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Variation and fate of heavy metals in municipal wastewater treatment plants.

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Variation and Fate of Heavy Metals in Municipal Wastewater Treatment Plants

by

Richard Gustav Zytner

A thesis
presented to the University of Windsor
in partial fulfillment of the
requirements for the degree of
M.A.Sc.
in
Department of Civil Engineering

Windsor , Ontario, 1984

To my parents

ABSTRACT

The City of Windsor has many metal plating industries and Windsor municipal wastewater is expected to contain various heavy metals. Thus, both the diurnal and daily variations in Cu, Cr, Cd, Ni, Zn and Pb concentrations were studied. The analyses were performed using a direct current plasma emission spectrometer and these values were compared with results obtained from an Atomic Absorption unit at regular intervals. Both results were found to be within reasonable agreement.

Presently, the City of Windsor treats the wastewater at two treatment plants. One has a conventional activated sludge system and the other has a modified primary system. Both plants add waste chemicals to remove phosphorous. Grab and composite samples were collected over a four month period at various points of the treatment system to provide both total and phase metal concentrations. These data were then used to calculate the removal efficiencies and apply mass balance for all metals in both the treatment plants.

Both treatment facilities showed significant diurnal variations. As the dry weather flow increased, so did the heavy metal concentrations. However, after extended periods of rainfall, the metals in the wastewater were diluted.

Mass balance calculations indicated that a significant amount of metals were being added through the waste chemicals used for phosphorous removal. This contribution was especially significant at the activated sludge plant where the primary effluent metal concentrations were often higher than the raw wastewater levels. On occassions, the effluent metal concentrations at both plants exceeded the influent levels. It was also observed that during dewatering, the mass ratio of metals in centrate to influent was greater than one percent.

Both plants showed significant removal of suspended metals with the efficiency approaching 75%. However, the removal of dissolved metals was relatively low. Even with comparatively low overall removal efficiencies, the effluent concentrations at both plants were well within the ranges reported in the literature. With respect to the sludge cake, the cadmium and zinc concentrations exceeded the Ontario Ministry of Agriculture guidelines for land application. Cadmium exceeded the limits five to seven times.

ACKNOWLEDGEMENTS

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Chapter I

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

Over the past decades, civilized mankind has been exposed more and more to heavy metals that are present in the environment [Schroeder and Darrow, 1973]. The earth is quickly becoming a planet, where rarely a man can find a place containing just the background metal levels. The heavy metal additions are a direct result of human activities which are located mainly in urban areas. Many of these activities, whether they be industrial or residential, produce wastewaters that are discharged into the municipal sewerage system for treatment. Once in the sewerage system, it becomes necessary to reduce metal concentrations to levels which will be acceptable for discharge to the environment. These metals appear both in the final wastewater effluent and the sludge which accumulates various heavy metals during treatment.

The difficulty in treating wastewater, for reduction in heavy metals, stems directly from the fact that in the field, fluctuations in nature and concentration occur for each metal species [Sommers et al., 1976 and Beckett, 1980]. These fluctuations are further complicated by the dilution that occurs in the sewer system due to infiltration, stormwater when sewers are combined, and the phase fractions at which the metal exist. The effects of these variables on the heavy metal concentration also change from one municipality to the other [Sommers, 1977].

With these types of problems, it becomes important to analyze and understand how the various treatment operations are functioning. For if the treatment operations are not performing satisfactorily, with respect to heavy metal removal, changes can be made to the treatment process, to reduce the environmental impact. Schroeder and Darrow [1973] feel that water is already one of the most toxic substances around and any further metal additions would only make the situation worse.

1.2 OBJECTIVE AND SCOPE

With more studies being done on pilot plants than actual treatment plants [Kalinske, 1981], it becomes necessary to evaluate the performance of existing plants, since often, some of the treatment steps perform differently in practise than predicted by theory. Keeping this in mind, both wastewater treatment plants in the City of Windsor were studied, from October 1983 to January 1984. One of these treatment plants is a modified primary treatment plant, and the other is an activated sludge treatment plant. The primary objectives of this study were:

1. to analyze and evaluate the variations in diurnal and daily samples, for both total and phase fraction metal concentrations at both treatment plants;
2. to calculate the metal removal efficiencies in the treatment plants, both overall and for specific unit operations; and
3. to carry out a mass balance for all the metals to determine if all the metals could be accounted for.

The resulting data were then compared to similar plants reported in the literature, to determine the effectiveness of the treatment plants in the City of Windsor.

In performing the metal analysis, a relatively new type of analytical machine was used in this study [Zander, 1983]. This machine, a Plasma Emission Spectrometer,[1] was developed in 1978 to determine heavy metal concentrations. The results obtained by this machine were compared to the standard Atomic Absorption technique, to determine if Plasma Spectrometer was reliable in analyzing wastewater for heavy metals.

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[1] Spectraspan V, Beckman Industries, Andover, Mass.

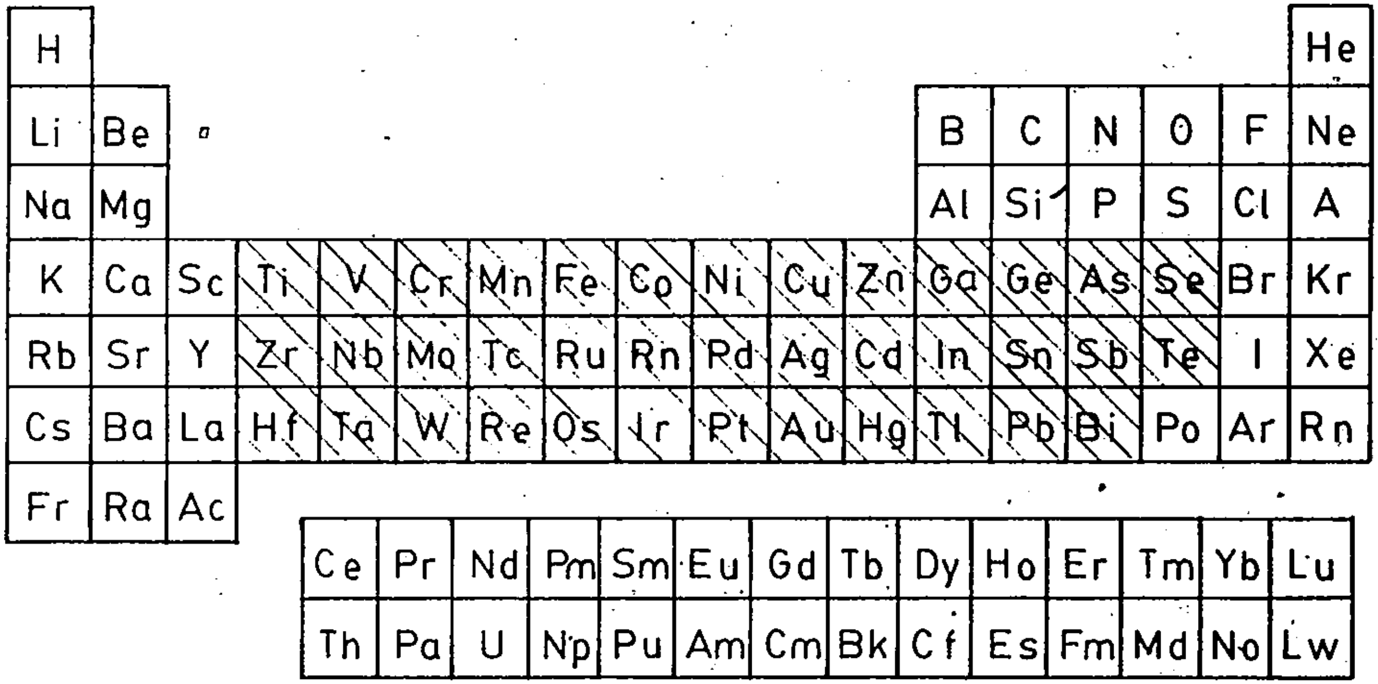
Chapter II

HISTORICAL REVIEW

2.1 DEFINITION OF HEAVY METALS

Heavy metals have become a huge concern in today's society due to their potential to contaminate the environment [Lester et al., 1979]. However, before the reasons of concern can be described, 'heavy metals' should be defined. According to Stokes and Davey [1981], heavy metals are those with a specific gravity greater than 4 or 5. Another view is that of Burrell, who feels that heavy metals are those elements which are bounded by titanium, hafnium, selenium and bismuth, as shown in the periodic table [Figure 2.1]. In spite of these differing views on the definition, an important fact which should be realized, is that heavy metals are present in the environment. They are in general toxic and must be considered when discussing environmental pollution.

With heavy metals being present in small amounts around the world, they are frequently referred to as trace elements. The concentration of these trace elements is usually less than 10^{-6} M. Metals like copper, Cu, cadmium, Cd, nickel, Ni, zinc, Zn, chromium, Cr, and lead, Pb, are of greatest concern because of their sensitive aquatic form and



H																	He
Li	Be											B	C	N	0	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rn	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	Ar	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

Figure 2.1: THE PERIODIC TABLE, WITH HEAVY METALS SHADED [Burrell, 1974]

toxicity to humans and plants [Burrell, 1976]. These metals are sensitive in aquatic forms, since they are highly reactive while dissolved in water. The name commonly used for this is transition elements.

2.2 SOURCES OF HEAVY METALS

The trace metals, which eventually find their way into a municipal wastewater facility, orginate from a variety of sources. These sources include; industrial discharges, surface runoff, domestic water supplies, sanitary wastes and sewer infiltration [Yost et al., 1981]. However, it should be noted that the amount from each category varies from city to city and individual studies should be made [Davis III et al., 1975].

2.2.1 Industrial Discharge

Until studies were completed on large cites like New York, it was felt by many organizations and public officials that if electroplating industries were properly regulated, metals could be withheld from the sewer system [Klein et al., 1974]. However, the study done on New York indicated that even if all electroplating contributions were eliminated, large amounts of metals would still be present. It was estimated that without the electroplating discharges, 84% cadmium, 80% chromium, 91% copper, 38% nickel, and 94% of zinc, would remain in the wastewater [Nielsen and Hrudey, 1983]. With the metal levels being so high, Klein et al., [1974] undertook the task of determining the main contributors of these non-electroplating heavy metals in the municipal wastewater system.

In completing studies on large residential areas, they observed that domestic sewage does contribute significant heavy metals [Table 2.1]. However, these levels still did not fully explain the total metals finally treated. Further investigations by Klein et al. [1974], showed that industries other than metal plating were discharging heavy metals. Table 2.2 shows metal concentrations from various selected industries. This list is different from the typical sources like the primary metal industries, fabricated metal parts, machinery, transportation equipment and chemicals.

TABLE 2.1

Metal Concentrations in Residential Wastewater

Pumping Station	Days of Sampling	Average Metal Concentration ug/L					Flowrate MLD
		Cu	Cr	Ni	Zn	Cd	
67th Rd.	18	110	70	10	240	2	.50
Aqueduct	12	150	3	10	150	5	.96
24th Ave.	21	190	9	10	130	1	2.00
75th Ave.	8	200	35	10	130	2	13.20
Ave. M	7	230	8	15	30	1	13.51

Ref: [Klein et al., 1974].

TABLE 2.2

Metal Concentrations In Discharges From Selected Industries

Industry	Average Metal Concentration ug/L				
	Cu	Cr	Ni	Zn	Cd
Meat Processing	150	150	70	460	11
Fat Rendering	220	210	280	3890	6
Fish Processing	240	230	140	1590	14
Bakery	150	330	430	280	2
Misc. Foods	350	150	110	1110	6
Brewery	410	60	40	47	5
Soft Drinks and Flavouring Syrup	2040	180	220	2990	3
Ice Cream	2700	50	110	780	31
Textile Drying	370	82	25	50	30
Fur Dressing and Dyeing	7040	20140	740	1730	115
Misc. Chemicals	160	280	100	80	27
Laundry	1700	1220	100	1750	134
Car Wash	180	140	190	920	18

Ref: [Klein et al., 1974].

In Ontario, Oliver and Cosgrove [1974] observed a pattern similar to that of New York. However, they did notice that the metal concentrations in the Ontario municipal wastewaters were higher when compared to world values. The higher levels were attributed to the high proportion of industrial wastes added to the sewage, as the result of extending sewer services to the industrial community [Brown and Hensley, 1973].

2.2.2 Surface Runoff

The heavy metals are washed into the sewer system via the rain gutters and manhole covers where the sources include all open areas and streets. The concentrations of metals in street runoff are high as seen in Table 2.3, and can have a significant effect on the domestic sewage when the sewers are combined. It has been observed that combined sewage can have a concentration 10 to 100 times that of domestic sewage [Williams et al., 1976]. Thus a significant addition in heavy metals is made by the surface runoff to the domestic wastewater.

TABLE 2.3

Comparison of Metal Concentrations on Street Runoff and Domestic Sewage

Metal	Street Runoff kg/h	Domestic Sewage kg/h	Ratio SRO/DOM
Cr	36.0	5.5	6.6
Ni	4.5	0.02	236.0
Fe	3583.0	24.5	146.0
Cu	16.3	0.08	211.0
Zn	63.5	0.38	167.0

Ref: [Williams et al., 1976].

The metal concentrations in the surface runoff, depends on various factors [Helsel et al., 1979]. These factors include pavement type, vehicles, vegetation, anti-skid compounds like salt and land use designation. Even though the above sources seem to provide a large proportion of the metals, they account for only 30% of the metals in runoff while the remainder of the metals comes from atmospheric contributions [Barkdoll et al., 1977]. They observed that the dust accumulation on the streets is rapid during the first 2 days of no precipitation, before reaching an asymptote value. Then during a storm, the actual concentration of metals in the runoff depends on the volume of water during the rainfall. If a large storm event occurs, a large volume of water is produced giving a small concentration, compared to a small storm, which produces a larger concentration of pollutants [Table 2.4].

TABLE 2.4

Metals in Surface Runoff-Average Concentrations

Metal	Concentration (uq/L) [Klein et al., 1974]	Concentration (uq/L) [Yost et al., 1981]
Cd	25	---
Cu	460	150
Cr	160	30
Ni	150	80
Zn	1600	620
Pb	---	900

2.2.3 Domestic Water Supplies

Water that is used for domestic purposes contains certain amounts of heavy metals, whether it be from aquifers or surface sources. Aquifers usually have the higher metal concentration [Wood et al., 1975]. Whatever may be the source for water, government regulations limit the metal concentrations that are allowed in the treated water. These limits can then be taken as the maximum levels that could be added by the domestic water to the municipal wastewater. Table 2.5 shows the present permissible levels of metal in the drinking water in Canada.

TABLE 2.5

Drinking Water Objectives for Heavy Metals

Metal	Concentration in ug/L
Zn	5000
Ni	250*
Cd	5
Cu	1000
Cr	50
Pb	50

Ref: [Ministry of the Environment, 1983].
*[Environment Canada, 1979].

2.2.4 Domestic Additions to Municipal Wastewater

The metals that are added to the wastewater from domestic sources are usually smaller in amounts and different from industrial sources, but yet quite significant. The domestic sources can be categorized as low volume yet highly chemically complex effluents, as compared to specific large volume industrial discharges [Atkins and Hawley, 1978]. In their study, it was observed that the domestic effluents were more difficult to treat than the industrial discharges, due to the above chemical complexities.

Furthermore, it has been observed that every metal or chemical substance ever known to humans at one time or another, does eventually appear in the domestic effluent. This fact can be attributed to the large quantities of chemical products available to the consumer for home use. A complete list of metals contained in every day consumer products was compiled by Atkins and Hawley [1978].

A point that should be stressed is that a single individual using various consumer products does not constitute a significant source of heavy metals. However, when a city contains a large number of residents, the quantities are significantly magnified. Further complicating the problem are the flows from sources other than individual residential units or industrial complexes. These sources include apartment buildings, restaurants, hotels, institutions such as hospitals, laboratories and shopping centres. All these locations can add significant amount of heavy metals to the wastewater [Maruyama et al., 1975].

