondary macronutrients, micronutrients, fillers, coatings, etc. may also be needed. However, the main inputs to the NPK factory come from ammonia plant, nitric acid plant, phosphate, potash, and dolomite mines as shown in Figure 4.1. The focus in this thesis is on the processes in the NPK factory.

Figure 4.2 shows these inputs together with wet and dry processes. In the wet section side two main types of processes exist: production by the mixed acid route and production by the nitrophosphate route. The nitrophosphate approach (ODDA process) provides a way to raise the P component in the product without utilizing phosphoric acid, albeit requiring a larger investment and interaction with other fertilizer processes [39]. The nitrophosphate route needs phosphate rock as the raw material, however, mixed acid process has options with or without phosphate rock. Figure 4.3 shows these routes with more information[1].

For a better comparison between nitrophosphate (ODDA) process and mixed acid route (with phosphate rock digestion type) Figure 4.4 is presented. As it is clear from this figure nitrophosphate, and mixed acid routes are different on how the mother liquor, or the concentrated solution of phosphate is produced. Filtration of digestion liquor in nitrophosphate route gives calcium nitrate while in the mixed acid route it ends in calcium sulfate.

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[1] There are some plants around the world that use Urea as the main source of Nitrogen and TSP/SSP (Triple/Single Super Phosphate) as P sources in the NPK production which are not scope of this research.

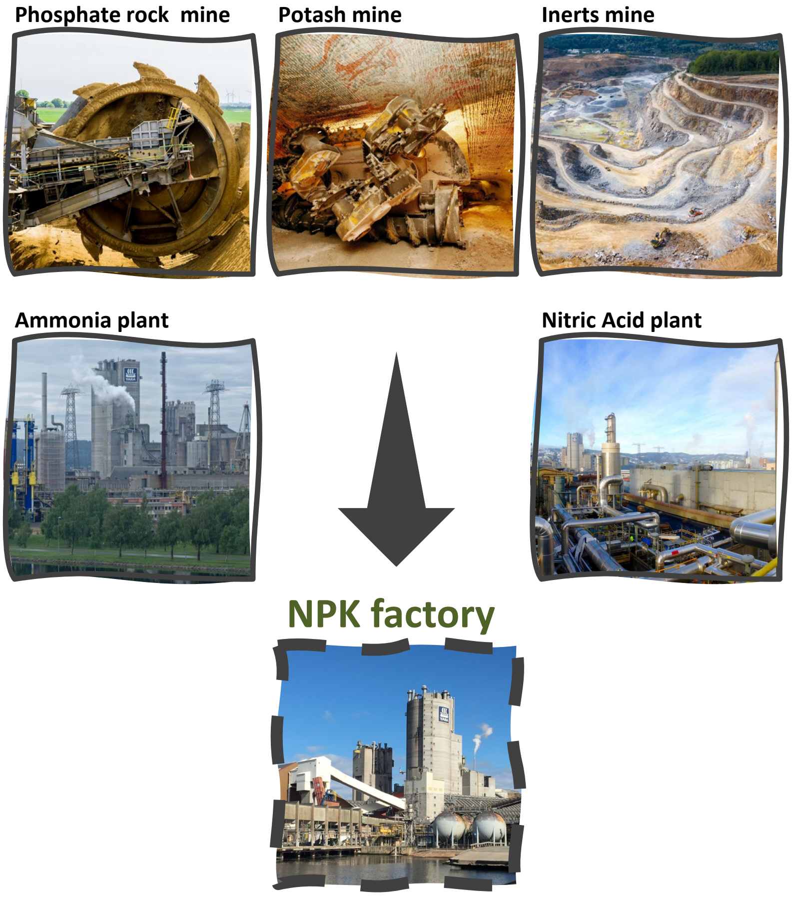

Figure 4.1: Different inputs to the NPK factory.

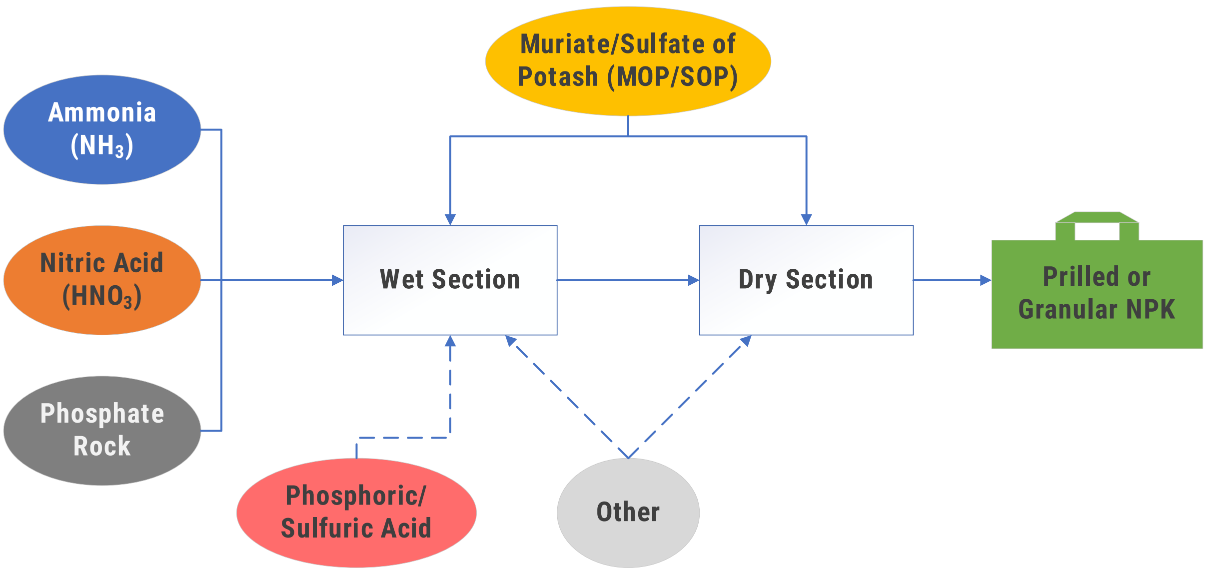

Figure 4.2: NPK production general flow chart.

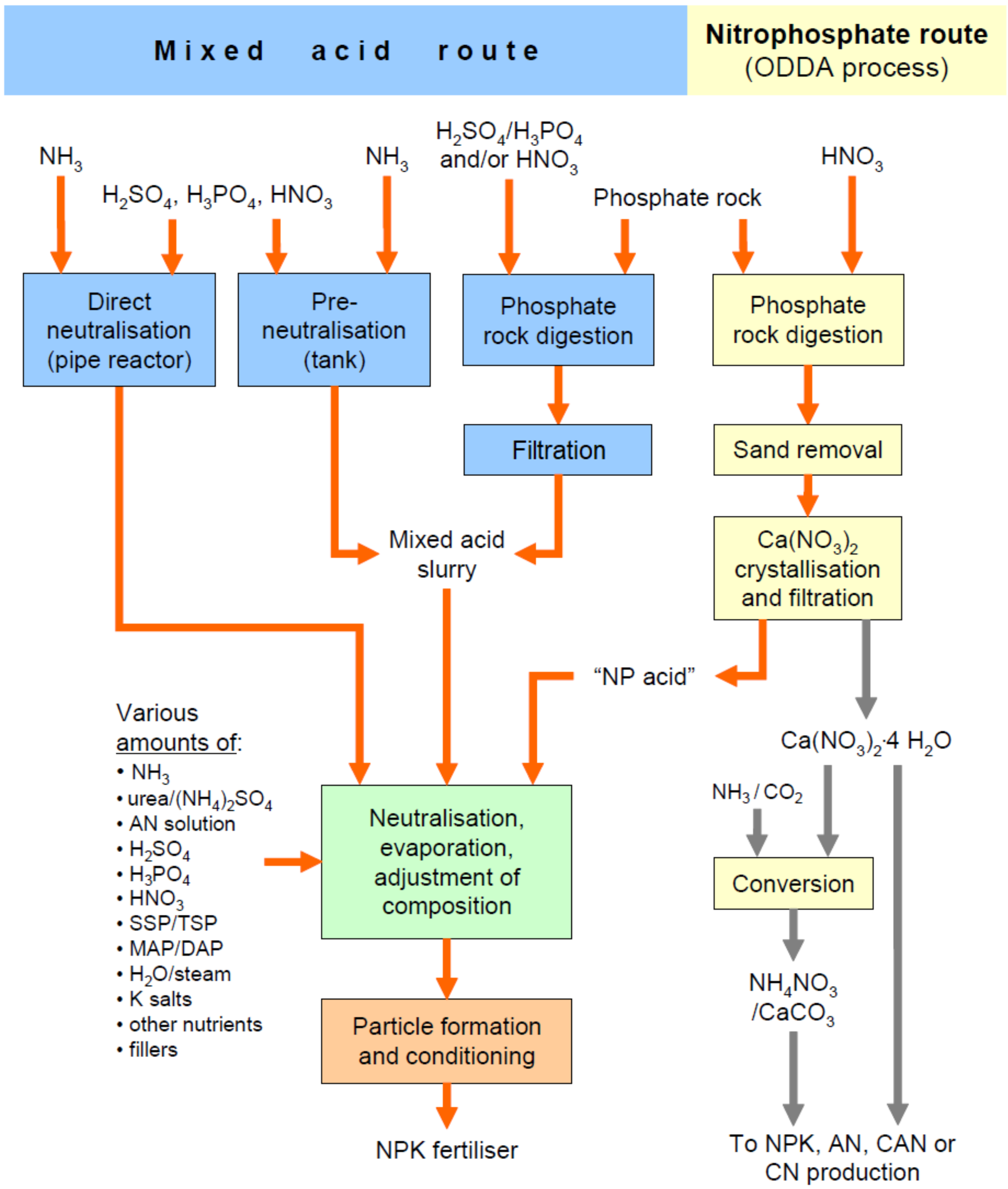

Figure 4.3: A holistic flow chart of the NPK fertilizers production in different plants in the world that use phosphate rock or SSP/TSP[1] as the raw material (from [39] with some modifications).

In this study the focus would be on the NPK production plant #3 in the Yara Porsgrunn located in Norway. So, from now on when the NPK production is discussed it means the right-hand side of the Figure 4.4.

[1] Triple Super Phosphate (TSP fertilizer) and Single Super Phosphate (SSP fertilizer).

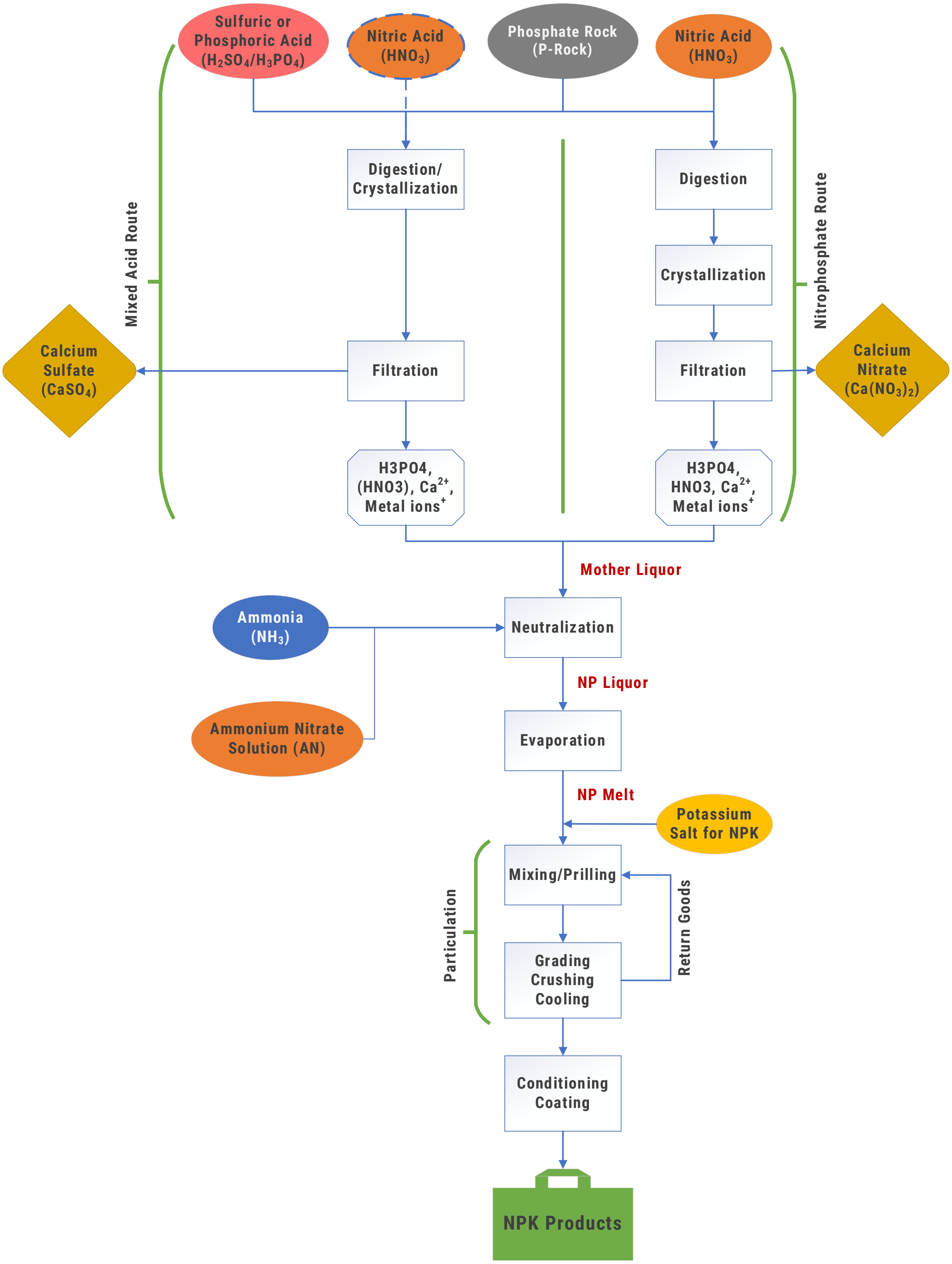

Figure 4.4: Two main NPK processes based on phosphate rock usage.

4.2 NPK production in Porsgrunn

As explained before, at Yara Porsgrunn plant, NPK production is based on Nitrophosphate (ODDA) route. Inputs and processes in this route are explained in the following sub-chapters.

4.2.1 Nitrophosphate Route Processes for Producing an NPK Product

Figure 4.5 shows an overview of the nitrophosphate route. Digestion, calcium nitrate (CN) removal (cooling, crystallization, and separation), neutralization, evaporation and particulation (mixing, prilling, screening, cooling, coating) are the main processes.

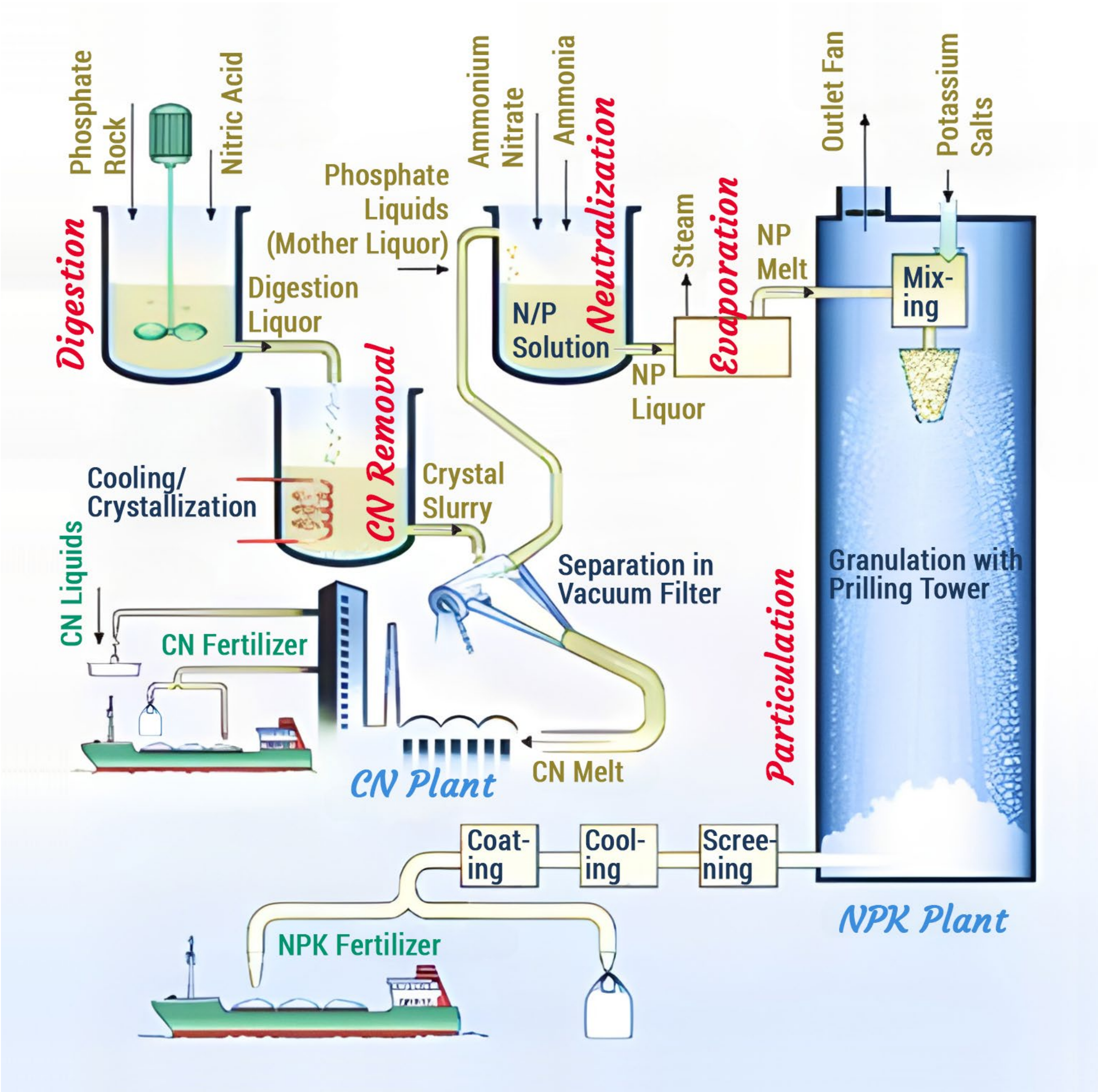

Figure 4.5: Nitrophosphate route processes (from [11] with modifications)

4.2.1.1 Digestion Step

The main purpose of this part, the first step in the wet section, is dissolving phosphate rock with nitric acid. This step may include adding other acids and raw materials as well. Two continuous stirred tanks in series are used for this aim.

