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# Industrial wastewater treatment at PCETP, India

## - A primary investigation of the heavy metals content

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CHALMERS UNIVERSITY OF TECHNOLOGY
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# Industrial wastewater treatment at PCETP, India -A primary investigation of heavy metal content

# Industriellt avloppsvattensrening i PCETP, Indien
- En förstudie om innehållet av tungmetaller

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Cover:
Overview of Perundurai Common Effluent Treatment Plant, PCETP, in SIPCOT industrial area, India (2004).

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## ABSTRACT

This Master Thesis was a primary investigation of a wastewater treatment plant, PCETP, which is located in the industrial area SIPCOT Perundurai, India. The treatment plant treats textile wastewater and uses the water for irrigation on agriforest land. The report analyses the concentration of heavy metals in the influent, effluent and sludge from this treatment plant. The research also studies whether there is any accumulation of heavy metals in the soil and plants on the agriforest land.

The result from the analyses shows that the effluent water has far less heavy metal concentrations than the influent water and the heavy metal builds up in the sludge. The effluent water quality is good, compared to Indian regulation for irrigation with wastewater. Despite this the results indicate that the soil of the agriforest land has slightly increased concentrations of heavy metals compared to the non-irrigated fields. However, the analyses show that there are no accumulations of heavy metals in the plants on the irrigated fields. The long-term effect of the irrigation is unsure, but those results imply that the soil will be polluted and the plants growth might be affected.

To reduce the heavy metal concentrations in effluent water other unit such as reverse osmosis or ion exchange could be added. To decrease the iron concentration PCETP should optimize the chemicals used in the process.

Key words: heavy metal, wastewater treatment, textile effluent, irrigation, India, PCETP

Industriellt avloppsvattensrening i PCETP, Indien
- En förstudie om tungmetaller

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## SAMMANFATTNING

I Indien används 85% av vattenkonsumtionen för bevattning. Då rent vatten inte finns i överflöd är det därför vanligt att man återanvänder avloppsvatten från industrin, för bevattning på åkermarker. En stor del av detta avloppsvatten kommer från textilindustrin, då denna är stor förbrukare av vatten. Eftersom textillindustrin tillsätter mycket kemikalier i sina processer är det viktigt att reningen av vattnet är tillfredställande. I fall bevattning med sämre vattenkvalité sker kan det leda till förorening av mark och grundvatten och därmed också till skada av människors hälsa.

Det här examensarbetet är utfört som en fältstudie på ett avloppsvattenreningsverk PCETP, Perundurai Common Effluent Treatment Plant, beläget i industriområdet SIPCOT i Perundurai, Indien. Reningsverket behandlar avloppsvatten från textilindustrier och återanvänder det renade vattnet som bevattningsvatten på jordbruksmark. Rapporten är en förstudie som omfattar studier av tungmetallerna kadmium, krom, järn, bly och zink, hur de avskiljs från vattnet och dess påverkan på jord och växter på de bevattnade fälten. Resultaten har jämförts med de lagar och förordningar som gäller i Indien. När det gäller textillavloppsvatten är tungmetaller en viktig parameter att kontrollera eftersom dessa används rikligt i textilprocessen och är farliga för miljön. Om tungmetaller kommer ut i naturen kan dessa bioackumuleras i marken och därmed påverka naturen långsiktigt.

Under fältarbetet i Indien har dygnsprover på in- och utgående vatten och stickprover på slam tagits varje dag under en veckas tid. På det bevattnade fältet har växt- och jordprover samlats in. Dessa prover har analyserats, dels i Indien med AAS och i Sverige med ICP-MS, för att påvisa koncentrationen av tungmetallsinnehållet av Cd, Cr, Fe, Pb och Zn. Resultatet från dessa analyser bekräftade att avloppsreningsverket, PCETP, renar vattnet bra med avseende på de lagar och bestämmelser som gäller i Indien. Tungmetall-koncentrationen i utgående vatten är mycket lägre än i ingående för de flesta ovanstående metallerna och större delen av tungmetallerna ansamlas i slammet. Även om resultatet indikerar på en bra rening har förhöjda halter av tungmetaller hittats i den bevattnade jorden. Dock påvisar inte detta resultat några förhöjda tungmetallshalter i växterna som växer på den bevattnade jorden. Den långsiktiga effekten av bevattningen är osäker, men om samma ökning av koncentrationen i jorden sker följande år kommer halterna av tungmetaller att vara dubbelt så höga som de för obevattnad mark inom 5-15 år.

För att förbättra avskiljningen av tungmetaller på reningsverket kan en processenhet läggas till, exempelvis jonbytare eller omvänd osmos membran. Även ordentlig översyn av kemikalieanvändning och eventuellt byte av fällningskemikalie skulle kunna leda till bättre och effektivare rening. PCETP är ett mycket bra och modernt reningsverk men det kan alltid förbättras ytterligare för att uppnå ett uthålligare samhälle.

Nyckelord: tungmetaller, avloppsrening, textile industri, bevattning, Indien, PCETP

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The MFS shall include two months fieldwork in a developing country resulting in a master dissertation or similar study. The purpose of a MFS is, at the same time as the research is carried out, for the student to acquire knowledge of developing countries and their problems. In other words, to get a brief view of how people live, work and of daily life in a developing country. It should also build relationships between Swedish students or institutes and universities or organizations in developing countries.

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# Contents

ABSTRACT V
SAMMANFATTNING VI
ACKNOWLEDGEMENT VII
PREFACE VIII
CONTENTS IX
ABBREVIATION XI

1 INTRODUCTION 1
  1.1 Objectives 2
  1.2 Scope 2
  1.3 Assumptions 2

2 LITERATURE STUDY 4
  2.1 Parameters 4
  2.2 Textile industries and heavy metal 8
  2.3 Soil, plant and heavy metals 10
  2.4 Groundwater and heavy metal 13
  2.5 Legislation 13
  2.6 Treatment of heavy metals 14

3 SITE DESCRIPTION 19
  3.1 Perundurai 19
  3.2 SIPCOT 20
  3.3 Perundurai Common Effluent Treatment Plant 20
  3.4 Early data 26
  3.5 The irrigated fields 26

4 MATERIALS AND METHODS 30
  4.1 Method 30
  4.2 Errors 33

5 RESULT 34
  5.1 Heavy metals in water and sludge 34
  5.3 Heavy metals in soil and plants 37
  5.4 Soil 39

5.5 Reliability 40

6 DISCUSSION 42
6.1 Water 42
6.2 Sludge 43
6.3 Soil and plants 44
6.4 Heavy metals through the treatment plant 47
6.5 Improvements 49

7 CONCLUSION 50

8 FURTHER AREA OF STUDY 51

9 REFERENCES 52

10 APPENDIX 59

# Abbreviation

*General*

| | |
|---|---|
| AAS | Atomic Absorption Spectrophotometer |
| ACF | Activated Carbon Filter |
| AVGF | Atomic Valves Gravity Filter |
| ICP-MS | Inductively Coupled Plasma-Mass Spectrometry |
| Milli q | Deionise water |
| PCETP | Perundurai Common Effluent Treatment Plant |
| TNAU | Tamil Nadu Agriculture University |
| TNPCB | Tamil Nadu Pollution Control Board |
| WET | Water Environment Technology |
| WTC | Water Technology Centre |

*Chemical*

| | |
|---|---|
| BOD | Biochemical Oxygen Demand |
| COD | Chemical Oxygen Demand |
| DS | Dry Solids |
| EC | Electrical Conductivity |
| PPB | Parts Per Billion, $10^{-9}$ |
| PPM | Parts Per Million, $10^{-6}$ |
| SS | Suspended Solids |
| TDS | Total Dissolved Solids |
| TS | Total Solids |
| TSS | Total Suspended Solids |

*Notification*

| | |
|---|---|
| Heavy metal | In this report heavy metal includes cadmium, chromium, iron, lead and zinc. |

# 1 Introduction

Textile is a major source of income and of great importance for India's economy. At the same time textile processing has major environmental impact. A large proportion of the environmental issues are related to the use and discharge of water. Textile manufacturing is among the major industrial water users. To produce one kg of textile fabrication about 200 litres of water is used (Workshop on impact of industrial effluent, 2000, EPA SV, 1998 and Devarajan, 2002*)*. A lot of chemicals are added to the process for cleaning and dyeing purposes. Obviously the wastewater effluent from this unit contains considerable amounts of hazardous pollutants, and where heavy metals are very common.

In India most of the effluent from the textile industry is discharged untreated into rivers. Today 70% of available water in India is polluted and two thirds of illness in India is related to water-borne diseases (Ghosh, 2002). Water treatment is a very important step to change these conditions and to achieve a sustainable situation. India's government has an awareness of this and limits for water effluent quality exist. Unfortunately, this regulation is not closely supervised and a lot of places do not follow the regulation. In newly developed industrial areas advanced wastewater treatment is used for textile effluent, as the one in this study area SIPCOT in Perundurai.

Effluents from the textile industry contain high concentrations of inorganic and organic chemicals and are characterized with residual COD and strong colour. Today methods like adsorption, chemical treatment, membranes, photolysis, chemical oxidation, reduction and ion–pair extraction are used around the world. Those methods are quite costly and some of them are less efficient. Membranes as ultra filtration, nano filtration and reverse osmosis are known to be very effective in the removal of dyestuffs.

Irrigation is responsible for 85% of India's water consumption (Plunkett, 2001). As mentioned above, a large quantity of wastewater is produced from textile factories. In India it is therefore common to reuse the textile effluent water for irrigation on agricultural land. Of course this has a lot of advantages for achieving a better wastewater management. The disadvantages of using textile wastewater for irrigation are related to bad water quality. After irrigation the water will infiltrate to the soil. Some water will find its way to river basins and tends to physically percolate into the groundwater. In the case the water is contaminated, for example with heavy metals, it can cause considerable damage to agricultural land, groundwater as well as to the health of living systems.

Some heavy metals are essential for human beings and plants. All of them are toxic if large intakes occur and the main issue is the bioaccumulation of them. Different elements of heavy metals effect humans in different ways, they can infect the interior organs, weaken bones, cause cancer, harm the nerve system and can even cause death.

Hence is it necessary to investigate and survey the content of the water used on irrigated fields. Even though the water concentration of heavy metals is low, accumulation can occur. This can give long term contaminated soil and groundwater. This report will do a primary investigation about the heavy metal situation in a particular wastewater treatment plant.

## 1.1 Objectives

This Minor Field Study is a primary investigation of the heavy metals content in the wastewater treatment plant in SIPCOT Perundurai.

The report will describe the treatment plant regarding influent-, effluent water and sludge, to observe the separation of heavy metals. In case of high concentrations of heavy metals found, guidelines will be provided to minimize the heavy metal concentrations in the effluent water.

This research will look into the impact from wastewater irrigation in terms of heavy metals in the soil and plants and try to understand if any long-term pollution occurs in the irrigated area.

The investigation determines what kind of industries that are connected to the Perundurai Common Effluent Treatment Plant, PCETP. This work will also include a survey of the limits for heavy metal loads for industrial effluents and water used for irrigation.

## 1.2 Scope

This report is a result of a master thesis in civil engineering at Chalmers University of Technology. The main scope of the study is to investigate the impact of using textile industry effluent for irrigation of agricultural land.

It comprises 20 weeks of work and consists of two parts, one literature study and one field-study. The literature part reviews the effect that heavy metals cause on soil, plants, humans and groundwater, and a brief text about Indian legislation. It also explains how heavy metals today are separated from wastewater and describes the parameters that have been measured during the investigation. The following chapter comprises a description of the site and treatment plant where the field study was done. Materials and methods describe how the field study was performed. When the results of all the analyses are listed there follows a discussion of the results. There is a conclusion after the discussion and finally a recommendation for future study.

## 1.3 Assumptions

All water samples are taken in PCETP area. The water and sludge samples were taken everyday between the 16th and the 23rd of October, except the 22nd. Soil and plant samples were collected on the 27th of October 2004. The collection was done over a short time period and can only give a rough estimation of the treatment plant’s capacity to separate heavy metals.

This report focuses on the wash water treatment plant in Perundurai, because the effluent is used for irrigation after treatment.

The water samples have only been collected from the influent and the effluent water in the wastewater treatment plant. The result will not show how each unit separates the heavy metals.

A selection of heavy metals has been made according to the elements commonly found in textile industries. The report focuses only on five elements; cadmium, chromium, iron, lead and zinc, where iron counts as a heavy metal.

The composite soil samples consist only of five samples from each field, which will only give a rough idea of the real situation. Plant samples have only been collected from the leaves, and not from the roots or the stem.

This report will not go into the different ways of the contamination of groundwater.

# 2 Literature study

The following literature review aims to introduce the reader to the different parts of the report. Information for this rapport has been collected through books, articles, reports, websites and by talking to people.

It is important to be critical to the information found in literature. Books, articles and reports can give incorrect information. New discoveries could always make a book out of date, but in some cases the fact will be the same for many years. It is easy to get information from Internet today and many companies use websites to sell their products. In these cases, companies will probably only provide information that gives them positive publicity. It is also easy for anyone to put information on the web, without proper reviewing.

## 2.1 Parameters

This report will investigate different parameters, which are related to the quality of the treatment processes, soil and plants. These parameters are described below.

### 2.1.1 Heavy metals

The most important parameters in this report are heavy metals. Heavy metals are those elements with larger atomic density than 5 g/cm$^3$ (Chunrong, 1999). Commonly said heavy metals are those metals in the periodic table with an atomic number greater than 20, excluding the alkali metals. This is due to the similarity of their chemical properties and environmental behavior. Many of them are trace metals in the earth crust and most of them are toxic even in very low concentrations (Mahimaraja, 1996 and Chunrong, 1999). Heavy metals tend to accumulate in soil mainly by adsorption mechanisms (Aucejo, 1996).

Heavy metals are not only toxic for plants. They are also toxic for human beings. For human beings some heavy metals are essential for growth, such as zinc. They are all toxic if larger amounts are ingested or inhaled. The main issue with heavy metals are the bioaccumulation due to long residence times. The residence time of cadmium in the soil has a range of 75-380 years. Lead and zinc have residence times of 1000-3000 years. However, half-life for cadmium is 15-1100 years and 740-5900 years for lead. Even though the ranges are wide in different soil conditions it is clear that heavy metal pollution is a very long-term matter (Alloway, 1995).

*Cadmium*

Cadmium, Cd, is a natural element in the earth's crust. It is found as a mineral combined with other elements such as oxygen, chlorine or sulphur. All soils and rocks, including coal and mineral fertilizers, contain a very small amount of cadmium. Thus if a higher concentration is found, the soil is probably contaminated (Alloway, 1995). Cadmium is, compared to other heavy metals, dissolved easy in nature (Pettersson, 1994). It is used in batteries, pigments, metal coatings and plastics. Cadmium has no essential biological function. It is not biodegradable, but can easily change form in the environment. Cadmium stays in the human body a very long time and the amounts could be built up from many years of exposure to low levels (ATSDR, 1999b).

Cadmium is highly toxic to plants and animals. Breathing high levels of cadmium severely damages the lungs and can cause death, especially after long-term exposure. Ingestion of cadmium can cause weak bones and kidney diseases. Animals given cadmium in food or water were found to have high blood pressure, iron-poor blood, liver disease and nerve- or brain damage. Animals exposed to cadmium during pregnancy can result in harm to the foetus in form of changes in birth weight, skeleton, behaviour and learning ability. The toxicity of the metal is determined by form not by concentration (Alloway, 1995). The Food and Drug Administration limits the amount of cadmium in food to 15 mg/l (ATSDR, 1999b).

### *Chromium*

Chromium, Cr, is an element found in rocks, animals, plants and soil. In the environment it occurs in several different forms that are pH dependent. The most common form is chromium (III), which is an essential nutrient helping the body to consume sugar, protein and fat. Chromium is used for chrome plating, colour pigments, leather tanning and wood preserving. Chromium enters the air, water and soil mostly in the chromium (III) and chromium (VI) forms. Chromium is strongly attached to the soil, so only small amounts can dissolve into water and therefore it does not enter the groundwater in larger amounts (Alloway, 1995 and ATSDR, 2001).

Ingesting large amounts of chromium (VI) can cause stomach upsets, convulsions, kidney- and liver damage, or even death. Chromium is human carcinogen. Breathing high levels of chromium (VI) can cause irritation to the nose such as runny nose, nosebleeds, ulcers and holes in the nasal septum. Skin contact with certain chromium (VI) compounds can cause skin wounds. Allergic reactions consisting of severe redness and swelling of the skin have been noted (ATSDR, 2001).

### *Iron*

Iron, Fe, is defined as an essential micronutrient due to involvement in the formation of chlorophyll. It is found in the earth's crust, often in combination with other chemical elements. Some iron compounds are considered to be soluble in the whole pH range, ferric and ferrous humates. The availability of iron is always increasing with decreasing pH (Sauchelli, 1969). Iron is an essential nutrient, which is involved in the oxygen transport inside human beings. Many enzymes throughout the body contain iron. The red blood cell contains haemoglobin, partly made from iron, which is a part and parcel of myoglobin, a special protein that helps the muscle tissue to store oxygen and also give muscles the red colour. The enzymes that are involved in energy production include iron. Proper functioning of the immune system relies, in part, on sufficient amounts of iron (Better health channel, 2004).

The body stores iron very efficiently, and too much iron can be toxic. Iron overload is a condition characterised by excessive absorption of iron through diet. Much of the additional iron is deposited in the liver, damaging this vital organ and causing it to enlarge. Abundance iron can be stored almost anywhere in the body. Iron overload can lead to a vast range of symptoms like, joint pain, constant fatigue, heart problems, hair loss, abnormal liver function, impaired memory, mood swings and depression (FAQ, 2003). Some studies suggest that iron overload may cause cancer, such as colorectal cancer (Better health channel, 2004). Harmful levels of iron may also be deposited in other organs, including the heart and the pancreas. It can also affect joints, leading to symptoms similar to arthritis (CATIE, 2001).

### *Lead*

Lead, Pb, naturally occurs in small amounts in the earth's crust. Lead can be found in all parts of our environment. Lead itself does not break down, but lead compounds are changed by sunlight, air and water. Once lead reaches the soil, it usually sticks to soil particles. Movement of lead from soil into groundwater will depend on the type of lead compound and the characteristics of the soil (ATSDR, 1999a). Due to low solubility it tends to accumulate and influence the microbial activities and thereby reduce the soil productivity (Alloway, 1995).

Lead can have an effect on almost every organ and system in the body. The most sensitive system is the central nerve system, particularly for children. Lead could also cause problems with the kidneys. At high levels lead may, decrease reaction time, cause weakness in fingers, wrists or ankles and possibly affect the memory. Lead may also cause anaemia and problems with the blood. It can also damage the male reproductive system. There is not enough evidence to clearly determine the carcinogenicity to people. Even low levels of exposure to lead can affect a child's mental and physical growth (ATSDR, 1999a).

### *Zinc*

Low levels of zinc, Zn, are essential for maintaining good health. If zinc levels are too low it will cause failure to eat, skin lesions, sexual immaturity, depression, and affect taste (Alloway, 1995). Zinc compounds are widely used in industry to make paint, rubber, dyes and wood preservatives. Depending on the type of soil, some zinc compounds can move into the groundwater and into lakes, streams and rivers. The solubility of zinc is highly dependent on the compounds, for example zinc phosphate is insoluble and zinc nitrate is very soluble (Sauchelli, 1969). In general zinc is considered to be very mobile and bioavailabel and can accumulate in crops and human diets. The availability of zinc decreases by increasing pH (ATSDR, 2003).

Zinc can cause stomach cramps, anaemia and changes in cholesterol levels. Harmful effects generally begin at levels 10-15 times higher than the amount needed for good health. Large doses ingested, even for a short time, can cause stomach cramps, nausea and vomiting. Inhaling large amounts of zinc (as dust or fume) can cause a specific short-term disease called metal fume fever. Applying low levels of certain zinc compounds on the skin causes skin irritation. Increases in deaths and decreased weight have been found in animals after ingesting very high amounts of zinc (ATSDR, 2003).

### 2.1.2 pH

pH is the negative log base of hydrogen ion concentration and is unit-less. The hydrogen-ion concentration is an important quality parameter. The concentration range for existence of most biological life is quite narrow and critical (Tchobanoglous, 1991). The hydrogen–ion concentration in water is closely connected with the extent to which water molecules dissociate (Kiely, 1997). The solubility of heavy metals is dependent on the pH, see Section 2.3.3, due to this a lot of process units are heavily dependent on pH such as chemical treatment, see Section 2.6.

