# Phosphorus

Papers of an Interdisciplinary Practical Training at the University of Graz

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# Abstract

This edited volume presents the work of 15 students that took the course *Interdisciplinary Practical Training – Time Bomb Phosphorus (scientific writing)* in the winter term 2011/2012 at the Karl-Franzens-University Graz, Austria. Teachers were: Prof. Dr. Walter Gössler, Dr. Maximilian Mrotzek and Mag. Andreas Kreuzeder. This volume consists of six papers on different topics related to phosphorus.

The students' work presented here is highly innovative. Students were asked to find a research gap and write a paper according to scientific standards in order to fill this gap. The resulting papers were subject to an internal review process within the group of students and lecturers. Either through pure literature research, laboratory work, modelling, or empirical research, students found interesting and even surprising results on different levels by working in small groups.

We decided to publish the results in the new ISIS reports series in order to make the students' findings publicly available and to illustrate that this teaching method, which focuses on scientific writing and emulates the scientific review process, is successful.

Maximilian Mrotzek, Andreas Kreuzeder, and Walter Gössler

Graz, 23. January 2013

# Kurzfassung

Dieses Sammelwerk beinhaltet die Arbeit von 15 Studierenden, die den Kurs *Interdisziplinäres Praktikum (IP) – Zeitbombe Phosphor (scientific writing)* im Wintersemester 2011/2012 an der Karl-Franzens-Universität Graz (Österreich) belegt haben. Die Lehrenden waren: Prof. Dr. Walter Gössler, Dr. Maximilian Mrotzek and Mag. Andreas Kreuzeder. Das Werk umfasst sechs Arbeiten zu unterschiedlichen Themen zu Phosphor.

Die hier präsentierten studentischen Arbeiten sind sehr innovativ. Die Studierenden wurden angewiesen eine Forschungslücke zu finden und ein Artikel nach wissenschaftlichen Standards zu schreiben, welcher diese Lücke füllt. Die resultierenden Artikel wurden dann einem internen Evaluierungsprozess durch Studierende und Lehrende unterzogen. Durch Literaturrecherche, Laborarbeit, Modellierung oder empirische Arbeit fanden die Studierenden in Kleingruppen- arbeit interessante und teilweise überraschende Ergebnisse auf verschiedenen Ebenen.

Wir haben uns entschlossen diese Ergebnisse in der neuen ISIS-Report Serie zu veröffentlichen, um so die Resultate der studentischen Arbeiten öffentlich zugänglich zu machen und darüber hinaus zu zeigen, dass diese Art der Lehrmethode (schreiben von wissenschaftlichen Artikeln und Durchführung eines Review-Prozesses) erfolgreich sein kann.

Maximilian Mrotzek, Andreas Kreuzeder, and Walter Gössler

Graz, 23. Januar 2013

# Content

# 1. Editorial

**Interdisciplinary Practical Training Courses at the University of Graz**

The University of Graz offers the unique study program *Environmental System Sciences* with four fields of specialization, both as a Bachelor and a Master program. Students can choose a specialization in Business Administration, Geography, Economics or Natural Sciences-Technology, which accounts for approximately 70% of their total courses. Additionally, a minor-specialization can be freely chosen under some conditions. This organization, together with further teaching and training in the fields of *system-sciences* offer an interdisciplinary structure with high regard to a broad methodology and a high standard of knowledge.

In its early days, the program of Environmental System Sciences was initiated by an active group of students. The tradition of active and independent student groups has so far continued and is the core of the organizational process for the Interdisciplinary Practical Training Courses, which are usually initiated in a highly participatory process by the students themselves. Additionally, the organizers are supported by an active group of students, which are themselves at different stages in their studies.

The Interdisciplinary Practical Training Courses are held on a Bachelor- and Master-degree level and are organized on various teaching frameworks. The experiences over the last years have proven the potential and also the pitfalls of this open format, which allows individual initiative and demands personal responsibility from both students and lecturers.

The content of this Interdisciplinary Practical Training *Time Bomb Phosphorus (scientific writing)* was divided into three areas:

*(1) Content-related orientation*
- Analysis and Description of market dynamics and development of scenarios
- Use of non-renewable resources
- Chemical analytical methods

*(2) Concepts and Methods*

The methods, such as *Material Flow Analysis* or *System Dynamics*, were addressed in the lecture and could be applied by the students in their subgroups if needed. Additionally, students had access to laboratories with state of the art analytical chemistry equipment.

*(3) Scientific Writing*

- Writing a scientific paper in English
- Realization of an internal review process of papers

**The role of phosphorus – a brief background**

The following short description is the initial background given to the students at the beginning of the course. It aims to highlight why phosphorus is an interesting and up-do-date topic.

>> Phosphorus (P) is, together with Nitrogen and Potassium, a central component of modern fertilizers. An increasing scarcity of raw materials, in this case rock phosphate, is especially noteworthy in the case of fertilizers. The prominent role of phosphorus as a central fertilizing component in agriculture makes its availability essential for modern food production and food security. The declining availability of rock phosphate is accompanied by a rise in demand due to the growth of human population and a change in consumption habits, especially the increasing consumption of 'phosphorous intensive' meat. Since a substitution is not possible, low quality phosphate ores have to be mined, which leads to a contamination of fertilizers with heavy metals that may find their way into the food chain. Due to the fact that phosphate rocks are found in only a few countries worldwide, the supply of phosphorus in most countries depends on imports, which makes national economies highly vulnerable. Additionally, phosphorus prices have proven to be highly volatile, as shown for instance by an increase in the price of rock phosphate from Morocco of a few hundred percent in 2008. <<

**Content of the articles**

Even though all papers of the students deal with phosphorus, the papers are diverse, ranging from the economic analysis of the failure of a phosphor recycling

company to a chemical empirical study where phosphorus speciation in urine is made. Nevertheless, we try to order the papers of the students into a logical sequence. This starts with papers that have a broader view on the topic, or when looking at them from a meta level, they have a wide applicability. The following papers then get more specific and might be concerned even with specific cases.

It starts off with the work of (1) '**Anja Kristin Holzer, Julia Hopfer, Christoph Wagner:** *Phosphorus speciation in urine by ion chromatography-inductively coupled plasma mass spectrometry'*. The authors describe that phosphorus, even though only in little doses, is absolutely necessary for almost every living organism. In their work inorganic phosphate and pyrophosphate in urine were quantified via inductively coupled plasma mass spectrometry (ICPMS) after separating it by ion chromatography. (2) '**Christoph Walcher / Franz Mlynek / Thomas Lanner:** *(Trace) Elemental "fingerprint" of rock phosphates and phosphorus containing fertilizers determined by ICPMS.'* In this paper, the authors show that, as every rock formation has its characteristic ratio of trace elements, it is possible to determine the origin of the phosphate in mineral fertilizer. The measurement was also based on ICPMS instrumentation. While these papers have a rather general claim, the following work is more specific towards phosphorus use on a country level. The next paper is (3) '**Rachel Miller / Margit Baier:** *Political Aspects behind the Phosphorus Crisis with special focus on Morocco/Western Sahara'.* Here, the two authors draw their attention on political insecurities in phosphor supplying countries. As example they take the worldwide main supplier Western Sahara/Morocco and how the resource depletion in this country has effects on the resource market and the country itself. As a method a qualitative scenario analysis was used. (4) '**Christian Tauber / Alexander Stiegler:** *The Austrian Phosphorus Demand: A Material Flow Analysis'* generate in their paper a Material Flow Analysis model for phosphorus in Austria that aims to provide a better understanding of the actual stocks and flows of phosphor. The last two papers are concerned with phosphor recycling techniques. (5) '**Elisabeth Dornisch**: *Phosphorus recycling from sewage sludge ash: Comparison of the PASCH, Mephrec and Ash Dec processes'.* The author describes and compares in her paper three different promising ash recycling technologies. As method she uses a SWOT-analysis. Finally, (6) '**Harald Gruber / Stefan Krammer / Martin Schönberg:** *From the Establishment to the Failure of the Ash-Dec Umwelt AG – A Dynamic Analysis.'* The authors analyze why the Ash-Dec Umwelt AG, which had a promising unique phosphate recovery technology, went bankrupt. A system dynamics model was designed to investigate the causes of this development.

**Limitations and disclaimer**

We have to make two limiting remarks to the results of this edited volume. The first one is concerned with the status quo of phosphorus availability. Current research[1] suggests that there is no shortage of phosphorus at least within the next decades. The main argument is that previous research did not include relevant factors such as geological knowledge or technological development sufficiently. When the course took place, the current debate was not that far as it is now and is therefore not reflected in the work of the students. However, this does not diminish the achievements of the students work as none of their papers has phosphorus availability as core topic. The student papers are rather dealing with topics which are independent of this current discussion.

Secondly, we want to highlight that the work presented here is the work by students done in a course during one semester. The students are no specialists in phosphorus research and it was the first time for them to write such an article and to do a peer-review. Thus, their work might contain errors and inconsistencies. Therefore, the following *disclaimer* applies: The readers of this edited volume are fully responsible for the use of the herein presented work. The editors and authors do not claim completeness, correctness or full consistency and will not be liable for any loss, damage or costs incurred by reason of using information from this publication.

[1] For example: Scholz, R.W., Wellmer, F.-W., Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus? *Global Environ. Change* (2012), http://dx.doi.org/10.1016/j.gloenvcha.2012.10.013

# 2. Articles

# Phosphorus speciation in urine by ion chromatography-inductively coupled plasma mass spectrometry

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## Abstract

The focus of the present work was the separation and quantification of inorganic phosphate (iP) and pyrophosphate (PPi) in urine. The urinary concentrations of these compounds are interesting due to their role as a clinical parameter for several disease patterns. A simple and fast method was developed, that allows a direct measurement of the diluted urine samples. The separation of the phosphorus compounds was carried out by ion chromatography and inductively coupled plasma mass spectrometry (ICP-MS) was the chosen phosphorus selective detector. A separation with a anion exchange column (150 x 4.6 mm, 5 μm) and citic acid (20 mM, pH 7.0) as mobile phase was optimized. Under the optimized conditions it was possible to separate phosphate and pyrophosphate in less than 5 minutes in real urine sample. Thanks to the low detection limits and the high sensitivity of the ICP-MS, an adequate quantification of the physiological amounts of urinary iP and PPi was aimed.

## 1 Introduction

### 1.1 Phosphate

Phosphorus is a macronutrient, which all organisms require for life. [Karl, 2000] In humans phosphorus is necessary for nerve functions, muscle contractions and to build bones and teeth. Furthermore phosphorus is a part of the energy storage processes and protein phosphorylation. Almost all of the phosphorus in the body occurs as phosphate, in which 85 % can be found in the skeletal system. The remaining 15 % are stored in cells, where they are required for DNA formation and biological metabolisms. [Themelis, et al., 2004]

A direct relationship has been found between urinary excretion of phosphate and its intake. Themelis, et al., 2004] Moreover phosphorus excretion depends on several factors like, physical activities, body size and environmental factors. [Sullivan, et al., 1982] [Vinneras, et al., 2002] Urinary phosphate levels out of range are caused by several diseases, thus the importance for the determination of urinary phosphate concentrations is given. [Claßen, et al., 1990]

Urine is the frequently used matrix to determine medical parameters, where phosphorus occurs at a pH between 4.8 and 6.6 as $H_2PO_4^-$ and $HPO_4^{2-}$. [Blais, et al., 2000] [Ganrot, et al., 2007]

Beside the ion chromatography, a special method of HPLC, the most common methods for the determination of phosphorus in urine are the high performance liquid chromatography and the capillary electrophoresis. [Themelis, et al., 2004]

### 1.2 Pyrophosphate

Pyrophosphate consists of two molecules of phosphate connected via an ester bond and it is generated by several biological processes. [Heinonen, 2001] Because of its influencing role in intracellular and extracellular cell functions, there are different pathways for production, degradation and the transport of PPi. [Terkeltaub, 2001] PPi is generated most times as a byproduct in many biological synthetic and regulatory reactions. Biosynthesis of all biological macromolecules and small metabolites, like amino acids, coenzymes and nucleotides are coupled to the liberation of PPi from nucleoside triphosphate (NTP). PPi is produced as main product not as a byproduct as usually during the enzyme hydrolysis of NTPs. [Heinonen, 2001] [Terkeltaub, 2001] It is also used as an energy source instead of ATP in many biochemical reactions, especially in lower organisms. [Heinonen, 2001]

PPi can affect many biochemical and physiological reactions, particularly by its inhibitor function. PPi has been shown to be bound strongly onto the calcium containing crystals. Thus for example inhibits the aggregation of hydroxyapatite and calcium oxalate. [Fleisch, 1978] [Fleisch, 1981] [Munoz, et al., 2009]

PPi prevents the precipitation of calcium phosphate in connective tissue matrices, the urinary tract, and in other

extracellular fluids. In the urinary tract PPi acts as natural inhibitor for urolitheasis. [Fleisch, 1978]

Lower urinary PPi indicates a deficient inhibitory capacity against crystallization, diagnosed as one of the possible causes of the lithiasis and renal calculi. Hence in stone former patients a lower concentration of PPi has been reported. [Fleisch, 1978] [O'Brien, et al., 1967] [Simonet, et al., 2003] [Sharma, et al., 1992]

A higher PPi excretion may lead to accumulations in cartilages, tendons and ligaments. [Koopman, 2005]

The concentrations of PPi indicate pathologic aspects include for example urolitheasis, renal calculi, pseudogout and calcification. [Heinonen, 2001] Therefore the measurement of PPi is of high interest.

Determination of PPi in urine is mainly based on chemical [Heinonen, et al., 1981] [Chang, et al., 1985] and enzymatic methods. [O'Brien, et al., 1967] [O'Brien, 1976] [P.H. Cartier, 1974] [Simonet, et al., 2003] [Baykov, et al., 1982] In clinical laboratories the identification of PPi is not common. [Simonet, et al., 2003]

### 1.3 Detection/method

In order to separate the phosphate and pyrophosphate properly ion chromatography was chosen. According to the different pKa values the ions are separated by an adequate mobile phase.

In table 1 literature data of several methods is listed. Rather low concentrations of PPi are expected, so a sensitive analyze method was required.

polyatomic interferences at m/z 31 and the high ionization potential of phosphorus. [Kovačevic, et al., 2005]

## 2 Experimental

### 2.1 Reagents and sample preparation

Water (18 MΩ cm) was prepared using a Milli-Q system (Millipore, Bedford, MA, USA). Sodium pyrophosphate tetrabasic decahydrate ($Na_4O_7P_2 \cdot 10\ H_2O$) was purchased from Sigma Aldrich (Wien, Austria) and the phosphorus standard solution was used from CPI International (Santa Rosa, CA, USA). Citric acid monohydrate was purchased from Fluka (Buchs, Schweiz) A group of seven volunteers provided urinary samples (University, Graz, Austria).

The standard mixtures were prepared with following stock solutions: a 10000 mg kg$^{-1}$ phosphorus solution and a 7200 mg kg$^{-1}$ sodium pyrophosphate tetrabasic decahydrate solution. The phosphorus concentration of the sodium pyrophosphate tetrabasic decahydrate STD is (13.9% P). Hence they were diluted and the prepared phosphorus stock solution contains 1000 mg kg$^{-1}$ P and the pyrophosphate stock solution contains 10 mg kg$^{-1}$ P. Urine samples were collected in polypropylene tubes and kept at low temperatures for a maximum of 1 hour. The specific gravity was determined with a total solid refractometer (Leica TS 400). Prior to analysis, samples were diluted (1+9) with Milli-Q water. For the preparation of the spiked samples, a defined amount of

*Table 1 Literature data of iP and PPi*

| sample | iP | PPi | unit | method | reference |
|---|---|---|---|---|---|
| urine | | 9.98 ±2.23 | mg/L | SPE-ICP-MS | [Munoz, et al.,2009] |
| urine | | 1.26-6.67 | mg/L | LC conductivity detector | [Simonet, et al., 2003] |
| 24 h urine | 270-870 | | mg/L | photometric detection | [Tietz, 2006] |
| morning urine | 400-1360 | | mg/L | photometric detection | [Krieg, et.al., 1986] |
| 24 h urine male | 0.49-1.05 | | g/day | photometric detection | [Sato, et al., 1981] |
| 24 h urine female | 0.36–0.63 | | g/day | photometric detection | [Sato, et al., 1981] |
| urine | 0.43 ±0.16 | | g/day | colorimetric detection | [Raines Bell, et al., 1977] |

The ICP-MS (inductively coupled plasma mass spectrometry) provides a very sensitive, accurate and fast analytical technique. Very low limits of detection can be achieved and small sample amounts of any matrix are required. [Blais, et al., 2000] [Becker, et al., 2003] Difficult to handle are the problems resulting from the

the PPi stock solution was added to the sample, to obtain a spike-concentration of 1 mg kg$^{-1}$ PPi after dilution (1+9).

To prove the stability of PPi, spiked urine samples (1 mg kg$^{-1}$) were prepared and stored at room temperature and at low temperature respectively. Samples were measured

directly, after one day, two days, 5 days and 7 days. Prior to analysis stored urine samples were diluted (1+9). All solutions were transferred to HPLC vials for analysis.

## 2.2 Chromatographic system

HPLC separation was carried out using a Dionex ICS-3000 TC chromatographic system (Sunnyvale, CA, USA) equipped with Dionex ICS Hamilton PRP-X100 anion exchange column (150 x 4.6 mm, 5 μm) and injector AS 1. Citric acid (20 mM, pH 7) was used as mobile phase. The column was operated at 40°C, 25 μl of sample were injected and the flow rate was set to 1.0 ml/min.

## 2.3 Detection system

The exit of the HPLC column was connected via the nebulizer of the quadrupole ICP-MS 7500ce (Agilent, Waldbronn, Germany). The measurement was performed with collisions/reaction cell in He mode to obtain a better signal/noise ratio. Table 3 shows the plasma conditions, which were applied for detection of phosphate and pyrophosphate.

*Table 3 ICP-MS parameters*

| Parameters | |
|---|---|
| Carrier gas flow | 1.02 L min$^{-1}$ |
| RF power | 1550 W |
| RF matching | 1.58 V |
| Nebulizer pump | 0.4 rps |
| Torch-H | 1.3 mm |
| Torch-V | 0.7 mm |
| Spray chamber temperature | 2°C |
| Sample depth | 5 mm |
| He flow rate (collisions/reaction cell) | 4.2 mL min$^{-1}$ |

## 3 Results and Discussion

### 3.1 Optimization of the detection

In addition to the initial instrument tune the ICP-MS was specifically tuned for phosphorus with a solution containing 500 μg L$^{-1}$ phosphorus, 1μg L$^{-1}$ lithium and 1μg L$^{-1}$ yttrium. The parameters were optimized for high sensitivity towards phosphorus as well as a low background signal (table 3). Due to the polyatomic interferences at m/z 31, no nitric acid was used.

A linear calibration curve for pyrophosphate in the range of 50 μg L$^{-1}$ to 1 mg L$^{-1}$ and in the range of 10 to 500 mg L$^{-1}$ for phosphate, was obtained. Different responses are observed by simultaneous measurement of the same amounts of iP and PPi. Possible reasons for that phenomenon could be the volatility during transport or more unlikely the different ionization in the plasma.

For unexplainable reasons, a small iP peak is visible by the calibration of PPi.

## 3.2 Chromatographic separation

Based on the different pKa values of Pi and PPi the ion chromatography was used as separation method. Under the prevailed conditions (pH 7.0) the phosphoric acid is one or two times deprotonated ($H_2PO_4^-$/$HPO_4^{2-}$) and eluates first ($t_{ret}$ 2.2). Pyrophosphate is three- and four times respectively deprotonated ($HP_2O_7^{3-}$/$P_2O_7^{4-}$) [Weast, 1986] and eluates later ($t_{ret}$ 4.2).

Several attempts were made to find an adequate mobile phase for the separation of phosphate and pyrophosphate. The first separation was tried to obtain with 100 mM citric acid. Because of the small time lag between the retention times, the concentration of the mobile phase was reduced to 50 mM later to 30 mM and 20 mM. In order to avoid tailing, fronting and to improve the resolution, the best separation was carried out with a 20 mM citric acid solution (pH about 7.0).

## 3.3 Quantification

The phosphorus species at m/z 31 were analyzed by ICP-MS. The low detection limit allows a direct determination of Pi and PPi in human urine.

To determine the error of measurement a solution with a defined concentration was determined with every measurement. The peak areas were averaged and the percentage divergence from the average was calculated. The obtained values allow a realistic estimation of the error of measurement.

The chromatographic separation of iP and PPi in urine is outlined in figure 1. The chromatogram below expresses the wide range of concentrations of iP and PPi in urine. To illustrate the low concentration of PPi the peak at the specific retention time was zoomed in. As visible in the chromatogram the spiked (1 mg L$^{-1}$) sample proves the right identification of PPi at 250 seconds, under the chosen conditions.
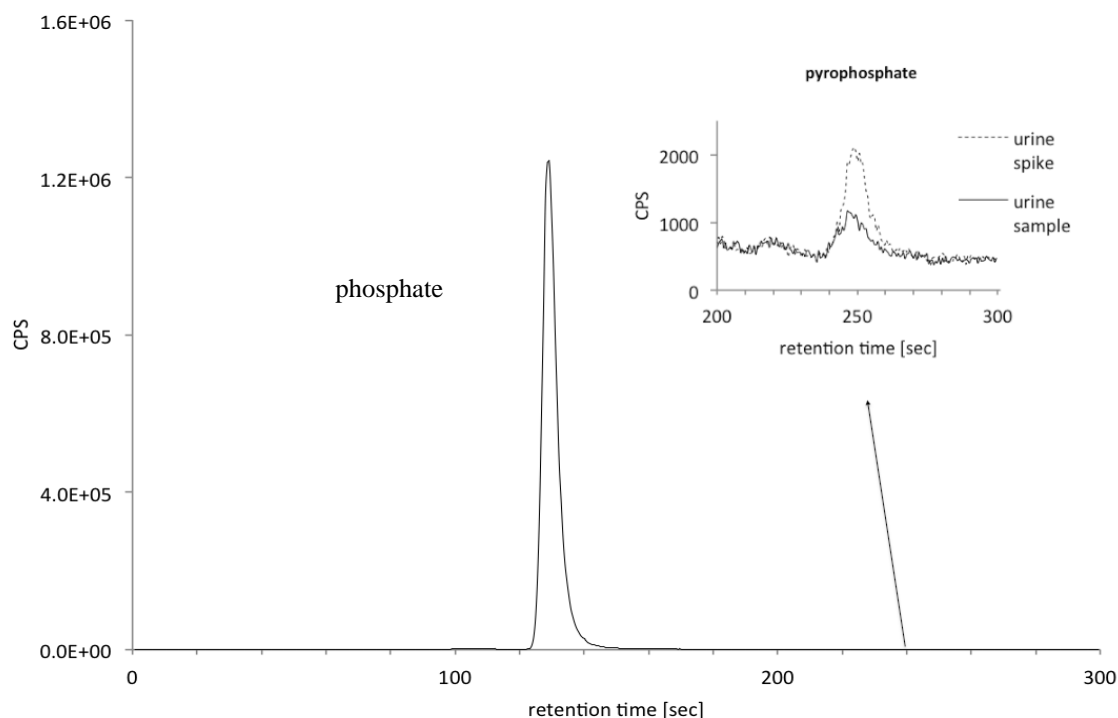
*Figure 1 Chromatogram of iP, PPi and spiked PPi (1mg $L^{-1}$) in diluted (1+9) urine.*

### 3.3.1 Quantification of urine samples

In the following table the results of the morning urine and spontaneous urine are shown. To make the results comparable, the urine samples were normalized with the specific gravity. It has to be outlined that not all urinary samples were detected three times. Furthermore those single values were measured with 30 mM citric acid as mobile phase. However the single values are compared with the others. Variations between the obtained concentrations of iP and PPi could be explained by the different sex, age and diet of the volunteers. For significant results a bigger number of samples are required.

In table 4 the obtained concentrations of iP and PPi in urine are listed.

*Table 4 iP and PPi concentrations of urine*

| Sex (age) | iP [mg kg$^{-1}$] | PPi [mg kg$^{-1}$] |
|---|---|---|
| Female 1 (23) | 878 | 1.3 |
| Female 1 (23) | 776 ± 2.8 | 1.1 ± 0.33 |
| Female 2 (23) | 882 ± 5.6 | 1.1 ± 0.14 |
| Female 3 (25) | 1375 | 2.8 |
| Male 1 (3) | 632 ± 2.9 | 1.9 ± 0.03 |
| Male 2 (23) | 1035 | 1.5 |
| Male 3 (23) | 125 ± 0.7 | 0.23 ± 0.04 |
| Male 4 (29) | 933 | 1.5 |
| Male 4 (29) | 1793 ± 1.5 | 2.7 ± 0.03 |

The range of iP varies more in comparison to the PPi concentrations. But a correlation between iP and PPi can be derived from the data. Generally lower iP concentrations come along with lower PPi concentrations and reverse. A correlation between iP and PPi with sex or age is undetermined, but cannot be excluded.

The results of female 1 (23) and male 4 (29) were achieved from urine samples of two different days. Noticeable is that the results of female 1 (23) are more likewise than those of male 4 (29). The concentration of both phosphorus compounds of male 4 (29) almost doubled. Perhaps the diet could be linked to the higher phosphorus excretion. The diet also could be a reason for the low values of male 3 (23).

The determined concentrations of iP are in the range of the literature values of [Tietz, 2006] [Krieg, et al., 1986] (table 1), except male 4 (29) with a higher value. However, the PPi concentrations are in the lower range of the cited values [Simonet, et al., 2003] or even below than the literature data [Munoz, et al., 2009]. This could be due to many reasons, for example different experimental conditions, not nomalized or in another way normalized values.

*Figure 2 Phosphate concentrations of the stability experiment-100% initial concentration*
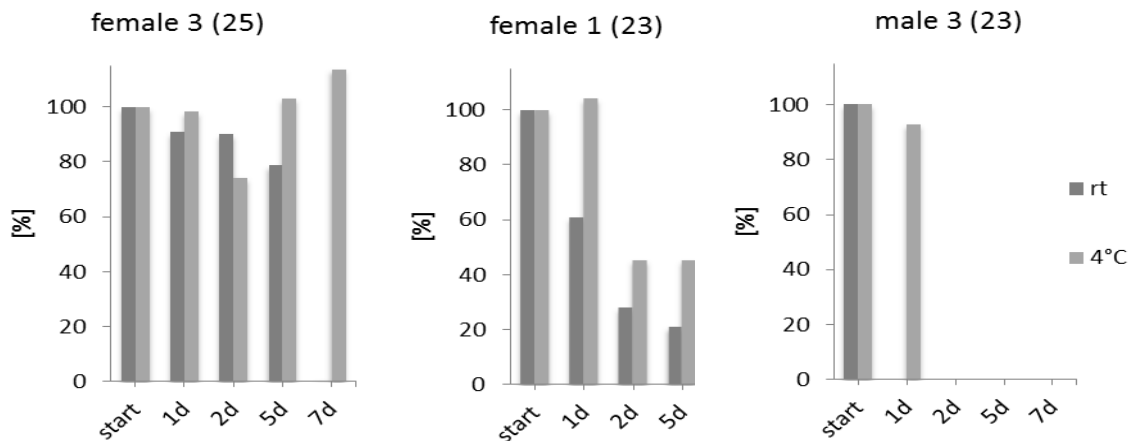


*Figure 3 Pyrophosphate concentrations of the stability experiment-100% initial concentration*

The results of the mentioned stability experiment are not adjusted for different urine densities and outlined in figure 2 and figure 3. For a better illustration 100% was defined as the initial concentration in the diagrams.

As obvious in figure 2 the stability of iP is demonstrated. The fluctuations are within the error of measurement. The urine samples of two out of three volunteers show a

stable iP concentration over seven days, equal if they were stored at room temperature or in the fridge (4°C).

Except the female 1 (23) urine sample, stored at room temperature, show a decreasing trend, whereas the

samples stored at low temperature are stable. Thus far we have no explanation for it.

Figure 3 reveals the PPi concentrations of the stability experiment. All three urinary samples show a clear trend, the PPi concentrations decrease over time. Stored at low temperature, the degradation is not that fast. Noticeable, are the missing plots of male 3 (23) and one plot of female 1 (23), which are under LOQ (limit of quantification) and moreover the increasing concentrations of the female 3 (25) urine sample, which are within the error of measurement. In the supplementary figure 4 and figure 5 demonstrate the results of the standard abbreviation without 100% as initial concentration.

# 4 Conclusion

The developed method provides a good opportunity to separate and quantify iP and PPi in urine. Advantages are for example the low detection limits and a fast analysis.

The separation under the chosen conditions was adequate. Parameters were selected due to a good resolution and a high sensitivity. In order to avoid interferences the use of solutions containing nitrogen was avoided. Citric acid was used as mobile phase because it fulfills the requirements best and achieves a good retention time for the analytes. One problem was the high concentration of iP in comparison with the rather small concentration of PPi. In order to quantify the PPi well, the distance between the peaks needed to be expanded. This was aimed with 20 mM citric acid as mobile phase.

To obtain reliable conclusions a higher number of volunteers is required. It would be interesting to explore the iP and PPi excretion of sex, age and diet related connections. In particular to focus on differences and similarities between them. Because of the mentioned reasons, it would be a good idea to continue the study.

The stability experiment indicates that the urinary phosphate is stable for at least one week. Other than the PPi, which seems to degrade over the time. Generally it is to notice, that the PPi is more stable, stored at low temperature.

A tool that allows the reliable determination of PPi was achieved to get a better understanding of phosphorus metabolism.

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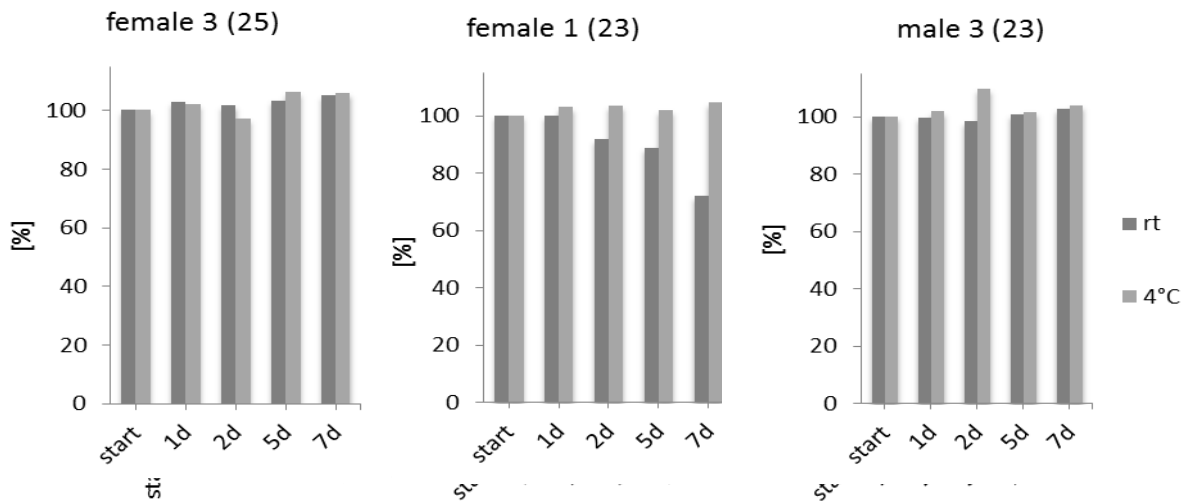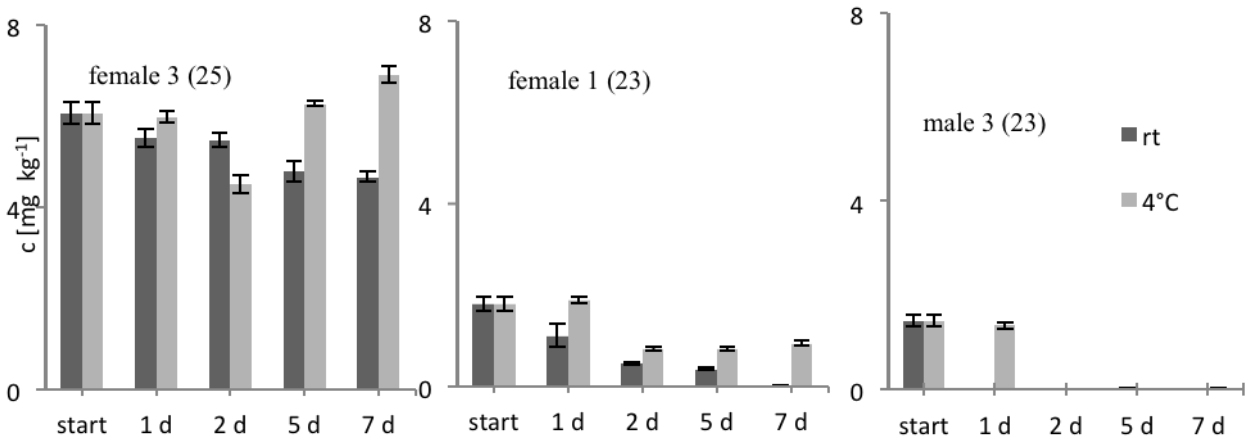
# 6 Supplementary



*Figure 4 Phosphate concentrations of the stability experiment*
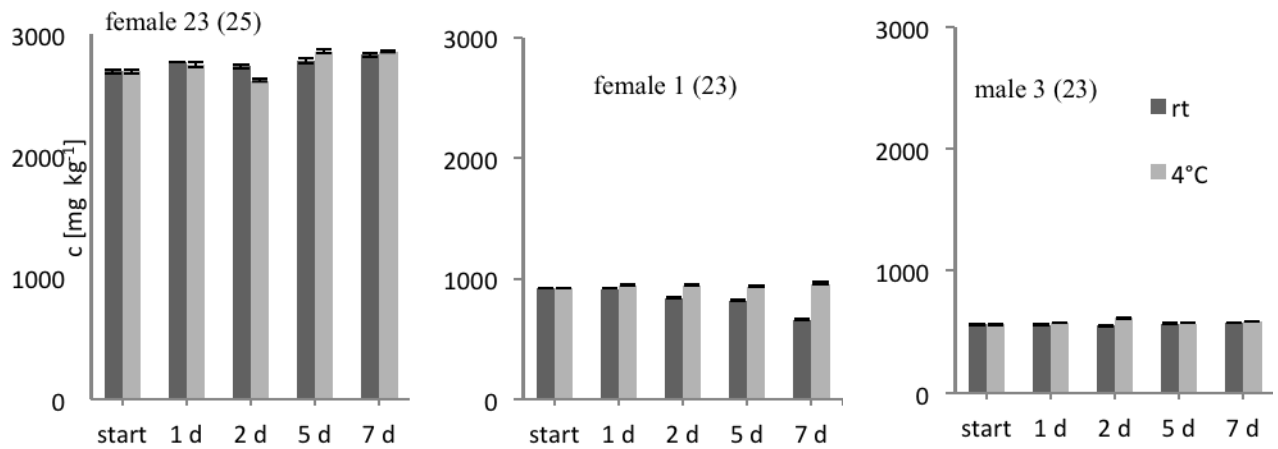


*Figure 5 Pyrophosphate concentrations of the stability experiment*

# (Trace) Elemental "fingerprint" of rock phosphates and phosphorus containing fertilizers determined by ICP MS

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## Abstract

Every rock formation in a region has its characteristic ratio of (trace) elements. Based on this, it is possible to determine the origin of mined rock phosphates due to its characteristic (trace) elemental pattern – the "fingerprint". Rock phosphates are the raw material for mineral fertilizers and therefore the same patterns are present in both materials.