The crops can't use phosphate rock[1] directly since it's not in a form they can use. The phosphorus will be converted by the nitric acid into phosphates, which the crops may absorb, and the nitrate nitrogen itself is a nutrition for the plants.

A combination of excess nitric acid, phosphoric acid, and calcium nitrate is produced when phosphate rock is digested in 64% nitric acid in the nitro phosphate process. Volume flow and residence time are important parameters to dissolve rock. Reaction (4.1) shows detail of the exothermic process at this stage which heats digestion liquid to ~ 60ºC.

$$3Ca_3(PO_4)_2 \times CaF_2\langle s\rangle + (20+x)HNO_3 \xRightarrow{Exothermic} 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF + xHNO_3 \quad (4.1)$$

Silica hexafluoride (H_2SiF_6) and silica tetrafluoride (SiF_4) are created when a portion of the hydrofluoric acid (HF) combines with silica oxides (SiO_2); these compounds will evaporate and be carried away by the off gases. Some other side reactions are also in this process that produce effluent (Reaction (4.2)).

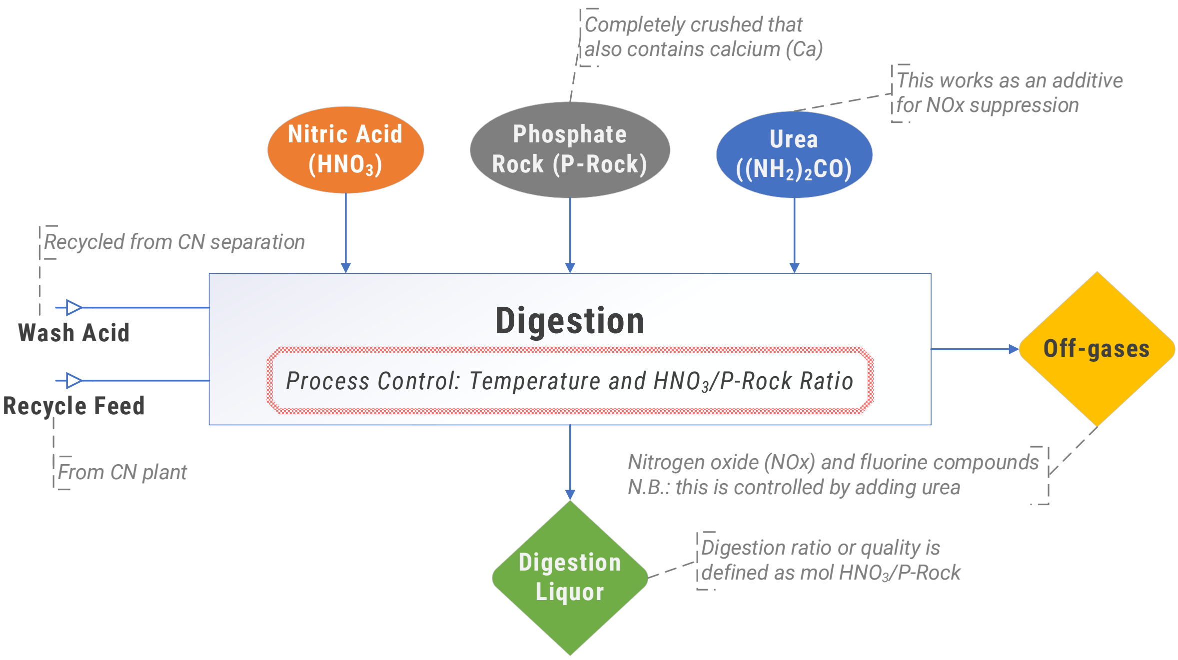

Figure 4.6: Digestion process in details

[1] Phosphate rock is simplified as $Ca_{10}(PO_4)_6F_2$ or in another arrangement as $3Ca_3(PO_4)_2{\times}CaF_2$. For more information about P-rocks refer to clause 2.3 in this report.

$$\begin{cases} 4HF + SiO_2 \Rightarrow SiF_4 + 2H_2O \\ 6HF + SiO_2 \Rightarrow H_2SiF_6 + 2H_2O \\ H_2SiF_6 \Rightarrow SiF_4 + H_2F_2 \\ 2HNO_3 + C \Rightarrow 2HNO_2 + CO_2 \\ 4HNO_2 + C \Rightarrow 4NO + 2H_2O + CO_2 \\ HNO_3 + 2NO + H_2O \Rightarrow 3HNO_2 \\ 2HNO_2 \Rightarrow NO + NO_2 + H_2O \end{cases} \tag{4.2}$$

The carbon content in the side reactions is dependent on the phosphate rock compositions. The bigger carbon amount in the P-rock, the higher carbon dioxide produced.

NO and NO_2 in the last row of the Reaction (4.2) are NOx. Urea reaction mechanism removes HNO_2, a precursor for NOx as shown in the Reaction (4.3).

$$\begin{cases} (NH_2)_2CO + HNO_3 \Rightarrow (NH_2)_2CO \times HNO_3 \\ (NH_2)_2CO \times HNO_3 + HNO_2 \Rightarrow N_2 + HNCO + 2H_2O + HNO_3 \\ HNCO + H_2O \Rightarrow NH_3 + CO_2 \\ HNCO + HNO_2 \Rightarrow CO_2 + N_2 + H_2O \end{cases} \tag{4.3}$$

However, an unwanted reaction may also happen and produce N_2O which hugely take part in global warming.

$$(NH_2)_2CO \cdots HNO_3 + HNO_3 \Rightarrow N_2O + HNCO + 2H_2O + HNO_3 \tag{4.4}$$

Due to this problem new ways are developed to reduce NOx emissions to reduce Urea usage and its consequences like N_2O. Ozone project is a solution to be used instead of Urea solution.

$$\begin{cases} NO + O_3 \Rightarrow NO_2 + O_2 \\ 2NO_2 + O_3 \Rightarrow N_2O_5 + O_2 \\ N_2O_5 + H_2O \Rightarrow 2HNO_3 \end{cases} \tag{4.5}$$

4.2.1.2 Crystallization

To be able to separate the calcium nitrate at later steps, crystallizing of the calcium is essential. This is carried out by water cooling process shown in the Figure 4.7 and based on the Reaction (4.6).

$$CA(NO_3)_2\langle aq\rangle + 4H_2O\langle l\rangle \xrightarrow{Exothermic} Ca(NO_3)_2 \times 4H_2O\langle s\rangle \tag{4.6}$$

Since this reaction is an exothermic type, the energy is removed at first step by cold water and at the second step by NH_3/water mixture.

Crystallization depends on the temperature, water content, and digestion ratio obtained in the previous step.

Remaining silica hexafluoride may also react in a side reaction (4.7) below.

$$CA(NO_3)_2\langle aq\rangle + H_2SiF_6\langle aq\rangle + 2H_2O\langle l\rangle \xrightarrow{Exothermic} CaSiF_6 \times 2H_2O\langle s\rangle + 2HNO_3 \tag{4.7}$$

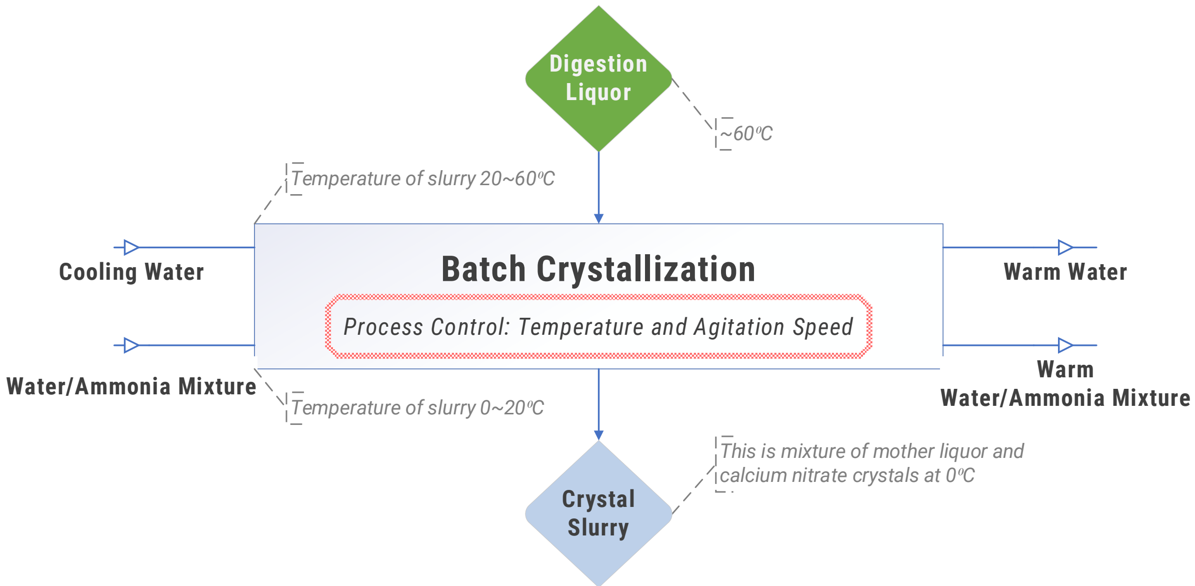

Figure 4.7: Generating the right calcium nitrate crystal size distribution.

4.2.1.3 Separation

After crystallization, calcium nitrate tetra hydrate[1] is removed from the crystal slurry by filtering or centrifugation to lower the calcium nitrate level and prevent the formation of apatite. The calcium reduced solution is called mother liquor. This step does not have main reaction, but there might be some side reactions like calcium hexafluorosilicate dihydrate[2] which is soluble in water and calcium nitrate tetra hydrate which is soluble in both water and nitric acid.

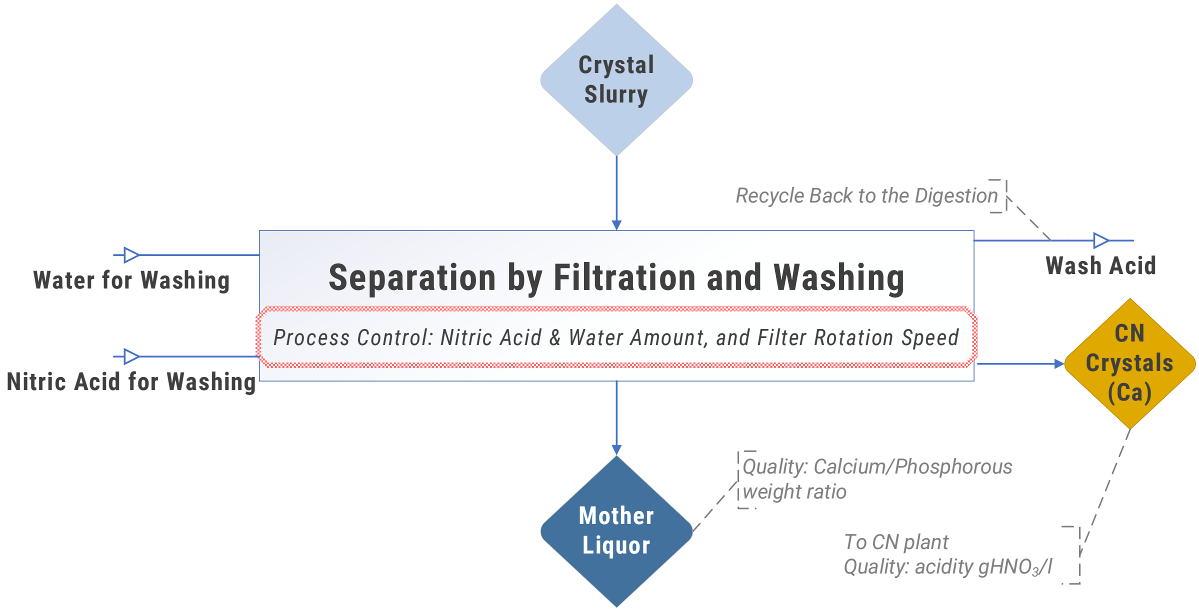

Figure 4.8: CN separation from mother liquid

In the other sections of the plant, calcium nitrate (CN) crystals are washed, refined, neutralized with ammonia, and then utilized as fertilizer or in other technical applications in either solid or liquid form. This part is not the topic of this study.

4.2.1.4 Neutralization

By adding extra nitric acid or ammonium nitrate[3], the mother liquor from the filters is modified to attain the proper nitrogen level. Then, ammonia is needed for neutralization of acids after digestion such that the pH is near to 5.8 (Figure 4.9).

Ammonia load limits entrainment of P and N in effluent water vapour and pH affects the mother liquid viscosity. Adjusting N/P and neutralizing acid are important, but keeping P soluble is also crucial.

---

[1] $Ca(NO_3)_2 \times 4H_2O$

[2] $CaSiF_6 \times 2H_2O$

[3] NH_4NO_3

All main reactions in this step are exothermic and energy released evaporates water from 30% to 10-20%). Temperature and pH must be controlled precisely to maintain the phosphorus in a form useful to the crops and avoid the tendency to reform apatite.

The neutralization in the tanks is done in stages to control pH and precipitation of undesired products, which may give high viscosity and operational problems. On account of this, the precipitation of calcium fluoride, di-calcium phosphate, and when pH rises, more di-calcium phosphate, is controlled and the liquid's viscosity is preserved [11].

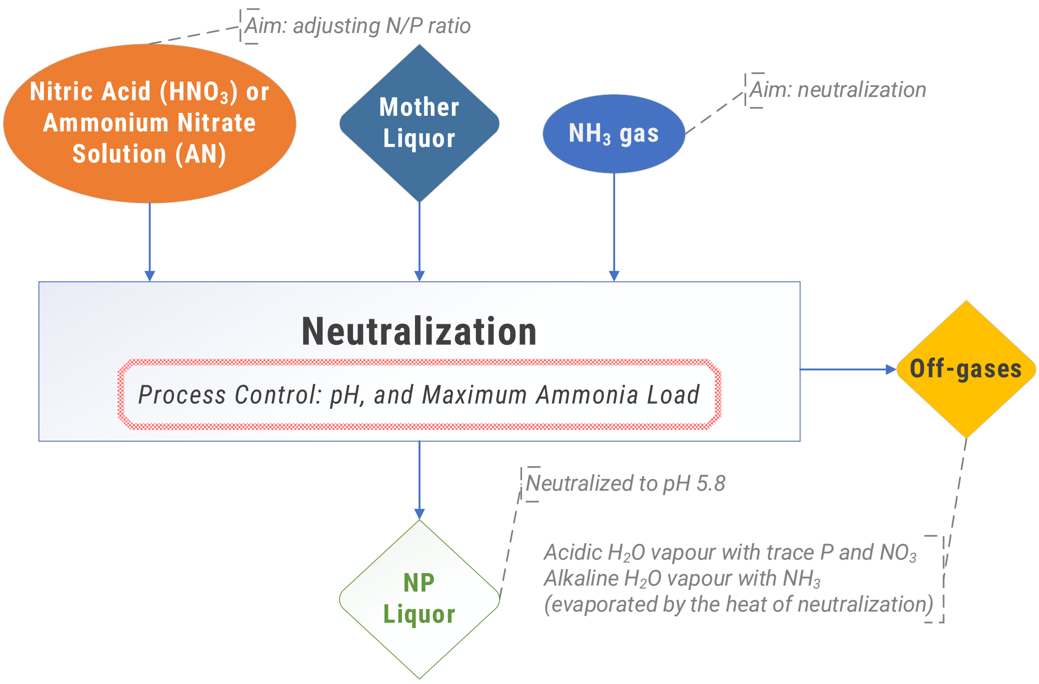

Figure 4.9: Purpose: Adjusting N/P ratio and neutralizing acid.