### 2.1.3 Electrical conductivity

Electrical Conductivity, EC, is the capacity of a solution to carry a current. It depends on the total concentration of ionized substances dissolved in the water. All ions contribute to conductivity. However the ions affect the conductivity differently through different valences and mobility. Micro Siemens per centimetre (μS/cm) is the unit for electrical conductivity. The higher the resistance of the water, the lower the conductivity. Since the electrical current increases with increasing temperature, the EC values are automatically corrected to a standard value of 25°C. The values are then technically referred to as specific electrical conductivity (Lake Access, 2004). The specific conductance of distilled water is about 1 μS/cm, which is low and the value of seawater is 50 000 μS/cm (U.S. Fish and Wildlife Service, 2004). Electrical conductivity is commonly used as a quick test for measuring the quality of water or soil.

### 2.1.4 Total dissolved solids

Total Dissolved Solids, TDS, describes the amount of dissolved compounds in the water and is similar to conductivity.

Water is a good solvent and picks up impurities easily. Dissolved solids refer to any minerals, salts, metals, cations or anions, which are dissolved in water. TDS consists of inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates). It also consists of some small amounts of organic matter that are dissolved in water. TDS concentration is the sum of the cations (positively charged ion) and the anions (negatively charged ions) in the water. TDS tells the quantity of dissolved ions but not the nature of them (WU CEQ, 2004). TDS is an indicator to determine the general quality of the water. High TDS concentration is not a health hazard but more an aesthetic matter. However, if higher TDS is found it can indicate that some metal levels, such as lead or aluminium, are very high.

### 2.1.5 Total suspended solids

Total Suspended Solids, TSS, includes all particles in a known volume of liquid not passing through a filter of 1.2 micrometer pore size. TSS is measured in mg/l. The filter-solid fraction consists of colloidal and dissolved solids of particles of both inorganic, organic molecules and ions. The particles have a size of $10^{-3}$-$10^{-6}$ m (Tchobanoglous, 1991). TSS is commonly used to measure the amount of particles removed during the treatment process.

### 2.1.6 Biological oxygen demand

Biological Oxygen Demand, BOD, measures the readily biodegradable organic carbon. There are a number of different tests developed to determine the organic content of wastewater. BOD measures the dissolved oxygen used by microorganisms when they are oxidizing organic matter. $BOD_5$ is the amount of dissolved oxygen used from the water sample by microorganisms as they break down the organic matter at 20°C, over a five days period. Clean waters have a $BOD_5$ value of less then 1 mg/l and wastewater has between 150-1000 mg/l (Kiely, 1997). $BOD_5$ is widely used around the world for measuring organic compounds in the wastewater but it has limitations. Firstly a high concentration of active bacteria is required. Secondly only the biodegradable organics are measured. Thirdly a particularly long period of time is necessary to obtain the results. Fourthly BOD does not have stoichiometric validity after the soluble organic present in the solution has been used (Tchobanoglous, 1991).

### 2.1.7 Chemical oxygen demand

Chemical Oxygen Demand, COD, is the amount of oxygen needed to chemically oxidize the organics in the water. A strong oxidizing agent, commonly used is potassium dichromate, which is used to oxidize the organic matter instead of microorganisms used in BOD. COD measures the same thing as BOD, but has the advantage of only taking two hours to produce the result. The temperature needs to be elevated and some inorganic compounds will interface with the test, so these have to be removed before hand. The COD is in general higher than the BOD because more compounds can be chemically oxidized than biologically oxidized. Different types of water have different translations between BOD and COD (Kiely, 1997 and Tchobanoglous, 1991).

## 2.2 Textile industries and heavy metal

The way of treating wastewater is dependent on the origin and the quality. In this report the wastewater comes from textile industries. Textile dyeing requires the input of a wide range of chemicals such as soda ash, sodium peroxide, acetic acid and colouring chemicals. In some of those chemicals heavy metals will be present. The metal may be used as an important content but may also be a trace mineral, because of contaminated chemicals. All chemicals that are not absorbed by the fabric will stay in the water, so heavy metals will occur in the wash water from the dyeing process. Not only pollution from the added chemicals will contribute to the pollution load. Unwanted raw material components such as grease and dirt are also a source. The origins of heavy metals and iron, commonly found in textile water effluent are described below.

- Cadmium and zinc are often found together due to the common origin in zinc blend that includes both these elements. They are used in orange pigments and also in different kinds of salts used in the textile process (Posner, 2004).
- Chromium is used in oxidation in the form of sodium dichromate. It can also be used in cotton and rayon dyeing and under chemical fixation. Both forms of chromium (VI) and chromium (III) are found in those chemicals (UNEP IE, 1994).
- Iron is often found in red pigments and as a trace mineral in chemicals.
- Lead is used in yellow pigment, but can also be used to increase the weight of the cloth (Posner, 2004).

The dyeing process will be described further on in the text. The whole textile industry includes growing, harvesting, production, treatment process and transport. It is important to understand that chemicals used in earlier treatment of the textile can be washed out in the dye or wash water.

### 2.2.1 Dyeing

Over the last decades a more environmental-friendly dyeing textile process has been developed, both by reducing the effluent emerging from dyes and by developing less harmful dyes. Unfortunately, these methods and chemicals are used more in developed areas and not in developing countries, which are the main dye producing countries. Chemical companies market a range of products, many under trade names rather than by chemical composition. Therefore identification of hazardous chemicals is difficult (UNEP IE, 1994).

Initially, different plant and animal related products were used for dyeing. Today high affinity is important. Affinity is the concentration between the pigment on the cloth and the concentration in the water after equilibrium adsorption has occurred. High affinity represents less colour chemicals left in the water. The residue in the wash water is hard to recover, so therefore it is desirable to reduce the water used per kg fabric (Åsnes, 1997).

#### 2.2.1.1 Case study: Dyeing process in Shakthi Knitting Private Limited

Below is a description of a dyeing industry, Shakthi Knitting Private Limited, located in SIPCOT Perundurai. This is a newly constructed dyeing and printing industry. They use 1 kg fabric to 8 litres of water, 1:8 MLR, Materiel Load Rate. The pre-treatment and dyeing is done in the same machine and the rest of the processes are all prepared in different machines. They use high technology and everything is computerized.

First the fabric undergoes a pre-treatment, which is washing the textile fabric with soap, free from oil and mineral substances. In order for the dye to fully penetrate the cloth and to provide the necessary dyeing action, large amounts of pre-dissolved salt, NaCl or

$Na_2SO_4$, are added to the bath. This will suppress the negative charge on the fibre surface and therefore increase the dye uptake (Ahmed, 2004). After that, sulphate is added to get a better colour yield. To gain better control of the process, the alkalinity is increased mainly through the addition of Soda ash. The pH will rise to 10-11, which also results in a covalent fixing of the dye to the cotton fabric (Ahmed, 2004). The amount of dye and time the dye is together with the fabric is determined by the absorbance of the colour to the fabric. Later the remaining dyes and salts are washed out with clean water. After that the pH is adjusted by adding acetic acid or HCl. The finished fabric should have a pH close to 7. If the pH gets too high the clothes will be itchy and if the pH is lower than 7 the textile will rip very easily. After adjusting pH, the clothes are washed with water and soap to remove the remaining unwanted substances. Subsequently, Shakthi Knitting Private Limited washes the fabric again to remove the soap and add softening agent. This is to make the fabric uniform and achieve a nice soft feel. Finally the fabric is dried in a dryer and placed in a mechanical compress to prevent that the fabric from shrinking or stretching later on.

## 2.3 Soil, plant and heavy metals

The effluent from PCETP is used for irrigation, and therefore the description of the effect heavy metals can have on the soil and plants on the irrigated land is important. This is provided below together with information about the soil and plants.

### 2.3.1 Soil

“Soil is the thin skin of the earth’s surface responsible for life being possible on the planet” according to Allen (1995). It is a porous material formed at the surface of the earth. Processes of weathering, biological, geological and hydrological phenomena create the soil. Over long periods of time the soil is built up with different types of layers. The soil is composed of rock and mineral fragments, organic material, aqueous and gaseous components. The minerals generally come from the weathering of rock fragments and the organic material comes from living organisms, dead plants and colloidal humus (Alloway, 1995). The organic matter acts as a cluster and creates voids in various sizes, the “soil pores”. These pores are filled with air or some with water.

Soil has an enormous capacity for absorbing and storing particles and is also suited for buffering physical and chemical influences. The soil is the most suitable habitat for many organisms. There are no sharp gradients of temperature in the soil as there are in the atmosphere. This is because radiation is basically unable to penetrate through the soil and also because the processes of exchange are slow and occur by diffusion. It is in the soil the roots of a plant derive their nutrient from the earth, and the roots are the most vulnerable organ system for many higher plants. Without soil, only few plants such as algae and mosses can live (Larcher, 1980).

### 2.3.2 Plant

Plant roots take up plant-nutrient elements in positively and negatively charged ionic form from the soil. Today it is known that at least 16 plant-nutrient elements are necessary for plants growth. The primary plant-nutrients are nitrogen, phosphorous and potassium, while the secondary nutrients are calcium, magnesium and sulphur. These six elements, the primary nutrients and secondary nutrients, are known as major elements or macronutrients. These elements are used in relatively large amounts by plants. Iron, manganese, copper, zinc, boron, molybdenum and chlorine are called trace elements or micronutrients. These elements are in relative abundance. On the other hand, they are as important as the major elements in the plant, but are only necessary in small amounts. The remaining nutrients are carbon, hydrogen and oxygen (Krishiworld, 2004).

### 2.3.3 Nutrient transportation

The transport from the soil to the plant is the same for heavy metals and nutrients. The nutrients the plant absorbs occur in the soil in both dissolved and bound form, but it is easier for the plant to take up the nutrients in dissolved form. However most of the nutrients in the soil are in bound form (almost 98%). They are bound in organic detritus, humus, insoluble inorganic compounds or incorporated in minerals. It is only a tiny fraction (less then 0.2%) of the nutrients, which are dissolved in the soil water. The remaining nutrients (2%) are absorbed on soil colloids (Larcher, 1980).

The pH in the soil is important as it affects the nutrient supply and also directly affects the plants vitality (Larcher, 1980). If soil pH decreases to extremely low (acidic) levels the nutrients will be more soluble. If the pH in the soil is extremely high (alkaline) many of the nutrients precipitate and will be insoluble (Alloway, 1995). If the metals are more soluble they will be more mobile and a higher concentration will occur in plants and groundwater. If the mobility is low, a higher accumulation of metals will be found in the soil. It is not only the pH that decides the mobility of the metals, it can also be different from metal to metal, see Table 2.1.

*Table 2.1 Heavy metals mobility*

| Cadmium | Chromium | Iron | Lead | Zinc |
|---|---|---|---|---|
| High mobility[1] | Low mobility[2] | Low mobility[3] | Low mobility[4] | High mobility[5] |

1). Pettersson, 1994. 2). Alloway, 1995. 3). PPO, 2005. 4). Alloway, 1995. 5). ATSDR, 2003.

The plant nutrients are based in the solid phase and their usual pathway to the plant root system is through the surrounding liquid phase. A root takes nutrients from the soil through three different ways;

- The plant root absorbs the nutrient ions, which are directly available from the soil solution. Those ions are $NO_3^-$, $SO_4^{2-}$, $Ca^{2+}$, $Mg^{2+}$, $K^+$ and P ions. The soil solutions replenish its ionic concentration by drawing ions from the solid phase of the soil (Larcher, 1980).

- Exchange nutrient ions. By releasing $H^+$ and $HCO_3^-$ the roots extract cat-ions as $K^+$, $Ca^{2+}$and $Mg^{2+}$ or an-ions as $(SO_4)^{2-}$, $Cl^-$ and $(NO_3)^-$ in the external solution (Larcher, 1980).
- Nutrient elements fixed in chemical compounds are liberated and form chelated complexes. Plant roots quickly take up metal chelates. Furthermore, some ions are freed more readily than others (Larcher, 1980).

The nutrients are transported from the root to the cell by the vascular system (Krishiworld, 2004). The nutrients enter the cell through a cell membrane. This can happen in three different ways. One way is if two ions of opposite charge are transported at the same time. In this way, the number of positive and negative charges will be even. Another way is when an ion in the cell is exchanged for another with the same charge. The third way is when the ion uses a specialized chemical that acts as a carrier. The carrier attracts anion outside the cell membrane and releases it inside the cell. The third way can only occur when there is already an electrical potential difference across the membrane (Larcher, 1980).

### 2.3.4 Heavy metals influence on soil and plants

Heavy metal pollution is the level when the content in the soil exceeds natural background levels and causes ecological destruction, by Chunrong (1999). Heavy metal pollution in soil is serious in many ways. It is both widespread and non-degradable, so it accumulates in the soil. The pollution infects more than just the soil, it also impairs the quality of crops, which leads to the food chain and infecting human health. It also influences the atmosphere and the quality of the water environment. Gaining control of the pollution sources is the most effective way to reduce the heavy metal pollution (Chunrong, 1999).

All the heavy metals are toxic in large amounts in plants, yet some of them are also plant-nutrients such as iron, copper and zinc. Those nutrients are essential for normal growth and development. The concentration of heavy metals may differ in stem, leaf and roots. The plant has different visual symptoms depending on whether the supplies of heavy metals are deficient or acceptable. Symptoms are generally similar from one plant species to another. One symptom is that plants can grow slowly, get a stunted growth or a lack of new growth. The plant can also get a symptom with the name Necrosis, which is death of plant tissue, sometimes in spots (EPN, 2005). Another symptom is that leaves can turn to yellow, almost ending as a totally bleached leaf. The bleaching of the leaves depends on the loss of chlorophyll, called Chlorosis. This yellowing can be generalized over the entire plant. In some plants, zinc excess will cause iron deficiency. Iron-excess will give a possible bronzing of leaves with tiny brown spots (EPN, 2005). Iron-excess occurs primarily in acidic soils, pH less than 5, where available soil concentrations are higher (MSUE, 1998). Typical heavy metal content in plant shoots is for cadmium 0.4 ppm, chromium 0.2 ppm, lead 6 ppm, iron and zinc 100 ppm (RIF GM, 2003). Some of those symptoms mentioned above depend not only on nutrient deficiency or the supply of toxic substances, but symptoms similar to these can also indicate environmental stress or other problems (UM, 2005).

## 2.4 Groundwater and heavy metal

Water has different pathways entering the soil. It is stored in the soil, consumed by plants or evaporates. The water that remains moves through the crop root zone in the soil and finally reaches the groundwater. If the water is contaminated, for example with heavy metals, it is possible for the contamination to follow the water pathway. If the contamination reaches the groundwater, it can be transported a long way and will move into the streams and even into the oceans. In this way the contamination can reach plants and harm animals and human beings a long way from the pollution spot. High pollution levels can be found very wide spread from the contamination source. Cleaning the groundwater from contamination is very costly and time consuming. Even though soil is hard to clean, the groundwater is harder and it is desirable to keep contamination from the groundwater.

The processes affecting the transport are complex. The transport rate depends mainly upon soil properties such as texture, chemical composition, structure, bedrock and of course varies widely between different chemical species. Heavy metals are transported through physical, chemical and biological interaction between rock matrix and the other species (Riley, 2000). Transportation in the groundwater is discussed very carefully in "Applied hydrogeology" by Fetter (2001). When the amount of water leaching through the soil is too low the amount of heavy metals will increase in the soil. This can lead to decreased crop yields (University of Nebraska Lincoln, 2004).

## 2.5 Legislation

The environmental legislation in India has been set up by the Ministry of Environmental and Forests (Ministry of Environmental and Forests, 2004). Each state is responsible for implementation of the legislation relating to prevention and control of the environmental pollution (Central Pollution Control Board, 2005). For Perundurai the Tamil Nadu Pollution Control Board, TNPCB, is the responsible institution. It was established in 1982. TNPCB have the observing function to ensure that the rules set up are followed. This includes inspection of sewage and trade effluent from treatment plants. Furthermore they collect samples of sewage or trade effluent, air emissions and noise to do analyses on, specific parameters. Finally they also monitor generation, transportation, storage, and disposal of hazardous waste (TNPCB, 2005).

The water "Prevention and Control of Pollution" Act 1974 amended 1988 is very important legislation. This is India's first attempt to deal with environmental issues. The act prohibits the discharge of pollution into water bodies beyond the given standards. The waste producers bear the responsibility to dispose of the waste to common sewage pipes or on their own area. Depending on where the disposal place of the wastewater is located; inland water, common sewage pipes, on land or to costal water, different maximum concentrations apply, see Appendix A. Section 25 requires the consent of the board for establishment, operation or processing by any industry that discharges sewage or trade effluent into streams, wells, sewers or lands.

There has been examples of very long turnaround times for TNPCB, up to 44 months to collect and analyses samples (Frontline, 2002). Recently TNPCB has strengthened by the enforcement, this has lead to lot of textile industries being forced to close down (The Hindi, 2005). The biggest issue for the textile industries is to meet the TDS limits.

TNPCB has closed down 135 tanneries without cleaning process connected to their wastewater system. According to TNPCB's homepage they have so far made an inventory of 25 706 industries in Tamil Nadu and certified 22 370 of them. If the laws not are followed, the board has the right to bring the case to court. If convicted, this can result in the minimum imprisonment of one year and six months up to a maximum of six years. It can also lead to an additional fine and of course the closing of the industries.

Legislation itself is not a problem in India, even though the discharge limits may be higher than in some developed countries (UNEP IE, 1994). The setback for India and Tamil Nadu is that the regulations and laws are not followed in practice. TNPCB has met enormous protests from all industries and is also accused of raising unemployment to even higher levels.

## 2.6 Treatment of heavy metals

Most of the heavy metal salts are soluble in water and form aqueous solutions. Consequently, it cannot be separated by ordinary physical separation. This is even more pronounced when the water has a lower concentration of heavy metals, in order of 1-100 mg dissolved heavy metal ions per litre (Fraunhofer IGB, 2002). Today there are different ways of removing heavy metals from the wastewater. Six main methods exist, sedimentation, chemical precipitation, adsorption, ion exchange, membrane filtration and biological treatment. To get an idea how PCETP and other treatment plants remove heavy metal these six methods are described below.

### 2.6.1 Sedimentation

Sedimentation is a physical treatment process, which uses gravity to separate suspended solids and particles from water. The particle velocity must be higher than the uplift velocity if the particles should settle. Sludge is collected at the bottom of the tank. The sludge emptying is often intermediate. In a wastewater treatment plant in Sweden 40% of the lead, zinc, chromium and cadmium are removed through primary sedimentation (Berg, 1986). Lead is one of the metals that is easily adsorbed by suspended materiel in wastewater and therefore easily removed by physical separation. Sedimentation is by itself not sufficient for removing heavy metals from the wastewater because it does not remove particles that are dissolved. It only removes the metals that already are in particle form or connected to other particles. Sedimentation in combination with the other methods may be sufficient to remove heavy metals. The most common combination is chemical precipitation followed by sedimentation.

### 2.6.2 Chemical precipitation

Chemical conditioning or coagulation is the addition of chemicals to modify the physical properties and change the stable solids that do not settle. Most colloids are electrically charged with the result that colloids of similar charge will repel each other. Therefore particles do not want to clog together to form bigger coagulates that can settle. Chemical precipitation is the addition of chemicals, usually lime, aluminium sulphate or ferric sulphate to the wastewater. The goal is that the chemicals and metals shall form insoluble precipitates. Metal precipitation is primarily dependent upon two factors: the concentration of the metal and the pH of the water. The pH should be where the newly formed complex has minimal solubility, so maximum coagulation occurs. The metal solubility as precipitated with sulphates is illustrated in Appendix B. However, the metals now only exist in another phase or state (that is as small solid particles). Metal removal is not complete until these metal solids are physically removed from the wastewater, typically by subsequent sedimentation or filtration (Ayres, 1994).

Several tests proved that pure lime ($Ca(OH)_2$) could effectively remove the colour and heavy metals from the textile wastewater (Tchbanoglous, 2003). Treatment with lime alone could be considered as competitive to the treatment with ferrous sulphate (Aivazidis, 2003). Lime has been found to be a better chemical to coagulate cadmium, nickel, zinc and often lead than aluminium sulphate while it is the opposite for chromium (Bergholm, 75/76).

