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DEPARTMENT OF CHEMISTRY

DIPLOMA THESIS

Evaluation of efficiency of wastewater treatment process in Prague city treatment plant.

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2015

DECLARATION

I declare that I have written my diploma thesis “Evaluation of efficiency of wastewater treatment process in Prague city treatment plant” on my own with the help of literature listed in References.

In Prague 10th April 2015

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ACKNOWLEDGEMENTS

I would like to express my gratitude to Prof. Ing. Jaromír Lachman, CSc, whose expertise, understanding, and patience, added considerably to my graduate experience.

A very special thanks goes to Ing. Matyáš Orsák, Ph.D, whose motivation and encouragement have enabled to finish this work. Dr. Orsák is the one professor who truly made a difference in my life. He provided me with direction, technical support and has became more of a mentor and friend, than a professor. I doubt that I will ever be able to convey my appreciation fully, but I owe him my eternal gratitude.

I want to say thank you to, Ing. Daniela Miholová, CSc, Ing. Miloslav Sulc, PhD, Ing. Marek Popov. They have assisted me in lab-work and helped me to find things that were needed for my experiments.

Finally, I wish to thank my family, for supporting me, and for believing in everything I do.

Student

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Summary

This study aims to evaluate the efficiency of wastewater treatment at Prague Waste wastewater treatment plant (Prague WWTP) through analysing the influents and effluents for the period from March to December 2014. Two samples were taken on monthly basis for each; influents and effluents, and selected indicators were measured in two reputations. Results were compared to small WWTP close to Prague in order to remark our results. Results were obtained from the Small WWTP for the same period.

Data were statistically contrasted and analysed to test the hypothesis; complying with the required limits, whether inflow contamination plays a key role for effluents concentration, and fluctuation through different climatic seasons through the year. Data from CULS meteorological station were used to test the possible effects on wastewater composition during storm events. Average removals were compared for different parameters.

It was found that the discharged effluents samples were complying with the standards set by regulating authorities in EU. The average removal for chemical oxygen demand (COD) was found to be 73 % for Prague WWTP compared to 95 % for the small WWTP. Ammonium and nitrite removal was 87 % and 56 % for Prague WWTP respectively, whereas ammonium and total N was 99.6 %, 85 % for the small WWTP respectively. Phosphate ions removal was 72 % for Prague WWTP, while for the small WWTP total Phosphorous was found to be 97 %. From these results we can say that removal efficiency in the small WWTP was better than Prague WWTP.

The correlation between effluents and influents concentration was tested in the selected parameters and only conductivity, COD, nitrites, chlorides and acid capacity have witnessed strong positive correlation. On the other hand, no significant correlation was found for the results from the small WWTP except ammonium content which witnessed strong positive correlation between inflow and outflow.

Strong positive correlations were existing between the indicators in the analysed influents samples for Prague WWTP; i.e., between conductivity and both of pH, chlorides and phosphate. In contrast, small WWTP influents' samples witnessed strong positive correlation between organic load parameters, such as ammonium, COD, BOD, total N and total P.

Key words: sewage treatment; waste water; NH_4^+, NO_2^-, NO_3^-, total phosphorous; COD; dissolved inorganic salts

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Section 1: Introduction

Municipal wastewater contains pollutants such as heavy metals, organic load and trace organic compounds from households and industrial sources (Sorme & Lagerkvist, 2002; Wilkie, Hatzimihalis, Koutoufides, & Connor, 1996). In a broad perspective, municipal wastewater or sewage can be defined as a combination of domestic effluents, either dissolved or as suspended matter (Rachid et al., 2008). Principal producers of wastewater are municipal (urban) areas; therefore, providing a high quality and effective sewer service to these areas involves carefully planning and adequate treatment (UN,ESA, 2005). There are many direct impacts of wastewater treatment processes, it affects on public health and environment and involve large amounts of energy consumption. The main purpose of a municipal WWTP is to minimize or eliminate the negative impacts of sewages (Abusoglu, Demir, & Kanoglu, 2012).

In the past, domestic wastewater treatment was basically confined to organic carbon removal. In recent years, increasing pollution in the receiving waters and more stringent effluent requirements for discharges to water surface bodies and sensitive zones have been the driving force in developing and implementing new treatment techniques to control, in addition to carbon, other significant parameters such as nitrogen, phosphorus, and priority pollutants. This new approach for wastewater management has greatly affected the concept of wastewater characterization (Orhon, Ateş, Sözen, & Cokgör, 1997). Pollutants are present in wastewater and sludge in a variety of forms; dissolved, exchangeable, attached to organic matters, occluded or co-precipitated with oxides, as carbonates and phosphate, ion crystals, and assimilated in biomass (Sterritt and Lester, 1984; Stasinakisa and Thomaidisb, 2010).

Section 2. Objective of Thesis

The aim of diploma thesis is to evaluate the wastewater treatment process in Prague city treatment plant.

Hypothesis:

1) The discharged effluents samples will conform to the required limits set by regulating authorities.

2) There will be fluctuation in selected required indicators and efficiency through different climatic seasons through the year.

3) There will be a correlation between the influents and effluents selected indicators which indicate that inflow contamination play key role for effluents concentration.

Chapter 2

Chapter 2: LITERATURE OVERVIEW

Section 2.1: Wastewater definition

Wastewater is the spent water after homes, commercial establishments, industries, public institutions, and similar entities have used their waters for various purposes. It is synonymous with sewage, although sewage is a more general term that refers to any polluted water (including wastewater), which may contain organic and inorganic substances, industrial wastes, groundwater that happens to infiltrate and to mix with the contaminated water, storm runoff, and other similar liquids. Certain sewage may not be spent water or a wastewater (A.P.Sincero& G.A.Sincero, 2003).

The keyword in the definition of wastewater is “used” or “spent”. That is, the water has been used or spent and now it has become wastewater. On the other hand, to become sewage, it is enough that water becomes polluted whether or not it had been used. When one uses the word wastewater, however, the meaning of the two words is blended such that they now often mean the same thing (A.P.Sincero & G.A.Sincero, 2003).

Section 2.2: The composition of wastewater

Wastewater is a complex mixture and can contain many types of contaminants. Domestic wastewater includes chemicals that are typically used in and discharged from the household. Grey wastewater is defined as wastewater without any input from toilets, which means that it corresponds to wastewater produced in bathtubs, showers, hand basins, laundry machines and kitchen sinks, in households, office buildings, schools, etc. The total grey wastewater fraction has been estimated to account for about 75 % volume of the combined residential sewage (Hansen & Kjellerup, 1994) mentioned by (Eriksson, Auffarth, Henze, & Ledin, 2002).

Wastewater is likely to carry pathogenic organisms that can transmit diseases to humans and other animals; contain organic matter that can cause odor and nuisance problems; hold nutrients that may cause eutrophication of receiving water bodies (McGraw-Hill, 2009) mentioned by (Kapshe, Kuriakose, Srivastava, & Surjan, 2013).

Even after treatment, wastewater discharges and the sewage sludge can contain a wide range of organic chemicals, and inorganic chemicals including metals and nutrients (Mathney, 2011).

Wastewater constituents can be broken down into three general categories:

Physical: thermal and solid properties.

Biological: pathogens, microbial ecology, biomarkers, and antibiotics.

Chemical: pH and alkalinity, ions and metals, fats, oils and grease (FOG), organics and nutrients, and micro-constituents.

Owing to the diurnal, seasonal, and regional fluctuations, wastewater characteristics can vary, becoming more or less concentrated with changing lifestyles, markets, weather patterns (Henze et al., 2002), or socioeconomic conditions (Campos and von Sperling, 1996), some of the most important characteristics are following in more details.

2.2.1-Physical

a. Solids

The solids characteristics can be influenced by wastewater source, region, or infrastructure. For example, the sewer lines in flat regions, such as the Netherlands, are more gradually sloped than those of alpine countries; as constituents enjoy a longer retention time in the pipes; more solids settle out or dissolve into the wastewater. On the other hand, sewer lines with steeper slopes encourage the oxidation of organic matter, whereas the anaerobic environment in less sloped pipes encourages hydrolysis. Solids concentration can also affect the viscosity of the wastewater, influencing its transport and dewatering properties (Nieuwenhuijzen, Kampschreur, & Mels, 2004).

b. Thermal

The thermal properties of wastewater, though variable by season and region, have a strong influence on treatment efficiency and resource recovery. The rate of chemical interactions tends to increase as temperatures rise, influencing bacterial growth and chemical metabolisms. In fact, some bacterial species will double their growth rate for each 10 ^{o}C increase in temperature, which may translate into faster or more efficient oxidation of organic matter or nitrification (Gerardi, 2006). However, cold water dissolves more oxygen than warm water; therefore, oxygen availability may be limited for oxidation or nitrification in warmer water (Metcalf and Eddy, 1991).

2.2.2-Biological characteristics

Treatment efficiency can be affected by biological characteristics, such as microbial ecology or antibiotics. Other constituents, such as pathogens, may influence the ability of wastewater products to be recovered and reused (Drexler et al., 2014).

2.2.3-Chemical characteristics

Chemical characteristics influence the treatment process, as they shape the environmental conditions for the biological community. Although nutrients and organic matter provide food for microorganisms, heavy metals or micro constituents may be toxic. From another aspect many chemical constituents, such as nitrogen and phosphorus, influence the quantity of recoverable products; and others such as cadmium or arsenic may also affect the quality of those products (Drexler et al., 2014).

a. General characteristics

Physical properties; such as the pH, alkalinity, and conductivity, which is influenced by the wastewater source.

pH: indicates the acidity or basicity of a solution, measured by the negative log concentration of H^+ ions. A low pH can inhibit biological treatment but a high pH can encourage ammonia volatilization or precipitation of compounds such as metal complexes. Alkalinity: typically measured as milligrams per liter of calcium carbonate, indicates the buffering capacity of a solution. High alkalinity may protect a biological community from pH shock but may delay pH adjustments for precipitation or flocculation (Eriksson et al., 2002).

Conductivity: indicates the ionic composition of wastewater by measuring how well a solution can carry an electric current. Although it does not differentiate between specific ions in a solution, conductivity can be used to determine the total dissolved solids (TDS) and gain a general understanding of water purity; a lower conductivity means a lower amount of ions, and therefore TDS, is present in the wastewater (Drexler et al., 2014).

b. Conventional ions and heavy metals

Ions may be positively or negatively charged as cations or anions, respectively. Some naturally occur in water and others result from the dissociation of salts and metal complexes or from the breakdown of organic material. Ions interactions, often influenced by pH, can cause precipitation or scaling within a treatment process. Similarly, precipitation can be encouraged as a means to recover resources such as struvite or heavy metals (Gerardi, 2006).

