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Final report for task 7 of the demonstration project "Sanitation Concepts for Separate Treatment of Urine, Faeces and Greywater " (SCST)

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Resource recovery and removal of pharmaceutical residues Treatment of separate collected urine

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η	dynamic viscosity
a^*,b^*	coordinates of CIE Lab system (specifying color)
AC	activated carbon
AOX	adsorbable organically bound halogens
AP	activity product
a_P	molar ratio of phosphate in desired product (precipitate)
a_s	molar ratio of Mg^{++} or Ca^{++} ions in the added precipitant
bn	billion
BWB	Berliner Wasserbetriebe
C^*	chroma in CIE Lab system (intensity of color)
C_0	initial concentration
C_d	detected concentration
cf	detected concentration factor
cf_{exp}	expected concentration factor
cf_{norm}	normalized concentration factor
CIE	Commission Internationale de l'Eclairage
CIE Lab	normalized color system of CIE
C_L,C_G	concentration of compound A in liquid and gas respectively [g/m^3]
C_M	concentration of substance X in mmol/l
COD	chemical oxygen demand
Conc	concentrate of evaporation process
Cond	condensate from steam stripping process
C_x	concentration of substance X as mg/l
DDD	defined daily dose
DF	dilution factor, resulting from steam condensed within the stripping column
Dist	distillate of evaporation process
G	friction velocity
H	Henry coefficient [gas mol fraction / liquid mol fraction]
H_C	Henry coefficient expressed in terms of volumetric concentrations [g/m^3 / g/m^3]
HSE	Hamburger Stadtentwässerung, meanwhile Hamburg Wasser (Hamburg water facilities)
k_{La}, k_{Ga}	global mass transfer coefficient for the liquid resp. gas phase [h^{-1}]
KETA	plant for sewage sludge de-watering and drying (KIärschlamm Enwässerungs und Trocknungsanlage)
KWB	KompetenzZentrum Wasser Berlin
L^*	lightness in CIE Lab system
LOD	limit of detection
LOQ	limit of quantification

M_s	molar weight of added precipitant as mg/mmol
m_s	amount of neede precipitant (mg)
M_x	mass of substance X for 1 mmol (mg/mmol)
N-depl	nitrogen depleted substrate from steam stripping process
nd	not detected
nm	not measured
NOX	nitrogen oxides
PhaR	pharmaceutical residues
rnc	removal efficiency not calculable
SCST	project 'sanitation concepts for the separate treatment of urine, faeces and greyweater
srf	stoichiometric rate factor
TN	total nitrogen
TP	total phosphorous
TS	total solids, dried solid contend (in German TR)
TUHH	Hamburg University of Technology
UVC	UV-light below 240 nm
V	volume
wwt	waste water treatment
x,y	mol fractions of compound A in liquid and gas phase respectively

Introduction

Within the EU-funded demonstration project 'Sanitation Concepts for the Separate Treatment of Urine, Faeces and Greyweater' (SCST), initiated, financed, and coordinated by Berlin Centre of Competence for Water (Kompetenzzentrum Wasser Berlin), Berliner Wasserbetriebe and Veolia Water the Institute of Wastewater Management and Water Protection of Hamburg University of Technology (TUHH) investigated processes for resource recovery and elimination of pharmaceutical residues from separate collected human urine.

The main processes for resource recovery were steam stripping for nitrogen extraction and vacuum evaporation for volume reduction and obtaining highly concentrated nutrient solutions. The processes precipitation, crystallization, and adsorption, were used for nutrient recovery as follow-up techniques. The effect of steam stripping and evaporation on the reduction of PhaR was investigated, as well as the effect of the additional processes UVC-radiation, ozonation.

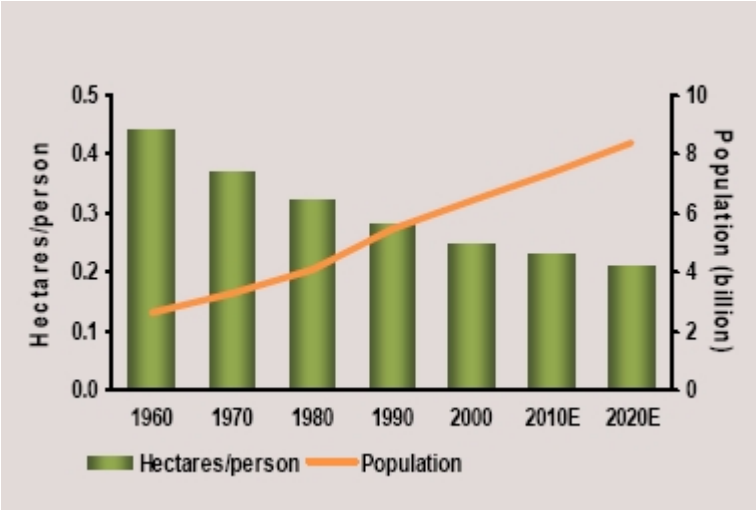
Background

Nutrients in wastewater, to a large amount emanated from human urine, have to be eliminated before being released to the aquatic environment, or as a more sustainable alternative they can be reused e.g. in agriculture. As a third and sustainable option for larger cities nutrients can be extracted and recovered in concentrated form for later use abroad.

The recovery of nutrients becomes interesting, since the value of fertilizers will increase due to the fact of limited phosphorous resources while world demand in fertilizer will rise in the coming years because of economical growth, and more important due to the constant population increase and thus a decrease of available arable land per person.

The reuse of nutrients contained in wastewater by spreading sewage sludge or separate collected urine onto fields can be an option in some areas. However, in many countries this is not allowed, mainly because of contamination of sludge with heavy metals respectively micropollutants such as pharmaceutical residues which are released to a large fraction via human urine into wastewater and the environment *[Larsen et al. 2004]*. Additionally for mega cities or larger cities where agricultural areas for application can only be found in a distance, the amounts of sludge or separate collected urine would be so large, that economical storage and transport to agricultural fields is questionable. Therefore, new approaches have to be found to reduce volumes of wastewater flows and to extract contained nutrients.

The separate collection and treatment of human urine might also allow a more specific treatment regarding pharmaceutical residues (PhaR). Already now, more and more PhaR are detected in surface, ground, and drinking water [*Daughton & Ternes 1999*], since nowadays wastewater treatment systems (wwt) are not designed to work as barrier against these. A large fraction of these micropollutants are released to the environment via urine. Thus, by finding treatment options for separate collected urine that eliminate these micropollutants, a great reduction of micropollutants in the environment could be achieved.



[*Yara & IFA 2006*]

Figure 1: Increasing population and reduced land availability for food production per capita

Nutrients

Nutrients such as nitrogen and phosphorous are essential for all forms of life. While the input in agriculture is used for increased crop production, nutrients in wastewater will lead to eutrophication of surface waters and to increasing deoxygenated areas -also called dead zones- in the costal areas of the oceans [*UNEP 2004*]. The nutrient flow is mainly linear from industrial fertilizer production for agriculture and food production over the consumer into the wastewater which is -after hopefully sufficient treatment- released to surface waters. Main focus in this study is on the nutrients nitrogen and phosphorous, being the ones with the largest fractions and the biggest impact in the environment.

In 1990, 60 % of all industrial fixed nitrogen was produced with the Haber Bosch process [*Galloway & Cowling 2002*]. Industrial nitrogen fixation does not deplete nitrogen resources but is very energy intensive. According to [*Patyk & Reinhardt 1997*] is the energy consumption for one metric ton of nitrogen fertilizer about 42 GJ/t N (11.7 kWh/kg N). In Germany the total energy consumption for production, transport and broadcasting of nitrogen fertilizer is about 49 GJ/t N (13.6 kWh/kg N)

It can be assumed that the world demand in fertilizer will increase in the coming years due to economical growth, leading -amongst others- to a change in diet (increased standard of living often leads to growing protein consumption per person, requiring more grain for animal feed), and even more important due to the population increase and thus a decrease of the available arable land per person, since almost no increase in farmable land is possible. At the same time the production of bio-fuels is becoming more and more a market, becoming additionally a competitor in arable land [*Yara & IFA 2006*]. An enormous factor, next to improved resource management, new crop varieties, and expanded agricultural knowledge are highly efficient fertilizers and also fertilizers affordable for people in low income countries to increase fertility of the available land.

Additionally to the demand of nitrogen in agriculture there is an increasing demand in pure ammonia and urea for industrial purposes such as plastic production and for combustion processes (e.g. waste incineration), where ammonia or urea is used for NO_X-removal of the off-gas (flue-gas).

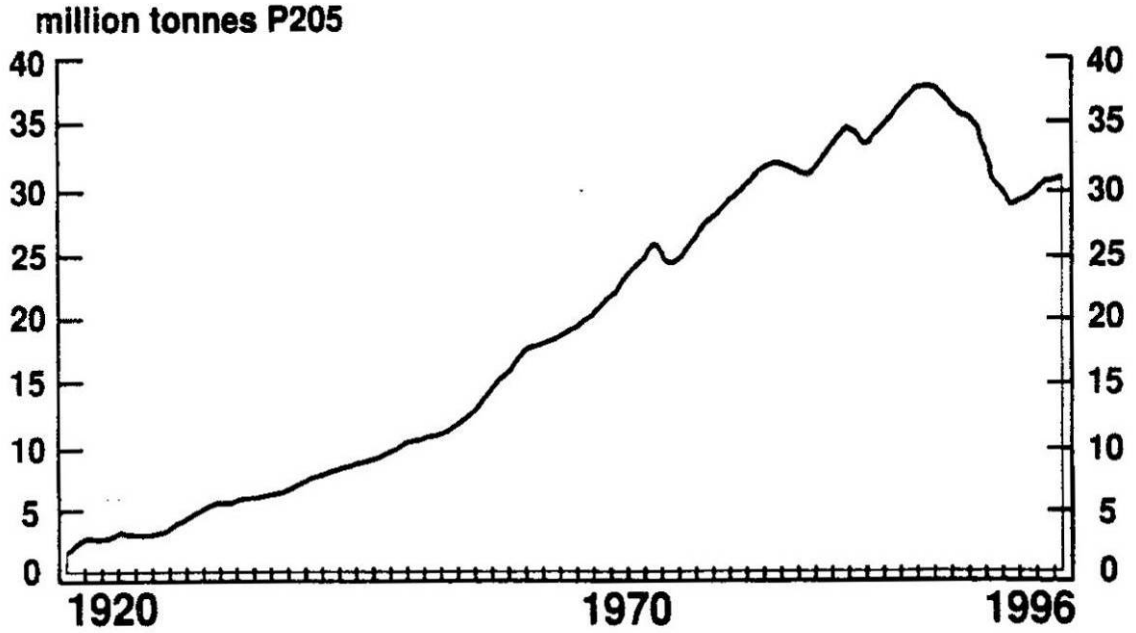
Next to the high energy demand for nitrogen synthesis resources in form of phosphorous and potassium for fertilizer production are limited. Especially for low income countries most mineral fertilizers are not affordable. On the other side urine has a high nitrogen content, and also high phosphorous and potassium contents, which make it a good source for fertilizer production. In Germany about 1.8 million tones of nitrogen are used in agriculture per year [*IFA 2005*]. The amount of nitrogen contained in human urine in Germany -if all urine was collected separately- would sum up to 20 % of this.

Phosphorus is the most valuable compound in urine, since depots of phosphorus are becoming scarce [*Udert, Larsen, & Gujer 2004*]. Yearly, around 38 million tones of phosphate (expressed as P_2O_5) are extracted worldwide [*Pinnekamp et al. 2003*]. The source for 'phosphorous-products' is so called phosphate rock, a general name given to natural calcium phosphates of various forms. The decrease of phosphate rock depots of good quality will induce an increase of phosphorus prices in the near future. The yearly consumption of phosphate rock is demonstrated in Figure 2. Phosphate consumption increased heavily until the nineties, following a slight decrease. The expected availability of phosphorous depots is depending on factors like growth of world population, trends in nutrition, land use patterns and on the definition of reserves, with is changing with the mining-techniques and processes.

Nevertheless the life expectation of phosphorous reserves is limited, according to [*Driver, Lijmbach, & Steen 1999*; *Pinnekamp et al. 2003*] to about one hundred years (Figure 3).

Phosphate usage in Western Europe can be divided in four categories [*Pinnekamp et al. 2003*].

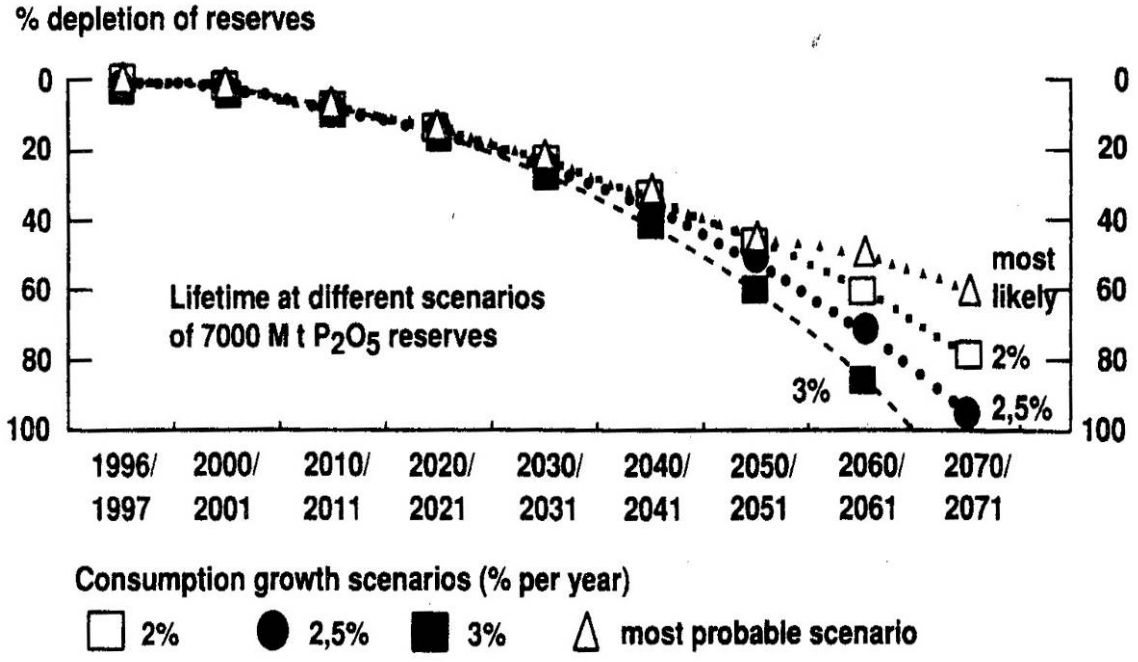
- 79 % for production of fertilizers
- 11 % fodder production
- 7 % washing and cleaning agents
- 3 % other industrial usage



[*Driver, Lijmbach, & Steen 1999*]

Figure 2: World phosphate rock consumption 1920 – 1995

Worldwide phosphate rock is mainly used for fertilizer production (about 80 %). Unfortunately, many phosphate reserves include contaminants. Most notable of these contaminants are cadmium, also uranium, nickel, chromium, copper and zinc. These metals are critical in the end products (fertilizers, detergent builders, food additives). The limits for cadmium content of sewage sludge for agricultural use is far more stringent than that applying to fertilizers. Thus, the content of heavy metals in sewage is mostly one or two orders of magnitude lower than those encountered in most commercial phosphate rocks [*Driver, Lijmbach, & Steen 1999*]. Due to high dilution of phosphorous in the raw wastewater recovery is normally done in high concentrated sludge streams [*Jardin & Pöpel 2001*; *Ueno & Fujii 2001*]. While nearly 50 % of all phosphorus in the municipal wastewater are coming from the urine fraction, urine adds nearly no heavy metals to it [*CIBA Geigy 1977*].



[*Driver, Lijmbach, & Steen 1999*]

Figure 3: Scenarios for lifetimes of phosphate rock reserves

If urine was collected and treated separately, not only resources could be recovered, also energy and land could be saved in conventional wastewater treatment plants that is normally required for removal of the high nitrogen and phosphorous content of urine [*Niederste-Hollenberg 2003*].

Pharmaceutical residues

In the last years more and more pharmaceutical residues (PhaR) were detected in surface, ground, and drinking waters [*Daughton & Ternes 1999*]. One of the main reasons is the low ability of today's conventional wastewater treatment to work as a barrier for PhaR [*Niederste-Hollenberg 2003*]. Residues are mainly released via the urine fraction, therefore implementation of alternative wastewater treatment like source separation systems are an option to reach systematic cleaning effects [*Larsen & Lienert 2004*; *Niederste-Hollenberg 2003*]. Before a reuse of nitrogen, phosphorus, and potassium by usage of urine as anthropogenic plant fertilizer can be recommended as safe solution the behaviour of PhaR during treatment and in the ecosystem soil needs to be clarified [*Larsen & Lienert 2004*; *Niederste-Hollenberg 2003*].

Pharmaceuticals are a very diverse group of chemicals. Also they change in types and amounts from year to year. Some substances were known for over 20 years to enter the environment as published by [*Garrison, Pope, & Allen 1976*; *Hignite & Azarnoff 1997*; *Norpoth et al. 1973*; *Tabak & Bruch 1970*]. Over time it became more aware to the public as chemical detection tools improved [*Daughton 2001*]. Hence, it took time until the degree of pollution by PhaR was realized. Additionally, yearly amounts of prescribed PhaR slightly increased in the last decade (29.5 bn DDD (= defined daily dose, [*CAS 2005*] in 1992 via 31.4

bn in 2003) [*Schwabe & Paffrath 2004*]. Due to this, potential concerns regarding PhaR in the environment increased and are summarized by [*Kolpin et al. 2002*]:

- abnormal physiological processes and reproductive impairment
- increased incidences of cancer
- development of antibiotic-resistant bacteria
- potential increased toxicity of chemical mixtures
- potential effects on humans and the aquatic environment just roughly understood.

In the year 2004 around 3000 active agents within 9000 medical products were used in health management [*Rote Liste® 2005*; *Schwabe & Paffrath 2004*]in Germany. Literature provides various approaches how to distinguish between hazardous and harmless substances. In general, it can be concluded a hazardous substance is persistent, bio-accumulating, and toxic [*Fitzke & Geißen 2007*] as well as very polar, what makes it harder to eliminate by classic wastewater treatment since polar molecules usually are very water soluble [*Heberer, Schmidt-Baeumler, & Stan 1998*; *Stackelberg et al. 2004*].

Thus, when it comes to elimination of pharmaceuticals via source separation systems the available treatment techniques have to be investigated in respect to urine for finding appropriate methods for PhaR removal respectively reduction.

Objective

The aim of a separate collection and treatment of urine is manifold.

The first step is to reduce and in a long term to avoid high nutrient loads in the wastewater. In areas with proper conventional wastewater management energy and space requirements of existing treatment plants can be reduced or used for optimized advanced treatment steps. In cases where functioning wastewater management is lacking, collecting urine separately can be a first step towards efficient nutrient management. In both cases accumulation of nutrients in surface waters can be reduced drastically and increasing formation of dead zones in the oceans can be avoided [*Gujer 2007*; *UNEP 2004*].

Next to reducing the accumulation in surface waters nutrients from separate collected urine shall be concentrated, extracted, and recovered to allow the production of marketable products for usage as fertilizer in agriculture or as resources for industrial processes. The direct use of urine instead of mineral fertilizer is an option in some areas and for some crops (e.g. production of plants used for energy production). However, often this option is limited due to constrains because of pharmaceutical residues contained in urine and due to socio-cultural reasons that cannot be disrespected.

Although not all consequences are fully understood regarding pharmaceutical residues released into the environment, the third objective of collecting and treating urine separately is to enable us to keep a large quantity of these problematic substances within a relatively small volume allowing appropriate and selective treatment.

Target products

In this study focus was on following different products obtained from separate collected urine.

The first target product is a concentrated nutrient solution, not only gaining the macronutrients nitrogen and phosphorous, but also the other nutrients, potassium and sulfur,

and additionally the trace elements, contained in urine. This concentrated nutrient solution could be source material for fertilizers or could be used as fertilizer itself. Other than in stored urine, pH should be in a neutral range towards acid conditions to avoid ammonia losses and odor nuisance. In case of direct use of the concentrated nutrient solution the product should be liquid and of low viscosity and free of pharmaceutical residues.

Next to a general concentration of all contained elements in urine extraction of nitrogen and phosphorous should lead to pure products such as ammonia water or different phosphate crystals (struvite and others). The products could be used directly in industry or agriculture or they could be considered raw material for other industrial or fertilizer products.

Since the questions of potential hazards from PhaR are not completely clear, from the current point of view all obtained products for use in agriculture should be free of pharmaceutical residues.

The value of a product is normally appointed by the market. For a new product or a product from 'new' resources a competition analysis with market analysis, consumer survey, competitor- and product analysis has to be conducted. This was not performed within this study. The costs for the obtained product can be derived from the energy demand for production which is given and discussed in each section.

Location, Material & Methods

Site description

The two plants in demonstration-scale, the unit for steam stripping of ammonia water from separate collected and stored urine and the evaporation unit for volume reduction and concentration of yellow water were set-up and operated at the wastewater treatment plant of Hamburg, Klärwerk Köhlbrandhöft, next to the plant for sewage sludge de-watering and drying (KETA). Infrastructure with water, electrical energy, and steam was provided by the Hamburg wastewater facility, Hamburg Wasser (former Hamburger Stadtentwässerung, HSE).

The evaporation unit was placed in a standard container, that was also used for storage of tools and supply. A four story scaffolding was erected as stand for the steam stripping reactor. For storage of untreated separate collected urine and for the processed urine 1 m^3 big-packs were used.

Picture 1: Demo site for urine treatment at Klärwerk Köhlbrandhöft, Hamburg

Substrates

Urine

Urine is the liquid excreta released over the kidneys. Physically it is an aqueous solution of numerous organic and inorganic substances. The composition of human urine can vary in a wide range. Factors like diet and habits influence the contained ingredients and concentrations as well as the change of the metabolism during daytimes and day and night. The usage of pharmaceuticals and hormones can also have an impact on the composition. Typical values of undiluted fresh urine are given in Table 1. More data from literature can be found in the appendix in Table 52.

Table 1: Typical concentrations of urine

	Daily average values from		**Typical Concentrations [mg/l]**		
	[*CIBA Geigy 1977*]	**[*Roempp 1997*]**	**derived from [*CIBA Geigy 1977*]**	**derived from [*Roempp 1997*]**	**Rink 1964, extracted from** [*von Wolffersdorff et al. 2004*]
Amount	1.25 l/d	1.5 l/d			1.25 - 1.5 l/d
pH	6.2	5.0 - 6.4			6.1
COD	15 000 mg/d		12 000		
Total-N	11 500 mg/d		9 200		9 150
Urea-N	9 600 mg/d	9 300 mg/d	7 700	6 200	7 700
Total P	1 200 mg/d		1 000		730 - 3 650
Total-S	1 300 mg/d		1 000		1 170 - 2 640
SO_4^{2-}-S	1 200 mg/d	2 400 mg/d	960	1 600	
Cl^-	4 800 mg/d	8 900 mg/d	3 800	5 930	4 400 - 6 600
K^+	2 700 mg/d	2 700 mg/d	2 200	1 800	1 833 - 6600
Na^+	5 200 mg/d	5 900 mg/d	4 200	3 930	2 933 - 4 400
Ca^{2+}	210 mg/d	500 mg/d	170	330	7.35 - 220
Mg^{2+}	120 mg/d	400 mg/d	100	270	126 - 209

Fresh urine from healthy persons contains hardly any micro-organisms [*Höglund 2001*]. During collection in separating toilets or waterless urinals, a contact with the enzyme urease will normally occur. Ubiquitous urease-positive bacteria, mainly growing in pipes are partially flushed into the collection tank [*Udert 2002*], where thereafter urea will be hydrolyzed into ammonia and bicarbonate within a little more than a day leading to an increase in pH. The hydrolysis of urea is also called ureolysis (Eq 1).

$$NH_2(CO)NH_2 + 2H_2O \rightarrow NH_3 + NH_4^+ + HCO_3^- \qquad \textbf{Eq 1}$$

The pH increase triggers the precipitation of struvite, hydroxylapatite and occasionally calcite [*Udert 2002*]. Also ammonia volatilization may occur during storage. Therefore,

stored urine has very different characteristics from fresh urine. A comparison of stored and fresh urine is given in Table 2.

Table 2: Reference values of fresh urine and stored urine.

		Fresh Urine	Stored Urine
Total Nitrogen	gN/m^3	9 200	9 200
Total Ammonia	gN/m^3	480	8 100
Urea	gN/m^3	7 700	0
Phosphate(1)	gP/m^3	740	540
Calcium	g/m^3	190	0
Magnesium	g/m^3	100	0
Potassium	g/m^3	2 200	2 200
Total Carbonate	gC/m^3	0	3200
Sulfate (2)	gSO_4/m^3	1 500	1 500
Chloride	g/m^3	3 800	3 800
Sodium	g/m^3	2 600	2 600
pH	-	6.2	9.1
Alkalinity	mM	22	490
COD	gO_2/m^3	10 000	10 000
Volume	l	1.25	1.25

(1) 95-100% of total phosphor

(2) about 90% of total sulfur

Note: Concentrations of fresh urine according to [*CIBA Geigy 1977*].
Concentrations of stored urine are derived from [*Udert 2002*]

As can be seen in Table 2 about 85% of nitrogen in fresh urine is present as urea, only 5% as total ammonia. The rest is organic nitrogen. After urea hydrolysis, total ammonia makes up to 90% of total nitrogen. This high ammonia concentration and the high pH can lead to ammonia volatilization during storage, transport or application. The equilibrium reaction between ammonium and ammonia can be described with following equation.

$$H^+ + NH_{3(aq)} \leftrightarrow NH_4^+ \qquad \textbf{Eq 2}$$

From Eq 2 the equilibrium constant k can be derived (Eq 3). This constant shows the ratio of ionogenic ammonia to dissociated ammonia, and is a function of temperature and pH.

$$k(T) = \frac{c[NH_4^+]}{c[NH_3] \times c[H^+]} \qquad \textbf{Eq 3}$$

An increase of pH and/or temperature moves this reaction to the side of ammonia ions in solution, as can be seen in Figure 4.

Additionally to the equilibrium between ammonium and ammonia in solution there is an equilibrium between ammonia in solution and ammonia in the surrounding gas phase:

$$NH_{3(aq)} \leftrightarrow NH_{3(gas)} \qquad \textbf{Eq 4}$$

The dynamic gas-liquid equilibrium does not mean that concentrations of the two phases become equal. It is the equality of chemical potentials that determines the state of equilibrium for each set of conditions of temperature and pressure. For dilute concentrations of most gases, the equilibrium-distribution curves can be described by Henrys law:

$$y = Hx \quad \text{or} \quad C_G = H_C * C_L \qquad \textbf{Eq 5}$$

with

x,y: mol fractions of compound A in liquid and gas phase respectively

H: Henry coefficient [gas mol fraction / liquid mol fraction]

C_L,C_G: concentration of compound A in liquid and gas respectively [g/m^3]

H_C: Henry coefficient expressed in terms of volumetric concentrations [g/m^3 / g/m^3]

Low values of H mean that at equilibrium with a small concentration of A in the gas phase will provide a large concentration in the liquid, meaning that compound A is very soluble in the liquid. High values of H mean compound A is not very soluble, but very volatile.

With lab experiments and model simulation the temperature dependency of the Henry coefficient for ammonia was derived. Data are given in Table 3 and Figure 50.

Table 3: Henry constant for ammonia in liquid-air at different temperatures

Temp [°C]	**H_c** [g/m^3 / g/m^3]	**1/H_c** [g/m^3 / g/m^3]
10	4,1 * 10^{-04}	2447
25	7,6 * 10^{-04}	1311
50	2,2 * 10^{-03}	463
75	6,1 * 10^{-03}	164
100	1,7 * 10^{-02}	58

Note:

Henry-coefficient for the system water/ammonium in dependency of the temperature (T in °C) function f = 3709.1*exp(-0.0416*T); extracted from [*Arevalo 2000*]

For the temperature range between 10 and 80 the Henry coefficient for ammonia is exponentially. This one of the main points, that makes the steam-stripping quite efficient compared to an air-stripping process.

The mass transfer can be described by global mass transfer coefficients

$$J = k_{La}\left(\left(1/H_C\right)C_G - C_L\right) \qquad \textbf{Eq 6}$$

$$J = k_{Ga}\left(C_G - H_C C_L\right) \qquad \textbf{Eq 7}$$

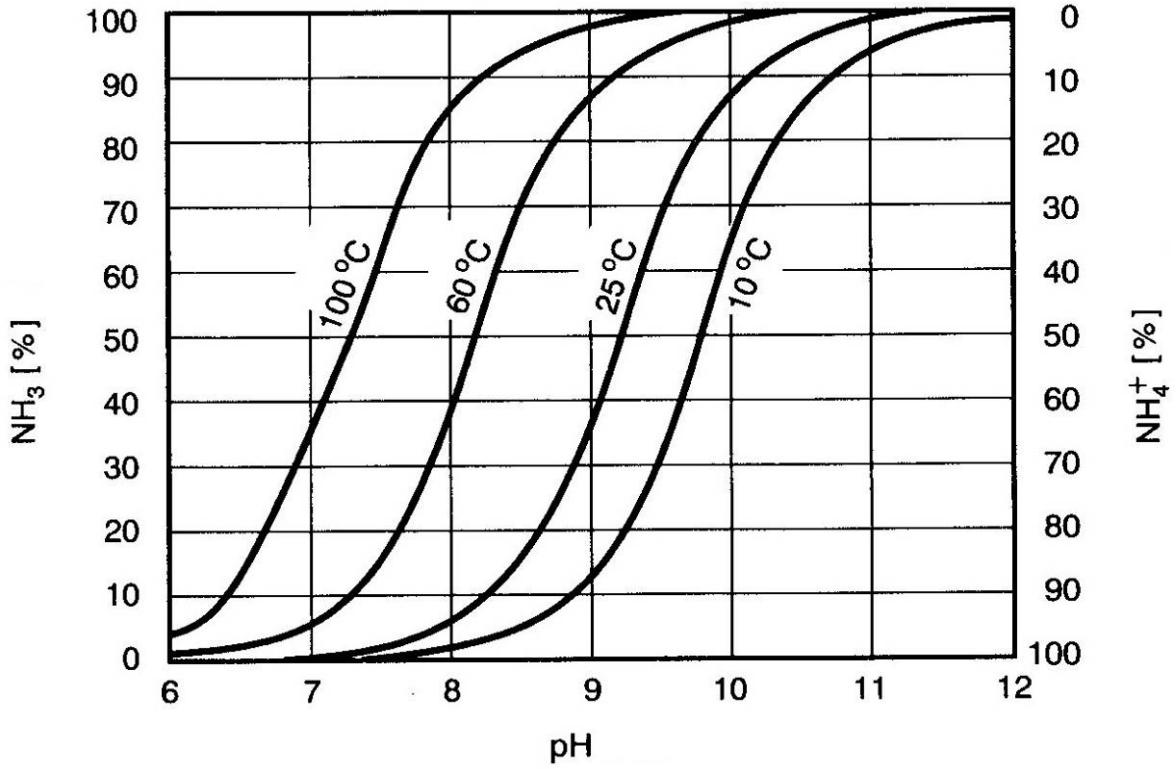
with

J: mass flow of A in the liquid or in the gas phase [g/m^{3}h]

k_{La}: global mass transfer coefficient for the liquid phase [h^{-1}]

k_{Ga}: global mass transfer coefficient for the gas phase [h^{-1}]

Since ammonia is volatile substantial losses of ammonia connected with odor problems can be expected at high pH. However, research shows that the loss of ammonia is marginal in closed storage [*Fittschen & Hahn 1998*].



[Meierer 1995]

Figure 4: Ammonia –Ammonium equilibrium dependent on pH and temperature

If separate collected urine is supposed to be transported in a sewer system volatilization of ammonia will be noticeable but still low. According to a test done by Buri and Schildknecht (1998) cited by [Udert 2002] , in a straight 2 km sewer the losses of ammonia at pH 9 and 15°C were 2% per hour. This low value may be acceptable for urine transportation, but it should be noted that a dramatic odor problem can occur. This problem can be solved by pre-treatment of urine, like pre-acidification, by stripping or bio-treatment.

The urea hydrolysis increases also the buffer capacity of the stored urine. The main buffering compounds are bicarbonate and ammonia. This high buffer capacity has a strong effect on the further treatment and application of urine. The direct usage of urine in the agricultural soils may affect the bacterial nitrification and cause nitrite accumulation in soils [*Burns et al. 1995*]. In most cases acidification of stored urine will be not be economically

feasible. But by extraction of ammonia e.g. via stripping buffer capacity and pH will be lowered again.

In fresh urine phosphorus can be found between 95 to 100% in dissolved form [*CIBA Geigy 1977*]. During storage of urine some phosphate will precipitate. This process is strongly dependent on the concentration of the cations calcium and magnesium which are the limiting factor for this process. Also potassium is affected to a small extend by precipitation during storage, since potassium can substitute ammonium in struvite [*Lind, Ban, & Byden 2000*]. Since ammonia concentration is much higher than the potassium concentration and since the magnesium concentration is the limiting factor, the loss of potassium can be neglected. The loss of potassium due to its substitution in hydroxylapatite is also presumably negligible [*Udert 2002*].

90% of sulfur in urine is present as sulfate. The rest are esters of sulfuric acid and neutral sulfur compounds [*CIBA Geigy 1977*]. Sulfate can be reduced biologically. Since elemental oxygen, nitrate and nitrite are missing and the iron concentration is very low, sulfate is the most favorable electron acceptor in stored urine. From this biological reaction hydrogen sulfide H_2S is produced.

Urine has a high COD of about 10 g COD/l. 85% of this COD is easily biodegradable. The main organic compounds are acids, creatinine, amino acids, carbon hydrates and urea [*CIBA Geigy 1977*]. Biological degradation may occur in storage tanks, if urine gets in contact with anaerobic micro-organism. Also fermenters may grow in urine. But methanogenic bacteria are likely to be inhibited by the high ammonia concentration [*Udert 2002*].

In stored urine precipitates of organic compounds can be found as well. According to [*Höglund 2001*] the concentration of organics in sedimented fraction of urine is substantially higher than the dissolved part of urine.

Micropollutants, here focus was on pharmaceutical residues can be contained in urine. Details about concentrations can be found in the chapter for pharmaceutical residues.

The contamination of urine with transmissible pathogens is mainly cross-contaminated from faeces [*Schönning, Leeming, & Stenström 2002*]. Most micro-organisms die-off during urine storage. Pathogens should not be able to multiply in the alkaline environment with high concentration of salts and ammonia. [*Höglund et al. 1998*].

Stored urine

Urine from two different sources was processed throughout the project.

One of the substrates was urine from a public toilet for males at Hansaplatz in Hamburg, Germany (Picture 2). The urinal is used by ~100 - 200 people per day. The urine is stored in an underground storage tank. Twice a month the stored urine is collected and transported by a honey sucker to the wastewater treatment plant Köhlbrandhöft in Hamburg.

Picture 2: Public Urinal at Hansaplatz in Hamburg, Germany. Foto: Groenwall, BSU

The urinal was installed by the city of Hamburg, namely Behörde für Stadtentwicklung und Umwelt (BSU). Cleaning and maintenance is done by a subcontractor. Collection and treatment is proceeded by Hamburg Wasser (former Hamburger Stadtentwässerung, HSE).

Substrate was received in March '05 and August '05. In Table 4 mean values of three randomly taken samples are presented.

The values were compared to values from literature (see Table 52). The found concentrations of macronutrients were about 30 and 50 % lower than literature values. It has to be noted, that values of substances of content given in medical literature usually represent the average of a 24 h sample. In the public urinal only a fraction of the 'total urine per day' is captured. For example, most likely there is little 'morning-urine' contained, which is supposed to have the highest nutrient concentrations. Additionally it can be assumed, that people drinking more, with a more diluted urine, are more tended to use a public urinal.

Even higher discrepancies could be found within the content of metals. Copper was by a factor 1 000 higher than stated in [*CIBA Geigy 1977*]. Nickel values were 70 times higher, iron 15 times, zinc, lead and chromium were 6 to 8 times higher than the values stated in above mentioned literature. Some of these high concentrations might be due to metals contained in drinking water pipes, or materials used in the set up or in the tank of the public toilet. Also diet plays a great role. Copper is used to a large extend in beverage production. Other metal elements are used as preservatives in food production. Gallium is rather unusually to be found in drinking water, but is commonly used in x-ray- contrast-substances.

The main part of organic acids, which are specially in the evaporation process of higher interest, were acetic acid and propionic acid.

Table 4: Urine from a public waterless urinal used by males at Hansaplatz, Hamburg, collected May 2005

pH		8.9
Conductivity	mS/cm	18 - 23
dry residue	g/l	30

TOC	mg/l	3 400
TC	mg/l	5 500
COD	mg/l	4 300

N-total	mg/l	4 300
P	mg/l	408
K^+	mg/l	1 360
Na^+	mg/l	2 085
Ca^{2+}	mg/l	5.7 - 8.6
Mg^{2+}	mg/l	0.1 - 0.3
Fe^{2+}	mg/l	1.2 - 2.3
Cu	mg/l	25.4
Zn	mg/l	3.9
Cd	µg/l	< 1
Ni	µg/l	166
Pb	µg/l	131
Ga	µg/l	15
Cr	µg/l	39

F^-	mg/l	110
Cl^-	mg/l	3 430
PO_4^{3-}	mg/l	1 250
SO_4^{2-}	mg/l	2 490
NO_2^-	mg/l	< 1
NO_3^-	mg/l	< 1

acetic acid	mg/l	1 660
propionic acid	mg/l	105
iso- butyric acid	mg/l	30
n- butyric acid	mg/l	< 4
iso- valeric acid.	mg/l	40
n- valeric acid	mg/l	< 2
caproic acid	mg/l	< 2

Note: Mean values of three samples. For values outside the 95% confidence interval the range was given.

The other substrate that was processed within this project was urine from the separating system of the Berliner Wasserbetriebe (BWB) from Klärwerk Stahnsdorf. At the time of collection the office building was fitted with waterless urinals of different systems and separating vacuum toilets, a modified Roediger separating toilet. At the building about 20 people were constantly working. Also meetings and seminars took place, that increased the number of contributors. Substrate was received in November '05 and March '06. Exemplary data are given in Table 5.

Again, most received values were 30 to 50 % lower than literature values. And again it can be assumed that the capture of only one fraction of the daily urine of a small population group leads to lower concentrations. At the same time, in this case it cannot be excluded that flushing water from the vacuum separating toilets was also captured, leading to dilution of the urine.

Table 5: Urine from the separating system Klärwerk Stahnsdorf, Berlin, Germany, collected Oktober May 2005.

pH		8.8
Conductivity	mS/cm	33.2
dry residue	g/l	18
COD	mg O_2/l	5 350
TN	mg/l	4 200
TP	mg/l	380
K^+	mg/l	1 200
Mg^{2+}	mg/l	8.4
Fe^{2+}	mg/l	9.5
SO_4^{2-}	mg/l	1 213

Note: Mean values of three samples

Processed urine

Beside of stored urine, also the products from the semi-technical plants were further treated.

The ammonia-depleted urine from the steam stripping which is also referred to as N-depleted urine was further processed by evaporation, crystallization, precipitation, adsorption, UVC-radiation and ozonation.

The concentrates from the evaporation step were further treated by crystallization, precipitation, and adsorption. More details can be found in these chapters.

Analytics

Since urine has a very complex matrix and a certain composition change depending on the source, the analytical methods have to be selected carefully. Some test kits, which are suitable for household wastewater, fail on the measurement of urine because of its matrix.

Ammonia

The analysis of ammonia was performed by using distillation and titration (Büchi 321; Distillation Unit, Dargatz). The method has three main steps: distillation, absorption in acidic solution (H_2SO_4) and titration with a base (NaOH). The advantage of this method is that since ammonia is distilled and caught in another solution, the complex salt matrix of urine cannot interfere with the measurement. Urea is also caught with this method as ammonia. Especially for fresh urine this has to be noted. Since in this work stored urine was used, it can be assumed that all the urea is already converted to ammonia.

In some of the first sets of the experimental part ammonia analysis was performed using test kits of Dr. Lange. These kits could not measure ammonia in the samples satisfyingly. Also the attempt to measure the ammonia content with stick tests did not bring any acceptable results.

Phosphate

Phosphate concentration was measured by Dr. Lange Cuvette-tests. For most of the measurement the test kit LCK 350 was used. Here total phosphor or phosphate concentration is analyzed by a photometric method. The control by the TUHH central lab using PE-Optima 2000 DV OES with ICP showed that the results of this test kit were in an acceptable range.

In the experimental start phase also a Dr. Lange test kit LCK 049 was used. The obtained results were significantly higher than the ICP-values. Also the accuracy of stick tests was tested. The analytical results did not show constant or comparable values.

