Hochschule für Angewandte Wissenschaften Hamburg
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Bachelor Thesis

Analytical Method Validation within the Implementation of a Monitoring Concept for Waste Water in the Industrial Zone of Tra Noc, Vietnam

Course of Studies: Environmental Engineering

submitted by
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Preposition

The constantly changing demand and supply of the resource water is influenced by climate change, the rise of the global populate, urbanization as well as the increase of consumption and affluence. The availability of clean, non-hazardous water is often not ensured as well as sufficiently protected in threshold and developing countries.

Since the last two decades Vietnam's economy has experiences huge growth and as a result the number of Industrial Zones is constantly increasing. Currently there are more than 200 registered Industrial Zones and even though it is mandatory, most of them don't possess sustainable waste water treatment. This naturally leads to severe environmental pollution, the decrease in life quality and health of the people as well as the flora and fauna.

In the context of a joint German-Vietnamese Cooperation, called AKIZ, a pilot project is currently being developed in the Mekong Delta Region. The project started in 2010 and takes place in the industrial zone of Tra Noc which is located just south of the city of Can Tho. In addition to the planning of a centralized waste water treatment plant, the project partners are compiling an integrated concept for waste water treatment in industrial zones. This is to guarantee the efficient, economical and ecological sustainable operation of the whole waste water system.

One of the main objectives of this project is the development of a monitoring program to observe and monitor the content of industrial waste water, particularly with regards to toxicity and pollution. The collected information will then be used to create a database to enable and support the decision making process on waste water treatment related questions.

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List of abbreviations

abs.	absolute
ATU	Allylthiourea
BMBF	Bundesministerium für Bildung and Forschung (engl.: Federal Ministry of Education and Research)
BOD	Biochemical Oxygen Demand
CEPIZA	Can Tho Export Processing and Industrial Zones Authority
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DONRE	Department of Natural Resources and Environment
Fig.	Figure
ICP	Inductively Coupled Plasma
IEEM	Institute of Environmental Engineering and Management (University of Witten, Germany)
ISE	Ion Selective Electrode
IZ	Industrial Zone
LAR	LAR Process Analysers AG, Berlin, Germany
NTRIW	National Technical Regulation on Industrial Wastewater
PE	Population Equivalent
PM	Photometric Method
rel.	relative
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
WWTP	Waste Water Treatment Plant

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1 Introduction

The AKIZ project is divided into six subprojects. The task of subproject 5 is the development and implementation of a monitoring concept for industrial waste water which is adapted to the specific local conditions, such as ecological and legal requirements, in Vietnam. It also has the ability to be expanded to other threshold and developing countries with similar framework. For the analysis of the waste water a containerized state of the art laboratory has been developed in Germany and adapted to the local conditions. At the end of 2010, it was then shipped and installed in the Industrial Zone (IZ) of Tra Noc. During the last year the relevant sampling locations and parameters were identified and analytical methods, such as photometric methods and COD, toxicity and inductively coupled plasma (ICP) measurement methods have been developed and evaluated.

1.1 Assignment

To dimension a Waste Water Treatment System based on European or North American Standards would most likely not lead to acceptable results as the water usage and waste water compounds can not be compared. Climate conditions, in this case particularly the temperature, are additionally influencing the waste water treatment. On these grounds, a reliable database filled with the analysed results of the compounds of the waste water, is indispensable for the technical and economical planning of sustainable treatment systems.

The containerized laboratory in Tra Noc has the responsibility to build such a database which can be seen as the heart of the monitoring concept. It is the objective of this work to evaluate the results of the monitoring activities 2012 and to validate the photometric methods used to analyze ammonium, nitrate, nitrite, total nitrogen, orthophosphate and total phosphorus in order to confirm the accuracy and measurement trueness of the monitoring results. It also aims to determine whether or not method modifications might be necessary and if samples can be preserved for some time to have a larger time frame to put the laboratory capacity most efficiently to work. Three different experiments were set up for this reason:

Experiment 1

Currently the parameters are measured with samples that have been prepared by filtering them with a membrane filter. Samples were measured for all parameters with filtered, as well as unfiltered samples, to verify that the filtering doesn’t result in any loss of the analytes.

Experiment 2

Ammonium and nitrate were measured with two different methods; the current photometric method and with an ion selective electrode (ISE). The aim here was to have a means of confirming the current results and to maybe even have a second, more time and fund efficient method for the measurement of those two parameters.

Experiment 3

The third experiment is about keeping the analyte concentration in the samples over a longer period of time constant in the sample and to find out if it is possible to preserve the sample. The preservation was done by acidifying one part of the sample and to freeze another part. The samples were then repeatedly measured over the course of two weeks and were compared with the current methods results.

1.2 Structure of this Work

This work at hand is divided into 4 parts. After the introduction the frame work is laid out, giving information on Tra Noc, the current Waste Water Treatment Situation as well as Environmental Guidelines. This is meant to get an understanding about the context of this study. The second part is about the monitoring activities which have taken place in Tra Noc beginning of the year 2012. The objective and planning criteria including the analysed parameter are described and the results are presented. The plausibility and accuracy of those results were then determined and discussed.

The following section engages in the improvement of the workflow in the laboratory and the validation of the current sample preparation. It would support the workflow and the efficient use of the limited personnel and monetary capacity of the laboratory if alternative methods such as an ion sensitive electrode would proof to be as accurate as the current method or, if the samples could be preserved without any loss of the analyte. Those options were revised and then validated. As part of validating the current methods the sample preparation was surveyed to ensure that the filtering of the sample doesn’t result in loss of the analyte.

The last part summarises everything that was presented and concluded in the other sections as well as gives recommendations and an outlook on future opportunities to ensure the quality standard of the analysis in the laboratory.

2 Framework

2.1 Geography and Climate [1]

The city of Can Tho is located in the Mekong Delta Region (South Vietnam), south of one of the arms of the Mekong River called Hau Giang and about 150 km south-west of Ho Chi Minh City. With an area of approx. 1,400 km^2 and about 1.2 million habitants (2004) Can Tho is one of the five biggest cities in Vietnam and the biggest of the Mekong Delta.

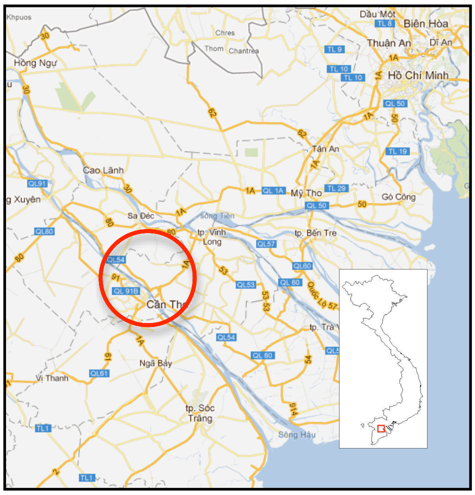

Fig. 1. Location of Tra Noc in the Mekong Delta Region

The Industrial Zone of Tra Noc is located about 12 km north of Can Tho bordering the Hau Giang at the north-east. In the west it is bordered by the Cai Chom channel and in the south by the National Route No. 91 which connects Can Tho with the south-western provinces of Hau Giang. The total area of the Industrial Zones amount to about 300 ha and is divided by the Sang Trang channel into Industrial Zone 1 and 2.

As part of South-East Asia, the Mekong Delta Region is part of an Earth Zone with a tropical climate and with two separate seasons. The monsoon season lasts from May to November and the dry season from December to April. The average temperature is about 27 ^{0}C with approx. 2,300 – 2,400 hours of sunshine per year and an average humidity of about 83 %.

2.2 Tra Noc und its Industries [2] [3]

The Industrial Zone of Tra Noc founded in 1998 is divided into two Industrial Parks. Tra Noc 1 covers an area of about 135 ha with 131 industries. Tra Noc 2 covers about 165 ha with 33 enterprises.

Those enterprises operate mainly in the field of seafood and food processing (e.g. fish, shrimp, rice or fruit), beverages (e.g. Saigon Bia or Pepsi Co.), garments, chemicals (e.g. pharmaceuticals) and fertilizer production.

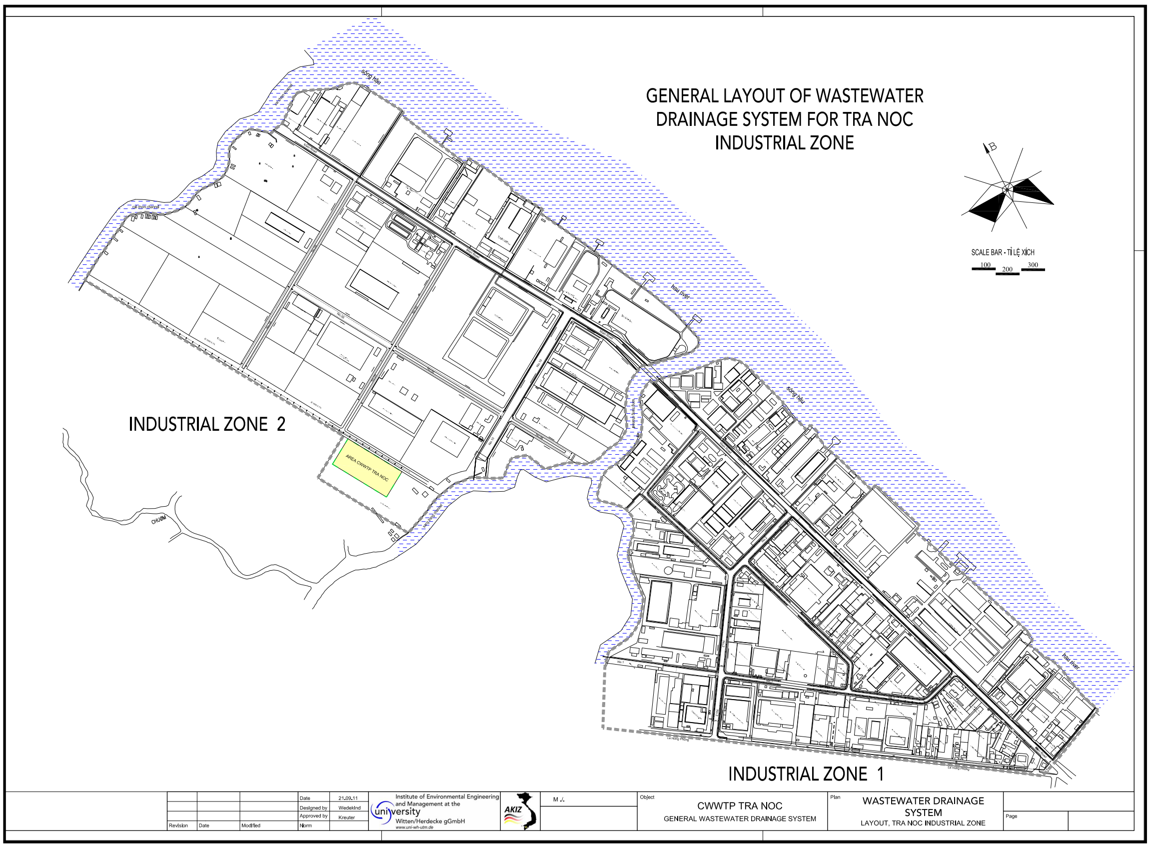

Fig. 2. Layout of Waste Water Drainage System for Industrial Zone 1 and 2 of Tra Noc (IEEM 2011)

Currently there is no exact data available regarding the amount and content of the discharged waste water into the sewerage system in Tra Noc IZ. The volume of released waste water from each factory differs from less than 100 m^3/d to 1,000 m^3/d, depending on size, field and current activity/productivity of the enterprise. However, the volume of waste water has been estimated within the AKIZ research and figures are also available, published by the Can Tho Export Processing and Industrial Zones Authority (CEPIZA).

Table 1. Estimation of Waste Water Load for Tra Noc IZ

Source and year	LAR and IEEM, 2011[2]	CEPIZA, 2011 [3]	Pöyry, 2020 [4]	Pöyry, 2030 [4]
Volume waste water, approx. [m^3/d]	15,000	12,000	17,300	22,500

To estimate the current compounds of the waste water in Tra Noc IZ is by far more difficult. The information given by the enterprises are mostly inconclusive. For example it also appears that the output of e.g. phosphorus, biological and chemical oxygen demand, nitrogen or toxic substances is unknown. Enterprises in the Industrial Zones in Vietnam are legally obliged to pre-treat their waste water if the limiting values are not met in a decentralized Waste Water Treatment Plant (WWTP), before they release it into the sewerage system. It is common knowledge that not all of the enterprises in Tra Noc operate such a pre-treatment plant and that many of the existing plants are not functioning properly.

A grab sample measurement was made by AKIZ and the Department of Natural Resources and Environment (DONRE) where waste water of a fish processing company was measured before and after the treatment. The results showed an increase in concentration of ammonium and orthophosphate after the treatment. The nitrite and nitrate levels remained stable. Even though it is not a representative measurement it does support the supposition of the currently poor treatment situation.

2.3 Environmental Guidelines and Limiting Values [5] [6]

Especially in Developing Countries the necessity of sustainable development in the field of waste water treatment und the protection of water quality of the receiving water facilities is of great importance. Referring to the Industrial Zones of Vietnam the sewerage systems and the pre-treatment plants are either in very poor condition or do not even exist. The highly polluted industrial waste water is released with very little or no treatment into the nearest body of water or coastal water area. In the case of Tra Noc, the waste water is released into the Hau Giang river or one of it's smaller anabranches.

Legally every Industrial Zone is bound to operate a centralized WWTP and to meet the National Technical Regulation on Industrial Wastewater (NTRIW). The allowed maximum concentration for each pollutant to be released, depends on the volume and the type of the receiving facility as well as the load of waste water. It is calculated as follows [5]:

(1) $c_{max} = c \cdot K_q \cdot K_f$

c_{max}	maximum concentration allowed to be released
c	concentration as found in table 1, NTRIW
K_q	coefficient, depending on volume of receiving water facility distinct by type (between 0.6 and 1.3), table 2 and 3, NTRIW
K_f	coefficient, depending on volume of discharged waste waster (between 0.9 and 1.2), table 4, NTRIW

The German *Gesellschaft für Internationale Zusammenarbeit* (GIZ) has proposed the following effluent standards for indirect discharge into the public drainage or sewerage systems in Vietnam.

These limit values are obligatory for all industrial or commercial waste water dischargers.

Table 2. Limit Values for indirect Discharge into Sewerage Systems in Vietnam (proposed by GIZ) [6]

Parameter	Unit	Limit value	Remark
Temperature	ºC	40	
pH	-	6.5 – 10.0	
COD	mg/L	2,000	minimum BOD/COD ratio: 1:4
Ammonia/ammonium	mg/L	200	if WWTP > 5,000 PE* or 500 m^3/d
	mg/L	100	if WWTP < 5,000 PE* or 500 m^3/d
Nitrite	mg/L	10	
Phosphorus	mg/L	15	

* = population equivalent

The values closely follow German standards. The lawful obligations for the discharge of waste water in Germany are specified in the law of water household (Wasserhaushaltgesetz, WHG) and the regulations of the Association for Sewage Treatment Technology (Abwassertechnische Vereinigung).

Table 3. Examplary Limit Value for direct and indirect Discharge of Waste Water in Germany

Parameter	Unit	Limit Value indirect Discharge [7]	Limit Value Discharge of Waste Water into Water Body [8]
Temperature	ºC	35	not specified
pH	-	6.0 – 9.0	not specified
COD	mg/L	not specified	110 – 200*
BSB_5	mg/L	not specified	20 – 25*
Ammonia/ammonium	mg/L	100	10
Nitrite	mg/L	10	not specified
Total nitrogen	mg/L	not specified	18 – 70*
Phosphorus	mg/L	not specified	2 - 3*

* value depending on industry (considered industries: breweries, juice and softdrink production, fish and meat meal factories, fish and meat processing, textile industry)

Tra Noc is a classic example where those legal matters have not been met yet. Authorities, responsible for the IZ, face a lack of reliable data and consistency which is problematic in the production processes used to estimate and plan such a WWTP. To dimension a WWTP by using European or American Standards, will not meet the requirements and won't lead to acceptable results. The load and contents can not be compared because of different guidelines for production processes. Additionally climatic conditions severely influence the treatment.

3 Implementation of the Monitoring Concept

3.1 Objective of the Monitoring Concept

It can no longer be ignored that water resources are limited and need to be protected. The need for Environmental Data Management is obvious, especially in Developing Countries where the population and technologies are continuously growing, the requirements are subject to constant changes.

The many complex substances that are discharged through industrial waste water have a direct impact on the sewerage system, the treatment process, facilities and outflow. If the content and load of waste water in a WWTP is neglected it can’t be expected that the effluent quality meets the legal value limits. Surveying and monitoring waste water is therefore necessary for an effective treatment process and hence for the sake of the public health and the environmental protection.

In the case of the IZ of Tra Noc the centralized WWTP and the new, closed sewerage system has not yet been built, but modelled by Vietnamese local authorities. The collected data during the initial concept development is also used to confirm or negate the estimated dimension of the planned centralized WWTP.

3.2 Planning Criteria

3.2.1 Timeline

The containerized laboratory of LAR Process Analysers AG has arrived at the end of 2010 in Tra Noc 1 at the premises of the water plant responsible for the water supply of Can Tho. Once the container and equipment was set up, the development of methods and the verification of results then took place in the first half of the year 2011. During this time sporadic collecting of data of various sampling points was done.

At the end of October 2011, the first interval of monitoring, two fixed nodes in Tra Noc 1 was carried out. From January to end of February 2012 the second interval of monitoring was accomplished. This data was evaluated and is now presented and discussed in this work.

The monitoring work in Tra Noc is ongoing, presumably until 2014.

3.2.2 Locations

The locations were chosen accordingly to the Topography Survey Report, Ha Khang Consultancy and Technical Planning and Survey of Geology Engineering Ltd. Co., August 2011, and the industries connected to the sampling point. The channels run along side the streets. At almost all intersections in Tra Noc 1 and 2, so called drainage nodes can be found. Each node is divided into up to four points (each corner of the intersection).

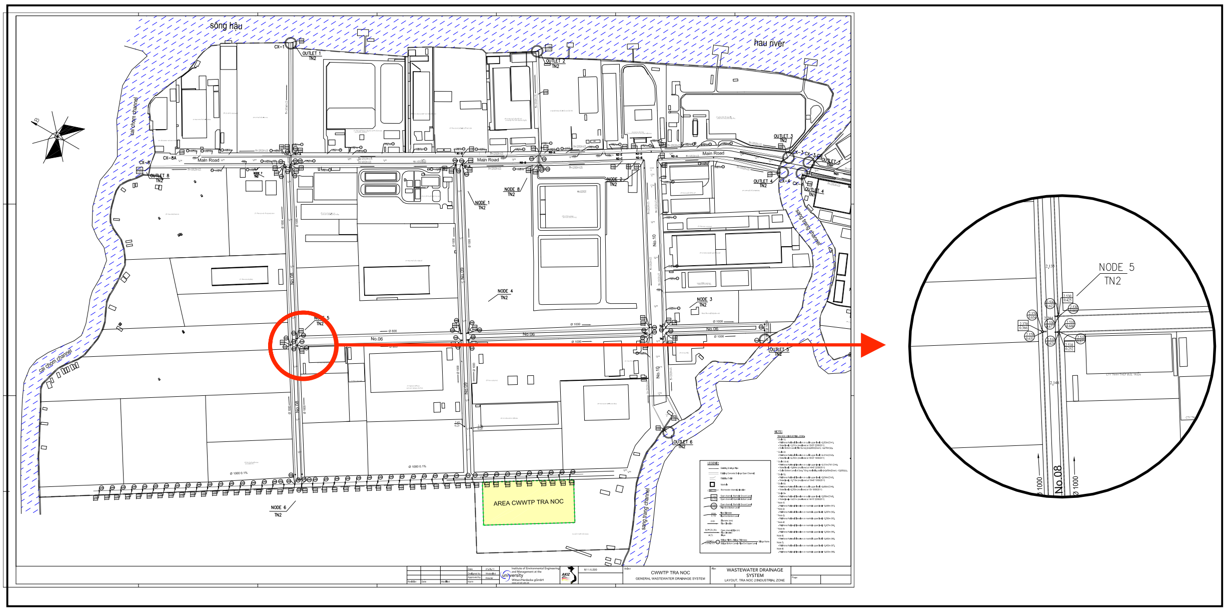

Fig. 3. Technical Drawing of Drainage System of Tra Noc 2 and Magnified Node 5

At these nodes the waste water of the connected enterprises are jointly passing by, moving towards one of the 14 outlets. The slopes in the sewerage system define the direction where the waste water is released into the receiving water facility. The documentation of the topographic survey show all directions of the slopes as well as where each enterprise is releasing their waste water into the system. Using this system it can be estimated beforehand what water load is to be expected. Working in the field showed some discrepancy within the data of the survey, which made it necessary to validate first hand and investigate all nodes.

In order to determine the drainage nodes with the highest water load and pollutants value, samples were taken at least twice at every node. The aim is to find the locations that can be taken as representatives for future monitoring and to estimate the inflow to the future WWTP.

4 Fundamentals

4.1 Sample Taking

To implement the Monitoring Concept, a suitable course of action for the sample taking needed to be developed. Besides locations, a sample taking interval and the type of sample taking needed to be ascertained. Furthermore, capacity, such as man power and costs, and also very importantly the tidal influence of the Hau Giang river, were main factors that needed to be taken into consideration.