The main neutralization reactions:

$$\begin{cases} HNO_3 + NH_3 \Rightarrow NH_4NO_3\langle aq\rangle^1 \\ Ca(NO_3)_2 + H_3PO_4 + 2NH_3 \Rightarrow 2NH_4NO_3 + CaHPO_4\langle s\rangle^2 \\ H_3PO_4 + NH_3 \Rightarrow NH_4H_2PO_4\langle aq\rangle^3 \\ H_3PO_4 + 2NH_3 \Rightarrow (NH_4)_2HPO_4\langle aq\rangle^4 \end{cases} \tag{4.8}$$

[1] AN: Ammonium Nitrate

[2] DCP: Di-Calcium Phosphate

[3] MAP: Mono-Ammonium Phosphate

[4] DAP: Di-Ammonium Phosphate

Remaining silica hexafluoride, calcium nitrate and calcium hexafluorosilicate dihydrate from previous steps may attend in the side reactions.

$$CaSiF_6 \times 2H_2O\langle s\rangle + 2Ca(NO_3)_2 + 4NH_3 + 2H_2O \Rightarrow 3CaF_2\langle s\rangle + 4NH_4NO_3 + SiO_2\langle s\rangle \quad (4.9)$$

$$H_2SiF_6 + 3Ca(NO_3)_2 + 6NH_3 + 2H_2O \Rightarrow 3CaF_2\langle s\rangle + 6NH_4NO_3 + SiO_2\langle s\rangle \quad (4.10)$$

4.2.1.5 Evaporation

A general overview of this step is shown in Figure 4.10. Evaporation lowers the water content of NP liquid under vacuum in two steps: step1) 0.8 bar, step2) 0.08 bar. Temperature and pressure must be controlled to remove water adequately and prevent precipitation.

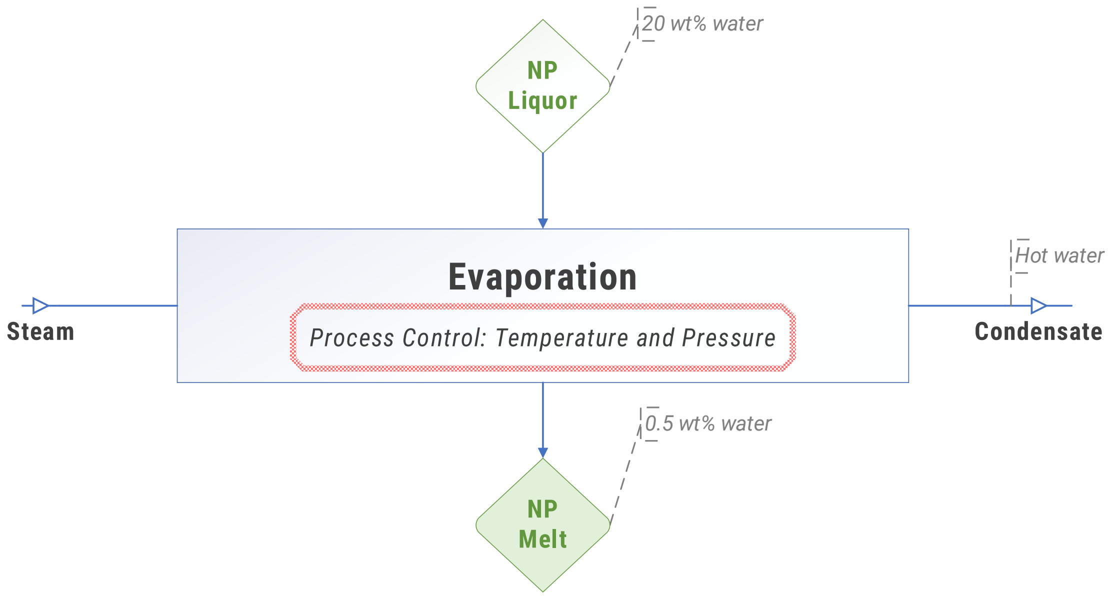

Figure 4.10: Removing water from the liquor.

Main reaction at this step is endothermic and the energy is obtained from condensing steam.

$$2H_2O\langle l\rangle \xRightarrow{Endothermic} 2H_2O\langle g\rangle \quad (4.11)$$

There are some side reactions from the outputs of the previous steps. The first side reaction is important since it affects gas cleaning.

$$\begin{cases} (NH_4)_2HPO_4 \Rightarrow NH_4H_2PO_4 + NH_3\langle g\rangle \\ 2NH_4H_2PO_4 \Rightarrow (NH_4)_2H_2P_2O_7 + H_2O \\ NH_4NO_3 \Rightarrow NH_3 + HNO_3 \\ CaF_2 + 2HNO_3 \Rightarrow 2HF + Ca(NO_3)_2\langle aq\rangle \\ 4HF + SiO_2 \Rightarrow SiF_4\langle g\rangle + 2H_2O\langle g\rangle \end{cases} \tag{4.12}$$

4.2.1.6 Adding Potassium Salts and Particulation

Particulation process or in other words prilling or granulation[1] are for easier handling and distribution on farm field. But salts are provided as a source of potassium, sulfur, and any other nutrients needed before the particulation step begins.

All nutrients are carefully regulated to ensure that the finished product has the proper concentrations. The finished particles are cooled, sieved for proper size distribution, and then treated with talcum and an oil/wax conditioning combination.

The various formulations for the finished product are designed with care to prevent goods with insufficient stability and a propensity to self-decompose when exposed to heat.

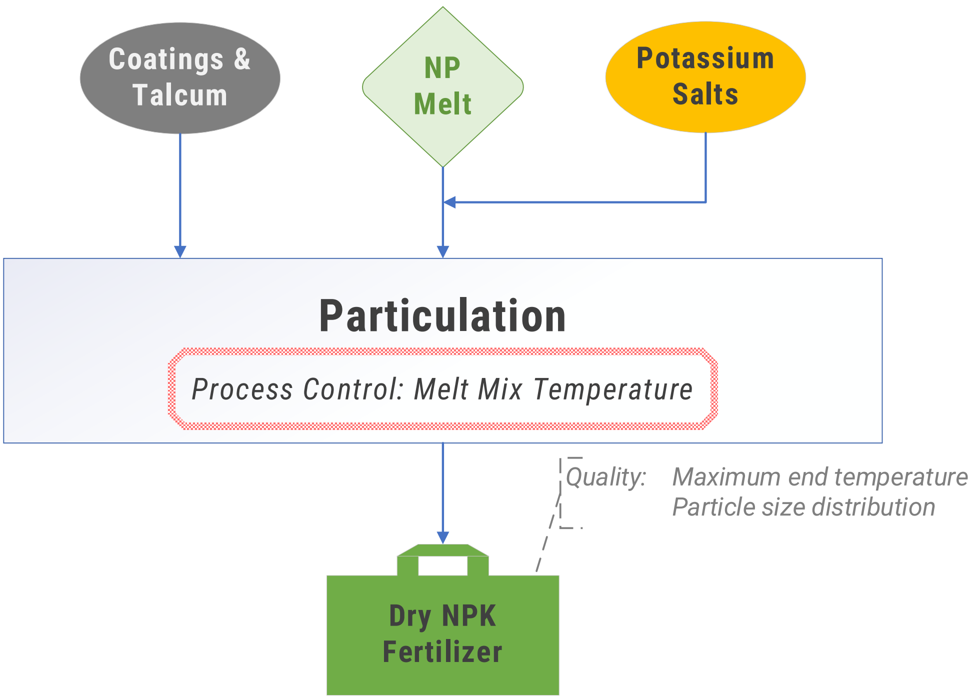

Figure 4.11: Adding potassium salts and then particulation.

[1] Prills are small, spherical, or pellet-shaped solid particles. Granules, on the other hand, are irregularly shaped solid particles.

Main reactions at this step are all exothermic and the released energy is removed by air.

$$\begin{cases} NH_4NO_3\langle aq\rangle \xRightarrow{Exothermic} NH_4NO_3\langle s\rangle \\ NH_4H_2PO_4\ \langle aq\rangle \xRightarrow{Exothermic} NH_4H_2PO_4\ \langle s\rangle \\ (NH_4)_2HPO_4\langle aq\rangle \xRightarrow{Exothermic} (NH_4)_2HPO_4\langle s\rangle \end{cases} \tag{4.13}$$

5 Guidance on Performing an LCA of the NPK

One of the problems with LCA studies is that there is no agreement on which effect areas or impact categories should be addressed specifically in each study [67]. Data sets from various LCA practitioners encompass various effect categories. GWP appears to be the sole effect category utilized by all research. As a result, the European LCA platform created the International Reference Life Cycle Data System (ILCD) manual, which seeks to give an in-depth guidance on conducting LCA research [60]. On the other hand, it is exceedingly wide, with little of it relevant or useful in terms of doing an LCA on fertilizer production.

As mentioned in Chapter 3, the results from the analysis are dependent on the life cycle perspective that is chosen. Cradle-to-gate is the relevant perspective to use in a life cycle assessment of an NPK production as an inorganic fertilizer, as well as being the chosen perspective for the report. There a not many studies that mainly focus on the fertilizer production or cradle to gate LCA on fertilizers which can help our modeling. An LCA case study at Democritus University of Thrace, to compare nitrate and compound fertilizers is one of the rare useful available assessments [73].

The sections that follow try to provide a simplified overview of the processes that must be taken to complete an LCA for NPK manufacturing. For general discussions regarding the LCA, refer to chapter 3.

5.1 Preparation for the Analysis

Preparation is a crucial step in conducting a comprehensive and accurate Life Cycle Assessment (LCA) analysis.

- Get familiar with LCA methodology: as presented in the chapter 3.
- Get familiar with NPK: as presented in the chapter 2.
- Understanding NPK production methods and processes: as described in the chapter 4.
- Which LCA software to use: there are several available software that can be used with included databases. SimaPro[1] is a commercial LCA software that was used for modeling. Even with the use of purchasable databases, they are limited, and knowledge of the software, processes and flows is required. The user must be able to understand and if necessary, edit inputs and outputs of the different processes.

[1] For more information see section 3.3.

5.2 Define the Goal

When defining the goal, the aim of the study must be set. A specific goal for cradle-to-gate assessment of an NPK fertilizer production with the focus on principal harmful substances end into the goal below

> To provide a holistic examination of environmental impacts of contaminants that come from production of a fertilizer produced in the NPK plant #3 in Yara – Porsgrunn.

It should also be noted that this work helps to

- learn general concepts of NPK fertilizers and LCA.
- find out about principal harmful substances from NPK.
- explore the existing standards for the NPK.
- understand principles for industrial production of an NPK product.
- explore the current data availability within Yara and external databases.
- gain indicative insight into impacts of Yara production.

5.3 Define the Scope

When determining the scope, all aspects that will be considered must be properly described. This step is critical to complete since it specifies the depth and breadth of the investigation, and any inaccuracies will have an impact on the outcomes. The functional unit and system boundary will affect whether the results can be easily compared.

The scope-phase may/must contain the following [67]:

- Function, functional unit and reference flow
- Life cycle inventory modelling
- System boundary and cut-off criteria
- Life cycle impact assessment methods and categories
- Type and sources of required data and information
- Data quality requirements
- Comparisons between systems
- Identification of critical review needs
- Intended reporting

Specifically, for NPK:

Scope

- Raw material sources for N, P, and K ➔ NPK production route ➔ required energy sources ➔ emissions monitoring and calculation.
- Functional units: impact equivalents per ton of product, e.g.: $kgCO_2e/tNPK$, or $kgCO_2e/tP_2O_5$.
- System boundary: as shown in the figures in the next clause.

5.3.1 System Boundary

It is critical to evaluate every aspect of the value chain while establishing the boundary. The border must be drawn to limit the complexity of the study while taking into account all elements.

The system boundary in an LCA denotes the boundaries defined between the product under consideration and the surrounding systems Figure 5.1 depicts the cradle-to-grave boundary groups. While dashed rectangular defines cradle-to-gate boundary condition which is discussed in this study.

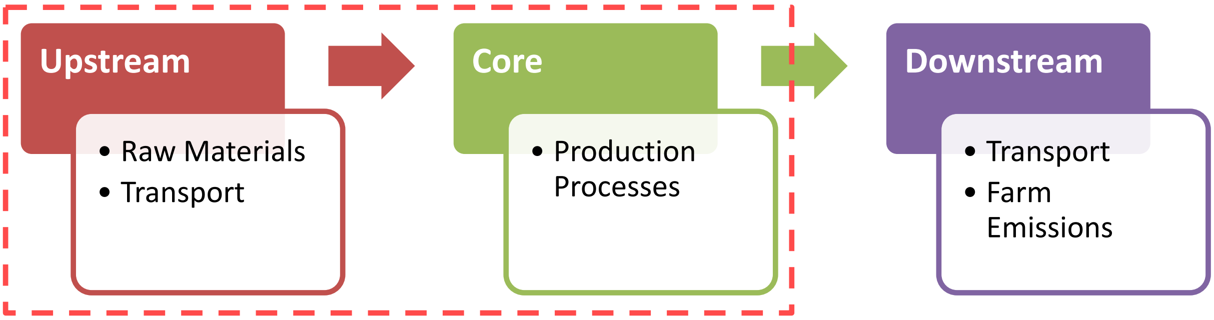

Figure 5.1: Cradle-to-grave and cradle-to-gate system boundaries of an NPK

Figure 5.2 shows a general assembly for the boundary limit of the NPK production in Yara Porsgrunn NPK#3.

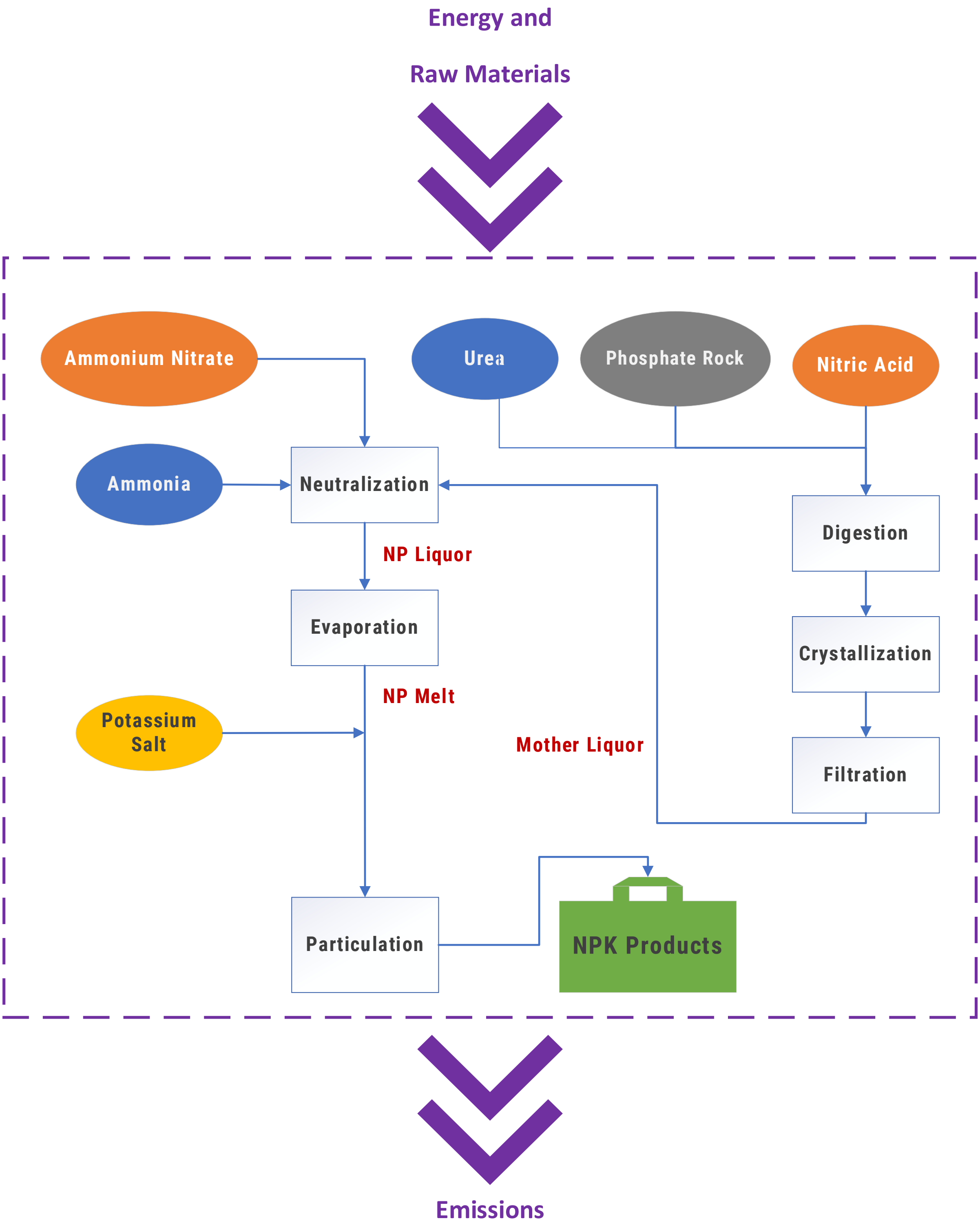

Figure 5.2: System boundary considered for NPK production.