Based on measurements done with ICP MS in this paper the ratios of 38elements were statistically calculated and related to different fertilizer samples to determine similarities between them and successfully trace back the origin of the rock phosphate used in fertilizer production.

## 1 Introduction

90 % of the mined rock phosphate (RP) is used for fertilizer production [Smil, 2000]. The mined RP contains high Phosphate (P) concentration (over 20%) and therefore its mining is cost-effective for now, but in the near future (conservative estimations predict a "peak-phosphorus" around 2035 [Cordell, 2010]) there will only be mines with low quality RP (low quantity of P, contaminations with heavy metals). Like oil, phosphorus deposits need millions of years to naturally renew itself, because of its slow cycling behavior [Cordell, 2009]. Those are the reasons why RP is considered as a non-renewable resource.

P is one of the three major macronutrients in plants (N nitrogen, P phosphorus, K potassium) and it is not replaceable with any other element. Because of the increasing demand on food more and more fertilizer (respectively mineral P containing fertilizer) is needed to meet requirements.

To guarantee a high quality of mineral fertilizers (low heavy metal content, high P content) it is necessary to know the origin of RP used in the production of those mineral fertilizers. To avoid the usage of bad quality RPs in fertilizer production and therefore lower the quality of the finished product, it is necessary to trace back the origin via the fingerprint technique.

In this paper the fingerprint technique was used and improved. The main hypotheses of the (trace) elemental fingerprint analysis are that each RP deposit (mine) has its characteristic (trace) elemental ratio and that this pattern – the "fingerprint" – can be recovered in mineral fertilizers, in which these RPs are processed. Works on these hypotheses were already carried out by Kratz, *et. al.* [Kratz, 2005], Charter, *et. al* [Charter, 1995] and Senesi, *et. al* [Senesi, 1981]. They came to the conclusion that these hypotheses are applicable.

One of the additional aims in this paper was to show if or if not the Rare Earth elemental pattern alone is sufficient for the fingerprint to trace back the origin of the RP used in fertilizer production.

## 2 Material and method

### 2.1 Sample description and preparation

The fertilizer samples F1 – F13, the RP samples RP1 – RP5 and additional information about the production was provided by an Austrian fertilizer producer. For the production of F1 – F13, a mixture of 80 % RP1 and 20 % RP4 was used. That is why different RP mixtures were also measured (Mix 1 – 8).

F14 – F18 were bought at a local hardware store. The origin of the raw material, used for the samples F14 – F18 is not stated on the packaging.

For quality control the certified reference material BCR® - 032 (Natural Moroccan Phosphate Rock) was used.

| Code | Description | Code | Description |
|------|-------------|------|-------------|
| F1 | 20-8-8+3+4 | F17 | 12-8-16+3+10 |
| F2 | 15-15-15+0+3 | F18 | Guano (11-6-3.5+3+2) |
| F3 | 24-14-0+0+3 | RP1 | Morocco K10 |
| F4 | 15-5-18+2.5+10.5 | RP2 | Morocco K20 |
| F5 | 21-7-7+2+4 | RP3 | Syria |
| F6 | 14-10-20+0+4 | RP4 | Algeria |
| F7 | 20-20-0+0+3 | RP5 | Egypt |
| F8 | 18-25-0+0+2 | Mix 1 | 80 % K20, 20% Syria |
| F9 | 26-14-0+0+0 | Mix 2 | 60 % K20, 40% Syria |
| F10 | 26-10-0+0+4 | Mix 3 | 40 % K20, 60% Syria |
| F11 | 12-12-17+2+5 | Mix 4 | 20 % K20, 80% Syria |
| F12 | 16-10-10+3+5 | Mix 5 | 80 % K10, 20% Algeria |
| F13 | 15-13-13+2+3 | Mix 6 | 60 % K10, 40% Algeria |
| F14 | 14.5-7-14.5+2+7 | Mix 7 | 40 % K10, 60% Algeria |
| F15 | 9-14-19+3+0.5(Fe) | Mix 8 | 20 % K10, 80% Algeria |
| F16 | 12-11-18+2.6+8 | BCR032 | Natural Moroccan RP |

**Table 1: Measured fertilizers (F) and rock phosphates (RP), number code description for fertilizers: N-P-K+Mg+S BCR032 = BCR® certified Reference Material**

The RP1 is a sample from the Khouribga mine in Morocco (called K10). The RP2 is basically K10 with 5 % podsol additive (podsol is a nutrient-poor soil, which is used as a diluent). As a result these two RPs have very similar elemental content. RP4 is from the Rouina mine in Algeria. With the provided documents it was not possible to determine the exact mines of RP3 and RP5.

The fertilizer samples were grinded with a Retsch ZM 1000 mill (Retsch GmbH, Haan, Germany) at 10000 rpm using a 1.0 mm T titanium sieve and a 12 teeth titanium rotor. The RP samples were grinded using the same mill with a 0.25 mm T titanium sieve. About 0.5 g of the grinded RP or fertilizer samples were digested in quartz tubes with 5 mL conc. $HNO_3$ using a microwave digestor (MLS GmbH ultraCLAVEIII Microwave Digestor, Sorisole, Italy). The program used for digestion is given in Table 2.

| Step | Time [min] | Temp 1 [°C] | | Temp 2 [°C] |
|------|-----------|-------------|---|-------------|
| 1 | 5 | 24 | → | 80 |
| 2 | 25 | 80 | → | 250 |
| 3 | 30 | 250 | → | 250 |

**Table 2: Digestion program**

After the digestion some colorless precipitate remained. The digested samples were diluted 1+199 in polypropylene tubes with ultrapure water (Milli-Q, 18 MΩ·cm) containing 10 % (v/v) $HNO_3$. The ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, Massachusetts, USA).

## 2.2 Analytical method

For analyzing the samples an ICP-MS 7500ce (Agilent Technologies GmbH, Waldbronn, Germany) was used. For optimization of the operation conditions a tuning solution (1 µg/l Li, Y, Tl, Ce, Co, Fe, Se, Cr in 2 % (v/v) $HNO_3$) was used.

In mode 1 no collision gas was used. The average count rate of $^{7}Li$ was $6*10^4$- cps, of $^{89}Y$ was $1.3*10^5$ cps and of $^{205}Tl$ was $8*10^4$ cps. The oxide ratio for mode 1 was ~16. In mode 2, helium was used as a collision gas, to reduce polyatomic ions. The average count rate of $^{7}Li$ was 64 cps, of $^{89}Y$ was $2*10^3$ cps and of $^{205}Tl$ was $4*10^3$. The oxide ratio for mode 2 was 0.78.

The ICPMS was calibrated for the elements shown in table 3 and the internal standard (IS) containing 500 µg/L of Be, In, Ge and Re in 10 % $HNO_3$ was added online. The calibration was done in the appropriate ranges from 10 ng/L to 100 mg/L.

| Isotope | IS | Mode | Isotope | IS | Mode |
|---------|-----|------|---------|-----|------|
| $^{7}Li$ | $^{9}Be$ | 2 | $^{107}Ag$ | $^{74}Ge$ | 2 |
| $^{11}B$ | $^{9}Be$ | 2 | $^{111}Cd$ | $^{74}Ge$ | 2 |
| $^{23}Na$ | $^{9}Be$ | 1 | $^{125}Te$ | $^{115}In$ | 2 |
| $^{24}Mg$ | $^{9}Be$ | 1 | $^{137}Ba$ | $^{115}In$ | 2 |
| $^{27}Al$ | $^{9}Be$ | 2 | $^{139}La$ | $^{115}In$ | 2 |
| $^{31}P$ | $^{9}Be$ | 1 | $^{140}Ce$ | $^{115}In$ | 2 |
| $^{39}K$ | $^{9}Be$ | 1 | $^{141}Pr$ | $^{115}In$ | 2 |
| $^{43}Ca$ | $^{9}Be$ | 1 | $^{146}Nd$ | $^{115}In$ | 2 |
| $^{45}Sc$ | $^{9}Be$ | 1, 2 | $^{147}Sm$ | $^{115}In$ | 2 |
| $^{51}V$ | $^{9}Be$ | 1 | $^{153}Eu$ | $^{115}In$ | 2 |
| $^{52}Cr$ | $^{9}Be$ | 1 | $^{157}Gd$ | $^{115}In$ | 2 |
| $^{55}Mn$ | $^{9}Be$ | 1 | $^{159}Tb$ | $^{115}In$ | 2 |
| $^{56}Fe$ | $^{9}Be$ | 1 | $^{163}Dy$ | $^{115}In$ | 2 |
| $^{59}Co$ | $^{9}Be$ | 1 | $^{165}Ho$ | $^{115}In$ | 2 |
| $^{60}Ni$ | $^{9}Be$ | 1 | $^{166}Er$ | $^{115}In$ | 2 |
| $^{65}Cu$ | $^{9}Be$ | 1 | $^{169}Tm$ | $^{115}In$ | 2 |
| $^{66}Zn$ | $^{9}Be$ | 1 | $^{172}Yb$ | $^{115}In$ | 2 |
| $^{71}Ga$ | $^{9}Be$ | 2 | $^{175}Lu$ | $^{115}In$ | 2 |
| $^{75}As$ | $^{74}Ge$ | 2 | $^{205}Tl$ | $^{185}Re$ | 2 |
| $^{82}Se$ | $^{74}Ge$ | 2 | $^{208}Pb$ | $^{185}Re$ | 2 |
| $^{85}Rb$ | $^{74}Ge$ | 2 | $^{209}Bi$ | $^{185}Re$ | 2 |
| $^{88}Sr$ | $^{74}Ge$ | 1 | $^{232}Th$ | $^{185}Re$ | 2 |
| $^{89}Y$ | $^{74}Ge$ | 2 | $^{238}U$ | $^{185}Re$ | 2 |
| $^{95}Mo$ | $^{74}Ge$ | 2 | | | |

**Table 3: Table of the measured Isotopes containing IS and mode**

## 2.3 Statistical analysis

The concentrations of selected elements in one sample were put in relation to each other to obtain a matrix of the element ratios (see figure 2 in the Appendix). For each sample (18 fertilizers, 5 rock phosphates and 8 RP mixes) such a matrix was calculated to get a specific "fingerprint".

The elements used for statistical analysis were: Li, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Ga, As, Se, Rb, Sr, Y, Mo, Ag, Cd, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Bi, Th, U.

See 3.2 in Results and discussion for information about excluded elements.

For the statistical analysis, a two sided Pearson´s correlation coefficient was calculated for these matrices using "IBM SPSS Statistics", version 19.0.0. The goal was to find significant similarities in the ratios of

(trace) elements in the different samples, to determine the origin of the RP used for fertilizer production.

# 3 Results and discussion

## 3.1 Quality control

To check the accuracy of the measurements BCR-032 was always measured alongside the samples. Therefore it was first compared with the certified values and values found in literature. Note: Only 0.5g of the BCR-032 was used for the analysis, instead of the suggested 1g. The 1.6 % mass loss after drying was considered.

| BCR-032 Natural Moroccan Rock Phosphate | | | | |
|---|---|---|---|---|
| Element | Unit | measured values | Certified values[a] | literature values[b] |
| | | Conc. ± SD | Conc. ± SD | Conc. ± SD |
| Al | [mg/kg] | 2224 ± 39 | 2910 ± 320 | 2750 ± 710 |
| As | [mg/kg] | 9.6 ± 0.2 | 9.5 ± 0.5 | 9.1 ± 5.6 |
| B | [mg/kg] | 22.5 ± 0.3 | 22.6 ± 2.2 | - |
| Ba | [mg/kg] | 96.4 ± 1.4 | - | 1300 ± 170 |
| Ca | [g/kg] | 350 ± 5 | 370 ± 3 | 373 ± 53 |
| Cd | [mg/kg] | 20.8 ± 0.3 | 20.8 ± 0.7 | - |
| Ce | [mg/kg] | 71.4 ± 1.7 | - | 85.8 ± 36.0 |
| Co | [mg/kg] | 0.58 ± 0.01 | 0.59 ± 0.06 | 0.58 ± 0.23 |
| Cr | [mg/kg] | 250 ± 6 | 257 ± 16 | 247 ± 136 |
| Cu | [mg/kg] | 31.5 ± 0.4 | 33.7 ± 1.4 | - |
| Eu | [mg/kg] | 7.5 ± 0.1 | - | 2.5 ± 2.1 |
| Fe | [mg/kg] | 1571 ± 17 | 1610 ± 70 | 1570 ± 220 |
| K | [mg/kg] | 718 ± 14 | - | 721 ± 274 |
| La | [mg/kg] | 105 ± 2 | - | 100 ± 35 |
| Lu | [mg/kg] | 2.54 ± 0.06 | - | 0.72 ± 0.89 |
| Mg | [mg/kg] | 2389 ± 43 | 2400 ± 60 | 2450 ± 635 |
| Mn | [mg/kg] | 16.6 ± 0.3 | 18.8 ± 1.3 | 18.0 ± 2.0 |
| Na | [mg/kg] | 5863 ± 73 | - | 6233 ± 1184 |
| Nd | [mg/kg] | 62 ± 1 | - | 72 ± 62 |
| Ni | [mg/kg] | 35.0 ± 0.6 | 34.6 ± 1.9 | - |
| P | [g/kg] | 146 ± 3,5 | 144 ± 1 | - |
| Rb | [mg/kg] | 3.5 ± 0.1 | - | 5.7 ± 2.4 |
| Sc | [mg/kg] | 10.3 ± 0.3 | - | 8.8 ± 4.4 |
| Se | [mg/kg] | 7.1 ± 0.2 | - | 10.0 ± 0.9 |
| Sm | [mg/kg] | 26.7 ± 0.5 | - | 53.2 ± 20.8 |
| Sr | [mg/kg] | 980 ± 16 | - | 1014 ± 590 |
| Th | [mg/kg] | 4.7 ± 0.1 | - | 3.0 ± 1.0 |
| U | [mg/kg] | 118 ± 1 | - | 116 ± 67 |
| V | [mg/kg] | 155 ± 3 | 153 ± 7 | 158 ± 9 |
| Yb | [mg/kg] | 15.5 ± 0.4 | - | 12.3 ± 6.4 |
| Zn | [mg/kg] | 251 ± 6 | 253 ± 6 | 260 ± 37 |

**Table 4: ICP-MS analysis of the rock phosphates reference material BCR-032, [a] Certified, [b] [Siddique, 2011].**

To check the accuracy of the obtained analytical data, a Z-score was calculated with formula 1 according to [FDA, 2012] and plotted (see Figure 1).

$$z = \frac{x_m - x_c}{\sigma}$$

**Formula 1: Formula to calculate the Z-score.**
$x_m$ = measured value, $x_c$ = certified value, $\sigma$ = standard deviation of certified value

$|Z\text{-score}| \geq 3$: not trustable values
$3 > |Z\text{-score}| > 2$: questionable values
$|Z\text{-score}| \leq 2$: reliable values
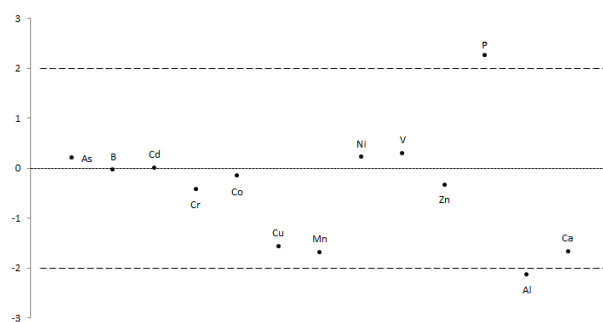


**Figure 1: Z-score of the certified elements**

As shown in figure 1, most of the Z-scores are below 1, which means a good reliability of the measured data. The Z-score of 3 elements (Ca, Cu, Mn) is between 1 and 2, which still means a good reliability. Only the z score of 2 elements (Al, P) is between 2 and 3 which means, that these are questionable values. Here it has to be said, that the certified values of Al, P and Ca refer to the oxides and not to the pure elements. Therefore the certified oxide values were calculated via mass percentage to the pure elements.

## 3.2 Analysis

The following elements were excluded from further analysis. B, Cu, Zn and Mg were excluded, because they are added as micronutrients in fertilizers. Na, K, Ca and P are bulk elements (no certainty that element source is RP alone). For Te, the concentration was below the noise of the measurement (<0.08 mg/kg).

Based on the present results it is possible to determine the origin of the RP used for fertilizer production in particular circumstances. The comparison of the values of the measurements done in this study and values found in literature [Awadalla, 2010; Pantelica, 1996] show that there are big differences in the element contents in RP of different mines, even in one region. Because of that it is only possible to relate the RP to a specific mine and not to a whole region.
Another problem is that fertilizer producers use mixtures of RP from different mines and not RP from a single mine as raw material.
At first it was tried to only compare the ratios of the REE but as shown in figure 3 in the Appendix the ratios of the REE in the analyzed RP are very similar and therefore it is not possible to distinguish between the RPs with a statistical significance. As a result, more elements (see section 2.3) were added to the calculation of ratios and correlations. On the other hand it is also not possible to relinquish the REEs. All

the elements mentioned in section 2.3 are needed to get a statistical significant result.

To relate a fertilizer to a RP with a statistical significance either the mixture of the used RPs has to be known, or a sophisticated database, including all possible mixtures of RPs, is needed. If only the pure RPs are analyzed, the statistical significance (correlation over 0.900) is only given for the main component of the mixture and the minor component can only be estimated.

The samples F1 – F13 show high correlation values with RP1 and RP2 (> 0.900), mediocre with RP3 (> 0.600) but show only a weak correlation (< 0.450) with RP4 and RP5. Further the mixtures 1-8 show a high correlation (> 0.800) with the samples F1 – F13. The strongest correlation occurs between mix 5 and each of the fertilizer sample F1 – F13.

| | Mix1 | Mix2 | Mix3 | Mix4 | Mix5 | Mix6 | Mix7 | Mix8 |
|---|---|---|---|---|---|---|---|---|
| F1 | 0.958 | 0.934 | 0.887 | 0.808 | 0.974 | 0.949 | 0.911 | 0.874 |

**Table 5: Correlation coefficients of the mixes with fertilizer sample F1.**

As shown in table 5, the correlation values should be seen as relative values. It cannot be said that correlation values >0.900 automatically imply an absolute link between the P-source origins. For example see table 5: Mix 1 has a correlation coefficient of 0.958 but Mix 5 has a correlation of 0.974. Thus Mix 5 is the sample with the highest correlation value (compared to all other considered samples) and can be seen as the origin of F1.

These reasons confirm the assumption that the elemental ratio of each RP can be recovered in the fertilizer because it is known that these fertilizers were produced with a mixture of 80 % RP1 and 20% RP4.

The samples F14 – F18 did not correlate with any of the measured RP or the values of various RP found in literature (Kola Peninsula/Russia[a,b], Abu Tartur/Egypt[c], Syria[d]) [[a]Zanin, 2005, [b]Zanin, 2006, [c]Awadalla, 2010; [d]Pantelica, 1996]. *Note: The correlations were calculated only with the elements which concentrations were given in the papers.*

Possible reasons why the samples F14 – F17 did not correlate are the insufficient information given in the papers (too few analyzed elements, no information about the exact origin of the analyzed RPs), also it is unknown where each fertilizer producer gets his RP from or even if the producer uses RP at all as the (main) source of P. Other possible P-sources are phosphogypsum, residues of phosphoric acid production and other various sources [Sattouf, 2007b]. The reason why F18 did not correlate with any of the RPs is that F18 was produced from Guano, which is the excrement of seabirds, some bats and seals.

## 4    Conclusion

In former studies, carried out by Sattouf [Sattouf, 2007a, 2007b], it was postulated that it is not possible to determine the origin of RP, used in fertilizer production, using only REE ratios as a characteristic fingerprint. On the whole this postulation can be confirmed. He also postulated that "[…] it is very difficult, if not impossible to trace back the origin of a P-fertilizer based on its elemental pattern alone" [Sattouf, 2007b]. This was disproven to a certain degree, as it was possible for F1 – F13 to determine the origin of the used RP using only their elemental pattern alone. But it was not possible to trace back the origin of F14 – F17 because only a limited number of RP samples were accessible and it was also not known which P-containing raw material (RP or e.g. phosphogypsum) was used for the fertilizer production.

For further research on this topic a broader range of RPs and fertilizer samples, with known P-source origin and mixing ratios are necessary to build up a sophisticated database for determining the origin of fertilizers with unknown P-source.

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# Appendix

Figure 2: Element ratios calculated in a matrix. For description see 2.3 Statistical analysis

