

Study of the Pathway of Heavy Metals in a Sewerage System

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**Thesis presented in partial fulfillment of the requirements for
the degree of Master of Chemistry at the University of
Stellenbosch**

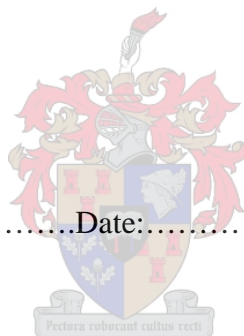
Promoter: Prof. Klaus R. Koch

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Declaration:

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously in its entirety or in part been submitted at any university for a degree.

Signature:.....Date:.....



Abstract

This thesis reports on an exploratory investigation of proposed sludge guideline limits of heavy metal (cadmium, chromium, copper, nickel, lead and zinc) concentrations for South Africa. The purpose of the study is to determine allowable heavy metal concentrations in sludge for use as fertilizer in agriculture that can be attained and is practically possible without being detrimental to the environment.

This determination was done by investigating the potential sources and concentrations of these heavy metals at the Potsdam Wastewater Treatment Works (WWTW) and also the efficiency of the treatment works in removal of these heavy metals. A heavy metal mass balance of both the influent at the Potsdam WWTW and the wastewater through the treatment works was calculated. This study also proposes possible interventions to minimize the levels of these heavy metals.

Results for the heavy metal mass balance of the influent showed that a large quantity of some metals were unaccounted for, this implies that either industries discharge illegally after hours or the present monitoring undertaken by the City of Cape Town is inadequate. The large percentage of unaccounted cadmium suggests another source, which should be further investigated.

The mass balance of the wastewater through Potsdam WWTW concluded that all these heavy metal limits were attainable, and that in some cases can be lowered even more. The treatment works has a high removal efficiency of these heavy metals, and a substantial reduction of these limits is justified. In the period of this study, the area under investigation gradually expanded, as more industries were established in it. Although the works was performing beyond its capacity it nevertheless was able to attain the rigorous heavy metal limits in sludge that are envisaged. There has also been a reduction in limits of heavy metals for discharge of final effluent into waterbodies; this study shows that these limits are also attainable.

Opsomming

Hierdie verhandeling doen verslag oor 'n verkennende ondersoek van voorgestelde slikriglynperke van swaarmetale (kadmium, chroom, koper, nikkel, lood en sink) konsentrasies vir Suid-Afrika. Die doel van die studie is om die toelaatbare swaarmetaalkonsentrasies in slik wat aangewend kan word as landboubemesting te bepaal wat haalbaar is en prakties moontlik is sonder om nadele vir die omgewing in te hou.

Die bepaling is gemaak deur die potensiaale bronne en die konsentrasies van swaarmetale by die Potsdamafvalwaterbehandelingsaanleg (AWBA) te ondersoek en ook die doeltreffendheid van die aanleg om die metale te verwyder te ondersoek. 'n Swaarmetaalmassabalans is vir die invloei en ook vir die afvalwater wat deur die aanleg vloei bereken. Met hierdie studie word ook ingrepe aanbeveel om die swaarmetaalvlakke te verminder.

Die invloei se swaarmetaalmassabalans dui daarop dat 'n groot hoeveelheid van sommige metale nie kan verreken word nie wat op sy beurt daarop dui dat die industrie onwettig sy uitvloei na-ure stort of dat die moniteering wat tans deur die Stad Kaapstad uitgevoer word onvoldoende is. Die groot hoeveelheid onverrekenbare kadmium dui op die teenwoordigheid van 'n bron wat verder ondersoek behoort te word.

Die massabalans van die afvalwater wat deur die Potsdam AWBA vloei bewys dat die perke vir al die swaarmetale haalbaar is en dat sommige selfs nog verder verminder kan word. Die aanleg het 'n hoë verwyderingsdoeltreffendheid van swaarmetale en derhalwe is 'n substantiale vermindering van die perke geregverdig. Gedurende die studie het die industrie in die studiegebied gelydelik uitgebrei soos wat nuwe industrieë toegevoeg is. Alhoewel die aanleg bo sy vermoë presteer het was dit desnieteenstaande moontlik om die streng swaarmetaalperke in die slik wat in die vooruitsig gestel word nou reeds na te kom. Die perke van swaarmetale vir die vrystelling van uitvloei in waterliggame is ook verminder en die studie dui daarop dat hierdie perke ook haalbaar is.

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Study of the Pathway of Heavy Metals in a Sewerage System

Chapter 1: Introduction

1.1 Background

There has been concern in recent years regarding increased levels of metals in sewage. High concentrations of metals in sewage may constitute an ecological threat and can endanger the use of the receiving water. Furthermore, high metal concentrations in raw sludge can upset anaerobic digestion delaying or inhibiting stabilization causing disposal problems and jeopardizing the long term use of digested sludge in agriculture. A large fraction of heavy metals in wastewater is accumulated in the sludge during conventional treatment. Many of the trace elements are also micronutrients, such as zinc, which improve plant growth and the feed value of the crop. Other metals, such as cadmium and lead, are of concern because of the potential of introducing them into the human food chain.

For the past seven years sludge guidelines in South Africa have been the centre of much debate. Currently land disposal and agricultural re-use of sewage sludge in SA must comply with the “Permissible Utilization and Disposal of Sewage Sludge, Edition 1 (WRC 1997)”. The guidelines deal with application of sewage sludge to land and permissible limits for organic and inorganic pollutants in sludge. The metal limits of the sludge guidelines were extensively debated and the new “Guidelines for the Utilization and Disposal of Wastewater Sludge” were proposed in March 2006, also under debate is the analytical method for determining metals in sludge. In the interim sludge metals are extracted using both the TCLP (leachable) and aqua regia (total) extraction methods. For soil the 1991 guidelines which are based on total metal content is still in use. Europe, Australia and the US tend to derive limits based on a combination of good practices i.e. what should be achievable and protecting soils from risk-based limits under nominal application scenarios rather than attempting to maintain background concentrations.

The WRC initiated a research program in 2000 to further develop the knowledge base for the management of sewage sludge in the South African context. Although the results of these

research projects do not give all the answers, they do enable the formulation of an updated “Permissible Utilisation and Disposal of Sewage Sludge, Edition 2” document. This new edition should combine the relevant aspects of the addendum and limits for metals, nutrients and organic pollutants based on scientific criteria to ensure credibility and acceptance.

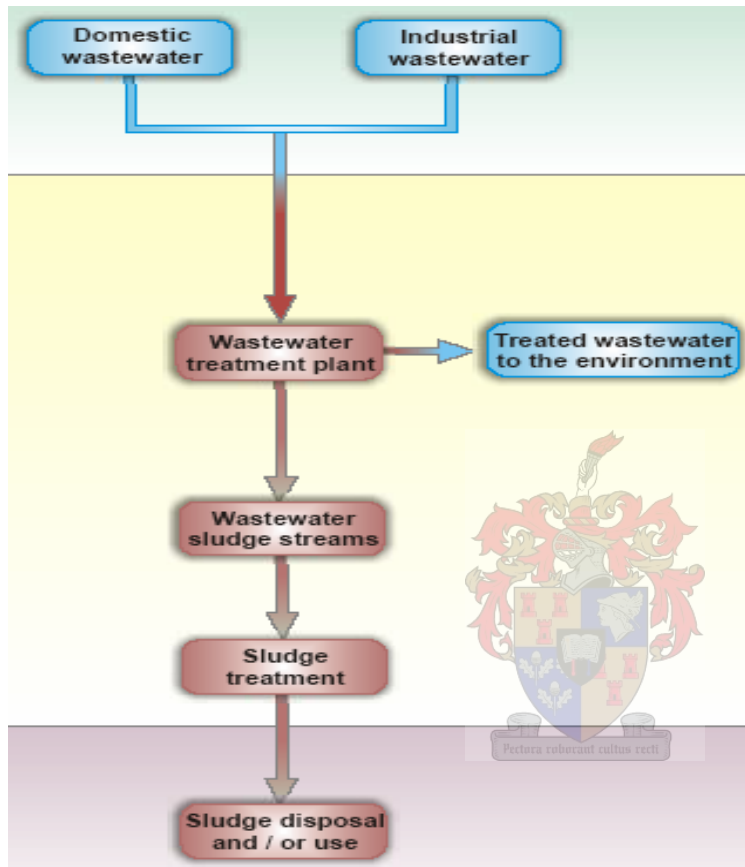


Fig. 1.1 Typical wastewater lifecycle

1.2 Heavy Metals and Sludge

Ever since man started walking this earth he has been plagued with the problem of his solid, liquid and gaseous wastes. The use of the land as a receptor of wastewater has been practiced for hundred of years throughout the world. With these early practices, some agricultural benefits were realized, however the primary consideration was disposal of the wastewater. As populations increased and land became more difficult to reserve for this purpose and the concern for public health increased, the use of sewage farms decreased. The increased threat of waterborne diseases resulted in the development of new wastewater treatment plants.

Sludge is produced as a necessary by-product of any water treatment process. Land disposal of these sludge is commonly practiced but it is prone to environmental and health hazards. A large fraction of metals in wastewater is accumulated in the sludge during treatment. The concentration of metals depends to a great extent on the amount of industrial effluent contribution to the wastewater system. In wastewaters from domestic sources only, the concentration of most metals is usually low. At high levels heavy metals in sludge are of primary concern because of their potential uptake by crops and thereby their entrance into the human food chain. Also, there is a concern for heavy metal buildup in the soil to phytotoxic levels and their migration to groundwater.

All metals have adverse effects for humans above certain concentrations especially cadmium, lead and hexavalent chromium. Metabolic interactions among the heavy metals are so potent that studies of these metals in isolation from each other can be seriously misleading. The potential toxicity of an intake of lead is greatly influenced by the concurrent intake of iron and that of cadmium by the concurrent intake of zinc and copper.

1.3 Land Application of Sludge

Land application of sludge is both economical and beneficial as it supplies all major essential nutrients (N, P, K, S, Ca and Mg) to crop land and also increases the humus content of soils. However sludge from industrialized or mixed areas contain elements in concentrations that cause direct or indirect symptoms of toxicity to vegetation. In addition to Cu, Zn, Cd, B, and Ni which are typical pollutants of residential origin, certain industries also release large amounts of V, Cr, Mn, Co, As, Ba, and Pb which can affect crop yields. Furthermore, some plants accumulate high concentrations of Se, Mo, Cd and Pb (accumulative toxin in the food chain), which are toxic to man and animals but do not affect normal plant growth.

The availability of heavy metals to plants, their uptake and their accumulation depend on a number of soil, plant and other factors.

1.3.1 Soil Factors

1. Soil pH – metals are more available to plants below pH 6.5.

2. Soil phosphorous – phosphorous interacts with certain metal cations to decrease their availability to plants.
3. Organic matter – they can chelate and complex heavy metals so that they are less available to plants.
4. Cation exchange capacity (CEC) – soils with high CEC ability are safer for sludge application.
5. Moisture, temperature and aeration – these can affect plant growth and uptake of metals.

1.3.2 Plant Factors:

1. Plant species and varieties – vegetable crops are more sensitive to heavy metals than grass.
2. Organs of the plants – grain and fruit accumulate lower amounts of metals than leafy tissues.
3. Plant age and seasonal effects – the older leaves of plants will contain higher amounts of metals.



1.3.3 Other Factors:

1. Reversion – with time metals may revert to unavailable forms in soil.
2. Metals – metals differ in their relative toxicities to plants and in their reactivity in soils.

Metals exist in different forms in municipal sewage sludge. Their form depends on the chemical properties of the sludge and on the chemistry of the metal. Using a sequential extraction procedure to fractionate metals, Stover et al. [1976] ranked the relative quantities of different forms of Cu, Zn, Pb, Cd, and Ni present in municipal sewage sludge as follows:

Cu: sulphides > carbonates > organic bound = adsorbed > exchangeable

Zn: organic bound > carbonates > sulphides > adsorbed > exchangeable

Pb: carbonates > organic bound > sulphides > adsorbed > exchangeable

Ni: carbonates > organic bound > exchangeable > adsorbed > sulphides

Cd: carbonates > sulphides > organic bound > adsorbed = exchangeable

Based on this data, less than 17 percent of the total amount of Cu, Zn, Pb, and Cd in sludge and approximately 22 percent of Ni are in the adsorbed and exchangeable fractions, that is,

the forms readily available to plants. The remainder of the metals is present in forms which require conversion to water-soluble, exchangeable, or adsorbed forms before uptake by plants. Additional data [Sommers, 1977; Stover et al., 1976] suggest that different chemical forms of a metal may predominate in different sewage sludge. Thus, the behaviour of a metal after incorporation into the soil may not be similar for different sludges.

1.4 Control of Discharges to Sewer

Discharges to sewers are subject to control for various reasons:

1. To ensure that no substances can cause damage to sewers
2. To minimize sources of danger to the public or to sewer maintenance personnel
3. To avoid flooding by the uncontrolled discharge of excessive volumes of water
4. To limit the concentration of substances which have a deleterious effect on the efficient operation of wastewater treatment works
5. To minimize harmful substances occurring in final effluent and sludge

In South Africa stormwater is excluded from the sewerage system and only sewage (domestic and industrial effluent should be allowed to enter system. If stormwater is allowed to enter the sewers they are bound to overflow and the large volumes arriving at the treatment works during wet weather would cause hydraulic overloading. Industries discharging toxic effluents must be controlled at the source. The limits imposed for toxic metals should be strictly adhered to as a poisoned biological filter or activated sludge plant will lead to reduced efficiency of plant performance. At certain concentrations metals are likely to inhibit sludge digestion or reduce the rate at which decomposition takes place. Closely associated with a control of metals is the control of pH, since metals will pass into the sewer in solution if the pH is too low. The stipulated pH requirement is not less than 5.5, however certain metals have an appreciable solubility at this pH.

No person or industry may discharge or increase the quantity or vary the nature of the industrial effluent without the written consent of the City Council into any wastewater system or increase the quantity or vary the nature of the effluent. It is prohibited to discharge stormwater or any substance other than wastewater into the wastewater system.

In order to control unwanted discharges into both stormwater and sewer, effluent inspectors check all dwellings to ensure that stormwater is not being discharged into sewers, and at industrial sites to ensure that effluent is not discharged into the stormwater system. In the Cape Metropole normally industrial effluent samples are collected four times during a six month period and charges are calculated on the mean of the last four results. Monthly billing is done according to the formula:

$$\text{Charge} = V_w \times \text{SVC} + V_{ie} \times T[(\text{COD}-1000)/1500] + V_{ie} \times T \times \text{SF}$$

Where: V_w = total volume in kilolitres of wastewater discharged during the month

SVC = sewerage volume charge (determined by City)

V_{ie} = total volume in kilolitres of industrial effluent discharged during the month

COD = chemical oxygen demand of the effluent in mg/l

T = cost of treating 1 kilolitre of wastewater (determined by City)

SF = surcharge factor = $\frac{\text{actual} - \text{specified limit}}{\text{specified limit}}$ (limit as per By-law)

From the above formula it is evident that if the COD is less than 1000 the second term is zero and if effluent complies with by-law limits then only the SVC charge will apply. In the case of the pH parameter, if (actual - spec. limit) results in a negative value, a positive value of the same magnitude must be substituted. The COD of industrial effluent is the rolling arithmetic average of four samples taken at any time during a six to twelve month period. The SF of industrial effluent is the latest value determined. The SF is cumulative for all parameters that are outside the limits set in the Industrial Effluent By-law.

1.5 Objectives

The primary aim of this project is to ascertain that lower metal limits can be achieved and not a compromised reached which could have short and long term detrimental effects on the receptors of sludge and to broaden the knowledge base for the management of sewage sludge.

Other goals envisaged could be:

- (i) To see to what level effluent is discharged illegally by industries.
- (ii) To investigate the efficiency of industrial effluent monitoring by the City Of Cape Town.
- (iii) To investigate the effectiveness of the WWTW in removing metals.

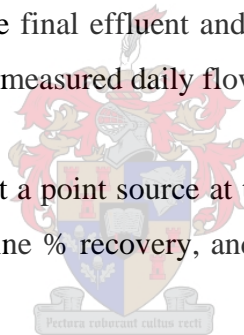
1.6 Project Design and Outline

Industries in the Montague and Killarney Gardens area were assessed for their metal loading on the Potsdam WWTW. The Potsdam WWTW was investigated for its effectiveness in the removal of metals.