There are some problems connected to the addition of chemicals. The first one is that the chemicals may consist of a considerably high amount of heavy metals. If pure chemicals are not added, it may even increase the amount of some heavy metals instead of reducing them (Berg, 1986). The second one is that compounds such as cyanide or ammonia can inhibit the precipitation of metals, and limit their removal so that the discharge limits are exceeded. The third is that not all metals have the same minimum solubility, see Appendix C. Instead the pH needs to be adjusted to an average value approximately pH 9 but of course the perfect pH is dependent on the specific water quality (Ayres, 1994). The fourth challenge is that hexavalent chromium cannot be removed as the other metals because it is soluble at all pH. Instead water with chromium (VI) is first treated with a chemical reduction process to change the form to chromium (III), which can be coagulated (UNEP IE, 1994). During the reduction process sulphur dioxide, sodium bisulphite or ferrous sulphate is added to the wastewater. After that the pH is lowered to 3.0 or less using acid (typically sulphuric acid). This process converts chromium from the hexavalent form to the trivalent form (Ayres, 1994).

### 2.6.3 Adsorption

Adsorption is a method that lets the wastewater pass through a tank with a specific material with good adsorption capacity. Today a lot of different adsorption materials are used. The most common is activated carbon (Malik, 2004 and Sengil, 2004). Absorption through activated carbon has been one of the most reliable and effective methods, but it is expensive. The activated carbon can be made from different materials consisting of carbon, see Chapter 3.3.2.1. Activated carbon is prepared from low cost materials, for example, mahogany or sawdust, which are considerably efficient for textile effluent. The quality of the effluent is dependent on the contact time, adsorbent dose and pH. In this case pH should be below 3. This is due to the surface of the activated carbon being positively charged by the increased amount of $H^+$. Since most of the dye's molecules are anion, a stronger attraction and adsorption will occur and therefore a more efficient treatment. Better adsorption will also occur at higher pH, above 10, because the heavy metals will precipitate, see Appendix C. Today all kinds of adsorption materials like clay minerals, fly ash, slag, alunite, chitosan, wood, mazinie cod and peat are being used, but the adsorption capacity is less than with activated carbon. According to research by

Şengil, A. and Özacar, M. (2004), pine dust has big potential for removal of metals. Even here low pH will increase adsorption of metal complex (Malik, 2004).

In 2004 Soo-Jin, P. conducted research into modified activated carbon filters by electrochemical oxidation treatment with acidic or basic electrolyte in the context of heavy metal adsorption behaviours. He found out that increased surface functional groups led to an increase of the adsorption of heavy metal ions.

### 2.6.4 Ion exchange

Ion exchange is considered to be one of the most common treatments to remove metals (Tchbanoglous, 2003). Ion exchange is the interchanging of ions between a solid phase and the liquid that surrounds the solids. An important process for making ion exchange possible is that exchange sites exhibit stronger holding capacity for certain ions than others. First ions with multiple charges are held more strongly than those of fewer charges. The same charge ions are held accordingly to their atomic weight, with heavier held more strongly (Liu, 2000). Materials used for exchange metals are zeolites, weak and strong anions and cation resins, chelating resins and biomass. Synthetic ion exchanges have better durability but natural resins are considered to be the cheapest option (Tchbanoglous, 2003). Chelating resins can even pick up metals through the background solution. However, if precipitation is used before ion exchange metal formation, that is hard to be removed by resins, can occur (Liu, 2000).

Most commonly the exchanging material is placed in a bed or a packed column and the water to be treated is passed through. When the resin capacity is exhausted the column is backwashed to remove trapped solids and the resin regenerated (Tchobanoglous, 1991). Ion exchange processes are highly pH dependent. Most metals bind better at higher pH due to less competition from protons for adsorption sites (Tchbanoglous, 2003).

Today methods that increase the natural ion exchange resins have been developed. For example, this can involve doping the bran with phosphate groups, enabling it to bind heavy metals. The binding capacities are comparable to or even higher than those of commercially available ion exchangers. After regeneration with acid, the bio-adsorbents can be reused several times. In bench scale experiments the bio-adsorbent proved suitable for the elimination of toxic heavy metals from various industrial wastewaters (Fraunhofer IGB, 2002).

### 2.6.5 Membrane filtration

Membrane filtration is pressing the water through a very fine membrane in either dead end or passed through systems. Today wide ranges of different membranes are used, such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

Membrane techniques can reduce the heavy metal concentration in wastewater to less than one quarter of the amount left after traditional chemical water treatment and precipitation methods (Koch membrane system, 2004). Ultrafiltration is effective for the removal of particles and macromolecules. Nanofiltration allows the separation of low molecular weight organic compounds and divalent salts. Reverse osmosis is suitable for removing ions and larger species from, for example dye bath effluents. The reverse osmosis membrane also removes the colour and desalinates the waste stream considerably. Only the use of ultrafiltration is not enough to get good quality in the effluent and further treatment is required. The use of membrane technology consisting of ultrafiltration followed by reverse osmosis has been very effective in wastewater treatment (Ŝostar-Turk, 2005).

Filtration through a membrane can also split the effluent into two streams. One of the two streams containing the dyestuff and most of the divalent ions is called reject stream. The other stream consists of water and some salts, depending on the kind of membrane used to pass through. The factors that limit membrane filtration are the durability of the membranes due to clogging and concentration polarization (Bes-Pih, 2002). Ismail Koyoncu found out during research in 2003, that maintaining pH 7 decreases clogging and gives longer membrane life.

### 2.6.6 Biological treatment

Many aquatic microorganisms, such as bacteria, yeast and algae can absorb dissolved metals from their surroundings onto their bodies. Microorganisms can be used for removing heavy metal ions successfully (Hussein, 2004). Biological methods such as biosorption or bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. Microorganisms assimilate metal either actively (bioaccumulation) and or passively (biosorption). Earlier studies demonstrate that biosorptive processes are often more applicable than the bioaccumulative processes. This is because living systems (active uptake) often require the addition of nutrients, therefore the BOD and COD may increase in the effluent. In addition, maintenance of a healthy microbial population is difficult due to metal toxicity and other unsuitable environmental factors. Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for recovery of heavy metals from industrial waste streams.

Although the mechanisms by which heavy metals affect biological treatment processes are not well defined, the general response of these processes to varying concentrations of metals is well documented. It has been reported that activated sludge microorganisms and process efficiency were restrained by cadmium, chromium and nickel at concentrations above 10 mg/l. However, trace amounts of heavy metals are still required by microorganisms for optimum growth (Soon-An, 2005).

### 2.6.7 Combinations of different techniques

Membranes in combination with physico-chemical processes are interesting to achieve good effluent quality. The quality of the effluent may be so good that the water could be reused in the industries (Bes-Pih, 2002).

The addition of activated carbon powder increased the oxygen uptake rate of activated sludge microorganisms. This is done by reducing the toxic effects of metals and supplying reaction sites for microorganisms and substrates. The addition of activated carbon powder into a biological treatment system to reduce the toxic effects of metals should be carried out as early as possible before the microorganisms become seriously impaired (Soon-An, 2005).

The most common method at present involves precipitation reactions followed by an adsorption process using synthetic resin ion exchangers. In the ion exchanger, the metal ions are bound to the resin and can be replaced by hydrogen ions. When the ion exchanger is saturated, it is regenerated with an acid. The result is a highly concentrated acidic salt solution, which can be further condensed. The ion exchanger can be reused. One disadvantage of using synthetic resins as ion exchangers is that they are produced from petroleum, a limited resource (Fraunhofer IGB, 2002).

# 3 Site description

## 3.1 Perundurai

Perundurai is located between the cities Coimbatore and Erode, but belongs to the Erode district. For location, see the map in Figure 3.1. Erode is one of the 30 districts in the state of Tamil Nadu in India. Erode was earlier a part of the Coimbatore district but since the 17th of September 1979, it has been its own district. It has an area of 8.2 $km^2$ that corresponds to 6.3% of the total state area. Erode is first of all an agriculture district and about 38% of the total area is cultivated. Agriculture provides employment to approximately 60% of the workforce (SIDO online, 2005).

The major crops grown are oilseeds followed by cereals. Beside these, crops such as sugarcane, turmeric and cotton are commonly cultivated. Erode is also an industrially developing district. One of the oldest and largest industries is the textile industry, where power loom weaving has a major role. The district also has a high concentration of handloom weaving, rice milling and edible oil expelling units. Other industries in the district are leather, chemical, plastic, paper and basic metal industries (SIDO online, 2005).

Perundurai is located on a flat plateau about 300 meters above sea level. There is 726 mm rainfall per year with almost 80% during the two monsoon periods. The temperature during the year is quite constant, between 24-37°C. The bedrock is mostly unclassified gneiss, but lime also occurs. The soil is Irugur, which is sensitive to erosion and the soil layer is 0.3-1.0 meter thick (Soil atlas erode district, 1998).

*Figure 3.1 Indian map showing the location of Perundurai*

## 3.2 SIPCOT

The government is promoting industrial growth in backward and hitherto underdeveloped areas that have potential to grow. SIPCOT is an organization arranging this in the state of Tamil Nadu, so far in 17 different areas (SIPCOT, 2004). Companies, willing to start up industries in that area, lease the land for 99 years and are guaranteed good infrastructure, electricity, sewage and water supply 24 hours a day.

### 3.2.1 SIPCOT Perundurai

SIPCOT Perundurai was started in the year 2000 and it is divided into two parts, the east and the west part, totally 1240 ha. SIPCOT only leases 732 ha of the total area and today 288 ha of the area is licensed. Currently 210 industries are located in the area within the fields of chemicals, textiles industries, food manufacturing, tanning and engineering products. SIPCOT has a common sewage plant, where black water from all industries is treated. The water comes by gravity in stone-laid drainage pipes and is then taken care of by oxidization ponds.

SIPCOT Perundurai industrial plan is an area designed for 54 different units within textile processing. Today there are only 10 units in operation and four units under construction. These four units will open in 2005. The processes run at the textile industries are dyeing, bleaching and yarning. The industries in SIPCOT are mainly working with cotton. The cotton contributes with much organic matter in the water effluent.

Each of the industries has two different pipe systems for wastewater. One system is taking care of the water from the first washing after dying, called the dye bath effluent. This water has always very high TDS, over 2100 mg/l and is therefore not measured. The other system is for the remaining effluents from acid wash, water washing, soap washing and softening water. All this is called wash water. The industries have a sensor that measures the TDS value from the wash water, ensuring that it does not exceed 2100 mg/l. If the value is higher a valve will close and direct the water back to the receiving tank to dilute with the other wash water. The textile has two different effluent wastewater streams. The dye bath has a high TDS, above 2100 mg/l, and the wash water has a lower TDS, below 2100 mg/l. Each industry will also measure the flow in both effluent pipes. All effluent from the industries is sent to Perundurai Common Effluent Treatment Plant, PCETP.

## 3.3 Perundurai Common Effluent Treatment Plant

Each industry bears the responsibility for dealing with the effluent water from their processing. Therefore the 14 textile units together formed PCETP. Each of the units has different shares in the treatment plant and consequently they are allowed different maximum flows that they can discharge to the treatment plant. The treatment plant only handles industrial effluent from those 14 textile industries. PCETP can operate 3600 $m^3$/d wash water (TDS below 2100 mg/l) and 450 $m^3$/d dye bath (no limits for TDS).

## 3.3.1 Dye bath treatment plant

The dye bath treatment uses an evaporator for cleaning the water. Before the evaporator the water is pre-treated in the form of sedimentation and fine screening. The evaporation unit is a high technology system that vaporizes the water in five different evaporation tanks, three falling and two forced circulation (vacuum) tanks. They reduce the power input by using two heat exchangers and by doing so recover heat from the outgoing water to the incoming water. The outcomes from the evaporation tanks are two different waters, distilled water that goes back to the industries and the second water that goes to solar dryer ponds. The water in the solar dryer ponds evaporates to the atmosphere in 10 days. The rest consists to 95% of sodium chloride, NaCl. The salt is collected from the bottom of the ponds and stored in sacks under roof. They produce 3.6 tons of salt each day and the space for storage is limited so this soon becomes a big and critical issue. At the time of writing an investigation is being made about purifying the salt so it can be reused in the textile industries.

## 3.3.2 Wash water treatment plant

The wash water treatment plant was opened in July 2002 and reduces COD and $BOD_5$ by 40-60%. They regularly measure pH, TSS, TS $BOD_5$, COD and TDS. The plant has no seasonal variation as the textile industry produces the same quantity the throughout the year. However, the hourly inflow varies widely in both quality and quantity. The receiving tank and the bar screens are designed for the peak flow, but the units down stream of the equalization tank are designed for an average flow and an average quality. The energy consumption is approximately 0.9 $kWh/m^3$ water treated and the cost is 12-20 $Rupees/m^3$ (2-4 $SEK/m^3$) treated water.

### 3.3.2.1 Flowchart

First the flowchart for PCETP is described and then the processing in each unit is described in detail. For a picture of the flowchart, see Appendix D. A number is connected to every unit.

First all wastewater comes through the bar screen (1) into the receiving sump (2). Afterwards the water is pumped 12 meters to the equalization tank (3). The water is spread out through three floating aerators in the tank. The water is then again pumped 12 meters with a centrifuge pump up to the flash mixing tank (4). There the water is mixed with lime, iron sulphate and polyelectrolyte. After that the water goes into the clariflocculator (5), where the particles coagulate and sink to the bottom as sludge. The outlet water from the clariflocculator goes to the clarified effluent sump (6). The water is pumped by means of the automatic valves gravity filter feed pumps to the Automatic Valves Gravity Filter, AVGF (7). The water used for backwashing in the AVGF goes back to the receiving sump (2). After the AVGF, hydrochloric acid, HCl is added and mixed into the water with a static mixer (8) to reduce the pH to 7.5-8.5. The water then goes to the stabilization sump (9). Afterwards the water is distributed into two parallel, identical systems. The water is pumped into an Automatic Carbon Filter, ACF (10). The backwashing water from the ACF goes back to the receiving sump (2). After the ACF the clean water goes through a magnetic flow meter (11), which register TDS and pH. Finally the water is pumped with a booster pump out to the field for irrigation.

The sludge from the bottom of the clariflocculator goes to the sludge sump (12) and then further to the sludge thickener (13). After the sludge thickener the sludge can go two different ways. Most of the sludge goes to the centrifuge (14) but before the centrifuge, more polyelectrolyte is added. The rest of the sludge goes to the drying beds (15). As a final point the sludge is packed in sacks and stored under a roof (16) until further notice.

### *Bar screen (1)*

The bar screen is where the wastewater first passes through and is situated in the influent of the Receiving sump. It is used to take care of rags and large objects in the wastewater, so that these objects do not destroy the forthcoming units, for example pumps. PCETP has two screens that are located inside the receiving sump. The shapes are rectangular, size 1.5 x 2.5 $m^2$. The clear openings (spaces between bars) of the first screen are 10-15 mm and clear openings of the second screen are 20 mm. The screen is hand-cleaned once a day and this is sufficient because the character of the water is good.

### *Receiving sump (2)*

The purpose of the receiving sump is to attain the same flow into the treatment plant. The diameter of the receiving sump is 8.0 meters and it has a depth of 2.3 meters. The flow into the treatment plant is about 132-150 $m^3/h$ and TDS is less then 2100 mg/l. In general, TDS is around 1800 mg/l, pH is about 8-9 and the retention time in the tank is approximately 45 minutes.

### *Equalization tank (3)*

The water is spread over three floating aerators, which distribute the water on to the surface of the equalization tank. The water is mixed with air so that an anaerobic process does not occur and settling of suspended solids is avoided. The equalization tank is there to equalize the temperature, quality and flow rate of the water. In other words, minimizing the fluctuation in those parameters for the downstream units. The equalization tank in PCETP has a diameter of 32 meters and a depth of 4 meters. The retention time in the tank is about 24 hours with a flow of 150 $m^3/h$.

### *Flash mixing tank (4)*

The mixing tank is an important unit when one substance must be completely mixed with another. The first goal for the mixing tank is to raise the wastewater pH to form metal hydroxide particles, by the addition of lime. The next step is to add iron sulphate and polyelectrolyte into the wastewater. Iron sulphate destabilizes the colloids so they are able to flocculate (Liu, 2000). The polyelectrolyte attaches to the metal solid particles and small metal hydroxide particles become entangled in the polyelectrolytes. This increases the particle size, which promotes settling (Ayres, (1994). This effect is illustrated in Figure 3.2

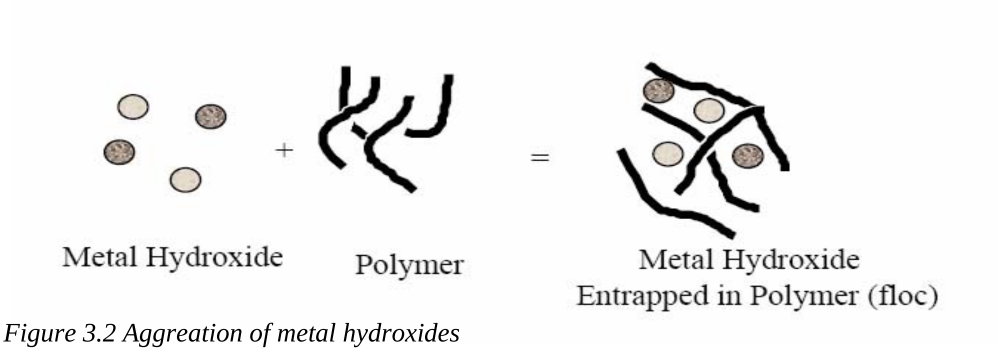

*Figure 3.2 Aggreation of metal hydroxides*

The mixing tank has a volume of 1.5 x 1.5 x 1.8 $m^3$ and the mixer is mechanical. In PCETP they add lime to raise the pH to 11. Water samples are collected about every two hours from the equalization tank so the dose of the chemicals can be regulated to the quality of the water. On average, the chemicals added in 1 litre wash water are 80-90 ml Lime, Ca(OH) 5% and 20 ml iron sulphate, $FeSO_4$ 5%. The water retention time in the flash mixing tank is about two minutes.

### *Clariflocculator (5)*

The clariflocculator is a tank where both flocculation and sedimentation takes place. Once the size of the particles is increased, they are able to settle so they can be removed from the wastewater. The particles go to the bottom of the tank since they are heavier than water. The water goes over the outfall, so here the sludge and the water go different ways. The pH during sedimentation must be maintained at approximately 9.0 to ensure that none of the metal hydroxides re-dissolve and become soluble in the water (Ayres, 1994). Inside the big tank (settling tank) is a vertical cylinder (downtank) open at the top and bottom, which acts as a flocculation chamber. The water from the mixing tank enters from the top of the downtank. In the downtank, a couple of mixers operate at slow speed to increase the size of the flocks. If the speed of the mixers is too rapid, it will destroy the flocks. After the water leaves the bottom of the downtank, the course of the water turns upward. The water rises slowly in the annular space between the settling tank and downtank while the flocks (as sludge) settles down to the bottom of the settling tank. The deposited sludge is scratched off from the bottom of the tank and pumped into the sludge sump. The cleaner water reaches the top, it flows out through the outfall, which extends all around the settling tank. The clariflocculator at PCETP has a diameter of 16.5 meters and a depth of 3.0 meters. The water retention time is four hours.

### *Clarified effluent sump (6)*

It is in the clarified effluent sump that the water is stored after the clariflocculator. The sump is used to provide a constant flow into the next unit, the AVG filter. The clarified effluent sump in PCETP has a retention time of 30 minutes. The dimension of the tank is 10.0 x 6.0 x 2.5 $m^3$.

### *Automatic valves gravity filter (7)*

The purpose of the filtering is to remove suspended solids, which did not settle in the sedimentation basin. The reason the particles do not settle could be that they are too small and do not have sufficient time to settle. The particles instead follow the water out (Ayres, 1994). The wastewater passes through the filter bed composed of granular material (Tchobanoglous, 1979). The removed particles are accumulated in the voids in the sand therefore the head increases. When the pressure gets too high, automatic backwashing starts to remove the suspended solids (Ayres, 1994). In PCETP, the sand filter is used because it is effective and made of cheap material. They have three different sand stones of a different density to increase the flow. The coarse material is on the bottom and the fine material on the top. The driving force in the sand filter is the capillary drainage system in the bottom. The flow in the filters is 7 $m^3/h$. This gives a retention time of approximately 10 minutes. The filter is backwashed for about 15 minutes with a flow of 50 $m^3/h$, in general twice a day. The backwash water from the sand filter goes back to the receiving sump.