Total hardness: the concentration of divalent cations, such as calcium or magnesium, may be used to estimate the scaling potential of wastewater. Other ions may affect treatment or recovery opportunities. For example, when present in concentrations of 1–15 mg l^{-1}, sulfides may encourage the growth of filamentous bacteria, such as *Beggiatoa*, *Nosticoidalimicola*, and *Thiothrix*, which may lead to poor settling of activated sludge (Gerardi, 2006).

Risk elements: The total content and forms of risk elements vary widely according to the nature of the individual element and the physicochemical processes involved in sludge wastewater treatment (Volesky, 1987) mentioned by (Drexler et al., 2014). Risk elements are essential in small amounts to aid biological function (Gerardi, 2006), but high levels can become toxic, hindering biological treatment. Elements, such as aluminum, may be added during treatment to facilitate precipitation or flocculation. As elements can precipitate and settle with sludge, the concentration in biosolids may be too high for reuse as a fertilizer. Pretreatment of risk elements using membranes (Fane et al., 1992) or bio sorbents (Volesky, 1987) at concentrated sources can help improve resource recovery opportunities downstream mentioned by (Drexler et al., 2014).

Risk elements can inhibit aerobic and anaerobic biological treatment processes, thereby causing possible deteriorations in effluent quality and reduced rates of anaerobic sludge digestion (Kugelman & McCarty, 1965; Poon & Bhayani, 1971; USPHS, 1965) mentioned by (Nielsen & Hrudey, 1983). Katsoyiannis & Samara (2007) observed strong positive correlations in wastewater samples, for bioluminescence inhibition with biochemical oxygen demand (BOD), COD and suspended solids (SS) (0.730, 0.730 and 0.751, respectively). The significant correlation found for toxicity with BOD and COD suggests that a large part of the toxic load of wastewater is accompanied with organic load. Significant correlations between EC_{50} (half maximal effective concentration) and COD have been observed by other investigators (Guerra, 2001).

Metals discharged in the treated sewage can be toxic to aquatic life and can cause natural waters to be unsuitable as potable water sources (Environment Canada, 1979) mentioned by (Nielsen & Hrudey, 1983).

c. Fats, oils and grease (FOG), and detergents

These substances can be beneficial and detrimental to wastewater treatment efficiency and resource recovery. High concentrations of surfactants can negatively affect the ability of activated sludge organisms to form flocs, requiring supplementary additives to prevent effluent from exceeding permit requirements (Gerardi, 2006). Similarly, FOG can encourage the growth of filamentous bacteria, such as *Microthrixparvicellaor Nocardioforms*, causing foaming in the activated sludge process, increasing treatment and operational costs (Gerardi, 2006). FOG can also clog pipes, decreasing transport efficiency, and devaluing wastewater infrastructure. However, if fed directly to an anaerobic digester, FOG can boost methane production, thereby increasing energy recovery (Drexler et al., 2014).

d. Organic material:

Organic matter consists of proteins, carbohydrates, lipids, and other macromolecules. Owing to its complexity and variability, organic material is measured by its oxygen demand, that is, how much oxygen would be required to fully oxidise, or break down, its constituents, as shown in the oxidation equation below (Henze et al., 2002):

$$C_{18}H_{19}O_9N + 17.5\ O_2 + H^+ \rightarrow 18\ CO_2 + 8H_2O + NH_4^+$$

Removing oxygen demand from wastewater before discharge is critical to prevent receiving waters from going anoxic when dissolved oxygen is used to oxidize the incoming organic material (Drexler et al., 2014).

Section 2.3: Water quality parameters

2.3.1-COD& BOD

COD does not differentiate between biologically available and inert organic matter, and it is a measure of the total quantity of oxygen required to oxidise all organic material into carbon dioxide and water, while BOD is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. Increase in BOD or COD and SS indicates reduction in the available dissolved oxygen in the water body which at times may diminish to levels that are lethal for most fish and other aquatic life. The effectiveness of wastewater treatment can be measured by using the changes in COD before and after intervention (Kapshe et al., 2013).

Oxygen demand can be measured and reported in a number of ways which is useful for determining treatability and recovery opportunities. For example, as BOD is typically more easily biodegraded than COD, the COD:BOD ratio indicates the amount of the recalcitrant material present (Drexler et al., 2014). COD is a useful parameter for the modeling of biological kinetics as it sets electron equivalence of the substrate, biomass and oxygen requirement, but it reflects also biodegradable organics and residual components; BOD_5 is now regarded as a poor index of relatively easily biodegradable substrate. Consequently, BOD_5: COD ratio may be conceived as an acceptable index of biological treatability, or more accurately a rough proportion of easily and slowly biodegradable organic matter. Presence of organic and inorganic matter in water is commonly measured in terms of BOD_5, COD, SS and TDS (Orhon et al., 1997).

COD characterizing

Various methods have been proposed for characterizing the readily and slowly biodegradable organic fractions. One was proposed by (Ekama et al., 1986) mentioned by (Orhon et al., 1997), the flow through activated sludge process method, has proved to be efficient but requires a complex pilot plant. The principle is the measurement of the Oxygen Uptake Rate in an activated sludge process operated under daily cyclic square wave loading conditions.

Mathieu & Etienne (2000) studied French settled sewage, and found that readily biodegradable and slowly bio degradable represent around 8.5 % and 48 % of total COD respectively. Ayaz & Akça (2001) examined wet land sewage treatment method on pilot scale at the city of Istanbul were they found that COD and suspended solid removal efficiencies were obtained as 90 % and 95 %, respectively and the effluent COD concentration at an average loading of 122 g COD/m2 day was satisfactory for the Turkish Water Pollution Control Regulation.

Dulekgurgen et al. (2006); Hu et al. (2002) indicate that in accordance with microbial degradation kinetics, the soluble readily biodegradable COD fraction consists of relatively small biodegradable particles, which are easily transported across cell membrane and then metabolized in minutes. On the other hand, utilization of the particulate biodegradable COD and the soluble slowly biodegradable COD or the rapidly hydrolysable COD fractions takes longer since these constituents comprise larger particles and require extracellular breakdown prior to their transport into the cells for biodegradation. It can be observed in Table 1 that there is a clear improvement in COD when the raw sewage passes through treatment in four different WWTPs in Surat, India.

Table 1. COD improvement in four WWTP in Surat, India.

Name of STP	Month and year	Cod Raw sewage	Cod treated sewage
Anjana	Apr-11	674.4	74.0
	Aug-11	573.8	71
Bhatar	Apr-11	390.4	86.4
	Aug-11	354	81.2
Karanj	Apr-11	491.5	81.1
	Aug-11	536.3	69.9
Singanpore	Apr-11	535.1	233.3
	Aug-11	490.4	206.8

(Kapshe et al., 2013)

2.3.2-Nutrients

Conventional nitrogen removal occurs through nitrification and denitrification, releasing nitrogen gas to the atmosphere or settling organic nitrogen in bio solids. Phosphorus is similarly settled in bio solids.

a. Total nitrogen

It may be present in wastewater as organic nitrogen, or inorganic. Inorganic nitrogen compounds are common wastewater contaminants, i.e., nitrate (NO_3^-), nitrite (NO_2^-), or ammonium (NH_4^+). Total nitrogen includes all these species, whereas total Kjeldahl nitrogen includes just organic nitrogen and ammonia (Constituents et al., 2014).

Nitrogen removal is important in preventing a wide range of public-health and environmental impacts. Inorganic nitrogen can contribute to eutrophication in natural water bodies, like rivers and lakes. High concentration of ammonium considered toxic to aquatic organisms. Nitrate can be easily transformed into nitrite and nitrite is a dangerous cancer inducer and may cause the disease of methemoglobinemia in infants. High concentrations of nitrate and nitrite severely limit the utilization of groundwater for drinking purposes. Therefore, there is a great need to remove N-compounds from various types of water. Biological processes combining sequential nitrification and denitrification are commonly used for N-compounds removal. The process of denitrification involves the reduction of nitrate to nitrite by anaerobic facultative bacteria that utilize nitrate as electron acceptor. Denitrifying bacteria are generally heterotrophic and need organic matters as electron donor. Nowadays the most common approach for the removal of nitrogen is the heterotrophic denitrification, such as the anoxic/oxic process in most wastewater treatment plants as tertiary treatment (Zhou et al., 2011).

Zhou et al. (2011) examined autotrophic denitrification process with sulfur limestone as the electron donor to remove nitrate and nitrite, especially from the low concentration water. This method can be applied in many cases such as eutrophicated surface water, underground water, or wastewater treatment plant effluent. However, for the higher concentration nitrate and nitrite removal, longer hydraulic retention time was necessary. Requiring of no carbon source, nutrients or oxygen supply, autotrophic denitrification proved to be a cheap and easy-to-manage process. In his experiment Influent concentration, hydraulic retention time and temperature are important factors that affect the denitrification efficiency.

Aerobic Nitrifications of NH_4^+ to NO_3^-

$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + 2H_2O$

$NO_2^- + 0.5O_2 \rightarrow NO_3^-$

The anaerobic denitrification involves the following reactions

$2NO_3^- + 10H^+ + 10e^- \rightarrow N_2 + 2OH^- + 4H_2O$

$2NO_2^- + 6H^+ + 6e^- \rightarrow N_2 + 2OH^- + 2H_2O$

(Khin & Annachhatre, 2004)

b. Total phosphorus

Phosphorus is equally essential for cellular function, as it is an important component of ATP as well as other complex organic compounds. Phosphorus (P) enters municipal wastewater treatment facilities from both domestic and industrial sources. Domestic contributions come from human wastes and detergents. Total P includes orthophosphate, condensed phosphates, and organic phosphates, typically partitioned in wastewater as 50 %, 35 %, and 15 %, respectively. Phosphorus can be removed from wastewater by transforming it from a soluble form into a solid that can be removed by sedimentation.

Two widely used processes are chemical precipitation and enhanced biological removal (Parson &Smith, 2008).

Chemical precipitation, the most commonly applied process, can remove up to 90 % of all influent P. The chemical precipitation of phosphorus is brought about by the addition of the salts of multivalent metal ions that form precipitates of sparingly soluble phosphates. Three types of metal precipitant are generally used for chemical phosphorus removal namely iron (II), iron (III) and aluminum. (Thistleton, Pearce, & Parsons, 2002).

Phosphorus can also be removed biologically from wastewater by incorporation into cells; these cells are then removed as sludge. Conventional biological treatment typically removes only 20 % of the P present, whereas encouraging the establishment of bacteria that can take up and store more P than they need for their normal metabolic requirements can increase this to 90 % (Parson &Smith, 2008).

