Possibilities and opportunities for recovery of nutrients other than phosphorus

An exploratory research

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Abstract

This study is an investigative research into the opportunities and possibilities for the recovery of nutrients excluding phosphorus. This research was commissioned by the Dutch Ministry of Infrastructure and Environment in connection with the Circular Economy policy document ‘Netherlands Circular 2050’. In our report we identify priority nutrients and study the possibilities for their recovery.In this study a long list of nutrients was narrowed down to the following shortened list: Boron, Cobalt, Copper, Potassium, Molybdenum, Selenium and Zinc.

We mapped several waste chains with their nutrient concentrations and have also described the composition of waste streams containing nutrients. The largest waste streams containing the prioritized nutrients are: sludge from WWTP’s (waste water treatment plants), ash from sludge WWTP’s and ash from MSWI (municipal waste incineration). We also created a framework for nutrient recovery strategies based on the flow properties, nutrient concentration and contamination. Nineteen (19) technologies were investigated to determine suitability for nutrient recovery and were matched to promising waste streams and the nutrients which can be recovered with them. Finally, the technologies were evaluated on technology readiness level (TRL), economic feasibility, and existence of restricting regulations of end products. All 19 technologies investigated are capable of producing end products with a potential demand. Almost half of the technologies have a promising technology readiness level. We propose nine (9) technologies that we recommend for further research in the field of nutrient recovery. This further research varies between TRL, economic feasibility and policy/regulation. Furthermore the legislation on nutrient recovery was briefly evaluated. It was concluded that the Dutch environmental legislation is restricting and complicating technical solutions for applying nutrient-rich flows for agricultural purposes.

We recommend further research for the following nutrient containing waste streams and technologies:

- Direct use of composted sludge, dried sludge and ash from energy wood
- Cleaning of Bioleaching sludge
- Separation of the liquid fraction of the separated digestate from digesters in the sugar industry.
- Separation of zinc, lead, cadmium and copper from fly ash by acid fly ash washing process FLUWA
- Polymer-assisted ultrafiltration (PAUF) for selective separation of tin, copper and nickel, together with recovery of zinc and lead.
- Ecophos process

- Phytoremediation with biomass for energy and recovery of nutrients from the ashes after incineration.

Key words: nutrients, recycling, recovery, circular economy, biobased economy, investigative research, critical nutrients

Contents

Summary

Nutrients are food for life. They are necessary for growth and a healthy life for humans, animals and plants. Soil can naturally contain nutrients or nutrients can be applied to soil in the case of nutrient deficiency. Artificial fertilizer can contain minerals from mined mineral ores. Because most fertilizer ingredients are sourced from mines, a fear of scarcity is present as well as criticism about the environmental impact of mining primary materials.

The policy document ‘Circular Netherlands 2050’ outlines a government wide program in the Netherlands to create a sustainable circular economy which aims to sustainably decrease use of raw materials while remaining economically profitable. One of the five priority sectos outlined in the program is ‘biomass and food’. It is from that priority sector that this study was commissioned by the Dutch Ministry of Infrastructure and Environment in order to investigate possibilities and opportunities for recovery of nutrients from waste.

Research on recovery of phosphorus has gained considerable attention and advancement in academia, and pilot projects have been carried out various private public partnerships during the lastdecade. For this reason nutrients other than phosphorus are the main focus of this study. The geographical scope of this study is the Netherlands and Europe.

Based on the criticality assessment method from (Graedel & et al, 2012) we chose the following indicators to prioritize nutrients:

- Significance to plants and animals
- Geographic concentration of ores,
- Ore depletion time
- Environmental impacts and
- Results of other criticality assessments

The potential prioritized nutrients were narrowed down to: Boron, Cobalt, Copper, Potassium, Molybdenum, Selenium and Zinc.

Next, the following six (6) Dutch waste flow chains were mapped including details on flow size and nutrient concentration of the above mentioned prioritized nutrients:

- Communal wastewater
- Industrial wastewater
- Solid waste from households and industry

- Biomass and livestock farming
- Slaughterhouse waste and animal cadavers and carcasses
- Coal chain

The largest waste streams containing the prioritized nutrients are: sludge from WWTP's, ash from sludge WWTP's and ash from MSWI. Sometimes data about concentrations of waste streams and the amount of waste streams was difficult to obtain, and the concentrations of waste streams vary due to changing inputs. Nevertheless, this study has generated more knowledge about the waste streams with the highest nutrient concentrations. In addition,the theoretically recoverable nutrients quantities in waste streams were identified. This initial evaluation was based on nutrient concentration and size of the waste stream.

In addition to the concentration of nutrients in a waste stream,the extent to which the waste stream is contaminated is also important to know, because it influences the possible recovery technique and the end product. We created a qualitative framework in which the type of recovery technique can be chosen based on the nutrient concentration and contamination of the waste stream. The available recovery techniques are: direct application, restricted application, cleaning, separation and extraction. In figure 0.1 the flows have been placed in the qualitative grid. The circle size corresponds to the size of the waste stream.

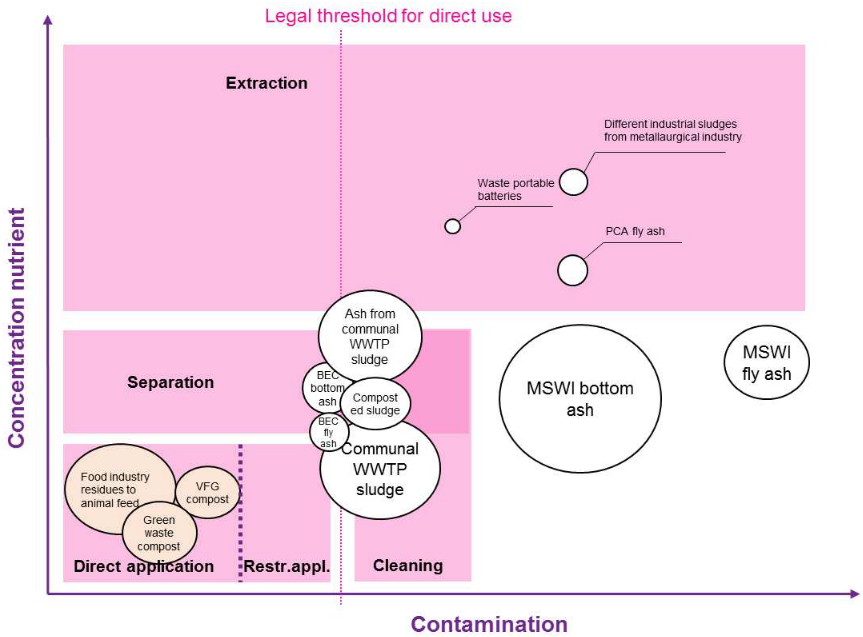


Figure 0.1 Relationship nutrient recovery strategies and concentration and contamination waste streams (populated with the results from chapter 3)

We investigated technologies for each recovery strategy and have provided more detailed information about them. Finally all relevant information has been brought together and summarized in table 0.1 and table 0.2.
Table 0.1provides information about which nutrients can be recovered using which technology. Table 0.2 further reviews technologies with respect to potential demand, technology readiness (TRL), economic feasibility, whether regulation restrictions exist and which technologies we recommend prioritizing for future research.

Table 0.1 Recovery options related to the prioritized nutrients

Strategy		Recovery option	unknown	B	Co	Cu	K	Mo	Se	Zn	other
Direct use	1	Dewatered communal sludge		x	x	x	x	x	x	x	x
	2	Composted sludge		x	x	x	x	x	x	x	x
	3	Dried sludge		x	x	x	x	x	x	x	x
	4	Ash from energy wood					x				
Cleaning	5	Sludge separated inorganic/organic	x								
	6	Bioleaching sludge	x								
	7	Ashdec proces sludge ash									x
	8	Extraction heavy metals from wastewater		x	x	x	x	x	x	x	x
Separation	9	Separated digestate food industry	x								
	10	Eutectic freezing liquid fractions residu	x								
Extraction	11	FLUWA MSWI fly ash				x				x	x
	12	PAUF MSWI fly ash				x				x	x
	13	Ecophos WWTP fly ash					x			x	x
	14	Stuttgart Sludge leaching	x								
	15	Reductive acid leaching batteries				x	x			x	x
	16	Ammonia leaching copper				x					
	17	Biorefinery: micro-algae		x	x	x	x	x	x	x	x
	18	Biorefinery: duckweed, azolla, hyacinth		x	x	x	x	x	x	x	x
	19	Phytoremediation biomass for energy	x								

Table 0.2 Recovery options related to the prioritized future research

Strategy		Recovery option	Potential demand	TRL	Economical feasible	No Regulation restrictions	Prioritized future research
Direct use	1	Dewatered communal sludge	+	+	+	-	
	2	Composted sludge	+	+	+	-	+
	3	Dried sludge	+	+	+	-	+
	4	Ash from energy wood	+	+	+	-	+
Cleaning	5	Sludge separated inorganic/organic	+	-	?	?	
	6	Bioleaching sludge	+	-	?	?	+
	7	Ashdec proces sludge ash	+	-	?	+	
	8	Extraction heavy metals from wastewater	+	-	?	?	
Separation	9	Separated digestate food industry	+	+	?	+	+
	10	Eutectic freezing liquid fractions residu	+	-	?	?	
Extraction	11	FLUWA MSWI fly ash	+	-	?	?	+
	12	PAUF MSWI fly ash	+	-	?	?	+
	13	Ecophos WWTP fly ash	+	+	?	+	+
	14	Stuttgart Sludge leaching	+	-	?	?	
	15	Reductive acid leaching batteries	+	-	?	?	
	16	Ammonia leaching copper	+	-	?	?	
	17	Biorefinery: micro-algae	+	+	-	+	
	18	Biorefinery: duckweed, azolla, hyacinth	+	+	-	+	
	19	Phytoremediation biomass for energy	+	+	+/-	+	+

About half of the technologies investigated have a positive technology readiness level. These include all (low tech) direct application technologies, separated digestate from food industry in cleaning technologies, Ecophos WWTP of fly ash, two biorefinery technologies and phytoremediation in the extraction category. The economic feasibility is unknown for most recovery techniques except for direct application. We recommend carrying out feasibility studies and establishing business cases.

Dutch environmental legislation is restricting and complicating technical solutions for applying nutrient-rich flows for agricultural purposes. Technology and the impact of applying a (processed) residual waste stream must comply with the precautionary principle of the Waste Framework Directive (Kaderrichtlijn Afvalstoffen) which states that it:'may not lead to overall adverse environmental or human health impacts'.

We recommend further research for the following technologies:

- Direct use of:
  - *Composted sludge (2)*
  - *Dried sludge (3)* - With reduced P (phosphorus) content and a good hygienic status combined with quality assurance, the application of communal sludge in the Netherlands can be an option in the future.

  - *Ash from energy wood (4)* can be reused as fertilizer (like in Sweden and Finland) if specific legislative aspects are developed
- *Cleaning of bioleaching sludge(6)*
- *Separation of t*he liquid fraction of the *separated digestate (9)* from digesters in the sugar industry
- Acid fly ash washing process FLUWA (11) to separate zinc, lead, cadmium, and copper from fly ash *Polymer-assisted ultrafiltration (PAUF) (12)* (added before the hydroxide precipitation), for selective separation of tin, copper and nickel, together with recovery of zinc and lead.
- *Ecophos process (13)*
- *Phytoremediation with biomass for energy (19)* - The absorbed nutrients can be recovered from the ashes after incineration

Although the direct application technologies perform well in the first mentioned evaluation categories, the use of the end products is restricted by law, due to the existence of organic micro pollutants and heavy metals in the favourable flows for recovery.

1 Introduction

Nutrients are essential for life and their future availability must be guaranteed. Tracking the flows of nutrients and routing them back into the biological cycle can prevent them from going to waste. The Dutch Nutrient Platform (DNP) was established in 2011 with the goal to address (worldwide) scarcity of nutrients and the geopolitical dependence of the Netherlands on countries outside Europe for the supplies. The members of the DNP are Dutch companies such as waste treatment facilities, suppliers for agricultural suppliers, engineering consultancies, water companies and water technology companies. Additionally, (semi) public organizations like water boards and the Ministry of Infrastructure and Environment as well as knowledge institutions are represented within the DNP. Initially, the focus was mainlyon phosphorus. From 2011-2016 several members of the DNP succeeded in recovering phosphorus from wastewater, sludge ash and other waste streams. The diverse members of the DNP expect that, in the short term, a significant part of the Dutch phosphoruswill be recovered and will be reused for agricultural purposes (closing the cycle).

In January 2017 the national policy program 'Circular Netherlands in 2050' started. The driving forces for a Circular Netherlands are sustainability (Ministry Infrastructure and Environment, in the following M IenM) and effectiveness (Ministry of Economics). The program will form the basis for the transition agenda. The ambition to recycle nutrients in the Netherlands is running ahead of the transition agenda.

In addition to phosphorus, other macro- and micronutrients also need to be addressed. Recent literature shows that depletion of micronutrients is currently a global problem (Chardon & Oenema, 2013); (de Haes & et al., 2012); Henckens, 2016; Platform Landbouw, Innovatie en Samenleving, 2014 ('LIS report'); Van der Weijden et al., 2014). According to (de Haes & et al., 2012) soil deficiencies of the micronutrients zinc and molybdenum haveled to reductions in crop yields. Zinc and selenium are lacking in human nutrition.. In many parts of Asia, Africa and South America nutritional zinc shortages lead to deficiency diseases. Additionally, selenium shortages appear to lead to deficiency diseases in developing countries. In the analysis of (Chardon & Oenema, 2013) six micronutrients were identified that are demonstrably essential for several plants or livestock species and that are potentially scarce: boron, cobalt, copper, molybdenum, selenium and zinc. In addition to these micronutrients, the following macronutrients are also important: phosphate, nitrogen, potassium, calcium, magnesium and sulphur.

From the DNP and M IenM an assignment was given to Tauw and WUR to explore the chances for recovery and reuse of nutrients other than phosphorus. the results of this exploration are presented in this report.

The determination of prioritized nutrients in the framework of this research is flexible-adaptive. The nutrients that will be prioritized is a sub-result of this research. Criteria that are part of the evaluation are not only scarcity and geopolitical dependency but also availability of waste, recoverability (in terms of degree of concentration, its chemistry which has influence on quality and properties of the waste and recovered products, as well as economic value) and potential business cases of recovery. Nutrients are not excluded in advance, but during the exploration in this report the most promising nutrients for recovery will come forward.

In this study, recycling is defined as recovery of nutrients. Recovery can take place by extraction of individual nutrients from residual flows, e.g. for use by industry, or by using the entire flow or part of it, e.g. in agriculture. Focus is on nutrients that are essential for plant and animal growth; other elements such as metals and rare earth minerals are excluded from this study. We would like to highlight that we focus on flows and not on stocks which means that we exclude the opportunity of landfill mining. However, residual flows that are currently landfilled are included.

The geographical scope for recovery of nutrients is primarily the Netherlands, but the application of recovered nutrients has the geographical scope of Europe or beyond.

The aim is to find chances for reuse on the short term, not to do a thorough and complete investigation. Knowledge gaps do not need to be completed but have to be emphasized. It is interesting to know why information is missing or certain recycling routes failed to be implemented. Could there be a prospect for the future?

Structure of the report

In the first chapter the importance, goal and scope of this research is covered.

The second chapter contains the results from a literature review on nutrients resulting in an overview of essential mineral nutrients and the presentation of criteria to assess and determine priority nutrients for this exploratory research. As said before, the prioritization in this study does not exclude any nutrients yet.

In the third chapter residual/waste streams with nutrient recovery potential are mapped for the Netherlands. Nutrient concentrations have been found through literature review and information shared by processing parties. Additionally, information about the total waste quantities are presented. The covered chains are: sewage sludge chains, industrial sludge, solid wastes from municipal and industrial origin and organic and livestock related wastes. These chains were identified after internal consultation within the project group. This chapter presents facts and available knowledge and does not focus on real chances of recovery.

With this background of priority nutrients and flows containing nutrients in mind, strategies for recovering nutrients are explored in chapter 4. Based on the flow properties, four strategies of recovery have been developed. For each strategy a literature review has been carried out and potential recovery techniques suited for mineral nutrients are presented. In this chapter actual chances for recovery become apparent without ranking of the best routes.

In chapter 5 the results are discussed with the goal to find and evaluate combinations of waste streams and techniques to recover mineral nutrients including a qualitative economic assessment. A prioritization of the most promising routes is presented.

In the final chapter we discuss our results and give conclusions and recommendations for further research.

2 Analysis of important nutrients for recovery

2.1 Introduction

This chapter aims to map the existing (mineral) nutrients and subsequently tries to limit the number of nutrients for recovery from residual flows based on their importance (prioritization).