2.2.5 Sewer Infiltration

The last source of heavy metals for the sewer system is infiltration. The amount of infiltration depends mainly on the condition of the sewer system. A well constructed system has low quantities of infiltration as compared to a poorly constructed one which allows large quantities of infiltration.

The metals enter with the ground water, after being dissolved by the groundwater contained in the soil [Wood et al., 1975]. Higher the metal concentration in the soil, higher will be the dissolved metal concentrations entering the sewers during infiltration.

2.3 TOXICITY OF HEAVY METALS

With the numerous sources of heavy metals now identified, it is important to examine why these metals should be removed before the wastewater is released into the environment. Of all the metals contained in the wastewater, some are highly toxic to living organisms while the others are essential micronutrients [Argaman and Weddle 1973]. However, excess of any element can be eventually toxic. For example a person can drink three litres of potable water per day with no side effects, but when he consumes 9-10 litres his liver might fail, indicating toxicity [Schroeder and Darrow, 1973]. Even with the extensive research already completed, the complex relationship between heavy metals and the living organisms is not fully understood. What is understood though is that every person now contains metal levels in him at higher concentrations than his forebearers [Schroeder and Darrow, 1973]. For lead alone, today's reference person has a lead concentration of 121 ug, which is 100 times higher than the concentration found in a primitive man.

The heavy metals which exist in the municipal sewage system can effect: (i) the process being used at the treatment plant whether it be aerobic or anaerobic, since both respond similarily to heavy metals, (ii) the environment quality as a result of metals released in the effluent, and (iii) the environment quality due to heavy metals being leached from the sludge [Yost _et al._, 1981].

The metals enter the environment through either the effluent or sludge. For the effluent the limits on concentration are the same as for potable water after dilution, whereas no limits presently exist for sludge. The only limits currently used for sludge are land application rates to ensure that the leachate concentration is a minimum, along with minimum plant uptake. However, even though the present effluent concentrations seem low, researchers Hannah _et al._ [1977] feel that they should be lower to protect the senstive life which exists.

The problem with the metals is that they can neither be created nor destroyed, leaving them mobile and reactive. Being so mobile and reactive, they are thought of as transients in the environment [Stokes and Davey, 1981]. Furthermore, with the bio-accumulation and persitence of these metals in the environment, they remain available for oxidative and reductive enzyene reactions. When these metabolic reactions occur, metals can be taken up by organisms and concentrated [Underwood, 1979]. Then as this procedure works its way up the food chain, the heavy metals can eventually find there way into the human system. The movement of the toxic elements up the food chain is illustrated in Figure 2.2, while Table 2.6, gives the toxic effects of various metals on aquatic life and human beings.

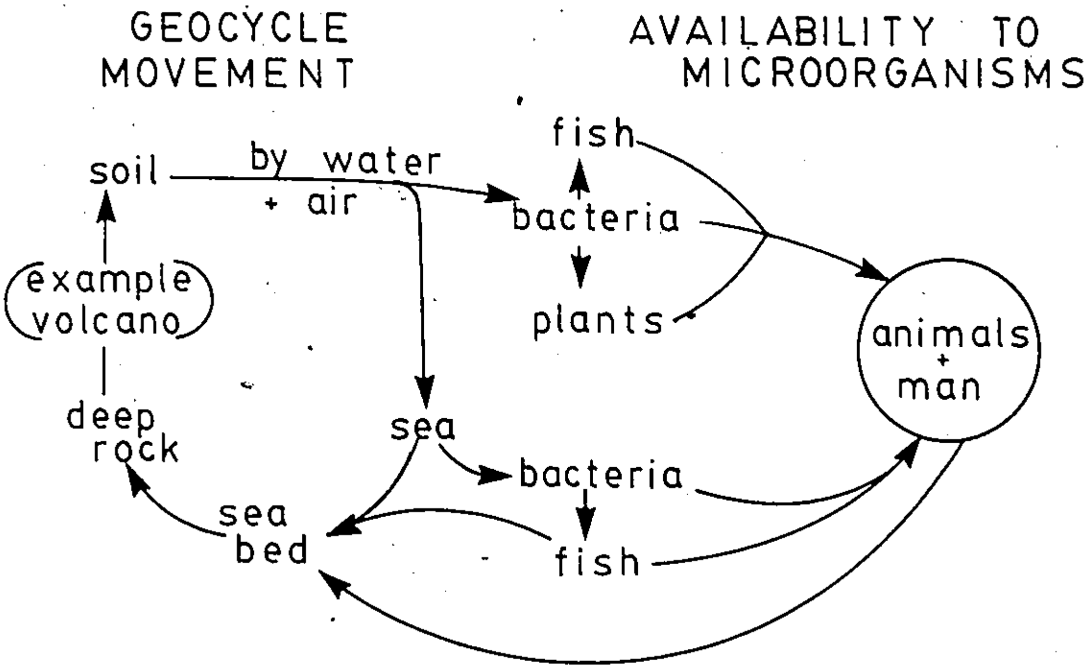


Figure 2.2 : MOVEMENT OF TOXIC ELEMENTS IN NATURE [Woods, 1974]

TABLE 2.6

Summary of Effects of Metals on Man and Aquatic Organisms

Metal	Effects on Man	Effects on Fish and Aquatic Organisms
Cd	Highly toxic, Cumulative, nonessential	Toxic
Cr	Unknown, nonessential	Toxic to lower organisms
Cu	Essential beneficial element	Highly toxic, varying with species and chemical factors
Ni	Very low toxicity	Low chronic toxicity
Pb	Cumulative poison, nonessential	Highly toxic
Zn	Essential benefical element	Toxic, varying with species and chemical factors

Ref: [Argaman and Weddle, 1973].

2.4 METHODS OF HEAVY METAL REMOVAL

2.4.1 General

Metals present in the wastewater can be divided into three phases; soluble, settleable solids, and non-settleable solids [Patterson et al., 1975]. The settleable solids can be defined as those solids which settle within the 30 minute time limit defined by the conventional Standard Methods test [APHA-AWWA-WPCF, 1980]. Soluble metals are those which pass through a 0.45 um filter. The non-settleable metals are the ones which cannot pass through the filter, but require longer than 30 minutes to settle.

The relative concentration of these three phases depends on the chemical matrix of the sewage [Lester et al., 1979]. Especially important is the presence of synthetic chelates like nitrilotriacetic acid, NTA, which can increase the solubility of metals over that of the natural effects [Chen, 1974]. The solubility phases are important in removing metals, since the type of treatment method for removing metals depends on these fractions. These phases vary at different plants, but their general pattern can be seen in Figure 2.3 It should be noted that the soluble metals are most difficult to remove, and as a result are desired to be in low concentrations.

Various treatment procedures exist for the removal of metals. However, the final treatment scheme chosen must be

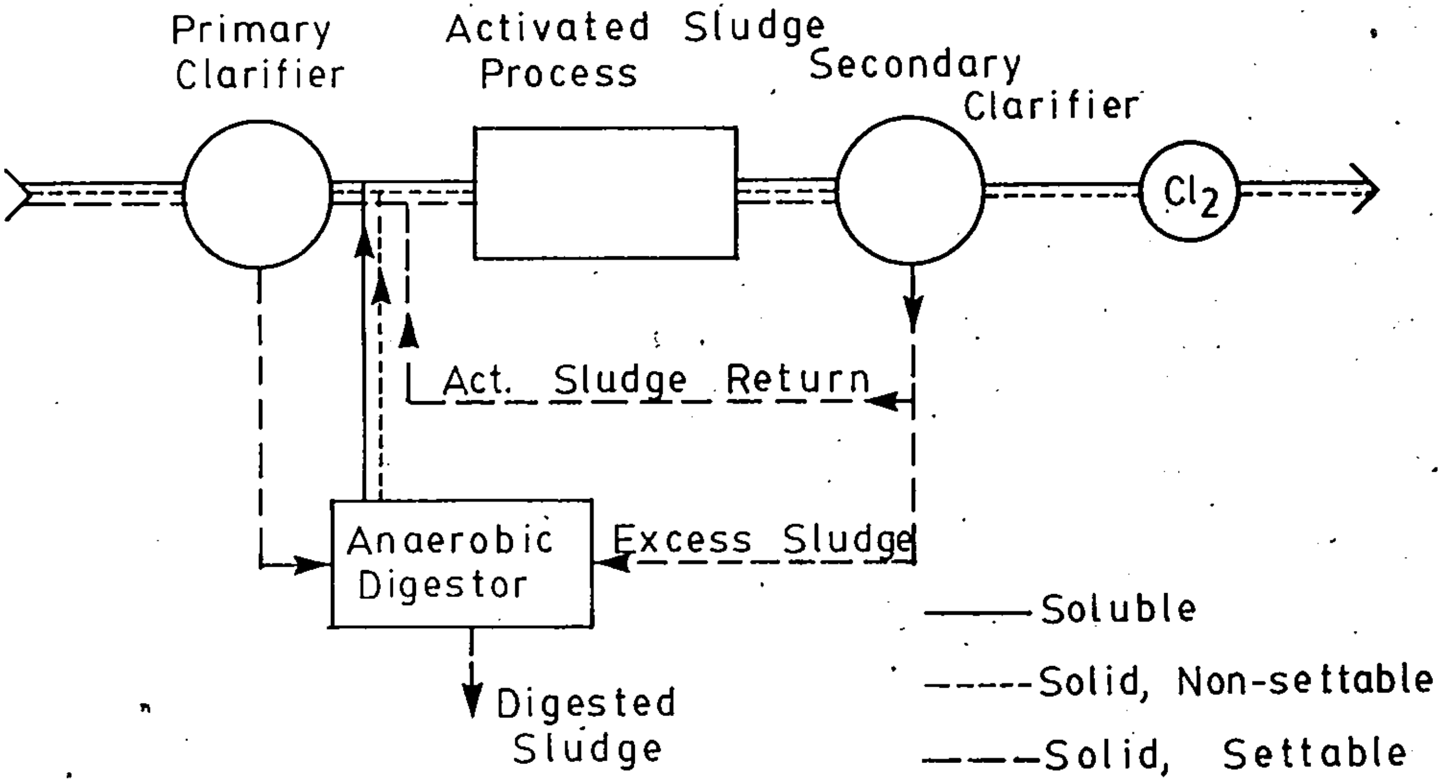


Figure 2.3: LIQUID AND SOLID PHASE PATHWAYS [Patterson et al., 1975]

such that it can handle the variability, complexity, and physiochemical properties of the metals [Sterritt and Lester, 1983]. The variability in the metals that exists is unpredictable since it arises from the varying contributions of the different sewage sources over a period of time. The time base can be diurnal, weekly, or yearly, and this results in difficulties in removing the heavy metals [Wood et al., 1975]. The conventional methods most often used for treatment include; plain sedimentation, chemical precipitation, and biological treatment [Yost et al., 1981]. Other available treatment options are: ion exchange, activated carbon, electrodialysis, reverse osmosis, sand filtration and microstraining. Generally these methods are not common, since they often are not economically feasible for municipal treatment. Keeping this in mind, the more conventional methods are described.

2.4.2 Physical and Chemical Methods

2.4.2.1 Physical Methods

In the initial stage of metal removal, whether it is a conventional activated sludge or a physical-chemical treatment plant, clarification is the first step. For removal by clarification, the important factor is the presence of insoluble metals. These suspended metals can be either naturally insoluble, or be precipitated out by chemical action. Most metals form insoluble ions very easily, with the most common form being the hydroxide [Benefield et al., 1982]. Less common forms are carbonates, sulfates, and phosphates, with pH being the most influencing factor [Stoveland et al., 1979].

The majority of soluble metals discharged into the sewer system become insoluble by the time they reach the treatment plant [Black, 1976]. This initial phase change occurs when the metals come in contact with the domestic wastewater, and precipitate out due to the presence of hydrogen sulfide [Wood et al., 1975]. The hydrogen sulfide is produced at the expense of sulfate, by the anaerobic bacteria which exist in an active slime layer on the sewer wall [Thistlethwaite, 1972]. The majority of the slime forms on the underwater surface, where the slime thickness depends on the water velocity. The actual process begins by the growth of the bacteria "Desulphvibrio desulphuricans", which reduce the organic sulfides in the waste to hydrogen sulfide. The amount of hydrogen sulfide generated is quite significant; it was observed that one mg/L of hydrogen sulfide was produced in a 3.2 km long sewer, with a diameter of 0.6 m, while running one-third full. Figure 2.4 shows how the metal solubilities are affected by increase in hydrogen sulfide concentration. Insolubility of metals increases with the increase in H_2S concentration.

The rate at which the trace elements are precipitated as insoluble metallic sulfides, occurs almost instantaneous-

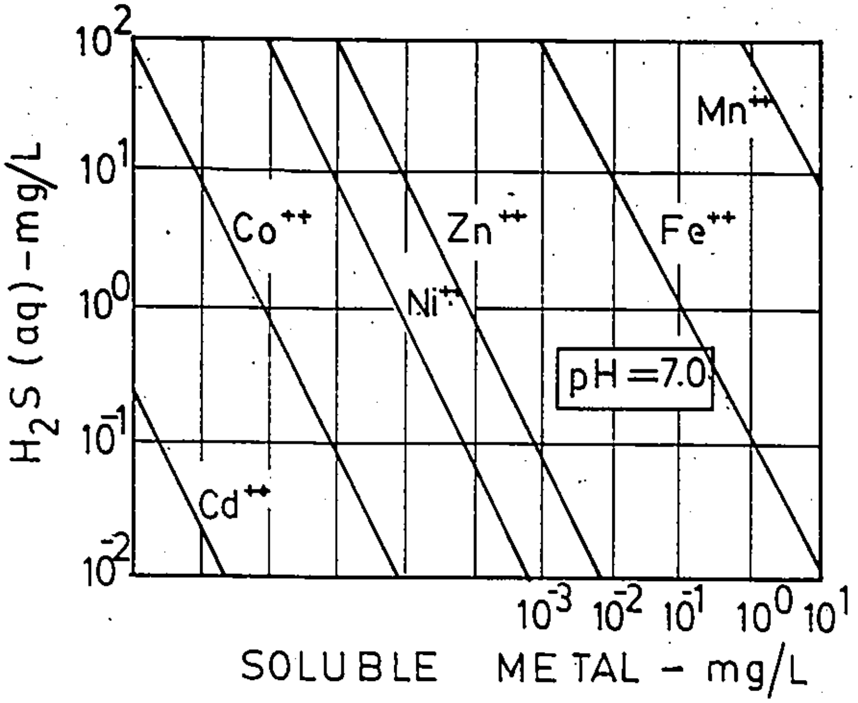


Figure 2.4: SOLUBILITIES OF METALLIC SULFIDES AT VARIOUS HYDROGEN SULFIDE CONCENTRATIONS [Wood <u>et</u> <u>al.</u>, 1975]

ly during the the first 30 sec. of contact [Jenkins <u>et</u> <u>al.</u>, 1964]. During the next 6-8 hours a slow increase in precipitation is observed. However, the actual rate depends on the amount of chelates present in the sewage as previously noted. If excessive natural chelates like fulvic or humic acids, ammonia, or synthetic chelates like NTA or EDTA are present, the natural precipitation can be reduced [Nomura and Young, 1974] because the metals are held in solution by the chelates. Figure 2.5 shows the effect of the chelate NTA on removal efficiency for various metals.

As previously stated, the natural occuring precipitation due to hydrogen sulfide is very important. This fact was confirmed by Oliver and Cosgrove, [1974] who observed that of all the dissolved metals entering the sewage treatment plant, less than 1% are removed by plain sedimentation. This low removal percentage indicates that chemical addition maybe required if a higher metal removal is needed.