Section 2.4: Eutrophication

While phosphorus and nitrates (which are a form of nitrogen) are essential nutrients for plants and animals, excessive amounts of both nutrients can lead to the following problems: eutrophication, accelerated plant growth, algae blooms, low dissolved oxygen levels and death for certain species of fish, invertebrates and other animals. Elevated levels of nitrates and nitrites are also associated with human harms such as blue baby syndrome, adverse pregnancy outcomes and cancer (US EPA, 2011). River pollution caused by human activity promotes the growth of bacteria in the water, which increases demand for dissolved oxygen but also takes away from the oxygen supply of aquatic wildlife (Wong & Lewis, 2013).

Eutrophication refers to the excessive accumulation of micro flora (like phytoplankton) and macro flora (large floating plants) in water bodies. It is closely associated with increased human activities in the catchment area. Although eutrophication typically is considered a result of the natural aging process of lakes, the primary reason for such excessive growth is the accumulation of nutrients like phosphates and nitrates in the water bodies. Assessment of phosphorous concentrations is very essential to the evaluation of the lake's characteristics (Akkoyunlu & Akiner, 2012; Brett & Benjamin, 2007).

Akkoyunlu & Akiner (2012) tested six parameters through which Eutrophication potential in a water body can be assessed instead of using the standard water quality index (WQI) that uses 15 chemistry parameters. Dissolved oxygen, PO_4, NO_3, NO_2, BOD_5, and COD are six parameters were named as the eutrophication parameters and used to obtain a new modified water quality index (WQI) that is called WQI_{eut} eutrophication. Linear relation was observed between WQI and WQI_{eut}, see the following Equation. This equation shows nothing but the correlation between WQI and WQI_{eut}. This correlation should be strong in order to say that WQI_{eut} is reliable.

$$WQI = 0.6931\ (WQI_{eut}) + 27.547\ (R^2 = 0.8835,\ p<0.000)$$

Section 2.5: Combined sewer overflow

Discharges form combined sewer systems (CSOs), by which a mixture of industrial wastewater, urban surface runoff, domestic wastewater and sewer deposits are discharged into receiving waters.

Pollution from rain water discharges to receiving waters was first identified in early 1970s. A major reason for the long-term persistence of poor quality waters is the continued existence of uncontrolled or poorly controlled discharges from combined sewer overflows (CSOs) and surface water runoff. The impact on rivers and lakes caused by CSO events is accepted as an important source of pollution. European regulations concerning water quality standards in rivers, which classifies the rivers according with the standards that different kind of fish need to live in, are mainly broken because of CSO discharges (Suárez & Puertas, 2005).

Weyrauch et al. (2010) in his conducted study on CSOs in Berlin, Indicated that receiving rivers in most historic cities in Europe (e.g., Paris, London or Rome), as well as North America (e.g., most cities in North-Eastern USA) have a combined sewer system.

During CSO, COD may by higher than normal values. Suárez & Puertas (2005) mentioned that the possible reasons for the increase in COD values in CSO events may be attributed to the removal of sediments from the sewer network. These sediments cannot be removed by wastewater, whose hydraulic energy is moderate, but can be removed by combined waters, which have more discharge, velocity, and shear stress.

The first-flush of pollutants has been identified in a relatively high proportion of the total storm pollution load that occurs in the initial part of the combined sewer runoff. (Gupta & Saul, 1996) mentioned by (Suárez & Puertas, 2005), defined the first-flush as the initial period of storm flow during which the concentration of pollutants was significantly higher than those observed during the latter stages of the storm event.

In contrast, Sztruh & Markovi (2002) carried out a long-term urban drainage monitoring study in Slovakia, and over 300 CSO chambers were visited and evaluated. Furthermore, wastewater samples were taken and analysed, and event mean concentration were produced from eight monitored storm events carried out in four combined sewer systems. It was found that first flush of organic material in combined sewer overflows cannot be confirmed in any of the eight measured storm events. It is assumed that organic material is continuously decomposed and removed by dry weather discharges and is transported towards a wastewater treatment plant before CSOs start to operate. They presented database considering the similarities could be used in other Central European states, such as Poland, Hungary or the Czech Republic.

Section 2.6: Storm water and sanitary water

Considering the pollutant source profiles (storm-water, sanitary sewage, groundwater and CSO data), Sanitary sewage was found to have higher concentrations of most pollutants than storm-water (except Pb and Zn), groundwater (except Hg), and CSOs (except Cd and Pb). Most pollutants exhibit higher concentrations in storm-water than in groundwater (except Hg). Storm-water has higher total suspended solids (TSS), total P, Cu, and Zn concentrations than CSOs. Groundwater has higher Zn concentration than CSOs. The highest bacteria levels are found in sanitary sewage. The highest concentrations of Pb and Cd found in CSOs may be explained by the erosion of sewer deposits or remobilization of in sewer settled particles (Gromaire et al., 2001)

Soonthornnonda & Christensen (2008) studied CSO in the Greater Milwaukee area, Wisconsin, U.S. It was found that between 27 % and 56 % of the total overflow is from sanitary sewage and most of the remaining from storm-water with possible minor contribution (≤8 %) from groundwater. Most TSS and metals (Cd, Cr, Cu, Pb, Ni, Hg, and Zn) are from storm-water, while sanitary sewage carries large contributions (≥28 %) of BOD_5, NH_3, and total phosphorus. The fraction of NH_3 is ≥58 %.

Section 2.7: Removal efficiency

Bahri (1998) surveyed 15 WWTPs in Tunisia. Total N and P removal efficiencies were 48 % (62 % for ammonium) and 63%, respectively. For trace elements, removals averaged: Zn 87 %; Cu and Fe 78 %; Pb 64 %; Cr 50 %; Mn 44 %; Co and Cd 17 %; and Ni13 %.

The removal efficiency depended on the type of treatment process. For example, activated sludge, stabilization ponds, and trickling filter were more efficient in Kjeldahl nitrogen removal (60-70 %) compared to the oxidation ditch which had higher removal efficiencies compared to stabilization ponds. For Cu, Fe, Pb and Zn, higher removal efficiencies were obtained with the oxidation compared to the activated sludge process or to the stabilization ponds and the following sequences were common in the influent and effluent:

Influent: Fe>> Zn>Pb>Mn>Cu>Ni>Co>Cd

Effluent: Fe>>Mn>Pb>ZN>Ni>Cu>Co>Cr>Cd

In another study, a pilot scale wetland treatment plant was constructed in Istanbul, Turkey. The treatment of domestic wastewater of Marmara research center campus was examined. Ayaz & Akça (2001) stated that removal values were as follows: COD 90 %, SS 95 %, total Kjeldahl nitrogen 77 %, total N 61 %, and PO_4^{-3} 39 %.

In Kanpur India the conventional type of sewage treatment plants were studied, were they found that these plants basically reduce the organic load, but are not very effective in reducing the levels of metals and pesticides except that a large fraction of these toxicants present in the wastewater is retained with the sludge generated by

WWTPs while the remaining part getting out with the treated wastewater/effluent (Singh, Mohan, Sinha, & Dalwani, 2004).

Metal removal efficiencies at Gold Bar WWTP, Edmonton, Canada were monitored. Removal values were as following in Table 2. Overall removal efficiencies for cadmium, chromium and copper were high and those for nickel and zinc were variable and generally low. It also appeared that, with the exception of cadmium, metals were predominantly removed by primary sedimentation. Geometric mean metal concentrations in the final effluent did not exceed the maximum levels allowed for Canadian drinking waters. Metal concentrations in the digested sludge samples, with the possible exception of nickel, would probably not inhibit sludge disposal by land application (Nielsen & Hrudey, 1983).

Table 2. Removal values for Gold Bar WWTP

	% Removal				
	Cd	Cr	Cu	Ni	Zn
primary treatment	39	68	60	50	44
overall treatment	92	92	93	43	54

Chapter 3

Chapter 3: Materials and Methods:

The study was carried out in 2014-2015 at the Czech University of Life Science in Prague, at the Department of Chemistry.

Section 3.1: Plant description

Prague City Wastewater Treatment Plant (Prague WWTP) located on an island in the Imperial Trojan basin, was put into operation in 1966. When established, one of the biggest in Europe, but soon ceased to fulfill the increasing demands on the quality of treated water. Therefore, in the 80th and then again in the 90s of the last century Prague WWTP made significant renovation and completion of some new buildings. It was mainly to increase the capacity of the biological treatment stage including the introduction of the wastewater nitrification process. Centrifuges machine for management and dewatering sludge were installed. New cogeneration unit were installed for the production of heat and electricity from biogas. Large automatic monitoring and control system of technological processes of water purification, sewage processing and energy production was built gradually. Prague WWTP is a mechanical-chemical-biological treatment plant with a design capacity of Q24=7 m^3/s, the current average inflow of wastewater, however, is about the value of 4 m^3/s. Prague WWTP is designed for purification of about 95 % of Prague wastewater. The municipal urban wastewater is a mixture of sewage, industrial wastewater and rainwater. Biological drying removes carbon pollution and partially nitrified ammonia nitrogen. Phosphorus is removed from the water by precipitation with ferric salts (available from < http://www.pvk.cz/>).

3.1.1-Sewerage system

Wastewater is fed into the treatment through Prague's central sewerage system. The network, based on the beginning of the last century, single species, which is a mixture of sewage and storm water discharged from a single outlet.

3.1.2-Major treatment machinery

8 screw pumps are used for pumping water from the upper horizon, 4 to drain the water from the bottom, Pump for gravel trap. Water granted in the form of gravitational

gradient with sufficient energy to pass through the following stages of treatment. 12 fine self-cleaning screens used to separate coarse impurities floating. In Prague WWTP there are eight old and four new secondary sedimentation tanks. Regeneration tank used to collect sludge from the new settlement tanks. Excess biological sludge after thickening centrifuge is mixed with the primary sludge and pumped into the two-stage digester at temperature of 55 °C. The resulting biogas is used in a cogeneration unit to produce energy and heat. Sludge water Fugatami of thickening and dewatering centrifuge is pumped back to the regeneration tank. Contaminants are transported by screw conveyor into a container, due to their diverse nature and often hazardous properties are disposed of in landfills.

Technological cleaning line consists of:

1.Gravel traps.
2. Fine screens.
3. Longitudinal aerated grit chamber.
4. Primary settling tanks.
5. Aeration tanks with fine bubble aerators.
6. Settling tanks.
7. Regeneration tank return sludge.