Color

To evaluate color as an indicator for the removal of PhaR during ozonation and UVC-radiation the transmitted spectral light of urine was measured by spectrophotographyand expressed according to the CIELab-system. In cylindrical coordinates chroma C^*_{ab} describes the intensity, the hue angle h_{ab} the color itself, while L^* stands for lightness. An increase of the color intensity will lead to a decrease of lightness. Equivalent, the calculated value of the color can increase, when lightness is decreasing.

Urine absorbs the violet/blue part of the spectral light because of the energy absorption of the conjugated π-electron system from the two middle pyrrol-rings of urobilin. The angle hue is changing only to a very small extend. L^* is affected strongly by turbidity. An increase of turbidity leads to a decreasing lightness. In this study turbidity related to color is expressed as the difference between absolute lightness ($L^* = 100$) and the relative lightness L^*. A correlation with standard turbidity measurements was not conducted.

The factor that is describing the intensity of color is chroma C^*. Concentrated fresh urine has a chroma of about $C^* = 20$. At a dilution of 1 : 10 slight yellow color was still

detectable by eye sight (C^* = 3). A dilution of 1 : 20 led to C^* = 1, where no yellow color was detectable by eye sight.

The spectral curve, needed for colour evaluation, was measured by using a Jasco spectro¬photometer V-550.

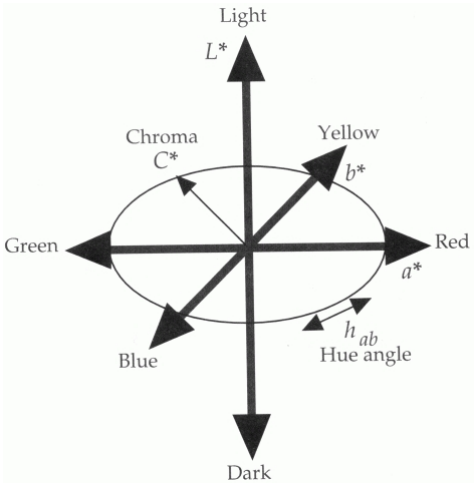


Figure 5: CIE-Lab system

Other Parameters

- TN: Dr.Lange Cuvette tests LCK338 (20-100 mg/l TN)
- TOC, TC: Autoanalyzer Analytic Jena
- COD: Dr.Lange Cuvette tests LCK114 (150-1000 mg/l)
- Fe^{+2} / Fe^{+3}: Dr.Lange Cuvette tests LCK320 (0.2-6.0 mg/l)
- SO4: Dr.Lange Cuvette tests LCK153 (40-150 mg/l)
- Mg^{+2}: Dr.Lange Cuvette tests LCK326 (0,5-50 mg/l)
- NO^{-3}: Dr.Lange Cuvette tests LCK340 (5-35 mg/l NO3-N)
- K: Dr. Lange Cuvette test LCK328 (depending on the analysis results by different dilutions, this kit did not bring acceptable results)
- TS (total solids): according to [*APHA, AWWA, & WEF 2005*]
- AOX: according to DIN EN ISO 9562, AOX - System M 2000 C
- BTEX: Headspace-gaschromatography PE Turbomatrix 40 Trap

- quantification of Na, K, Ca, Mg, P, Cu, Zn, Fe, N_{tot}, and trace elements
  PE Elan DRC II ICP-MS
  PE-Optima 2000 DV OES with ICP
  PE SIMAA AAS
- carboxylic acid and anions:
  Dionex-ionchromatography

Laboratory Equipment

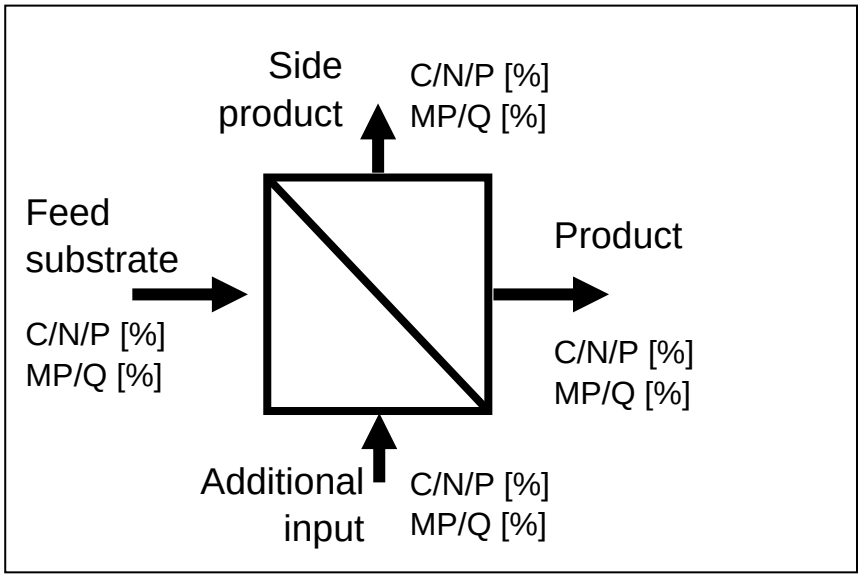
- pH: pH-electrodes for wastewater. WTW Microprocessor pH Meter pH 196
- Conductivity: WTW Conductometer LF 191
- Ammonia: Büchi 321; Distillation Unit, Dargatz
- Jar Test: with mixing speed regulation (100-1600 rpm)

Pharmaceutical Residues

All analyses regarding pharmaceutical residues were conducted by IWW Rheinisch-westfälisches Institut für Wasser Beratungs- und Entwicklungsgesellschaft mbH using HPLC-MS [*Butzen, Werres, & Balsaa 2005*].

General description of urine treatment processes

To each process a general description is given in the resuming conclusions of that process. This description is according to [*Maurer, Pronk, & Larsen 2006*]. The idea is to present all relevant flows in one simple scheme.



[*Maurer, Pronk, & Larsen 2006*]

Figure 6: General template for description of processes for urine treatment

The feed substrate in this report is either undiluted stored urine or N-depleted urine from the steam stripping process. Additional inputs are chemicals or energy, as far as relevant. In all processes one main product is obtained. At the same time normally a side product is produced that might need further treatment. The figures for carbon (C), nitrogen (N), phosphorous (P), micropollutants (MP, in this report representing PhaR), and volume flow (Q) are percentage of the input. They represent obtained results respectively data from literature where necessary. Especially in the case of PhaR only summarized quantitative numbers can be presented. More detailed information can be found in the chapter 'reduction/removal of pharmaceutical residues' of this report at the individual process description.

For statements regarding energy consumption the obtained values were compared to numbers from literature.

Processes for resource recovery

Steam stripping

Although nitrogen is not a limited resource, N-recovery from urine is economically useful in two ways. Energy and space requirements needed in conventional wwtp for nitrogen removal can be reduced drastically [*Maurer, Schwegler, & Larsen 2003*], since up to 70% of nitrogen in common wastewater stems from urine [*Otterpohl 2001*]. At the same time the production of nitrogen fertilizers doubles the number of energy consumption per kg treated nitrogen [*Niederste-Hollenberg 2003*].

In fresh urine nitrogen is present mainly in form of urea. Without any special treatment urea will be hydrolyzed within only a little more than a day into ammonia and bicarbonate, accompanied by an increase of pH. More details on the hydrolysis of urea and ammonia/ammonium equilibrium can be found in chapter 'Stored urine'.

General process description

Steam stripping is a thermal separation process in which heated wastewater is put in intimate contact with steam in a packed tower. The combined effects of the steam and heat, or temperature cause volatile ammonia (or organic material) to transfer from the liquid to the vapour phase. This material is then carried out with the vapour. As contacting proceeds down the tower, the wastewater becomes leaner in ammonia while the vapour phase becomes more enriched as it travels up the tower.

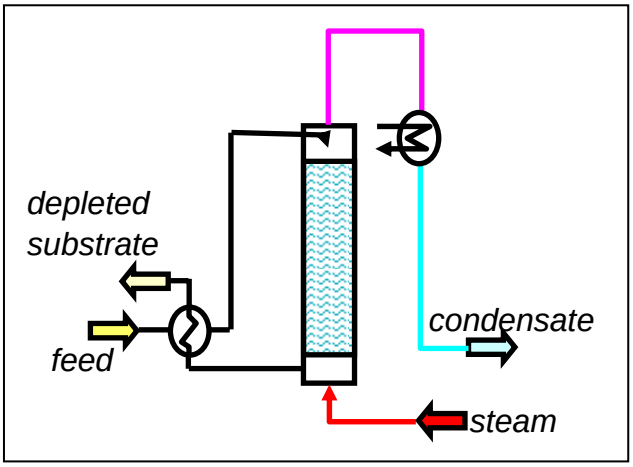
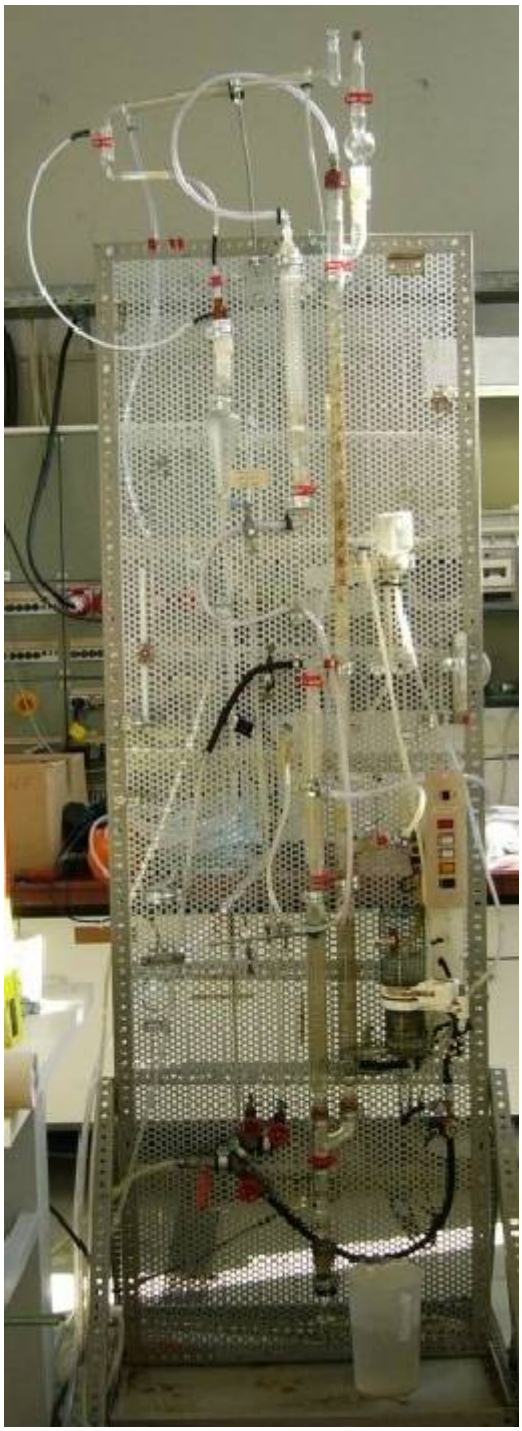


Figure 7: Scheme of steam stripping unit

Steam is normally injected at the bottom of the tower to provide heat and vapour flow. Depleted wastewater leaves the bottom of the tower. The wastewater is fed at the top of the tower and steam leaves the top heavily laden with ammonia. This steam/ammonia combination is condensed and can be processed further. While the wastewater is depleted from ammonia, a low-volume but concentrated water/ammonia solution is obtained as product.

Ammonia stripping in laboratory scale

Prior to operation of the large scale stripping unit a small steam stripping unit was used to gain first experiences regarding ammonia extraction from yellow water. The operating data were used at the large scale steam stripping process for progress enhancement.



Picture 3: Steam stripping in lab scale

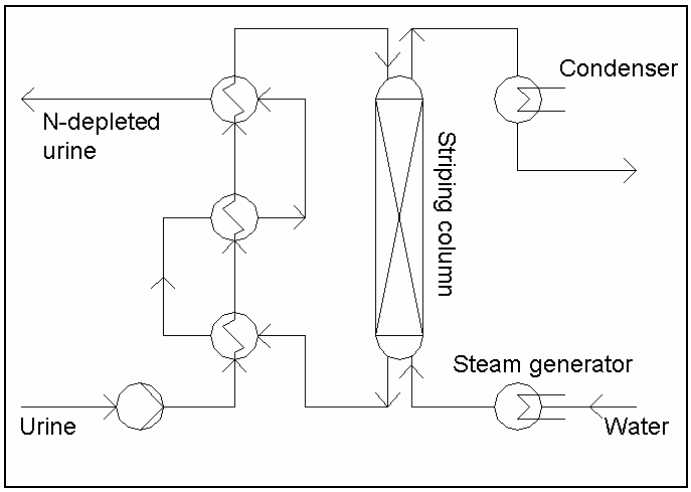


Figure 8: Scheme of steam stripping in lab scale

Reactor volume of the small steam stripping unit was 2 l (h=1.5m, D=2.5cm, filled volume: 2/3). Steam was generated at atmospheric pressure and a temperature of 100°C. Steam quantity could be adjusted between 0.2 and 0.9 kg/h. The volume of yellow water in the stripping reactor was 0.5 l.

During operation, the inflow of steam into the urine filled reactor caused a heavy foam production. Foam driven above the yellow water intake led to contamination of the condensed ammonia enriched steam. Since no mechanical foam destruction device could be implemented, a silicon based defoamer was used, applied to the urine inlet and the upper part of the stripping unit.

The steam was also used to heat up the substrate, thus the ammonia depleted substrate was also diluted by condensed water from the steam within the reactor.

Following parameter were varied:

Table 6: Parameters varied in lab scale steam stripping

Substrate	NH_3-solution, urine
pH	pH of feed urine was varied between 8.2 and 11.6
Temperature	Temperature of feed urine was varied between 20°C and 90°C

Steam stripping pilot plant

The steam stripping unit in pilot scale was set up at a place at the wastewater treatment plant in Hamburg, Klärwerk Köhlbrandhöft.

The stripping tower was manufactured from stainless steal at the metal building shop at TUHH. The column was 4.80 m high, and could be segmented into 5 parts: 1x connecting piece for urine input and steam exhaust, 1x socket for depleted urine outlet and steam intake, and 3 reactor tubes.

Connecting sockets and perforated plate

15 mm pall rings, filling for stripping unit

Reactor tubes for steam stripping unit

Picture 4, Picture 5, Picture 6: Parts of demo-size stripping reactor

The filling material for reaction surface extension was consisting in 15 mm metal pall rings with a surface of 360 m^2/m^3, and a free volume of 95 %.

For heat insulation mineral wool was used, protected by a cover of zinc plates.

The stripping tower was erected within a four story scaffolding.

Picture 7: Demo scale stripping unit in scaffolding on the right side of the container. Feed substrate in 1 m^3 big-packs on the left side of container

Heat exchange

Because of the high salt concentration of urine and the possibility of precipitation at higher temperatures, a tube bundle heat exchanger would be technically the best choice. Because of high expenditure in manufacturing tube bundle heat exchangers costs were too high for this demonstration project. Therefore a FeRo plate heat exchanging unit with 37 panels and a surface area of 2.94 m^2 was used.

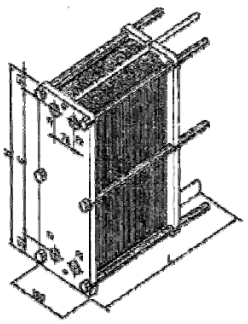


Figure 9: FeRo plate heat exchanger

Condenser

As a condenser a single tube condenser was built, which was installed next to the stripping column. Hot steam from the head of the stripping column entered the condenser from top, while service water was used in a cross flow to cool down the steam. The condensate was captured at the bottom of the condenser. The heat exchanging surface was 0.47 m^2. Maximum flow of cooling service water was 300 l/h.

Energy, water, steam

Electric energy, steam and process water was provided by HSE. Steam was available at 6 bar and a temperature of 160°C. Measuring of the steam quantity was conducted by volumetric measurement of the condensed off steam, and fraction comparison of the in- and outlet streams.

Procedure

Operation procedure of both, the lab scale plant and the pilot plant were quite similar. In the following the operation procedure of the pilot scale plant is described.

Urine was pumped by a spiral pump from the storage tank (feed container) through a flow meter and the heat exchanger into the column inlet at a height of 5.60 m. From the column sump the depleted urine flowed by gravity through the heat exchanging unit and a second flow meter into the collection tank for the N-depleted substrate. The filling height in the reactor was controlled by a visible tube outside of the reactor connected to the head and the sump of the column. The filling height could be adjusted by an overflow -variable in height- that was placed right after the outlet flow meter.

Residence time within the stripping column was about 15 min.

Steam was regulated by a regulation valve and introduced at the bottom of the column. The loaded off steam was removed at the head of the column and send through a condenser. The condensate was captured at the bottom of the condenser in a 1 l measuring cylinder. Samples from the condensate were taken directly from the condenser. The energy from the condensing process was not integrated in the process.

Picture 8: Steam valve of steam stripping plant in demo-size

At the beginning of each run 0.5l of a silicon based defoamer were added to the substrate. The N-depleted substrate was collected in a 1 m^3 Container, the condensate was collected in a 1 l measuring cylinder respectively collected directly in sampling bottles.

Temperature was measured on the outside of the steal cover of the stripping tower at the height of steam inlet, and at the height of the substrate inflow.

Several process sets were conducted, while different parameters were varied.

Table 7: Varied parameters during steam stripping in pilot scale

varied parameters	Inflow	70 - 110 l/h
	Steam flow	15 - 35 kg/h
	pH-value of initial substrate	8.5 - 11

Prior to the sets with elevated pH in the initial stored urine, pH was increase by adding NaOH respectively KOH into the feed container.

Samples were taken from the inflow from the feed container, from the N-depleted substrate directly from the outflow, and from the condensate directly from the condensate outflow. Volume and time were recorded in constant intervals, the samples were analyzed regarding to pH, TN, NH_4, and TP. Additionally spot samples were analyzed regarding SO_4, K and COD.

In total a volume of 2.5 m^3 was processed in several sets. In each set the plant was operated after a heat-up phase of 30 to 45 min. between 2 and 4 h. At times, more than one set was conducted in a row. Thus the maximum operation time of the plant was 8h/d. After

reaching a stable flow of condensate samples of condensate and N-depleted substrate were taken in intervals of 15 or 30 min.. Values given below are generally average values.

Since there was no device for steam-flow measurement, the equivalent of the liquified (completely condensed) volume of the steam per time (Q^{eq}_{steam}) was derived from the mass balance of the measured flow of substrate feed (Q_{feed}), the outflow of the N-depleted substrate (Q_{depl}), and the volume per time of condensate (Q_{cond}).

$$Q_{feed} + Q^{eq}_{steam} = Q_{cond} + Q_{depl} \qquad \textbf{Eq 8}$$

The amount of steam condensed within the reactor can be derived from

$$Q_{reactor} = Q_{depl} - Q_{feed} \qquad \textbf{Eq 9}$$

from the steam condensed within the stripping column the dilution factor (DF) can be expressed as

$$DF = \frac{Q_{feed}}{Q_{depl}} \qquad \textbf{Eq 10}$$

Results

Ammonia stripping in laboratory scale

In the small stripping unit pH and temperature of the feed substrate were varied. The ratio between Q_{feed} and Q^{eq}_{steam} was varied between 0.3 and 2.2. In all cases ammonia analytics was performed by using stick tests. Each sample was measured 2 times. In case of a deviation of more than 10 % a third measurement was conducted. The average NH_3-concentration of the feed substrate was 4.7 g/l.

Table 8: Results of lab scale steam stripping, sorted regarding highest NH_3-concentration in condensate

Q_{feed} [l/h]	Q^{eq}_{steam} [l/h]	Q_{feed}/Q^{eq}_{steam} [-]	c_{NH3} cond [g/l]	c_{NH3} depl urine [g/l]	reduct [1 [%]	pH $_{feed}$ [-]	temp $_{feed}$ [2
0,48	0,85	0,56	2,96	0,18	94,6	8,9	
0,51	1,41	0,36	2,93	0,13	96,8	8,9	
1,08	1,13	0,96	5,9	0,74	83,3	11	
0,34	0,99	0,34	1,34	1,41	73,5	11,2	
0,37	1,29	0,29	1,6	0,38	92,4	11,4	
1,61	0,74	2,18	8,44	1,36	74,8	11,6	
0,51	1,01	0,5	3,46	0,74	87,9	8,2	x
0,61	0,97	0,63	3,26	0,23	94,9	10,8	x
0,67	1,09	0,61	3,02	0,33	92,2	11,4	x

[1)] ammonia reduction from feed to N_depl

[2)] elevation of $temp_{feed}$ from 20°C to 93°C

In total ammonia concentrations of more than 200 % of the substrate concentration could be reached in the condensed off-steam. Ammonia concentrations in the depleted substrate were between 5 and 10 % of the initial ammonia concentration. The pH of the treated substrate remained stable throughout the process, which showed, that the maximum of ammonia extraction was not reached.

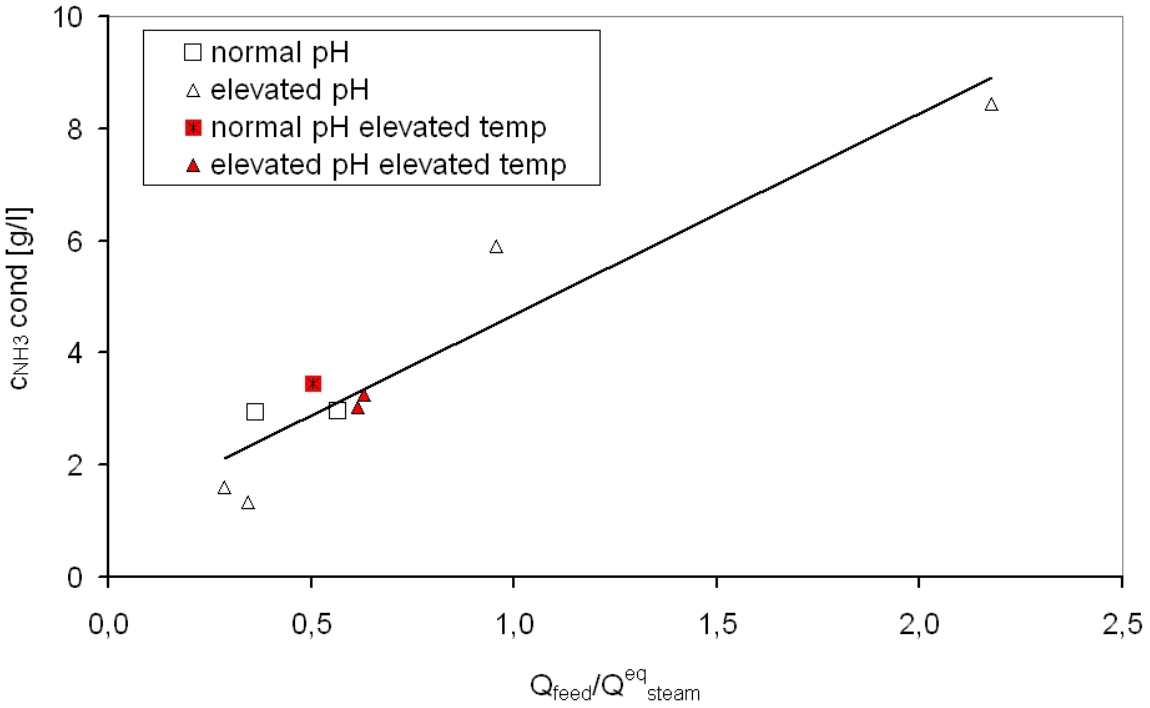


Figure 10: NH_3 concentration in condensate over ratio of Q_{feed}/Q^{eq}_{steam}, lab scale

In Figure 10 the NH_3 concentration in the yielded condensate is set in relation to the volume flow of substrate flow divided by steam flow. The different input parameters are shown with different symbols. As can be seen the NH_3 concentration in the condensate was not influenced by an increase of pH of the feed substrate or by an increase of feeding temperature.

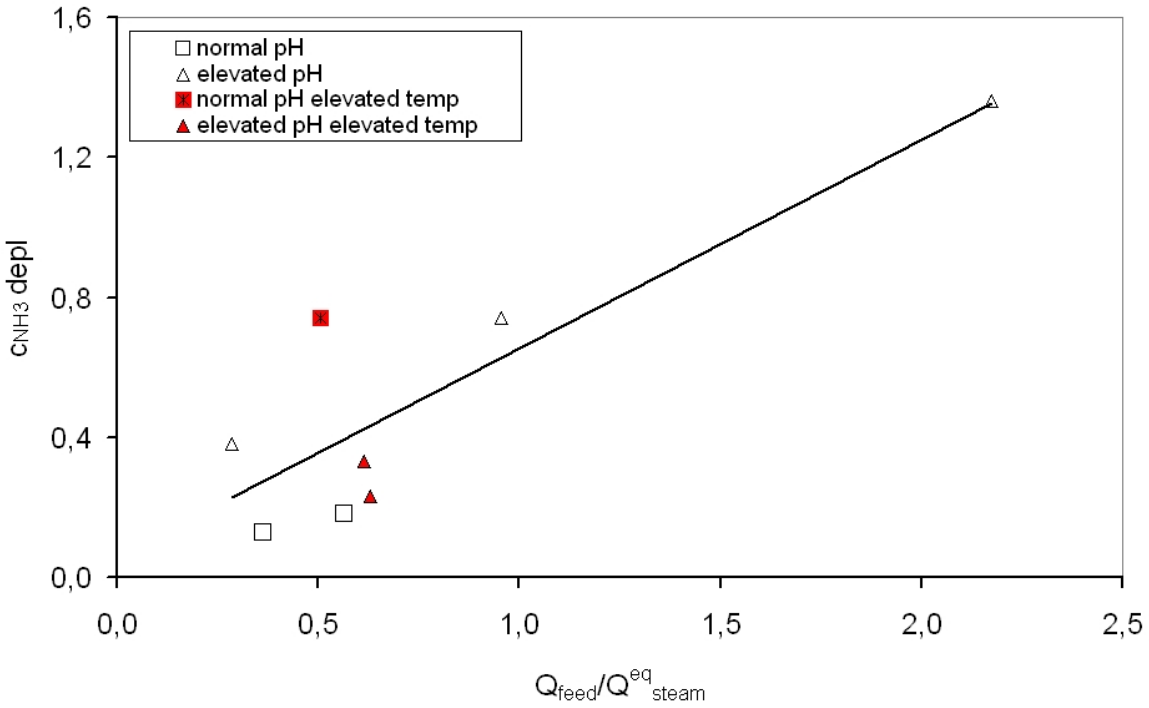


Figure 11: NH_3 concentration in N-depleted substrate over ratio of Q_{feed}/Q^{eq}_{steam}, lab scale

In Figure 11 the NH_3 concentration in the depleted substrate is set in relation to the volume flow of substrate flow divided by steam flow. Again, the different input parameters are shown with different symbols. Again, an effect of an increase of pH of the feed substrate or by an increase of feeding temperature on the depletion can not be clearly stated.

When setting NH_3 concentrations of condensate and depleted substrate in relation to the feed pH, as shown in Figure 51 and Figure 52 in the appendix, in both cases an increase in concentration at higher pH can be assumed.

Steam stripping pilot plant

A total more than 2 m^3 urine was processed in the steam stripping pilot plant. Volume flows, steam flow and feed pH were varied according to Table 9.

Table 9: Varied parameters during pilot plant steam stripping

Ref.Nr. [1]	varied parameter
M1-M4	Q_{feed}/Q^{eq}_{steam}
P1-P4	elevated pH of feed substrate, Q_{feed}/Q^{eq}_{steam}
F1-F3	high Q_{feed}/Q^{eq}_{steam}, analytics by external laboratory

[1] Reference number

During the sets M1 to M4 the ratio Q_{feed} / Q^{eq}_{steam} was varied between 2.4 and 3.6. In the sets P1 to P4 pH was elevated using NaOH. Because of heavy foaming problems substrate

flow had to reduced drastically. In both cases ammonia analytics was performed by using Dr. Lange test kits and stick tests. Within the sets F1 to F3 the ratio between Q_{feed} and Q^{eq}_{steam} was varied between 3.5 and 4.1. The analysis of NH_3 was performed by using the Büchi-distillation method.

Table 10: Process parameters during steam stripping in demo scale

Ref Nr.	process time [h]	Q_{feed} [l/h]	Q^{eq}_{steam} [l/h]	Q_{feed}/Q^{eq}_{steam} [-]	pH feed [-]
M1	3	82	33	2,5	8,9
M2	3	82	34	2,4	8,9
M3	1	72	20,1	3,6	9
M4	2	61	21,1	2,9	8,9
P1	1,5	29	15,9	1,8	9,3
P2	1	27	19,1	1,4	9,8
P3	2,5	28	17,4	1,6	10,2
P4	1	24	24,2	1,0	9,3
F1	2	81	23	3,5	9
F2	3	95	23	4,1	8,8
F3	2,5	98	25	3,9	8,9

Table 11: Results of steam stripping pilot scales tests

Ref Nr.	Q_{cond} [l/h]	c_{NH3} feed [g/l]	c_{NH3} depl urine [g/l]	c_{NH3} cond [g/l]	reduct (2 [%]	pH feed [-]	pH depl [-]	pH cond [-]
M1	6,0	4,2	0,38	65,4	91	8,9	5,9	9,4
M2	11,0	5,8	0,114	52,0	98	8,9	5,8	9,0
M3	12,6	5,8	0,17	23,1	97	9,0	5,6	9,3
M4	7,0	7,4	0,16	74,3	98	8,9	5,6	9,3
P1	8,6	7,4	>0,001	21,4	100	9,3	8,95	7,35
P2	10,9	6,6	>0,001	15,8	100	9,8	10,4	9,3
P3	10,3	6,3	>0,001	16,2	100	10,2	10,4	9,9
P4	15,6	7,4	>0,001	8,3	100	9,3	7,9	9,3
F1	2,2	2,1	0,08	108	96	9,0	5,4	9,6
F2	2,4	3,5	0,33	121	91	8,8	5,5	9,5
F3	3,5	3,6	0,18	116	95	8,9	5,5	9,6

[2)] ammonia reduction from feed to N_depl

Nitrogen could be depleted from the original substrate very well. The ammonia concentration in the depleted substrate was in nearly all cases less than at least 10% of the original value. As long as the initial pH was not adjusted, the pH of the depleted substrate was decreased by steam stripping from nearly pH 9 to below pH 6, which makes the steam stripping indeed a very expedient process prior to the evaporation. Ammonia concentrations in the condensate were between 15 and 34 times higher than in the initial substrate. Thus ammonia solution of more than 12 % could be reached.

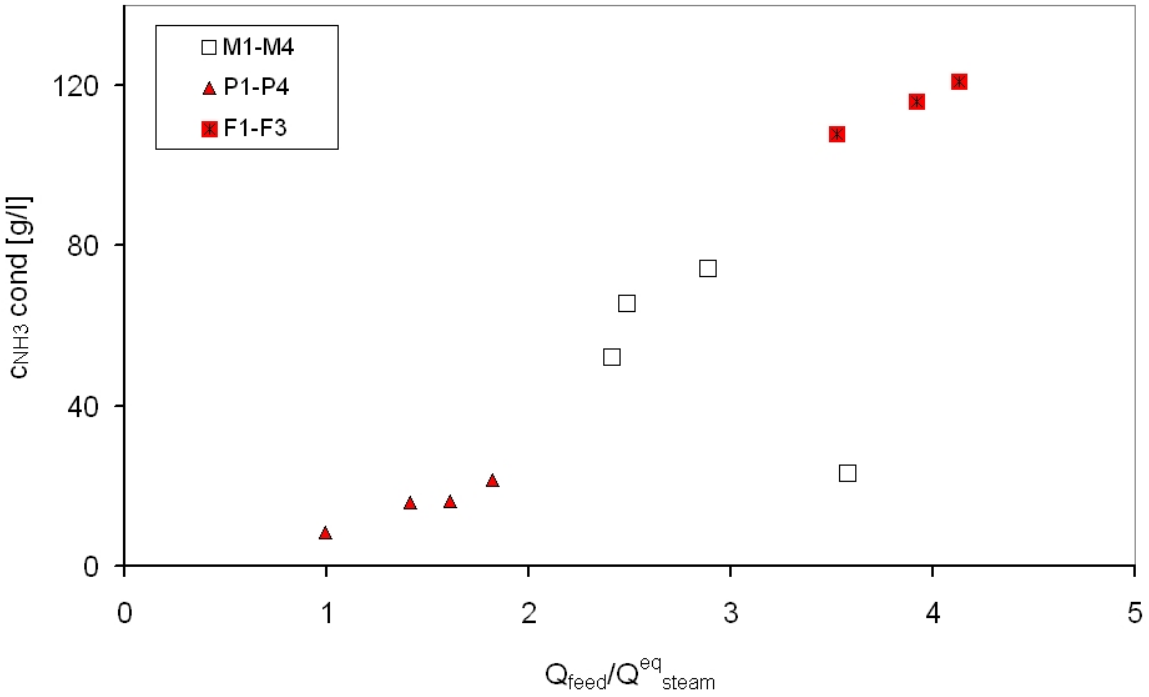


Figure 12: NH_3 concentration in condensate over ratio of Q_{feed}/Q^{eq}_{steam}, pilot scale

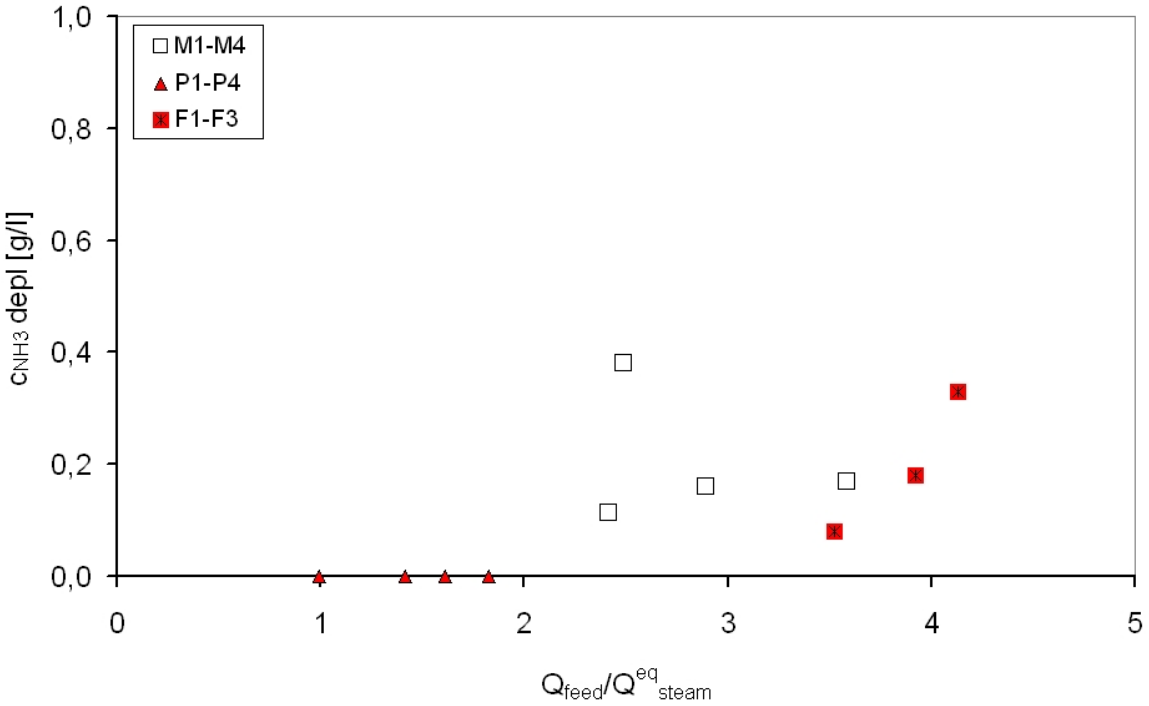


Figure 13: NH_3 concentration in N-depleted substrate over ratio of Q_{feed}/Q^{eq}_{steam}, pilot scale

Table 12: Mass flows in pilot scale steam stripping unit

Ref Nr. [1]	Q_{feed} [l/h]	Q_{Ndepl} [l/h]	Q_{cond} [l/h]	Q^{eq}_{steam} [l/h]	$Q_{reactor}$ [l/h]	DF	$Q_{reactor}/Q^{eq}_{steam}$
M1	82	109	*6,0*	33,0	27,0	0,75	82%
M2	82	105	*11,0*	34,0	23,0	0,78	68%
M3	72	80	12,6	20,1	7,5	0,91	37%
M4	61	75	*7,0*	21,1	14,0	0,81	67%
P1	29	36	8,6	15,9	7,3	0,80	46%
P2	27	35	10,9	19,1	8,2	0,77	43%
P3	28	35	10,3	17,4	7,1	0,80	41%
P4	24	33	15,6	24,2	8,6	0,74	36%
F1	81	102	*2,2*	23,0	20,8	0,80	90%
F2	95	116	*2,4*	23,0	20,6	0,82	90%
F3	98	120	*3,5*	25,0	21,5	0,82	86%

Mass flows of each set can be found in Table 12 as well as the dilution factor of the N-depleted substrate which was resulting from steam condensed within the reactor. Between 7 and 27 kg of steam condensed within the reactor resulting in dilution of 10 to 25 % of the N-depleted substrate.

In the condensate no phosphorous could be detected. The reduction of the concentration in the N-depleted substrate was nearly completely compensated by integrating the dilution factor. Therefore, obviously no precipitation occurred within the stripping reactor. This was proved by visual observation of the filling material as well as of substrate pipes.

Table 13: Phosphorous contend during pilot scale steam stripping

Ref Nr.	P_{feed} C_0 [mg/l]	P_{Ndepl} C_d [mg/l]	P_{cond} [mg/l]	C_d / C_0	P^{exp}_{Ndepl} [2] [mg/l]	P^{norm}_{Ndepl} [3] [-]
M3	431	376	>0,1	87%	390	0,96
P2	395	300	>0,1	76%	315	0,95
P3	440	326	>0,1	74%	324	1,01
P4	431	312	>0,1	72%	343	0,91

[2] The expected concentration of phosphorous in the N-depleted substrate is calculated by $P^{exp}_{Ndepl} = P_{feed} * DF$

[3] The normed concentration of phosphorous in the N-depleted substrate is calculated by $P^{norm}_{Ndepl} = P_{Ndepl} / DF$

Table 14: COD, potassium, sulphur and phosphorous contend during pilot scale steam stripping

Ref Nr.		COD mg O_2/l	Red.[1]	K mg/l	Red.[1]	K^{norm}	S mg/l	Red.[1]	S^{norm}	P mg/l	Red.[1]	P^{norm}
F2	urine feed	2 590		1 198			354			207		
F2	condensate	370	14%	<1	-		58,3	16%		<2	<1	
F3	condensate	1 080	42%	1,1	0,1%		83,3	24%		<2	<1	
F2	N-dep. substrate	1 790	69%	930	78%	1,06	298	84%	0,97	162	78%	1,05
F3	N-dep. substrate	1 428	55%							178	85%	0,95

[1] Reduction regarding initial concentration of feed substrate

The reduction in the N-depleted substrate was more or less equivalent to dilution of steam for heat up of the system, condensed within the reactor.

Energy

During the lasts sets of the demo-scale steam stripping unit about 25 kg steam at 160°C were used per 100 l substrate. This is equivalent to an energy demand of 680 MJ/m^3 (188 kWh / m^3 processed substrate). From this energy the main part was used for heating up the substrate in the column. Only about 1/6 of that energy was used for the stripping of ammonia itself.

Thus, major energy saving can be obtained by improvements in heat insulation of the column, heat exchanger and pipes and by energy recovery. In the demo-size plant, an energy potential in form of heat of 65 MJ/m^3 was not used resulting from the condensing and cooling down of the condensate. The steam-stripping plant in semi-technical size in this project was not designed towards energy efficiency.

With proper insulation, energy recovery, and slight changes in process control such as a fractionated condensation, it should be possible to reach literature values of 150 -200 MJ/m^3 (40 - 55 kWh/m^3).

Conclusion

Within the steam-stripping plant in semi-technical scale, designed to process substrate from ~800 people 25 - 35 l/(m^3 urine) of an ammonia solution containing up to 120 g NH_3 /l could be produced from urine which contained between 2 and 7.4 g NH_3/l. Up to 50 times of the initial NH_3-contend could be condensed in 1/40 of the volume. In the remaining N-depleted substrate a reduction of 90 to 98 % could be reached. Thus the resulting NH_3 concentration of 6 - 10 mmol/l in the depleted substrate would be somewhat equivalent to the phosphorous concentration of 5 mmol/l and could be completely removed by subsequent MAP-precipitation.