2.4.2.2 Chemical Methods

The type of chemicals used to precipitate metals in a treatment facility, varies according to its availability and cost. Whenever possible, the most economical chemical is used. Some of the chemicals presently used include: lime, alum, ferric chloride and ferric sulfate. The effectiveness of each depends on the metal concentration in the wastewater. For higher the metal concentration, higher the removal efficiency. This is true for any precipitation process. In addition, chemicals like alum and lime are also used for phosphorus removal, thus serving two purposes [Aulenbach, 1983]. In a field study in Grand Rapids, Michigan, it was observed that metals also had an affinity for chemicals used

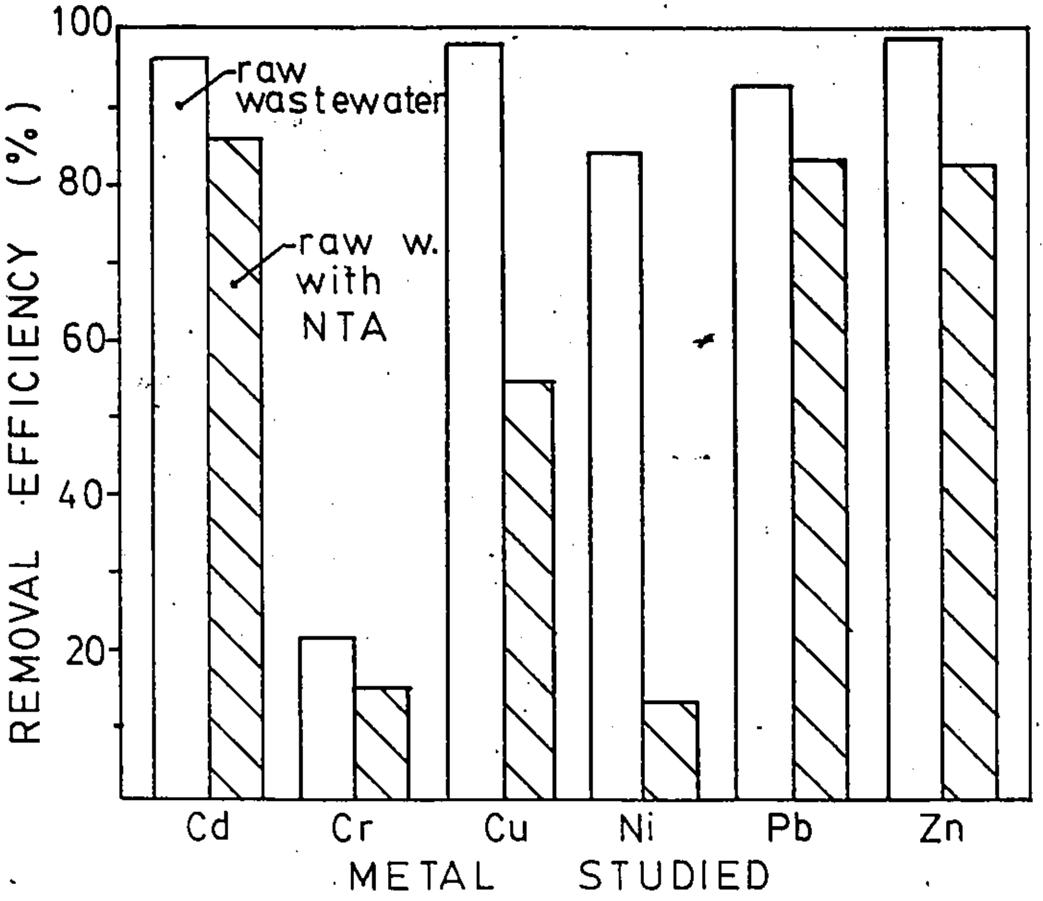


Figure 2.5: HOW HEAVY METAL REMOVAL IS AFFECTED BY NTA [Argamn and Weddle, 1973]

in phosphorous removal [Yost et al., 1981]. These chemicals include iron oxides, ferric chloride and hydroxide precipitate. However, difficulty does exist in making theoretical predictions due to the presence of substances like ligands, carbonates, sulfates, and chlorides. Whatever chemicals are added, a caution should be exercised since the chemicals themselves may be contaminated with heavy metals [Table 2.7].

The actual precipitation of metals when chemicals are added is not only pH dependent, but also depends on concentration of metal ions in solution [Olver et al., 1975 and Argro and Culp, 1972]. Solubility product approach is used to understand how the metal hydroxides are formed. The solubility product, Ksp, is defined by:

$$Ksp = [Mx^{2}][(OH^{-})^{2}]/[Mx(OH)_{2}] \qquad 2.1$$

where,

Mx = metal concentration,

OH^{-} = hydroxyl concentration and

$Mx(OH)_{2}$ = metal hydroxide concentration.

This equation indicates that when pH increases, the concentration of hydroxyl ions increases, requiring a corresponding increase in $[Mx(OH)_{2}]$ to keep the solubility product constant. Various solubility products can be seen in Table 2.8, while Figure 2.6 shows the general pattern of metal solubility as a function of pH.

TABLE 2.7

Heavy Metal Content in Commercially Available Phosphorous Removal Chemicals

Chemical and Supplier	Concentration in mg/L					
	Cd	Cr	Cu	Ni	Pb	Zn
$FeCl_3$						
A	80	80	15	40	275	400
B	20	180	160	50	2100	14500
C	1.4	661	12	42	113	260
$FeCl_2$						
A	0.1	36	5.6	7	0.1	1.7
B	1	20	9.0	19	1.5	2.3
$FeSO_4$						
A	0.1	3.3	0.5	6.5	0.1	5.6
B	0.2	51	240	29	4.6	860
Alum						
A	0	1	1.0	1.0	0.5	1
B	0.7	47	0.8	1.2	0.8	2.2
C	0.2	0.2	1.0	0.1	1	2.5
Lime						
A	0.2	0.6	3.0	3.0	1.0	25

A, B, and C were not identified

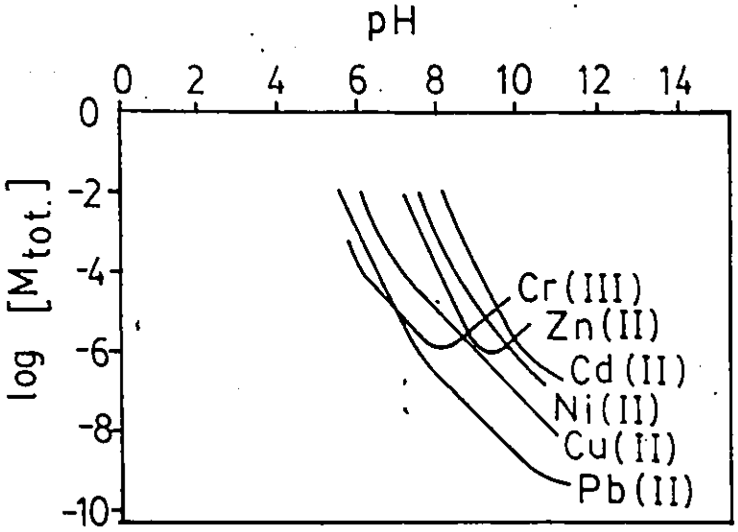
Ref: [Black, 1976].

TABLE 2.8

Solubility Products of Metal Hydroxides

Compound	Ksp * [Oliver *et al.*, 1975]
$Cr(OH)^-$	1.0×10^{-30}
$Cu(OH)^-$	3.0×10^{-19}
$Pb\,O(OH)^-$	1.6×10^{-15}
$Ni(OH)^-$	2.1×10^{-17}
$Zn(OH)^-$	1.8×10^{-14}

* Ksp = solubility product



$$[M_{tot.}] = [M] + \sum_n [M(OH)_n]$$

Figure 2.6: SOLUBILITY OF PURE METAL HYDROXIDES vs. pH [Nilsson, 1971]

The actual solubilities and-optimum pH conditions shown in Table 2.8 and Figure 2.6 do not hold true in practise. The problem with theoretical calculations is that they do not account for the complexity of the wastewater. Generally the solubilities are greater than the calculated values. This is due to numerous causes such as: incomplete reactions, poor separation of coloidal precipitates, the formation of complex metal ions (or ion speciation) and electrolite effects. Furthermore the age of the precipitated hydroxide is also a factor, because, the older the precipitate the harder it is for the ion to resolubilize [Benefield *et el.*, 1981].

Once the metals are precipitated, whether naturally or aided by chemicals, they can readily be removed by settling out of the particles. Stone [1955,1956], observed that the metal ions become enmeshed in settling flocs and are settled out. This was confirmed by the use of sterile wastewater to prove that no biological uptake occurred. Another study by Brown and Hensley [1973] shows the direct relationship between amount of metal removed and the amount of suspended solids removed. This is shown in Figure 2.7 . This plot which is logarithmic in nature, indicates that as suspended solid removal increases so does the heavy metal removal at an exponential rate, i.e. asymptotically approaches completion of heavy metal removal.

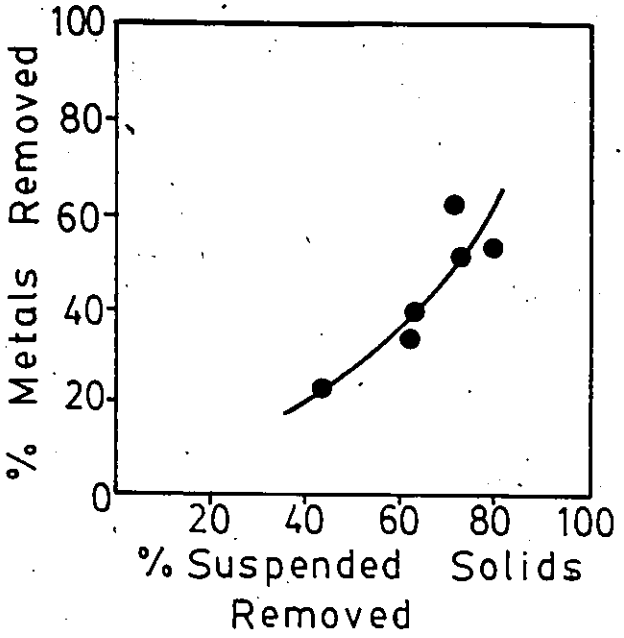


Figure 2.7: RELATIONSHIP BETWEEN METALS AND SUSPENDED ~~SOLIDS~~
[Brown and Hensley, 1973]

It has been suggested that the wastewater retention time in the clarifier be increased, to obtain the maximum removal of metals by plain sedimentation [Stoveland et al., 1979]. When chemical precipitation is used, the addition of polymers should be investigated. The polymers would introduce chemical bonding and settling would not have to rely only on physical bonding to remove suspended particles [Huck et al., 1977].

2.5 ACTIVATED SLUDGE

2.5.1 General

The activated sludge operation improves the quality of the primary effluent through biological action. This biological process can be either aerobic or anaerobic. However, studies have shown that of the two processes, aerobic is superior to anaerobic in heavy metal removal. This superiority is a direct result of the long term capability for metal removal exhibited by aerobic bacteria [Neufeld and Herman, 1975].

In an activated sludge process, the majority of metal removal occurs by three mechanisms:

1. physical trapping of precipitated metals in the sludge flow matrix,
2. binding of the soluble metal to extracellular polymers,
3. accumulation of soluble metals by the biclogical cells [Brown and Lester, 1979 and Nelson et al., 1981].

However, even though researchers have agreed that all these mechanisms occur, it is still not clear which mechanism is the dominant one, since differing views exist. Neufeld and Hermann [1975], noted that the biological uptake of the metals in the activated sludge process is insignificant, when compared to entrapment and binding. On the other hand, Jenkins et al. [1964], state that physical entrapment of suspended metals is insignificant to biological uptake. These differences in opinion are justified, since the behaviour of heavy metals in the activated sludge process depends on several changing factors [Sterritt and Lester, 1981]. These variables include both plant operation parameters and physical-chemical factors. The plant operation parameters include sludge age, suspended solids removal and dissolved oxygen concentration, while the physical-chemical factors include temperature, pH, metal ion concentration, metal solubility, metal valency and particle size.

2.5.2 Physical Entrapment of Insoluble Metals

In this process, the metal ions in suspended form are removed. These metal ions had either escaped primary treatment or were precipitated in the aeration tank due to the changing chemical environment. The environment changes through the bacteria which are thought of as "bags of enzymes", capable of performing hydrolysis and oxidation reactions [Kiang and Metry, 1982]. The other important factor is the pH.

The precipitation occurs as a result of various metal ions present which have strong tendency to interact with the cations and anions in solution. The positively charged ions may go through an anion-exchange process, while the negative ions are subjected to the cation exchange phenomenon. However, one difficulty that does exist is that theoretical predictions are hard to make due to changing environment in the aeration tank.

After the precipitation has occurred, the actual removal takes place when the suspended ions become physically entrapped or entangled in the biological floc. Then subsequent settling in the secondary clarifier removes the metals as the flocs are settled out.

2.5.3 Binding of Metal Ions to Extracellular Polymer

For the removal of metals by this mechanism, it has been shown that the floc forming bacteria produce extracellular polymers, which provide binding sites for the metal ions [Chen et al., 1974 and Sterritt and Lester, 1983]. Among all the bacteria present in the aeration tank, it has been seen that the "zoogloea ramigera" is most efficient in metal removal [Neufeld, 1976].

The polymers that are produced by the bacteria are in the form of either loose slime or capsule [Brown and Lester, 1979]. The polysacharide slime increases the viscosity of the activated sludge, while the capsule forms a transparent cover around the cell wall. Also, the slime polymer remains in solution and is released in the effluent in colloidal form, while the capsular polymer remains attached to the flocs and settles out with the sludge. This difference means that any metals adsorbed to the capsular polymer, will be removed in the secondary clarifier.

Observations have shown that, in the conventional activted sludge process, the concentration of the capsular polymers is higher than the slime polymers [Brown and Lester, 1979]. This fact is of imprtance due to the metal removing capabilities. In fact, any metal adsorbed by the slime polymer will remain in the effluent since the slime does not settle out. A few studies have been performed to determine ways of increasing the capsular polymers concentrations to improve effluent quality [Takii, 1977 and Dugan , 1975]. They have demonstrated that certain strains of bacteria, grown in the presence of excess carbohydrate substrates, increase the capsular concentrations. Furthermore, Matson and Charachlis [1976], have shown that the extracellular polymer capsule growth may be increased by increasing these ratios of carbon to nitrogen, carbon to phosphorous and carbon to sulphur in the growth medium.

As previously suggested, the polymers have a certain affinity for metals. The metals are adsorbed in the ion form since the high molecular weight extracellular capsular polymers provide many functional groupings that act as binding sites [Cheng <u>et</u> <u>al.</u>, 1975]. These high molecular weight polymers include polysacharide, proteins, RNA and DNA. Also, within the matrix exist groups of phosphoryl, carboxyl, sulphydryl and hydroxyl which act as ligands [Hunter <u>et</u> <u>al.</u>, 1983].

Many of the capsular polymers are negative in charge, giving the surfaces an overall negative charge. It has been observed that among the metals, iron has the highest affinity while nickel has the lowest affinity [Bagby and Sherrard, 1981]. The degree of affinity in decreasing order is:

$Fe>Pb>Cu>Cd>Hg>Cr>Zn>Ni.$

Chen [1974], noticed that cadmium, chromium, copper and zinc are associated primarily with activated sludge particles larger than 8 um in diameter as compared to nickel, lead and manganese which are associated with smaller particles.

The initial adsorption of the metal ions is very rapid, usually between 3 and 10 minutes due to the chemical structure of the capsular polymer [Cheng *et al.*, 1975]. It is beleived that the adsorption follows the Freudlich and Langmuir isotherms, as the initial uptake is quite fast, followed by a slow long term constant rate.

The number of binding sites can be increased by modifying the bacteria used, adjusting the pH and controlling the sludge age. Even though pH adjustment is considered one of the most important factors in increasing the number of binding sites [Nelson *et al.*, 1981], sludge age modification is used most often. Sludge age is easier to change and is preferred over pH adjustment [Neufeld and Hermann, 1975 and Brown and Lester, 1982]. As Figure 2.8 shows, an increase in sludge age, θc , considerably improves the adsorption of cadmium. It has even been proposed that a further increase in sludge age to between 9 and 15 days, would give optimum removal [Sterrit and Lester, 1981].