Following: Block diagram of wastewater treatment technologies at Prague WWTP

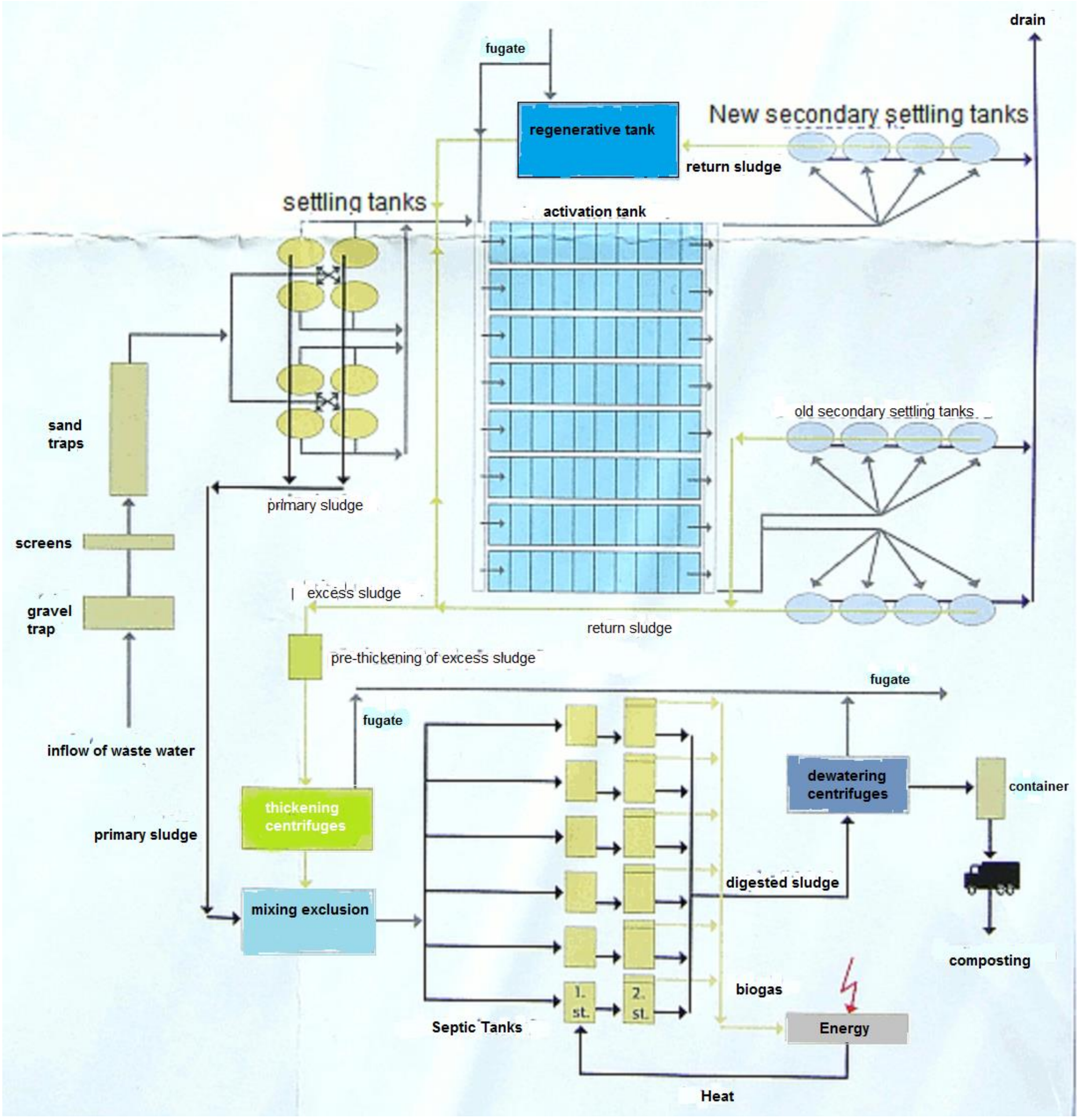


Figure 1. Block diagram of wastewater treatment technologies at Prague WWTP

Section 3.2: Sampling

Samples obtained monthly from Prague WWTP during the period from March 2014 until December 2014 on monthly basis. Wastewater were collected from the influent (raw wastewater) after sand traps and before the settling tanks process, and the effluent of the secondary settling tanks, which is discharged to river Vltava, two samples for each. All samples were collected in plastic vessels and were kept frozen until analysed on (-20 °C). The samples where filtered to remove large impurities through Cat

No 1004 150 4 filter papers, and the filtrate was collected and used for all tests in this study.

Mandatory parameters for wastewater will indicate the removal efficiencies and the change in water characteristics through seasons. These parameters are NH_4^+, NO_3^-, NO_2^- (inorganic nitrogen), phosphate ions, Chemical Oxygen Demand (COD). Alternatively the parameters which are not included in the standard wastewater: pH values potentiometrically, Cl-titrimetrically, hardness of water (Ca^{2+}, Mg^{2+}) titrimetrically, acid capacity, and risk elements Cd and Pb.

Section 3.3: Analysis

3.3.1-Physicochemical analysis

Standard techniques were used to analyze the different parameters: pH (pH meter Schott Glass main Typ CG842, Germany), electrical conductivity (Inolabcand level1 wtw, Germany) measured at 25ºC, COD (potassium dichromate method (Afnor 1979)), Ca and Mg (EDTA titrimetric method), Cl (titrimetric method), acid capacity (titrimetric method). Ammonium, nitrite, nitrate and phosphate were analyzed by spectrophotometric method (Afnor 1979) using Thermo Spectronic Heʎios Y spectrophotometer. Details of the measurement are given in Table 3. Cadmium and lead were measured by atomic absorption after acidifying by 0.5 ml of HNO_3 for 50 ml sample. A spectrometer Varian SpectrA 280Z with graphite atomiser was used and programmable sample dispenser Varian 120. The concentration of Cd and Pb were determined out in argon atmosphere in a pyrolytic graphite tube with platform. Detailed parameters of the measurement are given in the Table 4

Table 3. Spectrophotometer parameters of measurement

Test	Wavelength	Equation
Ammonium	410	A =0.0072×conc
Nitrite	520	A =0.0320×conc
Nitrite	435	A =0.0059×conc
Phosphate	385	A= 0.0025×conc+0.0060

Table 4. The parameters of measurement of Cd and Pb in Wastewater samples using Varian AA 280Z spectrometer

Element	Cadmium	Lead
Calibration	standard addition method	standard addition method
Wavelength (nm)	228,8 (0,5)	283,3 (0,5)
Background correction	Zeeman	Zeeman
Evaluation	peak area	peak area
Modifier	(NH4)2HPO4	(NH4)2HPO4
Pyrolysis temperature	650 °C	850 °C
Atomization temperature	2150 °C	2400 °C
Bulk concentration	3 µg/L	30 µg/L
Sample volume on platform	30 µL	30 µL

3.3.2-Replicates and statistical analysis

All experiments were conducted in two replicates. Data were contrasted and statistical analyses were performed on them. For all measurements averages, correlations, significances and standard deviations were calculated using Excel 2007.

Chapter 4

Chapter 4: Results

Section 4.1: General remarks

It can be observed that when the raw sewage passes through the treatment process, there is an improvement in all parameters except the total hardness, nitrate, Cd and Pb; Cd and Pb influents' were already in very low values (Tables 5 & 6). The COD of treated sewage declines substantially indicating the removal of the organic matter from the sewage. There is marked reduction in the total nitrogen in the measured parameters; NH_4^+ and NO_2^-. However, the NO_3 is significantly increased, during the treatment process. Physiochemical characteristics of influents and effluents samples in Prague center treatment plant over the studied period are listed in Table 5 and 6 respectively.

Higher concentrations of ammonium and chlorides detected in October influents were consistent with higher conductivity and pH which probably means that the electrolytes load of wastewater was high in this period, nevertheless COD did not confirm that it was the highest month in terms of organic matter. Presumably, the values lower than the expected level in September is due to overflow storm, high volume of storm flow dilute nutrients in influents and effluents. Obtained data for precipitation at the period of sample shown that 38 mm were precipitated in 11th and 12th of September (weather station at Czech University of Life Science).

Specific effluents indicators' values were correlated to concentrations of influents. This was clear in ammonium, chlorides, phosphate, nitrite, COD, acid capacity and conductivity. On the contrary, nitrates, Pb, Cd, Ca and Mg effluents concentration does not appear to be related to influents concentration. These findings would indicate that the influents concentrations of organic compounds have high effect on the overall concentration of the effluents. Moreover, substances such as risk elements have already very low values in influents which make the treatment process effect not clear on them.

Coefficient of variation was estimated for influents and was limited for pH 2.5 %. It was in range of 30 % for conductivity ammonium, chlorides, total hardness, acid capacity and COD. It was much higher for nitrate, lead and cadmium with 46 %, 59 % and 95 % respectively.

Table 5. Descriptive values of element concentration for influents in Prague city treatment plant.