### *Static mixer (8)*

Most of the coagulant formed has now been removed and the pH can be reduced to the desirable effluent limits. In PCETP a static mixer is placed on the pipe to the stability tank and is designed with baffles. This mixes the water hydraulically with hydrochloric acid, $HCl$.

### *Stabilization sump (9)*

In the stabilization sump the pH in the water stabilizes, resulting in fixed pH at 7.5-8.5 before the water goes to the carbon filter. The sump also ensures a constant flow to the next unit, for example when the AVGF is backwashed. The retention time is 30 minutes in the stabilization sump in PCETP.

### *Activated carbon filter (10)*

The most effective method to take away unwanted materials such as odour, heavy metals organic and inorganic pollutants is to use an ACF. Activated carbon can be prepared from anything consisting of carbon, for example hardwood or nut shell. The materials are heated to 200-1000ºC without oxygen and are activated by reheating to a high temperature whilst providing steam. This will give a fine capillary structure with a surface area of 1000-2000 $m^2/g$ (Hammar, 1998). The carbon will adsorb the pollution and in that way remove the substance. PCETP has two granular carbon filters, one in each system. The volume of the tanks is 10 $m^3$ and each tank is under a pressure of 2.5-3.5 kPa. The retention time in ACF is eight minutes. The thickness of the carbon bed is 0.5-0.75 meter and it is made of coconut shells. The coconut shells are used for two years before they are replaced. The filter is backwashed every eight hours for 15 minutes. The back washing and the first filtrate go to the receiving sump.

### *Magnetic flow meter (11)*

The magnetic flow meter measures Q, pH and TDS in the effluent water. This unit forms the last control of the water before it goes to the field for irrigation. The effluent water has a flow of about 139 $m^3/h$, pH around 7.5 and a TDS of 1700 mg/l.

### *Sludge sump (12)*

The sludge sump is a tank where the sludge is collected before it goes to the sludge thickener. This tank is essential to achieve a constant flow into the next unit. The sludge sump in the treatment plant has a diameter of 1.5 meters and a depth of 3.0 meters. The incoming SS is 2-3%.

### *Sludge thickener (13)*

The purpose of the thickener is to increase the solids content of the sludge by removing a portion of the liquid fraction. The thickener has a slow speed mixer. The mixer has the function of making air channels in the sludge, which makes it easy for the water to escape. Another function of the mixer is to scratch the sludge into the middle of the tank where the sludge is taken out. In PCETP the sludge thickener has a diameter of 6.0 meters and a depth of 2.0 meters. The DS after the thickener is 3-6%.

### *Centrifuge (14)*

The centrifugation separates liquids from solids by considerably increasing the gravity power. Due to different density between the solids and the liquid the solids go immediately to the periphery and the water stays closer to the centre and can than be separated. PCETP has two centrifuges but only uses one at a time. The centrifuge extracts the water so the outlet DS is 25%. Each day 10-15 tons of sludge is produced.

### *Drying beds (15)*

Sludge-drying beds are used to dewater digested sludge. The bed is similar to slow filtration through sand. The bed is filled up with one meter of sludge and it stays untouched for 20 days. Under the sand layer there are drainpipes to collect the separated water. After drying, the sludge is removed and packed into bags and stored under a roof. The sand has three different fractions to increase the flow speed through the bed. The five drying beds are a complement to the centrifuge. They are used instead of the centrifuge when capacity is not sufficient. The dimensions of each bed are 11 x 5.0 x 1.0 $m^3$.

*Storage of sludge (16)*

The sludge is packed into bags and stored under a roof until later. PCETP has made an investigation regarding the use of sludge for brick production. The result was very positive and at the time of writing PCETP has applied for approval for this.

## 3.4 Earlier data

PCETP do not measure the heavy metals continuously. TNPCB do take their own samples to ensure that limits are followed a couple of times a year. Some measuring has been done at the treatment plant connected to an earlier master thesis. The result from those studies can be seen in Appendix E.

## 3.5 The irrigated fields

TNPCB has provided the limits (see Appendix A) and the regulation that PCETP needs to follow. The industries need to ensure that the water is below the regulation limits and disposed of on their own land. Therefore PCETP was constructed in connection with an agroforest field close to the treatment plant. The aim of this field is to take care of all the effluent water from the treatment plant. The irrigation land is 21 ha in size and there are many different trees and grasses in the fields. The main species are Eucalyptus, Casurina, Jetropha, Neem tree, Korai, Sambai and Elephant grass. The compilation of the vegetation, name, size and purpose can be seen in Table 3.1. Plants with high transpiration are chosen to ensure that all water is consumed. In addition, Casurina is a nutrient-fixing tree while biodiesel can be extracted from Jetropha. The plantation is two years old and after 10 years the forest can be harvested. The irrigation during the day is through drainage channels dug by hand. The direction of water changes continuously to feed water into different areas. There are 17-20 different effluent pipes but only 4-6 are used at the same time. Nighttimes rain guns are used to distribute the water. So far has 1500 $m^3$/d irrigated water being placed on 21 ha fields. The irrigation has been going on for two years, which means that the fields has received 52 100 $m^3$/ha.

*Table 3.1 Compilation of the area and the purpose of the plants*

| Plant | Area [ha] | Products |
|---|---|---|
| **Eucalyptus** | 12 | Oils in health and cosmetic products, paper, timber |
| **Korai grass** | 2.4 | Mat making |
| **Casurina** | 4 | Nutrient fixing tree, fuel, timber |
| **Jatropha** | 0.8 | Bio diesel plant |
| **Sambai** | 0.8 | Traditional curtains |
| **Elephant grass** | 0.4 | Animal food |
| **Neem tree** | 0.6 | Timber, medicine value, fuel |

### 3.5.1 Eucalyptus, Eucalyptus globules

Eucalyptus, see Figure 3.3, is a quickly growing tree and also the tallest known tree. The tree can be used in papermaking and as timber. The oil that is extracted from the fresh leaves has three different areas of use, medical, industrial and aromatic. Medical use is as a medicine against infections, antiseptic and for microbial diseases of the lungs and bronchitis. Industrial use comes from the content of terpenes, which are used for flotation purposes in mining operations. Aromatic use is for the aroma in perfumes (Botanical.com, 1995).

*Figure 3.3 Eucalyptus*

*Figure 3.4 Casurina*

### 3.5.2 Casurina, Casuarina glauca

Casurina, see Figure 3.4, is a coniferous tree and grows, compared to other trees, in inhospitable sites, for example very saline sites. It is a medium size tree 15 meters tall, occasionally reaching 25 meters. Casurina has been planted in agro forestry areas primarily for fuel wood but also as windbreak and reserve fodder. The wood has a high calorific value (about 5000 Kcal/kg) and tends to burn slowly with little smoke or ash (NFTA, 1991).

### 3.5.3 NeemTree, Azadirachta indica

Neem, see Figure 3.5, is a native tree in India and can rise up to 35 meters. It carries leaves all year round, thereby providing a constant source of shade. The tree grows quickly and grows in the poorest of soil and weather conditions. It is resistant to more than two hundred different types of insects, as well as various mites, nematodes, fungi, bacteria and even some various viruses (Page Wise, 2002). Therefore the Neem tree is an ideal source of timber for carpentry. The Neem oils have contraceptive properties and antiseptic properties and thereby ideal for use as a medicine. The wood can also be used as fuel.

*Figure 3.5 Neem tree*

### 3.5.4 Jatropha

Jatropha grows in hot dry tropical climates and originates from South America. The tree grows to a height of eight meters and can survive dry periods by shedding leaves, see Figure 3.6. It can be up to 50 years old. The fruits contain up to three seeds that contains 33% oil (FAO, 2004a). This oil can be used for lighting oil, lacquer, soap and as textile lubricant. Recently it has become popular to use the oil in small diesel engines. Jatropha oil is modified by transesterification, heating with alcohol and a catalyst. After this it can be directly used as diesel fuel (Agrawal, 1990). Jatropha is also used for medical purpose for its cleansing effects. The wood is also used as fuel or for basket making.

*Figure 3.6 Jatropha*

### 3.5.5 Korai, Cyperus rotundus

Korai, see Figure 3.7 is a perennial grass that reaches 75 cm in height. The stems are 3-sided and have a triangular cross section. The leaves are green and have a shiny appearance but are only 5-8 mm wide. (UF IFAS, 2004). It is a common plant around the world and in India it is used for mat making.

*Figure 3.7 Korai*

### 3.5.6 Elephant grass, Pennisetum purureum

This tall perennial grass can grow up to 4.5 meters high. Elephant grass, see Figure 3.8, needs a lot of water and thereby it is found in areas with over 1000 mm of rainfall (FAO, 2004b). It grows well in moderate to heavy texture and highly fertile soil. It is most widely grown for fodder grass, but is low in protein if not cut very young. However it has a high value of sugar and leaf-steam ratio.

*Figure 3.8 Elephant grass*

### 3.5.7 Sambai, Typha angustifolia

*Figure 3.9 Sambai*

Sambai is a perennial and aquatic grass. The leaves are narrow and sword-shaped and will rise up to two meters and have distinctive fruiting spikes, see Figure 3.9. Sambai prefers lower pH and has a rapid growth rate and can take over a big area quickly (The Rock Family's Homepage, 2004). It grows where the soil remains saturated most of the growing season and preferably covered with about 30 cm of water. The leaves are widely used as bedding and matting material and for manufacturing of baskets. In India it is also used for traditional curtains. Most of the plant can be used for food for humans and is also a good source of biomass and fuel.

# 4 Materials and methods

## 4.1 Method

Samples were collected at the treatment plant, PCETP from influent water, effluent water and sludge. Soil and plant samples were taken from the irrigated fields. Water samples were analysed at PCETP laboratory for BOD, COD, pH, TDS and TSS. All heavy metals concentrations, pH in soil, conductivity in soil and soil texture were analysed in either or both WTC laboratory, Coimbatore and at Chalmers Environmental Chemical laboratory. The samples were prepared before the analyses could be done.

### 4.1.1 Collection

The water and sludge samples were taken between the 16th and the 23rd of October except for the 22nd, when the treatment plant was closed due to Ayudha Pooja, a national holiday. All soil and plant samples were collected on the 27th of October.

*Water*

Personnel at the treatment plant took the water samples. Every two hours, samples were taken for heavy metals analyses from the influent water before the bar screens and from the effluent water after the ACF. Each sample had a volume of one litre. The 12 samples taken on one day were mixed into one litre composite samples. Altogether, seven influent and seven effluent water samples were taken. All the other water samples, for analyses at PCETP, for influent and effluent were collected from the equalization tank and before the ACF.

*Sludge*

Personnel at the PCETP also collected the sludge samples. Seven sludge samples were collected in plastic bags, once a day, during the peak hour. The samples were taken after passing through the centrifuge unit.

*Soil*

The soil samples were collected from a 10 x 10 $m^2$ area. In this area, five samples were taken at random locations on each depth, 0-15 cm and 15-30 cm. The samples were collected by digging a v-shaped cut. A 1.0-1.5 cm thick slice was taken through the whole exposed face of the v-shaped cut. After collecting the soil samples the bulk was quartered[1]. The same procedure was done for each soil of the seven major crops and for two reference samples. The reference samples were taken in a non-irrigated area, but in close connection to the irrigated fields. The soil was placed and stored in polythene bags to prevent external contamination. An assistant worker at WTC laboratory and the authors took these samples.

*Plant*

Leaves were collected from the seven major cultivated species and reference samples were collected from three trees, Eucalyptus, Neem and Casurina. All the samples were taken by workers at the PCETP or by the authors. Trees and grass plants were selected at random in the field and leaves were collected from different parts of those plants.

### 4.1.2 Preparation before analyses

To measure pH, conductivity and heavy metals in sludge, soil and plants the samples needed to be dried. To measure the total heavy metal concentrations, digestion was necessary. Before available concentrations could be analysed the samples needed to be dissolved. To be able to measure conductivity and pH the soil needed to be mixed with water. In the soil both available and total heavy metal concentrations have been analysed. For the water, sludge and plant samples, only total heavy metals have been analysed. The preparation done at WTC in India is named method 1 and method 2 corresponds to the preparation done at Chalmers Environmental Chemical laboratory.

*Drying*

Sludge, soil and plant samples were spread out on newspapers and placed on the floor in a corridor at WTC for air drying over a couple of days. When the soil was dry it was crushed and sieved through a two mm screen, the sludge was only dried and crushed. The plants were cut and ground to pieces (Devarajan, 1987).

*Digestion method 1*

The digestion of water, sludge, soil and plant samples were made through dissolving the samples with acids. The mix of sample and acid was stored over night and the following day put on a 90°C hot plate. The weight of the samples and the volume of the added acids differ between different sample types, this can be seen in Appendix F. The sludge, the soil and the plant samples were ready when the solution had turned into a milk colour. If the samples dried out before they got the right colour some perchloric acid was added

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[1] Quartered is done through dividing the thoroughly mixed soil into four equal parts. Reject the two opposite quarters and remix the remaining two parts, repeat this procedure until about half to one kg of soil is left (Subanshchandrabose, 1989).

(Devarajan, 1987). The water was ready after 270 minutes. The standard for water is taken from ISO 15587-2, first edition. After the samples were chilled, they were diluted with distilled water up to a specific volume, see Appendix F.

*Digestion method 2*

To do the digestions in Chalmers Environmental Chemical laboratory, microwave MARS 5 was used. To do this, the samples were mixed with acid (see Appendix F) and placed into closed fluorocarbon vessels. The vessels were placed into the microwave oven under pressure and heat. The heating program for digestion is different for the sample types, see Appendix F. To certify that the method was correct, one blank sample and one standard reference material were prepared for each run in the microwave oven. When the samples were chilled they were transferred to plastic test tubs. The samples were then filled with milli q water to the original volume in case of evaporation during digestion.

*Dissolved method 1 and 2*

To dissolve the heavy metals in the soil the shake method was used. An amount of soil was mixed with acid (see Appendix F) and was shaken for two hours. After shaking the sample solution was filtered through a filter paper.

*Mixing with water*

To measure conductivity and pH, 20 grams of soil was mixed with 50 ml of distilled water. The samples were left untouched for 30 minutes (Jackson, 1967).

### 4.1.3 Analyses

Samples treated according to method 1 were analysed in the Atomic Absorption Spectrophotometer, AAS, while samples treated according to method 2 were analysed with ICP-MS. For description of the different analyses equipment see Appendix G.

Conductivity was measured according to Piper (1966). pH was measured according to Jackson (1973) with a “Potentiometry Elico pH meter”.

The texture of the soil was analysed by a method based on feeling the texture of the soil by hand. The soil is moistened with water in the hand. The mixture is rubbed between the thumb and the fingers to decide whether the sample is gritty, soapy or sticky. In this way you determine the texture of the soil within the guidelines, see Appendix H. The relative proportion of sand, silt and clay can approximately be found through a Triangular textural diagram (Appendix I).

BOD, COD, pH, TDS, TSS and flow, Q, for the water were measured according to standard procedures outlined by AOAC 1962 and Anon 1965, specified in Appendix J.

## 4.2 Errors

In this report some samples have concentrations below the detection limit for a parameter (notice the difference between absent and not detectable). The detection limit is different for the two different pieces of equipment used to analyze the heavy metals, AAS and ICP-MS. The AAS equipment can detect down to ppm while the ICP-MS can detect as low concentrations as ppb.

The soil and plant samples were taken in October, which is in the middle of the rain season, so this may interfere with both soil and plant samples.

Balance errors may also have occurred. The amount of samples was small and was lightweight. This meant that the smallest breath of air, wind or other instruments in the room could affect the balance and therefore make it imprecise.

Some of the soil samples in the second layer could not be taken at the right depth because the soil thickness was not thick enough. Those samples were taken as deep as possible before hitting the bedrock.

It should also be mentioned that the time between when the samples were taken and when they were analysed was long. The time between the collection and first analyses was one month. To do the second analyses the samples were sent by Indian speed post and analysed in Sweden two months after collection.

# 5 Result

This chapter includes all the results from the analyses. It is mentioned in Chapter 4 that all analyses of heavy metals were done with two different methods (method 1 and 2). Method 1 has high detective limits and has complex preparations. The results derived from method 1, see Appendix K, were recorded as no detection of heavy metals, except for iron and zinc. Due to this, the results of heavy metals shown in this report are from method 2, which was analysed at Chalmers, see Appendix L.

Concentrations in water are usually presented in mg/l, in sludge and soil mainly in mg/kg and in plants commonly presented in parts per billion, ppb. All the results in the text below are presented in parts per million, ppm. The reason for this is to make it easier to compare the concentrations from all the different sample types; water, sludge, soil and plants to each other.

## 5.1 Heavy metals in water and sludge

The amount of heavy metals in the influent water varies from day to day. The values of heavy metals from the influent water are higher than those for effluent water. In Figures 5.1-5.5, influent, effluent and sludge concentrations for each element can be seen. Note that the scale on the y-axis is different for the influent, effluent (left side) and the sludge (right side).

All the samples analysed by method 2 were sent to Sweden by post. During transportation to Sweden, one day of water samples leaked out. Therefore no results exists from the 21st of October, neither influent nor effluent. No results exist from the 22nd when the treatment plant was closed. In the following figures a value between 20th and 23rd has been extrapolated to achieve a continuous line.

### 5.1.1 Cadmium

The cadmium concentration from the influent is higher than the effluent concentration, but a high peak occurs on the 19th, in the effluent water that is much higher than the influent concentration, see Figure 5.1. The average concentrations of the influent and effluent were 0.019 ppm and 0.014 ppm. On the 23rd an increased amount of cadmium was recorded in the influent and the sludge. The average cadmium load in sludge was 0.113 ppm.

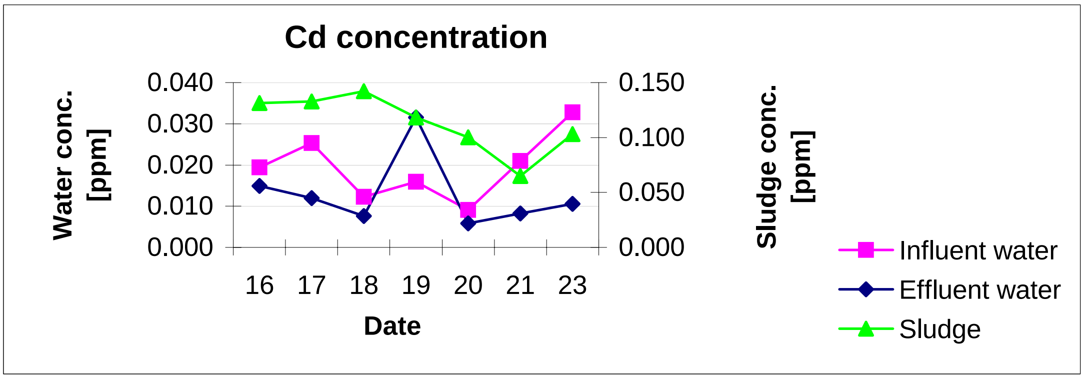

*Figure 5.1 Cadmium concentration in water and sludge*

## 5.1.2 Chromium

The amount of chromium in the influent fluctuates between 1.2-10.0 ppm. In the effluent the difference is lower, but those values are below the concentration of the blank samples and are therefore not countable. During this week, the sludge concentration of chromium goes slowly down. The sludge values were 82-188 ppm.