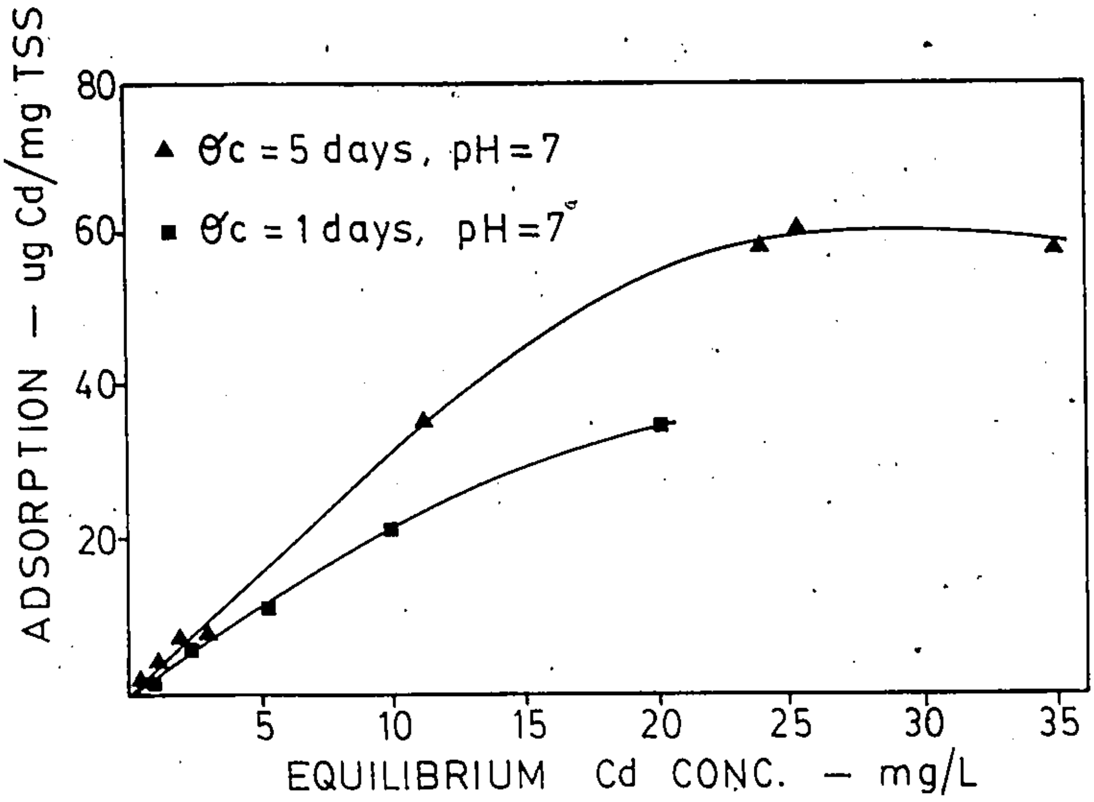


Figure 2.8: CADMIUM ADSORPTION FOR DIFFERENT SLUDGE AGES (θc) [Neufeld and Herman, 1975]

2.5.4 Bio-accumulation of Soluble Metals by Bacteria Cells

A property of all living organisims is the ability to concentrate ions within the organism [Neufeld and Herman, 1975]. In activated sludge systems, this ability to accumulate metal ions in the cells is dependent on the solubility of the metal in the aeration tank [Kodukula et al., 1983]. Studies have shown that greater the solubility, higher the degree of metal accumulation, where the ions are initially adsorbed on the floc surfaces before being taking up by the cells [Lewandowski et al., 1980].

The metal uptake due to metabolism is a slow process and depends on the viability of the activated sludge. Brown and Lester [1979], have reported four ways by which bacteria accumulate and concentrate the metal ions beyond those necessary as enzyeme cofactors. These methods include chelate formation by the binding of metals to organic ligands, shifts in metal valencies, substitution of one metal for another and biomethylation. The accumulation continues until equilibrium is reached between metals in solution and in cell. Neufeld and Hermann [1975] had determined that by the time equilbrium was reached, the metals were concentrated 10 to 20 % by weight of biological cells without any toxic effects.

2.5.5 Kinetic Model for Heavy Metal Bio-Accumulation

In studying the metal accumulation by sludge cells, Neufeld and Nowak, [1977] used the following analytical approach. In general the specific rate of accumulation on biological sludge is a function both of the physical and chemical environment for the sludge and is expressed as:

$$r=f(C,\ Q,\ pH,\ \gamma,\ T,\ .\ .\ ) \qquad 2.2$$

where:

r=overall rate of metal accumulation on biomass, mg metal/g biomass,

C=liquid phase metal concentration in intimate contact with biomass, mg/L,

Q=quantity of metal already associated with biomass, mg metal/g biomass,

pH=negative log of the hydrogen ion concentration,

γ=a measure of physical resistance to mass transfer,

T=temperature.

Equation 2.2 can be simplified by making an assumption that C and γ are the variables of concern along with Q, which is a dependent variable. Thus the new equation becomes:

$$r=f(C,\ \gamma,\ Q) \qquad 2.3$$

Since there is an upper limit to the quantity of metal that can be accumulated by the biomass, as is seen through experiments, Equation 2.3 can be written deterministically.

Therefore,

$$r = [K1C^{a} - K2(Q/(A-Q))^{b}]f(\gamma) \qquad 2.4$$

where:

K1=forward rate constant,

K2=reverse rate constant,

a,b=exponents, and

A=maximum level of a heavy metal that can be associated with the biological solids, mg metal/g biomass.

In order to determine realistic values for K1, K2, a, b, and A, Equation 2.4 must be evaluated at isotherm conditions at a constant pH, and at flow rates greater than the minimum required to negate the kinetic resistance of film diffusion. Taking the above conditions into consideration, Equation 2.4 can be simplified to:

$$r=K1C^{a} - K2[Q/(A-Q)]^{b} \qquad 2.5$$

However, when equilibrium is reached, the two rates are equal, causing r to become zero. Therefore, an equilbrium equation can be derived for the sludge metal interactions as:

$$K1Ce^{a} = K2[Qe/(A-Qe)]^{b} \qquad 2.6$$

which can be simplified to:

$$Qe = ACe^{a/b}/[(K2/K1)^{1/b} + Ce^{a/b}] \qquad 2.7$$

where Qe = level of metal associated with the floc phase when the equilbrium concentration of metals in the liquid phase is Ce.

2.5.6 Completing the Activated Sludge Treatment

After leaving the aeration tank, the wastewater must be clarified to obtain a proper effluent. By settling out the biological floc, the metals are also removed. Whatever the mechanism, it is expected that greater the settling efficiency larger will be the the removal of metals. However, studies have shown that the proportion of dissolved metal to total metal increases as the treatment process progresses. Thus, a greater efficiency in clarification does not significantly reduce the quantity of dissolved metals. Luckily, the soluble metal concentration is fairly low in the municipal wastewater [Table 2.9].

TABLE 2.9

Phase Distribution of Heavy Metals in Raw Sewage

Metal	Total Range ug/L	Average Percent Distribution Soluble	Insoluble
Cd	6-40	17	83
Cr	60-1400	7	93
Cu	60-1200	38	62
Pb	<50-1100	5	95
Ni	<30-1800	67	33
Zn	110-2400	24	76

Ref: [Black, 1976].

For the removal of the remaining dissolved metals, which are low in concentration, tertiary treatment must be used [Neufeld, 1975, Vuceta, 1979, and Maruyama et al., 1975]. The treatment methods most commonly used include ammonia stripping, recarbonation, multimedia filtration, carbon adsorption, ion exchange and reverse osmosis.

2.5.7 Effect of Heavy Metals on Activated Sludge

Many studies have been done on the effect of metals on the efficiency of activated sludge treatment. However, it is difficult to compare all the results, since some of the tests were completed on acclimated sludge, while others on non-acclimated sludge. Generally, a common belief is that acclimated sludge is less affected by metals than the non-acclimated one [Barth et al., 1964].

Acclimation can be defined as the time required for various species of bacteria in the aeration tank to become tolerant to the metals. Varma [1976] theorized that the toleration occurs as the result of some mutation of the existing species or the production of enzymes which can detoxify the metals. Another view is that the acclimation occurs when additional enzymes are produced to take the place of the damaged enzymes [Bagby and Sherrard, 1981]. If the transformation does not occur, then the metabolism rate will be affected reducing the efficiency of treatment. In some cases, the efficiency of treatment improves when new enzymes are produced. However, even when the bacteria become acclimated, upsets can occur when heavy shockloads are imposed on the aeration tank.

The eventual metal toxicity depends on a variety of factors including metal concentration, type of metal, form of metal, species of bacteria present, suspended solids concentration and sludge age. Ghosh [1972] observed that of all these parameters, the most critical is the form of the metal. The toxicity increased when the soluble ion concentration was high, since the ions were readily bio-accumulated by the bacteria.

Barth et al. [1964] carried out a number of studies to determine the toxic level for the bacteria. They observed that the metals are non-synergistic, with no effect on treatment efficiency when the total combined metal concentration does not exceed 10mg/L. Table 2.10 gives the individual thresholds of various metals.

A study by Bagby and Sherrard [1981] indicated that initially some stimulation occurs in the bacterial growth before some toxic concentration is reached and the biological metabolism is stopped. This observed stimulation by the metals can be seen in Figure 2.9 . After the optimum metal concentration is reached, the initial effect is the damaging or inactivation of some of the critical enzymes. This initial effect then causes a chain reaction by reducing the metabolism rate, followed by a reduction in new growth. If

TABLE 2.10

Threshold Concentrations for Various Metals in the Air Activated Sludge Process

Metal	Conc. in ug/L	Type of Activated Sludge
Zn	2.0	Carbonaceous
	5.0-10.0	Carbonaceous
	1.0	Nitrification
Ni	1.0-2.5	Carbonaceous
	1.0	Nitrification
	2.0	Nitrification
Cr	10.0	Carbonaceous
	1.0	Nitrification
	10.0	Nitrification
	1.0	Nitrification
Pb	10.0	Carbonaceous
Cu	1.0-10.0	Carbonaceous
	1.0	Nitrification
	2.0	Nitrification
Cd	1.0	Carbonaceous
	5.0	Nitrification
Cr	10.0	Carbonaceous

Ref: [Kiang and Metry, 1982].

the increase in metal concentration continues, the crossover concentration will be reached, at which time toxicity occurs. Once in the toxicity zone, any further increase in metal concentration will result in complete failure if enough enzymes are damaged and insufficient energy available to increase the metabolism rate.

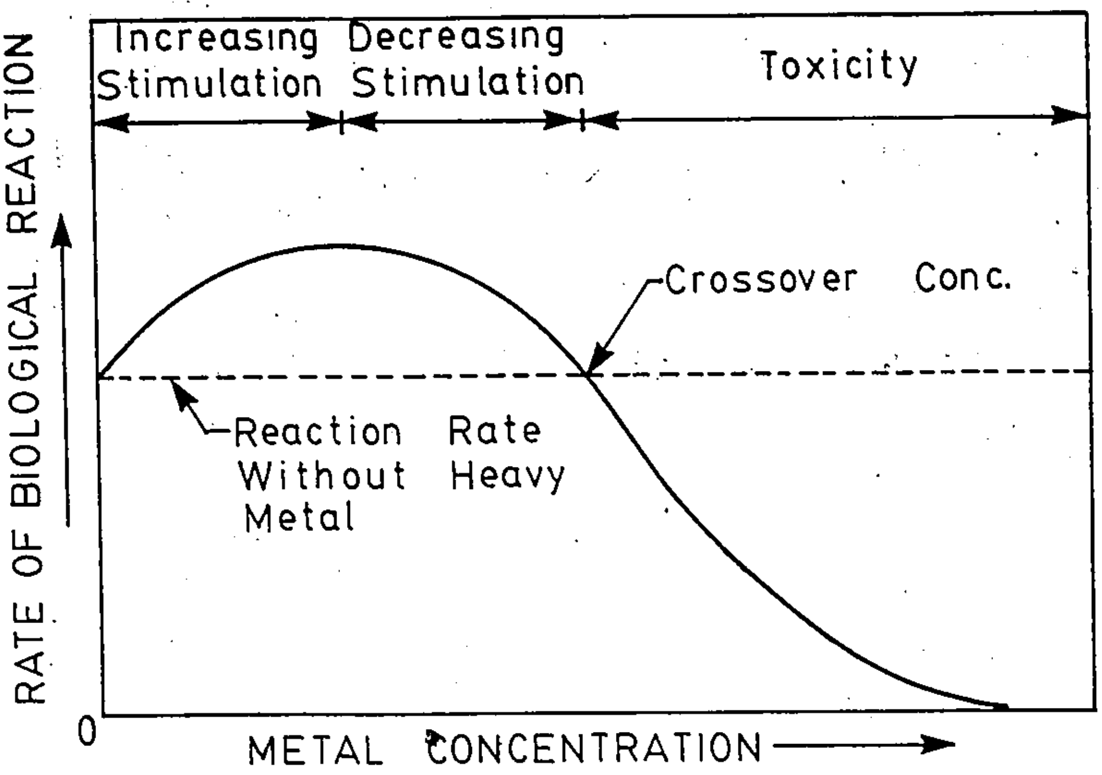


Figure 2.9: GENERAL EFFECT OF HEAVY METALS ON BIOLOGICAL REACTIONS [Bagby and Sherrard, 1981]

The metal with the most effect on the biological process is mercury, while the one with the least effect is zinc [Mowat, 1976]. The remaining metals fall into the pattern shown below;

Hg>Ag>Cr(III)>Al>Fe>Cu>Ni>Cd>Co>Cr(VI)>Sn>Zn.

With the toxicity reducing the efficiency of BOD reduction, it is important to control the effects of metals. In studying various control parameters, it was seen that changes to sludge age, organic loading rate and MLSS reduce the metal impact. The studies showed an increase in any one of these three, would decrease the proportion of active cells tied up as complexes with the metals, resulting in better biological activity and thus improving effluent quality [Nilsson, 1971, and Oliver and Cosgrove, 1974].

As noted previously, a combined metal concentration of 10mg/L results in only a 5% reduction in the conventional activated sludge treatment efficiency. However, even though the anaerobic systems respond to the non-toxic levels like the aerobic bacteria, they fail suddenly and completely when the threshold toxic level is exceeded. This sensitivity is especially critical for sludge digestion which has been observed to fail quite suddenly [McDermott *et al.*, 1965]. Also sensitive to small amounts of metals is the aerobic nitrification stage [Barth *et al.*, 1964].

2.6 METALS IN TREATMENT PLANT SLUDGE

No matter what treatment technique is used, the removal of heavy metals from the wastewater can occur without great difficulty. However, in treating wastewater for heavy metals, the metals are only separated from the wastewater. These separated metals then end up in the sludge, with their exact concentration depending on the removal technique used.

The problem with the sludge is that the metals concentrate in the it; sometimes 10,000 times that of the influent [Black, 1976]. He further noted that even when insignificant metal concentations exist in the influent, the metal content in the sludge can be high. The final metal concentration determines the method of disposal chosen.

The sludge disposal method chosen should be such that there is no environmental contamination, now or in the future. Presently the methods used include incineration, disposal on the farm fields, lagooning, sanitary landfill, dewatering and composting for garden use and ocean dumping. The average break down is about 30% for incineration, 15% for ocean disposal, and 55% for all types of land disposal, which includes roughly 25% for croplands [Cornwell and Westerhoff, 1973].

However, recent concerns regarding the high cost of incineration, ocean pollution, ground water contamination from landfill leachates, and crop uptake of metals, all the present methods are under some suspicion [Wozniak and Huang, 1982, Garrigan, 1977 and Epstein and Chaney, 1978]. What is now required are cost effective methods of sludge disposal which reduce the possibilty of environmental contamination.

2.7 REMOVAL EFFICIENCIES OF HEAVY METALS

Many studies have been done on the removal of metals from domestic wastewater, as seen in Table 2.11. However, due to the variations that exist with the sewage characteristics and types of removal techniques used, the removal efficiencies are always different at the various treatment plants, ranging from 10 to 100% [Patterson, 1976]. It has even been observed through studies on the same plants that the efficiencies change due to factors which are not fully understood.