First the concept of ‘importance’ of raw materials is explored by a review of scientific methodologies that aim to determine important raw materials (2.2). Based on these insights we assess the importance of mineral nutrients with our chosen indicators: essentiality for plants and animals (2.3.2), geographic concentration of ores (2.3.3), ore depletion time (2.3.3), environmental impacts (2.3.4) and results of other criticality assessments (2.3.5).

Finally a summary of the analysis of the most important nutrients is presented (2.5). As said before, this prioritization does not exclude any nutrients yet.

2.2 Review of scientific methodologies to determine importance of raw materials

Importance of raw materials is a concept that is highly subjective, because it is based on value judgements. We take the point of view that importance is related to availability. (van der Voet, 2013) states that in the present debate on resource availability, three related concepts play a role: depletion, scarcity and criticality.

Depletion means that a resource amount present in geological/natural stocks on earth is being reduced. As nutrients remain on earth, there is no depletion as such but the amount of ores with a certain concentration of metals can get depleted.

Scarcity means that the amount available in terms of feasibility of economic recovery and technical recovery for use, is or will be insufficient in the near future (depending on the subjective definition of time). At a regional scale, scarcity can be affected by geopolitical effects when nutrients are sourced from elsewhere.

Criticality means that the resource is scarce and at the same time essential for the present society. Usually this means that it cannot be replaced easily by another resource.

(van der Voet, 2013)

The scientific community adopted the concept of resource criticality. Several researchers developed their own methodologies for raw material criticality assessments depending on the questions being asked.

(Helbig, Wietschel, Thorenz, & Tuma, 2016) compared several material criticality assessments. Criticality Assessments consist of 3 fields of assessment: supply risk, vulnerability and environmental impact. Sets of indicators are used to help determine the criticality of raw materials. Figure 2.1 illustrates the content of a criticality assessment and a variety of indicators per field of assessment that have been used in different studies.

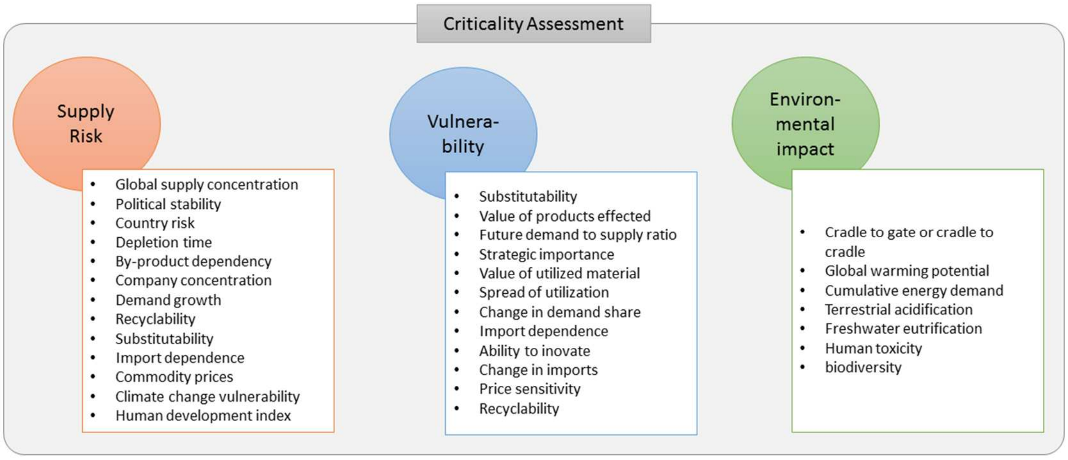


Figure 2.1 Structure criticality assessment and possible indicators

Some indicators are used in several fields of assessment. It is the practitioner's choice and value assessment where an indicator belongs to.

(Helbig, Wietschel, Thorenz, & Tuma, 2016) found out that each study has a different conclusion on material criticality depending on the chosen scope - for example national or technological scope. In each study the indicators varied due to difference in scope and aim of the analysis. (Helbig, Wietschel, Thorenz, & Tuma, 2016). (Graedel & et al, 2012) created a summary on the relevance of material related characteristics depending if a corporate, national or global scope is chosen for the criticality assessment. The summary is shown in table 2.1. One can clearly see that for example geopolitical factors are crucial on corporate level and important on national level. However on a global level geopolitical factors are unimportant. This explains the different conclusions in different criticality assessments.

Table 2.1 Relevant Material-Related Characteristics for Different Organizational Levels (Graedel & et al, 2012)

		using corporation	using nation	global
1	focus	relevance to that firm's product line	relevance to national industry and population	all uses of a material, wherever they happen
2	time scale	1−5 years	5−10 years	10−100 years
3	supply potential	crucial	very important	very important
4	technological change	very important	worth consideration	impossible to predict
5	geopolitical factors	crucial	important	unimportant
6	social factors	moderately important	very important	unimportant
7	environmental implications	important	important	moderately important
8	intensity of competition	crucial	depends on national industry composition	unimportant

2.3 Criticality of nutrients

2.3.1 Introduction

The mentioned scientific methodology from (Graedel & et al, 2012) is adapted by us to assess the criticality of nutrients for the Netherlands. This study is called ‘Possibilities and opportunities for recycling of other nutrients than phosphorus’.

The aim of this study is to identify opportunities for recycling in order to make a critical nutrient less critical. In accordance to the budget and schedule of this study the following indicators are chosen for the criticality assessment:

- **Essentiality for plants and animals**: Essentiality relates to the indicator substitutability. Nutrients are essential to all life, especially those without a substitute. An effective composition of a nutrient mix as fertilizer sustains high and future proof crop yields (Cordell et al., 2011)
- **Geographic concentration of ores**: Because nutrients are essential to life, a shortage of supply can have severe health effects (LIS, 2012). Geographic concentration of minable nutrients is an important indicator because few countries with high reserves could exploit their power and make other countries vulnerable
- **Ore depletion time (R/P)**: The necessity to find a recycling technique for nutrients is among other criteria motivated by the depletion time
- **Environmental impacts (such as Global Warming Potential and Energy Demand)**: Recycling is often attributed to have a lower environmental impact than mining because recycling uses less energy to recreate a new material – popular examples are aluminum (The Aluminum Association, 2017) and glass (Glass Packaging Institute, 2017) recycling. With the help of life cycle assessment (LCA) environmental impacts across a supply chain can be quantified. A high environmental impact of a mining activity can give motivation to find a recycling technique with less damaging environmental effects

Additionally to these indicators the evaluations from (Chardon & Oenema, 2013) (Landbouw, 2014) (European Commission, 2014) are taken into account to create a shortlist of critical nutrients.

2.3.2 Long list of essential mineral nutrients

Various mineral nutrients are essential for the growth of plants and the health of animals and humans. The essential nutrients for plants and animals were taken as the starting points for te long list. On the basis of concentrations in plants, a distinction is made between so-called macronutrients and micronutrients (trace elements). Macronutrients are required by plants in relatively large quantities and consist of N, P, K, Ca, Mg, and S. Micronutrients are present in low quantities below 200 ppm. The list of micronutrients that are essential for plant growth varies, but contains at least B, Cl, Co, Cu, Fe, Mn, Mo, Ni and Zn. Some nutrients may be essential for specific plants, or can be beneficial for plant growth. Some mineral nutrients that are not essential for plants can be essential for animals (table 2.2).

Table 2.2. Essential nutrients for plants and animals (based on (Chardon & Oenema, 2013) and (Voortman, 2012); an (x) indicates that the element is not essential for all plants

Element name	Symbol	Classification[1]	Essential for plants	Essential for animals
Aluminium	Al	micro	(x)	
Boron	B	micro	x	
Calcium	Ca	macro	x	x
Chlorine	Cl	micro	x	x
Cobalt	Co	micro	(x)	x
Chromium	Cr			x
Copper	Cu	micro	x	x
Fluorine	F			x
Iron	Fe	micro	x	x
Iodine	I	micro	(x)	x
Phosphorus	P	macro	x	x
Potassium	K	macro	x	x
Magnesium	Mg	macro	x	x
Manganese	Mn	micro	x	x
Molybdenum	Mo	micro	x	x
Nitrogen	N	macro	x	x
Sodium	Na	micro	(x)	x
Nickel	Ni	micro	(x)	x
Sulphur	S	macro	x	x

Element name	Symbol	Classification[1]	Essential for plants	Essential for animals
Selenium	Se	micro	(x)	x
Silicon	Si	micro	x	x
Tin	Sn			x
Vanadium	V	micro	(x)	x
Zinc	Zn	micro	x	x

[1] Classification based on the amounts required by plants

Also organic matter is of interest. Organic matter has a direct relationship with soil fertility, the uptake of nutrients and crop yield, and is an important component in various waste streams. Organic matter is a subject that is addressed in the transition agenda Biomass and food. Organic matter is therefore not within scope of this study.

2.3.3 Geographic concentration and resource depletion in ores

For several nutrients, supply risk and estimated depletion time of the mineral ores is shown in Table 2.3. The indicator geographic concentration describes whether a few countries own most of the mineral or not. 'High' means that only a few countries have this specific resource, indicating a high geopolitical relevance of this mineral. 'Low' means that several countries have the resource, meaning low dependence. A high geographic concentration may indicate a high geopolitical risk, especially when the resources are mainly located outside Europe, as is the case for B, I, Mo and V. Data about yearly production and reserves are strategic. The USGS sometimes discloses this data for the United States of America. It can be expected that this data only represents an order of magnitude.

The indicator R/P represents the reserves-to-production ratio, which is the depletion time of the mineral in years when the amount of known reserves (R) are mined at the current rate (P). It is a static indicator, but the values of R and P are changing over time. New reserves might be discovered and production could decrease due to better recycling techniques or another reason for a reduced demand. The R/P value can also be a strategic indicator: the lower the value the higher the demand and the price that can be asked for this mineral. Values above 50 years generally do not worry decision makers. If the value is low, mining companies start investigating new reserves which then increases the R/P value again.

Table 2.3 Production characteristics of several nutrients, based on (U.S. Geological Survey, 2017)

Symbol	Geographic concentration [1]	Production (k ton/year), estimated for 2016	R/P
B	High [2]	9.400 [2]	40
Ca (stone crushed)	Low	1.480.000 [3]	Z [4] (as 'lime')
Co	Medium	123	57
Cu	Medium	19.400	37
Fe (iron Ore)	Medium	1.360.000	60
I	High [2]	32 [2]	237
K (potash K_2O)	Medium	39.000	110
Mg (MgO)	High [2]	27.700 [2]	307
Mn	Medium	16.000	43
Mo	High	227	66
N (fixed ammonia)	Low	140.000	Z [4] (from air)
Na (soda ash)	Low	53.600	Z [4]
Ni	Low	2.250	35
P (fhosphate rock-ore)	High	261.000	260
S	Low	69.300	Z [4] (from mineral oil)
Se	Medium	2,2 [2]	45
Si	High	7.200	Z [4]
V	High	76	250
Zn	Medium	11.900	18

[1] High = the top 3 countries have > 75% of the world production,
Medium = top 3 countries >50% and < 75% of the world production,
Low = top 3 countries <50% the world production
[2] excluding USA
[3] USA only
[4] Z = amply available

2.3.4 Environmental impact of sourcing

The data found on environmental impact are cradle-to-gate lifecycle inventories of minerals and metals. The processes mining, concentration of ore, purification of concentrate, refining intermediates into metals or alloys and making a product mix in form of element are represented in these inventories. They are shown in Table 2.4.

Most of these processes are not located in the Netherlands and to some extend in other European countries, hence the environmental impacts (except for global warming potential) are mostly local to where the processes are located. It is a moral question whether this data fits in the geographic scope of Europe that is handled in this study. However one can use these insights to require that recovery techniques should perform better than the techniques used for refining primary minerals to ensure sustainable business practices.

Table 2.4 Environmental impact for the sourcing of primary metals (Nuss & Eckelman, 2014)[A]

Symbol	GWP	Cumulative energy demand	Terrestrial acidification	freshwater eutrofication	human toxicity
	CO_2 eq./kg	MJ eq/kg	kg SO_2-eq/kg	kg P-eq/kg	CTUh /kg
B	1,50	27,30	0,01	5,3E-04	2,8E-07
Ca	1,00	5,80	0,00	1,4E-05	1,3E-08
Co	8,30	128,00	0,09	4,0E-03	3,8E-06
Cu	2,80	53,70	0,39	1,3E-01	2,7E-04
Fe	1,50	23,10	0,01	7,3E-04	4,1E-07
Mg	5,40	18,80	0,00	1,9E-04	1,2E-06
Mn	1,00	23,70	0,01	6,7E-04	3,3E-07
Mo	5,70	117,00	0,16	5,4E-01	9,0E-04
Ni	6,50	111,00	1,50	1,4E-02	2,3E-05
Se	3,60	65,50	0,23	5,5E-02	1,1E-04
V	33,10	516,00	0,14	4,3E-07	4,4E-09
Zn	3,10	52,90	0,04	5,1E-03	5,9E-05

[A] I, K, N, Na, P, S en Si are not metals and hence not mentioned in this list. For comparison Energy demand and GWP values for N-fertiliser are 40 MJ/kg N, 6,17 kg CO2-eq./kg and for P-fertiliser 13,31 MJ/kg P2O5, 0,73 kg CO2-eq./kg **(Brentrup & Pallière, 2012)**.

2.3.5 Criticality assessments from other literature sources

The European Commission started in 2010 to assess and monitor critical non-energy materials. In 2014 the list has been reviewed for a second time. Critical materials are assessed on their economic importance and supply risk for the EU. The economic importance is related to the gross value added of end use 'mega sectors' in the EU. This means that the agricultural sector is part of the scope of the EC criticality analysis next to a lot of other sectors. (European Commission, 2014). Out of the 14 identified critical raw materials by the European Commission there are two mineral nutrients on the list: Cobalt and Magnesium. On the candidate list consisting of 54 raw materials the following mineral nutrients are also on the list: Borates, Chromium, Copper, Manganese, Molybdenum, Nickel, Potash, Selenium, Silicon, Tin, Vanadium and Zinc.

Criticality of elements can be based on industrial use and/or agricultural use. For criticality for agricultural use, (Chardon & Oenema, 2013) looked in their analysis at the content of mineral nutrients in the soil and excluded nutrients that have high contents in soil and for which no scarcity in agriculture is expected. Therefore, Cr is not included in their shortlist as no scarcity for agriculture is expected, even though it is indicated by the EU as critical raw material.

Magnesium is on the EU list of critical raw materials, but has not been mentioned by (Chardon & Oenema, 2013) and (Landbouw, 2014) as a critical nutrient; it does have a high geographic concentration but the reserves will last for decades.

(Chardon & Oenema, 2013) made the assumption that a high median content of a mineral nutrient in the soil or elsewhere in the environment lead to no expected scarcity or price increase with significant impact on agriculture. Hence the elements Al, Cl, Fe, I, Mn, Na and Si are not seen as critical. A number of elements are considered to be essential in animal nutrition. However on the basis of feedstock feed a shortage is not expected to occur. These elements are: As, B, Cr, Ni, Pb, Si, Sn, V. Because Boron is also essential for plants it is still included in their shortlist (Chardon & Oenema, 2013).

In table 2.5 the shortlists in regard to nutrients from the different studies are summarized.

Table 2.5 Nutrients of importance for the Netherlands and Europe based on different studies

Nutrient	(LIS, 2012)	(Chardon & Oenema, 2013)	(Landbouw, 2014)	(European Commission, 2014) candidates
Boron	X	X	X	X
Chromium				X
Cobalt	X	X		X
Copper	X	X		X
Potassium	X		X	X
Molybdenum	X	X	X	X
Selenium	X	X	X	X
Zinc	X	X	X	X
Nickel	X			X
Manganese	X			X
Magnesium				X
Tin				X
Vanadium				X

2.4 Economic aspects

The cost value of nutrients will play a role in determining perspectives for possible business cases on nutrient recovery. Because of that in this paragraph prices of minerals are presented.

The prices of minerals are dynamic, some fluctuate more than others, and prices may differ per country depending whether a country imports or owns this resource itself. The data in are based on the US market and can be seen as an order of magnitude.