The concentration of metals (Cu, Cr, Zn, Cd, Ni, and Pb) was analysed by means of AES-ICP at the source (industrial and domestic). Twelve industries that have been identified as a source of metal contamination were sampled. Monthly data for the past three years was used. The Wesfleur (domestic stream) was evaluated to see what contribution domestic effluent makes towards the total metal content as this works has two separate influent streams, a domestic and an industrial stream. The Water Control Inspectors determined flow values for each industry.

The influent at the Potsdam Wastewater Treatment Works (WWTW) was sampled and analysed monthly. Furthermore the final effluent and the sludge of the WWTW was sampled and analysed. The Plant Operators measured daily flow values by means of flow meters.

A tracer, lithium was discharged at a point source at the furthest industry from the plant and a mass balance evaluated to determine % recovery, and also the distribution and flow at which effluent travels along the sewers.



1.7 Mass Balance Technique

The law of conservation of matter states that matter is conserved, neither created nor destroyed. Thus, if we know the amount of material that enters a chain of processes, and keep an account of all the amounts in different paths, we can calculate quantities of materials that are hard to measure. For example, we can calculate the amount of material entering the atmosphere if we know the amounts that went in, the transformations, and the waste streams to land and water. This method is called the Mass or Material Balance technique.

An example of a process from everyday life is sewage treatment. Wastewater is generated in your homes and is collected with the sewer system and transported to a treatment plant. When asked what happens to the sewage at the plant, most people say that the pollutants are removed from the water and the relatively clean water is then discharged to a water body. But what

happens to the pollutants that are removed? In the treatment process, these pollutants are transferred from the water to the air, and to solid material, sludge, or biosolids, and a small amount remains in the clean water. These waste products must be taken care of so that they do not affect the environment. A mass balance can be used to determine how much pollutant is in each of its various forms. Many environmental problems have been caused by neglecting to think of the pollutants in terms of the conservation of matter and a mass balance.

1.8 Specific Project Objectives

1. Mass balance of metals in the influent from all the different sources coming into the Potsdam WWTW.
2. Mass balance of metals in the wastewater through the Potsdam WWTW.
3. Efficiency of Potsdam WWTW in removing metals.



Chapter 2 – Wastewater Treatment Systems

2.1 Potsdam WWTW

2.1.1 Background

The Potsdam WWTW, situated west of Koeberg Road opposite the Caltex Refinery, serves a catchment bounded by Tygerberg in the east, the N1 and Sable Road in the south, the coastline in the west and the existing developments in West Beach, Sunningdale, Parklands and Du Noon in the north. Recorded flows at the Potsdam WWTW over the period July 2003 to September 2005 revealed an average daily flow of 34.2 MI/d.

Potsdam WWTW also needs to serve new developments east of the N7 up to the Tygerberg and as far north as Potsdam Road extension (generally known as the De Grendel Development Area), as well as undeveloped land between the Diep River and the N7. These areas drain naturally to Potsdam WWTW. The Greater Potsdam Catchment Area includes the area north of the existing developments of West Beach, Sunningdale and Parklands up to the watershed between Blaauwberg Hill and Koeberg Hill. All the land south of the urban edge slopes towards the lower areas at the Diep River and Rietvlei. Potsdam is located downstream of this catchment area and forms a natural focal point for the provision of treatment facilities for the whole area.

The Greater Potsdam Catchment Area comprises an area of approximately 10 000 ha, with about 5 000 ha still available for urban development. Close to 675 ha may still be developed in the De Grendel Proposed upgrading of wastewater treatment and associated infrastructure in the Blaauwberg area.

2.1.2 Treatment Processes at Potsdam WWTW

Flow arrives at the inlet works from up to four pump stations, namely the Table View East Pump Station, Koeberg Road Pump Station (PS), Du Noon PS and Racecourse Road PS. In addition, a small amount of flow gravitates to the works from Bothasig. The inlet

works is equipped with three screens that screen out any solid materials from the influent flow. In the event of the screens being blocked or when the inflow exceeds the capacity of the screens the raw sewage overflows and is directed to reed beds. The influent is then split (to the biofilter works and the activated sludge works) and passes through a flume where the flow is measured. The influent then passes through degritting systems and the grit is removed to 6 m³ skips, which are collected from time to time.



Fig. 2.1 Aerial view of Potsdam WWTW

The secondary treatment process entails the biological treatment of the liquid to reduce its nutrient load and Chemical Oxygen Demand (COD). During the biological treatment process bacteria are formed which feed on the pollutants (e.g. nitrogen, and phosphates) and in so doing remove them from the liquid.

2.1.2.1 Activated Sludge Plant (ASP)

The activated sludge works was constructed in 1996 and 1997 and operates as follows:

- A splitter splits the flow to two Primary Settling Tanks (PST) (25 m diameter tanks fitted with baffles for scum removal).
- The settled sewage is passed to the settled sewage pump station. Variable speed pumps pump the liquid through a flume where it is measured. It then flows into a bioreactor.
- The bioreactor consists of two separate streams, each with a modified UCT configuration.
- The flow from the two streams is then combined and flows in an open channel to a flow splitter where it is then split to six 25 m diameter clarifiers.
- The final effluent passes through a flow meter and the maturation ponds with a chlorination facility en route. The chlorination facility is not currently in use but uses chlorine gas drawn drum installation as well as UV disinfection.
- The final effluent then flows into the Diep River at the same point as the biofilter system effluent.

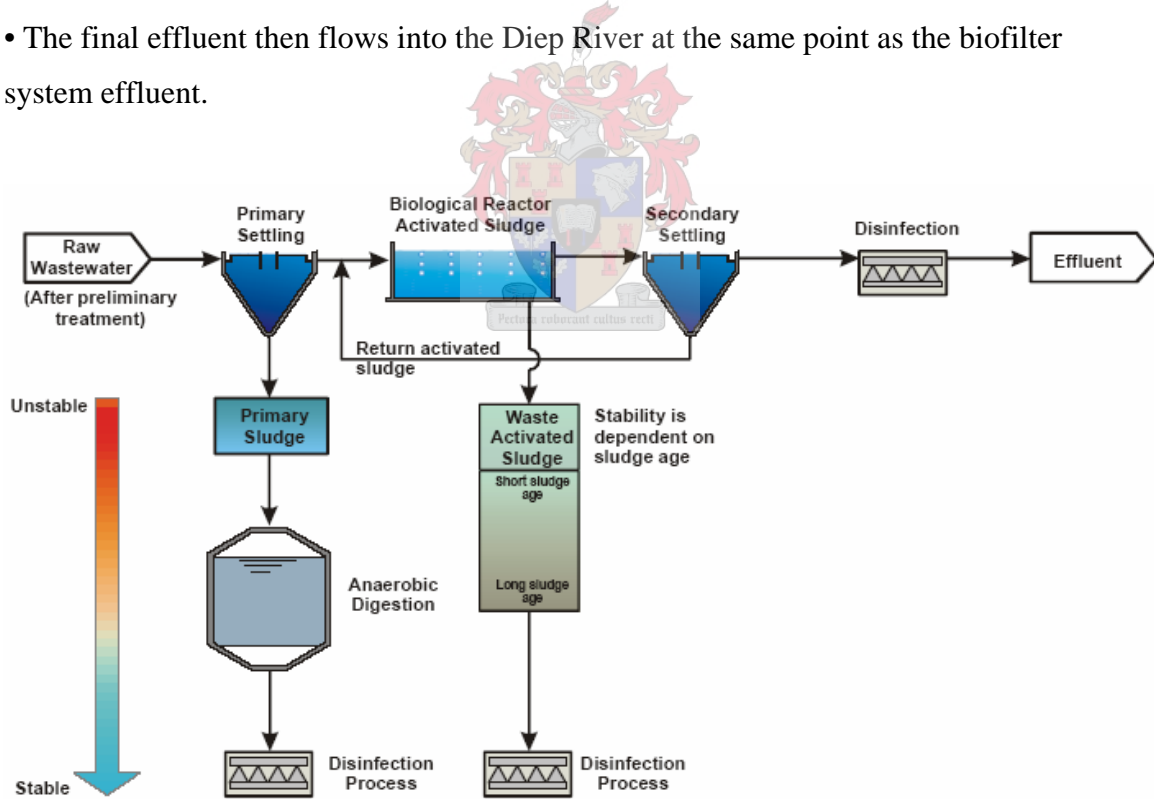


Fig.2.2 Wastewater treatment process (ASP)

The activated sludge processes are as follows:

The activated sludge process is an aerobic (oxygen-rich), continuous-flow biological method for the treatment of wastewater, in which organic matter is utilized by micro-organisms for life-sustaining processes, that is, for energy for reproduction, digestion, movement, etc. and as a food source to produce cell growth and more micro-organisms. During these activities of utilization and degradation of organic materials, degradation products of carbon dioxide and water are also formed. The activated sludge process is characterized by the suspension of micro-organisms in the wastewater, a mixture referred to as the mixed liquor. Activated sludge is used as part of an overall treatment system, which includes primary treatment of the wastewater for the removal of particulate solids before the use of activated sludge as a secondary treatment process to remove suspended and dissolved organic solids.

The conventional activated sludge process consists of an aeration basin, with air as the oxygen source, where treatment is accomplished. Soluble organic materials are absorbed through the cell walls of the micro-organisms and into the cells, where they are broken down and converted to more micro-organisms, carbon dioxide, water, and energy. Insoluble particles are adsorbed on the cell walls, transformed to a soluble form by enzymes (biological catalysts) secreted by the micro-organisms, and absorbed through the cell wall, where they are also digested and used by the micro-organisms in their life-sustaining processes.

The micro-organisms that are responsible for the degradation of the organic materials are maintained in suspension by mixing induced by the aeration system. As the micro-organisms are mixed, they collide with other micro-organisms and stick together to form larger particles called floc. The large flocs that are formed settle more readily than individual cells. These flocs also collide with suspended and colloidal materials (insoluble organic materials), which stick to the flocs and cause the flocs to grow even larger. The micro-organisms digest these adsorbed materials, thereby re-opening sites for more materials to stick.

The aeration basin is followed by a secondary clarifier (settling tank), where the flocs of micro-organisms with their adsorbed organic materials settle out. A portion of the settled micro-organisms, referred to as sludge, are recycled to the aeration basin to maintain an active population of micro-organisms and an adequate supply of biological solids for the adsorption of organic materials. Excess sludge is wasted by being piped to separate sludge-handling processes. The liquids from the clarifier are transported to facilities for disinfection and final discharge to receiving waters.

2.1.2.1 Biofilter Plant

The biofilter works operates as follows:

- A splitter splits the flow to primary settling tanks (five 17.5 m. diameter tanks).
- In addition there are two 12.2 m. diameter PSTs that are currently not in use.
- The settled sewage flows by gravity to the settled sewage pump station. The settled sewage is pumped in two separate streams to the biofilters (each stream consists of four biofilters).
- The effluent from the biofilters then flows to the humus tanks.
- The effluent then flows through eight maturation ponds before it enters the Diep River just upstream of the by-pass channel.
- The humus sludge is returned to the splitter at the end of the inlet works from where it passes to the primary tanks for settlement.
- The primary and humus sludge is removed by gravity from the primary sedimentation tanks and then pumped to the raw sludge holding tank from where it undergoes dewatering.

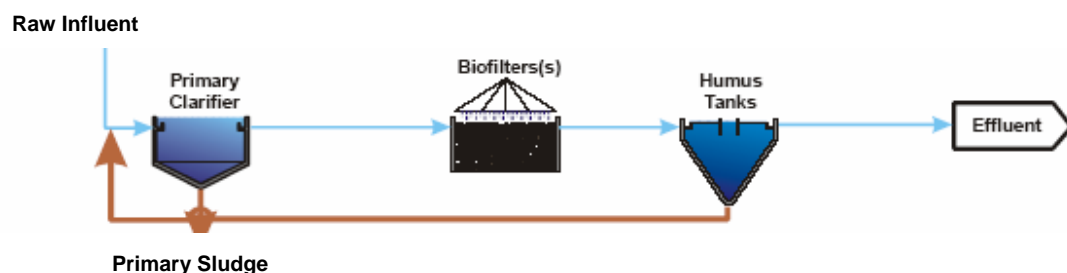


Fig. 2.3 Wastewater treatment process (Biofilter Plant)

2.1.2.3 Sludge Treatment

- The primary sludge is joined with the sludge from the biofilter works and is pumped to the holding tank.
- The waste activated sludge (WAS) is thickened in a dissolved air flotation (DAF) tanks.
- The thickened waste activated sludge is then pumped into a holding tank.

The sludge dewatering installation was constructed in 1997 just to the north of the site along with a compost plant. The City of Cape Town subsequently closed the compost plant and moved the belt presses to a more central position on the site, away from the nearest downstream neighbour.

The dewatering complex operates as follows:

- Primary and secondary sludge are stored separately in sludge holding tanks.
- The primary sludge holding tank is covered and the sludge is mixed using external mixing pumps. The secondary sludge holding tank is open and the sludge is mixed using coarse bubble diffusers.
- Three belt presses can be used to dewater either primary or waste activated sludge. A dedicated pump station that draws water from the final effluent stream of the biofilter works provides wash water to the belt presses.
- Dewatered sludge cake is conveyed via screw conveyors to twin hoppers which hold the sludge until it is trucked for offsite disposal.
- The filtrate and wash water from the belt presses drain back to various points on the works. At present approximately 13.5 tons of dry solids are produced per day, and this is either wasted at Vissershok Landfill site or used in the manufacture of compost at Vissershok.

2.2 Treatment of Metals by Industry

The recovery of metals from effluent has a number of benefits. It minimizes pollution of the environment, reduces the chances of poisoning the WWTW and the recovery of expensive and precious metals is a huge cost saving to the industry. According to convention, the majority of current metal recovery technologies are physical or chemical in nature. Biological systems however, are gaining in popularity as they are increasingly

being proved to be as effective as physical methods while operating at substantially lower costs. Membrane systems are still being developed and most potential applications involve the use of membranes as either filtration devices or as metal ion chelators in combination with other adsorbent material.

There are a number of strategies available, including cementation, solvent extraction, evaporation, ion exchange, chemical precipitation, biological treatment and membrane processing.

2.2.1 Chemical Precipitation

The conventional method for removal of metals is chemical precipitation of the metal as a hydroxide or sulphide. Traditionally hydroxide precipitants such as lime and caustic soda are favoured over sulphide due to the much higher cost of chemically produced hydrogen sulphide (H_2S) and the hazards associated with its manipulation.

2.2.1.1 Hydroxide Precipitation

The most common precipitation method in local industries is hydroxide. The solubility of heavy metals is highly pH dependent. Adjusting the effluent pH can cause the precipitation of the metals that are subsequently removed by sedimentation or filtration. A flocculating or coagulating agent is added to improve the sedimentation characteristics of the precipitate. The pH chosen for the precipitation will depend upon the range of metals to be removed and must be optimized for each individual effluent. Chromium precipitates as a hydroxide only if it is in the trivalent state. Therefore hexavalent chromium must first be reduced to the trivalent state before hydroxide precipitation. Fig. 2.4 gives the theoretical solubility as a function of pH of metal hydroxides for certain metals.