The topographic data was used to decide at which times of day and where the samples needed to be taken. It's been important to rule out a dilution of the waste water in the sewerage system from the inwards pushing water from the Hau Giang River. Therefore the depth of a fixed point (Outlet 1 in Tra Noc 1) was always measured as well as the depth at each sampling point. This data was used to evaluate the results considering a possible dilution.

The priority for the monitoring done in the beginning of 2012, was to get information from as many different nodes as possible. The strategy was to take samples at one or maybe two locations with an expected high load of pollutants four times per sampling day. In addition, two to three extra locations were chosen where samples were taken two times per sampling day. At those locations lower results were to be expected. Since the development is an ongoing process the sample taking strategy is continuously evaluated and adjusted.

4.2 Relevant Parameter to Evaluate Industrial Waste Water [6] [9]

Industrial waste water is defined as the water which was used for any producing or processing operation and which is afterwards released directly into a body of water or indirectly into a sewerage system by an enterprise.

The degree of the impurity of waste water is defined by the extent of different measureable parameters. They represent pollutants and are referred to as the quality or characteristics of waste water. Those characteristics are described by chemical, biological and physical parameters and are chosen because of their validity on the impact on the Environment. The extent of those parameters is used to design and operate pre-treatment plants, sewerage systems and WWTP. The following is an introduction of the parameters used for the development of the monitoring concept in Tra Noc and is not a complete list of parameters that is or can be used to reveal the quality of industrial waste water.

The parameters are divided into physical and chemical parameters. The BOD is described within the chemical parameters because of its close relation to the COD and because it is determined by measuring oxygen concentration which is a chemical parameter. Within this work no biological parameters were examined and are therefore left out.

4.2.1 Chemical Parameters

Biochemical Oxygen Demand [10] [11]

The biochemical oxygen demand (BOD) is the amount of oxygen needed by microorganism for the aerobic decomposition of the organic substances in a water body. Over a certain period, commonly 5 days (n = days, BOD_n) at 20 ºC the oxygen that is used by a mirco-organism for the oxidation of organic substances is measured. The result is the sum of all biologically degradable compounds in the water and it is not conclusive regarding the composition of single bonds and is therefore called a sum parameter. The BOD result does allow a prediction of the state of pollution of water. Unpolluted water has a BOD_5 of 5 mg/L or less.

It is common practice especially in the treatment of industrial waste water to only measure the BOD of the decomposition of carbons. The oxygen demand of the biological oxidation of ammonia, ammonium and nitrite into nitrate is not taken into account. The nitrification where oxygen is used for the oxidation of ammonia to nitrite and then nitrate is suppressed by adding allylthiourea (ATU) as an inhibitant.

Chemical Oxygen Demand [11]

Similar to the BOD is the chemical oxygen demand (COD) a sum parameter to quantify the amount of oxidable substances in water. The COD clearly specifies the amount of oxygen that is needed to oxidize those substances as if oxygen were the oxidizing agent.

The biological degradable as well as the non degradable organic compounds and some inorganic substances are determined. Therefore the COD is always higher than the BOD. The ratio of BOD_5 and COD gives information about the kind of compounds in the waste water and about the ability of decomposition.

Table 4. Meaning of Ration BOD_5 and COD [12]

$BOD_5 \triangleq 50-100\ \%$ COD	The substances are easily biodegrated
$BOD_5 \triangleq 25-50\ \%$ COD	Decomposition of substances is difficult
$BOD_5 \triangleq 12-25\ \%$ COD	Usually the ratio after the biological treatment

Dissolved Oxygen [13 14]

The dissolved oxygen (DO) content is the concentration of dissolved oxygen in a liquid and is limited by physical conditions such as temperature and partial pressure. There are two main sources of dissolved oxygen in running or surface waters - the atmosphere and aquatic, phototrophic organism (e.g. algae). The atmospheric oxygen is mixed into the water through movement such as wind but mostly conditioned by Dalton's Law of partial pressures, where the sum of all partial pressures p_i within ideal gases equals the total pressure P_{total} of the mixture.

$$(2) \qquad P_{total} = \sum_{i=1}^{n} p_i$$

An equilibrium between the gas in the liquid and the gas in the atmosphere is set up. In pure water the ratio of gases in the atmosphere is equal to the ratio of gases in the water. The ability of oxygen to dissolve in water decreases with increasing temperature and the increasing content of other dissolved substances such as salts and other dissolved gases.

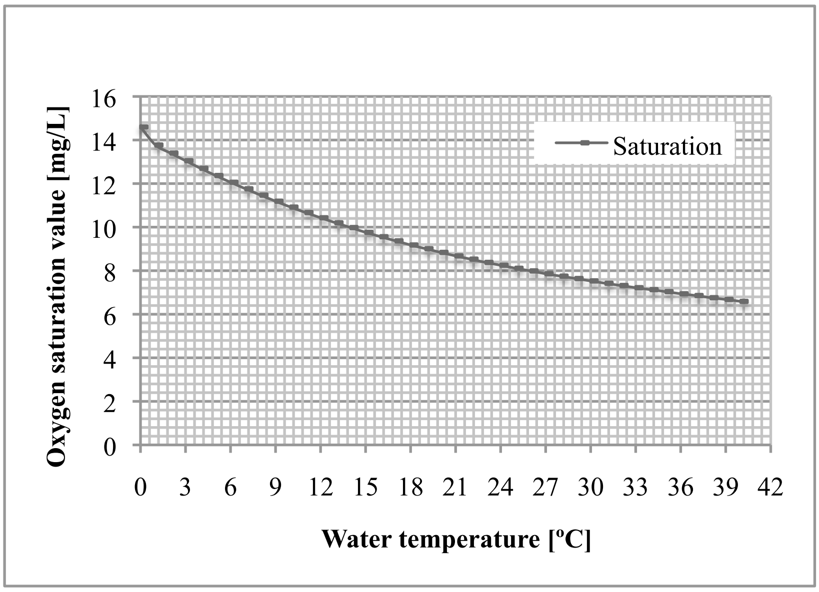

Fig. 4. Oxygen Saturation at Total Pressure of 1013 bar in Water Vapour Saturated Atmosphere [14]

Since most aquatic organism need oxygen for respiration a fish-critical concentration of about 3 mg O_2/L has been defined.

The parameter of DO is a measured variable for the regulation of Waste Water Treatment. Oxygen is essential for the aerobic metabolic activity of the nitrifying bacteria during nitrification to oxidize ammonia to nitrate. For this part of the biological treatment, oxygen is inserted into the aeration tank where an oxygen concentration of 3 mg/L is sufficient.

Nitrogen [15] [16]

Nitrogen is an essential nutrient and required by plants and animals for the building of amino acids. If there is a surplus supply in a water body it will lead to severe environmental problems such as eutrophication. A small amount of molecular nitrogen is soluble in water but it is of no importance for the determination of pollution or for water treatment. More important is total bounded nitrogen which is composed of all inorganic and organic nitrogen bounds such as ammonia (NH_3)/ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-) and organic bounded nitrogen (proteins, amino acids, urea, etc.).

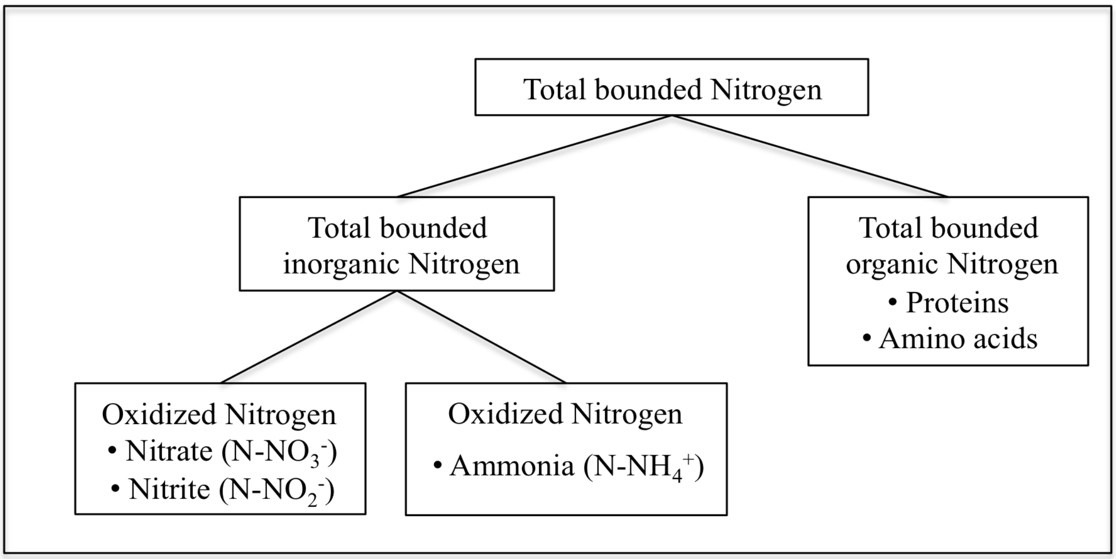

Fig. 5. Ligated Nitrogen in Waste Water

Within the Waste Water Treatment the elimination of nitrogen is an essential element, because of its high impact on the Environment. The elimination is done through the microbiological process of nitrification and denitrification. Nitrification is the oxidation of ammonium (nitrogen valency of -3) through nitrate to nitrite (nitrogen valency of +5). Autotrophic organisms called nitrificants use the ammonium nitrogen as hydrogen-donator and dissolved carbon dioxide as carbon source.

The following reaction equation is underlying the nitrification process:

$$NH_4^+ + 1{,}5\ O_2 \longrightarrow NO_2^- + 2\ H^+ + H_2O + 230\ kJ \qquad \text{Nitritation}$$

$$NO_2^- + 0{,}5\ O_2 \longrightarrow NO_3^- + 75\ kJ \qquad \text{Nitratation}$$

$$NH_4^+ + 2\ O_2 \longrightarrow NO_3^- + 2\ H^+ + H_2O + 305\ kJ \qquad \text{Nitrification}$$

The denitrification is a reduction process and can be seen as the inversive process of the nitrification. The significant difference is that the reduction process does not take place at the stage of ammonium but at the stage of elemental nitrogen. This way, the unwanted nutrient nitrogen in the treated waste water is eliminated by being released into the atmosphere as a gas.

$$2\ NO_3^- + H_2O \longrightarrow N_2 + 2{,}5\ O_2 + 2\ OH^- \qquad \text{Denitrification}$$

Under anoxic conditions, certain heterotrophic organisms such as *pseudomonas* and *microoccus* are able to use the bonded oxygen of nitrate and/or nitrite for the decomposition of organic compounds. In this case both compounds are taking over the role of the molecular oxygen as hydrogen-donator.

Phosphorus [15] [16]

Phosphorus is an essential nutrient for the metabolic reaction in the cells of organism. The element phosphorus can be found in the inorganic and organic ligated state. Substances containing phosphorus can be dissolved, polymer chained and particulate. Most of the phosphorus is inorganic and dissolved as orthophosphate (PO_4^{3-}). Orthophosphates are the salts of phosphoric acids (H_3PO_4) and can be divided into three groups:

Primary orthophosphate:	NaH_2PO_4 (Sodium dihydrogen phosphate)
Secondary orthophosphate:	Na_2HPO_4 (Disodium hydrogen phosphate)
Tertiary orthophosphate:	Na_3PO_4 (Trisodium phosphate)

Orthophosphate is the only form available for living organisms but otherwise ligated phosphorus can be transformed into orthophosphate. Therefore total phophorus is generally measured in addition to orthophosphate. Digestion is necessary for measurement, where all polymer phosphates and organic phosphates are converted into orthophosphates which can be then again be measured with the same analytical method.

Total phosphorus is composed of all inorganic and organic phosphorus compounds and provides an estimate of the amount of potentially available phosphorus

4.2.2 Physical Parameters

Temperature [17]

As already shown, many parameters are influenced by temperature (cf. conductivity, dissolved oxygen) and the temperature is needed for a correct evaluation and in order to get comparable results when a reference temperature is used.

As for the treatment in WWTP temperature is an even more important factor since the biological decomposition of the aerobic and anaerobic treatment depends highly on temperature. If the temperature is very high, the construction material of the sewerage system can be damaged.

Almost all found ammonia and nitrite oxidazing organism are mesophil and have their optimum temperature sitting between 25 ºC und 30 ºC. The optimum temperature for activated sludge in WWTP that can be found in literature, lies between about 25-35 ºC [16]. Nitrification will slow down at about 12 ºC and the bacteria growth will stop at below 8 ºC.

pH [18]

pH is the measurement of the activity of hydrogen-ions (H^+) in a liquid solution. It is an important parameter for the efficiency of the treatment process in a WWTP, because the biological as well as the chemical treatment are very sensitive to changes of the pH. The pH is defined as the negative logarithm to the base 10 of the hydrogen-ion activity in mol/L. It ranges in from 0 to 14 where pH 7 is the value for neutral water. At the value of pH 7 the activity of hydrogen-ions c_p equals 10^{-7}.

The change of pH is not only governed by what is added to it but also by the buffer capacity of the liquid. In Waste Water Treatment, the term acid capacity or alkalinity has been established even though acid capacity is normally used for waters with little or no buffering substances. It is defined as the specific amount of chloric acid (HCl) that can be added to the waste water until the pH of 4.3 is reached ($K_{S\,4.3}$). Acid capacity indicates the presence of alcalinic substances such as phosphate, ammonia, sulphide-ions, organic substances, carbonates and bicarbonates.

For the efficiency of the nitrification within the Waste Water Treatment, the pH and an adequate acid capacity is of great importance. During the process of nitrification, nitric acid is formed. This acid must be neutralized by the waste water's acid buffer system as soon as it is formed. It must be ensured that the ratio of nitrogen to acid capacity is sufficient to prevent a drop of the pH value to below 4 during the nitrification stage.

Table 5. Dependency of the Nitrification Process on pH [18]

Waste water values in aeration tank	Example 1	Example 2	Example 3
pH	6.4	6.6	7.0
Temperature [ºC]	8	8	8
Oxygen content in aeration tank [mg/L]	1	2	1
Total nitrogen in inflow to aeration tank [mg/L]	40	40	40
Ammonium ($N\text{-}NH_4^+$) in outflow [mg/L]	12.9	5.2	1.2

Conductivity [19]

In waste water the conductivity is used as a sum parameter to determine the concentration of ions. It depends on the concentration of substances in the water, the valence of the kations and anions and their movement which again depends on the temperature. Therefore the measurement of conductivity is normed to be measured at, respectively determined by using a compensation curve for either 20 ºC or 25 ºC.

Conductivity provides a conclusion about the total content of dissolved salts. High conductivity or a significant increase indicates the extent of pollution within the water. Most common salts that can be found in water are sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^+), potassium (K^+) as well as chloride (Cl^-), sulfide (S^{2-}), hydrogen carbonate (HCO_3^-), carbonate ($CO_3^{\ 2-}$) and nitrate (NO_3^-).

Redox Potential [20]

The redox potential describes the ratio of oxidated to deoxidated substances. An energy transfer takes place where oxidizing substances act as electron donators and deoxidizing ones as electron acceptors. This results in a difference in voltage which is a measure of free enthalpie. The redox potential indicates the electro-chemical condition in a liquid. In waste water the potential can vary between a highly oxidizing ambience of +800 mV and a highly deoxidizing milieu of -300 mV. In oxygen rich water the potential is high and many oxidizing bonds such as iron and manganese oxide, nitrate and sulfate are found. A low potential points to an absence of oxygen as well as deoxidizing bonds such as iron (II), manganese (II) and organic substances.

Most substances that are found in the intake of WWTP’s are in their deoxidized form. They will be oxidized through the aerobic decomposition which then leads to an increase of the redox potential. After the aeriated phase of the biological treatment the redox potential decreases because of incoming waste water and even more because of the beginning denitrification. During the anaerobic phase of denitrification the oxidizing substance nitrate is decomposed.

The measurement of redox potential is used to regulate the process of nitrification and can as well be used for the regulation of phosphorus elimination.

5 Analytical Methods and Monitoring Results

This section details the principle of operation and clarifies the analytical methods. After the general outline, the principle and procedure of each method is described. Furthermore, within the parameter, the results of the monitoring activities of January and February 2012 are presented.

The sampling took place between one and two times per week. Each sample contained 2 to 3 Litre of water in a plastic canister. Starting at 9.00 am with an interval of two hours, four samples were taken at two to four different locations. The sample name is chosen accordingly and contains the location and time. For example the sample TN1_N2P1_1100 is taken in Tra Noc 1 at node 2 point 1 at 11.00 am. For the experimental part other information was added:

_F	filtered
_uF	unfiltered
_H_2SO_4	approx. 0.5 % sulphuric acid was added after sample taking
_fr	sample was kept in a freezer after sample taking

Experience showed that owing to capacity insufficiency more than one time per week and ten to twelve samples each time, were not manageable.

5.1 Materials

The following chemicals were used for the photometric and ISE determination:

Table 6. List of Chemicals

Name	Molecular Formula	CAS-No.	Distributer
2,6-dimethyl phenol	C_8H_{1O}	576-26-1	-
Aluminium potassium sulfate dodecahydrate	$AlH_{24}KO_{20}S_2$	7784-24-9	Merck KGaA
Ammonium chloride	NH_4Cl	89485-85-8	Merck KGaA
Ammonium heptamolybdate tetrahydrate	$(NH_4)_6Mo_7O_{24}$	12027-67-7	-
Disodium pentacyano nitrosyl ferrate	$C_5FeN_6 * 2 Na$	14402-89-2	-
Ethylenediamine tetra acetic acid (EDTA)	$C_{10}H_{16}N_2O_8$	94108-75-5	-
Hydrochloride fumeric 37 %	HCl	9004-54-0	Merck KGaA
L(+)-ascorbic acid	$C_6H_8O_6$	89924-69-6	-
N-(1-naphthyl) ethylenediamine dihydrochloride	$C_{12}H_{16}Cl_2N_2$	551-09-7	Merck KGaA
Ortho-Phosphoric acid 85%	H_3PO_4	9066-91-5	Merck KGaA
Potassium antimony (III) oxide tartrate trihydrate	$K_2(SbO)_2 C_8H_4O_{10}$	28300-74-5	Merck KGaA
Potassium dihydrogen phosphate	KH_2PO_4	7778-77-0	Merck KgaA
Potassium nitrate	KNO_3	96193-83-8	Merck KgaA
Sodium dichlorisocyanurate	$C_3Cl_2N_3NaO_3$	2893-78-9	Merck KGaA
Sodium hydroxide	$NaOH$	13010-73-2	-
Sodium nitrite	$NaNO_2$	82998-40-1	Merck KGaA
Sodium peroxodisulfate	$Na_2S_2O_8$	7775-39-5	-
Sodium salicylate	$C_7H_5NaO_3$	94413-51-1	Merck KGaA
Sulfanilamide	$C_6H_8N2O_2S$	63-74-1	Merck KGaA
Sulphuric acid	H_2SO_4	7664-93-9	-
Trisodium citrate	$C_6H_5Na_3O_7$	8055-55-8	Merck KGaA

5.2 Tube Tests

The following materials were used:

Table 7. List of Materials

Parameter	Test Identifier	Measurement Range	Distributer
Ammonium	985 005	1.0 – 40.0 mg/L NH_4-N	Machery-Nagel GmbH & Co. KG
Nitrate	985-064	0.3 – 22.0 mg/L NO_3-N	Machery-Nagel GmbH & Co. KG
Nitrite	985-069	0.1 – 4.0 mg/L NO_2-N	Machery-Nagel GmbH & Co. KG
Orthophosphate	985-080	0.30 – 15.00 mg/L P	Machery-Nagel GmbH & Co. KG
Total Nitrogen	985-092	3.0 – 60.0 mg/L N	Machery-Nagel GmbH & Co. KG
Total Phosphorus	985-080	0.30 – 15.00 mg/L P	Machery-Nagel GmbH & Co. KG

5.3 Devices and Software

The following devices and electrodes were used for the photometric, ISE and suspended solids determination:

Table 8. List of Devices and Software

Apparat	Model	Manufacturer
Photometer	Nanocolor 500 D	Machery-Nagel GmbH & Co. KG
pH/Ionmeter	867 pH Module	Metrohm GmbH
Electronic Scale	ABS 120-4	KERN & Sohn GmbH
Heating Block	Nanocolor Vario compact	Machery-Nagel GmbH & Co. KG
Magnetic Stirrer	R 1000	Carl Roth GmbH & Co. KG
Cabinet Drier	UFB 400	Memmert GmbH & Co. KG
ISE Software	tiamo^{TM}	Metrohm GmbH
ISE NH_3	-	Metrohm GmbH
ISE NO_3^-	-	Metrohm GmbH

5.4 General on Measurement Proceeding

5.4.1 Preparation Materials and Devices

All beaker, glass cuvettes, containers, volumetric flasks and other materials used, were cleaned by hand using detergent specifically for laboratory equipment and tap water. Afterwards everything was rinsed properly with purified water three times and left on a rack to dry or put inside an incubator at about 80 ºC.

The pipettes and the electrodes for pH, DO, redox potential and conductivity were checked on a regular bases and calibrated if necessary and possible. The photometer used for all measurements was a single beam filter photometer with an silicone photo element. The wavelength ranges from 340 to 860 nm and the samples were measured in round glass tubes. The photometer is designed for round glass tubes of 16 mm optical depth. Before each measurement series, a blank value was measured and automatically subtracted by the photometer software.