5.4 Life Cycle Inventory Analysis

Data must be gathered in line with the system's goal, scope, and boundaries. The conventional method is as follows [67]:

- Identifying processes within the system boundary (as presented in chapter 4)
- Planning data collection (number of meetings were held to get familiar with Yara's monitoring system-PIMS)
- Data collection
- Validation of Data
- Reference of Data to a Functional Unit
- Compilation of data to a "Life Cycle Inventory"

5.5 Impact Assessment

For the impact assessment, the following must and should be done:

- Classification and characterization (must)
- Normalization (optional[1, 2])
- Grouping and weighting (optional[1])

A comprehensive LCA, according to the ILCD guide, must evaluate various impact categories[3]. According to the ILCD manual, the following effect categories should be investigated if relevant [60]:

- Global Warming Potential (GWP)
- Acidification Potential (AP)
- Eutrophication Potential (EP)
- Photochemical Ozone Creation Potential (POCP)
- Primary Energy Demand (PED), renewable
- Primary Energy Demand (PED), non-renewable.

Nevertheless, heavy metals are often considered as impact categories due to their potential adverse effects on human health and the environment. Some common impact categories related to heavy metals in LCA include:

- Human toxicity: It considers factors such as the toxicity of specific metals, exposure routes, and the potential for bioaccumulation or biomagnification in the food chain.
- Ecosystem Toxicity: This category focuses on the potential impacts of heavy metals on ecosystems and their inhabitants.

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[1] It is optional with valid reason like if there is no need to compare the results.

[2] The numbers are normalized, and the various effect categories are given a relative weight, to achieve standardization.

[3] Each LCA impact category has a unique set of units. These units can be standardized to Pt. for discussion and comparison purposes.

- Freshwater and Marine Eutrophication: Heavy metals can contribute to eutrophication, which is the excessive enrichment of water bodies with nutrients. Eutrophication can lead to harmful algal blooms, oxygen depletion, and disruption of aquatic ecosystems.
- Acidification: Certain heavy metals, such as lead (Pb) and cadmium (Cd), can contribute to acidification of ecosystems. Acidification affects soil and water pH, potentially harming vegetation, aquatic life, and soil organisms.

In this study, two models, one with heavy metal emissions and another without heavy metal emissions are considered to see heavy metal emissions effects to different categories by comparison.

5.6 Interpretation and Evaluation

This phase includes the following [67]:

- Identification of significant issues in the Life Cycle Inventory Analysis results
- Evaluation of results
    - Completeness check
    - Sensitivity check
    - Consistency check
    - Uncertainty check
- Conclusions, limitations, and recommendations

Any problems with the study should be identified and, if feasible, remedied. If the study's degree of completion falls short of the scope's requirements or the aim, either higher-quality data must be employed, or the goal and scope must be changed.

It is crucial to recognize the processes that significantly influence the effect evaluation. This aids in determining which elements may be enhanced or altered to lessen effects.

5.7 Reporting and Critical Review

This phase consists of the following [60]:

- Reporting (must)
- Confidential report (can)
- Critical review from independent, experienced reviewer (not required for internal studies)

Finally, the study's findings must be presented in a technical report with impartial results and techniques that can be duplicated. It must be evaluated if the report will be intelligible to a non-technical audience if it is used to make decisions. If appropriate, a confidential report may be included.

The reviewer must be objective, educated in LCA techniques, and skilled in the verification and auditing of such analyses. Furthermore, the reviewer should be technically knowledgeable about the system under examination.

In the case of “Cradle-to-Gate” of NPK it can be restated as

- A report that includes methods, findings, and conclusions
- Confidential report (any part needed)
- Review by an independent EPD-verifier

As previously stated, a third-party EPD verifier must certify the LCA on NPK. The full assessment of GWP, AP, and EP[1] will typically be sufficient for a product to receive EPD approval; however, it should be thoroughly investigated if additional impact categories will need to be addressed.

[1] Global warming (GWP), acidification (AP), and eutrophication (EP) potentials.

6 Basic Calculations and Data Collection

Chapter 4 helped to understand the various stages for production of NPK products in Yara Porsgrunn NPK plant #3 based on the Nitrophosphate route. The final focus of this thesis is understanding and finding a methodology for the assessment of the heavy metals' emissions due to each type of the NPK product. As discussed in section 2.3 the bigger the P value in an NPK product, the higher heavy metals emissions probability. Based on this between all products that have been produced in 2022 in NPK plant #3, the NPK 20-10-10 is chosen[1].

In the following sub-chapters raw materials, and heavy metal emissions calculations and conventional emissions data collection are discussed.

6.1 Raw material for the NPK 20-10-10

As described in previous chapters, for each of N, P, and K different sources are available that are explained in following clauses. Designing a true recipe is based on operational experience and plant characteristics. However, there are some empirical rules to steer ingredients amounts to be calculated.

6.1.1 P_2O_5 Content from Phosphate Rock

Phosphate rock can be provided from different mines with different compositions[2]. Table 6.1 shows the composition of commonly used phosphate rocks in Yara Porsgrunn.

It is generally better to use only one type of phosphate rock when producing NPK fertilizers, unless there is only a small amount of one type left or if we need to reduce the level of substances in a particular rock by blending it with another type that has fewer contaminants.

One ton of NPK 20-10-10 contains 10% or 100 kg of P_2O_5. Phosphate rock requirement can be calculated by dividing the P_2O_5 content in the product by the P_2O_5 content in the P-rock. Assuming from Table 6.1, 33.6% of P_2O_5 in the Youssofia P-rock,

$$P - rock = 10\% \cdot 1000/33.6\% = 298\ kg \text{ phosphate rock}^{3} \qquad (6.1)$$

[1] Yara Porsgrunn NPK 2022 products are listed in Appendix B.

[2] Yara Porsgrunn imports P-rock from different suppliers and test for their compositions in the lab. So, relevant data are available, however, values from references are used for generalization.

[3] For easier calculations, it is assumed that there is no P loss during the production process. For more accuracy the P content in the sand removal process should also be considered.

Table 6.1: Typical analyses of various phosphate rocks [74].

Mine (Country)	P_2O_5 [%]	CaO [%]	SiO_2 [%]	CO_2 [%]	F [%]	Cl [%]	Fe_2O_3 [%]	Al_2O_3 [%]	MgO [%]
Siilinjärvi (Finland)	36.8	54.6	0.9	4.7	2.6	0.006	0.3	0.2	0.8
Kola (Russia)	39.2	52.0	2.0	0.2	3.1	0.002	0.8	0.8	0.1
Youssofia (Morocco)	33.6	53.1	1.9	3.4	4.0	0.02	0.2	0.3	0.5

Some part of this phosphate rock is Ca which ideally is completely separated in the separation step and will be used in the CN plant and this portion would not end in the final NPK product. However, the separation process is not a hundred percent efficient process. Thus, the Ca amount in the mother liquor shows whether all the Ca crystals are separated or not.

Considering 0.5 kgCa/kgP as an approximate yearly average value in the mother liquor[1], Calcium amount which will end in final NPK product can be estimated.

$$33.6\%P_2O_5 \equiv 14.7\%P \xrightarrow{\frac{kgCa}{kgP}=0.5} 33.6\%P_2O_5 \equiv 7.4\%Ca \tag{6.2}$$

Therefore, 7.4% Ca is not separated and will end in the final NPK product. For Youssofia Ca content can be calculated as

$$53.1\%CaO \equiv 38.0\%Ca \tag{6.3}$$

Now it is possible to calculate how much Ca goes to the CN plant and should be subtracted from 298kg of the P-rock.

$$\begin{gathered} P-rock_{CN} = 298 * (1 - 7.4\%) * 38.0\% = 105kg \\ P-rock_{NPK} = 298 - 105 = 193kg \end{gathered} \tag{6.4}$$

[1] For more information see Appendix C.

Therefore, 298 kg of Youssofia phosphate rock is needed for producing 1 ton of NPK 20-10-10, however, 193kg of it goes to the final NPK product and the rest goes to the CN plant. These values are 255 and 168 for Kola and 272 and 174 for Siilinjärvi phosphate rocks.

6.1.2 N content from Nitric Acid and Ammonia

At Yara's Porsgrunn plant ammonia and nitric acid are the sources of Nitrogen, and are shown as nitrate or NO_3-N , and ammonium, or NH_4-N. The N content is divided between NO_3-N and NH_4-N, and you can assume that a ratio between those two of approximately 0.7 (NO_3-N:NH_4-N) giving the consumption for nitric acid and ammonia respectively. This ratio helps balance the pH of the final product, reaching a pH of 5.8 and as ammonium ions release nitrogen gradually over time, providing a sustained nutrient supply.

By considering the ratio of NO_3-N over NH_3-N equals to 0.7[1], it can be written

$$NO_3 - N = 0.7NH_3 - N \tag{6.5}$$

$$total - N = NO_3 - N + NH_3 - N = 1.7NH_3 - N \tag{6.6}$$

$$NH_3 - N = total - N/1.7 \tag{6.7}$$

$$NO_3 - N = 0.7total - N/1.7 \tag{6.8}$$

One ton of NPK 20-10-10 which has 15% of nitrogen, nitric acid and ammonia can be calculated

$$NO_3 - N = 0.7 \cdot 20\% \cdot 1000/1.7 = 82kg \text{ nitrogen from nitric acid} \tag{6.9}$$

$$NH_3 - N = 20\% \cdot 1000/1.7 = 118kg \text{ nitrogen from ammonia} \tag{6.10}$$

The pure HNO_3 and NH_3 can be calculated as

$$HNO_3 = \frac{63}{14} \cdot NO_3 - N = \frac{63}{14} \cdot 82 = 370kg \text{ nitric acid}^2 \tag{6.11}$$

$$NH_3 = \frac{17}{14} \cdot NH_3 - N = \frac{17}{14} \cdot 118 = 143kg \text{ ammonia} \tag{6.12}$$

---

[1] Some references may prefer NH_3-N over NO_3-N ration as 1.4.

[2] From the experience each 100kg of P-rock needs 126 kg nitric acid for digestion. So, for 298kg of the P-rock there might 375 kg of nitric acid be needed. However, not all of it can be allocated to the NPK20-10-10.

6.1.3 K_2O Content from Potassium Salt

Assuming the potassium comes from MOP[1], the "K_2O content" of MOP is about 60%[2]. So, 1 ton of NPK 20-10-10 containing 10% "K_2O" requires,

$$MOP = 10\% \cdot 1000/60\% = 167kg \text{ potash} \tag{6.13}$$

6.1.4 Rest of the recipe

The rest of the recipe can be water content, coating oil, complementary nutrients, talcum or fillers. To simplify this part, we will only consider fillers for this analysis. Fillers can be different materials such as gypsum, sand, or dolomite. In this study dolomite is considered.

$$\begin{aligned} Dolomite, etc. \\ &= total\ NPK - Ammonia - Nitric\ Acid - Phosphate\ Rock \\ &- Potash = 1000 - 193 - 370 - 143 - 167 = 127kg^3 \end{aligned} \tag{6.14}$$

As discussed in the previous chapter, some urea might also be added to the system for controlling the NOx emissions. This can be seen in Appendix G. Since urea amount is small, its nitrogen content is assumed not to be entered in NPK's nitrogen content but in the rest of the recipe.

6.2 NPK 20-10-10 Bill of Material

In previous headings the easy calculation methodology for NPK 20-10-10 was discussed. It is worth mentioning that real-world calculation needs experience and a lot of knowledge from the production unit, details of ongoing process, working equipment efficiency, raw material detail specification, etc.

Figure 6.1 gives bill of material and a general overview of all calculations results for producing one ton of NPK 20-10-10. Phosphate rock figure represents the amount needed based on Youssofia P-rock.

[1] Muriate of potash or potassium chloride

[2] If we use SOP instead of MOP this value is different. SOP or Sulfate of potash contains 50% as K2O.

[3] For Kola and Siilinjärvi P-rocks, required dolomite amount are calculated as 152kg and 146kg respectively.

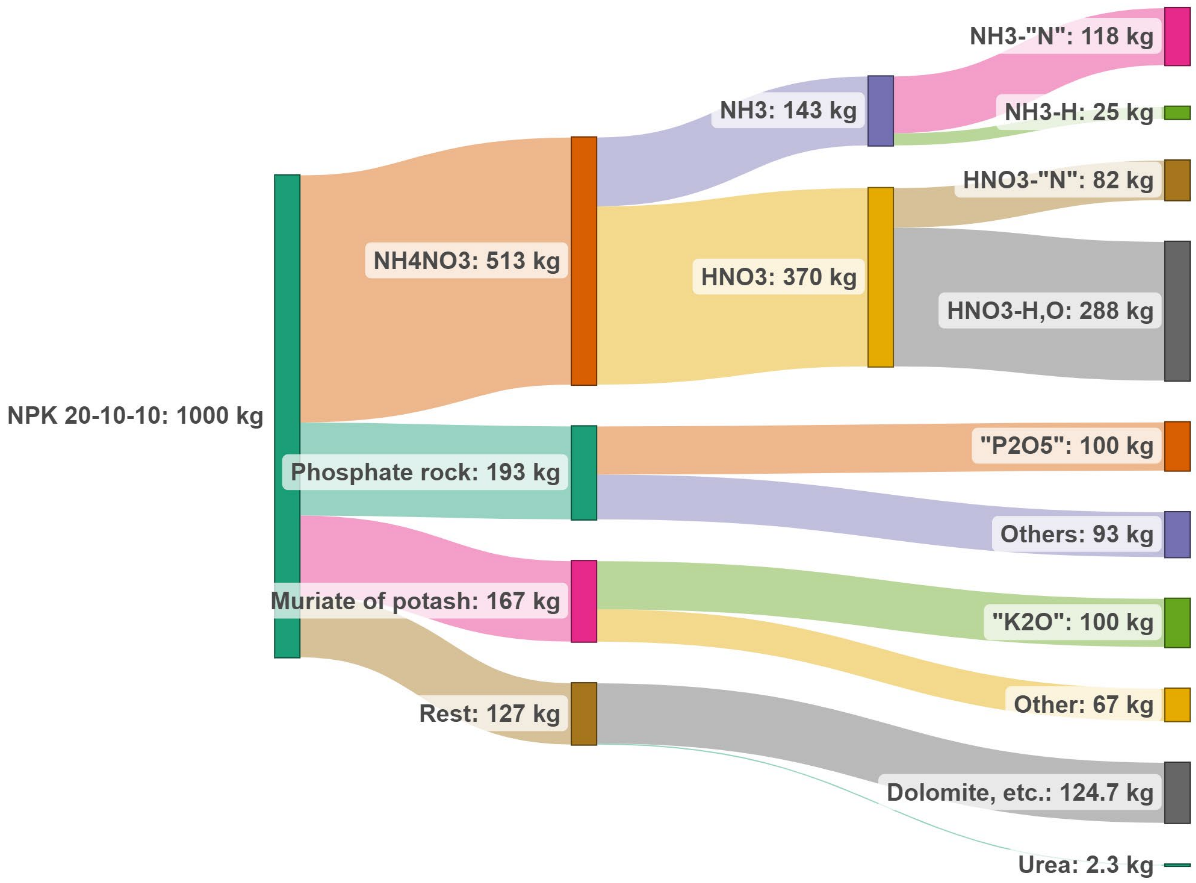


Figure 6.1: Sankey diagram of Bill of Material (BOM) required for producing one-ton NPK 20-10-10 production.

6.3 Emissions from NPK production

Following emissions from the NPK production at Yara Porsgrunn is challenging as they can be listed as emissions to the soil, air or water. The conventional emissions are monitored and can be understood by checking the P&IDs and PFDs and finally checking DCS system. While for heavy metals a different methodology and boundary assumption is needed. These two parts will be discussed in this section.

6.3.1 Conventional Emissions

There is not a clear scientific approach for classifying emissions. However, the main reason in this study to classify the emissions in two groups is that heavy metals are calculated, and others are monitored continuously. Conventional emissions to air are NO, N_2O, CO_2, Fluoride, escaped Ammonia, etc. Conventional emissions to water are Ammonia, Nitric Acid, P, etc.

In the LCA we prefer to have data for each process step, however, sometimes it is not possible. In this study emissions to water could not be obtained for each step, however, for the emissions to air it was possible thanks to online monitoring.

In order to track emissions to air, a specific boundary, based on availability of emission measurement points are defined. Figure 6.2 shows groups of boundaries that categorize these emission points to air. The Blue boundary contains emissions during digestion, crystallization and filtration. Neutralization and evaporation are included in the Green boundary and particulation is considered in the Purple boundary.

The emissions analyses output is mostly in [kg/hr] unit at Yara Porsgrunn monitoring system (PIMS) with possibility to export hourly data to an excel file. Thus, total yearly emission and from that, emission per ton of an NPK product[1] could be calculated.

In any case that the total yearly emission figure could not be calculated from the exported excel file, an average value has been considered for each emission type from each emission point. NPK plant #3 has worked 88.8% of the year or almost 7778 hours. So, the total emission could be calculated in kg or tons.

In the Blue boundary one more assumption should be considered. Some part of the total emissions in this boundary must be allocated to Ca crystals. $P - rock_{CN}$ and $P - rock_{NPK}$ were calculated in the previous section and their weight ratio will be used for true emission allocation. For the carbon dioxide emissions carbon content of the P-rock was considered for the calculation.

[1] Many different types of products were produced in 2022 in Yara Porsgrunn as listed and marked for NPK plant #3 in Appendix B.