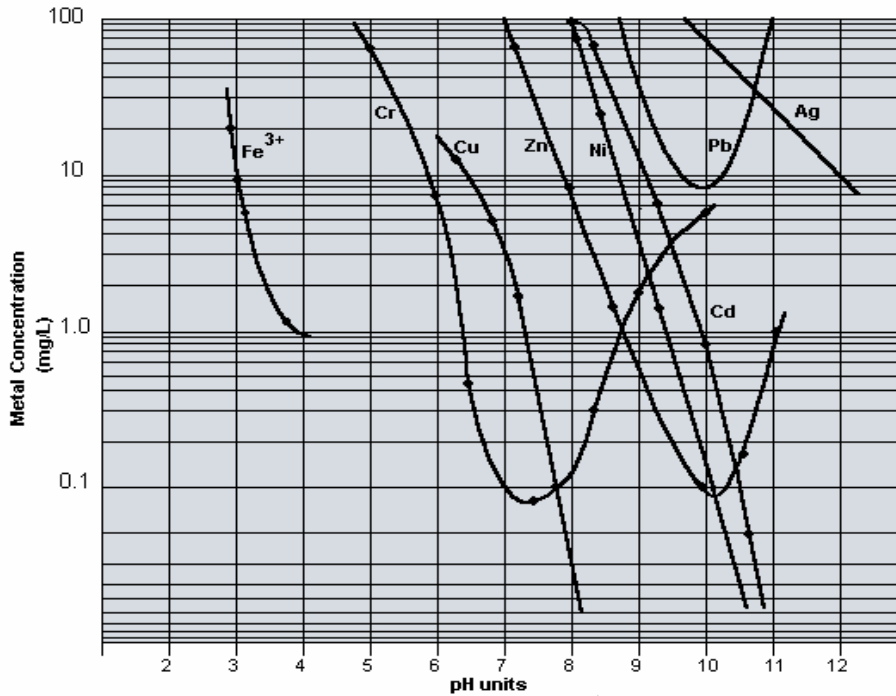


Fig. 2.4 Metal hydroxide solubility curves

A typical layout for a continuous treatment system is shown in Fig. 2.5. Allowance is made for a portion of the sludge to be recycled to provide a seed to aid the growth of newly formed precipitate. The two widely used chemicals used to cause precipitation are lime $\text{Ca}(\text{OH})_2$ and caustic soda (NaOH). For example copper:

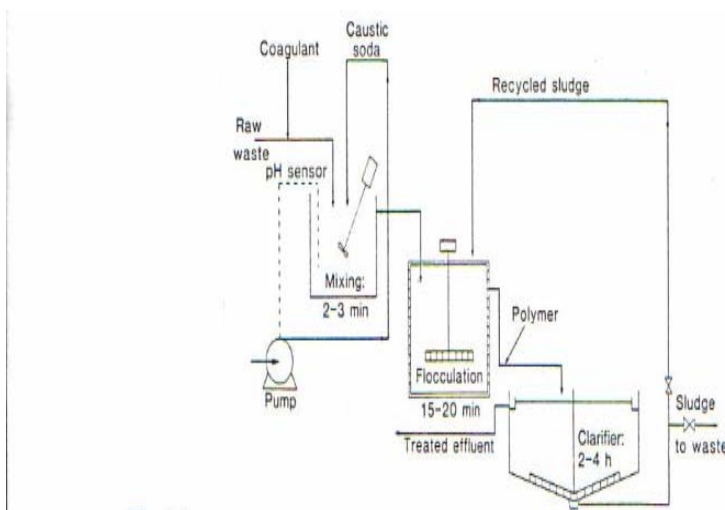
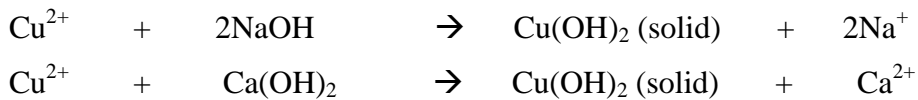


Fig. 2.5 Continuous treatment system

The disadvantages and advantages of $\text{Ca}(\text{OH})_2$ (lime) are:

- Its relative insolubility demands that it be used as a slurry, thus equipment such as dosing pumps or pneumatic valves which do not get blocked by solid particles are required.
- The sludge volume produced is greater than when NaOH is used.
- It is cheaper than NaOH.
- It produces dense sludge that is easier to dewater.
- It is necessary for the removal of high ammonia concentrations by air stripping.

The disadvantages and advantages of NaOH (caustic soda) are:

- Higher price.
- Higher residual solubility of metal hydroxides.
- Forms a very light and gelatinous sludge that settles poorly and is difficult to dewater.
- It requires no complicated dosing system.

2.2.2 Activated Carbon Adsorption

Activated carbon will adsorb many metals that are organically complexed. Granular carbon is preferred to powdered carbon because it can be regenerated and reused. It also offers an additional filtering action thereby removing metal containing solids.

The mechanism of adsorption can be physical adsorption due to Van der Waals forces of attraction, exchange adsorption due to electrostatic forces induced by charged functional groups on the carbon surface or chemisorption in which the adsorbate reacts with the carbon surface and is chemically bound to the carbon. Activated carbon can also effect trace metal removal by chemical reduction. Carbon behaves as a reducing agent in the presence of oxidized metals such as dichromates and permanganates, forming Cr(III) and Mn(IV) which are readily insoluble at neutral pH values precipitating as $\text{Cr}(\text{OH})_3$ and MnO_2 .

2.2.3 Ion Exchange

Ion exchange involves the reversible exchange of ions between a solution and a solid phase that are in direct contact. The solid phase can be a neutral zeolite or a synthetic resin consisting of a crosslinked polymeric network with charged functional groups which attract oppositely charged ionic species and retain them by electrostatic forces. Once the ionic exchange resin becomes saturated by the replacement metal it can be regenerated by flushing with an acid or alkaline solution. The metals are thus concentrated into a small volume, yielding up to 500 times concentrated regenerant brine. In some case valuable metals can be recovered from the brine by electrolysis.

Ion exchange has been used as a polishing process after hydroxide precipitation and coagulation treatment. Because the ion exchange effluent is of a good quality the water can be reused in the manufacturing process. A disadvantage of this process is the high initial cost of this sophisticated system, as well as operation and maintenance requirements and cost of regenerating chemicals.

2.2.4 Reverse Osmosis

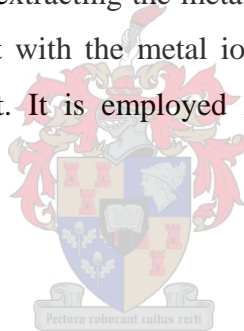
It is a treatment system utilizing semi-permeable membranes. It operates at pressures up to 40 atmospheres and produces a concentrate on one side of the membrane and a clear permeate on the other. Both the size of the ion and its charge tend to affect the portion that will pass through the membrane, thus an absolute separation usually is not achieved. Large metallic ions and those that carry a higher positive charge such as nickel, zinc, copper, arsenic and cadmium do not pass through the membrane with the same freedom as do lower, positively charged ions such as sodium and potassium.

It operates at pressures up to 40 atmospheres. A great deal of pumping energy is required to force the liquid through the membrane from the lesser to the more concentrate solution, because the pressure must overcome the osmotic pressure between the solutions thus the name reverse osmosis.

2.2.5 Other Removal Methods

Methods not widely used are:

- Ultrafiltration – a substantial pressure is required to force liquid through a membrane while relatively large sized particles are retained and concentrated in the liquid portion that does not pass through the membrane.
- Electrodialysis – separation via differing ionic size, charge and charge density of solute ions, using ion exchange membranes
- Ozone treatment – its effectiveness results from both the oxidation of organo-metallic complexes, which otherwise maintain a significant portion of the metal in solution, and the oxidation of the metal to a higher less soluble oxidation state.
- Cementation – a process in which a dissolved metal is in contact with a more active metal, such as iron or zinc, and becomes cemented to it.
- Solvent Extraction – involves extracting the metal by contacting the solution with an organic reagent that will react with the metal ion and result in its conversion to a dissolved form in the solvent. It is employed mainly for selective recovery e.g. platinum group metals (PGM).



Chapter 3 – Instrumentation

3.1 Theory of Inductive Coupled Plasma (ICP)

An ICP includes the following components: a sample introduction system, ICP torch, high frequency generator, transfer optics and spectrometer and computer interface.

3.1.1 Sample Introduction Process

The function of the sample introduction system is to deliver uniform sample amounts to the plasma for excitation of atomic/ionic emission. The sample introduction system combines a sample together with a carrier gas and transports it to the plasma's central channel. The process of delivering a liquid sample into the plasma involves the breaking up of a stream of liquid with a carrier gas. The liquid droplets and carrier gas combine to produce an aerosol. A device known as a nebulizer carries out this process. Tubing fitted on a peristaltic pump controls the flow of the liquid sample into a nebulizer. The speed of the pump and the physical size of the tubing regulates the amount of sample that enters the nebulizer. The nebulizer forms an aerosol by pneumatic or ultrasonic means. There are two basic types of pneumatic nebulizers, V-groove and Concentric glass.

The aerosol must be injected into the plasma at a uniform rate without causing plasma destabilization. In addition to this the aerosol that is injected into the plasma must also contain a sufficient number of small droplets that are reproducible and representative of the sample. A spraychamber is used to remove the larger droplets from the aerosol while providing a uniform flow of aerosol to the torch. The aerosol is sprayed directly into a spray chamber that removes the larger droplets from the aerosol. The spraychamber allows the aerosol to travel to the transfer tube and torch through an indirect route. While passing through the chamber the larger droplets fall out of the aerosol and are removed through a drain, tubing and peristaltic pump to waste.

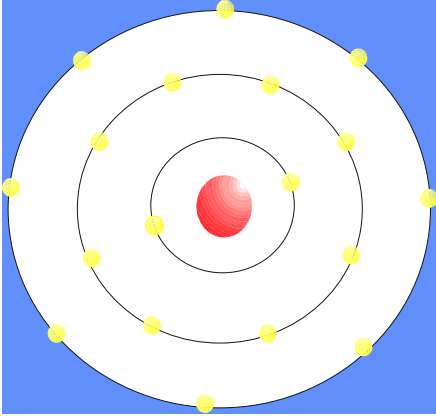
3.1.2 Torch

The torch confine ionized argon gas in the RF field of the induction coil and introduces the fine sample aerosol from the spraychamber to the plasma preheating zone. A standard torch assembly consists of three concentric tubes. The outer wall forms the channel that carries the plasma gas flow. The plasma flow keeps the plasma from overheating the torch. The intermediate tube separates the auxiliary flow from the plasma. The auxiliary gas flow provides a positive pressure at the base of the plasma that lifts the plasma and keeps it from interacting with the top of the auxiliary and injector tubes. The injector tube is the inner most tube and carries the sample aerosol to the plasma. The flow of the sample aerosol is determined by the carrier gas flow rate. The design of the torch produces low pressure at the center of the plasma. By design the sample is fed through this low pressure region. As the sample passes through the plasma it rapidly changes state. The plasma as an excitation source offers two physical means for emission, atomization and ionization.



3.1.3 Excitation

The sample to be analyzed must first be heated to a very high temperature. This is done by introducing a sample into an excitation source. Atoms become excited by absorbing energy, usually by collision with other atoms (that is by heat). The absorbed energy causes an electron in the outer shell to move to a higher energy orbit. Such excited atoms are unstable, and the electron quickly returns to a less energetic orbit. The energy difference between the two orbits is ejected from the atom in the form of light. The light is of a wavelength that is characteristic of the atom and therefore the element. A spectrometer that is set to a wavelength of interest will then measure the intensity of the light emitted at that wavelength. The intensity of the light is proportional to the number of atoms in the excitation source of the element of interest.



3.1 Diagram of a typical orbital

A gas is an electrical insulator. A plasma conducts electricity. Only a small fraction of the atoms in a gas need to be ionized to form a plasma. Argon gas in the ICP plasma normally has less than 1% ions. An inductively coupled plasma is achieved by the ionization of argon gas in a radio frequency magnetic field.

Ionization in a plasma is triggered when argon is passed through a rapidly changing magnetic field and is then seeded with electrons from a spark discharge. The electrons from the spark discharge accelerate through the gas and the changing magnetic field. The accelerated electrons collide with argon atoms and knock electrons from them. The electron collisions with the argon atoms cause the release of more electrons from other argon atoms, resulting in argon ions. These collisions are sustained by the influence of the magnetic field. Through the influence of the magnetic field the argon atoms and ions continue to collide forming more ions. The formation of ions allow a plasma state to form and become self sustained.

When ions re-combine with free electrons, the approaching electron loses energy by emitting light over a wide range of wavelengths. The emission over the wide range of wavelengths is known as a continuum. The plasma generates a baseline of continuum emission that comes mainly from the re-combination of ion pairs. Once the free electron is trapped by the ion it is constrained to exist in specific orbits. Upon recombination of an electron with a singly-charged ion the atom no longer carries a charge and is no longer an ion. Ions also emit light through ionic emission. An ion will absorb energy, usually by

collision with other ions and atoms. The absorbed energy causes an electron of the ion to move to a higher energy orbit. The electron in the ion quickly returns to a lower orbit level. The energy difference between the two orbits is ejected from the ion in the form of light. The light is of a wavelength that is characteristic of the ion and therefore the element.

As the atomic structure of an ion of a certain element is physically different from the atomic structure of an atom of the same element, an ion of a certain element will emit light at different wavelengths than an atom of the same element. The background emission of the plasma consists of the continuum emission of ion recombination, the ionic emission from the argon ions and atomic emission of the excited argon atoms.

Atomization is the physical process where gaseous molecules are broken down into simple elements. Molecules are atomized by heat. Argon ions and electrons, under the influence of the magnetic field flow in the horizontal plane of the RF coil. The ions and electrons collide with the neutral argon atoms. The collisions with the neutral argon atoms result in the generation of temperatures of up to $10,000^{\circ}\text{K}$. In theory, the point of the greatest activity between ions, electrons and neutral atoms will be the point of the highest temperature. Particles in the form of an aerosol are carried through the central channel for excitation to atomic and ionic states.

3.1.4 Optics

An ICP-AES optics system gathers the radiated emissions from the plasma. The emissions are then separated into their characteristic wavelengths. The characteristic wavelengths of interest are then analyzed. There are basically two different types of ICP-AES spectrometers on the market: sequential and simultaneous. These terms relate to the way optics separate the characteristic wavelengths for analysis.

There are two basic simultaneous configurations currently commercially available: Rowland circle and Echelle.

An Echelle simultaneous ICP-AES uses a polychromator that gathers the radiant emissions and focuses this incident light onto two stationary dispersive elements. The first dispersive element is a grating. The grating is usually ruled to disperse the incident light into a spectrum across the vertical optics plane. The second dispersive element is generally a prism. The prism is manufactured and mounted to project the vertical spectrum from the grating into a two dimensional optical matrix. The prism does this by further dispersing the vertically orientated full spectrum across the horizontal optics plane. Having been dispersed in two planes the resulting image now represents a two dimensional optical matrix. The matrix is composed of a composite of the entire spectrum where lowest wavelength is positioned in one extreme, (i.e. lower right hand corner) and the highest wavelength is positioned in the opposite extreme, (i.e. upper left hand corner). The two dimensional spectrum is then observed by a solid-state detector.

3.2 Characteristics of Inductive Coupled Plasma

3.2.1 Spectrometer

The instrument used was a simultaneous reading Varian Vista ICP using solid-state detector technology with an axially viewed torch. It has an Echelle-based polychromator with a 400mm focal length that utilizes a single Charge Coupled Device (CCD) detector. The resolution of the system is less than 0.0072 nm at 200 nm and 0.013nm at 327.4nm. Argon was used as a purge gas. The instrument utilizes six argon emission lines to update the calibration. The instrument is able to perform determinations across the entire spectrum, both UV and visible. The instrument is able to determine all desired elements in one analytical method pass.

The instrument is able to operate with temperature changes of up to 2.5°C per hour without any degradation of performance. The instrument includes a cooled cone type interface to help eliminate the cool end of the axial plasma to help minimized self-absorption and physical interferences.

3.2.2 Detector

This solid-state detector is a charge-coupled device with over 70,000 pixels arranged in continuous angled arrays that are matched exactly to the spectral image of the echelle

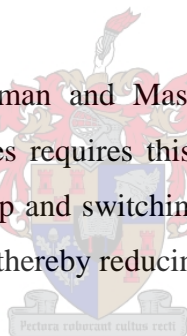
optical system. Each detector pixel has anti-blooming protection to enable the simultaneous measurement of trace level analytes in the presence of major matrix constituents. The detector is cooled by a Peltier device to a temperature of at least -35°C to minimize detector dark current thereby enhancing instrument performance and detection limits.

3.2.3 RF Generator

The RF generator is run at a frequency of 40 MHz. The generator has an optimal power output range of 700 - 1500 watts and is computer controllable in 10-watt increments. The RF generator has power transfer efficiency into the plasma of at least 75% to eliminate the need of inefficient secondary matching networks. The stability of the power output is better than 0.1%.

3.2.4 Sample Introduction System

The instrument consists of a Sturman and Masters spraychamber with a V-groove nebulizer. The nature of the samples requires this type of rugged system. The system includes a 3-channel peristaltic pump and switching valve system for improving sample introduction and washout efficiency thereby reducing sample carry-over.