All reagents, stock and standard solutions have been stored in a refrigerator at about 6-8 ºC. They were stored in glass bottles, and where necessary owing to light sensitivity in brown bottles.

With every measurement series a blank solution (purified water) and a standard solution was prepared and measured. The reagents and the standards respectively the stock solutions were renewed when the measuring results weren't plausible anymore (cf. 4.3). For example if:

- the findings in the blank solution were too high
- within the recovery rate of the standard solution a deviation of more than 10 %
- the results between the nanocolor tube test (used as reference) and the measured result significantly differed.

A new calibration was made every time the reagents and solutions were newly prepared.

5.4.2 Preparation of Sample, Reagents and Solutions

After sample taking, they were stored in a 2 L PE canister and brought back to the laboratory. About 200 ml was then immediately filtered with a 45 µl membrane filter. The filtered samples were filled into another PE or glass bottle and stored in a refrigerator at about 6-8 ºC. The samples in the 2 L canister were brought to an external laboratory at the University of Can Tho to measure BOD_5. The reagents and stock solutions were all prepared by filling the designated amount of the specific chemical into a volumetric flasks. The flask was filled up to three-fourth and shaken carefully until the solids were dissolved. The volumetric flask was then filled up to the calibration mark. If an acidic solution e.g. sulphuric acid needed to be added, it was added last.

Most of the stock solutions had a concentration of 1,000 mg/L. The needed standard solutions range between 0,01 and 20 mg/L. To prepare the standard solution series, the stock solution was diluted in steps of the factor 10. 10 ml stock solution were pipetted into a 100 ml volumetric flask and filled to the calibration mark.

5.4.3 Calibration

The obtained standard solution was used to prepare the standard solution series for the calibration. The measurement of each standard solution is conducted the same way samples were measured as described under chapter 5 for each method.

After the measurement the calibration curve was created. The measured value of the solution was plotted on the y-axis and mass concentration in milligram per Litre was plotted on the x-axis. The blank value was then calculated and equivalents the y-axis intercept. The equation describing the regression curve as well as the coefficient of determination (R^2) were determined. Only calibration curves with a $R^2 > 0.995$ were used.

5.4.4 Evaluation of Concentration

The calibration curve for the photometric methods show a linear behaviour in the calibrated range. The equation received from the linear regression is in the form of:

$$A = m \cdot c + b \tag{3}$$

The equation converts for the concentration c in mg/L, including the dilution factor to:

$$c = \frac{A - b}{m} \cdot d \tag{4}$$

A	measured extinction
b	y-axis intercept, extinction of calculated blank solution value
m	accent of the calibration curve, in milligram per Litre (mg/L)
d	dilution factor

5.5 Method Principles and Presentation of Results

5.5.1 Method Description - Ammonium [21] [22]

The method for determining ammonium was developed according to the DIN 38406-5: German standard methods for examination of water – Determination of Ammonium, and it was adjusted to meet the projects specific occurrences. The proceeding of preparation and measurement is described as follows:

Principle of Method

Ammonia reacts in water to ammonium ions:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

The equilibrium of this reaction is determined by the pH of the solution. In acidic solutions ammonia almost completely reacts to ammonia-ions. At a pH value of 9.2 the ratio is 1:1. The equilibrium can be calculated as follows:

$$\log \frac{a\left(NH_4^+\right)}{a\left(NH_3\right)} = \log K - pH \qquad (5)$$

The equilibrium constant K is also depending on the temperature, e.g. for the temperature of 25 ºC, in Litreature can be found the value 4.78 for the negative log(K).

The ammonia-ions react at a pH of about 12.6 with hypochlorite-ions to monochloramine

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$$

In the next step the monochloramine reacts with thymol to 2 N-chloro-2-isopropyl-5-methylchinon-monoimine:

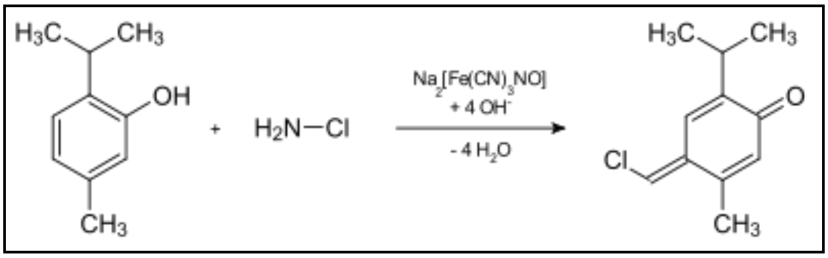

Fig. 6. Monochloramine reacts with Thymol to 2 N-chloro-2-isopropyl-5-methylchinon-monoimine [23]

In the last step N-chloro-2-isopropyl-5-methylchinon-monoimine reacts with another thymol molecule to indephenol which in an alcalinic medium will show a blue coloration.

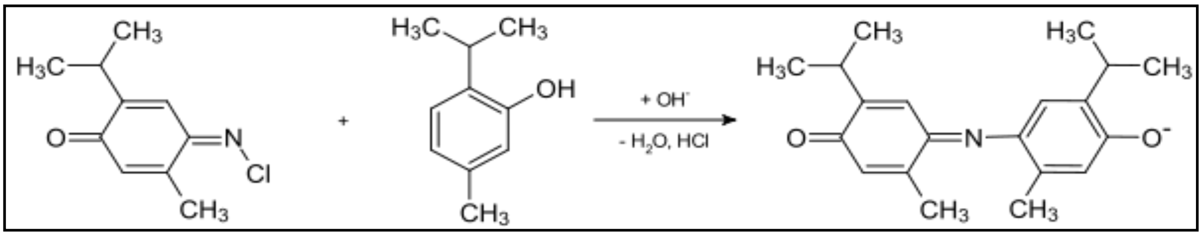

Fig. 7. N-chloro-2-isopropyl-5-methylchinon-monoimine reacts to Indephenol [23]

Preparation Reagents and Solutions

- Buffer solution: 32.5 g trisodium citrate, 32.5 g sodium salicylate and 0.242 g disodium pentacyano nitrosyl ferrate dissolved in 250 ml
- Reagent solution: 3.2 g tri sodium hydroxide dissolved in 50 ml by stirring and warming up. At room temperature, 0.2 g sodium dichloroisocyanurate was added and filled up to 100 ml
- Ammonium stock solution (c = 1,000 mg/L): 1.91 g ammonium chloride dissolved in 500 ml

Calibration

5 ml of the following standard series was prepared: 0.5, 1.0, 2.0, 5.0 and 10.0 mg ($N\text{-}NH_4^+$)/L. The standard series has been prepared and measured just as the samples, using standard solution instead of sample. The calibration curve was created as previously described under 5.4.3.

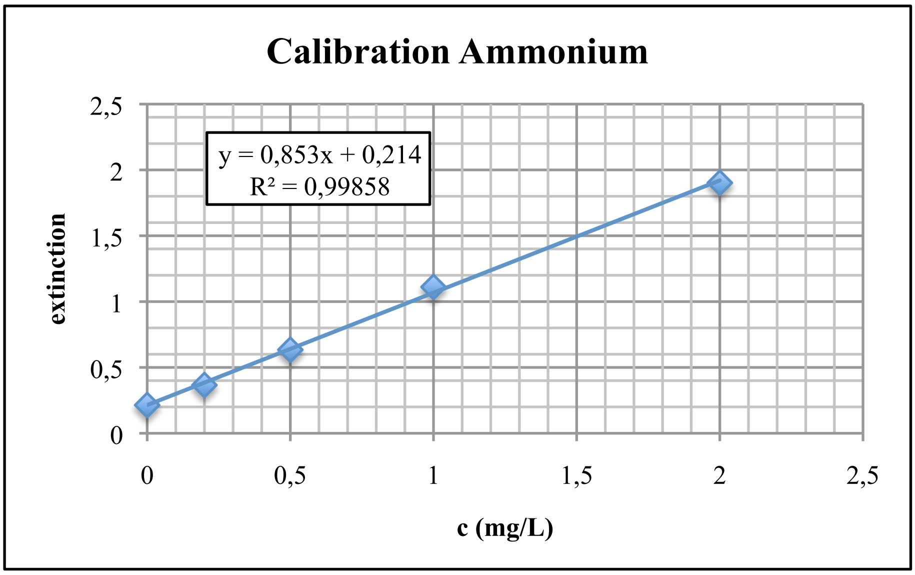

Fig. 8. Calibration Curve for Ammonium, 19.12.2011

Preparation and Measurement of Ammonium

5 ml of sample solution was warmed up to room temperature and pipetted into a round glass tube. If a concentration outside the calibrated range was expected, a corresponding dilution of the sample with pure water was necessary. To the content of the round glass tube, 0.5 ml of buffer solution and 0.5 ml of reagent solution were added and mixed properly. The extinction was measured with the photometer after 15 minutes at a wavelength of 690 nm.

5.5.2 Ammonium Results of Monitoring Activity

In the first week of January samples were taken twice at node 7 point 2, node 8 point 3 and at three different outlets (OL) in Tra Noc 1.

Table 9. Ammonium Results, Locations N7P2, N8P3 and Outlet N6OL1, N4OL7 and N4OL6 in Tra Noc 1

Sample	Dilution	Results 03.01.2012 c [mg/L]	Results 05.01.2012 c [mg/L]
Standard 1 mg/L	1	1.01	0.94
TN1_N7P2_0900	20	20.30	22.09
TN1_N7P2_1100	20	24.20	9.99
TN1_N7P2_1300	20	14.87	22.23
TN1_N7P2_1500	20	24.45	19.30
TN1_N8P3_0900	20	27.55	16.04
TN1_N8P3_1100	20	18.97	21.03
TN1_N8P3_1300	20	19.34	42.61*
TN1_N8P3_1500	20	18.76	22.06
TN1_N6OL1_1100	20	32.12	34.77
TN1_N6OL1_1500	20	22.44	16.83
TN1_N4OL7_1100	5	2.47	1.17
TN1_N4OL7_1500	5	2.91	1.33
TN1_N4OL6_1100	20	8.30	14.56
TN1_N4OL6_1500	20	10.43	9.12

* dilution factor 50

During the course of the day the ammonium concentration was rather stable (table 9.). A comparison between the two days shows similar results for all locations. A single result, N8P3_1300 was slightly noticeable because of it's significantly higher value. This sample of January 5th was measured two times. The first time it was diluted 1:20 and the extinction was just out of the calibrated range. This indicates a concentration between 40 and 45 mg/L which complies with the received value of 42.6 mg/L.

Table 10. Ammonium Results, Locations N1P1, N2P1 and N2P2 in Tra Noc 1

Sample	Dilution	Results 10.01.2012 c [mg/L]	Dilution	Results 20.02.2012 c [mg/L]
Standard 1 mg/L	1	1.00	1	1.12
TN1_N1P1_0900	20	9.61	10	8.42
TN1_N1P1_1100	20	8.23	10	13.24
TN1_N1P1_1300	20	5.74	10	19.40
TN1_N1P1_1500	20	8.96	10	< 2
TN1_N2P1_1100	20	6.89	10	16.78
TN1_N2P1_1500	20	6.78	10	19.33
TN1_N2P2_1100	20	2.60	50	31.54
TN1_N2P2_1500	20	5.46	10	7.21

The sampling dates of the locations N1P2, N2P2 and N2P2 in Tra Noc 1 (table 10.) were about six weeks apart. Here it becomes apparent that the concentrations of the analytes are underlying grave changes not only over the course of a day but also over time. The ammonium concentration for N2P1 on the second date, 20th of February, is between 2.4 and 2.9 times higher than what was previously on the 10th of January recorded. For sample N1P1 the course of concentration is very different between the two days. In January the values stay constant whereas in February the value reaches a peak of 19.40 mg/L around noon and subsequently decreases to below 2 mg/L in the afternoon. It is obvious that the production mode of the enterprises can't be assumed to be constant and therefore predictable.

Table 11. Ammonium Results, Locations N3P3, N8P1 and N8P2 in Tra Noc 1;
Location N5P1 in Tra Noc 2

Sample	Dilution	Results 12.01.2012 c [mg/L]	Dilution	Results 13.02.2012 c [mg/L]
Standard 1 mg/L	1	1.02	1	1.31
TN1_N3P3_0900	5	2.36	1	0.27
TN1_N3P3_1100	50	50.59	1	1.95*
TN1_N3P3_1300	50	44.08	20	3.47
TN1_N3P3_1500	50	53.58	20	3.54
TN1_N8P1_1100	5	3.60	1	1.43
TN1_N8P1_1500	5	3.51	1	4.98
TN1_N8P2_1100	20	10.41	-	-
TN1_N8P2_1500	20	7.88	-	-
TN2_N5P1_1100	-	-	50	(80.9)
TN2_N5P1_1500	-	-	50	52.2

* tube test: 2.1 mg/L

The samples taken at locations N3P3 and N8P1 (table 11.) were taken one month apart. Additionally, on both dates in each case, one other location was visited. On first sight the values from locations N3P3 at 11.00, 13.00 and 15.00 and the values of location N5P1 are noticeable, because of their much higher values. Most of the ammonium concentrations in Tra Noc that were detected so far range between 1.0 and 15.0 mg/L. A few times the concentration came up to 30 mg/L, but anything above seemed unusual. Therefore the results of location N3P3 and N5P5 were re-evaluated.

The three ammonium values from January 12th for location N3P3 were measured 4 days after sample taking with a dilution of 1:20. Those first measurement results were outside the calibration range but still indicated that the concentrations probably lie closely in the range of the concentrations that were determined with the dilution of 1:50.

The value 80.9 mg/L of the sample N5P1_1100 is higher than the total nitrogen (76.32 mg/L) concentration which means either the ammonium value is too high or the total nitrogen is too low, since the total nitrogen is the accumulation of all nitrogen compounds contained in the sample. After re-evaluation, the total nitrogen result was assumed accurate which means the ammonium value was false. It is suspected that a measurement error occurred (also cf. 6.3.1 Ammonium Results of ISE Measurement).

The other results appear conclusive, except for the too high standard value of 1.31 mg/L. Since the tube test result which was used as a reference confirms the accuracy of the measurement, the results were used and the standard solution was renewed.

Table 12. Ammonium Results; Outlet N7OL1 in Tra Noc 1;
Location N4P3 and N4P4 in Tra Noc 2

Sample	Dilution	Results 07.02.2012 c [mg/L]
Standard 1 mg/L	1	1.32
TN1_N7OL1_0900	25	30.19
TN1_N7OL1_1100	25	17.91
TN1_N7OL1_1300	25	27.49
TN1_N7OL1_1500	25	29.98
TN2_N4P3_1100	25	21.80
TN2_N4P3_1500	25	22.0
TN2_N4P4_1100	10	3.3*
TN2_N4P4_1500	10	5.70

* tube test: 2.9 mg/L

The outlet 1 in Tra Noc 1 and the locations N4P3 and N4P4 in Tra Noc were sampled on January 7th (table 12.). The results appear very stable and conclusive, except for the too high standard value of 1.32 mg/L for a 1.0 mg/L standard. Since the tube test result, used as a reference confirms the accuracy of the measurement, the results were used.

5.5.3 Method Description - Nitrate [21] [24]

The method for determining nitrate was developed according to the DIN 38405-9: German standard methods for examination of water – Determination of Nitrate, and was adjusted to meet the projects specific occurrences. In the following, the procedure of preparation and measurement are described.

Principle of Method

If a sulphuric acid and phosphoric acid solution with 2,6-dimethyl phenol is added to a sample, the nitrate-ions react to 4-nitro-2,6-dimethyl phenol. The extinction of this complex can now be photometricly measured to determine the present nitrate.

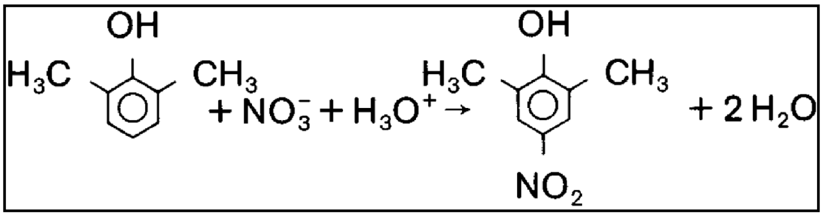

Fig. 9. Reaction Equation of the Nitration of 2,6-dimethyl phenol [24]

Chloride can interfere severely with this method and lower the recovery rate of nitrate down to approx. 60 %. It's coactive necessary to ensure that chloride is not present in the sample.

Reagents and Solutions

- Sulphuric acid-phosphoric acid solution: 50 ml sulphuric acid, 98 % and 40 ml phosphoric acid, 85 % were carefully mixed together.
- 2,6-dimethyl phenol solution: 0.1 g of 2,6-dimethyl phenol dissolved in 100 ml
- Nitrate stock solution (c = 1,000 mg/L): 0.73 g potassium nitrate dissolved in 1 Litre

Calibration

To calibrate, 5 ml of the following standard series was prepared: 0.5, 2.0, 5.0, 10.0, 15.0 and 20.0 mg ($N-NO_3^-$)/L. The standard series was prepared and measured as described below using standard, instead of sample solution. The calibration curve was created as described under 5.4.3.

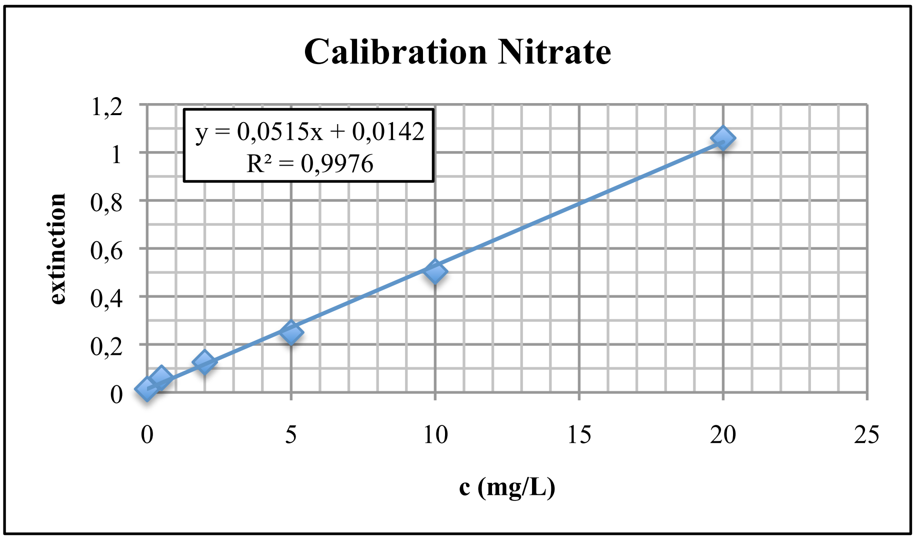

Fig. 10. Calibration Curve Nitrate, 20.12.2011

Preparation and Measurement of Nitrate

0.5 ml of sample solution warmed up to room temperature were pipette into a round glass tube with 5 ml of the acidic solution. If a concentration outside the calibrated range was expected, a corresponding dilution of the sample with pure water was necessary. To the content of the round glass tube 0.5 ml of 2,6 dimethyl phenole solution was added and mixed. The extinction was measured with the photometer after 10 minutes at a wavelength of 365 nm.

5.5.4 Nitrate Results of Monitoring Activity

In the first week of January samples were taken twice at node 7 point 2, node 8 point 3 and at three different outlets (OL) in Tra Noc 1.

Table 13. Nitrate Results, Locations N7P2, N8P3 and Outlet N6OL1, N4OL7 and N4OL6 in Tra Noc 1

Sample	Dilution	Results 03.01.2012 c [mg/L]	Results 05.01.2012 c [mg/L]
Standard 10 mg/L	1	10.00	9.83
TN1_N7P2_0900	1	1.92	1.38
TN1_N7P2_1100	1	1.80	1.39
TN1_N7P2_1300	1	2.23	4.39
TN1_N7P2_1500	1	2.23	0.87
TN1_N8P3_0900	1	1.05	2.76
TN1_N8P3_1100	1	10.35	3.38
TN1_N8P3_1300	1	9.07	2.37
TN1_N8P3_1500	1	8.93	2.35
TN1_N6OL1_1100	1	1.12	1.10
TN1_N6OL1_1500	1	1.24	1.03
TN1_N4OL7_1100	1	< 0.5	1.34
TN1_N4OL7_1500	1	< 0.5	1.03
TN1_N4OL6_1100	1	2.78	4.76
TN1_N4OL6_1500	1	1.88	0.95

According to table 13 and analogical to ammonium the nitrate concentration was quite constant during the course of the day for each location.

The comparison between the two days show also similar results, except at location N8P3. Here, at the 3rd of January, the value increases after 9.00 am from 1.1 mg/L to a maximum of 10.4 mg/L. Two days later on the same location the concentration stays in lower range between 2.4 and 3.4 mg/L.