| Element | Code | F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 | F10 | F11 | F12 | F13 | RP1 | RP2 | RP3 | RP4 | RP5 | F14 | F15 | F16 | F17 | F18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | Mean [mg/kg] | 0,28 | 0,87 | 0,77 | 0,23 | 0,24 | 0,50 | 1,19 | 1,44 | 0,77 | 0,55 | 0,70 | 0,59 | 0,44 | 1,79 | 1,74 | 0,19 | 0,44 | >0,01 | 0,04 | 0,05 | 0,05 | 0,21 | 0,02 |
| | SD [mg/kg] | 0,01 | 0,00 | 0,02 | 0,01 | 0,01 | 0,01 | 0,01 | 0,02 | 0,01 | 0,02 | 0,01 | 0,04 | 0,02 | 0,01 | 0,05 | 0,05 | 0,03 | 0,01 | | 0,00 | 0,01 | 0,00 | 0,01 | 0,00 |
| Al | Mean [g/kg] | 0,52 | 1,43 | 1,18 | 0,40 | 0,54 | 0,76 | 2,06 | 1,90 | 1,51 | 0,81 | 0,98 | 1,12 | 0,81 | 2,70 | 2,17 | 0,70 | 1,61 | 3,93 | 1,25 | 0,92 | 1,62 | 0,77 | 0,40 |
| | SD [g/kg] | 0,01 | 0,01 | 0,02 | 0,01 | 0,01 | 0,01 | 0,05 | 0,13 | 0,03 | 0,03 | 0,05 | 0,01 | 0,00 | 0,11 | 0,03 | 0,01 | 0,03 | 0,04 | 0,01 | 0,01 | 0,02 | 0,02 | 0,05 |
| As | Mean [mg/kg] | 4,31 | 7,62 | 6,96 | 2,83 | 2,70 | 7,39 | 10,10 | 14,94 | 6,91 | 6,01 | 5,57 | 5,50 | 7,38 | 15,58 | 22,09 | 2,18 | 6,60 | 22,58 | 1,56 | 1,78 | 1,66 | 3,41 | 3,85 |
| | SD [mg/kg] | 0,08 | 0,08 | 0,11 | 0,11 | 0,04 | 0,11 | 0,24 | 0,46 | 0,16 | 0,11 | 0,26 | 0,04 | 0,06 | 0,29 | 0,40 | 0,06 | 0,10 | 0,20 | 0,06 | 0,01 | 0,07 | 0,06 | 0,17 |
| B | Mean [mg/kg] | 4,34 | 8,67 | 8,92 | 536,97 | 8,69 | 6,00 | 11,89 | 14,86 | 9,10 | 1995,41 | 476,28 | 11,66 | 13,13 | 20,97 | 19,05 | 36,17 | 44,01 | 27,20 | 219,78 | 69,23 | 203,71 | 144,20 | 11,49 |
| | SD [mg/kg] | 0,09 | 0,14 | 0,14 | 21,28 | 1,23 | 0,19 | 0,28 | 1,60 | 0,51 | 54,85 | 21,72 | 0,43 | 0,24 | 0,36 | 0,32 | 0,70 | 1,12 | 0,37 | 2,98 | 0,33 | 3,53 | 3,30 | 0,45 |
| Ba | Mean [mg/kg] | 23,87 | 46,27 | 37,57 | 18,12 | 19,70 | 28,30 | 60,35 | 60,00 | 45,99 | 30,43 | 34,14 | 34,33 | 36,00 | 98,56 | 97,53 | 184,85 | 24,30 | 88,54 | 7,96 | 17,48 | 9,80 | 113,29 | 3,47 |
| | SD [mg/kg] | 0,14 | 0,64 | 0,36 | 0,61 | 0,21 | 0,41 | 1,56 | 1,05 | 0,87 | 0,44 | 1,35 | 0,36 | 0,47 | 1,99 | 1,66 | 4,23 | 0,44 | 1,81 | 0,22 | 0,56 | 0,82 | 2,88 | 0,27 |
| Bi | Mean [mg/kg] | 0,01 | 0,01 | 0,02 | 0,01 | 0,02 | 0,03 | 0,05 | 0,05 | 0,04 | 0,05 | 0,04 | 0,04 | 0,04 | 0,06 | 0,07 | 0,04 | 0,06 | 0,08 | 0,01 | 0,02 | 0,03 | 0,02 | 0,01 |
| | SD [mg/kg] | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| Ca | Mean [g/kg] | 28,54 | 34,56 | 33,10 | 14,99 | 25,77 | 20,69 | 47,00 | 52,20 | 30,40 | 24,88 | 25,57 | 42,21 | 37,77 | 349,37 | 346,72 | 329,38 | 339,66 | 307,23 | 14,65 | 15,51 | 22,16 | 32,99 | 52,82 |
| | SD [g/kg] | 0,16 | 0,47 | 0,59 | 0,78 | 0,41 | 0,30 | 1,36 | 2,82 | 0,60 | 0,46 | 1,04 | 0,52 | 0,90 | 7,53 | 8,06 | 6,84 | 5,35 | 7,84 | 0,09 | 0,35 | 0,30 | 0,64 | 4,71 |
| Cd | Mean [mg/kg] | 3,26 | 5,87 | 5,48 | 1,87 | 2,64 | 5,26 | 8,01 | 9,59 | 5,15 | 4,10 | 4,87 | 4,02 | 4,92 | 17,25 | 15,64 | 5,88 | 15,43 | 2,16 | 1,71 | 1,29 | 1,94 | 1,63 | 1,40 |
| | SD [mg/kg] | 0,05 | 0,08 | 0,03 | 0,06 | 0,04 | 0,05 | 0,22 | 0,25 | 0,08 | 0,07 | 0,22 | 0,05 | 0,08 | 0,44 | 1,30 | 0,13 | 0,31 | 0,04 | 0,02 | 0,02 | 0,01 | 0,05 | 0,10 |
| Ce | Mean [mg/kg] | 7,52 | 17,80 | 14,60 | 5,60 | 7,39 | 10,95 | 26,80 | 26,23 | 18,65 | 14,15 | 13,88 | 12,77 | 11,18 | 43,79 | 40,93 | 16,22 | 214,99 | 338,46 | 29,70 | 99,18 | 41,98 | 1178,15 | 3,05 |
| | SD [mg/kg] | 0,08 | 0,52 | 0,11 | 0,25 | 0,04 | 0,18 | 0,58 | 0,32 | 0,39 | 0,25 | 0,63 | 0,13 | 0,13 | 0,66 | 0,84 | 0,28 | 2,66 | 4,85 | 0,13 | 1,10 | 0,27 | 26,44 | 0,35 |
| Co | Mean [mg/kg] | 0,16 | 0,34 | 0,40 | 0,08 | 0,10 | 0,18 | 0,44 | 0,42 | 0,34 | 0,17 | 0,21 | 0,28 | 0,20 | 0,50 | 0,45 | 0,22 | 0,48 | 9,98 | 0,91 | 2,73 | 0,82 | 1,04 | 0,35 |
| | SD [mg/kg] | 0,01 | 0,01 | 0,01 | 0,00 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,00 | 0,01 | 0,00 | 0,00 | 0,02 | 0,02 | 0,01 | 0,02 | 0,41 | 0,01 | 0,01 | 0,02 | 0,03 | 0,02 |
| Cr | Mean [mg/kg] | 52,35 | 106,12 | 103,01 | 37,90 | 41,30 | 83,63 | 148,11 | 216,97 | 96,55 | 75,61 | 89,64 | 75,48 | 87,41 | 311,03 | 265,68 | 77,58 | 183,12 | 12,19 | 20,97 | 11,89 | 23,76 | 32,34 | 3,20 |
| | SD [mg/kg] | 0,83 | 2,26 | 2,39 | 1,86 | 0,49 | 1,55 | 5,62 | 10,66 | 1,86 | 1,74 | 4,53 | 1,72 | 0,97 | 12,83 | 8,59 | 1,99 | 7,28 | 0,90 | 1,05 | 0,47 | 0,82 | 2,70 | 0,70 |
| Cu | Mean [mg/kg] | 9,20 | 18,92 | 551,59 | 7,62 | 7,79 | 12,30 | 15,71 | 29,08 | 14,16 | 11,73 | 14,60 | 12,93 | 12,23 | 34,78 | 30,90 | 6,87 | 8,48 | 10,47 | 186,75 | 10,09 | 20,72 | 13,50 | 8,51 |
| | SD [mg/kg] | 0,39 | 0,23 | 12,46 | 0,47 | 1,47 | 0,29 | 0,32 | 0,79 | 0,35 | 0,28 | 0,66 | 0,44 | 0,26 | 0,64 | 0,51 | 0,84 | 0,07 | 0,27 | 3,33 | 0,37 | 0,14 | 0,46 | 0,96 |
| Dy | Mean [mg/kg] | 3,37 | 8,10 | 6,74 | 3,14 | 2,90 | 5,56 | 11,38 | 13,21 | 7,03 | 5,75 | 7,72 | 5,93 | 5,45 | 19,44 | 16,77 | 3,49 | 22,18 | 35,26 | 2,86 | 4,65 | 4,45 | 25,99 | 0,37 |
| | SD [mg/kg] | 0,03 | 0,13 | 0,06 | 0,14 | 0,01 | 0,06 | 0,33 | 0,19 | 0,14 | 0,16 | 0,35 | 0,06 | 0,05 | 0,32 | 0,36 | 0,05 | 0,36 | 0,47 | 0,05 | 0,04 | | 0,54 | 0,04 |
| Er | Mean [mg/kg] | 2,73 | 6,37 | 5,36 | 2,52 | 2,27 | 4,53 | 8,94 | 10,63 | 5,53 | 4,52 | 6,16 | 4,64 | 4,45 | 15,28 | 13,24 | 2,80 | 13,61 | 22,53 | 1,80 | 2,48 | 2,74 | 11,23 | 0,24 |
| | SD [mg/kg] | 0,05 | 0,13 | 0,06 | 0,10 | 0,02 | 0,08 | 0,17 | 0,12 | 0,16 | 0,08 | 0,27 | 0,06 | 0,02 | 0,25 | 0,23 | 0,04 | 0,23 | 0,32 | 0,03 | 0,01 | 0,03 | 0,22 | 0,02 |
| Eu | Mean [mg/kg] | 0,68 | 1,65 | 1,38 | 0,63 | 0,62 | 1,11 | 2,35 | 2,63 | 1,47 | 1,20 | 1,54 | 1,22 | 1,07 | 4,08 | 3,45 | 0,84 | 6,84 | 10,99 | 0,86 | 2,27 | 1,32 | 16,03 | 0,07 |
| | SD [mg/kg] | 0,01 | 0,02 | 0,01 | 0,03 | 0,00 | 0,02 | 0,05 | 0,02 | 0,03 | 0,02 | 0,07 | 0,01 | 0,01 | 0,06 | 0,06 | 0,01 | 0,07 | 0,17 | 0,01 | 0,00 | 0,01 | 0,27 | 0,00 |
| Fe | Mean [g/kg] | 0,43 | 1,04 | 0,80 | 0,31 | 0,34 | 0,64 | 1,17 | 1,07 | 0,90 | 0,57 | 0,70 | 0,77 | 0,68 | 1,70 | 1,70 | 0,66 | 2,41 | 3,73 | 1,93 | 2,26 | 1,76 | 1,31 | 0,82 |
| | SD [g/kg] | 0,01 | 0,03 | 0,04 | 0,02 | 0,01 | 0,01 | 0,08 | 0,06 | 0,03 | 0,01 | 0,03 | 0,03 | 0,02 | 0,04 | 0,05 | 0,02 | 0,14 | 0,29 | 0,24 | 0,07 | 0,12 | 0,13 | 0,06 |
| Ga | Mean [mg/kg] | 0,46 | 1,04 | 0,94 | 0,34 | 0,38 | 0,69 | 1,48 | 1,65 | 1,06 | 0,75 | 0,82 | 0,78 | 0,71 | 2,17 | 2,00 | 0,63 | 3,12 | 3,91 | 0,59 | 0,80 | 0,71 | 4,65 | 0,20 |
| | SD [mg/kg] | 0,01 | 0,01 | 0,03 | 0,01 | 0,01 | 0,02 | 0,03 | 0,12 | 0,02 | 0,01 | 0,04 | 0,01 | 0,01 | 0,05 | 0,05 | 0,01 | 0,07 | 0,06 | 0,00 | 0,02 | 0,02 | 0,11 | 0,03 |
| Gd | Mean [mg/kg] | 3,18 | 7,69 | 6,38 | 2,95 | 2,86 | 5,22 | 10,81 | 12,40 | 6,71 | 5,49 | 7,22 | 5,63 | 5,07 | 18,54 | 15,98 | 3,57 | 27,71 | 40,72 | 3,58 | 8,13 | 5,61 | 57,28 | 0,41 |
| | SD [mg/kg] | 0,05 | 0,10 | 0,06 | 0,13 | 0,03 | 0,09 | 0,28 | 0,16 | 0,10 | 0,11 | 0,35 | 0,07 | 0,05 | 0,28 | 0,31 | 0,07 | 0,41 | 0,52 | 0,03 | 0,07 | 0,02 | 1,14 | 0,01 |
| Ho | Mean [mg/kg] | 0,87 | 2,06 | 1,73 | 0,81 | 0,74 | 1,46 | 2,90 | 3,42 | 1,79 | 1,47 | 1,99 | 1,51 | 1,42 | 4,93 | 4,29 | 0,90 | 4,83 | 7,88 | 0,60 | 0,88 | 0,93 | 4,46 | 0,08 |
| | SD [mg/kg] | 0,01 | 0,03 | 0,02 | 0,03 | 0,01 | 0,03 | 0,07 | 0,04 | 0,05 | 0,03 | 0,08 | 0,02 | 0,01 | 0,07 | 0,09 | 0,01 | 0,08 | 0,11 | 0,01 | 0,00 | 0,01 | 0,10 | 0,01 |
| K | Mean [mg/kg] | 70,32 | 128,32 | 0,49 | 143,07 | 53,56 | 162,67 | 0,76 | 1,14 | 0,40 | 0,84 | 142,90 | 77,38 | 105,60 | 0,73 | 0,60 | 0,23 | 0,87 | 1,98 | 129,79 | 129,65 | 139,41 | 158,09 | 31,46 |
| | SD [g/kg] | 0,36 | 1,95 | 0,01 | 6,79 | 0,50 | 1,68 | 0,02 | 0,08 | 0,01 | 0,02 | 5,56 | 0,87 | 1,85 | 0,04 | 0,01 | 0,01 | 0,01 | 0,05 | 0,26 | 0,82 | 0,99 | 3,55 | 3,15 |
| La | Mean [mg/kg] | 19,07 | 43,93 | 37,67 | 16,39 | 16,61 | 31,17 | 60,90 | 73,11 | 39,86 | 31,88 | 41,47 | 32,72 | 30,80 | 105,36 | 92,20 | 22,31 | 150,57 | 186,57 | 19,27 | 48,68 | 27,62 | 753,43 | 2,81 |
| | SD [mg/kg] | 0,16 | 0,73 | 0,32 | 0,98 | 0,23 | 0,52 | 1,65 | 0,77 | 0,73 | 0,66 | 1,70 | 0,36 | 0,26 | 1,79 | 1,58 | 0,37 | 2,23 | 2,33 | 0,04 | 2,77 | 0,19 | 14,90 | 0,08 |
| Li | Mean [mg/kg] | 0,40 | 1,09 | 0,83 | 1,14 | 0,42 | 0,56 | 1,43 | 1,25 | 1,06 | 3,37 | 1,59 | 0,82 | 0,64 | 1,76 | 1,48 | 1,01 | 2,06 | 1,39 | 0,94 | 8,39 | 1,32 | 0,67 | 3,51 |
| | SD [mg/kg] | 0,02 | 0,02 | 0,02 | 0,05 | 0,01 | 0,01 | 0,03 | 0,08 | 0,02 | 0,07 | 0,08 | 0,01 | 0,02 | 0,06 | 0,02 | 0,01 | 0,04 | 0,03 | 0,01 | 0,39 | 0,03 | 0,03 | 0,44 |
| Lu | Mean [mg/kg] | 0,44 | 1,00 | 0,85 | 0,40 | 0,35 | 0,73 | 1,40 | 1,70 | 0,86 | 0,71 | 0,97 | 0,72 | 0,72 | 2,41 | 2,09 | 0,43 | 1,72 | 2,91 | 0,32 | 0,35 | 0,43 | 0,84 | 0,03 |
| | SD [mg/kg] | 0,01 | 0,02 | 0,01 | 0,00 | 0,01 | 0,01 | 0,04 | 0,02 | 0,01 | 0,02 | 0,04 | 0,01 | 0,01 | 0,04 | 0,04 | 0,01 | 0,02 | 0,04 | 0,01 | 0,00 | 0,01 | 0,03 | 0,00 |
| Mg | Mean [g/kg] | 18,31 | 1,83 | 1,18 | 18,72 | 14,84 | 1,06 | 1,69 | 2,57 | 1,38 | 1,11 | 19,01 | 16,21 | 9,53 | 2,15 | 1,93 | 2,52 | 7,19 | 2,34 | 13,29 | 22,90 | 14,11 | 16,99 | 14,26 |
| | SD [g/kg] | 0,19 | 0,03 | 0,02 | 0,86 | 0,24 | 0,02 | 0,04 | 0,13 | 0,02 | 0,02 | 0,84 | 0,29 | 0,19 | 0,07 | 0,04 | 0,04 | 0,09 | 0,05 | 0,04 | 0,23 | 0,07 | 0,39 | 1,22 |
| Mn | Mean [mg/kg] | 5,93 | 11,75 | 14,44 | 6,24 | 4,25 | 6,35 | 14,31 | 9,36 | 11,44 | 8,82 | 9,76 | 6,99 | 5,05 | 9,57 | 9,20 | 7,16 | 14,23 | 1131,17 | 242,13 | 416,06 | 32,92 | 238,10 | 41,10 |
| | SD [mg/kg] | 0,99 | 2,12 | 1,32 | 1,46 | 1,20 | 0,11 | 0,95 | 1,10 | 0,50 | 4,74 | 1,64 | 0,33 | 0,32 | 0,37 | 0,76 | 0,16 | 0,15 | 19,08 | 3,38 | 5,49 | 0,75 | 16,57 | 4,62 |
| Mo | Mean [mg/kg] | 0,59 | 1,04 | 1,04 | 0,54 | 0,41 | 1,12 | 1,60 | 1,25 | 0,97 | 0,80 | 1,16 | 0,76 | 1,43 | 2,75 | 2,94 | 1,95 | 2,43 | 4,30 | 49,46 | 2,74 | 2,90 | 0,59 | 0,24 |
| | SD [mg/kg] | 0,03 | 0,02 | 0,01 | 0,01 | 0,05 | 0,02 | 0,04 | 0,03 | 0,03 | 0,01 | 0,06 | 0,01 | 0,02 | 0,04 | 0,07 | 0,05 | 0,06 | 0,05 | 0,58 | 0,06 | 0,02 | 0,03 | 0,01 |
| Na | Mean [g/kg] | 2,45 | 4,88 | 2,26 | 2,01 | 2,29 | 4,35 | 3,21 | 3,76 | 2,31 | 1,78 | 4,06 | 3,35 | 3,81 | 5,00 | 4,54 | 3,40 | 9,16 | 6,71 | 2,16 | 2,51 | 2,08 | 2,89 | 7,77 |
| | SD [g/kg] | 0,02 | 0,06 | 0,02 | 0,09 | 0,02 | 0,04 | 0,07 | 0,18 | 0,04 | 0,04 | 0,16 | 0,02 | 0,06 | 0,10 | 0,10 | 0,06 | 0,09 | 0,16 | 0,02 | 0,01 | 0,01 | 0,05 | 0,66 |
| Nd | Mean [mg/kg] | 11,69 | 28,12 | 23,91 | 10,65 | 10,90 | 19,01 | 40,50 | 45,87 | 25,45 | 20,81 | 26,50 | 21,01 | 18,38 | 70,13 | 59,85 | 14,37 | 149,01 | 192,71 | 16,61 | 46,15 | 25,71 | 427,83 | 1,98 |
| | SD [mg/kg] | 0,14 | 0,42 | 0,20 | 0,49 | 0,03 | 0,30 | 0,75 | 0,39 | 0,61 | 0,27 | 1,08 | 0,29 | 0,12 | 1,14 | 1,17 | 0,18 | 2,24 | 3,09 | 0,17 | 0,36 | 0,04 | 8,02 | 0,04 |
| Ni | Mean [mg/kg] | 7,61 | 11,88 | 18,43 | 5,94 | 5,42 | 10,25 | 19,88 | 19,82 | 11,15 | 8,98 | 12,33 | 9,93 | 11,84 | 40,88 | 31,73 | 8,33 | 15,30 | 23,02 | 5,45 | 6,69 | 4,08 | 7,40 | 2,81 |
| | SD [mg/kg] | 0,13 | 0,27 | 0,36 | 0,35 | 0,94 | 0,30 | 0,36 | 0,65 | 0,14 | 0,21 | 0,73 | 0,44 | 0,27 | 1,29 | 0,73 | 0,59 | 0,44 | 0,59 | 0,19 | 0,12 | 0,12 | 0,25 | 0,52 |
| P | Mean [mg/kg] | 34,68 | 70,34 | 63,95 | 22,20 | 32,74 | 50,83 | 95,89 | 119,83 | 68,59 | 45,65 | 57,32 | 49,18 | 64,56 | 158,72 | 159,41 | 148,28 | 143,88 | 146,06 | 29,52 | 61,63 | 32,47 | 45,03 | 22,68 |
| | SD [mg/kg] | 0,68 | 0,78 | 1,15 | 0,47 | 0,09 | 1,62 | 1,02 | 2,10 | 0,52 | 1,20 | 1,82 | 0,12 | 2,12 | 3,53 | 4,20 | 3,72 | 1,61 | 3,13 | 0,04 | 2,04 | 0,17 | 0,96 | 2,23 |
| Pb | Mean [mg/kg] | 0,54 | 1,33 | 1,05 | 0,41 | 0,52 | 1,09 | 1,67 | 1,42 | 1,18 | 0,73 | 0,83 | 0,84 | 0,88 | 2,02 | 2,46 | 1,76 | 2,73 | 17,47 | 0,68 | 1,17 | 0,73 | 1,47 | 0,33 |
| | SD [mg/kg] | 0,00 | 0,02 | 0,01 | 0,01 | 0,01 | 0,02 | 0,05 | 0,01 | 0,03 | 0,01 | 0,04 | 0,00 | 0,00 | 0,02 | 0,04 | 0,03 | 0,04 | 0,16 | 0,02 | 0,02 | 0,01 | 0,09 | 0,01 |
| Pr | Mean [mg/kg] | 2,62 | 6,30 | 5,38 | 2,37 | 2,46 | 4,26 | 9,09 | 10,29 | 5,75 | 4,67 | 5,92 | 4,71 | 4,13 | 16,79 | 13,55 | 3,28 | 35,20 | 43,94 | 4,15 | 11,83 | 6,29 | 123,52 | 0,50 |
| | SD [mg/kg] | 0,02 | 0,11 | 0,04 | 0,10 | 0,01 | 0,08 | 0,19 | 0,09 | 0,15 | 0,08 | 0,26 | 0,06 | 0,04 | 0,27 | 0,34 | 0,04 | 0,43 | 0,44 | 0,03 | 0,15 | 0,03 | 2,24 | 0,03 |
| Rb | Mean [mg/kg] | 13,54 | 12,34 | 5,17 | 8,77 | 9,19 | 8,12 | 2,55 | 2,33 | 1,85 | 1,37 | 19,56 | 12,63 | 11,10 | 3,61 | 3,00 | 1,03 | 3,96 | 4,60 | 5,15 | 38,57 | 7,86 | 10,01 | 4,58 |
| | SD [mg/kg] | 0,13 | 0,18 | 0,02 | 0,29 | 0,08 | 0,08 | 0,07 | 0,10 | 0,02 | 0,03 | 0,85 | 0,13 | 0,10 | 0,15 | 0,04 | 0,04 | 0,07 | 0,07 | 0,04 | 0,40 | 0,04 | 0,22 | 0,59 |
| Sc | Mean [mg/kg] | 2,04 | 4,67 | 4,41 | 1,69 | 1,89 | 3,14 | 6,88 | 8,35 | 4,34 | 3,09 | 4,22 | 3,39 | 3,23 | 11,93 | 10,16 | 3,92 | 5,20 | 22,35 | 3,35 | 3,92 | 3,54 | 3,95 | 0,73 |
| | SD [mg/kg] | 0,02 | 0,09 | 0,01 | 0,07 | 0,02 | 0,06 | 0,17 | 0,59 | 0,19 | 0,08 | 0,24 | 0,09 | 0,04 | 0,28 | 0,13 | 0,16 | 0,08 | 0,29 | 0,01 | 0,10 | 0,04 | 0,05 | 0,12 |
| Se | Mean [mg/kg] | 1,37 | 2,67 | 2,37 | 1,25 | 1,08 | 2,20 | 3,51 | 4,08 | 2,16 | 2,50 | 2,62 | 1,88 | 1,78 | 6,47 | 5,71 | 1,44 | 39,22 | 13,95 | 2,02 | 1,52 | 3,53 | 3,67 | 2,03 |
| | SD [mg/kg] | 0,11 | 0,15 | 0,11 | 0,05 | 0,04 | 0,19 | 0,22 | 0,24 | 0,12 | 0,18 | 0,16 | 0,08 | 0,04 | 0,24 | 0,32 | 0,12 | 0,70 | 0,31 | 0,17 | 0,09 | 0,09 | 0,25 | 0,08 |
| Sm | Mean [mg/kg] | 2,24 | 5,44 | 4,62 | 2,07 | 2,10 | 3,67 | 7,90 | 8,72 | 4,88 | 4,02 | 5,13 | 4,07 | 3,51 | 13,61 | 11,57 | 2,72 | 26,09 | 35,09 | 3,31 | 8,12 | 5,10 | 57,05 | 0,36 |
| | SD [mg/kg] | 0,03 | 0,08 | 0,03 | 0,10 | 0,02 | 0,06 | 0,15 | 0,10 | 0,11 | 0,06 | 0,24 | 0,06 | 0,03 | 0,22 | 0,25 | 0,05 | 0,33 | 0,46 | 0,03 | 0,10 | 0,06 | 0,87 | 0,03 |
| Sr | Mean [g/kg] | 0,15 | 0,23 | 0,21 | 0,14 | 0,16 | 0,13 | 0,31 | 0,32 | 0,24 | 0,31 | 0,22 | 0,21 | 0,22 | 0,92 | 0,86 | 1,59 | 2,39 | 1,56 | 0,17 | 0,23 | 0,24 | 3,90 | 0,19 |
| | SD [g/kg] | 0,00 | 0,00 | 0,00 | 0,01 | 0,00 | 0,00 | 0,01 | 0,01 | 0,00 | 0,01 | 0,01 | 0,00 | 0,00 | 0,01 | 0,02 | 0,04 | 0,05 | 0,03 | 0,00 | 0,00 | 0,00 | 0,08 | 0,01 |
| Tb | Mean [mg/kg] | 0,52 | 1,25 | 1,04 | 0,49 | 0,46 | 0,85 | 1,76 | 2,02 | 1,08 | 0,89 | 1,18 | 0,91 | 0,82 | 3,03 | 2,59 | 0,56 | 4,06 | 6,19 | 0,49 | 0,97 | 0,78 | 5,97 | 0,06 |
| | SD [mg/kg] | 0,01 | 0,02 | 0,00 | 0,02 | 0,01 | 0,01 | 0,05 | 0,03 | 0,02 | 0,02 | 0,05 | 0,01 | 0,01 | 0,05 | 0,04 | 0,01 | 0,07 | 0,07 | 0,00 | 0,01 | 0,00 | 0,10 | 0,00 |
| Te | Mean [mg/kg] | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 | >0,08 |
| | SD | | | | | | | | | | | | | | | | | | | | | | | |
| Th | Mean [mg/kg] | 0,61 | 1,46 | 1,34 | 0,43 | 0,65 | 0,89 | 2,37 | 1,88 | 1,40 | 1,15 | 1,09 | 1,14 | 0,87 | 3,86 | 3,63 | 0,90 | 13,93 | 5,93 | 2,33 | 8,61 | 3,61 | 8,63 | 0,63 |
| | SD [mg/kg] | 0,01 | 0,03 | 0,02 | 0,02 | 0,01 | 0,02 | 0,02 | 0,03 | 0,04 | 0,02 | 0,05 | 0,01 | 0,01 | 0,05 | 0,08 | 0,02 | 0,15 | 0,10 | 0,02 | 0,15 | 0,02 | 0,21 | 0,06 |
| Tl | Mean [mg/kg] | 0,05 | 0,06 | 0,05 | 0,03 | 0,03 | 0,05 | 0,08 | 0,06 | 0,05 | 0,12 | 0,07 | 0,05 | 0,06 | 0,16 | 0,13 | 0,07 | 3,63 | 6,38 | 0,19 | 0,09 | 0,28 | 0,01 | 0,02 |
| | SD [mg/kg] | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,01 | 0,00 | 0,00 | 0,05 | 0,09 | 0,01 | 0,01 | | 0,00 | 0,00 |
| Tm | Mean [mg/kg] | 0,40 | 0,93 | 0,78 | 0,37 | 0,33 | 0,66 | 1,30 | 1,55 | 0,81 | 0,66 | 0,90 | 0,67 | 0,65 | 2,22 | 1,93 | 0,40 | 1,84 | 3,12 | 0,27 | 0,33 | 0,38 | 1,18 | 0,03 |
| | SD [mg/kg] | 0,00 | 0,02 | 0,01 | 0,02 | 0,00 | 0,01 | 0,00 | 0,01 | 0,03 | 0,02 | 0,02 | 0,01 | 0,01 | 0,04 | 0,04 | 0,00 | 0,03 | 0,07 | 0,00 | 0,03 | 0,00 | 0,03 | 0,00 |
| U | Mean [mg/kg] | 26,02 | 57,10 | 50,03 | 19,48 | 25,31 | 37,17 | 76,54 | 99,36 | 54,18 | 37,93 | 44,95 | 42,45 | 39,03 | 116,38 | 109,13 | 52,99 | 42,87 | 26,26 | 21,14 | 11,98 | 20,10 | 18,54 | 0,21 |
| | SD [mg/kg] | 0,25 | 0,52 | 0,39 | 0,45 | 0,26 | 0,57 | 0,77 | 1,14 | 1,02 | 0,55 | 2,15 | 0,45 | 0,31 | 1,61 | 2,34 | 0,75 | 0,42 | 0,35 | 0,14 | 0,11 | 0,09 | 0,45 | 0,00 |
| V | Mean [mg/kg] | 54,04 | 95,36 | 87,46 | 34,45 | 34,52 | 84,87 | 133,67 | 130,95 | 90,70 | 69,09 | 68,70 | 65,97 | 86,16 | 234,16 | 311,20 | 56,84 | 48,74 | 36,49 | 22,87 | 19,16 | 22,94 | 38,02 | 2,30 |
| | SD [mg/kg] | 0,27 | 1,49 | 1,17 | 0,37 | 1,52 | 0,37 | 1,56 | 2,00 | 1,43 | 1,45 | 3,45 | 1,26 | 1,01 | 7,97 | 7,36 | 1,45 | 0,53 | 1,56 | 0,16 | 0,12 | 0,50 | 1,10 | 0,27 |
| Y | Mean [mg/kg] | 48,61 | 111,60 | 94,57 | 43,99 | 41,57 | 79,40 | 156,67 | 190,58 | 98,90 | 79,40 | 106,66 | 82,45 | 80,42 | 270,14 | 239,64 | 59,84 | 214,18 | 278,34 | 26,17 | 33,91 | 40,09 | 156,64 | 3,96 |
| | SD [mg/kg] | 0,47 | 1,47 | 1,00 | 1,91 | 0,15 | 0,92 | 4,66 | 6,60 | 1,83 | 1,87 | 4,78 | 0,72 | 0,56 | 3,30 | 5,04 | 1,08 | 4,05 | 4,67 | 0,12 | 0,32 | 0,36 | 2,74 | 0,36 |
| Yb | Mean [mg/kg] | 2,52 | 5,83 | 4,93 | 2,33 | 2,06 | 4,18 | 8,19 | 9,81 | 5,05 | 4,17 | 5,66 | 4,22 | 4,15 | 14,06 | 12,17 | 2,51 | 10,92 | 18,67 | 1,02 | 1,31 | 1,69 | 5,45 | >1 |
| | SD [mg/kg] | 0,02 | 0,10 | 0,06 | 0,10 | 0,02 | 0,07 | 0,15 | 0,13 | 0,09 | 0,08 | 0,24 | 0,03 | 0,04 | 0,21 | 0,23 | 0,04 | 0,18 | 0,23 | 0,05 | 0,02 | 0,04 | 0,18 | |
| Zn | Mean [mg/kg] | 69,82 | 129,81 | 1218,26 | 102,31 | 51,68 | 89,49 | 167,09 | 180,72 | 109,01 | 82,15 | 164,46 | 80,94 | 95,84 | 288,25 | 250,80 | 166,69 | 127,15 | 84,93 | 160,60 | 62,45 | 122,22 | 249,80 | 67,88 |
| | SD [mg/kg] | 0,74 | 3,42 | 20,44 | 4,02 | 0,29 | 1,38 | 3,22 | 2,61 | 2,40 | 1,52 | 8,28 | 1,20 | 1,10 | 6,04 | 4,94 | 3,58 | 1,42 | 1,21 | 1,66 | 0,63 | 1,70 | 32,76 | 6,28 |

**Table 5: Total element content of all measured samples**

**Table 6: Pearson's correlation coefficient of measured fertilizers and rock phosphates**

Pearson Correlation matrix (each variable has the statistics: Pearson Correlation, Sig. (2-tailed), N). Sig. (2-tailed) = .000 and N = 1435 for all pairs unless noted; selected Sig. values in the F18/RP5 area are .001–.132.

| | RP1 | RP2 | RP3 | RP4 | RP5 | F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 | F10 | F11 | F12 | F13 | F14 | F15 | F16 | F17 | F18 | Mix1 | Mix2 | Mix3 | Mix4 | Mix5 | Mix6 | Mix7 | Mix8 | BCR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RP1 | 1 | .989** | .702** | .793** | .130** | .952** | .974** | .987** | .993** | .978** | .974** | .976** | .953** | .939** | .986** | .984** | .942** | .961** | .797** | .737** | .811** | .425** | .082** | .993** | .961** | .915** | .838** | .928** | .899** | .860** | .821** | .993** |
| RP2 | .989** | 1 | .729** | .769** | .129** | .924** | .951** | .978** | .994** | .986** | .984** | .972** | .960** | .953** | .981** | .989** | .962** | .984** | .792** | .759** | .795** | .477** | .087** | .978** | .959** | .915** | .839** | .893** | .870** | .840** | .809** | .981** |
| RP3 | .702** | .729** | 1 | .809** | .192** | .610** | .577** | .610** | .711** | .691** | .610** | .598** | .601** | .599** | .721** | .847** | .618** | .669** | .492** | .496** | .515** | .784** | .072** | .773** | .830** | .885** | .926** | .702** | .742** | .774** | .791** | .737** |
| RP4 | .793** | .769** | .809** | 1 | .210** | .841** | .769** | .729** | .810** | .714** | .730** | .867** | .619** | .605** | .817** | .728** | .630** | .714** | .707** | .771** | .761** | .440** | .082** | .872** | .906** | .932** | .935** | .915** | .952** | .979** | .990** | .839** |
| RP5 | .130** | .129** | .192** | .210** | 1 | .130** | .120** | .123** | .155** | .155** | .141** | .124** | .107** | .123** | .169** | .139** | .131** | .165** | .398** | .366** | .541** | .064* | .047 | .122** | .121** | .119** | .113** | .124** | .126** | .129** | .131** | .116** |
| F1 | .952** | .924** | .610** | .841** | .130** | 1 | .985** | .946** | .949** | .881** | .927** | .898** | .842** | .821** | .938** | .915** | .830** | .974** | .888** | .819** | .870** | .304** | .082** | .958** | .934** | .887** | .808** | .974** | .949** | .911** | .874** | .961** |
| F2 | .974** | .951** | .577** | .769** | .120** | .985** | 1 | .984** | .968** | .930** | .965** | .954** | .911** | .895** | .952** | .957** | .899** | .921** | .865** | .797** | .958** | .301** | .082** | .958** | .922** | .860** | .764** | .938** | .900** | .852** | .806** | .969** |
| F3 | .987** | .978** | .610** | .729** | .123** | .946** | .984** | 1 | .983** | .975** | .988** | .990** | .969** | .959** | .963** | .988** | .962** | .967** | .817** | .763** | .822** | .357** | .085** | .959** | .923** | .859** | .763** | .893** | .854** | .806** | .762** | .973** |
| F4 | .993** | .994** | .711** | .810** | .155** | .949** | .968** | .983** | 1 | .981** | .985** | .970** | .847** | .939** | .992** | .990** | .949** | .975** | .828** | .784** | .832** | .437** | .089** | .982** | .961** | .915** | .837** | .919** | .895** | .863** | .829** | .986** |
| F5 | .978** | .986** | .691** | .714** | .155** | .881** | .930** | .975** | .981** | 1 | .978** | .987** | .984** | .983** | .972** | .993** | .986** | .989** | .750** | .708** | .775** | .451** | .080** | .947** | .921** | .868** | .795** | .842** | .810** | .772** | .734** | .956** |
| F6 | .974** | .984** | .610** | .730** | .141** | .927** | .965** | .989** | .985** | .978** | 1 | .981** | .964** | .961** | .966** | .994** | .970** | .988** | .831** | .797** | .926** | .365** | .091** | .948** | .911** | .846** | .747** | .866** | .830** | .791** | .751** | .956** |
| F7 | .976** | .972** | .596** | .667** | .124** | .898** | .954** | .990** | .970** | .987** | .981** | 1 | .991** | .985** | .954** | .990** | .982** | .973** | .756** | .701** | .778** | .358** | .082** | .933** | .893** | .826** | .727** | .841** | .797** | .746** | .700** | .951** |
| F8 | .953** | .960** | .601** | .619** | .107** | .842** | .911** | .969** | .947** | .984** | .964** | .991** | 1 | .996** | .925** | .978** | .992** | .972** | .695** | .655** | .718** | .393** | .076** | .903** | .865** | .799** | .704** | .780** | .738** | .691** | .648** | .925** |
| F9 | .939** | .953** | .599** | .605** | .123** | .821** | .895** | .959** | .939** | .983** | .961** | .985** | .996** | 1 | .918** | .974** | .990** | .975** | .694** | .661** | .717** | .395** | .083** | .892** | .853** | .787** | .692** | .758** | .717** | .672** | .631** | .908** |
| F10 | .986** | .981** | .721** | .817** | .169** | .938** | .952** | .963** | .992** | .972** | .966** | .954** | .925** | .918** | 1 | .978** | .926** | .961** | .810** | .755** | .828** | .423** | .091** | .973** | .955** | .913** | .839** | .921** | .898** | .866** | .831** | .975** |
| F11 | .984** | .989** | .647** | .728** | .139** | .915** | .957** | .988** | .990** | .993** | .994** | .990** | .978** | .974** | .978** | 1 | .980** | .990** | .794** | .752** | .804** | .400** | .080** | .953** | .921** | .861** | .769** | .865** | .830** | .789** | .750** | .965** |
| F12 | .942** | .962** | .618** | .630** | .131** | .830** | .899** | .962** | .949** | .986** | .970** | .982** | .992** | .990** | .926** | .980** | 1 | .986** | .717** | .693** | .734** | .415** | .087** | .902** | .866** | .802** | .708** | .760** | .731** | .690** | .652** | .914** |
| F13 | .961** | .984** | .669** | .714** | .165** | .874** | .921** | .967** | .976** | .989** | .988** | .973** | .972** | .975** | .961** | .990** | .986** | 1 | .781** | .760** | .789** | .440** | .094** | .935** | .906** | .850** | .761** | .821** | .792** | .759** | .726** | .938** |
| F14 | .797** | .792** | .492** | .787** | .398** | .868** | .865** | .817** | .828** | .750** | .831** | .756** | .695** | .694** | .810** | .794** | .717** | .781** | 1 | .974** | .966** | .227** | .108** | .821** | .793** | .745** | .660** | .840** | .825** | .807** | .784** | .803** |
| F15 | .737** | .759** | .496** | .771** | .366** | .819** | .797** | .763** | .784** | .708** | .797** | .701** | .655** | .661** | .755** | .752** | .693** | .760** | .974** | 1 | .907** | .278** | .111** | .776** | .755** | .715** | .639** | .768** | .765** | .766** | .757** | .749** |
| F16 | .811** | .795** | .515** | .761** | .541** | .870** | .858** | .822** | .832** | .775** | .826** | .778** | .718** | .717** | .828** | .804** | .734** | .789** | .966** | .907** | 1 | .230** | .108** | .817** | .789** | .739** | .657** | .830** | .808** | .781** | .752** | .807** |
| F17 | .425** | .477** | .784** | .440** | .064* | .304** | .301** | .357** | .437** | .451** | .365** | .358** | .393** | .395** | .423** | .400** | .415** | .440** | .227** | .278** | .230** | 1 | .040 | .482** | .532** | .582** | .621** | .352** | .381** | .409** | .426** | .459** |
| F18 | .082** | .087** | .072** | .082** | .047 | .082** | .082** | .085** | .089** | .088** | .091** | .082** | .076** | .083** | .091** | .088** | .087** | .094** | .108** | .111** | .108** | .040 | 1 | .096** | .094** | .081** | .074** | .078** | .076** | .078** | .077** | .080** |
| Mix1 | .993** | .978** | .773** | .872** | .122** | .958** | .958** | .959** | .982** | .947** | .948** | .933** | .903** | .892** | .973** | .953** | .902** | .935** | .821** | .776** | .817** | .482** | .086** | 1 | .994** | .967** | .909** | .960** | .948** | .926** | .899** | .991** |
| Mix2 | .961** | .959** | .830** | .906** | .121** | .934** | .922** | .923** | .961** | .921** | .911** | .893** | .865** | .853** | .955** | .921** | .886** | .906** | .793** | .755** | .789** | .532** | .084** | .994** | 1 | .989** | .950** | .958** | .956** | .946** | .929** | .978** |
| Mix3 | .915** | .915** | .885** | .932** | .118** | .887** | .860** | .858** | .915** | .868** | .846** | .826** | .799** | .787** | .913** | .861** | .802** | .850** | .745** | .715** | .739** | .582** | .081** | .967** | .989** | 1 | .985** | .939** | .954** | .957** | .950** | .943** |
| Mix4 | .838** | .839** | .926** | .935** | .113** | .808** | .764** | .763** | .837** | .785** | .747** | .727** | .704** | .692** | .839** | .768** | .708** | .761** | .660** | .639** | .657** | .621** | .074** | .909** | .950** | .985** | 1 | .892** | .923** | .942** | .947** | .878** |
| Mix5 | .928** | .893** | .702** | .915** | .124** | .974** | .938** | .893** | .919** | .842** | .866** | .841** | .780** | .758** | .921** | .865** | .768** | .821** | .840** | .768** | .830** | .352** | .076** | .960** | .958** | .939** | .892** | 1 | .993** | .972** | .946** | .950** |
| Mix6 | .899** | .870** | .742** | .952** | .126** | .949** | .900** | .854** | .895** | .810** | .830** | .797** | .738** | .717** | .898** | .830** | .731** | .792** | .825** | .765** | .808** | .381** | .076** | .948** | .958** | .954** | .923** | .993** | 1 | .992** | .977** | .931** |
| Mix7 | .860** | .840** | .774** | .979** | .129** | .911** | .852** | .806** | .863** | .772** | .791** | .746** | .691** | .672** | .866** | .789** | .690** | .759** | .807** | .766** | .781** | .409** | .070** | .926** | .946** | .957** | .942** | .972** | .992** | 1 | .996** | .900** |
| Mix8 | .821** | .809** | .791** | .990** | .131** | .874** | .806** | .762** | .829** | .734** | .751** | .700** | .648** | .631** | .831** | .750** | .652** | .728** | .784** | .757** | .752** | .426** | .077** | .899** | .929** | .950** | .947** | .946** | .977** | .996** | 1 | .867** |
| BCR | .993** | .981** | .737** | .838** | .116** | .961** | .969** | .973** | .986** | .956** | .956** | .951** | .925** | .908** | .975** | .965** | .914** | .938** | .803** | .749** | .807** | .459** | .080** | .991** | .978** | .943** | .878** | .950** | .931** | .900** | .867** | 1 |

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).