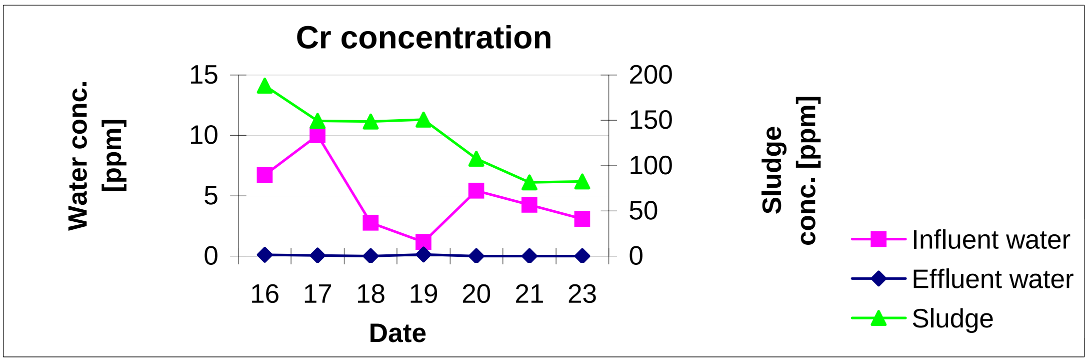

*Figure 5.2 Chromium concentration in water and sludge*

## 5.1.3 Iron

The effluent has some peak values of iron, higher than the values of the influent. The variation of the concentrations for the influent was 81-177 ppm and for the effluent 75-534 ppm. Iron values for the sludge are much higher than for the water, 116 526-131 197 ppm.

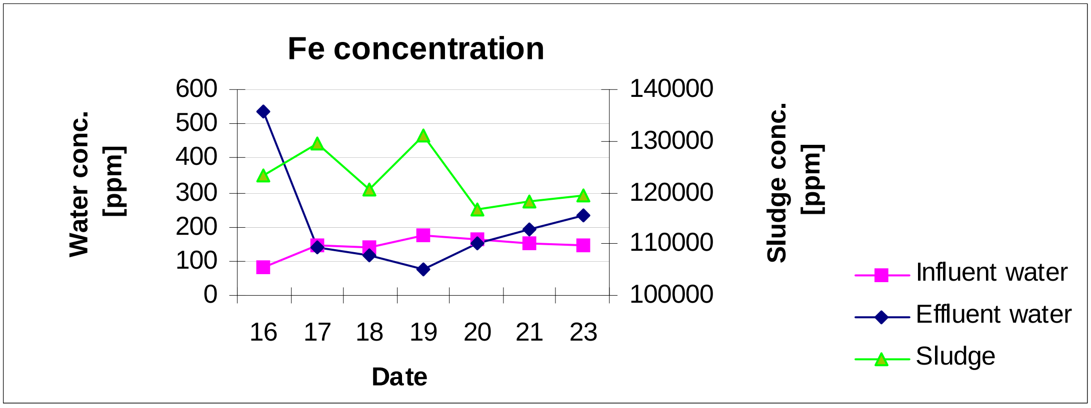

*Figure 5.3 Iron concentration in water and sludge*

### 5.1.4 Lead

The day after the treatment plant was closed, the 23rd, a higher value was recorded in the influent and the effluent for lead, just as for cadmium. The average load of lead in the influent was 0.293 ppm and for the effluent 0.143 ppm. In the sludge, the average concentration was 3.916 ppm, which is higher than for the water.

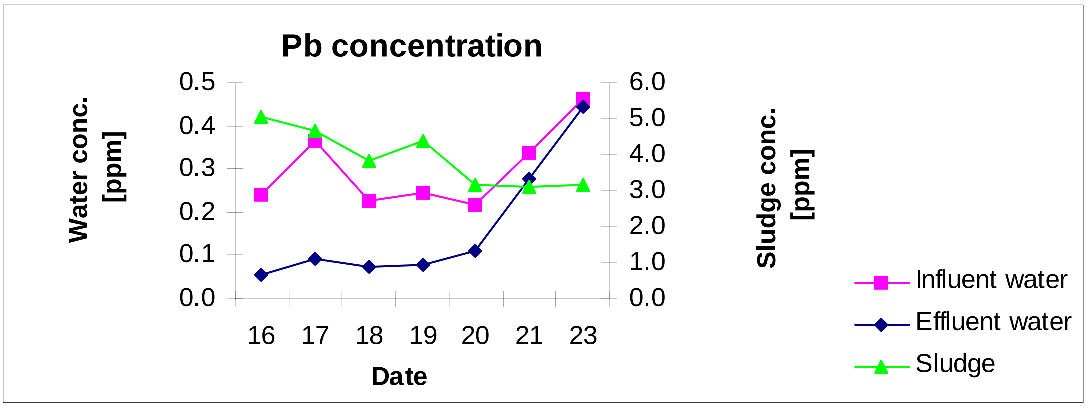

*Figure 5.4 Lead concentration in water and sludge*

### 5.1.5 Zinc

The load of zinc in the influent varies greatly from day to day. The values for the influent were 19-80 ppm, while the values for the effluent were 2.4-8.3 ppm. The sludge also has a variation like the water and the values for the sludge were 270-366 ppm.

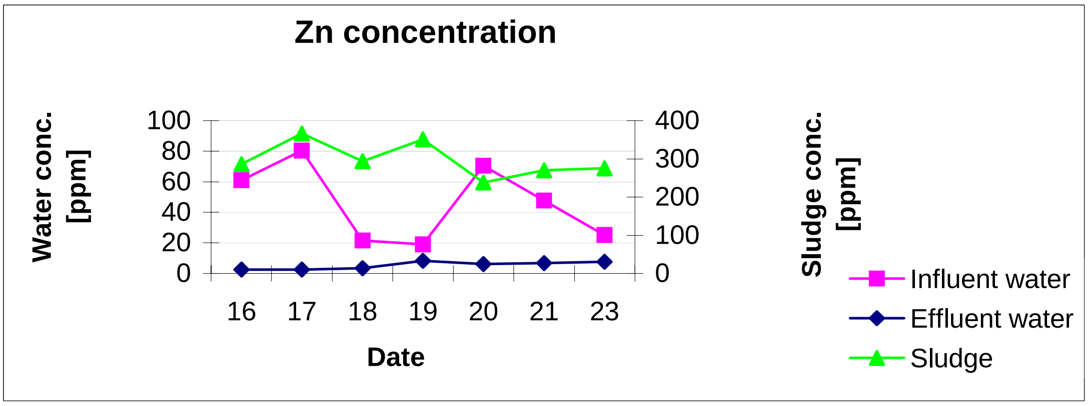

*Figure 5.5 Zinc concentration in water and sludge*

## 5.2 Water

The BOD, COD, pH, TDS and TSS are daily average values and can be seen in Appendix J. In this appendix the flow, Q, for the influent and effluent can also be seen.

The water inflow rate decreased on the 21st and was even less on the 23rd of October, but was kept between 1600 $m^3$/d to 2200 $m^3$/d. The pH in the influent only fluctuated between 8.15-8.6. The TDS was around 1700 mg/l, less than the 2100 mg/l that is the critical limit for the textile industry effluent. The BOD was between 100-200 mg/l and the COD was more than double, approximately 540 mg/l. The TSS was approximately 200 mg/l.

All of the effluent values seem to be quite constant. The pH was roughly 7.6. The TDS concentration was only 1720 mg/l ± 40 mg/l through the whole week. COD was approximately 220 mg/l, $BOD_5$ was reduced to 26 mg/l and TSS was about 18 mg/l.

## 5.3 Heavy metals in soil and plants

### 5.3.1 Cadmium

The cadmium concentration in the soil is low, around 0.034 ppm. The upper layer and the second layer show no difference in accumulation concentrations for cadmium. The reference soil samples have slightly less cadmium concentrations than the irrigated soil, 0.028 ppm compared to 0.036 ppm. The available fraction in the soil is in the range of 5%-100% of the total concentration. Compared to other heavy metals the available fraction of cadmium is high in the soil. In most cases the cadmium concentration is higher in the plants, 0.047-0.216 ppm, than in the soil, see Figure 5.6. The highest value was found in Eucalyptus trees.

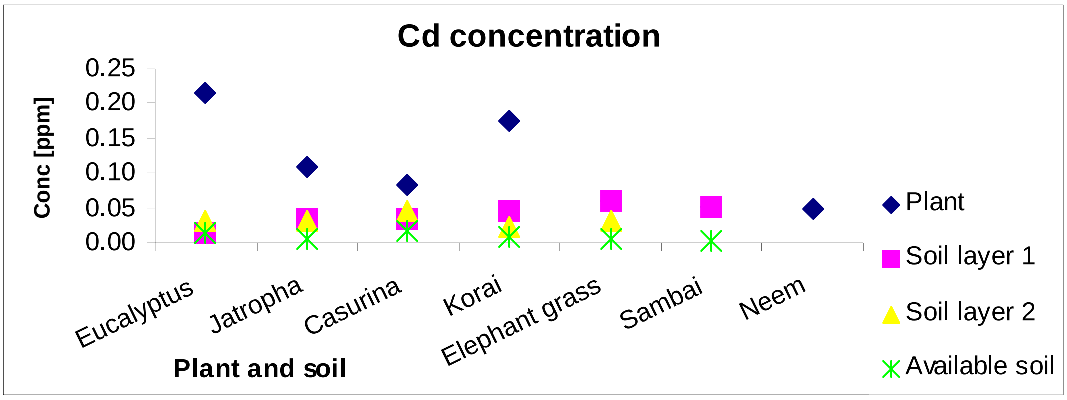

*Figure 5.6 Cadmium concentration in plant and soil*

## 5.3.2 Chromium

Concentration of chromium was on average 78 ppm in the reference soil sample, compared to 86 ppm in the irrigated soil sample. The chromium concentrations are rather constant between the different soil depths, but a small trend is that higher concentrations occur in the lower depths. Only a few percentages were available fractions. All the plants had chromium levels below the detection limit for the ICP-MS or below the blank sample levels.

## 5.3.3 Iron

The iron concentration in the soil was 17 000-20 000 ppm, except in the soil where Elephant grass and Sambai grow. There the concentration were 30 000 ppm. A slightly higher concentration of iron is found in the deeper soil. Iron has an average concentration of 22 500 ppm in the irrigated field and only 17 900 ppm on average in the reference soil sample. Availability in the soil is very low, it is much lower than the values in the plants. Iron values in the plants vary greatly for all the plants, from 80-289 ppm, but in comparison to the soil the values in the plants are very low. The soil concentrations are almost a factor 100 higher.

## 5.3.4 Lead

There is no difference in lead concentration for the different soil depths and the concentration is quite constant, approximately 4 ppm. The irrigated soil has on average a lead concentration of 4.58 ppm and the reference soil samples had a value of 3.64 ppm. The available fraction in the soil is very low. The variation of lead concentration in the plants is wide, from 0.704 to 2.241 ppm. Figure 5.7 shows that the soils have higher concentrations of lead than the plants.

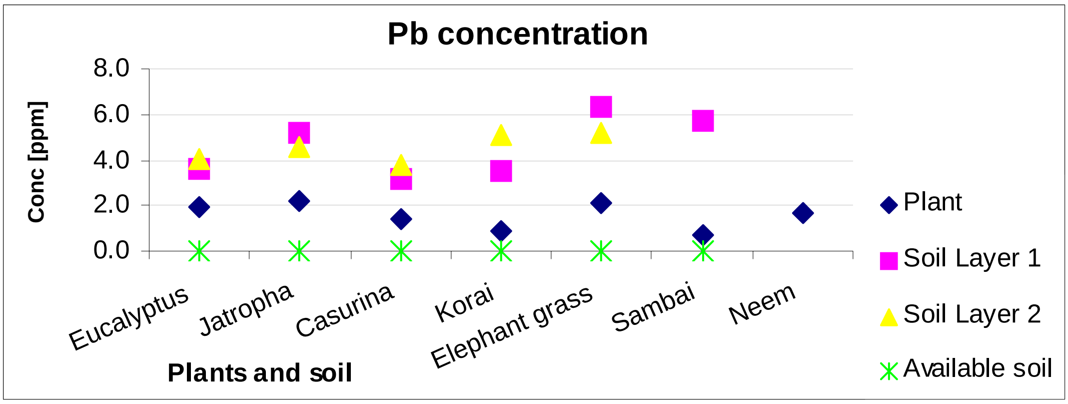

*Figure 5.7 Lead concentration in plant and soil*

### 5.3.5 Zinc

Zinc concentration was approximately 35 ppm in the soil, but the soil where Eucalyptus grows has higher values. The average concentration of zinc was 37 ppm for the irrigated fields and for the non-irrigated fields it was 29 ppm. The result shows no differences between the concentrations of heavy metals in the soil for the two layers. The available fraction is very small in the soil. Zinc has a higher value in the plants, 23-60 ppm, than most of the other soils.

## 5.4 Soil

The conductivity is higher in the soils that have been irrigated, while pH is roughly the same in the irrigated fields and the reference soils samples, approximately a pH of 8.5 to 9, see Table 5.1. There was no specific difference in pH for the different depths in the soil. The soil where Korai grows has higher conductivity. The soils where Elephant grass and Eucalyptus grow are the only soils where the pH is above 9.

All the soil was found to be sandy loam except where Sambai grows. Where a higher content of clay was found and therefore determined as sandy clay, all the samples from the second layer were found to have slightly more clay, but still in the range of sandy loam. The contents of sandy loam are according to United States Department of Agriculture 0-20% clay, 50%-100% sand and 0-30% silt and the contents of sandy clay is >35% clay, >45% sand (see Appendix I).

*Table 5.1 pH and conductivity[2] in soil*

| Soil sample number | pH | Conductivity [µS/cm] |
|---|---|---|
| Reference soil 1, layer 1 | 8.67 | 90 |
| Reference soil 1, layer 2 | 8.64 | 80 |
| Reference soil 2, layer 1 | 8.57 | 120 |
| Reference soil 2, layer 2 | 8.74 | 120 |
| Eucalyptus, layer 1 | 9.01 | 360 |
| Eucalyptus, layer 2 | 9.01 | 390 |
| Jatropa, layer 1 | 8.41 | 270 |
| Jatropa, layer 2 | 8.71 | 290 |
| Casurina, layer 1 | 8.46 | 190 |
| Casurina, layer 2 | 8.50 | 190 |
| Korai, Layer 1 | 8.82 | 1790 |
| Korai, layer 2 | 8.61 | 1500 |
| Elephant grass, layer 1 | 9.07 | 460 |
| Elephant grass, layer 2 | 9.03 | 440 |

## 5.5 Reliability

To completely understand the results it is important to be aware of all the steps involved in the preparation of the samples.

To investigate how reliable the digestion was, one sample of reference material was placed during each run in the microwave oven, MARSH 5. Those materials were also analysed by ICP-MS. The reference material result was then compared with old results from earlier analysis with the same material. To compare those results: average, standard deviation, relative difference and confidence interval (95%) were used. Those values can be seen in Appendix M. The results from this run show a confidence interval that is lower than in the earlier analysis. If the value of the relative difference is small, the results will be in accordance with earlier reference material analysis. In this case the relative difference was approximately 10% or less. The confidence interval and the relative difference confirmed that this digestion worked properly.

To measure whether the procedure itself had any influence on the result, blank samples were prepared. This means that each microwave run included a blank sample. The blank samples were done by not adding any sample material, only adding acids. A comparison between the blank samples and results from the collected samples shows how effective the digestion is. The results can be seen in Appendix M, where the averages of the blank

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[2] Soil pH and conductivity were measured the10th November 2004 at WTC.

samples and the field samples are presented. The highest concentrations of iron were found in blank samples for the sludge, 233.5 ppm. Comparing these blank samples to the iron sludge concentrations, 61 389 ppm, it is obvious that they are relatively negligible. Except for chromium the results are acceptable. Due to that the concentrations of chromium in plants and effluent are below the blank samples, this report assumes those concentrations as not detectable.

To ensure the reliability of the result, it is important to look at the concentration of Rh in each analysed sample, see the figure in Appendix M. The figure shows that the variation is low and acceptable.

During the preparation of available heavy metals in the soil fraction, high colour occurred in the filtrate in two of the samples. Half of the amount was filtered twice and all four samples were analysed. The result was that the concentration is much less, 15 ppm to 3 ppm, in the samples that was re-filtered. If everything should have been correct, no differences should have occurred. Iron will very easily precipitate in different formation and is pH dependent. Oxidization could have taken place during the shaking. Later during the filtration flocculation could occur, with the result that lots of iron got trapped in the filter. The conclusion is that the iron available soil concentration may not be correct.

Many of the results of heavy metals were displayed as no detection in analysis with the ASS, (Method 1). One reason could be the digestion method, which maybe did not work properly and therefore the heavy metals did not dissolve, as they should. According to ISO 15587-2 a vapour recovery system should be placed on top of each vessel during heating. Unfortunately a vapour recovery system did not exist at WTC. This resulted in high vaporisation and the samples dried up. To reduce the effect of evaporation, acid was added as described in Section 4.1.2 digestion method 1. The effect of this is a bit unclear. This in combination with irregular heating during almost a week and difficulties in deciding when the samples were finished may have caused uncertainties.

Another aspect of reliability is the analysing in the AAS. The sludge, soil and plant samples were never filtered before run in the AAS. Therefore the dirt in the samples could have plugged the narrow tubes, which lead the samples into the flame.

# 6 Discussion

It is important to keep in mind that the aim of this report is to do a primary investigation; the collection was both limited in time and resources. To better understand the real situation more soil and plant samples should be collected. Water and sludge samples need to be taken under a longer time and continuously. Finally more parameters such as water infiltration rate through the soils are important to draw the right conclusions. The discussion below is based on the results that have been analysed and it is a first estimation of the real situation.

## 6.1 Water

The relatively constant values in pH, TDS, COD, $BOD_5$, TSS and flow are probably due to the fact that the samples were taken in the equalisation tank, where the water already is mixed. Influent water, used for heavy metals analyses, was collected from the bar screens and therefore shows more fluctuating values. The inflow rate under the analysed period is far less than the treatment plant is constructed for, 2200 $m^3$/d compared to 3600 $m^3$/d. This may also affect the result either in a positive or a negative way in the different units. Most of the parameters of the treatment plant are quite constant in the effluent and this points towards good operations with few problems.

TDS is one of the parameters that PCETP does not reduce at all. Most probably the influent contribution to TDS has different origin than the effluent. The influent TDS come from dying processes and the effluent TDS has its origin in chemical treatment with iron sulphate or other added chemicals.

The structure for the influent water is similar between cadmium and lead, the concentration goes both up and down during the same period. A similar structure in the influent can be found between chromium and zinc. One reason for this could be that one dye used in the textile process includes more of the two heavy metals. The connection between influent and effluent metal concentrations is weak.

The quality of effluent water is far below the Indian regulation limits as seen in Table 6.1. As seen in the table below no concentration limits exists for iron. According to Indian legislation the irrigated water has very good quality.

*Table 6.1 Effluent quality compared to Indian legislation of disposal water on land*

| | PCETP effluent concentrations [ppm] | Indian limits for disposal water on land [ppm] (TNPCB, 2004) |
|---|---|---|
| **Cadmium** | 0.014 | 1 |
| **Chromium** | No detection | 1 |
| **Iron** | 208 | - |
| **Lead** | 0.143 | 1 |
| **Zinc** | 5.068 | 15 |

Comparing effluent water quality in the old data, as seen in Appendix E, with the results from this investigation, shows much lower concentrations in earlier studies. For example zinc was earlier measured as 0.12 ppm but the result in this study shows an average concentration of 5 ppm. The reason for this can be, for example, changed properties on the influent or reduced removing capacity in some of the units of the treatment plant. It can also depend on the analyses method, which is not correctly performed or samples could have been contaminated after collection.

## 6.2 Sludge

Like the water, the sludge has a variation of heavy metals. Before the national holiday the 22nd, when the treatment plant was closed, a downward trend can be observed for the concentration of heavy metals in the sludge. The explanation may be reduced dying at the factories because of the upcoming holiday. A comparison of heavy metal concentration is done between a median value published by Leeper (1987), PCETP average and Ryaverkets (a treatment plant) annual average in the sludge, see Table 6.2. The value in the table shows that the sludge in PCETP has far lower concentrations compared to the other two. Only chromium has slightly higher concentration in PCETP than Ryaverket had. The low values in PCETP can be interpreted differently; firstly the removing of heavy metals is not working properly and therefore the concentrations of the effluent are increased. Secondly the concentrations in the sludge can be lower due to the fact that the produced sludge volume is large, so the load of removed heavy metals can be efficient. PCETP do produce 15 ton TS sludge per day, that is a big volume compared to the small quantity of water treated, 3600 $m^3$/d. Ryaverket produces 40 ton TS per day but treats a higher volume of water, 304 000 $m^3$/d.