Table 2.6. Price of several minerals/nutrients

Symbol	Price (US$/kg)	Data source	Visited on
B	0,40	https://minerals.usgs.gov/minerals/pubs/commodity/boron/mcs-2016-boron.pdf	
Ca	0,01	https://minerals.usgs.gov/minerals/pubs/commodity/stone_crushed/mcs-2016-stonc.pdf	
Co	28,88	https://minerals.usgs.gov/minerals/pubs/commodity/cobalt/mcs-2016-cobal.pdf	14-12-16
Cu	5,74	http://www.infomine.com/investment/metal-prices/copper/5-year/	14-12-16
Fe	0,08	https://minerals.usgs.gov/minerals/pubs/commodity/iron_ore/mcs-2016-feore.pdf	
I	28,00	https://minerals.usgs.gov/minerals/pubs/commodity/iodine/mcs-2016-iodin.pdf	
K	0,22	http://www.infomine.com/investment/metal-prices/potash/5-year/	14-12-16
Mg	2,09	http://www.infomine.com/investment/metal-prices/magnesium/5-year/	14-12-16
Mn	1,74	http://www.infomine.com/investment/metal-prices/manganese/all/	14-12-16
Mo	15,25	http://www.infomine.com/investment/metal-prices/molybdenum-oxide/5-year/	14-12-16
N	0,52	https://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2016-nitro.pdf	
Na	0,16	https://minerals.usgs.gov/minerals/pubs/commodity/soda_ash/mcs-2016-sodaa.pdf	
Ni	11,43	http://www.infomine.com/investment/metal-price-futures/nickel/3-month/5-year/	14-12-16
S	0,10	https://minerals.usgs.gov/minerals/pubs/commodity/sulfur/mcs-2016-sulfu.pdf	
Se	50,27	https://minerals.usgs.gov/minerals/pubs/commodity/selenium/mcs-2016-selen.pdf	
Si	3,00	https://minerals.usgs.gov/minerals/pubs/commodity/silicon/mcs-2016-simet.pdf	
V	9,70	https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2016-vanad.pdf	
Zn	2,73	http://www.infomine.com/investment/metal-prices/zinc/5-year/	14-12-16

2.5 Prioritization of the nutrients for recovery

This research aims to discover opportunities for recycling of other nutrients than P. The following seven nutrients are essential in agriculture and require specific attention for recovery from residual flows because of potential supply risks: B, Co, Cu, K, Mo, Se and Zn (**Table 2.7**).
The choice is based on the collected data from the earlier subchapters. The reasons for importance are given in **Table 2.7**.

Table 2.7 Prioritization of the nutrients for recovery

Nutrient	Reasons for importance
Boron	• Very high geopolitical mining concentration • 12% of global use is in agriculture • Mentioned by all 4 assessments
Cobalt	• The European Commission (2010) indicates cobalt as an element with a (slightly) increased risk of supply disruption due to the fact that production is mainly taking place in Congo • GWP and energy demand for mining are considerably high
Copper	• High environmental mining impacts • Medium geographic concentration • Competing in other sectors
Potassium	• Medium geographic concentration • Is a macro nutrient and hence a higher amount is needed in fertilizer in comparison to the nutrients
Molybdenum	• Very high geopolitical mining concentration • Mentioned by all 4 assessments • Scoring high in several environmental impact categories
Selenium	• Mineral reserves are restricted • Co-product of copper production, present production capacity does not meet the estimated agricultural need • 30% of global use is in agriculture • Mentioned by all 4 assessments
Zinc	• Mineral reserves are very restricted • High geopolitical mining concentration • Mentioned by all 4 assessments

Opportunities for recycling are however not limited to this list as economic drivers and potential business cases may allow efficient recycling of other nutrients as well.

Nitrogen is not among the selected prioritized of nutrients. Even though nitrogen is an essential nutrient, it is not scarce: atmospheric nitrogen is fixed by bacteria and by the fertilizer industry.

3 Waste flows in the Netherlands and their properties

3.1 Introduction

The goal of this study is to find possibilities for nutrient recovery other than phosphorus. In order to identify possible streams from which nutrients can be recycled an overview of residual organic and inorganic flows has to be created. In this chapter, flow charts map these flows for different chains:

- Communal waste water chain in NL (3.2)
- Industrial waste water chain in NL (3.3)
- Solid wastes from households and industry chain in NL (3.4)
- Biomass and livestock farming chain in NL (3.5)
- Slaughterhouse waste and animal cadavers and carcasses chain in NL (3.6)
- Coal chain in NL (3.7)

Streams that currently do recycle nutrients are also included in the flow charts (shaded box indicates the recycling application). Additionally the properties of the streams are investigated such as size of the stream per year and concentrations of the nutrients mentioned in the shortlist from chapter 2.5 per stream. Streams for which data has been found are colored in green; streams for which no data could be found are colored black.

This chapter focuses on giving an overview of flows and their nutrient contents. In chapter 3.8 a short summary is given, together with an indication of flows that have perspectives for nutrient recycling based on their properties.

3.2 Communal waste water chain in NL

The DNP has focused a lot on the communal waste water chain as a source for phosphorus recovery. The communal waste water chain has a relatively stable and high material flow. This is the motivation to examine the presence of other nutrients in this chain.

Communal waste water treatment plants (WWTP) are treating waste water from households, together with rain water and a limited flow from industry. After treatment at the WWTPs, the cleaned water is discharged to surface water and the residual sludge is either composted, dried, mono- or co- incinerated (Ringoot, Reitsma ea, Thermische hydrolyse als de motor voor centrale slibverwerking, H2O 25 maart 2014). For 2018, GMB expects to export (a part of) their compos-ted sludge for agricultural use outside the Netherlands (France). At the moment composted sludge is used for co-firing at coal power plants. Because the sludge is only a small fraction of the fuel in a coal fired power plant, the concentration of the ashes is almost completely determined by the coal. The coal ashes are currently used in the cement industry. Coal ashes are examined in subchapter 3.7.

From 2018 onwards, the ash from mono-incineration of sewage sludge from SNB and HVC is expected to be supplied to Ecophos. Then, mono-incinerated sewage sludge will be used to extract phosphoric acid together with Al/Fe and Mg/Ca solutions (De Ruiter, 2015). The residual from this process still contains nutrients.

Currently also, part of the communal sewage sludge is co-incinerated at waste-to-energy plants. The inputs of co-incineration are from different sources and sludge is not a major input stream. As a result, the nutrients present in sludge are covered in subchapter 3.4 by waste incineration.

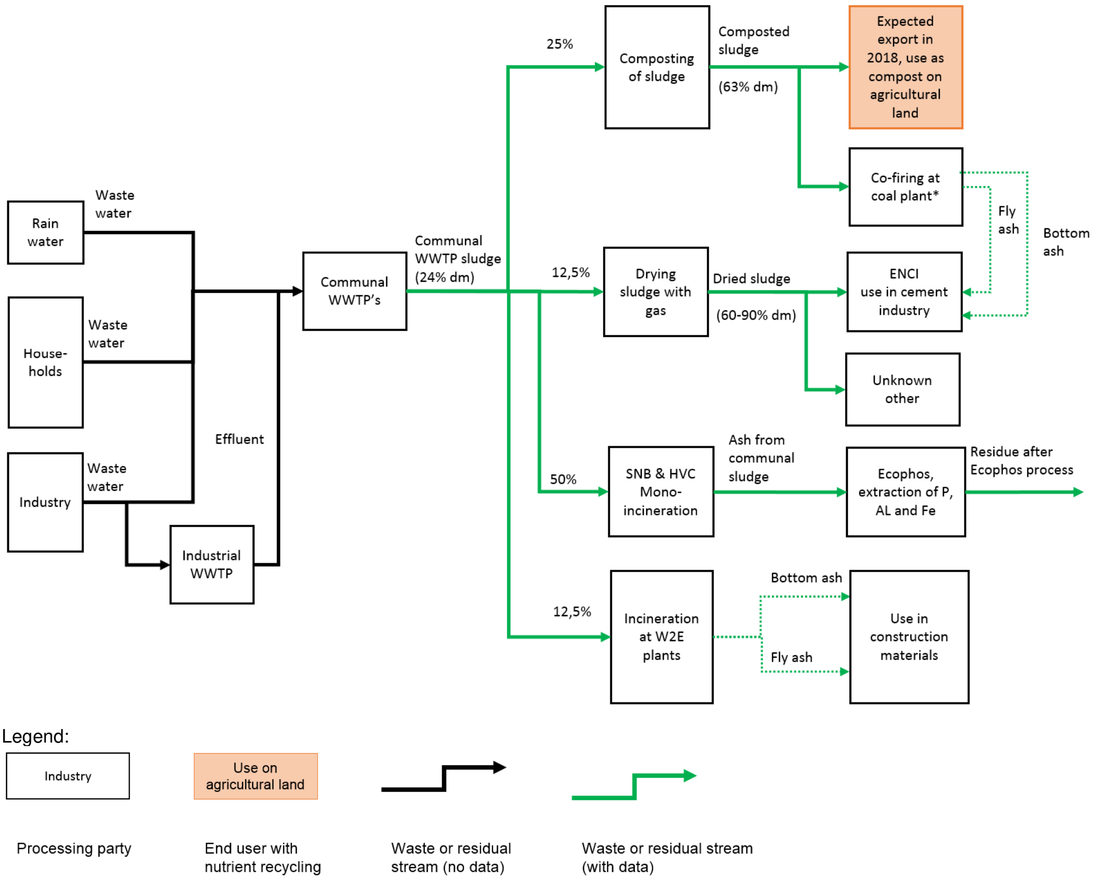


Figure 3.1 Communal waste water chain in NL

Table 3.1 shows the concentrations of nutrients in the residual streams for which data has been found. The gradient scale goes from red (no or very low concentration) via yellow (5 % of maximum value in comparison to all streams examined in this study including other chains) to green (highest concentration). When there were no data found in literature about certain nutrient concentrations a '-' symbol was used. However this does not necessarily mean that no traces are present, just that they were not measured or reported. Also important to note is that these values are sometimes averages of measurements repeated over a longer period and from different treatment sources. These values are hence indications and can vary per batch and treatment facility due to change in inputs.

For the communal waste water chain this means that in comparison of all shortlist nutrients Potassium has the highest concentration, in this case for composted sludge and in the expected residue after the Ecophos process. The concentrations of zinc can be also worth to examine.

Table 3.1 Nutrient concentrations in the communal water treatment chain

Residual stream	source of information	B Boron	Co Cobalt	Cu Copper	K Potassium	Mo Molyb-denum	Se Selenium	Zn Zinc
		mg/kg in dm	mg/kg in dm	mg/kg in dm	mg/kg in dm	mg/kg in dm	mg/kg in dm	mg/kg in dm
Communal WWTP sludge (24 % ds)	(CBS, 2016) - NL	-	-	425	-	-	-	1.000
Composted sludge (63% dm)	(GMB, 2016) - NL	-	-	499	4.683	9	5	1.568
Dried sludge	(ECN, 2017) #2899 - ES	31	155	500	740	250	75	1.000
ash from communal sludge incineration	(CBS, 2016) - NL	-	17	1.101	-	30	3	2.828
Residue after extraction of P, Al and Fe from sludge ash (Ecophos process)	(Ecophos, 2017) - NL	-	-	660	19.000	-	-	2.400

The concentration of copper and zinc from communal WWTP sludge increases after mono-incineration. This happens because of loss of water and dry matter (e.g. organic matter and elements such as nitrogen) during incineration. Values for potassium have not been included in (CBS, 2016), and we have no other data for potassium content of communal sludge. However, it is expected that communal sludge has also a considerable potassium concentration like dried sludge and sludge ash. Interesting to note is that corrosion of water and sewage pipes leads to a high copper concentrations in communal WWTP sludge (CBS, 2016). The copper concentration might decrease in the future in the case that copper pipes are replaced by PE pipes.

Sludge from communal WWTP's can contain pharmaceuticals and personal care products (PPCP's), toxic metals (like antimony and tin) and pathogens (E. coli species may be used as an indicator). The concentrations and amount of contaminants can differ from treatment plant to treatment plant. (Healy & et al, Health and Water Quality Impacts Arising from Land Spreading of Biosolids, 2017). Heating by drying and composting will sometimes kill the pathogens. Organic micro pollutants are removed during incineration. Anyhow the metals and also most of the nutrients will stay in the residue.

Table 3.2 shows the total amounts of nutrients per stream and nutrient. It is important to note that the last four mentioned streams are sub streams from the communal WWTP sludge stream. Due to uncertainties the amounts do not exactly add up. The communal waste water chain contains more than 300 ton per year of zinc and around 400 ton potassium.

Table 3.2 Total amounts of nutrients per stream per year for the communal waste water chain in N

Residual stream	Size of flow in NL in kt/year dm		B Boron t/y in dm	Co Cobalt t/y in dm	Cu Copper t/y in dm	K Potassium t/y in dm	Mo Molyb-denum t/y in dm	Se Selenium t/y in dm	Zn Zinc t/y in dm
Communal WWTP sludge (24 % ds)	336,0		-	-	143	-	-	-	336
Composted sludge (63% dm)	84,0	*	-	-	42	393	1	0	132
Dried sludge	42,0	*	1	7	21	31	11	3	42
ash from communal sludge incineration	70,0	*	-	1	77	-	2	0	198
Residue after extraction of P, Al and Fe from sludge ash (Ecophos process)	7,0	*	-	-	5	133	-	-	17

* estimation

3.3 Industrial waste water chain in NL

Some industrial plants have their own waste water treatment plant on site. We distinguish food and non-food industry, and have three different categories of industrial sludge (Figure 3.2). Residual flows from the food industry are often already reused in agriculture as animal feed or fertilizer product. Organic sludge from the food industry can be an input for biogas production through digestion. When the digestate is low on heavy metals it can be directly applied on agricultural land.

Hazardous organic sludge, paper sludge and other (hazardous) combustible sludge is incinerated at waste-to-energy plants. The ashes are processed to be used in building materials. Non-recyclable sludge that is also non-combustible is landfilled such as DND-sludge[1] .

[1] DND = Detoxification, Neutralization, Dewatering; in Dutch: ONO = ontgiften, neutraliseren, ontwateren

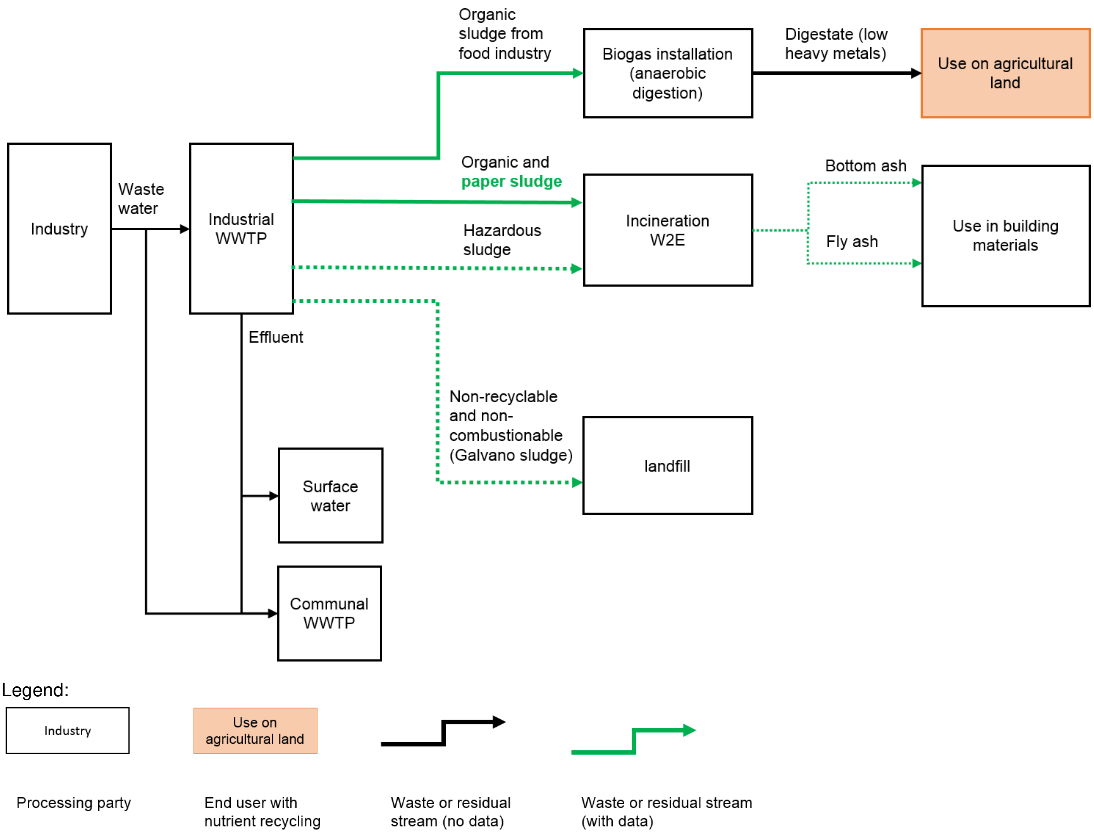


Figure 3.2 Sludges from industrial waste water in NL

Table 3.3 shows the concentrations of nutrients in the residual streams for which data has been found. The gradient scale goes from red (no or very low concentration) via yellow (5 % of maximum value in comparison to all streams examined in this study including other chains) to green (highest concentration). When there were no data found in literature about certain nutrient concentrations a '-' symbol was used. However this does not necessarily mean that no traces are present, just that they were not measured or reported. Also important to note is that these values are sometimes averages of measurements repeated over a longer period and from different treatment sources. These values are hence indications and can vary per batch and treatment facility due to change in inputs.