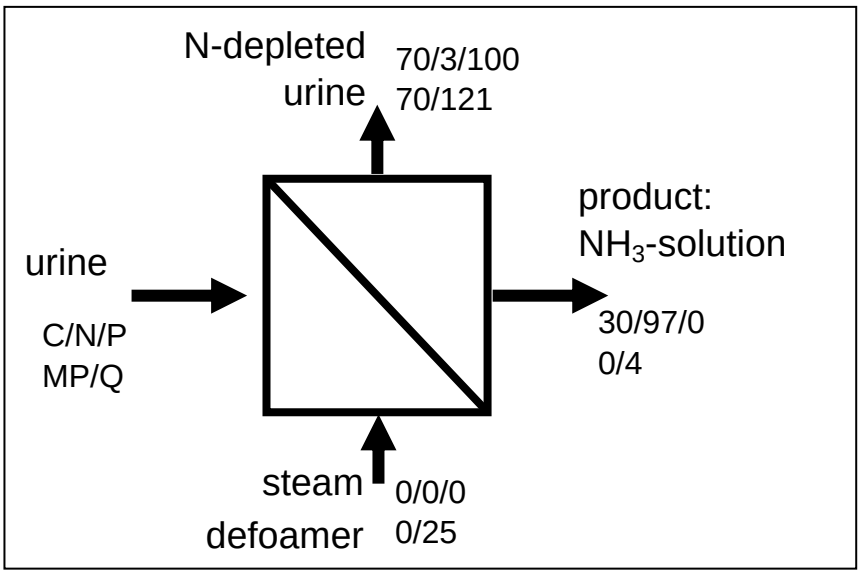


Figure 14: Scheme of steam stripping process with quantitative in- and output modified according to [*Maurer, Pronk, & Larsen 2006*]

A fine steam adjustment as well as slight process modifications such as improved energy recovery and a fractionated condensation would lead to even higher ammonia concentrations in the yielded product and lower energy consumption.

Pre-treatment of the substrate was not necessary. The pH of hydrolyzed urine is in a range suitable for the stripping process. Precipitation within the system was not observed.

Evaporation

Introduction

Human urine contains all nutrients (macro- and micro-) and also trace elements that are considered to be important for the growth of plants. In addition to phosphorus and nitrogen, high concentrations of the nutrients potassium and sulfur increase the fertilizing quality of urine. Because a continuous application to land (~20m^3 urine/ha land) is normally not feasible, large storage volumes are needed. For densely populated areas volume reduction and concentration of contained substances by evaporation is an option.

Material & Methods

Equipment

For volume reduction two types of evaporators were used. In laboratory scale a rotation evaporator (RotaVap) was operated to gain information about the behaviour of the substrate during evaporation (e.g. foaming, splashing, change of boiling point). The rotating glass bulb with a volume of 500 ml was heated in an oil bath. Using a water-jet pump, the system was set at a vacuum of -300 m bar. Per hour about 150 - 200 ml were evaporated and extracted from the system as distillate. The glass bulb was refilled manually every 30 min to obtain a larger volume of concentrate.

To demonstrate technical feasibility and to obtain larger quantities of concentrates, a 'Prowadest mini' evaporation unit in demo-scale from the company KMU Umweltschutz GmbH was operated in batch. With an evaporation rate of 4 - 10 l/h and temperatures between 70 - 80°C at a pressure of -300 mbar a substrate equivalent of 80 persons could be processed. Distillate was constantly extracted from the system. The evaporation bulb was refilled automatically when liquid level dropped below a defined level within the bulb.

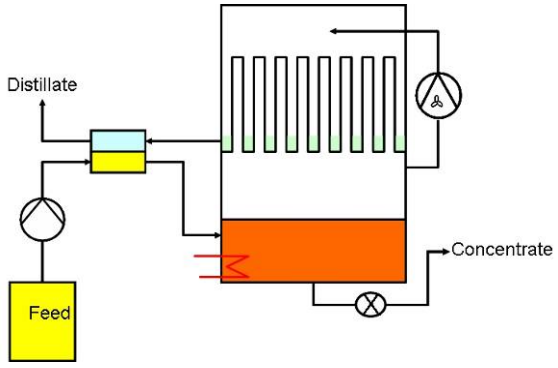


Figure 15: Scheme of evaporation process

Picture 9: Evaporation plant Provadest 'Mini', KMU

In the first evaporation set in demo-scale the feed substrate was prepared in 60 l canisters that were refilled manually subsequently. For later sets, the feed substrate was stored and prepared in a 1 m^3 tank outside of the container. The feed substrate was sucked by a water jet pump into the evaporation bulb. Several sensors were controlling the filling level of the evaporation bulb. The evaporation bulb was heated in an oil-bath. The saturated off gas was cooled in a heat-exchanger. The produced distillate was captured in two 60 l tanks, which were emptied manually on a continuous base. The volume that was extracted via distillate output was replaced automatically from the feed tank. Foaming and splashing within the evaporation bulb were controlled by automatic addition of a silicon based defoamer.

Substrates

Two substrates were processed: stored urine and N-depleted urine. In several runs the pH of the stored urine was lowered using H_2SO_4 respectively H_3PO_4 to avoid excessive losses of Nitrogen in form of ammonia.

Table 15: Parameters varied in the pilot scale evaporation plant

Substrate	urine N-depleted urine
pH	pH of feed urine was varied between pH 4.5 and pH 8.9 using H_2SO_4 respectively H_3PO_4

Table 16: Feed substrates for evaporation process (average values)

	pH	cond. mS/cm	TOC mg/l	TN mg/l	NH_4-N mg/l	PO_4-P mg/l	P mg/l	K mg/l	S mg/l	COD mgO_2/l	TS(* g/l
Stored urine	8.8	21		3 970		360	207	1198	354	4 120	7.8
Stored urine, pH7, H_3PO_4	7.3	23		4 180	3 640	1 140				4 300	8.0
Stored urine, pH4,7, H_2SO_4	4.7	24	2 190	3 150							30
N-depl. urine	6.7	11,5	75	210	120	299	170	930	298	1720	14.4

*) TS stands for total solids (not the german Trockensubstanz)

Concentration factor

In order to express the concentration efficiency of different parameters, a concentration factor cf is used which is calculated by dividing the detected concentration with the initial concentration.

detected concentration factor: $$cf = \frac{conc_{\det}}{conc_{init}}$$ **Eq 11**

To allow better comparison of different concentrates and their parameters a normalized concentration factor cf_{norm} is used. For normalizing the concentration factor, the detected concentration factor is divided by the expected concentration factor cf_{exp}. The expected concentration factor is derived from the analysis of total solids (TS). In pre-tests the concentration factor derived from TS proved best to be equivalent to the concentration factor derived from volumetric balance. In the case of the demo-scale evaporation plant the large volumes handled did not allow a precise volumetric balance.

expected concentration factor: $$cf_{\exp} = \frac{TS_{\det}}{TS_{init}}$$ **Eq 12**

normalized concentration factor: $$cf_{norm} = \frac{cf_{\det}}{cf_{\exp}}$$ **Eq 13**

In the distillate volatile substances such as organic acids are captured. For evaluation of these substances, the expected concentration is assumed to be equal to the initial concentration. It is neglected that the volume will be lower than the initial volume and thus that the concentration should be higher.

in case of distillate: $$cf_{\exp}^{dist} = cf_{init}$$ **Eq 14**

$$cf^{dist} = cf_{\exp}^{dist} = cf_{norm}^{dist}$$ **Eq 15**

In case of non volatile substances that are contained to some extend in the distillate the percentage of the initial concentration is given where needed for comparison.

Results

Acidification of stored urine

The acid capacity of stored urine is very high. Here an m-value of 32 mmol/l was measured. Thus, for an acidification of 1 liter urine from pH 9 to pH 6 4 ml of 96 % H_2SO_4 respectively 3 ml of 85 % H_3PO_4 were needed.

Evaporation time

Evaporation of large quantities of urine under above given conditions is a time consumptive process. For obtaining 17 litres (the liquid contend of the demo-scale evaporation plant) of a 12 fold concentrate at a evaporation rate of 1.6 l/h 5 d are needed. In the first set, the evaporation time is contained in the names of the concentrates and distillates.

Evaporation of stored urine acidified with H_2SO_4.

About 300 litres of urine were acidified subsequently in 60 l containers by adding a total volume of 1.65 l 95 % H_2SO_4. Samples were taken in intervals in the beginning of 4 later in intervals of 32 and 63 h.

In Table 17, Table 18, Table 56, and Table 57 the parameters of the obtained concentrates and distillates are presented.

Table 17: pH, conductivity, TOC, TN and total solids (TS) during first set of evaporation..

	pH	cond. [mS/cm]	*cf*	TOC [mg/l]	*cf*	TN [mg/l]	*cf*	TS [g/l]	*cf*
feed average	4,67	24		2.190		3.150		30	
Conc 1250	5,30	54	*2,3*	4.050	*1,9*	4.040	*1,3*	69	*2,3*
Conc 1750	4,65	83	*3,4*	6.500	*3,0*	4.880	*1,6*	104	*3,5*
Conc 3975	5,52	126	*5,2*	14.030	*6,4*	6.050	*1,9*	224	*7,5*
Conc 7750	3,76	274	*11,4*	10.020	*4,6*	6.640	*2,1*	379	*12,7*
Dist 1250	8,12	0,5	*0,0*	134	*0,1*	70	*0,0*	-0,1	*0,0*
Dist 1750	3,65	0,2	*0,0*	633	*0,3*	8	*0,0*	-0,1	*0,0*
Dist 3975	7,04	1,5	*0,1*	381	*0,2*	412	*0,1*	0,6	*0,0*
Dist 7750	3,72	0,3	*0,0*	664	*0,3*	-	*0,0*	0,1	*0,0*

Note

1) TOC and TN analyzed by autoanalyzer analytic Jena AG. Samples for measuring conductivity were not diluted prior measurement
2) Complete table can be found in the appendix

The analysis of TOC and TN in the concentrated urine with the autoanalyzer analytic Jena AG proved to be not sufficient. Already in non-concentrated urine the matrix and the high basic buffer capacity of urine causes problems in the analytics of many parameters. Thus, additionally total nitrogen, phosphorous and potassium of six samples were measured in an external laboratory. The results showed that nitrogen and phosphorous can be captured

completely in the concentrate. The low concentrations of potassium of two concentrates are not due to losses into the distillate. Formation of crystals did not occur in this step which can be seen on the fact that the metals relevant for crystal-formation could be detected in the expected concentrations in the concentrates (see Table 56).

Table 18: Nutrients during concentration process

	feed Urine	Conc 1250	Conc 1750	Conc 3975	Dist 1250	Dist 1750	Dist 3975
TN mg/l	4 330	10 100	16 400	27 500	130	40	320
cf_{det}		*2,3*	*3,8*	*6,6*	*3 %*	*1 %*	*7 %*
P mg/l	408	988	1 472	3 037	<2	<2	<2
cf_{det}		*2,4*	*3,6*	*7,4*	*< 0,5 %*	*< 0,5 %*	*< 0,5 %*
K mg/l	1 360	3 290	1 125	2 420	1,57	0,57	1,5
cf_{det}		*2,4*	*0,8*	*1,8*	*0,1 %*	*0,04 %*	*0,1 %*
cf_{exp}		2,3	3,5	7,5			

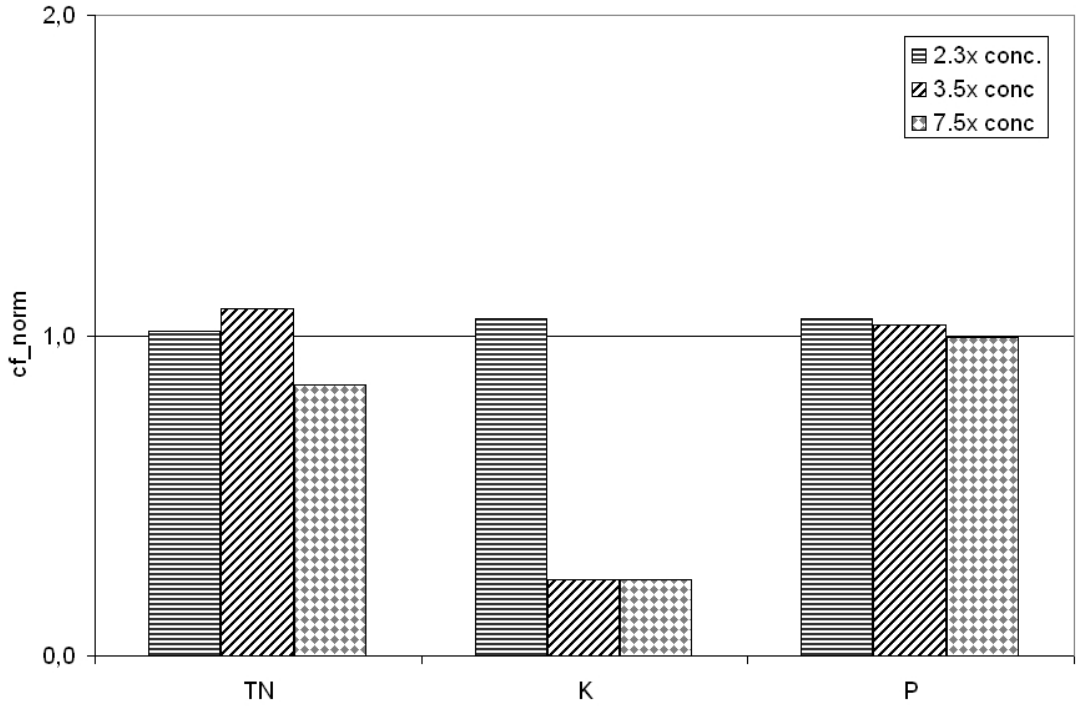


Figure 16: Nutrients in concentrates after evaporation

Different trace elements were analyzed in samples of feed substrate and each three concentrates and distillates by a spectro-quant analysis (Table 56). The reduction of copper, zinc, nickel, and lead in the second concentrate is most likely due to interferences of other highly concentrated substances within the concentrates.

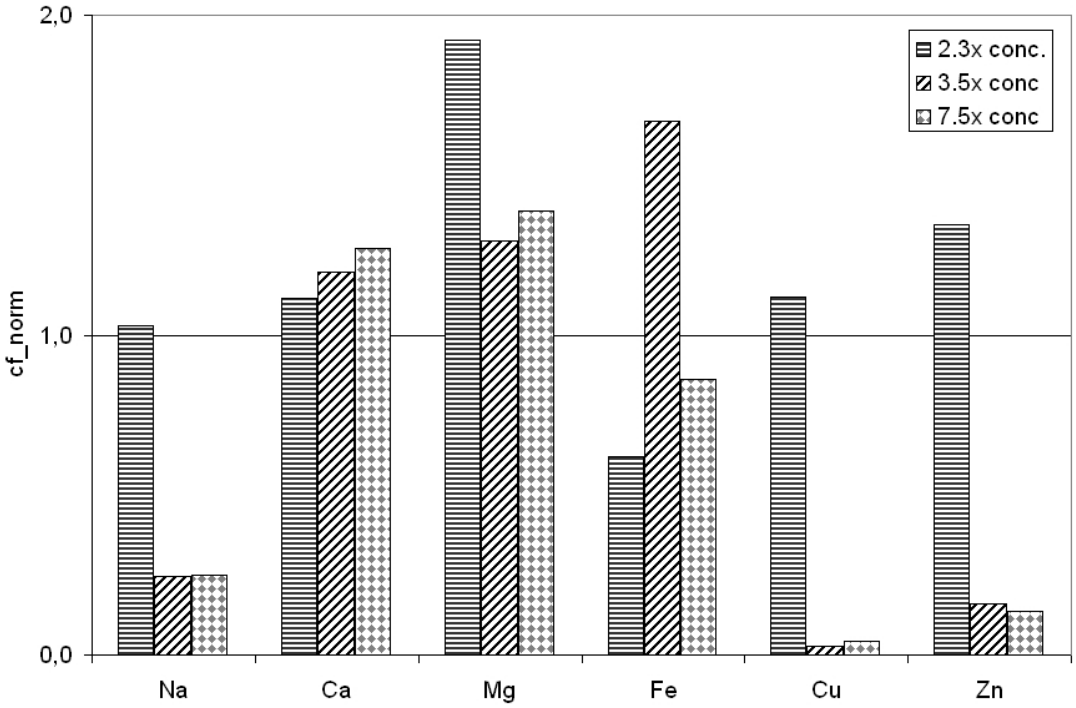


Figure 17: Metals in concentrates during evaporation

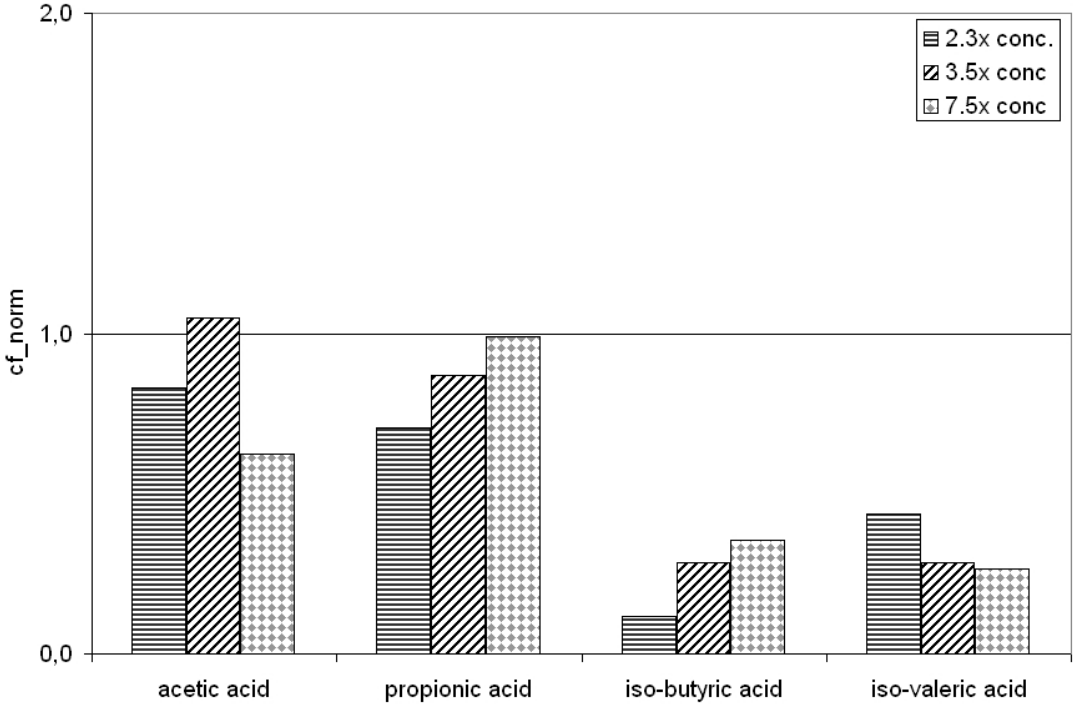


Figure 18: Organic acids in concentrates during evaporation

The samples of feed substrate, three concentrates and three distillates were also analyzed regarding carbon acids (Table 57). Caproic acid and n-valeric acid were not detected in any sample. While the boiling point of the carbon acids is increasing with their complexity

(from acetic acid: 118°C to valeric acid: 187°C) the concentration factor in the distillate of the later ones is drastically higher as can be seen in Figure 19.

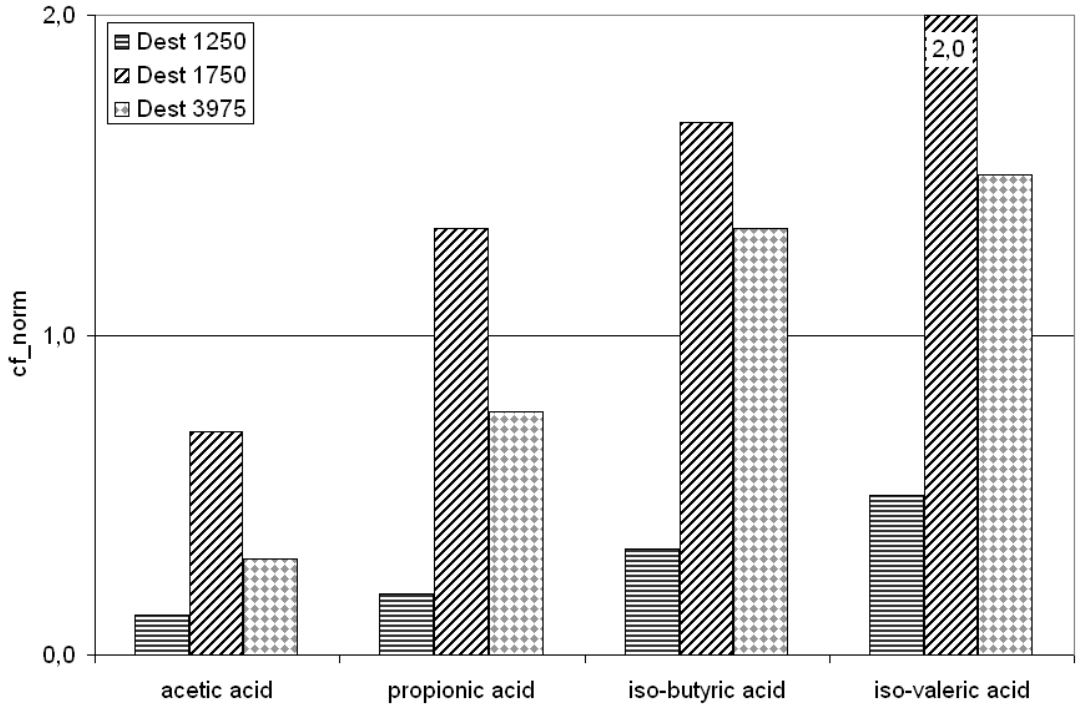


Figure 19: Organic acids in distillates during evaporation

Since n-butyric acid was not detected in the initial feed substrate, it is not included in Figure 18 and Figure 19. Assuming that the maximum concentration of in the feed substrate n-butyric acid can be 4 mg/l the following normalized concentration factors can be derived:

Table 19: Normalized concentration factor for n-butyric acid, with assumption that maximum initial concentration of feed substrate is 4 mg/l

	n-butyric acid cf_{norm}(*
Conc 1250	*3,3*
Conc 1750	*5,0*
Conc 3975	*5,7*
Dest 1250	*nd*
Dest 1750	*30*
Dest 3975	*23*

*) assumed that maximum initial concentration = 4 mg/l

Thus, from Table 20 it can be seen that large amounts of n-butyric acid, but also iso-valeric, propionic acid, iso-butyric acid, and even acetic acid to some extend show an increase in the total mass balance (sum of normalized concentration factors of concentrate and distillate should equal 1).

Table 20: Total mass balance of organic acids

	acetic acid	propionic acid	iso-butyric acid	*n-butyric acid* (*	iso-valeric acid
$cf_{Cond1250}+cf_{Dist1250}$	0,96	0,89	0,45	4.3	0,93
$cf_{Cond1750}+cf_{Dist1750}$	1,75	2,20	1,95	35	2,29
$cf_{Cond3975}+cf_{Dist3975}$	0,93	1,75	1,69	28	1,77

*) assumed that maximum initial concentration = 4 mg/l

Evaporation of stored urine acidified with H_3PO_4

Sulfuric acid causes surface corrosion on 'non high-grade steel elements' within the evaporation plant. In our case valves and weld seams were affected. Therefore in the next set approximately 3 ml of 85 % H_3PO_4/(l urine) was used to yield the same pH-lowering potential as 4 ml of 96 % sulfuric acid.

Nearly 1 m^3 was concentrated by evaporation down to a concentrate of 17 l which is equivalent to a concentration of 57 times. The feed substrate was prepared in several sets of 200 to 400 litres in a 1 m^3 container. Because of the large volumes and the refilling of not completely emptied tanks pH adjustment proved to be more difficult than expected. Therefore the average pH of feed substrate was around pH 7.3 causing extraction of ammonia into the distillate.

By addition of H_3PO_4 the phosphorous contend of the feed substrate was more than tripled from initially 320 mg P/l to 1,150 mg P/l.

Table 21: Concentrates and distillates from evaporation

	pH	cond mS/cm	*cf*	TOC mg/l	TN mg/l	NH_4-N mg/l	*cf*	P mg/l	*cf*	COD mgO_2/l	*cf*	TS g/l	*cf*
feed avr.	7.3	21				3 640		1150		2590		8,8	
Conc 24	5,54	351	*17*	163	138	27 000	*7*	33300	*29*	36400	*14*	212	*24*
Conc 27	5,38	381	*18*	114	141	24 000	*7*	31500	*27*	32370	*12*	238	*27*
Conc 53	5,51	716	*34*	228	156	32 000	*9*	59400	*52*	67040	*26*	465	*53*
Conc 57	5,43	1005	*48*	210	162	28 700	*8*	58500	*51*	71640	*28*	499	*57*
Dist 24	5,41	5,0	*24%*	183	152	420	*12%*	5,9	*0,51%*	322	*12%*	0,2	*2,5%*
Dist 27	9,05	3,0	*14%*	173	134	279	*8%*	0,36	*0,03%*	1032	*40%*	0,4	*5,0%*
Dist 53	8,99	8,1	*38%*	85	174	1500	*41%*	0,22	*0,02%*	344	*13%*	0,4	*4,7%*
Dist 57	9,24	9,6	*46%*	89	189	4000	*110%*	0,14	*0,01%*	259	*10%*	0,2	*1,8%*

Note : Complete table can be found in the appendix

From Table 21 it can be seen that all the expected phosphorous was found in the concentrates, while the distillate was nearly free of phosphorous. The reduction of phosphorous in Figure 20 is also most likely due to limitations of analysis at extremely high concentrations. For the measurement of conductivity at high concentrations the substrate has to be diluted sufficiently. Samples in Figure 20 were diluted 1:100 but obviously not enough.

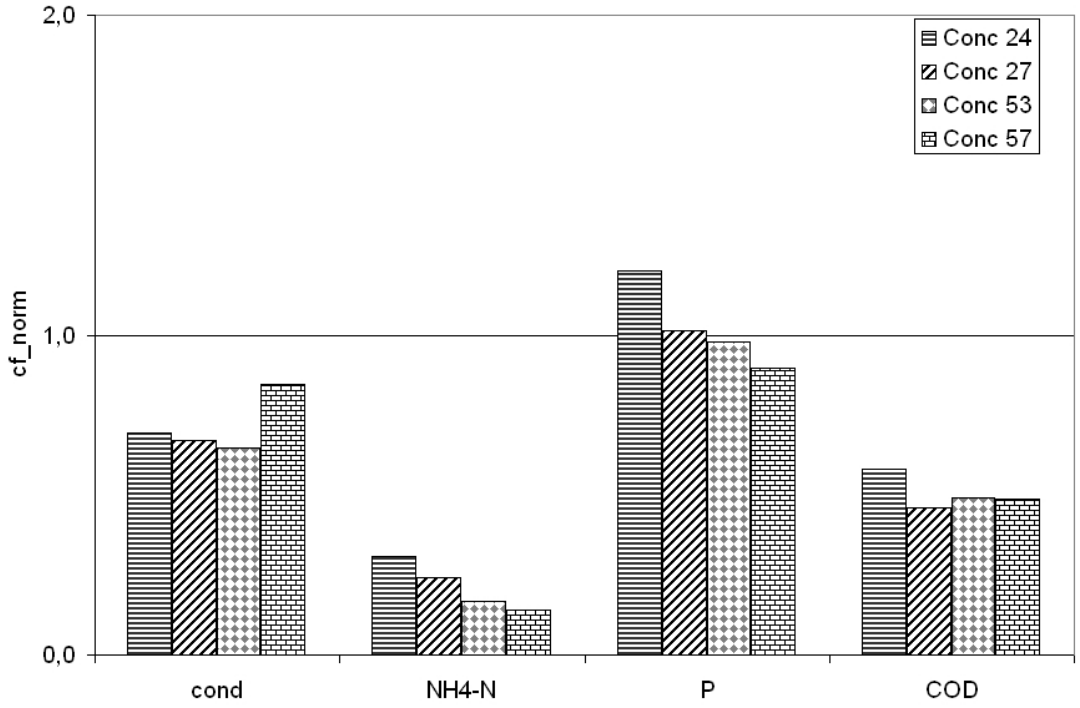


Figure 20: Conductivity, NH_4, P and COD in concentrates after evaporation

Evaporation of N-depleted urine after steam stripping

More than 900 l N-depleted urine from the steam stripping process were concentrated by evaporation yielding in 17 l of 55 fold concentrate.

Table 22: pH, conductivity, total organic carbon, total nitrogen, ammonium, COD and total solids (TS) of concentrates and distillates from N-depleted urine after steam stripping and evaporation

	pH	cond mS/cm	*cf*	TOC mg/l	TN mg/l	NH_4-N mg/l	COD mgO_2/l	*cf*	TS g/l	*cf*
feed average	6,77	11,53				120	1720			
Conc Ndep 24	6,03	226	*19,6*		220	2128	37110	*21,6*	142	*24,4*
Conc Ndep 32	5,74	391	*33,9*	1622	196	1400	65690	*38,2*	188	*32,4*
Conc Ndep 55	5,82					2560			319	*55,0*
Dist N_depl 24	6,77	11,5	*100%*	54	22		2362		0,51	
Dist N_depl 32	9,44	1,3	*11%*	4,7	56		153			

Phosphorous, potassium and sulfur were analyzed by ICP (Table 59). The results presented in Figure 21 lead to the conclusion that the measurement of dried solid content was not precise, since the normalized concentrations of P, K, S, and even COD have all the same off-set. It can be assumed, that P, K, and S are completely captured in the concentrates.

Since pH was not reduced in this evaporation step extraction of ammonia into the distillate occurred.

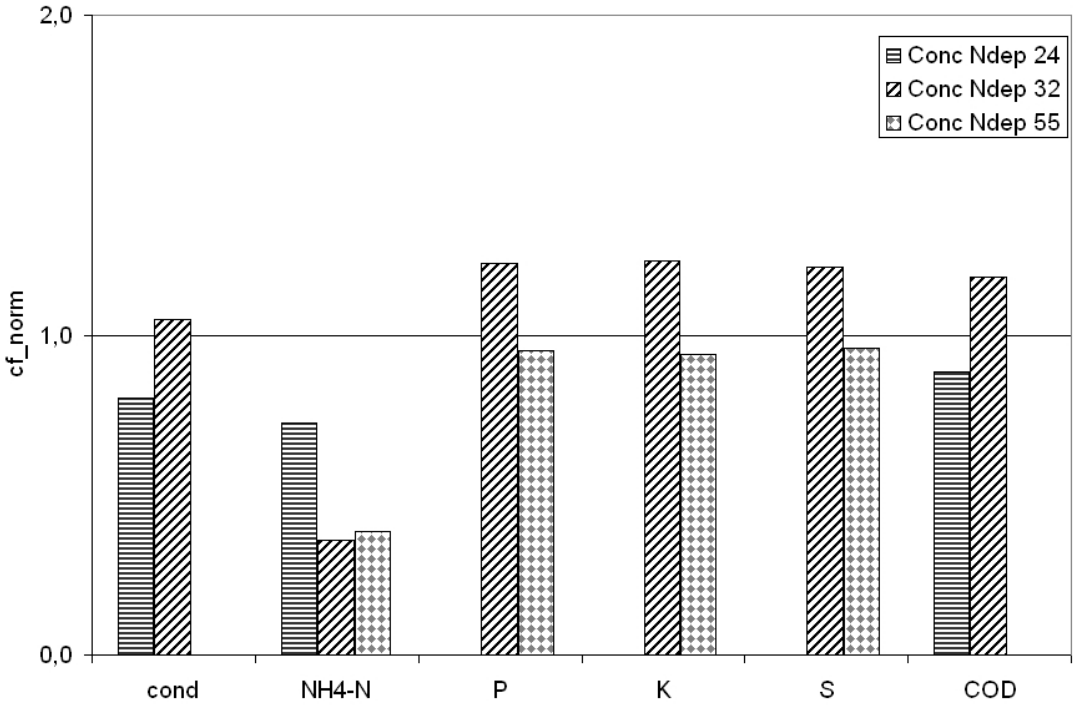


Figure 21: Conductivity, NH_4-N, phosphorous, potassium, sulfur and COD of concentrates from N-depleted urine after steam stripping and evaporation

Boiling point

Behavior of foaming, and splashing was investigated. In the small lab-scale RotaVap evaporator the phenomenon could be observed visually. Foaming occurs normally only with fresh substrate, especially with stored urine. N-depleted urine from the steam stripping process showed drastically less foaming. While foaming will still occur, even after a while at high temperatures, the phenomenon of splashing is even more severe. Because of the very diverse matrix of urine splashing occurs even at high agitation as proceeded in the RotaVap. Foaming could be controlled in most cases by addition of small fractions of oil or even better by addition of a silicone based defoamer.

The change of boiling point was also observed under atmospheric pressure. The higher concentrated a concentrate is, the higher the boiling point. At the same the temperature within the concentrate is still increasing leading to constant boiling retardation (delay of boiling point). This is leading to heavy splashing which can cause system failures. In case of the demonstration plant splashing of the concentrate was leading to several shut downs of the plant, since level sensors were affected. In Figure 54 it can be seen that the N-depleted substrate and the distillate of the evaporation process show a very similar boiling behavior as water.

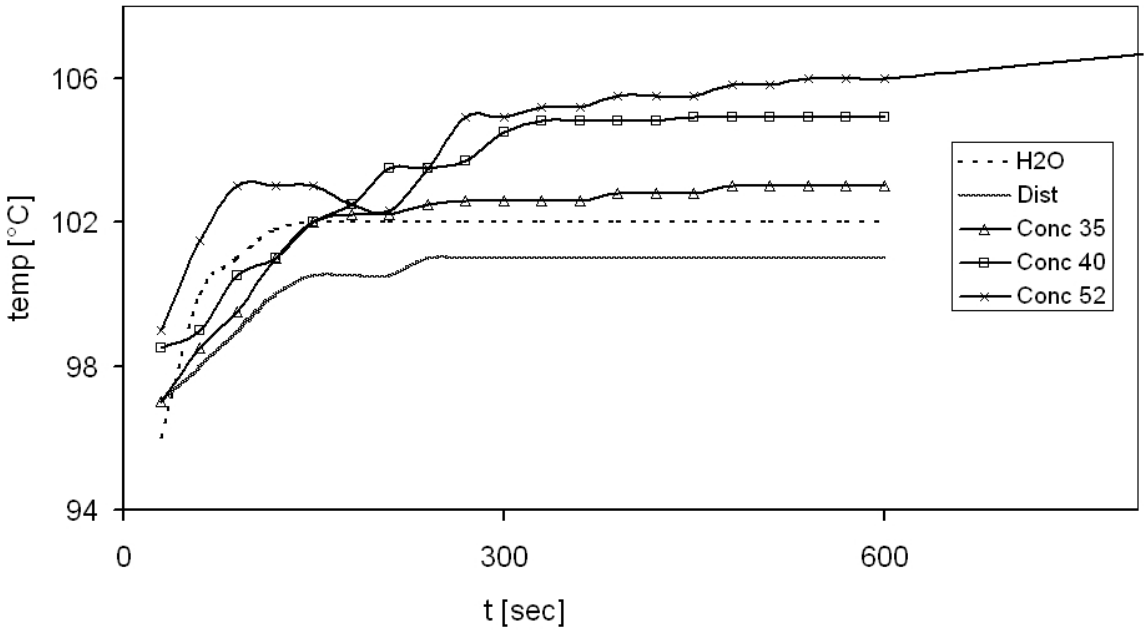


Figure 22: Determination of boiling point of concentrates, and distillate compared to H_2O

Viscosity

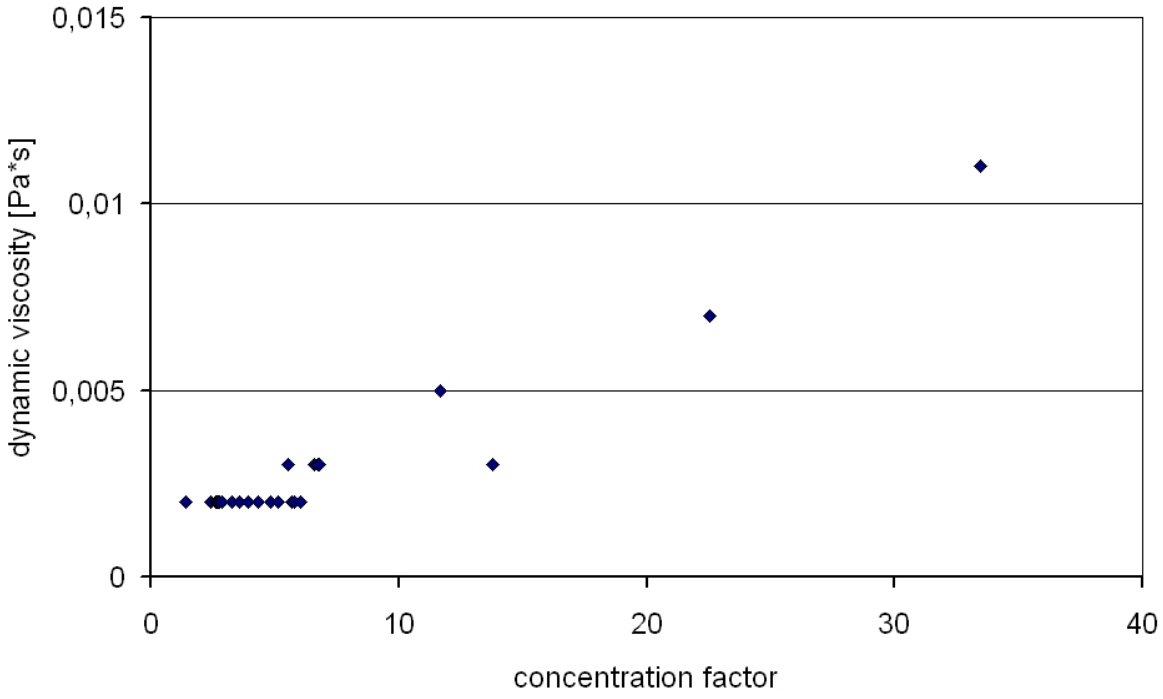


Figure 23: Dynamic viscosity (η) of different concentrates behaving as Newton liquids

The concentrates obtained in above described sets behaved all like Newton liquids and were not depending on friction velocity. However, there was an increase in viscosity with increasing concentration, as can be seen in Figure 23. Even at concentrations of about 50 fold the viscosity was less than e.g. olive oil ($\eta_{olive\ oil}$ = 0.084 Pa*s).

For more detailed information a part of the concentrate obtained from the demo-size evaporation plant was further concentrated in a laboratory evaporator (RotaVap). Thus concentrations of up to 125 fold were obtained looking like thick sludge.

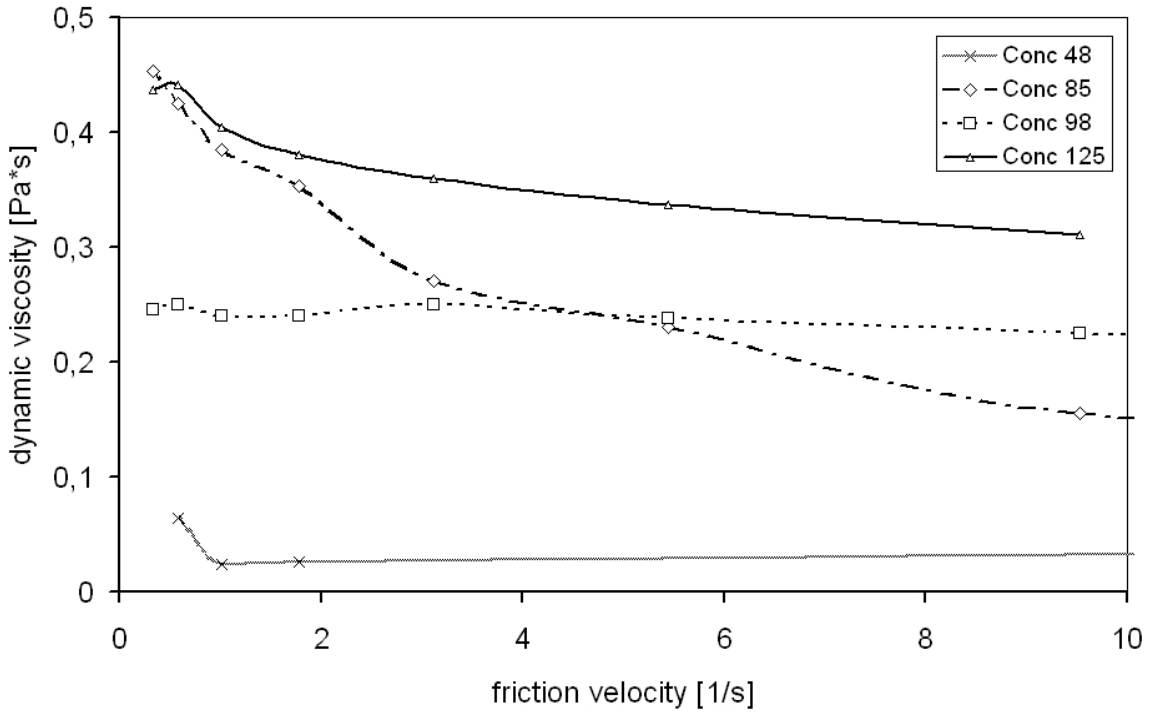


Figure 24: Dynamic viscosity (η) of high concentrated concentrates over friction velocity showing thixotropic behavior

With increasing friction velocity G the dynamic viscosity decreased (see Figure 24) which is described as thixotropic behavior, allowing processing by pumping and mixing without excessive energy input.