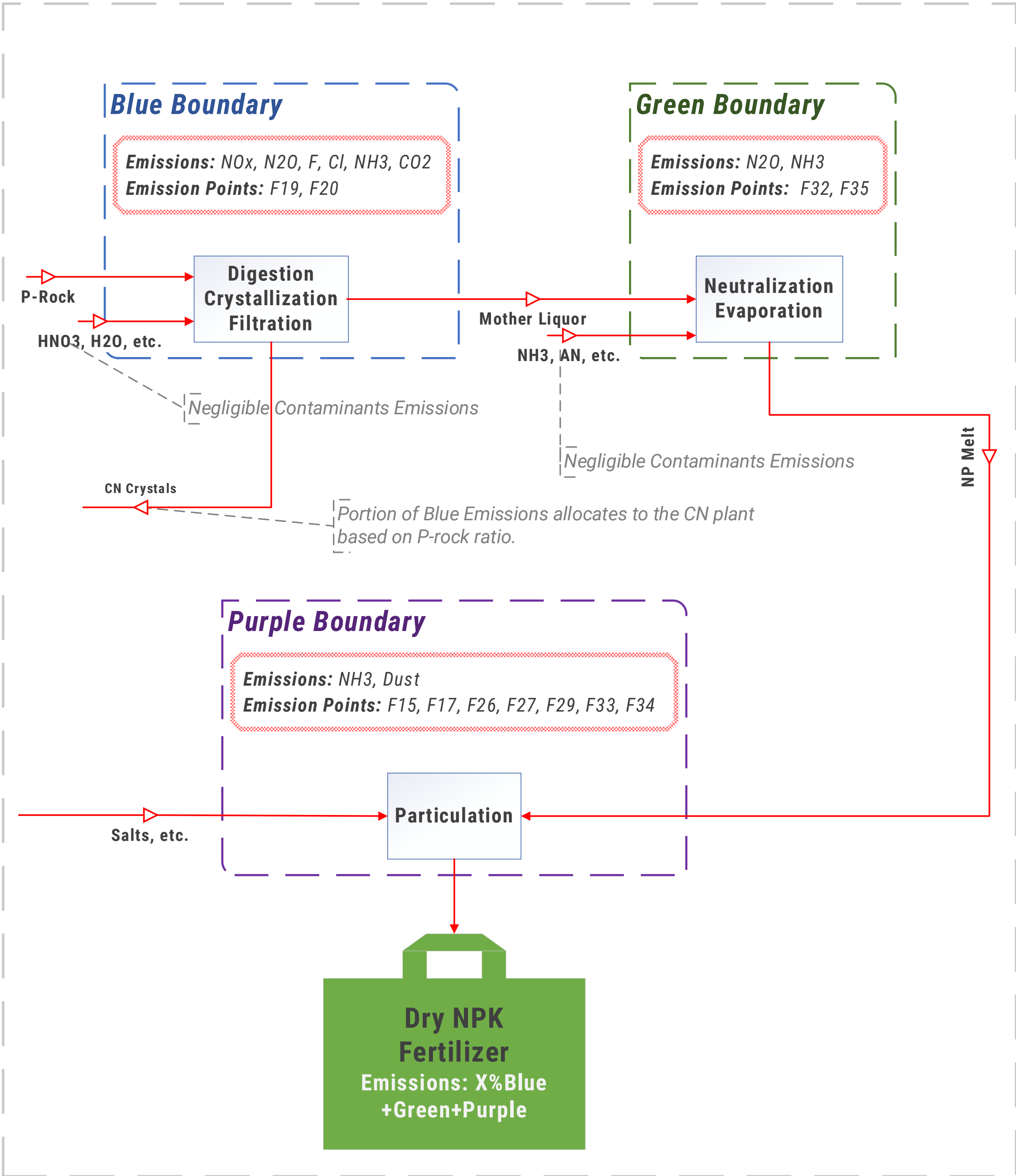


Figure 6.2: Boundary limit for conventional emissions.

6.3.2 Heavy Metal (HM) Emissions

Calculation of heavy metal emissions from NPK fertilizer production are based on prior work. The main assumption in their work was based on earlier studies [75] showing that heavy metals in raw materials mainly follow the phosphorus in the NPK/CN production.

A group of researchers performed several theoretical assessments [76] in 2002 which was updated by others in 2018 based on similar principles [5].

Current work uses the same methodology for calculating the heavy metal emissions based on different raw materials input in the process unit. Mercury (Hg), Copper (Cu), Arsenic (AS), Chromium (Cr), Nickel (Ni), Zink (Zn), Cadmium (Cd), and Lead (Pb) emissions can be calculated using this methodology [5].

For the heavy metals a different methodology and boundary limit is needed. Figure 6.3 depict this boundary limit clearly. Since a high portion of heavy metals are originated from solid raw materials, other inlets are not shown[1].

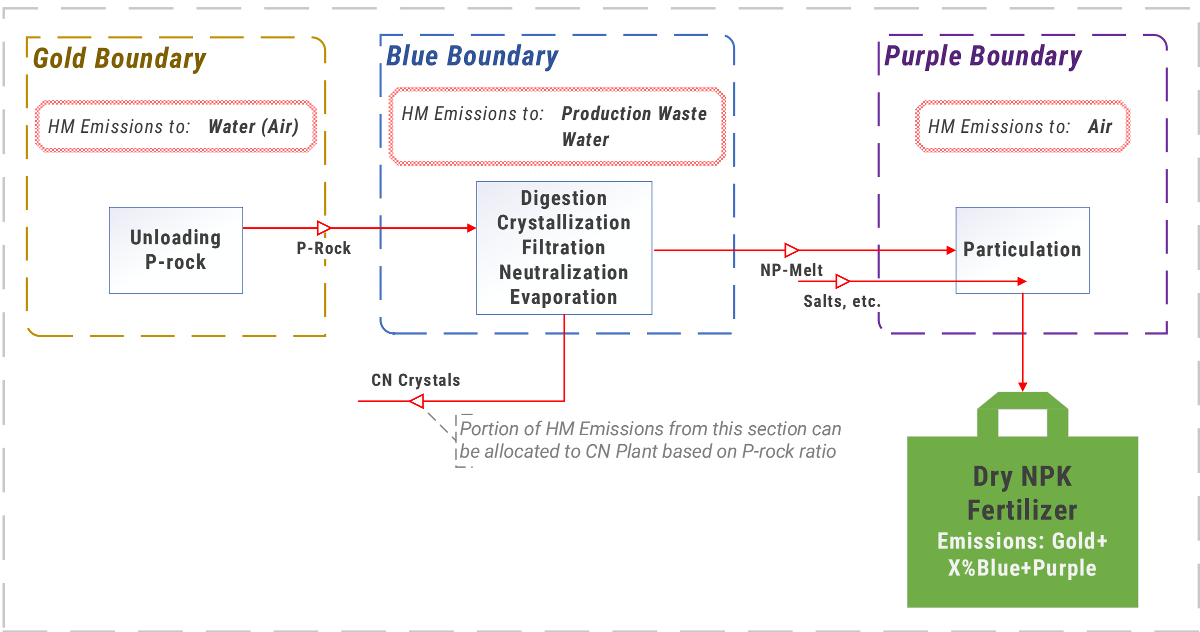


Figure 6.3: Boundary limit for heavy metal emissions.

Table 6.2 shows heavy metals concentration in different types of P-rocks, salts and dolomite.

[1] Raw water used for process and cooling water in NPK production is taken from Norsjø. Heavy metals contents in the raw water are in the scale of the $\mu g/l$ based on data from NGI (The Norwegian Geotechnical Institute). They are not considered in the calculations since the added heavy metal emissions from solid materials are important based on this study assumptions.

Table 6.2: Average heavy metal concentrations in mineral sources [5].

Element	Unit	Youssofia	Kola	Siilinjärvi	MOP	SOP	Dolomite
Hg	**mg/kg**	0.005	0.005	0.005	0	0.001	0.001
Cu	**mg/kg**	25	32	14	0.64	0.41	0.2
As	**mg/kg**	5.5	0.15	1.1	0.02	0.05	0.27
Cr	**mg/kg**	170	0.8	1.3	0.06	0.04	0.04
Ni	**mg/kg**	30	1.8	2.7	0.16	8.8	0.9
Zn	**mg/kg**	220	17	7.2	1.5	2.5	6
Cd	**mg/kg**	9.7	0.05	0.1	0.02	0.04	0.06
Pb	**mg/kg**	2.6	2.8	10	1.4	1.4	0.9

6.3.2.1 Raw Material Unloading Emissions

As shown in Figure 6.3, heavy metal emissions start from the unloading stage (Gold boundary). Raw potassium and phosphate salts are delivered by ship and discharged at the quay into the site's available raw material storage tanks. In order to unload raw materials, bucket cranes are employed.

Figure 6.4 shows the unloading locations. About two-thirds of the unloading occurs by the deep-water quay (1), with the remaining one-third occurring from the main quay (2). The raw material is then transported to the allocated bunkers via subsequent conveyor belts.

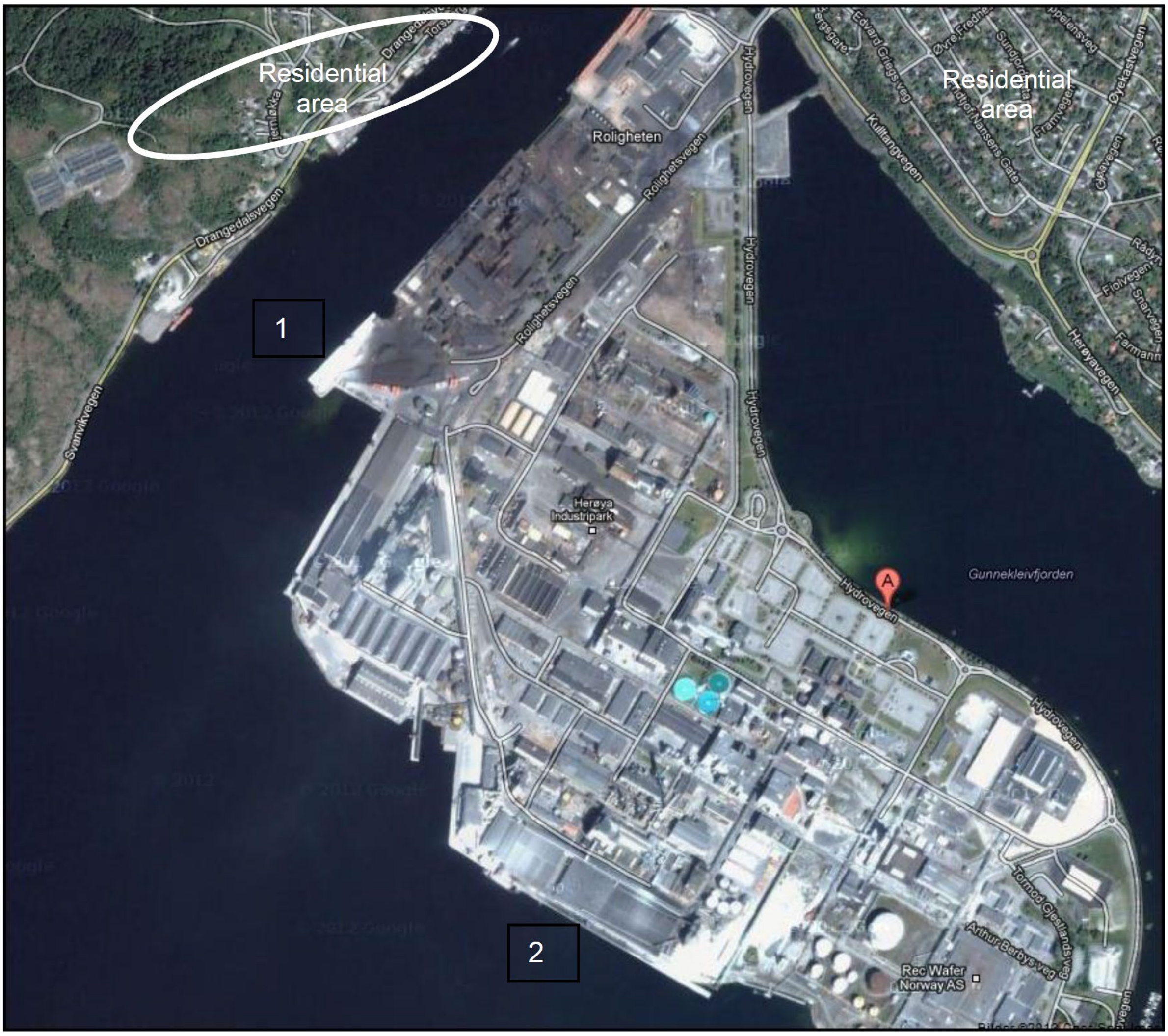


Figure 6.4: Herøya Industry park, with Yara Porsgrunn production plant and deep water quay (1) and main quay (2) [5].

The air will be exposed to particles at this stage. Moreover, some of the particles will land on the quay area's concrete which will be collected, and the area will be washed afterwards.

As stated before, for calculation of heavy metal emissions, the composition of the particles released into the air and water is expected to be the same as the composition of the raw materials.

Nonetheless, it should be emphasized that the majority of dust emissions during unloading are likely to end up in the sea near the quay. Theoretically, all emissions from offloading might be categorized as emissions to water.

Formula (6.15) and (6.16) are used for calculating heavy metal "i" emissions to air (HM_i^{air}) and water (HM_i^{water}) during unloading. In these formulas "j" and "k" indicate P-rock and Salts (additives) types respectively, and W is the total mass of raw material type j or k that has been unloaded while x_i indicates fraction of the heavy metal type i in the raw material type j or k.

From the experiments a specific emission factor for air and water (SP^{air} and SP^{water}) can be found for each type of raw materials. These values are available from previous works by Yara team [5].

$$HM_i^{air} = \sum_j SP_j^{air} \cdot W_j \cdot x_{i,j} + \sum_k SP_k^{air} \cdot W_k \cdot x_{i,k} \tag{6.15}$$

$$HM_i^{water} = \sum_j SP_j^{water} \cdot W_j \cdot x_{i,j} + \sum_k SP_k^{water} \cdot W_k \cdot x_{i,k} \tag{6.16}$$

6.3.2.2 Emissions to Water during Production

Emissions to water are mostly seen in the wet part of the NPK manufacturing based on nitrophosphate process before salts are added. However, there are some wash water from subsequent processes that are recycled back into nitrophosphate process section and conservatively we can assume that it has 10% of the heavy metals in the salts [5].

Formula (6.17) is used for calculating heavy metal "i" emissions to water (HM_i^{water}) during production. In this formula "j" and "k" indicate P-rock and Salts (additives) types respectively; and W is the total mass of raw material type j or k that has been used while x_i indicates fraction of the heavy metal type i in the raw material type j or k.

From the experiments a specific emission factor to water during production (SP_P^{water}) can be estimated. Correction factors (CF_i^{water}) are added based on a sampling and analysis effort to compensate for divergence from the theoretical assumption that the heavy metal to P ratio in prills and prill dust is equal. Both SP and CF values are available from previous works by Yara team [5].

$$HM_i^{water} = SP_P^{water} \left(\sum_j (W_j \cdot x_{i,j}) + 0.1 \cdot \sum_k (W_k \cdot x_{i,k}) \right) \cdot \mathrm{CF}_\mathrm{i}^{\mathrm{water}} \tag{6.17}$$

6.3.2.3 Emissions to Air during Production due to the Prilling and Conditioning

It is presumable that dust from the prilling and finished product lines in the NPK manufacture emits heavy metals into the atmosphere.

$$\begin{aligned} HM_i^{air} = {} & SP_P^{air,Prill} \left(\sum_j (W_j \cdot x_{i,j}) + \sum_k (W_k \cdot x_{i,k}) \right) \cdot \mathrm{CF}_\mathrm{i}^{air,Prill} \\ & + SP_P^{air,Finish} \left(\sum_j (W_j \cdot x_{i,j}) + \sum_k (W_k \cdot x_{i,k}) \right) \cdot \mathrm{CF}_\mathrm{i}^{air,Finish} \end{aligned} \tag{6.18}$$

Formula (6.18) is used for calculating heavy metal "i" emissions to air[1] (HM_i^{air}) during production. In this formula "j" and "k" indicate P-rock and Salts (additives) types respectively; and W is the total mass of raw material type j or k that has been used while x_i indicates fraction of the heavy metal type i in the raw material type j or k.

From experimental data, a specific emission factor to air during production (SP_P^{air}) can be estimated. Correction factors (CF_i^{air}) are added based on a sampling and analysis effort to compensate for divergence from the theoretical assumption that the heavy metal to P ratio in prills and prill dust is equal. Both SP and CF values are available from previous works by Yara team [5].

6.3.2.4 Emissions to Waste during Production

The methodology for calculating this part is similar to what we saw in formula (6.17). However, due to the confidentiality although it has been calculated, it is not considered in the LCA.

6.3.3 Emissions Figures

For the monitored and calculated emissions figures, please see Appendix D and E.

6.4 Steam, Electricity, and Water Usage for the NPK Production

As these data might be different from one plant to another, plant-based discussions for the consumptions are made in Appendix F.