*Table 6.2 Sludge concentration comparing with mean values*

| | PCETP average concentrations [ppm] | Sludge median [ppm] (Leeper, 1987) | Ryaverket [ppm] (Gryaab, 2004) |
|---|---|---|---|
| **Cadmium** | 0.113 | - | 1 |
| **Chromium** | 130 | 250 | 29 |
| **Iron** | 122 673 | 21 000 | - |
| **Lead** | 3.92 | 700 | 34 |
| **Zinc** | 297 | 3000 | 625 |

The sludge concentration is much higher in this report than the earlier measured data at PCETP, especially when it comes to iron where the concentration is 0.154 ppm compared to 120 000 ppm. The old measuring levels are really low and knowing that PCETP uses iron sulphate in the process, these values are unrealistic.

## 6.3 Soil and plants

The pH differs more between the irrigated fields than between the different depths in each soil. The soils with lower pH have no detection of available heavy metal fractions. No connection is found between pH and conductivity in these results. The non-irrigated soil has lower conductivity than the irrigated soils. The result does not show a clear connection between conductivity and concentration of heavy metals in soils or plants. Heavy metals are in this case not the major source for the conductivity but the irrigation changes the conductivity.

One surprising result was that the reference plant samples had higher concentrations of heavy metals than the plants that had been irrigated, see Table 6.3. There are two explanations for the higher concentrations of heavy metals in the non-irrigated plants. Firstly the plant concentrations of heavy metals are low and therefore harder to prepare and analyse. Secondly the non-irrigated plant samples were collected from young newly bought plant samples and earlier up-take of heavy metal is unclear. Therefore it is not correct to say that the plants on the fields are unaffected by the irrigation

*Table 6.3 Reference and plant samples*

| | **Cadmium [ppm]** | **Chromium [ppm]** | **Iron [ppm]** | **Lead [ppm]** | **Zinc [ppm]** |
|---|---|---|---|---|---|
| **Eucalyptus reference sample** | 0.725 | No detection | 252.411 | 1.907 | 45.531 |
| **Eucalyptus** | 0.216 | No detection | 230.664 | 1.953 | 40.649 |
| **Casurina reference sample** | 0.047 | No detection | 270.483 | 1.107 | 45.873 |
| **Casurina** | 0.082 | No detection | 248.916 | 1.387 | 27.666 |
| **Neem tree reference sample** | 0.074 | No detection | 243.328 | 2.112 | 26.265 |
| **Neem tree** | 0.05 | No detection | 159.433 | 1.634 | 25.479 |

Some of the plants had a higher concentration of cadmium and zinc than the soil samples had, see Appendix L. Those two metals are more movable than the other ones and therefore the plant up-take is favoured by this. The concentrations of the other heavy metals were lower in the plant than in the soils, and they showed also lower mobility. This is shown in Table 2.1. The available fraction in soil should be higher for those minerals with high mobility. This is only correct for cadmium, which has a high percentage of available metal in the soil. The reasons why zinc did not show higher concentrations of available metal could be due to the analysing method that did not work properly.

The plant average concentrations in the irrigated fields are comparable with literature levels for plant leaves. The concentration of heavy metals in the plants in the field is not so high for cadmium, lead and zinc, see Table 6.4. The concentrations in the leaves are higher for iron in the plants in the fields, than what was found in the literature. The iron concentration found in literature may not be correct for plants growing in red soil, because red soil has naturally high iron concentrations in the soil and plants growing there. The concentrations of chromium were not detected as mentioned before.

*Table 6.4 Heavy metals concentrations in PCETP plants and values found in literature*

| | Literature Concentration (RIF GM, 2003) [ppm] | PCETP concentration [ppm] |
|---|---|---|
| **Cadmium** | 0.4 | 0.11 |
| **Chromium** | 0.2 | No detection |
| **Iron** | 100 | 195 |
| **Lead** | 6 | 1.55 |
| **Zinc** | 100 | 37 |

The soil that had the highest concentration of heavy metals was where Elephant grass and Sambai grows. Those two grasses like to grow in water and therefore may PCETP has increased the irrigation on those fields. The higher value found in the soil cannot be detected in the plants growing there. The plant Jatropha has in general higher loads of all five heavy metals, but this is not related to the soil. Casurina soil has lower concentrations and you can se a tendency to this in the plant. The heavy metal concentrations of the plant that were recorded are iron and after that zinc, the rest of the metals had no specific order. The concentrations of heavy metals in soil is highest for iron followed by chromium, zinc, lead and cadmium, see Appendix L. After two years of irrigation higher heavy metal concentrations in soils were not related to higher plant concentrations. There is no evidence of a simple relationship.

The water will pass easily through the soil with a sandy loam texture, especially in the upper layer where the sand fraction is larger. The soil in the upper layer will promote high water flow through the soil, eluviations. In the second soil layer, there is a small tendency for reduced water flow and therefore deposition of materials could occur, illuviation. In these result only two soils, Eucalyptus and Korai, show higher accumulation of heavy metals in layer two. The reason why not more soils show this result can be due to that the soils only had small differences in texture between the soil depths. It can also depend on that the irrigated water concentrations were too small to show any differences of heavy metal accumulations. If the soil water has a high concentration of heavy metals, soil as for example, sandy loam will promote movement of the heavy metal down to the groundwater. This will lead to further distribution of contamination and therefore also decreases the contamination in the soil. The information in this investigation is not sufficient to decide whether the groundwater will be contaminated in the long-term.

The result for all soils shows that the irrigated soil has higher concentrations of heavy metals than the non-irrigated soils, see Figure 6.1. This indicates that the wastewater irrigation does affect the soil content of heavy metals.

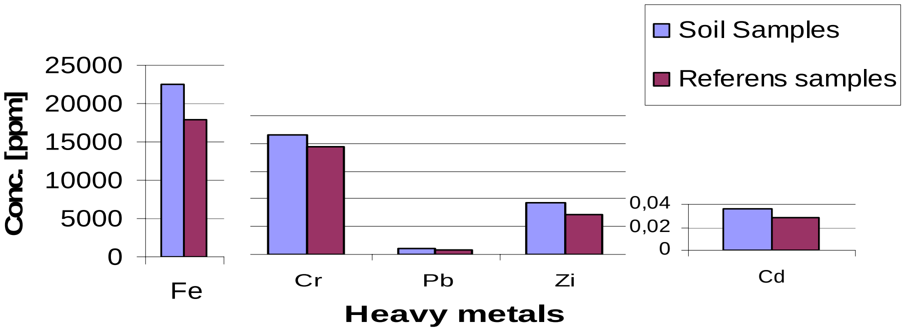

*Figure 6.1 Reference and soil samples*

The Table 6.5 below shows the quantities, milligram of each heavy metal that has so far been added per square meter. The amount iron added per square meter is considerably higher compared to the other heavy metals.

*Table 6.5 Quantities of each heavy metal added on the irrigated fields*

| Heavy Metal | Mass [mg/m$^2$] |
|---|---|
| Cadmium | 0.07 |
| Chromium | 0.48 |
| Iron | 1069.12 |
| Lead | 0.74 |
| Zinc | 26.04 |

No limits have been found for soil contamination in India. A comparison with the Swedish regulation of contaminated sediment soil, as seen in Table 6.6, shows that no soils in SIPCOT are contaminated. However, this table also shows the comparing value. Only chromium shows increased concentrations in the soils at PCETP and according to those regulations the soil was probably contaminated with chromium. In the same table United Kingdom, UK, trigger threshold values are shown and those limits are even higher than the Swedish limits. United States, US, limits for toxic soils are also shown in Table 6.6 and are much lower than the first two mentioned. The question is whether the land will be contaminated in the long-term. It is not easy to answer this question with so few data and so different reference limits. However, if no changes appear in the next decades the soil will start to be polluted. Most likely increased concentrations of heavy metals will be found in the soil and the plants growing there. The plants may be affected and will as a result suffer from reduced growth.

To get a better picture of the real plant and soil conditions more samples with more spreading should be taken to ensure that the samples illustrate reality.

*Table 6.6 Heavy metal in soil*

| | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **PCETP average irrigated soils concentration** | 0.04 | 86 | 22572 | 4.58 | 37 |
| **Swedish threshold limits (Naturvårdsverket, 2002)** | 0.4 | 120 | - | 80 | 350 |
| **Swedish comparing values (Naturvårdsverket, 2002)** | 0.15 | 45 | - | 25 | 100 |
| **PCETP / Swedish comparing values**[3] | 0.25 | 191 | - | 0.18 | 0.37 |
| **UK trigger threshold (Contaminated land, 2000)** | 3 | 600 | - | 500 | 300 |
| **US toxic soil limits (Leeper, 1987)** | 10 | 0.06 | - | 50 | - |

## 6.4 Heavy metals through the treatment plant

The cadmium concentrations were low through the treatment plant and the influent water concentrations were fluctuating. The cadmium concentrations of the effluent were only slightly lower than for the influent. The separation of cadmium is modest but the cadmium concentration in the effluent is still very low. The sludge cadmium concentration was high and it is possible to see the connection to the influent, but the concentration is not varying as much as in the influent. The concentrations in the soils were low but only slightly less than in the irrigated water. Due to irrigation with effluent water, a raised cadmium load may occur in the soil. This will cause a problem since cadmium is movable and can easily be taken up by the plants.

The concentration of chromium in the influent was high and very varying. The effluent concentration was low and very constant and the sludge concentration was high. This information indicates a good and efficient separation. The effluent concentration of chromium was very low compared to the soil content and should therefore cause little influence on the soil.

The effluent has often higher concentration of iron than the influent. The separation is not efficient but it is not surprising because addition of iron during the chemical treatment. The levels of iron were high in the effluent and especially in the sludge. The sludge concentration is not constant and this gives reasons to believe that the separation is not stable. Even though that the effluent concentration was high it is hard to see the influence on the soil because the natural iron soil concentration is already very high in red soil.

All the lead concentrations were very low. The influent concentration was as for the other heavy metals very fluctuating and can be explained by the different dyes, which have been used. The separation of lead is good, the sludge concentration is related to the inlet quality and has less variations. Concentration of lead in the soil was high and the influence from the irrigated water is low.

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[3] The values in the situation, SIPCOT, divided by comparing values shall be under one if the soil is unaffected and not contaminated in any way.

Influent zinc concentration was very variable and high and the effluent concentration was steady and low. The sludge concentrations were quite high but the separation of heavy metals in the water is moderate. The effluent has high concentrations compared to the levels already existing in the soil. The zinc concentration could be a serious problem if the irrigation keeps going on, to the same extent. Concentrations in the plants may also rise due to the mobility of zinc.

The effluent quality is good in most of the cases, but all the heavy metals that are removed do not stay in the sludge. The mass balance, Appendix N, shows the amount of heavy metals in the influent, effluent and the sludge. The amount of metal is not in balance; the differences between the influent load and the effluent load are far more than the amount in the sludge. The reason can be that the analyses methods are incorrect. Another reason can be that by the time the samples were taken the flow rate of the influent was nearly half of what they usually have. Thirdly the time difference between the influent and the producing of the sludge can interfere with the results. Therefore it is not accurate to compare the sludge amount of heavy metals and the water taken during the same time.

It is difficult to draw a conclusion about the future of the contamination in the soil. A calculation, which builds on the differences between the concentrations of heavy metals in non-irrigated soil and the irrigated soil, can give an indication about the situation. For the case that the heavy metal concentrations in the soil are going to increase at the same rate, as they have for the last two years, and under the same conditions, it will take between 4 to 15 years before the concentration of heavy metals in the soil is double that of the reference soil, see Table 6.7. For iron it will take about four years before the concentration is double that of its reference value. Iron effluent levels are only 1% of the soil levels. The reasons for the differences may depend on that the heavy metals in general are much higher in the effluent, than the analyses in this report show.

*Table 6.7 Heavy metals increase in the soil*

| | **Cadmium** | **Chromium** | **Iron** | **Lead** | **Zinc** |
|---|---|---|---|---|---|
| **Difference in conc., irrigated and non-irrigated soil [ppm]** | 0.009 | 8.118 | 4638.042 | 0.937 | 7.796 |
| **Increasing of conc. after 2 years** | 31% | 10% | 26% | 26% | 27% |
| **Year to double the conc.** | 4.4 | 17.2 | 5.7 | 5.8 | 5.5 |

## 6.5 Improvements

It is hard to find improvements on an already modern and developed treatment plant. PCETP is today using considerably high amounts of iron sulphate to treat the water. The levels of iron sulphate should be reduced to achieve lower iron concentration and TDS in effluent water. It should be possible to do this and at the same time keep the treatment plants efficiency. Another way to lower the iron concentrations is to change the chemical from iron sulphate to lime. Lime has been proven to be as efficient as iron sulphate to treat textile effluent. To make a final polish of the effluent water a new unit could be added in the process, for example ion exchange or reverse osmosis. It is wise to ensure that the new unit is working properly on the current water quality before investing money. Especially reverse osmosis where clogging is a problem, which can be increased by high TDS.

# 7 Conclusion

Perundurai Common Effluent Treatment Plant, PCETP uses new technology and units to simplify operations, for example AVG filter. The plant is well operated and it has a constant effluent water quality.

PCETP treats effluent water from 14 textile industries in the area. Tamil Nadu Pollution Control Board, TNPCB, regulates the limits for industries to dispose water. The limits for heavy metals differ from where the water is placed, to surface water, common sewage, on land (irrigation) or to coastal areas. The 14 textile units in SIPCOT have started PCETP to achieve a good quality of the wastewater, so now it is the treatment plant's responsibility to follow the regulation. The limits TNCPB set up for disposal of wastewater on land is achieved with good margin at PCETP. In this case the textile factory has no limits for the concentration of heavy metals in the water before it is sent to the treatment plant. PCETP has by its self set up two limits for the amount of wastewater each industry can send to them, one for TDS below 2100 mg/l and one for TDS above 2100 mg/l.

The efficiency in separation of heavy metals is found through comparing the concentrations in influent water to the sludge and the effluent water. The concentrations of heavy metals differ among the metals and the treatment of the metals has different success rates. The separation of cadmium is moderate, but due to very low influent concentrations the effluent still has low values. Chromium treatment is good and very efficient. Iron effluent concentration is higher than the influent and has even higher values in the sludge. The poor separation results for iron are related to the high amount of iron sulphate that is added in the process. The separation of lead during the treatment is running well. Removing zinc from the water is decent, but still the effluent concentrations are high.

Increasing the separation of heavy metals at PCETP may not be necessary. Some improvement can be done to polish the effluent further, for example to extend the treatment plant with another unit such as ion exchange or reverse osmosis. To improve the control of the high iron concentration one suggestion is to look over the amount of chemicals used in the process and even change the coagulate, iron sulphate.

All the soil samples show that the soil that has been irrigated has higher concentrations of heavy metals. The impact does exist, but so far the soil is not contaminated and the plant shows no signs of any increased levels of heavy metals. The long-term effects of irrigation are a bit unsure. The soil concentration of heavy metals will double within 4-15 years if the same increase rate, as in the past two years, continues. Zinc and cadmium are the heavy metals that could change the natural soil content the most. This is because the concentration in effluent water and soil are almost the same. The addition of heavy metals can cause the site to be polluted and plant growth may be affected in the long-term.

# 8 Further area of study

This master thesis is only a primary investigation to see whether PCETP has any problems with separation of heavy metals. Unfortunately the time for doing a master thesis is short, therefore it is necessary to broaden and to follow up this investigation. Below a few suggestions are listed.

- Investigate the amount of chemicals added to the process in PCETP, to understand the efficiency and look into the possibility to change the coagulate.
- Proper investigations of the soil, to understand how the irrigated water infiltrates through the soil to the groundwater. Also study the spread of the pollutants, both heavy metals and others parameters.
- Another field study in less than five years, to see how the concentration of heavy metals in plant and soil has changed. At the same time increase the number of soil and plant samples to get more reliable results.
- Heavy metals are not the only pollution load for the irrigated field. Different kinds of salts can also bring down the growth of the plants. Therefore it is necessary to look over other parameters such as salt, which is not mentioned in this report.

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# 10 Appendix

Appendix A.: Indian tolerance limits

Appendix B.: Solubility of heavy metals as sulphides

Appendix C.: Solubility of heavy metals

Appendix D.: Flow chart

Appendix E.: Heavy metal concentrations from earlier analyses at PCETP

Appendix F: Preparation before analyses

Appendix G.: Short description about ICP-MS and AAS

Appendix H.: Texture class

Appendix I.: Triangular textural diagram

Appendix J.: Data results analyses / measured at PCETP

Appendix K.: Results of heavy metals analyses, method 1, India

Appendix L.: Results of heavy metals analyses, method 2, Sweden

Appendix M.: Reference material / blanc samples

Appendix N.: Mass Balance

# APPENDIX A.

## India tolerance limits

Tolerance Limits for Discharge of Trade Effluent into inland surface water, public sewers, on land irrigation and marine coastal areas (TNPCB, 2005).

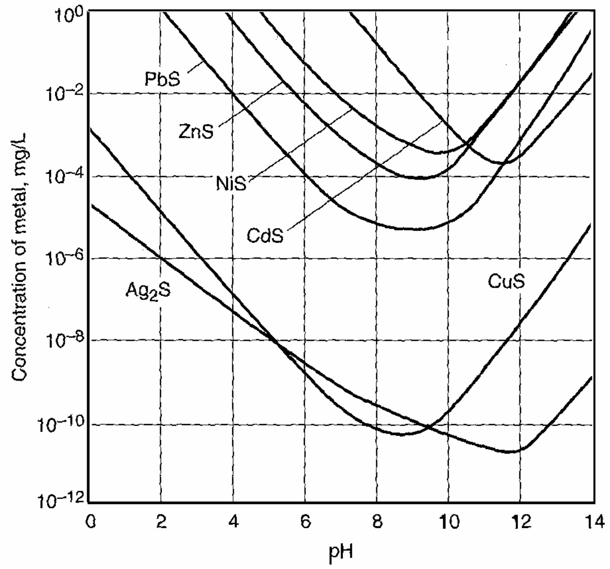
| Characteristics | Inland Surface Waters | Public Sewers | On Land for Irrigation | Marine Coastal Areas |
|---|---|---|---|---|
| **Colour & Odour** | - | - | - | - |
| **Suspended Solids [mg/l]** | 100 | 600 | 200 | a. For process waste waters-100<br>b. For cooling water effluent 10 % above TS matter of influent cooling water |
| **Particle Size of Suspended Solids** | Shall pass 580 micron I.S.Sieve | - | - | a. Floatable solids maximum 3 mm<br>b. Settable solids maximum 850 microns |
| **Dissolved Solids (inorganic) [mg/l]** | 2100 | 2100 | 2100 | - |
| **pH Value** | 5.5 to 9 | 5.5 to 9 | 5.5 to 9 | 5.5 to 9 |
| **Temperature** | 40°C at the point of discharge | 40°C at the point of discharge | 40°C at the point of discharge | - |
| **Oil & Grease [mg/l]** | 10 | 20 | 10 | 20 |
| **Total Residual Chlorine [mg/l]** | 1.0 | - | - | 1.0 |
| **Ammoniacal Nitrogen (as N) [mg/l]** | 50 | 50 | - | 50 |
| **Total Kjeldahl Nitrogen (as N) [mg/l]** | 100 | - | - | 100 |
| **Free Ammonia (as $NH_3$) [mg/l]** | 5.0 | - | - | 5.0 |
| **BOD, 3 days at 27°C [mg/l]** | 30 | 350 | 100 | 100 |
| **COD [mg/l]** | 250 | - | - | 250 |
| **Arsenic (as As) [mg/l]** | 0.2 | 0.2 | 0.2 | 0.2 |
| **Mercury (as Hg) [mg/l]** | 0.01 | 0.01 | 0.01 | 0.01 |

| Characteristics | Inland Surface Waters | Public Sewers | On Land for Irrigation | Marine Coastal Areas |
|---|---|---|---|---|
| Lead (as Pb) [mg/l] | 0.1 | 1.0 | 1.0 | 1.0 |
| Cadmium (as Cd) [mg/l] | 2.0 | 1.0 | 1.0 | 2.0 |
| Hexavalent Chromium (as $Cr^{+6}$) [mg/l] | 0.1 | 0.2 | 1.0 | 1.0 |
| Total Chromium (as Cr) [mg/l] | 2.0 | 2.0 | 1.0 | 2.0 |
| Copper (as Cu) [mg/l] | 3.0 | 3.0 | 3.0 | 3.0 |
| Zinc (as Zn) [mg/l] | 1.0 | 15 | 15 | 15 |
| Selenium (as Se) [mg/l] | 0.05 | 0.05 | 0.05 | 0.05 |
| Nickel (as Ni) [mg/l] | 3.0 | 3.0 | 3.0 | 3.0 |
| Boron (as B) [mg/l] | 2.0 | 2.0 | 2.0 | 2.0 |
| Percent Sodium [%] | - | 60 | 60 | - |
| Residual Sodium Carbonate [mg/l] | - | - | 5.0 | - |
| Cyanide (as CN) [mg/l] | 0.2 | 2.0 | 0.2 | 0.2 |
| Chloride (as Cl) [mg/l] | 1000 | 1000 | 600 | - |
| Fluoride (as F) [mg/l] | 2.0 | 15 | 2.0 | 15 |
| Dissolved Phosphates (as P) [mg/l] | 5.0 | - | - | - |
| Sulphates (as SO4) [mg/l] | 1000 | 1000 | 1000 | 1000 |
| Sulphides (as S) [mg/l] | 2.0 | - | 2.0 | 5.0 |
| Pesticides | Absent | Absent | Absent | Absent |
| Phenolic Compounds (as C6H5OH) [mg/l] | 1.0 | 5.0 | 5.0 | 5.0 |
| Radio Active Materials | | | | |
| a. Alpha emitters [micro curie/ml] | $10^{-7}$ | $10^{-7}$ | $10^{-7}$ | $10^{-7}$ |
| b. Beta emitters [micro curie/ml] | $10^{-6}$ | $10^{-6}$ | $10^{-6}$ | $10^{-7}$ |