sample Date	pH	conductivity µS.cm^{-1}	Cl mg.l^{-1}	NO$_2$ mg.l^{-1}	NH$_4$ mg.l^{-1}	Total hardness mmol.l^{-1}	Ca mg.l^{-1}	Mg mg.l^{-1}	Acid capacity mmol.l^{-1}	NO$_3$ mg.l^{-1}	PO$_4$ mg.l^{-1}	C.O.D mg.l^{-1}	Pb ug.l^{-1}	Cd ug.l^{-1}
Mar-14	**8.18**	**1226**	**106.3**	**2.21**	**83.0**	**2.6**	**60.0**	**25.2**	**6.2**	**12.6**	**0.37**	**550.0**	**3.01**	**0.011**
Apr-14	**8.24**	**1265**	**109.4**	**2.09**	**56.1**	**2.6**	**57.0**	**27.0**	**5.4**	**11.6**	**0.32**	**800.0**	**2.42**	**0.033**
May-14	**7.94**	**1004**	**104.2**	**4.82**	**77.0**	**2.2**	**56.0**	**19.8**	**3.9**	**7.9**	**0.37**	**550.0**	**4.78**	**0.071**
Jun-14	**8.22**	**1238**	**115.0**	**0.24**	**27.2**	**0.9**	**21.0**	**9.0**	**1.8**	**5.3**	**0.32**	**533.9**	**3.96**	**0.036**
Jul-14	**8.1**	**1138**	**111.5**	**4.04**	**73.4**	**2.6**	**67.0**	**21.0**	**5.8**	**19.4**	**0.41**	**784.0**	**3.40**	**0.010**
Aug-14	**7.67**	**864**	**105.9**	**1.92**	**34.5**	**2.2**	**43.0**	**27.6**	**3.2**	**6.7**	**0.26**	**441.0**	**2.32**	**0.021**
Sep-14	**7.94**	**380**	**30.4**	**0.62**	**77.1**	**2.6**	**57.0**	**27.0**	**5.4**	**15.8**	**0.2**	**636.1**	**0.88**	**0.012**
Oct-14	**8.32**	**1628**	**139.7**	**0.12**	**105.8**	**1.8**	**43.0**	**16.8**	**6.8**	**4.7**	**0.36**	**727.0**	**0.79**	**0.005**
Nov-14	**8.16**	**1366**	**111.1**	**2.45**	**90.5**	**3.0**	**88.0**	**19.8**	**7.9**	**10.2**	**0.35**	**388.3**	**1.53**	**0.005**
Dec-14	**7.91**	**1278**	**113.3**	**2.40**	**70.8**	**2.9**	**64.0**	**31.2**	**7.1**	**8.0**	**0.39**	**1000.0**	**0.76**	**0.012**
Average	**8.07**	**1138.70**	**104.68**	**2.09**	**69.54**	**2.33**	**55.60**	**22.44**	**5.34**	**10.22**	**0.34**	**641.03**	**2.38**	**0.021**
STD	**0.20**	**335.52**	**27.98**	**1.53**	**24.19**	**0.61**	**17.60**	**6.51**	**1.90**	**4.72**	**0.06**	**186.75**	**1.41**	**0.020**
CV	**2.46**	**29.46**	**26.73**	**73.01**	**34.79**	**26.34**	**31.66**	**29.00**	**35.70**	**46.25**	**18.94**	**29.13**	**59.04**	**94.842**
Min	**7.67**	**380.00**	**30.38**	**0.12**	**27.18**	**0.90**	**21.00**	**9.00**	**1.75**	**4.68**	**0.20**	**388.31**	**0.76**	**0.005**
Max	**8.32**	**1628.00**	**139.74**	**4.82**	**105.83**	**3.03**	**88.00**	**31.20**	**7.90**	**19.41**	**0.41**	**999.98**	**4.78**	**0.071**

Table 6. Descriptive values of element concentration for effluents in Prague center treatment plant over ten months:

sample Date	pH	conductivity µs.cm^{-1}	Cl mg.l^{-1}	NO$_2$ mg.l^{-1}	NH$_4$ mg.l^{-1}	Total hardness mmol.l^{-1}	Ca mg.l^{-1}	Mg mg.l^{-1}	Acid capacity mmol.l^{-1}	NO$_3$ mg.l^{-1}	PO$_4$ mg.l^{-1}	C.O.D mg.l^{-1}	Pb ug.l^{-1}	Cd ug.l^{-1}
Mar-14	6.96	932	103.3	0.94	10.8	2.5	62.0	23.4	1.9	91.7	0.080	110.0	4.00	0.103
Apr-14	7.33	930	104.2	0.5	6.8	2.1	51.0	19.8	2.1	101.5	0.145	330.0	4.12	0.113
May-14	6.8	711	79.0	2.7	9.1	1.9	47.0	17.4	1.5	61.2	0.030	100.0	4.71	0.059
Jun-14	7.01	960	107.6	0.5	6.7	1.4	29.0	15.6	1.1	121.7	0.145	126.2	0.86	0.035
Jul-14	6.99	758	82.5	1.0	8.0	2.2	57.0	18.6	1.5	100.5	0.035	235.2	2.75	0.089
Aug-14	7.19	920	72.0	0.5	4.6	2.8	69.0	25.2	2.3	84.4	0.095	186.2	3.35	0.192
Sep-14	6.87	433	40.8	0.2	4.2	2.1	51.0	19.8	2.1	52.3	0.055	127.2	4.80	0.053
Oct-14	6.84	1008	106.8	0.8	11.2	2.8	58.0	31.8	2.6	93.7	0.135	163.6	1.89	0.087
Nov-14	7.16	1001	105.9	1.5	6.4	2.9	67.0	28.2	2.8	83.3	0.110	126.2	4.38	0.071
Dec-14	7.11	965	103.3	0.7	20.7	2.6	78.0	14.4	2.5	125.0	0.110	250.0	0.93	0.005
Average	7.03	861.80	90.53	0.92	8.86	2.32	56.90	21.42	2.01	91.54	0.09	175.46	3.18	0.080
STD	0.17	179.94	21.90	0.71	4.78	0.47	13.61	5.62	0.55	23.07	0.04	74.85	1.50	0.051
CV	2.42	20.88	24.19	77.13	53.92	20.21	23.92	26.25	27.17	25.20	45.81	42.66	47.24	63.068
Min	6.80	433.00	40.79	0.18	4.24	1.38	29.00	14.40	1.05	52.34	0.03	100.00	0.86	0.005
Max	7.33	1008.00	107.63	2.66	20.73	2.85	78.00	31.80	2.75	124.99	0.15	329.99	4.80	0.192

Section 4.2: Removal efficiency:

A comparison of average sewage influent and effluent composition was made to investigate the overall removal efficiency; percentage of removal demonstrated in Table 7. Total hardness, cadmium and lead contents were not affected by the treatment process. Good ammonium, nitrite, phosphate and COD removal was captured on constant basis. Negative values for nitrite were found in June and October which means that the nitrite content in outflow was higher than in inflow. The bias of the values for these two months is more explained in the discussion part.

Table 7. Percentage of removal in Prague WWTP during the study period

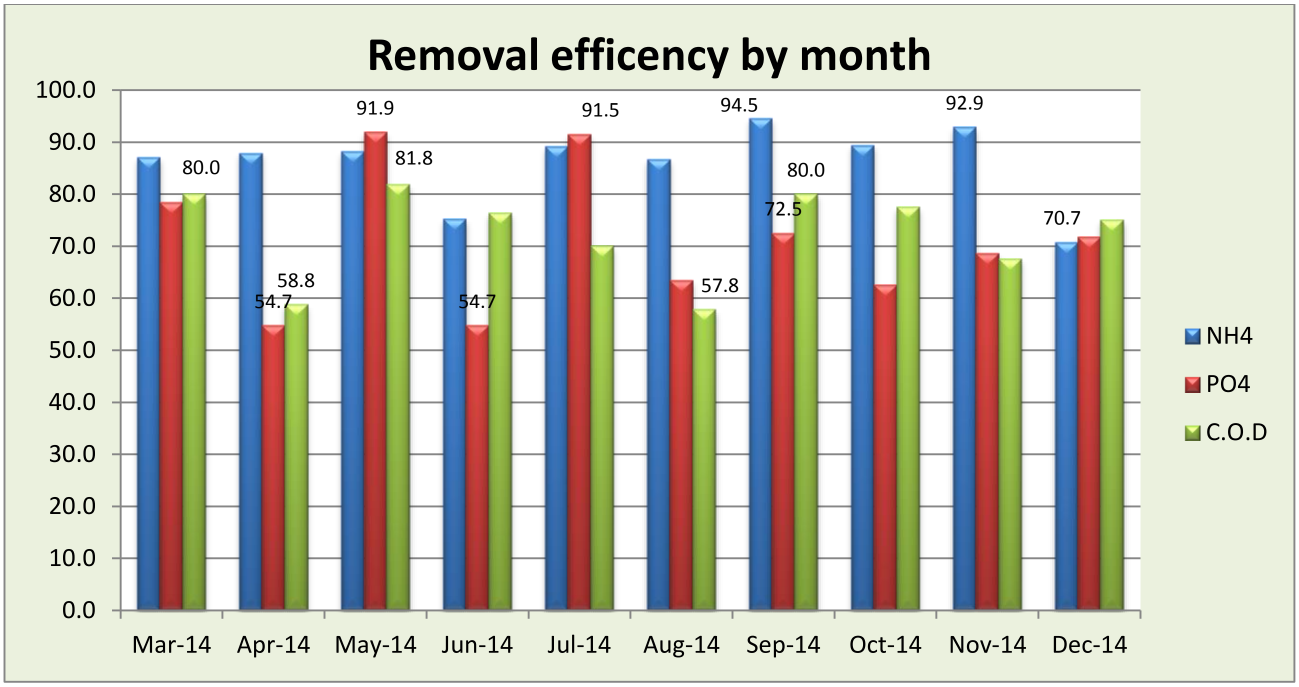
sample Date	NH_4 mg.l^{-1}	NO_2 mg.l^{-1}	PO_4 mg.l^{-1}	C.O.D mg.l^{-1}
Mar-14	87.0	57.7	78.4	80.0
Apr-14	87.9	75.6	54.7	58.8
May-14	88.2	44.7	91.9	81.8
Jun-14	75.2	-	54.7	76.4
Jul-14	89.2	74.5	91.5	70.0
Aug-14	86.7	76.0	63.5	57.8
Sep-14	94.5	71.3	72.5	80.0
Oct-14	89.4	-	62.5	77.5
Nov-14	92.9	40.1	68.6	67.5
Dec-14	70.7	71.4	71.8	75.0

The highest removal value for ammonium was in September; 94.5 %, and the lowest was in December; 70.7 %. Phosphate ions removal recorded the highest value in May 91.9 %; and the lowest values were in April and June with 54.7%. COD reached the highest to 81.8 % at May and the lowest 57.8 % at August. These values are presented in Figure 2. Average COD removal ratio was 72 % while that of ammonium was 87 % and nitrite was 72 %. Removal was 72 %, 13 % and 62 % for phosphate, chlorides and acid capacity respectively (Table8).

Table 8. Average removal ratio in Prague WWTP during the study period

Type	Cl mg.l^{-1}	NO_2 mg.l^{-1}	NH_4 mg.l^{-1}	Acid capacity mmol.l^{-1}	PO_4 mg.l^{-1}	C.O.D mg.l^{-1}
Removal efficiency	13.5	55.9	87.2	62.3	71.9	72.6

Figure 2 Ratio of removal efficiency by month in Prague WWTP during the study period



Section 4.3: Correlation data

Pearson’s r correlation was used to compare association between chemical measures. Strong positive correlations were detected between inflow and outflow measures of Cl, NO_2, COD, acid capacity and conductivity as follows in Table 9.

Table 9. Person’s correlation between influents and effluents samples indicators

Chemical measure	Conductivity	Cl	NO_2	COD	Acid capacity
Person’s r	0.87*	0.85*	0.75*	0.70*	0.73*

*Significant correlation $P< 0.05$.