Energy

The evaporation process is energy consumptive. The small evaporation unit that was operated to process urine and N-depleted urine in demo-scale had an energy demand of about 2 200 MJ/m^3 (611 kWh/m^3). More efficient evaporation processes are possible, such as used in large-scale desalination plants with vapor compression distillation (VCD) and specific energy requirements of as low as 150 - 180 MJ/m^3 [*Maurer, Pronk, & Larsen 2006*]. Because of the high salt contend and the extremely diverse matrix of urine processes such as thin film evaporation might be prawn to failure caused by a break in the film leading to precipitation and thus to incrustation. However, in the evaporation unit Prowadest Mini precipitation or incrustation was observed neither within the bulb, nor in pipes. This is explained by the high temperatures within the bulb and of the concentrate.

Conclusions

Highly concentrated solutions could be obtained from stored urine and from N-depleted urine. Concentration factors of 55 fold and more could be reached which means to gain 18 l of concentrate from 1 m^3 of separate collected urine. Concentrates up to 60 fold had a low viscosity. Phosphorous, potassium, and sulfur were captured in the concentrates. The distillate contained carbon acids, leading to COD values in the range of the initial COD.

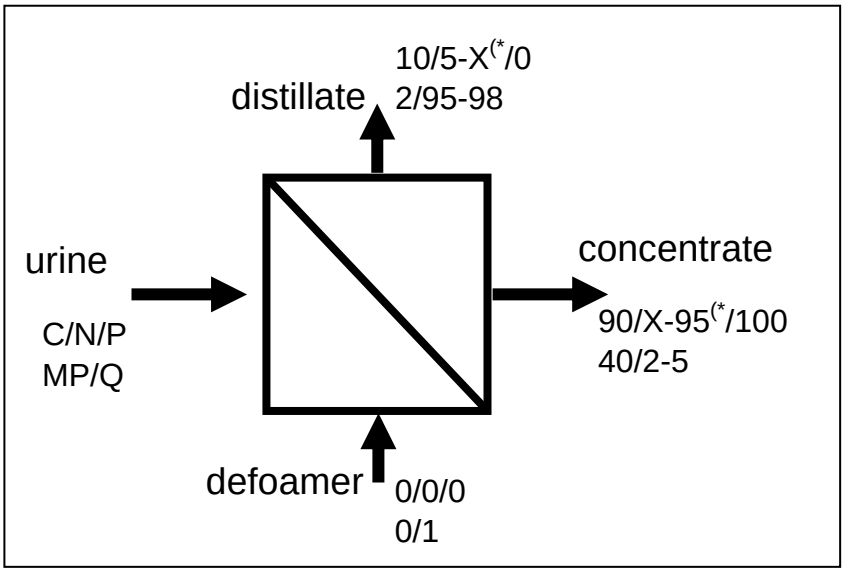


Figure 25: Process scheme for evaporation modified according to [*Maurer, Pronk, & Larsen 2006*]

*) strongly depending on pH of initial substrate

As [*Maurer, Pronk, & Larsen 2006*] stated, the two main obstacles for evaporation of urine are loss of ammonia and the high energy demand. Acidification of stored urine requires large quantities of acid. Since sulfuric acid can lead to corrosion in most regular evaporation plants, phosphoric acid might be the only alternative, when using conventional evaporation units. While prices for phosphoric acid are about 3x higher than for sulfuric acid the yielded concentrate will also be more valuable because of its high P-content. During the conducted evaporation experiments approximately 1.5 g/l P was added to the source separated urine. It has to be noted that for producing P-fertilizer phosphoric acid is one of the main source materials. However, since phosphorus is a limited resource the practice of using phosphoric acid in the treatment of urine to enhance the process and for improving product value is questionable and can be further discussed.

Evaporation of N-depleted urine is an option. pH and buffer capacity are both reduced by the stripping of ammonia. In this project the pH of the large volume of N-depleted substrate was not as low as it possibly can be, since the N-depleted substrate was produced in several sets, where focus was not always on maximum N-depletion.

In laboratory tests it could be proved, that foaming of yellow water can be controlled easily by the addition of anti-foaming agents. Because of the very inhomogeneous matrix of urine a constantly occurring boiling retardation (delay of boiling point) leads to splashing if

no action is taken. Most effective seems to be the agitation of the substrate. However, in the used pilot plant this was not possible.

Within the evaporation bulb no crystal precipitation was observed. Some flock forming and after a while crystal growth occurred in the stored concentrates.

Crystallization, Precipitation, Adsorption

Introduction

Crystallization of phosphate salts from urine, precipitation and adsorption was investigated in lab scale. Stored urine, nitrogen depleted urine and concentrated urine were used as source. Different precipitants (MgO, $MgCl_2$, $CaCO_3$, $Ca(OH)_2$, $CaCl_2$) were used for precipitation and crystal formation. The precipitants were compared depending on their phosphate removal efficiencies. Zeolites and a burned clay mineral were used for adsorption of NH_4^+ and PO_4^{3-}. Also the ability of zeolites working as seed crystals in stored and concentrated urine was investigated.

Crystallization

Process description

Crystallization describes the formation of crystals from liquid solutions, melt, or from gas phase. In aqueous solutions crystallization can be achieved by evaporation or cooling, until at the given temperature conditions the saturation concentration of the substance focused on is exceeded. In cases of over-saturation the crystallization can be triggered by seed crystals or nuclei. The products of conventional crystallization can often be redissolved when the original conditions of temperature and concentration are restored.

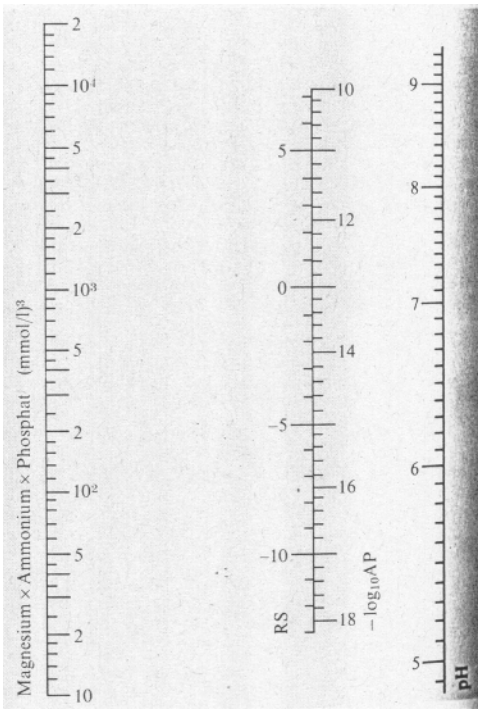


Figure 26: Nomogram of Magnesium ammonium phosphate $\{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\}$ [*CIBA Geigy 1977*]

The formation of crystals can be described by nomograms. In Figure 26 and Figure 27 two examples from [*CIBA Geigy 1977*] are given. On the scale in the middle values of the absolute saturation are given as negative log of the activity product (AP) as well as

information regarding the relative supersaturation (RS). While '0' on the RS-scale is describing the solubility product '1' is stating the crystal formation product. A negative value means that the concentrations of the components are not high enough to reach the solubility product. Thus, the solution is not saturated and crystals will dissolve. Values between '0' and '1' describe a meta-stabile region, where crystals can grow as long as seed crystals are present. At values above '1' spontaneous crystal formation should occur. [*CIBA Geigy 1977*]

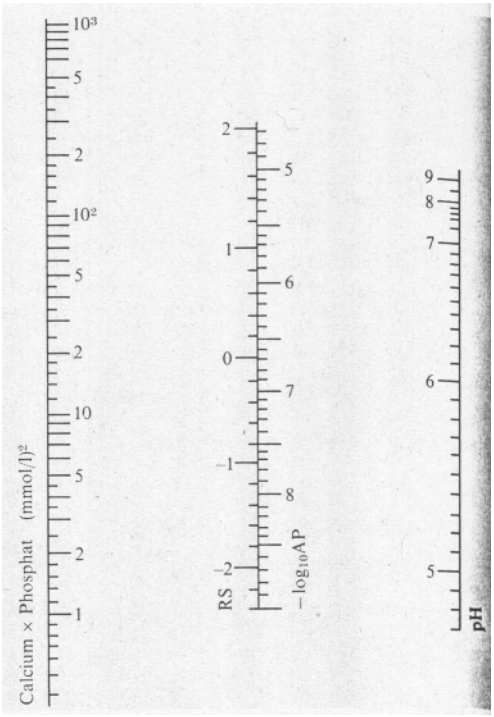


Figure 27: Nomogram of Calcium hydrogenic phosphate $\{Ca^{2+}\}\{HPO_4^{2-}\}$ [*CIBA Geigy 1977*]

Thus, at pH 9 and concentrations of ammonium, magnesium, and phosphate of each higher than 50 mmol/l MAP crystal formation can be expected. Likewise, at pH 9 and concentrations of calcium and phosphate of each higher than 30 mmol/l crystal formation of calcium phosphate can be expected.

In an oversaturated solution, the crystallization process will be induced by nucleation which means that very small particles (nuclei, only a few nanometers in size) are being formed. If these particles are thermodynamically stable, crystal growth begins. If the nucleation does not result in stable nuclei, the crystallization process will fail and the solution will stay oversaturated. In this case the nucleation can be assisted by adding crystals to the system serving as nuclei. These added crystals are referred to as seed crystals. Crystallization processes depend mainly on pH, temperature, and components in the system.

Material &Methods

To investigate the crystallization process concentrates from the evaporation process were further evaporated in glass vials in a drying oven, as well as stored in 500 ml glass bottles at ~20°C (room temperature) and at 5°C (fridge). TN, TP and pH were measured on a regular base. Crystals observed by eye vision were filtered over a filter with pore size of 1 mm. The

structure of the gained crystals was documented by pictures. Samples were analyzed by X-ray diffractometry.

Picture 10: Crystals after drying in a glass valve of 12x concentrate

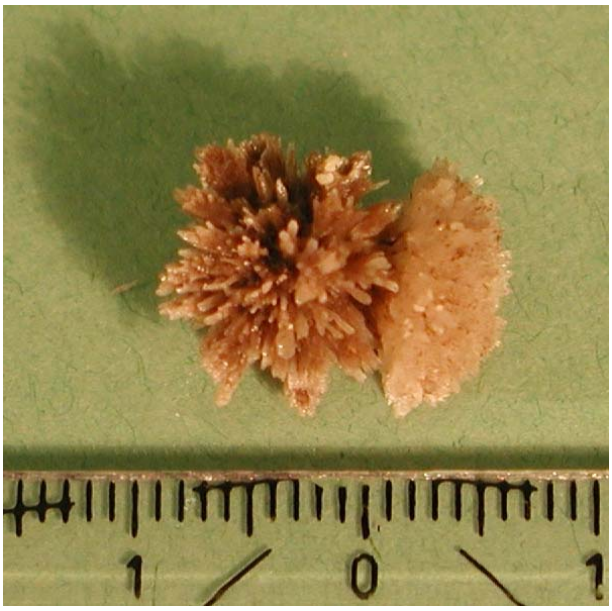
Results

From a 12x concentrate, that was acidified with H_2SO_4 prior to evaporation, a total of about 2 g/l of sodium ammonium hydrogen phosphate hydrate $Na(NH_4)HPO_4 \cdot 4H_2O$, and sodium ammonium sulfate NH_4NaSO_4 was obtained within two weeks. Crystals were analyzed qualitatively by X-ray diffractometry. Measurements of TP and TN did not allow a more detailed interpretation of the quantity.

Picture 11: Stercorit ($H(NH_4)Na(PO_4) \cdot 4H_2O$) washed crystals and grinded washed crystals from self crystallization from concentrated urine

In the dried residue of the 12x concentrate a total of 380 g/l was measured. Samples of the crystals that were obtained showed additionally to sodium ammonium sulfate and ammonium hydrogen phosphate hydrate signals of sylvit (KCl), and halit (NaCl).

From a 50x concentrate, that was acidified with H_3PO_4 prior to evaporation, about 24 g/l of stercorite, $H(NH_4)Na(PO_4) \cdot 4H_2O$ were obtained within four weeks storage at room temperature Picture 11.



Picture 12: Potassium Ammonium Phosphat ($0.73\ NH_4H_2PO_4 \cdot 0.27\ KH_2PO_4$)

In samples of the 50x concentrate that were stored at 5°C over a period of 6 weeks 16 g/l of potassium ammonium phosphate ($0.73\ NH_4H_2PO_4 \cdot 0.27\ KH_2PO_4$) were found. The crystals from this sample showed two very different structures with different colors: One brown crystal with a structure similar to a tree with branches, the other one white and much denser. Both of these were grown together when obtained from the substrate. Prior to X-ray-diffractometry they were separated but showed nearly identical signals.

Also in these cases measurements of TP and TN did not allow a more detailed interpretation of the quantity of contained substances.

Precipitation

Process description

Precipitation is the removal of a solved substance in form of crystals, flocks, or amorphous precipitate by adding a precipitant. Often 'precipitation' is applied to crystallizing systems and usually refers to supersaturation being generated by the addition of a third component that induces a chemical reaction to produce the solute or lowers its solubility [*Jones 2002*]. These systems commonly have rapid formation of the solid phase, which usually implies ‘fast crystallization’. Because of this fast formation precipitates (the obtained product) often have an amorphous pattern. Also, precipitation is often an irreversible process, i.e., many precipitates are virtually insoluble substances produced by a chemical reaction. [*Mullin 2002*]

The main product to be yielded from source separated urine is magnesium ammonium phosphate (MAP) also called struvite, a relatively insoluble crystalline precipitate [*Donnert & Salecker 1999*]. Struvite can be used as a slow-release non-burning fertilizer [*Ueno & Fujii 2001*]. It has an equimolar ratio of magnesium, ammonium and phosphate ions.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6\,H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad \textbf{Eq 16}$$

In the crystallization processes of struvite [*Çelen & Türker 2001*] could show that there is a pH reduction in the solution which suggests that HPO_4^{2-} precipitates rather than PO_4^{3-} (Eq 15)

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6\,H_2O \rightarrow MgNH_4PO_4.6H_2O + H^+ \qquad \textbf{Eq 17}$$

In urine magnesium is normally the limiting factor for struvite formation. The ratio phosphate/ammonia is very low (1/38).

The optimum pH for struvite formation is between 8.8 and 9.4. Since at lower pH struvite is soluble and most of the phosphate in urine is present as $H_2PO_4^-$ and HPO_4^{2-} struvite formation can be expected to be lower.

$$(Ca, Mg)(K, NH_4)(PO_4).6H_2O \qquad \textbf{Eq 18}$$

In struvite precipitation of small amounts of Ca (Mn and Fe) may substitute for Mg and K may substitute for NH_4^+ (Eq 16) [*Lind, Ban, & Byden 2000*]

Material & Methods

Experiments were conducted in a jar test system. The speed of the mixing system for 5 samples was adjustable from 100 to 1600 rpm. Different Ca and Mg salts were used as precipitant. Doses were calculated according to following equations:

$$m_S = \frac{a_P}{a_S} * C_M * V * M_S * srf \qquad \textbf{Eq 19}$$

and

$$\frac{C_P}{M_P} = C_M \qquad \textbf{Eq 20}$$

with

- C_P: concentration of phosphate as mg/l PO_4-P
- M_P: mass of phosphate for 1 mmol (mg/mmol)
- C_M: concentration of phosphate as mmol/l PO_4-P
- m_S : needed amount of added precipitant (mg)

V : volume of the sample (l)
M_S : molar weight of the added precipitant as mg/mmol
srf : stoichiometric rate factor
a_p : molar ratio of phosphate in desired product
a_s : molar ratio of Mg^{++} or Ca^{++} ions in the added salt

For MAP the stoichiometric rate of magnesium/phosphate is 1/1. For calcium phosphate salts, the product phosphate ratio changes depending on the salt that will precipitate. The ratio of the expected precipitates lies between 0.67 for $Ca_3(PO_4)_2$ and 0.6 for hydroxylapatite. However, for calculation the product molar phosphate ratio a_P was set to be 1.

The stoichiometric rate factor (srf) was used for the ratio between the added salt and the theoretical calculated amount needed by the stoichiometric rate (Eq 19). A factor srf greater than 1 means, that the addition is higher than the theoretical need. The doses varied from a stoichiometric rate factor regarding P from 1 to 3, in one case up to srf 19.

$$srf = \frac{\text{amountof precipitant}}{\text{stoichiometric need}} \qquad \textbf{Eq 21}$$

The precipitant was given directly to the beaker before 200 ml of urine sample was added. Mixing time was varied in different sets between 6 and 45 min following sedimentation at different time intervals. After the sedimentation phase a sample from the supernatant was analyzed regarding phosphate and ammonia.

Following salts were used for precipitation of MAP respectively calcium phosphate:

1. Magnesium oxide (MgO): low solubility; light basic effect
2. Magnesium chloride ($MgCl_2$): weak acidic effect; high solubility
3. Calcium carbonate ($CaCO_3$): very low solubility in water
4. Calcium hydroxide ($Ca(OH)_2$): high basic effect; widely used in treatment plants
5. Calcium chloride ($CaCl_2.(2H_2O)$): very well soluble in water; acidic effect

Results

Addition of Mg-salts to stored urine

In a first set a wide range of MgO dosage was investigated. Addition of MgO induces an increase of pH. However, the effect of pH change on stored urine is negligible due to the high buffer capacity of hydrolyzed urine. For a stoichiometric rate factor of 2 the addition of about 1 g MgO per litre urine causes a pH increase from 8.8 to pH 9.0.

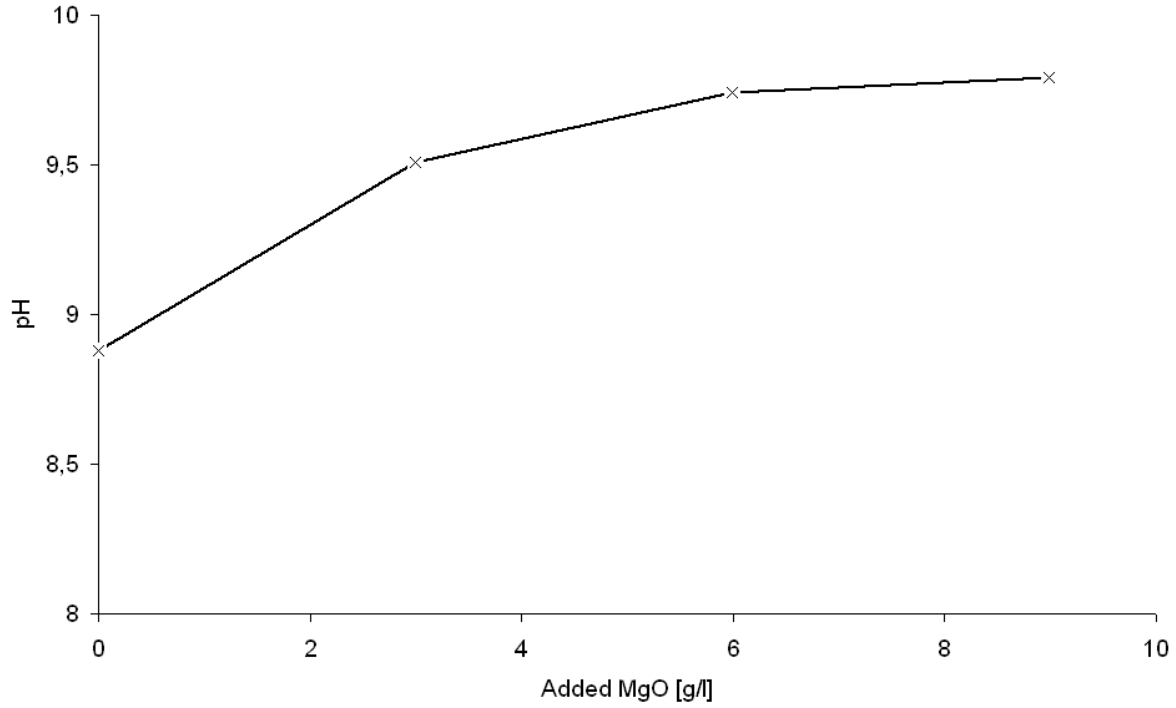


Figure 28: pH change after addition of MgO to stored urine

At the same time MgO dosages above srf 3 (~1.4 g MgO /l) did not lead to increased P-removal in the samples of stored urine.

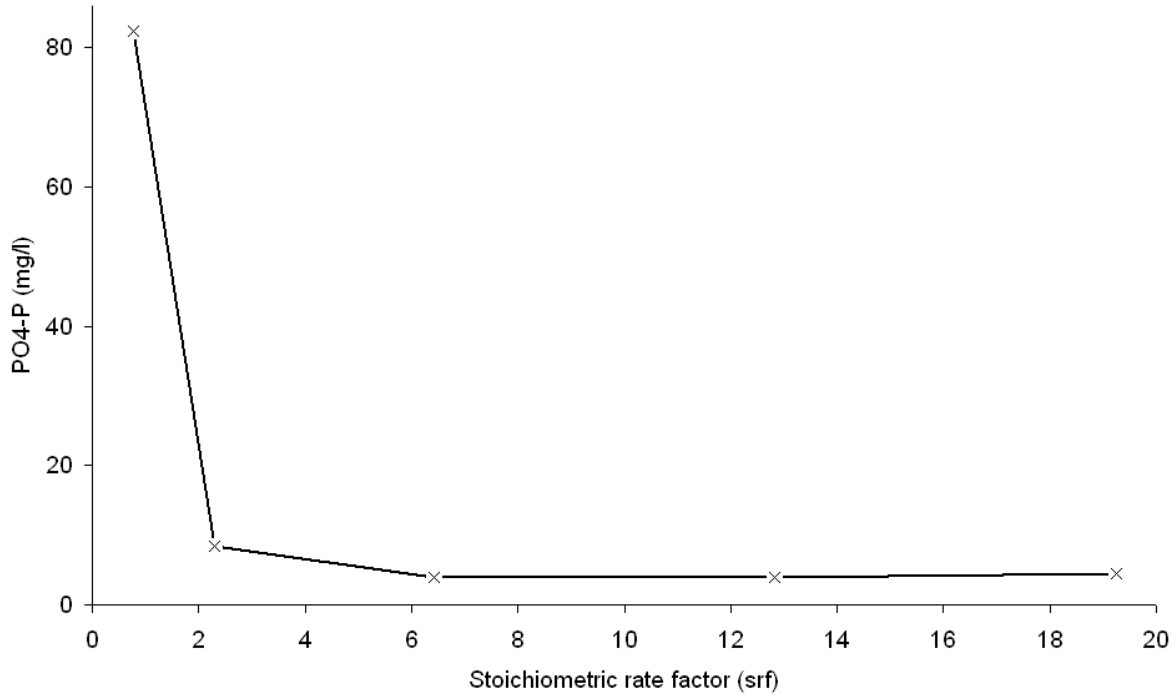


Figure 29: Phosphate concentrations in urine after dosage of MgO, srf 1 - 20

In a second set dosages below srf 2 were investigated in more detail.

Table 23: Phosphate concentrations after dosage of MgO, srf 1 - 1.8

MgO srf	PO_4-P_{feed} mg/l	PO_4-P mg/l	*Reduction %*
1	362	71	*80%*
1,2	362	22	*94%*
1,4	362	8,6	*98%*
1,6	362	6,5	*98%*
1,8	362	5,9	*98%*

At a stoichiometric rate factor of 1.5 nearly 98% phosphate were removed (Table 23, and in appendix Figure 55). The effect of mixing and sedimentation time was also observed. Intervals were varied between 5 and 45 minutes. The influence on P-removal was small and is presented in the appendix (Table 61 - Table 63, and Figure 56).

Because of the low solubility of MgO, often $MgCl_2$ is used as precipitant. Because of its higher molecular weight, dosages have to be more than doubled. Removal rates are comparable to MgO (Table 64, Figure 59). Again, the effect on pH in stored urine was small (Table 24, Figure 58)

Table 24: Addition of $MgCl_2$

srf		1x	2x	3x
$MgCl_2$ added [g/l]	0	1.1	2.2	3.3
$(PO_4)_{initial}$	362			
$(PO_4)_{end}$		22	5.8	4.9
removal rate		94%	98%	99%
pH	8.9	8.8	8.7	8.7

Addition of Mg-salts to N-depleted substrate

The composition of the N-depleted feed substrate for MAP-precipitation is given in Table 25.

Table 25: The composition of nitrogen depleted urine, compared to stored urine

	N-dep(*	stored
PO_4-P (mg/l)	322	359
PO_4-P (mmol/l)	10.4	11.6
NH_3-N (mg/l)	119	3642
NH_3-N (mmol/l)	8.5	260
pH	6.8	8.8
Conductivity (mS/cm)	17.2	33

*) average values from the experiments

The phosphate content in comparison to the tested urine described above was lower and the ammonia stripping removed about 97 % of total ammonia. The experiments were carried out for MgO and $MgCl_2$.

Table 26: MgO and $MgCl_2$ addition to N-depleted urine

	MgO	MgO	$MgCl_2$ *$6H_2O$	$MgCl_2$ *$6H_2O$
srf	1.36	2.72	1.36	2.72
PO_4-P_i [mg/l]	276	276	276	276
PO_4-P_e [mg/l]	85	28.7	274	270
Removal [%]	69	90	0.7	2.2
pH_i	6.0	6.0	6.0	6.0
$pH_{\text{after mix}}$	9.0	9.8	5.9	5.8
$pH_{\text{after sed}}$	9.0	9.8	6.0	5.8

Because of the pre steam-stripping pH and buffer capacity was reduced. The effect is shown in Figure 30. Therefore, MgO addition had a much stronger effect on the pH of N-depleted substrate than in case of the stored urine.

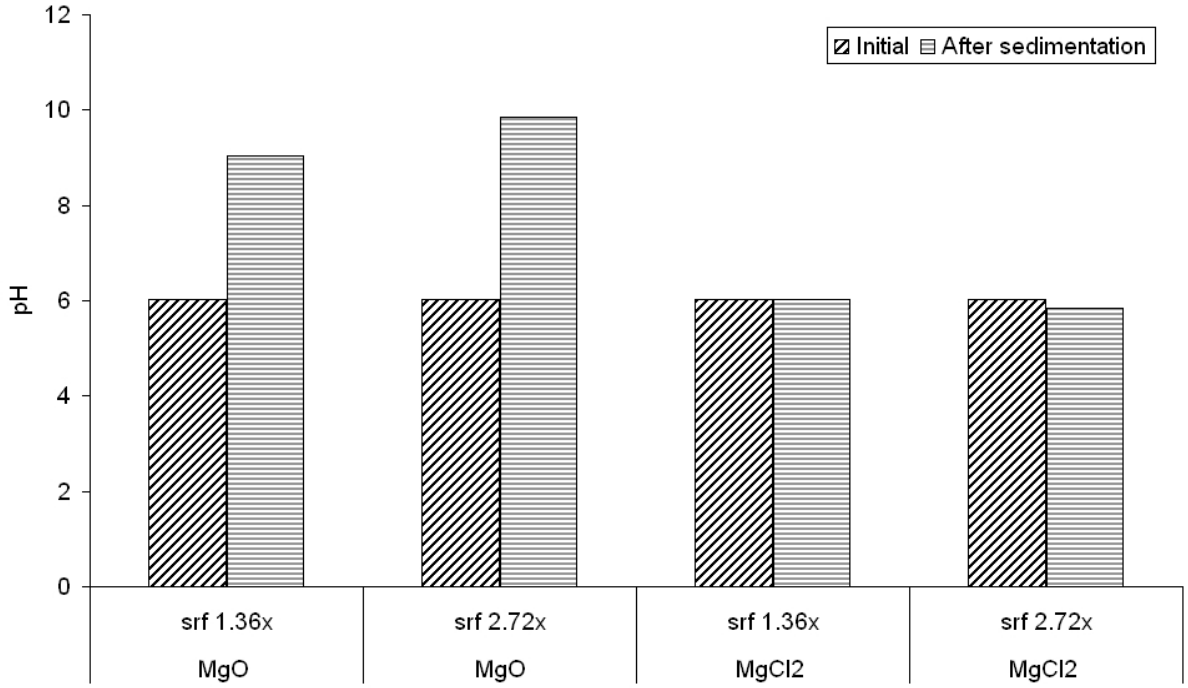


Figure 30: pH change in N-depleted substrate after addition of MgO and $MgCl_2$

At the same time pH of N-depleted urine can be adjusted in this case by addition NaOH (Figure 31).

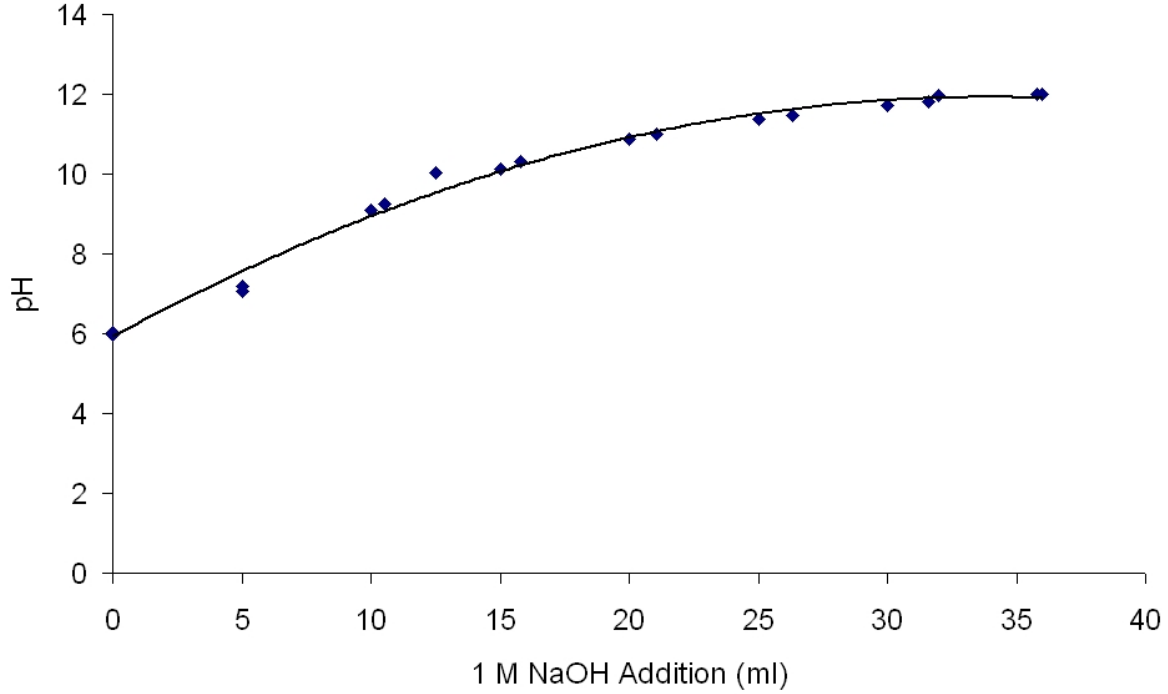


Figure 31: pH change by addition of 1M NaOH (NH_3-N = 119 mg/l))

Without pH adjusting results of P-reduction by addition of MgO and $MgCl_2$ is presented in Table 26 and Figure 32. Since the low pH of N-depleted urine of about 6 was even decreased by the addition of $MgCl_2$ Nearly no P could be removed. MgO addition raised the pH up to more than 9, where conditions are optimal for MAP crystallization.

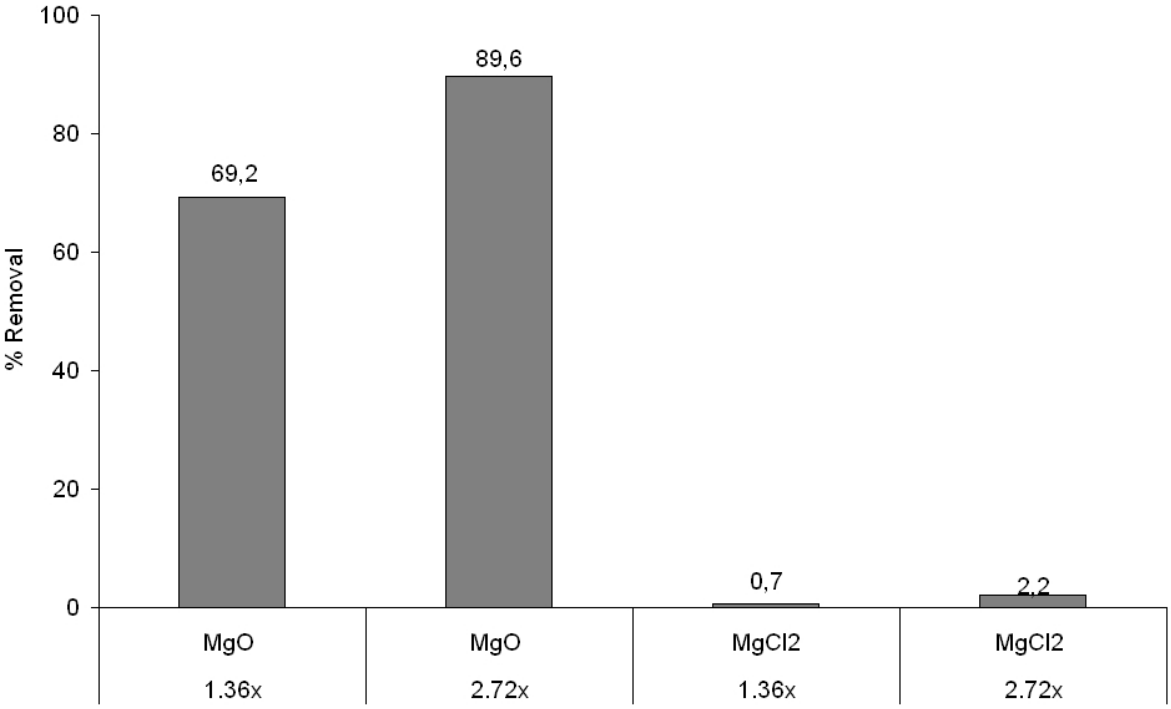


Figure 32: N-dep, comparison of phosphate removal for MgO and $MgCl_2$ addition (PO_4-P_I = 276 mg/l)

In a next step P-removal efficiency of $MgCl_2$ in N-depleted urine was investigated at different pH. pH was raised by addition of NaOH to $pH_{initial}$ 8, 10, and 12. As can be seen in Table 27 pH decreased by addition of $MgCl_2$ drastically. Thus, even after NaOH addition for a pH-increase to $pH_{initial}$ = 10 P-removal was negligible (Table 27, Figure 60).

Table 27: $MgCl_2$ addition to N-dep substrate; phosphate end concentrations at different pH values (PO_4-P_I = 276 mg/l)

srf	2.7	2.7	2.7	2.7
PO_4-P_e [mg/l]	270	272	266	83
Removal [%]	2.2	0.7	2.4	69
$pH_{initial}$	6.0	8	10	12
$pH_{after\ mix}$	5.8	7.2	8.2	10.2
$pH_{after\ sed}$	5.9	7.3	8.6	10.4

P-removal efficiency at different srf for $MgCl_2$ in N-depleted urine at an elevated pH of 12 is presented in Table 28 and Figure 61 in the appendix.

Table 28: $MgCl_2$ addition to N-dep substrate; phosphate end concentrations at different saturation rate factors (PO_4-P_I = 2767 mg/l)

srf	1.4x	1.7x	2.0x	2.4x
PO_4-P_{end} [mg/l]	50	10	12	5
Removal [%]	81	96	96	98
$pH_{initial}$	12	12	12	12
$pH_{after\ mix}$	11,3	11,0	10,7	10,4
$pH_{after\ sed}$	11,1	10,8	10,5	10,3

Addition of Ca-salts to stored urine

Additionally to the use of Mg-salts as precipitants three Ca-salts were used for precipitation.

Table 29: Stored Urine; Comparison of phosphate removal for different calcium salts (srf=2)

	$Ca(OH)_2$	$CaCl_2$	$CaCO_3$ (Powder)
srf	2x	2x	2x
PO_4-$P_{initial}$ [mg/l]	210	210	359
PO_4-P_{end} [mg/l]	199	74.7	356
P-removal [%]	5.2	64	0.8
pH	8.7	8.7	8.6

The solubility of calcium chloride is the greatest of the three salts used as precipitant. The one of calcium carbonate is the lowest. This was equivalent to the removal rate because of the Ca^{2+} ion concentration and the solubility equilibrium. The solubility equilibrium of

calcium phosphate salts depend on the calcium concentration, a higher concentration which is achieved by a more soluble calcium salt causes a higher supersaturation and driving force to form calcium phosphate salts.

Addition of Ca-salts to N-depleted urine

For precipitation using Ca-salts the pH of the N-depleted urine was raised to pH 12 using NaOH.

Table 30: Ca-precipitants in N-depleted urine; phosphate concentrations at pH 12 and srf 2.7

	$CaCO_3$	$Ca(OH)_2$	$CaCl_2$
srf	2.7	2.7	2.7
PO_4-$P_{initial}$ [mg/l]	276	276	276
PO_4-P_{end} [mg/l]	262	30.8	4
P-removal [%]	5.1	89	99
$pH_{initial}$	12	12	12
$pH_{after\ mix}$	12.0	12.5	11.6
$pH_{after\ sed}$	12.0	12.6	11.6

Again, the low solubility of $CaCO_3$ caused little precipitation. The pH was not dramatically influenced by the addition of the precipitants.

Comparison of precipitation in urine and N-depleted urine

Precipitation of ammonium and phosphate is technically well feasible in both substrates. While the low pH of N-depleted urine will inhibit formation of crystals, it can be easily be increased by addition of NaOH, $Ca(OH)_2$ and presumably also by the addition of MgOH which however is assumed to be not that stable. It has to be noted that in case of addition of $Ca(OH)_2$ to N-depleted urine no tests were conducted at the initial pH of the N-depleted substrate.

Table 31: Stored and N-depleted urine comparison depending on the phosphate removal performance by salt addition

	Stored		N-Depleted	
	srf	*Removal (%)*	srf	*Removal (%)*
MgO	1.5x	*98*	2.7x	*90*
	1x	*80*	-	-
$MgCl_2$	2x	*98*	2.4x	*98**
	1x	*94*	1.7x	*96**
$Ca(OH)_2$	2x	*5.2*	2.7x	*89**
$CaCl_2$	2x	*64*	2.7x	*99**

* pH was adjusted to 12

The conducted experiments represent a first screening of different precipitants for the N-depleted substrate. More detailed investigation might be promising.

Precipitation with MgO in concentrated urine

To the 50 fold concentrate from the evaporation process MgO and $MgCl_2$ were added as precipitants. Because of the extremely high phosphorous concentration in the concentrate, saturation rate factors below and equal 1 were used.

Table 32 MgO addition to 50 fold concentrate

srf	0.07	0.25	0.5	1
MgO addition [g/l]	5	18.7	37.4	74.8
PO_4-P $_{Initial}$ [g/l]	57.5	57.5	57.5	57.5
PO_4-P $_{End}$ [g/l]	56.5	49.4	36.7	10.5
P-Removal[%]	1.7	14	36	82
$pH_{Initial}$	5.0	5.0	5.0	5.0
$pH_{after\ mix}$	4.9	5.2	5.4	5.9
$pH_{after\ sed}$	4.5	4.7	4.9	5.4

The results in Table 32 show that the removal of phosphate in concentrate is possible with MgO addition. Although the pH was not increase, P-removal rate at srf 1 was 82 %, which is comparably to the P-removal at srf 1 in untreated stored urine. This is due to the high concentrations, far beyond the saturation concentration (see Figure 26). Therefore removal efficiency within the same time frame was equivalent to the one yielded at stored urine. However, the addition of large quantities of MgO also caused an increase in the solution temperature. At an addition of srf 1 MgO the temperature within the sample raised from room temperature up to 65ºC. The produced solution was highly viscous. A separation of solid and liquid phase was difficult at first. Obviously reaction times at those high concentrations are higher. At the same time it could be observed that the product was more of a crystal-form instead of the amorphous precipitate in the experiments with stored urine.

Precipitation with $MgCl_2$ in concentrated urine

The solubility of $MgCl_2$ is higher than the one of MgO. Therefore $MgCl_2$ at three saturation rate factors was use as precipitant in the 50 fold concentrated urine from the evaporation process. Because of high buffer capacities of the concentrate the pH was not altered prior precipitant dosage.