[1] For air emissions usually Cu, Ni, and Zn are not considered. I did not find any clear reason for this. But it might be from regulations.

7 Results and Discussion

The modeling process used to analyze data and derive insights is presented in Appendix H. Three processes were defined i) NP 20-10 liquor (includes Digestion, Crystallization, Separation, and Neutralization steps), ii) NP 20-10 melt (includes Evaporation stage), and iii) NPK 20-10-10 (potassium addition and particulation). Product life cycle assessment is done and then it is delved into the results obtained from the analysis, highlighting key findings and trends. and discussing based on findings.

7.1 A Complete Product Life Cycle

Calculation based on one ton of NPK or equivalent P_2O_5 makes comparisons challenging since the amount of harmful substances emitted to the environment due to the one ton NPK production are not big. It has already been discussed that harmful substances originate mainly from phosphate rock. And it was reported that in 2021 almost 50,000 tons P_2O_5 was produced[1] in the NPK plant #3. Considering all 50,000 tons of P_2O_5 as a reference NPK 20-10-10, the equivalent of 500,000 tons can be calculated.

Figure 7.1 shows network diagrams for each process involved in the NPK 20-10-10 production. The main reason for bringing this figure is to show how vast and interconnected this network can be. Figure 7.2 shows the same network with higher cut-off value.

[1] For details see Appendix B.

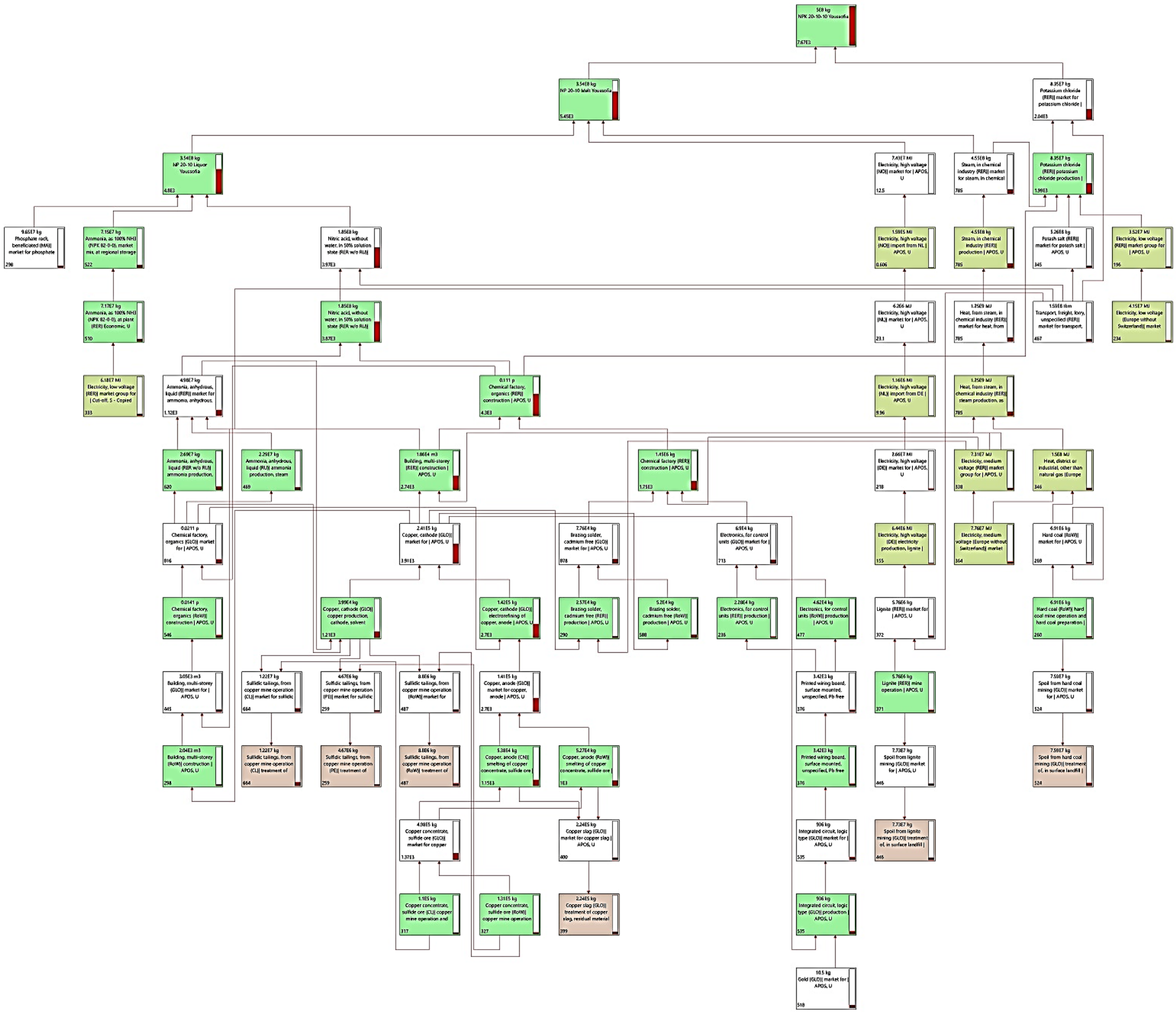


Figure 7.1: Inspecting the results of modeling; the life cycle overview for NPK 20-10-10 production from Youssofia P-rock (cut-off 3%).

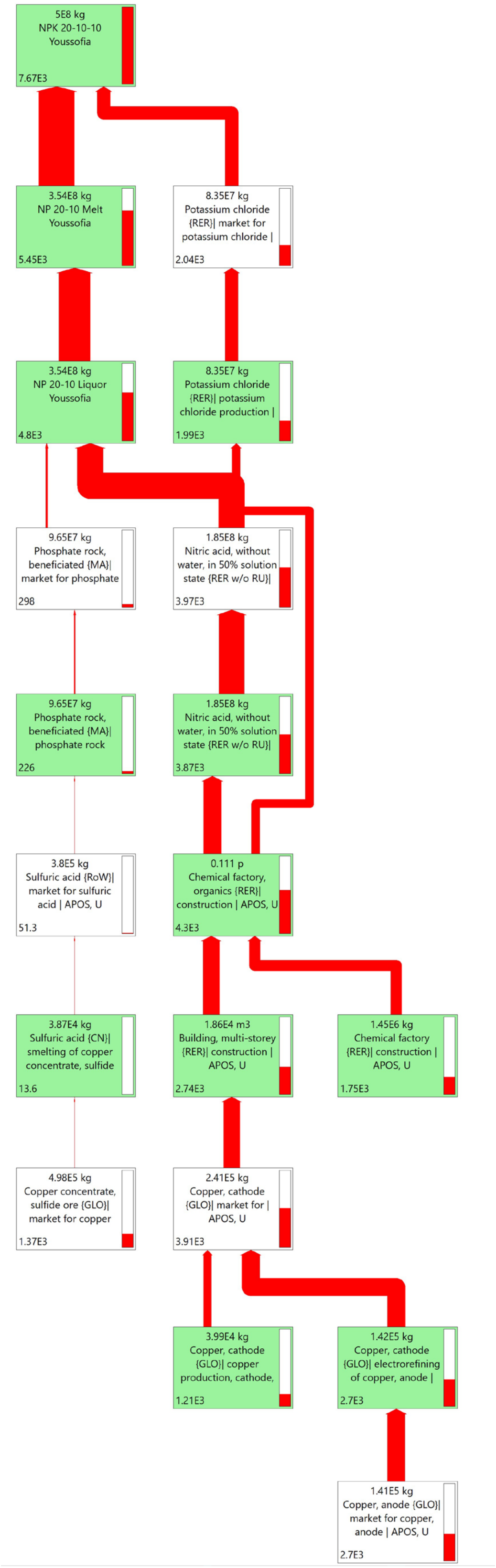


Figure 7.2: Human noncarcinogenic toxicity- process contribution network diagram for NPK 20-10-10 production from Youssofia P-rock (cut-off 15%).

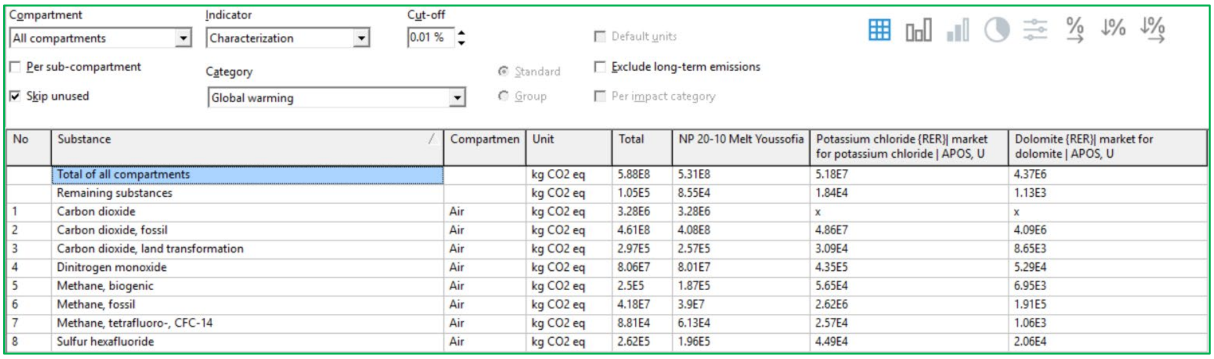
Line weight in Figure 7.2 shows the effect of different processes while sections with an effect of less than 15% are not shown (cut-off). It was predictable that NP Liquor, which involves wet section stages from NPK production, will have the biggest contribution to the impact as line weight shows the same thing. This is because the major sources of emissions are from input material at this step and processes of the wet section of NPK production.

7.1.1 Global Warming Potential Impact Category

This category has been extensively studied in different case studies because it assesses the potential contribution of a product or activity to climate change by measuring its greenhouse gas emissions, typically expressed in terms of carbon dioxide equivalents (CO_2e).

Figure 7.3 shows the contributors list from life cycle assessment for global warming. It shows the total CO_2 equivalent emission to atmosphere for producing 500,000 tons NPK 20-10-10 which is estimated 588,000 tons CO_2e.

SimaPro shows life cycle impact assessment results in a neat way that can be investigated and interpreted better and easier. Figure 7.4 shows that carbon dioxide from fossil fuel and nitrous oxide have the highest contribution in global warming.



No	Substance	Compartmen	Unit	Total	NP 20-10 Melt Youssofia	Potassium chloride {RER}| market for potassium chloride | APOS, U	Dolomite {RER}| market for dolomite | APOS, U
	Total of all compartments		kg CO2 eq	5.88E8	5.31E8	5.18E7	4.37E6
	Remaining substances		kg CO2 eq	1.05E5	8.55E4	1.84E4	1.13E3
1	Carbon dioxide	Air	kg CO2 eq	3.28E6	3.28E6	x	x
2	Carbon dioxide, fossil	Air	kg CO2 eq	4.61E8	4.08E8	4.86E7	4.09E6
3	Carbon dioxide, land transformation	Air	kg CO2 eq	2.97E5	2.57E5	3.09E4	8.65E3
4	Dinitrogen monoxide	Air	kg CO2 eq	8.06E7	8.01E7	4.35E5	5.29E4
5	Methane, biogenic	Air	kg CO2 eq	2.5E5	1.87E5	5.65E4	6.95E3
6	Methane, fossil	Air	kg CO2 eq	4.18E7	3.9E7	2.62E6	1.91E5
7	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	8.81E4	6.13E4	2.57E4	1.06E3
8	Sulfur hexafluoride	Air	kg CO2 eq	2.62E5	1.96E5	4.49E4	2.06E4

Figure 7.3: Inventory (LCI) results window in SimaPro after doing the assessment for 500,000-ton NPK 20-10-10 (cut-off 0.01%, cradle-to-gate).

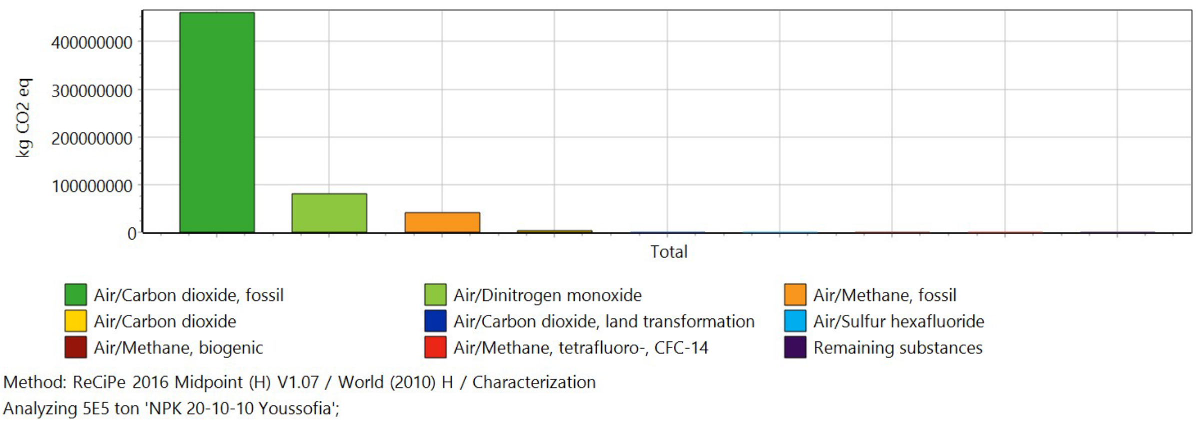


Figure 7.4: Global warming impact assessment and equivalent carbon dioxide emission to the atmosphere during producing 500,000-ton NPK 20-10-10 (cut-off 0.01%).

7.1.1.1 NPK 20-10-10 Product Carbon Footprint

As mentioned, the estimated carbon dioxide equivalent (CO_2e) emissions to the atmosphere resulting from the production of 500,000 tons of NPK 20-10-10 is a total of approximately 588,000 tons CO2e. So, 1.175 $tCO_2e/tNPK$ can be calculated. This is called a product carbon footprint.

The product carbon footprint is often determined through a life cycle assessment (LCA) methodology by cradle to gate perspective. Fertilizer producers usually use Fertilizer Europe's (FEU)[1] calculator and methodology for estimating their products carbon footprint [77]. product carbon footprint for NPK 20-10-10 from Yara Porsgrunn calculated by FEU calculator is equal to 0.727 (2019 vintage).

The reason for this difference has been investigated and the following issues could be found.

- Ecoinvent data in SimaPro for Nitric Acid is not site specific and it gives in the best case an average for European fertilizer plants. While in Yara-Porsgrunn, the Nitric Acid plant has been optimized significantly during last decade and has more than 33% less global warming potential. It has the highest impact in the product carbon footprint deviation since almost 37% of NPK 20-10-10 is nitric acid.
- Ecoinvent data in SimaPro for the imported potash is not site specific and it is from European average with has more than 70% less global warming potential. It has a high impact in the product carbon footprint deviation since almost 17% of NPK20-10-10 is potash.
- The steam emission factor from Yara Porsgrunn plant is much lower (~60%) than an average emission factor for European counties reported in the ecoinvent database.

Considering all these deviations, the total carbon footprint result from SimaPro can be declined from 1.175 to 0.840 $tCO_2e/tNPK$ which is closer to the 0.727 $tCO_2e/tNPK$ figure from FEU calculator.

7.1.2 Influenced Categories

Results of the characterization step are shown in Figure 7.5. All impact scores are displayed on 100% scale and the colors indicate the contribution of different steps. It is clear from this figure that the wet section has the highest contribution. This could be expected since the wet section has the high amount of raw materials, emissions and most effective production stages inside.

[1] Fertilizers Europe represents the interests of the majority of mineral fertilizer manufacturers in the European Union. Fertilizers Europe has created a Carbon Footprint Calculator (CFC) and a methodology for estimating direct and indirect GHG emissions associated to the manufacture of certain fertilizer products in an effort to reduce the carbon footprint of the fertilizer industry.

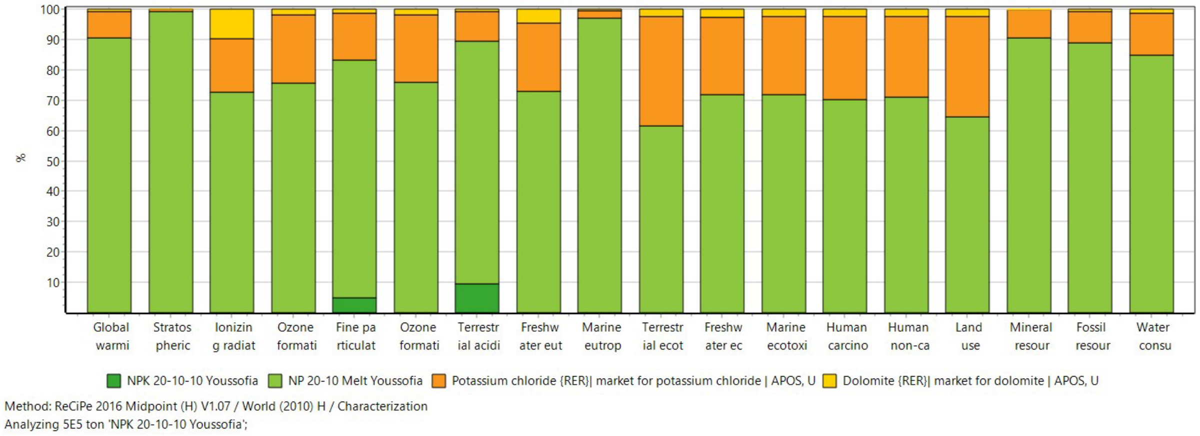


Figure 7.5: Inventory and impact assessment results.