Other parameters witnessed strong positive correlation among them. Correlation was found in influents samples between chlorides (Cl^-) content and conductivity, r= 0.92 with significance value $P<0.001$, and between (PO_4^{3-}) and conductivity, r= 0.74 with significance $P<0.05$. Moderate positive correlation was observed between conductivity and pH, r=0.65 with significance value $P<0.05$. Strong positive correlation was detected between ammonium (NH_4^+) content and acid neutralizing capacity; Person's correlation was 0.82 with significance $P<0.05$. As we obtained higher content of nitrates in effluents we tested correlation between conductivity and NO_3^- in effluents, and correlation was positive, r=0.7 with $P<0.05$.

Section 4.4: Physicochemical characteristics

4.4.1-Conductivity

Conductivity of wastewater influents and effluents through the investigated period is shown in Figure 3. Inflow and outflow samples values correlate with each other during the same period, r=0.87. The highest value was recorded in October and the lowest was in September.

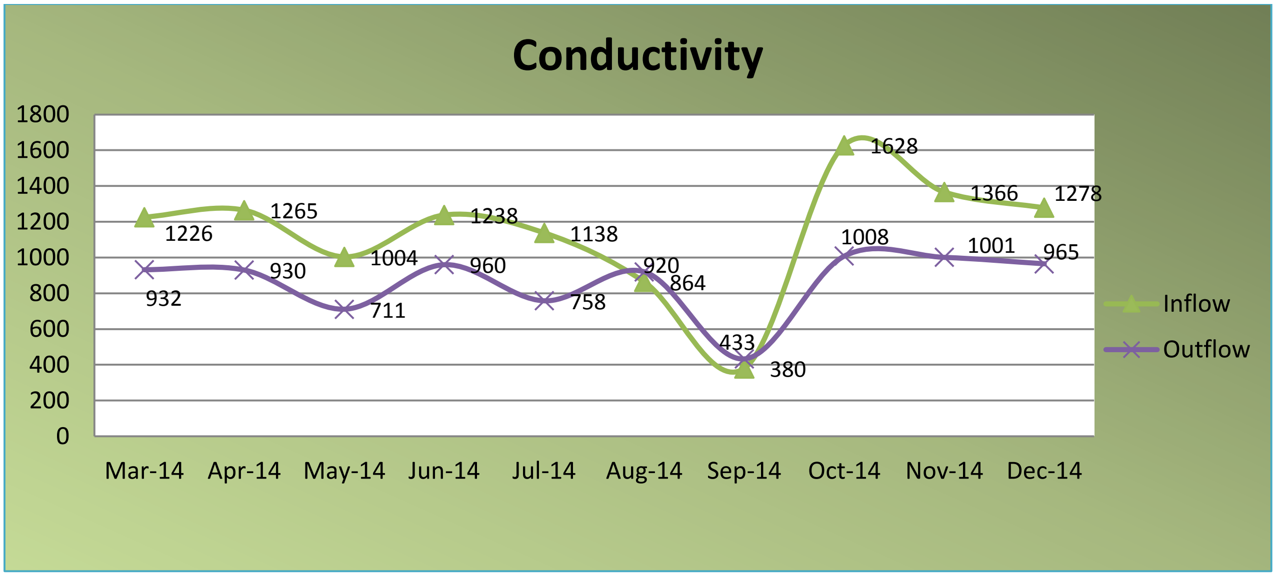


Figure 3. Conductivity of Prague WWTP samples during the study period

4.4.2-Chlorides content

Content of chlorides as presented in Figure 4, shows the highest and lowest values for both influents and effluents in October and September respectively. Person's correlation between inflow and outflow concentration; r= 0.85; *P*<0.001.

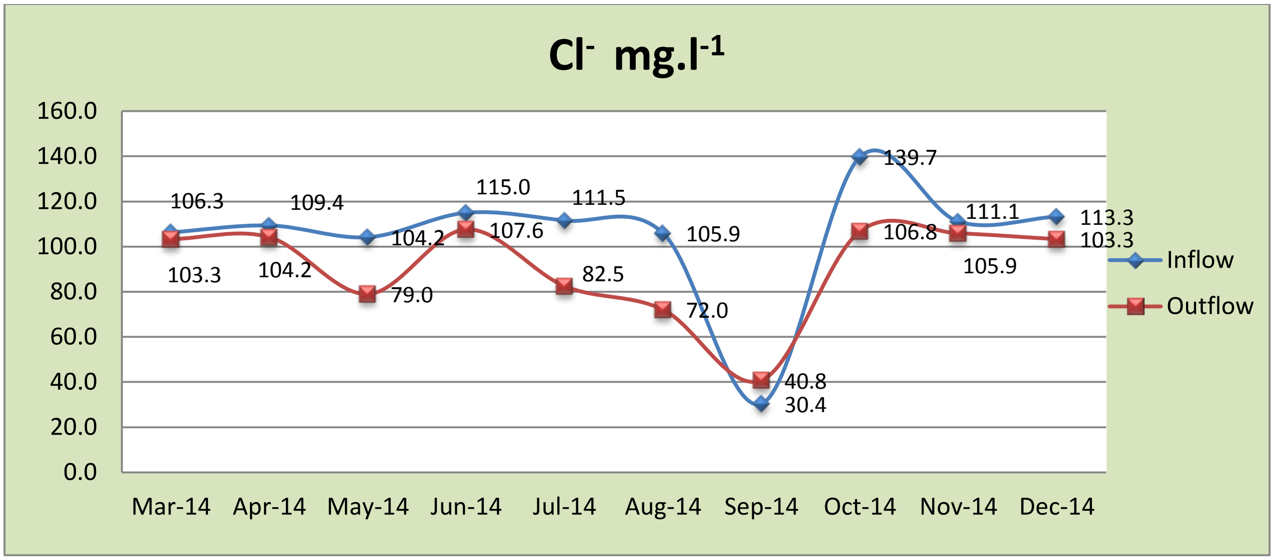


Figure 4. Chlorides content of Prague WWTP samples during the study period

4.4.3-Ammonium content

Figure 5 shows the difference between the ammonium content before and after treatment. Average removal efficiency was 87 % for the whole period as mentioned in Table 7. The highest value for effluents concentration was in October and the lowest was in June.

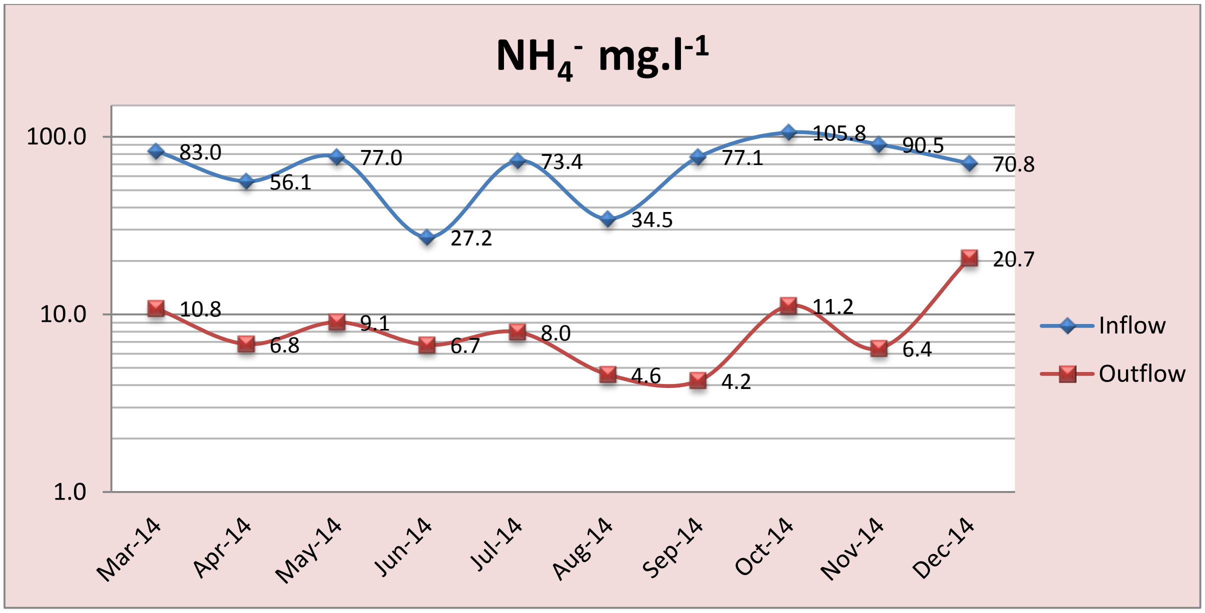


Figure 5. Ammonium Content of Prague WWTP samples during the study period

4.4.4-Acid capacity neutralization

Inflow and outflow samples indicated by acid capacity analysis demonstrated in Figure 6. The removal average was 62 % and the correlation between inflow and outflow was strong; 0.73 with $P<0.05$.

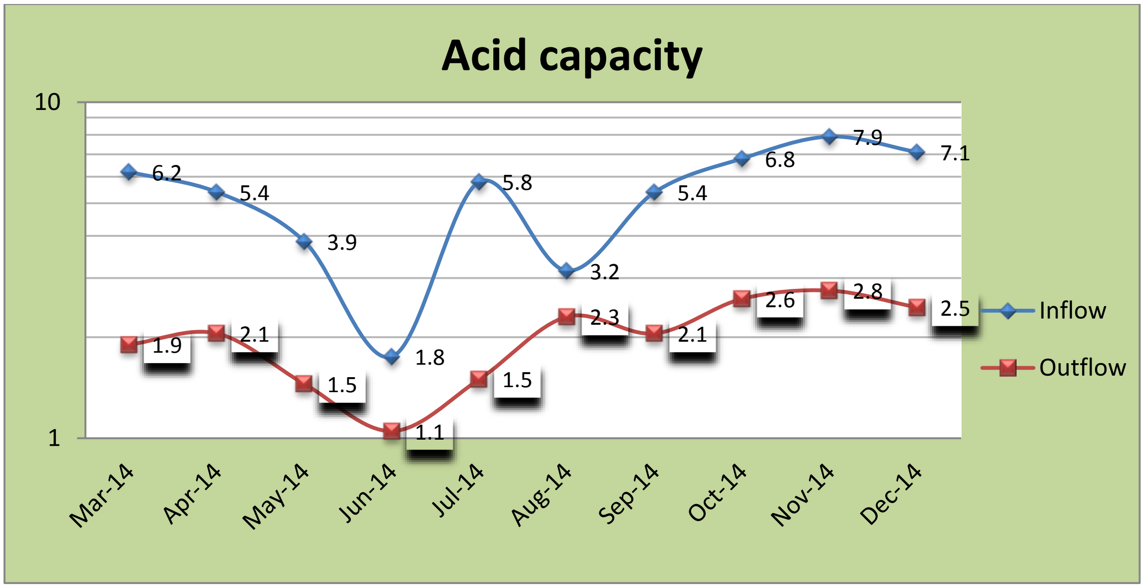


Figure 6. Acid capacity of Prague WWTP samples during the study period

4.4.5-Nitrate content

It was found that nitrate content in inflow was much less than outflow. This might be caused by the nitrification process and transferring of different forms of nitrogen during the treatment to nitrate; more explained in discussion. Figure 7 illustrates the difference between effluents and influents content of nitrates.