3.2.5 Software

The software is able to display calibration curves and wavelength peaks for all of the elements analyzed simultaneously. The software is able to provide three different forms of background corrections. The software is able to do two forms of spectral interference corrections. Traditional Interfering Element Corrections (IEC) is available and the system is also able to calculate these values automatically. The system also has advanced, Fast Automated Curve-fitting Technique (FACT) available to help correct for severely structure backgrounds. The system is able to apply spectral interference correction in addition to background correction post sample analysis, eliminating the need to reanalyze the sample. The instrument is able to read both background and emission data simultaneously and allow for manual or automatic background correction. The software has a library of analytical wavelengths containing at least 33,000 lines whose relative

intensities are determined on the instrument optical system. Calibration equations include linear, weighted fit, non-linear, and forced through blank options. The software includes automatic optimization of key instrument parameters.

3.2.6 Performance

Table 3.1 Axial 3σ detection limits using 30 second integration

Element	LOD ($\mu\text{g/l}$)	Element	LOD ($\mu\text{g/l}$)
Al	0.1	Fe	0.1
As	1.0	K	0.3
B	0.1	Mg	0.01
Ba	0.03	Mn	0.03
Be	0.01	Na	0.15
Ca	0.01	Ni	0.3
Cd	0.05	Pb	0.8
Co	0.2	Se	2.0
Cu	0.3	V	0.2
Cr	0.15	Zn	0.2

Table 3.2 Instrument resolution

Element	Wavelength (nm)	Resolution (nm)
Cadmium	214.435	< 0.008
Chromium	267.716	< 0.010
Copper	327.396	< 0.013
Nickel	231.604	< 0.010
Lead	220.353	< 0.008
Zinc	213.856	< 0.008

The instrument has an analytical linearity in excess of 5-6 orders of magnitude with the ability to use alternate wavelengths that are measured simultaneously.

3.3 Calibration and Validation

3.3.1 Calibration

For industrial effluent a four-point calibration curve was established with concentrations of 0.5, 1.0, 2.0 and 5.0 ppm covering the optimum working range of the samples. These calibration standards were made up from a 100 ppm combined stock standard. The standards for the wastewater and sludge were 0.05, 0.10, 0.20, 0.50 and 1.0 ppm. These were made up from a 25 ppm stock standard. The original standard concentration was a 1000 ppm solution bought from Merck Chemicals. The correlation coefficient for all the standards was always greater than 0.9999. The standards and blank were run after every 15 samples. The analytical quality assurance (AQC) standard or check standard used was from the SABS and which was tested by almost 70 laboratories. The working and check standard should not differ by more than 10 %. Reagent blanks were also analysed and carried all the way through the sample preparation stages.

3.3.2 Matrix Spike Recovery

Matrix spike evaluation was carried out for both industrial effluent and wastewater to validate both methods. Three batches of 10 samples were carried out at a frequency of once a month to ascertain repeatability and reproducibility. For industrial effluent the samples were spiked with 2 ppm standard solution, analysed, averaged and the 95% confidence interval (CI) for all the analytes calculated as seen in table 3.3.

Table 3.3 % Recoveries for industrial effluent

	Batch 1	Batch 2	Batch 3
Cadmium	92.4 ± 2.1	96.4 ± 1.6	89.2 ± 2.0
Chromium	91.4 ± 5.8	94.1 ± 6.5	90.3 ± 3.6
Copper	96.0 ± 2.6	98.2 ± 2.5	96.1 ± 2.6
Nickel	86.7 ± 3.6	90.5 ± 3.1	87.8 ± 2.9
Lead	88.3 ± 5.1	93.2 ± 2.7	88.4 ± 2.9
Zinc	97.9 ± 2.4	98.0 ± 4.6	97.6 ± 4.8

Average % recovery for all three batches of industrial effluent is shown in table 3.3. The relatively high CI is due to the fact that all the samples had different matrices as they come from different industries.

Recoveries for wastewater

The wastewater samples were similarly spiked with 0.5 ppm standard, averaged and the 95% confidence interval calculated as shown in table 3.4.

Table 3.4 % Recoveries for wastewater

	Batch 1	Batch 2	Batch 3
Cadmium	82.7 ± 0.9	81.0 ± 1.1	80.7 ± 0.9
Chromium	81.8 ± 1.1	80.2 ± 0.9	75.9 ± 2.0
Copper	83.9 ± 1.4	85.5 ± 1.7	86.7 ± 0.9
Nickel	78.1 ± 0.6	76.4 ± 0.9	76.4 ± 0.6
Lead	77.5 ± 1.4	75.8 ± 1.1	77.9 ± 1.2
Zinc	89.4 ± 3.2	88.6 ± 5.5	86.7 ± 1.2

The lower % recovery is due to the complex matrix and vigorous digestion procedure.

The lower CI for wastewater is because the sample matrices were all the same.

3.4 Analytical Methods

3.4.1 Industrial Effluent Analysis

- To a 50ml sample is added 5ml of 1:2 nitric acid.
- The solution is digested and evaporated to almost dryness insuring that it does not go completely dry as some volatile metals like chromium may be lost.
- Cool and add about 20ml water and a further 2.5ml of the nitric acid and boil to dissolve the precipitate.
- Cool to room temperature and filter through a GF/A filter paper, make up to the mark in a 100ml volumetric flask and mix well.
- Dilution is thus two times and further dilutions are made if concentrations fall outside the calibration range.
- Read on ICP.

3.4.2 Wastewater Analysis

- To a 250 ml sample is added a digestion reagent composed of a 2:5:3 volume ratio mixtures of 70% perchloric acid, 65% nitric acid and deionised water respectively.
- The solution is evaporated until 10ml is left and then very slowly digested until it starts to fume.

- Cool, add water and boil for about 5 minutes.
- Cool to room temperature and filter through a GF/A filter paper.
- Make up to the mark in a 50ml volumetric flask and mix well. The sample is thus concentrated 5 times.
- Read on ICP.

3.4.3 Sludge Analysis

- Weigh about 5g sludge sample into an Erlenmeyer flask, add 10ml digestion reagent (same as in wastewater analysis) and evaporate slowly on a hot plate.
- If sample contains a lot of organic matter, place a stemless funnel on the mouth of the flask when level falls below about 50ml, to allow some refluxing to take place.
- Remove funnel when brown fumes become less.
- Boil very slowly until white dense perchloric fumes evolve when sample level is very low. Continue heating at low heat until there is about 1ml liquid left. Do not boil to dryness.
- Remove from hot plate and allow to cool.
- Add about 20ml deionised water and boil slowly for 5 minutes.
- Cool and filter into 100 ml volumetric flask and make up to mark with deionised water.
- A reagent blank is also prepared using the same procedure as above.
- Read both on ICP.

The sludge concentration is calculated according to the following formula:

$$\text{Concentration (mg/kg)} = (\text{reading } \mu\text{g/l} - \text{reagent blank}) \times 0.1 / \text{mass} \times (100 / \% \text{total solids})$$

All the above methods were developed and validated over the years in the Wastewater and Industrial Effluent laboratories of the City of Cape Town's Scientific Services.

Chapter 4 – Metal loading

4.1 Results of Industrial Effluent

Twelve industries were identified as contributors of metals into the Potsdam WWTW by the city's water pollution inspectorate. The industries were metal platers, radiator reconditioners, rust removers, paper manufacturers, metal and steel component manufacturers, and chemical and detergent manufacturers. The volume of effluent discharged by these industries was also determined. This was done by taking the total water consumption as determined by the water-meter reading and subtracting the amount of water used in product, for domestic purposes, steam generation, gardening, etc.

Samples of effluent were taken on the premises of these industries where factory effluent is discharged directly into the sewer system. Frequency of sampling was once every 6 weeks. Study was carried out over a 3 year period from July 2003 to June 2006 resulting in 24 samples being taken. The analytical results of the 24 samples for each of the industries were averaged and the average metal output per year for the period calculated, using the following calculation:

$$\text{Mass of metals (kg)} = [\text{Volume discharged (kl/year)} \times \text{Ave. metal conc. (mg/l)}] / 10^3$$

Table 4.1 Average yearly total mass loading (kg) of metals by industry

Firms	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
A	0.012	2.67	4.13	3.89	1.70	6.56
B	2.505	18.61	25.05	18.61	0.72	32.56
C	0.022	<0.01	1.84	0.22	1.25	21.99
D	<0.001	6.94	874.31	2.31	2.31	27.76
E	<0.001	0.05	0.21	<0.01	0.05	0.53
F	<0.001	6.07	1.43	0.21	1.11	0.90
G	<0.001	0.13	0.26	0.13	0.13	2.60
H	0.010	18.48	5.18	11.15	0.88	2.93
I	<0.001	19.80	14.15	29.71	1.42	28.29
J	3.587	35.87	107.61	35.87	71.74	753.25
K	0.103	0.21	14.36	0.41	10.47	49.04
L	2.164	23.81	22.12	17.07	16.35	304.21
Total Metal Content	5.9	132.6	1070.7	119.6	108.1	1230.6

4.2 Results of Influent to Potsdam WWTW

The influent to the Potsdam WWTW is a mixture of wastewater from industrial and domestic sources. The works was sampled once a month for the 3 year period. An automatic sampler was installed at a point after the 3 incoming streams, Montague Gardens, Killarney Gardens and the Caltex Refinery, pass through the screen and combine. A 200ml sample is taken every hour for 24 hours and composited. The monthly results were averaged and the total metal incoming per year calculated according to the following formula:

$$\text{Mass of metals/year} = [\text{Ave. cumulative flow (MI)} \times \text{Ave. metal conc. } (\mu\text{g/l})] / 10^3$$

Table 4.2 Average yearly mass (kg) of metals in influent at Potsdam WWTW

	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	2.5	35.6	141.1	29.3	30.7	331.0
Total Flow (MI)/year	12345					
Total Mass (kg)/year	31	440	1742	362	379	4086

4.3 Result of Influent to Wesfleur WWTW (Domestic)

The Wesfleur WWTW is the only plant in the Greater Cape Town area that has two completely separate streams for industrial and domestic wastewaters. The analysis of the domestic stream gives an indication of the concentration of metals discharged by domestic sources. Assuming domestic discharge on average is the same for all households the average metal content can be taken as a domestic source for the Potsdam WWTW.

Table 4.3 Average yearly mass (kg) of metals from domestic sources

	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	0.3	8.1	53.6	6.3	7.3	175.1
Total Flow (MI)/year	11698					
Total Mass (kg)/year	3.5	95	627	74	85	2048

4.4 Results of Final Effluents

The Potsdam WWTW has two treatment processes namely; the biofilter and the activated sludge process (ASP). These processes are dealt with fully in chapter 2. The calculation is done similarly to that of the influent.

Table 4.4 Average yearly mass (kg) of metals in final effluents - ASP

	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	0.1	2.7	4.5	13.9	1.1	30.4
Total Flow (MI)/year	2911					
Total Mass (kg)/year	0.3	8	13	41	3	89

Table 4.5 Average yearly mass (kg) of metals in final effluents - Biofilter Plant

	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	0.3	3.8	12.2	15.7	1.7	44.1
Total flow (MI)/year	3526					
Total mass (kg)/year	1.1	4	43	56	6	156

4.5 Results of Sludge

There are two sludge streams namely the primary sludge and secondary sludge as explained in chapter 2. The concentration of the metals is calculated on dry mass basis of sludge.

Table 4.6 Average yearly mass (kg) of metals in sludge

	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (mg/kg)	4	63	245	50	53	502
Mass sludge (tonnes)/year	5000					
Total mass (kg)/year	20	315	1225	250	265	2510

4.6 Mass Balance of Metals

4.6.1 Influent Balance

Mass Balance Equation:

Mass of metals (industry) + Mass of metals (domestic) = Mass of metals (influent)

Table 4.7 Average yearly mass (kg) of metals from all sources

Source	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Industry	5.9	133	1071	120	108	1231
Domestic	3.5	95	627	74	85	2048
Influent	30.9	440	1742	362	379	4086
Unaccounted	21.5	212	44	168	186	807

Table 4.8 Comparison by percentage of metals from sources

Source	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Industry	19	30	62	33	29	30
Domestic	11	22	36	20	23	50
Unaccounted	70	48	3	47	48	20

As can be seen from the data a huge percentage of metals are unaccounted for, especially for cadmium (70%) suggesting another source that could be further investigated. Chromium, nickel and lead about 50% are unaccounted for and zinc and copper unaccounted for is less than 20%.

4.6.2 Metal Balance of WWTW

Mass Balance Equation:

Mass of metals (effluent) + Mass of metals (sludge) = Mass of metals (influent)

Table 4.9 Mass (kg) of metals through works

Source	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Effluent	1.4	11	56	96	9.2	244
Sludge	20	315	1225	250	265	2510
Influent	31	440	1742	362	379	4086
Unaccounted	9.6	114	461	16	105	1332

Table 4.10 Comparison by percentage of metals in treatment works

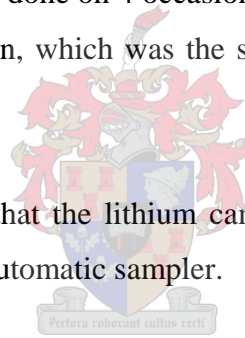
Source	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Effluent	5	3	3	27	2	6
Sludge	65	72	70	69	70	61
Unaccounted	30	25	27	4	28	33

The unaccounted for portion is similar for all the metals except nickel which also had the lowest efficiency.

4.7 Lithium Tracer Recoveries in Sewer

Lithium was used as a tracer to determine what recoveries can be achieved in a sewer system. A litre of a 250g/l solution of lithium was decanted into the sewer at the furthest factory from the Potsdam WWTW. An automatic sampler was setup at the inlet of the works. The sampler was set up to sample 200ml influent at 10 minute intervals for 2 hours giving 24 samples. This was done on 4 occasions and analysed on the ICP. Lithium was detected on only one occasion, which was the second sample i.e. at the 20 minute mark.

The only explanation for this is that the lithium came through in a batch and had not dispersed and was missed by the automatic sampler.



Chapter 5 - Efficiency of Potsdam WWTW

Until now little is known about the efficiency of the Potsdam WWTW in removal of metals. This study aims to evaluate on a six monthly cycle over 3 years what impact the increased industrial activity has had on the efficiency of the plant.

5.1 Results of Influent to Potsdam WWTW

Monthly results were averaged into six month cycles so that a more accurate assessment of the efficiency of the works could be made.