Table 3.3 Concentrations of nutrients in the industrial sludge chain in NL

Residual stream	source of information	B Boron mg/kg in dm	Co Cobalt mg/kg in dm	Cu Copper mg/kg in dm	K Potassium mg/kg in dm	Mo Molyb-denum mg/kg in dm	Se Selenium mg/kg in dm	Zn Zinc mg/kg in dm
sludge from production of potatoe products	(CBS, 2016) - NL	-	-	50	-	-	-	350
sludge from production of dairy products	(CBS, 2016) - NL	-	-	20	-	-	-	200
sludge from processing vegetables and fruits	(CBS, 2016) - NL	-	-	50	-	-	-	170
paper sludge	(Kuokkanen, & et al, 2008) - FI	-	-	7	120	-	-	12
Paper sludge ash	(Marsland & Whiteley, 2015) - UK	-	11	290	21	31	10	1.966
DND sludge	(Steketee & Langevoort, 2014), data from 1990ies - NL	-	-	4.050	-	-	-	11.000
DND sludge/ filter cake mixed sample		-	-	18.000	-	310	-	1.050
Enamel glaze sludge		-	-	293	-	-	-	79.882
Filter dusts from production of ceramic industry		-	-	-	-	-	-	39.000
Zinc iron salt residue from galvanization		-	-	-	-	-	-	720.000
Floatation sludge from cleaning used blasting grit		-	-	39.000	-	-	-	23.000
Petroleum refinery – sludge from biological WWTP	(Tauw bv, 2010) - NL	-	-	390	-	-	-	3.600
Petroleum refinery – sludge from the oil / water / sludge separator		-	58	680	-	63	-	4.400

Information on non-organic industrial sludge is difficult to obtain as an open source due to confidentiality related issues, and information could not or barely be derived from open online sources such as CBS (Office for Dutch National Statistics) and Eurostat. However, in (CBS, 2016) concentrations of copper and zinc in wastewater in µg/l are given for selected industries. The concentrations vary a lot between industries and between production plants. Copper concentrations were relatively high for the textile industry (38-354 µg/l) and ship-building. Zinc concentrations are relatively high for metal refining industries (52-1.803 µg/l) and textile industry.

The grey shaded rows of the table relate to non-organic sludge. This information is derived from (Steketee & Langevoort, 2014) who conducted a literature research on landfill mining. They researched which hazardous non-combustible streams were used to be landfilled until around the end of last century. The data may be outdated because waste management regulation has changed dramatically in the EU and the Netherlands and recycling technologies advanced greatly which led to increased recycling and less landfilling. A few streams with high concentrations of specific nutrients are highlighted below (in landfill):

- DND sludge/ filter cake is a waste with high copper (18.000 mg/kg dm) and nickel (72.500 mg/kg dm) concentrations.
- Residues of the ceramic industry contain high zinc concentrations, for example in filter dust (39.000 mg/kg dm) and enamel/glaze (80.000 mg/kg dm). However the data are very outdated; the ceramics industry has been employing efficient technologies to reduce wastes e.g. by spray painting or micro-filtration plat to recover glaze (Villeroy&Boch, 2017). Zinc iron salt residue from galvanization contains high zinc concentration (720.000 mg/kg dm). There have been high technological advancements in regard to resource efficiency in the galvanization industry. Processes are designed this way that metals are recycled internally in the factory. When the content of the galvanizing tub/bath reaches a certain level of contamination the whole content is brought to a waste company. The above mentioned flow and concentration could hence be found at a waste company but with a much lower volume than 15-20 years ago.
- Residues from cleaning used blasting grit also contain relatively high copper and zinc concentrations. Blasting grit is used to clean and/or roughen materials/ constructions made out of iron, non-ferro metallic, asphalt or stone. During gritblasting contaminations and old coatings are removed from the surfaces. The residues of ray grid cleaning are still landfilled.

DND sludge may be an interesting possibility to recover zinc and copper, although the concentration and flow of the stream are very unpredictable. However, this flow is not investigated further due to the high uncertainties, the same is true for zinc iron salt residue from galvanization.

Sludge composition of a petroleum refinery are derived from (Tauw bv, 2010), and high concentrations of zinc occur in the sludge from an industrial biological waste water treatment plant and from the oil/water/sludge separator.

Also the Dutch registry[2] of EU International Waste Shipment Directive was asked for information. The waste shipment permits (EVOA's[3]) are freely available online. Since 2017 only limited quantitative information is available in the EVOA's permit publications. Until 2016 there was information about the volumes and mass in dry matter available, but not about composition of the flow and concentrations of nutrients. The EVOA notifications are not freely available.

[2] In Dutch: Inspectie Leefomgeving en Transport
[3] In Dutch: Europese Verordeling Overbrenging Afvalstoffen

Table 3.4 shows the total amounts of nutrients in the industrial sludge chain in the Netherlands. All values are estimated by the authors.

Table 3.4 Total amounts of nutrients per stream per year for industrial sludges chain in NL

Residual stream	Size of flow in NL in kt/year dm		B Boron t/y in dm	Co Cobalt t/y in dm	Cu Copper t/y in dm	K Potassium t/y in dm	Mo Molyb-denum t/y in dm	Se Selenium t/y in dm	Zn Zinc t/y in dm
sludge from production of potatoe products	5,0	*	-	-	0	-	-	-	2
sludge from production of dairy products	10,0	*	-	-	0	-	-	-	2
sludge from processing vegetables and fruits	10,0	*	-	-	1	-	-	-	2
paper sludge	4,0	*	-	-	0	0	-	-	0
Paper sludge ash	-	*	-	-	-	-	-	-	-
DND sludge	50,0	*	-	-	203	-	-	-	550
DND sludge/ filter cake mixed sample	2,0	*	-	-	36	-	1	-	2
Enamel glaze sludge	0,1	*	-	-	0	-	-	-	4
Filter dusts from production of ceramic industry	0,0	*	-	-	-	-	-	-	1
Zinc iron salt residue from galvanization	0,4	*	-	-	-	-	-	-	288
Floatation sludge from cleaning used blasting grit	0,5	*	-	-	20	-	-	-	12
Petroleum refinery – sludge from biological WWTP	5,0	*	-	-	2	-	-	-	18
Petroleum refinery – sludge from the oil / water / sludge separator	5,0	*	-	0	3	-	0	-	22

* estimation

3.4 Solid wastes from households and industry chain in NL

Many Dutch municipalities separately collect vegetable, fruit and garden (VFG[4]) wastes to produce compost (keurcompost) that can be applied on agricultural land (Certificeringscommissie Keurcompost, 2015). The VFG waste is increasingly used for anaerobic digestion and biogas production before it is composted.

According to (Vereniging Afvalbedrijven, 2014) 41 % of the Dutch municipal solid waste (MSW) that is incinerated can be classified as VFG waste. In order to increase the separation of organic and non-organic streams an additional separation step is sometimes included after the collection of waste. MSW can be separated into a solid fraction and an organic wet fraction[5]. Also out of date products from industry can undergo such a separation process. The organic wet fraction is used for biogas production. That digestate together with the solid waste fraction from MSW and industry as well as hazardous household waste are incinerated at a solid waste incineration plant. Fly ashes and bottom ashes are the residues. In the Netherlands these outputs of incineration plants are huge waste streams with 1.924 kton bottom ash and 111 kton fly ash per year.

[4] In Dutch: groente, fruit en tuinafval (GFT)
[5] In Dutch: ONF = Organische Natte Fractie

Non-recyclable and non-combustible wastes are landfilled. Used cooking oils and animal fats are collected separately in order to produce biodiesel. The byproducts of biodiesel production like glycerines and potassium sulfates can be used in agriculture.

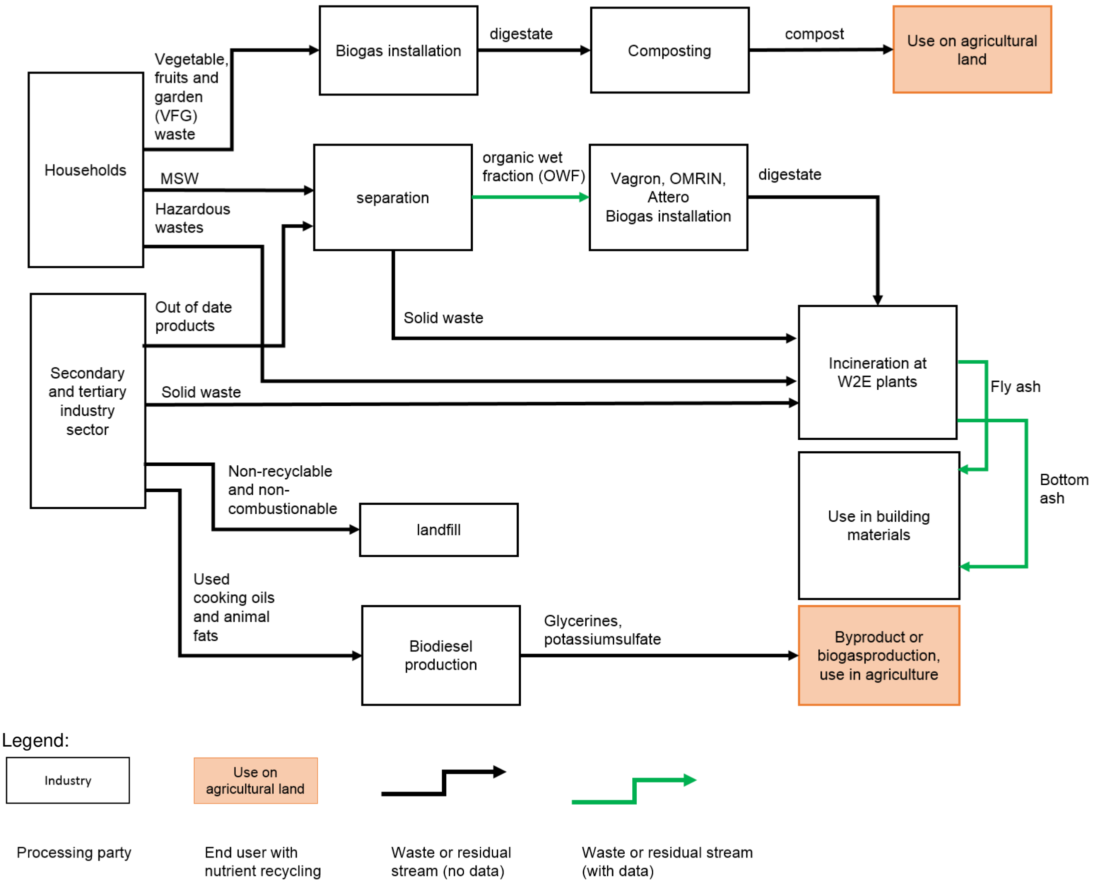


Figure 3.3 Solid wastes from households and industry chain in NL

Table 3.5 shows the concentrations of nutrients in the residual streams for which data has been found. The gradient scale goes from red (no or very low concentration) via yellow (5 % of maximum value in comparison to all streams examined in this study including other chains) to green (highest concentration). When there were no data found in literature about certain nutrient concentrations a '-' symbol was used. However this does not necessarily mean that no traces are present, just that they were not measured or reported. Also important to note is that these values are sometimes averages of measurements repeated over a longer period and from different treatment sources. These values are hence indications and can vary per batch and treatment facility due to change in inputs.

Table 3.5 Concentrations of nutrients in the solid wastes chain in NL

Residual stream	source of information	B Boron mg/kg in dm	Co Cobalt mg/kg in dm	Cu Copper mg/kg in dm	K Potassium mg/kg in dm	Mo Molyb-denum mg/kg in dm	Se Selenium mg/kg in dm	Zn Zinc mg/kg in dm
Organic Wet Fraction (OWF)	(ECN, 2017) #3198 - NL	-	18	471	18.311	34	2	1.226
bottom ash MWIP	Tauw internal, 2017, averages - NL	-	40	2.851	7.765	26	5	3.802
fly ash MWIP		-	26	1.426	34.021	775	17	25.754

For three streams data has been found. Concentrations of copper are relatively high in bottom and fly ashes of MWIP's. Potassium is high in Organic Wet Fraction, probably to a large extent dissolved in the water fraction of OWF. Potassium is also high in fly ash from MWIP. The concentration of zinc in ashes of MWIP's is high, especially in the fly ash. The fly ash also contains relatively high concentrations of molybdenum.

Table 3.6 shows the total amounts of nutrients in the solid waste chain in the Netherlands. High amounts of Potassium, zinc and copper could be recovered from MWIP bottom ashes. From fly ash high amounts of potassium and zinc could be recovered.

Based on the available data the stream organic wet fraction is not very promising for recycling potassium because it is input for waste incineration and the potassium content is higher in fly ashes than in OWF and because the theoretic recoverable amount of potassium is higher in fly ash than in OWF.

Table 3.6 Total amounts of nutrients per stream per year for the solid wastes chain in NL

Residual stream	Size of flow in NL in kt/year dm	B Boron t/y in dm	Co Cobalt t/y in dm	Cu Copper t/y in dm	K Potassium t/y in dm	Mo Molyb-denum t/y in dm	Se Selenium t/y in dm	Zn Zinc t/y in dm
Organic Wet Fraction (OWF)	90,0 *	-	2	42	1.648	3	0	110
bottom ash MWIP	1.924,3	-	77	5.486	14.942	50	10	7.316
fly ash MWIP	110,8	-	3	158	3.770	86	2	2.854

* estimation

In addition to the big streams mentioned above another possible source for fertilizer production are portable batteries. A concept of this has been presented at the Nutrient Platform on 23rd of March 2017 by Brimstone fertilizers.

In the European Union (28 countries) 212.000 tons (NL 7.849 ton) of portable batteries and accumulators have been brought on the market in 2015; only 84.000 tons (NL 3.430 tons) have been collected separately as waste (Eurostat, 2016). This means that the battery waste collection rate is below 50%. Most batteries are collected and treated via the municipal solid waste chain although they are hazardous waste. This means they end up in waste incineration plants. Moreover, 10% of the portable batteries in the EU are zinc-carbon batteries; more than 70 % of all battery sales in the EU are alkaline Zn-MnO_2 batteries (EPBA, 2017). For recycling, the metals from crushed alkaline batteries are mechanically separated, and the waste black mass is treated chemically to separate zinc, manganese and potassium (Tanong & et. al., 2014).

3.5 Biomass and livestock farming chain in NL

This chain focusses on residual flows from agriculture, landscaping and livestock. Organic wastes can come from the sectors agriculture, horticulture, forestry and landscaping. Clean organic waste like roadside mowings can be composted. This compost can be used on agricultural land. Another part is incinerated at waste incineration plants or combusted decentralized for example in domestic homes. The ashes are predominantly reused as a filling material in the building industry. Another fraction is incinerated in a biomass incinerator for energy production (BEC). Biomass wastes can also be used as input for co-digestion with manure.

Manure contains many nutrients and is applied directly on agricultural land or after anaerobic digestion. The use of manure on agricultural land is regulated by the Dutch government and the EU (Rijksoverheid, 2017). Because of a higher manure production than can be used in Dutch agriculture, part of the manure is exported for agricultural use abroad.

Chicken manure is mono-combusted, and the ashes are exported, The ash has a high phosphorus and potassium concentration, and the nutrients are recovered by use of the ash as fertilizer.