# APPENDIX B.

## Solubility of heavy metals as sulphides

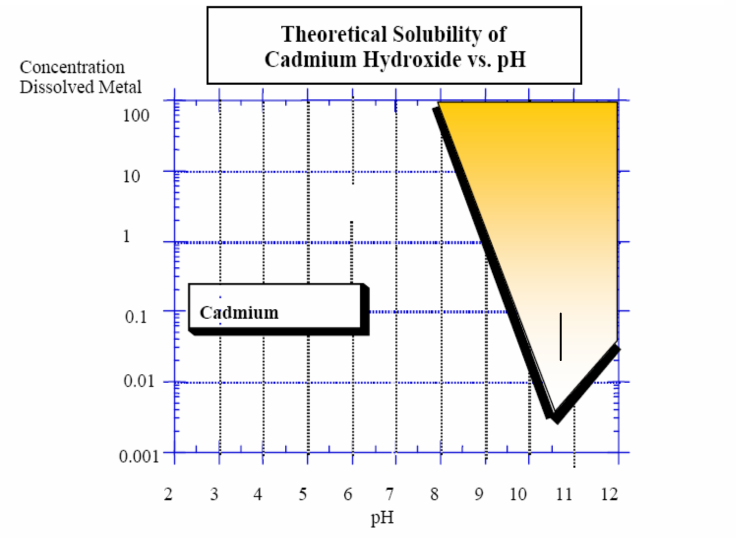
Residual soluble metal concentration as a function of pH for the precipitation of metals as sulphides (Tchobangolous, 2003).

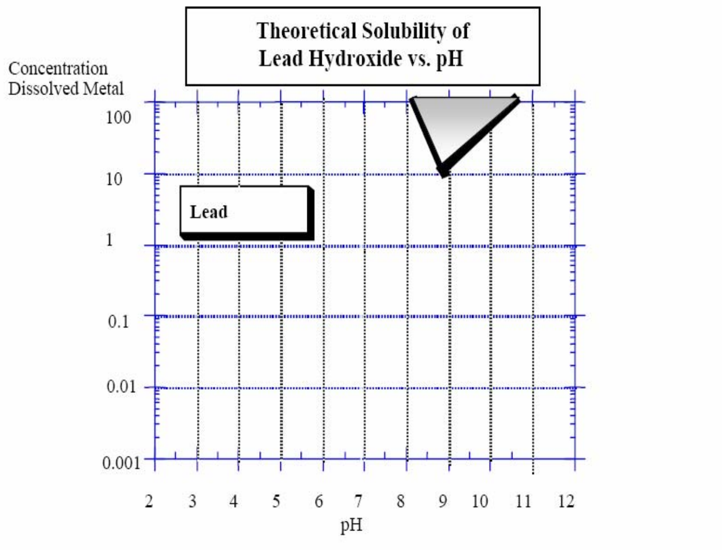


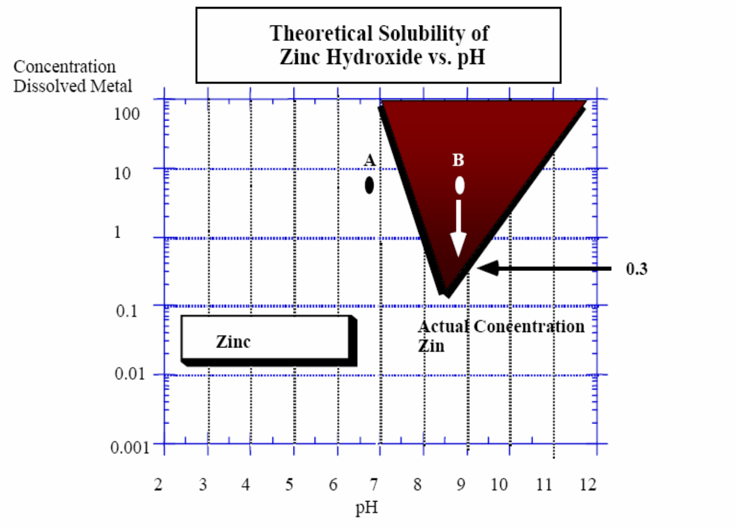
## APPENDIX C.

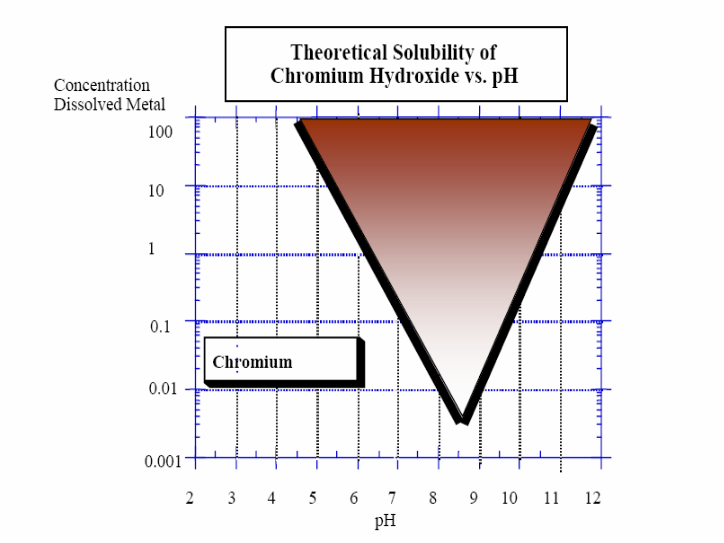
## Solubility of heavy metals

Those figures are based on an ideal wastewater. Some variations in the exact values of the metal concentrations will occur due to the presence of other substances in the wastewater (Ayres,1994).



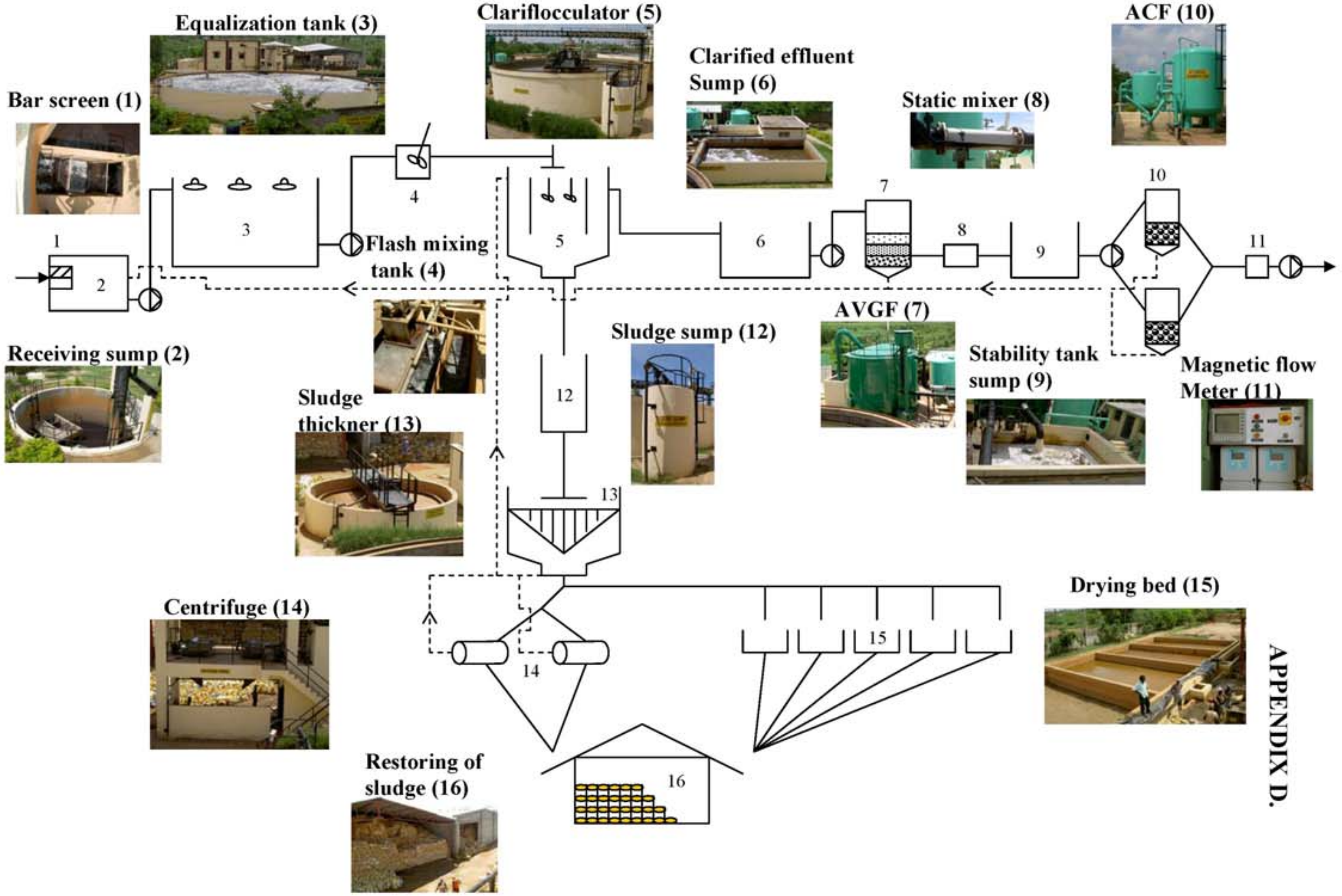






# APPENDIX D.

## Flowchart of PCETP



## APPENDIX E.

# Heavy metal concentrations from earlier analyses at PCETP

*Effluent water:* Heavy metals concentrations (Matha, 2003).

| Element | Effluent water concentration [ppm] |
|---|---|
| **Chromium** | 0.02 |
| **Iron** | 0.75 |
| **Lead** | 0.01 |
| **Zinc** | 0.12 |

*Sludge*: Heavy metals concentrations (Chandra, C. Sckrn, 2004).

| Element | Sludge concentration [ppm] |
|---|---|
| **Cadmium** | 0.013 |
| **Chromium** | 1 |
| **Iron** | 0.154 |
| **Lead** | 1.22 |
| **Zinc** | 0.96 |

# APPENDIX F.

## Preparation before analyses

*Digestion method 1*: The amount of amples and acids in the digestion (Devarajan, 1987).

| Sample | Amount of sample | Perchloric acid | Nitric acid, 69% | Triple acid mixture* | Dilute with distilled water to: |
|---|---|---|---|---|---|
| **Water** | 40 ± 0.2 ml | - | 10 ± 0.2 ml | - | 40 ml |
| **Sludge** | 0.5 gram | 30 ml | - | - | 250 ml |
| **Soil** | 0.5 gram | 30 ml | - | - | 100 ml |
| **Plant** | 2 grams | - | - | 12 ml | 25 ml |

***Tripleacid mixture (180 ml):**

135 ml Nitric acid
30 ml Sulphuric acid
15 ml Perchloric acid
Mix all the chemicals to one solution in a bottle.

*Digestion method 2:* The amount of samples and acids in the digestion.

| Sample | Amount of sample | Nitric acid | Hydrogen peroxide |
|---|---|---|---|
| **Water** | 10 ml | 1.1 ml | - |
| **Sludge** | 0.5 gram | 10 ml | - |
| **Soil** | 0.5 gram | 10 ml | - |
| **Plant** | 0.5 gram | 8 ml | 2 ml |

*Digestion method 2:* Heating program in the Microwaves MARS 5.

| Sample | Stage | Max. Power [W] | Power [%] | Ramp [min] | Pressure [psi] | Temperature [°C] | Hold [min] |
|---|---|---|---|---|---|---|---|
| **Water** | 1 | 1200 | 100 | 10:00 | 300 | 160 | 00:00 |
| | 2 | 1200 | 100 | 10:00 | 300 | 170 | 00:00 |
| **Sludge & Soil** | 1 | 1200 | 100 | 02:00 | 300 | 165 | 02:00 |
| | 2 | 1200 | 100 | 03:00 | 300 | 175 | 10:00 |
| **Plant** | 1 | 1200 | 100 | 08:00 | 300 | 130 | 02:00 |
| | 2 | 1200 | 100 | 05:00 | 300 | 150 | 10:00 |

*Dissolved method 1 and 2:* The amount of soil samples and acids in the dissolved.

| Method | Amount soil | DTPA extraction* | $NH_4Cl$ (1M unbuffer) | Filter paper |
|---|---|---|---|---|
| **Method 1 (Devarajan, 1987)** | 20 grams | 40 ml | - | Whatman No. 1 |
| **Method 2 (Bertil, 1995)** | 12.5 grams | - | 50 ml | H 00 |

*** DTPA extracting solution (1 litre):**

14.92 ml of 0.1 M TEA, Analar reagent grade $(HOCH_2\ CH_2)_3\ N$
1.967 grams of 0.005 M DTPA, diethlenetriamine penta acetic acid
1.47 grams of 0.01 M $CaCl_2 \times 2H_2O$

Mix all the chemicals to one solution into a bottle. Add approximately 20 ml of distilled water to the solution. Let the chemicals and the distilled water dissolves and add distilled water to approximately 0.9 liter. Adjust the pH to 7.3 ± 0.05 with 1:1 N HCl while stirring. Finally make up the volume of the solution to 1 liter with distillated water.

# APPENDIX G.

## Short description about ICP-MS and AAS

### ICP-MS

ICP-MS (Inductively coupled plasma-mass spectrometry) is an analytical technique, which is based on conduct the sample into plasma with temperature around 5000K (WET, 2004). In the plasma the samples will dissociate into molecules and ionise into atoms. The ions are then transported into vacuum through a cone and moves into a quadrupled mass spectrometer. In the mass spectrometer, the ions are sorted by mass and detected using a scanning electron multiplier (Byggnadsmaterial, 2005 and AGU, 1995).

### AAS

The electronic energy levels for atoms are specific for each element. This is utilized in Atomic Absorption Spectrophotometer, AAS, where the samples are sucked up into a flame and converted to free atom vapour. A lamp is directed to the vapour, which emit light with specific wavelength. The element will absorb the light in their wavelengths. The amount of radiation from a specific energy is detective. In this way the amount of heavy metal can be detected (Colgate geology, 2003 and Onsager, 2005).

# APPENDIX H.

## Texture class

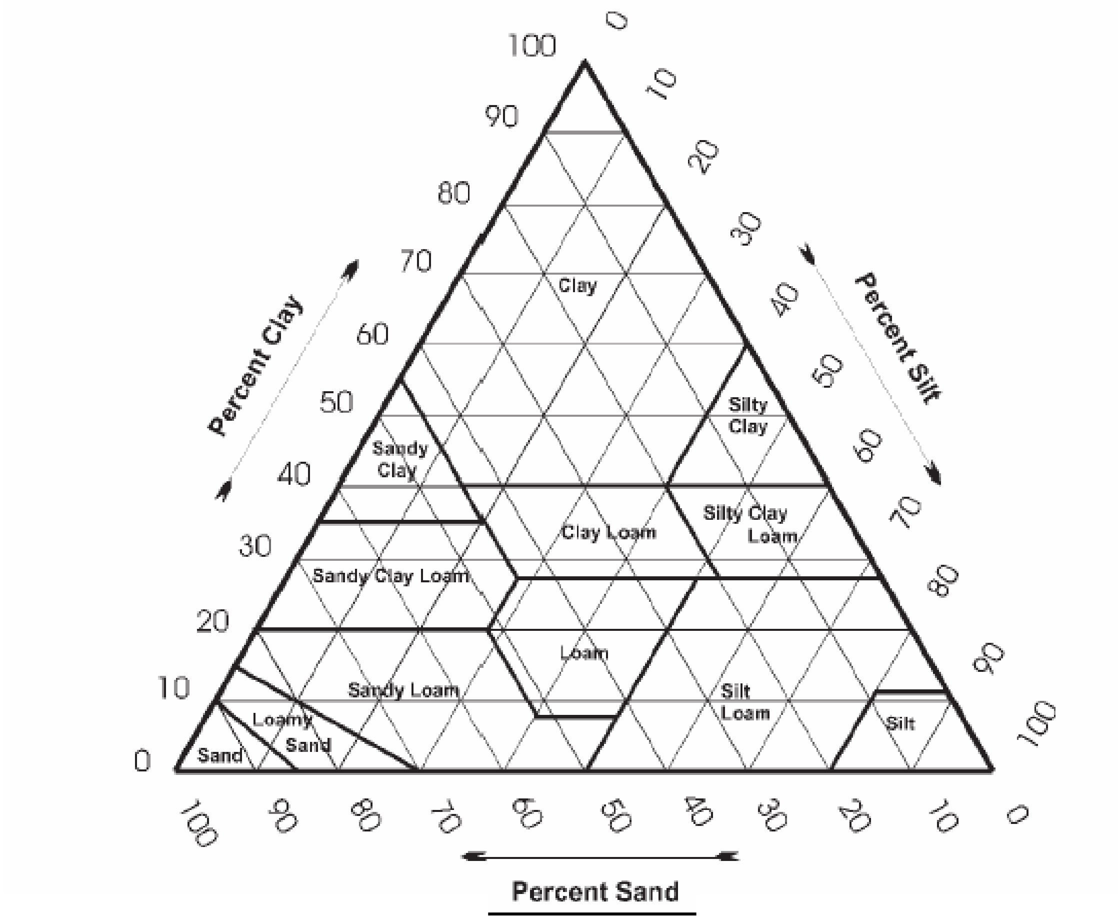
*Classification of texture class from the feel method* (M. Subanshchandrabose, 1989).

| Textural class | Feel of fingers | Ball formation | Stickiness | Ribbon formation |
|---|---|---|---|---|
| **Sand** | Very gritty | Does not form ball | Does not stain fingers | No |
| **Loamy sand** | Very gritty | Forms, very easily broken | Very little stain fingers | No |
| **Sandy loam** | Moderately gritty | Forms fairly firm ball but is easily broken | Definitely stain fingers | No |
| **Loam** | Neither very gritty nor very smooth | Forms firm ball | Yes | No |
| **Silt loam** | Smooth or slick “buttery” feel | Yes | Yes | Slight tendency to ribbon with flaks surface |
| **Clay loam** | Slightly gritty feel | Moderately hard ball when dry | Definitely stains fingers | Ribbons out on squeezing but ribbon breaks |
| **Silty clay loam** | Very smooth | Yes | Yes | Shows some flacking on ribbon surface similar to |
| **Clay** | Very smooth | Forms hard ball which dry cannot be crushed by fingers | Yes | Squeezes at right moisture into long (1”-3”) ribbons |

APPENDIX I.

## Triangular textural diagram

Content of different soil textures according to triangular textural diagram (Soil Texture, 2005).