Table 5.1 – Half yearly average mass (kg) of metals in influent

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	July 2003 To Dec.2003	1.8	21.2	114.6	36.9	22.5	236.8
Total Flow (MI)		6293					
Total Mass (kg)		11	133	721	232	142	1464
Average (µg/l)	Jan.2004 To June 2004	1.3	20.2	120.9	15.8	14.7	198.0
Total Flow (MI)		6297					
Total Mass (kg)		8	13	761	100	93	1247
Average (µg/l)	July 2004 To Dec.2004	2.2	36.0	142.6	23.5	42.8	350.3
Total Flow (MI)		6679					
Total Mass (kg)		15	240	952	157	286	2340
Average (µg/l)	Jan.2005 To June 2005	2.3	35.5	153.6	31.4	30.1	318.7
Total Flow (MI)		5756					
Total Mass (kg)		13	204	884	181	173	1834
Average (µg/l)	July 2005 To Dec.2005	3.3	45.1	137.6	29.7	40.0	399.5
Total Flow (MI)		6127					
Total Mass (kg)		20	276	843	182	245	2448
Average (µg/l)	Jan.2006 To June 2006	4.0	55.7	177.5	37.5	36.1	485.9
Total Flow (MI)		5883					
Total Mass (kg)		24	341	1088	230	221	2977

5.2 Results of Final Effluent of Potsdam WWTW

Table 5.2 – Half yearly average mass (kg) of metals in final effluent– ASP

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	July 2003 To Dec.2003	0.2	2.6	8.0	17.0	1.3	26.3
Total Flow (MI)		2852					
Total Mass (kg)		0.6	7.4	23	49	3.7	75
Average (µg/l)	Jan.2004 To June 2004	0.1	1.7	4.1	13.1	0.9	28.0
Total Flow (MI)		2930					
Total Mass (kg)		0.3	5.0	12	38	2.6	82
Average (µg/l)	July 2004 To Dec.2004	0.1	1.7	1.1	11.5	0.4	12.6
Total Flow (MI)		3128					
Total Mass (kg)		0.3	5.3	3.4	36	1.3	39
Average (µg/l)	Jan.2005 To June 2005	0.1	3.5	4.8	13.8	1.4	31.4
Total Flow (MI)		2824					
Total Mass (kg)		0.3	10	14	39	4.0	89
Average (µg/l)	July 2005 To Dec.2005	0.2	4.8	5.4	15.6	1.5	37.8
Total Flow (MI)		2889					
Total Mass (kg)		0.6	14	16	45	4.3	109
Average (µg/l)	Jan.2006 To June 2006	0.1	2.7	2.6	11.8	0.8	53.5
Total Flow (MI)		2842					
Total Mass (kg)		0.3	7.7	7.4	34	2.3	152

Table 5.3 Removal Efficiency of ASP

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
% Efficiency	Jul-Dec 03	89	88	93	54	94	89
	Jan-Jun 04	92	92	97	17	94	86
	Jul-Dec 04	96	95	99	51	99	96
	Jan-Jun 05	96	90	97	56	95	90
	Jul-Dec 05	94	89	96	48	96	91
	Jan-Jun 06	98	95	99	69	98	89

Table 5.4 – Half yearly average mass (kg) of metals in final effluent– Biofilter plant

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Average (µg/l)	July 2003 To Dec.2003	0.3	2.0	9.8	16.8	1.3	26.7
Total Flow (MI)		3404					
Total Mass (kg)		1.0	6.8	33	57	4.4	91
Average (µg/l)	Jan.2004 To June 2004	0.2	2.1	10.9	10.6	1.3	33.6
Total Flow (MI)		3367					
Total Mass (kg)		0.7	7.1	37	36	4.4	113
Average (µg/l)	July 2004 To Dec.2004	0.2	3.3	14.1	13.4	1.9	39.8
Total Flow (MI)		3514					
Total Mass (kg)		0.7	12	50	47	6.7	140
Average (µg/l)	Jan.2005 To June 2005	0.2	4.0	10.9	14.5	1.7	35.2
Total Flow (MI)		3005					
Total Mass (kg)		0.6	12	33	44	5.1	106
Average (µg/l)	July 2005 To Dec.2005	0.4	6.2	16.3	14.0	2.6	51.1
Total Flow (MI)		3220					
Total Mass (kg)		1.3	20	53	45	8.4	165
Average (µg/l)	Jan.2006 To June 2006	0.4	5.0	11.1	24.7	1.6	78.3
Total Flow (MI)		3005					
Total Mass (kg)		1.2	15	33	74	4.8	235

Table 5.5 Removal Efficiency of Biofilter

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
% Efficiency	Jul-Dec 03	83	91	91	55	94	89
	Jan-Jun 04	85	90	91	33	92	83
	Jul-Dec 04	91	91	90	43	96	89
	Jan-Jun 05	91	89	93	54	94	89
	Jul-Dec 05	88	86	88	53	94	87
	Jan-Jun 06	90	91	94	34	96	84

As can be seen from the % removal efficiencies that both ASP and Biofilter Plants have a reasonably good efficiency except for nickel. The ASP has slightly better removal

efficiency than the Biofilter. The good efficiency of the plant results in that the final effluent discharged is of a good quality but the result is a higher concentration in the sludge because the metals are never destroyed but merely goes from one medium to another.

The following graphs shows the trends in concentration of metals from July 2003 - June 2006 taken as a six monthly average for influent and the two effluent treatment processes

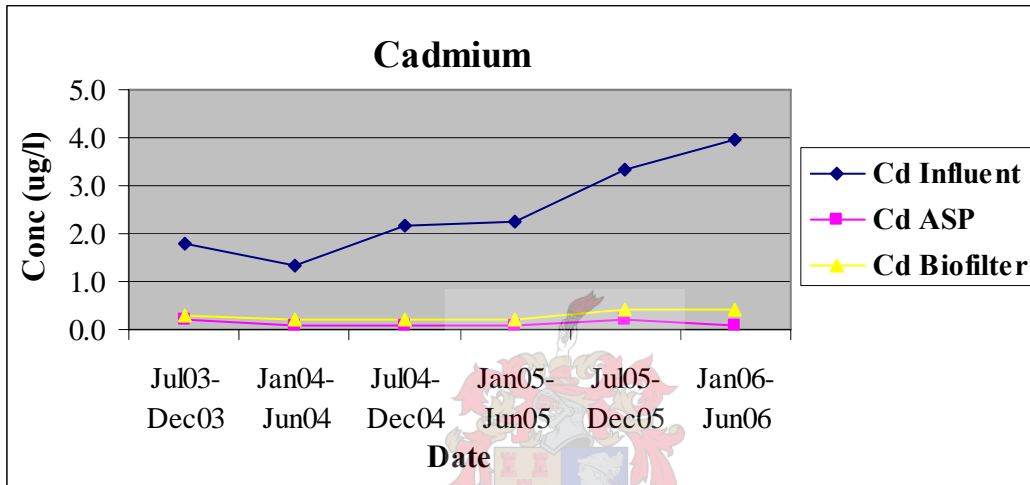


Fig. 5.1 Plot of trends in influent and final effluent (Cadmium)

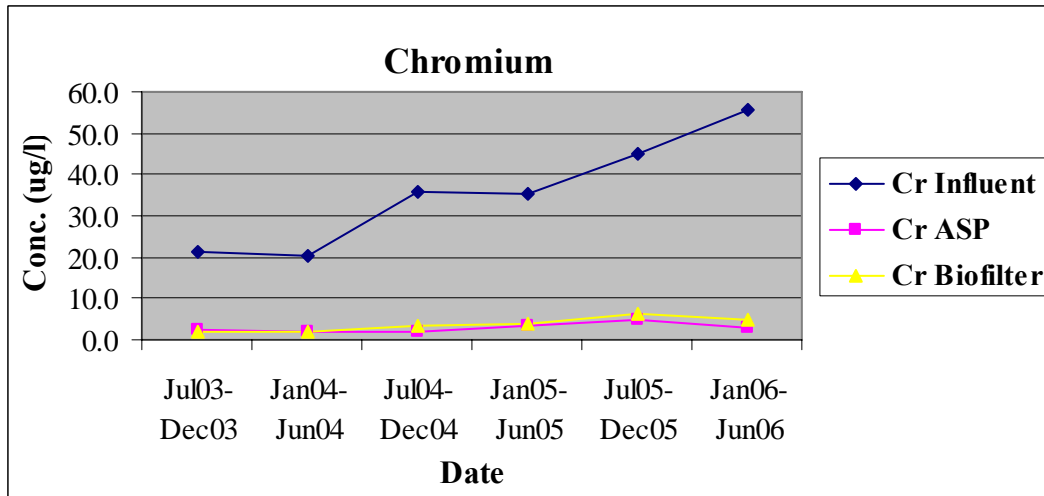


Fig. 5.2 Plot of trends in influent and final effluent (Chromium)

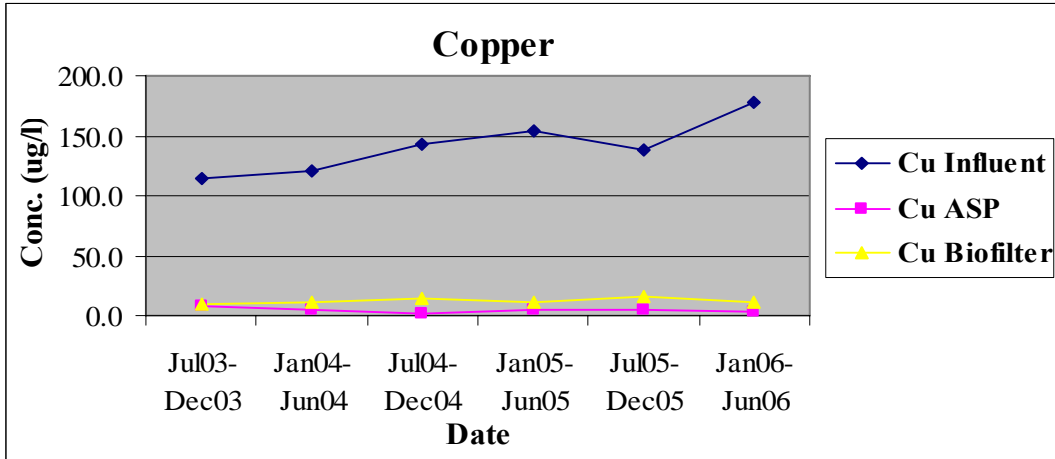


Fig. 5.3 Plot of trends in influent and final effluent (Copper)

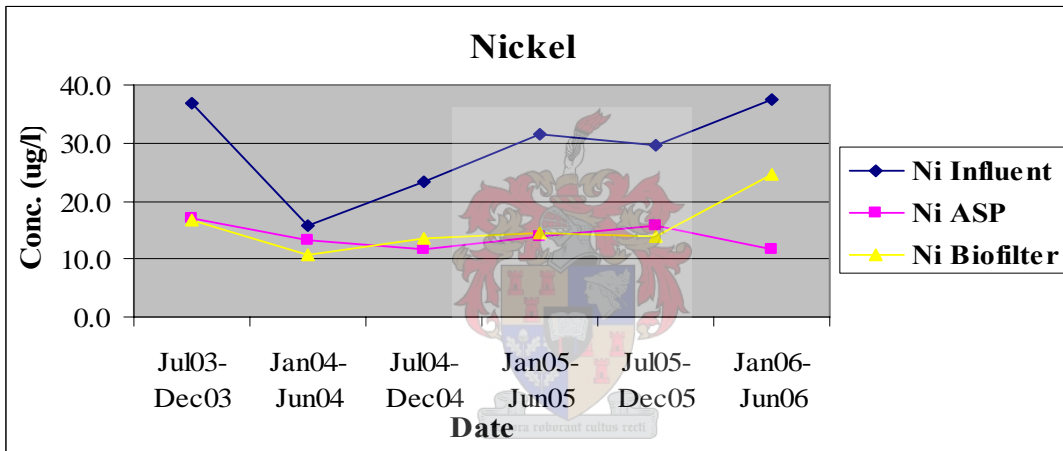


Fig. 5.4 Plot of trends in influent and final effluent (Nickel)

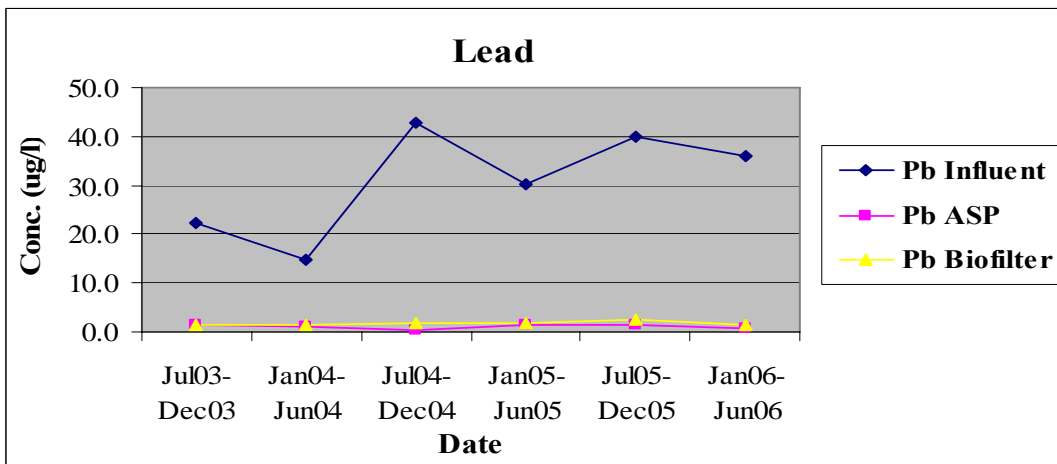


Fig. 5.5 Plot of trends in influent and final effluent (Lead)

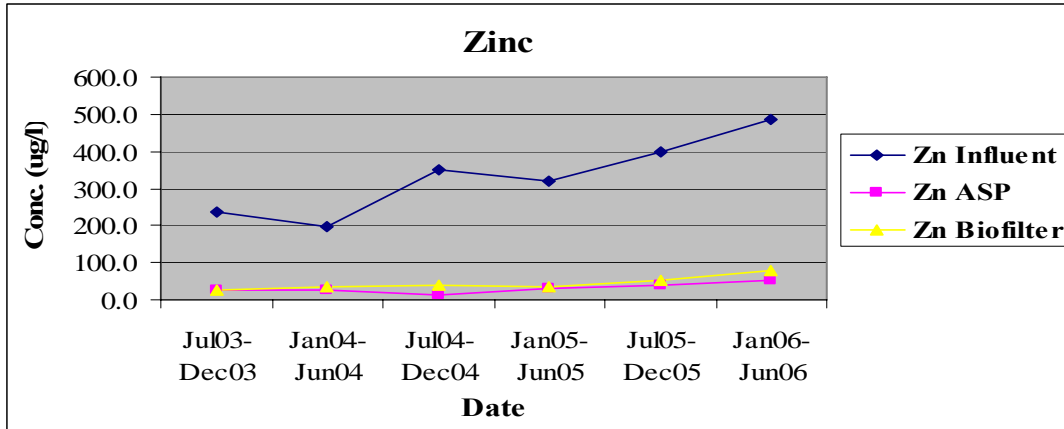


Fig. 5.6 Plot of trends in influent and final effluent (Zinc)

It can be seen from all the graphs without exception that there is an upward trend in all the metals. There is a significant increase in the concentration of the metals in the influent from July 2003 to June 2006, added with the increase in the flow causing a significant increase in the metal loading of the plant. The treated effluent however did not show a marked increase especially the activated sludge plant. The activated sludge plant is much better in removing metals than the biofilter treatment.

5.3 Results of Sludge

Table 5.6 – Half yearly average concentration (mg/kg) of metals in primary sludge

Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Jul.2003 to Dec.2003	3.5	50	222	47	56	487
Jan.2004 to Jun.2004	2.8	45	248	36	52	508
Jul.2004 to Dec.2004	3.0	45	236	36	65	500
Jan.2005 to Jun.2005	4.6	63	282	44	73	601
Jul.2005 to Dec.2005	4.6	62	266	36	67	589
Jan.2006 to Jun.2006	7.0	93	286	51	71	649

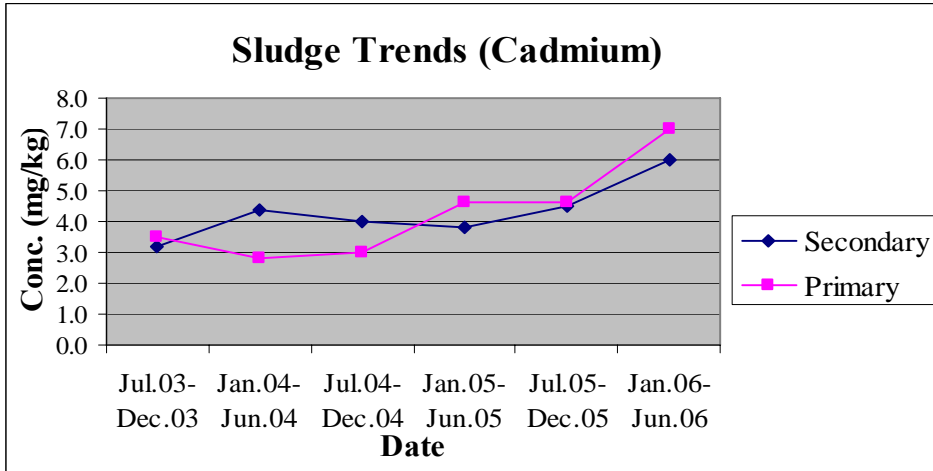


Fig. 5.7 Plot of sludge trends (Cadmium)