Similar to the addition of MgO a temperature increase was observed, but temperatures did not exceed 30°C. For all tested srf values phosphate removal was above 50%. The highest P-removal achieved was for the srf 0.5 with a removal of 64 %. The lowest dosage with srf 0.1 was able to remove 54 % of phosphate, which was more than the stoichiometrically expected value of 10 %, as it can be seen from the removal efficiency. This can be explained by the fact, that not only MAP was formed but also other phosphate-crystals, probably

induced by the formation of MAP. The comparably low P-removal rate at sfr 1 is probably due to the pH reduction by adding large quantities of $MgCl_2$.

Table 33: $MgCl_2$ precipitant in concentrated urine

srf	0.1	0.5	1
$MgCl_2.6H_2O$ [g/l]	38	189	377
PO_4-$P_{initial}$ [g/l]	57.5	57.5	57.5
PO_4-P_{end} [g/l]	26.7	20.5	23.2
PO_4 Removal [%]	54	64	60
Removal Efficiency [%]*	536	129	60
pH	4.2	2.2	0.82

* Removal efficiency is the molar rate of actual removed phosphate to the added $MgCl_2$

Adsorption

Adsorption on different materials is a widely used process in wastewater treatment. Zeolites are well known for their adsorption properties and their cheap prices. In a work conducted at Istanbul Technical University, a zeolite (clinoptilolite) was used on separately collected urine [*Beler-Baykal et al. 2004*]. The highest surface concentration attained under experimental conditions employed was 15.4 mg ammonium per gram of clinoptilolite for an initial concentration of 110 mg ammonia per liter. The highest removal was 98 %, obtained for a loading of 1 mg ammonium per gram clinoptilolite, which would cause a need of 6 kg of clinoptilolite per liter urine with a NH_3 concentration of 5 - 6 g per liter. The recovery efficiency by washing with tap water was 63%.

Material & Methods

For the investigation of adsorption a bottle test was used. Selected amounts of zeolite and urine were given to a 250 ml bottle. Thereafter the closed bottle was mixed for 5 min following a 48 hours adsorption time. 50 g of zeolite were mixed with 100 ml of urine. Since the bottles were closed the ammonia the loss of ammonia due to evaporation should be negligible. Additionally a reference bottle with urine only was observed.

Following adsorbents were used:

1. Zeogranul: granulate form with the diameter 1 - 2 mm.
2. Zeolite: granulate form with the diameter 3 - 5 mm
3. burned clay mineral: filter material with high surface area
4. activated carbon is well known for its good adsorption properties and it is widely used in water and wastewater treatment processes. The activated carbon used was Degussa Degusorb HKW1.

   Unfortunately no clinoptilolite could be used because of supply problems.

Results

Phosphate and ammonia removals are presented in Figure 33 and Table 65. As can be seen from Figure 33 the removals for ammonia and phosphate achieved by both zeolites are over 50 %. In case of zeogranul and for an initial concentration of 360 mg/l PO_4-P and 3544 mg/l NH_3-N the end concentrations of 14.8 mg/l PO_4-P and 178 mg/l NH_3-N were achieved.

The adsorption of ammonia and phosphate per gram of zeolite is presented in the appendix in Table 65. With a maximum adsorption rate of 5.86 mg NH_3-N per gram zeolite literature values for clinoptilolite could not be verified. At the same time little data exist regarding phosphate reduction by addition of zeolites. Especially in case of zeogranul high removal rates of 96 % could be achieved.

The process handling was very simple, and the product might have a chance to get used in agriculture. The 48 hour adsorption time was not varied. A shorter time might be achievable. The amount of zeogranul needed to remove phosphate and ammonia was very high (nearly 0.5 kg/litre urine), the usage of zeogranul as a polishing stage after another ammonia or phosphate removal process might be more useful.

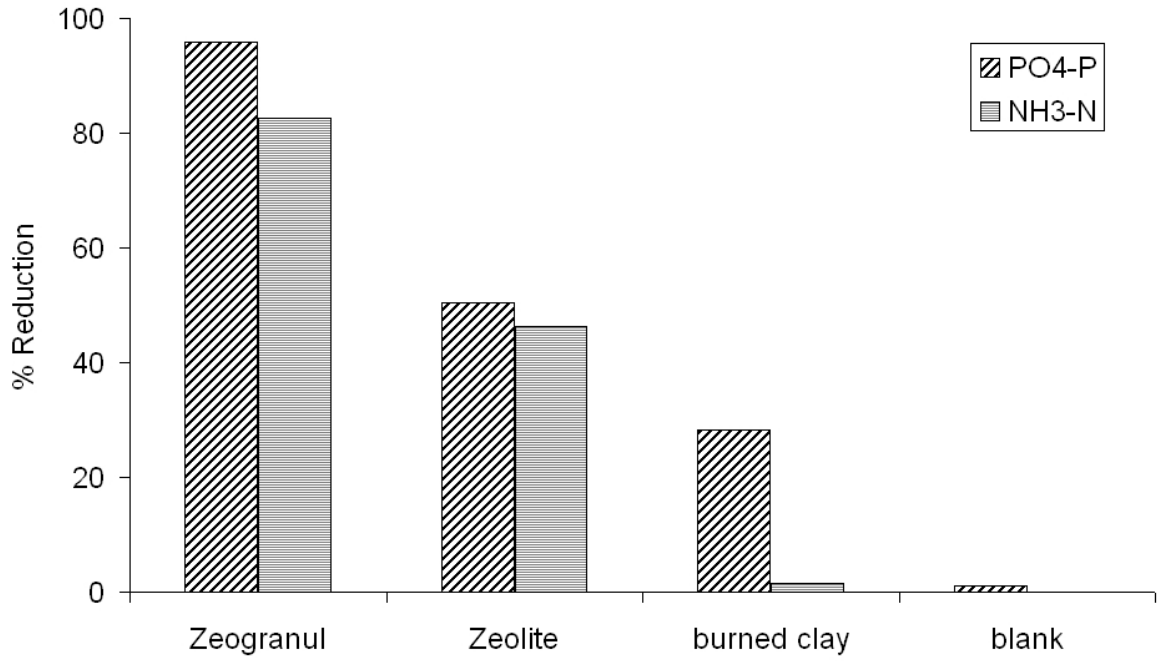


Figure 33: Stored Urine adsorption of phosphate and ammonia on zeolites

Addition of activated carbon

Activated carbon (AC) is well known for its adsorption capacity due to its very high surface area. Thus, different dosages of activated carbon were tested. The dosages used were higher than the normally used for wastewater. The experiment was carried out with 30 minutes mixing and respectively 30 minutes sedimentation in an open beaker.

Table 34: Stored Urine activated carbon (AC) addition; phosphate and ammonia removal

AC dosage [g/l]	5	50	250
PO_4-P $_{initial}$ [mg/l]	360		
PO_4-P $_{end}$ [mg/l]	348	260	17.8
PO_4-P removal [%]	3.3	27.8	95.1
Adsorption mg PO_4-P/ g AC	0.48	0.4	0.27
NH_3-N $_{initial}$ [mg/l]	3482		
NH_3-N $_{end}$ [mg/l]	3236	3306	2955
NH_3-N removal	7.1	5.1	15.1
Adsorption mg NH_3-N /g AC	9.84	0.7	0.42

The high dosages of 50 and 250 g AC/l had only experimental purposes. Practically they are not applicable due to the high costs. Longer adsorption times might have been more sufficient. The usage of activated carbon as polishing step can be possible.

Conclusions

The removal efficiency for phosphate in all investigated substrates was found to be depending on the dosage of precipitants. MgO and $MgCl_2$ had given over 95% phosphate removal by lower dosages. For nitrogen depleted urine except MgO a pH adjustment was needed and high phosphate removals could be achieved for MgO, $Ca(OH)_2$ and $CaCl_2$.

The usage of zeolites for ammonia and phosphate removal was possible. However, the amount of zeolite needed for removal of ammonia and phosphate was very high. Although costs for zeolites are normally low, transport costs will be high. The use of zeolites for a polishing step after another ammonia or phosphate removal process seems reasonable.

Processes for the reduction/removal of pharmaceutical residues

The effect of steam stripping and evaporation on the reduction of PhaR in urine was investigated as well as ozonation and UVC-radiation as additional processes. Stored and processed urine was treated and investigated as it was. Samples were not additionally spiked. Focus was on selected PhaR which are commonly referred to in literature and which are presented in Table 38 and Table 39.

The detection limit (LOD) of PhaR in urine matrix was different from the LOD in aqueous solutions, such as condensates and distillates. In most cases it could be lowered throughout the running time of the project. In Table 35 nowadays LODs are given.

Table 35: Level of detection of PhaR

	LOD urine matrix	LOD aqueous solutions
16α-Hydroxyestron	10 µg/l	0,02 µg/l
17α-Ethinylestradiol	50 µg/l	0,02 µg/l
Acetylsalicylic acid	0,5 µg/l	0,02 µg/l
Bezafibrate	0,5 µg/l	0,02 µg/l
β-Sitosterol	2 µg/l	0,01 µg/l
Carbamazepine	0,5 µg/l	0,02 µg/l
Clofibric acid	0,5 µg/l	0,02 µg/l
Diclofenac	0,5 µg/l	0,02 µg/l
Estradiol	10 µg/l	0,01 µg/l
Estriol	100 µg/l	0,02 µg/l
Estrone	10 µg/l	0,01 µg/l
Fenofibrat	0,5 µg/l	0,02 µg/l
Fenoprofen	0,5 µg/l	0,02 µg/l
Gemfibrozil	0,5 µg/l	0,02 µg/l
Ibuprofen	0,5 µg/l	0,02 µg/l
Indometacin	0,5 µg/l	0,02 µg/l
Ketoprofen	0,5 µg/l	0,02 µg/l
Mestranol	5 µg/l	0,01 µg/l
Pentoxifylline	0,5 µg/l	0,02 µg/l
Phenacetin	0,5 µg/l	0,02 µg/l
Phenazone	3 µg/l	0,02 µg/l

If not stated otherwise blank values in the following tables about PhaR concentrations mean that the concentration was below the limit of detection. If parameters were not measured, this is stated separately. In the figures parameters that were not found in the initial substrate are not listed.

Steam stripping and evaporation

The process description can be found in the chapters 'Steam stripping' and 'Evaporation'.

Samples were taken during the steam stripping process from initial substrate, condensate, and N-depleted substrate. During evaporation samples were taken from initial substrate, concentrate, and distillate during the evaporation of untreated stored urine.

UVC-radiation

The UVC-radiation system consisted in a UVC reactor and a feed tank. Substrate was circulated through the reactor.

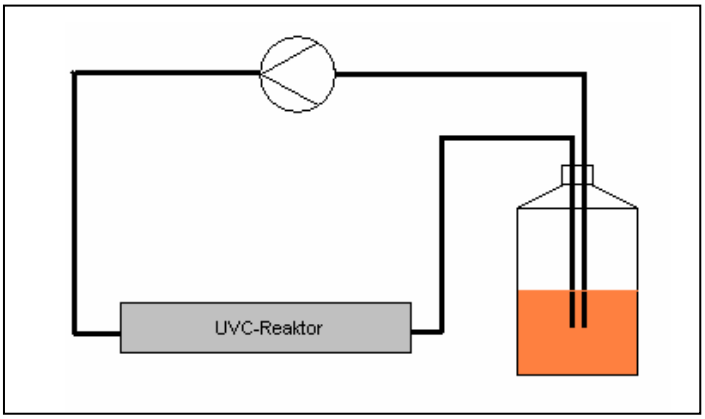


Figure 34: Scheme of UVC-radiation

Two different samples were processed. Untreated stored urine and N-depleted urine were pumped with a flow of 12l/h from a feed bottle trough a tube containing a UVC-lamp by a diaphragm pump (ProMinent B 02.035). The lamp was a sterilAir UVC ½ 4VHS with 16W (5.3W @ 254nm + 185nm), and a high ozone-output. Samples were taken after 20, 74, and 120 hours for the stored urine, respectively 27, 74, and 140 hours for the N-depleted urine. Different time intervals result from adjustments prior the second set of UVC-radiation. Therefore following UVC-dosages were applied:

Table 36: UVC-dosages for stored urine and N-depleted urine

Stored urine	N-depleted urine
0.4 kWh/l	0.6 kWh/l
1.6 kWh/l	1.6 kWh/l
2.7 kWh/l	3.2 kWh/l

Reason for the selection of high energy dosages were prior experiments for removal of urochromes from urine [*Tettenborn et al. 2006*] .

Ozonation

Ozone is highly reactive. Materials/molecules that have chemical double bonds, or that contain oxidisable elements can be oxidised by ozone. The specific and direct reaction of ozone with organic substances is due to an electophilic addition that leads to a splitting of the C=C double bonds (Crigée mechanism). Reaction rate constant is rather slow in the range of $k_D = 1.0 - 10^3\ M^{-1}s^{-1}$ [*Gottschalk, Libra, & Saupe 2000*]. During indirect reaction secondary oxidants, especially hydroxyl radicals (OH°), are formed by the decay of ozone. These react non-selectively and immediately ($k = 10^8 - 10^{10}\ M^{-1}s^{-1}$) with solutes.

Most pharmaceuticals have an aromatic molecular structure. These aromatic rings can be attacked by ozone according to the Crigee-mechanism.

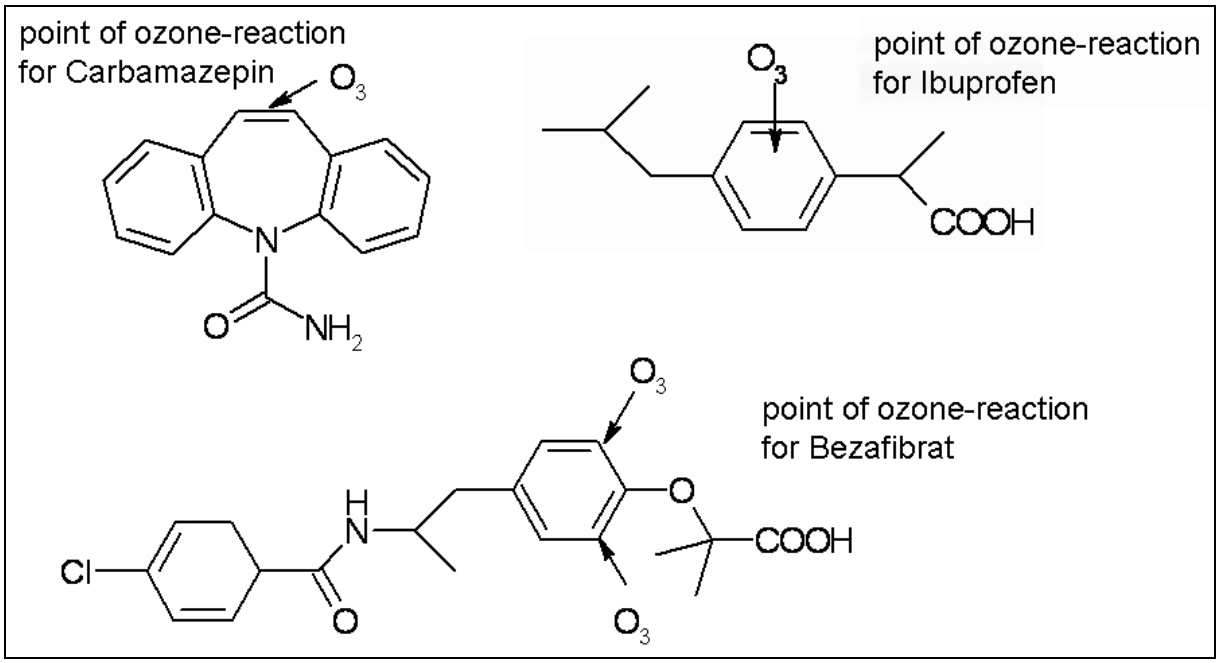


Figure 35: Examples for point of ozone attack at carbamazepine, ibuprofen, and bezafibrate [*Huber et al. 2003*]

The ozone was produced by an ozone-generator from Sander. Substrate was filled in a 2 l bottle were it was percolated with ozone. The ozone-uptake was derived from the difference between O_3 in-put and O_3 out-put, measured by ozone-analyzers. The ozone-gasflow was saturated with H_2O prior entering the reaction bottle to avoid evaporation. The off-gas was treated in a sodium-thiosulphate solution and thereafter released into the fume-hood.

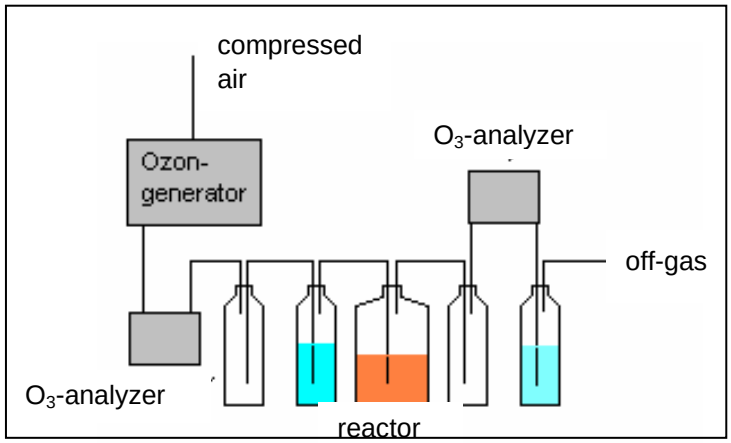


Figure 36: Scheme of Ozonation

Gas flow was 10 l/h, initial volume of substrate 600 ml. Samples were taken after 1, 3, 6, and 24 hours, respectively. Therefore the consumed ozone dosages (ozone-uptake) varied depending on the ozonated substrate. Results are given in respect to consumed ozone dose.

Stored urine and N-depleted urine at different pH values were ozonated.

Table 37: Input parameter of ozonation, dosage is representing the consumed amount of ozone

Urine	
pH	dosage [g O_3/L]
8.9	1.0
8.9	1.6
8.8	0.6
8.8	4.1
8.7	0.8
8.7	5.9

Urine	
pH	dosage [g O_3/L]
7	2.0
4	0.5
4	0.9

N-depleted urine	
pH	dosage [g O_3/L]
7.9	0.7
7.9	4.8
6.7	1.4
6.7	1.9
4	0.6
4	1.3

Again, the dosages used were selected according to prior experiments for removal of urochromes from urine [*Tettenborn et al. 2006*].

Results

Untreated urine

In the urine used as initial substrate for the different processes eight of 21 tested parameters, which are commonly referred to in literature, were detected (Table 38, Figure 37). It has to be noted that the contributors at the two locations represent only a fraction of the population. More details regarding the source location and number of users can be found in the chapter about 'Stored urine'.

Ibuprofen and bezafibrate were the PhaR with by far the highest concentrations (nearly all samples above 200 µg/l, and up to 850 µg/l). β-sitosterol, diclofenac and carbamazepine were detected in ranges between 10 and 50 µg/l. Phenacetin (detected in four of six samples),

Pentoxifylline (detected in five of six samples), and phenazone (detected in three of six samples) were mainly detected in the range just above the detection limit of 1 μg/l and 10 μg/l.

Table 38: Concentrations of pharmaceutical residues found in urine from a public urinal at Hansaplatz, Hamburg (HH) and from the separation system Stahnsdorf, Berlin (B) in order of highest concentration of average (Avr.).

		HH March 05	HH Mai 05	B Okt 05	B Nov 05	HH Dez 05	B Mai 06	*Avr.*	*Stand. dev.*	*95% Conf*	*Min*	*Max*
Ibuprofen	μg/l	411	511	398	794	417	442	***496***	*138*	*121*	*398*	*794*
Bezafibrate	μg/l	202	192	846	207	230	495	***362***	*241*	*211*	*192*	*846*
β-Sitosterol	μg/l	31	52	30	22	18	40	***32***	*11*	*10*	*18*	*52*
Diclofenac	μg/l	27	17	9	45	17	14	***21***	*12*	*10*	*9*	*45*
Carbamazepine	μg/l	23	29	11	13	20	4	***17***	*8*	*7*	*4*	*29*
Phenacetin	μg/l	23	< 1	< 1	1	2	1	***7***	*9*	*8*	*1*	*23*
Pentoxifylline	μg/l	8	9	< 1	3	7	6	***7***	*2*	*2*	*3*	*9*
Phenazone	μg/l	< 3	< 1	< 1	2	4	2	***3***	*1*	*1*	*2*	*4*

Table 39: Substances below detection limit resp. not detected in urine samples

Substances not detected	Amount in [μg/l]
Clofibric acid	< 1,0
Estrone	< 10
17α-Ethinylestradiol	< 50
Fenofibrat	< 1,0
Fenoprofen	< 1,0
Indometacin	< 1,0
Ketoprofen	< 1,0

Acetylsalicylic acid	no
Gemfibrozil	no
Estradiol	no
Estriol	no
Mestranol	no
16α-Hydroxyestron	no

The samples were also analyzed regarding substances in Table 39. None of them was found in any sample. In one case 17a-ethinylestradiol was detected in a N-depleted substrate at a concentration of 11 μg/l, although it could not be detected in the initial stored urine. The change of matrix by steam stripping might have changed interferences that avoided detection in the stored urine. The LOD in the matrix of stored urine was actually above 50 μg/l.

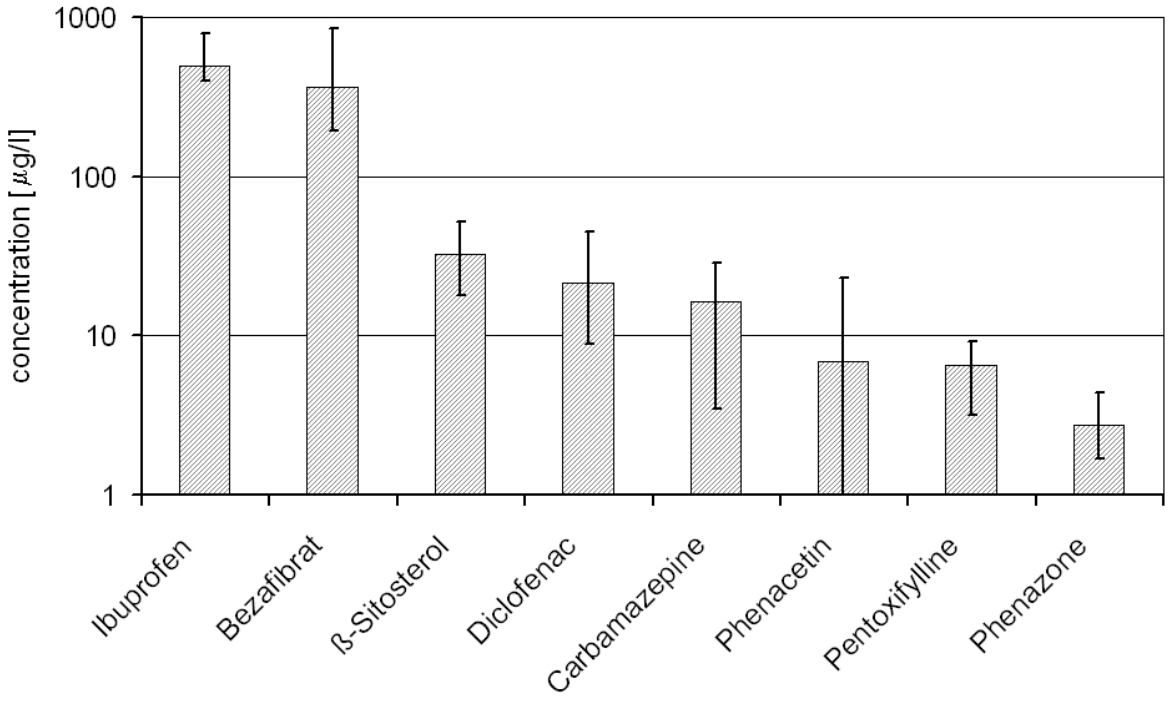


Figure 37: Average concentrations and the minimum and maximum concentrations of PhaR found in urine presented on a logarithmic scale

Steam stripping

Lab scale steam stripping

In the lab scale stripping unit the behavior regarding heat and volatility of PhaR was investigated. In two different sets one sample of the feed substrate and each two samples of the N-depleted substrate after steam stripping and each two samples of the condensate were taken. Results are presented in Table 40 and Table 68.

Table 40: Average initial concentration of PhaR and average normalized concentrations of PhaR found in N-depleted substrate and condensate in lab scale

	C_0 µg/l	N-dep C_d/C_0	Cond C_d/C_0
Ibuprofen	411	0.72	0.009
Bezafibrate	202	0.82	0.005
β-Sitosterol	31	0.82	0
Diclofenac	26	0.67	0.027
Phenacetin	23	0.35	0.011
Carbamazepine	23	0.48	0.012
Pentoxifylline	8	0	0

The dilution effect of steam condensed within the stripping column was in average 81 % (Eq 10). When excluding the dilution effect of the steam ((C_d/C_0)/DF), it can be

calculated that there was obviously no reduction in bezafibrate and in β-sitosterol in the N-depleted substrate. A retention time of 3 - 5 min at 100°C could not affect theses substances. Diclofenac and ibuprofen could be reduced by 18 and respectively 12 %. Phenacetin and carbamazepine were reduced respectively by 57 and 41 %. Pentoxifylline was not detected; neither in the N-depleted substrate nor in the condensate.

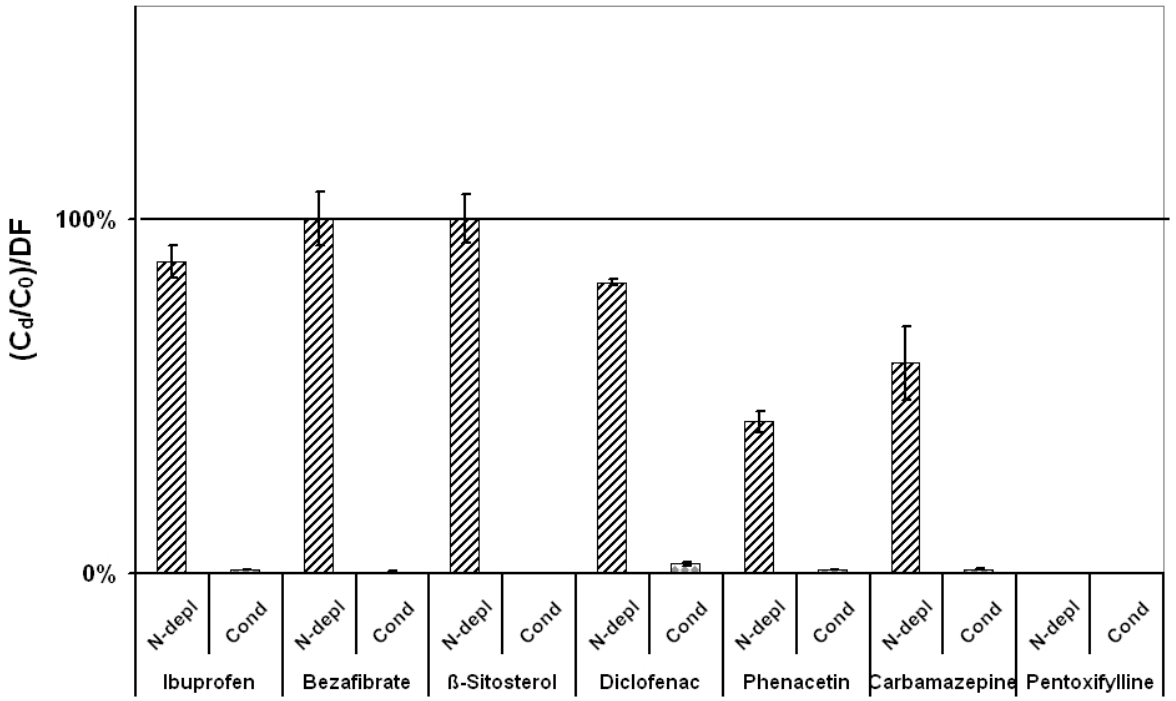


Figure 38: Average normalized concentrations and their standard deviation of N-depleted substrate and condensate from lab scale steam stripping process regarding feed concentration in order of highest initial concentration. The dilution effect is excluded. Pentoxifylline could be detected neither in the N-depleted substrate nor in the condensate.

About 1 % of the amount of the initial substrate concentration of ibuprofen, phenacetin, and carbamazepine could be found in all samples of the condensed off-steam. In three of four samples of the condensed off-steam traces (0.1 - 2.5 µg/l) of bezafibrate could be found. β-sitosterol could not be found in any sample of the condensate. The amount of diclofenac in the condensed off-steam was between 1.5 and 4.2 % (0.4 - 1.1 µg/l) of the initial concentration in the feed substrate.

Demo scale steam stripping

During the steam stripping process in demo-scale with overheated steam one sample of the feed substrate and each one sample of N-depleted substrate and of condensate of two different sets were taken. The detected concentrations are given in Table 41.

The residence time inside of the stripping column was about 15 min, thus nearly 5 times higher as in the laboratory plant. The temperature inside of the column was only slightly higher, because of the filling height in the column of 1.5 m instead of 0.4 m in the laboratory plant. When stripping with overheated steam of 160°C temperatures within the

column will not increase dramatically above 100°C, since the stripping reactor is no over-pressure area, thus overheated steam will be expanded when entering the reactor.

β-Sitosterol and pentoxifylline were eliminated completely. Carbamazepine was obviously not affected; instead a reforming of carbamazepine breakdown products is possible. Values of phenazone and phenacetin were 2 and 4 times respectively 20 and 30 times higher in the N-depleted substrate than in the analyzed sample of the initial feed substrate. This could be due to interferences of ammonia, carbonate, and/or pH on the analytical methods, since these parameters were influenced by the steam stripping process. A reformation process in this case is not presumably. Reductions of ibuprofen, bezafibrate and diclofenac were more or less in the range of the dilution of the N-depleted substrate by steam condensed within the stripping column (see Table 12, Eq 10).

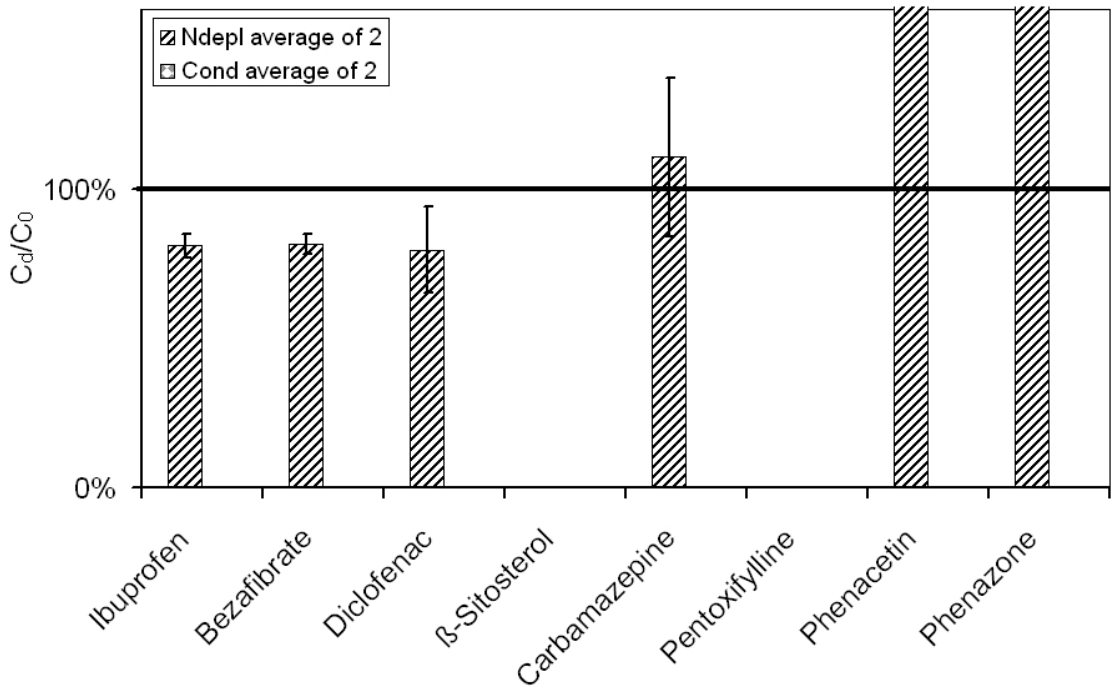


Figure 39: Concentrations of N-depleted substrate and condensate from demo scale steam stripping process regarding feed concentration in order of highest initial concentration. Pentoxifylline was neither found in any N-depleted substrate nor in any condensate. High values for phenacetin and phenazon might be due to analytical interferences. The dilution effect is not excluded.

The condensate was nearly free of PhaR, only traces of ibuprofen were found (0.25 - 0.55 % of the initial concentration). Since phosphorous-balance did not show substrate overflow into the condensate, and also no other PhaR could be detected in the condensate, traces of ibuprofen were obviously stripped out of the substrate.

Table 41: Substances detected in samples from the demo scale steam stripping plant. Of two sets one sample was taken

		initial conc C_0	N_depl Set_1 C_d	N_depl Set_2 C_d	Cond Set_1 C_d	Cond Set_2 C_d
Ibuprofen	µg/l	794	675	611	2,0	4,4
Bezafibrate	µg/l	207	176	162	<1	<1
Diclofenac	µg/l	45	42	29	<1	<1
β-Sitosterol	µg/l	22	<1	<1	<1	<1
Carbamazepine	µg/l	13	11	17	<1	<1
Pentoxifylline	µg/l	3,2	<1	<1	<1	<1
Phenazone	µg/l	1,7	3,7	4,3	<1	<1
Phenacetin	µg/l	1,0	23	34	<1	<1

Evaporation

During the evaporation process samples of two concentrates and two distillates were taken and analyzed regarding their PhaR content (Table 42). For the 3.5 fold concentrate an evaporation time of 30 h was needed, for the 12 fold concentrate evaporation time was 4 d 6 h.

Again, for better comparison in Figure 40 the PhaR concentrations were normalized with the concentration factor cf and the normalized concentration factor cf_{norm} (Eq 11 - Eq 13). For evaluation of the distillate, the expected concentration is assumed to be equal to the initial concentration (Eq 15) (Table 70).

In the 3.5 fold concentrate the expected amount (3.5 x of initial concentration) of carbamazepine, phenacetin, phenazone and pentoxifylline could be detected. 50 % of the expected concentrated amount of bezafibrate and less than 30 % of the expected concentrated amount of diclofenac and ibuprofen were detected.

Again in both concentrates β-sitosterol was not detected.

Table 42: PhaR detected in samples from the evaporation process.

		feed	Conc 3.5x	Conc 12x	Dist 3.5x	Dist 12x
Ibuprofen	µg/l	417	274	37	166	231
Bezafibrate	µg/l	230	494	86	<1	<1
Carbamazepine	µg/l	20	85	141	2,5	<1
β-Sitosterol	µg/l	18	<1	<1	<1	<1
Diclofenac	µg/l	17	17	6,3	<1	<1
Pentoxifylline	µg/l	6,6	25	50	<1	<1
Phenazone	µg/l	4,4	17	79	<1	<1
Phenacetin	µg/l	2,4	8,9	<1	<1	<1

In the distillate belonging to the 3.5 x concentrate, 40 % of the initial concentration of ibuprofen and 12 % of the initial concentration of carbamazepine could be detected.

In the 12 x concentrate the amount of phenazone exceeded the expected concentrated amount. About 60 % of the expected concentrated amount of carbamazepine and pentoxifylline could be detected in the concentrate. Traces of diclofenac, ibuprofen and bezafibrate could also be detected, but no phenacetin at all.

In the distillate belonging to the 12 x concentrate, 60 % of the initial concentration of ibuprofen could be detected, but none of the other parameters.

It can be noted, that at an evaporation time of 4.25 d at temperatures of 80°C five of eight PhaR could be reduced by more than 97 %. Phenazone was because of its complex structure obviously not effected. Also pentoxifylline and carbamazepine proved to be persistent to thermal treatment. Ibuprofen and to a slight extend carbamazepine proved to be volatile.

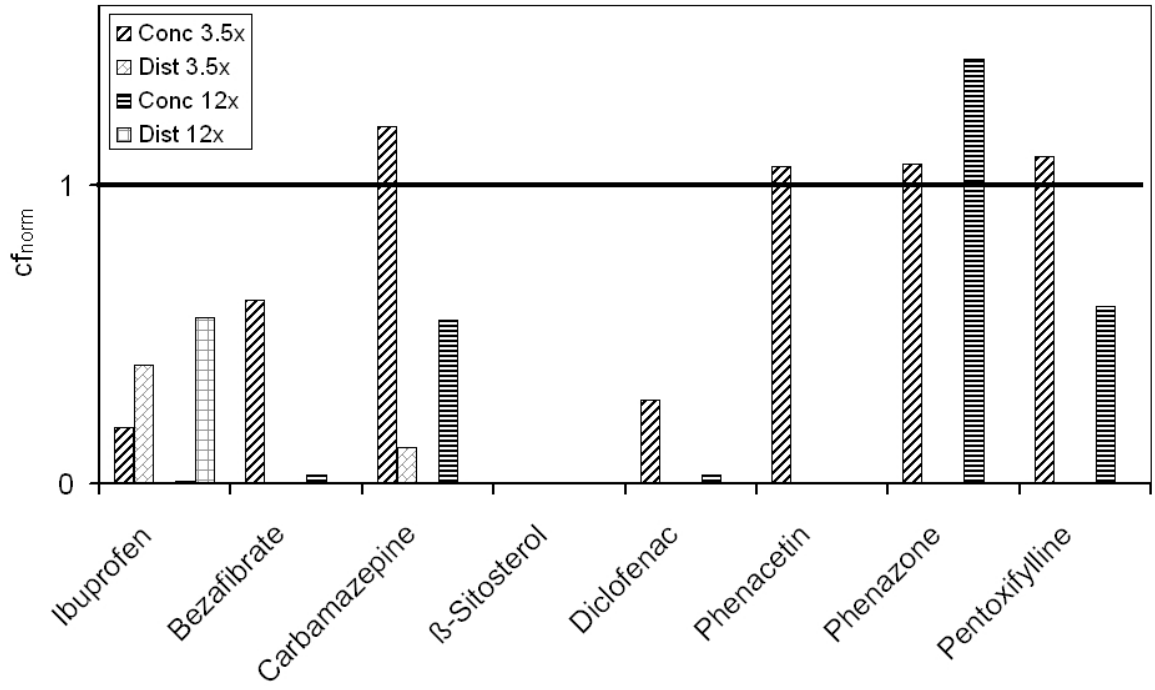


Figure 40: Normalized PhaR concentrations of a 3.5 fold and 12 fold concentrate and the distillates from the demo scale evaporation process

UVC-radiation

Urine and N-depleted urine was treated by UVC-radiation as described above. The results are presented in Figure 41 and in Table 71, respectively Figure 42 and Table 72 for the N-depleted substrate. It has to be noted that the energy input in the two sets was altered.