Table 14. Nitrate Results, Location N1P1, N2P1 and N2P2 in Tra Noc 1

Sample	Dilution	Results 10.01.2012 c [mg/L]	Dilution	Results 20.02.2012 c [mg/L]
Standard 10mg/L	1	10.02	1	10.61
TN1_N1P1_0900	1	1.03	1	1.96
TN1_N1P1_1100	1	0.87	1	1.22
TN1_N1P1_1300	1	0.95	1	2.74
TN1_N1P1_1500	1	0.77	2	1.70
TN1_N2P1_1100	5	19.90	1	11.19
TN1_N2P1_1500	5	26.31	2	7.18
TN1_N2P2_1100	1	0.83	1	13.09
TN1_N2P2_1500	1	1.24	2	3.80

The sampling dates of the three locations in table 14 were about six weeks apart. At N1P1 the concentration of nitrate appears to be generally low (between 0.87 and 2.74 mg/L) and unlike ammonium, there isn't a significant difference between the two sampling dates. However, what is different, is the unusually high concentration at location N2P1 (up to 26.31 mg/L) on the 10th of January. It is much higher than the ammonium concentration (6.9 and 6.8 mg/L) on this location. So far ammonium had always been higher than nitrate and nitrite. Therefore, the results were re-evaluated. The samples N2P1 of January 10th were first measured undiluted and the concentration was above the calibration range. The extinctions still indicate a concentration between 20 and 25 mg/L which confirms the obtained results.

Table 15. Nitrate Results, Locations N3P3, N8P1 and N8P2 in Tra Noc 1;
Location N5P1 in Tra Noc 2

Sample	Dilution	Results 1 12.01.2012 c [mg/L]	Dilution	Results 13.02.2012 c [mg/L]
Standard 10 mg/L	1	9.42	1	9.30
TN1_N3P3_0900	1	< 0.5	1	0.95
TN1_N3P3_1100	1	< 0.5	1	1.71
TN1_N3P3_1300	1	< 0.5	2	22.57
TN1_N3P3_1500	1	< 0.5	2	15.73
TN1_N8P1_1100	1	6.04	2	26.49
TN1_N8P1_1500	1	15.37	2	13.40
TN1_N8P2_1100	1	3.84	-	-
TN1_N8P2_1500	1	< 0.5	-	-
TN2_N5P1_1100	-	-	1	1.42
TN2_N5P1_1500	-	-	1	< 0.5

The measurements done one month apart at the locations N3P3 and N8P1, table 15 show again how different the concentrations and composition of the waste water can be. All results are conclusive and appear accurate.

Table 16. Nitrate Results; Outlet N7OL1 in Tra Noc 1;
Locations N4P3 and N4P4 in Tra Noc 2

Sample	Dilution	Results 07.02.2012 c [mg/L]
Standard 10 mg/L	1	9.03
TN1_N7OL1_0900	1	5.46
TN1_N7OL1_1100	1	6.68
TN1_N7OL1_1300	1	6.23
TN1_N7OL1_1500	1	7.30
TN2_N4P3_1100	1	< 0.5
TN2_N4P3_1500	1	1.73
TN2_N4P4_1100	1	6.14
TN2_N4P5_1500	1	7.65

The outlet 1 in Tra Noc 1 and the locations N4P3 and N4P4 in Tra Noc were so far only sampled once, on January 7th (table 16.). The results appear very stable over the course of the day and they are conclusive.

5.5.5 Method Description - Nitrite [20 24]

The method for determining nitrite has been developed according to the DIN EN 26777: German standard methods for examination of water - Determination of Nitrite; was adjusted to meet the projects specific occurrences. In the following, the procedure of preparation and measurement are described.

Principle of Method

The nitrite in the sample reacts in an acidic solution (pH 1.9) with 4-amino benzene sulfonamide and in the presence of orthophosphoric acid. It forms a diazonium salt which becomes a light pink colour when it reacts with the added N-(1-naphthyl) ethylenediamine dihydrochloride.

The result can be influenced if interfering substances such as chloramine, chlorine, thiosulfate or iron (III)-ions are present.

Reagents and solutions

- Sulfanilamide solution: 0.5 g sulfanilamide dissolved in 35 ml of hydrochloricd fumeric acid, 37 % (HCl) solution (5 ml HCl + 30 ml distilled water) and added up to 50 ml
- N-naphtyl ethylendiamine solution: 0.5 g N-(1-naphtyl)ethylendiamine dichloride dissolved in 500 ml
- Nitrite stock solution (c = 100 mg/L): 0.5 g sodium nitrite dissolved in 1 Litre

Calibration

For calibration 5 ml of the following standard series was prepared: 0.01, 0.05, 0,10 and 0.20 mg (N-NO_2^-)/L. The standard series has been prepared and measured as described below using standard instead of sample solution.

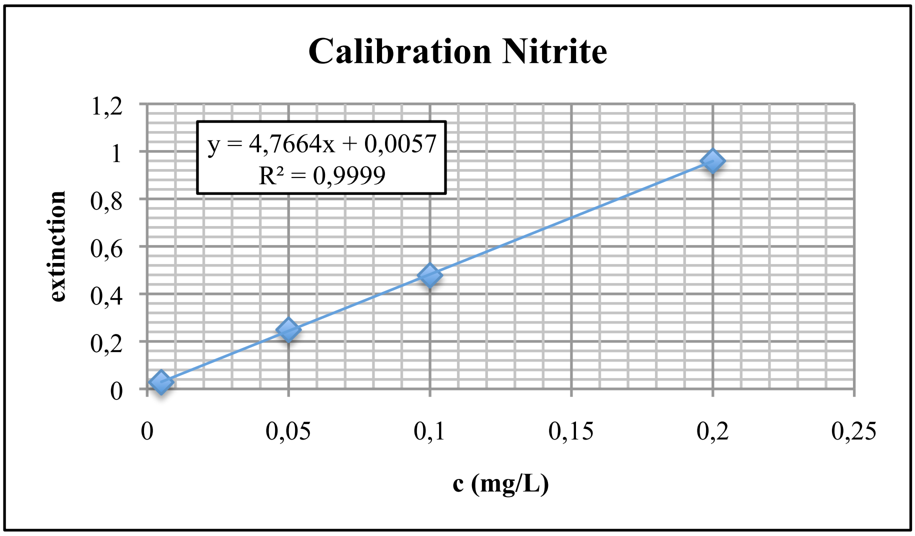

Fig. 11. Calibration Curve Nitrite, 02.11.2011

Preparation and Measurement of Nitrite

5 ml of sample solution warmed up to room temperature were pipette into a round glass tube. If a concentration outside the calibrated range was expected, a corresponding dilution of the sample with pure water was necessary. 0.2 ml sulfanilamide solution and 0.2 ml N-naphtyl-ethylendiamine solution were added and mixed. The extinction of each solution was measured with the photometer after 15 minutes at a wavelength of 540 nm.

5.5.6 Nitrite Results of Monitoring Activity

Table 17. Nitrite Results; Monitoring February 2012

Sample	Dilution	Results 07.02.2012 c [mg/L]	Results 13.02.2012 c [mg/L]	Results 20.02.2012 c [mg/L]
Standard 0.1 mg/L	1	0.10	0.11	0.11
TN1_N7OL1_0900	10	0.31	-	-
TN1_N7OL1_1100	20	1.26	-	-
TN1_N7OL1_1300	20	0.59	-	-
TN1_N7OL1_1500	20	0.84	-	-
TN2_N4P3_1100	1	0.02	-	-
TN2_N4P3_1500	1	0.02	-	-
TN2_N4P4_1100	10	0.30	-	-
TN2_N4P5_1500	10	0.33	-	-
TN1_N3P3_0900	1	-	0.11	-
TN1_N3P3_1100	1	-	0.07	-
TN1_N3P3_1300	20	-	0.89	-
TN1_N3P3_1500	20	-	0.90	-
TN1_N8P1_1100	10	-	0.43	-
TN1_N8P1_1500	10	-	0.39	-
TN1_N1P1_0900	10	-	-	0.36
TN1_N1P1_1100	10	-	-	0.11
TN1_N1P1_1300	10	-	-	0.16
TN1_N1P1_1500	1	-	-	0.16
TN1_N2P1_1100	20	-	-	1.16
TN1_N2P1_1500	20	-	-	1.26
TN1_N2P2_1100	10	-	-	0.30
TN1_N2P2_1500	5	-	-	0.26
TN2_N5P1_1100	1	-	-	0.01
TN2_N5P1_1500	10	-	-	0.16

The parameter nitrite could not be measured in January owing to logistical difficulties i.e. the ordering of missing chemicals. Fortunately the nitrite results of February (table 17.) as well as the results of former monitoring activities in 2011 were constant and always very low, between 0.01 and 1.26 mg/L, as would be suspected for this parameter. The concentrations were mostly significantly below 1 mg/L, only three results were between 1.1 and 1.3 mg/L. Without any exception the results were plausible and appear fully reliable. It is suspected that it can be taken for granted that the concentration of the samples from January are all below 1.5 mg/L as well.

5.5.7 Method Description - Total Nitrogen [21]

The total nitrogen measurement follows the same principle as the nitrate measurement and the same calibration as for nitrate is used. Before the measurement of total nitrogen a digestion of the sample is necessary where all the nitrogen is dissolved.

Reagent for digestion

- Sodium hydroxide solution (1.5 Mol): 30 g of sodium hydroxide dissolved in 500 ml

Preparation and Measurement of Total Nitrogen

5 ml of sample solution warmed up to room temperature were pipette into a round glass tube. 0.5 ml of sodium hydroxide and approximately 50 mg of sodium peroxodisulfate were added and mixed. The round glass tube was then headed up for one hour at 100 ºC. After the glass tube had cooled down to room temperature (about 30 minutes) the measurement proceeded as described for nitrate (cf. 5.5.3).

5.5.8 Total Nitrogen Results of Monitoring Activity

Table 18. Total Nitrogen Results, Locations N7P2, N8P3 and Outlet N6OL1, N4OL7 and N4OL6 in Tra Noc 1

Sample	Dilution	Results 03.01.2012 c [mg/L]	Dilution	Results 05.01.2012 c [mg/L]
Standard 10 mg/L	1	10.00	1	9.83
TN1_N7P2_0900	5	45.93	5	50.01
TN1_N7P2_1100	5	75.37	5	69.54
TN1_N7P2_1300	5	84.60	5	42.05
TN1_N7P2_1500	5	58.17	5	59.05
TN1_N8P3_0900	5	73.62	5	57.01
TN1_N8P3_1100	10	122.56	5	66.04
TN1_N8P3_1300	10	103.72	5	73.72
TN1_N8P3_1500	5	66.24	5	37.00
TN1_N6OL1_1100	1	(4.54)	12.5	125.76
TN1_N6OL1_1500	5	97.81	12.5	112.76
TN1_N4OL7_1100	1	8.84	5	68.76
TN1_N4OL7_1500	1	6.04	5	85.37
TN1_N4OL6_1100	1	10.80	5	40.98
TN1_N4OL6_1500	1	16.41	5	52.54

In the first week of January samples were taken twice at node 7 point 2, node 8 point 3 and at three different outlets (OL) in Tra Noc 1. All results of table 18 appear plausible and conclusive except for two values. The concentration of 4.54 mg/L for sample N6OL1_1100, January 3rd, is far too low and considered a false finding. For this sample ammonium and nitrate accumulate to already more than 30 mg/L. Considering the other results taken at the same location, which were around 100 mg/L and above, the 4.54 mg/L result must be a matter of mismeasurement.

The second noticeable value for total nitrogen of 10.8 mg/L was the sample N4OL6_1100, January 3rd. Ammonium and nitrate added up to 11.08 mg/L and an unknown value for nitrite needed to be added. Presuming that the nitrite concentration was insignificantly small and that there was an uncertainty within each method of 5 – 10 % the small deviation can be explained. It is impossible to say which of the true values is a little bit higher or lower, but it can be said, that the concentrations for nitrogen at this location are within acceptable abuttals of measurement accuracy.

Table 19. Total Nitrogen Results; Locations N1P1, N2P1 and N2P2 in Tra Noc 1

Sample	Dilution	Results 10.01.2012 c [mg/L]	Dilution	Results 20.02.2012 c [mg/L]
Standard 10mg/L	1	10.02	1	10.61
TN1_N1P1_0900	1	14.94	1	11.13
TN1_N1P1_1100	1	16.14	10	21.73
TN1_N1P1_1300	1	17.95	1	(19.58)*
TN1_N1P1_1500	1	17.02	1	8.62
TN1_N2P1_1100	5	50.60	5	27.28
TN1_N2P1_1500	5	52.05	5	30.68
TN1_N2P2_1100	1	12.10	5	52.25
TN1_N2P2_1500	1	19.08	5	19.41

* out of range

The sampling dates of the three locations in Tra Noc 1 in the table above were about six weeks apart. At location N1P1 the concentrations of total nitrogen appeared conclusive over the course of the day and in a similar range between the two sampling days. For the other two locations, the analytes were obviously underlying changes again connected to changes of production activity of the enterprises. The measurement of sample N2P2_1100 on the 20th of February stands out in particular. The finding was 52.25 mg/L whereas the other samples of the same location on two different days lied between 12.10 and 19.41 mg/L. This result was re-evaluated and no reason could be found as to why the value should be false.

Table 20. Total Nitrogen Results, Locations N3P3, N8P1 and N8P2 in Tra Noc 1; Location N5P1 in Tra Noc 2

Sample	Dilution	Results 12.01.2012 c [mg/L]	Dilution	Results 13.02.2012 c [mg/L]
Standard 10mg/L	1	9.41	1	9.05
TN1_N3P3_0900	1	8.80	5	17.76
TN1_N3P3_1100	5	68.08	10	17.07
TN1_N3P3_1300	5	67.31	10	31.85
TN1_N3P3_1500	5	76.56	10	51.84
TN1_N8P1_1100	5	19.61	10	67.78
TN1_N8P1_1500	5	24.95	10	90.31
TN1_N8P2_1100	5	38.65	-	-
TN1_N8P2_1500	5	19.80	-	-
TN2_N5P1_1100	-	-	5	76.32
TN2_N5P1_1500	-	-	10	98.28

At the two locations N3P3 and N8P1 the samples were taken one month apart (table 20.). As expected the results comply with the results of the other nitrogen compounds. The indifferent values between the two days on each location mirror the unpredictable changes in the composition of waste water.

Table 21. Total Nitrogen Results; Outlet N7OL1 in Tra Noc 1; Location N4P3 and N4P4 in Tra Noc 2

Sample	Dilution	Results 07.02.2012 c [mg/L]
Standard 10 mg/L	1	9.02
TN1_N7OL1_0900	5	35.64
TN1_N7OL1_1100	5	30.68
TN1_N7OL1_1300	5	34.57
TN1_N7OL1_1500	5	40.88
TN2_N4P3_1100	5	17.96
TN2_N4P3_1500	5	22.33
TN2_N4P4_1100	5	15.24
TN2_N4P4_1500	5	15.62

The results of outlet 1 in Tra Noc 1 and the locations N4P3 and N4P4 in Tra Noc 2 sampled January 7th were very stable over the course of the day and the results could be confirmed as being reliable (table 21.).

5.5.9 Method Description - Orthophosphate and Total Phosphorus [21 26]

The methods for determining phosphorus were developed according to the DIN EN ISO 6878: German standard methods for examination of water - Determination of Phosphorus, and were adjusted to meet the projects specific occurrences. In the following, preparation and measurement procedures are described.

Principle of Method

The orthophosphate-ions react in an acidic solution with molybdate and antimony-ions and form an antimony-phosphorus molybdate-complex. This complex is reduced with ascorbic acid to a new, highly coloured molybdenum blue complex. The extinction of this complex can now be photometricly measured to determine the present orthophosphates.

Considering the equilibrium of heptamolybdate in watery solutions [27]

$$Mo_7O_{24}^{6-} + 4\ H_2O \longrightarrow 7\ MoO_4^{2-} + 8\ H^+$$

the following equation arises:

$$PO_4^{3-} + 12\ MoO_4^{2} + 24\ H^+ + 3\ NH_4^+ \longrightarrow (NH_4)_3[P(Mo_3O_{10})_4] + 12\ H_2O$$

For the total phosphate measurement a thermal digestion with peroxosulfate is necessary. Polyphosphates and organic phosphorus bondings can be determined after they are hydrolized with sulphuric acid to molybdate-reactive orthophosphate. For substances which are difficult to decompose a nitric acid/sulphuric acid - digestion is needed.

Reagents and solutions

- Sodium peroxodisulfate solution: 15 g sodium peroxodisulfate and 7 ml sulphuric acid, 98 % dissolved in 1 Litre
- Acidic molybdate solution: 6 g ammonium heptamolybdate tetrahydrate, 0.14 g potassium antimony (III) oxide tartrate trihydrate and 50 ml sulphuric acid, 98 % dissolved in 1 Litre
- Ascorbic acid solution: 50 g L(+)-ascorbic acid dissolved in 1 Litre
- Phosphorus stock solution (c = 1,000 mg/L): 4.39 g potassium hydrogen phosphate dissolved in 1 Litre

Calibration

To calibrate, 4 ml of the following standard series was prepared: 0.5, 1.0, 2.0, 2.5 and 3.0 mg ($P\text{-}PO_4^{3-}$)/L. The standard series was prepared and measured as described below using standard instead of sample solution. The calibration curve was created as described under 5.4.3.

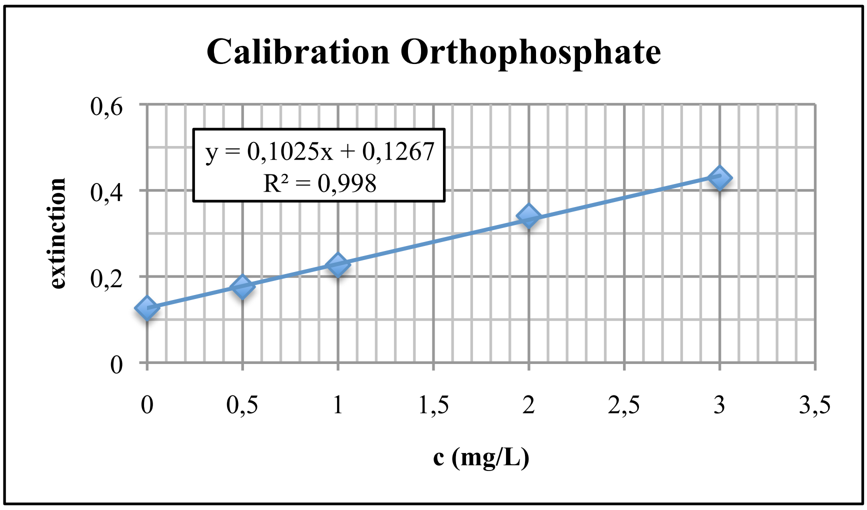

Fig. 12. Calibration Curve for Orthophosphate, 13.01.2012

Preparation and Measurement of Orthophosphate

4 ml of sample solution, warmed up to room temperature were pipetted into a round glass tube. If a concentration outside the calibrated range was expected, a corresponding dilution of the sample with pure water was necessary. To the content of the round glass tube 0.3 ml sodium peroxodisulfate, 0.2 ml ascorbic acid and 0.2 ml acidic molydbate solution were added and mixed. The extinction was measured with the photometer after 10 minutes at a wavelength of 585 nm.

Preparation and Measurement of Total Phosphorus

4 ml of sample solution, warmed up to room temperature were pipette into a round glass tube. 0,3 ml of sodium peroxodisulfate were added and the tube was heated up for one hour at 100 ºC. After the digestion 0.2 ml of each molybdate- and ascorbic acid solution were added and mixed. After 10 minutes the extinction was measured at a wavelength of 585 nm.

5.5.10 Orthophosphate Results of Monitoring Activity

In the first week of January samples were taken twice at node 7 point 2, node 8 point 3 and at three different outlets (OL) in Tra Noc 1.

Table 22. Orthophosphate Results, Locations N7P2, N8P3 and Outlet N6OL1, N4OL7 and N4OL6 in Tra Noc 1

Sample	Dilution	Results 03.01.2012 c [mg/L]	Results 05.01.2012 c [mg/L]
Standard 1 mg/L	1	0.95	0.92
TN1_N7P2_0900	10	8.11	2.89
TN1_N7P2_1100	10	3.84	0.76
TN1_N7P2_1300	5	3.47	1.44
TN1_N7P2_1500	1	0.97	2.10
TN1_N8P3_0900	5	3.09	6.83
TN1_N8P3_1100	10	19.68	(11.61)
TN1_N8P3_1300	10	18.03	5.10
TN1_N8P3_1500	10	21.14	12.78
TN1_N6OL1_1100	20	(45.98)	10.04
TN1_N6OL1_1500	5	2.89	10.77
TN1_N4OL7_1100	1	n.d.	n.d.
TN1_N4OL7_1500	1	n.d.	n.d.
TN1_N4OL6_1100	2.5	2.17	3.56
TN1_N4OL6_1500	2.5	2.05	1.69

For the three locations N7P2, N8P3 and N8P4 the concentrations vary during the course of the day as well as within the two dates of sample taking, even though the dates were only two days apart. The two values of table 22 in brackets needed to be re-evaluated because they were higher than the total phosphorus values (cf. 5.5.11).

The sample N6OL1_1100 was measured with a lower dilution factor the first time and the extinction was above the calibrated range. Still, the result of this measurement indicated a concentration around 45 mg/L which matches the second measurement with a concentration of 45.9 mg/L. This concentration isn't considered plausible because the total phosphorus lies at 24 mg/L. It is not possible to know for sure if the total phosphorus result is correct but most likely the orthophosphate value wasn't, since none of the overall orthophosphate findings were above 30 mg/L. This conclusion can be supported by the too low, false total nitrogen concentration (4.54 mg/L). It can be suspected that this sample had a difficult matrix and contains substances that are interfering with the photometric methods.