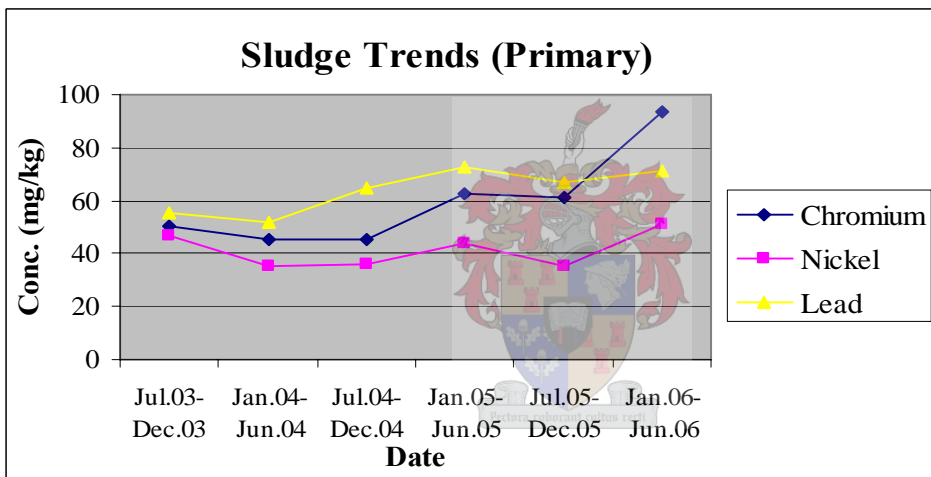


Fig. 5.8 Plot of sludge trends for primary sludge (Cr, Ni, Pb)

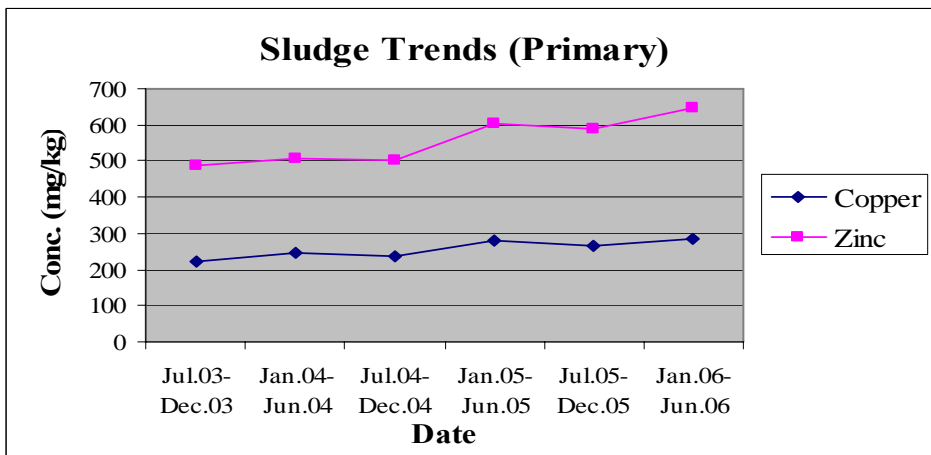


Fig. 5.9 Plot of sludge trends for primary sludge (Cu, Zn)

Table 5.7 – Half yearly average concentration (mg/kg) of metals in secondary sludge

Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Jul.2003 To Dec.2003	3.2	54	208	62	32	348
Jan.2004 To Jun.2004	4.4	52	220	55	31	392
Jul.2004 To Dec.2004	4.0	48	212	43	37	430
Jan.2005 To Jun.2005	3.8	57	235	56	38	417
Jul.2005 To Dec.2005	4.5	68	252	49	53	453
Jan.2006 To Jun.2006	6.0	94	269	57	53	616

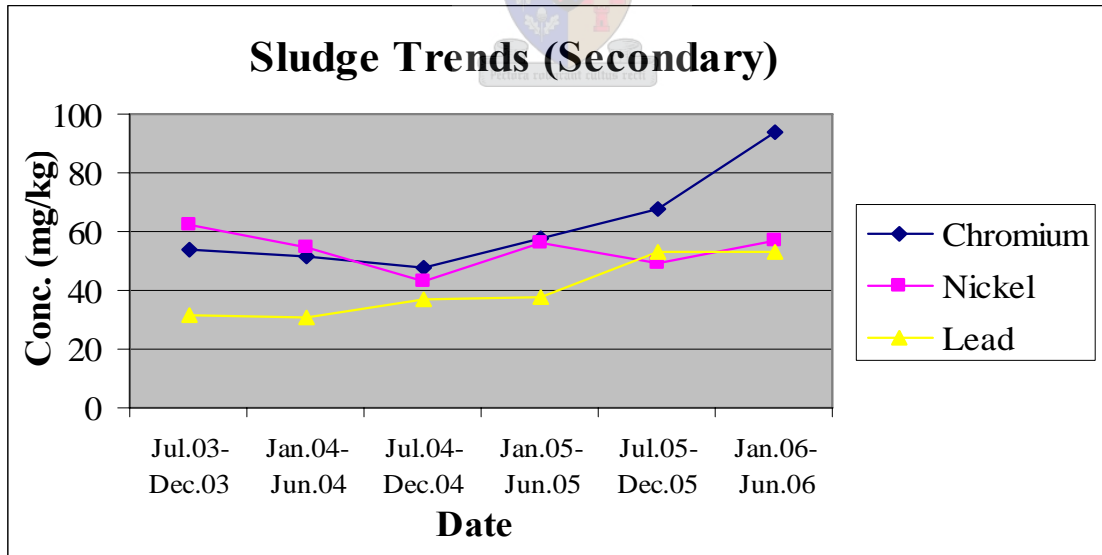


Fig. 5.10 Plot of sludge trends for secondary sludge (Cr, Ni, Pb)

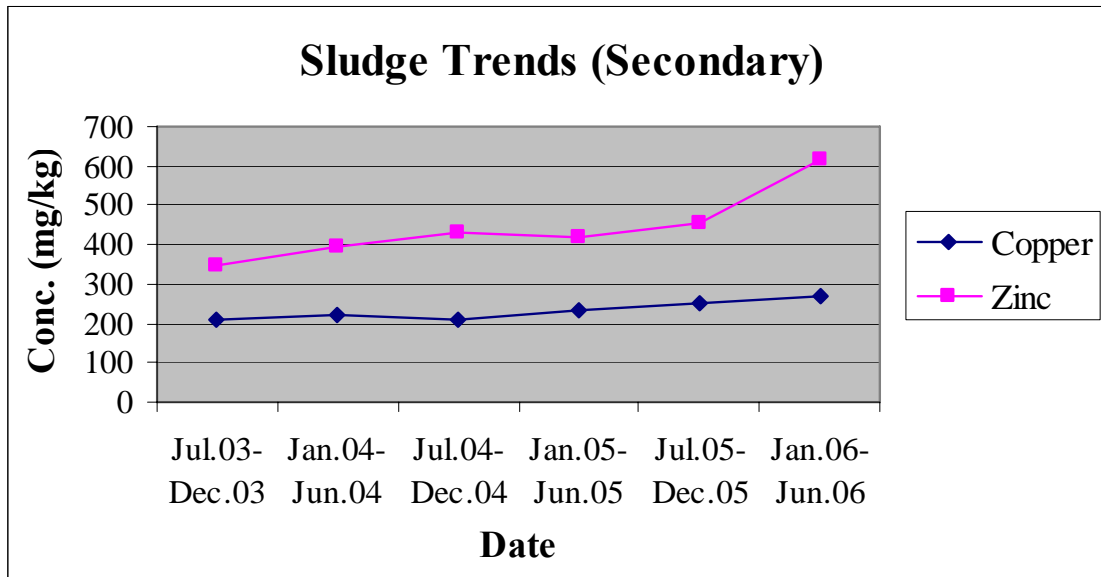
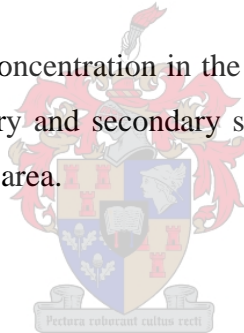


Fig. 5.11 Plot of sludge trends for secondary sludge (Cu, Zn)

The increased trend in the metal concentration in the sludge over this period can also be seen from the data on both primary and secondary sludge. This is definitely due to the increased industrial activity in this area.



Chapter 6: Conclusion

All the specific objectives of the project were achieved although mass balance into works was less successful with a large fraction being unaccounted for.

6.1 Mass Balance of Influent

A mass balance in a sewer system is extremely difficult to perform and quantify as was seen from the lithium tracer experiment. Three years of data was collated for this exercise and it can be assumed that it is good enough to make certain assumptions. The Works efficiencies can be deemed very accurate and reliable as can be seen from the standard deviations.

Table 6.1 Comparison of metals (%) contributed by the different sources

Source	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Industry	19	30	62	33	29	30
Domestic	11	22	36	20	23	50
Unaccounted	70	48	2	47	48	20

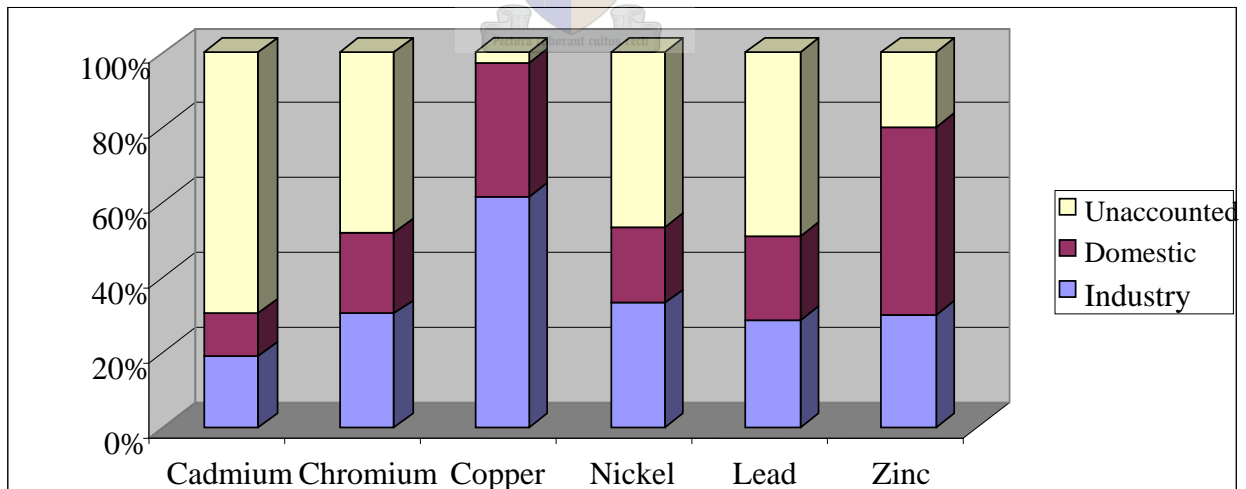


Fig. 6.1 Graphic comparison of sources of metals

The unaccounted for portion in the mass balance is quite large especially for cadmium which would suggest an unknown source that should be further investigated. Chromium,

lead and nickel has an unaccounted for portion of close to 50%. This might be due to illegal discharging by industries i.e. discharging after hours. The WWTW was sampled by means of automatic samplers that sampled for 24 hours and industrial effluent was sampled during office hours. Industries were requested to have automatic samplers installed but only two were eager to comply. Twenty-four hour sampling and hourly analysis was carried out, and nothing sinister was detected but this was only done on 3 occasions, which was too few to pick up anything sinister. More frequent 24 hour monitoring should be carried out in the future.

These results also suggest that the sampling frequency of the City is inadequate. The more frequent the sampling the more accurate the final assessment of the quality of the industries effluent quality. However staff resources are hopelessly inadequate to monitor and analyse such a large number of samples.

The fact that a large percentage of zinc was from domestic sources contributed to the less than 20 % unaccounted for figure. Because the domestic source is a relatively constant source and not haphazard as in an industrial source, this makes mass balance more accurate. The accuracy of the copper mass balance is due to the fact that a large percentage of copper from industrial sources was from only two big industries. The one has a relatively constant concentration of copper in the effluent and an automatic sampler sampled the other.

6.2 Mass Balance of Wastewater Treatment Works (WWTW)

Table 6.2 Metal balance of WWTW in percentage

Source	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Effluent	5	3	3	27	2	6
Sludge	65	72	70	69	70	61
Unaccounted	30	25	27	4	28	33

The concentrations of the metals in sludge are all similar between 60% and 70%. The unaccounted for portion is also similar (25-32%) except for nickel which is 4%. No

satisfactory explanation can be given for this result, but it also correlates with the low efficiency in removal of this metal. It could be due to the speciation of nickel in sludge, which is different from all the other metals, with a large amount in the adsorbed and exchangeable fractions.

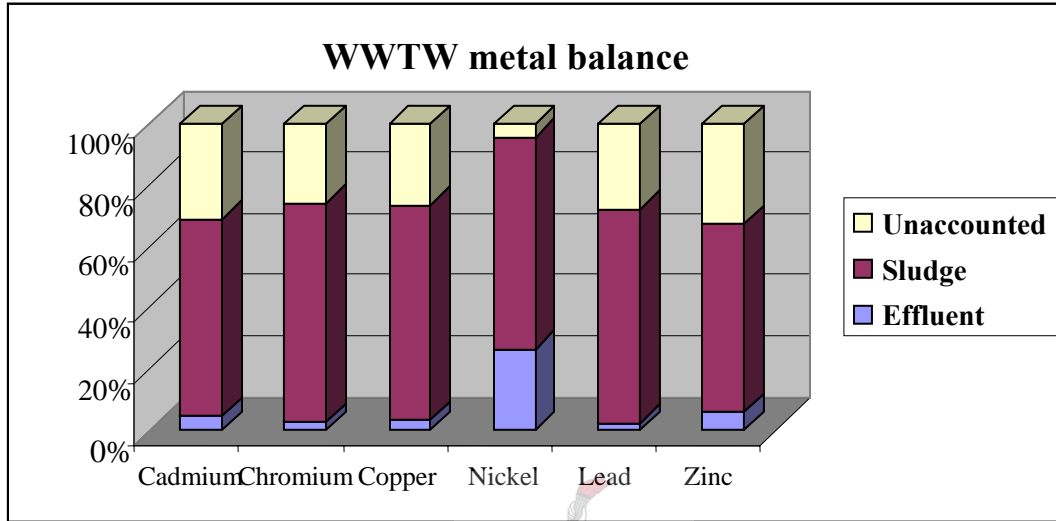


Fig. 6.2 Graphic depiction of WWTW metal balance

6.3 Wastewater Treatment Works Efficiency

Table 6.3 DWAF limits ($\mu\text{g/l}$) compared to final effluents

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
ASP	Jun03-Dec03	0.2	2.6	8.0	17	1.3	26
	Jan04-Jun04	0.1	1.7	4.1	13	0.9	28
	Jun04-Dec04	0.1	1.7	1.1	12	0.4	13
	Jan05-Jun05	0.1	3.5	4.8	14	1.4	31
	Jun05-Dec05	0.2	4.8	5.4	16	1.5	38
	Jan06-Jun06	0.1	2.7	2.6	12	0.8	54
Biofilter	Jun03-Dec03	0.3	2.0	10	17	1.3	27
	Jan04-Jun04	0.2	2.1	11	11	1.3	34
	Jun04-Dec04	0.2	3.3	14	13	1.9	40
	Jan05-Jun05	0.2	4.0	11	15	1.7	35
	Jun05-Dec05	0.4	6.2	16	14	2.6	51
	Jan06-Jun06	0.4	5.0	11	25	1.6	78
DWAF Limits	New 2005	8	20	6	-	10	50
	Old 1984	50	50	1000	-	100	5000

The data shows that the final effluents of both plants are well within the new 2005 limits set by the Department of Water Affairs and Forestry (DWAF) for cadmium, chromium and lead. Copper and zinc are within limits for the ASP and not the biofilter plant but there is an upward trend for zinc and it could well exceed the limits in future if no action is taken. Both processes of the Potsdam WWTW are extremely efficient with regard to its metal removal efficiency. The ASP is much better than the biofilter plant. Suggest either doing away with biofilter plant and upgrading ASP to accommodate the higher volume or improving it drastically.

6.4 Metals in Sludge

There are three sludge/biosolids guidelines within the state departments but the DWAF guidelines are the ones that municipalities try to adhere to.

Table 6.4 Comparison of sludge limits (mg/kg) to Potsdam WWTW

	Period	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Primary Sludge	Maximum	12	124	396	95	117	909
	Average	5	60	257	42	64	556
Secondary Sludge	Maximum	8	114	327	98	82	758
	Average	4	62	232	54	41	442
Sludge Guidelines	Old DWAF	15.7	2373	50.5	575	50.5	353.5
	New 2006	40	1200	1500	420	300	2800
	Health	20	1750	750	200	400	2750
	Agriculture	20	1200	1200	200	1200	3000

The old DWAF limits for copper and zinc were ridiculously low and it could not have been attained even if industrial limits were lowered, because the major source is from domestic (see table 6.1). The new 2006 DWAF limits are more realistic but I still think it is too high. Lead and cadmium limit could have stayed the same and would have been attained with stricter measures and better housekeeping from industries. DWAF limits for chromium and nickel can be lowered as concentrations are well within the limits. If a small treatment works with heavy industrial influent can cope with these guidelines so can all the other works.