**Figure 3: Spider chart of elemental pattern of measured Rare Earth Elements. Values are represented as decadic logarithm.**

# Political Aspects behind the Phosphorus Crisis

## with special focus on Morocco/Western Sahara

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## Abstract

Phosphorus as a vital element intrinsically tied to all living beings, food chains and plant growth, is more and more depleted and its position as a non-renewable and scarce resource becomes increasingly a topic in science. This development draws special attention to the political insecurities in supply countries that have the potential to even worsen the problem of scarcity of Phosphorus in the future. This paper shows on the example of Western Sahara/Morocco how resource depletion and fundamental change in political structures in an occupied territory can influence not only the country or region but also the worldwide resource market. As methods, first a causal loop diagram will give an overview on the connection between Western Sahara's phosphorus production and different areas on a supra-national scale, second a comparison to South Sudan and third a simplified qualitative scenario analysis for simulating possible future development are used. The results show that Western Sahara's phosphate industry is intimately connected with the global phosphorus market and that various future scenarios are possible, if the region becomes independent peacefully. Concluding, a political change in this region can cause a total restructuring of the phosphorus market concerning trade cooperation and supplier-costumer partnerships.

## 1. Introduction

While the whole world currently talks about decreasing oil production, only few people concern themselves with the problematic issue of the essential non-renewable element of phosphorus and its depletion. Phosphorus – amongst others – is needed for modern food production in the form of mineral fertilizer. This fertilizer usually is produced with phosphate rock, which is mined in only a few places in the world, especially in China (24% of world production in 2007), USA (20 %) and Morocco (19%) [Jasinski 2008]. The very concentrated occurrence of the convertible form of phosphorus on only a few spots in the

world causes various problems, such as the simultaneous violation of multiple international law – as is the case of Morocco – where the occupation of Western Sahara (censured by the United Nations) is inter alia caused by the giant phosphorus reserves [Cubby 2007; 27; Botha 2010; 237, 248].

This paper deals with the phosphorus scarcity as a future threat and its political aspects with special focus on the case of Western Sahara. Even though research has been done on Morocco and Western Sahara's legal situation [Botha 2010; Pearce 2011; Simanowitz 2009; McCutcheon 2011; Cisse and Mrabet 2004], none give attention to the possible effects on the world phosphorus market that can be caused by a change in the political and legal structure of Western Sahara. There is no study that analyzes the possible consequences if Western Sahara were to actually gain its independence through a non-violent process.

The aim of this work is (1) to show how political change in Western Sahara can impact the global phosphorus market, and (2) if Western Sahara can become independent with the help of the UN.

This paper will answer how political changes in Morocco/Western Sahara can affect the global phosphorus market. The first chapter describes the phosphorus crisis, history, and legal situation of Morocco and Western Sahara. Chapters 2 and 3 are a description of the applied methods and presenting our results. In the further sub-chapters we compare Sahara to South Sudan to show that gaining independence non-violently is possible, and then apply a simplified scenario analysis after Shoemaker [1995].

### 1.1. Phosphorus Problem on a Global Scale

In times where scarcity occurs in multiple contexts – such as scarcity of funds, jobs, raw materials, human capital etc. – the scarcity of a chemical element whose existence is essential looks quite odd at first glance. Phosphorus shows us that even a substance which is contained by every plant and every creature can become scarce in its usage and represent a non-renewable resource.

### Food Security

The constant growing population and the thereby even worsened situation concerning global food security, require an increase in agricultural output. This cannot be reached without mineral fertilizers which can only be produced with the mining of phosphate rock. Since efforts to increase the accessibility of fertilizers to poor farmers in developing countries to sooth hunger crises still don't bring the desired success today, accessibility and affordability of sufficient nutrition for less wealthy people will become even more problematic in the future [Cordell 2010; 59-62]. The issue of phosphorus scarcity prospectively adds a price increase for mineral fertilizer throughout supply shortages and as a consequence rising prices for food in general. This amongst others will also cause limited access to meat and dairy products in emerging markets like China and India, where the demand for such products has exploded due to growing incomes.

### Supply

Unlike other necessary nutrients for food production (i.e. nitrogen), phosphorus is not freely and sufficiently available in the geosphere [Déry 2007]. Phosphorus mainly occurs in a bounded form as phosphate. When plants grow, they bind the phosphorus from the soil in its substance and through harvesting the phosphorus is taken away from the land within the crops, leaving nothing left for further plants to grow. In earlier times manure was used for bringing back the phosphorus into the soil. The use of mined phosphate rock is relatively new and closely related to the green revolution. It slightly began to be used around 1850 and had its "take off" in around 1950. Since then fertilizer production and also an improved output is absolutely dependent on phosphorus rock mining [Cordell 2010; 86].

In the 19th century European soils were widely phosphorus-deficient because the only way to return phosphorus to the fields was manure distribution. In England farmers found that bone meal (from near cutlery production) enhanced plant growth and so bones became a widespread fertilizer, even though this didn't work on all soil types [Johnston 2001; 9-10].

Today's common agricultural activities need mineral fertilizer to maximize the output as all farmers aim to maximize their profits. Without mineral fertilizers no competitive production would be possible in world markets and certainly no food security, in the sense of all people having access to sufficient nutrition, would be possible. Pearce [2011] points out that three billion people wouldn't be living today if the green revolution with its technologies for nitrogen binding and other fertilizing hadn't taken place. This implicates that if we're running low in artificial fertilizer, the global food production will decrease on a scale that causes dramatic hunger crises and reduces world population strictly [Pearce 2011]. Since phosphorus in its most concentrated and useable form – phosphate rock – is mined on a large scale for fertilizer production, phosphate rock reserves in all parts of the world are more and more depleted. As an aggravation the big scale phosphate deposits in the world are unevenly distri-
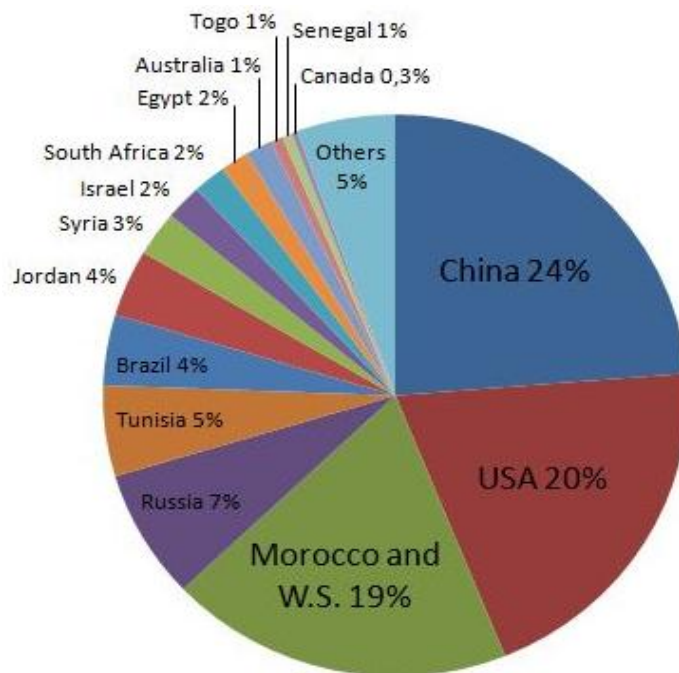


*Figure 1*: world phosphate rock production 2007 by country (total 147 million tons). *Source*: [Jasinski 2008]

buted and are controlled by only a few countries (see Figure 1). Worldwide about 170 million tons of phosphate rock were mined in 2010 [Pearce 2011], 70 to 80 percent of this total global production came from the US, China and Russia. Remarkably the six IMPHOS (Institut Mondial du Phosphate – World Phosphate Institute) Member companies - CPG (Tunisia), OCP (Morocco), JPMC (Jordan), ICS (Senegal), FERPHOS (Algeria) and IFG (Togo) – produce approximately 30 percent of global phosphate rock production, but contributed in the year 2004 around 50 percent of total global phosphate rock exports [Cisse and Mrabet 2004; 23].

The biggest producers are the USA and China, but these countries focus mainly on their own national markets to secure food production [Pearce 2011]. Furthermore China "imposed a 135 percent tariff" in 2008 to (successfully) prohibit export of phosphate rock [McCutheon 2011]. However, while Morocco accounts only for 15 percent of total global production, it contributes around 50 percent of global exports [Pearce 2011]. Europe as an extreme example is very dependent on phosphate rock imports and thereby is very sensitive to price fluctuations due to scarcity effects.

Various scientists tried to simulate and estimate future phosphorus deposit development and came to different results ranging from 16 billion to 60 billion tons of remaining phosphate rock reserves [Syers 2011; 37]. The Fertilizer Development Center (IFDC) estimates total reserves at about 60 billion tons with around 51 billion only situated in Morocco, second China with 3,7 billion tons and third the US with 1,8 billion [Van Kauwenbergh 2010]. Recently scientists revised their appraisals upward based on this report of the IFDC [Syers 2011; 38].

But no matter how many tons actually are left in the world, everything points to the fact that a disproportionately big part of all reserves is located in the desert of Western Sahara respectively under the control of Morocco [Van Kauwenbergh 2010]. And additionally it is apparent that in the future the US will pass the leading production position to Morocco for lack of reserves and advanced depletion of its resources.

If it continues at this rate, the world will concentrate on Morocco when it comes to fertilizer supply, agricultural production and food security.

## 1.2. MOROCCO AND WESTERN SAHARA

### Colonialization

In the late 19th century, there was a European rush to capture territorial land within Africa. With most of the Americas already settled and established, countries were looking for the next wave of territorial expansion. The French, Spanish, and English were among other countries competing against each other; Spain claimed Western Sahara in 1884. Western Sahara was originally considered a Spanish military outpost, especially during the Spanish Civil War when Saharawi' were recruited for fighting.

During the 1950s and 1960s, the French territories in Africa (Algeria, Morocco, and Mauritania) surrounding Spanish territories fought and won their independence from France; this decolonization movement gained momentum across Africa. To reassert its authority in the territory, Spain decided to increase its presence and power within Western Sahara. Spain began to develop administrative, industrial, commercial, and educational structures based on the structures of Spain. Spain also increased the budget in order to build infrastructure and encourage investments- specifically in mineral exploration of oil and iron [Botha 2010; 83]. By the early 1960s, Spain had multiplied its budget for Western Sahara development with the focus to build the infrastructure for the planned phosphate industry.

Despite the development in Western Sahara, many Saharawi were dissatisfied with the unfair hierarchy and colonial experience - they wanted independence. With increased pressure from the Saharawi and the international community and waning Spanish popularity, in 1974 Spain reluctantly abdicated Western Sahara. Before leaving, however, Spain met with the leaders of Morocco and Mauritania and agreed on a deal the two countries would split the territory between them once Spain decolonized.

Almost immediately after Spain left Western Sahara, Morocco denied Western Sahara as an independent state and declared it as a province of Morocco. Morocco hoped that its claim would be legally upheld by the International Court of Justice (ICJ), but their claim was rejected after Morocco failed to prove territorial rights of Western Sahara. Due to its increased interest in Western Saharan natural resources and need for expansion, Morocco decided to invade and annex Western Sahara in 1975, despite in violation of UN Resolutions and the ICJs' ruling. Since then, Morocco has occupied Western Sahara.

### Resources

During the Spanish colonization, Western Sahara was thought to be a wasteland until a large phosphate reserve in Bu Craa was found in the 1940s. Much of the development and investments from Spain thereafter were to develop an infrastructure for phosphate production. Because of this explosion of development, the world's largest conveyor belt (100 kilometers) transports phosphates from Bu Craa to the harbor where it's processed and exported. As Botha [2010] observed, "Anyone visiting the harbor… would have see up to five bulk vessels lining up, one after the other, waiting to be loaded [249]".

Since the Spanish concession, Morocco has taken over the Western Saharan phosphate industry. Through exploitation of Western Saharan phosphate mines, Morocco has become first in the world in phosphate exports, and the US Geological Survey estimates that in 2010 Morocco produced twenty-six million tons, second only behind China with sixty-five million tons [Jasinski 2010; 188-199]. According to the World Phosphorus Institute, the Moroccan/Western Saharan reserves account for 46-63% of the world reserve total [Cisse and Mrabet 2004; 24], almost twice as much as the second biggest reserve (China).

Of the million-tons produced by Morocco, over half originates from Western Sahara; the income Morocco earned from Bu Craa in 2008 alone was around $1.7 billion [Botha 2010; 250]. The production volume is expected to intensify because of higher market prices and demand. The constantly rising price of phosphate will substantially increase the profit for OCP (Morocco's state phosphorus company); since 2007 the price increased over 800% [Botha 2010; 250].

It is hard to argue that the Moroccan takeover of the Western Saharan phosphate industry has been beneficial to the Saharawi. Not only have the Moroccans reaped insurmountable profits from exploitation of Western Saharan resources, but they have also marginalized Saharawi society. Before the Moroccan occupation, most of the 1600 workers in the mines were Saharawi, today only 200 of 2000 workers are Saharawi- the rest are Moroccan [Botha 2010; 249].

### Legal Situation

Western Sahara is officially recognized by the United Nations (and other international organizations) as a 'non-self-governing territory', which characterizes a nation whose people do not yet have full level of self-government [Simanowitz 2009; 300]. The Saharawi Arab Democratic Republic (SADR) is a state that claims sovereignty over Western Sahara; the SADR control 20-25% of their stated territory while Morocco controls the other 75-80%. The SADR is a full-fledged state that exercises autonomy over the Saharawi-liberated regions. The SADR is officially recognized as a sovereign representative of Western Sahara by

fifty-eight countries and is a member of the African Union.[1]

According to international law, Morocco is an occupy power of Western Sahara and has no sovereignty over it. The Saharawi people have been waiting for an UN-backed referendum (*UN Resolution 1514*) that will allow them to vote for either (1) independence, or (2) as a continued territory of Morocco [MINURSO Mission]. Despite efforts by the international community, the referendum has been continually blocked by the Moroccans and their allies. With only a few exceptions, almost all African colonies have achieved independence through internationally sanctioned means. All UN members are required to uphold this right and any other procedure or blocking of this would be in violation of international law- Morocco has twice violated its agreement and obligations to hold a referendum.[2]

In addition to violating *UN Resolution 1514*, Morocco's invasion of Western Sahara has simultaneously violated and breeched a host of international laws and agreements. These include:

- *UN Resolutions 2625* which states that the use of military force to occupy Western Sahara is in violation of UN. The resolution states that any use of "military threat or force to violate the existing…boundaries…the act of force will never be recognized as legal [Botha 2010; 154]".

- *Article 49 of the Geneva Convention* states that the occupying power (Morocco) may not settle its nationals or population into the territory it occupies (Western Sahara).

- *General Assembly Resolution 1514 (XV)* affirms that the Moroccan exploration and exploitation of Western Sahara resources are in violation of international law.

SADR and the POLISARIO (the Saharawi rebel liberation movement) [United Nations – MINURSO n.y.] have been working and advocating for independence from Morocco through internationally legal means and ways of the United Nations system. Today, not one country or international organization has officially recognized Moroccan sovereignty rights on the Saharawi.

The UN has passed over a hundred solutions regarding Morocco and Western Sahara, but all have been blocked or not passed because of Morocco's allies, particularly France, Britain, and the United States. This has established a standard where UN resolutions about Western Sahara are passed but not enforced [Simanowitz 2009; 300].

The Moroccan exploitation of Western Sahara natural resources are in breach of international law not only for Morocco, but also for the countries that buy and import Western Sahara phosphorus. This fruitful and advantageous trading gives Morocco leverage over other nations and has been instrumental in helping to ensure that no action has been taken by the UN Security Council against Morocco. Through support of these countries Morocco has succeeded in avoiding internationally established legal obligations towards Western Sahara for the last thirty-years. A major help from their partners was the French and American veto threats that resulted in the UN Security Council's failure to establish the occupation issue under *Chapter VII of the UN Charter*, which would have allowed for sanctions against Morocco.

There is strong support for Moroccan presence in Western Sahara, in particular because of the mineral exports. This control gives Morocco power to deal trading for political support because these countries all have special interests in Morocco and its resources (primarily phosphorus)[3]. The US also sees Morocco as a key ally in the war against terrorism; in June 2004 the US granted Morocco 'major non-NATO ally' status - only 15 other nations hold this title [Botha 2010; 119]. Shortly afterwards, a free trade agreement was signed between the two countries, although Congress insisted that none of the Moroccan imports would be from Western Sahara.

An analysis done by Botha [2010] of *Article 73 of the UN Charter* examined the Moroccan exploitation of Western Sahara resources. The legal opinion of the General Assembly on the issue was "if further exploration and exploitation activities were to proceed in disregard of the interests and wishes of the people of Western Sahara, they would be in violation of the principles of international law application to mineral resource activities in Non-Self-Governing Territories" [237]. This means that Morocco would need to consult with authorized representatives of Western Sahara and be granted permission in order to legally continue with its mining activities. Morocco did not, and has not.

## 2 Methods

This chapter will show the three methods we have chosen to use in this paper. The first method is a causal loop diagram (CLD) to illustrate the status quo of the interrelationships between the situation in Western Sahara and its phosphorus resources on a global scale. The second method is a comparison of Western Sahara to South Sudan to show **if** a non-violent way to independence is possible for Western Sahara. Finally, as a third method a simplified scenario analysis using the methods of Shoemaker [1995], will show the impacts that a change in political status (Western Saharan freedom) can have on the world phosphorus issue.

The three methods are linked as follows: The first method will describe the status quo of Western Sahara in a very simplified way to enable the look on all most important variables at once (see point *"A"*, *Figure 2*).

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[1] The number of countries recognizing SADR fluctuates, with some suspending recognition and others acknowledging it.
[2] Settlement Plan and Baker Plan

[3] The US, an outspoken supporter of Morocco, lists phosphorus as a rare element that is crucial to national security.
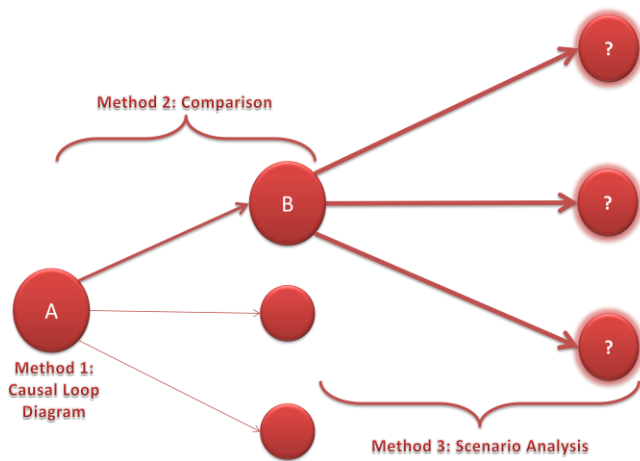
***Figure 2:*** **How the three methods are connected.**
*Source: created for this research*

This will be the starting point for our comparison method that will show that independence of Western Sahara is realistic and one of several possible future situations from now. Other possible developments (see the spots below point *"B", Figure 2*) like a violent path to independence, the maintenance of the current Moroccan rule or a full-fledged civil war were not considered here, because this would have gone too far for this research and the authors decided to concentrate on this special case. The peaceful way to independence is a basic assumption of this paper for simplification issues. The third method will then analyze, which consequences can arise out of this new status quo (the changed political situation) in relation to the global phosphorus market by building three different possible scenarios.

## 2.1. Causal Loop Diagram

The first method is a causal loop diagram that enables a simplified look on complex situations and correlations visualizes the present situation of Western Sahara in interdependency with selected subject areas of the world. This allows us to highlight key factors that mainly influence the phosphorus cycle concerning Western Sahara and also serves as a preparation for the scenario analysis that follows as a third method.

## 2.2. Cross Country Comparison Method

The second method that we use is a cross-country comparison method to the country of South Sudan. Our reasoning for first analyzing a comparison is to investigate whether Western Saharan independence from Morocco is realistically possible through nonviolent means; proving that it's possible is crucial to the continuation and validation of our research. If independence isn't possible then one can assume that everything will stay "as-is" with no changes in the political and social situation in Western Sahara, and no changes to the phosphorus cycle and market.

There are multiple countries that would be suitable for comparison with Western Sahara, all varying in degrees in similarities and differences. The countries we considered as candidates for our comparison method was:

1)  *East Timor-* Situated in the Indian Ocean just north of Australia, Timor was invaded by the Indonesians days after Portugal withdrew its colonial empire, despite Timor declaring independence. The region suffered through decades of war and suffering before increased international pressure persuaded Indonesia to allow for a referendum in 1999. The UN set up a peacekeeping force, Unmiset, and is still there today.
2)  *Sudan/South Sudan-* South Sudan became the newest country in 2011 after a successful referendum voted for independence from Sudan. A peace agreement in 2005 ended decades of war and fighting; the UN played a large role in the peace-keeping and referendum process.
3)  *Eritrea-* Located along the Red Sea, Eritrea achieved independence from Ethiopia in 1993 after a 32-year armed conflict [BBC News Africa]. The UN initially set up operations to help patrol the negotiated borders between the two countries, but eventually withdrew from being unable to fulfill its mandate.

In comparative research, one chooses two cases (here Western Sahara and South Sudan) which have similar characteristics so that the chosen variables are able to operate in similar contexts. In order to conduct and analyze a cross-country comparison method, we examined the literature work of Hantrais [1995] and James [1987] who look at the different approaches and their benefits and issues associated with a comparison method. Hantrais [1995] suggests that there has been a growing interest in international comparisons, particularly for governmental bodies when it can be used a tool to "assess the transferability of policies between member states". A comparison helps to "understand how each system operates and why it yields the outcomes it does" [James 1987; 209] referencing historical development, economic structure, political organization, social statistics, and other relevant variables.

South Sudan was chosen because comparison is easier within one continent, because the conflicts are more likely to share at least *some* common factors (i.e. political framework, historical background) [James 1987; 210]. Sudan is also the most recent country to gain its independence. Although there are intense differences between the two, South Sudan seems to be the best example of proving possibility of Western Saharan independence.

This method structure will compare South Sudan and Western Sahara: (1) main issues, (2) the main actors and sources of pressure, (3) the role of the UN and third-party countries, and (4) the competition for resources. First, we look at the main issues from the conflict at hand. Second, we examine who the main actors are within the area and where the pressure of change is originating from (i.e. citizens, UN, NGOs, etc). Third, we investigate the role of the United Nations and third-party countries in the context of the conflict and the peace process. Finally, we investigate the role that resources play in the conflict and the size of role they play.
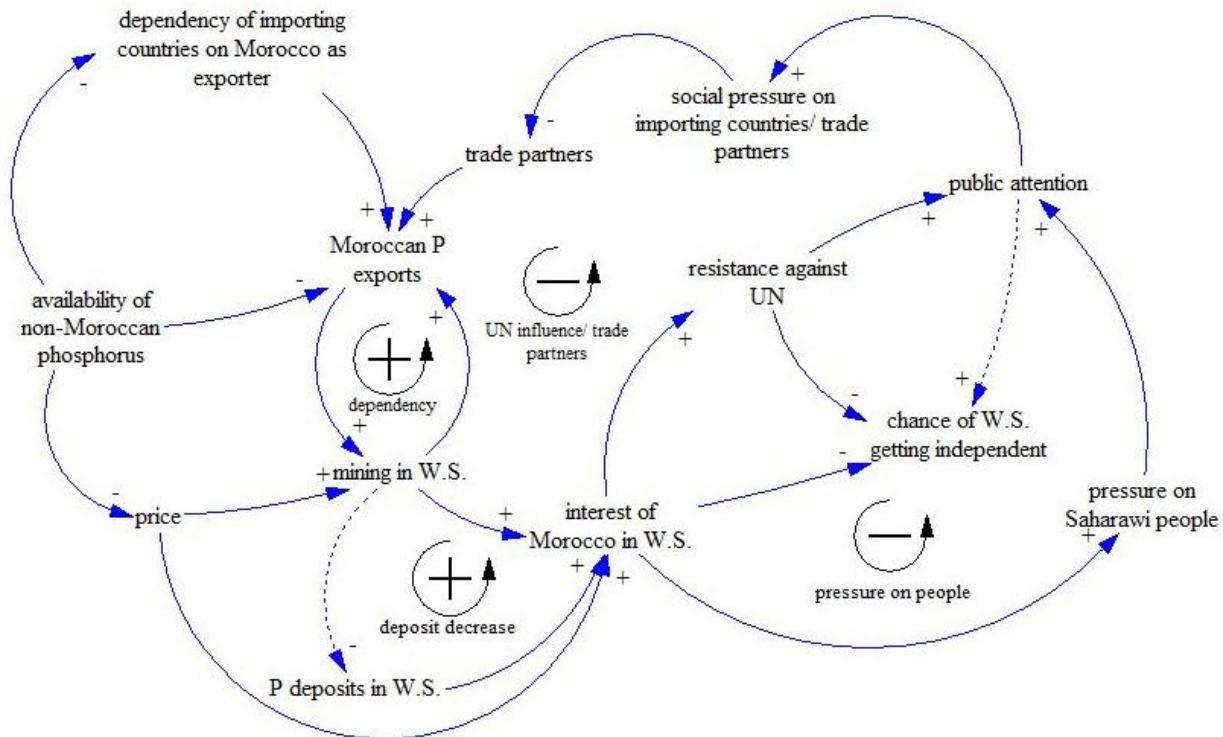
***Figure 3*: Causal loop diagram describing the status quo of Western Sahara in correlation with the world.**
***Source*: created for this research**

## 2.3. Scenario Analysis

The third method applied in this paper is a simplified qualitative scenario analysis after Shoemaker [1995]. In his paper he concentrates on scenario planning for companies but also gives the example of a scenario analysis for South Africa in the 1980's. This shows that the application to a political and social problem on a national scale is also possible. Furthermore he describes the scenario building in a "step-by-step process [Shoemaker 1995; 25]" that allows a well-founded substructure for our scenarios. We use the scenario analysis because it allows simplifying very complex systems of change and estimating future developments. In addition this qualitative approach allows the incorporation of elements "that were not or cannot be formally modeled [Shoemaker 1995; 27]".

The scenario generation will be executed in the first seven steps of Shoemaker's Scenario Planning Process, which carries the scenario analysis further to decision making and actual planning measures [Shoemaker 1995; 28-29]:

1. Definition of Scope and Time Frame
2. Identification of Major Stakeholders
3. Identification of Basic Trends
4. Identification of Key Uncertainties
5. Construction of Initial Scenario Themes
6. Consistency and Plausibility Check
7. Development of Learning Scenarios

We stopped after the 7th step which generated Learning Scenarios that are "tools for research and study" [Shoemaker 1995; 29]. We also shortened the 7th step to further simplify the method and adapt it towards the goal of this work. This is only possible because the outcome of step 5 mainly equates to the outcome of step 7. Any further deepening and concretization would have gone too far for the aim of this paper.

## 3 Results

### 3.1. Results of the Causal Loop Diagram

The causal loop diagram in *Figure 3* shows the main factors of influence that describe the Status Quo in Western Sahara. In the center of our model stands the "Moroccan phosphorus export" quantity (including the phosphorus mined in Western Sahara). This variable influences the "mining in W.S." because the more Morocco exports, the more phosphorus has to be mined (proportionally) in Western Sahara. This leads also to the conclusion that if more phosphorus is mined in Western Sahara[4], Morocco can export more because we assume that an increased supply is not raising the national demand.

As an (only) influencing factor the "availability of non-Moroccan phosphorus" (P) on the world market, which is also determined by the total phosphorus reserves in the world, impacts (negatively) the depen-

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[4] The mined phosphorus in W.S. can increase for example because of discovery of phosphate rich rock layers, etc.

dency of importing countries on Morocco as an exporter, (negatively) the Moroccan P exports and (also negatively) the Phosphorus world market price[5]. The "dependency of importing countries on Morocco's exports" furthermore influences the Moroccan exports because the more dependent the rest of the world becomes to Moroccan P the more P will be exported. A rising world market "price" in addition increases mining in Western Sahara by reason that a higher phosphorus price makes mining more profitable. Furthermore a higher price also increases the interest of Morocco in Western Sahara because of the greater chance of making profit. This means that decreasing availability of non-Moroccan phosphorus that accompanies with the lowering total phosphorus reserves in the world[6] increase the significance of Moroccan and Western Saharan exports gradually and tightens the current situation.

If we now concentrate on the big circle on the right side, two possibilities of influence arise: one including the pressure on the Saharawi people and one including the (Moroccan) resistance against the UN. The first one's starting with the Moroccan exports again: The more Morocco exports, the more it has to mine in Western Sahara. The more P is mined in Western Sahara, the more depleted get the "deposits of phosphorus on Western Saharan" territory (less P left). Here it is very important to note that, due to the enormous reserves located in Western Sahara, depletion of deposits will take a long time and will only be substantial in the long run. So the effect of reduced phosphorus deposits shrinking "Morocco's interest" in the occupation of Western Sahara can be nearly disregarded but for the sake of completeness it is to point out.

Because of the big phosphorus deposits in Western Sahara, Morocco has big interest in the region. The higher the interest is, the more "pressure" will be put "on the Western Saharan people" through the occupation and this will further lead to more global "public attention". Moreover we assume that a higher public attention raises the "social pressure on (from Morocco) importing countries" and trade partners, so that they sanction phosphorus from Western Sahara and so reduce trade partners for Morocco[7]. This furthermore causes fewer exports for Morocco and a decreasing interest in Western Sahara.

The "chance of Western Sahara to get independent" is one of the things we want to find out. It is primarily

influenced by the "interest of Morocco in Western Sahara" which lowers the chance if it is high. Secondarily the chance of Western Sahara to get independent is influenced by the grade of resistance Morocco offers "against the UN", which is again influenced (positively) by this mentioned interest (cumulative effect!). We assume here that if Morocco resists more and more against the UN this will also raise "public attention", which has the ability to increase the chance for Western Sahara's independency. Furthermore this public attention to the fact that Western Sahara is occupied illegally (according to international law) puts social pressure on the importing countries and so reduces trade partners and thereby Moroccan exports the same way as described before.

## 3.2. Results of the Cross-Country Comparison – Sudan

| Republic of South Sudan | Western Sahara |
|---|---|
|  |  |
| *Population:* 7.5-9.7M *Religion:* Islam, Christian *Language:* Arabic, English *Area:* 619,700 km² *Main exports:* Oil | *Population:* 260,000 *Religion:* Islam *Language:* Arabic *Area:* 252,299 km² *Main exports:* phosphorous, fish, oil |
| **Overview of key data** | *Source*: [BBC "Country Profile"] |

### Background of the Comprehensive Peace Agreement (CPA)

The governments of North and South Sudan signed the CPA on January 2005. This agreement had groundwork and regulations on power-sharing, security logistics, distribution of resources, and terms of independence for South Sudan. In addition, it was decided that after a six-and-a-half-year timetable in which South Sudan would have a referendum (vote) on the decision of autonomy or continued integration with the North. During those six-and-a-half-years an interim governing system was set-up and there was assistance from the international community for monitoring and operationalizing. In January 2011, the referendum was successful in establishing an overwhelming support (98%) for South's independence.

### Main Issues

Since Sudan's break from colonial Britain in 1956, tension between North and South Sudan thwarted unification due to differences between religion and state, wealth, political power, control over resources, and

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[5] The more available phosphorus from other destination than Morocco is, the
- less dependent importing countries become on Morocco's exports.
- less Morocco can export because of competition.
- lower is the price of phosphorus on the world market.

[6] This is also due to the extremely high reserves located in Morocco/Western Sahara that increase the importance of Morocco as an exporter alongside with further depletion of phosphorus deposits all over the world.

[7] This should at least be true for the amounts of phosphorus that origins from Western Sahara territory.

unequal socio-economic development. There was a large disparity between the social classes: North is more urbanized and has a better infrastructure, while the South was profoundly underdevelopment and had poor quality of essential services (i.e. education and clean water. The South resented what they believed to be North domination and lack of attention, and felt the North failed to consider South's needs and were being kept out of their own government.

**Western Sahara:** Tensions between Western Sahara and Morocco have thwarted negotiations and peace deals due to differences in political power, control over resources, and unequal socio-economic growth. To help understanding, these two countries can be thought of as North and South Sudan- Morocco is the North and Western Sahara is the South. Morocco (just as Sudan did) took over political control of its southern neighbor and subsequently over the Western Sahara resources. While Western Sahara is not as underdeveloped as the South, it does lack important infrastructure and services (i.e. educational facilities, adequate health care) that gives Morocco an advantage. This difference in development has also created the socio-economic gap between Moroccans and Western Saharawi. Also, Morocco has also instituted Moroccan law over most of Western Sahara land, giving Western Sahara little-to-no say over the government, voting and elections, or the ability to govern itself.

We feel it is important to note that a principal difference between the two regions is that the Saharawi have fought for their rights and independence primarily through legal and diplomatic means, and *not* through violence or terrorism. This is substantially different from Sudan where violence and wars run rampant and have resulted in nearly 2 million deaths.