N8P3_1100 will be proven to be reliable when it is discussed under 5.6.3 Plausibility for Results of Phosphorus.

Table 23. Orthophosphate Results; Locations N1P1, N2P1 and N2P2 in Tra Noc

Sample	Dilution	Results 10.01.2012 c [mg/L]	Dilution	Results 20.02.2012 c [mg/L]
Standard 1 mg/L	1	0.90	1	0.95
TN1_N1P1_0900	1	n.d.	1	n.d.
TN1_N1P1_1100	1	n.d.	1	n.d.
TN1_N1P1_1300	1	n.d.	1	0.52
TN1_N1P1_1500	1	n.d.	1	n.d.
TN1_N2P1_1100	5	6.10	5	8.48
TN1_N2P1_1500	5	5.20	5	9.63
TN1_N2P2_1100	1	n.d.	5	8.98
TN1_N2P2_1500	1	n.d.	1	n.d.

The sampling dates of the three locations in the table above were more than a month apart. Contrary to the nitrogen results at these locations, the concentration of orthophosphate stayed stable or was even not detectable (table 23.). The 8.98 mg/L of sample location N2P2_1100 was the only noticeable value here because for the other three measurements at this location no orthophosphate could be detected. The results appeared all accurate and conclusive which indicates that the phosphorus concentration in the released waste water can change from not detectable to quite perceivable.

Table 24. Orthophosphate Results, Location N3P3, N8P1 and N8P2 in Tra Noc 1; location N5P1 in Tra Noc 2

Sample	Dilution	Results 12.01.2012 c [mg/L]	Dilution	Results 13.02.2012 c [mg/L]
Standard 1 mg/L	1	0.90	1	1.14
TN1_N3P3_0900	1	0.55	1	1.07
TN1_N3P3_1100	1	2.56	1	< 0.5
TN1_N3P3_1300	1	2.57	5	9.34
TN1_N3P3_1500	1	2.55	5	8.03
TN1_N8P1_1100	10	8.05	5	12.05
TN1_N8P1_1500	10	8.14	5	11.93
TN1_N8P2_1100	10	9.13	-	-
TN1_N8P2_1500	1	2.35	-	-
TN2_N5P1_1100	-	-	10	20.25
TN2_N5P1_1500	-	-	5	11.68

The time difference between the two sampling dates was one month and the values again show how different the concentrations over time can be. In table 24, at N3P3 on the 12th of January the concentration increased slightly after 9.00 am from 0.6 to consistently 2.6 mg/L. On the 13th the concentration on the same location increases after 11.00 am from around 1 mg/L to almost 10.0 mg/L. Comparatively at locations N8P2 and N5P1 the concentration decreased between 11.00 am and 3.00 pm. Overall, all results can be confirmed plausible and appear accurate.

Table 25. Orthophosphate Results; Outlet N7OL1 in Tra Noc 1; Locations N4P3 and N4P4 in Tra Noc 2

Sample	Dilution	Results 07.02.2012 c [mg/L]
Standard 1 mg/L	1	0.99
TN1_N7OL1_0900	5	10.49
TN1_N7OL1_1100	5	10.41
TN1_N7OL1_1300	5	11.11
TN1_N7OL1_1500	5	13.03
TN2_N4P3_1100	1	2.25
TN2_N4P3_1500	1	2.32
TN2_N4P4_1100	5	3.81
TN2_N4P4_1500	5	4.14

The results of outlet 1 in Tra Noc 1 and the locations N4P3 and N4P4 in Tra Noc 2 sampled January 7th were considered very stable for nitrogen levels over the course of the day and all results are considered conclusive (table 25.).

5.5.11 Total Phosphorus Results of Monitoring Activity

In the first week of January samples were taken twice at node 7 point 2, node 8 point 3 and at three different outlets in Tra Noc 1.

Table 26. Total Phosphorus Results, Locations N7P2, N8P3 and Outlet N6OL1, N4OL7 and N4OL6 in Tra Noc 1

Sample	Dilution	Results 03.01.2012 c [mg/L]	Results 05.01.2012 c [mg/L]
Standard 1 mg/L	1	0.95	0.92
TN1_N7P2_0900	10	20.17	**6.56**
TN1_N7P2_1100	10	22.02	27.07
TN1_N7P2_1300	10	17.35	**4.91**
TN1_N7P2_1500	10	14.63	15.50
TN1_N8P3_0900	10	18.42	20.17
TN1_N8P3_1100	10	26.20	**9.38**
TN1_N8P3_1300	10	25.62	14.53
TN1_N8P3_1500	10	25.81	23.19
TN1_N6OL1_1100	10	(24.06)	19.10
TN1_N6OL1_1500	10	7.73	21.14
TN1_N4OL7_1100	1	n.d.	0.68
TN1_N4OL7_1500	1	n.d.	n.d.
TN1_N4OL6_1100	2.5	3.44	5.82
TN1_N4OL6_1500	2.5	3.10	4.14

The sample N6OL1_1100 from the 3rd of January, table 26 was already discussed for total nitrogen and orthophosphate. It seems that the sample contains substances that interfere with the method and therefore the value is most likely not accurate.

Furthermore, three results from the measurement taken on the 5th stand out. N8P3_1100 will be proven as reliable when it is discussed under 5.6.3 Plausibility for Results of Phosphorus. The total phosphorus concentration was assumed too low, considering the other values at this location. As for N7P2, there was a conspicuous drop in concentration at 11.00 and 15.00. Only more data over time can fully confirm the accuracy of these figures.

Table 27. Total Phosphorus Results; Locations N1P1, N2P1 and N2P2 in Tra Noc 1

Sample	Dilution	Results 10.01.2012 c [mg/L]	Dilution	Results 20.02.2012 c [mg/L]
Standard 1 mg/L	1	0.90	1	0.95
TN1_N1P1_0900	10	< 5.0	1	< 0.5
TN1_N1P1_1100	10	< 5.0	1	< 0.5
TN1_N1P1_1300	10	< 5.0	1	1.52
TN1_N1P1_1500	10	< 5.0	1	< 0.5
TN1_N2P1_1100	10	18.97	10	18.44
TN1_N2P1_1500	10	17.17	10	22.95
TN1_N2P2_1100	10	< 5.00	20	15.90
TN1_N2P2_1500	10	< 5.00	1	0.87

The samples from the 10th of January were measured with a dilution 1:10 and the extinction of six samples was below the lowest calibrated concentration of 0.5 mg/L. Since no undiluted measurement was made, it stays unknown if the concentrations of total phosphorus on the 10th of January were as low as they were six weeks later.

Table 28. Total Phosphorus Results; Location N3P3, N8P1, N8P2 and N5P1 in Tra Noc 1

Sample	Dilution	Results 12.01.2012 c [mg/L]	Dilution	Results 13.02.2012 c [mg/L]
Standard 1 mg/L	1	0.90	1	1.14
TN1_N3P3_0900	1	3.21	1	1.70
TN1_N3P3_1100	20	11.59	1	1.32
TN1_N3P3_1300	10	17.53	10	12.38
TN1_N3P3_1500	10	13.65	10	11.64
TN1_N8P1_1100	16	15.91	5	(16.93)*
TN1_N8P1_1500	16	12.45	10	16.48
TN1_N8P2_1100	20	12.13	-	-
TN1_N8P2_1500	5	6.10	-	-
TN2_N5P1_1100	-	-	40	34.10
TN2_N5P1_1500	-	-	40	22.95

* measurement was out of range

All results at all four locations in the table above appeared conclusive and plausible. Comparing the results it becomes apparent that the phosphorus concentration was not underlying as significant changes as the nitrogen compounds.

Table 29. Total Phosphorus Results; Outlet N7OL1 in Tra Noc 1; Locations N4P3 and N4P4 in Tra Noc 2

Sample	Dilution	Results 07.02.2012 c [mg/L]
Standard 1 mg/L	1	0.99
TN1_N7OL1_0900	10	18.77
TN1_N7OL1_1100	10	14.26
TN1_N7OL1_1300	10	27.46
TN1_N7OL1_1500	10	15.00
TN2_N4P3_1100	5	5.25
TN2_N4P3_1500	5	5.57
TN2_N4P4_1100	5	6.15
TN2_N4P4_1500	5	5.90

The results for N7OL1, N4P3 and N4P4 in table 29 were for total phosphorus, as already for the other parameter, conclusive and appeared accurate.

5.6 Quality Assurance

It is a viable necessity to ensure the quality of the measured values to confirm their accuracy and to survey the plausibility of the results. In order to do so, following measures were determined and taken.

5.6.1 Reference Values

A standard solution was measured with every measurement series. Also one of the samples of each series was measured with a Machery-Nagel nanocolor tube test from a test-kit. Those values were used as a reference to revise the measured sample results. The results were considered accurate if either

- the recovery rate of the standard solution deviates less than 10 % respectively for 1 mg/L standards not more than 0.2 mg/L, or
- the photometricly measured value was within the range of 15 % of the tube test value or for values below 3.5 mg/L within 0.5 mg/L (for nitrite within 0.1 m/L)

Ideally both conditions were met but as the results show, in practice often only one criteria was applied. The reference values for all parameter from January and February 2012 are presented below. The values in brackets did not meet the quality assurance criteria.

Table 30. Reference Values for Ammonium

Date	Standard 1 mg/L [mg/L]	Deviation relative [%]	Photometric result [mg/L]	Tube test result [mg/L]	Deviation relative [%]
03.01.2012	1.01	1.0	27.6	24.5	14.8
05.01.2012	0.94	- 6.0	-	-	-
10.01.2012	1.0	0	-	-	-
12.01.2012	1.02	2.0	-	-	-
07.02.2012	(1.32)	32.0	3.3	2.9	13.8
13.02.2012	(1.31)	31.0	2.0	2.1	-4.8
20.02.2012	1.10	10.0	13.2	(9.4)	40.4

For each measurement series for the parameter ammonia one of the two criteria were met (table 30.) and for the 3rd of January both criteria were met. Three times in January no tube test result were determined.

Table 31. Reference Values for Nitrite

Date	Standard 10 mg/L [mg/L]	Deviation relative [%]	Photometric result [mg/L]	Tube test result [mg/L]	Deviation absolute [mg/L]
03.01.2012	10	0	1.9	1.6	0.3
05.01.2012	9.83	- 1.7	-	-	-
10.01.2012	10.02	0.2	-	-	-
12.01.2012	9.42	- 5.8	-	-	-
07.02.2012	9.03	- 9.7	-	-	-
13.02.2012	9.30	- 7.0	-	-	-
20.02.2012	10.61	3.9	-	-	-

No tube test kits for nitrate were available after the 3rd of January but the all standard measurement met the quality assurance criteria (table 31.).

Table 32. Reference Values for Nitrite

Date	Standard 0.1 mg/L [mg/L]	Deviation relative [%]	photometric result [mg/L]	tube test result [mg/L]	Deviation absolute [mg/L]
07.02.2012	0.10	0	0.30	0.20	0.10
13.02.2012	0.11	10.0	-	-	-
20.02.2012	0.11	10.0	0.26	0.2	0.06

In January no nitrite was measured. The measurement of the reference values in February complied with the quality assurance criteria (table 32.).

Table 33. Reference Values for Total Nitrogen

Date	Standard 10 mg/L [mg/L]	Deviation relative [%]	photometric result [mg/L]	tube test result [mg/L]	Deviation relative [%]
03.01.2012	10	0	6.0	6.0	0
05.01.2012	9.83	- 1.7	-	-	-
10.01.2012	10.02	0.2	14.9	(11.0)	35.5
12.01.2012	9.42	- 5.8	8.8	(4.0)	120
07.02.2012	9.03	- 9.7	40.88	44.0	-7.1
13.02.2012	9.30	- 7.0	-	-	-
20.02.2012	10.61	3.9	11.1	11.0	0.9

The calibration that is used for total nitrogen is the same as for nitrate. Therefore the standard measurements of nitrate are used as reference for total nitrogen as well. The quality assurance criteria were met for all standard measurements and for three out of five tube test determinations (table 33.)

Table 34. Reference Values for Orthophosphate

Date	Standard 1 mg/L [mg/L]	Deviation relative [%]	photometric result [mg/L]	tube test result [mg/L]	Deviation relative [%]
03.01.2012	0.95	- 5.0	2.2	2.3	- 4.3
05.01.2012	0.92	- 8.0	-	-	-
10.01.2012	0.90	- 10.0	-	-	-
12.01.2012	0.90	- 10.0	-	-	-
07.02.2012	0.95	- 5.0	8.48	(11.1)	-23.6
13.02.2012	1.14	14.0	1.07	1.13	-5.3
20.02.2012	0.99	- 1.0	3.81	4.4	-13.4

For the measurement series that was measured on the 7th of February the tube test determination did not met the quality assurance criteria (table 34.). All standard measurements and the other three tube tests results were within the constraints.

Table 35. Reference Values for Total Phosphorus

Date	Standard 1 mg/L [mg/L]	Deviation relative [%]	photometric result [mg/L]	tube test result [mg/L]	Deviation relative [%]
03.01.2012	0.95	- 5.0	22.0	(16.2)	35.8
05.01.2012	0.92	- 8.0	-	-	-
10.01.2012	0.90	- 10.0	< 5.0	< 5.0	not to determine
12.01.2012	0.90	- 10.0	-	-	-
07.02.2012	0.95	- 5.0	18.8	(13.1)	43.5
13.02.2012	1.14	14.0	28.2	27.1	4.1
20.02.2012	0.99	- 1.0	< 0.5	< 0.5	0

The calibration that is used for total phosphorus is the same as for orthophosphate. Therefore the standard measurements of orthophosphate are used as reference for total phosphorus as well. Therefore all standard measurements (table 35.) as stated with orthophosphate were within the limit, only two out of the five tube test results were as well. Two were 36 and 44 % off and one deviation couldn't be determined because only a range of concentration was known.

5.6.2 Plausibility for Results of Nitrogen Compounds

The parameter total nitrogen is defined as the sum of all nitrogen containing compounds. Those compounds are ammonium, nitrate, nitrite and organic bounded nitrogen (proteins, amino acids, urea, etc.). Logically, total nitrogen must be higher than all the other nitrogen parameter combined, especially since the organic bounded nitrogen is not measured and is unknown. If the total nitrogen result is lower than the sum it needed to be determined which parameter value or values were false. Most of the times this was done by re-evaluating the raw data, comparing the former results and using experience (cf. 5.6.4).

The following two tables show exemplary the plausibility of the monitoring results presented before. It was presumed that the nitrite values were insignificantly low and therefore were not considered unless the sum of ammonium and nitrate deviates 2 mg/L from the total nitrogen result. In order to evaluate the results a coefficient was constituted.

$$\kappa_N = \frac{c_{TN}}{c_{NH_4^+} + c_{NO_3^-}} \tag{6}$$

κ_N	Coefficient for the comparison of nitrogen compounds
c_{TN}	Concentration of total nitrogen [mg/L]
c_{NH4+}	Concentration of ammonium [mg/L]
c_{NO3-}	Concentration of nitrate [mg/L]

Table 36. Comparison and Determination of Plausibility for Nitrogen Compounds for the Monitoring Activity Results, first Week of January 2012

	03.01.2012				05.01.2012			
Sample	Results Ammonium c [mg/L]	Results Nitrate c [mg/L]	Results TN c [mg/L]	K_N	Results Ammonium c [mg/L]	Results Nitrate c [mg/L]	Results TN c [mg/L]	K_N
TN1_N7P2_0900	20.30	1.92	45.93	2.1	22.09	1.38	50.01	2.1
TN1_N7P2_1100	24.20	1.80	75.37	2.9	9.99	1.39	69.54	2.1
TN1_N7P2_1300	37.16	2.23	84.60	2.1	19.64	4.39	42.05	1.7
TN1_N7P2_1500	24.45	2.23	58.17	2.2	19.30	0.87	59.05	2.9
TN1_N8P3_0900	27.55	1.05	73.62	2.6	16.04	2.76	57.01	3.0
TN1_N8P3_1100	18.97	10.35	122.56	4.2	21.03	3.38	66.04	2.7
TN1_N8P3_1300	48.36	9.07	103.72	1.8	42.61	2.37	73.72	1.6
TN1_N8P3_1500	18.76	8.93	66.24	2.4	22.06	2.35	37.00	1.5
TN1_N6OL1_1100	**32.12**	**1.12**	**(4.54)**	**0.14**	34.77	1.10	125.76	3.5
TN1_N6OL1_1500	22.44	1.24	97.81	4.1	16.83	1.03	112.76	6.3
TN1_N4OL6_1100	**8.30**	**2.78**	**10.80**	**0.97**	14.56	4.76	40.98	2.1
TN1_N4OL6_1500	10.43	1.88	16.41	1.3	9.12	0.95	52.54	5.2

The table 36 reveals that the samples contain an unpredictable amount of unknown nitrogen compounds. A coefficient K_N below 1 means the result can’t be plausible.

Only the coefficient of the two marked results in the table 36 was below 1. Both results have been discussed earlier and it was concluded that the sample N6OL1_1100 must have a difficult matrix and some unknown substances was interfering with the measurement. The nitrogen concentrations for sample N4OL6_1100 were confirmed as correct and the small deviation is explained by the interval of uncertainty of the methods.

Table 37. Comparison and Determination of Plausibility for Nitrogen Compounds for the Monitoring Activity Results, Locations N1P1, N2P1 and N2P2 in Tra Noc 1

	10.01.2012				20.01.2012			
Sample	Results Ammonium c [mg/L]	Results Nitrate c [mg/L]	Results TN c [mg/L]	K_N	Results Ammonium c [mg/L]	Results Nitrate c [mg/L]	Results TN c [mg/L]	K_N
TN1_N1P1_0900	9.61	1.03	14.94	1.4	8.42	1.96	11.13	1.1
TN1_N1P1_1100	8.23	0.87	16.14	1.8	13.24	1.22	21.73	1.5
TN1_N1P1_1300	5.74	0.95	17.95	2.7	**19.40**	**2.74**	**(19.58)****	**0.88**
TN1_N1P1_1500	8.96	0.77	17.02	1.7	< 2	1.70	8.62	3.2
TN1_N2P1_1100	6.89	19.90	50.60	1.9	**16.78**	**11.19**	**27.28**	**0.98**
TN1_N2P1_1500	6.78	26.31	52.05	1.6	19.33	7.18	30.68	1.2
TN1_N2P2_1100	2.60	0.83	12.10	3.5	31.54	13.09	52.25	1.2
TN1_N2P2_1500	5.46	1.24	19.08	2.8	7.21	3.80	19.41	1.8

** out of range

The two marked results in the table above, sample N1P1_1300 and N2P2_1100 show total nitrogen values that were just slightly smaller than the sum of the compounds ammonium and nitrate. For sample N1P1 it can be explained by the total nitrogen measurement where the extinction was out of the calibrated range. A second measurement with a higher dilution most likely would have been a little higher. It naturally can only be speculated, but experience thus far showed that the measurements out of range came very close to the actual value of the second measurement within the calibrated range.

The other marked row of sample N2P1 in table 36 has a total nitrogen concentration 0.69 mg/L lower than the sum of ammonium and nitrate. Supposably a very small nitrite value and an unknown organic bound nitrogen value need to be considered as well. Therefore the results were re-evaluated. The re-evaluation wasn't conclusive and all measurements appeared accurate. In those cases, where the difference between the sum of nitrogen compounds and total nitrogen was very small it can presumably explained by the uncertainty of measurement. The same is true for the four marked values in table 38 where the sum of ammonium and nitrate is in very close range to the total nitrogen values.

Table 38. Comparison and Determination of Plausibility for Nitrogen Compounds for the Monitoring Activity Results, Locations N7OL1, N4P3 and N4P4 in Tra Noc 1

	07.02.2012			
Sample	Results Ammonium c [mg/L]	Results Nitrate c [mg/L]	Results TN c [mg/L]	K_N
TN1_N7OL1_0900	**30.19**	**5.46**	**35.64**	**1.0**
TN1_N7OL1_1100	17.91	6.68	30.68	1.2
TN1_N7OL1_1300	**27.49**	**6.23**	**34.57**	**1.0**
TN1_N7OL1_1500	29.98	7.30	40.88	1.1
TN2_N4P3_1100	**21.80**	**< 0.5**	**17.96**	**0.8**
TN2_N4P3_1500	**22.0**	**1.73**	**22.33**	**0.9**
TN2_N4P4_1100	3.3	6.14	15.24	1.6
TN2_N4P4_1500	5.70	7.65	15.62	1.2

The other results which are not presented above have been evaluated and were confirmed as plausible. In total, out of all measurements from January and February eight results reviewed for plausibility were standing out. Seven results were confirmed to be still reliable because the absolute deviation did not exceed the sum of 10 % from each sample which can be explained by the uncertainty of measurement. Only one sample N6OL1_1100, as repeatedly discussed for several parameter, was detected to be not plausible.

5.6.3 Plausibility for Results of Phosphorus

The parameter total phosphorus is defined as the sum of all phosphorus containing compounds. Logically, total phosphorus must be higher than orthophosphate. If the total phosphorus concentration is lower than the orthophosphate's, it needed to be determined which of the two parameter values was false. This was done by re-evaluating the raw data, comparing the former results and using experience (cf. 5.6.4).

The following table shows exemplary the plausibility of the monitoring results presented before.