Characterized results in Figure 7.5 do not help in understanding the magnitude of the final effect on different impact categories. Figure 7.6 shows that production of equivalent NPK 20-10-10 in 2022 has the highest impacts on following three categories.

1. Human carcinogenic toxicity
2. Freshwater ecotoxicity
3. Marine ecotoxicity

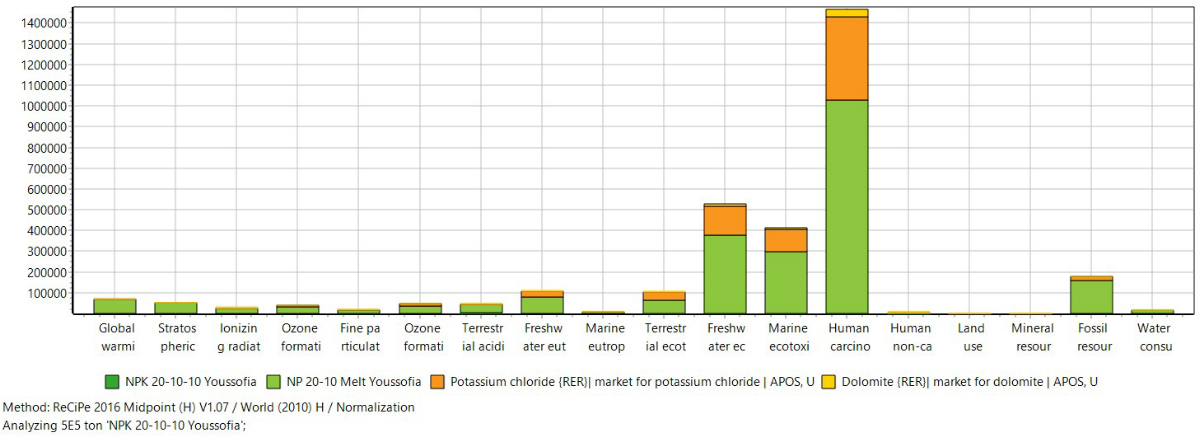


Figure 7.6: Normalized impact assessment results. The single score (Pt) is calculated by applying a weighting factor of each impact category to normalize the score of damage assessment.

These three categories together with some other impact categories are described in the next part. But they have an identical unit and Recipe method uses “kg 1,4-DCB” (kilograms of 1,4-Dichlorobenzene) unit for them. The unit “kg 1,4-DCB” refers to the use of 1,4-Dichlorobenzene (1,4-DCB) as a reference substance for comparison. In other words, the amount of a substance required to cause the same Potentially Affected Fraction (PAF) as 1 kilogram of 1,4-DCB.

By exploring each of these three categories it can be found which substance is impacting more. Figure 7.7 shows that chromium VI, Nickel and Arsenic emissions to water and air have the highest impacts. However, it is important to know that Water/Chromium VI has 97% influence in this part.

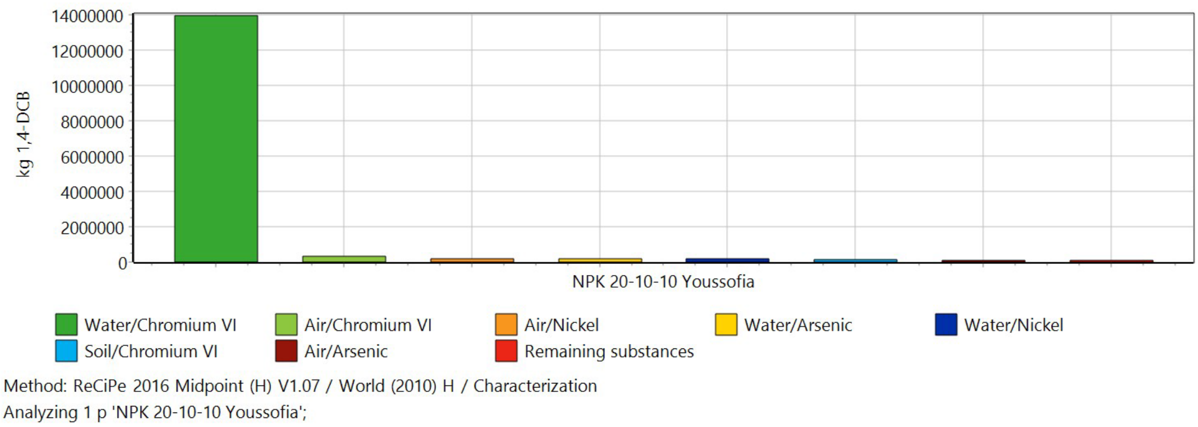


Figure 7.7: Characterized results for contributors in Human Carcinogenic category while blending 500,000 tons NPK 20-10-10.

Figure 7.8 shows that zinc and copper emission to water have the highest contribution in freshwater ecotoxicity similar to what can be understood from Figure 7.9 for Marine ecotoxicity.

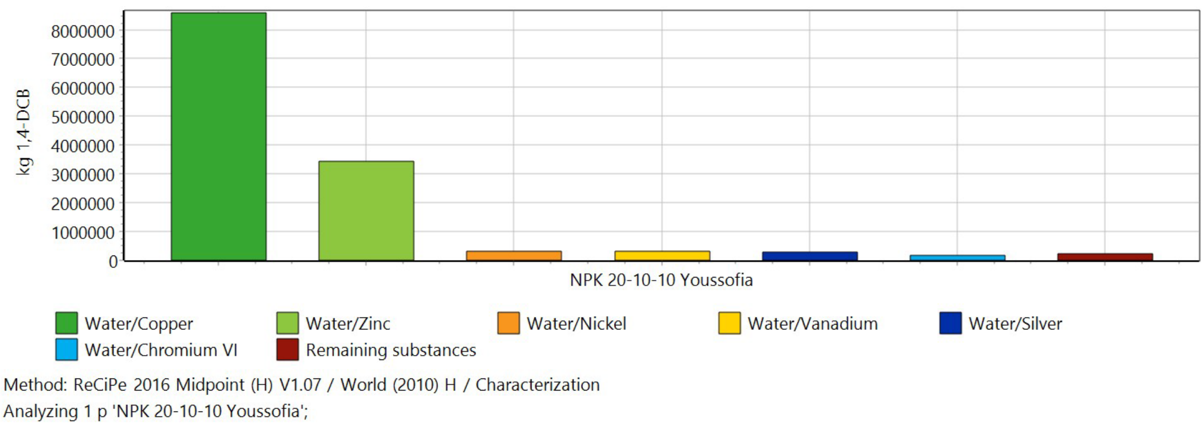


Figure 7.8: characterized results for contributors in Freshwater ecotoxicity category while blending 500,000 tons NPK 20-10-10.

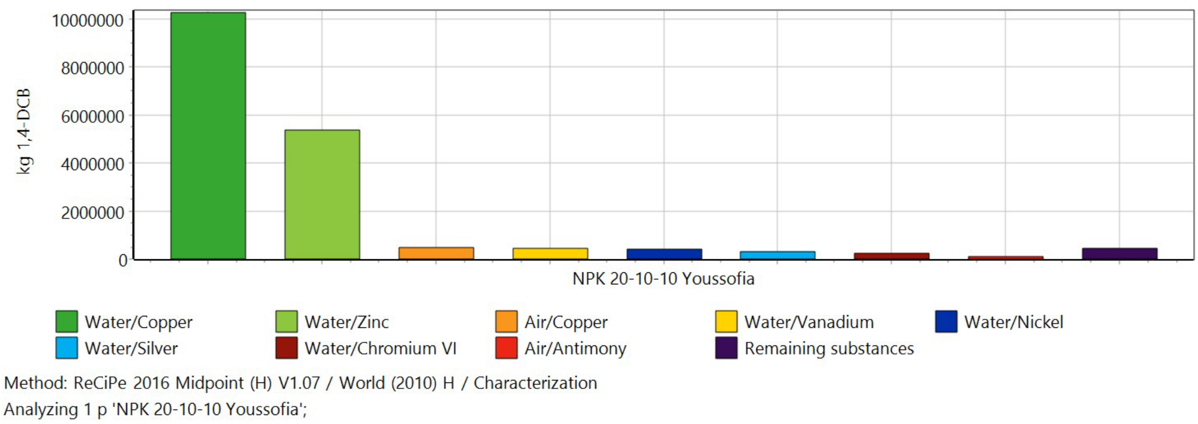


Figure 7.9: characterized results for contributors in Marine ecotoxicity category while blending 500,000 tons NPK 20-10-10.

7.1.2.1 Mostly Influenced Categories by Heavy Metals

The focus in this thesis is understanding the effects of heavy metal emissions during production. Heavy metal emissions during production are less than 1.1 % of total heavy metal content in raw materials (see Appendix E for details), therefore most of it will end in the final product. So, it is hard to follow heavy metal emissions impacts from production stages. Thus, two similar cases were defined one without heavy metal emissions and the other with heavy metal emissions figures calculated in section 6.3.2.

Table 7.1 shows a comparison of standardized results for these two cases. Standardization is done by SimaPro's automatic normalization of the values and relative weighting of the different impact categories. Any difference in results for these two cases can be expected as the effect of heavy metals emissions during production. Impacts are in the following categories. These categories have been described briefly in Table 3.2 but will be repeated here again.

- Terrestrial, Marine and Freshwater ecotoxicity: this aims to understand the potential risks posed by chemicals or substances released into the soil through various activities, such as industrial processes, agricultural practices, or waste disposal. It considers both direct toxicity to organisms living in the soil and indirect effects on higher trophic levels through the food chain. Substances with high ecotoxicity potential can disrupt soil functions, such as nutrient cycling, water retention, and biological activity. The effects of substances on terrestrial organisms can contribute to biodiversity loss in affected ecosystems.
- Human carcinogenic and non-carcinogenic toxicity: they aim to evaluate the potential adverse health effects of substances on human beings. Carcinogenic toxicity assessment focuses on determining the potential of substances to cause cancer in humans. Non-carcinogenic toxicity considers a range of toxicological endpoints, including acute and chronic toxicity, neurotoxicity, reproductive toxicity, developmental toxicity, and other specific health effects.

Table 7.1: LCIA results Comparison for with and without heavy metal emissions (export from SimaPro). All figures are normalized to have an identical similar unit (Pt).

Impact category	NPK 20-10-10 Youssofia	NPK 20-10-10 Youssofia no HM	Difference
Global warming	73,446	73,446	0
Stratospheric ozone depletion	50,949	50,949	0
Ionizing radiation	31,859	31,859	0
Ozone formation, Human health	41,004	41,004	0
Fine particulate matter formation	19,124	19,124	0
Ozone formation, Terrestrial ecosystems	48,623	48,623	0
Terrestrial acidification	49,298	49,298	0
Freshwater eutrophication	110,917	110,917	0
Marine eutrophication	7,339	7,339	0
Terrestrial ecotoxicity	106,253	106,140	113
Freshwater ecotoxicity	528,516	528,504	12
Marine ecotoxicity	414,992	414,955	37
Human carcinogenic toxicity	1,465,442	1,465,415	27
Human non-carcinogenic toxicity	7,662	7,659	3

Table 7.2: LCIA results Comparison for with and without heavy metal emissions (export from SimaPro).

Impact category	Unit	NPK 20-10-10 Youssofia	NPK 20-10-10 Youssofia no HM	Difference
Global warming	kg CO2 eq	587,566,069	587,566,069	0
Stratospheric ozone depletion	kg CFC11 eq	3,051	3,051	0
Ionizing radiation	kBq Co-60 eq	15,316,804	15,316,804	0
Ozone formation, Human health	kg NOx eq	843,694	843,694	0
Fine particulate matter formation	kg PM2.5 eq	489,114	489,114	0
Ozone formation, Terrestrial ecosystems	kg NOx eq	863,635	863,635	0
Terrestrial acidification	kg SO2 eq	2,020,408	2,020,408	0
Freshwater eutrophication	kg P eq	72,024	72,024	0
Marine eutrophication	kg N eq	33,821	33,821	0
Terrestrial ecotoxicity	kg 1,4-DCB	1,614,789,750	1,613,075,778	1,713,973
Freshwater ecotoxicity	kg 1,4-DCB	13,312,749	13,312,442	307
Marine ecotoxicity	kg 1,4-DCB	18,043,114	18,041,522	1,593
Human carcinogenic toxicity	kg 1,4-DCB	15,092,091	15,091,817	274
Human non-carcinogenic toxicity	kg 1,4-DCB	239,431,984	239,338,017	93,967

7.2 Different Phosphate Rocks Usage Effects

Heavy metal emissions depend on the phosphate rock mine because they have different contaminants contents and different emission factors to the environment during unloading (as explained in section 6.3.2).

Figure 7.10 shows total emissions of different heavy metals from unloading to the final production process. As an example, due to the composition and emission factors, Youssofia phosphate rock emit more cadmium (Cd) while phosphate rock from Siilinjärvi pollute the environment with lead (Pb) more. The emissions are at most 1.1 percent of their total content in the phosphate rock. So, it can be assumed that almost all the heavy metals will be transferred into the final product.

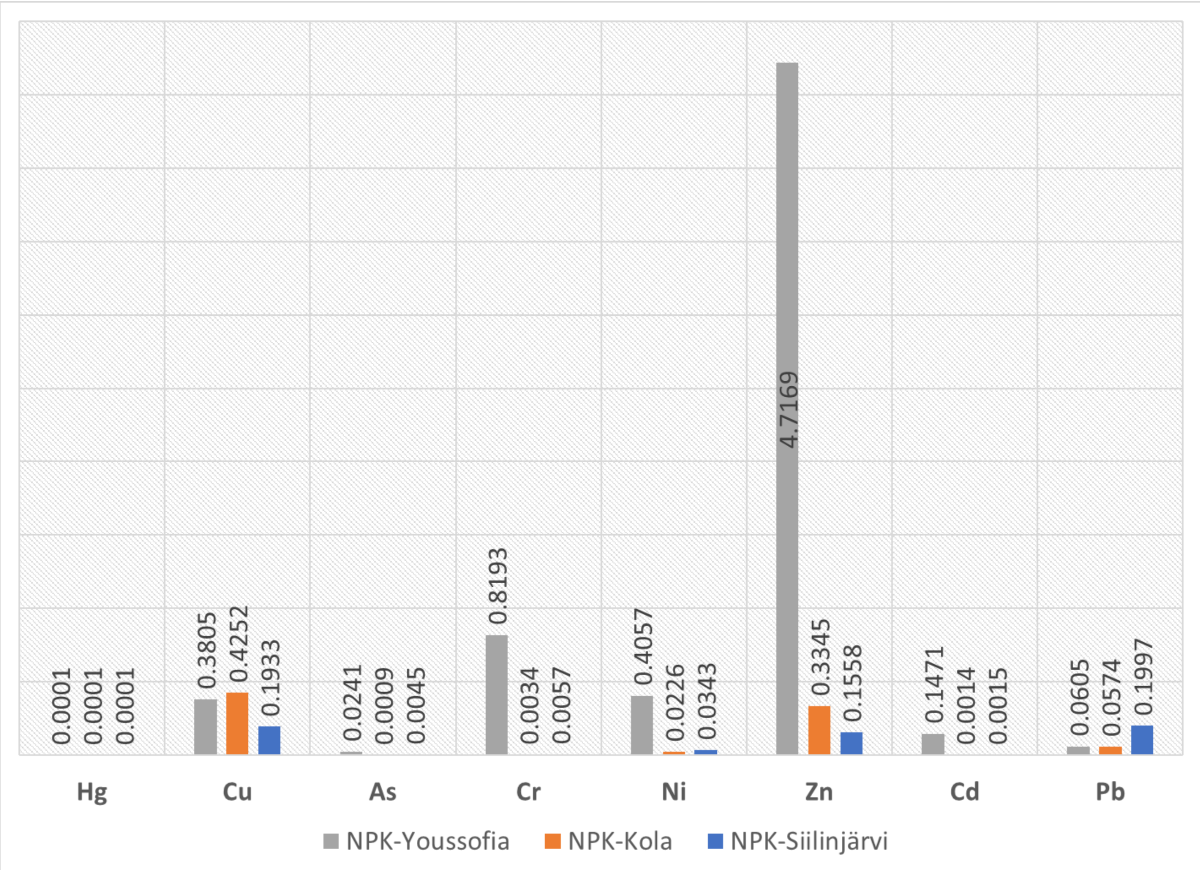


Figure 7.10: Heavy metal emissions during producing NPK 20-10-10 by using different phosphate rocks (milligram of heavy metal emissions to the environment per kilogram of P_2O_5).

Figure 7.11 shows how much heavy metal will remain in the final product. This is calculated by mass balance by subtracting emissions from content of the heavy metals in the raw materials. For critical heavy metals like cadmium (Cd) it can be seen how important raw materials are since NPK produced from Youssofia has much more cadmium in the final NPK 20-10-10.