The Potsdam WWTW is going to be upgraded to 100 MI/day from its presently capped 47MI/day. It is also envisaged that the works will supply non-potable water to the Milnerton Golf Course, the Theo Marais sportsfields, Sappi Paper, four schools in Milnerton and Table View, public open spaces and the Table View beachfront dunes. Potential new users include the oil refinery, Kynoch and local farmers. Future extensions to other industrial users and residential developments in the area are also envisaged. A new development on the farm De Grendel will also utilise the treated effluent and install a dual water reticulation network for domestic irrigation. If the present effluent metal concentrations can be attained in the future it will definitely be feasible to use the effluent as a non-potable water supply.



References

1. Guideline Series on the Permissible Utilisation and Disposal of Wastewater Sludge
“Requirements for the agricultural use of wastewater sludge” Vol.2, Water Research Commission, 2002
2. Herselman J. E., Steyn C.E. and Snyman H.G., “Background to proposed metal limits for the new SA sludge guidelines on agricultural use of biosolids” Jan. 2005
3. Crites R.W., “Land use of wastewater and sludge” Environmental Science and Technology, Vol.5, No5, p140-145, 1984
4. Roberts P., Hegi H.R., Weber A. and Krahenbuhl, “Metals in municipal wastewater and their elimination in sewage treatment” Progress Water Technology, Vol. 8, no.6 p301-306, Pergamon Press 1977
5. “Potable (Drinking) Water and Wastewater Industrial Effluent By-Law” Approved 31 May 2006
6. Hulskotte J.H.J. and van Gijlswijk R.N., “Metal Balance of Sewer Systems”, Netherlands Organisation for Applied Scientific Research, March 2003
7. Karvelas M., Katsoyiannis A. and Samara C, “Occurrence and fate of heavy metals in the wastewater treatment process”, Science Direct, Vol.53, Issue10, P1202-1210, Dec. 2003.
8. “Mass Balance Technique” Environmental Decision Making, Science and Technology Carnegie Mellon University, 2003
9. “Hydroxide Precipitation” Hoffland Environmental Inc. Wastewater Treatment Systems
10. Mack C., Burgess JE, Duncan JR, “Membrane Bioreactors for metal recovery from wastewaters”, Water SA, Vol.30, No. 4, P521-532, Oct. 2004
11. McSweeney Larry, “Varian Vista Service Course Introduction”
12. Varian Vista Software Manual, 1999
13. Snyman H.G., and Herselman J. E., “Guidelines for the Utilisation and Disposal of Wastewater Sludge” Vol.1, March 2006
14. Underhill L. and Bradfield D., “Introstat”, University of Cape Town, p201-224, Juta & Co., 1994
15. City of Cape Town Media Release, “Major boost for Cape Town water supply”, 2006

Appendix A

Potsdam Influent Metals (ug/l)

Date	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Jul-03	0.6	21.4	118.8	33.0	26.8	249.4
Aug-03	3.4	17.6	136.0	38.4	24.8	262.8
Sep-03	0.8	11.6	93.6	24.4	15.6	155.8
Oct-03	2.8	39.4	129.6	50.6	29.2	307.2
Nov-03	1.2	18.6	76.0	21.8	15.0	180.8
Dec-03	2.0	18.4	133.8	53.0	23.4	264.6
Jan-04	1.2	20.2	108.2	9.0	19.4	205.0
Feb-04	0.8	35.2	239.4	22.6	13.4	195.8
Mar-04	1.0	15.4	103.4	11.4	15.8	249.2
Apr-04	3.0	26.8	129.6	27.0	16.2	216.0
May-04	1.0	10.8	62.6	12.6	10.0	148.8
Jun-04	1.0	12.8	82.4	12.0	13.4	173.2
Jul-04	N/S	44.2	229.2	28.4	44.8	471.0
Aug-04	1.8	41.4	126.6	18.8	54.6	275.8
Sep-04	2.0	25.4	110.6	19.8	36.2	311.2
Oct-04	2.8	43.4	136.0	30.5	42.3	382.5
Nov-04	2.0	25.4	110.6	19.8	36.2	311.2
Dec-04	N/S	N/S	N/S	N/S	N/S	N/S
Jan-05	1.0	24.8	144.6	14.2	20.0	273.2
Feb-05	1.6	32.2	118.2	21.8	26.2	321.6
Mar-05	2.8	32.8	133.4	27.0	32.0	268.8
Apr-05	5.4	65.2	266.8	70.8	50.6	529.6
May-05	1.4	33.0	137.2	21.6	28.2	315.2
Jun-05	1.4	24.8	121.4	32.8	23.8	203.6
Jul-05	3.0	39.4	141.2	52.8	36.2	399.0
Aug-05	4.4	30.2	149.8	19.4	46.0	511.4
Sep-05	1.4	37.0	115.8	22.2	17.2	236.0
Oct-05	2.4	89.6	176.6	38.2	40.0	450.0
Nov-05	2.0	40.6	115.0	20.6	30.0	261.2
Dec-05	6.8	33.6	127.4	25.2	70.8	539.6
Jan-06	1.0	18.8	117.2	11.4	23.8	243.4
Feb-06	2.4	41.0	192.8	29.8	36.2	526.0
Mar-06	6.0	84.0	277.2	39.6	61.4	641.2
Apr-06	4.6	80.8	223.0	80.8	48.8	602.6
May-06	2.0	38.4	113.4	39.4	19.2	481.0
Jun-06	7.8	71.4	141.4	23.8	27.0	421.4
Ave.	2.5	35.6	141.1	29.3	30.7	331.0
Std. Dev.	1.80	20.33	50.83	16.28	14.71	135.70

Appendix B

Wesfleur Influent Metals (ug/l)

Date	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Jul-03	0.0	13.6	87.8	7.4	5.0	197.6
Aug-03	0.4	6.4	56.8	5.6	8.6	136.6
Sep-03	0.4	10.2	58.4	4.2	5.8	182.2
Oct-03	0.4	9.2	40.0	5.2	6.6	151.2
Nov-03	0.4	7.0	48.4	5.6	7.0	139.2
Dec-03	0.4	N/S	53.8	9.2	7.2	213.2
Jan-04	0.4	6.2	62.0	5.4	7.4	166.0
Feb-04	0.0	7.6	50.6	5.0	6.8	166.0
Mar-04	0.4	N/S	44.6	6.2	5.2	157.0
Apr-04	0.4	8.2	44.4	6.0	9.4	156.4
May-04	0.2	4.2	40.2	4.8	6.4	127.2
Jun-04	0.2	5.0	49.8	4.0	7.4	150.0
Jul-04	N/S	8.0	61.2	7.0	5.6	196.0
Aug-04	0.2	4.2	36.2	4.8	6.4	113.4
Sep-04	0.2	3.6	31.4	4.4	6.6	108.8
Oct-04	0.4	4.8	36.2	5.1	4.0	126.5
Nov-04	0.2	3.6	31.4	4.4	6.6	108.8
Dec-04	N/S	N/S	N/S	N/S	N/S	N/S
Jan-05	0.4	8.0	46.0	6.6	7.8	155.8
Feb-05	0.2	9.8	34.0	5.0	6.6	137.8
Mar-05	0.4	7.8	40.4	5.2	5.8	152.6
Apr-05	0.4	8.6	37.0	5.8	6.0	141.4
May-05	0.2	9.6	58.6	6.8	6.4	155.0
Jun-05	0.2	9.2	69.4	7.6	10.0	186.4
Jul-05	0.4	10.8	81.2	9.4	8.8	164.2
Aug-05	0.4	7.2	48.0	4.6	7.8	171.0
Sep-05	0.4	12.2	63.8	8.4	9.4	206.2
Oct-05	0.4	9.4	48.6	7.0	7.0	147.4
Nov-05	0.4	13.2	64.0	9.8	14.6	239.0
Dec-05	0.4	10.2	51.4	8.6	9.2	171.4
Jan-06	0.4	9.2	64.0	7.0	8.0	168.8
Feb-06	0.4	7.8	64.4	6.2	8.8	246.4
Mar-06	0.4	8.8	50.4	6.8	7.0	255.2
Apr-06	0.4	9.0	85.2	7.2	6.4	221.8
May-06	0.4	9.2	74.8	6.0	6.4	358.4
Jun-06	0.4	5.4	61.4	7.8	7.0	254.6
Ave.	0.3	8.1	53.6	6.3	7.3	175.1
Std. Dev.	0.12	2.56	14.80	1.55	1.85	50.89

Appendix C

Potsdam FE-Activated Sludge Plant Metals (ug/l)

Date	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Jul-03	0.6	7.9	29.3	24.7	3.8	56.1
Aug-03	0.1	2.1	5.4	17.8	1.2	39.3
Sep-03	0.0	1.3	1.8	13.8	0.8	16.9
Oct-03	0.1	1.7	2.2	11.5	1.0	19.5
Nov-03	0.1	1.1	1.6	20.6	0.6	15.5
Dec-03	0.1	1.3	7.7	13.4	0.2	10.2
Jan-04	0.0	1.0	7.4	9.9	0.3	10.8
Feb-04	0.0	1.5	0.4	12.0	0.0	6.9
Mar-04	0.1	1.7	1.2	8.7	1.1	16.3
Apr-04	0.1	2.5	6.6	27.9	1.6	65.2
May-04	0.1	2.6	7.4	9.0	1.6	41.6
Jun-04	N/R	0.9	1.7	10.8	0.8	27.3
Jul-04	N/S	N/S	N/S	N/S	N/S	N/S
Aug-04	0.1	0.9	1.1	6.6	0.4	15.5
Sep-04	0.1	1.0	1.0	11.4	0.4	11.1
Oct-04	N/R	2.1	0.9	14.7	0.0	5.5
Nov-04	0.1	2.0	1.3	11.5	0.6	13.8
Dec-04	0.0	2.4	1.3	13.5	0.5	17.2
Jan-05	0.1	2.2	0.7	10.2	0.4	20.6
Feb-05	0.0	2.4	0.7	8.2	0.3	18.6
Mar-05	N/R	2.5	1.4	8.5	1.1	20.5
Apr-05	0.1	3.2	1.1	26.9	1.4	35.7
May-05	0.3	5.7	16.9	13.7	2.8	42.6
Jun-05	N/R	4.8	8.1	15.0	2.6	50.3
Jul-05	0.1	5.5	10.1	13.5	2.1	50.0
Aug-05	N/S	N/S	N/S	N/S	N/S	N/S
Sep-05	N/S	N/S	N/S	N/S	N/S	N/S
Oct-05	0.6	5.8	8.9	20.0	2.1	53.1
Nov-05	0.1	4.0	1.3	15.5	1.4	20.5
Dec-05	0.1	4.0	1.4	13.5	0.5	27.4
Jan-06	0.0	3.7	2.6	10.5	0.8	50.7
Feb-06	0.1	2.4	2.1	14.9	0.8	66.4
Mar-06	0.1	2.5	2.8	10.0	1.0	75.7
Apr-06	0.1	2.2	2.9	11.7	0.5	21.3
May-06	N/S	N/S	N/S	N/S	N/S	N/S
Jun-06	N/S	N/S	N/S	N/S	N/S	N/S
Ave	0.1	2.7	4.5	13.9	1.1	30.4
Std Dev	0.15	1.70	5.95	5.30	0.88	19.64

Appendix D

Potsdam FE-Biofilter Plant Metals (ug/l)

Date	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Jul-03	0.6	2.8	12.3	22.4	1.4	35.5
Aug-03	0.2	2.5	8.2	17.2	1.4	29.1
Sep-03	0.2	1.8	9.2	12.9	1.4	24.1
Oct-03	0.2	1.9	8.1	13.1	1.4	28.1
Nov-03	0.2	1.4	7.0	20.3	1.2	23.5
Dec-03	0.1	1.4	13.9	15.1	0.8	19.7
Jan-04	0.1	1.2	12.9	10.7	0.5	23.2
Feb-04	0.0	2.1	6.3	11.4	0.0	12.5
Mar-04	0.3	1.8	6.9	8.6	1.5	20.1
Apr-04	0.3	3.2	14.0	13.1	2.2	56.8
May-04	0.3	2.6	14.0	8.7	2.0	53.3
Jun-04	N/R	1.8	11.5	10.9	1.4	35.8
Jul-04	0.0	1.5	8.6	7.6	1.3	24.1
Aug-04	0.1	1.4	6.3	7.3	0.5	23.1
Sep-04	0.6	5.4	26.5	16.1	3.7	62.4
Oct-04	N/R	3.9	17.5	18.3	1.2	48.2
Nov-04	0.2	3.1	12.1	11.7	1.7	35.0
Dec-04	0.3	4.3	13.7	19.2	2.8	46.1
Jan-05	0.1	2.5	7.6	11.0	0.9	23.2
Feb-05	0.1	3.1	6.6	10.1	1.3	30.4
Mar-05	0.1	3.2	6.5	10.3	1.2	19.8
Apr-05	0.3	4.8	11.5	28.5	1.2	27.5
May-05	0.5	6.5	21.7	12.4	3.5	61.4
Jun-05	N/R	4.1	11.3	14.6	1.9	49.1
Jul-05	0.2	4.6	15.1	12.9	1.4	48.2
Aug-05	0.3	3.1	14.1	11.1	2.5	52.3
Sep-05	0.3	5.4	17.2	10.8	2.4	53.6
Oct-05	0.7	8.9	22.5	20.3	3.7	61.5
Nov-05	0.5	8.7	26.0	13.7	4.2	57.2
Dec-05	0.1	6.2	2.9	15.2	1.3	33.9
Jan-06	0.1	3.7	3.3	10.5	0.7	18.9
Feb-06	0.5	3.6	4.8	14.6	0.7	65.9
Mar-06	0.2	3.6	10.8	11.6	1.7	80.0
Apr-06	0.4	5.0	14.0	20.5	1.5	40.4
May-06	0.4	4.8	16.4	26.7	2.2	148.6
Jun-06	0.8	9.2	17.3	64.3	2.6	116.2
Ave	0.3	3.8	12.2	15.7	1.7	44.1
Std Dev	0.20	2.12	5.87	9.73	0.96	27.61

Appendix E

Potsdam Primary Sludge Metals (mg/kg)

Date	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
9-Jul-03	4	52	220	46	52	435
6-Aug-03	3	47	199	59	43	423
3-Sep-03	3	59	210	45	58	476
8-Oct-03	3	50	203	34	58	485
5-Nov-03	5	46	215	50	56	588
3-Dec-03	3	48	286	46	66	516
7-Jan-04	2	41	266	41	55	576
4-Feb-04	2	52	181	31	43	394
10-Mar-04	4	35	293	41	58	494
11-Apr-04	N/S	N/S	N/S	N/S	N/S	N/S
5-May-04	N/S	N/S	N/S	N/S	N/S	N/S
9-Jun-04	3	53	253	29	50	566
7-Jul-04	3	46	312	24	95	537
4-Aug-04	2	39	220	21	43	445
8-Sep-04	3	49	233	41	72	507
6-Oct-04	24	46	229	67	57	541
3-Nov-04	4	45	185	26	57	471
8-Dec-04	N/S	N/S	N/S	N/S	N/S	N/S
5-Jan-05	3	40	248	30	50	561
2-Feb-05	4	57	246	28	67	641
2-Mar-05	5	79	396	36	111	703
6-Apr-05	8	92	312	95	74	663
4-May-05	N/S	N/S	N/S	N/S	N/S	N/S
8-Jun-05	3	44	207	30	63	438
6-Jul-05	2	44	198	29	52	402
3-Aug-05	4	61	266	36	65	523
2-Sep-05	4	70	280	37	79	641
5-Oct-05	6	66	312	49	53	563
6-Nov-05	5	61	219	33	61	496
5-Dec-05	7	67	321	29	93	909
5-Jan-06	3	42	247	26	50	539
4-Feb-06	12	183	333	142	92	713
6-Mar-06	1	90	252	39	61	587
4-Apr-06	9	124	391	74	117	856
3-May-06	10	111	317	71	78	757
4-Jun-06	N/R	99	176	47	29	444
Ave.	5	64	257	45	64	559
Std. Dev.	4.3	30.9	57.4	24.2	19.8	124.8