What is known is that, when evaluating removal rates, it is important to consider the phase distribution of the metals in the raw wastewater. This information is important, since soluble metals are the most difficult to remove and high concentrations would result in reduced removal efficiencies when conventional treatment is used. Unfortunately, the majority of studies do not report the phase fractions, which would allow for proper comparisons. What is reported are the general trends. When the proportion of soluble metals is high as for nickel, the removal is low. On the other hand when the soluble fraction is low, the removal is high. This general pattern was also observed in the Ontario plants. Furthermore, even though the Ontario studies report lower removal efficiencies, they indicate improved removal during primary settling. This is probably a direct result of using chemicals to remove phosphorous.

TABLE 2.11

Overall Metals Removal Efficiencies of Different Plants

City	Treatment Received	Efficiency (%) Cd	Cr	Cu	Ni	Zn	Pb
Anderson, Indiana	Sec.	59	88	86	41	75	75
Buffalo, NY.	Sec.	38	62	61	11	41	74
Grand Rpds., Michigan	Sec.	--	19-66	13-57	18-41	35-51	--
Muncie, Indiana	Sec.	--	78	68	0	70	82
Pittsburgh, Pa.	Sec.	67	67	56	10	65	81
Wahiawa, Hawaii	Step	59	32	74	42	71	73
Winnipeg, Manitoba	Pure	--	68	77	0	80	49
Avg. of 6 Cities near Kansas City	----	16	37	49	--	47	49
4 Ontario Cities	Lag.	0	13	13	40	42	0
5 Ontario Cities	Prim.	13	69	30	21	42	48
11 Ontario Cities	Act.	28	76	80	53	67	70

Sec. = Secondary Treatment
Trk. Flt.=Trickling Filter
Step=Step Aeration
Lag.=Lagoon Systems
Act.=Actvated Sludge
Prim.=Primary Treatment
Pure=Pure Oxygen
Con.=Convential Activated Sludge

Ref: [Yost et al., 1981].

All the studies referred to here have stated that when the raw wastewater had a total metal concentration less than 10 mg/L, no inhibition of the biological process occurred. Futhermore, it is reported that the relationship between suspended solids and metal removal holds true. As more solids are removed, so are more metals. A problem that was reported by many plants concerned the sludge digester. A few activated sludge plants have reported that when the supernatant from the digester is recycled, a problem with toxification occurs [Brown and Hensley, 1973]. The toxic effects occur since the supernatant is highly concentrated in metals and thus increases the metal concentration entering the aeration tank.

Another observation made in the various reports is concerning the treatment reliabilty of biological treatment. Researchers like Netzer and Crawford [1983] believe that if a more consistent effluent is desired, physical-chemical treatment should be used. By using physical-chemical, they feel that a removal efficiency better than 90% could be attained, without upsetting the treatment facility.

Chapter III

BACKGROUND ON THE WINDSOR TREATMENT FACILITIES STUDIED

3.1 GENERAL

Presently, the Water Pollution Control System for the City of Windsor includes two treatment plants. The two treatment facilities are the West Windsor Pollution Control Plant, and the Little River Pollution Control Plant. West Windsor receives the wastewater from the River Front interceptor sewer, which serves the old part of the city [Harding and Romano, 1981]. There is also a second trunk sewer for West Windsor, called the Western-Grand Marais Sanitary Trunk, servicing the new developments in the southern part of the city. This trunk is continually expanding westward, to provide wastewater treatment for the municipality of Sandwich West [Figure 3.1]. The majority of industries in Windsor are located in the West Windsor Treatment area. The Little River plant services the east side of the city and receives mostly domestic wastewater. The municipalities of Tecumseh, St. Clair Beach and Sandwich South are included in this area [Figure 3.1].

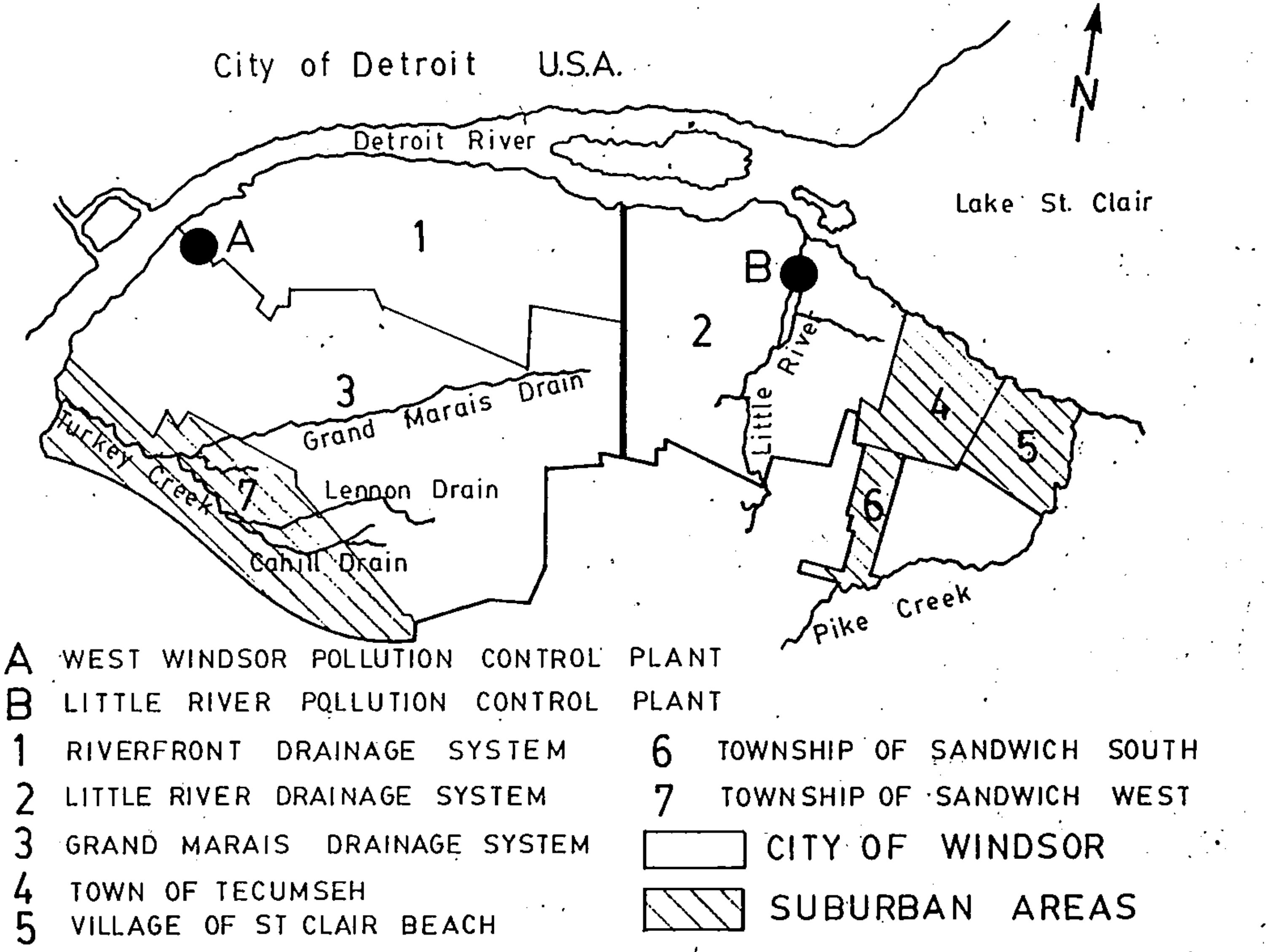


Figure 3.1: TREATMENT AREAS SERVED

3.2 LITTLE RIVER POLLUTION CONTROL PLANT

3.2.1 General

The Little River Pollution Control Plant is located on the east side of Little River, at the intersection of Jerome Street and Mckinley Street. The plant has room for an ultimate capacity of 72 million litres per day (16 MGD). Presently the plant provides secondary treatment for 36 MLD (8 MGD), with phosphorous removal facilities incorporated [Harding and Romano, 1981]. The various Little River treatment process can be seen in Figure 3.2.

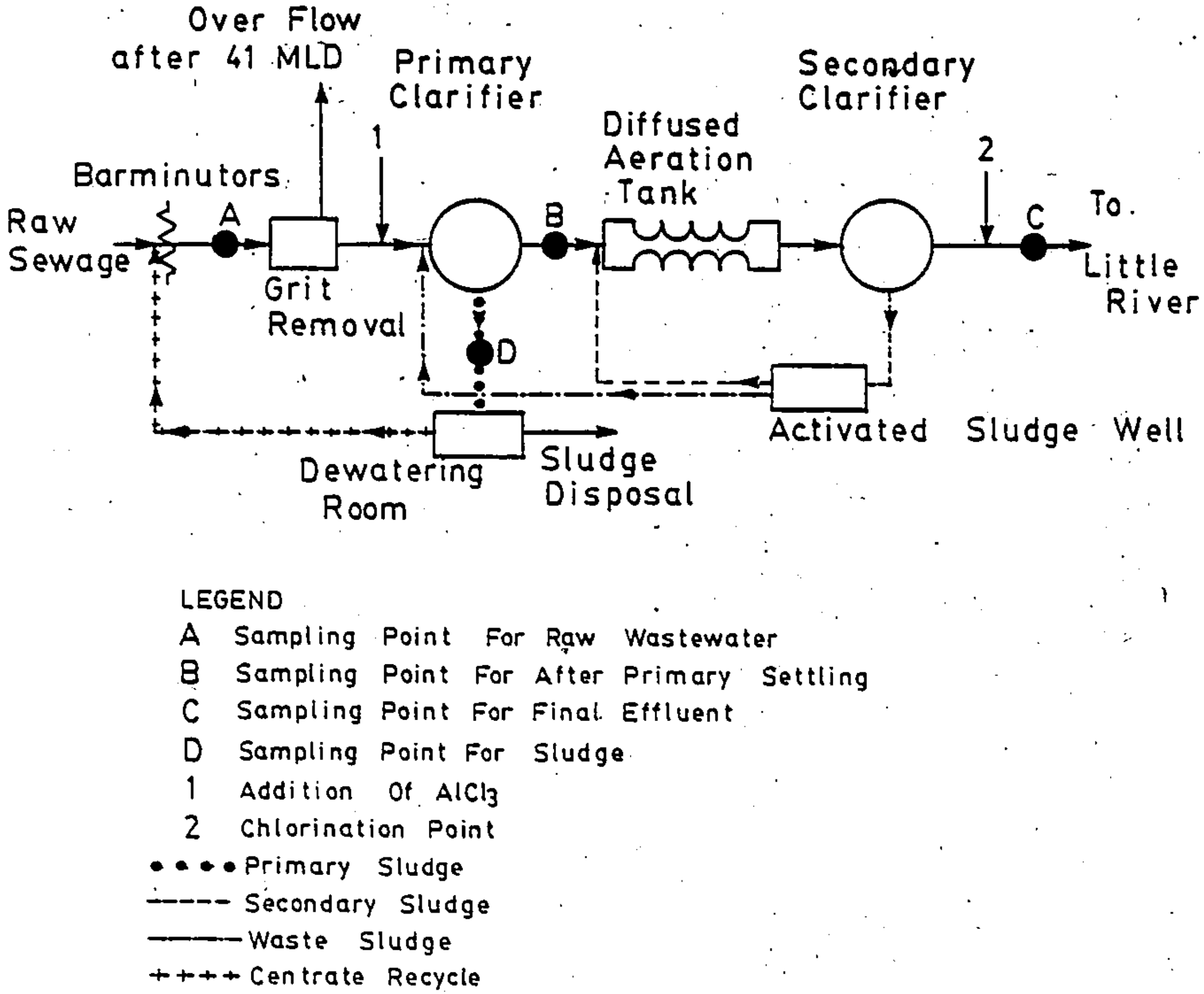


Figure 3.2: LITTLE RIVER POLLUTION CONTROL PLANT

3.2.2 Inlet Works

The raw sewage enters the inlet chamber through two large collector sewer trunks. Large screens and barminuters remove and 'masserate' all large particles.

3.2.3 Grit Removal

The sewage then flows into the raw well where it is lifted some 20 m by pumps to flow by gravity through the remaining processes.

At the first grit removal chamber, the velocity of the sewage is reduced, allowing the heavier material to drop. A circular submerged plough rakes the grit to a side pit for removal by a conveyor.

The second system is a larger, more efficient, aerated grit removal system. By aerating the sewage to remove grit, oxygen is also added to the wastewater. With the flat topography in Windsor, sewers have minimum grades and this can cause the sewage to become septic. By adding the oxygen the wastewater is freshend, which enhances further treatment.

3.2.4 Chemical Addition

After leaving the grit chamber the phsophorous precipitating chemical is added. During this study $AlCl_3$ was the chemical added. The mixing occurs through turbulence in the channel on the way to the primary setling tanks.

3.2.5 Primary Settling Tanks

The flow is distributed equally to the primary tanks. These tanks have a unique structure, which eliminates the necessity of constructing special sludge thickening tanks, since the entire centre drop section performs this function.

3.2.6 Aeration Tank

The flow from the primary tanks is taken by open concrete channel to the activated sludge tanks. Diffused air is injected into the the tank to provide the necessary oxygen for the bacteria. The wastewater spends approximately three hours in the tank before being released to the final settling tanks.

3.2.7 Final Settling Tanks - Activated Sludge - Chlorination

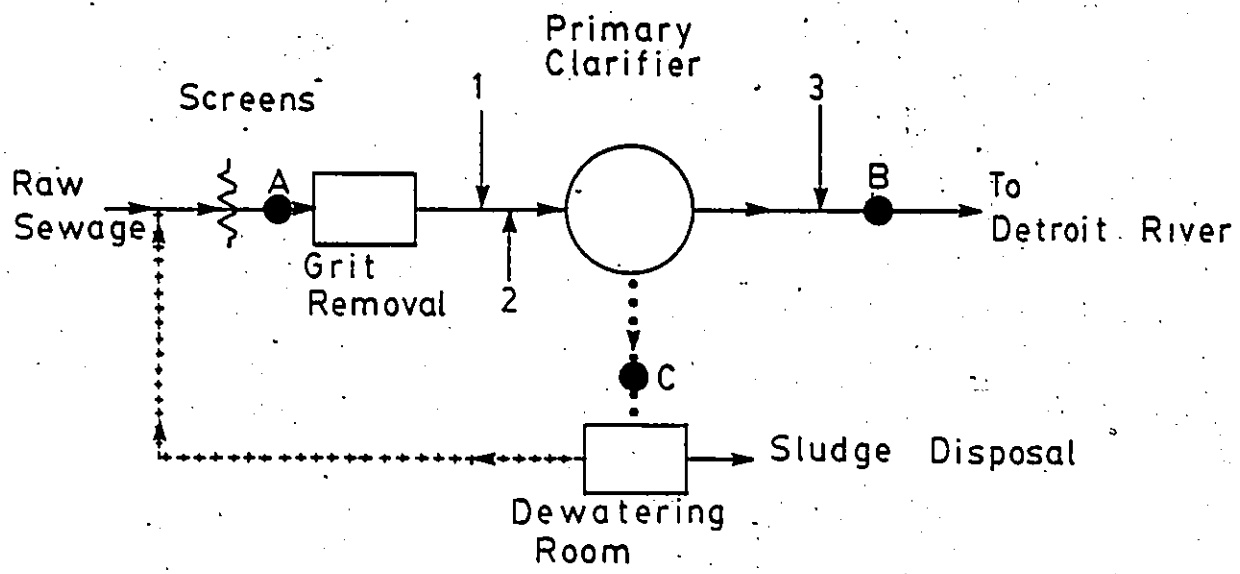
The wastewater now enters the final settling tanks where the activated sludge is settled out and pumped to the activated sludge sludge well. From the well, activated sludge is returned to the aeration tank to maintain the bacterial population. Periodically a portion of it is wasted to the head of the primary clarifier. The clear effluent overflows the weirs to the chlorine contact chamber from where it is discharged into the Little River.