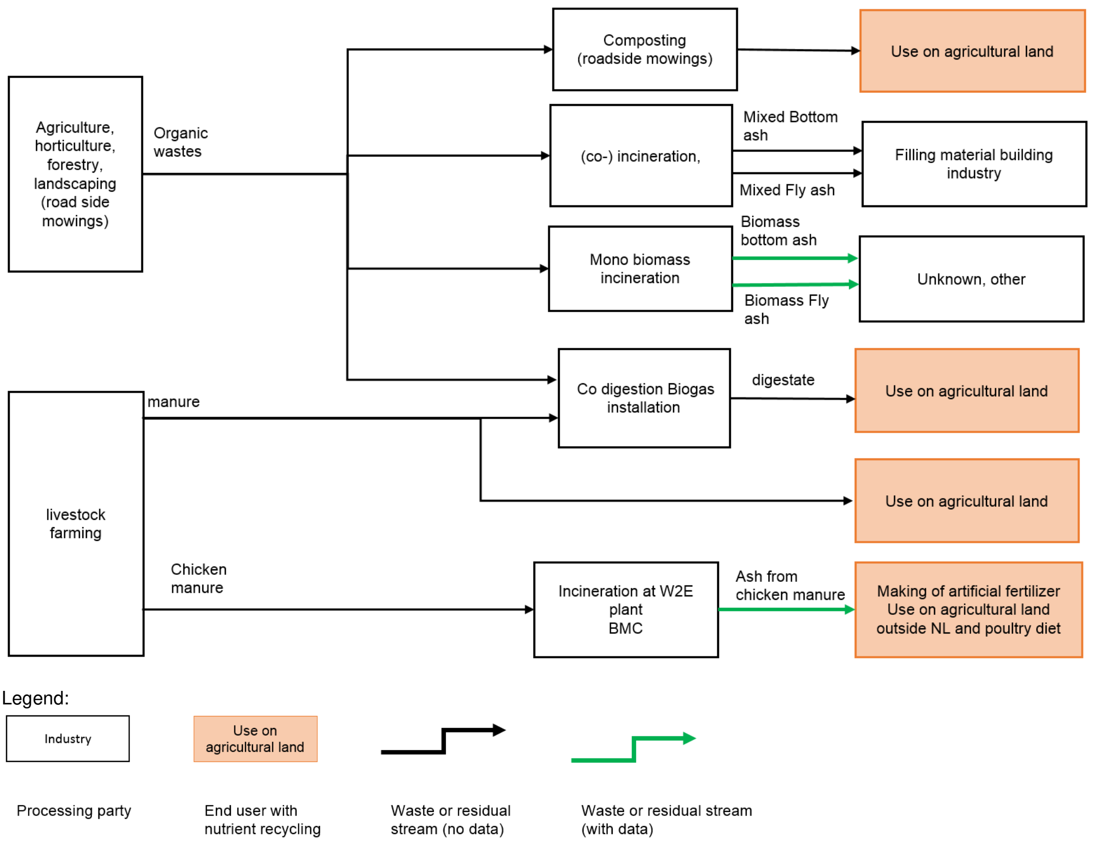


Figure 3.4 Biomass and livestock chain in NL

Table 3.7 shows the concentrations of nutrients in the residual streams for which data has been found. The gradient scale goes from red (no or very low concentration) via yellow (5% of maximum value in comparison to all streams examined in this study including other chains) to green (highest concentration). When there were no data found in literature about certain nutrient concentrations a '-' symbol was used. However this does not necessarily mean that no traces are present, just that they were not measured or reported. Also important to note is that these values are sometimes averages of measurements repeated over a longer period and from different treatment sources. These values are hence indications and can vary per batch and treatment facility due to change in inputs.

Table 3.7 Concentrations of nutrients in the biomass and livestock chain in NL

Residual stream	source of information	B Boron mg/kg in dm	Co Cobalt mg/kg in dm	Cu Copper mg/kg in dm	K Potassium mg/kg in dm	Mo Molyb-denum mg/kg in dm	Se Selenium mg/kg in dm	Zn Zinc mg/kg in dm
BEC bottom ash	Tauw internal, 2017, averages - NL	-	-	980	12.500	6	-	3.000
BEC fly ash		-	-	405	17.500	9	-	4.075
Bottom ash combustion of wood chips	(Obernberger & Supanicic, 2009) - AT	-	-	148	-	-	-	453
Coarse fly ash combustion of wood chips		-	-	195	-	-	-	2.464
Fine fly ash combustion of wood chips		-	-	175	-	-	-	5.850
Coarse fly ash combustion of bark		-	-	162	-	-	-	3.024
Fine fly ash combustion of bark		-	-	152	-	-	-	6.828
Ash from chicken manure	(ECN, 2017) #3499 - NL	107	52	307	112.416	119	5	2.747

The concentrations and quality of biomass ashes from biomass incinerators vary a lot between the installations but also at the same installation over time. This is due to the mixes of inputs that vary over time, like pruning wood from parks, wood chips from pine trees (Pels, 2011)

Table 3.8 shows the total amounts of nutrients in the biomass and livestock chain in the Netherlands. There are no mono-incineration plants for wood chips and bark in the Netherlands, hence these flows do not occur.

Table 3.8 Total amounts of nutrients per stream per year for the biomass and livestock chain in NL

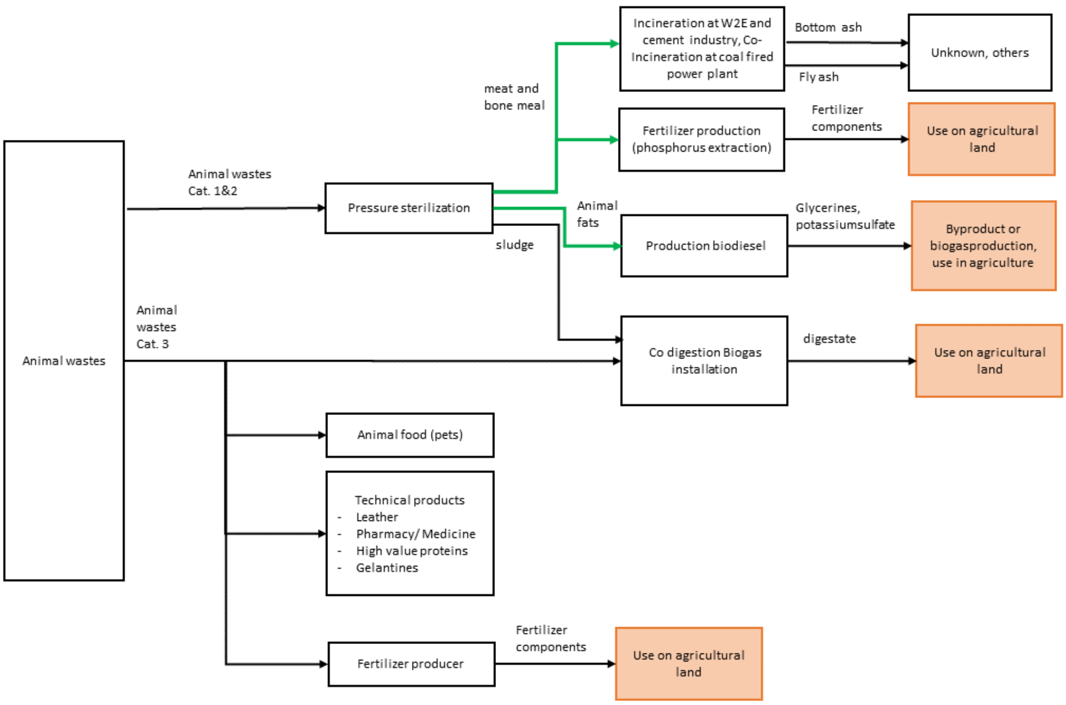
Residual stream	Size of flow in NL in kt/year dm	B Boron t/y in dm	Co Cobalt t/y in dm	Cu Copper t/y in dm	K Potassium t/y in dm	Mo Molyb-denum t/y in dm	Se Selenium t/y in dm	Zn Zinc t/y in dm
BEC bottom ash of B-wood incinerator	19,0	-	-	19	238	0	-	57
BEC fly ash of B-wood incinerator	6,0	-	-	2	105	0	-	24
Bottom ash combustion of wood chips	-	-	-	-	-	-	-	-
Coarse fly ash combustion of wood chips	-	-	-	-	-	-	-	-
Fine fly ash combustion of wood chips	-	-	-	-	-	-	-	-
Coarse fly ash combustion of bark	-	-	-	-	-	-	-	-
Fine fly ash combustion of bark	-	-	-	-	-	-	-	-
Ash from chicken manure	60,0	6	3	18	6.745	7	0	165

3.6 Slaughterhouse waste and animal cadavers and carcasses chain in NL

Animal wastes occur at animal farms, slaughter industry, food processing industry and laboratories. There are 3 categories of animal wastes in the Dutch legislation. Category 1 and 2 wastes are seen as hazardous waste: category 1 as major hazard, category 2 as minor hazard. Category 3 material is meat that is not destined for human consumption but is eligible for animal feed (Rijkswaterstaat, 2017).

Category 1 and 2 animal wastes are collected separately by a rendering company (Rendac). In the Netherlands these wastes undergo a pressure sterilization. The products out of this process are sludge, meat and bone meal, and animal fats. Sludge can be used for co-digestion. Meat and bone meal is mostly incinerated by the cement industry (ENCI) and by E.ON, a power plant (De Ruijter et al., 2015). Phosphorus can also be extracted from meat and bone meal which is then used for artificial fertilizers. Animal fats are used in biodiesel production (NVWA, 2017).

In the Netherlands Darling Ingredients is processing category 3 material into several products like animal foods and technical products. The inputs are also very diverse: raw milk from healthy animals, hooves, hair, feathers and horns of animals approved for human consumption, products of animal origin, kitchen wastes. (NVWA, 2017).



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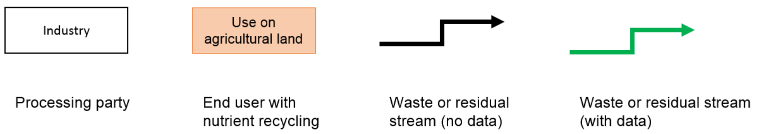

Figure 3.5 Slaughterhouse waste and dead animals chain in NL

Table 3.9 shows the concentrations of nutrients in the residual streams for which data has been found. The gradient scale goes from red (no or very low concentration) via yellow (5 % of maximum value in comparison to all streams examined in this study including other chains) to green (highest concentration). When there were no data found in literature about certain nutrient concentrations a '-' symbol was used. However this does not necessarily mean that no traces are present, just that they were not measured or reported. Also important to note is that these values are sometimes averages of measurements repeated over a longer period and from different treatment sources. These values are hence indications and can vary per batch and treatment facility due to change in inputs.

Table 3.9 Concentrations of nutrients in the slaughterhouse waste and dead animals chain in NL

Residual stream	source of information	B Boron mg/kg in dm	Co Cobalt mg/kg in dm	Cu Copper mg/kg in dm	K Potassium mg/kg in dm	Mo Molyb-denum mg/kg in dm	Se Selenium mg/kg in dm	Zn Zinc mg/kg in dm
Meat & bone meal	(ECN, 2017) #2193 - NL	-	2	31	6.000	-	-	138

Table 3.9 only gives data on meat and bone meal. The other animal wastes are already recycled, in agriculture or as animal feed. Meat and bone meal has a relatively high potassium concentration.

The amounts of meat and bone meal produced in the Netherlands are not publicly available but can be derived from unpublished material of Smit et al. (2015) who studied phosphorus flows in the Netherlands. They estimated for 2011 an amount of 84 ton of meat and bone meal incinerated in the Netherlands. Combined with Table 3.9 this would give an annual flow of 504 ton potassium, next to almost 3 million kg P as calculated by Smit et al. (2015).

3.7 Coal chain in NL

The composition of coal ash is dependent on the quality of the coal, and co-fired material also has a small influence (see also subchapter 3.2). In table 3.10 one can see the concentrations of nutrients in coal ash.

Table 3.10 Concentrations of nutrients in coal ash

Residual stream	source of information	B Boron mg/kg in dm	Co Cobalt mg/kg in dm	Cu Copper mg/kg in dm	K Potassium mg/kg in dm	Mo Molyb-denum mg/kg in dm	Se Selenium mg/kg in dm	Zn Zinc mg/kg in dm
coal ash at coal fired power plant	(van der Sloot & et al, 1985) - global	2.013	155	500	740	250	75	1.000
fly ash at coal fired power plant		475	5.000	303	-	300	335	3.100

In comparison to the other streams investigated, coal ashes contain higher amounts of boron, cobalt and selenium. Hence coal ash can be a source for different nutrients than already covered. The amounts of coal ashes produced in the Netherlands are between 1,5 (av) and 2 mln (max) ton fly ash/year (Compendium voor de Leefomgeving, 2017). That means 713 ton/y B, 7.500 ton/y Co, 455 ton/y Cu, 450 ton/y Mo, 500 ton/y Se and 4.650 ton/y Zn.

In the long run however the amounts are expected to decrease according to plans of the Dutch government who wants to shift to the production of renewable energies and to eliminate the use of fossil fuels by 2050. Right now the ashes are used in the cement industry.

3.8 Economic aspects

With the information about waste streams, concentrations and the nutrient prices in paragraph 2.4 the theoretical value per ton of the waste stream is estimated, see table 3.11.

Table 3.11 Estimation of value waste streams related to the specific nutrient

Nutrient	Max. concentration in mg/kg d.m.	Stream	Price in USD/kg	Value in USD per t waste stream d.m.
Gold	11	Gold ores	38.812,35	426,94
Boron	2.013	PCA coal ash	0,4	0,81
Boron	200	sewage sludge, anaerobic digestion	0,4	0,08
Cobalt	5.000	PCA fly ash	28,88	144,40
Cobalt	40	BEC bottom ash of B-wood incinerator, higher values for clean mono streams	28,88	1,16
Copper	39.000	Floatation sludge from cleaning used blasting grit	5,74	223,86
Copper	2.851	bottom ash MWIP	5,74	16,36
Copper	1.033	sewage sludge ash	5,74	5,93
Potassium	34.021	BEC fly ash of B-wood incinerator	0,22	7,48
Potassium	34.021	fly ash MWIP	0,22	7,48
Potassium	4.200	sewage sludge ash	0,22	0,92
Molybdenu	775	fly ash MWIP	15,25	11,82
Selenium	335	PCA fly ash	50,27	16,84
Selenium	75	Dried sludge	50,27	3,77
Zinc	72.000	Zinc iron salt residue from galvanization	2,73	196,56
Zinc	79.882	Enamel glaze sludge	2,73	218,08
Zinc	39.000	Filter dusts from production of ceramic industry	2,73	106,47
Zinc	25.754	fly ash MWIP	2,73	70,31
Zinc	23.000	Floatation sludge from cleaning used blasting grit	2,73	62,79
Zinc	11.000	DND sludge	2,73	30,03
Zinc	6.633	sewage sludge ash	2,73	18,11
Zinc	4.400	Petroleum refinery – sludge from the oil / water / sludge separator	2,73	12,01
Zinc	3.802	bottom ash MWIP	2,73	10,38
Zinc	3.600	Petroleum refinery – sludge from biological WWTP	2,73	9,83

3.9 Summary of residual streams with available data

In this chapter the waste streams and their composition and concentration of relevant nutrients are investigated. Sometimes data about concentrations of waste streams and the amount of waste streams were difficult to obtain, and the concentrations of waste streams may vary due to changing inputs. Nevertheless, the investigation has delivered more knowledge about the waste streams with the highest nutrient concentrations and the theoretical recoverable nutrients quantities in waste flows are identified.

Zinc:
- Bottom ash and fly ash from MWIP's
- Composted sludge from WWTPs
- The residue of the Ecophos process

Potassium:
- The residue of the Ecophos process
- Composted sludge from WWTPs
- Bottom ash and fly ash from MWIP's

Copper:
- Bottom ash from MWIP's

Boron, cobalt and selenium:
- Coal ash contains significant amounts of boron and coal fly ash cobalt and selenium

In the next chapter the opportunities to recover the prioritized nutrients in the identified waste streams are identified in more detail.

4 Opportunities for nutrient recovery

4.1 Introduction

With the background of priority nutrients and flows containing nutrients in mind strategies for recovering nutrients are explored in this chapter. Four strategies of recovery have been developed in chapter 4.2.

In chapter 4.3 the demand side of possible recovered nutrient products is elaborated.

For each strategy a literature review has been carried out and potential recovery techniques suited for mineral nutrients are presented in chapter 4.4. In this chapter real chances of recovery become visible without ranking of the best routes. In paragraph 4.5 a summary of the opportunities is presented.

4.2 Strategies for nutrient recovery

In Figure 4.1 four different strategies for nutrient recovery are shown in a value pyramid. The product on the top of the pyramid has the highest value and is the lowest in volume and mass at the same time. The higher on the pyramid the purer the product is.

At the bottom of the pyramid the residual stream is completely reused with no or little processing. The direct applied stream contains a mix of nutrients and maybe also other ingredients such as organic matter. Direct application (e.g. in agriculture) can take place when the contaminations on the stream are within legal limits.

When the stream is contaminated the stream may be cleaned. The end product is similar to the clean stream, but extra processing is needed, for example contaminants such as plastics, medical residues or heavy metals are removed. The removed contaminants are wastes.

Another strategy is separation of the residual flow. Different mixes of nutrients could be separated based on their physical and chemical properties, for example separating a solid and a liquid fraction. This results in products of smaller size; the division of nutrients may vary per fraction and results in different nutrient mixes of the products.