Table 39. Comparison and Determination of Plausibility for Phosphorus Compounds for the Monitoring Activity Results, first Week of January 2012

	03.01.2012			05.01.2012		
Sample	Results Orthophosphate c [mg/L]	Results TP c [mg/L]	K_{Ph}*	Results Orthophosphate c [mg/L]	Results TP c [mg/L]	K_{Ph}*
TN1_N7P2_0900	8.11	20.17	2.5	2.89	6.56	2.3
TN1_N7P2_1100	3.84	22.02	5.7	0.76	27.07	35.6
TN1_N7P2_1300	3.47	17.35	5.0	1.44	4.91	3.4
TN1_N7P2_1500	0.97	14.63	15.1	2.10	15.50	7.4
TN1_N8P3_0900	3.09	18.42	6.0	6.83	20.17	3.0
TN1_N8P3_1100	19.68	26.20	1.3	**11.61**	**9.38**	**0.8**
TN1_N8P3_1300	18.03	25.62	1.4	5.10	14.53	2.8
TN1_N8P3_1500	21.14	25.81	1.2	12.78	23.19	1.8
TN1_N6OL1_1100	**45.98**	**24.06**	**0.5**	10.04	19.10	1.9
TN1_N6OL1_1500	2.89	7.73	2.7	10.77	21.14	2.0
TN1_N4OL7_1100	n.d.	n.d.	-	n.d.	0.68	-
TN1_N4OL7_1500	n.d.	n.d.	-	n.d.	n.d.	-
TN1_N4OL6_1100	2.17	3.44	1.6	3.56	5.82	1.6
TN1_N4OL6_1500	2.05	3.10	1.5	1.69	4.14	2.4

* K_{Ph} = Coefficient for phosphorus: ratio of TP and orthophosphate result

Just us for the plausibility check of the nitrogen compounds, a coefficient K_{Ph} was determined to investigate if there is a dependency between total phosphorus and orthophosphate. If the coefficient were in similar for all samples it could be concluded in which concentration range the other parameter would be found. Apparently there is no pattern to be found, the coefficients vary significantly, even for one location on the same day. But the coefficient allows a statement about the plausibility because a K_{Ph} below 1 means at least one of the results can’t be accurate. Of all the results presented before, only the two marked ones in the table above (table 39.) are inconclusive. The results needed to be re-evaluated.

The re-evaluation for sample N8P3 wasn’t conclusive and all measurements appeared accurate. In those cases, where the difference between the phosphorus and orthophosphate is very small it can presumably explained by the uncertainty of measurement (cf. 5.7 Uncertainty of the Methods).

The sample of location N6OL1 was already discussed in the last section about the plausibility of nitrogen and the re-evaluation lead to the conclusion that none of the parameter results for this sample can be trusted because there seemed to be substances in the sample which have influenced the measurement.

5.6.4 Practical Experience

Another less scientific but valuable means of quality assurance is the use of practical experience. Waste water, as pointed out before, is often underlying severe change when it comes to its composition. If one value of one parameter stands out for one location because it is significantly higher or lower than all other results determined for this location, it can not be concluded that the value must be false. But, as more data available for one location as higher the likelihood to pick out those results that don't match former results. That way suspicious samples can be repeatedly measured or re-evaluate.

Contrariwise if the concentrations of one location and day respectively days, were in the same range, it can be concluded that the results have a high possibility of being accurate.

5.7 Uncertainty of the Methods [28] [29]

A true value, in the case of this work a true concentration value, can never be determined because all measurements are afflicted with uncertainties. This means that every measurement result can only be seen as an estimated value for the true value respectively an expected value of the measurand. The uncertainty is divided into the systematic measurement deviation and the random deviation. The sum of both defines the interval in which the true value can be found. In addition the expanded uncertainty can be determined by stating the level of confidence. The level of confidence provides the probability of finding the true value within a certain interval. For the expanded uncertainty the standard uncertainty is multiplied by a coverage factor k. The choice of the factor k is based on the level of confidence desired.

For the photometric methods used in the laboratory of Tra Noc the measurement uncertainty hasn't been determined at this point but estimated. The uncertainty of the methods in this work are estimated with 10 % with a level of confidence of 95 % ($k = 2$).

6 Analytical Method Validation

6.1 Objective of Validating Methods [30]

The results of analytical measurements are the foundation for decision-making, often with consequences on a large scale for the environment and economic processes. It is therefore of great importance to be able to judge and guarantee the reliability, quality and consistency of analyteical results. Method validation is the process used to confirm that the analytical procedure employed for a specific analysis is suitable. The validation of methods is an integral, essential part of any good analytical practice.

Analytical methods need to be validated or re-validated: [31]

- before their introduction into routine use;
- whenever the conditions change for which the method has been validated (e.g. an instrument with different characteristics or samples with a different matrix); and
- whenever the method is changed and the change is outside the original scope of the method

6.2 Method Validation in the LAR Laboratory in Tra Noc

The status quo in January 2012 of the photometric methods which are used to determine ammonium, nitrate, nitrite, total nitrogen, orthophosphate and total phosphorus and are the use of a normative document where the developed methods are described. The alignment of plausibility is found in chapter 5.

Generally the attained results with the developed methods were plausible and appeared accurate at the time of measurement. Still, there are discrepancies e. g. about whether or not some parameter should be measured unfiltered in order to not result in the loss of analyte. Also it was often challenging or even impossible to measure all parameters in an acceptable timeframe. Therefore methods of sample preservation were tried out. Now, in order to validate the accuracy of the results and to improve the workflow in the laboratory the following experiments have taken place.

6.3 Comparison with the Ion Selective Electrode (ISE)

6.3.1 Objective

The measurement with an ISE is a faster and cheaper procedure to measure certain parameter such as ammonium and nitrate than the photometric methods. It has the advantage that the colouration or turbidity is not effecting the measurement as well as a wider measurement range. The calibration ranges from 0.5 to 10 mg/L whereas the calibration of the photometric method is only linear for up to 2 mg/L. The experiment was set up in order to find an alternative, more efficient method and to be able to have another means of reference to evaluate the results.

6.3.2 Layout and operation mode of an ion selective electrode [32 33]

An ion selective electrode belongs to the potentiometric measurement procedures. The layout includes two electrodes: the ISE, specific to one kind of ion and a reference electrode (either build into one element or as a separate electrode), which are connected through a volt meter. The potential of the reference electrode stays constant whereas the electrochemical potential of the ISE is influenced by the activity of the specific ion. The outcome of this is a change of voltage between the two electrodes and this difference is used as the measurand to evaluate the concentration. The relation between the concentration of ions to be measured and the measured voltage is described by the Nernst equation:

$$(7) \qquad U_{ion} = U_{ion}^{0} \pm \frac{RT}{zF} \cdot \ln(a_{ion})$$

U_{ion}	Potential of the electrode
U^0_{ion}	Standard potential of the electrode at point of reference
±	algebraic sign, + for positive charged ions and – for negative charged ions
R	universal gas constant, R= 8.314472 J K^{-1} mol^{-1}
T	absolute temperature
F	Faraday constant, F = 9.64853399 10^4 C mol^{-1}
z	number of moles of electrons transferred in the cell reaction
a_{ion}	activity of the relevant ion

Kations lead to a positive gradient because of their positive charge whereas anions lead to a negative gradient. The potential of the ISE is build by the chemical reciprocal effect happening at the membrane which functions as an ion exchanger. If the sensory head is dipped into the sample solution and the concentration of nitrate is higher than the nitrate concentration of the electrolyte solution inside the electrode, the nitrate ions are transported inside the electrode into the electrolyte solution. The result is a negative charge.

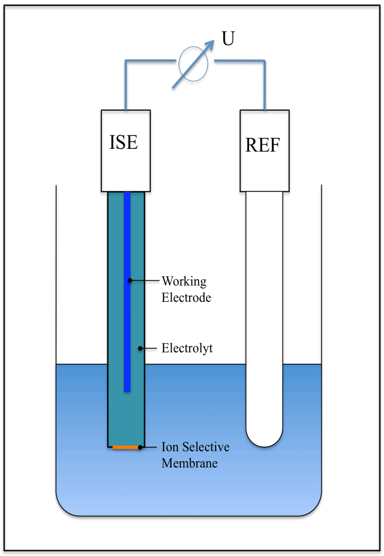

Fig. 13. Schematic layout of an ISE

To compensate this charge, Ag^+ ions of the AgCl layer of the working electrode are reduced. This leads to a negative charge in the AgCl layer which is now compensated with Ag^+ ions of the silver conductor inside the AgCl layer. This leaves an electron inside the conductor and causes the electric voltage that can now be measured. If the concentration of nitrate is lower than the concentration in the electrolyte solution inside the electrode the reactions are happening the opposite way.

Very often the ISE also reacts to other ions besides the relevant ones. Those ions interfere with the measurement. For example the NH_4^+-ISE reacts also sensitive to the presence of potassium because it shows a similar chemical behaviour. If potassium is present it can lead to higher findings.

6.3.3 Calibration Curve and Evaluation of Concentration

The calibration curve was created as described under 4.1.3. The calibration curve for the ISE method shows a logarithmic behaviour in the calibrated range. The equation received from the regression is in the form of:

(8) $A = m \cdot \ln(c) + b$

The equation converts for the concentration c in mg/L including the dilution factor to:

$$(9)\qquad c = e^{\frac{A-b}{m}} \cdot d$$

A	measured voltage (mV)
b	y-axis intercept, extinction of calculated blank solution value
m	accent of the calibration curve, in milligram per Litre [mg/L]
d	dilution factor

6.3.4 Preparation and Measurement with the NH_4^+-ISE

Reagents and Solutions

- Buffer solution: 100 g sodium hydroxid (NaOH) and 16 g EDTA dissolved in 1 Litre
- Ammonia stock solution (c = 1,000 mg/L): 1.91 g ammonium chloride (NH_4Cl) dissolved in 500 ml

Calibration

20 ml of the following standard series was prepared: 0.5, 1.0, 2.0, 5.0 and 10.0 mg (N-NH_4^+)/L. The standard series has been prepared and measured as described below using standard instead of sample solution.

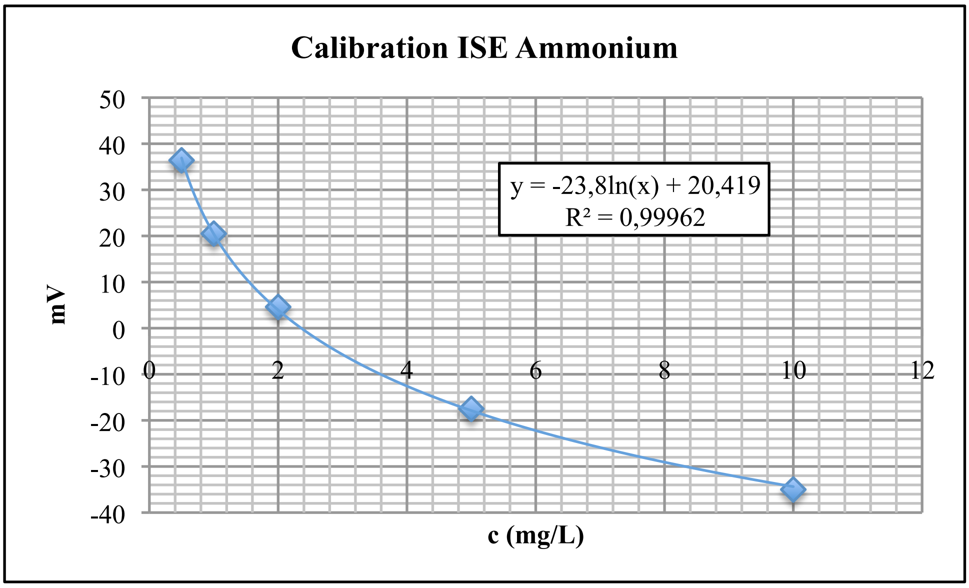

Fig 14. Calibration curve for $NH4^+$ - ISE, 08.02.2012

ISE Measurement of Ammonium

20 ml of sample solution warmed up to room temperature were pipetted into a small beaker. If a concentration outside the calibrated range was expected, a corresponding dilution of the sample with pure water was necessary. 1 ml of buffer solution is added as well as a magnetic stirrer. While the solution is stirred at a low to medium speed the ISE and the reference electrode were dipped into the beaker and the voltage (mV) is measured until the value is stable.

6.3.5 Results for NH_4^+-ISE Measurement

In total 18 measurements were made, each for ISE and with the photometric method. The samples were taken on three different days on nine different locations. All samples were measured filtered and unfiltered. In order to evaluate the results a coefficient for photometricly measured and the ISE values was constituted.

$$\kappa_M = \frac{M_P}{M_{ISE}} \tag{10}$$

κ_M	Coefficient of method comparison
M_P	Concentration of photometric measurement [mg/L]
M_{ISE}	Concentration of ISE measurement [mg/L]

Table 40. Comparison of ISE and Photometric Method Results for the Parameter Ammonium

	Sample	ISE Result [mg/L]	PM* Result [mg/L]	Deviation absolute [mg/L]	Deviation relative [%]	k_M
07.02.2012	TN2_N7OL1_1100_F	13.75	17.91	4.16	-23.2	1.3
	TN2_N7OL1_1100_uF	13.41	21.95	8.54	-38.9	1.6
	TN2_N4P3_1100_F	16.20	21.83	5.63	-25.8	1.3
	TN2_N4P3_1100_uF	14.18	20.77	6.59	-31.7	1.5
	TN2_N4P4_1100_F	4.26	3.34	0.92	27.5	0.8
	TN2_N4P4_1100_uF	1.94	(28.55)	-	-	-
13.02.2012	TN2_N3P3_1100_F	1.18	1.95	0.77	-39.5	1.7
	TN2_N3P3_1100_uF	1.01	1.71	0.70	-40.9	1.7
	TN2_N5P1_1100_F	(4.25)	(80.89)	-	-	-
	TN2_N5P1_1100_uF	(4.12)	(85.11)	-	-	-
	TN2_N8P1_1100_F	0.88	1.43	0.55	-38.5	1.6
	TN2_N8P1_1100_uF	0.77	1.28	0.51	-39.8	1.7
20.02.2012	TN1_N1P1_1100_F	9.34	13.24	3.90	-29.5	1.4
	TN1_N1P1_1100_uF	9.81	12.49	2.28	-21.5	1.3
	TN1_N2P1_1100_F	11.97	16.78	4.81	-28.7	1.4
	TN1_N2P1_1100_uF	11.55	14.82	3.27	-22.1	1.3
	TN1_N2P2_1100_F	39.46	31.54	7.92	25.1	0.8
	TN1_N2P2_1100_uF	38.77	(49.77)	-	-	-

* PM = photometric method

The values of N4P4 and N2P2, table 40 measured unfiltered with the photometric method are not plausible and are discussed in the next section 6.4.2. These two samples were taken out of the evaluation. The results for location N5P1 needed to be re-evaluated and are discussed below.

For each measuring row one sample has been measured with a tube test as a reference value:

Table 41. Comparing Results of Photometric Method, ISE and Tube Test

Sample	Result [mg/L]	Result ISE [mg/L]	Tube Test [mg/L]
TN2_N4P4_1100_F	1.1	4.4	2.9
TN2_N3P3_1100_F	1.7	1.2	2.1
TN1_N1P1_1100_F	11.8	9.3	9.4

6.3.6 Discussion of the NH_4^+-ISE Results

Both methods show constant, plausible results. The relative deviation lies between 21 and 40 % and all values came out in the same measurement range of each other except for the samples of location N5P1. All concentrations measured with the ISE were lower than with the photometric method, except for two values of two different locations. A reason for the consistent lower results could be the interference of amine or present metals. Mercury and silver interfere by complexing with ammonia This can happen if the amount of EDTA that was added wasn't sufficient.[34]

A coefficient was formed to investigate the relation between the methods and support the conclusion of a good compliance. The two times were the ISE value came out higher, the coefficients were 0.8 and for all other plausible results it lied between 1.3 and 1.7.

It seems now that both methods deliver accurate results and it needs to be determined which one is assumed closer the true value. The results of sample N5P1 are the ones that stand out the most. Obviously one of the methods must have been influenced by something. Assuming that the concentration of the filtered and unfiltered sample are identical (cf. 6.4), the results can be seen as a repeat determination. Looking at both methods separately the results were in a close range of each other which supports the assumption. But the results of both methods for sample N5P1 were outstanding far from each other and at least one of them must be completely false. After investigating both values for plausibility the only reference point left was experience. All ammonium values in Tra Noc so far have been far below 80 mg/L. Also the total nitrogen results are an indicator that the photometric method was disturbed. The total nitrogen results lie between 70 and 76 mg/L but the ammonium results could still be explained by the interval of measurement uncertainty.

The tube test values have been defined as reference values but an examination of the tube test values and the two methods (cf. table 39) didn't lead to a conclusion, which of the methods is more accurate. On the first measurement date the tube test result lies in the middle of the two methods result. The second value complies better with the photometric method and the third with the ISE measurement. In order to come to a finding which method is delivering the more accurate results more data is necessary. It's also recommendable to determine the uncertainty of both methods.

Nevertheless, with the data at hand the ISE appears to be an alternative, maybe even more accurate method in comparison to the photometric measurement. The results came out stable and plausible and none of the measurements seemed to have been influenced by other ions. The disadvantage of the ISE measurement is the new calibration which is needed before every measurement, but leaves this method still as a faster alternative. It is also less prone to measurement errors because the samples often don't need any dilution and less reagents are added.

6.3.7 Preparation and Measurement with the NO_3^--ISE

Reagents and Solutions

- Aluminium sulfate solution: 34.2 g aluminium sulfate ($Al_2(SO_4)_3$) and 4.9 ml of sulphuric acid dissolved in 1 Litre
- Nitrate stock solution (c = 1,000 mg/L): 0.73 g potassium nitrate (KNO_3) dissolved in 1 Litre

Calibration

For calibration 20 ml of the following standard series was prepared: 0.5, 2.5, 5.0, 10.0 and 20.0 mg ($N\text{-}NO_3^-$)/L. The standard series has been prepared and measured as described below using standard instead of sample solution.

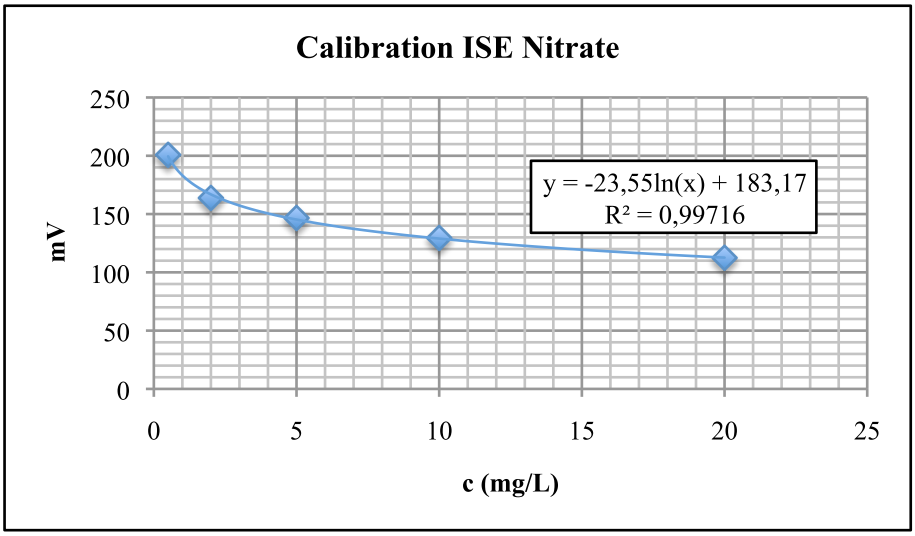

Fig. 15 Calibration Curve for NO_3^- -ISE

Measurement of Nitrate

The measurement is exactly the same as with the NH_4^+-ISE (cf. 6.3.4), only the reagent solution is different. Instead of buffer solution, 1 ml of aluminium sulfate solution is added.

6.3.8 Results for NO_3^--ISE Measurement

In total 18 measurements were made, each for ISE and with the photometric method. The samples were taken on three different days on nine different locations. All samples were measured filtered and unfiltered.

Out of the 18 results 2 of ISE determinations could not be used because the results were out of the calibration range. The remaining 16 results were evaluated.