# APPENDIX J.

## Data results analyses / measured at PCETP

*Influent water:* Completive values for the whole day.

| Date | BOD$_5$ [mg/l] | COD [mg/l] | pH [mg/l] | TDS [mg/l] | TSS [mg/l] | Q [$m^3$/d] |
|---|---|---|---|---|---|---|
| **2004.10.16** | 116 | 531 | 8.4 | 1700 | 212 | 2076 |
| **2004.10.17** | 108 | 514 | 8.15 | 1730 | 186 | 2023 |
| **2004.10.18** | 183 | 516 | 8.6 | 1670 | 188 | 1883 |
| **2004.10.19** | 166 | 5526 | 8.4 | 1680 | 230 | 1982 |
| **2004.10.20** | 112 | 530 | 8.5 | 1720 | 194 | 2207 |
| **2004.10.21** | 186 | 563 | 8.6 | 1620 | 196 | 1738 |
| **2004.10.23** | 132 | 582 | 8.6 | 1620 | 298 | 1656 |
| **Analyzing method** | Anon, 1965 | Anon, 1965 | Jackson, 1973 | AOAC, 1962 | AOAC, 1962 | |

*Effluent water:* Completive values for the whole day.

| Date | BOD$_5$ [mg/l] | COD [mg/l] | pH [mg/l] | TDS [mg/l] | TSS [mg/l] | Q [$m^3$/d] |
|---|---|---|---|---|---|---|
| **2004.10.16** | 26 | 219 | 7.8 | 1740 | 19 | 2076 |
| **2004.10.17** | 28 | 228 | 7.5 | 1760 | 18 | 2200 |
| **2004.10.18** | 23 | 224 | 7.7 | 1720 | 17 | 1950 |
| **2004.10.19** | 24 | 234 | 7.8 | 1700 | 19 | 2056 |
| **2004.10.20** | 24 | 228 | 7.5 | 1760 | 19 | - |
| **2004.10.21** | 28 | 227 | 7.5 | 1670 | 18 | - |
| **2004.10.23** | 26 | 238 | 7.5 | 1680 | 19 | - |
| **Analyzing method** | Anon, 1965 | Anon, 1965 | Jackson, 1973 | AOAC, 1962 | AOAC, 1962 | |

APPENDIX K.

## Results of heavy metals analyses, method 1, India

*Influent and effluent water:* Total heavy metals concentration.

| Water | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **2004.10.16 Influent** | No detection | No detection | 4.1 | 3.6 | 0.8 |
| **2004.10.16 Effluent** | No detection | No detection | 6.8 | 1.9 | 0.1 |
| **2004.10.17 Influent** | No detection | No detection | 3 | 1.5 | 0.9 |
| **2004.10.17 Effluent** | No detection | No detection | 5.3 | 0.9 | 0.3 |
| **2004.10.18 Influent** | No detection | No detection | 3.6 | 0.7 | 0.4 |
| **2004.10.18 Effluent** | No detection | No detection | 4.6 | 0.4 | 0.2 |
| **2004.10.19 Influent** | No detection | No detection | 2.4 | No detection | 0.3 |
| **2004.10.19 Effluent** | No detection | No detection | 3.9 | No detection | 0.2 |
| **2004.10.20 Influent** | No detection | 1.5 | 4.2 | No detection | 0.6 |
| **2004.10.20 Effluent** | No detection | No detection | 2.4 | No detection | 0.2 |
| **2004.10.21 Influent** | No detection | No detection | 5.5 | No detection | 0.4 |
| **2004.10.21 Effluent** | No detection | No detection | 6.7 | No detection | 0.2 |
| **2004.10.23 Influent** | No detection | No detection | 3 | No detection | 0.4 |
| **2004.10.23 Effluent** | No detection | No detection | 3.4 | No detection | 0.2 |

*Sludge:* Total heavy metals concentration.

| Sludge | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **2004.10.16** | No detection | No detection | 120 000 | No detection | 200 |
| **2004.10.17** | No detection | No detection | 125 000 | No detection | 250 |
| **2004.10.17** | No detection | No detection | 122 500 | No detection | 250 |
| **2004.10.19** | No detection | No detection | 120 000 | No detection | 250 |
| **2004.10.19** | No detection | No detection | 130 000 | No detection | 200 |
| **2004.10.19** | No detection | No detection | 115 000 | No detection | 200 |
| **2004.10.23** | No detection | No detection | 122 500 | No detection | 200 |

*Soils:* Total heavy metals concentration.

| Soil | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Reference soil 1, 0-15 cm** | No detection | 10 | 10 500 | No detection | 30 |
| **Reference soil 1, 15-30 cm** | No detection | No detection | 21 000 | No detection | 40 |
| **Reference soil 2, 0-15 cm** | No detection | 80 | 27 000 | No detection | 40 |
| **Reference soil 2, 15-30 cm** | No detection | No detection | 24 500 | No detection | 20 |
| **Eucalyptus, 0-15 cm** | No detection | No detection | 30 000 | No detection | 10 |
| **Eucalyptus, 15-30 cm** | No detection | No detection | 25 500 | No detection | 10 |
| **Jatropa, 0-15 cm** | No detection | No detection | 24 000 | No detection | 20 |
| **Jatropa, 15-30 cm** | No detection | 90 | 26 000 | No detection | 40 |
| **Casuarina, 0-15 cm** | No detection | No detection | 23 000 | No detection | 40 |
| **Casuarina, 15-30 cm** | No detection | No detection | 24 000 | No detection | 40 |
| **Korai, 0-15 cm** | No detection | 30 | 22 500 | No detection | 30 |
| **Korai, 15-30 cm** | No detection | No detection | 29 000 | No detection | 40 |
| **Elephant grass, 0-15 cm** | No detection | No detection | 32 500 | No detection | 40 |
| **Elephant grass, 15-30 cm** | No detection | 70 | 32 000 | No detection | 40 |

*Soil:* Available heavy metals concentration.

| Available soil | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Reference soil 1, 0-15 cm** | No detection | No detection | 11.6 | No detection | 0.8 |
| **Reference soil 1, 15-30 cm** | No detection | No detection | 10.4 | No detection | 0.6 |
| **Reference soil 2, 0-15 cm** | No detection | No detection | 5.2 | No detection | 0.6 |
| **Reference soil 2, 15-30 cm** | No detection | No detection | 9.6 | No detection | 0.4 |
| **Eucalyptus, 0-15 cm** | No detection | No detection | 18.8 | No detection | 0.4 |
| **Eucalyptus, 15-30 cm** | No detection | No detection | 15.2 | No detection | 0.6 |
| **Jatropa, 0-15 cm** | No detection | No detection | 150 | No detection | 0.8 |
| **Jatropa, 15-30 cm** | No detection | No detection | 135 | No detection | 1 |
| **Casuarina, 0-15 cm** | No detection | No detection | 125 | No detection | 0.8 |
| **Casuarina, 15-30 cm** | No detection | No detection | 120 | No detection | 0.8 |
| **Korai, 0-15 cm** | No detection | No detection | 115 | No detection | 0.8 |
| **Korai, 15-30 cm** | No detection | No detection | 110 | No detection | 0.8 |
| **Elephant grass, 0-15 cm** | No detection | No detection | 100 | No detection | 0.8 |
| **Elephant grass, 15-30 cm** | No detection | No detection | 100 | No detection | 0.6 |

*Plant:* Total heavy metals concentration.

| Plants | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Eucalyptus, reference sampels** | 6.25 | No detection | 60 | 22.5 | 18.75 |
| **Eucalyptus** | 3.75 | No detection | 56.25 | 10 | 18.75 |
| **Jatropa** | 1.25 | No detection | 91.25 | 10 | 18.75 |
| **Casuarina, reference samples** | 1.25 | No detection | 81.25 | 10 | 25 |
| **Casuarina** | No detection | No detection | 68.75 | 8.75 | 18.75 |
| **Korai** | No detection | No detection | 37.5 | 15 | 25 |
| **Elephant grass** | No detection | No detection | 50 | 11.25 | 18.75 |
| **Sambai** | No detection | 6.25 | 120 | 7.5 | 18.75 |
| **Neem tree, reference samples** | No detection | No detection | 70 | 8.75 | 12.50 |
| **Neem tree** | No detection | No detection | 56.25 | 13.75 | 12.50 |

## APPENDIX L.

# Results of heavy metals analyses, method 2, Sweden

*Influent and effluent water:* Total heavy metals concentration.

| Water | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **2004.10.16 Influent** | 0.02 | 6.72 | 81.04 | 0.24 | 61.04 |
| **2004.10.16 Effluent** | 0.01 | No detection | 534.15 | 0.05 | 2.43 |
| **2004.10.17 Influent** | 0.03 | 10.01 | 145.07 | 0.37 | 80.37 |
| **2004.10.17 Effluent** | 0.01 | No detection | 142.21 | 0.09 | 2.48 |
| **2004.10.18 Influent** | 0.01 | 2.76 | 138.95 | 0.23 | 21.46 |
| **2004.10.18 Effluent** | 0.01 | No detection | 115.81 | 0.07 | 3.48 |
| **2004.10.19 Influent** | 0.02 | 1.17 | 176.86 | 0.24 | 18.90 |
| **2004.10.19 Effluent** | 0.03 | No detection | 74.85 | 0.08 | 8.32 |
| **2004.10.20 Influent** | 0.01 | 5.41 | 162.10 | 0.22 | 70.47 |
| **2004.10.20 Effluent** | 0.01 | No detection | 151.97 | 0.11 | 6.16 |
| **2004.10.23 Influent** | 0.03 | 3.09 | 145.04 | 0.46 | 25.07 |
| **2004.10.23 Effluent** | 0.01 | No detection | 233.38 | 0.44 | 7.54 |

*Sludge:* Total heavy metals concentration.

| Sludge | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **2004.10.16** | 0.13 | 188.46 | 123276.36 | 5.07 | 286.18 |
| **2004.10.17** | 0.13 | 149.43 | 129379.72 | 4.65 | 365.89 |
| **2004.10.17** | 0.14 | 148.55 | 120656.25 | 3.81 | 294.02 |
| **2004.10.19** | 0.12 | 150.71 | 131196.65 | 4.40 | 350.69 |
| **2004.10.19** | 0.10 | 107.49 | 116525.69 | 3.16 | 238.37 |
| **2004.10.19** | 0.07 | 81.50 | 118330.10 | 3.14 | 270.37 |
| **2004.10.23** | 0.10 | 82.41 | 119349.68 | 3.17 | 275.39 |

*Soil:* Total heavy metals concentration

| Soil | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Reference soil 1, 0-15 cm** | 0.03 | 80.63 | 17 092.01 | 3.51 | 25.68 |
| **Reference soil 1, 15-30 cm** | 0.03 | 83.81 | 17 868.72 | 3.48 | 33.32 |
| **Reference soil 2, 0-15 cm** | 0.02 | 81.68 | 20 222.66 | 4.12 | 30.64 |
| **Reference soil 2, 15-30 cm** | 0.03 | 65.22 | 16 552.44 | 3.45 | 27.17 |
| **Eucalyptus, 0-15 cm** | 0.01 | 93.72 | 19 947.23 | 3.65 | 31.47 |
| **Eucalyptus, 15-30 cm** | 0.03 | 102.15 | 22 894.43 | 4.05 | 33.98 |
| **Jatropa, 0-15 cm** | 0.03 | 76.36 | 20 619.80 | 5.23 | 37.49 |
| **Jatropa, 15-30 cm** | 0.03 | 80.37 | 21 218.80 | 4.60 | 35.43 |
| **Casuarina, 0-15 cm** | 0.03 | 67.13 | 17 310.93 | 3.19 | 30.78 |
| **Casuarina, 15-30 cm** | 0.05 | 84.30 | 21 064.44 | 3.80 | 36.10 |
| **Korai, 0-15 cm** | 0.04 | 73.67 | 19 501.70 | 3.56 | 30.17 |
| **Korai, 15-30 cm** | 0.02 | 86.79 | 22 214.49 | 5.08 | 34.09 |
| **Elephant grass, 0-15 cm** | 0.06 | 99.17 | 30 008.79 | 6.30 | 48.62 |
| **Elephant grass, 15-30 cm** | 0.03 | 84.73 | 25 574.11 | 5.22 | 40.83 |
| **Sambai, 0-15 cm** | 0.05 | 97.11 | 27 937.87 | 5.68 | 48.01 |

*Soil:* Available heavy metals concentration.

| Soil available | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Reference soil1, 0-15 cm** | 0.005 | 1.791 | 1.804 | 0.001 | 0.102 |
| **Reference soil 2, 0-15 cm** | 0.019 | 2.116 | 15.629 | 0.015 | 0.148 |
| **Eucalyptus, 0-15 cm** | 0.014 | 2.247 | 35.712 | 0.024 | 0.168 |
| **Jatropa, 0-15 cm** | 0.006 | 2.086 | 1.256 | 0.001 | 0.058 |
| **Casuarina, 0-15 cm** | 0.016 | 2.329 | 1.347 | 0.004 | 0.139 |
| **Korai, 0-15 cm** | 0.008 | 2.464 | 2.042 | 0.006 | 0.128 |
| **Elephant grass, 0-15 cm** | 0.006 | 2.870 | 1.390 | 0.001 | 0.093 |
| **Sambai, 0-15 cm** | 0.003 | 3.105 | 1.443 | 0.001 | 0.097 |
| **Eucalyptus, 0-15 cm, 2nd filtrate** | 0.013 | 3.452 | 3.677 | 0.008 | 0.147 |

*Plant:* Total heavy metals concentration.

| Plants | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Eucalyptus, reference samples** | 0.72 | No detection | 252.41 | 1.91 | 45.53 |
| **Eucalyptus** | 0.22 | No detection | 230.66 | 1.95 | 40.65 |
| **Jatropa** | 0.11 | No detection | 289.03 | 2.24 | 59.98 |
| **Casuarina reference samples** | 0.05 | No detection | 270.48 | 1.11 | 45.87 |
| **Casuarina** | 0.08 | No detection | 248.92 | 1.39 | 27.67 |
| **Korai** | 0.18 | No detection | 80.00 | 0.88 | 55.43 |
| **Elephant grass** | 0.06 | No detection | 121.20 | 2.09 | 23.31 |
| **Sambai** | 0.05 | No detection | 238.52 | 0.70 | 27.22 |
| **Neem tree reference samples** | 0.07 | No detection | 243.33 | 2.11 | 26.26 |
| **Neem tree** | 0.05 | No detection | 159.43 | 1.63 | 25.48 |

## APPENDIX M.

## Reference material / blanc samples

*Reference material, earlier studies.*

| Sample | Cadmium | Chromium | Iron | Lead | Zinc |
|---|---|---|---|---|---|
| **RM JDP** | 2.7 | 80.3 | 50163.3 | 147.0 | 1511.9 |
| **RM JDP** | 3.0 | 102.6 | 59421.5 | 167.5 | 1712.7 |
| **RM JDP** | 2.8 | 81.4 | 53515.4 | 155.9 | 1592.6 |
| **RM JDP** | 3.0 | 110.5 | 60807.5 | 165.0 | 1699.4 |
| **Average** | 2.87 | 93.68 | 55976.91 | 158.83 | 1629.13 |
| **Stdev.** | 0.16 | 15.18 | 5001.91 | 9.36 | 94.89 |
| **RSD** | 5.6% | 16.2% | 8.9% | 5.9% | 5.8% |
| **Confidence interval (95%)** | 0.2 | 14.9 | 4901.9 | 9.2 | 93.0 |

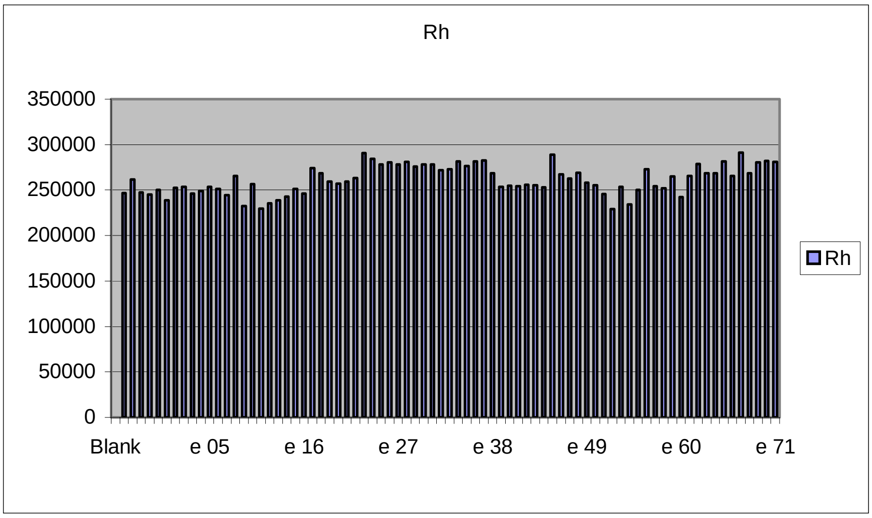
*Reference material, methods 2.*

| Sample | Cadmium | Chromium | Iron | Lead | Zinc |
|---|---|---|---|---|---|
| **RM 2** | 2.9 | 64.4 | 47949.7 | 139.3 | 1672.4 |
| **RM 3** | 3.1 | 91.8 | 59159.5 | 154.5 | 1781.5 |
| **RM 4** | 3.3 | 100.4 | 64689.0 | 163.3 | 1878.7 |
| **RM 7.1** | 3.3 | 100.4 | 64689.0 | 163.3 | 1878.7 |
| **RM 7.2** | 3.4 | 104.8 | 67514.6 | 169.2 | 1943.1 |
| **RM 9** | 3.2 | 104.0 | 62807.1 | 153.8 | 1780.5 |
| **Average** | 3.2 | 94.3 | 61134.8 | 157.2 | 1822.5 |
| **Stdev.** | 0.19 | 15.35 | 7021.55 | 10.57 | 96.78 |
| **RSD** | 5.9% | 16.3% | 11.5% | 6.7% | 5.3% |
| **Confidence interval (95%)** | 0.2 | 12.3 | 5618.4 | 8.5 | 77.4 |

*Water, plant, soil and sludge samples:* Average on blank samples.

| Sample | Cadmium [ppm] | Chromium [ppm] | Iron [ppm] | Lead [ppm] | Zinc [ppm] |
|---|---|---|---|---|---|
| **Influent water** | 0.019 | 4.859 | 141.508 | 0.293 | 46.219 |
| **Effluent water** | 0.014 | 0.047 | 208.726 | 0.143 | 5.068 |
| **Water, blank sample** | No detection | 1.322 | 12.682 | 0.014 | 0.772 |
| **Relatively influent water** | No detection | 27.195 | 8.962 | 4.597 | 1.669 |
| **Relatively effluent water** | No detection | 2805.732 | 6.076 | 9.430 | 15.226 |
| **Plant** | 0.079 | 0.051 | 106.808 | 0.802 | 18.889 |
| **Plant blank sample** | 0.002 | 3.653 | 1.426 | 0.033 | No detection |
| **Relatively plant** | 2.329 | 7196.710 | 1.335 | 4.142 | No detection |
| **Soil, layer 1 & 2** | 0.017 | 41.175 | 10483.54 | 2.121 | 17.177 |
| **Soil, blank sample** | 0.002 | 0.157 | 18.116 | No detection | 1.038 |
| **Relatively soil** | 13.894 | 0.382 | 0.173 | No detection | 6.045 |
| **Sludge** | 0.057 | 64.957 | 61389.07 | 1.960 | 148.765 |
| **Sludge blank sample** | 0.006 | No detection | 233.484 | 0.307 | 4.237 |
| **Relatively sludge** | 10.585 | No detection | 0.380 | 15.685 | 2.848 |

*Diagram over Rh values*



# APPENDIX N.

## Mass Balance

The table below describes the incoming, outgoing load and the heavy metals in the sludge. The different between incoming and outgoing of heavy metals suppose to be in the sludge. In this table the iron values is not include depends on the treatment plant adding iron in the process.

| Elements | Incoming load [g/d] | Outgoing load [g/d] | Sludge [g/d] | Incoming - Outgoing load [g/d] |
|---|---|---|---|---|
| **Cadmium** | 37.12 | 26.64 | 1.70 | 10.48 |
| **Chromium** | 9427.11 | 182.75 | 1946.90 | 9244.36 |
| **Lead** | 567.64 | 276.71 | 58.74 | 290.94 |
| **Zinc** | 89665.38 | 9831.44 | 4459.09 | 79833.94 |