The last option for nutrient recovery is extraction, the product will be a pure mineral nutrient. Hence, the volume of the product will be low but the value of a pure mineral is high. The residue that remains after extraction needs to get a proper destination.

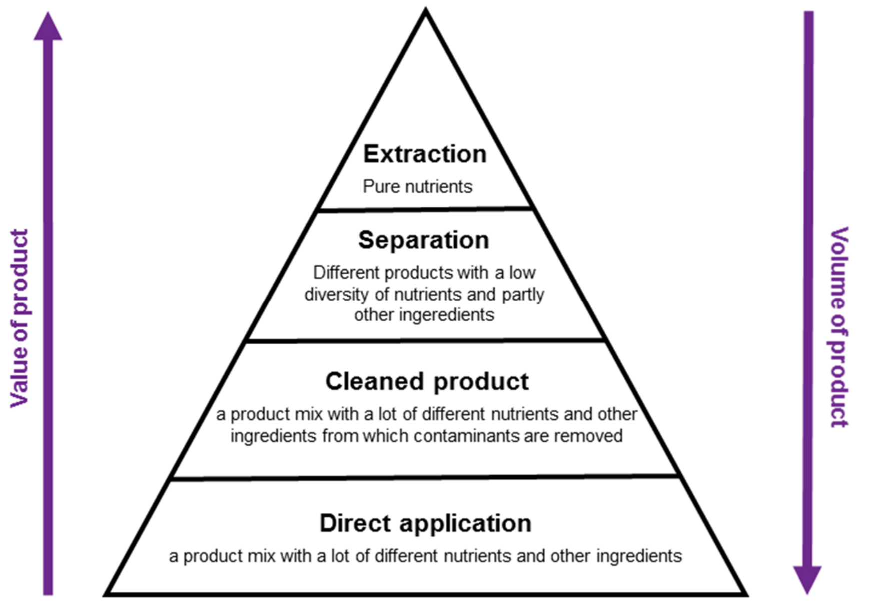

Figure 4.1 Strategies for nutrient recovery

In general, the higher one climbs the value pyramid the more advanced technology has to be applied. To make extraction economic feasible the concentration of the nutrient has to be high in the (waste) stream and the market value of the refined product has to justify the costs for extraction.

The feasibility of the 4 strategies and the connected opportunities for (waste) streams and nutrients recovery are largely dependent on the concentration of the nutrient in the (waste) stream and the contamination of this stream. In Figure 4.2 an ‘empty’ picture shows this relationship. Also, the legal threshold(s) for direct application is incorporated. This figure can be ‘filled’ with cases to show the possible ways of reuse and accompanying bottlenecks and necessary roadmaps.

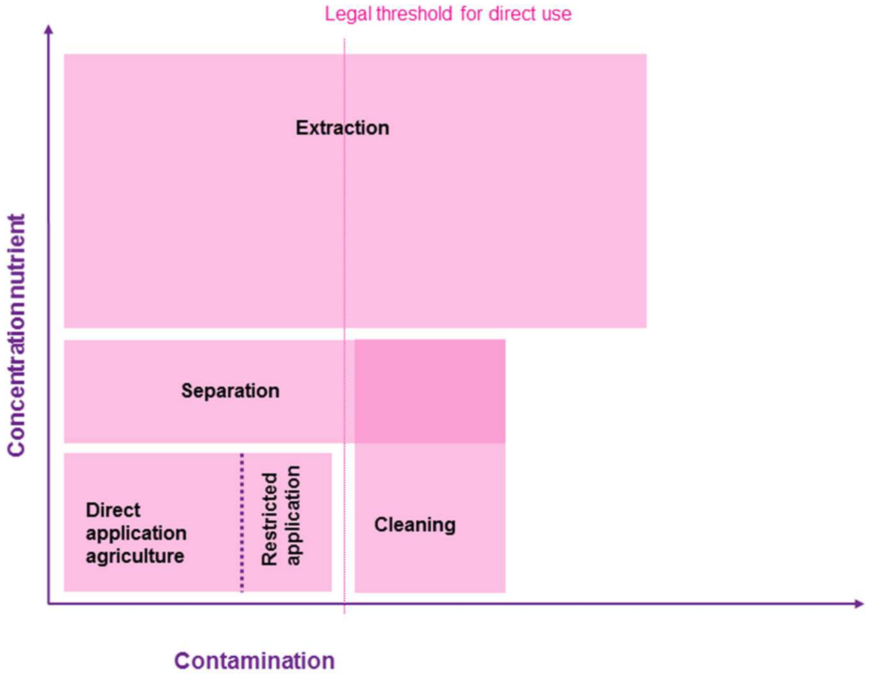

Figure 4.2 Relationship nutrient recovery strategies and concentration and contamination waste streams (empty)

In the following the 4 recovery strategy scenarios are explained in further detail.

Direct application

If contamination is below legal thresholds, the stream can be applied directly for agricultural use provided the nutrients are present in usable form. The legal context of direct application of waste streams is complex in the Netherlands and will be described more in detail in chapter 4.4.2. Direct use of a residual flow involves no specific treatment of the flow, and no changes in the nutrient contents of the product. For specific contaminations, direct application may be allowed with restrictions. This is a scenario for ‘low hanging fruits’; where no additional technology is needed to close the nutrient cycle.

Cleaned stream

Streams of this category exceed legal threshold of contaminants. Cleaning means to **remove undesired physical substances** from a residual flow, aimed at use of the major part of this flow. Undesired substances can be plastics, heavy metals, organic pollutants, pathogens. Cleaning is broadly **achieved through mechanical action and/or extraction**. In some cases the nutrient content of the flow changes, e.g. when (some of) the heavy metals are removed.

Separation

Separation means to **split the flow into two or more parts**, aimed at using both parts for different purposes, or only the most valuable part or the least polluted part. Some nutrients can be concentrated in a specific fraction, and/or nutrients can be separated from pollutants. **Separation processes use the differences in either size, shape, mass, density or chemical affinity** between the constituents of a mixture. Usually there is **only physical** movement and no substantial chemical modification. Generally, a mixture of nutrients will be available. The separated flows for nutrient recovery have to be clean, additional cleaning process may be needed. Removal of water to concentrate the flow also fits into this section.

Extraction

Extraction aims to retrieve pure nutrients. Extraction is a **separation process consisting in the separation of a substance from a matrix whereby additional force is used**. Often a substantial **chemical modification** takes place. These products have the highest market value because of their ease of application (for example in artificial fertilizers and customized nutrient mix in fertilizers), and have a broader range of potential users. Because pure nutrients are extracted the contamination of the residual stream is less relevant because it stays in the waste stream and not in the product. The residual flow needs a proper destination.

The determination of the most feasible and practical strategy depends on several aspects. If contaminations are within legal limits, a specific flow can be used as it is. Direct use saves costs for treatment, but often the flow has a large volume with higher costs for application. Purified nutrients are much easier to store, transport and use, and have a higher value compared to nutrients that are present at low concentrations and mixed with other nutrients. Therefore, the best strategy will be determined by the balance between costs for transport, storage and application, and costs for extraction. In the BioNPK project, recovery of minerals from residual flows from food processing industry was studied (sugarbeet, potato, wheat). Many business cases appeared to be negative. Extraction of minerals from these flows required quite some energy and other inputs, and 'no treatment' appeared to be the best option from an economic point of view. In 2013, cost price to produce traditional fertilizers was often much lower than what is feasible from industrial residual flows (Vermeulen et al, 2013).

4.3 Potential users of recovered nutrients

4.3.1 Introduction

Nutrients are essential for plant and animal production, and potential users are therefore agri-culture, livestock, forestry and fishery. Next to direct application in agriculture, other potential customers for nutrients from residual flows are the fertilizer industry and the livestock feed industry through which nutrients also go to agriculture. Nutrients can have other applications than for plants and animals, and for recovered nutrients non-agricultural users may be more applicable because of food safety and/or public opinion. In the next paragraphs the demands of several potential uses are elaborated in more detail:

- Agriculture and livestock
- Forestry
- Fertilizer industry and other industries

4.3.2 Demands in agriculture and livestock

Crop production demands fertilizer, and livestock production demands nutrients in feed.

Crop production in agriculture is the largest user of nutrients, and regular additions of nutrients to the soil are needed to compensate for nutrient export by harvested crops and for nutrient losses. Crops absorb a range of nutrients, and therefore agriculture can use products that contain a (preferably optimal) mixture of nutrients. Precision agriculture asks for a balanced mix of nutrients; the nutrient concentrations may vary during the seasons. Customized nutrient mixes are a hot topic at the moment. A current discussion is However, specific fertilizers with single nutrients are needed as well to balance crop nutrient demand and nutrient supply. The use of an optimal balance of nutrients can is necessary for (precision) agriculture. Taylor made mixtures of recovered nutrients can be used in this type of agriculture.

A product with recovered nutrients must be permitted for use as fertilizer. Bulk products with a nutrient mixture must compete with animal manure, and use by farmers will be determined by price and product properties. When the product has similar properties as manure (liquid and a high volume) prices will be negative. For purified single nutrients, prices can be compared with current fertilizers.

For livestock and fishery, feed products are required. In addition to feed products, specific nutrients are added to the diets to optimize mineral nutrition of the animals.

For use as feed, there is a range of requirements: product registration, risk analysis (HACCP), traceability, and concentrations of undesired substances must be within limits (EC, 2002; Hoving et al., 2012). In contrast to the negative price of manure-like products, feed can have a positive price based on feeding value.

4.3.3 Demands of forestry

In Sweden and Finland, ashes are returned to forests to prevent acidification and maintain the nutrient balance. In Dutch forests, only potassium is a relevant nutrient to add, as all other nutrients are amply available (Pels, 2011). Therefore, there is no demand for nutrients in forestry, except potassium. Eventually forestry optimized artificial fertilizers may be demanded.

4.3.4 Demands in fertilizer industry and other industries
Fertilizer industry can incorporate residual flows in their processes to produce single and compound fertilizers. As raw material, the residual flows have to compete with ores. Processing of the residual flows can reduce risks to public health, but public opinion on products from anthropogenic waste can still play a role. In Dunkirk, Ecophos constructs two separate plants to be able to separately treat the ashes from mono-incinerated communal waste water sludge ash and have a separate destination of recovered nutrients, mainly phosphorus.

For recovery of metals in metallurgical processes, the (pre-concentrated) waste stream must contain a certain minimum amount of metal and there are also demands regarding contaminants which result in increased emissions to water or air.

4.4 Nutrient recovery techniques

4.4.1 Introduction
This paragraph discusses nutrient recovery techniques along the strategies as described in paragraph 4.2. Single techniques may be used to recover nutrients from residual flows, but often a combination of techniques will be applied. For example, pre-treatments such as filtration can be applied to remove solid particles before a flow is treated in a crystalliser. Or techniques can be combined to first capture and concentrate nutrients from diluted flows (e.g. using plants or membranes), and subsequently use the concentrated flow directly in agriculture as feed or fertilizer, or to extract nutrients (Mehta et al., 2015).

Figure 4.3 shows the nutrient concentration and contamination grid, and the position of various flows (chapter 3). It is an indicative figure, where the diameter of a circle indicates the size of the flow. For different nutrients, the position of the flows can vary as concentrations differ for different nutrients, and the elements Cu and Zn can both be seen as a recoverable resource and a contamination.

The orange shaded circles in the bottom left represent residue streams where direct application is already employed. VFG Compost and Green Waste Compost are regular products from organic wastes. Food industry residues that are used in animal feed consist of products such as beet pulp and potato steam peel. Size of the flows is estimated based on BVOR (2016) and Smit et al. (2014). Example for a flow that is applied in agriculture after a separation step is Betafert, which is the solid fraction of the digestate of sugar beet residues. As nutrients in these flows are already recycled, these flows will not further be discussed in the present study.

Cleaning, separation or extraction may be applied to products from communal waste water treatment that have concentrations of contaminants that are around the legal threshold for agricultural application. EU regulation thresholds and country specific regulations differ, and regulations in the Netherlands prevent direct agricultural application of these products. Export of sludge can be an option (STOWA, 2014), and actions to enable export of composted sludge to France are in progress (GMB, 2016).

Most nutrient concentrations increase from sludge to composted sludge to ash from mono-incinerated sludge. This is not valid for all nutrients, as e.g. nitrogen is lost to the air during incineration.

Ashes from biomass incineration (BEC fly ash and BEC bottom ash) are smaller flows than ash from communal waste water treatment but with similar properties. Metal content in BEC ashes can be lower, depending upon the quality of the processed biomass (e.g. A or B wood). Flows from various industries and solid waste incineration are not suitable for direct agricultural use, but some flows may have sufficiently high nutrient concentrations that allow extraction of specific nutrients.

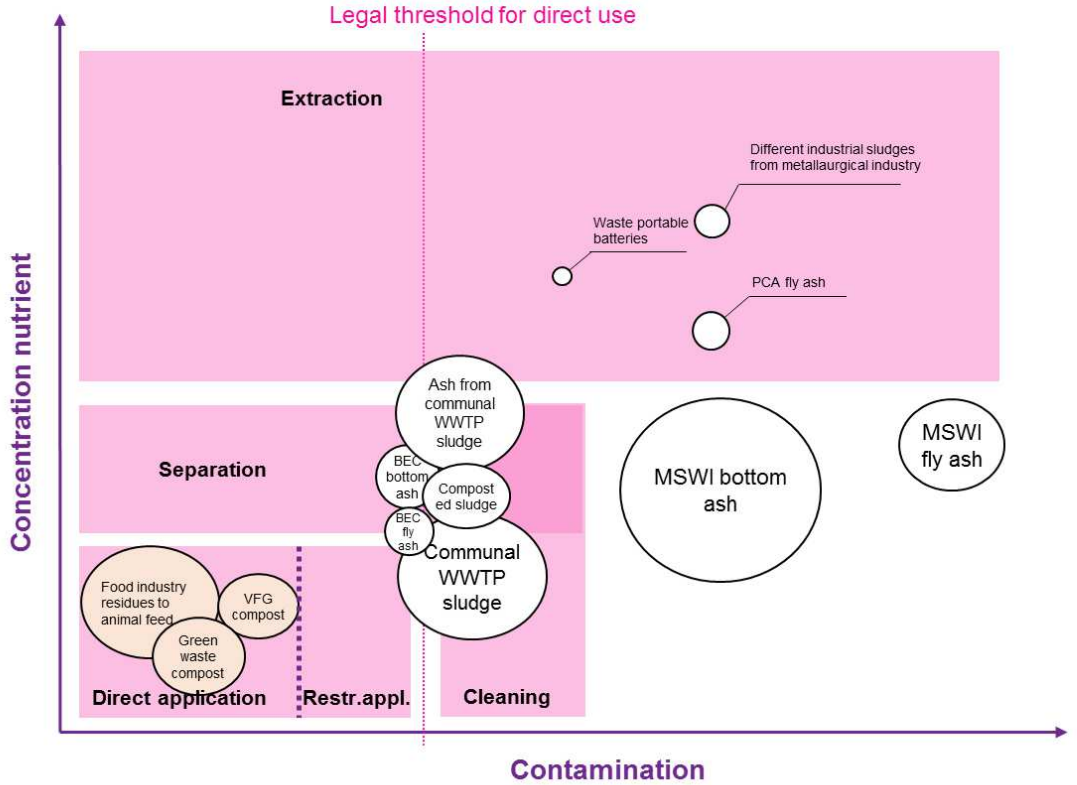

Figure 4.3 Relationship nutrient recovery strategies and concentration and contamination waste streams (filled with the results from chapter 3)

4.4.2 Direct use without treatment

Direct use of waste flows without specific treatment or extraction of specific nutrients is one way to close the nutrient cycle. In the present report, direct use without treatment is defined as application to fields in agriculture. Use in specific biomass production, e.g. algae or energy crops, is regarded as a recovery technique and described in paragraph 4.4.6.

There are sufficient techniques available to apply residual products to fields in agriculture, the major ones being manure spreaders, both for solid manure and slurry.

Most products that can be used directly are already used as animal feed or fertilizer product, e.g. VGF-compost and several products from the food industry (De Ruijter et al., 2015). In Sweden and Finland, ash from energy wood is recycled as fertilizer for which specific legislative and technical aspects have been developed (Stig Emilsson, 2006; Swedish Forest Agency, 2008). Rationale behind the ash recycling is to compensate for nutrient depletion and counteract acidification, aiming to return only the amount of heavy metals that was present in the harvested trees.
Direct agricultural use of sludge from communal wastewater treatment does not occur in the Netherlands, due to maximum tolerated heavy metal concentrations and the restriction on mixing with other products. However, sludge characteristics vary between WWTPs, and relatively clean sludge might be used as fertilizer or soil conditioner (STOWA 2014). This has been explored by Water board Hunze en Aa's in the project 'Vruchtbaar slib' (Fertile sludge) (Koop, 2016; Van der Maas, 2016). The project concluded that there are opportunities for renewed use of sludge in agriculture if technical, economic and social aspects are improved: reduced P content, hygienic status and quality assurance.