**Main Actors**

The United Nations played a significant role in the peace and freedom initiative of Sudan. The UN played the role of mediator and consultant with Sudan regional governments and organizations that were involved in the peace negotiations. The recognition of South's self-determination from the international community was an important role in the successful implementation; some UN members were compelled to recognize and back the independence movement. Alongside recognition, third-party countries also contributed military and police personnel to help ensure the agreed-upon ceasefire and to help along the peace-building process[8] (see *Table 1*). Although the United States thought peace efforts by the Sudanese government were benign, the European Union decided that engaging in constructive dialogue would help bring about peaceful results. In addition, countries have committed to provide financial assistance to contribute toward desperately-needed development; for example, the UK has pledged £90million to help aid in healthcare, education, and security development [Lazaridis 2011].

| Table 2 | Country Contributors to MINURSO |
|---|---|
| **Military Personnel** | Argentina, Austria, Bangladesh, Brazil, China, Croatia, Djibouti, Egypt, El Salvador, France, Ghana, Guinea, Honduras, Hungary, Ireland, Italy, Jordan, Malaysia, Mongolia, Nepal, Nigeria, Pakistan, Paraguay, Poland, Republic of Korea, Russian Federation, Sri Lanka, Uruguay and Yemen |
| **Police Personnel** | Egypt, El Salvador, Jordan |
| | *Source:* [United Nation- MINURSO] |

**Western Sahara:** As mentioned earlier, Morocco has good trade relations with developed and powerful countries such as France and the US- this has helped protect Moroccan interests and continued occupation in Western Sahara. Like the South, the recognition of Western Saharan's right to self-determination from the international community is an important step in the successful implementation of the independence movement. Just as in the Sudan conflict, some countries that have recognized Western Saharan independence are contributing military and police personnel to the UN Mission (see *Table 2*) to help ensure the agree-upon ceasefire and to help the peace-building process.

The current third-party support for Morocco can change, though. A few decades ago there was relatively little civil society activism regarding Sudan. However, concerted efforts by peace and human rights activists, religious groups, and NGOs across the globe eventually forced these countries to reverse their stance and join the campaign for freedom [Botha 2010; 124-125]. A similar campaign may have value for the

| Table 1 | Country Contributors to UNMIS |
|---|---|
| **Military Personnel** | Australia, Bangladesh, Belgium, Benin, Bolivia, Brazil, Burkina Faso, Cambodia, Canada, China, Croatia, Denmark, Ecuador, Egypt, El Salvador, Fiji, Finland, Germany, Ghana, Greece, Guatemala, Guinea, India, Indonesia, Japan, Jordan, Kenya, Kyrgyzstan, Malaysia, Mali, Moldova, Mongolia, Namibia, Nepal, Netherlands, New Zealand, Nigeria, Norway, Pakistan, Paraguay, Peru, Philippines, Poland, Republic of Korea, Romania, Russian Federation, Rwanda, Sierra Leone, Sri Lanka, Sweden, Switzerland, Tanzania, Thailand, Turkey, Uganda, Ukraine, United Kingdom, Yemen and Zambia |
| **Police Personnel** | Argentina, Australia, Bangladesh, Bosnia and Herzegovina, Brazil, Canada, China, Egypt, El Salvador, Ethiopia, Fiji, Gambia, Germany, Ghana, India, Indonesia, Jamaica, Jordan, Kenya, Kyrgyzstan, Malaysia, Mali, Namibia, Nepal, Netherlands, Nigeria, Norway, Pakistan, Philippines, Russian Federation, Rwanda, Samoa, Sri Lanka, Sweden, Turkey, Uganda, Ukraine, United States, Yemen, Zambia and Zimbabwe. |
| | *Source:* [United Nation- MINURSO] |

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[8] We recognize that the UN, NGOs, and other relief organizations contributed immense humanitarian assistance to the Sudanese people. While we do not wish to ignore or minimize this important aspect, we will not focus on the humanitarian aid aspect.

Morocco-Western Sahara conflict. It can be said that the more international backing for Western Sahara- and the less for Morocco- increases the ability of the UN and the Security Council to enforce resolutions.

**United Nations Role**

Under *Resolution 1590*, the UN established the United Nations Mission in the Sudan (UNMIS) after determining that the situation in Sudan was a reliable and constant threat to international peace and security [UNMIS Mission]. UNMIS was to deal with the main issues of support for the peace process, governance, security, and humanitarian aid.

During the CPA negotiation talks, the UN provided technical and logistical assistance to Sudan through the UNMIS operations and personnel. After the CPA was finalized and signed, the UN created the UNMIS Mandate that commissioned tasks to support the successful implementation of the CPA. Some of the core efforts were [UNMIS Mission]:

   i.    To monitor and verify implementation and compliance of ceasefire agreement
   ii.   To assist North and South in restructuring police and law enforcement services which were in following of democratic policies, and to aid in law enforcement training
   iii.  To assist in protecting humans rights of Sudanese and combating vindication through promoting long-term peace
   iv.   To assist in development and consolidation of a national legal framework, and then promoting the rule of law
   v.    To provide parties of the CPA guidance, overseeing, and technical and logistical assistance for the preparations and the conducting of free and fair elections and referenda

**Western Sahara**   Under *Resolution 690*, the UN established the United Nations Mission for the Referendum in Western Sahara (MINURSO) after determining that the situation in Morocco and Western Sahara needed assistance in seeking a peaceful solution to the conflict. Similar to Sudan, MINURSO was to deal with the main issues of support for the peace process, governance, and security. Some of the core tasks of the MINURSO mandate were [United Nations – MINURSO n.y.]:

   i.    To monitor and verify implementation and compliance of ceasefire agreement (since 1991)
   ii.   Verify the reduction of Moroccan troops in Western Sahara
   iii.  Identify and register qualified Western Saharan voters for the referendum
   iv.   Organize and ensure a free and fair referendum and proclaim/verify the results

One can see that the mandates for UNMIS and MINURSO are similar in structure and core tasks; both are commissioned to monitor and verify compliance to the established ceasefire agreements, and to oversee the successful operations and results of the voting

referendum for South and Western Sahara independence.

**Competition for Resources**

The current historical happenings in Sudan can be correlated with the discovery and exploration of oil and other natural resources[9]. Upon discovering oil in the south, the Sudanese government re-commissioned the region to the north and created the pseudo-state named Unity; this allowed for the Sudanese government to claim the oil was a North resource. *Article 9* of the 1998 Constitution of the Sudan states: "All natural resources… are public property and shall be governed by law. The State shall prepare plans and …financial and human resources necessary to exploit these resources [Goldsmith *et al.,* 2002; 203]". This allowed the central government to claim ownership of oil-producing regions in the south.

This exploitation of petroleum resources in the south has been a large contributor to the humanitarian and livelihood needs of southern peoples[10]. It has been argued that northern revenues from oil production finance the conflict and fighting[11], while also suggesting that foreign oil developers (see *Table 3*) have been more concerned with petroleum production and profits than with peace [Goldsmith *et al*., 2002; 188].

| *Table 3*   Oil Companies in Sudan (as of 2001) |
| --- |
| Mobil (USA) |
| Royal Dutch Shell (Netherlands) |
| OMV-AG (Austria) |
| Elf-Aquitaine (France) |
| Lundin Oil/IPC (Sweden) |
| TotalFina (France/Belgium) |
| Agip (Italy) |
| Talisman Energy (Canada) |
| China National Petroleum Corporation (China) |
| *Source:* [Goldsmith *et al*., 2002; 226-227] |

The issues surrounding the ownership of south's resources required an arrangement where the revenues promoted the welfare and profess of all Sudanese. Goldsmith et al [2002] mentions that oil production can reduce the likelihood of (future) conflict through "economic development that is evenly distributed between different social and economic groups" [221]. The federal resource infrastructure pre-CPA favored the North rather than the South which sought for

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[9] Other natural resources found in Sudan include gold, silver, iron, tin, cooper, granite, uranium, iron ore, lead manganese, and marble.

[10] It is estimated that Sudan contains about 1% of the world's oil reserves, or about 1-3 billion barrels of oil. This has an estimated value of several billion US dollars [Goldsmith et al 2002; 223].

[11] Revenues from Sudan oil have been suspected to finance the government's military action and purchasing of weaponry to be used against the citizens of oil-rich South Sudan. Although in a 2001 report to the UN Commission on Human Rights, the Sudanese government rejected those accusation and claimed the oil revenues were being invested for development in the South [Goldsmith et al. 2002; 228].

greater control and management over their own resources [Goldsmith *et al.,* 2002; 201].

Under the CPA South Sudan received 50% of Sudan's oil revenues during the six-and-a-half-year interim period; after the successful referendum in 2011 each country received ownership of oil fields in their own respected regions- no cross-border ownerships. Today, South Sudan's economy is highly oil-dependent and rich in natural resources. However, while the South has rights over the oil, the refineries and the oil pipeline to the Red Sea are in Sudan, therefore, they are sometimes forced to work together.

**Western Sahara**   The issues surrounding Western Saharan resources were discussed earlier. Western Sahara is similar to South Sudan in resource issues in the aspect that another country was exploiting and profiting from "stolen" resources. North Sudan took the oil resources from the South, and Morocco is taking phosphorus resources from Western Sahara. Like North Sudan, Moroccan phosphorus traders are argued to be more concerned with phosphorus imports and exports and the global market, than with peace and ethical issues in Western Sahara. Those who import Morocco's phosphorus exports directly and indirectly support the continuation of the illegal occupation of Western Sahara and undermine the efforts of the UN peace-process [Eyckmans and Gurr 2010].

## 3.3. Results of the Scenario Analysis

Before starting the iterative process of scenario generation, the initial position of the analysis has to be pointed out briefly. As discussed at the beginning of *Section 2*, the initial point of the scenario analysis is not the current situation in Western Sahara, but the status **if** Western Sahara has become independent. Now we have to answer the question: **when** this will happen?

We discussed that South Sudan was freed in 2011 after 55 years under the rule of North Sudan. In the case of Western Sahara, which was left by its Spanish colonial rulers in 1975, the time until independence can be approximated to this, and it is modified by the fact that there was no war, we can presume that freedom for Western Sahara will be reached around 2020 – the initial point of our scenario analysis.

### Definition of Time Frame and Scope

To define the time frame it is important to rate in which period most of the affects of the political change on the world phosphorus market development will occur. If we consider that peak phosphorus is expected around 2035 [Cordell 2010; 36], this gives us the first hint towards our time frame. In the case that there are bigger reserves than currently expected, as Van Kauwenbergh [2010] estimates, this peak can be delayed, which allows our timeframe to span from 2020 to 2040 – twenty years. Only in this long period eventually a new phosphorus industry can settle down in Western Sahara. Big changes in infrastructure take a long time.

The scope deals with the question "What knowledge would be of great value… that far down the road?

[Shoemaker 1995; 28]" by analyzing the past for relevant variables. In this case the relevant issues have been described in the previous chapters in great detail: phosphorus scarcity, former occupation by Morocco, final independence of Western Sahara, the system of national phosphate mining in Western Sahara[12], world phosphate rock price fluctuations, and world demand for Western Saharan phosphates.

### Identification of the Major Stakeholders

The most important stakeholders are summarized in *Table 4*. As we can see, the most important will be the first government of independent Western Sahara: here we presume that the current political representatives for Western Saharan, the SADR, will assume office and consequently bear the challenge of rearranging the national phosphate mining industry (among other things). It is here that the international phosphate mining companies become important because they can bargain with the former Moroccan mining companies for mining rights.

The Moroccan government plays an important role through exerting influence across the new border. This and other changes concerning a new government, treatment of the local people (and their behavior), and building advanced infrastructure will in all probability be monitored by the UN and the African Union.

Finally, the countries that import much from Morocco and Western Sahara (mainly EU and US), will try to re-negotiate their trade positions, which will have a major impact on the local situation of Western Sahara and Morocco.

| *Table 4* | **Major Stakeholders** |
|---|---|
| Sahrawi Arab Democratic Republic (SADR) | |
| International Phosphate Mining Companies | |
| Moroccan Mining Companies | |
| United Nations | |
| Moroccan monarch/ government | |
| Importers (esp. US and EU) | |
| African Union | |
| Saharawi people | |
| | *Source: created for this research* |

### Identification of Basic Trends

Due to the fact that the period from 2020 to 2040 is quite far from present time, these basic trends that shouldn't be uncertain at all are hard to figure out from our present situation. However, what is probable to a very high degree is that the UN will guard and monitor a new Western Saharan leadership/government after gaining independence as they did in the case of Sudan. Due to the fragile situation after the liberation, the UN will necessarily monitor to secure human rights, prevent new suppression of the people by the new leaders and for peacekeeping, especially if the UN has pushed the progress towards an independent status. Like other

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[12] Dominance of Morocco before independence: All phosphate rock reserves belonged to the Office Cherifien des Phosphates, a Moroccan state agency, and through the "almost unlimited executive powers of the Moroccan monarch" indirectly to one man: King Mohammed VI of Morocco [Pearce 2011].

examples showed recently in the 'Arab Spring' people in North Africa tend to demonstrate for democratic systems, which also need a securer of fair elections that can also be supported by a UN monitoring.

What's additionally assured is that phosphorus as an irreplaceable fertilizer additive will experience a price increase because of the depletion of the deposits and an increase in environmental regulations which complicate and raise the cost of the mining[13]. Even if there will be improved and widespread recycling techniques for phosphorus and new off-shore deposits were found, prices will rise because these techniques are much more expensive than common mining.

As a third basic trend the striving for phosphate earnings of the new government/leaders of Western Sahara is more or less unambiguous. The new rulers will try to merchandise the phosphate deposits and for that purpose they will have to set up contracts to mining companies (either Moroccan or international[14]).

The population growth will, in all likelihood, continue to be positive, but at the same time the growth rate will decrease due to improved wealth in emerging economies (i.e. China and India) and further decrease of birth rates in the developed world[15] [United Nations 2005]. This will cause a constantly growing demand for fertilizer to feed the growing population and thereby an increased demand for phosphorus.

## Identification of Key Uncertainties

As mentioned before, the time frame accentuates uncertainties because it lies that far in the future. Nevertheless we will try to highlight the most important uncertainties concerning the future development of an independent Western Sahara and the world phosphorus market.

One of the most interesting questions is how Western Sahara will cope with the problem of sustaining its very lucrative phosphate industry without the present Moroccan companies. It's not likely that there will be insufficient candidates for exploitation rights of the huge Western Saharan deposits, but the choice will be very exciting for observers because of the danger of cooperating with another partner who exploits the region for its resources.

Another uncertainty will be the development of the technologies for phosphorus recycling and off-shore mining worldwide. If these techniques become widely-used and cost-efficient, they can turn into a competition for Western Saharan phosphate exports and cause a decrease in Western Sahara's relevance in the world phosphorus market. Off-shore mining as well as recycling phosphorus out of sewage sludge or other waste

is nowadays still too expensive to become an actual competitor to onshore mining. If this becomes competitive it could decrease the importance of phosphorus mining at the current level and this would induce a financial loss for Western Sahara that relies on its phosphorus as the most important economic business unit.

How the new government will treat its population and how stable a new regime will be in the future, is also not for sure. A change in leadership doesn't necessarily have to cause an improvement in human rights, participation and democracy even though a UN monitoring will/would work towards such goals. It's also not clear if the new government can maintain its position if intricacies occur.

Another important issue is the future trade association of which countries will trade phosphates with Western Sahara. It is likely that the US will keep purchasing its phosphorus from Morocco, while other countries which supported Western Sahara on its way to independence will not cooperate/ trade with Morocco and focus on Western Sahara as a phosphate supplier.[16]

*Table 5* sums up the key uncertainties in six questions which can be answered by 'yes' or 'no' to prepare for the correlation matrix (*Table 6*).

| Table 5 | *Key Uncertainties* |
|---|---|
| $U_1$ | Will Western Sahara create its own industry with local companies for sustaining the mining industry? |
| $U_2$ | Will Western Sahara cooperate with a US or European company for sustaining the mining industry? |
| $U_3$ | Will Western Sahara cooperate with a Moroccan company for sustaining the mining industry? |
| $U_4$ | Are recycling technologies and off-shore mining becoming cost-efficient and profitable? |
| $U_5$ | Is the new government treating the population in a way that won't cause another revolution in the near future? |
| $U_6$ | Will the US switch from Morocco to Western Sahara as a main supplier in phosphorus? |
| | *Source: created for this research* |

To find out about the interrelationships among the uncertainties the correlation matrix in *Table 6* gives an overview. If a 'yes' in $U_1$ leads to a higher probability of a 'yes' in $U_2$, these are linked with a '✚'; if the probability gets lower with a '━' and if it has no influence they are linked with a '*0*'. If the correlation is unknown the linkage results in a '**?**'.

The correlation matrix shows that while $U_1$ and $U_2$ have various influences (mainly positive) on the other uncertainties, $U_3$ is primarily negative and $U_4$ has hardly any or only unknown interrelationships with others. $U_5$ and $U_6$ are positively related again.

Concerning the recycling and offshore mining this suggests that the technologies do not influence which country supports Western Saharan phosphate industry.

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[13] This is due to the fact that in the process of phosphate rock mining a lot of dangerous and toxic wastes accrue and have to be treated afterwards. Today regulations are not yet that strict but in the future further investment in the issue of sustainability will also focus on these toxic and often also radioactive wastes.

[14] Cooperation with Morocco isn't impossible but quite uncertain because of the long lasting fight for freedom against the Moroccan occupants.

[15] US, EU, Australia, Japan

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[16] Countries of the African Union for example are more likely to trade with Western Sahara than with Morocco.

| Table 6 | | | Correlation Matrix | | | |
|---|---|---|---|---|---|---|
| | $U_1$ | $U_2$ | $U_3$ | $U_4$ | $U_5$ | $U_6$ |
| $U_1$ | x | + | − | 0 | + | + |
| $U_2$ | x | x | − | 0 | + | + |
| $U_3$ | x | x | x | 0 | − | − |
| $U_4$ | x | x | x | x | ? | ? |
| $U_5$ | x | x | x | x | x | + |

*Source: created for this research*

Also the technologies do not alter the probability of a new stable situation concerning the government in a direct way.

Cooperation with the US and the EU would increase stability due to more steady trade cooperation and knowledge transfer. It would also make a switch on the US from Morocco to Western Sahara as a main supplier more probable.

If a cooperation with Morocco is realized this would reduce the probability of a very stable new government and the chance to take over US as a costumer.

## Construction of Initial Scenario Themes

In the course of the analysis three main scenarios accentuated and are presented as followed:

### Scenario 1 – Cooperation with US and EU

After becoming independent, Western Sahara cooperates with a US phosphate mining company to insure further growth in the phosphate industry as the major national business unit and to guarantee the needed knowledge base for the Western Sahara industry. This cooperation is a "win-win" situation for both sides because the US phosphate reserves are estimated to be depleted by 2040 and the full-fledged phosphate mining companies are running out of resource. On the other side Western Sahara got rid of the Moroccan occupiers and now lacks an executive company with certain knowledge to maintain the phosphate mining and – through that – resume proceedings in the phosphate mining industry.

The EU – in addition to the US – serves as a main investor. This lowers trading between the US and the EU with Morocco due to the new competition on the world market and the preference for products that are produced by a 'home company' (Americans will prefer phosphates from an American company over phosphates from a Moroccan company). Through cooperation with the US and EU, Western Sahara becomes a competitive player in the world phosphate market and develops a strong phosphorus industry.

Furthermore, phosphate mining becomes more environmentally acceptable because of higher production standards and regulations which are also due to the cooperation with the EU.

Concerning technologies, recycling of phosphorus and off-shore mining stay non-significant and aren't a competition for mined phosphate rock (yet) due to high price differences. Phosphate rock remains the main source for phosphorus for fertilizer production, but the regional concentration of remaining reserves increases. Even though phosphorus deposits become smaller around the world, Western Sahara and Morocco can compete because of their large reserves. Additionally the estimations on how much phosphate rock reserves are left in the world were constantly adjusted upwards and thereby peak phosphorus was delayed,

### Scenario 2 – New Technologies

Recycling and off-shore mining become cost efficient and profitable because of the price increase of mined phosphate rock, which became scarce over the years and had to face bad reputation due to radioactive waste production and other pollution occurring in the process of mining.

Peak phosphorus was met in 2035 and thereby phosphate rock prices exploded and pushed on the developments in the recycling branch and in new discoveries of mineable deposits (off-shore) in different countries. This created a very hard competition for Western Saharan reserves, which still are immense, but have to struggle higher environmental regulations. Nevertheless Western Sahara builds its new independent economy for lack of competitive alternatives on the resource, but not as successfully as in *Scenario 1* and with additional losses through the higher environmental regulations and expensive compliance.

The additional alternatives for investments in the phosphorus market weakened the interest of the US and the EU in Western Sahara. Western Sahara tries to build a phosphate mining industry for their own but it is difficult because of problematic circumstances.

The low success in the mining industry- and the thereby lower income- also impairs the situation of the Saharawi people. Even though they are no longer suppressed by Morocco the new government (SADR) now faces poverty and unemployment due to the weak industry. This will also destabilize the new government because of a high grade of dissatisfaction within the society.

### Scenario 3 – Cooperation with Morocco

Even though Western Sahara became independent, it further cooperates with Morocco as a knowledge supplier and partner in the phosphate mining industry. A new contract secures fairness concerning the apportionment of profits between Western Sahara and the Moroccan companies. This secures the maintenance of the phosphate industry and through that makes economic growth in Western Sahara possible.

Although recycling and off-shore mining became more relevant over the last years, these are still no real competition for the huge phosphate rock reserves in the region.

The Saharawi people are not totally satisfied with this new situation because there are still Moroccans 'involved' in their resource industry. This can lead to demonstrations or even a revolution against the new government (SADR) and cause major instability of the new political situation.

The US has become a big purchaser not only of Moroccan but also of Western Saharan phosphates and consequently created a strong phosphate industry in Western Sahara.

### Consistency and Plausibility Check

The assumptions concerning the basic trends, time frame, scope and key uncertainties turned out to be realistic and plausible. Consequently the three developed scenarios have proven in discussion to stand a plausibility and consistency check.

### Development of Learning Scenarios

The developed Initial Scenarios from above can be assumed as the learning scenarios that can be used for research and study.

## 4. Conclusion

This paper concentrates on the political side of the phosphorus crisis and shows that a political change in one problematic country can change the global phosphorus market in a dramatic way.

The Causal Loop Diagram revealed the interrelationships between the Western Saharan phosphorus industry and the world phosphorus market, as well as the UN activities in the region. This showed that Western Sahara's industry and reserves are an important section on a global scale and also is intimately connected to other parts of the worldwide phosphorus trade system.

The Comparison Method illustrates on the example of South Sudan that a peaceful process to independence for Western Sahara is possible. Even though the two regions have their differences, the similarities that have been worked out allow a comparison and gives insight in a possible future development.

This finding allows us to proceed with a Scenario Analysis which creates three different future scenarios about what happens if Western Sahara actually achieves independence. The first scenario assumes cooperation with the US and the EU by excluding Morocco from the future Western Saharan phosphorus industry. This strengthens Western Sahara's role in the world market and makes it a big player on global scale. The second scenario acts on the assumption that recycling and off-shore mining techniques become relevant on the world market and – in addition to stricter environmental regulations – undermine the development of a new Western Saharan phosphate mining industry. The third scenario supposes cooperation with the Morocco, which supports Western Saharan phosphate industry but brings reluctance and counter movements from the side of the population and thereby raises instability of the new political situation.

As we can see with the help of these scenarios the liberation of Western Sahara can have various impacts on the world phosphorus market, which can certainly never be assessed without incorporating other essential facts into the analysis. We must take into account the interaction of multiple areas such as technology, politics, financial aspects, economic developments, environmental regulations, etc if we want to analyze the future.

The only thing that can be ascertained is that a major change in the political situation of a region as important to the phosphorus market as Western Sahara would have great impacts not only on the rate of depletion of phosphate rock and the technologies that are invented and applied, but also on the network of trade cooperation on a global scale and on the financial status of competitors and trade partners.

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# The Austrian Phosphorus Demand
# A Material Flow Analysis

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## Abstract

As a key element in our body (ATP, DNA), Phosphorus (P) is essential for human life in general. Nevertheless this non-renewable resource is only available in a few countries worldwide making imports inevitable for Austria nowadays.

Thus, to generate a general understanding of the imports driven P demands, the main national P stocks and flows for 2009 in Austria were defined and quantified. Moreover, a detailed study on the material flow analysis (MFA) was conducted. For this issue a MFA model based on the free software STAN2 was developed. With this model the main P losses that occur in the waste sector could be identified. It so was possible to predict quantitively about 60% of the national P imports to be potentially replaceable by a more effective fertilizer use as well as P recoveries from waste. Especially a consequent bio waste separation would yield recycled amounts, which are in the range of the total Austrian P-fertilizers imports. According to a study for Switzerland, the biggest P recovery potential lies in the sewage sludge. However, as a result of this work undertaken here with the focus on Austria, waste separation has a higher potential than the separation and usage of sewage sludge in Austria.

## 1 Introduction

Phosphorus (P) is an essential element for all forms of life on earth. Animals, plants and human beings need a certain amount of P for physical health every day. As an example, in human bodies P is a fundamental component within DNA, RNA and ATP, making a continuous uptake inevitable. This uptake of about 1.2g/(person day) [Cordell *et al.*, 2009] is mainly achieved by food consumption originating from agricultural products. These products on the other hand take up their P from the soil. As a consequence of European farmlands exhaustion in the last century [Konrad, 1997], fertilization became inevitable when one still wants to have a rich harvest. This anthropogenic addition of P to the soil is mainly due to phosphate in mineral fertilizers, which globally account for about 80% of the phosphate usage [Steen, 1998].

In consideration of the phosphorus need, food industry, production, consumption and composting play a major role in the global P-cycle. Amongst others the introduced areas will crucially be affected by a global depletion of P reserves, which possibly will occur in 80-400 years (see [Brunner, 2010]).

Consequently, a greater knowledge of the demand and consumption of this non-substitutable element is necessary for developing recommendations for a more sustainable use in future times.

Therefore, various international [Neset *et al.*, 2008; Vuuren *et al.*, 2010] and national (see e.g. [Binder *et al.*, 2009; Smit *et al.*, 2010; Schroeder *et al.*, 2010]) analysis have been performed defining P-demands, consumption and losses. Already multiple publications deal with the national P-flow in Austria, focusing either on contributions to certain systems, or displaying whole national cycles [Lindenthal, 2000; Seyhan, 2006; Kreuzeder, 2011; Kroiss *et al.*, 2011c; Thaler *et al.*, 2011] of the last decade.

However, there is no material flow analysis (MFA), which includes data of the very last years and would display the state of the art. Furthermore, a comparison between Austria and a culturally and economically similar country has not been done yet, although recently H. Rechberger has indicated this research gap regarding the necessity of such a comparative study [Rechberger, 2011].

In order to fill this gap, this paper presents an updated MFA for the years 2009 and 2010. The necessary in- and out-flows were defined for the main national processes. Thus allows an identification of stocks and losses in the Austrian P-cycle.

Additionally, a comparison to our neighbouring country Switzerland will be presented in this paper, which displays similarities and differences in the P-household. Comparative studies like this one reveal advantages and disadvantages between existing systems. Consequently, they allow retrieving recommendations for a more sustainable P-treatment in the future.

As an introduction to this work, the method of MFA

is described at first. In the following section the developed model is presented. Results of the MFA as well as the comparison between the P-flows in Switzerland and Austria are discussed, finally leading to recommendations for a more sustainable P-household in Austria.

## 2 Method

The investigation of phosphorus flows in Austria was established with the method "material flow analysis" (MFA). The software we used is called STAN2 and can be downloaded at the Technical University Vienna. This software provides a graphical interface with all important components like stocks, flows, system boundaries etc. for developing a MFA model.

### 2.1 Material Flow Analysis (MFA)

MFA is a systematic approach to flows and stocks within a certain space and time frame. Within the defined system boundary a MFA model represents sources, pathways and sinks of a specific material. The investigated material can be an element, a substance or goods. The MFA follows the law of conservation of matter. This means that elements or energy cannot be destroyed. Instead, its elements can flow and accumulate in the system or can be exported or imported via the system boundaries [Brunner and Rechberger, 2004]. The method of MFA is a flexible and fast way to get rough estimates for the flow of a certain substance in a system. These advantages were the reason for having chosen it as the method in our examination. In this paper, the substance under investigation is phosphorus. This way of modelling allows us to create subsystems and combine them with others or connect them to other main systems. Processes and systems work according to the principle of mass balance [Brunner and Rechberger, 2004].

To apply this method, the following steps are necessary [Kreuzeder, 2011]:

- Selection of relevant substances, appropriate system boundaries, processes and goods.

- Assessment of mass flows of goods and substances concentrations.

- Calculation of substance flows and stocks of the system.

- Schematic presentation and interpretation of the results.

### 2.2 Uncertainty Consideration

When developing the model, these steps stated above were followed closely albeit iteration was necessary. The data source was put in relation to the relative uncertainties of the model parameters and they were distinctively heterogenic. The uncertainties of flows could be empirically assessed because the data type and the relative uncertainties were correlating with each other ordinarily. Following the assumptions made by Binder et al. (2009), the model parameters can be distinguished in five different data types [Binder et al., 2009]:

- Statistics, which follow the rule of standardization and well-defined surveys from official sources or organizations, will be defined as good data sources with an uncertainty < 5%.

- Own surveys naturally have a strong volatility of quality because of the origin of the basis data. In our thesis the uncertainty will be estimated in a range from 5-25%.

- Calculations with rough standard values indicate great inaccuracy of parameters. The uncertainty will be estimated in a range from 20-40 %.

- Generalised and rough projections have inaccuracies which will be estimated in a range from 30-50%.

- As long as only a few references exist, one can only get rough estimates and the inaccuracies are estimated > 40%.

These assumptions were adopted from Binder because of the comparability of the data sources and also for establishing a better comparison of the Austrian and Swiss model.

### 2.3 Data evaluation and integration

In this work the data collection and their revision follow the data's actual availability. Furthermore, the calculations of the used data correspond to the five different types of data as described above. The minimum and maximum concentrations of phosphorus were multiplied by flows of goods. The mean value as well as the corresponding error was also calculated. Various sources of data and existing models were taken into consideration to complete the model and to minimize the variability of certain flows. It was also of importance that the major flows are in the focus of our work in order to point to the phosphorus flows and stocks in Austria. Processes and data calculations of the model from Seyhan [Seyhan, 2006] for Austria and Binder [Binder et al., 2009] for Switzerland were adopted to minimize inaccuracies and for establishing a basis for a comparison between the Austrian and Swiss phosphorus flows. Our main data sources were online statistics like Statistic Austria or official institutes like Agrar-Markt Austria or the Federal Ministry of Agriculture, Forestry, Environment and Water Management.

## 3 Results

In this section the model specifically developed for Austria will be introduced. All quantified P-flows are visualized as material flows and all graphics in this work refer to the phosphorus-cycle in Austria. The thickness of the arrows is proportional to the quantity of the flow. This type of diagram is called Sankey-Diagram which allows a quick and easy identification of important flows of the system. Furthermore, the rectangles represent processes and can include sub processes. In addition, the stocks - if defined - are visualized in the rectangles. All quantities describing stocks and flows are stated in the appendix in more detail.

The main system consists of the following processes:
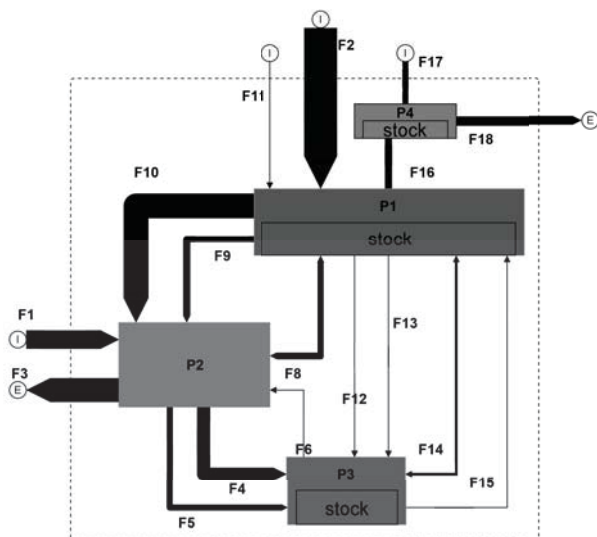
Figure 1: Model results of the main system.

- Water/Environment
- Agriculture
- Industry/Household
- Waste Treatment

The results of these processes will be presented one after the other. Before doing so, the main system will be discussed. It is shown in Fig. 1. Furthermore, all important stocks, stock growths and flows, which will be discussed, are presented in Table 1 and 2 with their error.

## 3.1 Main system

In Austria the phosphorus balance is mainly dominated by *agriculture (P1)*, *food industry (P2)* and *waste treatment (P3)*. Austria imports approximately 24.8 kt P/a and exports about 20 kt P/a. Whereas the imports are dominated by fertilizers for agriculture, the exports are dominated by food exports from the industry. The biggest flows in the system are food/fodder (F10) from agriculture to *industry/household* and waste water (F4) from *industry/household* to waste management. The biggest growth of the phosphorus stock occurs in the process *waste treatment* with about 9.8 kt P/a.