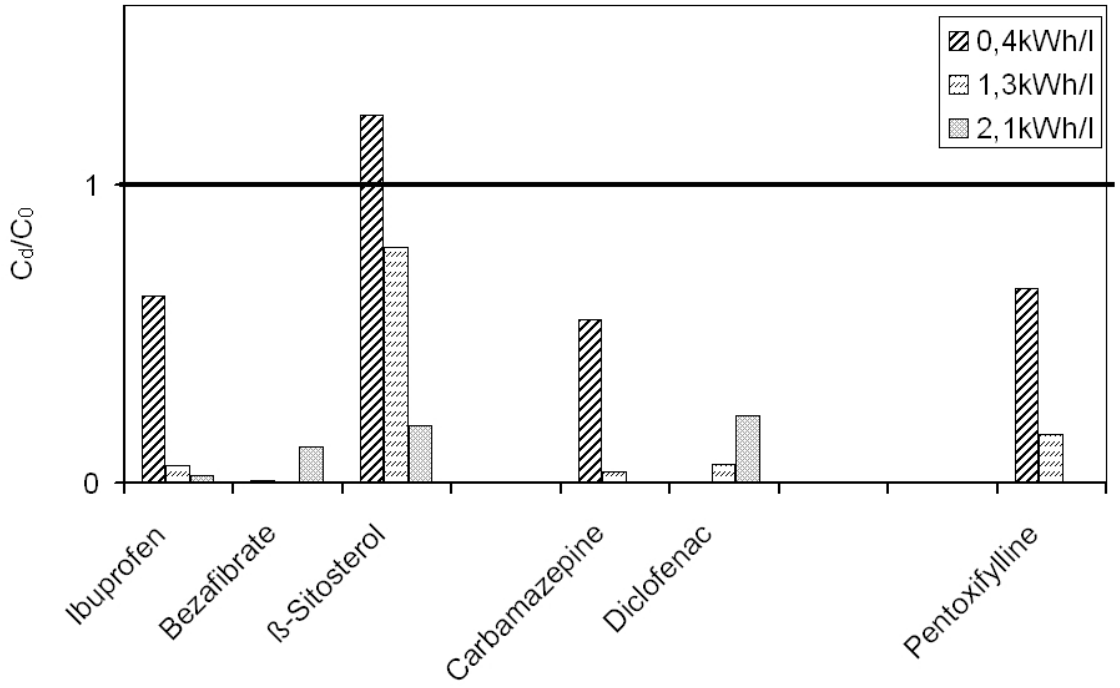


Figure 41: PhaR in urine treated with UVC radiation

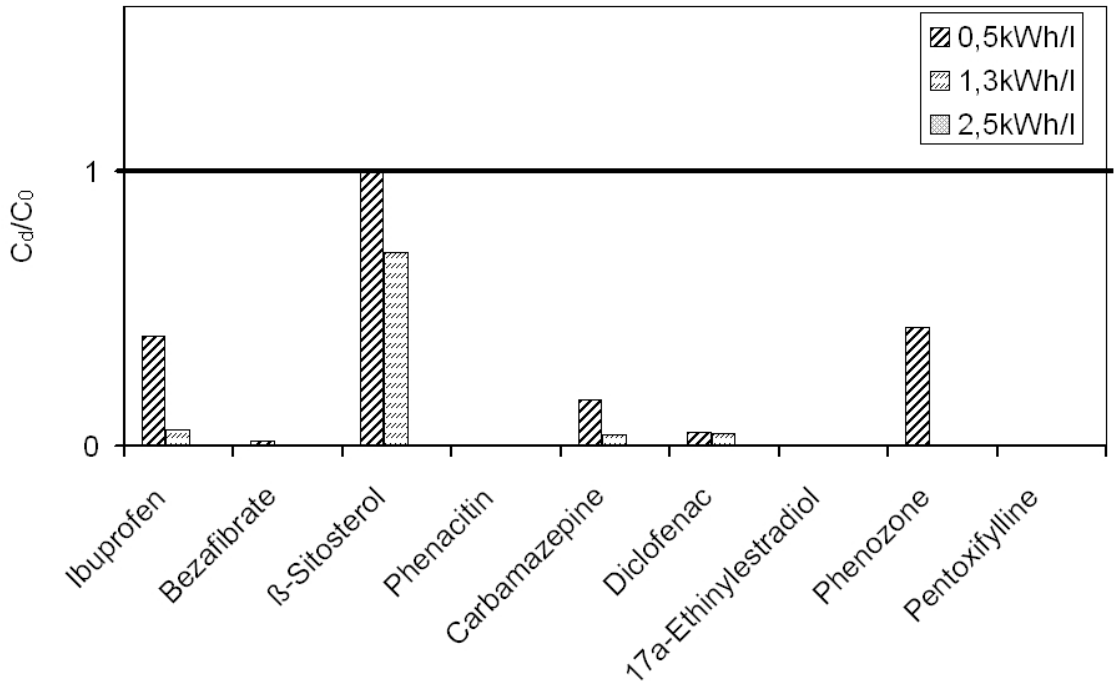


Figure 42: PhaR in N-depleted urine treated with UVC radiation

Besides the fact that introduced energy dosages were high, in both cases nearly all PhaR could be reduced completely by UVC-radiation.

In Table 43 the PhaR-removal per energy input is presented. Removal efficiency seemed to be drastically higher in most cases when treating N-depleted substrate with UVC-radiation. In cases of complete removal the removal efficiency was not calculable which is marked by rnc.

Table 43: Removal efficiency of UVC radiation

type of substrate	stored urine			N-depleted urine		
applied UVC dose [kWh/l]	0.4	1.3	2.1	0.5	1.3	2.5
	removal/ (kWh/l)	removal / (kWh/l)	removal / (kWh/l)	removal / (kWh/l)	removal / (kWh/l)	removal / (kWh/l)
Ibuprofen	93 %	72 %	46 %	120 %	72 %	rnc
Bezafibrate	248 %	76 %	42 %	197 %		rnc
β-Sitosterol	-58 %	16 %	38 %	0 %	23 %	rnc
Phenacetin (*	- (*	- (*	- (*	rnc	rnc	rnc
Carbamazepine	113 %	74 %	rnc	167 %	74 %	rnc
Diclofenac	rnc	72 %	37 %	190 %	73 %	rnc
17α-Ethinylestradiol (*	- (*	- (*	- (*	rnc	rnc	rnc
Phenazone	- (*	- (*	- (*	114 %	rnc	rnc
Pentoxifylline	87 %	64 %	48 %	rnc	rnc	rnc

*) Phenacetin, 17α-ethilylestradiol, and phenazone were not detected in the initial substrate of stored urine

Quite some PhaR are known to be instable under photolytic conditions. Several authors reported e.g. about carbamazepine degradation rates of 25 - 42 % during sun-light radiation [*Andreozzi et al. 2002*; *Doll & Frimmel 2003*]. Of diclofenac [*Buser, Poiger, & Müller 1998*] reported degradation rates of more than 90 % by natural photolytic processes.

ß-sitosterol as a phytosterol being most persistent against UVC-light is noteworthy but because of its structure and its natural occurrence in plants reasonable.

Ozonation

Untreated stored urine

Two sets of untreated stored urine from different locations were treated with ozone. Results can be found in Figure 43 and Table 73 respectively Figure 44 and Table 74.

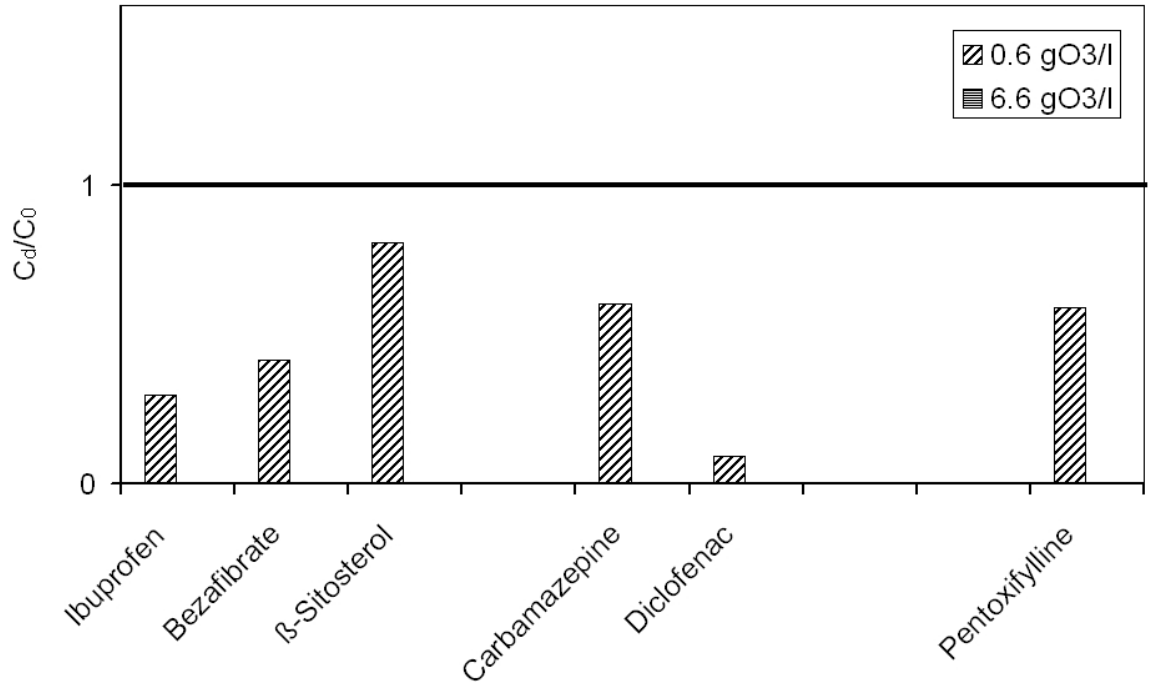


Figure 43: PhaR in urine ($HH_{march05}$) treated with ozone

Ozone dosages were about a factor of 10^3 higher than the ones used ozonation of river water or wwtp effluent [*Ternes et al. 2003*]. Reason is the high COD of about 10 g O_2 /l in urine and its complex matrix. At the same time PhaR concentrations are in the range of a few microgram up to several hundred microgram also a factor of 10^3 higher than in surface waters or wwtp effluents.

At dosages less than 1 g O_3/l all PhaR were drastically reduces but still detectable. Diclofenac was reduces the most. ß-sitosterol in urine was similar to the results from UVC-radiation the most persistent one. At a high ozone dosage of 6.6 g O_3/l all PhaR were below detection limit.

At a second set of ozonation of urine the reduction efficiency was similar. Only diclofenac was removed completely at a ozone dose of less than 1 g O_3/l. At an ozone dosage of 5.9 g O_3/l 2 5 of the initial concentration of bezafibrate could be detected and 7 % of the initial concentration of ibuprofen was detected. The value for diclofenac exceeded the initial concentration by nearly 3 times after ozone dosages of 5.9 g O_3/l. Since in all other cases of all investigated PhaR diclofenac was the one that was reduced the most by ozone, this fact is disregarded.

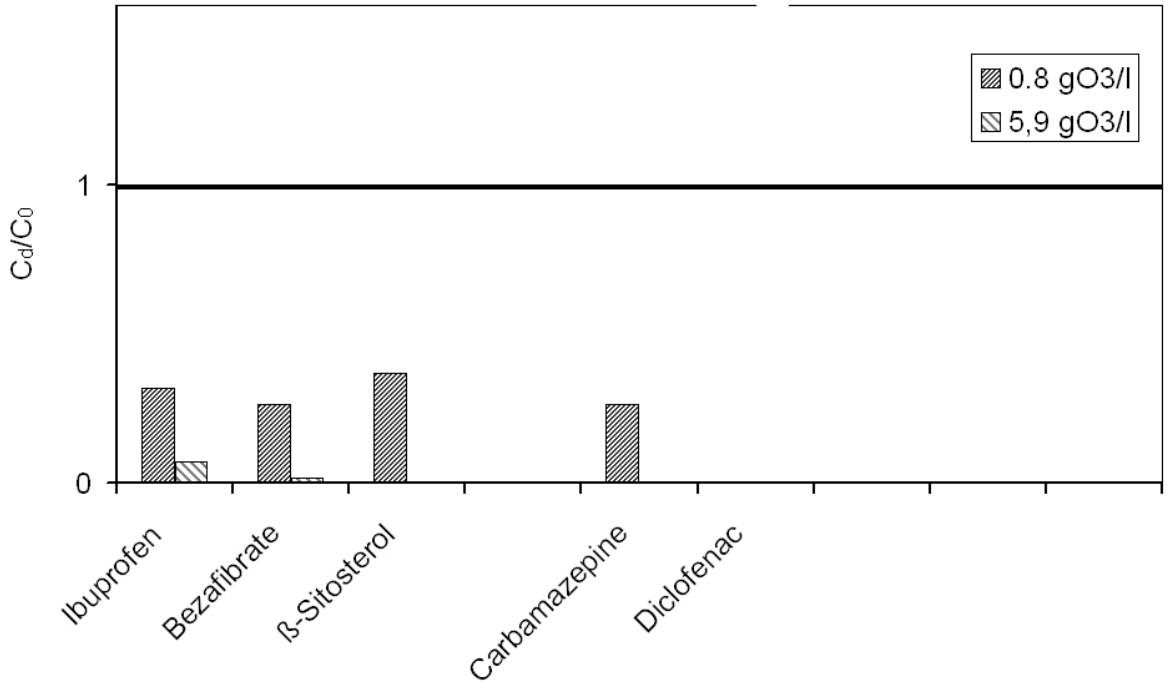


Figure 44: PhaR in urine (B_{oct05}) treated with ozone. Diclofenac not included

N-depleted urine after steam stripping

Also N-depleted urine was treated with ozone. Results can be found in Figure 45 and Table 75.

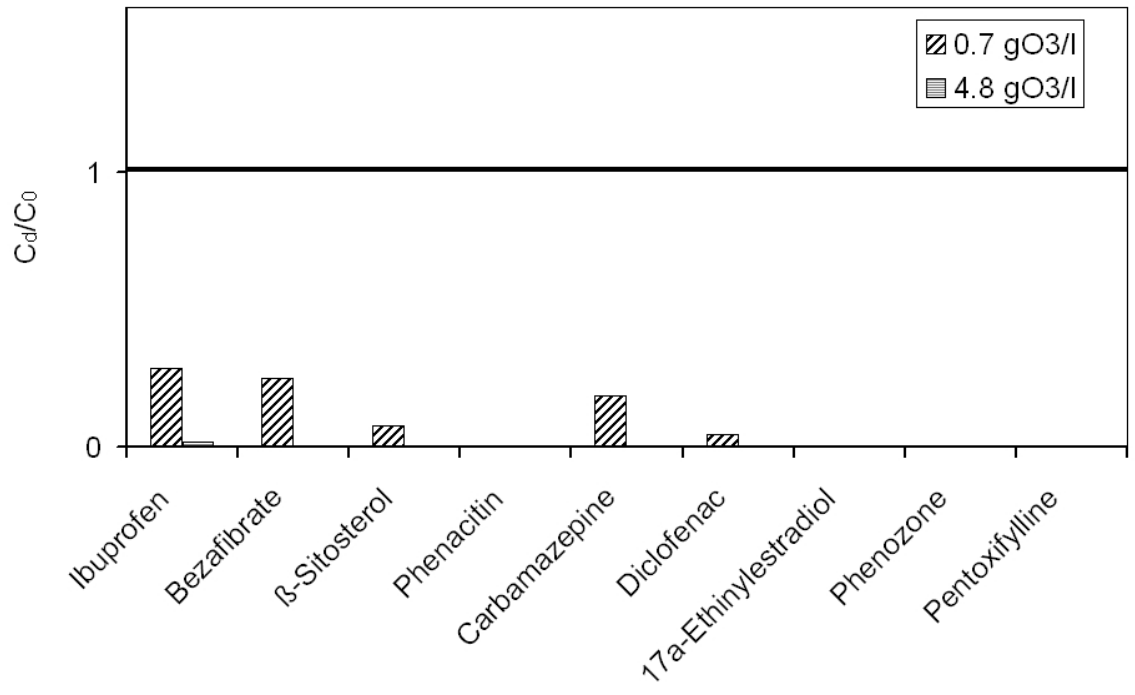


Figure 45: PhaR in N-depleted urine treated with ozone

The substance 17α-ethinylestradiol was detected in the initial N-depleted substrate but could not be found after dosages of 0.7 or 4.8 g O_3/l. The initial concentrations of phenazone and pentoxifylline were just above the LOQ. So the complete removal at ozone dosage of 0.7 g O_3/l was expected. Phenacetin was also similar to the UVC radiation of N-depleted urine completely eliminated already at the lowest dose. ß-sitosterol, which seemed to be the most persistent PhaR at the other ozonation and UVC-radiation experiments, was removed more than ibuprofen, bezafibrate and carbamazepine.

The removal efficiency for urine and N-depleted urine per g O_3 consumed during ozonation is presented in Table 44. In cases of complete removal the removal efficiency per gram ozone was not calculable which is marked by rnc.

Table 44: Removal efficiency of PhaR per gO_3/l

type of substrate	urine $_{HH}$		urine $_{B}$		urine $_{N\_depl}$	
applied ozone dose [g O_3/l]	0.6	6.6	0.8	5.9 l	0.7	4.8
	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l
Ibuprofen	117%	15%	85%	16%	102%	20%
Bezafibrate	97%	rnc	92%	17%	107%	rnc
β-Sitosterol	32%	rnc	79%	rnc	132%	rnc
Phenacetin	- (*	- (*	- (*	- (*	rnc	rnc
Carbamazepine	67%	rnc	92%	rnc	116%	rnc
Diclofenac	151%	rnc	rnc	-31%	136%	21%
17α-Ethinylestradiol	- (*	- (*	- (*	- (*	rnc	rnc
Phenazone	- (*	- (*	- (*	- (*	rnc	rnc
Pentoxifylline	69%	rnc	- (*	- (*	rnc	rnc

*) Phenacetin, 17α-ethilylestradiol, and phenazone were not detected in the initial substrate of stored urine$_{HH}$ and urine$_{B}$, additionally pentoxifylline was also not detected in the initial substrate of stored urine$_{B}$

UVC-radiation (Table 43) and even more ozonation of N-depleted urine showed a higher reduction of most PhaR than from the matrix of urine. While in not pretreated stored urine β-sitosterol was reduced by 32 % respectively 79 % per gO_3/l in the N-depleted substrate a complete removal should be received at a dosage of 1 gO_3/l. Bezafibrate and carbamazepine showed similar tendencies. Only diclofenac and ibuprofen did not show such a clear effect. For diclofenac the high initial concentration could be a reason, why it was not affected by pretreatment of the urine. For the other substances, the reduction of ammonium in the urine might have increased the efficiency, since one competitor (in this case the ammonium) for the ozone molecules was removed by steam stripping, making more ozone available for the reaction with PhaR.

pH-variations

Most pharmaceutical residues do have an aromatic structure. Carbon double-bounds can be attacked via a direct selective reaction of ozone according to the Crigée-mechanism. While at high pH values a large quantity of ozone is consumed for formation of radicals that attack

components very fast but non-selectively, in an acidic environment the direct selective reaction is supported.

Therefore urine from B '06 was acidified with 17 ml HPO_3/l substrate (pH-reduction from pH 9 to pH 4). The acidified solution was thereafter treated with ozone. Already the acidification had some effect on most PhaR (Table 45, Figure 62).

Table 45: Influence of acidification on PhaR in urine

		pH 8.9 C_0	pH7 C_d	C_d / C_0	pH4 C_d	C_d / C_0
Bezafibrate	µg/l	495	405	*0.82*	413	*0.83*
Ibuprofen	µg/l	442	438	*0.99*	354	*0.80*
β-Sitosterol	µg/l	40	49	*1.22*	23	*0.56*
Diclofenac	µg/l	13.9	10.4	*0.75*	9.2	*0.66*
Pentoxifylline	µg/l	5.6	7.1	*1.27*	3.9	*0.70*
Carbamazepine	µg/l	3.5	9.6	*2.74*	7.9	*2.26*
Phenazone	µg/l	2.1	2	*0.95*	< 1.0	*0*
Phenacetin	µg/l	1.4	2.5	*1.79*	1.4	*1.0*

The N-depleted substrate was acidified with 2.5 ml HPO_3/l N-depl substrate (for pH reduction from pH7 to pH4) (Table 46, Figure 63).

Table 46: Influence of acidification on PhaR in N-depleted urine

		pH 7 C_0	pH 4 C_D	C_d / C_0
Bezafibrate	µg/l	649	636	*0.98*
Ibuprofen	µg/l	590	480	*0.81*
β-Sitosterol	µg/l	87	8.4	*0.10*
Diclofenac	µg/l	22	16	*0.71*
Pentoxifylline	µg/l	6.3	7.6	*1.21*
Carbamazepine	µg/l	14	13	*0.94*
Phenazone	µg/l	1.8	2.1	*1.17*
Phenacetin	µg/l	4.5	1.8	*0.40*

ß-sitosterol was affected the most by acidification. Reduction of more than 40 % and in the N-depleted substrate of more than 90 % were observed.

Ozonation at low pH

To investigate ozonation efficiency at low pH stored urine and an acidified batch of the same stored urine were treated. Samples were taken in intervals of 80 minutes respectively 230 minutes. The O_3-uptake within the same time intervals was reduced by roughly 50 % by

acidification (Table 47) since a radical chain-reaction of OH° radicals and O_3-molecules was not supported in the acidic environment.

Table 47: Ozone uptake at different pH

	t = 80 min	t = 230min
stored urine pH 8.9	0.97 g O_3/l	1.59 g O_3/l
stored urine at pH 4	0.50 g O_3/l	0.86 g O_3/l
N-depl urine pH 7	1.37 g O_3/l	1.94 g O_3/l
N-depl urine pH 4	0.63 g O_3/l	1.26 g O_3/l

Ozonation of stored urine at low pH

The detected concentration of PhaR in ozonated urine and acidified urine is presented in Table 48.

Table 48: Influence of ozone on PhaR in acidified urine

		stored urine pH 9					acidified stored urine pH 4				
			0,97 gO_3/l		1,59 gO_3/l			0,5 gO_3/l		0,86 gO_3/l	
		feed C_0	C_d	*C_d/C_0 [%]*	C_d	*C_d/C_0 [%]*	feed C_0	C_d	*C_d/C_0 [%]*	C_d	*C_d/C_0 [%]*
Bezafibrate	µg/l	495	159	*32*	47	*10*	413	249	*60*	97	*23*
Ibuprofen	µg/l	442	163	*37*	57	*13*	354	266	*75*	209	*59*
β-Sitosterol	µg/l	40	40	*99*		*0*	23		*0*		*0*
Diclofenac	µg/l	14		*0*		*0*	9.2		*0*		*0*
Pentoxifylline	µg/l	5.6	1.7	*30*		*0*	3.9	4.1	*105*	1.9	*49*
Carbamazepine	µg/l	3.5		*0*		*0*	7.9	3.8	*48*	3.1	*39*
Phenazone	µg/l	2.1		*0*		*0*					
Phenacetin	µg/l	1.4		*0*		*0*	1.4		*0*		*0*

While within the same timeframe only half of the amount of O_3 was consumed by the acidified sample, reduction rates at the more or less same O_3-consumptions were except for ß-sitosterol in the same range. In case of carbamazepine the initial concentration were so low, that comparison seems to be not significant. ß-sitosterol seemed to be degraded mainly by direct O_3-reaction since as well as during the ozonation of N-depleted urine, as well as during ozonation of acidified urine removal was significantly higher than in the untreated stored urine.

In Figure 46 the bars were sorted according to the ozone uptake. The two bars in the middle of each set present with 0.9 g O_3/l and 1.0 g O_3/l nearly the same amount of ozone consumption, one in the acidified substrate the other in the untreated stored urine. It can be seen that for most cases, except for ß-sitosterol, reduction rates were in the same range.

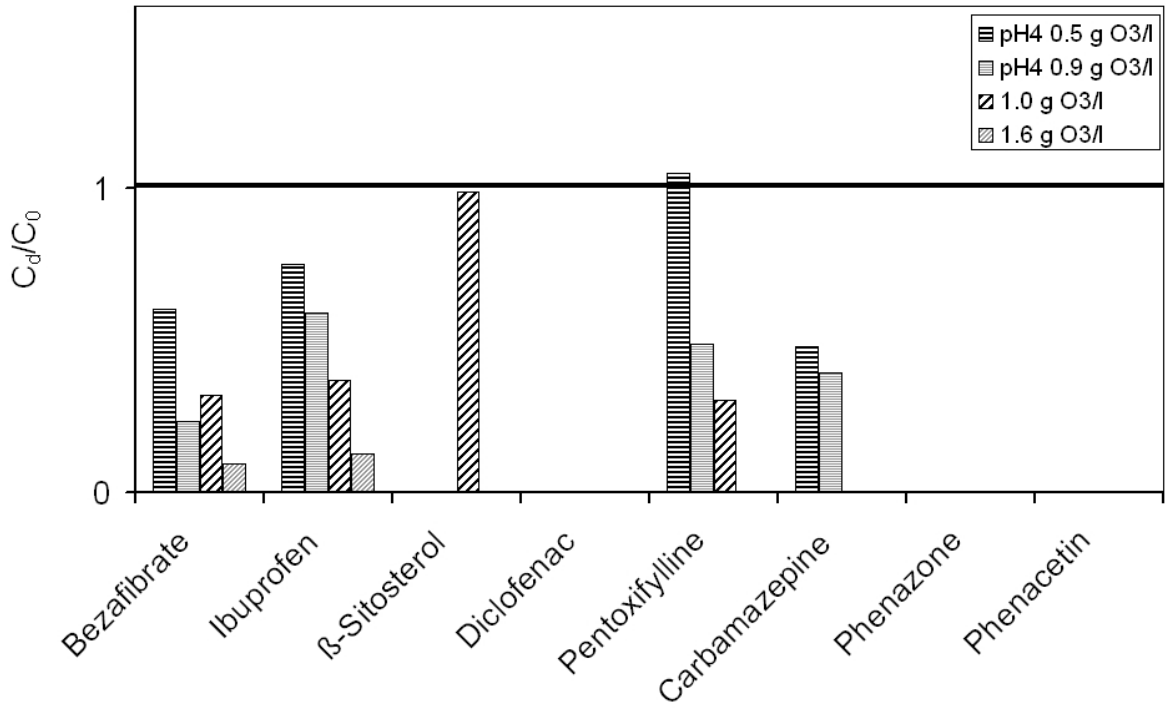


Figure 46: PhaR in acidified and non-acidified urine. Samples were taken at similar ozonation times, but ozone-uptake from acidified urine was significantly lower. At the same time removal efficiency was not significantly changed.

Ozonation of N-depleted substrate at low pH

Also N-depleted urine was acidified from initially pH 7 to pH 4. The N-depleted urine and the acidified N-depleted urine were treated with ozone. Again ozone uptake was reduced by nearly half the amount by acidification. The results are presented in Table 49.

Table 49: Influence of ozone on PhaR in acidified N-depleted urine

		pH 7	1,37 gO_3/l		1,94 gO_3/l		pH 4	0,63 gO_3/l		1,26 gO_3/l	
		C_0	C_d	*C_d/C_0 [%]*	C_d	*C_d/C_0 [%]*	C_0	C_d	*C_d/C_0 [%]*	C_d	*C_d/C_0 [%]*
Bezafibrate	µg/l	649	335	*52*	167	*26*	636	362	*57*	147	*23*
Ibuprofen	µg/l	590	390	*66*	274	*46*	480	326	*68*	265	*55*
β-Sitosterol	µg/l	87	28	*32*		*0*	8,4		*0*		*0*
Diclofenac	µg/l	22		*0*		*0*	16		*0*		*0*
Pentoxifylline	µg/l	6.3	6.6	*105*	3.5	*56*	7.6	7.1	*93*	3	*39*
Carbamazepine	µg/l	14	6.6	*46*	3.6	*25*	13	7.7	*57*	5.1	*38*
Phenazone	µg/l	1.8		*0*		*0*	2.1		*0*		*0*
Phenacetin	µg/l	4.5		*0*		*0*	1.8	1.6	*89*		*0*

Also in Figure 47 the bars were sorted according to the ozone uptake. The two bars in the middle of each set present with 1.3 g O_3/l and 1.4 g O_3/l nearly the same amount of ozone consumption, one in the acidified N-depleted substrate the other in the non acidified N-depleted urine.

In this case the reduction of all PhaR, that can be compared with each other was significantly higher in the acidified substrate. When excluding the competitor ammonium the effect of enhancing the direct reaction according to the Crigée-mechanism was supported.

As expected do obviously all PhaR have a more intensive reaction with ozone itself than with the produced radicals. However, it seems that most PhaR can also be reduced by radicals to some extend, except ß-sitosterol, which seems to be persistent against UVC-radiation and reaction with radicals.

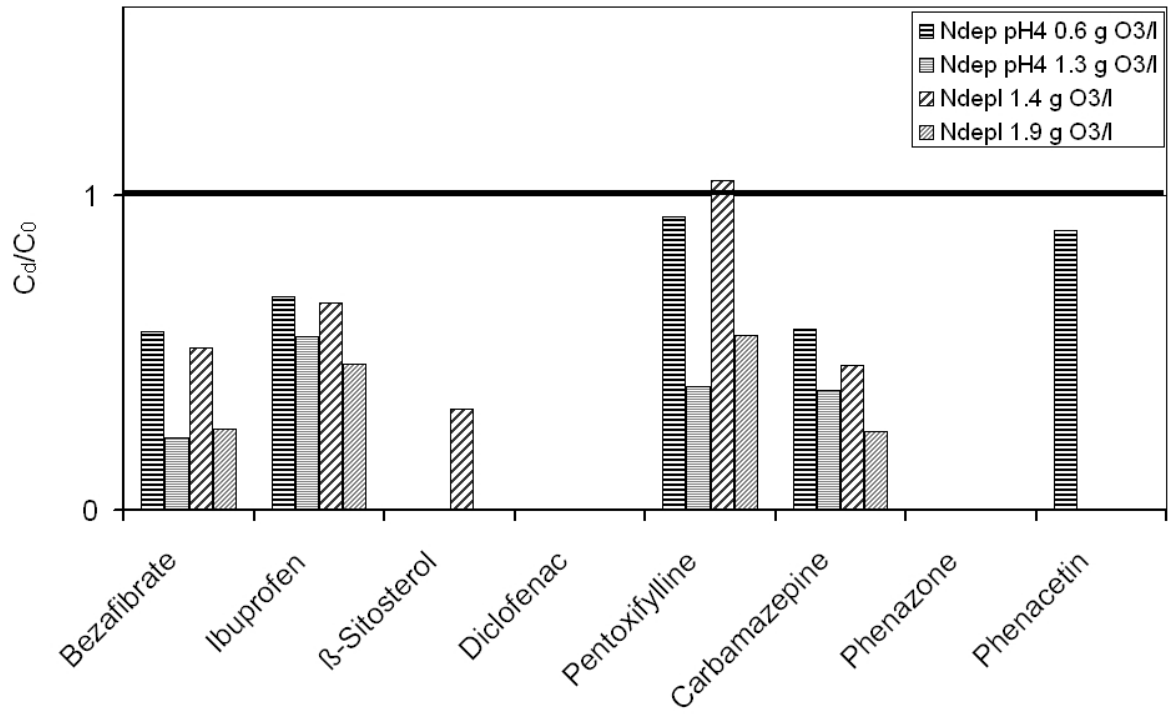


Figure 47: PhaR in acidified and non-acidified N-depleted urine. Samples were taken at similar ozonation times, but ozone-uptake from acidified N-depleted urine was significantly lower. At the same time removal efficiency was increased significantly in all cases.

Table 50: Removal efficiency per g O_3 for acidified and non-acidified urine, and N-depleted urine

type of substrate	Stored urine				N-depleted urine			
	'regular' pH 8.9		acidified to pH 4		'regular' pH 7		acidified to pH 4	
applied ozone dose [g O_3/l]	1.6	1.0	0.9	0.5	1.4	1.9	0.6	1.3
	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l	removal/ g O_3/l
Bezafibrate	57%	68%	85%	79%	35%	39%	72%	59%
Ibuprofen	55%	63%	46%	50%	24%	28%	53%	34%
β-Sitosterol	rnc	1%	rnc	rnc	48%	rnc	rnc	rnc
Diclofenac	rnc	rnc	rnc	rnc	rnc	rnc	rnc	rnc
Pentoxifylline	rnc	70%	57%	-10%	-3%	23%	11%	47%
Carbamazepine	rnc	rnc	68%	104%	38%	39%	71%	48%
Phenazone	rnc	rnc	rnc	rnc	rnc	rnc	rnc	rnc
Phenacetin	rnc	rnc	rnc	rnc	rnc	rnc	19%	rnc

Side products of ozonation

Due to the high TOC content, the selective reaction of ozone might also lead to fragmentary mineralization products from organic components [*Gulyas 2003*] Because of the high chloride concentration of up to more than 4 g/l the formation of AOX could be expected by the ozonation of urine.

Analytics regarding AOX formation were conducted. However, because of its high ammonium and chloride content the LOD for AOX was in the range of 1 mg/l. This value was not exceeded during the ozonation of urine for PhaR removal.

Indicators for removal of PhaR

Since the analytics regarding PhaR in urine are costly other indicators for the removal of PhaR might be beneficial. In case of UVC-radiation and ozonation the change of color throughout ozonation was measured. Chroma and turbidity were derived as described in [*Tettenborn et al. 2006*] (values are given in Table 77 and Table 78). Both, chroma and turbidity decreased as expected during ozonation but not during low UVC-radiation (see Figure 48, Figure 49, and Figure 64 to Figure 67).

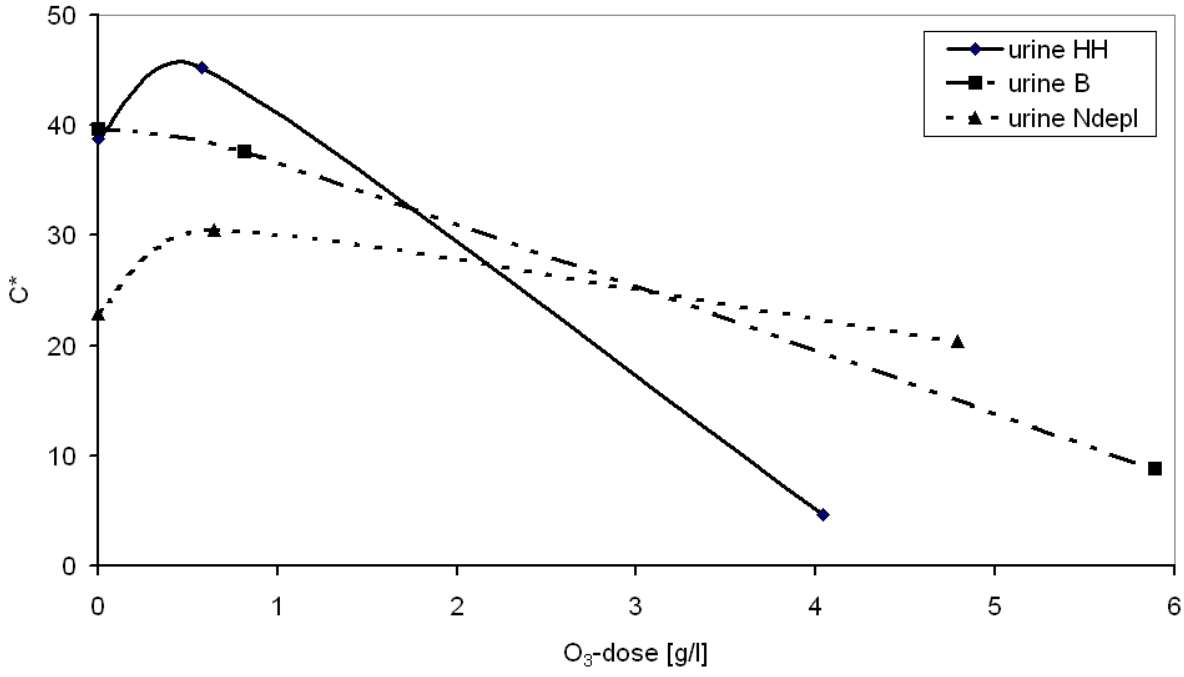


Figure 48: Colorvalue chroma of urine and N-depleted urine during ozonation

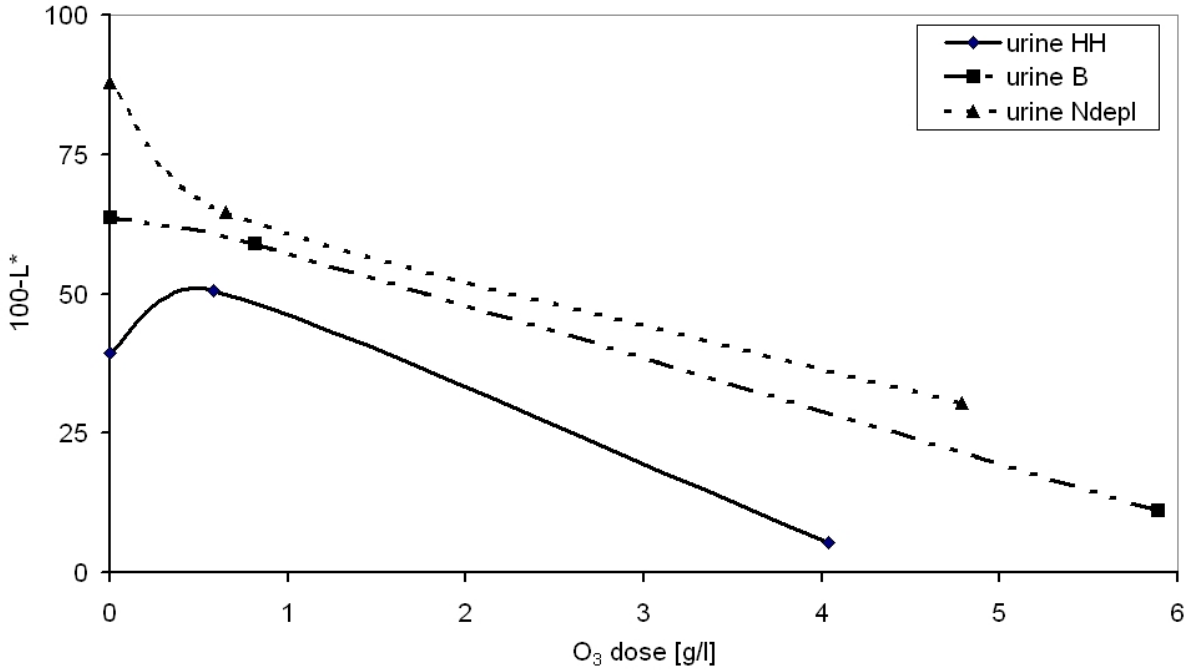


Figure 49: Colorvalue (100-lightness) of urine and N-depleted urine during ozonation

However, color reduction in all experiments was little after ozone-input sufficient for removal of PhaR. During UVC-radiation a color reduction could not be obtained by the applied dosages. From previous experiments [*Tettenborn et al. 2006*] it is known that color can be removed by ozone and UVC-radiation dosages about tow to three times higher than for the removal of PhaR needed. Thus it can be stated that decolorized urine will not contain any PhaR, but color as an indicator for the removal of PhaR seems not to be sensitive enough.

Energy

According to [*Bünning 1996*] energy requirements per kg produced O_3 are between 6.5 and 10 kWh when using oxygen as feed gas. For preparation of oxygen another kWh is needed for 1 N m^3 of oxygen. When producing ozone from air 14 kWh are needed per kg ozone.

Therefore with an energy input of 15 - 45 kWh/m^3 substrate (1 - 3 g O_3/l) all PhaR could be removed from urine. For acidified N-depleted urine the amount might be a little lower. The energy input for ozonation of urine was about 500 times higher than for the treatment of wwtp effluent [*Ternes et al. 2003*]. However, at the same time volume per person and day of urine is about 300 times lower (compared to entire wastewater processed in German municipal treatment plants in 2001, including domestic, industrial, infiltration, and rain water from [*Brenk et al. 2006*]: $10.5*10^9 m^3$/a; divided by connected German population). Concentrations of PhaR in urine are about 10^3 times higher than in wwtp effluent.

The energy input by UVC-radiation in this study was about 2 MWh/m^3 substrate. Reason for this high energy input might be the matrix of urine, not allowing UVC-light to penetrate all through the substrate. Improvements of this process should be possible. Although energy requirements of the UVC-radiation were extremely high the effect could clearly be stated.

Conclusion

All selected treatment processes did affect PhaR concentrations in urine.

During steam stripping in lab scale slight reductions of carbamazepine (41 %) and phenacetin (57 %) were observed. However steam stripping with overheated steam in demo scale could not verify this result. Here only β-sitosterol and pentoxifylline were eliminated completely. The ccondensate from the steam-stripping unit was mainly free of PhaR. Residence time within the stripping column were between 5 and 15 minutes. Temperatures around 100°C.

After four days and six hours (4d 6h) in the evaporation process at a temperature of around 80°C all PhaR, except carbamazepine, phenazone, and pentoxifylline were reduced by more than 95%. Significant traces of carbamazepine could be found in the distillate after 30 h. Also, more than 50 % of the initial concentration of ibuprofen was found in the distillate after 4d 6h.

Although most substances were not easily affected by thermal influences, sufficient time and temperatures at boiling point did remove most PhaR. ß-Sitosterol was affected the most.

By high dosages (~2 kWh/l) of UVC-light nearly all PhaR could be reduced by more than 90 % from the matrix of urine. While in this case ß-sitosterol proved to be the most persistent, bezafibrate and carbamazepine were reduced the most by UVC-light.

By ozonation a dosage of 2.5 g O_3/l was found to be sufficient to eliminate all PhaR.

UVC-radiation and ozonation were more effective, when the substrate was steam-stripped before, since competition of substances such as ammonium was reduced. The reduction of pH seemed to influence ß-sitosterol the most.

Ozone consumption over time was less in the acidified urine, but PhaR reduction was depending more on ozone consumption than on time. However, in both acidified substrates, but even more in the N-depleted acidified substrate the efficiency of PhaR-reduction was slightly increased by combination of acidification and ozonation.

Energy requirements for the ozonation of urine for PhaR-removal was in this study about 2 times higher than the amount that would be needed for ozonation of the wwtp effluents.

Costs of urine treatment in general

For a detailed statement regarding the costs and value of the obtained products several economical tools are needed such as a market evaluation, analysis of competitive products, cost-benefit calculation including sustainability indicators and factors respecting environmental protection. In this study focus was set on technical aspects of realization of plants in demo-scale and the scientific output from the operational tasks. Energy requirements and quantities of additional chemicals or other required input material were measured, discussed for each process, and compared to literature values. These data can be used for an estimation of individual process costs.

In general, the costs of separate collection and treatment of urine are expected to be in a comparable range with conventional methods since the processes investigated in this study are similar to the ones used in conventional wastewater treatment and fertilizer production from fossil resources. While the scale of the fertilizer industry using fossil resources currently cannot be reached the benefits regarding sustainability and environmental protection of separate collection and treatment of urine have to be included in a cost analysis. These benefits for examples are reduced accumulation of nutrients in surface waters and costal ocean regions especially in areas with inadequate wastewater treatment, and reduced requirements for nutrient removal in conventional wastewater treatment plants. Additionally the benefit of spared fossil resources and of a more sustainable system with closed loops has to be noted.