Table 42. Comparison of ISE and Photometric Method Results for the Parameter Nitrate

	Sample	ISE Result [mg/L]	PM Result [mg/L]	Deviation absolute [mg/L]	k_M
07.02.2012	TN2_N7OL1_1100_F	31.26	6.68	24.58	0.2
	TN2_N7OL1_1100_uF	25.13	< 0.5	24.88	$9.9 * 10^{-3}$
	TN2_N4P3_1100_F	12.47	< 0.5	12.22	0.02
	TN2_N4P3_1100_uF	5.17	< 0.5	4.92	0.05
	TN2_N4P4_1100_F	31.26	6.14	25.12	0.2
	TN2_N4P4_1100_uF	27.97	5.83	22.14	0.2
13.02.2012	TN2_N3P3_1100_F	0.74	1.71	0.97	2.3
	TN2_N3P3_1100_uF	0.33	2.97	2.64	9
	TN2_N5P1_1100_F	1.51	1.42	0.09	0.9
	TN2_N5P1_1100_uF	1.40	< 0.5	1.15	0.2
	TN2_N8P1_1100_F	(37.86)*	26.49	-	-
	TN2_N8P1_1100_uF	(39.17)*	29.25	-	-
20.02.2012	TN1_N1P1_1100_F	1.44	1.22	0.22	0.8
	TN1_N1P1_1100_uF	1.43	0.93	0.50	0.7
	TN1_N2P1_1100_F	17.20	11.19	6.01	0.7
	TN1_N2P1_1100_uF	12.54	4.62	7.92	0.4
	TN1_N2P2_1100_F	13.09	13.09	0	0.1
	TN1_N2P2_1100_uF	12.37	13.91	1.54	1.1

* out of range

6.3.9 Discussion of NO_3^--ISE Results

Now, looking at the results of the nitrate measurement, the results show that the ISE is not an alternative method for this parameter. The values of the ISE measurement are generally higher, sometimes even up to a 100 times. There seemed to be no pattern to find a relation between the two methods results and no systematic deviation could be found. The coefficient varies from 0.009 and 9 which is a decimal power of 3. The only conclusion possible is that at least one of the methods is not delivering reliable results. The imprecision of the standard measurement is for both methods around 10 % and no tube tests for a reference were made because at the time there was no test kit available.

This makes it difficult to confirm which results are correct, with only the results from this experiment at hand. Still, it can be said that the correctness of the photometric method was discussed and verified under 5.5.4.
Also experience from former monitoring activities in 2011 when the tube test kit was available, confirmed the compliance between photometric results for nitrate with the reference value of the test tube measurement. Comparing the ISE nitrate results with the results of total nitrogen some of the nitrate results are even higher than the total nitrogen which makes them not plausible.

It may be concluded that the ISE measurement was influenced and the results are incorrect. The presence of chloride in a sample can lead to higher findings, but some of the results are so significantly higher that there must be at least one other reason for the incorrect results. The membrane of an ISE is very sensitive and if there were for example detergents in waste water the NO_3^--ISE is prone to failure. To confirm or eliminate the influence of chloride or detergents, further tests could be made to finally confirm, that the NO_3^- -ISE is no alternative to the current method.

6.4 Comparison of filtered and unfiltered samples

So far all parameters were measured with samples that have been filtered with a 45 µm membrane filter. For the measurement of e.g. ammonium it should not make a difference if the sample was filtered since all ammonium-ions are assumed to be completely dissolved into the liquid phase. This is also expected for nitrate, nitrite and orthophosphate. For other parameters such as phosphorus and total nitrogen it can be suspected that the concentration in the unfiltered sample will be higher. Contrary to ammonium, nitrate, nitrite and orthophosphate-ions, some nitrogen and phosphorus bondings are not fully dissolved but can be found attached to the sedimentation material and suspended particles.

Therefore all those parameter were measured filtered and unfiltered using the photometric methods. The parameter ammonium and nitrate were also measured with the ISE as described in the last experiment. The results of this experiment were also taken into consideration to evaluate the two parameter. Furthermore, for validation a coefficient for filtered and unfiltered samples was constituted:

(11) $$k_{uF/F} = \frac{uF}{F}$$

$\kappa_{uF/F}$	Coefficient for unfiltered and filtered sample results
uF	Unfiltered sample concentration [mg/L]
F	Filtered sample concentration [mg/L]

The suspended solids of each sample were as well determined to use as a reference on the influence of particles on the photometric measurement.

The suspended solids were measured by filtering 100 ml of each sample through a glass fibre membrane, using a closed system composition and a vacuum pump. The membrane filter was first dried at 105 ºC in a cabinet drier for at least one hour and then the weight was determined with a laboratory precision scale. After filtration the membrane filters were again dried at 105 ºC for at least 12 hours and then weight again. The suspended solids are calculated as follows:

(12) $$c_{ss} = \frac{w_2 - w_1}{V} \cdot 1{,}000$$

c_{ss}	Concentration suspended solids [mg/L]
w_1	Weight of membrane filter before filtering [mg/L]
w_2	Weight of membrane filter after filtering [mg/L]
V	Volume of filtered sample [ml]

6.4.1 Ammonium Results of filtered and unfiltered Samples

15 samples on three different days from 15 locations were measured with the photometric method and compared.

Table 43. Comparing Ammonium Results of Photometric Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
07.02.2012	TN2_N7OL1_0900	30.11	17.83	95	12.28	0.6
	TN2_N7OL1_1100	17.80	21.86	66	4.06	1.2
	TN2_N4P3_1100	21.74	20.76	76	0.98	1.0
	TN2_N4P4_1100	3.29	28.47	17	25.18	8.7
13.02.2012	TN2_N3P3_0900	0.27	< 0.2[*]	9	0.17	0.4
	TN2_N3P3_1100	1.95	1.71	13	0.24	0.9
	TN2_N3P3_1300	3.47	3.92	14	0.45	1.1
	TN2_N3P3_1500	3.54	3.35	< 5	0.19	1.0
	TN2_N5P1_1100	80.89	85.11	126	4.22	1.1
	TN2_N5P1_1500	52.23	54.92	188	2.69	1.1
20.02.2012	TN2_N8P1_1100	1.43	1.28	< 5	0.15	0.9
	TN2_N8P1_1500	4.98	5.19	< 5	0.21	1.0
	TN1_N1P1_1100	13.24	12.49	440	0.75	0.9
	TN1_N2P1_1100	16.78	14.82	80	1.96	0.9
	TN1_N2P2_1100	31.54	49.77	200	18.23	1.6

[*] for calculation, the value 0.1 (the middle between 0 and 0.2) was used

Nine of those 15 samples were also measured with the ISE. The results of this method were discussed under 6.3.6 and came to the conclusion that the results can be seen as valid. They were therefore also used in this section to validate the measuring of filtered and unfiltered samples.

Table 44. Comparing Ammonium Results of ISE Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
07.02.2012	TN2_N7OL1_1100	13.75	13.41	66	0.34	0.98
	TN2_N4P3_1100	16.20	14.34	76	1.86	0.89
	TN2_N4P4_1100	4.43	2.10	17	2.33	0.47
13.02.2012	TN2_N3P3_0900	1.18	1.01	13	0.17	0.86
	TN2_N5P1_1100	4.25	4.12	126	0.13	0.97
	TN2_N8P1_1100	0.88	0.77	< 5	0.11	0.88
20.02.2012	TN1_N1P1_1100	9.34	9.81	440	0.47	1.1
	TN1_N2P1_1100	11.97	11.55	80	0.42	0.96
	TN1_N2P2_1100	39.46	38.77	200	0.69	0.98

6.4.2 Discussion Ammonium Results of filtered and unfiltered Samples

The results for ammonium are very consistent and confirm the expectation that the ammonia-ions are fully dissolved. Eleven out of the 15 photometricly measured values and eight out of nine values measured with the ISE comply very well. The sample N3P3_0900 has a coefficient of 0.4 but still can be considered as complying because the values are in such a low range and the absolute deviation of 0.17 mg/L is insignificantly small. The small deviations between the filtered and unfiltered values can be explained by the deviation that arises because of the method uncertainty which still needs to be determined.

As for the values that don't comply, it is impossible the establish a connection between suspended solids and the high deviations. As seen in table 41, the sample N1P1_1100 has by far the highest concentration of suspended solids (440 mg/L) and the values of filtered and unfiltered fully comply. Whereas the sample N4P4_1100 with a very low concentration of suspended solids (17 mg/L) showed the highest deviation with 25 mg/L apart from each other. If particles had influenced the measurement a lower concentration for the unfiltered sample are to be expected, because the particles are responsible for scattering the light which leads to incorrect results. The same is true for turbidity or colouration of the sample which might absorb the light at a certain wavelength, leading to lower findings. Nevertheless, the findings for ammonium are explicit as is also confirmed by the ISE measurement. Ammonium can be measured filtered without any loss.

6.4.3 Nitrate Results of filtered and unfiltered Samples

14 samples on three different days from 14 locations were measured with the photometric method and compared.

Table 45. Comparing Nitrate Results of Photometric Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
07.02.2012	TN2_N7OL1_1100	6.68	< 0.5*	66	6.43	0.04
	TN2_N4P3_1100	< 0.5*	< 0.5*	76	0	1.0
	TN2_N4P4_1100	6.14	5.83	17	0.31	0.95
13.02.2012	TN2_N3P3_0900	0.95	1.20	9	0.25	1.26
	TN2_N3P3_1100	1.71	2.97	13	1.26	1.74
	TN2_N3P3_1300	22.57	25.68	14	3.11	1.14
	TN2_N3P3_1500	15.73	21.72	< 5	5.99	1.38
	TN2_N5P1_1100	1.42	< 0.5*	126	1.17	0.18
	TN2_N5P1_1500	< 0.5*	< 0.5*	188	0	1.0
	TN2_N8P1_1100	26.49	29.25	< 5	2.76	1.10
	TN2_N8P1_1500	26.49	20.98	< 5	5.51	0.79
20.02.2012	TN1_N1P1_1100	1.22	0.93	440	0.29	0.76
	TN1_N2P1_1100	11.19	4.62	80	6.57	0.41
	TN1_N2P2_1100	13.09	13.91	200	0.82	1.06

* for calculation, the value 0.25 (the middle between 0 and 0.5) was used

The ISE measurement for nitrate doesn’t show reliable results and can not be used to support the evaluation of the photometric measurement.

6.4.4 Discussion Nitrate Results of filtered and unfiltered Samples

The comparison of filtered and unfiltered samples showed less consistent results compare to ammonium and nitrite. Of the 14 measured samples in table 43, six values are having a coefficient between 0.75 and 1.15 and have a high accordance between filtered and unfiltered samples. The absolute deviation of sample N3P3_0900 and N1P1_1100 is so insignificantly small (0.3 mg/L), they can be seen as compatible. Based on the assumption that the measurement uncertainty of this measurement lies around 10 %, the deviation for N8P1_1500 can be explained and is therefore considered compatible as well. That leaves nine compatible results and five none compatible.

This means a general tendency that the filtered and unfiltered sample results are in accordance. Out of the five incompatible results only the samples N7OL1_1100 and N2P1_1100 showed a difference in concentration between filtered and unfiltered that can not be considered the same measurement range anymore (coefficient of 0.04 and 0.4). The two samples have a similar concentration of suspended solids (66 and 80 mg/L) and it is possible that particles have influenced the measurement. But it can not be taken for certain because other samples with a higher suspended solids concentration had very compatible results. There is also a possibility that the method for nitrate measurement was impaired and substances in the waste water effected the measurement which has lead to less accurate results with a higher uncertainty.

Overall, the results substantiate that there is no difference in concentration for nitrate between unfiltered and filtered results, because the deviations can be explained otherwise.

5.4.5 Nitrite Results of filtered and unfiltered Samples

14 samples on three different days from 14 locations were measured filtered and unfiltered with the photometric method and compared.

Table 46. Comparing Nitrite Results of Photometric Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
03.02.2012	TN2_N7OL1_1100	1.26	0.04	66	1.24	0.03
	TN2_N4P3_1100	0.02	0.08	76	0.06	4.0
	TN2_N4P4_1100	0.30	0.29	17	0.01	0.97
13.02.2012	TN2_N3P3_0900	0.11	0.11	9	0	1.0
	TN2_N3P3_1100	0.07	0.07	13	0	1.0
	TN2_N3P3_1300	0.89	0.89	14	0	1.0
	TN2_N3P3_1500	0.90	0.89	< 5	0.01	0.99
	TN2_N5P1_1100	0.01	0.09	126	0.08	9.0
	TN2_N5P1_1500	0.16	0.13	188	0.03	0.81
	TN2_N8P1_1100	0.43	0.43	< 5	0	1.0
	TN2_N8P1_1500	0.39	0.38	< 5	0.01	0.97
20.02.2012	TN1_N1P1_1100	0.11	0.11	440	0	1.0
	TN1_N2P1_1100	1.16	0.06	80	1.10	0.05
	TN1_N2P2_1100	0.30	0.36	200	0.06	1.2

6.4.6 Discussion Nitrite Results of filtered and unfiltered Samples

The findings for nitrite in Tra Noc are generally very low with almost all results far below 1.0 mg/L. This naturally leads to a high relative deviation with just small differences between the absolute results.

Of the 14 measured samples, ten comparisons were in very high accordance between the filtered and unfiltered sample with a coefficient between 0.8 and 1.2 and a absolute deviation not more than 0.6 mg/L. As well as already for ammonium and nitrate, there can't be a connection established between the suspended solids and the deviating findings of nitrite. The four values with higher deviations standing out, N7OL1_1100, N4P3_1100, N5P1_1100 and N2P1_1100, were not the same that were standing out for ammonium. This confirms the assumption that the measured suspended solid concentration can not be used as a reference.

As for the results of the two samples N4P3 and N5P1, where the coefficients were 4.0 and 9.0, the nitrite concentration is in such a low range that the difference probably can be explained by the inaccuracy of the method. The inaccuracy increases in the lower calibration range. The absolute deviation is only 0.06 and 0.08 mg/L.

Looking at the two other results that were noticeable, N7OL1 and N2P1, the filtered values are significantly higher than the unfiltered and the suspended solid concentration were still rather low in concentration. The sample N2P1_1100 was measured twice for filtered and unfiltered. The first time with a dilution factor 10 and the extinctions measured were out of range. The extinction of the filtered sample was above the calibrated range and the extinction of the unfiltered sample was below. That allows the assumption that the final results measured with no dilution for the filtered and the dilution factor 20 for the unfiltered sample are correct. It can only be speculated what has influenced the measurement and had lead to the difference in concentration. It could have been the particles, maybe in combination with a colouration of the sample.

At the end it is also questionable how important it is for the parameter nitrite to research the reason for the deviations in the method as long as the results are coming out so low and the values are not making any difference for the planning and maintaining a waste water treatment system.

The results for nitrite show a very high accordance between filtered and unfiltered samples. It can be said that it is fully dissolved in the liquid phase and that there is no loss if the sample is filtered before measurement.

6.4.7 Total Nitrogen Results of filtered and unfiltered Samples

24 samples on three different days from 24 locations were measured with the photometric method and compared.

Table 47. Comparing Total Nitrogen Results of Photometric Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
07.02.2012	TN2_N7OL1_0900	35.64	32.24	95	3.4	0.90
	TN2_N7OL1_1100	30.68	26.31	66	4.37	0.86
	TN2_N7OL1_1300	34.57	37.48	65	2.91	1.08
	TN2_N7OL1_1500	40.88	33.60	93	7.28	0.82
	TN2_N4P3_1100	17.96	25.63	76	7.67	1.43
	TN2_N4P3_1500	22.33	27.67	80	5.34	1.24
	TN2_N4P4_1100	15.24	13.97	17	1.27	0.92
	TN2_N4P4_1500	15.62	45.84	16	30.22	2.93
13.02.2012	TN2_N3P3_0900	17.76	13.56	9	4.20	0.76
	TN2_N3P3_1100	17.07	19.18	13	2.11	1.12
	TN2_N3P3_1300	31.85	50.50	14	18.65	1.59
	TN2_N3P3_1500	51.84	98.08	< 5*	46.24	1.89
	TN2_N5P1_1100	76.32	69.91	126	6.41	0.92
	TN2_N5P1_1500	98.28	35.04	188	63.24	0.36
	TN2_N8P1_1100	67.78	67.00	< 5*	0.78	0.99
	TN2_N8P1_1500	90.31	61.75	< 5*	28.56	0.68
20.02.2012	TN1_N1P1_0900	11.13	15.71	570	4.58	1.41
	TN1_N1P1_1100	21.73	55.65	440	33.92	2.56
	TN1_N1P1_1300	19.58	20.37	392	0.79	1.04
	TN1_N1P1_1500	8.62	2.93	10	5.69	0.34
	TN1_N2P1_1100	27.28	24.95	80	2.33	0.91
	TN1_N2P1_1500	30.68	31.17	56	0.49	1.02
	TN1_N2P2_1100	52.25	50.50	200	1.75	0.97
	TN1_N2P2_1500	19.41	17.08	64	2.33	0.88

6.4.8 Discussion Total Nitrogen Results of filtered and unfiltered Samples

As stated before the unfiltered results for the parameter total nitrogen are expected to be higher since it is suspected that the filtration results in a loss of organic nitrogen which is bound within the particles. It's the objective of this measurement to find out if the current practiced measurement of filtered samples is actually delivering accurate results.

More than half (13 out of 24) of the filtered values found in table 45 were higher than the unfiltered, which was not to be expected. Out of these 13 values, eight results are in a close range to each other and show a high compliance (coefficient between 0.85 and 1.25). All together 12 filtered and unfiltered samples comply very well. Which leaves the question open, if there is a loss of total nitrogen after filtering. An investigation of the twelve less complying values showed five results with a higher concentration for the filtered samples. The contemplation of the suspended solids doesn't lead to a relation that could confirm with no doubt the loss of data because of particles that influence the photometric measurement. It can also not be confirmed that there is a higher total nitrogen concentration in the unfiltered sample if the suspended solids concentration is high (cf. sample N3P3_1500 and N1P1_1100).

It can be speculated that about half of the time, depending on the location, the difference between filtered and unfiltered sample for total nitrogen is insignificant and filtering therefore doesn't make a difference. In the other half of the measurements either the digestion was insufficient and the particles in the sample resulted in a loss owed to the photometric measurement; or the measurement was accurate and the concentration in the unfiltered sample is truly by far higher than in the filtered. That would mean the filtered sample result is not mirroring the actual concentration which is much higher. In that case the photometric method could not be used. To come to a final conclusion more comparing measurements are recommended.

6.4.9 Orthophosphate Results of filtered and unfiltered Samples

10 samples on three different days from 10 locations were measured with the photometric method and compared.

Table 48. Comparing Orthophosphate Results of Photometric Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
07.02.2012	TN2_N7OL1_1100	10.41	9.96	66	0.45	0.96
	TN2_N4P3_1100	2.25	4.96	76	2.71	2.20
	TN2_N4P4_1100	3.81	2.91	17	0.90	0.76
13.02.2012	TN2_N3P3_0900	1.07	< 0.5*	9	0.82	0.23
	TN2_N3P3_1100	< 0.5*	0.58	13	0.33	2.32
	TN2_N5P1_1100	20.25	21.23	188	0.98	0.95
	TN2_N8P1_1100	12.05	11.60	< 5	0.45	0.96
20.02.2012	TN1_N1P1_1100	< 0.5*	4.07	440	3.82	16.28
	TN1_N2P1_1100	8.48	8.93	80	0.45	1.05
	TN1_N2P2_1100	8.98	7.50	200	1.48	0.85

* for calculation the value 0.25 (the middle between 0 and 0.5) was used.

6.4.10 Discussion Orthophosphate Results of filtered and unfiltered Samples

The difference between filtered and unfiltered samples for the parameter orthophosphate is expected to be insignificant. For 50 % of the ten measurements it can be easily confirmed (table 46.) since the coefficient is lying between 0.85 and 1.05 which means deviations can be explained with the interval of uncertainty for the measurements. The concentrations of the samples N3P3_0900 and 1100 are in a low range (≤ 1 mg/L) and the inaccuracy of the method increases towards the lower end of the calibration range. These two results are therefore also seen as compatible. Sample N4P4_1100 has an absolute deviation of 0.9 mg/L which is considerably small. That makes it eight out of ten measurements where the filtered and unfiltered concentrations comply.

Only the results for N4P3_1100 and N1P1_1100 are standing out and the reason for the discrepancy can only be speculated. As a final conclusion it can be said that the measurement of filtered samples for orthophosphate doesn't underlie any loss in concentration because of the filtration.

6.4.11 Total Phosphorus Results of filtered and unfiltered Samples

24 samples on three different days from 24 locations were measured with the photometric method and compared.

Table 49. Comparing Total Phosphorus Results of Photometric Method for Filtered and Unfiltered Results

	Sample	Result, filtered [mg/L]	Result, unfiltered [mg/L]	Suspended solids [mg/L]	Deviation absolute [mg/L]	$k_{uF/F}$
07.02.2012	TN2_N7OL1_0900	18.77	23.69	95	4.92	1.26
	TN2_N7OL1_1100	14.26	15.66	66	1.40	1.10
	TN2_N7OL1_1300	27.46	29.75	65	2.29	1.08
	TN2_N7OL1_1500	15.00	21.64	93	6.64	1.44
	TN2_N4P3_1100	5.25	7.21	76	1.96	1.37
	TN2_N4P3_1500	5.57	6.97	80	1.40	1.25
	TN2_N4P4_1100	6.15	14.43	17	8.28	2.35
	TN2_N4P4_1500	5.90	7.62	16	1.72	1.29
13.02.2012	TN2_N3P3_0900	1.70	0.94	9	0.76	0.55
	TN2_N3P3_1100	1.32	1.17	13	0.15	0.89
	TN2_N3P3_1300	12.38	12.79	14	0.41	1.03
	TN2_N3P3_1500	11.64	12.13	< 5	0.49	1.04
	TN2_N5P1_1100	34.10	35.08	126	0.98	1.03
	TN2_N5P1_1500	22.95	21.97	188	0.98	0.96
	TN2_N8P1_1100**	(16.93)	(16.52)	< 5	(0.41)	(0.98)
	TN2_N8P1_1500	16.48	17.21	< 5	0.73	1.04
20.02.2012	TN1_N1P1_0900	< 0.5*	1.74	570	1.49	6.96
	TN1_N1P1_1100	< 0.5*	29.26	440	29.01	117.04
	TN1_N1P1_1300	1.52	9.26	392	7.74	6.09
	TN1_N1P1_1500	< 0.5*	24.02	10	23.77	96.08
	TN1_N2P1_1100	18.44	19.26	80	0.82	1.04
	TN1_N2P1_1500	22.95	19.67	56	3.69	0.86
	TN1_N2P2_1100	15.90	27.05	200	11.15	1.70
	TN1_N2P2_1500	0.87	2.01	64	1.14	2.31

[*] for calculation the value 0.25 (the middle value between 0.5 and 0) was used.