## 3.2 Water/Environment (P4)

The subsystem *water/environment* has a phosphorus stock of around 7.9 kt P, which represents P in lakes and groundwater. This stock accumulates around 2.9 kt P/a. The imports from inside the system into the process *water/environment* is due to erosion (F16) from the process *agriculture* and is around 4.3 kt P/a. The erosion includes the aggregated phosphorus emission of all entry paths in Austria like ground water, erosion through agriculturally used areas, point sources and so on [Schilling *et al.*, 2009]. Imports from
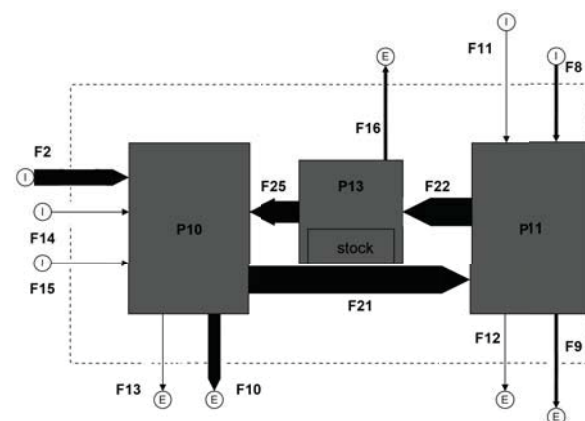


Figure 2: Model results of the process agriculture.

outside the system boundaries (F17) are mainly expected to originate from German rivers, which statistically contain a greater P concentration than Austrian ones (see Apendix).

## 3.3 Agriculture (P1)

The central sub processes in the process *agriculture* are *agriculture plants (P10)*, *agriculture animals (P11)* and *soil (P13)*. These sub processes have an enormous exchange of phosphorus between each other and build a cycle which is shown in Fig. 2. The main out-flows are food/fodder (F10), food (animals) (F9) and erosion (F16). The biggest flow in this cycle is the fertilizer (agric. direct) (F22) which represents the farmyard manure and goes from *agriculture animals* to *soil*, with a quantity of around 38.6 kt P/a. The import of animals (F11) and fertilizer (sewage sludge) (F15) are negligible in this process. Only the flow fertilizer (organic agriculture) (F14) with a quantity of around 2.1 kt P/a is worth mentioning as an import in relation to fertilizer imports (F2) with around 9 kt P/a and fodder imports (F8) with around 4.2 kt P/a.

Farmyard manure feeds the soil and raises the stock in the soil. Through erosion and harvest the raise of phosphorus stock in the soil will be minimized. This means that the raise of P-stock in the soil will be reduced and this reduction leads to a growth in the stock of the process *water/environment*. As a consequence, the stock of P in the *soil* will shrink by 7.5 kt P/a and the stock of *water/environment* will grow by 2.9 kt P/a.

## 3.4 Industry/Household (P2)

This process represents all private households and the food industry in Austria. *Industry/household* consists of the sub processes *industry (P5)*, *household (P6)* and *waste (P12)*. The main imports into the process are food/fodder (F10) from *agriculture* with around 13.4 kt P/a, imported food (F1) with around 11.2 kt P/a and food (animals) (F9) from the sub process *agriculture animals* with around 4.3 kt P/a. The import of fertilizer for private household is negligible. Exported

Table 1: Main P-flows and stock/stock growths of the MFA model.

| Flow/Stock | Flow of P $\pm$ Error [kt/a] |
| --- | --- |
| F1 import food (Food, fodder) | 11.2 $\pm$ 4.1 |
| F2 import fertilizer | 9.1 $\pm$ 0.9 |
| F3 export food (food, fodder) | 14.6 $\pm$ 4.1 |
| F4 waste water | 8.2 $\pm$ 0.4 |
| F5 waste (manmade, bio) | 3.9 $\pm$ 0.2 |
| F8 fodder | 4.2 $\pm$ 0.4 |
| F9 food (animals) | 4.3 $\pm$ 0.8 |
| F10 food/fodder | 13.4 $\pm$ 1.3 |
| F11 import (animals) | 0.5 $\pm$ 0.1 |
| F12 animal waste | 0.2 $\pm$ 0.1 |
| F13 crop waste | 0.1 $\pm$ 0.0 |
| F14 fertilizer organic | 2.1 $\pm$ 0.1 |
| F15 fertilizer (sewage sludge) | 0.1 $\pm$ 0.0 |
| F16 erosion | 4.3 $\pm$ 0.2 |
| F17 import water | 4.0 $\pm$ 0.2 |
| F20 food (general) | 10.6 $\pm$ 0.7 |
| F21 fodder (agric. direct) | 26.2 $\pm$ 2.6 |
| F22 fertilizer (agric. direct) | 38.6 $\pm$ 7.7 |
| F23 waste/waste water industry | 1.0 $\pm$ 0.9 |
| F24 waste/waste water house | 11.1 $\pm$ 0.7 |

Table 2: Main model results as basis for discussion. If not stated otherwise, the P values are based on the year 2009.

| Imports/Exports | kt P/a |
| --- | --- |
| Total Imports | 24.8 $\pm$ 5.8 |
| Total Exports | 19.6 $\pm$ 3.3 |
| Total Imports 2010 | 28.7 $\pm$ 4.8 |
| **Variation in stocks** | **kt P/a** |
| Agriculture | -7.5 $\pm$ 1.7 |
| Water/Environment | 2.9 $\pm$ 0.4 |
| Waste Treatment | 9.8 $\pm$ 0.2 |
| Stocks (total) | 5.3 $\pm$ 2.8 |

food (food, fodder) (F3) is the biggest export flow with around 14.5 kt P/a which reflects the Austrian trade of groceries. Furthermore, fodder (F8) flows from *industry* to *agriculture animals* with a quantity of 4.2 kt P/a. One of the three flows between the sub processes is food (general) (F20), which represents the phosphorus quantity of food for food consumption. This is the biggest flow with a quantity of around 10.6 kt P/a. Waste/wastewater industry (F23) and waste/wastewater household (F24) represent the flow of waste to the sub process *waste* with a quantity of around 12.1 kt P/a.

There are no stocks available in the process *industry/household* and in its sub processes because the waste of industry and household will be deposit in the process *waste treatment*. Private stocks in the sub process *household* are expected to be small in comparison to the in- and out-flows. Due to a balanced trade of goods, industrial stocks are negligible, too. Thus, both are neglected in our representation.

### 3.5 Waste Treatment (P3)

The process *waste treatment* contains the two sub processes *water treatment (P7)* and *storage (P9)*. The main imports are given by waste water (F4) originating from the process *industry/household* (approx. 8.2 kt P/a). Comparable small inflows are obtained from animal (F12) and crop waste (F13) from *agriculture*. An amount of about 3.9 kt P/a originates from biological waste (F5) from private households and food industry. The main out-flow of this process is fertilizer (organic agric.) (F14) originated from the sub process *storage*. About 1.6 t P/a sewage sludge (F15) products are used as fertilizer in agriculture.

All in all, there is a growth of approx. 9.8 kt P/a in the stock.

## 4 Discussion

In this section the results of the material flow analysis are discussed. At first, the main effects on the Austrian system are taken into consideration. Accordingly a comparison to the P-flows in Switzerland is presented.

### 4.1 The Austrian Phosphorus flows

Table 2 summarizes the main results of the Austrian P-cycle. We differentiate between the total imports in 2009 and 2010 because of their significant variation in P-fertilizer imports, which will be discussed later. In general, the data of Table 2 refers to the year 2009, as this data was used for the calculation. Detailed values of certain flows are stated in the appendix.

Following the model results, on the one hand, Austria exhibits a general need for the import of P from other countries, mainly in form of mineral fertilizer as well as food and fodder for humans and animals respectively. On the other hand, there are various elements in the Austrian cycle, where P is deposited, i.e. P highly accumulates in waste repositories, which in turn leads to a stock growth.

A decrease of P within an existing stock is only detected in the process *agriculture*, which possibly originates from crop growth and erosion. At this point of explanation it should be mentioned that a net decreasing P-stock in agricultural soil is questionable and possibly results only from high uncertainties in the model. Furthermore, according to Schroeder et. al. [Schroeder *et al.*, 2010] Austria has a soil surplus of 2 kg P/(ha*a). Nevertheless, this value does not influence the following considerations at any point.

However, from the MFA three main possibilities for the reduction of the national P demands can be deduced.

Firstly, one way to reduce the P demand from foreign trade is an extraction of P directly from waste water. Therefore various techniques are developed and tested (see e.g. [Pinnekamp *et al.*, 2007; Pinnekamp, 2007; Sengupta and Pandit, 2011]), leading to a possible use of P as fertilizer.

With respect to the possibility of recycling P from waste water, it has to be noted that already a high amount of waste water is generally treated in sewage plants [UMWELTBUNDESAMT, 2011], leading to a total recovery potential of about 7 kt P/a [Kroiss *et al.*, 2011a]. Nevertheless, based on this value from the MFA only about 3% are determined to be used actually for agricultural fertilization. By assuming a general (technical) recovery efficiency of 70-80% [Cornel, 2002], an agricultural usable amount of 4.9 - 5.6 kt P/a will be achieved.

Obviously, a general application of P originating from waste water is limited because of a legally demanded

fertilizer quality, especially in consideration of its heavy metal content [AMA, 2010].

Secondly, a more efficient use of agricultural fertilizer seems obvious. Despite the fact, that the MFA does not include detailed information about the fertilization behaviour and small private stocks of Austrian farmers, a possibility to reduce the mineral fertilizer imports was identified. To be more precise, the developed model considers P-imports in form of fertilizer as they have been published for 2009, which are about 30% smaller than in 2010 and in previous years (e.g. 2008) [FAO, 2011; LEBENSMINISTERIUM, 2011a]. In contrast, flows that should be affected at first glance (e.g. crop production, food consumption), do not show significant changes between 2009 and 2010 [AWI, 2011; L20, 2010; AMA, 2011; LEBENSMINISTERIUM, 2011b]. Moreover, the whole Austrian system still provides a net accumulation of P in stocks. In other words, a lack of P did not occur in the year 2009 at all. Consequently, a more efficient use of P fertilizer on agricultural farmlands is assumed to have avoided general deficiencies.

Thirdly, a separation of biological waste shows a high potential for a reduction of P-imports. Kroiss et al. [Kroiss et al., 2011b] consider only about 30% of the total amount of private organic waste to be stored separately. From the developed MFA we can predict about 13 kt P/a, leaving private households and industry in form of pure biological waste in the case of a consistent separation. Based on the simulation, an actual use of approximately 61% will finally lead to about 8 kt P/a for fertilization.

In sum, Figure 3 shows the three just mentioned saving/recovery potentials of P in Austria (grey) as well as their sum (grey, first bar) in comparison to the total imports in 2010 (black). It is obvious that the national P imports using these three activities cannot totally be substituted, especially when taking the Austrian food/fodder import demand into account. Nevertheless, at least an import reduction with respect to P-fertilizers seems feasible. Especially the three mentioned aspects tackle the substitution/saving of mineral fertilizer. Following the presented considerations, they sum up to about 17 kt P/a, which even tops the P-fertilizer imports of 2010 (about 13 kt P/a).

Despite the convenient reduction potential of the Austrian P-imports through the aspects discussed earlier, the real implementation of those depends on various technical, political and social aspects. Those have been taken into account only up to a small extend but should be kept in mind.

## 4.2 Comparison to Switzerland

The comparison of the P-flows per capita of Austria and Switzerland depicts the differences and similarities between the two countries. The main flows and
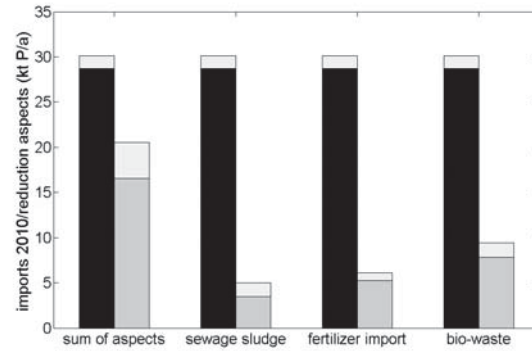


Figure 3: The P recovery and saving potential by the considered aspects (grey) and their sum (grey) in comparison to total P-imports of 2010 (black)

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Table 3: Main P-flows and stock growths of Austria in 2009 and Switzerland in 2006.

| Comparison of P | Austria kg/(cap*a) | Switzerland kg/(cap*a) |
|---|---|---|
| imports totally | 3.0 | 2.3 |
| exports totally | 2.4 | 0.5 |
| fertilizer import | 0.8 | 1.0 |
| agriculture cycle (cumulative value) | 3.9 | 4.0 |
| stock growth totally | 0.6 | 1.7 |
| stock growth soil | -1.0 | 0.5 |
| water export | 0.6 | 0.3 |

stock growths are listed in Table 3 and will be discussed now.

The imported fertilizer in Austria is around one fourth higher than the imported fertilizer of Switzerland per capita. In regard to the fewer fertilizer import in Austria for the year 2009, there was nearly an equal value for imports in the years before and in 2010. Furthermore, a big difference between the overall exports of the two countries is also worth mentioning. Austria exports nearly five times more phosphorus and imports of around 0.7 kg P/(cap*a) more than Switzerland. Due to the strong exports of food in Austria, the imports and exports of phosphorus differ from those in Switzerland.

The biggest flows in the overall system are in the sub process *agriculture* which builds up a cycle. This cycle has related flows of phosphorus in both countries and thereby nearly the same amount of phosphorus per capita and year.

The overall stock growths of phosphorus in both countries are not comparable per capita; Austria accumulates around 0.6 kg P/(cap*a) and Switzerland accumulates around 1.7 kg P/(cap*a). Furthermore, in Switzerland the stock of the soil is growing by 0.5 kg P/(cap*a) and in Austria the stock of the soil is shrinking by 1 kg P/(cap*a). The export of P in Switzerland via rivers and erosion is 50 % less per capita and year than in Switzerland.

According to Binder et. al. [Binder et al., 2009], the overall potential of phosphorus recycling is around 1.8 kg P/(cap*a) for Switzerland. Due to the reduction

through exports of animal waste and the amount of recycled phosphorus (which is partly already used) an overall potential of P around 1.3 kg P/(cap*a) is more suitable. In Austria the overall potential of phosphorus recycling is around 1.7 kg P/(cap*a). According to Binder et. al. [Binder *et al.*, 2009], the biggest unused P-potential for Switzerland lies in the preparation and usage of sewage with a quantity of around 0.8 kg P/(cap*a). In Austria the recycling potential of sewage is around 0.7 kg P/(cap*a). In comparison to Switzerland, Austria has a greater recycling potential in solid waste, for example, in solid bio waste. The reason for this is an easier application in practice. A policy which leads to a better separation of organic waste could be a first course of action in Austria.

In sum, the comparison shows that Austria and Switzerland have a similar agriculture cycle. Furthermore, the stock growth of the soil is completely different between the analysed countries. By recovering around 60 % of the overall recycling potential of phosphorus in Austria the imports of P fertilizer are not necessary anymore.

## 5  Conclusion

In this work a material flow analysis (MFA) for Phosphorus (P) in Austria for the years 2009 and 2010 was presented. Since the main Austrian P-flows are associated with agricultural production, the model focused on flows originating from this area.
Austria actually has a need of P-imports, which potentially will be reduced by avoiding losses in the national cycle.
These losses lead to a general growth of P-stocks, which mainly occurs in the waste sector and is only reduced by the removal of nutrients from the soil in agricultural production and due to erosion.
However, with the help of the presented model three main possibilities were identified which consequently could lead to a more sustainable P-treatment.
As a first point, the model allows a P-fertilizer import reduction of about 30% with respect to the latest values in 2010. Due to this reduction, affected flows such as crop production and food import (export) do not show significant changes. This finally leads to the assumption that a more effective use of P-fertilizer is possible. At least a certain "buffering capacity" of the soil originating from its huge stocks possibly facilitates the use of a smaller amount of P mineral fertilizer in 2009 in comparison to the years 2008 and 2010.
The second aspect covers the issue of the P-recovery from waste water, which would results in 4.9 - 5.6 tP/a by an assumed recycling efficiency of 70-80% [Cornel, 2002].
Finally, the third potential is identified when taking a look at the separation of biological waste in households and industry. A strict separation will in total lead to about 8 kt P/a, which could be used as organic fertilizer on agricultural fields.

In sum, all three activities together achieve about 60% of the total P-imports of 2010. Although a scenario of a total substitution seems not to be realistic when considering the national food (fodder) import demand. However, at least a reduction of P-fertilizer imports seems possible. A reduction is achieved only by separation of biological waste in the households and the following use of compost on agricultural fields. This recycling of P can lead to about 13 kt P/a, which is about the same amount that has been imported by P-fertilizers in 2010 and 2008.

The comparison of the MFA model of Austria and Switzerland shows the similarity in the agriculture cycle, but it also depicts the differences in accumulation of phosphorus in the soil. Furthermore, it points out that through waste separation a big amount of phosphorus could be recovered in Austria. In contrast to the study of Binder et. al.[Binder *et al.*, 2009], which leads to the biggest recovery amount of P from sewage sludge, the biggest recovery potential of phosphorus in Austria is in the waste separation. According to our work, a better separation of organic waste could be a first course of action.

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## Apendix
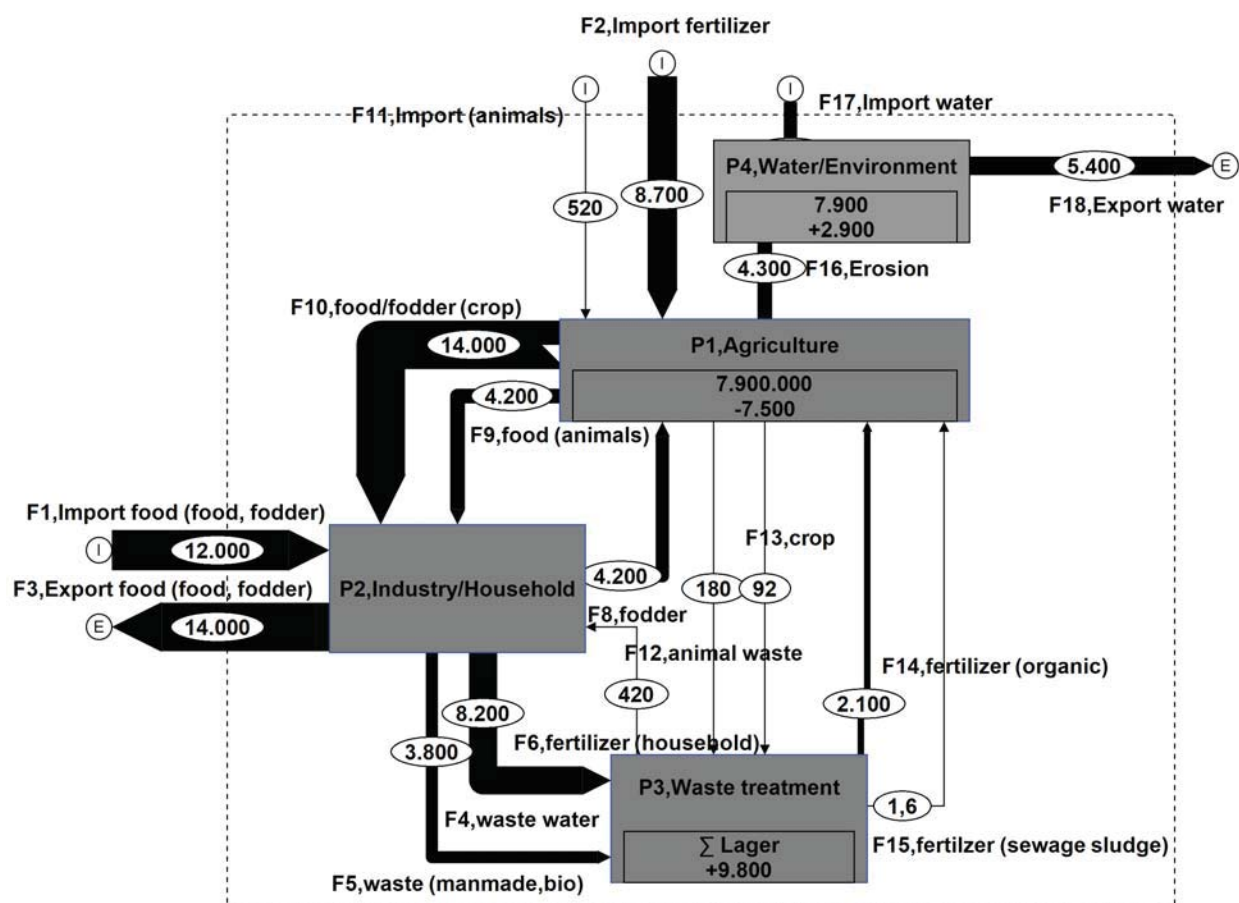


Figure 4: This Figure represents the main system. Variations to the presented values of Tab.4 possibly occur due to balancing of the software STAN2. Table 4 rather represents the collected literature data. In general literature as well as model value only differ within the presented uncertainty.
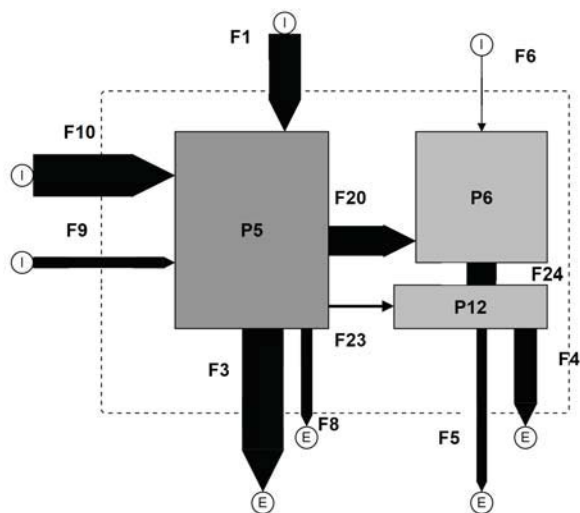
Figure 5: Model results of the sub processes *industry/household*.
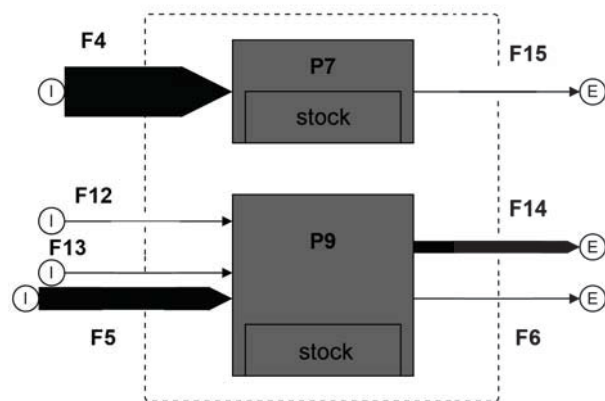


Figure 6: Model results of the sub processes *waste treatment*.

Table 4: Data basis of phosphorus flows.

| Flow | flow of good [1000 t/a] | | P concentration [g P/kg] | | flow of P [t/a] | comment |
|---|---|---|---|---|---|---|
| F1 import food (food, fodder) | 317.4 ± 15.9 | [STA, 2011a] | 0.2-7.7 | cited in [Seyhan, 2006] and in [Binder et al., 2009] | 11217 ± 4147 | calc. seperately |
| F2 import fertilizer | 20.8±2.1 | [FAO, 2011] | | | 9058 ± 906 | |
| F3 export food (food, fodder) | 4936.2 ± 246.8 | [STA, 2011a] | 0.2-7.7 | cited in [Seyhan, 2006] and in [Binder et al., 2009] | 14568 ± 4115 | calc. seperately |
| F4 waste water | | | | [Kroiss et al., 2011a] | 8235 ± 412 | |
| F5 waste (manmade, bio) | 770.1 ± 38.5 | [BMLFUW, 2011] | 5.00±0.25 | [Kroiss et al., 2011b] | 3851 ± 193 | |
| F6 fertilizer (household) | 93.5 ± 4.7 | [Kroiss et al., 2011b] | 4.5 | calc. by [Kroiss et al., 2011b] | 421 ± 21 | calc. by [Kroiss et al., 2011b] (5%assumed) |
| F8 fodder | 880 ± 85 | | 4.76 | [Binder et al., 2009] | 4189 ± 422 | calc. seperately |
| F9 food (animals) | 908.7 ± 190.8 | | 4.75 | [Binder et al., 2009] | 4316 ± 754 | calc. seperately |
| F10 food/fodder (crop) | | [STA, 2011b] | | cited in [Seyhan, 2006] | 13444 ± 1344 | calc. seperately |
| F11 import (animals) | 74.3 ± 14.1 | [STA, 2011b] | 7.06 | [Binder et al., 2009] | 524 ± 66 | |
| F12 animal waste | 26 ± 8.6 | [STA, 2011b] | 7 | [Binder et al., 2009] | 182 ± 53 | |
| F13 crop waste | 105 ± 52.5 | | 0.87 | [Binder et al., 2009] | 91 ± 38 | estimated |
| F14 fertilizer organic | 467.5±23.8 | [Kroiss et al., 2011b] | 4.5 | calc. by [Kroiss et al., 2011b] | 2104 ± 105 | calc. by [Kroiss et al., 2011b] |
| F15 fertilizer (sewage sludge) | | | | | 1.6 ± 0.5 | [Schroeder et al., 2010] |
| F16 erosion | | | | | 4300 ± 215 | [Schilling et al., 2009] |
| F17 import water | $(26800\pm1340)\cdot10^3$ | [WASSERWERK.AT, 2011] | $0.15 \cdot 10^{-3}$ | [EEA, 2011] | 4010 ± 201 | calc. seperately |
| F18 export water | $(77200\pm 3860)\cdot10^3$ | [WASSERWERK.AT, 2011] | $0.07 \cdot 10^{-3}$ | [EEA, 2011] | 5404 ± 270 | calc. seperately |
| F20 food (general) | $(4518\pm 226)\cdot10^3$ | [LEBENSMINISTERIUM, 2011c] | 0.2-7.7 | cited in [Seyhan, 2006] and in [Binder et al., 2009] | 10647 ± 725 | |
| F21 fodder (agric. direct) | | [STA, 2011b] | | cited in[Seyhan, 2006] | 26222 ± 2622 | calc. seperately |
| F22 fertilizer (agric. direct) | | [STA, 2011b] | | cited in [Seyhan, 2006] | 38646 ± 7729 | calc. seperately |
| F23 waste/waste water ind | | | | | 1018 ± 855 | calc. by balancing |
| F24 waste/ waste water hous | | | | | 11068 ± 725 | calc. by balancing |
| F25 plant growth | | [STA, 2011b] | | cited in [Seyhan, 2006] | 39666 ± 3967 | calc. seperately |

Table 5: Data basis of phosphorus stocks.

| Stock | stock of good [1000 t/a] | | P concentration [g P/kg] | | stock of P [t/a] | comment |
|---|---|---|---|---|---|---|
| water/environment | $(66162 \pm 3308) \cdot 10^3$ | [Beiwl and Muehlmann, 2008] | $3\text{-}15 \cdot 10^{-6}$ | [Beiwl and Muehlmann, 2008] | $7920 \pm 1584$ | includs groundwater and lakes |
| soil | | | | [Seyhan, 2006] | $(79200 \pm 1984) \cdot 10^3$ | calc. seperately |
| water treatment | | | | | | not known |
| storage | | | | | | not known |

Mrotzek, Kreuzeder and Gössler (Eds.): Phosphorus

# Phosphorus recycling from sewage sludge ash

## - Comparison of the PASCH, Mephrec and Ash Dec processes -

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## Abstract

The rising worldwide demand of phosphorus – used as fertilizer – and the imminent phosphorus scarcity resulted in increasing prices in the past years. This led to an increasing interest in methods for phosphorus recycling using waste water, sewage sludge or sewage sludge ash as raw material. Starting with ash higher process efficiencies and phosphorus yields are achieved with less use of chemicals. However, these processes in general are very energy and cost-intensive compared to processes starting with waste water or sludge. Via the comparison of the three most promising ash recycling technologies – the Mephrec®, Ash Dec® and PASCH process – with a set of different process indicators the advantages and disadvantages of the particular technologies, as well as their position and future prospects on the market were shown. Regarding the results the three processes were quite similar, but the lower phosphorus prices of the two metallurgic processes - Mephrec® and Ash Dec® - made them more competitive to the phosphorus price on the world market. With the internal and external indicators of the comparison a SWOT-analysis of the phosphorus recycling technologies from sewage sludge ash in general was performed, showing possible future opportunities as well as necessary strategies for their long-term competitiveness.

## 1 Introduction

The element phosphorus is essential for all life forms since it occurs as phosphate in RNA and DNA and is crucial for the cellular metabolism. Therefore, phosphorus is very important for plant growth and consequently also as a fertilizer for food crops. [Gilbert, 2009] Considering the permanently growing world population, providing enough food represents a global challenge. Sufficient supply with phosphorus, which is not substitutable, is a prerequisite for high crop yields. However, phosphorus reserves in the form of phosphate rock are limited and non-renewable. The different experts' opinions about the run out of the phosphorus reserves lie between 50 to 125 years, depending on the demand of fertilizer in the future. The uneven distribution of the worldwide phosphorus reserves additionally contributes to the tense situation. A large part of the resources is located in Morocco and Western Sahara, which are politically unstable. Further reserves are situated in China, the United States and South Africa. Probably phosphorus will become a strategic mineral in some countries, comparable to oil and its value and price will rise significantly. [Cordell, 2010]

So far, the public awareness concerning an upcoming shortage in phosphorus is astonishingly low. However, a high interest in methods to find and utilize new phosphorus resources is expected to go hand in hand with the increasing demand. It may become necessary to change consumption patterns and develop technologies towards a more sustainable resource management. [Brunner, 2010]

In this context, recycling of phosphorus can play a crucial role. Various techniques for phosphorus recovery or precipitation from wastewater already exist. The different technologies which are available today can be categorized according to the used raw materials, like wastewater, sludge or ash. Furthermore, three recovery processes can be distinguished, namely precipitation, precipitation in combination with wet-chemical extraction and thermal treatment. In the precipitation process, dissolved phosphate in waste water is precipitated or adsorbed without co-precipitation of disturbing metal ions. However, the gained amount of phosphorus out of the liquid phase is rather low compared to the technologies using sludge or ash. The treatment of sludge, which has a higher concentration of phosphorus, requires a more complex procedure where the phosphorus needs to be dissolved using strong acids, heat or pressure. During the wet-chemical extraction also metals are solubilized, which have to be separated from the phosphorus before its precipitation is performed. Therefore high amounts of chemicals are needed making the process complex and expensive. Via the incineration of the sludge all organic substances, like toxic compounds and almost all volatile metals are removed. For the elimination of the remaining metal ions a thermal-metallurgical or wet-chemical treatment of the ash is necessary. Using sewage sludge ash as raw material higher amounts of phosphorus are received using less chemicals and producing an almost directly usable end-product. [Horn et al., 2010]

In literature much information about the technologies themselves and also some comparisons between the different technologies regarding their complexity and efficiency are available. [Horn et *al.,* 2010] In an intensive study of the RWTH Aachen [Pinnekamp, 2007b] a detailed comparison, using a huge set of indicators, between several recycling methods using sewage water or sludge was performed. However, no detailed comparison (via an indicator set) of the different recycling technologies utilizing sewage sludge ash as raw material could be found.

Therefore a detailed set of indicators for their comparison was created in this paper. Next to the needed effort (costs and the amount of energy and chemicals) the effectiveness and profitability of the process, as well as the quality of the produced fertilizer are crucial parameters of the recycling systems. By this comparison the feasibility, disadvantages and advantages of the chosen technologies were shown and it was tried to figure out if one of the methods could be ranked first or if no ranking would be possible. After comparing the chosen technologies a SWOT-analysis for the phosphorus recovery processes from sewage sludge ash in general was performed. It should point out the strengths and weaknesses as well as the opportunities and risks of the recycling methods and show when and how phosphorus recycling from ash could be an interesting and renewable option for the future.

## 2 Materials and Methods

For the comparison of the three chosen technologies for phosphorus recycling from sewage sludge ash a detailed indicator set was performed. The internal indicators listed possible weaknesses or strengths of the particular technology, regarding their requirements, process complexity and economic feasibility, whereas the external indicators pointed out possible risks and opportunities of the particular technologies compared to competing technologies on the market or the fossil phosphorus rock recovery. In the end a concluding SWOT-analysis using the internal factors as process strengths and weaknesses and the external factors as risks and opportunities on the market was performed.

### 2.1 Internal indicators

Starting with the internal factors (see Table 1)) first of all the requirements of the waste water treatment plant (WWTP) like required volume or the minimum size of the plant, as well as structural requirements for the particular processes were described in a few key words. For numerical data, like the required minimum size or volume and the number of process steps the particular numbers or amounts are given. In the next step the complexity of the particular technologies were examined, regarding the number of process steps and possibly pre- and post-treatments of the raw material or end-product. The recycling potential of the process was divided into the percentage of possible recyclable amount of phosphorus which occurs in the inflow, in the possible yield of the process and in the potentially recovered amount of phosphorus in kg per year. In the next point the amount of required energy and the needed chemicals (amount and costs) as well as their influence and the impact of the waste-products on the environment were compared. The needed amount of energy and chemicals (amount and price) as well as the particular impact on the environment could only be estimated and classified in low or high because almost no detailed information was available. As next indicators the required investments for the process and building and the general costs per year, as well as the economic profitability, regarding the reached price per kg phosphorus were shown. For the investment costs and economic feasibility the given numbers should be seen as approximate values and for the price of kg phosphorus per year the range of the lowest and highest price, described in the cited literature, was taken. As last internal factors the bioavailability – depending on the citric acid solubility – and the quality of the end-product (e.g. heavy-metal pollution) as well as the experience of the particular processes so far and possible other process advantages were discussed.