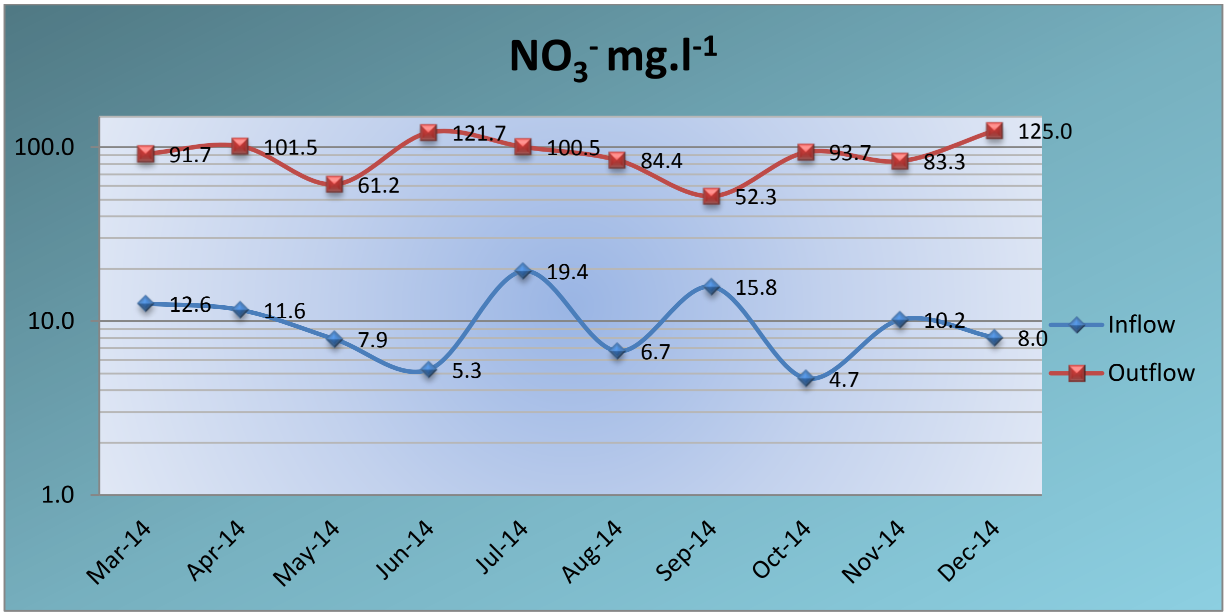


Figure 7. Nitrate content of Prague WWTP samples during the study period

4.4.6-Phosphate content

Phosphate content removal was effective with removal efficiency average 72 %, the difference between inflow and outflow is illustrated in Figure 8. The correlation between influents and effluents values was not significant.

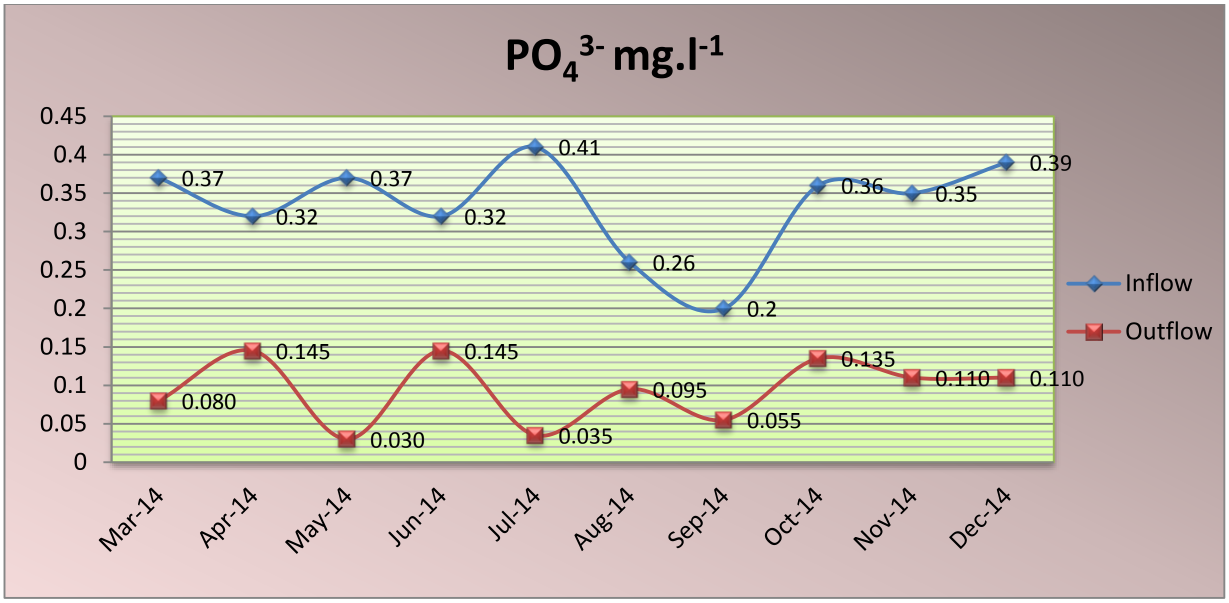


Figure 8. Phosphate content of Prague WWTP samples during the study period

4.4.7-COD content

COD removal average was 72.6 %, Person's correlation between influents and effluents was strongly positive; r= 0.7 with $P<0.05$. The highest influents value was recorded in December with 1000 mg.l^{-1} and the lowest was 388 mg.l^{-1} at November, while the highest for effluents was 330 mg.l^{-1} at April and the lowest was 110 mg.l^{-1} in May.

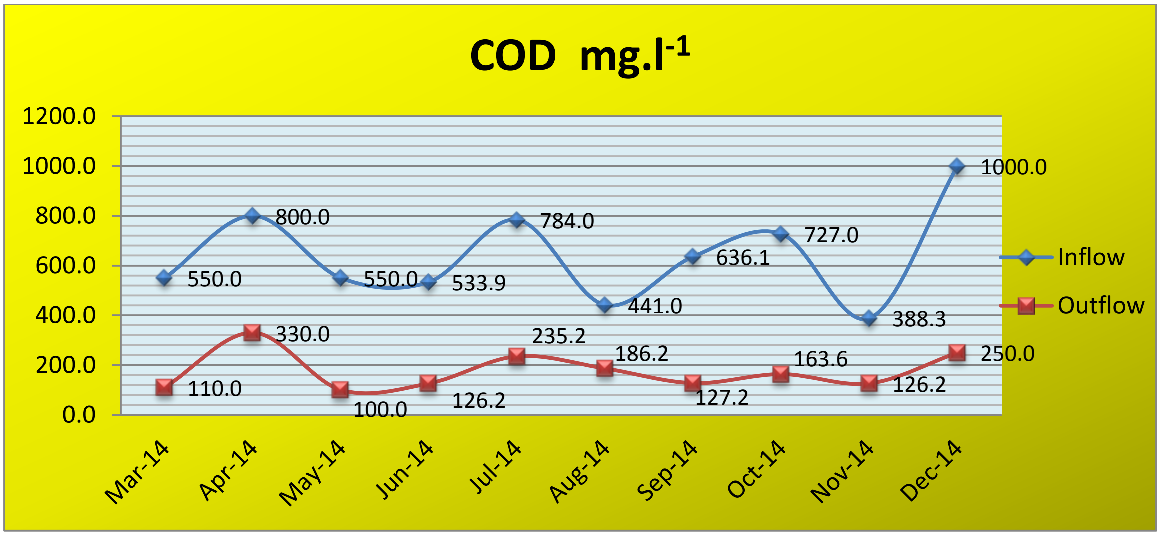


Figure 9. COD Content of Prague WWTP samples during the study period

Section 4.5: Given data for small wastewater treatment plant

In order to compare the results and removal efficiency from Prague WWTP, comparable results were obtained from small wastewater treatment plant for a small city located close to Prague and based on non-disclosure agreement name of the treatment plant, and other details about the treatment plant and treatment processes are not mentioned. The study period for the given data is the same; however, the sampling time was different. Wastewater sources and treatment processes are different than Prague city. Influents and effluents parameters are represented in Tables 10 and 11 respectively. Removal ratios through the whole period and average removal ratios are presented in Table 12. The main aim from comparison is to contrast and evaluate removal efficiency for Prague wastewater treatment plant, though the diverse conditions between the two plants.

Table 10. Concentration of selected indicators in influents in small WWTP

Date	COD mg.l^{-1}	BOD$_5$ mg.l^{-1}	N-NH$_4$ mg.l^{-1}	total N mg.l^{-1}	total P mg.l^{-1}
Mar-14	620	340	36.2	59.0	9.9
Apr-14	660	360	35.8	60.2	9.5
May-14	680	340	33.5	55.2	8.2
Jun-14	1,040	640	102.6	142.2	14.8
Jul-14	940	490	88.4	134.4	10.4
Aug-14	590	290	37.1	60.2	9.6
Sep-14	660	360	34.9	59.2	11.0
Oct-14	480	240	38.1	60.5	8.3
Nov-14	650	340	49.9	92.0	8.8
Dec-14	500	240	53.1	95.2	9.6
Average	682	364	51	82	10
STD	177	120	25	33	2
C.V	26	33	48	40	19

Table 11. Concentration of selected indicators of effluents in small WWTP

Date	COD mg.l^{-1}	BOD$_5$ mg.l^{-1}	N-NH$_4$ mg.l^{-1}	total N mg.l^{-1}	total P mg.l^{-1}
Mar-14	24	3	0.1	16.2	0.3
Apr-14	31	4	0.1	15.9	0.2
May-14	41	6	0.1	6.6	0.2
Jun-14	23	4	0.5	4.4	0.2
Jul-14	22	4	0.2	9.5	0.2
Aug-14	32	5	0.2	3.4	0.2
Sep-14	37	5	0.2	6.6	0.4
Oct-14	33	5	0.2	13.6	0.3
Nov-14	24	4	0.2	16.2	0.2
Dec-14	31	4	0.2	14.9	0.6
Average	30	4	0.2	10.7	0.3
STD	6	1	0.1	5.2	0.1
CV	22	19	57.7	48.3	47.0

Table 12. Removal ratios by month in small WWTP

Date	COD mg.l^{-1}	BOD$_5$ mg.l^{-1}	N-NH$_4$ mg.l^{-1}	total N mg.l^{-1}	total P mg.l^{-1}
Mar-14	96.1	99.1	99.7	72.5	97.0
Apr-14	95.3	98.9	99.7	73.6	97.9
May-14	94.0	98.2	99.7	88.0	97.6
Jun-14	97.8	99.4	99.5	96.9	98.6
Jul-14	97.7	99.2	99.8	92.9	98.1
Aug-14	94.6	98.3	99.5	94.4	97.9
Sep-14	94.4	98.6	99.4	88.9	96.4
Oct-14	93.1	97.9	99.5	77.5	96.4
Nov-14	96.3	98.8	99.6	82.4	97.7
Dec-14	93.8	98.3	99.6	84.3	93.8
Average	95.3	98.7	99.6	85.1	97.1

Chapter 5

Chapter 5: Discussion

The primary objective of the present study was to evaluate and compare the efficiency of a wastewater treatment in Prague WWTP. Influents were analysed prior to treatment to characterize wastewater organic and inorganic load. Final effluents were examined for being suitable for environmental discharges, and our results have revealed that effluents were always conforming to the required limits set by regulating authorities in EU. The Urban Wastewater Treatment Directive (UWTD) 91/271/EEC (EUR-LEX) which applies to wastewater discharges to all surface waters.