3.2.8 Sludge Dewatering and Disposal

The sludge separated from the wastewater and stored in the primary tank drop section, is pumped underground to a sludge holding tank in the dewatering building. When the holding tank is full, approximately every three days, the sludge is dewatered via centrifuges. The cake is transferred to trucks for hauling to the sanitary landfill site, while the centrate is recycled to the head of the plant for mixing with the incoming wastewater.

3.3 WEST WINDSOR POLLUTION CONTROL PLANT

The West Windsor Pollution Control Plant is located on a 36 acre site on the south-east corner of Ojibway Parkway and Sandwich Street, having an ultimate capacity of 265 million litres per day (60 MGD). The existing plant provides physical-chemical treatment for 155 million litres per day (34 MGD). It also provides grit removal and chlorination for additional 265 MLD (65 MGD) of storm water coming from the combined sewers [Harding and Romano, 1981]. Figure 3.3 shows the layout of the various treatment schemes at West Windsor.



LEGEND

A Sampling Point For Raw Wastewater
B Sampling Point For Effluent
C Sampling Point For Sludge
1 Addition Of $FeCl_3$
2 Addition Of Polymer
3 Cholorination Point
● ● ● ● Sludge
+ + + + Centrate Recycle

Figure 3.3 WEST WINDSOR POLLUTION CONTROL PLANT

3.3.1 Inlet Works

The raw sewage enters the inlet chamber through two large sewers. The inlet pipes into the plant contain mechanically cleaned bar screens which prevent particles larger than 7.5 mm from entering the pumping station. The wastewater is lifted a total of 15 m to the grit removal facility. From there the flow proceeds by gravity.

3.3.2 Grit Removal

Before entering the grit chamber, automatically cleaned bar screens spaced 2.5 mm apart remove the remaining debris that could damage the treatment equipment. An aerated system is used which induces a helical flow pattern to enhance the grit separation. After separation, the grit is washed to remove the adhering organic matter before being hauled away to sanitary landfill site.

3.3.3 Chemical Additions

After the wastewater passes through the grit chamber, phosphorous precipitation chemicals are added to the wastewater. During this study $FeCl_3$ was the chemical added. Turbulance in the channels provides the mixing.

Before entering the clarifiers, polyelectrolyte is added to the wastewater to enhance flocculation and sedimentation of the phosphorous precipitate and any other suspended matter. During this study, Alkapam 3000 was used.

3.3.4 Clarification

The flow is equally proportioned to each of the six clarifiers. The wastewater enters the clarifier from the bottom, through a vertical centre pipe. Here the flow is directed from the centre ring in a downward motion to the outside of the clarifier. A peripheral baffle retains the floating scum, while the settled solids are collected in a sludge hopper at the bottom of the clarifier.

The clear effluent overflows the weirs and is directed to the chlorination chamber. After disinfection the treated wastewater is discharged into the Detroit River.

3.3.5 Sludge Dewatering and Disposal

The accumulated sludge in the clarifiers is pumped underground to the sludge holding tanks in the dewatering building. When the tanks are full, roughly every three days, the sludge is transferred to centrifuges for dewatering. The dewatered sludge is conveyed to sludge cake hoppers where it is mixed with wood chips to allow for composting, for use as landfill in the city. The centrate is recycled to the head of the plant and mixed with the incoming wastewater.

Chapter IV

PROCEDURES ON SAMPLE COLLECTION AND ANALYSIS

4.1 LOCATION OF SAMPLING POINTS

4.1.1 Little River Treatment Facility

~~To analyze the metals at the Little~~ River plant, the majority of samples were taken from the raw sewage, primary effluent, final effluent, and sludge [Figure 3.2]. However, since the waste secondary sludge is fed back to the head of the primary clarifier to be dewatered with the primary sludge, only one sludge sample was available for analysis. These samples were further augmented by taking some additional samples from the the grit chamber and centrate recycle line.

Both composite and grab samples were collected from Little River Treatment Plant. Grab samples were manually collected. Enough grab samples were gathered in volume and number to provide a composite sample at the end of the day. However, for the sludge samples, sampling was not as easy, since Little River dewaters only when the sludge tanks are full. With this being the case, sludge samples could only be collected on dewatering days.

4.1.2 West Windsor Treatment Faciltiy

To analyze the metals in the West Windsor facility, the majority of samples were taken from the influent, effluent and sludge points during treatment [Figure 3.3]. These samples were also supplemented with samples from the aerated grit removal chamber, and centrate return line.

The type of samples taken were grab and daily composites. Fortunately for this study, West Windsor had installed continuous samplers which fed the influent and effluent directly to the laboratory. For sludge samples the same procedure used at Little River was used. The only exception is that the sludge sample was just primary sludge, not combined primary and secondary sludge.

4.2 SAMPLE COLLECTION

The steps outlined herein apply to all the samples collected from both the Little River Pollution Control Plant and the West Windsor Polution Control Plant.

The type of samples taken were either a grab sample or composite sample as previously stated. The grab samples were taken at an interval of every four hours at Little River and every two hours at West Windsor. The quality control groups at both treatment plants take composite samples for a 24 hour period to monitor the daily operating performance based on the conventional parameters of the plants. For this study the control groups just increased the volume of samples taken and thus provided the author with samples of sufficent quantity to perform the analysis. Some of these composite samples were used to determine the phase fraction of the metals between suspended and dissolved.

Once the samples were collected, the following steps were followed for sample preparation and storage.

1. 1 L linear polyethelene bottles were used since they absorb insignificant amounts of metals.
2. Bottles were washed and scrubbed with a hot detergent solution, then rinsed with tap water. Following the water rinsing, bottles were washed with 6N HCl acid. After allowing the acid film to soak for 30 minutes, the bottles were again rinsed with tap water, followed by distilled water. This final rinsing was followed by draining and drying the bottles in a dust free location [O'Haver, 1976 and Patterson and Koduk-la, 1982].
3. For samples to be analyzed for total metals, 5 ml of concentrated HNO_3 were added to the container before collection. The acid would lower the pH to less than 2, ensuring that no metals would be absorbed by the bottles. This step was not required if the samples were used to determine dissolved metal concentrations.
4. After the samples were in the containers, the bottles were brought to the laboratory. At this point pH

measurements were made to check whether the pH indeed was less than 2.

5. When pH measurements were complete, the samples were placed in a temperature controlled refrigerator, with a temperature of 4°C. The samples were stored here until they were analyzed.

4.3 SEPARATION OF METAL PHASES

To separate the dissolved and suspended metal phases, the collected samples had to be filtered. The filtration was performed on samples not acidified, according to the following procedure.

1. Filtration was performed soon as possible when samples were brought back to the laboratory, ensuring accurate analysis.
2. All utensils used for filtration were acid washed with 6N HCl to avoid any contamination. They were then rinsed with distilled water.
3. To avoid clogging of the Type HA 0.45 um glass fibre filter, the initial filtration was performed by a 934AH glass fibre filter.
4. Final filtration was performed by using a Type HA 0.45 um glass fibre filter.
5. The final filtrate volume was acidified by adding 5 mL of concentrated HNO_3

6. Filtrate was then poured into a linear polyethelene bottle, and stored in the refrigerator.

4.4 CONCENTRATION OF SAMPLES

To carry out accurate analysis of samples, which have low metal concentrations, Arqaman and Weddle [1973] and O'-Haver, [1976], suqgest that concentration thru evaporation should be carried out before anaylsis. Furthermore, this is also done by the personnel at the Windsor Wastewater Lab. The concentration factor the City of Windsor uses is 10 [Faust, 1983], and their results have been found to be quite satisfactory when compared with the Ministry of Environment results on the same samples. With this in mind, a concentration factor of 10 was chosen for this study. However, with the plasma unit beinq relatively new, a further check was made with Beckman Industries [Seely, 1983]. This conversation confirmed the proposed procedure.

The procedure used to concentrate the samples was the same for all the samples. The only difference concerned the initial volume taken for evaporation. When the sample was a composite one the intial volume was 400 mL, while for the qrab samples only 200 mL were taken. The difference was to allow for calibrating the plasma intrument for sample variances. It should be noted that the same volume of acid added to the standards was added to the samples to maintain a consistent matrix. The remaininq steps listed below were the same for all samples.

1. Clean acid washed beakers and graduated cylinders are used.
2. The beakers and the measured amount of sample were then placed on a hot plate with magnetic stirrers, and placed under a fume hood.
3. The amount of acid added was 5% of initial sample volume. However, if the total sample volume was close to the initial sample volume, the acid added for acidification was taken into consideration.
4. The beaker was then covered with a watch glass to prevent any contamination and splattering loss of the sample.
5. When sample volume became 10% of initial volume, evaporation was halted. Just before heat was turned off the watch glass was rinsed off with deionized water to return to the solution any metals that had condensed on the watch glass. To bring the sample to proper volume, the remaing solution and beaker rinsings were poured into a clean graduated cylinder. Volume was brought up to 10% of initial by adding distilled-deionized water.
6. Finally the sample was transferred to a 100 mL polyethylene container and stored in the refrigerator until analyzed.

4.5 PREPARATION OF SLUDGE SAMPLE FOR ANALYSIS

Since complete mass balances were required to complete this study, it was imperative that the metal concentrations in the sludge be determined. A study by Delfino and Enderson [1978], described many ways to analyze the sludge, and the one eventually chosen was the nitric digestion procedure. The selection of this method was based on the ease of application and the proven 95% confidence limit in metal determination.

The following points indicate the procedure used to prepare the sludge for metal analysis.

1. A wet sludge sample was weighed and then dried at 105 to 110°C.
2. Following the inital drying, the sample was ground up into smaller pieces before being placed in a muffle furnace at 550°C.
3. The dried sludge was then weighed on an analytical balance. Sludge was then placed in a covered beaker.
4. Distilled-deionized water was then added to the dried sludge sample, followed by 10 mL of concentrated HNO_3 Stirring was performed during this step.
5. The beaker was placed on a hot plate, and the solution brought to near dryness. All digestion procedures were performed under a fume hood.
6. Nitric acid was continually added in small increments until the solution became clear.

7. The remaining solution was filtered through a 0.45 um filter to remove any mineral residue.
8. The filterate was then diluted to 40 mL, to allow easy determination.
9. The metal concentrations were reported as mg/kg, on a dry weight basis.

4.6 INSTRUMENTATION USED TO ANALYZE SAMPLES

In analyzing the complex wastewater samples, a multi-element Spectraspan V was used. This instrument uses a three electrode direct current argon plasma source for optical emission spectrometry and hence is called the Direct Current Plasma (DCP). Since the development of the 3 electrode DCP in 1978 by Carl Hildebrand and T. J. Karlinski, it has received little coverage in the scientific literature [Zander, 1982]. This lack of coverage can be attributed to the great popularity of the Atomic Absorption Unit has in research. Fortunately, some result oriented researchers were using the DCP in data generation, leading to its present emergence.

The DCP jet illustrated in Figure 4.1 uses three electrodes. Two of the electrodes are anodes, while the third is a cathode, all in the inverted Y configuration. This unfamiliar shape provides an excellent viewing zone. By having the present configuration, the aerodynamic turbulance caused by the rushing plasma is moved up and away from the viewing zone, reducing the background interference. As can be seen by Figure 4.2, the relative background is low when compared to the peak intensity of the line, giving more stable analysis.

To produce the plasma, which is a fourth state of matter under atmospheric pressure, argon gas is fed to the electrodes. A direct current is then applied to the electrodes resulting in the plasma jets. This plasma has temperature varying between 5000° and 10000°K, which is sufficient for complete element analysis.

During the analysis, the sample is nebulizied into a fine spray having 3-10 um diameter droplets. These droplets are consequently delivered to the plasma through the sample tube [Figure 4.1]. On contact with the plasma, the sample becomes atomized, where atomization occurs as energy is imparted to the molecules. The energy is applied in terms of temperature, where higher the temperature, greater the resulting radiation emission. This radiation is in the form of a wavelength were each element has a specific characteristic wavelength. Thru optics the wavelength is directed to a monochromator which establishes an intensity for the sample analyzed.

The sample concentration is determined by comparing the sample intensity to the standard intensity curve. This intensity curve for comparisons is generated by running through the instrument a high and low standard of the same

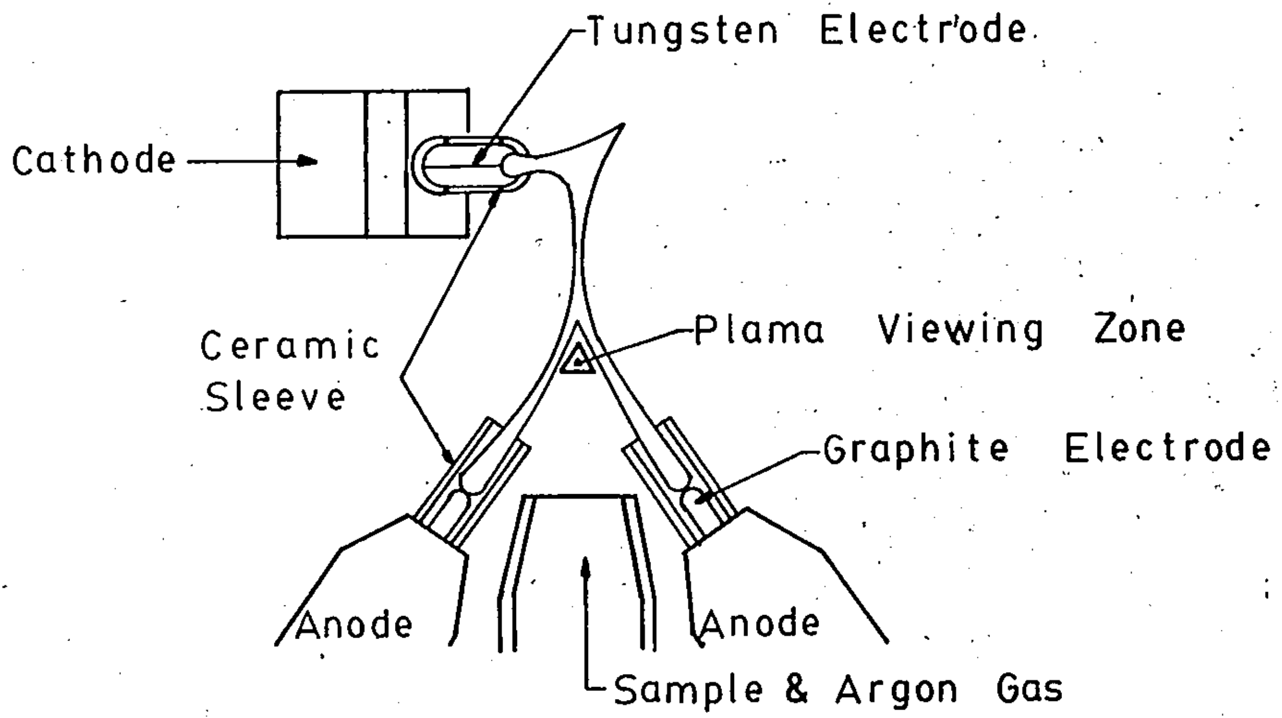


Figure 4.1: REPRESENTATION OF THREE ELECTRODE PLASMA JET

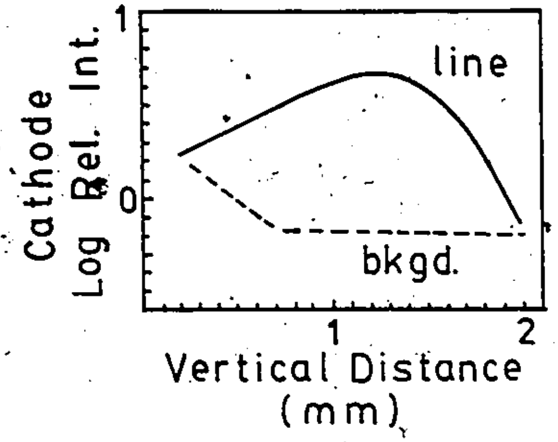


Figure 4.2: Background Interference for DCP
[Decker, 1980]

matrix as the sample. The generated curve remains in effect until the electrodes are physically altered through movement, or tip erosion from the argon gas.