### 2.2 External indicators

Regarding the external factors (see Table 1) a detailed comparison of the indicators, as at the internal ones, was rather complex. Therefore the evaluation was performed in a more qualitative way with rating the results with + (positive effect or better properties of the process), - (negative effect or worse properties of the process) and ± (same effect, or equal properties). As first external factor the reached phosphorus prices of the three processes were compared to the current world market price of fertilizer produced from phosphorus rock of 1.25 €/kg (January 2011) [Sartorius, 2011]. The next indicator compared the complexity and the costs of the particular processes with easier recycling technologies in general (e.g. from waste water). These two indicators should point out possibly risks and negative properties of the processes compared to easier technologies or to fertilizer from fossil phosphorus rock. The next four indicators should discuss positive opportunities and potentially side-effects of the recycling technologies from sewage sludge ash. The first indicator showed the long-term efficiency of the technologies due to their high throughputs and yields. In the second one the benefit of the technologies from the probably rising phosphorus rock price, due to its non-renewability was rated. Whereas the other two indicators should illustrate possible by-products or other advantages of the technologies, like the possible recycling of heavy metals or the generation of electricity during the process, which would cause an additional profit. Furthermore, the phospho-

rus recycling from sewage sludge ash serves also as a successful reutilization of an original technical waste product, which normally would have to be disposed in landfills.

## 2.3 SWOT-analysis

After the definition of the internal and external indicators and the comparison of the three processes a SWOT-analysis for the recycling technology of sewage sludge ash in general was performed, using the internal factors as strengths and weaknesses and the external ones as opportunities and risks. The SWOT-analysis is normally used as strategic planning method for the evaluation of strengths and weaknesses and the opportunities and risks of a new project, product or a whole company itself. The analysis has its mutual origins in the work of business policy academics at the Harvard Business School and other American business schools from the 1960s. [Hill & Westbrook, 1997] The idea behind the SWOT-analysis is the "analysis of the internal and external environment with the aim of identifying internal strengths in order to take advantage of its external opportunities and avoid external (and possible internal) threats, while addressing its weaknesses." [Panagiotou, 2003] General questions for the definition of the internal strengths and weaknesses for a technology are: [SWOT-Analysis]

– *What is the core competence of the technology? Does the technology produce high product yields and only low amounts of waste? Does the technology produce the desired end-product in a high quality?*
– *Where is further development necessary? In which areas of the technology are still weak points? Are there high investment and production costs?*

Between the internal indicators and the external indicators a clear separation is necessary, in order to prevent any mix-up. [Houben et al., 1999] General questions for the definition of external opportunities and risks would be: [SWOT-Analysis]

– *Why is this technology better than already existing ones'? How is the long-term efficiency of the technology compared to others? What are its the future prospects?*
– *Are there other and especially cheaper and less complex technologies on the market? Is the reached market price of the end-product competitive to the existing one?*

After the definition of the internal strengths and weaknesses of the technology itself and the external opportunities and risks of the technology on the market a matrix combing the four different points was performed, containing strategies and solutions for the improvement and defense of the technology. The combination of internal strengths and external opportunities should point out possibilities to raise the positive effects and improve the opportunities of the technology in the future. [Panagiotou, 2003] The combination of weaknesses and risks was used for a detailed analysis of necessary external input, which could prevent the fail of the technology. Via the combination of in-

ternal strengths and external risks or internal weaknesses and external opportunities strategies which could change or neutralize risks or weaknesses with the strengths or opportunities were tried to determine. [Houben et al., 1999; Nige & William, 1989]

## 3 Results

Before the implementation of the indicator set the different ways of phosphorus recycling from sewage sludge ash in general and the chosen processes were discussed.

### 3.1 Phosphorus recycling from sewage sludge ash

For the phosphorus recycling from sewage sludge ash the preceding incineration of the sewage sludge is necessary. Compared to the dumping or the direct use of sewage sludge this technic requires a higher amount of energy and increasing costs. One of the main reasons for rising costs is the need of the mono-incineration of sewage sludge, in order to reach the necessary concentrations of phosphorus in the ash. Normally the sewage sludge is burned in waste incineration plants as energy-rich fuel. However, after the incineration with other waste the phosphorus concentration in the received ash is way too low for any recycling purpose. [Sartorius, 2011] Via the incineration process almost all organic pollutants and endocrine substances occurring in the sewage sludge ash are destroyed or removed. Phosphorus stays completely in the ash and the average percentage lies at 6.2%. [Wiebusch & Seyfried, 1998] Heavy metals, like Pb, Cd, Cr, Cu, Ni, Zn and Hg occur only as trace elements. However, their concentration is usually too high for the direct application of the sewage sludge ash as agricultural fertilizer. The thresholds of the fertilizer regulation are often exceeded. Therefore a further treatment of the sewage sludge ash – e.g. an acidic digestion – is necessary. In general, for the phosphorus recycling from sewage sludge ash two different processes have been developed: wet-chemical or thermic-metallurgic treatment. [Pinnekamp, 2007a]

### 3.1.1 Wet-chemical treatment: PASCH

In the wet-chemical recovery process of phosphorus from the sewage sludge the first necessary step is the transfer of phosphorus in the liquid phase. Therefore strong acids, like sulfuric or hydrochloric acid are employed, which solubilize up to 90% of the phosphorus. However, in the same step also heavy metals are washed out of the ash, which have to be removed before the precipitation process and disposed properly. This is the main problem making the wet-chemical recovery to a constructional very complex and cost-intensive process. [Horn et al., 2010] In order to reach a phosphorus end-product, which could be directly applied as fertilizer for agricultural purpose many steps are necessary. In this paper the wet-chemical "PASCH" technology will be presented and discussed in detail. Other possible wet-chemical processes like the "BioCon" or the "Sephal" processes were not pre-

sented due to their low experience level (only laboratory scale) and high amounts of needed chemicals. [Horn et *al.*, 2010]

The PASCH process (Phosphorus recovery from ash) was investigated and developed from the Institute of Environmental Engineering (ISA) of RWTH Aachen University and several partner organizations. It enables the recovery of phosphorus from mono-incinerated sewage sludge ash or ashes from the incineration of meat and bone meal. [Dittrich et *al.*, 2009] Starting by leaching the ash with 7% hydrochloric acid in a stirred tank at normal temperatures of 20-25°C over 90% of the entire phosphorus is solubilized. [Montag, et *al.*, 2011] Via a parallel plate precipitator the remaining solid residues are separated from the leaching solution and dehydrated by centrifugation. After washing the solid filter the waste water can be reused for the dilution of the hydrochloric acid. The leach solution, containing a precipitate of phosphorus and metal compounds, have to be purified from the heavy metals (iron, lead, cadmium, copper, zinc) via a complex solvent extraction process. In the two-step Mixer-Settler- device an organic extraction solvent causes the separation of the metal ions, which precipitate as hydroxides. The phosphorus stays in the raffinate and can be discovered via a normal phosphorus precipitation with magnesium or calcium compounds. [Horn et *al.*, 2010; Pinnekamp, 2007a]

### 3.1.2 Metallurgic treatment: Mephrec®, ASH DEC®

In the first step of the thermic-metallurgic treatment the phosphorus-containing sewage sludge ash is mixed with solved calcium and magnesium chloride to receive a water content of around 30%. Afterwards the mixture is heated in a closed oven- system to a temperature between 850-1000°C. During this process the heavy metals react with chloride and evaporate. The occurring gas mixture is enriched with heavy metals and their particular chlorides and has to be cleaned with a wet scrubber and disposed probably. In order to reach the heavy metal threshold of the fertilizer regulation in the end-product about 50-100 g Chloride/kg ash are necessary at a process temperature of 1000°C. [Horn et *al.*, 2010; Adam et *al.*, 2007] During this process the ash phosphates are transformed in bioavailable magnesium phosphates, with solubility in citric acid of almost 100%. [Adam et *al.*, 2007] The two thermic-metallurgic technologies "Mephrec®" and "ASH DEC®" were further discussed in this paper. Other possible metallurgic technologies, like the "Thermphos" (developed 2006 in the Netherlands) or "Ulophos" process were not further discussed, because the first one could only be operated with low iron sewage sludge, whereas the second one was developed for the processing of meat and bone-meal. [Ingitec, 2009]

The metallurgic Mephrec® process was developed by the engineering company for foundry industry "Ingitec®" in Leipzig and first tests were performed on a pilot system at the Technical University of Freiberg, Germany. The process combines the generation of phosphate slag and

syngas production for the generation of electricity. For this process dried sewage sludge (25% dry matter) and sewage sludge ash, as well as ashes from the incineration of meat and bone meal are compressed to briquettes. In the first step the smelt-gasification of the briquettes together with coke (energy supply and reducing agent) and oxygen at 2000°C in a shaft furnace is performed. The produced liquid slag is tapped between 1450-1500°C and granulated in a water bath. During this process all organic compounds are transformed into syngas (carbon monoxide and hydrogen fuel gas), which can be further utilized for energy production. Low melting metals (e.g. Zn, Cd, Hg) are also transferred in the gaseous phase, segregated as dust and can be concentrated and reused in chemical metallurgy, whereas high melting metals (e.g. Fe, Cu, Cr, Ni ) stay in the solidifying slag. The granulate, containing over 90% of the entire phosphorus from the used briquettes, is free from organic pollutants and almost all heavy metals. After a mechanical treatment the end-product fulfills the thresholds for heavy metals of the fertilizer regulation and has a phosphorus bioavailability over 90%. Beside the promising end-product the process main advantage, compared to other recycling methods from sewage sludge ash is the use of the produced heat for electricity generation. [Ingitec, 2009; Horn et *al.*, 2010; Herrmann, 2009; Scheidig et *al.*, 2009]

The ASH DEC process was developed in 2001 by the Austrian company "ASH DEC Umwelt AG" and the process became part of the European SUSAN-project (Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery) in 2005. [Herrmann & Bachleitner, 2008] However, the company failed end of 2008 due to the economic crises and the enormous decrease of the world market price for phosphorus rock. The thermal phosphate recovery process ASH DEC® was acquired in the beginning of 2011 by the Finnish company "Outotec Oyj". [Herrmann, 2011]

The mono-incineration of sewage sludge completely eliminates organic pollutants, but the amount of heavy metal compounds in the incineration residues (high content of phosphorus) are still above the limits for agricultural application. Therefore in the thermochemical ASH DEC® process heavy metals are removed from the ashes and the containing phosphorus is transformed into a plant available phase. During the first process step the ash is treated with acids and chloric compounds (magnesium- or calcium chloride) to convert the heavy metals into metal chlorides. After drying the mixture the heavy metals, like cadmium, mercury, lead, copper and zinc, are evaporated at temperatures of 950°C in the rotary furnace. Afterwards the burned residues are mixed with potassium and nitrogen in order to receive the desired nutrient combination in the fertilizer product. In the last step the mixture is pelletized to provide a proper handling of the product. [Pinnekamp, 2007a; Adam et *al.*, 2009]

## 3.2 Comparison of Meprhec®, Ash Dec® and PASCH (indicator set)

After the short information about the technical realization of the particular processes they were compared via the prepared indicator set and the results were listed in table 1. For the comparison of the three chosen technologies Mephrec®, Ash Dec® and PASCH the results of the indicator set were discussed and compared.

### 3.2.1 Comparison of the internal indicators

Starting with the internal factors the examined volume of the plant for all processes had an input of 30.000 t of ash or dried sludge per year. As plant requirements beside special furnaces, like a shaft or rotary furnace for the Mephrec® and Ash Dec® process and a special extraction device (Mixer-Settler) for the PASCH process are needed. For the Ash Dec® and the PASCH process the mono-incineration of sewage sludge to ash is required. However, this could also be performed via an external incineration plant, which in turn would generate additional transport costs. [Sartorius, 2011] In the Mephrec® process the incineration of sewage sludge and other starting materials is already included. [Ingitec, 2009]

Regarding the complexity of the processes the Mephrec® process consists only of one general process step, the smelt gasification at almost 2000°C and the subsequent water quenching. However, as additional pre-treatment the briquetting of the raw material is necessary, as well as the mechanical post-treatment of the obtained phosphorus-slag product. [Ingitec, 2009] The Ash Dec® process seems to be more complex, having two general process steps: firstly treatment with water and magnesium or calcium-chloride for the dissolving of the ash and secondly the chloride calcination at almost 1000°C for the removal of heavy metals and organic pollutant. [Pinnekamp, 2007a] As pre-treatment the already mentioned mono-incineration is necessary and as post-treatment the received product has to be dried, which is the same for the PASCH process. However, the general three process steps make the wet-chemical process to the most complex one: firstly, the dissolving of the ash in 7% hydrochloride acid, secondly the complex solvent extraction for the removal of heavy metals and thirdly the precipitation of the phosphorus with magnesium compounds are required. [Pinnekamp, 2007a; Montag, et al., 2011]

The recycling potential of the three processes is quite similar. The percentage of phosphorus in the inflow (sewage sludge ash) lies at around 85-90% and the process efficiency and phosphorus yields at about 90%. [Pinnekamp, 2007a; Sartorius, 2011; Ingitec, 2009] The potentially recovered phosphorus per year for the PASCH process is estimated with 1 650 t of phosphorus per year. [Montag, et al., 2011] For the other two processes no data could be found for this indicator.

For the amounts of energy and needed chemicals no detailed numbers could be found. However, regarding the process temperatures the metallurgic Mephrec® and Ash Dec® processes seem to require high amounts of energy, whereas the PASCH process – running at low temperatures – will need lower amounts. Regarding the demand of chemicals the Mephrec® process does best, because no chemicals are applied. The Ash Dec® process needs high amounts of magnesium- and calcium chloride for the calcination step (up to 100 g Cl/kg), which are rather cheap chemicals. [Pinnekamp, 2007a; Ingitec, 2009] The PASCH process uses 7% hydrochloric acid and special extraction solvents like Alamine 336® and Tributylphosphate, which results in higher prices compared to the other processes. However, the employed chemicals are also in a low-medium price range. [Pinnekamp, 2007a] The impacts of the used chemicals and the process-by-products for the three processes were all rated as rather low. The segregated heavy metals in the waste gas flow of the two metallurgic processes could be re-concentrated and recycled for the metallurgic industry [Ingitec, 2009] and the extraction solvents of the PASCH process are regenerated and reintegrated in the process. [Horn et al., 2010]

The investment and general costs per year for the processes are only approximate values. The PASCH process seems to need less investment (only ~ 5 Mio) compared to the two metallurgic processes (~9-13 Mio), but the operating costs seem to be higher. [Everding & Pinnekamp, 2011; Ingitec, 2009; Herrmann & Bachleitner, 2008] However, these costs served only for a general orientation.

The achieved price for one kg phosphorus have to be compared to the world market price of fertilizer from phosphorus rock of 1.25 €/kg (January 2011) [Sartorius, 2011] Regarding the shown price ranges from the best and worst prices described in the literature only the Mephrec® and Ash Dec® processes seem to produce a competitive phosphorus fertilizer with prices of 1.20-1.50 €/kg P and 0.80 - 2.20 €/kg P respectively. [Ingitec, 2009; Sartorius, 2011] The achieved product from the PASCH process with a price range of 4.40-5.50 €/kg P would be way too expensive. [Everding & Pinnekamp, 2011]

The quality of the particular end products was rated for all processes with high, because the citric acid solubility lies over 90% and also the heavy metal concentrations are under the thresholds of the fertilizer regulation. [Ingitec, 2009; Pinnekamp, 2007a] However, the plant availability of the produced fertilizers still has to be measured in further plant and field experiments.

The degree of experience for all three processes is still only half-technic, because no large scale plants have been realized yet. [Horn et al., 2010] However, there have been many pilot projects and many future projects were already started or are in development, which

| Indicators | | | Mephrec® | ASH DEC® | PASCH |
|---|---|---|---|---|---|
| **Internal factors** | Requirements to WWTP | Volume | 30.000 t/a | 30.000 t/a | 30.000 t/a |
| | | Constructional requirements | Shaft furnace | Mono-incineration Rotary furnace | Mono-incineration Mixer-Settler extractor |
| | Complexity of technology | Process steps | 1 step | 2 steps | 3 steps |
| | | Pre-treatment | Briquetting of sewage sludge and ash | Mono-incineration of sewage sludge to ash | Mono-incineration of sewage sludge to ash |
| | | Process principles (process-temperature) | Smelt-gasification & quenching with water (1450-2000°C) | Treatment with water and $MgCl_2/CaCl_2$ Chloride calcination (950-1000°C) | Treatment with 7%-HCL Solvent extraction Precipitation with Mg-compounds (20-25°C) |
| | | Post-treatment | Mechanical re-processing | Drying of end-product | Drying of end-product |
| | Recycling potential | % of recycled P in inflow | 85-90% | 85-90% | 85-90% |
| | | Yield of phosphorus | 90% | 90% | 90% |
| | | Potentially recovered P per year | n.d. | n.d. | 1 650 t P/a |
| | Energy | Amount | high | high | low |
| | Needed chemicals | Type/Amount | n.d. | $MgCl_2/CaCl_2$ (50 – 100 g Cl/kg) | 7%-HCL, Alamine 336®, Tri-butylphosphat |
| | | Price | low | low | medium |
| | Influence and consequences for environment | Impact of waste and by-products | low (Heavy metals and chlorides in waste gas → recycling) | low (Heavy metals and chlorides in waste gas stream → recycling) | low (leaching and re-extraction residues → recycling or re-integration) |
| | | Used chemicals | / | Low ($MgCl_2$, $CaCl_2$) | Low (HCL diluted) |
| | Investments and costs | Investments for building | 8.5 Mio € | 10-13 Mio € | 4.8 Mio € |
| | | General cost per year | 4.8 Mio € /a | n.d. | 7.24 Mio €/a |
| | Economic profitability | Price/kg P | 1.20-1.50 €/kg P | 0.80 - 2.20 €/kg P | 4.40 – 5.50 €/kg P |
| | Quality of the end-product | Bioavaibilty of P | High (phosphorus-slag) | High (Mg-phosphates) | High (Mg- or Ca-phosphates) |
| | | Heavy-metal pollution of end-product | Below threshold | Below threshold | Below threshold |
| | Experience | | half-technic (pilot projects) | half-technic (pilot projects) | half-technic (pilot projects) |
| | Other advantages | | Syngas production → electricity generation | / | / |
| **External factors** | Reached phosphorus price compared to phosphorus price on the world market | | ± | ± | - |
| | Complexity and costs of the technology compared to easier recycling technologies (e.g. from waste water) | | - | - | - |
| | Long-term technology (high investment costs, but high throughputs and yields) | | + | + | + |
| | Phosphorus rock as non-renewable resource - Technologies benefit from rising price of phosphorus rock | | + | + | + |
| | Possible recycling of heavy metals/generation of electricity as additional profit | | + | + | + |
| | P-Recycling from sewage sludge ash as reutilization of a technically waste product | | + | + | + |
| | Sources | | [Ingitec, 2009; Sartorius, 2011] | [Ingitec, 2009; Pinnekamp, 2007a; Sartorius, 2011; Horn et al., 2010] | [Pinnekamp, 2007a; Sartorius, 2011; Montag, et al., 2011; Everding & Pinnekamp, 2011] |

**Table 1: Comparison of the Mephrec®, the ASH DEC ® and the PASCH-process via the indicator set.**

will provide new and hopefully more detailed data for the large scale realization.

As last internal indicator other advantages of the particular processes were described. Here the Mephrec® process presented an opportunity for additional profit, because the as by-product released syngas could be easily used for electricity production. [Ingitec, 2009]

### 3.2.1 Comparison of the external indicators

Regarding the results of the external indicators in general there were almost no differences between the particular processes. Only the achieved product prices for the two metallurgic processes are lower and therefore their competitiveness to the price of fertilizer from phosphorus rock on the world market would be higher than of the wet-chemical process. [Sartorius, 2011] Comparing the process complexity and costs to easier technologies, like phosphorus recycling from waste water all three recycling processes have a worse performance. However, looking at the long-term efficiency of the technologies the recycling from ash offers high throughputs and results in high yields compared to technologies using water or sludge. Therefore the high investment costs should be compensated in some years. [Sartorius, 2011; Sartorius et al., 2011] Furthermore, the price of fertilizer produced from phosphorus rock will increase in the following years, because phosphorus rock is a non-renewable resource, which will run out in the next decades. (Cordell, 2010) Hence, the recycling technologies will benefit from the rising world market price. [Everding & Pinnekamp, 2011]

Beside the received fertilizer end-product other by-products like syngas (only Mephrec®) or heavy metals, regenerated and recycled from the gas flow, are produced and could be used for an additional profit. [Ingitec, 2009; Everding & Pinnekamp, 2011] Moreover the used raw material, sewage sludge ash is a technical waste product which normally has to be disposed on landfills.

## 4 Discussion

After the detailed discussion of the particular internal factors for each process none could be named as the best recycling method. Considering the constructional requirements, the phosphorus recovery potential, the quality of the end product and the technical experience all methods are quite similar. However, comparing the two metallurgic processes with the wet-chemical one it was clearly visible that the process principles are less complicated and the lower demand of chemicals has a positive effect on the environment. Furthermore the achieved phosphorus prices are almost competitive with the world market price, whereas the PASCH process is still too expensive. The Mephrec® process seems to have an interesting advantage, due to the generation of syngas. This could be used further for electricity production, but the higher demand of ener-gy (higher process temperatures) has to be considered as well.

Regarding the external indicators the position and opportunities of the three processes on the market where quite similar. All technologies have too high investment and also operating costs which reduce their competitiveness compared to the mining and utilization of phosphorus rock. However, presuming the increase of the world market price of phosphorus rock, due to its non-renewability and the diminishing resources phosphorus recycling from sewage sludge ash may be a promising future and long-term technology.

For a concluding illustration the internal (strengths and weaknesses) and external factors (opportunities and risks) of the phosphorus recycling from sewage sludge ash in general were packed in a SWOT-analysis (see table 2) giving possible application strategies and future prospects.

The combination of the internal process strengths and the external opportunities of the technology on the market led to the following statements and strategies. The high throughputs and product yields will allow cheaper prices in the long term. However, in order to reach a better competiveness and future feasibility also additional optimizations (process principle, energy and chemical demand, quality of end-product) of the different processes as well as the increase of the world market price for phosphorus rock would be necessary.

Through combining the external opportunities with the process weaknesses a neutralization or even transformation of the negative process parameters should be achieved. The high investment and operating costs could be lowered by considering the saved money for the normally necessary depletion of the raw material and by the reintegration of used chemicals in the process. Furthermore the recycled heavy metals from the waste gas flow could be sold to the metallurgic industry, which would cause an additional profit and protect the environment at the same time.

By using the internal process strengths the external risks should be minimized. The problem of the expensive and complex technology compared to simpler ones', e.g. recycling from waste water could be compensated via the higher throughputs and achieved product yields of recycling from ash. These processes are long-term technologies which are indeed more cost-intensive, but will be more feasible in the long term.

As last point the processes weaknesses were combined with the external risks to show weak points where an intervention from the outside is necessary. The expensive and complex processes having high investment and operating costs as well as the cheaper competing technologies make recycling from ash rather unattractive at the moment. Therefore subventions and governmental aid are necessary for the realization of these promising future technologies.

| SWOT | Strengthss | Weaknesses |
|---|---|---|
| | - High yield of phosphorus<br>- Less demand of chemicals<br>- Electricity generation | - High investment costs<br>- High operating costs<br>- High price for P/kg<br>- Chemicals and heavy metals in waste stream |
| **Opportunities**<br><br>- Rising future price of phosphorus rock (non-renewable resource)<br>- Long-term technology, high throughput and yields<br>- Possible recycling of heavy metals and chemicals<br>- Re-utilization of an technically waste product | **Strengthss-Opportunities**<br><br>- optimization of technology and rising price of fossil phosphorus rock<br> → Future feasibility<br>- High production and yields<br> → Cheaper prices possible | **Weaknesses-Opportunities**<br><br>- High investment and general costs, but utilization of technical waste product<br> → No depletion costs<br>- Chemicals in waste water<br> → Reintroduce into process<br>- Heavy metals in gaseous waste phase but possible re-use in metallurgic industry<br> → Additional profit |
| **Risks**<br><br>- Expensive and complex technology, cheaper competing technologies<br>- Cheap price of rock phosphorus | **Strengthss-Risks**<br><br>- Cheaper and less complex technologies available, but less throughput and yield<br> →Advantage as long-term technology<br>- Electricity generation (only Mephrec®)<br> → Additional profit | **Weaknesses-Risks**<br><br>More expensive and complex technology, no feasibility or competitiveness yet<br> → Subventions and government aid necessary |

**Table 2: SWOT-Analysis of phosphorus recycling from sewage sludge ash.**

# 5    Conclusion

Summarizing the results of the comparison of the three recycling processes from sewage sludge ash, only slight differences could be detected. Regarding constructional requirements, recovery potentials, quality of the end product and the technical experience all methods are quite similar. However, for some indicators, e.g. number of process steps, demand of chemicals, and reached phosphorus price, the two metallurgic processes Mephrec® and Ash Dec® achieved better results compared to the wet-chemical PASCH process. Furthermore, the Mephrec® process allows the similar production of fertilizer and electricity production, due to the generation of syngas. However, the higher demand of energy has to be considered as well.

The analysis of the external indicators, showing the position and future prospects of the processes on the market were quite similar. Therefore the subsequent SWOT-analysis using the internal indicators as strengths and weaknesses and the external indicators as risks and opportunities was performed for phosphorus recycling from sewage sludge ash in general. Via the combination of strengths with risks and weaknesses with opportunities the future feasibility of these long-term technologies and possible additional profits, via recycling and utilization of by-products could be shown. As biggest weak point (combination of weaknesses and risks) the high investment and operating costs have to be mentioned. However, governmental aids and subventions of investors could be a solution to overcome initial difficulties and to realize this promising future technology in the next years.

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# From the Establishment to the Failure of the Ash-Dec Umwelt AG
## – A Dynamic Analysis

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## Abstract

In the last decade the Ash-Dec Umwelt AG developed a unique phosphate recovery technology treating ash substrates chemically and thermally. In this study the development and various reasons for the bankruptcy of this joint-stock company are being analyzed. New data was generated and assessed in order to show the structure and the behaviour of a company dealing in the phosphorus recovering business. Furthermore certain key features were scrutinized by using system dynamics. In other words, by using Vensim™PLE a dynamic model of the Ash-Dec Umwelt AG was built and the interaction of the elements of the system was examined closely. The received and analyzed data show possible policy recommendations on the one hand for firms dealing in the phosphate recovering branch and on the other hand for law-makers sustaining forward-looking technologies.

## 1 Introduction

Phosphorus is an essential element of the biosphere and exists in various organic and inorganic forms. For instance, it can be found in bones, within mitochondria, cell membranes and even occurs as calcium phosphate or phosphate rock which has been a crucial component of agricultural fertilizers, especially since the green revolution. Although the total range of phosphorus resources is unknown, it is obvious that an increasing demand for fertilizers, hence a higher or constant agricultural production, will result in the depletion of the phosphorus stock [Cordell, 2010]. Experts argue that the exploitation of phosphorus resources combined with the difficulties in recovering this essential element would certainly lead to "peak phosphorus" (the point in time when the maximum rate of global phosphorus extraction is reached) within the next decades [Abelson, 1999; Brunner, 2010; Cordell, 2010; GPRI, 2008; Greuling, 2011].

Were this true, scarcity would cause higher market prices of phosphorus and consequently of fertilizers resulting in a more extensive technology research. In addition, higher prices would be an incentive for entrepreneurs in order to build up new business concepts.

In the last years new types of phosphate recovery technologies were developed by visionary companies, such as Mephrec® that is based on a metallurgic treatment process, or PASCH that relies on a wet-chemical treatment [Sartorius, 2011]. One of the companies that seemed to have discovered a very efficient recovering technology was the Ash-Dec Umwelt AG that ran a pilot plant in Leoben, Austria [UFH, 2011]. The Ash-Dec Umwelt AG aimed at producing phosphorus fertilizer out of incinerated sewage sludge. Unexpectedly this joint-stock company went bankrupt in 2010 [Boerse-Express, 2010].

However, this paper is a new approach because it provides data from the establishment to the failure of the Ash-Dec Umwelt AG, a firm dealing in the phosphorus business. In other words, no similar research has been done before, putting the analysis of the structure and the behaviour of a phosphate-recovering company together. Since the interaction of various legal, economic, institutional and technological reasons that have contributed to the failure of the Ash-Dec Umwelt AG are still unclear the system is analyzed by system dynamics. One of the main focuses beside the simulation is the derivation of several policy recommendations, such as government actions, possible actions of the Ash-Dec Umwelt AG and preventive steps of other companies investing in new technologies, such as the phosphorus recovery.

## 2 Method

The software Vensim™PLE was used in order to build up the model of the Ash-Dec Umwelt AG. Generally,

Vensim™ can be used as interactive software in order to develop and analyze dynamic simulation models. Models are constructed graphically and can be fed with data and underlying mathematical equations [Vensim, 2011; Sterman, 2000].

Before building up the model, the interaction relationship between the elements of the system was analyzed by developing a so-called causal loop diagram (CLD)-based thought model. This design was developed around our assumption that the Ash-Dec Umwelt AG failed because there was a lack of willingness to invest (see *Figure 1* in the 'A Figures'-section). Additionally, various other factors, such as the market, technologies, etc. were included in order not to depend on a single key element. The stock and flow structure of the Ash-Dec Umwelt AG was constructed on the basis of the CLD and of further literature research that is presented within the following chapters.

At first, the stocks of the systems were defined according to the main elements of the annual financial statements and the consolidated income statement of the Ash-Dec Umwelt AG but always having the CLD based design in mind. In concrete, a standardised balance sheet was developed according to Lachnit [2004] and Kueting and Weber [2009] in order to improve the comparability and the analysis of the accounts.

Secondly, inflows and outflows were added. In other words, a stock and flow structure – that constitutes the design basis of the model – was constructed.

Thirdly, after that parameters and variables had been included, the model structure was built by connecting the elements of the subsystems. Additionally, the model was filled with real data and for the lack of scientific available measurements approximate numbers for several parameters were estimated. The outcomes and the structure of the model were examined closely.

Finally, a sensitivity analysis was made by changing system inputs in order to make it possible to derive policy recommendations.

## 3 Results: The Model of the Ash-Dec

The following description presents the constructed Vensim™-model (see *Figure 2, 3 and 4* in the 'A Figures' section) in three main steps. The interaction of the elements of the system is also defined by explaining the theoretical background for our assumptions (see *Table 1* in the 'B Appendices'-section).

### 3.1 Balance Sheet

Firstly, the stocks and their in- and outflows of the balance sheets are scrutinized. There are two central elements in this sub-model: the assets and the capital.

Firstly, the assets are composed of the monetary values of the current- and the long-term- assets describing the allocation of resources (see *Figure 4* in the 'A Figures' section). The current assets are being determined by the cash assets on the bank accounts of the Ash-Dec Umwelt AG and by the trade receivables [Annual Statements, 2004-2008]. The elements that play a decisive role are the long-term assets which are

the sum of the monetary values of the plant and the office equipment, the pilot plant (with a value of 1.3 million Euros) and the industrial plant (with an assumed value of 12 million Euros) [Annual Statements, 2004-2008]. The building of the pilot plant depends on the building permission that the Ash-Dec Umwelt AG received in 2007, and on the ability to raise the needed capital. The industrial plant, however, can only be built if an additional capital of at least 12 million Euros can be accumulated and after an environmental impact assessment is carried out.

The second central element is the capital that is representing the source of the finance and is distinguished into the following two accounts (see *Figure 3* in the 'A Figures' section). Financial inflows from shareholders are accounted to the equity capital, whereas loans from a bank are accounted to the debt capital. The equity capital is composed of two inflows. Firstly, the recapitalisation is the amount of the after-tax profit that stays within the company, and is therefore the annual surplus reduced by the dividend. In the case of a loss it is called debit carryover reducing or depleting the equity. Depletion leads - in the case that the investors refuse to be liable with their private property - to bankruptcy. The second inflow is the payment volume that depends on the willingness of shareholders or business angels to invest into the company [Wirtschaftsblatt, 2006]. Since shareholders show a higher willingness to invest into a technology that is in a higher developmental stage, a so-called 'technology-trust factor sub-model' was constructed: The trust in the Ash-Dec technology depends on the research of the company before building the pilot plant (Ash-Dec Research), on the research with external partners (ETH Zürich, TU Wien and within the SUSAN-project) and on the research in the pilot plant in Leoben [Bioland, 2010]. In detail, the Ash-Dec method was patented and was used in the pilot plant as a 'proof of concept' before trying to realize a large scale power plant [Hermann, 2011a]. All of the research activities increase the trust that the technology is profitable and will lead to dividends that initiate payments in the amount of 1.4 million Euros up to 15 million Euros [Annual Statements, 2004-2008].

The payment volume of the debt capital was conducted in the same way as the payment volume in the equity capital, meaning that potential credit grantors are only willing to give out loans if they trust that the new technology will lead to interest payments [Annual Statements, 2004-2008].

### 3.2 Profit and Loss Account

The profit and loss statement (see *Figure 3* in the 'A Figures' section) represents the dependency on the annual surplus (or loss) that can be distributed to shareholders (in the case of a surplus and of a positive decision for dividend payments). In the case of a surplus it is assumed that 40% is distributed to the shareholders, whereas 60% remain in the company for further investments. The annual surplus is calculated by subtracting the interest which are in the Ash-Dec case

about 3% of the debt capital [Annual Statements, 2004-2008] and the Austrian corporate income tax of 25% (with a minimum payment of 3.500 Euros for joint stock companies) from the EBIT (earnings before interest and taxes).