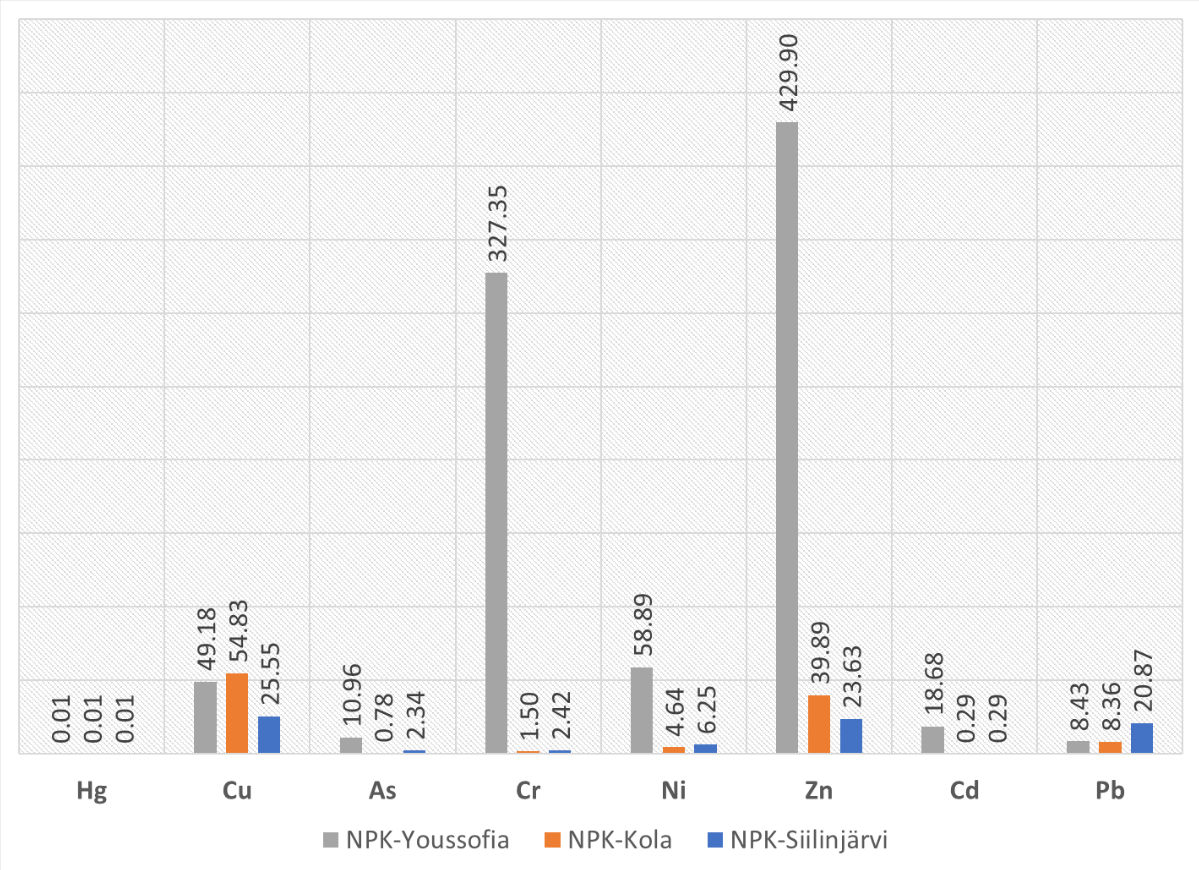


Figure 7.11: Heavy metal content expected to be in the final NPK 20-10-10 product (milligram of heavy metal per kilogram of P_2O_5).

So, specifically in terms of final products heavy metals impacts to the environment, Youssofia phosphate rock is expected to have the higher impact to the environment compared to the Kola and Siilinjärvi phosphate rocks by Cd, Zn, Ni, Cr, and As emissions.

However, from the cradle-to-gate impact assessment perspective, Figure 7.12 and Figure 7.13 show that Youssofia phosphate rock is not more harmful comparing Siilinjärvi and Kola phosphate rocks for many categories.

Table 7.3 and Table 7.4 give details of LCIA impacts on different categories for Siilinjärvi and Kola cases. Negative figures mean that the NPK produced from Youssofia phosphate rock has higher adverse impacts to the environment for that category comparing to the Siilinjärvi or Kola cases.

Figure 7.12: LCIA results comparison for NPK 20-10-10 production from different phosphate rocks.

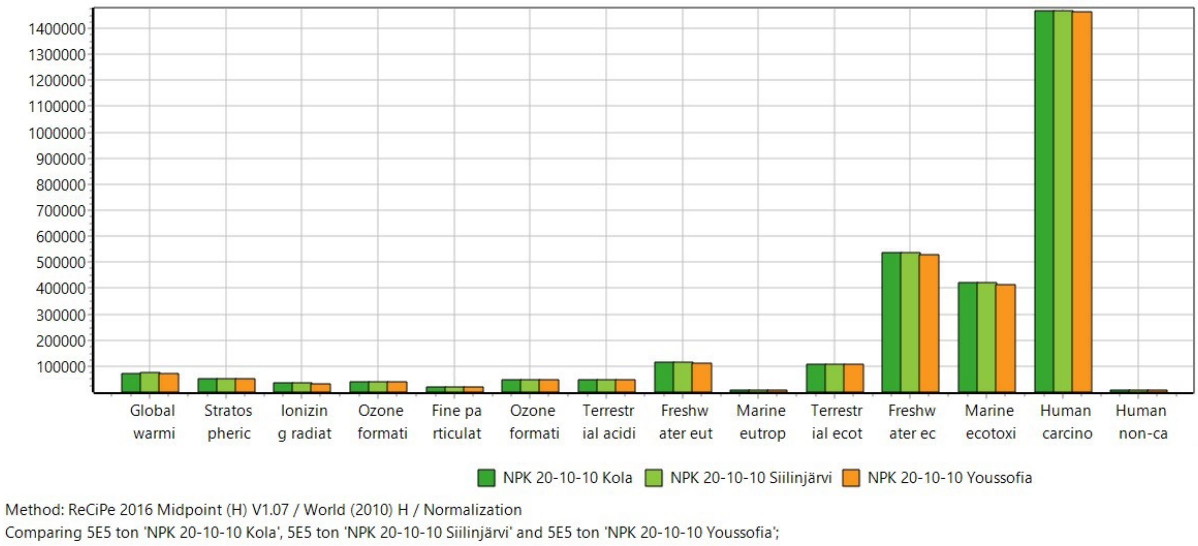


Figure 7.13: LCIA normalized results for NPK 20-10-10 production from different phosphate rocks.

Table 7.3: LCIA results comparison for NPK 20-10-10 production from different phosphate rocks (export from SimaPro).

Impact category	Unit	NPK 20-10-10			
		Siilinjärvi	Siilinjärvi minus Youssofia	Kola	Kola minus Youssofia
Global warming	kg CO2 eq	592,295,596	**4,729,527**	588,054,504	**488,435**
Stratospheric ozone depletion	kg CFC11 eq	3,052	**2**	3,052	**1**
Ionizing radiation	kBq Co-60 eq	16,950,070	**1,633,266**	16,965,272	**1,648,467**
Ozone formation, Human health	kg NOx eq	812,009	**-31,685**	811,840	**-31,854**
Fine particulate matter formation	kg PM2.5 eq	464,278	**-24,836**	464,122	**-24,992**
Ozone formation, Terrestrial ecosystems	kg NOx eq	831,866	**-31,769**	831,689	**-31,947**
Terrestrial acidification	kg SO2 eq	1,991,882	**-28,526**	1,991,414	**-28,994**
Freshwater eutrophication	kg P eq	74,669	**2,645**	74,557	**2,533**
Marine eutrophication	kg N eq	34,526	**705**	34,493	**672**
Terrestrial ecotoxicity	kg 1,4-DCB	1,626,590,593	**11,800,843**	1,626,472,127	**11,682,377**
Freshwater ecotoxicity	kg 1,4-DCB	13,514,571	**201,822**	13,516,877	**204,127**
Marine ecotoxicity	kg 1,4-DCB	18,296,762	**253,648**	18,299,217	**256,102**
Human carcinogenic toxicity	kg 1,4-DCB	15,117,288	**25,197**	15,113,273	**21,183**
Human non-carcinogenic toxicity	kg 1,4-DCB	238,666,905	**-765,079**	238,668,975	**-763,009**

Table 7.4: Normalized LCIA results comparison for NPK 20-10-10 production from different phosphate rocks (export from SimaPro).

Impact category	NPK 20-10-10			
	Siilinjärvi	Siilinjärvi minus Youssofia	Kola	Kola minus Youssofia
Global warming	74037	591	73507	61
Stratospheric ozone depletion	50974	25	50973	24
Ionizing radiation	35256	3397	35288	3429
Ozone formation, Human health	39464	-1540	39455	-1548
Fine particulate matter formation	18153	-971	18147	-977
Ozone formation, Terrestrial ecosystems	46834	-1789	46824	-1799
Terrestrial acidification	48602	-696	48590	-707
Freshwater eutrophication	114991	4073	114818	3900
Marine eutrophication	7492	153	7485	146
Terrestrial ecotoxicity	107030	776	107022	769
Freshwater ecotoxicity	536528	8012	536620	8104
Marine ecotoxicity	420826	5834	420882	5890
Human carcinogenic toxicity	1467889	2447	1467499	2057
Human non-carcinogenic toxicity	7637	-24	7637	-24

7.3 Accumulation

The results obtained indicate that heavy metal emissions to air, water, and soil comprise less than approximately 1.1% of heavy metals content in the raw materials. This percentage may vary for different principal heavy metals, suggesting that the contribution of heavy metals to the overall emissions is relatively small.

While the individual emission figures may not be substantial, it is important to consider the potential consequences of long-term accumulation of heavy metals in the vicinity of the production area. Heavy metals are known for their toxic properties and can pose risks to both the environment and human health. Even at low levels, persistent exposure or accumulation of heavy metals can lead to adverse effects over time.

It has been discussed that heavy metal emissions and their potential impacts are regulated by environmental standards and guidelines and compliance with these regulations and the implementation of best practices for emissions control and management can help minimize the potential adverse effects of heavy metal accumulation in the long term. Based on this production plant area is tested for accumulated emissions on a yearly basis.

8 Conclusion and Further Work

The fertilizer industry is facing increasing complexity due to evolving regulations, environmental concerns, customization demands, technological advancements, market dynamics, and the need for ongoing research and innovation. Adapting to these challenges and staying ahead of the curve is essential for companies operating in this sector.

Current and upcoming regulations and European directives are explained in detail in this work. Regulations regarding contaminants amounts in NPK fertilizers or their production processes can be influenced by various factors such as scientific research, environmental concerns, health considerations, and evolving agricultural practices. Over time, regulations tend to become more stringent to ensure the safety of agricultural practices and protect the environment. Governments and international organizations often set limits on the allowable levels of heavy metals in fertilizers to prevent their accumulation in soil, crops, and ultimately the food chain. These limits aim to safeguard human health and minimize environmental contamination.

Advancements in analytical techniques and monitoring capabilities may lead to more accurate detection and measurement of heavy metals, prompting regulatory bodies to adjust the limits accordingly. Additionally, emerging scientific studies and evidence on the potential risks associated with certain heavy metals may influence regulatory decisions.

It is important to note that mitigation techniques should be implemented in conjunction with adherence to relevant regulations and standards established by governmental authorities or international organizations. Additionally, local conditions and specific requirements may influence the choice and effectiveness of these techniques. A classification of heavy metal mitigations techniques is listed in this work.

Life Cycle Assessment (LCA) is a valuable tool for the fertilizer industry to assess and improve the environmental performance of their products and processes. To perform a life cycle assessment for an industrial plant, it is crucial to have a clear understanding of the main processes involved. This study has provided a comprehensive explanation of these processes, which serves as a foundation for conducting a thorough LCA.

Nevertheless, for considering heavy metals emissions impacts it is needed to estimate their emissions in the first place. Heavy metal emissions during the fertilizer production process can be theoretically estimated and calculated using Yara's internal methodology.

The findings derived from the analysis reveal that the emissions of heavy metals into the air, water, and soil during the fertilizer production process amount to less than approximately 1.1% of the heavy metal content present in the raw materials. It is important to note that this percentage is subject to variation based on the specific heavy metal under consideration. Consequently, the outcomes suggest that heavy metal contributions to the overall emissions remain relatively minor in magnitude.

LCIA has shown that by ignoring/addition of heavy metal emissions to air and water, Terrestrial ecotoxicity, Freshwater ecotoxicity, Marine ecotoxicity, Human carcinogenic toxicity, and Human non-carcinogenic toxicity impact categories are affected.

In this study, the Global Warming Potential (GWP100) result obtained from the Life Cycle Impact Assessment (LCIA) analysis, specifically up to the factory gate, shows a resemblance to the product carbon footprint calculated using the Fertilizer Europe Methodology. By accounting for and subtracting major differences in primary and secondary data, the findings indicate a good alignment in the assessment of the greenhouse gas.

The following aspects are recommended for further study or improvement in future research:

- Considering the minimal levels of heavy metal emissions during NPK production processes, the primary impacts are anticipated to occur at the farm level. Thus, it is strongly advised to conduct a more comprehensive life cycle assessment such as cradle-to-grave to obtain a thorough understanding of the exercise's implications.
- The Yara Porsgrunn plant is an integrated facility that encompasses various stages of production, including ammonia production, nitric acid plant, and NPK plant. However, due to the complexity of modelling three plants and time limitations, real-time data for ammonia and nitric acid plants were not incorporated. Instead, for ammonia and nitric acid inputs, the SimaPro database for the Region Europe (RER) was utilized.
  Although the exclusion of real-time data for ammonia and nitric acid plants does not directly impact the investigation of heavy metals, it is recommended to further enhance the model by incorporating actual data from these two plants. This addition would enable a more comprehensive analysis, considering the effect of real-time data on other impact categories beyond heavy metals.
- While heavy metal emissions during the production process may not be intensive, their accumulation over the years can be significant and warrants investigation. Understanding the long-term implications of heavy metal accumulation is crucial for addressing potential risks, implementing effective mitigation measures, and ensuring sustainable practices in order to minimize the potential adverse effects on the environment and human health.
- Yearly average emissions have been used in this work. However, there has been a recent realization that it is possible to precisely track production time and assess conventional emissions and raw materials during specific periods. This capability allows for the utilization of time and product-specific data in Life Cycle Impact Assessment (LCIA). By incorporating this approach, a more accurate analysis of the environmental impact can be achieved.

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Appendices

Appendix A Project Description

University of
South-Eastern Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Life cycle assessment of an NPK fertilizer production with the focus on principal harmful substances.

USN supervisor: Main supervisor: Marianne S. Eikeland,
Co-supervisor: Gamunu Samarakoon Arachchige

External partner: Yara International, Energy & Environment Department
External Supervisor: Stephane Bungener

Task background:
Yara has been calculating emissions footprint of its products aiming to delivered to customers Environmental Product Declarations (EPD). In this respect, the carbon footprint of its products for 10 years has already been calculated and are verified by 3rd party auditors and are delivered to customers as a part of the product package. Customers make use of this information for their GHG accounting and product carbon footprint calculations. While the carbon footprint is still a voluntary declaration by Yara, it is believed that it will eventually become a mandatory declaration due to regulations, stakeholder pressure and higher standards.
Yara wants to pay attention to other potentially harmful substances which will also be included in EPD in the years to come. Thereby, the company is to investigate

- Methodologies to calculate the life cycle impact of harmful substances on Yara NPK products
- Hotspots of harmful substances and technical solutions towards avoiding them

LCA: Life cycle assessment (LCA) is described as a holistic approach to identifying the environmental consequences of a product, process, or activity through its entire life cycle and to identifying opportunities for achieving environmental improvements. Industries/organizations are focusing on measuring and reducing emissions from their operations due to many reasons. Some of the reasons are ethical responsibilities, identifying and analysing the financial costs and benefits of environmental actions by the organization, and environmental regulations which are becoming increasingly demanding.

Task description:
The objectives of the master's thesis are to calculate the life cycle footprint at the factory gate of a typical NPK grade (e.g. NPK 15×3). The LCA must cover key harmful substances facing stricter regulations in medium term (~2030). To accomplish this, the following tasks are proposed:

- Literature review of harmful substances stemming from the fertilizer industry, and relevant regulations
- Literature review of modelling approaches for LCA in the fertilizer industry or similar process industries
- Identification of "Cradle to factory gate" impact of harmful substances for an NPK product
- LCA Modelling of NPK production process and consequential upstream processes.
- Identification of mitigation techniques to reduce harmful substance use and the impact
- A high-level assessment of costs and requirements (Optional)
- Discussion on the next steps for Yara and the systemization of methodologies and calculations to other products and plants

Student category: EET, EPE, IIA or PT students (reserved to Mohammad Hesan)

Is the task suitable for online students (not present at the campus)? Yes

Practical arrangements:
SimaPro and the Ecoinvent database are the tool of choice for LCA in Yara. The relevant process descriptions, production and emission data are available by Yara.

Supervision:
As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

Signatures:

Supervisor (date and signature): 03.02.23 Marianne S. Eikeland

Student (write clearly in all capitalized letters): MOHAMMAD HESAN

Student (date and signature): 31-Jan-2023 Mohammad Hesan