Use of sludge in agriculture is further investigated in the Wageningen UR project Sludge2Soil (Regelink, 2017) using techniques of solid-liquid separation and extraction of phosphorus by struvite precipitation.

Metals and Pharmaceuticals and Personal Care Products (PPCP) require attention and regulation to prevent accumulation in the soil upon repeated application, next to pathogen concentrations in biosolids and micro-plastics (Healy & et al, Health and Water Quality Impacts Arising from Land SPreading of Biosolids, 2017).

Dutch legislation is restricting the use of (direct application) of possible nutrient rich residual streams. In the fertilizer law (meststoffenwet) and the fertilizers decree (Besluit gebruik meststoffen) legal thresholds are set. They also regulate whether a product can be used as a fertilizer and under which conditions. When the 'product' has the status of 'waste' additional legal restrictions apply (for example no mixing, waste treatment permit, administrative requirements for

transport and others). In order to lose that status ‘waste’ the applied technology and impact of use have to comply to the precautionary principle of the Waste Framework Directive (Kaderrichtlijn Afvalstoffen):’ may not lead to overall adverse environmental or human health impacts’. This principle shall also part of the policy for a circular Netherlands and hence also for this study.
The above mentioned laws are applicable to all strategies, technology inputs and endproducts.

4.4.3 Cleaning

Cleaning means to remove undesired physical substances from a residual flow, aimed at use of the major part of this flow. Undesired substances can be plastics, heavy metals, organic (micro) pollutants, or pathogens. Cleaning results in minor changes in nutrient content of the flow (e.g. some of the heavy metals may be removed) and the end product with a mixture of nutrients is most likely to be used in agriculture or biomass production.

Removal of plastics and metals

Metals in metallic form can be removed using magnets, plastics and other inert materials such as stones and glass can be removed by mechanical separation such as sieving. This is applied to VFG waste that is cleaned before and after anaerobic digestion and/or composting.

Removal of pathogens

Pathogens can be removed by high temperatures or by addition of chemicals. For export of manure within the EU, the product must have been at 70°C for at least one hour (EC, 2011). With this treatment, all nutrients remain in the product, but there is a risk of nitrogen loss by ammonia volatilization. Incineration of products is at much higher temperatures and removes pathogens and part of other pollutants such as organic substances. During incineration, C and N are lost.

Composting can be another method to increase temperatures for a prolonged time and reduce pathogens, if properly carried out (Vinneras, 2013).
Pathogens can also be removed or reduced by sanitization with ammonia, which has been studied with sewage sludge, manure and source separated human excreta (Fidjeland et al., 2015; Nordin et al., 2015; Vinneras, 2013). Sufficient reductions were often found for bacteria, but not always for parasitic nematodes. The ammonia originates in the product itself when urea degrades and pH increases, and the concentration can be increased by addition of urea. Addition of urea enriches the product with N. This technique requires closed systems to maintain elevated concentrations of ammonia, and careful field application to prevent ammonia losses.

Removal of heavy metals

Removal of heavy metals in this chapter is aimed to reduce the heavy metal content of the flow to enable to use this flow, e.g. as fertilizer in agriculture or biomass production. The heavy metals may be recovered as well (see Chapter 4.4.5 – extraction) or may end up in a residual product without reuse of the metals.

Heavy metals can be removed from different flows:

- **From wastewater:** wastewater treatment is an example of removal of heavy metals from the wastewater where the heavy metals are concentrated in the sludge. The treated water is low in heavy metals, is currently discharged to surface waters but can also be used for irrigation purpose. This way, nutrients still present in the water (mainly potassium) can be used.
- **From sludge:** removal of heavy metals from sludge from wastewater treatment might increase the use of sludge as fertilizer or soil conditioner and thus increase nutrient reuse. The feasibility to clean sludge from communal wastewater treatment, especially removal of heavy metals, has been explored by STOWA (2014). Three processes were compared:
    - Separation into an organic and inorganic fraction
    - Electrolysis
    - Leaching

  They concluded no heavy metal removal techniques were available at sufficiently low costs. STOWA (2014) recommended to further explore options to separate inorganic and organic fractions using acids and bases, as these techniques are applied in metal industry and had lowest costs. Bioleaching is possibly an alternative for chemical leaching, especially for digested sludge, which contains sulphides. There is much practical experience with bioleaching of tailings or ores with low metal contents, especially with copper ores. Bioleaching of wastewater sludge has been investigated at laboratory scale (e.g. Ito et al (2008), Tichy (1998), Steketee et al (2000). Over the years, bioleaching has been developed as an environmentally friendly and cost-effective technology for the removal of heavy metals from the sludge. However, there are still various technical problems associated with the bioleaching process, which need to be addressed while developing the process on a larger scale. (Pathak, Dastidar, & Sreekrishnan, 2009)

- **From ash:** ashes are generally treated with extraction techniques (see chapter 4.4.5). Egle et al. (2016) give an overview of technologies to recover P, and of these technologies the Ashdec process is the only one that aims at removing metals from the ash product instead of extracting P. At a temperature of 900-1000ºC, volatile heavy metals (Cd, Cu, Pb and Zn) are removed, but other metals such as As, Cr and Ni remain in the product. Pilot plant has been operational, but the product is not yet market ready (Egle et al., 2016; P-Rex, 2015).

A research consortium has an ongoing project (2016-2019) aimed at extraction and marketing of metals from waste water, sludge and fly ash (Waterforum, 2016). Preliminary research showed opportunities to recover (scarce) heavy metals and rare earth metals such as copper, zinc, gold and palladium. Extraction of these metals improves quality of effluent, sludge and ash. Lower concentrations of copper and zinc increase options to use sludge from communal wastewater treatment.

4.4.4 Separation

Separation means to split the flow into two or more parts, aimed at using both parts for different purposes, or only the most valuable part or the least polluted part. Generally, a mixture of nutrients will be available, and these flows will generally be used in agriculture or in biomass production (e.g. algae, duckweed). Removal of water to concentrate the flow also fits into this section.

Current examples are solid-liquid separation of animal manure, where both fractions are used in agriculture but where transport distances for the different fractions may vary, and solid-liquid separation of digestate from digesters at the sugar industry. From the latter, the solid fraction is used in agriculture, and the liquid part is treated in a waste water treatment plant or concentrated by evaporation (Vermeulen et al., 2013).

A range of techniques can be distinguished to separate flows (Table 4.1). Several techniques are used or have been studied for use in processing of animal manure (Schröder et al., 2009; Velthof, 2011). For recovery of nutrients from water-rich residual flows from sugar, starch and ethanol industry, techniques have been studied in the bioNPK project (Vermeulen et al., 2013).

Separation of flows and the division of nutrients over the different fractions can be influenced by conditions (e.g. temperature, pH) and by use of flocculants. Combinations of techniques are often applied, e.g. a relatively simple solid-liquid separation and a further treatment of the liquid fraction. For manure, the liquid fraction from a screw press filter, band press filter or centrifuge can be concentrated using reverse osmosis. To prevent membrane fouling, reverse osmosis is preceded by techniques as ultrafiltration or filters to extract solid particles (Velthof, 2011).

To concentrate minerals, water can be removed from a liquid fraction by evaporation, membrane distillation, or eutectic freeze crystallization or concentration (Vermeulen et al, 2013).

Table 4.1. Some techniques to separate flows

Technique	Description
Static screen or rotating drum screen	Simple separators that have a high capacity but limited efficiency
Screw press filter	A screw squeezes the material in a perforated cylinder
Belt press filter	The product is pressed between filtering cloths and belts using rollers

Technique	Description
Centrifuge	Centrifugal force helps to increase the rate of settling
Membrane filtration	Pressure and semipermeable membranes separate a flow. The pore size of the membrane determines the particle size that is separated from the liquid. Pore size decreases from microfiltration to ultrafiltration, nanofiltration and reverse osmosis
Eutectic Freeze concentration	Separate liquids (with eg NH4) by freezing

4.4.5 Extraction

Extraction aims to retrieve pure nutrients. These products have highest market value because of their storability and ease of application, and have a broader range of potential users. After extraction of the nutrients, a residual flow remains that needs a proper destination. Extraction may consist of a combination of techniques, generally a technique to concentrate the nutrients is included.

Current examples are:

- P extraction from wastewater flows by struvite precipitation (K- and NH4-struviet) or by CaP
- N recovery by ammonia stripping and acid air scrubbing
- Extraction of P from mono-incinerated sewage sludge ashes

Extraction from ashes

Most research on nutrient recovery from ashes has been focused on phosphorus recovery from mono-incinerated sewage sludge ash (Egle et al., 2016). The present study focuses on recovery of other nutrients than phosphorus, and the technologies to extract P may be used to recover other elements as well, or the waste products from these techniques may be considered for extraction of other elements.

Several techniques to extract elements from ashes have been studied and are under development, but few are applied at pilot scale or full scale. For recovery of nutrients, two techniques are most promising and already applied at pilot or full scale: acid extraction and ammonia leaching.

Acid extraction and further separation

A possibility to separate heavy metals from fly ash is the acid fly ash washing process FLUWA (Fromm & et al, 2017). In Switzerland, more than half of the MSW incineration plants use FLUWA to mobilize heavy metals such as zinc, lead, cadmium and copper from fly ashes. The process is currently aimed at cleaning the ashes from the heavy metals for safe landfilling, but recovery of these and other metals is possible and studied in the SESAM project (Fromm & et al, 2017).

For recovery, the metals are dissolved by adding acid to the fly ash and the product is split using vacuum belt filtration into a rigid filter cake and a heavy metal containing liquid ash filtrate. The filtrate can be used to extract metals for which different methods are available. One route is by hydroxide precipitation resulting in a sludge that contains zinc, lead and cadmium that can be refined to marketable zinc. In this process, other metals are lost, and to extract these other metals as well, polymer-assisted ultrafiltration (PAUF) is added before the hydroxide precipitation. PAUF is based on selective bonding of heavy metals with water-soluble polymers. Using an ultrafiltration membrane, the bound metal ions are separated from the non-bound ions that pass the membrane and are treated with hydroxide precipitation. The bound heavy metals are released by a pH change, and the unloaded polymers can be reused. The released metals pass the membrane and can be captured. This way, selective separation of tin, copper and nickel seems possible, together with recovery of zinc and lead. The entire process is studied in a pilot plant in Germany (Fromm & et al, 2017).

After consultation of the Vereniging Afvalbedrijven it turns out that the members are interested in recovery of zinc from MSW incineration. However, there are a number of practical problems to be solved, especially regarding the economics of the process. In case of extraction, the moisture content of the fly ash increases sharply, and therefore the amount of material which needs disposal. Existing pathways for useful application as filler are based upon treatment of dry material. So, this application becomes impossible or additional treatment (drying, milling) is needed. Also, the application as building material for filling up German mines could become impossible or more expensive.

Application as filler and building material in mines are considered to be useful. It is conceivable that, after extraction of zinc, the current useful applications are not feasible anymore and that the amount of material which has to be landfilled rises. That means that the incineration branch becomes less sustainable regarding the percentage of residues which gets a useful application. This trend would undermine the goal of the policy of the European Commission which aims to decrease landfilling (European Commission, 2017).

The question is how recovery of a small amount of a scarce or critical raw material is valued against a ‘low grade’ useful application of much material, in which the critical metals get lost. But maybe it is possible to combine extraction of zinc with new useful applications of the residue, eventually in combination with other waste streams. Further research is needed to get a complete picture of the possibilities. This discussion illustrates that the processing of the complete waste stream needs to be evaluated and not only the recovery of the nutrients.

Acid extraction will also be applied by Ecophos in extraction of phosphorus acid from mono-incinerated sewage sludge ash (De Ruiter, 2015). In this process, other ions are being extracted with selective ion exchangers, resulting in Al/Fe and Mg/Ca solutions. Stuttgart Sludge leaching also applies acid extraction, and the remaining product after P extraction may be used for recovery of metals (P-Rex, 2015b).

Waste batteries is another flow where acid leaching allows recovery of metals. (Sobianowska-Turek & et al, 2016) researched the reductive acidic leaching of waste material of the zinc-carbon batteries (Zn-C) and zinc-manganese batteries (alkaline Zn-MnO_2); all of them portable accumulators. 'The research data proved that the reductive acidic leaching (H_2SO_4 + $C_2H_2O_4$) of the battery's black mass allows to recover 85,0 % of zinc and 100 % of manganese. Moreover, it was found that after the reductive acidic leaching it is possible to recover nearly 100 % of manganese, iron, cadmium, and chromium, 98,0 % of cobalt, 95,5% of zinc, and 85,0 % of copper and nickel from the solution with carbonate method.'

Ammonia leaching

This is a process developed and patented by Elemetal to recover copper and zinc from MSWI bottom ash, copper containing sludges, non-ferrous streams etcetera. There are four process steps: leaching with an ammonia containing liquid, solvent extraction (for separating copper and zinc), stripping and electro winning. For MSWI bottom ash, successful batch pilot tests were performed at a scale of 500 tons in 2014. The technical feasibility was proven during this pilot project, but due to low metal prices it was decided to revise the process and make it more scalable. Elemetal redeveloped the process during 2015 until now in order to be able to process non-ferrous concentrates from bottom ash and other recycling markets like treatment of End of Life vehicles and WEEE. With the help of an European LIFE grant (http://www.elemetalpcr.com) successful prototype tests were performed during the first half of 2017 to refine pure copper and zinc from non-ferrous input streams, see figure 4.4 for the pilot plant. The economic feasibility is under evaluation and commercial scale facilities are not realized until now. Next phase will be scaling up to a demonstration plant (Elemetal, 2017).

Figure 4.4 Pilotplant Elemetal / Inashco for recovery of copper and other metals from non-ferrous fractions

4.4.6 Production of biomass on waste flows

Biomass production can be used to extract and concentrate nutrients from diluted flows and increase the perspectives of keeping nutrients available in the agricultural system and/or for future extraction (Phytoremediation). These extracted nutrients from diluted flows may also replace fertilizers and thus reduce demand for mined nutrients.

The use of biomass to extract nutrients from residual flows is often aimed at effluent polishing; cleaning a wastewater flow before discharge. Biomass production on waste flows can be carried out with different plant species that grow under water, float on the water surface or root in soil and grow above the water surface (e.g. algae, duckweed, reed, willow) (Huurman & Van der Weide, 2015; Otte et al., 2014).

Biomass can be produced for use in the food chain, e.g. as fertilizer or feed for fish and livestock, in the non-food chain for extraction of specific components, and as energy source. The destination of biomass products in either food or non-food chains is affected by the source of the residual flow with possible contaminations, and by the opportunities for valorization of the system. Current Dutch laws are likely to forbid this practice at the time of writing this report.

Through biorefinery, the biomass can be processed into various products. Sanders et al. (2016) describe biorefinery of grass and maize to improve the feed composition of cattle and pigs and thus reduce the need to import animal feed. Their system is based upon separation into protein, fiber and a mineral concentrate, whereby all products are used within agriculture. This process does not recover nutrients that are otherwise lost and therefore is out of the scope of the present report.

Within biorefinery concepts, nutrients do play a role and the need to include nutrient recovery in biorefinery is emphasized by Carey et al. (2016). However, nutrients are also seen as internal flow where nutrients are recycled within a system to produce and refine biomass (Chen et al., 2017). Most biorefinery technologies aim at extraction of high value products, and there is hardly any focus on nutrients as one of the products from biorefinery. This is caused by the small scale of most initiatives, and the limited value of nutrients that hinders a good business case (Van der Werf, 2017). Recovery of nutrients from biomass products with biorefinery needs large scale operations and is therefore an option for the long term. On the shorter term, feasible options are recovery as feed and further use of the nutrients through manure management and use of biomass in energy plants and recovery of nutrients from the ash.