The EBIT on the other hand is calculated by subtracting costs from revenues. In our model there are four main sources for costs.

Firstly, the company spent a substantial amount for research and development (that led to a higher trust in the technology, leading to capital payments). The expenditures amounted to about 1.3 million Euros in 2003 increasing from then onwards by an annual rate of 11%. For the different types of research financial subsidies of about 1 million Euro annually were provided by the Austrian Research Promotion Agency (Forschungsförderungsgesellschaft, FFG) [SUSAN, 2008, Annual Statements, 2004-2008].

The second source of costs are wages that depend on the amount of employees (initially 5; it is assumed that in the case of a realization of a pilot or industrial plant 5 additional employees are hired) as well as the average wage that amounted to 45.000 Euros per employee and is expected to raise annually by 2% [Annual Statements, 2004-2008].

Thirdly, the costs for material in the case of production were considered as high as 700.000 Euros in the pilot plant and to be 7 million Euros per industrial plant (net costs), whereas fourthly, the depreciation of the long-term assets is 30% [Annual Statements, 2004-2008].

The revenues on the other hand depend on the amount of the sold product (the Phoskraft™-fertilizer) multiplied with its price. These factors will be scrutinized in the chapter 3.3 Competition.

### 3.3 Competition

In this subchapter the dependency on the amount and on the price of the Phoskraft™-PK12-20 fertilizer - meaning that it is a compound of phosphorus (12%) and potassium (20%) - in the context of competition with a conventional fertilizer is analysed (see *Figure 2* in the 'A Figures' section).

It is assumed that consumers are only willing to buy the cheapest available fertilizer, either recycled or conventionally produced. The price of Phoskraft™-fertilizer depends on the costs per recycled kilogramme of phosphorus, which amounts initially for 2,65 Euros per kg (base year 2012, calculating 2,199€/kg; starting in 2003 from 2,65€/kg with a decrease of 2,05% p.a.) in the industrial plant and assumed 3,5 Euros per kg in the pilot plant, with an annual price reduction caused by technological progress of 2,05% [Sartorius, 2011]. The price of conventional P amounts for 0,5 Euros per kilogram in 2003 with a price spike of 4 Euros per kilogram in 2008 which is referred in this paper as phosphorus bubble, since the average long term price increase amounts for 4,765% per year [Sartorius, 2011]. The price of the added K (Potassium) that has to be acquired for both types of

fertilizers is assumed to be the same for both fertilizers and is therefore extraneous in the competition.

In the case that the Phoskraft™-fertilizer is the cheaper variant and that a selling allowance (that was given to the Ash-Dec Umwelt AG in 2006) exists, all the produced fertilizer (250 tons in the pilot plant and 2.500 tons in the industrial plant per year) can be sold with an estimated mark-up of 10%. If the Ash-Dec Umwelt AG offers a more expensive product it will not able to sell any fertilizer and will remain a research and development company [Hermann, 2011].

## 4 Discussion of the Model

In order to get an idea of the drawing up of the Ash-Dec Umwelt AG the balance sheets of the years from 2003 to 2008 were analyzed. This means, that all data was structured and it was tried to calculate various ratios. Since our major view in this paper is on building a dynamic model of a phosphorus-recycling company and given the fact that a detailed analysis of all balance sheets could even fill at least another paper we simply want to provide some findings. Furthermore, the list of possible ratio-calculations out of the annual statements was narrowed down because the pilot plant did not make any real turnover.

For the Ash-Dec Umwelt AG there was always a high risk of insolvency. The reason for this is that the equity ratio was very low throughout the years. In concrete, a low equity ratio means that beside the risk of insolvency several other negative effects could arise, such as that the company has to pay higher interest rates or that the company (as a borrower) is not able to pay back the credit.

As the model shows, the lack of capital was one of the main reasons why the Ash-Dec got bankrupt. The Ash-Dec Umwelt AG was not able to realise an industrial plant since a capital of 20 up to 25 million € would have to be accumulated for the construction and for the commissioning and since the Austrian Research Promotion Agency cancelled approved subsidies in 2010 [Hermann, 2011a; Hermann 2011b]. The bankruptcy of the Ash-Dec Umwelt AG occurred one month after signing the first contract for an industrial plant in Germany [Hermann, 2011a].

In the following subchapters the interaction relationships between the main elements of the system are discussed. The five subchapters (4.1 to 4.5) correspond to the various elements or views of the initial CLD-based thought model describing reasons for the lack of the willingness to invest. Specifically, an analysis of the Vensim™-model is performed by confronting data generated out of the model and theoretical (partly literature-based) background.

### 4.1 New Technology

As listed above, one of our main assumptions is, that the Ash-Dec Umwelt AG failed because there was a lack of willingness to invest. Were this true, higher funding and monetary subsidies would be provided when technologies are in a higher stage of develop-

ment.

In the Communication [2011/0031] to the European Parliament and the Council the Commission of the European Union refers to the choice of financing instruments. In this communication not only the choice of the right instrument is being scrutinized but also the connection between financial supports of new technologies and the stage of the technological development. It is argued that the public has to offer financial aid or subsidies when high risks for the private sector do exist due to low technological development and/ or an early state in the project development phase. Shortly, public financial aid for research and development projects can limit or decrease uncertainties when the risks for the private market are too high [Commission, 2011].

Additionally, in Strebel et al. [2007] it is pointed out that during economic slowdowns or weaknesses fewer investments are made into research and development (R&D) because financial funds very often depend on the total revenues. It is a matter of fact, that the dependence of R&D on the revenues enhances economic recessions [Strebel et al., 2007].

In our construction of the model and within the simulation the stage of the technology research was included. In other words, a distinction was made between Ash-Dec research, in-plant research and research with external partners because more research obviously leads to better knowledge of the processes regarding a real plant realisation. A further element that could influence (debt and equity) payment behaviour is the existence of company-patents. A case in point is the patented Ash-Dec-Technology (three international patents concerning the thermal phosphate recovery process acquired by the Outotec Oyj, a Finnish company who is continuing and investing into the former Ash-Dec research) [Outotec, 2011].

To cut a long matter short, more and better research will result in a higher willingness to invest into a company or project and as consequence – as it is also shown in the Vensim-model – equity capital could be increased.

## 4.2 Market Permission of Organic Fertilizer

After some years of research a pilot plant was realized in Leoben, Austria. But before the market was entered and the produced fertilizer Phoskraft™ could be sold there were several obstacles to overcome [Artho Bovis, 2009 and 2011].

Firstly, there were difficulties to get the legal permission to sell a fertilizer that is produced out of the ash of sewage sludge. Since the Ash-Dec Umwelt AG had also to test the fertilizer in field trials [Ash-Dec Umwelt AG, 2008] it can be said that a considerable time delay did exist until the Ash-Dec Umwelt AG was able to enter the market.

Secondly, in addition to the process of the legal permission the components of a fertilizer have to be below certain threshold values for heavy metals defined in different regulations (in Austria: §9 Düngemittelgesetz 2006; in Germany Düngemit-telverordnung bezüglich Klärschlammasche) [Ash-Dec Umwelt AG, 2008; DüMV, 2004/2006/2008].

Thirdly, the fertilizer has to be sold at a certain price level. Phoskraft™ should be offered cheaper or at the same price as the products of similar fertilizers. Statistics show a tendency of constantly increasing fertilizer prices [AMA, 2011]. The price for phosphate rock seemed to be very stable for years. But in 2007, the price went up significantly. As demand decreased during the economic crisis in 2008 the prices went down again. The market for phosphate rock is mainly driven by the demand of the fertilizer industry because the majority of the mined phosphorus goes into the fertilizer production. Unexpectedly, the prices for fertilizer were not as volatile as the price for phosphate rock.

Economic data and the price levels on the markets play a decisive role because they provide information if the company and its processes show profitability or not. Shortly, revenues have to be reached in order to cover costs and to generate an annual surplus [Strebel et al., 2007].

To sum up, if the above listed problems are met successfully, at least a sustainable existence can be guaranteed.

## 4.3 The Approval for the Industrial Facility

Several factors that influence the realisation of a pilot and a real industrial plant as well can be distinguished.

As it is shown in the model, a certain amount of capital is needed for the realisation of a plant. On the one hand the monetary aspect plays a decisive role and on the other hand legal (bureaucratic) proceedings can lead to considerable time delays.

In our case, the pilot plant was realised in Leoben, Austria, and not in Vienna due to time delays caused by staffing changes within the municipal authorities as well as in the district heating corporation in Vienna, Austria.

A second reason for delays might be that for the plant (pilot or industrial) an environmental impact assessment has to be conducted. This means, that the effects of the processes of the plant on various environmental media are analyzed scientifically and interdisciplinary with the participation of local citizens.

Shortly, the influence of time and delays and linked to this a later start of production processes should not be underestimated regarding to a firm's success.

Since Outotec Oyj purchased the know-how and the intellectual property rights in early 2011 the Ash-Dec technology is back on track. Under favourable circumstances, the first industrial plant would be able to start production in the year 2013. That implies a time delay of 19 years since the basic mechanisms of the process have been investigated [Hermann, 2011a].

## 4.4 The Availability of Sewage Sludge Ash

The availability of a certain amount of sewage sludge ash limits the number of production sites for the Ash-Dec Umwelt AG. Due to the low population density in

Austria the rentable sites are limited to the 'conurbation Vienna'. Therefore the only source for sewage sludge is the sewage plant Simmering/Vienna where the amount of sewage sludge (the incinerated sludge is the main input of the Ash-Dec fertilizer production) exceeds the limit for a possible realisation of an industrial phosphorus-recovery plant.

At the moment a biogas plant is being realised at the mentioned site in Simmering/Vienna. In this facility the sludge is processed to extract the biogas which is used to generate electricity. In this context the question arises if any implications for the ash production do exist, what form of output can be gained after burning the sludge and what are the consequences if an electricity generating facility is in competition with firms dealing in the phosphate recovering branch. These topics are shortly discussed in the following section.

## 4.5 Volatility of Fertilizer Price

After the comparison of different outputs of the model-runs we reached the conclusion that in the years 2008 and 2009 it was possible to sell Phoskraft™ because it was cheaper than the conventional PK (Phosphorus, Potassium) fertilizer (*Figure* 5). It is possible that a wrong trend-extrapolation of the Ash-Dec Umwelt AG – they assumed that the prices would develop in the same way – contributed to the failure of this joint-stock company (*Figure 5* shows the so-called 'phosphorus-bubble').
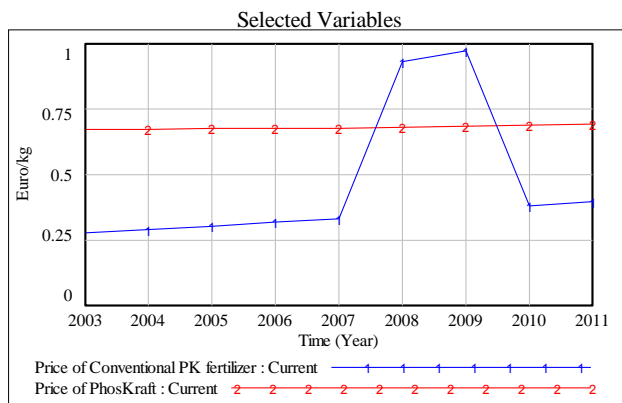


*Figure 5:* Development of the fertilizer prices with a production output of the pilot plant

We tried a type of sensitivity analysis by changing some model-inputs. In concrete, we assumed that the industrial plant would have been realised, technological progress would reduce the production costs of Phoskraft™ and that the price of conventional fertilizer would increase since phosphorus is getting scarcer and scarcer. Ceteris paribus, the revenues are predicted to rise leading to an increasing annual surplus. *Figure 6* shows that beginning in 2028 the price of the conventional fertilizer will outnumber Phoskraft™.

Briefly, the price of Phoskraft™ will get competitive. Were this true, one might argue that the Ash-Dec Umwelt AG was a quite visionary company that was founded 20 years too early to yield a profit. Due to operating costs and the absence of any revenues the bankruptcy was unavoidable. In our model the equity is depleted leading to bankruptcy in 2010.
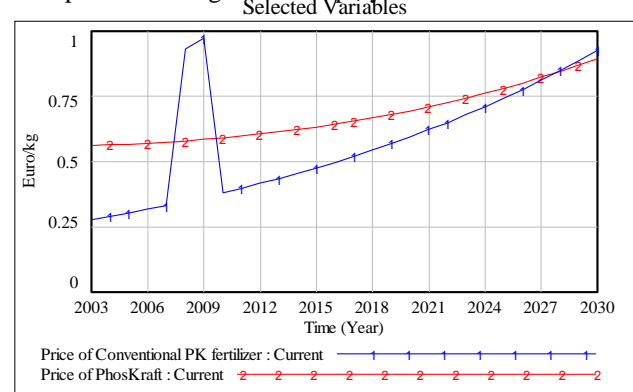


*Figure 6:* Development of the fertilizer prices with a production output of the industrial plant

## 4.6 Limitations

We are aware of possible limitations of our model. Since the process of modelling is linked to a subjective perception of parts of reality we can only present our access and our understanding of the structure of the Ash-Dec Umwelt AG. The chosen perspectives are mainly influenced by our background, which includes systems sciences, business administration and economics. Nevertheless we tried to develop an interdisciplinary approach including technical, in particular, chemical and physical aspects.

## 5 Conclusions and Recommendations

For all the reasons we have mentioned above, several policy recommendations can be derived from our research. These recommendations are not only limited to firms dealing in the phosphate recovering branch but have also a major significance for law-makers and for developers of new forward-looking technologies and projects.

However, following implications – ranging from concrete recommendations to very general ones – can be derived from our model and literature research:

- The higher the stage of technology development is the better future success can be proved. This will result in a higher willingness to invest (but obviously in decreasing interest rates for the provided capital since risks are being minimized).
- Investments in new technologies should also be made during economic crisis in order to break the 'vicious circle'. In other words, R&D expenditures should not be a percentage of revenues.
- Public subsidies play a decisive role for new technologies since unknown technologies and projects constitute hazardous businesses for private financiers, especially in Austria. In concrete, public funding is indispensable for sustaining forward-looking technologies when there is a lack of risk capital from private creditors.

One might argue that the money should be used

differently, e.g. given to a good cause, but investments in new technologies and projects offer on the one hand job possibilities (and prevent brain-drain) and the other hand might decrease the reliance on imports from other countries (especially from politically unstable ones).

- "Time is money", this proverb is true especially for start-up companies because the earlier products can be sold on the market, the faster revenues and profits can be reached. Therefore, all bureaucracy measures, e.g. building permissions and market barriers (stringent conditions) or an environmental impact assessment, should be accomplished as fast as possible.
- Phosphorus recycling should not be seen as a cure-all: agriculture should try to use fertilizers in a more efficient way. Another idea might be to increase a plant's uptake of phosphorus in order that phosphorus is used more efficiently.
- As far as we are informed, the ability for recycling phosphate out of sewage sludge ash remains the same when the sewage sludge is used in various upstream processes in order to generate electricity. In the final output just a small variation of the composites can be distinguished. Therefore, increasing investments in biogas-facilities at sewage treatment plants do not provide a substantial threat to the availability of phosphorus-containing ash. Inasmuch as the generated heat can be used for district heating the biogas technology may provide additional revenues. Shortly, from our point of view, it is not completely clear if the combination of two plants – a biogas-facility and a phosphate-recovering plant – can lead to an increased yield of energy. But if we are striving for a future amelioration of technical efficiency and a resource independency as well, the necessity of a combination of these two facilities should be discussed broadly [BAM/SUSAN, 2009; Hermann, 2011b].
- The question arises as to whether there is a second way of recovering phosphorus for fertilization. With the increasing number of biomass plants in Austria more and more wood ash is produced. Maybe wood ash could be an option to the ash of sewage sludge. This development would minimize the reliance on 'urban-phosphorus-mining' and on phosphate-exporting countries.

As assumed, the model and our research work show that various factors – economic, institutional, technological and legal ones – contributed to the failure of the Ash-Dec Umwelt AG. (see *Figure 1* in the 'A Figures'). As it was discussed above that the right choice of the point of time of the entry into a market plays a decisive role and seems to be an additional plausible factor why the Ash-Dec Umwelt AG went bankrupt.

To sum up, it is a pity that the Ash-Dec Umwelt AG has not realised an industrial plant in Austria and that the patents were sold to the Outotec Oyj company although our model results show that the industrial plant could have generated high profits in future. Con-sequently, a Finnish company invests and pins its hopes on the extremely promising Ash-Dec-technology that was initially financed with Austrian development funds.

## Acknowledgement

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## A Figures

*Figure 1* shows a CLD-influenced thought model. It was developed according to the basic assumption that the Ash-Dec Umwelt AG was not able to realise an industrial plant because there was a lack of capital. Our first dynamic-hypothesis was that investors have been deterred from injecting cash into new projects caused by various factors, such as the volatility of the fertilizer price, the development stage of technology, problems with the approval for the industrial facility (environmental impact assessment), the availability of a certain amount of sewage sludge near to the production site and the selling allowance of the product. (The minus at the arrowhead in *Figure 1* symbolizes "the more...the less is the willingness to invest".) *Figures 2, 3 and 4* show the plot of the model-structure in Vensim™PLE. They are described in the sections number 3 and 4.
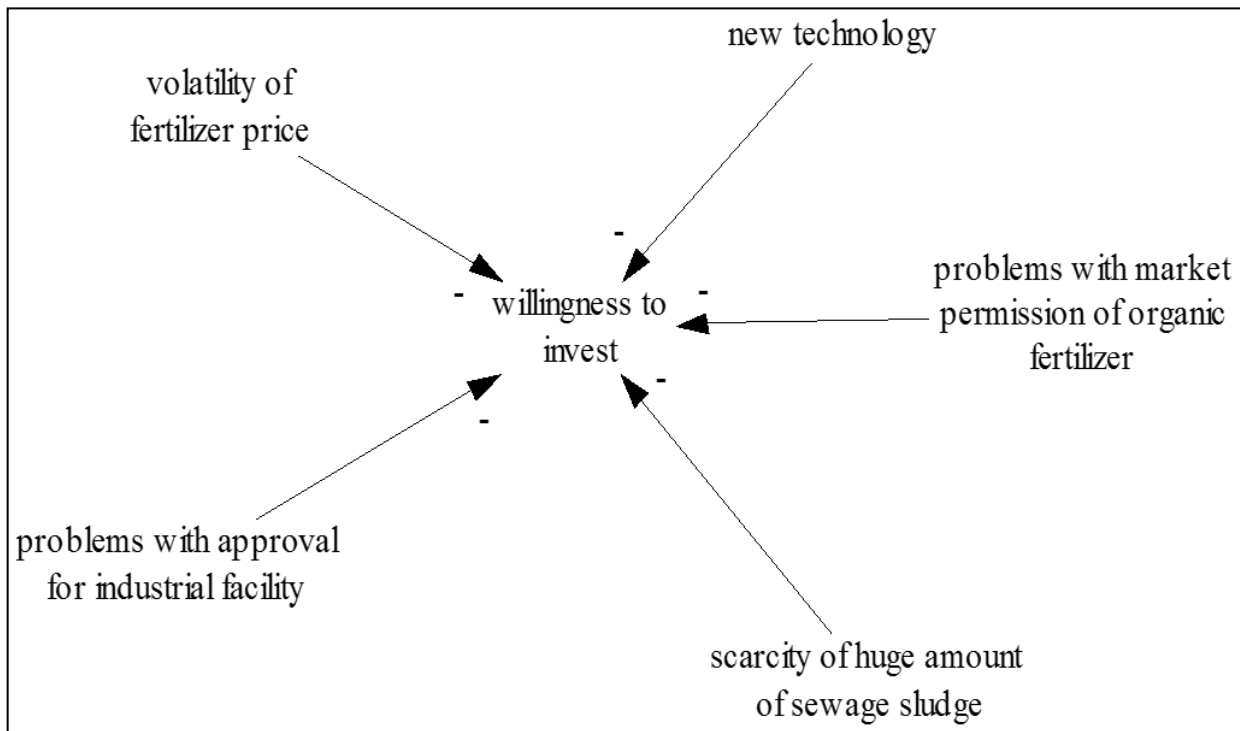


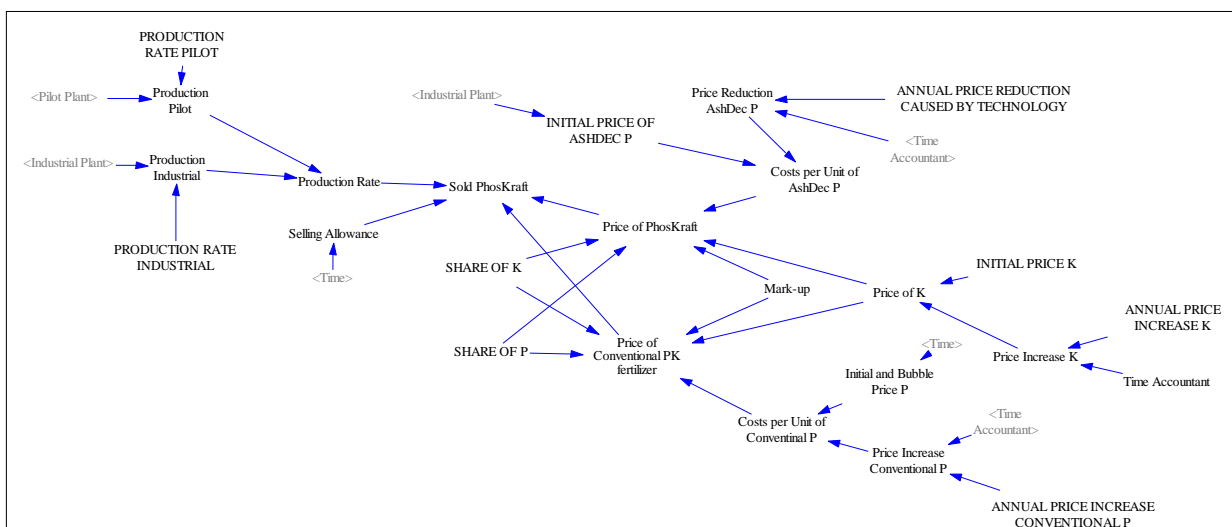*Figure 1:* A CLD-influenced thought model
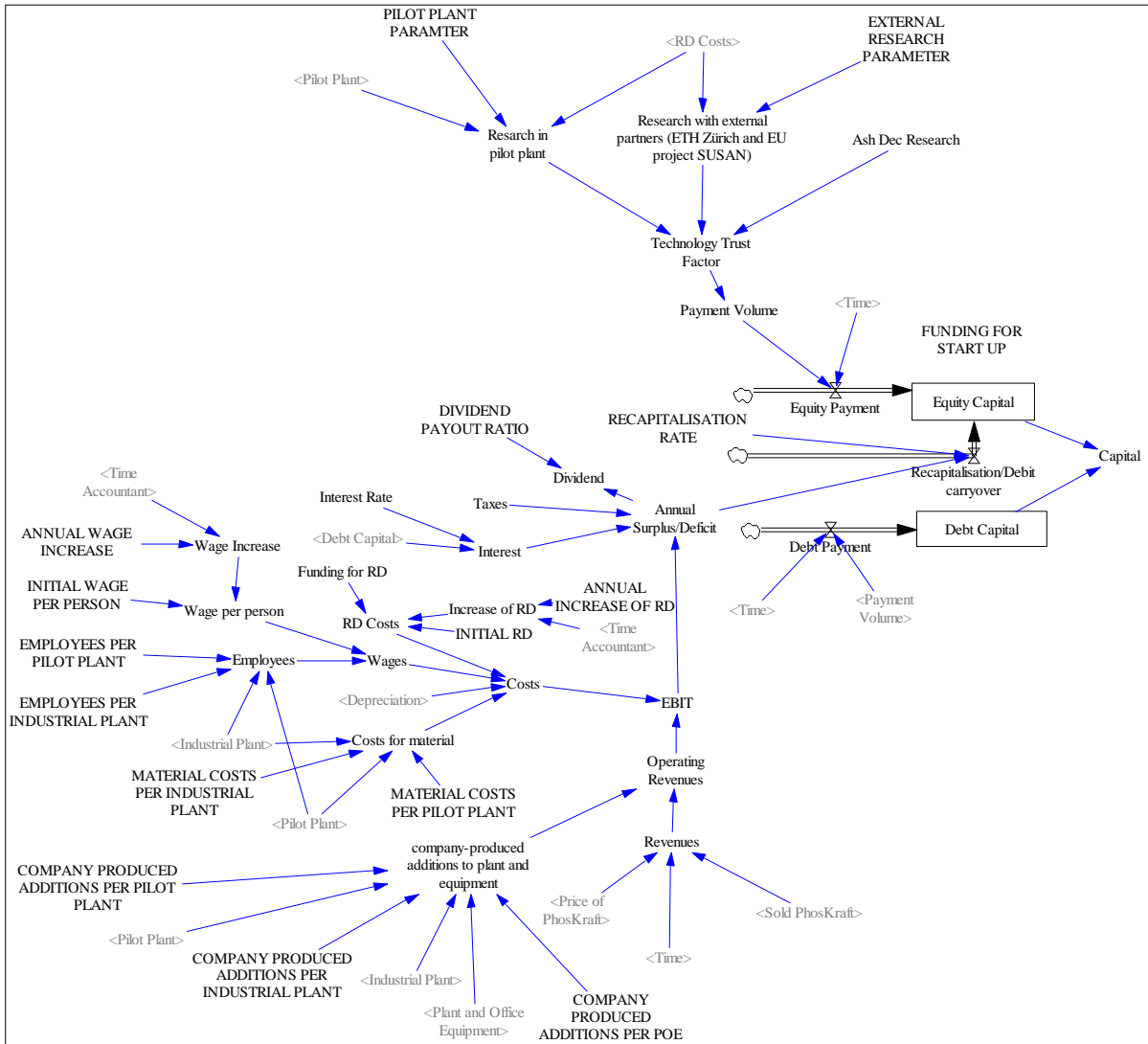


*Figure 2:* Vensim™-Model I: 'competition'

*Figure 3*: Vensim™-Model II: 'capital'



*Figure 4*: Vensim™-Model III: 'assets'

Mrotzek, Kreuzeder and Gössler (Eds.): Phosphorus
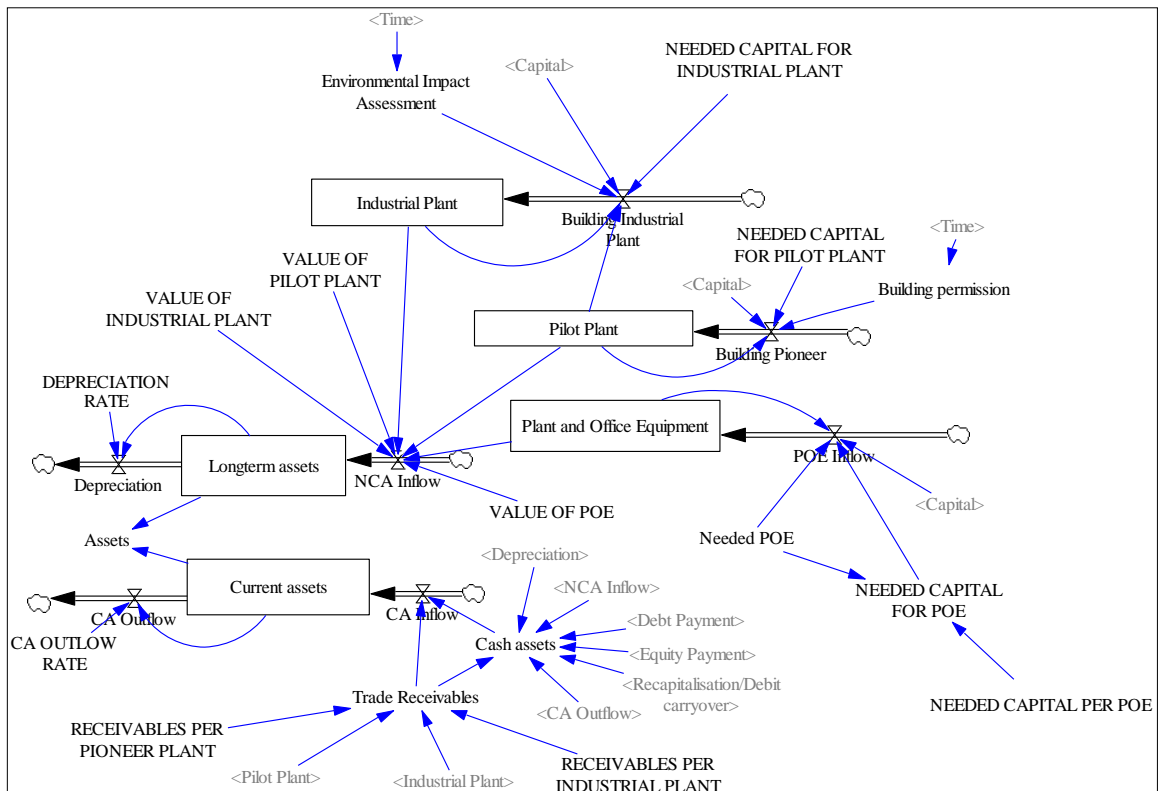
## B  Appendices

In the following data table (*Table 1*) the most important definitions of the variables and parameters, hence the elements of the model that was constructed with Vensim™PLE are presented.

The purpose is to show that our assumptions are well-thought-out and not plucked out of the air. In other words, literature and scientific background for our estimations is provided.

*List of Variables and Parameters*

| Name | Unit | Source/ Background |
|------|------|--------------------|
| Price Increase K (Potassium) | 1/Year | A rise in the price of Potassium (K) that is a nutrient in the PK 12/20 fertilizer is expected |
| Price Of K | Euro/kg | Calculation based on fixed retail price |
| Share Of K | 1/kg | [Ash-Dec Umwelt AG, 2008]; 20% Potassium-share in the PK12-20 fertilizer; K20 (Potassium Chloride or optionally P-Sulphate) |
| Share Of P | 1/kg | [Ash-Dec Umwelt AG, 2008]; 12% Phosphorus-share in the PK12-20 fertilizer; P205 as treated sewage sludge ash |
| Normal Price Increase P | 1/Year | [Sartorius, 2011] |
| Selling Allowance | dimensionless | [Annual Statements, 2004-2008];in 2004 the selling allowance for Austria; later for other countries |
| Production Rate Pilot Plant | kg/(Pilot Plant*Year) | assumption: 250.000 kg of fertilizer per year |
| Production Rate Industrial Plant | kg/(Industrial Plant*Year) | assumption: 100 times higher than the output of the pilot plant |
| Price Reduction caused by technological progress | 1/Year | [Sartorius, 2011]; reduction of 0.9795 per year |
| Costs per Unit of AshDec P | Euro/kg | [Sartorius, 2011]; estimations for production-costs for pilot and industrial plant; lower in the industrial plant |
| Needed Capital for Pilot Plant | Euro/Pilot Plant | [Annual Statements, 2004-2008]; about 1.3 million €, calculated: activated capital between that years |
| Needed Capital for Industrial Plant | Euro/Industrial Plant | [Sartorius, 2011] |
| Environmental Impact Assessment | dimensionless | estimated time delays |
| Depreciation Rate | 1/Year | [Annual Statements, 2004-2008]; depreciation of buildings and machinery (5 years), of „Geschäfts- und Betriebsmittel" (3 years), estimation: 0.3 |
| Funding For Start Up | Euro | [Ash-Dec Umwelt AG, 2008]; First deposit of 430,000 € |
| Technology Trust Factor | dimensionless | Estimated 1.7 million € are supplied if $> 7$, another 2 million € supplied if $> 10$ |
| Interest Rate | 1/Year | [Annual Statements, 2004-2008]; average interest rate of 3% throughout the years |
| Interest | Euro/year | amount of interest payments: Debt Capital*Interest Rate |
| Taxes | dimensionless | corporate tax in Austria: 25% |
| Funding for RD | Euro/Year | [Annual Statements, 2004-2008]; approximately 1 million € per year |
| Employees | Employee | estimation based on [Ash-Dec Umwelt AG, 2008]; start with 5 employees, doubling with the start-up of pilot plant; additional 5 employees needed for industrial plant |
| Wage Increase | 1/Year | estimated 1% net wage increase per annum |
| Material Costs Per Pilot Plant | Euro/(Pilot Plant*Year) | [Ash-Dec Umwelt AG, 2008];70,000 €; increase after plant commissioning |
| Material Costs Per Industrial Plant | Euro/(Industrial Plant*Year) | It is assumed that the industrial plant has a 100 times higher capacity than the pilot plant |
| Increase of RD | 1/Year | [Annual Statements, 2004-2008]; 0.11 per annum |

*Table 1*: List of the most important elements of the model

# 3. Closing Remarks

The Interdisciplinary Practical Training Courses on phosphorus was an interesting experience for the teachers. We were actually surprised by the quality of the students' work, especially considering the fact that they did not only work for this course but simultaneously had to do other course work, write their theses, or work part-time. We are very pleased with the final results and have already designed a course on "silver" for the summer term in 2013 following the same teaching methodology.

We recommend including this course setting of writing a paper in small groups and giving a peer review in the Interdisciplinary Practical Training Courses. We believe that students are compelled to tackle a problem more deeply if they can work in small groups. This allows to fully concentrate on the work while support from the supervisors can be much more specific and targeted. Moreover, students learn to write scientific papers and provide peer reviews, both of which are key competences they do not usually learn in other courses.

To conclude, we would like express our gratitude to the students, whose work is most sincerely appreciated.