Generally the precision of the DCP is represented by a coefficient of variation, which usually lies around 2% when the instrument is properly optimizied [Decker, 1980]. However, it should be noted that the precision is dependent on the samples and standards having a matrix as indentical as possible. The reported detection limits for the metals analyzed in this study by the Spectraspan V, are shown in Table 4.1.

TABLE 4.1

Heavy Metal Detection Limits for the Spectraspan V

Metal	ug/L
Cd	8
Cr	2
Cu	2
Ni	2
Pb	23
Zn	2

Ref: [Spectrametrics, 1980].

Chapter V

VERIFICATION OF RESULTS

5.1 GENERAL

While using an analytical method slightly different from that recommended in Standard Methods [APHA-AWWA-WPCF, 1980], the results obtained must first be verified. The verification is important since studies by Beckett [1980] and Van Loon et al. [1973], reported that many researchers publish data without first ensuring that their values are accurate. Keeping this fact in mind, a few checks were performed to gain confidence in the values reported.

5.2 VALIDATION OF STANDARDS

The basis for any analysis hinges on the confidence acquired for the standards. This was important since the metals analyzed by the DCP were compared to the standard solutions.

The dilution of the standards was done in two stages to reduce the error. This was necessary since the reference solution was certified[2] at 1000 mg/L ±1% and the required standards were at a concentration of 1 mg/L. If not done in two stages to minimize the error, any small error introduced

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[2] Fisher Atomic Absorption Standard, Fair Lawn, New Jersey

while reducing the concentration from 1000 mg/L to 1 mg/L, would greatly be magnified.

The first step involved reducing the concentration from 1000 to 10 mg/L, using the following procedure;

1. A 1 litre acid washed flask was partially filled with distilled deionized water.
2. 10 mL of each metal standard was transferred into the flask, via volumetric pipettes. Multi-element standards were used since the wastewater contains all the elements in combination, and the standard matrix should be as close as possible to the sample matrix (Dreler, 1983).
3. 50 mL of concentrated nitric acid was added to the flask, to ensure metals would stay in solution. Solution was then diluted to 1000 mL by adding distilled deionized water.
4. Standard was then transferred to a linear polyethylene bottle for storage in the refrigerator. The standard bottles were treated in the same fashion as the sample bottles to ensure that if any extraneous metals were added during bottle preparation, a relative correction was applied thru the matrix.

With the new 10 mg/L reference standard now available, the required 1 mg/L standard was prepared using the same procedure. The only difference was the amount of reference solution taken. For the 1 mg/L standard, 100 mL of 10 mg/L solution was required. When a blank was required, the same procedure was followed again, the only difference being that no metal solution was added. However, even when standards are carefully mixed, they must still be checked.

In order to check the quality of each standard, the standards were run as samples against each other. In this fashion the straight line shown in Figure 5.1 was produced, indicating consistency with the standards. If the line would not have been straight, something would have been wrong with the standards, since DCP works on a straight line calibration. Furthermore, any time a new standard was made, it was checked against the already existing standards, to ensure that the quality was maintained.

Similarily blanks were checked against the standards. These blanks contained distilled water, distilled-deionized water, and acids used to prepare samples and equipment. By checking the blanks, it could be determined whether metals were being added to the samples, and if the matrix was correct. In all tests, the blanks gave zero concentrations indicating that the matrix was properly put together.

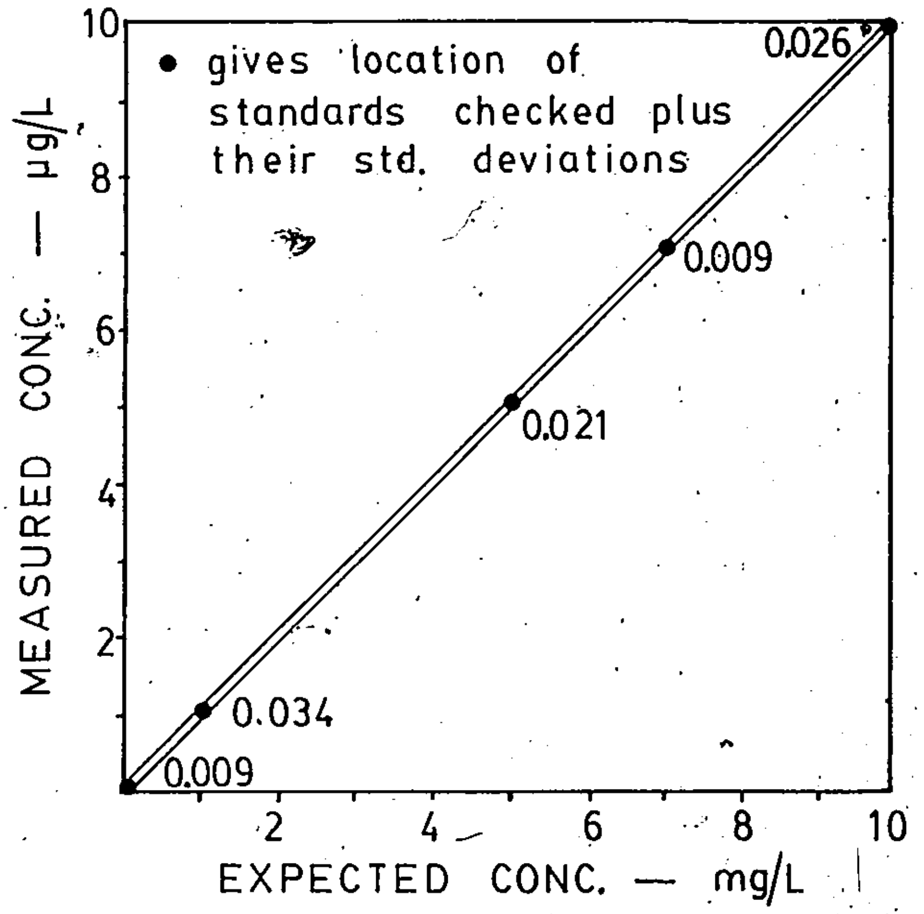

Figure 5.1: STANDARD VERIFICATION CURVE

5.3 DETECTION LIMITS

After verifying the standards, the next step involved the determination of the detection limits. Various detection limits were already evaluated by Beckman, as reported earlier. However, when a new machine is purchased checks must be made to gain confidence in the values obtained. The required ranges of concentrations for this research was established, and the distilled-deionized water was spiked with known concentrations of metals. These solutions were then analyzed in the machine to determine their recoveries.

Figures 5.2 and 5.3 show that two ranges of concentrations were analyzed. Two different sets were used because the metal concentrations in the samples were expected to drop one order of magnitude. Both figures indicate that the recoveries were almost perfect, giving a straight line. Furthermore, the calculated standard deviations for 6 repeats were 2 ug/L for the 0 to 100 ug/L range, and 5 ug/L for the 0 to 1000 ug/L range. These low standard deviations and straight line relationship, apparently indicate that the DCP readings were accurate in the entire ranges.

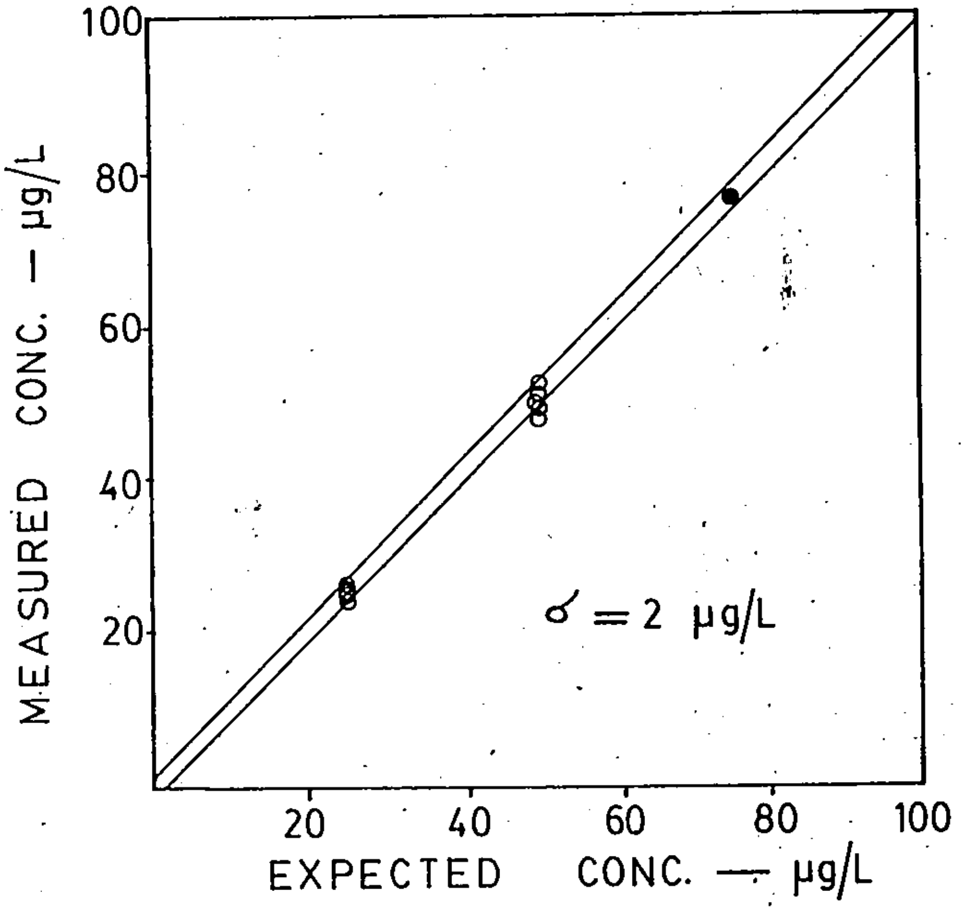

Figure 5.2: RECOVERY OF SPIKED DISTILLED DEIONIZED WATER, 0-100 μg/L RANGE

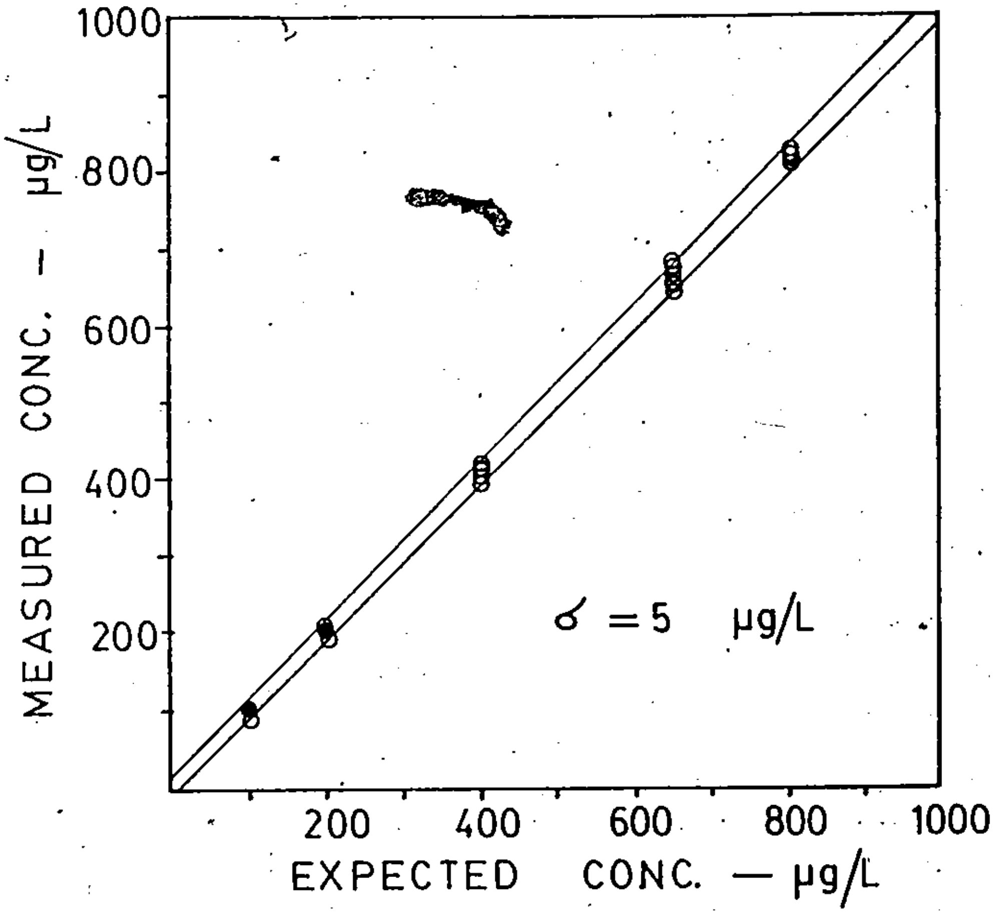

Figure 5.3: RECOVERY OF SPIKED DISTILLED DEIONIZED WATER, 0–1000μg/L RANGE

5.4 VERIFICATION OF EVAPORATION

After determining that DCP could accurately measure the metal concentrations in the required ranges, the concentration technique had to be checked. Since each wastewater sample was to be concentrated ten times to improve accuracy [Marumaya *et al.*, 1975], the possibility existed that some metal loss might occur during the process. In order to check this, distilled deionized water was spiked with different known concentrations of metal and then concentrated. After concentrating the samples, they were analyzed and the observed values are shown in Figures 5.4 and Figure 5.5 As can be seen, no apparent loss of metal occurred in both ranges, coinciding with low standard deviations. This indicated that evaporation could easily be used to concentrate the samples, in order to determine metals in the wastewater with confidence.