It was expected to have special characteristics form the warm season to the cold season, but this hypothesis was not uniformly supported. Wastewater load was variable through the year, but there were no specific trends for fluctuation through the year. A specific event such as storms is one reason for high fluctuations in wastewater constituents. Data was obtained from Czech University of Life Science (CULS) metrological station shows only one investigated period which witnessed high amount of precipitation. Storm events in combined sewer system may cause dilution for wastewater constituents (Suárez & Puertas, 2005) as was present in September samples.

Another purpose of the study was to test the changes in removal efficiency between the periods of year. Removal efficiency diversified through the year as shown in Figure 2. This may be related to many reasons. One major reason which was studied by many authors is temperature (Ahsan et al., 2005; Lishman, Legge, & Farquhar, 2000) which may affect wastewater constituents and efficiency of removal; at low temperature there will be lower efficiency while in high temperature the efficiency will be relatively higher. Bahri (1998) in his survey on 15 Tunisian WWTP stated that the contaminations load of influents changes with time. Moreover, the composition of effluent at a treatment plant has varied with time; he referred to different reasons; depending on the efficiency of the treatment plant and the proportion of water produced by different activities.

Removal in nitrites witnessed negative values in June and October due to higher concentration of nitrite in outflow than in inflow; this may be caused by the transferring of different nitrogen forms to nitrites during the treatment process. Another reason mentioned by (Metcalf and Eddy, 1991) that the increase in nitrite in effluents indicate insufficient aeration step or that a change in pH or toxicity disturbed the nitrifier population.

In our conducted experiment nitrate concentration was found to be appreciated in effluents than influents; this could be a product of nitrification process for other forms of nitrogen during treatment. Metcalf & Eddy (1991) refer increased content of nitrates in effluents to anoxic zone that is not developing or the BOD food source in the effluent is lower than usual.

It was proposed that the change in influents constituents concentration will cause a reasonably change in effluents concentration which would be the result of relatively fixed reduction treatment. Strong positive correlation was found between ingoing and outgoing in many indicators; conductivity, COD, nitrites, chlorides and acid capacity.

Conductivity was a key factor in our analysis, as positively correlated with many other measurements. Levlin (2010) found that conductivity can be used to monitor the changes in wastewater treatment processes. His experiment revealed that the main step which causes reduction in conductivity is biological nitrogen removal.

As we obtained higher content of nitrates in effluents we examined person's correlation between conductivity and nitrates in effluents. Conductivity has moderate positive correlation with nitrates, r=0.7 with $p<0.05$ which indicate that nitrates contribute by a significant part in the conductivity. Strong positive correlation was found between chlorides (Cl^-) and conductivity, r= 0.92 with significance value $P<0.001$, and between PO_4^{3-} and conductivity, r= 0.74 with significance $P<0.05$. This is likely caused by the existence of strong electrolyte as chlorides (Cl^-) and (HPO_4^{2-}) increase electrical conductivity. Moderate positive correlation was observed between pH and conductivity, r=0.65 with significance value $P<0.05$. This may be explained by that the conductivity of a solution depends on the concentration of all the ions present, which carry the electrical current, the greater their concentration is, the greater the conductivity. These ions move at different velocities through solutions so they contribute differently to conductivity. The most mobile anion is the hydroxyl ion (OH^-). Since pH is a measure of the concentration of hydrogen and hydroxyl ions, for basic solution the higher the (OH^-) concentration is, the higher the pH the greater the conductivity will be (A.P.Sincero & G.A.Sincero, 2003).

Strong positive correlation was detected between ammonium (NH_4^+) content and the acid neutralizing capacity. Person's correlation was 0.82 with significance $P<0.05$. The probable reason is that ammonium buffer the solution from acidifying by acid, the more ammonium content the more acid needed to change the pH (A.P.Sincero & G.A.Sincero, 2003).

Risk elements; Pb and Cd influents' were found to be in very low values, inflow and outflow concentration differences were not significant, presenting in very low values cause no clear effect detected by the treatment process. Inorganic elements; Ca, Mg were measured through the total hardness, results demonstrate that there were no significant removal for influents contents, influents and effluents contents intermingle with each other.

In order to associate the results from Prague WWTP, other outcome were obtained from small WWTP for a small city located close to Prague and based on non-disclosure agreement name of the treatment plant, and other details about the treatment plant and treatment process are not mentioned. The aim is to compare the removal ratio, through the differences between the two plants. The study period was the same; however, the sampling time was different. Wastewater sources are different; more industrial contribution in the small city than Prague city in addition to different treatment process, methods of analysis were the standards. Influents and effluents parameters are represented in Tables 10 and 11 respectively. Data from small WWTP was contrasted and statistical analyses were performed on them. For all measurements, averages, correlations, significances and standard deviations were calculated using Excel 2007.

The obtained data from the small wastewater treatment plant gave good indication that organic load fluctuate through the year with inflow coefficient of variation 20 % for P total, 40 % for N total, 48 % for ammonium, and around 30 % for COD and BOD_5. This variation was found to be comparable to results from Prague WWTP.

Very strong positive correlation between ammonium and total N, r=0.98 with *P*<0.001 in small WWTP, while in our analysis we did not estimate total nitrogen. However, it appears from the strong correlation that ammonium concentration could be a good indication for total nitrogen concentration. Moreover, Ammonium has a strong positive correlation with total phosphate, r= 0.75 with *P*<0.001.

COD was a key factor for the obtained results from the small WWTP. It was positively correlated with all organic load parameters, COD was used by many authors to track the changes through the wastewater treatment processes (Hua, An, Winter, & Gallert, 2003; Orhon et al., 1997). In small WWTP ammonium has strong positive correlation with COD, r=0.85 with significance *p*<0.001. The correlation between ammonium and COD was not significant in our data for Prague WWTP. The obtained data has total phosphate concentration which was found to be positively correlated with COD; r= 0.76 with *P*<0.05. In our data we have estimated phosphate ions not total phosphate, and no significant correlation was found between COD and phosphate ions concentration. Person's correlation between Biochemical Oxygen Demand (BOD) and COD was 0.98 with *P*<0.001 which indicate that the ratio of biodegradable to slowly biodegradable organic content was almost fixed. For small WWTP the increase in COD synchronizes with increase in BOD, ammonium, total nitrogen and total phosphorous concentrations.

The reduction comparison of the treatment process based on our analysis for Prague WWTP with obtained results from Small WWTP was as follows:

The average removal for COD was found to be 73 % for Prague WWTP, while it was 95 % for the small WWTP. Ammonium and nitrite removal was 87 % and 56 % respectively for Prague WWTP. Ammonium and total N removal for the small WWTP were 99.6 %, 85 % respectively. Phosphate ions removal was 72 % for Prague WWTP and total P removal for the small WWTP was found to be 97 %. From these results we can say that removal efficiency for organic load in the small WWTP was better than Prague WWTP and this might be caused by; 1. Treatment and management of low volume of wastewater is simpler. 2. The treatment process differs between Prague

WWTP and Small WWTP. 3. The differences in wastewater composition between the two plants. These matters need more research and refining.

The parameters of wastewater affected by combined sewer overflows, as a result, storm events relation with wastewater constituents needs more monitoring with more events under study. The trend of wastewater influents concentration through warm and cold season needs more investigation with more parameters and longer period covered. Since we could not find significant correlation between COD and other organic load parameters such as ammonium and phosphate in Prague WWTP, correlations between organic load indicators need more analysis, especially that a very strong positive correlation was present in small WWTP data. Comparative and in depth studies need to be done on many WWTPs in the Czech Republic for better understanding of different conditions consequences on wastewater treatment; i.e., treatment procedures, volume capacity and sources variations.

Chapter 6

Chapter 6: Conclusion

In the light of the experimental results summarized and evaluated in the preceding sections, the concluding remarks of this study may be expressed as follows. Wastewater characterization was carried out at Prague WWTP. The results were then compared to results from small WWTP to evaluate efficiency. Whereas the treatment system was highly efficient for the removal of water contaminants, it did not achieve the quality for the Small WWTP reduction. However, the wastewater effluents quality conformed to regulations set by EU. Wastewater composition through the year was not following specific trend. Water contamination in influents is a key factor of the final effluents concentration in Prague WWTP, through the positive correlations that was found between influents and effluents. However, results from small WWTP were not confirming this relation. Wastewater parameters such as chlorides, phosphate and pH found to affect conductivity through the positive correlation found between them. Despite ammonium and nitrite removals achieved, nitrate was increasing in concentration most probably due to nitrification process. Risk elements, Ca and Mg existed in low values in influents samples; accordingly no clear removal was recognized for these parameters. Small WWTP results show that organic load parameters are positively correlated with each other; COD, BOD, NH_4^+, total P and total N, which we could not confirm in our analysis for Prague WWTP. Regardless of the mentioned constraints, the system was able to remove a large portion of biodegradable compounds from contaminated waters which was presented in COD removal.

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List of Abbreviations

BOD: Biological oxygen demand

COD: Chemical oxygen demand

CULS: Czech University of life Science

FOG: Fats, oils and grease

SS: Suspended solids

TDS: Total dissolved solids

TSS: Total suspended solids

WWTP: Waste water treatment plant