[**] out of range

6.4.12 Discussion Total Phosphorus Results of filtered and unfiltered Samples

The parameter total phosphorus was expected to have higher findings in the unfiltered samples. This can be confirmed for 19 out of the 24 measured samples (cf. table 47.). The five samples, where the values for the unfiltered samples are lower, were having compatible results with a coefficient close to 1 or, if in a lower concentration range, a small absolute deviation.

In total there are eleven complying results within close range of each other and a coefficient between 0.85 and 1.1. The other 13 samples showed anything from small (1.1 mg/L) to big differences (29 mg/L) in concentration between the filtered and unfiltered measurement. As already for the other parameters concluded, no relation between suspended solids and the measurement outcome for total phosphorus can be determined. The difference between filtered and unfiltered sample was sometimes high and sometimes low, independently of the suspended solids concentration. That makes it difficult to come to any conclusion. The mostly higher unfiltered sample values indicated that the photometric measurement was not impaired by particles. It additionally indicates that for some samples there can be a significantly high and unpredictable loss of phosphorus concentration if the sample is filtered. To come to a final conclusion more comparing measurements are recommended.

6.5. Evaluation of Methods to Preserve Analytes in Samples

The composition of the waste water at the many sampling locations in Tra Noc during the monitoring activities in 2011 and beginning 2012 was unknown and the concentration of the different parameters could not be predicted. Hence, for every sample and every parameter the right dilution needed to be determined. For many samples it meant at least one repeated measurement. If the quality standards (standard and tube test measurement as reference values) weren't met, the complete measurement series needed to be repeated. This was very time consuming and the measurements were time crucial because the analytes in the sample can change quickly. Ideally the samples were analysed within hours after sample taking. The amount of samples, the repetition measurements and the personnel capacity made it impossible to get all results of all parameters within the same day.

In order to find out if there could be a bigger time frame for the analysis, sample preservation methods were tested. Currently all samples are preserved by filtering them with a 45 µm membrane filter after sample taking and storing them in a refrigerator at approximately 8 ºC. The samples were often measured after several days of sample taking.

In Literature it can be found that the preservation of samples is generally difficult and no method has proven certain. It always depends on the circumstances which in the case of the laboratory in Tra Noc are especially the climatic conditions.

According to the American Water Works Association the sample can be preserved as follows: [34]

Ammonium

Refrigerate at 4 ºC for 24 hours or preserve samples for up to 28 days by lowering the pH to 2 or less with concentrated sulphuric acid.

Nitrate

Refrigerate at 4 ºC for 48 hours or preserve unchlorinated samples concentrated sulphuric acid and store at 4 ºC. NOTE: When sample is preserved with acid, nitrate and nitrite can not be determined as individual.

Nitrite

Never use acid preservation. Make the determination promptly on fresh samples to prevent bacterial conversion of nitrite to nitrate or ammonium. For short-term preservation for 1 to 2 days, freeze the sample at −20°C or store at 4°C.

Orthophosphate

Never use acid preservation. Preserve sample by freeing at or below – 10 ºC.

Total Phosphorus

Preserve samples by lowering the pH to 2 or less with concentrated sulphuric or chloric acid and store at 4 ºC, or freeze without any addition.

In this experiment the samples for the measurement of ammonium, nitrate, nitrite and orthophosphate were first filtered and then divided into three parts. One part was kept refrigerated at 6 to 8 ºC, a second part had approx. 0.5 % sulphuric acid added until a pH value below 2 and was kept in the refrigerator as well. The third part was stored in a freezer and defrosted just before measurement. The same was done for the total nitrogen and the total phosphorus preparation only without the filtering. The samples for the ammonium measurement were neutralized again before determination using a 1.5 molar sodium hydroxide (NaOH) solution. Each sample was measured for each parameter at the day of sample taking and the value of this measurement was referred to as T_0. The refrigerated samples were analysed again after 24 hours, 48 hours, 7 and 14 days. The frozen samples were analysed after 48 hours and 7 days.

6.5.1 Ammonium Results for Preservation Methods

The samples were taken on the same day (07. Jan. 2012) at three different locations. Owing to a capacity bottleneck the measurements started on the 08. Jan. which is when T_0 was determined.

Table 50. Comparison of Ammonium Results for Preservation Methods

Sample	T_0 Result [mg/L]	T_{1d} Result [mg/L]	T_{2d} Result, [mg/L]	T_{7d} Result [mg/L]	T_{14d} Result, [mg/L]
TN2_N7OL1_1100	17.80	18.63	18.95	12.88	11.93
TN2_N7OL1_1100_H_2SO_4	-	10.02	23.44	17.15	13.80
TN2_N7OL1_1100_fr	-	-	21.80	10.43	-
TN2_N4P3_1100	21.74	25.21	15.04	-	3.51
TN2_N4P3_1100_H_2SO_4	-	10.84	27.67	21.25	15.51
TN2_N4P3_1100_fr	-	-	24.56	14.24	-
TN2_N4P4_1100	3.29	3.54	4.50	3.88	2.31
TN2_N4P4_1100_H_2SO_4	-	1.20	5.22	4.32	20.63
TN2_N4P4_1100_fr	-	-	4.28	2.51	-

6.5.2 Discussion of Preservation Results for Ammonium

The current method results showed for all three samples a small increase after the first day and the tendency to decrease after 7 to 14 days (table 48.). For sample N4P3 the change in concentration is not as significant as it is for the other two samples with higher T_0 concentration. The concentration in N4P3 decreases about 1 mg/L after two weeks with a starting point of 3.3 mg/L. The sample N7OL1 started with 17.80 mg/L and decreased after two weeks to 11.9 mg/L. The findings for sample N4P3 after 14 days are only a fraction of the former concentration. The concentrations decreased from 21.7 to 3.5 mg/L. But with only one measurement of a sample in a low range it can not be concluded that the change in smaller concentration will be small, too.

The samples that had sulphuric acid added don't show any consistency and the concentrations were bouncing up and down over time. One problem that occurred and could be partly responsible of the inconsistent results was the neutralisation of the sample. Adding the sodium hydroxide solution resulted in a significant dilution of the sample (up to the factor 2). The dilution factor was always a uneven number and not determined fully accurate which probably lead to an unknown measurement error. This preservation method was also very time consuming because of the neutralisation. Overall, the preservation of samples by adding sulphuric acid did not come to a satisfying result for the parameter ammonium.

The frozen samples seem to stay in the same but increased concentration range at least until the second day and then decrease towards the seventh day. For the first two days it appeared that the deviation in concentration for the current method and the frozen samples didn’t exceed the expected uncertainty interval of the current method, and therefore the analysis of ammonium within the first two days of sample taking seemed to have come to acceptable results if the sample was frozen after sample taking.

6.5.3 Nitrate Results for Preservation Methods

The samples were taken on the same day at three different locations.

Table 51. Comparison of Nitrate Results for Preservation Methods

Sample	T_0 Result [mg/L]	T_{1d} Result [mg/L]	T_{2d} Result, [mg/L]	T_{7d} Result [mg/L]	T_{14d} Result, [mg/L]
TN2_N7OL1_1100	5.46	8.27	3.32	2.41	5.98
TN2_N7OL1_1100_H_2SO_4	-	10.88	3.82	3.79	9.21
TN2_N7OL1_1100_fr	-	-	4.15	6.14	-
TN2_N4P3_1100	< 0.5	5.15	0.97	< 0.5	0.64
TN2_N4P3_1100_H_2SO_4	-	4.39	0.62	< 0.5	0.83
TN2_N4P3_1100_fr	-	-	0.72	0.64	-
TN2_N4P4_1100	6.14	9.79	5.88	5.67	7.77
TN2_N4P4_1100_H_2SO_4	-	8.22	5.59	6.37	7.36
TN2_N4P4_1100_fr	-	-	5.90	5.57	-

6.5.4 Discussion of Preservation Results for Nitrate

The concentrations of the current method and the concentration of the samples which had sulphuric acid added, were underlying unpredictable changes. They all increased after 24 hours and seemed to develop similar over time. Both don’t appear trustworthy – one day the values comply well and the next the changes are significantly (cf. table 49.). On the contrary the frozen samples seem to stay in a close range to the actual T_0 results even after 7 days. If the concentration in the frozen samples also increased at T_{1d} like the others did, can not be said because no measurement was made. It can be suspected that the frozen samples for the parameter nitrate deliver accurate results between two and seven days after sample taking.

6.5.5 Nitrite Results for Preservation Methods

The samples were taken on the same day at three different locations.

Table 52. Comparison of Nitrite Results for Preservation Methods

Sample	T_0 Result [mg/L]	T_{1d} Result [mg/L]	T_{2d} Result, [mg/L]	T_{7d} Result [mg/L]	T_{14d} Result, [mg/L]
TN2_N7OL1_1100	1.26	> 0.2	3.76	3.71	0.26
TN2_N7OL1_1100_H_2SO_4	-	0.19	0.18	0.10	0.01
TN2_N7OL1_1100_fr	-	-	0.59	0.58	-
TN2_N4P3_1100	0.02	0.02	0.20	0.14	0.13
TN2_N4P3_1100_H_2SO_4	-	< 0.01	< 0.01	< 0.01	0.01
TN2_N4P3_1100_fr	-	-	0.03	0.03	-
TN2_N4P4_1100	0.30	0.21	0.29	0.28	3.33
TN2_N4P4_1100_H_2SO_4	-	0.06	0.15	0.10	0.03
TN2_N4P4_1100_fr	-	-	0.30	0.28	-

6.5.6 Discussion of Preservation Results for Nitrite

The concentrations of the samples measured with the current method are changing unpredictably. There was first a significant decrease for sample N1OL7 from 1.3 to below 0.2 mg/L after 24 hours. One day later, after 48 hours there was a high increase to about 3.7 mg/L before it decreased severely some time after day seven to 0.3 mg/L. For sample N4P3 the results comply after the first day and then increased from 0.02 to 0.2 mg/L. The sample N4P4 showed another behaviour. It complied with the T_0 value until the seventh day before it increased significantly to 3.3 mg/L.

The added acid seemed to have the effect of a decreasing concentration, which can be observed in all three samples. This preservation method as well as the current method can be bowed out as a way to preserve the nitrite concentration in a sample.

The frozen sample results comply very well for sample N4P3 and N4P4. The concentration of sample N7OL1 after day 2 and day 7 comply also very well, but are only about half the concentration of the T_0 value of this sample. There is an indication that freezing the samples is a way of preservation that will deliver highly accurate results for at least seven days after sample taking. To confirm this indication more measurements are necessary because the data at hand is not sufficient as proof.

6.5.7 Total Nitrogen Results for Preservation Methods

The parameter total nitrogen was measured with unfiltered samples because it was expected that the unfiltered samples would deliver the concentration without any loss from the filtering process. As it turned out, the measurement of unfiltered samples didn't deliver reliable results. Therefore the findings of this measurement can not be validated owing that it can not be confirmed that any of the measured values are reliable and accurate.

6.5.8 Phosphorus Results for Preservation Methods

The samples were taken on the same day at three different locations.

Table 53. Comparison of Orthophosphate Results for Preservation Methods

Sample	T_0 Result [mg/L]	T_{1d} Result [mg/L]	T_{2d} Result, [mg/L]	T_{7d} Result* [mg/L]	T_{14d} Result, [mg/L]
TN1_N1P1_1100	< 0.5	< 0.5	< 0.5	(4.54)	< 0.5
TN1_N1P1_1100_H_2SO_4	-	< 0.5	< 0.5	(2.17)	< 0.5
TN1_N1P1_1100_fr	-	-	< 0.5	(1.82)	< 0.5
TN1_N2P1_1100	8.48	8.61	12.83	(11.80)	11.84
TN1_N2P1_1100_H_2SO_4	-	3.48	6.07	(5.98)	7.21
TN1_N2P1_1100_fr	-	-	9.75	(7.46)	5.29
TN1_N2P2_1100	8.98	9.84	10.41	(10.16)	10.78
TN1_N2P2_1100_H_2SO_4	-	6.97	6.15	(3.16)	8.24
TN1_N2P2_1100_fr	-	-	8.48	(6.07)	6.60

* Standard 1 mg/L was 0.64 mg/L

The concentration of orthophosphate in the sample N1P1 is below the minimum measurable quantity. There might be even no orthophosphate at all in the sample. It can not be validated.

The values of the measurement of day seven can not be confirmed to be accurate because the measurement does not meet the quality assurance criteria stated under 4.3. This doesn't leave enough data to evaluate whether or not the samples can be preserved for the orthophosphate measurement.

Even though with only this small amount of data at hand it is noticeable that the orthophosphate concentration seems to have increased over time. This leaves room for speculation that total phosphorus was biologically decomposed to orthophosphate. More measurements are recommended to come to a sustainable conclusion.

The data available for the evaluation of total phosphorus is likewise not sufficient. The samples were measured unfiltered. The result for N1P1 at T_0 is assumed to be false which leaves no reference to compare the following measurements with. The measurements on day 7 and 14 can not be confirmed accurate either because they don’t meet the quality assurance criteria. Two samples measured on two different days is not enough data to come to any conclusion.

7 Conclusion

The evaluation and validation of the monitoring activity results confirmed all the current photometric methods used in the laboratory in Tra Noc were suitable. Validating the methods was problematic as the samples that were taken, can only be seen as grab samples. No more than two samples from the same location were taken over a period of up to six weeks. The findings for each parameter at the same locations were sometimes in a close range to each other and other times, differed severely. The variation in results can be attributed to various reasons namely:

- The waste water may have been diluted by either heavy rainfall or the tidal influence of the receiving water bodies. At high tide the water from the Hau River or the attached channels entered the drainage system.
- The composition of the waste water discharged by the enterprises could have changed during the course of the day or over time owing to production processes and volume.
- Errors occurred in the analytical process e.g. interchanged samples or outlier

The effect on the concentration due to dilution can be mostly eliminated ase the samples were taken during the dry season and sampling was postponed on days with heavy rainfall. The days and times of sample taking were also pre-decided with the projects engineer, who was monitoring the water levels in the drainage system to minimize tidal influence on the samples. The change in composition of the waste water remained unknown and it is therefore difficult to impossible to know whether the findings differed because of the change in the enterprises discharge or owing to of errors made during analyses.

To ensure that no measurement errors occurred, the plausibility was investigated and samples were re-evaluated if findings stood out, e.g.:

- significant changes in concentration for one location,
- unusual high or low findings based on experience and
- unplausible findings

The outcome of the investigation of plausibility was consistently positive. Out of the 68 samples measured, only two results of the nitrogen compounds were identified as unplausible. This equates to 3 % of unplausible results. For the plausibility of phosphorus compounds one result was confirmed as unplausible. Out of these three unplausible results two were from the same sample N6OL1_1100 which was identified as unreliable. The plausibility of the results was highly confirmed but doesn't fully confirm good analytical practice. The methods accuracy still needs to be investigated.

The problem verifying the accuracy of the methods was, that the samples used were real samples with an unknown concentration of analyte, and that every sample was only measured once i.e. no repeated measurements were made.

As a reference point, the coefficient of determination (R^2) of the calibration function, as well as the reference values of the standard and tube test measurements were used. The coefficient of determination is a measure for the performance of adaptation. Since it is known that the parameters show a linear behaviour within the calibrated ranges, it can be said that a high coefficient verifies a high accordance with the regression curve. The analytical practice aims for a coefficient of 0.999. The coefficients of determination never fell below 0.995. This is generally a very good result but it can not be attached to much importance to the coefficient of determination as it still doesn't reveal the accuracy of the method. However, it does prove the measurements were made with diligence.

Now, the very good accordant standard measurements also confirm the precise mode of operation and that the methods, as developed, were delivering reliable results. The state of accuracy can be investigated by using another already validated method. The nanocolor tube test kits provided a validated method where the distributer declared an uncertainty of ± 3 %. The outcome of the comparison of the tube test and photometricly measured results are as follows:

Ammonium:	Four tube tests were made and three of them confirmed the photometricly measured values. The fourth tube test result was 9.4 mg/L compared to 13.2 mg/L.
Nitrate:	Only one tube test was made and it confirmed the photometricly measured value.
Nitrite:	Two tube test and they confirmed the photometricly measured value.

Total Nitrogen: Five tube tests were made and three of them confirmed the photometricly measured values. The fourth tube test result was 11.0 mg/L compare to 14.9 mg/L and the fifth was 4.0 to 8.8 mg/L.

Orthophosphate: Four tube tests were made where three confirmed the photometricly measured values. The fourth tube test result was 11.1 mg/L compared to 8.5 mg/L.

Total Phosphorus: Four tube tests were evaluated in which two of them confirmed the photometricly measured values. The third tube test result was 16.2 mg/L compared to 22.0 mg/L and the forth was 13.1 to 18.8 mg/L.

Between one and five data sets were available for each method to investigate the particular accuracy. It needs to be mentioned that this was not enough data to allow a final statement. However, what can be said is that most of the results showed a high accordance. The data sets that didn't meet the requirement of a deviation less than 15 % can nevertheless be considered in the same measurement range. The uncertainty of the photometric methods is an assumed 15 % but it is also possible that it may be higher, depending on the parameter, which would explain most of the differing data sets. It is therefore recommended to collect more data and establish the uncertainty and precision of the methods. More data sets of tube test and photometric method results (at least 10 per method) including repeated measurements also need to be compared.

Irrespective of the afore mentioned difficulties none of the measures taken to investigate the accuracy and reliability of the methods has given reason to doubt that the methods are nothing but suitable for their purpose. The Author believes if further investigations were followed, the outcome would be in a good accordance between the validated tube test and the current laboratory methods.

Within the validation process, the photometric method for the parameter ammonium and nitrate was compared with ISE measurements. The ISE measurement is not a validated method and for nitrate, the results of both methods didn't comply at all. The evaluation resulted in false ISE determinations because the values didn't withstand the plausibility check. For ammonium on the other hand, the results of both methods were in good accordance, which supports the assumption of the suitability of the current methods.

Furthermore, the influence of the sample preparation on the concentration value for all parameters were investigated. It was suspected that filtering the samples with a membrane filter results in a loss of concentration for total nitrogen and total phosphorus but not for ammonium, nitrate, nitrite and orthophosphate. The concentration of suspended solids was used as a reference to investigate if part of the analyte is bound to particles in the sample and would be eliminated by filtering.

The evaluation of the measurement of filtered and unfiltered samples showed no indication that the concentration for ammonium, nitrate, nitrite and orthophosphate would result in a lower, false concentration. The evaluation of total nitrogen and total phosphorus was inconclusive. For none of the parameters a relation between the suspended solids and the gained values could be established. The reason for this purpose might be incorrect suspended solids results owing to measurement errors during the analysis e.g. the particles sedimented on the bottom of the container and the sample wasn't shaken before filtering. Another reason which most likely has influenced many of the determinations was the interference of particles with the photometric measurement. A repeated investigation is recommended. It needs to be ensured that the suspended solids results are reliable by validating the method and that no particles might influence the photometric measurement. A suitable digestion for total nitrogen and total phosphorus needs to be determined which can be found within the DIN norm of the parameter.

The last part that was investigated within the validation process, were preservation methods, as immediate analysis of the samples wasn't always possible. The specifics published by the American Public Health Association, American Water Works Association and the Water Environment Federation provided the basis for the experimental set up. Each sample was acidified, kept frozen and refrigerated. It turned out that none of the recommended preservation methods could be confirmed as reliable to contain any of the analytes over a longer period of time unchanged in the sample. This does not mean that preserving samples must be eliminated as invalid. The data determined in this work was often inconclusive and mostly insufficient. Only three samples were investigated and for total nitrogen and total phosphorus unfiltered samples were used. The experiments comparing filtered and unfiltered samples as well as preserving samples took place at the same time. At this point it was expected that the unfiltered samples would deliver the correct concentration for total nitrogen and total phosphorus. Unfortunately this could not be confirmed and the unfiltered sample results were proven unreliable. Therefore no evaluable data was available for these two parameters.

Acidifying the samples appeared to not work for any of the other parameter. For nitrite and orthophosphate, it confirms the information found in literature that added acid would lead to changes in the sample. Ammonium and nitrate are supposed to be preservable with sulphuric acid but this could not be confirmed as the data at hand also did not indicate that it could. The best results were attained with freezing the samples. The results of ammonium, nitrate, nitrite and orthophosphate indicated that freezing the sample might preserve the analyte over days or maybe even weeks. It is recommended to set up a new investigation using more samples, following meticulously the timeline of analysis and meeting the refrigerator temperature requirements of 4 ºC instead of the current 6 – 8 ºC.

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Appendix (see CD-ROM)

I. Calibrations

II. Evaluation Monitoring Activities 2012

III. Evaluation Experiment 1_ISE

IV. Evaluation Experiment 2_filtered/unfiltered Samples

V. Evaluation Experiment 3_Preservation Methods

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Place, Date Signature