Overall, the raw material 'urine' proved to be an ideal resource for products usable in agriculture and industry. Combined with further demonstration and above mentioned market analysis, an upscaling of the pilot plants seems promising.

Table 51: Main factors of investigated processes

Process	yield; significant side effects	requirements; beneficial conditions	possible synergetic effects	beneficial pre-process	necessary follow up regarding	energy requirements [MJ/m^3]	obtained product
Steam stripping	N-recovery; pH reduction; reduction of buffer capacity	hydrolyzed substrate needed	energy for heating process	storage, MAP-precipitation	P-recovery , PhaR thereafter with grey water	150	NH_3-solution
Evaporation	volume reduction; reduction of most PhaR	low pH for reduction of loss of ammonia	energy for heating process	steam stripping; other pH reducing processes	post processing of concentrate and distillate; PhaR	200	Concentrated nutrient solution
MAP-precipitation	P-recovery	low buffer capacity		steam stripping and evaporation possible, but not necessary	N-recovery, PhaR thereafter with grey water	~ 30	Struvite
Crystallization	P-recovery	high N and P concentrations	cooling after concentration processes at high temperatures	evaporation	post processing of depleted substrate (N, COD, PhaR)	~ 20	P-crystals
Adsorption(*	nutrient recovery				post processing of depleted substrate (N, COD, PhaR)	~ 30	Nutrient enriched adsorbent
Ozonation	PhaR-removal	reduction of NH_3, COD, and pH	radical reaction increased at high temperatures (**	steam stripping acidification	nutrient recovery and COD removal	115	Substrate free of PhaR
UVC-radiation (***	PhaR-removal	reduction of NH_3, COD, and pH		steam stripping acidification	nutrient recovery and COD removal	7000	Substrate free of PhaR
Storage	hygienization/ stabilization				N, P, COD, PhaR treatment / usage	-	Substrate free of pathogens

*) high amounts of required adsorbent in lab-scale

**) was not investigated

***) very high energy requirements in lab set-up

Summary

The main goals for the treatment of separately collected urine are nutrient recovery, to improve the handling of the substrate, and to remove contained pharmaceutical residues. All of this is possible. However, no process suits every purpose. In Table 51 the aim and beneficial side effects of each process are listed as well as beneficial pre-processes and necessary follow-up steps.

For extraction of nitrogen from separate collected urine steam stripping proved to be very efficient. Main advantage of steam stripping in comparison to air stripping is the high temperature, were a high ammonia mass transfer is guaranteed. The initial substrate could be depleted from nitrogen by more than 97 %. The extracted ammonia was collected in a more than 12 % ammonia solution. Per cubic meter treated substrate 20 to 30 liters of ammonia solution could be obtained. The N-depleted substrate would need further treatment regarding contained phosphorous, COD, and -if required- pharmaceutical residues.

For phosphorous recovery MAP-precipitation still seems to be the most efficient and economical way. Pretreatment by steam stripping did not enhance the process. However, low pH values obtained by steam stripping could be regulated by the precipitant.

Evaporation is probably one of the most controversial discussed processes. Aim is to reduce the volume and to yield a highly concentrated nutrient solution. Both could be reached. More than 50 fold concentrates could be obtained (20 l concentrate from 1 m^3 substrate). While phosphorous was completely recovered in the concentrate, nitrogen losses due to ammonia volatilization were high. Acidification of stored urine cannot be an economical solution because of the high buffer capacity of stored urine. Steam stripping, biological pretreatment, or acidification of fresh urine are some options to avoid excessive losses into the distillate during evaporation. The concentrate could be used directly in agriculture as highly enriched nutrient solution or further processed by crystallization to gain an easy to handle solid product for agriculture. The distillate would need further treatment to remove COD and owing to circumstances to remove or recover nitrogen.

Because of concentrations above saturation crystal forming was obtained at storage of the concentrates. This process could be enhanced by technical means, yielding pure and dry products.

For adsorption literature values could not be reached. Adsorption rates for ammonium were 83 % with an adsorption of 5.9 mg NH_4-N / g zeogranul. For phosphorous adsorption rates of 96 % were obtained with an adsorption of 0.7 mg PO_4-P / g zeogranul. Thus about 1 kg adsorption material would be needed per liter of stored urine. The use of zeolite in a subsequent step after steam stripping and MAP-precipitation seems reasonable.

The two thermal treatment processes also had an impact on pharmaceutical residues. ß-sitosterol and pentoxifylline were affected the most by the stripping process itself. More important might be the generally higher removal rates in the subsequent ozonation after steam stripping.

During evaporation only carbamazepine, phenazone and pentoxifylline were found in a 12 fold concentrate. Especially phenazone proved to be very stable under evaporating conditions. Even in higher enriched concentrates phenazone is likely to be detected in large quantities. Ibuprofen and to a small extend carbamazepine could be detected in the distillate, thus they can be considered volatile.

With UVC-radiation all PhaR could be removed. ß-sitosterol was the one most persistent against UVC-treatment. High removal rates were obtained on bezafibrate, diclofenac, and phenacetin. Energy requirements exceeded the energy demand of ozonation by roughly a factor 100.

With the ozonation of stored urine all pharmaceutical residues could be removed. Again, phenacetin and diclofenac were affected the most. Acidification of stored urine did not lead to significant improved PhaR removal, probably because of ammonium present as competitor for the direct ozone reaction. However, acidification of N-depleted substrate did show a significant increased removal for bezafibrate, ß-sitosterol, and pentoxifylline.

Conclusion

Since urine has an energy potential of at about 900 MJ/(m^3 urine) [*Dockhorn & Dichtl 2004*; *Maurer, Schwegler, & Larsen 2003*; *Niederste-Hollenberg 2003*; *Patyk & Reinhardt 1997*] the energy demand of the investigated processes, except UVC-radiation were in comparable ranges with nutrient removal at conventional wastewater treatment plants and fertilizer production. Optimization of the treatment processes should allow competitive products and treatment procedures. Also for the removal of pharmaceutical residues the energy demand was in a comparable range as in conventional wastewater treatment concepts, at the same time space requirements for the ozonation of urine would be drastically lower than for the ozonation of wwtp effluent.

Especially the combination of steam-stripping and precipitation did yield high valued products. For reduction of energy consumption a combination of the two thermal processes steam stripping and evaporation should lead to high energy savings. Also other industrial thermal processes, such as e.g. thermal waste treatment, should be considered for synergetic effects in combination with steam stripping and evaporation. For removal of PhaR process for the combination of steam stripping and ozonation was beneficial.

Overall, marketable products could be gained from separate collected urine in semi-technical scale. A market analysis was not conducted; instead energy requirements and quantities of required input material were discussed and compared to literature values. In most cases the overall costs for production of pure substances or fertilizer products from urine is expected to be in the same range compared to produces from fossil materials.

While no process allows nutrient recovery and PhaR removal at drastically lower economical conditions than the conventional treatment system, the investigated processes can present one piece of a puzzle for new sanitation systems and allow their application where needed.

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Appendix

Processed substrate - urine

Table 52: Excerpt of mean values of urine found in literature

		modified from **[1]**	modified from **[2]**	modified from **[3]**	modified from **[4]**
TN	[g/d]	9.2 - 11.5	7 - 25	5.2 - 9.6	
P	[g/d]	0.8 – 2.0	0.5 - 1.5	0.5 - 1.1	1.0
S	[g/d]	1.2 – 1.5			
K	[g/d]	1.6 – 3.9	1.3 - 4.0	2.5 - 3.6	2.5
Ca	[g/d]	0.18 – 0.24	0.25 - 0.3		
Mg	[g/d]	0.11 – 0.13	0.1 - 0.2		

Note: values are stated as substance release per day

[1] [*CIBA Geigy 1977*]

[2] [*Hofstetter & Eisenberger 1996*]

[3] [*Jocham & Miller 1994*]

[4] [*Alken & Walz 1998*]

Table 53: Reference values of fresh urine and stored urine in mmol/l.

	Fresh Urine [mmol/l]	**Stored Urine** [mmol/l]
Total Nitrogen	657	657
Total Ammonia	34	579
Ammonia NH_3	0.02	193
Urea	550	0.0
Phosphate(1)	24	17
Calcium	4.7	0.0
Magnesium	4.1	0.0
Potassium	56	56
Sulfate (2)	6.9	6.9
Chloride	107	107
Sodium	113	113

(1) 95-100% of total phosphor

(2) about 90% of total sulfur

Note: Concentrations of fresh urine according to [*CIBA Geigy 1977*].
Concentrations of stored urine are derived from [*Udert 2002*]

Ammonia solution

Nitrogen is essential for all forms of life, and ammonia is one of the many forms (and which are readily inter-converted) in which nitrogen exists in the environment.

Physical properties:

- colorless gas with a pungent, suffocating odor
- highly water-soluble and soluble in chloroform and ether
- easily liquefied under pressure
- melting Point (°C): -78
- boiling Point (°C): -33
- specific Gravity: 0,771 g/l (0°C, 100 kPa)
- can be liquefied at 20 °C by a pressure of 800 - 900 kPa
- solubility in water:

  at 0°C and 100 kPa: 880 g (1142 l) NH_3 per liter
  at 20°C 520
  at 40°C about 340 and
  at 100°C 75 g NH_3 per liter

Table 54: Density and contend of a aqueous ammonia solution [[*Küster, Thiel, & Fischbeck 1972*]]

density [g/cm^3]	Weight. -%	Mol/ Litre	g (NH_3) /l
0,998	0,05	0,03	0,46
0,996	0,51	0,30	5,09
0,994	0,98	0,57	9,71
0,976	5,25	3,01	51,3
0,966	7,77	4,41	75,1
0,956	10,40	5,84	99,5
0,948	12,58	7,00	119
0,936	16,06	8,83	150
0,922	20,27	10,97	187
0,918	21,50	11,59	197

At unusually high levels toxic effects can be observed. Acute (2-4d after contact) toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants.

"Total ammonia" refers to the sum of ammonia (NH_3) plus the ionised form (NH_4^+). The toxicity of liquid ammonia solutions is primarily due to the presence of NH_3, the percentage of which increases with pH and temperature.

Therefore, the toxicity of "total ammonia" is greater in more alkaline waters at higher temperatures. It is also more toxic under conditions of decreased oxygen concentrations. Under most natural conditions of pH and temperature, total ammonia has moderate acute toxicity to aquatic life. No data are available on the short-term effects of total ammonia to plants, birds, or land animals.

Chronic (Long-Term) Ecological Effects Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. Chronic effects can be seen long after first exposure(s) to a toxic chemical. Under most natural conditions of pH and temperature, total ammonia has moderate chronic toxicity to aquatic life. No data are available on the long-term effects of total ammonia on plants, birds, or land animals.

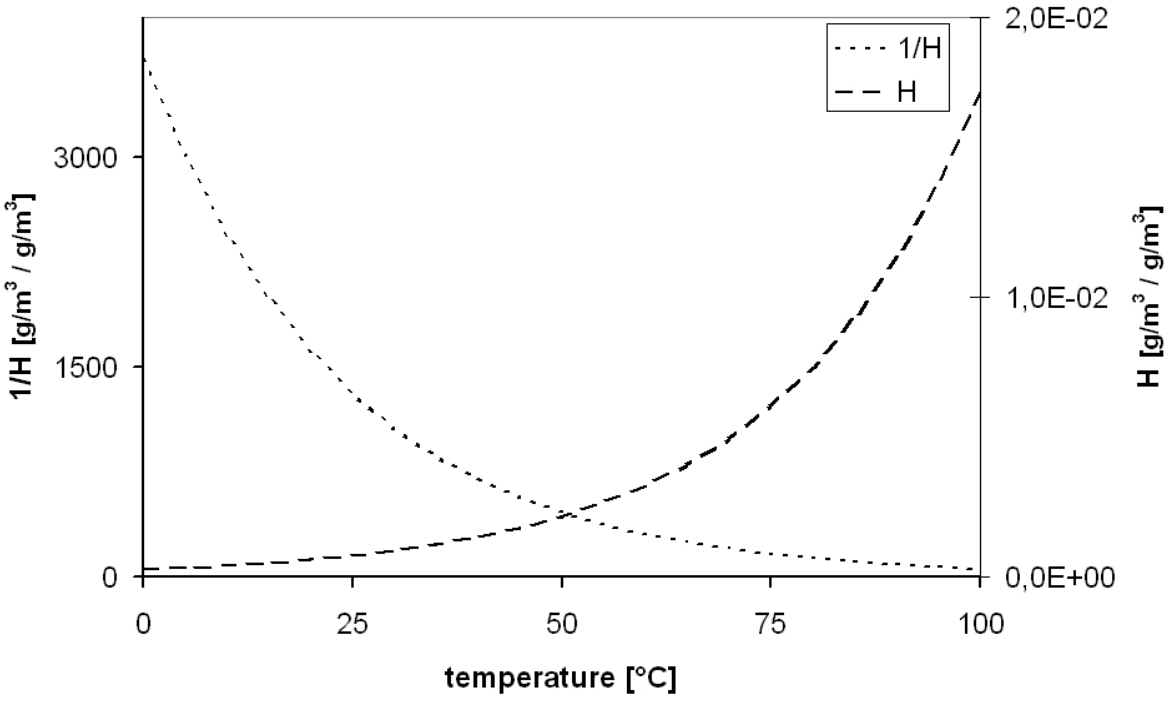

Figure 50: Henry coefficient for ammonia [*Arevalo 2000*]

Lab scale steam stripping

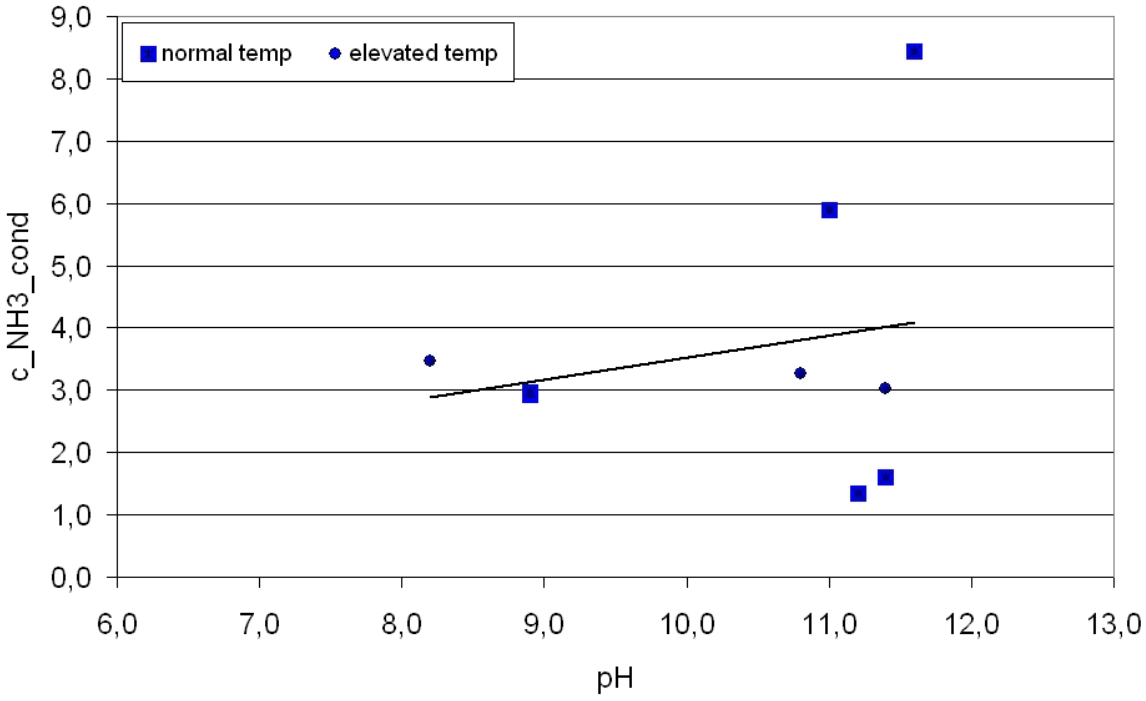

Figure 51: NH_3 concentration in condensate affected by pH

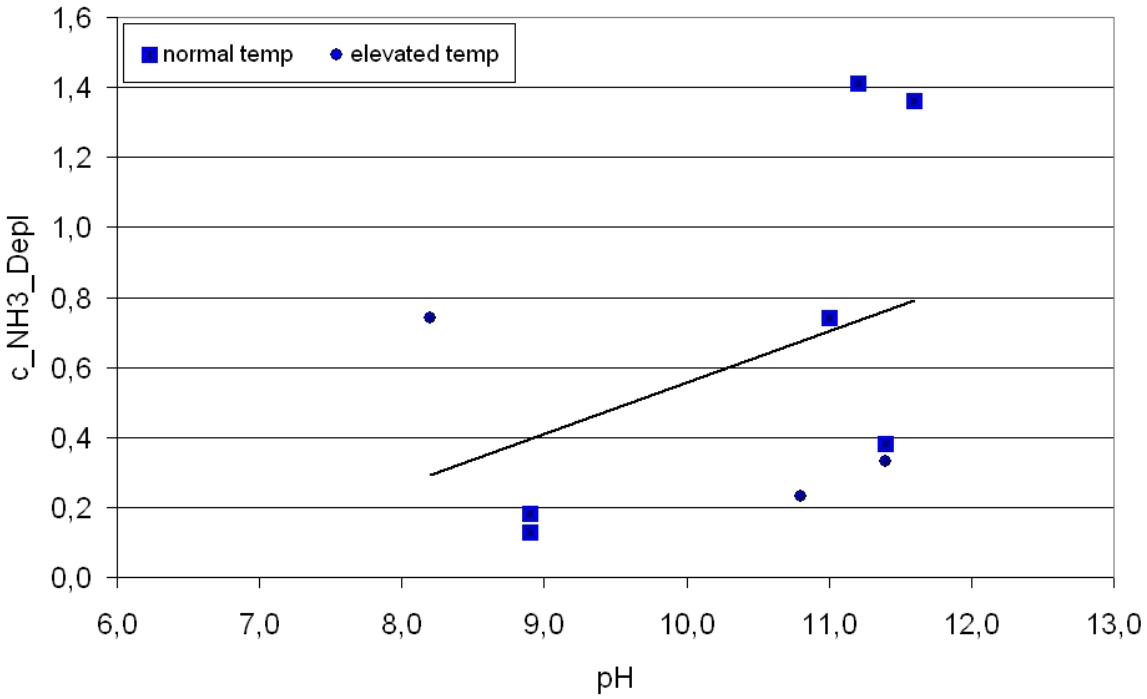

Figure 52: NH_3 concentration in N-depleted substrate affected by pH

Evaporation of hydrolyzed urine acidified with H2SO4.

Table 55: pH, conductivity, TOC, TN and total solids (TS) during first set of evaporation.
TOC and TN analyzed by autoanalyzer analytic Jena AG. Samples for measuring conductivity were not diluted prior measurement.

	pH	cond. [mS/cm]	*cf*	TOC [mg/l]	*cf*	TN [mg/l]	*cf*	TS [g/l]	*cf*	org. fatty acids [ml] BKT
feed average	4,67	24		2.190		3.150		30		
Conc 0240	4,91	36	*1,5*	2.600	*1,2*	3.320	*1,1*	43	*1,4*	
Conc 0500	4,62	45	*1,9*	4.030	*1,8*	3.790	*1,2*	63	*2,1*	
Conc 0750	4,98	51	*2,1*	1.710	*0,8*	2.890	*0,9*	63	*2,1*	
Conc 1000	4,32	57	*2,4*	2.470	*1,1*	3.860	*1,2*	77	*2,6*	
Conc 1250	5,30	54	*2,3*	4.050	*1,9*	4.040	*1,3*	69	*2,3*	
Conc 1500	3,93	65	*2,7*	5.360	*2,5*	4.400	*1,4*	82	*2,8*	25
Conc 1750	4,65	83	*3,4*	6.500	*3,0*	4.880	*1,6*	104	*3,5*	43
Conc 2000	4,94	78	*3,3*	6.670	*3,0*	5.110	*1,6*	117	*3,9*	59
Conc 3975	5,52	126	*5,2*	14.030	*6,4*	6.050	*1,9*	224	*7,5*	
Conc 7750	3,76	274	*11,4*	10.020	*4,6*	6.640	*2,1*	379	*12,7*	
Dist 0240	9,24	9,2	*0,4*	570	*0,3*	2.345	*0,7*	1,4	*0,1*	
Dist 0500	9,14	3,2	*0,1*	623	*0,3*	915	*0,3*	0,9	*0,0*	
Dist 0750	5,38	0,9	*0,0*	441	*0,2*	166	*0,1*	0,0	*0,0*	
Dist 1000	4,26	0,3	*0,0*	197	*0,1*	27	*0,0*	-0,1	*0,0*	

Dist 1250	8,12	0,5	*0,0*	134	*0,1*	70	*0,0*	-0,1	*0,0*	
Dist 1500	4,29	0,4	*0,0*	417	*0,2*	38	*0,0*	0,0	*0,0*	5,5
Dist 1750	3,65	0,2	*0,0*	633	*0,3*	8	*0,0*	-0,1	*0,0*	9,1
Dist 2000	9,08	0,3	*0,0*	717	*0,3*	55	*0,0*	0,2	*0,0*	21
Dist 3975	7,04	1,5	*0,1*	381	*0,2*	412	*0,1*	0,6	*0,0*	
Dist 7750	3,72	0,3	*0,0*	664	*0,3*	-	*0,0*	0,1	*0,0*	

Table 56: Metals during concentration process

	feed Urin	Conc 1250	Conc 1750	Conc 3975	Dist 1250	Dist 1750	Dist 3975
Na mg/l	2 085	4 945	1 780	3 890	2,13	0,96	3,05
Ca mg/l	7,13	18,3	29,8	67,9	1,56	2,66	0,97
Mg mg/l	0,19	0,84	0,86	1,98	<0,1	<0,1	<0,1
Fe mg/l	1,73	2,46	10,1	11,2	<0,1	4,29	<0,1
Cu mg/l	25,4	65,3	2,38	7,83	0,99	<0,05	0,07
Zn mg/l	3,88	12,0	2,17	3,97	2,76	<0,05	<0,05
Cd µg/l	<1	<1	na[*]	<1	na	na	na
Ni µg/l	166	518	na	226	na	na	na
Pb µg/l	131	412	na	98	na	na	na
Gd µg/l	15	42	na	128	na	na	na
Cr µg/l	39	188	na	111	na	na	na
cf_{exp}	1	2,3	3,5	7,5	1	1	1

*) na: not analyzed

Table 57: Organic acids during concentration process

	feed urine	Conc 1250	Conc 1750	Conc 3975	Dist 1250	Dist 1750	Dist 3975
acetic acid mg/l	1 660	3 170	6 090	7 770	210	1 160	500
propionic acid mg/l	105	170	320	780	20	140	80
iso- butyric acid mg/l	30	8	30	80	10	50	40
n- butyric acid mg/l	<4	30	70	170	<4	120	90
iso- valeric acid. mg/l	40	40	40	80	20	80	60
n- valeric acid mg/l	<2	<2	<2	<2	<2	<2	<2
caproic acid mg/l	<2	<2	<2	<2	<2	<2	<2
cf_{exp}	1	2,3	3,5	7,5			

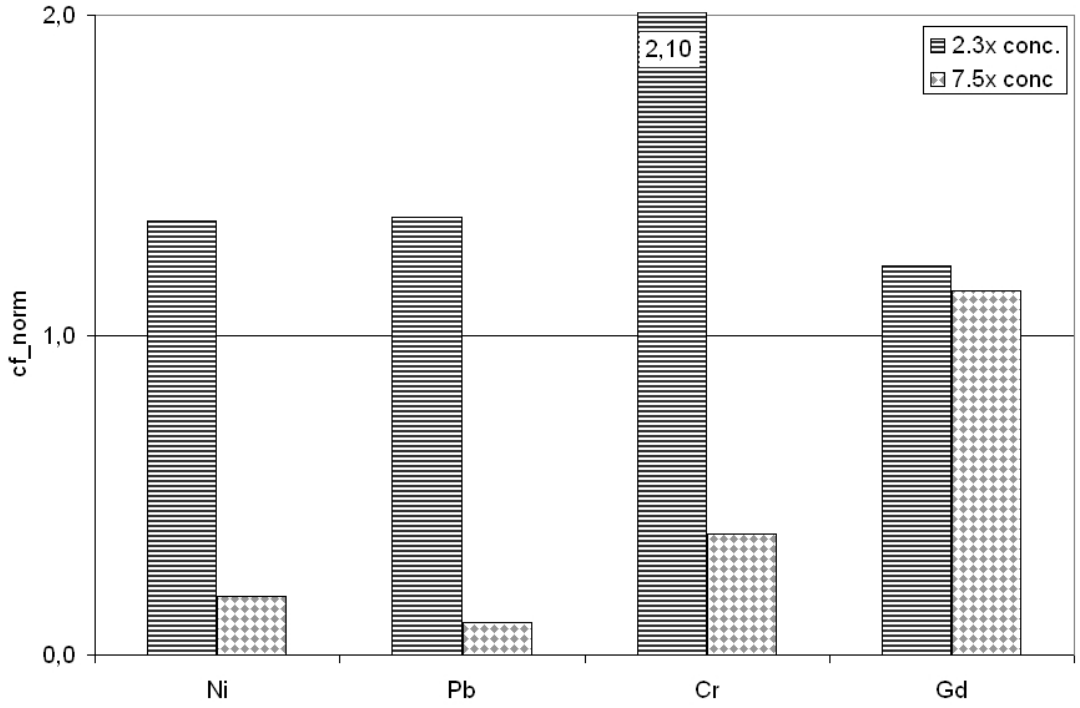

Figure 53: Trace metals in concentrates during evaporation

Evaporation of hydrolyzed urine acidified with H_3PO_4.

Table 58: Concentrates and distillates from evaporation

	pH	cond mS/cm	*cf*	TOC mg/l	TN mg/l	NH_4-N mg/l	*cf*	P mg/l	*cf*	COD mgO_2/l	*cf*	dry solids g/l	*cf*
feed avr.	7.3	21				3 640		1150		2590		8,8	
Conc 04						8 260	*2*	4360	*4*				*4*
Conc 05	8,98	63,2	*3*	52	6,9							44	*5*
Conc 19	5,58	225	*11*	54	119							171	*19*
Conc 24	5,54	351	*17*	163	138	27 000	*7*	33300	*29*	36400	*14*	212	*24*
Conc 25	5,47	351	*17*	82	141							222	*25*
Conc 27	5,38	381	*18*	114	141	24 000	*7*	31500	*27*	32370	*12*	238	*27*
Conc 46	5,7					27 314	*8*	57500	*50*			402	*46*
Conc 49	5,25	640	*30*	250	161							435	*49*
Conc 53	5,51	716	*34*	228	156	32 000	*9*	59400	*52*	67040	*26*	465	*53*
Conc 57	5,43	1005	*48*	210	162	28 700	*8*	58500	*51*	71640	*28*	499	*57*
Dist 04	7,87	4,4	*21%*	19	129							0,2	*2,1%*
Dist 24	5,41	5,0	*24%*	183	152	420	*12%*	5,9	*0,51%*	322	*12%*	0,2	*2,5%*
Dist 25	8,39	3,3	*15%*	167	128							0,3	*3,1%*
Dist 26	8,2	4,1	*20%*	46	131							0,3	*3,0%*
Dist 27	9,05	3,0	*14%*	173	134	279	*8%*	0,36	*0,03%*	1032	*40%*	0,4	*5,0%*
Dist 40	8,24	5,3	*25%*	71	148							0,2	*2,2%*
Dist 53	8,99	8,1	*38%*	85	174	1500	*41%*	0,22	*0,02%*	344	*13%*	0,4	*4,7%*
Dist 57	9,24	9,6	*46%*	89	189	4000	*110%*	0,14	*0,01%*	259	*10%*	0,2	*1,8%*

Evaporation of N-depleted urine

Table 59: Phosphorous, potassium, and sulfur concentrations in concentrates and distillates from N-depleted urine after steam stripping and evaporation

	P mg/l	*cf*	K mg/l	*cf*	S mg/l	*cf*
feed average	170		930		298	
Conc Ndep 32	6.730	*40*	37.100	*40*	11.700	*39*
Conc Ndep 55	8.900	*52*	48.100	*52*	15.700	*53*
Dist N_depl 32	<2		1,48		7,3	

Boiling point

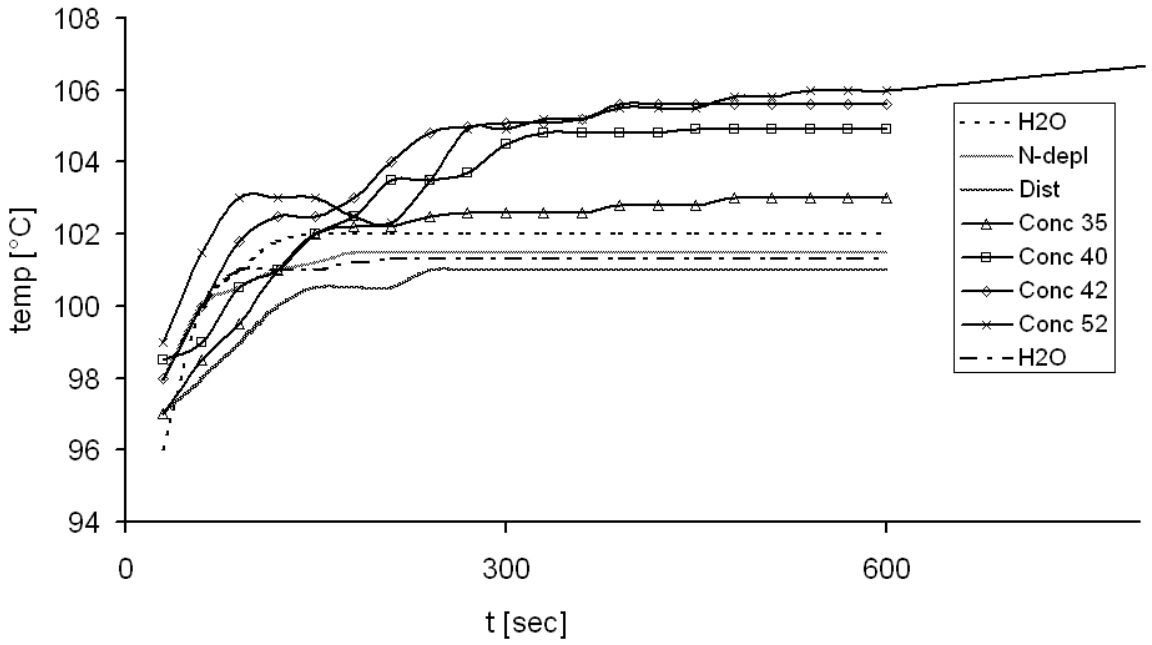

Figure 54: Determination of boiling point of concentrates, distillates, N-depleted substrate compared to H_2O

Precipitation

Table 60: Phosphate concentrations after dosage of MgO, srf 1 - 20

MgO srf	Added MgO g/l	PO_4-P_{feed} mg/l	PO_4-P mg/l	*Reduction* %	pH 8,9
0	0				
0,8	0,36	370	82,4	*78%*	
2,3	1,1	370	8,5	*98%*	
6,4	3,0	360	4,0	*99%*	9,5
13	6,0	360	3,9	*99%*	9,7
19	9,0	360	4,5	*99%*	9,8

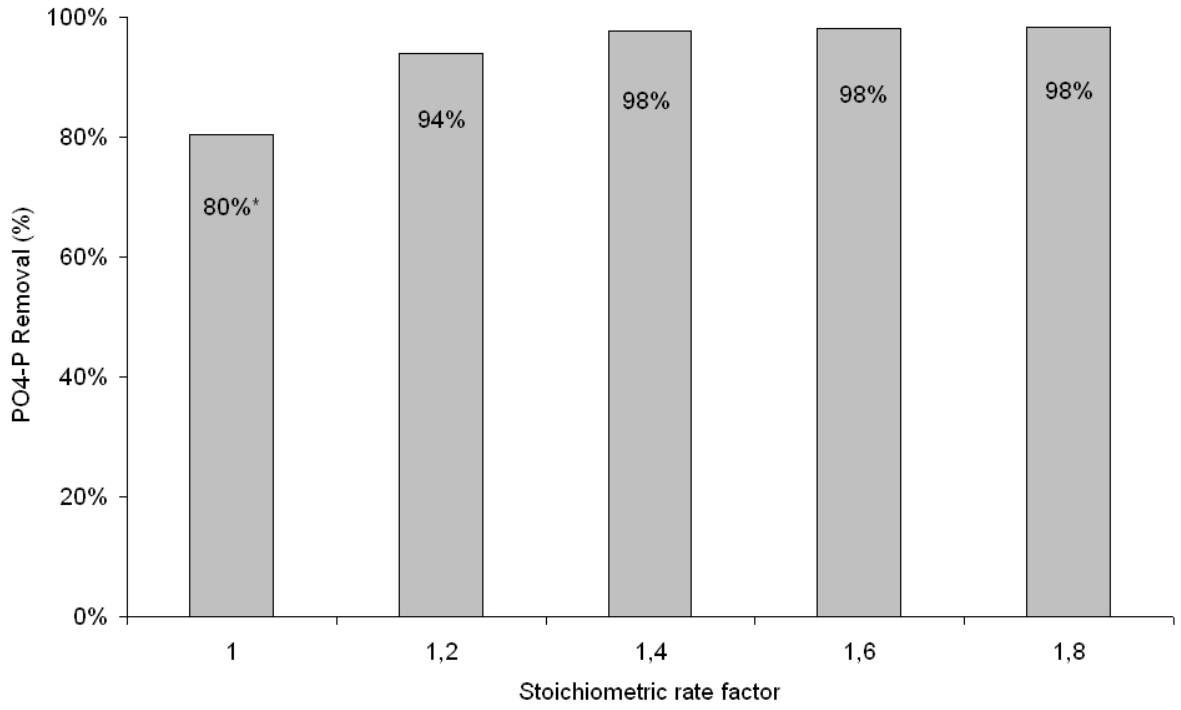

Figure 55: Reduction of phosphate concentrations in urine after dosage of MgO, srf 1 - 2

*) Mixing time here 30 minutes. For all others 15 minutes

Effect of mixing and sedimentation time on P-reduction

Table 61: MgO addition; effect of mixing time on the phosphate end concentration (srf 2; sedimentation time 30min, PO_4-P_i = 358 mg/l)

srf	mixing time	PO_4-P_e[mg/l]
2	15	5.48
2	30	5.44
2	45	5.10

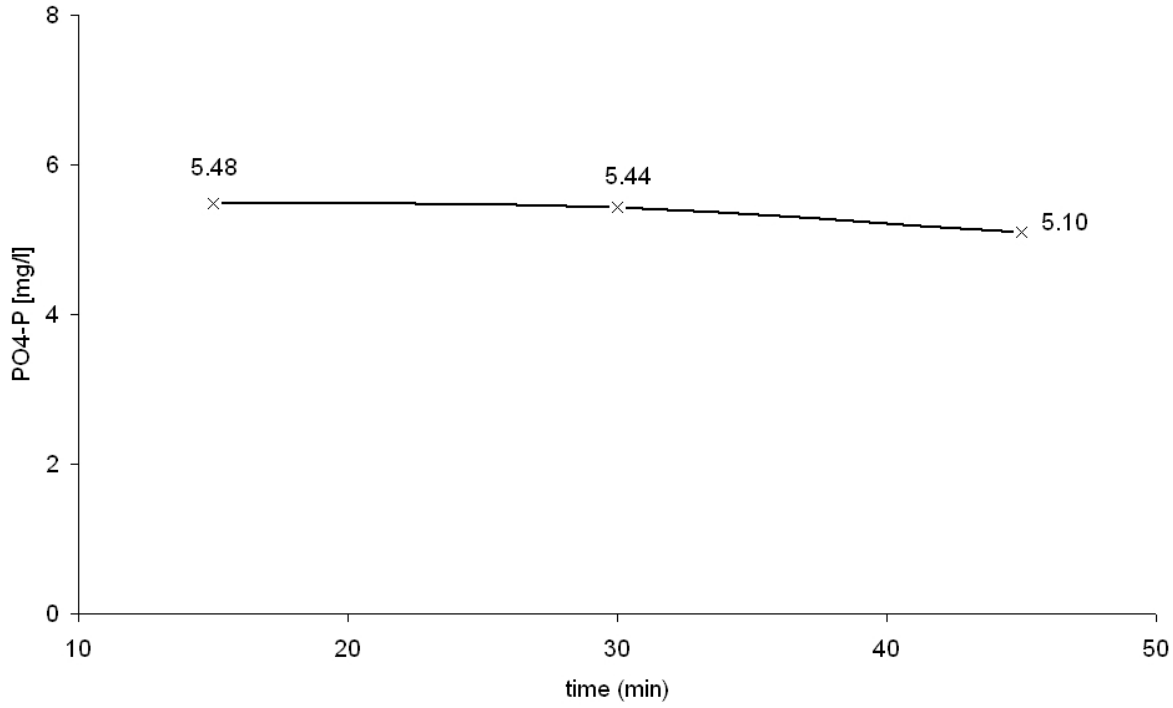

Figure 56: MgO addition; effect of mixing time on the phosphate end concentration (srf 2; sedimentation time 30min, PO_4-P_i = 358 mg/l)

Table 62: Effect of mixing and sedimentation time on phosphate concentration (Stored Urine MgO addition srf=2x, PO_4-P_i= 362mg/l)

Srf	2x				
Mixing Time (min)	6	6	15	30	30
Sedimentation Time (min)	5	10	30	15	30
PO_4-P End Concentration (mg/l)	10.2	8.0	5.5	5.3	5.4
PO_4-P Removal (%)	97	98	99	99	99

Table 63: Effect of mixing and sedimentation time on the phosphate concentration (Stored Urine MgO addition srf=1x; PO_4-P_i= 362mg/l)

Srf	1x		
Mixing Time (min)	15	15	30
Sedimentation Time (min)	15	30	30
PO_4-P End Concentration (mg/l)	83	77	71
PO_4-P Removal (%)	77	79	80