<u>Some examples of biomass types and their use are given below:</u>

- Micro-algae were produced by Ingrepro, which were used in shampoo, tooth paste and feed for dogs and horses. Ingrepro was the largest algae producer in the EU with about 15 ton of algae per year that were used, but was declared bankrupt in 2013 (Algenweb, 2013). Other initiatives to produce algae have risen (e.g. Algae Innovations Haarlemmermeer, Nutress), generally focusing on high quality products, food, and/or feed without focus on recovery of nutrients from residual flows.
- Water plants such as duckweed, azolla and water hyacinth can be used to recover nutrients from diluted flows. Duckweed can be grown on digested manure and used as animal feed (Kroes et al., 2016). Manure is a product that already can be used as a fertilizer, and production of duckweed on such flows has a limited contribution to nutrient recovery. Better perspectives within the scope of the present study are with production of water plants on flows from which nutrients are not yet being recovered. Duckweed can be used for effluent polishing and has good quality as animal feed, though a risk analysis and proper legal processes have to be carried out for practical application (Hoving et al., 2012).
- Biomass for energy can be a woody crop that is used in a biomass energy plant. Willow can be grown on wastewater for phytoremediation and effluent polishing but also on dredging sludge, and the *absorbed nutrients can be recovered from the ashes after incineration*.

Because of space requirements only a part of the wastewater can be treated (Otte et al., 2014).

4.5 Summary of recovery opportunities

Opportunities are based on the most promising combinations of (waste) steams with an relatively high content of nutrients, existing techniques and demand. In this paragraph a summary of the information from chapter 4 is giving, including the information from chapters 1-3). They are presented in a random order with a number. In the next chapter (5) the opportunities are prioritized.

Direct use without treatment

Most products that can be used directly are already used as animal feed or fertilizer product, e.g. VGF-compost and several products from the food industry. Direct agricultural use of *dewatered sludge from communal wastewater (1)* treatment does not occur in the Netherlands, due to maximum tolerated heavy metal concentrations and the restriction on mixing with other products (although because of the high organic content it would be an effective soil conditioner). Composting or drying of sludge (with spare heat) will reduce pathogens. Actions to enable export of *composted sludge (2)* to France are in progress (GMB, 2016). Perhaps export of *dried sludge (3)* to other countries is an opportunity (VvZB 2017). With reduced P content and a good hygienic status combined with a quality assurance the application of communal sludge in the Netherlands can be an option in the future. *Ash from energy wood (4)* can be reused as fertilizer (like in Sweden and Finland) if specific legislative aspects are developed.

Cleaning

Further exploration of heavy metal removal from *sludge separated inorganic and organic fractions (5)* using acids and bases is recommended by STOWA. *Bioleaching (6)* can be an alternative. The *Ashdec process (7)* for P recovery also recovers As, Cr and Ni. *Extraction of heavy metals from wastewater (8)* will increase options to use sludge from communal wastewater treatment.

Separation

The liquid fraction of the *separated digestate (9)* from digesters at the sugar industry. To concentrate minerals, water can be removed from a liquid fraction by evaporation, membrane distillation, or *eutectic freeze crystallization or concentration (10).*

Extraction

A possibility to separate zinc, lead, cadmium and copper from fly ash is the acid fly ash washing process *FLUWA (11).* With polymer-assisted ultrafiltration *(PAUF) (12)* (added before the hydroxide precipitation), selective separation of tin, copper and nickel seems possible, together with recovery of zinc and lead. In the *Ecophos process (13)*, after the extraction of phosphorus other ions are being extracted with selective ion exchangers, resulting in Al/Fe and Mg/Ca solutions. *Stuttgart Sludge leaching (14)* also applies acid extraction, and the remaining product after P extraction may be used for recovery of metals. The *reductive acidic leaching of batteries (15)* allows to recover 85,0 % of zinc and 100 % of manganese, iron, cadmium, and chromium, 98,0 % of cobalt, 95,5 % of zinc, and 85,0 % of copper and nickel. *Ammonia leaching copper (16)* from MSWI bottom ash is a process developed by Technical University Delft and used by Elemetal/Inashco. Biorefinery technologies aim at extraction of high value products, but also nutrients do play a role, but until now the limited value of nutrients hinders a good business case. It needs large scale operations and is therefore an option for the long term. The possible biorefinery technologies for the future are application of *micro-algae (17),* water plants such as *duckweed, azolla and water hyacinth (18)*. Finally *phytoremediation with biomass for energy (19)* can be an opportunity. The absorbed nutrients can be recovered from the ashes after incineration.

5 Prioritization of nutrient recovery

5.1 Introduction

In previous chapters a prioritization of nutrients is presented (without excluding the others), an overview of waste streams is given, connected to these nutrients, followed by strategies for nutrient recovery. This results in a list of potential recovery options. In this chapter these potential recovery options are presented related to the individual prioritized nutrients. After that, the recovery options are evaluated in a table with the following criteria:

- Potential demand
- Technical feasible (TRL, Technology Readiness Level)
- Economic feasible
- Regulation restrictions
- Prioritized for additional research in the future

5.2 Recovery options related to prioritized nutrients

In table 5.1 the recovery options identified in paragraph 4.5 are presented in relation to the individual nutrients selected in paragraph 2.5 and the concentrations in waste streams in paragraph 3.9.

Table 5.1 Recovery options related to the prioritized nutrients

Strategy		Recovery option	unknown	B	Co	Cu	K	Mo	Se	Zn	other
Direct use	1	Dewatered communal sludge		x	x	x	x	x	x	x	x
	2	Composted sludge		x	x	x	x	x	x	x	x
	3	Dried sludge		x	x	x	x	x	x	x	x
	4	Ash from energy wood					x				
Cleaning	5	Sludge separated inorganic/organic	x								
	6	Bioleaching sludge	x								
	7	Ashdec proces sludge ash									x
	8	Extraction heavy metals from wastewater		x	x	x	x	x	x	x	x
Separation	9	Separated digestate food industry	x								
	10	Eutectic freezing liquid fractions residu	x								
Extraction	11	FLUWA MSWI fly ash				x				x	x
	12	PAUF MSWI fly ash				x				x	x
	13	Ecophos WWTP fly ash					x			x	x
	14	Stuttgart Sludge leaching	x								
	15	Reductive acid leaching batteries				x	x			x	x
	16	Ammonia leaching copper				x					
	17	Biorefinery: micro-algae		x	x	x	x	x	x	x	x
	18	Biorefinery: duckweed, azolla, hyacinth		x	x	x	x	x	x	x	x
	19	Phytoremediation biomass for energy	x								

5.3 Evaluation recovery options

In table 5.2 the recovery options are presented in relation to the prioritization for additional research in the future.

Table 5.2 Recovery options related to the prioritized future research

Strategy		Recovery option	Potential demand	TRL	Economical feasible	No Regulation restrictions	Prioritized future research
Direct use	1	Dewatered communal sludge	+	+	+	-	
	2	Composted sludge	+	+	+	-	+
	3	Dried sludge	+	+	+	-	+
	4	Ash from energy wood	+	+	+	-	+
Cleaning	5	Sludge separated inorganic/organic	+	-	?	?	
	6	Bioleaching sludge	+	-	?	?	+
	7	Ashdec proces sludge ash	+	-	?	+	
	8	Extraction heavy metals from wastewater	+	-	?	?	
Separation	9	Separated digestate food industry	+	+	?	+	+
	10	Eutectic freezing liquid fractions residu	+	-	?	?	
Extraction	11	FLUWA MSWI fly ash	+	-	?	?	+
	12	PAUF MSWI fly ash	+	-	?	?	+
	13	Ecophos WWTP fly ash	+	+	?	+	+
	14	Stuttgart Sludge leaching	+	-	?	?	
	15	Reductive acid leaching batteries	+	-	?	?	
	16	Ammonia leaching copper	+	-	?	?	
	17	Biorefinery: micro-algae	+	+	-	+	
	18	Biorefinery: duckweed, azolla, hyacinth	+	+	-	+	
	19	Phytoremediation biomass for energy	+	+	+/-	+	+

Direct use of communal sludge (dewatered, composted or dried) on the one hand is promising, because it is cost effective and sustainable related to the organic substances and the nutrients. However the organic micro pollutants and heavy metals will block the direct application in the Netherlands and perhaps the application in other European countries (France, England, Denmark) in the future (> 5 years).

Cleaning of the sludge can make the application more realistic. At this moment research projects are carried out to investigate direct application after cleaning. Chances for bioleaching should be considered.

Separation of sludges from the food industry can be promising. Sometimes part of the separated sludges are already re-used. The other parts (liquids) must be evaluated for cleaning/-concentrating (with spare heat) that will make application as a fertilizer possible.

Extraction of nutrients from ashes (MSWI, fly ash, check bottom ash, coal ash) might be promising for the future. A more detailed check of the research projects outside the Netherlands is recommended. For more diluted waste flows, biological processes are more cost effective than chemical processes, so phytoremediation and biorefinery processes are also selected for further investigation.

6 Discussion, conclusion and recommendations

6.1 Discussion

The goal of this study was to investigate opportunities for nutrient recycling (other than phosphorus) from waste streams. In order to do so promising waste flows and technologies to reuse nutrients from these streams were researched.

We contributed to biobased economy related research especially by mapping waste streams and matching (existing) technologies for recovery for nutrients other than phosphorus which has not been done before. This report gives an intensive overview on multiple topics that have to be considered in order to evaluate opportunities for nutrient recycling.

This report tries to cover the most important aspects but may not get very detailed on some points. However the gathered and interpreted information gives a clear distinction of flows and technologies with high and low potential for nutrient recovery. We give recommendation on which technology-waste stream match what kind of further research can be meaningful for nutrient recovery.

The prioritized nutrients for the Dutch economy have been determined with the following indicators:

- Essentiality for plants and animals,
- Geographic concentration of ores
- Ore depletion time
- Environmental impacts and
- Results of other criticality assessments

The important nutrients are narrowed down to: Boron, Cobalt, Copper, Potassium, Molybdenum, Selenium and Zinc. Nitrogen is not among the selected important nutrients. Even though nitrogen is an essential nutrient, it is not scarce: atmospheric nitrogen is fixed by bacteria and by the fertilizer industry. The important nutrients are present in several waste flows. The largest are MSWI bottom ash and Communal WWTP sludge (sludge and ash from sludge incineration). The important nutrients in these flows are accompanied by other sometimes useful substances, like organic matter and phosphorus, and by pollutants like PAH and heavy metals. Therefore there is a need for extraction and cleaning techniques to recover the nutrients and produce useful products.

All of the 19 technologies investigated are capable of producing end products with a potential demand. Almost half of the technologies have a promising technology readiness level. These include direct use (technology) for streams like WWTP sludge and clean biomass ashes from energy wood. Also the separation of digestate coming from food industry has been implemented. The Ecophos process for WWTP fly ash, 2 biorefinery technologies and phytoremediation biomass for energy. Except for the Ecophos process and to some degree the separation of digestate the technologies can be classified as low tech solutions. It is therefore reasonable that most of them are also economically feasible. For the majority of technologies it is not clear yet whether they are economically feasible also in combination with suitable waste flows.

All direct application technologies are not suitable yet for the Netherlands due to restricting regulations. The reason isthe presence of contaminations which are mostly above the legal threshold determined by Dutch legislation. Nonetheless we recommend further research on the application of composted and dry sludge from WWTP's as well as ash from energy wood. The composition of sludge varies per waterboard, some do have almost complying compositions while others exceed the thresholds regularly. In combination with another technology the composition of the sludge could get more stable. Further research should focus on the one hand on complemental technologies and the desirability of adjusting legislation and environmental effects of the direct application of sludge.

Also ash from energy wood should get some attention for further research. Currently there are no clean energy wood ash streams in the Netherlands, possibilities to create streams without contaminations can be investigated as well as the desirability of adjusting legislation and environmental effects of the direct application of ash from energy (clean) wood.

When a waste stream is not suitable for direct application it can be made suitable with an additional cleaning process. Already existing cleaning processes are available for removing plastics (mechanical separation such as sieving), metals (using for example magnets) and pathogens (thermal treatment with low and high temperatures and sanitization with ammonia). Removing heavy metals from the waste stream is in a low TRL. We recommend to further investigate bioleaching of WWTP sludge as an alternative to chemical leaching. Over the years, bioleaching has been developed as an environmentally friendly and cost-effective technology for the removal of heavy metals from the sludge. However, there are still various technical problems associated with the bioleaching process, which need to be addressed while developing the process on a larger scale.

Separation techniques have been studied and applied in processing of animal manure and water-rich residual flows from sugar, starch and ethanol industry. Several separation techniques can be combined to process residual flows into useful end products. Possible combinations are simple solid-liquid separation and further treatment of the liquid fraction for example with evaporation. We see opportunities in the separation of the liquid fraction of digestate from the food industry.

Additional research can focus on the investigation of additional flows to digest and economic feasibility.

Extraction of nutrients from ashes (MSWI, fly ash, check bottom ash, coal ash) might be promising for the future. A more detailed check of the research projects outside the Netherlands is recommended to explore the possibilities of these techniques. The Ecophos process is on a high TRL for the recovery of phosphorus acid, also Al/Fe and Mg/Ca solutions can be obtained. Our research showed that there are also other nutrients present in the residual Ecophos stream. Therefore we recommend further research in recovering additional nutrients from this stream for example potash and zinc.

The FLUWA process is used in Switzerland to mobilize heavy metals such as zinc, lead, cadmium and copper from fly ashes of MSWI's. The process is currently aimed at cleaning the ashes from the heavy metals for safe landfilling, but recovery of these and other metals is possible and studied in the SESAM research project. In combination with polymer-assisted ultrafiltration (PAUF) we see a great potential to recover the above mentioned nutrients. The further development of FLUWA in combination with PAUF are still in the research phase and thus low in TRL. Also research has to be done if the end-product can be used or under which circumstances the end product can be used as fertilizer.

For more diluted waste flows, biological processes are more cost effective than chemical processes, so phytoremediation and biorefinery processes are also selected for further investigation.

We expect that the identified flows sludge from WWTP's, ash from sludge WWTP's and ash from MSWI are relatively stable in size for the coming decades and pose great opportunities for nutrient recovery. However, to reach a circular economy it is questionable if incineration of municipal waste (and recovery of nutrients) is a desirable development. Putting more effort in separating clean flows before incineration - for example better separation of VGF waste for digestion – might yield a better input flow for nutrient recovery from the view point of a biobased economy. Steering waste streams for reuse, repair and recycling or reducing waste can decrease the amount of MSWI ashes and can also change their composition.

6.2 Conclusions

- The important nutrients are narrowed down to: Boron, Cobalt, Copper, Potassium, Molybdenum, Selenium and Zinc.
- The largest waste streams containing the important nutrients are sludge from WWTP's, ash from sludge WWTP's and ash from MSWI

- All of the 19 technologies investigated are capable of producing end products with a potential demand. Almost half of the technologies have a promising technology readiness level.
- Dutch environmental legislation is restricting and complicating technical solutions for applying nutrient-rich flows for agricultural purposes. Technology and the impact of applying a (processed) residual stream has to comply to the precautionary principle of the Waste Framework Directive (Kaderrichtlijn Afvalstoffen):'may not lead to overall adverse environmental or human health impacts'.

6.3 Recommendations

The important nutrients are present in several waste flows. The largest are MSWI bottom ash and Communal WWTP sludge (sludge and ash from sludge incineration). The important nutrients in these flows are accompanied by other sometimes useful substances, like organic matter and phosphorus, and by pollutants like PAH and heavy metals. Therefore there is a need for extraction and cleaning techniques to recover the nutrients and produce useful products.

About half of the technologies investigated have a positive technology readiness level. These include all (low tech) direct application technologies, separated digestate from food industry in cleaning technologies, and Ecophos WWTP of fly ash, two biorefinery technologies and phytoremediation in the extraction category. The economic feasibility is unknown for most recovery techniques except for direct application. We recommend carrying out feasibility studies and putting up business cases.

We recommend further research for the following technologies:

- Direct use of:
  - *Composted sludge (2)*
  - *Dried sludge (3)* - With reduced P content and a good hygienic status combined with a quality assurance the application of communal sludge in the Netherlands can be an option in the future.
  - *Ash from energy wood (4)* can be reused as fertilizer (like in Sweden and Finland) if specific legislative aspects are developed.
- *Cleaning of Bioleaching sludge(6)*
- *Separation of* the liquid fraction of the *separated digestate (9)* from digesters at the sugar industry
- Separation of zinc, lead, cadmium and copper from fly ash by acid fly ash washing process *FLUWA (11)*
- *Polymer-assisted ultrafiltration (PAUF) (12)* (added before the hydroxide precipitation), for selective separation of tin, copper and nickel, together with recovery of zinc and lead.
- *Ecophos process (13)*

- *Phytoremediation with biomass for energy (19)* - The absorbed nutrients can be recovered from the ashes after incineration.

Although the direct application technologies perform well in the first mentioned evaluation categories, the use of the end products is restricted by law, due to the existence of organic micro pollutants and heavy metals in the favourable flows for recovery. Environmental impact assessments of the sourcing and processing of waste chains as well as environmental impacts should also be part of further research for promising technological routes.

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