Appendix F

Potsdam Secondary Sludges Metals (mg/kg)

Date	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
9-Jul-03	6	85	310	61	31	322
6-Aug-03	2	45	115	50	27	278
3-Sep-03	2	45	183	51	36	343
8-Oct-03	2	45	194	42	30	337
5-Nov-03	4	52	219	98	33	408
3-Dec-03	3	52	229	72	34	397
7-Jan-04	3	44	226	69	35	438
4-Feb-04	2	40	120	38	21	235
10-Mar-04	N/S	N/S	N/S	N/S	N/S	N/S
7-Apr-04	5	57	228	74	33	379
5-May-04	6	68	299	42	38	480
9-Jun-04	6	49	225	52	28	428
7-Jul-04	3	53	239	31	40	421
4-Aug-04	2	48	195	24	34	388
8-Sep-04	3	48	205	46	39	433
6-Oct-04	6	42	203	54	35	425
3-Nov-04	6	49	219	58	39	475
8-Dec-04	4	48	209	46	37	437
5-Jan-05	4	53	230	58	39	527
2-Feb-05	4	51	199	41	33	390
2-Mar-05	4	63	236	39	41	407
6-Apr-05	5	66	281	95	41	430
4-May-05	3	50	234	50	36	390
8-Jun-05	3	61	228	54	38	355
6-Jul-05	3	60	250	47	39	356
3-Aug-05	4	60	237	46	41	346
2-Sep-05	4	63	259	35	78	585
5-Oct-05	4	71	250	61	49	348
6-Nov-05	5	64	241	32	67	518
5-Dec-05	7	89	272	75	46	563
6-Jan-06	4	54	223	50	35	395
4-Feb-06	5	91	240	66	31	518
6-Mar-06	6	111	327	48	82	758
4-Apr-06	7	94	286	64	54	587
3-May-06	8	101	292	68	72	702
4-Jun-06	N/R	114	245	48	44	733
Ave.	4	62	233	54	41	444
Std. Dev.	1.6	20.0	44.4	16.4	13.9	119.7

Appendix G - Industrial Effluent

Cadmium (mg/l)

Industry	7/03 02	8/20 03	10/20 03	11/20 03	2/20 04	3/20 04	4/20 04	5/20 04	7/20 04	8/20 04	10/20 04	11/20 04	2/20 05	3/20 05	4/20 05	5/20 05	7/20 05	9/20 05	10/20 05	11/20 05	2/20 06	3/20 06	4/20 06	5/20 06	Ave.	Std.Dev.
A	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.03	0.00	0.04	0.01	0.01	0.01	0.00	0.00	0.00	0.09	0.01	0.01	0.020
B	0.47	0.16	0.20	0.24	0.29	2.59	1.10	0.20	0.22	0.31	0.04	0.50	0.78	0.51	0.17	0.18	2.20	0.83	0.09	0.03	2.15	1.90	0.55	1.10	0.70	0.758
C	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.10	0.03	0.01	N/S	0.01	0.00	0.03	0.041
D	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.003
E	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N/S	0.00	0.003
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	N/S	0.00	0.005
G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.006
H	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.05	0.01	0.013
I	0.00	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.007
J	0.01	0.01	0.00	0.00	0.01	0.01	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.00	0.00	0.01	0.005
K	0.01	0.01	0.00	0.02	0.03	0.06	0.14	0.02	0.03	0.03	0.32	0.04	0.01	0.03	0.02	0.02	0.03	0.03	0.08	N/S	0.00	0.00	0.01	0.16	0.05	0.072

Chromium (mg/l)

Industry	7/20 03	8/20 03	10/20 03	11/20 03	2/20 04	3/20 04	4/20 04	5/20 04	7/20 04	8/20 04	10/20 04	11/20 04	2/20 05	3/20 05	4/20 05	5/20 05	7/20 05	9/20 05	10/20 05	11/20 05	2/20 06	3/20 06	4/20 06	5/20 06	Ave.	Std.Dev.
A	1.7	1.6	2.9	1.6	0.6	1.2	2.2	4.4	3.2	1.5	0.2	4.3	2.0	2.1	0.8	4.0	2.8	2.0	2.0	3.2	1.0	5.1	0.1	1.4	2.2	1.34
B	1.5	0.7	0.9	1.4	1.4	3.3	0.4	0.5	3.2	0.2	0.5	78.6	3.9	2.4	0.3	1.6	4.6	2.5	1.2	0.2	1.8	0.4	2.5	10.1	5.2	15.78
C	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.04
D	0.6	0.1	0.1	0.1	0.1	0.6	0.6	0.4	0.2	0.2	0.4	0.6	0.1	0.4	0.1	1.2	0.1	0.1	0.8	0.1	0.1	0.6	0.3	0.1	0.3	0.29
E	0.1	0.1	0.2	0.2	0.0	0.1	0.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	N/S	0.0	0.1	0.10
F	2.8	1.6	74.7	0.5	5.8	2.3	5.8	0.9	21.3	1.4	0.8	0.2	2.6	1.1	0.1	1.1	1.7	40.4	2.8	0.1	0.3	85.4	N/S	10.6	11.5	22.98
G	0.0	0.0	0.1	0.2	0.0	0.4	0.1	0.1	0.1	0.0	0.1	0.0	0.2	0.6	0.0	0.3	0.0	0.3	0.5	0.0	0.2	0.1	0.0	0.1	0.1	0.17
H	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	45.8	19.8	44.5	28.9	28.9	30.3	21.7	42.2	3.8	2.0	0.7	5.4	2.8	0.3	14.7	10.2	18.9	16.30
I	1.2	3.7	1.2	1.7	0.8	0.3	1.5	1.6	1.0	2.3	0.9	1.7	1.7	1.6	0.7	1.2	0.6	0.4	1.8	4.5	0.4	0.4	1.1	1.0	1.4	0.99
J	0.2	0.0	0.1	0.1	0.0	0.3	0.1	0.0	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.0	0.1	0.1	0.10
K	0.3	0.1	0.0	0.4	0.1	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	N/S	0.0	0.0	0.0	0.1	0.11

Appendix H - Industrial Effluent

Copper (mg/l)

Industry	7/20 03	8/20 03	10/20 03	11/2 003	2/20 04	3/20 04	4/200 4	5/20 04	7/20 04	8/20 04	10/20 04	11/20 04	2/20 05	3/20 05	4/20 05	5/20 05	7/20 05	9/20 05	10/20 05	11/20 05	2/20 06	3/20 06	4/20 06	5/20 06	Ave.	Std. Dev.
A	1.5	1.1	1.5	0.7	6.5	1.1	1.0	6.9	8.3	1.0	8.8	5.7	2.6	2.1	1.2	14.2	4.2	1.3	2.0	4.6	1.4	1.9	0.1	2.6	3.4	3.41
B	4.9	4.1	3.7	1.7	4.1	3.8	0.8	2.8	17.5	5.5	1.3	22.6	14.8	12.8	5.2	5.2	8.7	8.5	3.1	0.5	8.7	2.6	12.2	12.2	7.0	5.73
C	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	8.3	2.5	0.3	N/S	0.4	1.1	2.5	3.35
D	67.1	6.4	7.1	9.0	9.1	8.8	523.0	8.0	18.9	25.7	5.7	6.3	3.9	24.1	50.1	51.8	3.6	5.6	24.3	5.6	8.7	15.7	5.4	12.2	37.8	104.73
E	0.1	0.5	0.1	0.1	0.2	0.3	0.2	0.1	0.1	0.2	0.5	0.1	0.0	0.3	0.1	0.5	0.9	3.5	0.5	0.0	0.1	0.0	0.1	N/S	0.4	0.72
F	0.3	0.1	13.3	18.7	1.1	0.3	0.6	0.1	1.3	0.1	0.2	0.1	1.2	2.5	0.6	0.4	0.5	6.0	0.3	0.1	0.1	12.3	1.3	N/S	2.7	5.06
G	0.1	0.1	0.2	0.3	0.1	0.2	0.3	0.2	0.4	0.5	0.4	0.1	0.2	0.4	0.1	0.3	0.1	0.1	0.4	0.1	0.0	0.1	0.1	0.3	0.2	0.14
H	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	16.8	8.8	7.2	4.6	14.1	9.1	3.5	8.1	2.4	0.4	0.4	0.5	1.1	0.1	4.0	3.7	5.3	5.03
I	1.5	0.9	1.0	3.2	1.3	0.4	0.2	1.4	1.4	3.3	1.2	0.5	0.3	3.1	0.3	0.1	0.4	0.2	0.2	0.9	0.4	1.2	0.2	0.3	1.0	0.97
J	0.3	0.0	0.3	0.4	0.3	1.1	0.1	0.0	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.1	0.1	0.3	0.32
K	1.3	0.5	0.5	2.2	10.5	4.5	38.1	7.4	5.0	6.0	14.5	3.4	5.3	2.7	5.9	16.8	1.6	5.2	6.2	N/S	1.8	7.5	3.0	12.2	7.0	8.04

Lead (mg/l)

Industry	7/20 03	8/20 03	10/20 03	11/2 003	2/20 04	3/20 04	4/200 4	5/20 04	7/20 04	8/20 04	10/20 04	11/20 04	2/20 05	3/20 05	4/20 05	5/20 05	7/20 05	9/20 05	10/20 05	11/20 05	2/20 06	3/20 06	4/20 06	5/20 06	Ave.	Std. Dev.
A	0.7	1.0	4.3	1.0	0.6	1.0	0.8	1.6	2.2	3.2	0.6	2.0	0.8	1.7	0.6	3.3	1.2	2.0	0.5	0.8	0.2	1.5	0.2	0.7	1.4	1.04
B	0.5	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.2	0.1	0.0	0.8	0.2	0.1	0.2	0.1	0.2	0.2	0.0	0.1	0.6	0.1	0.0	0.4	0.2	0.20
C	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	7.0	0.3	0.1		0.5	0.6	1.7	2.97
D	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.2	1.4	0.2	0.2	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.28
E	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.0	0.1	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.2	0.8	0.1	0.1	0.0	0.0	0.1	N/S	0.1	0.16
F	0.4	0.1	17.7	1.6	0.4	0.2	0.7	0.1	0.3	0.0	0.1	0.0	0.4	0.6	0.2	0.2	0.3	15.1	0.4	0.0	0.0	8.4	1.0	N/S	2.1	4.84
G	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.3	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.2	0.0	0.1	0.1	0.0	0.0	0.1	0.07
H	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	2.3	0.7	1.1	1.1	2.6	1.6	0.5	0.8	0.1	0.8	0.2	0.1	0.5	0.0	1.4	0.1	0.9	0.79
I	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.2	0.4	0.1	0.1	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.1	0.1	0.10
J	0.2	0.0	0.2	0.1	0.1	1.1	0.1	0.0	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.0	0.0	0.2	0.33
K	0.6	0.5	0.3	6.6	8.0	3.9	16.7	3.0	2.7	5.0	19.7	19.2	6.9	2.5	1.5	4.4	1.4	7.0	0.4	N/S	1.7	2.5	1.2	1.4	5.1	5.81

Appendix I - Industrial Effluent

Nickel (mg/l)

Industry	7/20 03	8/20 03	10/20 03	11/20 03	2/20 04	3/20 04	4/20 04	5/20 04	7/20 04	8/20 04	10/20 04	11/20 04	2/20 05	3/20 05	4/20 05	5/20 05	7/20 05	9/20 05	10/20 05	11/20 05	2/20 06	3/20 06	4/20 06	5/20 06	Ave.	Std. dev.
A	2.1	0.7	1.1	1.0	0.6	2.8	1.3	23.2	1.8	0.5	0.5	0.7	6.6	0.8	1.6	7.1	7.0	1.5	3.6	5.8	1.3	2.1	1.0	2.7	3.2	4.8
B	4.9	4.4	4.5	2.6	5.0	2.2	4.8	6.7	3.5	12.6	3.4	8.0	7.4	4.5	5.6	6.9	10.3	8.5	3.2	3.7	3.2	4.3	1.7	3.1	5.2	2.6
C	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.7	0.4	0.1	N/S	0.1	0.1	0.3	0.3
D	0.6	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.1
E	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	N/S	0.0	0.0
F	0.0	0.0	8.4	0.3	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.2	0.0	0.0	0.2	0.3	0.1	N/S	0.4	1.7
G	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.3	0.0	0.2	0.1	0.2	0.4	0.0	0.1	0.2	0.0	0.0	0.1	0.1
H	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	33.4	13.1	3.5	15.5	16.8	22.4	15.3	26.6	4.8	1.3	0.6	4.1	1.5	1.8	9.1	11.9	11.4	9.9
I	2.7	3.5	1.3	9.5	4.7	0.5	0.1	0.6	0.5	2.0	5.7	0.2	0.2	1.5	0.5	2.5	0.4	3.9	1.6	4.3	3.2	0.1	0.9	0.5	2.1	2.3
J	0.1	0.2	0.0	0.0	0.1	0.1	0.0	0.1	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	0.0	0.0	0.1	0.1
K	0.4	0.0	0.0	0.2	0.1	1.1	0.6	0.2	0.0	0.4	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.2	N/S	0.0	0.0	0.0	0.1	0.2	0.3

Zinc (mg/l)

Industry	7/20 03	8/20 03	10/20 03	11/20 03	2/20 04	3/20 04	4/20 04	5/20 04	7/20 04	8/20 04	10/20 04	11/20 04	2/20 05	3/20 05	4/20 05	5/20 05	7/20 05	9/20 05	10/20 05	11/20 05	2/20 06	3/20 06	4/20 06	5/20 06	Ave.	Std. dev.
A	3.2	2.4	8.8	1.3	0.9	2.1	1.4	3.6	5.9	4.2	0.8	7.9	3.6	1.0	1.4	6.8	2.8	4.2	3.6	2.9	1.7	4.8	53.0	2.1	5.4	10.4
B	1.5	6.0	6.6	8.7	2.1	12.1	7.7	6.1	17.6	7.4	2.5	40.3	3.8	9.9	3.2	5.6	11.7	12.3	2.6	1.9	10.0	17.0	9.4	12.9	9.1	8.1
C	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	97.8	31.5	12.5	N/S	3.5	4.0	29.9	39.6
D	1.7	0.8	1.1	0.8	0.1	0.8	1.3	6.3	0.5	4.0	0.5	0.6	0.2	0.4	0.1	1.2	0.7	0.8	0.8	0.6	0.9	1.1	1.1	1.5	1.2	1.3
E	0.9	0.9	0.3	3.1	0.8	1.5	1.2	0.7	0.6	0.9	0.7	0.7	0.6	0.4	0.2	1.0	1.2	1.8	1.0	1.3	1.2	1.0	1.0	N/S	1.0	0.6
F	1.1	1.0	9.3	0.9	0.1	0.9	1.2	0.9	0.8	0.6	0.9	0.5	0.4	1.0	0.7	1.1	0.9	2.9	0.7	0.8	0.6	9.9	1.7	N/S	1.7	2.6
G	0.8	0.8	2.0	3.5	1.0	2.6	1.8	1.5	1.4	2.3	1.2	1.6	1.1	1.7	0.1	2.8	1.0	0.7	5.7	1.1	3.5	5.4	2.4	1.1	2.0	1.4
H	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	4.6	3.5	3.3	3.7	1.2	0.4	0.6	3.9	0.7	4.8	3.1	0.9	4.4	1.0	5.8	6.0	3.0	1.9
I	2.9	1.5	2.4	5.2	2.1	1.9	5.6	1.8	2.8	3.9	1.9	1.1	0.4	1.9	0.7	0.8	1.1	1.1	1.9	1.8	1.2	1.2	1.1	1.6	2.0	1.3
J	3.3	3.1	2.5	1.3	1.3	3.0	1.5	1.8	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	1.2	1.6	2.1	0.8
K	3.3	4.5	7.6	16.0	41.1	78.5	18.4	9.5	22.7	18.3	34.4	7.7	84.7	19.3	15.7	8.4	19.8	20.7	48.0	N/S	9.8	6.0	14.0	41.3	23.9	22.0