Addition of $MgCl_2$

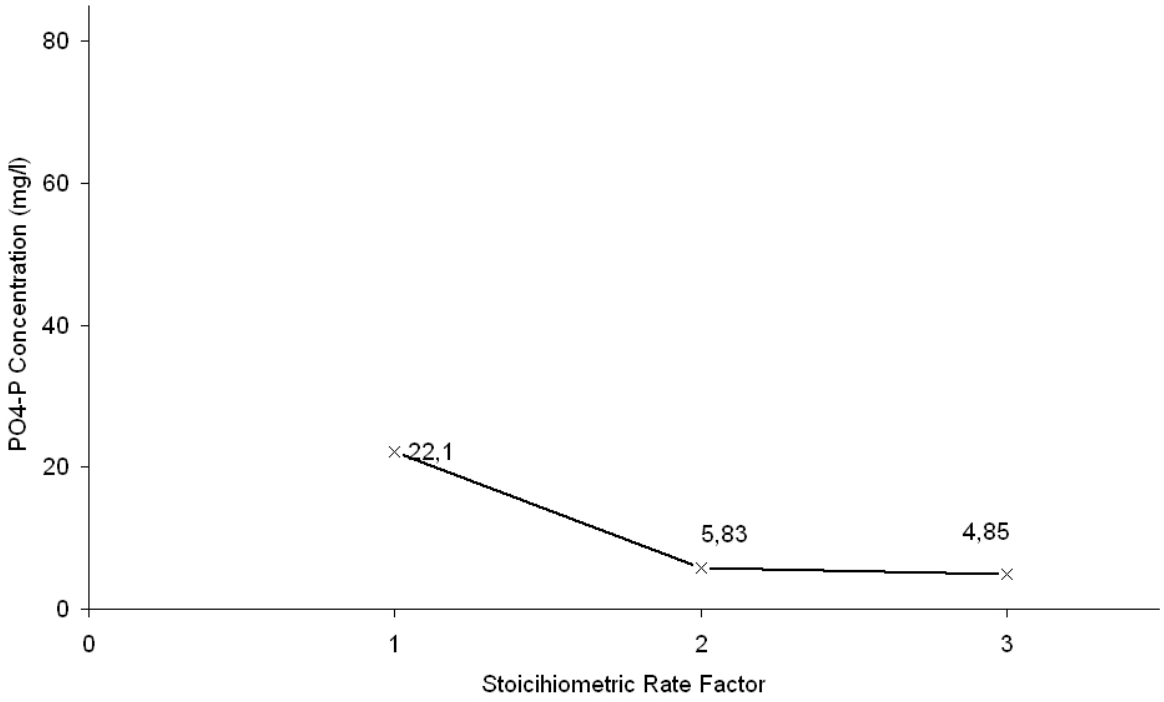

Figure 57: PO_4 concentration after addition of $MgCl_2$

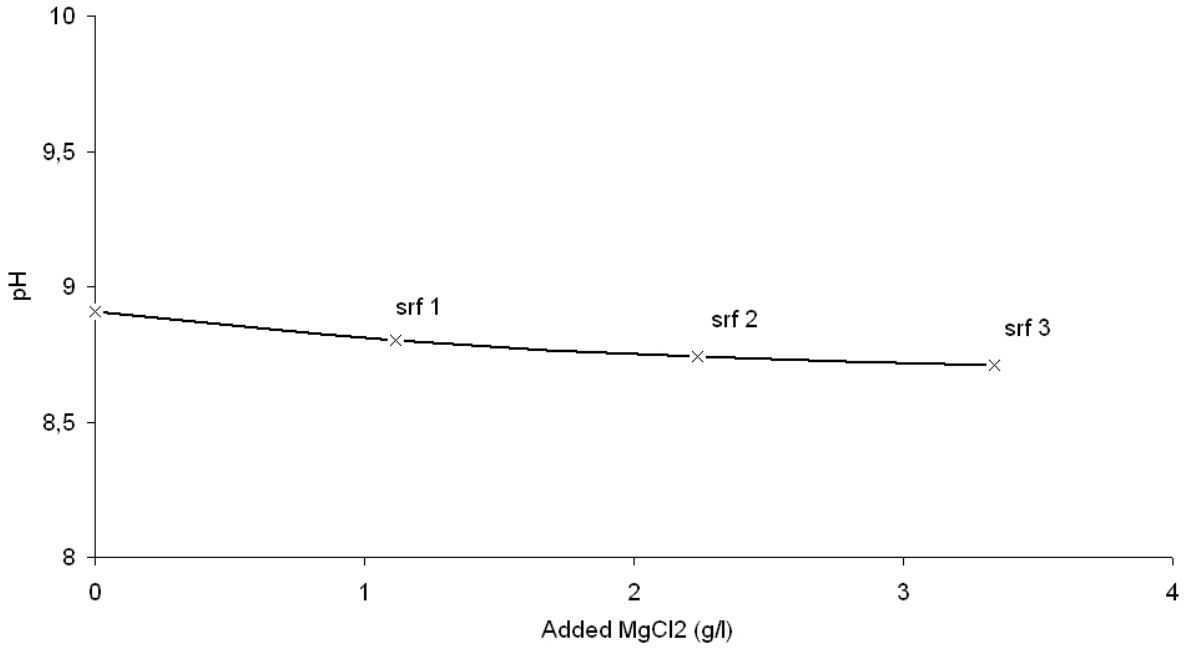

Figure 58: pH change after addition of $MgCl_2$

Comparison MgO and $MgCl_2$

Table 64: Removal rates comparison of addition of MgO and $MgCl_2$

srf	1x	2x	3x
MgO	80,4%	98,5%	nm (*
MgCl2	93,9%	98,4%	98,7%

*) nm: not measured

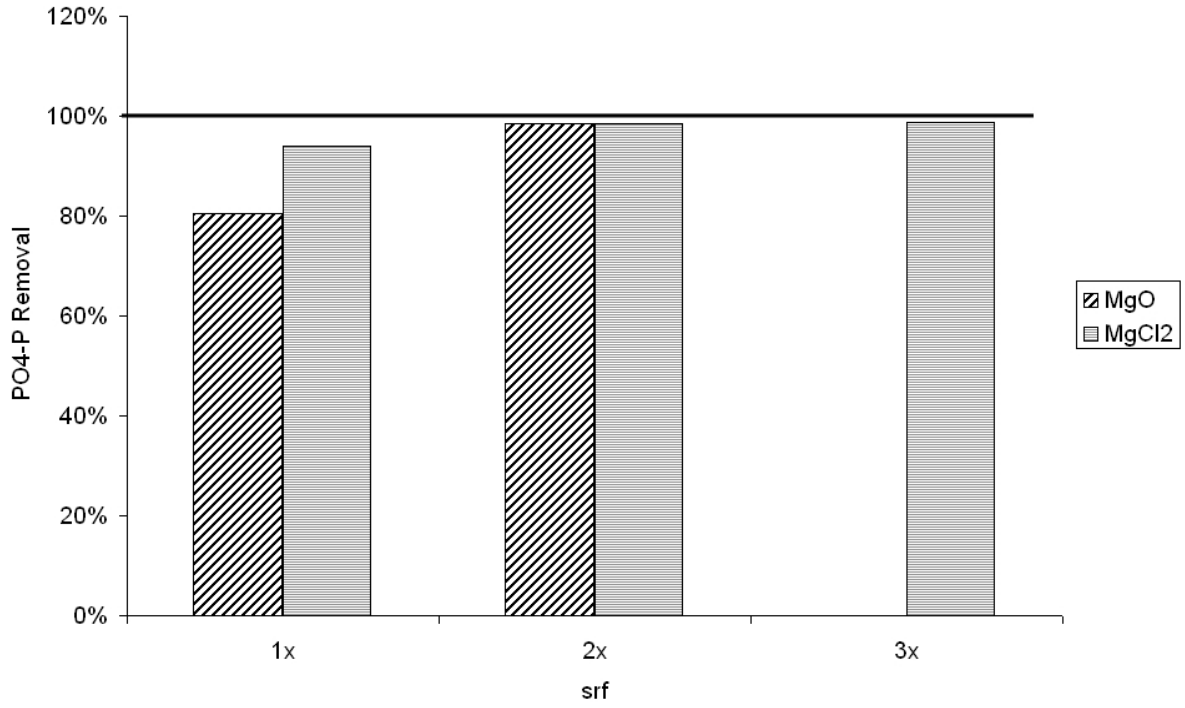

Figure 59: Removal rates comparison of addition of MgO and $MgCl_2$

P-removal at different pH by addition of $MgCl_2$

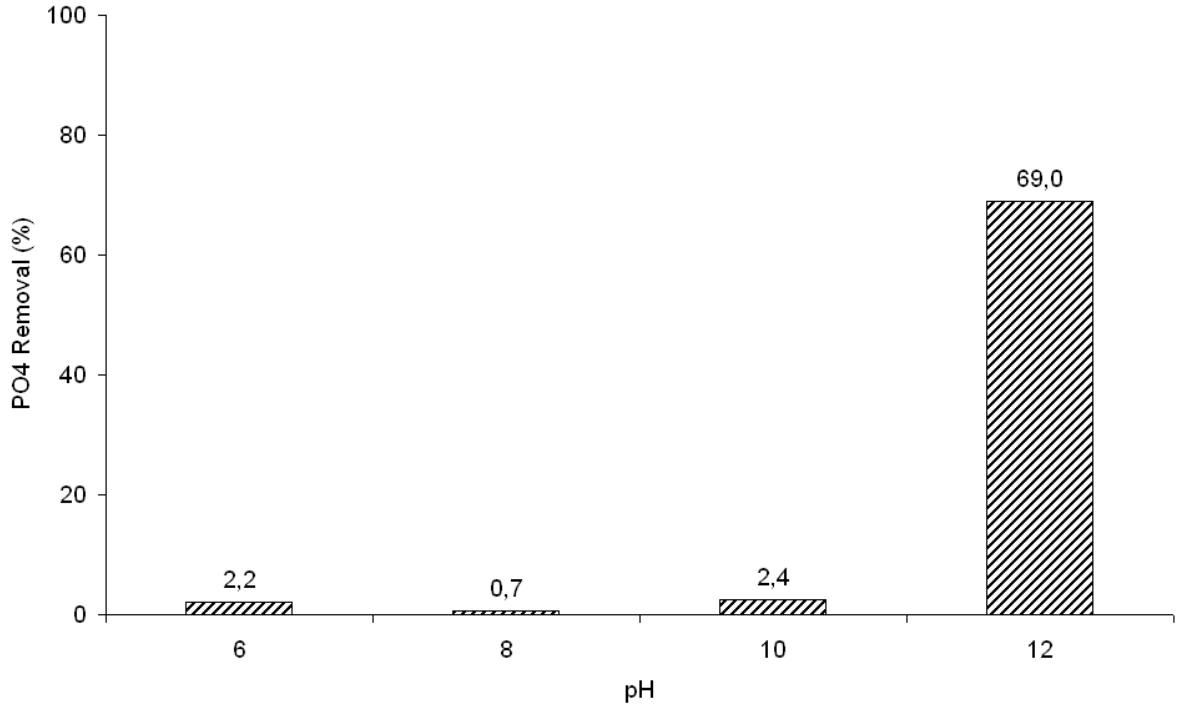

Figure 60: N-dep substrate with $MgCl_2$ addition; pH dependence of phosphate removal for srf 2.7 (PO_4-P_I = 276 mg/l)

P-removal at elevated pH by addition of $MgCl_2$ at different srf

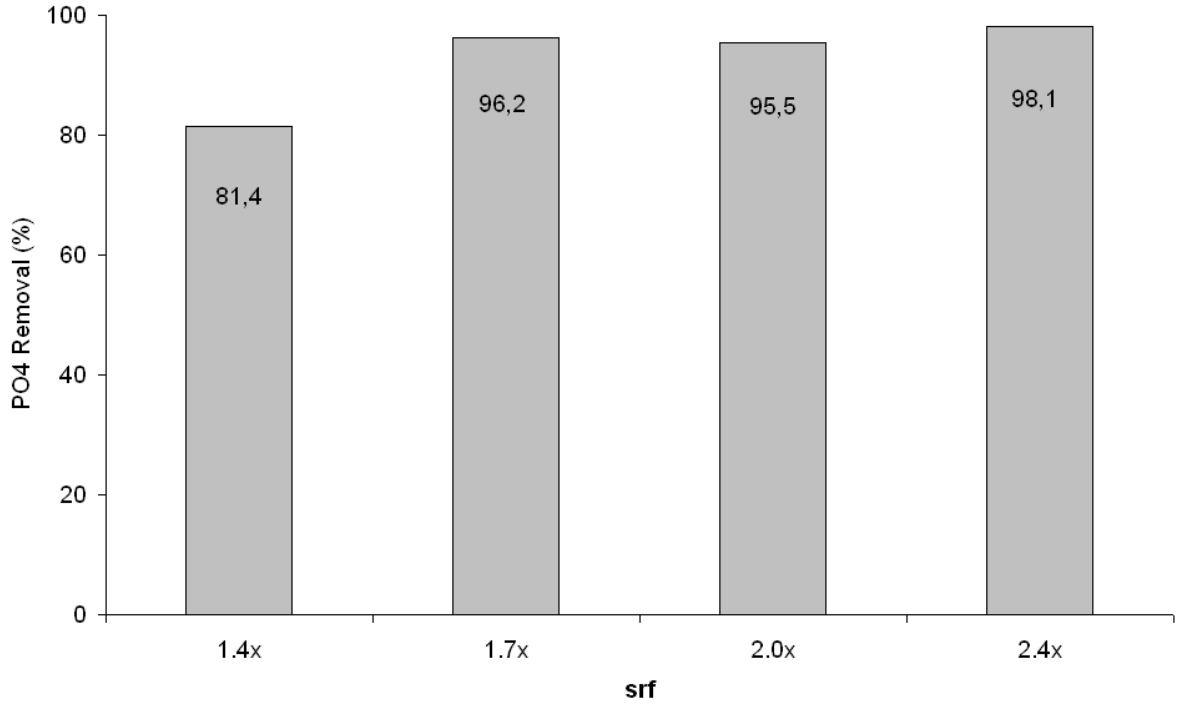

Figure 61: N-dep substrate added with $MgCl_2$; phosphate removal at pH 12 (PO_4-P_I = 266.5 mg/l)

Adsorption

Table 65: Adsorption and/or precipitation/crystallization of PO_4 and NH_3 after addition of zeolites

	initial	Zeogranul	Zeolite	burned clay	blank
PO_4 [mg/l]	360	14,8	178	258	356
%		96	50	28	1
adsorption mg PO_4-P / g Zeolite		0,69	0,36	0,20	0,01
NH_3 [mg/l]	3544	616	1905	3488	3544
%		83	46	2	0
adsorption mg NH_4-N / g Zeolite		5,86	3,28	0,11	0,00

Seed crystals

Zeolites were used as seed crystal material. For the experiment a dosage of 20g/l was used, the zeolites were crushed into a powder form. From the experiments it was seen that no change in the phosphate concentration was achieved.

Also for seed crystal experiments, the amount of $CaCO_3$ (25 g/l) used was less than the ones given by literature (100g/l).

Table 66: Stored Urine $CaCO_3$ addition, phosphate removal (PO_4-P_I = 359mg/l)

Srf	2x	2x		
Amount added	2,29 g/l	2,29 g/l	25 g/l	25g/l
Type	powder	marmor	powder	marmor
Initial PO_4-P [mg/l]	359	359	359	359
PO_4-P End [mg/l]	356	356	358	368
(PO_4)-P Removal (%)	0.8	0.8	0.2	-2.6
pH	8.66	8.65	8.64	8.67

To see if the hydrogen carbonate present was causing an inhibition, another experiment was conducted. A sample of stored urine was acidified to a pH 2 and then carbonate was tried to be stripped by aeration and mixing. The pH thereafter was increased to 12 and 100 g/l of calcium carbonate in powder form (precipitated) was added. After mixing and sedimentation time analysis for phosphate was done, but no noticeable removal was detected (max removal was 1.7 %). Longer mixing and sedimentations times were not conducted, but could probably help to obtain a noticeable effect.

Seed crystals in concentrated urine

To initiate crystallization by adding a porous medium different amounts of the zeolite zeogranul was added to the a 12 fold concentrate from the evaporation process. In other experiments high removal of phosphate were obtained by addition of zeogranul. Although anions are normally not adsorbed onto zeolites, PO_4^{3-} has the tendency to get attached to

surfaces in general. In the experiments were zeolites were used as seed crystals, it was assumed, that the surface of zeolites provide a good interaction with phosphate ions, leading to some sort of nucleation.

For the experiment zeogranul was crushed into little particles in order to remain suspend and increase the surface area. After 30 minutes mixing and 30 minutes sedimentation the supernatant was analyzed.

Table 67: 12 fold concentrate, zeolite as seeding crystals; phosphate removal (PO_4-P_I = 2120 mg/l)

Dosage [g/l]	-	1	5	25
PO_4-P_E [mg/l]	3 880	3 800	4 000	3 780
PO_4-Removal [%]	0.0	2.1	-3.1	2.6

No noticeable removal of phosphate was detected (Table 67). Zeogranul usage as seeding crystal was not successful.

Removal of PhaR

Table 68: Substances detected in sample from the lab scale steam stripping plant. Of two sets each two samples were taken

		initial conc		N-dep				Cond			
		C_0 set 1	C_0 set 2	C_d set1		C_d set2		C_d set1		C_d set2	
Ibuprofen	µg/l	380	442	358	283	267	270	3,8	4,1	4,0	3,5
Bezafibrate	µg/l	188	216	216	157	138	148	2,5	0,4	<0,1	0,1
β-Sitosterol	µg/l	29	33	31	27	21	21	<1,0	<1,0	<1,0	<1,0
Diclofenac	µg/l	23	30	19	17	17	18	0,7	1,1	0,4	0,7
Phenacetin	µg/l	19	28	10	6,8	8,6	6,9	0,3	0,2	0,2	0,3
Carbamazepine	µg/l	17	28	19	6,7	9,2	9,0	0,3	0,3	0,3	0,2
Pentoxifylline	µg/l	8,9	7,7	<1,0	<1,0	<1,0	<1,0	<0,1	<0,1	<0,1	<0,1

Table 69: Percentile concentration C_d/C_0 in N-depleted substrate and condensate regarding initial feed concentration from the demo-scale steam stripping process

	N_depl Set_1	N_depl Set_2	Cond Set_1	Cond Set_2
Ibuprofen	85 %	77 %	0 %	1 %
Bezafibrate	85 %	78 %	no	no
Diclofenac	94 %	65 %	no	no
β-Sitosterol	no	no	no	no
Carbamazepine	84 %	1.37 x	no	no
Pentoxifylline	no	no	no	no
Phenazone	2.18 x	2.53 x	no	no
Phenacetin	22.9 x	33.8 x	no	no

Table 70: Normalized concentration factor cf_{norm} of PhaR detected in concentrates and distillate from evaporation process

	Conc 3.5x	Conc 12x	Dist 3.5x	Dist 12x
Ibuprofen	0,19	0,01	0,40	0,55
Bezafibrate	0,61	0,03	-	-
Carbamazepine	1,19	0,58	0,12	-
β-Sitosterol	-	-	-	-
Diclofenac	0,28	0,03	-	-
Pentoxifylline	1,10	0,63	-	-
Phenazone	1,07	1,50	-	-
Phenacetin	1,06	-	-	-

Table 71: PhaR in untreated stored urine during UVC-treatment

		feed	0,4kWh/l		1,3kWh/l		2,1kWh/l	
		C_0	C_d	C_d/C_0	C_d	C_d/C_0	C_d	C_d/C_0
Ibuprofen	µg/l	511	320	*63 %*	30	*6 %*	13	*3 %*
Bezafibrate	µg/l	192	1,6	*1 %*	1,1	*1 %*	23	*12 %*
β-Sitosterol	µg/l	52	64	*123 %*	41	*79 %*	10	*19 %*
Carbamazepine	µg/l	29	16	*55 %*	1,1	*4 %*	<1,0	*no*
Diclofenac	µg/l	17	<1,0	*no*	1,1	*6 %*	3,9	*23 %*
Pentoxifylline	µg/l	9,2	6	*65 %*	1,5	*16 %*	<1,0	*no*

Table 72: PhaR during UVC-treatment of N-depleted substrate

		feed	0,5kWh/l		1,3kWh/l		2,5kWh/l	
		C_0	C_d	C_d/C_0	C_d	C_d/C_0	C_d	C_d/C_0
Ibuprofen	µg/l	470	189	40 %	28	6 %	<1,0	no
Bezafibrate	µg/l	363	6,2	2 %	<1,0	no	<1,0	no
β-Sitosterol	µg/l	270	270	100 %	190	70 %	<1,0	no
Phenacetin	µg/l	40	<1,0	no	<1,0	no	<1,0	no
Carbamazepine	µg/l	27	4,4	17 %	1,1	4 %	<1,0	no
Diclofenac	µg/l	22	1,1	5 %	1	4 %	<1,0	no
17α-Ethinylestradiol	µg/l	11	<1,0	no	<1,0	no	<1,0	no
Phenazone	µg/l	2,3	1	43 %	<1,0	no	<1,0	no
Pentoxifylline	µg/l	1,5	<1,0	no	<1,0	no	<1,0	no

Table 73: PhaR in stored urine during ozonation. Urine from HH, Mai '05

		feed	0.6 g O_3/l		6.6 g O_3/l	
		C_0	C_d	C_d/C_0	C_d	C_d/C_0
Ibuprofen	µg/l	511	152	30 %	1	0
Bezafibrate	µg/l	192	79,8	42 %	<1,0	no
β-Sitosterol	µg/l	52	42	81 %	<1,0	no
Carbamazepine	µg/l	29	17,3	60 %	<1,0	no
Diclofenac	µg/l	17	1,6	9 %	<1,0	no
Pentoxifylline	µg/l	9,2	5,4	59 %	<1,0	no

Table 74: PhaR in stored urine during ozonation. Urine from B Okt. 05

		feed	0.8 g O_3/l		5.9 g O_3/l	
		C_0	C_d	C_d/C_0	C_d	C_d/C_0
Bezafibrate	µg/l	846	222	26 %	14	2 %
Ibuprofen	µg/l	398	126	32 %	29	7 %
β-Sitosterol	µg/l	30	11	37 %	<1,0	no
Carbamazepine	µg/l	11	2,9	26 %	<1,0	no
Diclofenac	µg/l	8,8	<1,0	no	25(*	282 %(*

*) Diclofenac value seems unreasonable. Thus diclofenac is not included in Figure 44

Table 75: PhaR during ozonation of N-depleted substrate

		feed	0.7 g O_3/l		4.8 g O_3/l	
		C_0	C_d	C_d/C_0	C_d	C_d/C_0
Ibuprofen	µg/l	470	134	29 %	8,6	2 %
Bezafibrate	µg/l	363	90	25 %	<1,0	no
β-Sitosterol	µg/l	270	21	8 %	<1,0	no
Phenacetin	µg/l	40	<1,0	no	<1,0	no
Carbamazepine	µg/l	27	4,9	18 %	<1,0	no
Diclofenac	µg/l	22	1	4 %	<1,0	no
17α-Ethinylestradiol	µg/l	11	<1,0	no	<1,0	no
Phenazone	µg/l	2,3	<1,0	no	<1,0	no
Pentoxifylline	µg/l	1,5	<1,0	no	<1,0	no

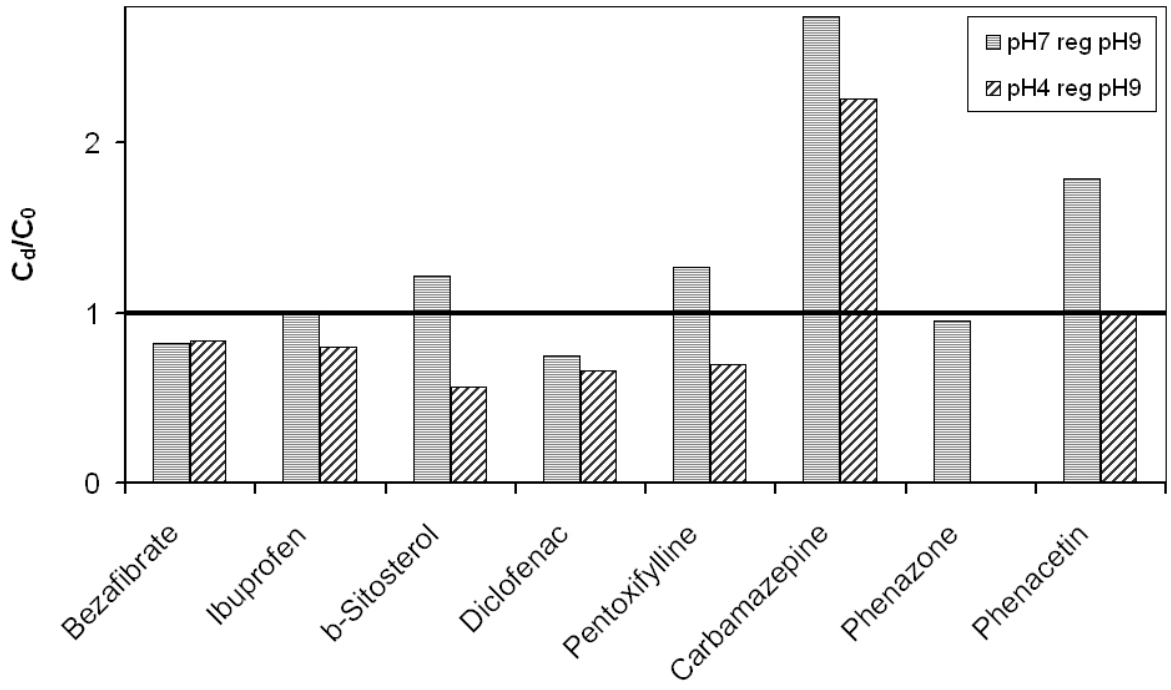

Figure 62: Detection of PhaR in urine influenced by acidification

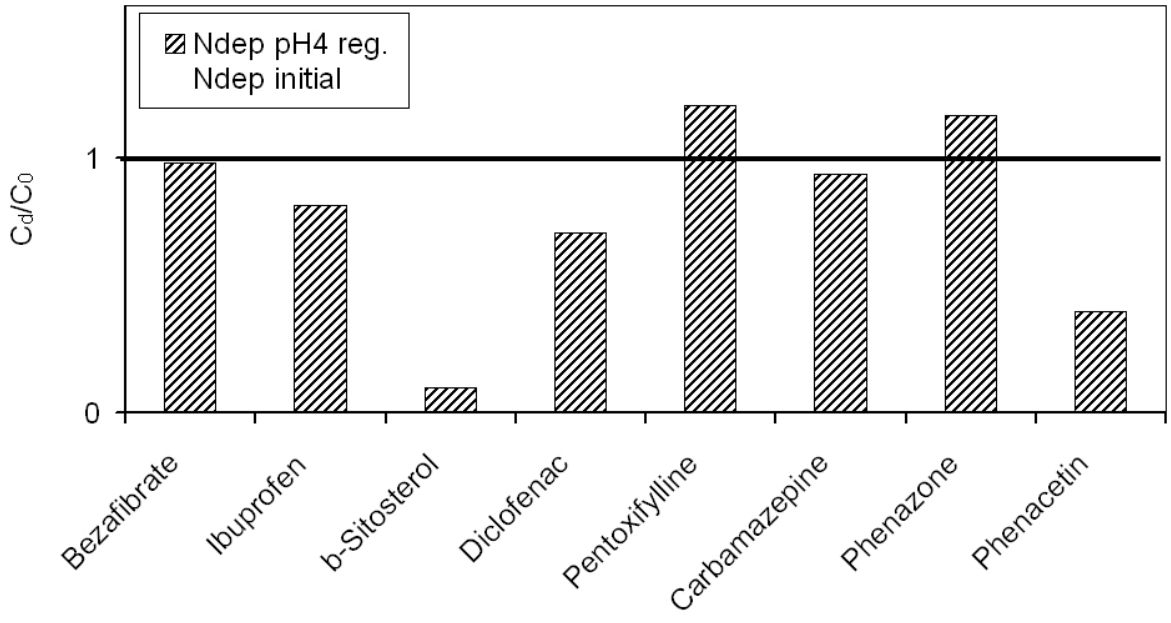

Figure 63: Detection of PhaR in N-depleted urine influenced by acidification

Table 76: Influence of ozone on PhaR in acidified urine

		feed	0,97 gO_3/l		1,59 gO_3/l	
		pH 9	C_d	C_d/C_0	C_d	C_d/C_0
Bezafibrate	µg/l	**495**	159	32 %	47	10 %
Ibuprofen	µg/l	**442**	163	37 %	57	13 %
β-Sitosterol	µg/l	**40**	40	99 %		0 %
Diclofenac	µg/l	**14**		0 %		0 %
Pentoxifylline	µg/l	**5,6**	1,7	30 %		0 %
Carbamazepine	µg/l	**3,5**		0 %		0 %
Phenazone	µg/l	**2,1**		0 %		0 %
Phenacetin	µg/l	**1,4**		0 %		0 %

		feed			2,02 gO_3/l	
		pH7				[%]
Bezafibrate	µg/l	405			167	41
Ibuprofen	µg/l	438			53	12
β-Sitosterol	µg/l	49				0
Diclofenac	µg/l	10				0
Pentoxifylline	µg/l	7,1				0
Carbamazepine	µg/l	9,6				0
Phenazone	µg/l	2				0
Phenacetin	µg/l	2,5				0

		feed	0,5 gO_3/l		0,86 gO_3/l	
		pH4		[%]		[%]
Bezafibrate	µg/l	413	249	60	97	23
Ibuprofen	µg/l	354	266	75	209	59
β-Sitosterol	µg/l	23		0		0
Diclofenac	µg/l	9,2		0		0
Pentoxifylline	µg/l	3,9	4,1	105	1,9	49
Carbamazepine	µg/l	7,9	3,8	48	3,1	39
Phenazone	µg/l					
Phenacetin	µg/l	1,4		0		0

Table 77: CIE-Lab values for ozonated and UVC-radiated urine and N-depleted urine

	O_3-dose	UVC-dose	L*	a*	b*	100-L*	C^*_{ab}	h_{ab}
$urine_{HH}$	0		61	4,3	38,5	39	39	83,6°
	0,6		49	12	43,7	51	45	75,2°
			91	0,28	7,7	8,8	7,7	87,9°
	4,0		95	0,15	4,6	5,4	4,6	88,1°
$urine_{B}$	0		36	10,5	38,3	64	40	74,7°
	0,8		41	10,1	36,3	59	38	74,5°
			56	6,1	32,2	44	33	79,3°
	5,9		89	0,58	8,8	11	8,8	86,2°
			93	0,15	5,7	7,4	5,7	88,5°
$urine_{N\text{-}depl}$	0		12	8,9	21,1	88	23	67,2°
	0,7		35	9,0	29,1	65	30	72,8°
			51	6,3	27,5	49	28	77,2°
	4,8		70	2,9	20,3	30	20	81,9°
			78	1,5	15,7	22	16	84,6°
$urine_{HH}$		0	61	4,3	38,5	39	39	83,6°
		0,4	46	15,5	49,0	54	51	72,5°
			54	14,2	54,7	46	56	75,4°
		1,3	56	13,7	55,8	44	57	76,3°
		2,1	60	12,2	57,1	40	58	77,9°
$urine_{N\text{-}depl}$		0	12	8,9	21,1	88	23	67,2°
		0,5	28	12,1	34,7	72	37	70,7°
			30	13,5	37,7	70	40	70,3°
		1,3	34	12,5	39,1	66	41	72,3°
		2,5	42	9,7	38,0	58	39	75,6°

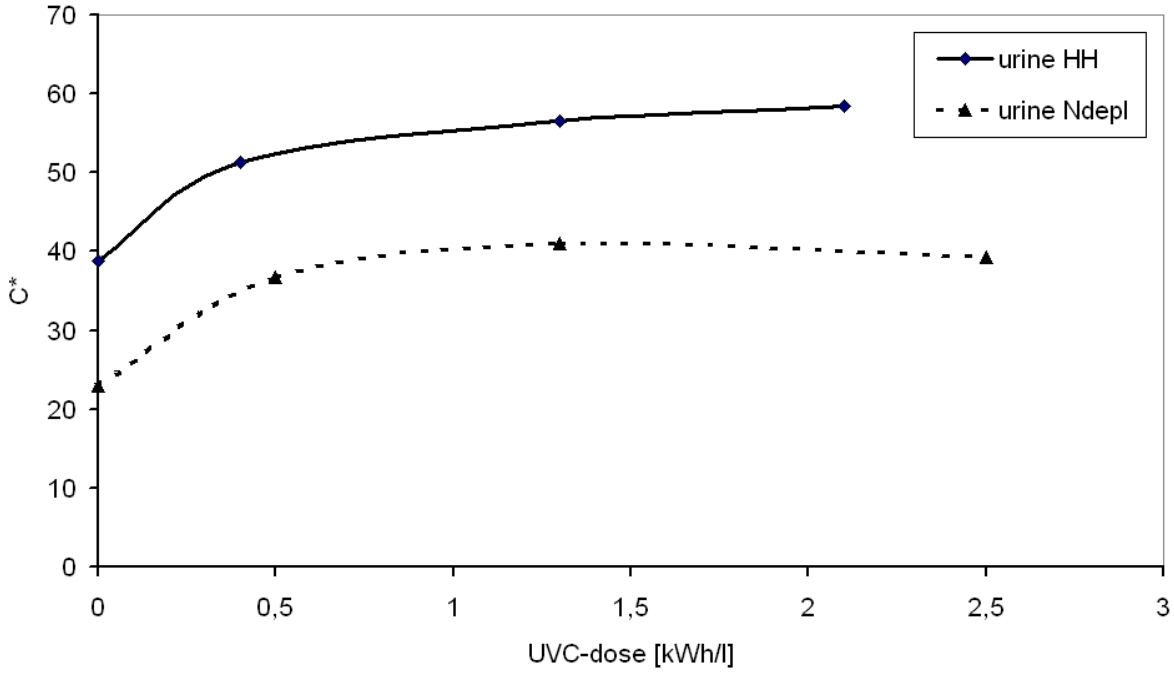

Figure 64: Chroma of urine and N-depleted urine during UVC-radiation

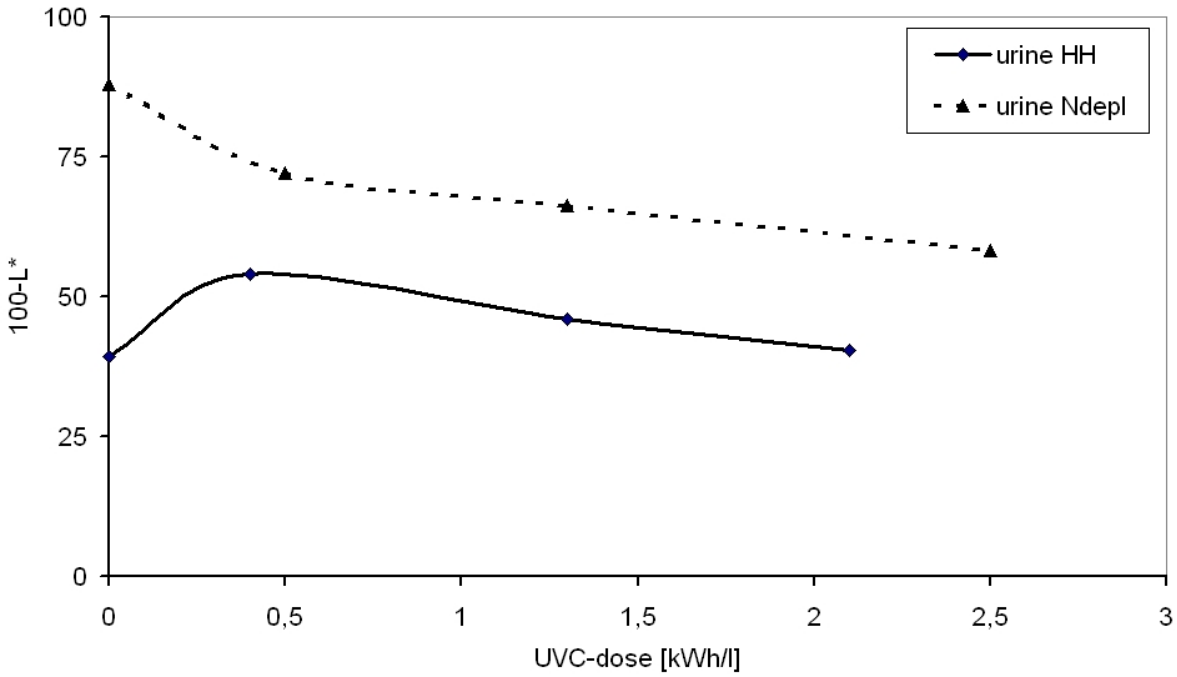

Figure 65: Turbidity of urine and N-depleted urine during UVC-radiation

Table 78: CIE-Lab values for ozonated and acidified urine and N-depleted urine

	O_3-dose	L*	a*	b*	100-L*	C^*_{ab}	h_{ab}
$urine_{pH9}$	0	35,1	11,2	38,4	64,9	40,0	73,7°
		32,0	13,9	38,9	68,0	41,3	70,3°
	0,97	40,1	10,9	37,4	59,9	39,0	73,7°
	1,59	59,5	4,58	28,8	40,5	29,2	81,0°
$urine_{pH7}$	0	27,1	12,4	36,0	72,9	38,0	71,0°
		22,4	12,3	31,5	77,6	33,8	68,6°
		30,5	8,31	28,6	69,5	29,7	73,8°
	2,02	50,8	3,30	21,4	49,2	21,7	81,2°
$urine_{pH4}$	0	28,1	11,0	33,5	71,9	35,3	71,9°
		19,2	9,85	25,9	80,8	27,7	69,2°
	0,5	22,6	8,60	25,4	77,4	26,8	71,3°
	0,86	27,2	8,05	23,3	72,8	24,6	70,9°
urine-$Ndepl_{pH7}$	0	13,3	16,1	32,1	86,7	35,9	63,3°
	1,37	31,0	12,3	37,0	69,0	39,0	71,6°
	1,94	52,5	6,71	34,7	47,5	35,4	79,1°
urine-$Ndepl_{pH4}$	0	3,6	10,8	20,7	96,4	23,3	62,3°
		11,1	10,4	24,1	88,9	26,2	66,6°
	0,63	18,1	9,99	26,1	81,9	28,0	69,1°
	1,26	27,7	8,12	26,1	72,3	27,3	72,7°

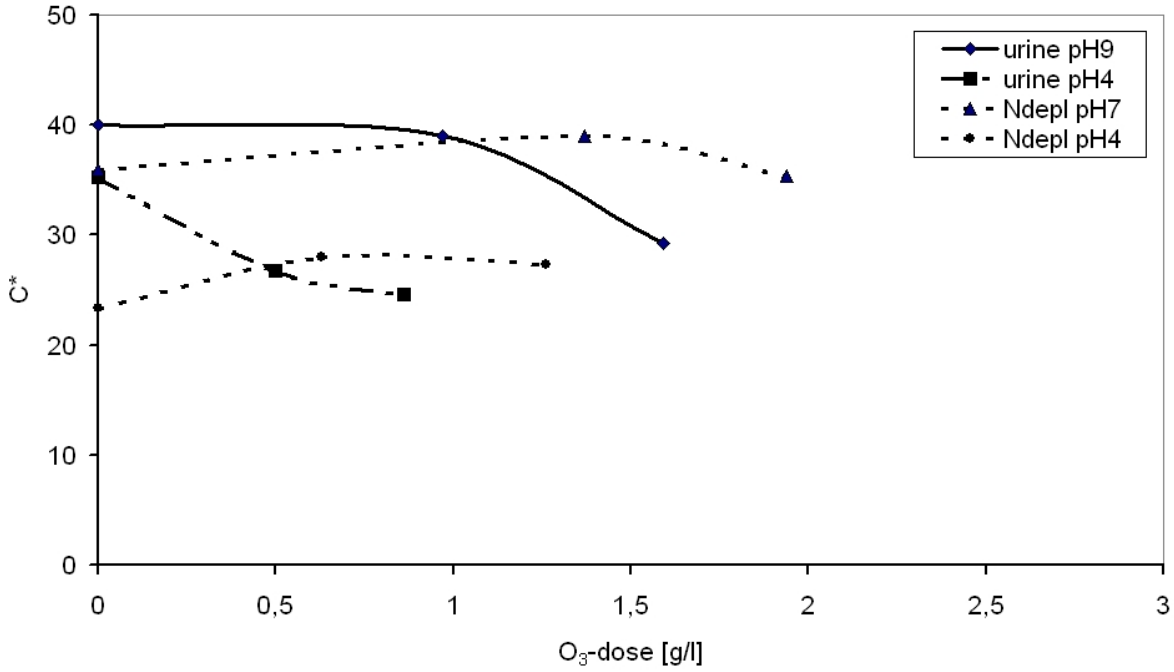

Figure 66: Colorvalue chroma of urine and N-depleted urine during ozonation

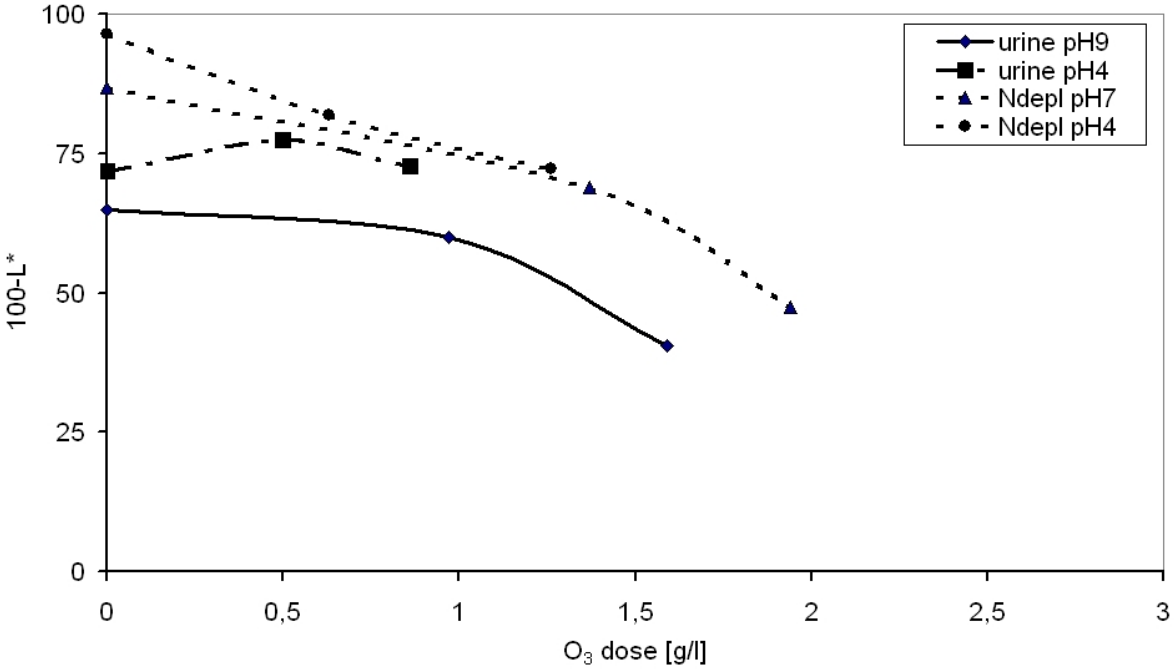

Figure 67: Colorvalue turbidity of urine and N-depleted urine during ozonation