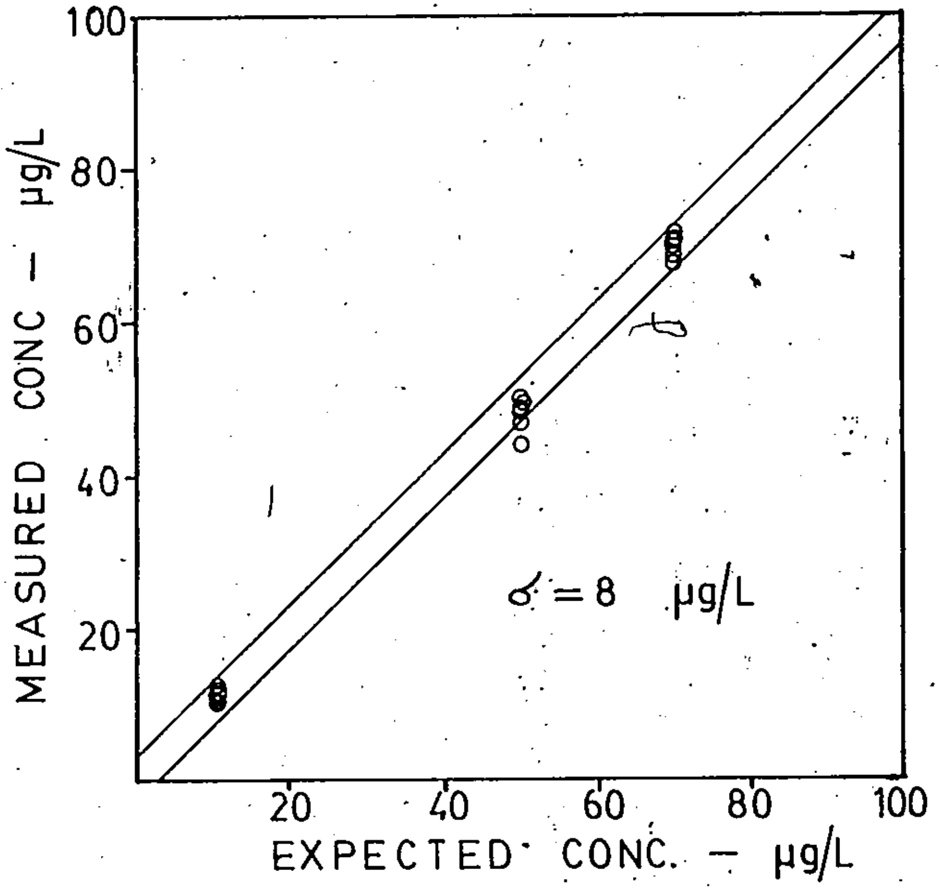

Figure 5.4: RECOVERIES OF CONCENTRATION TECHNIQUE — 0 to 100 μg/L RANGE

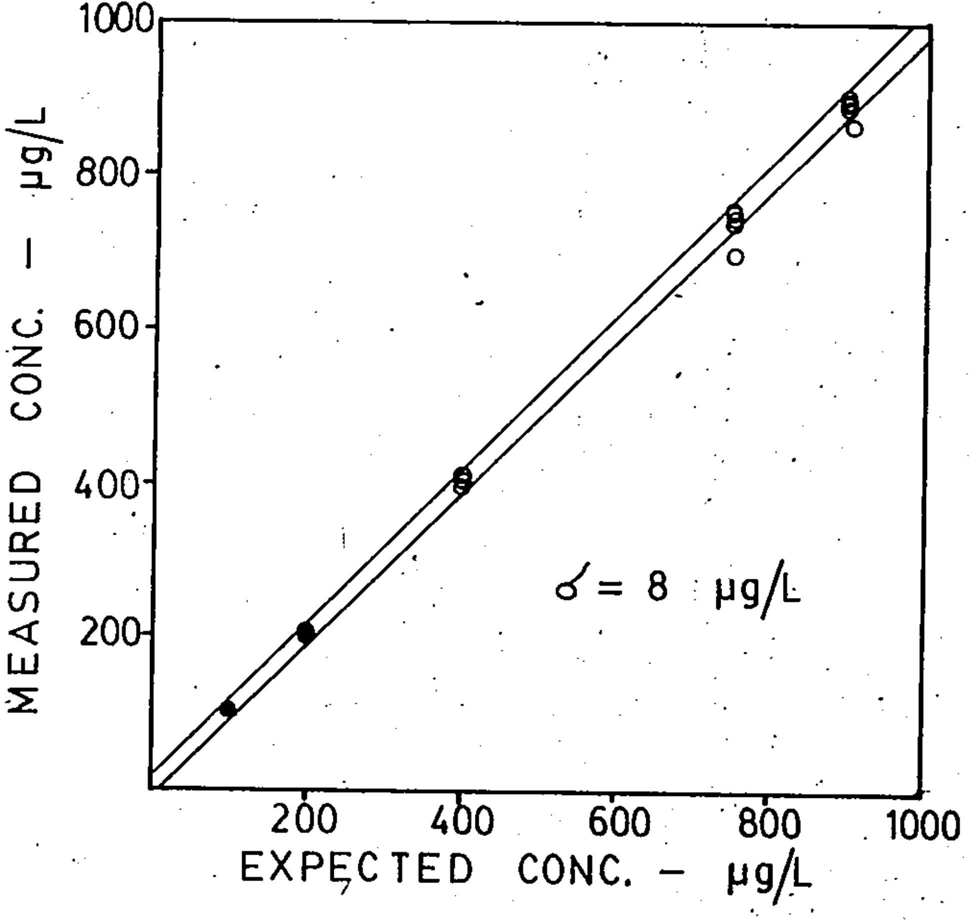

Figure 5.5: RECOVERIES OF CONCENTRATION TECHNIQUE —— 0 to 1000 µg/L RANGE

5.5 VERIFICATION OF WASTEWATER ANALYSIS

Even though the tests completed on the distilled-deionized water were satisfactory, tests on wastewater still had to be verified. The reason for further checks was that the wastewater sewage contains many substances of unknown concentrations. When these substances enter the DCP, the analysis can be affected due to the spectral interferences which may occur. These interferences can either increase or decrease the measured concentrations.

Raw wastewater and primary effluent were used to determine how the plasma worked with the developed matrix. These samples were spiked with metals and analyzed. After the initial anlysis, it was observed that there was some specteral interferences occurring, especially with zinc.

With the specteral interference present, there were two methods available to correct the matrix problems. One was to determine what caused the interference, and add it to the matrix, or else use the background compensator. Since the wastewater compostion is quite variable, with many elements present, the first method would have been quite troublesome, with no guarantee on the accuracy of results. With this in mind the second option was chosen. The DCP is equipped for background compensation and is relatively easy to initiate.

In order to perform background corrections, a digiscan was first run to see how each element behaved within the matrix. These digiscans indicated, that of the six metals analyzed, only zinc, nickel and chromium, require the corrections. Once the proper corrections were entered, for both sides of the peak, absolute corrections were applied to each sample. With these corrections, the spiked samples were rerun, giving adequate analysis as indicated by Figure 5.6 and Figure 5.7 . Furthermore, satisfactory standard deviations were obtained, indicating that the wastewater samples could easily be analyzed with confidence.

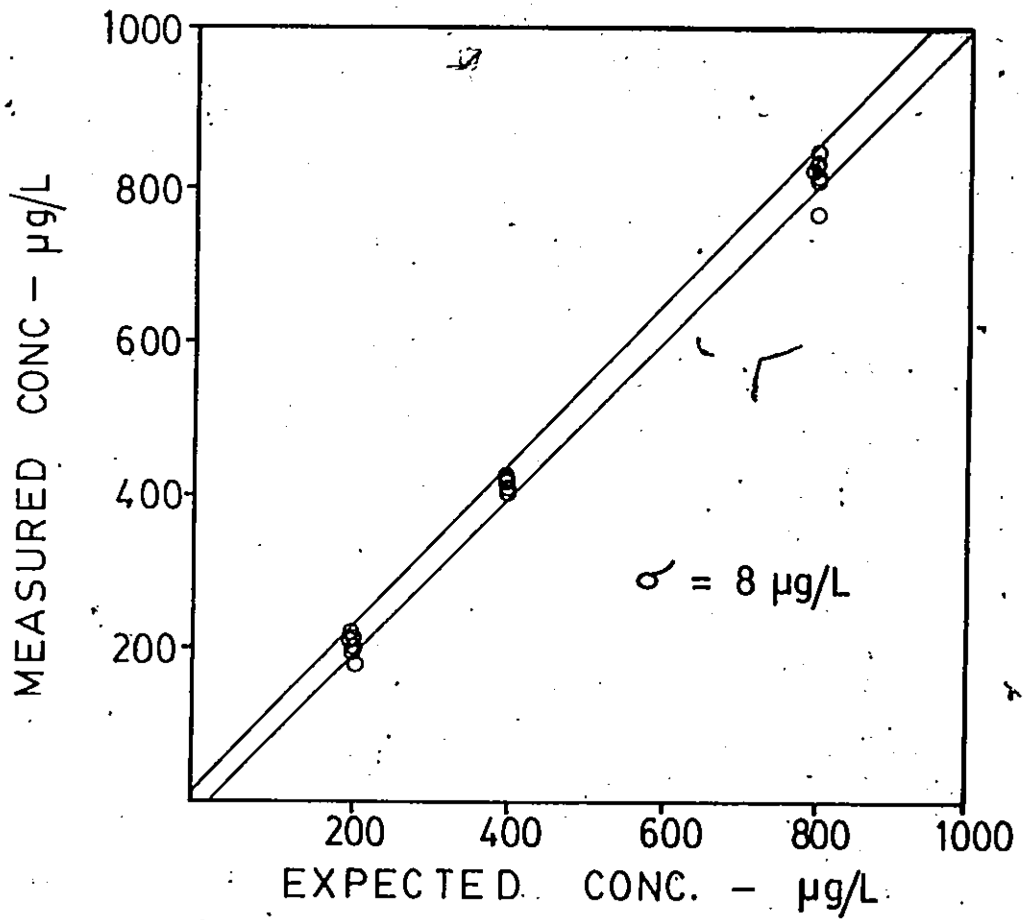

Figure 5.6: RECOVERIES OF LITTLE RIVER RAW WASTEWATER SPIKED WITH COMPOSITE METALS

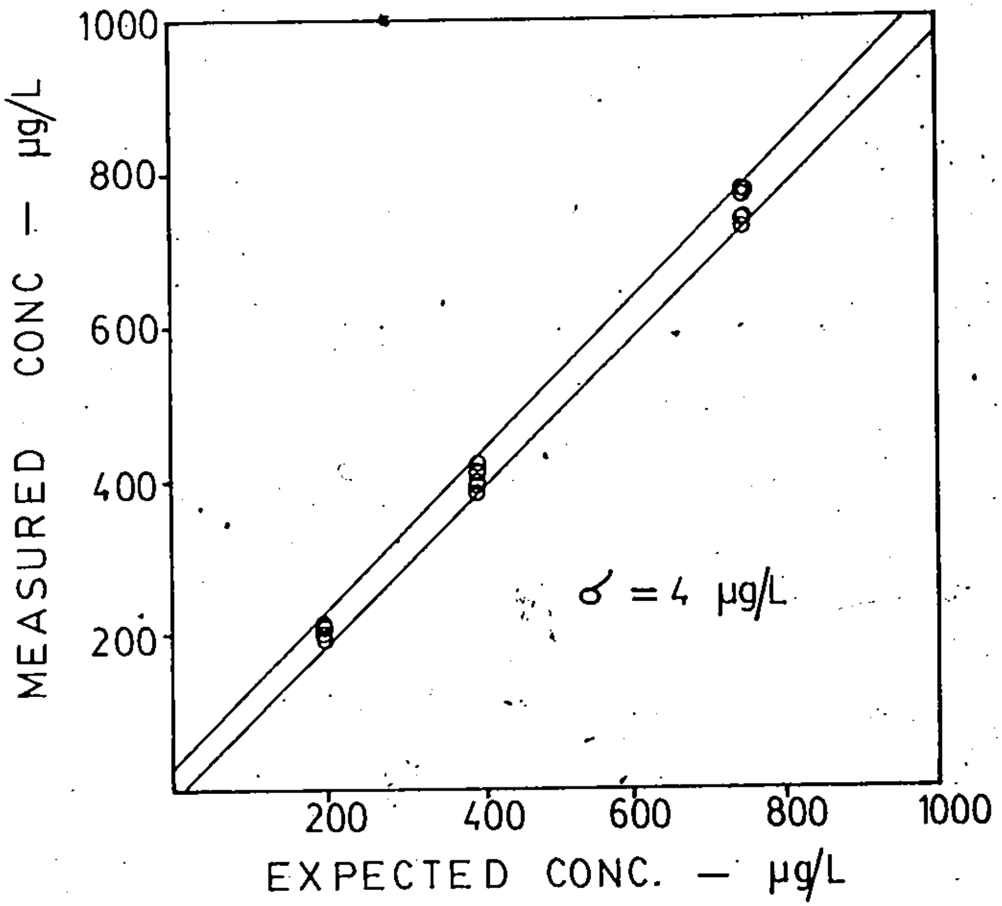

Figure 5.7: RECOVERIES OF LITTLE RIVER PRIMARY EFFLUENT SPIKED WITH COMPOSITE METALS

5.6 COMPARISON OF DCP WITH ATOMIC ABSORPTION

Even though sufficient proof now exists that the DCP machine is acceptable for heavy metal analysis in wastewater, one final check had to be performed. It is possible that certain errors in the technique existed, which might have gone unnoticed. This possibility of errors was checked by comparing the DCP data to data done in a independent lab.

With excellent cooperation from the City of Windsor Wastewater Lab, an independent check was possible. Indentical samples were analyzed both with the DCP and the City of Windsor Atomic Absorption unit. It is important to mention that the Wastewater Lab prepared the samples differently, since they adhere to the standard AA procedures outlined in the Standard Methods [APHA-AWWA-WPCF, 1980].

With the difference in sample preparation and analysis, certain differences in concentration values were expected. But as Table 5.1 indicates, these differences were in general acceptable. The samples of Dec 1, 1983 were analyzed after considerable storage in the refrigerator, showing no metal absorption by the container.

Finally, repeatability of the analysis was tested by reanalyzing the samples. This indicated that the second analysis was within 5% of the first, giving acceptable repeatability.

TABLE 5.1

Comparisons Between DCP and AA

		Metal Concentrations in ug/L					
Remarks	Type	Ni	Cd	Zn	Pb	Cu	Cr
West Windsor	DCP	82	8	416	87	120	82
Raw	AA	80	5	367	84	114	54
Dec 1, 1983	diff.	2	3	49	3	6	28
West Windsor	DCP	73	8	140	35	30	18
Effluent	AA	70	5	114	40	30	14
Dec 1, 1983	diff	3	3	26	5	-	4
West Windsor	DCP	142	6	697	86	143	215
Raw	AA	103	4	585	56	125	134
Feb 1, 1984	diff.	39	2	112	30	18	81
West Windsor	DCP	82	2	150	18	4	20
Effluent	AA	84	3	134	17	20	19
Feb 1, 1984	diff.	2	1	16	1	4	1
Little River	DCP	40	9	416	120	110	43
Raw	AA	60	9	420	120	90	50
Mar 1, 1984	diff.	20	-	4	-	20	7
Little River	DCP	14	9	282	32	32	13
Effluent	AA	8	9	100	40	20	5
Mar 1, 1984	diff.	6	-	182	8	12	8

DCP = Direct Current Plasma
AA = Atomic Absorption
diff.= difference between DCP and AA

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Chapter VI

RESULTS AND DISCUSSION

6.1 GENERAL

It was noted in the literature that each treament plant investigated had its own diurnal variations in metal concentrations. Identifying the exact cause of the variations is like identifying a fingerprint, since they are directly related to the various sources contributing the wastewater. With this in mind, emphasis was placed on studying diurnal and daily variations in concentrations for each metal.

Since the total metal concentration is an important parameter in treating the wastewater, emphasis was placed on determining the total heavy metals. However, reports have shown that the dissolved ions are the most difficult parts of metals to remove. Consequently, a few studies were carried out investigating the phase fractions of the metals in the raw wastewater, and observing them as treatment progressed. The patterns observed in Windsor were compared to those reported in other studies.

In any study on a treatment plant, whether it be a full scale or a pilot plant, removal efficiencies must be investigated. By calculating removal efficiencies, researchers can compare the results obtained for similar treatment plants and also determine how the indidvidual plants are performing.

No matter how a study is planned originally, many new interesting observations come forth during the course of the investigation. This study was no exception. While completing the diurnal calculations for Little River, it became quickly apparent that the feed chemicals and centrate recycling were having an influence on the observations. Since speculations on reasons are not sufficient as proof, further investigation was warranted.

These investigations involved the determination of the effects of feed chemicals and centrate recycle on the concentration of heavy metals at Little River. Even though the early results did not warrant it, similar studies were carried out at the West Windsor treatment plants in order to obtain a good comparison.

6.2 LITTLE RIVER

6.2.1 Diurnal Variations

6.2.1.1 Lead

As can be seen from Figure 6.1, the diurnal variations for lead raw wastewater vary from 34 to 98 ug/L. Generally the concentrations are lowest in the early morning, coinciding with reduced dry weather flow. Also various peaks are observed which exceed the normal range of concentrations. These peaks are due to the recycle of the centrate from the sludge dewatering centrifuges. In order to determine this effect, centrate was collected from the treatment plant and analyzed for metals. With the centrate flow rate being roughly 0.057 MLD, occurring once every three days, the metal concentration values listed in Table 6.1 will cause increases in the metal concentrations in the influent to the treatment plant. Since the sludge is dewatered when the sludge tanks are full, about every three days, and since the metals collected in the sludge varies from day to day, these peaks change accordingly.

On further analyzing the diurnal variations, one interesting observation is made. It appears that the primary effluent often has a higher lead concentration than the raw wastewater. This increase can be related to a combination three factors; (i) relatively low influent concentrations (ii) addition of waste $AlCl_3$ to remove phosphorous, and (iii) the recycling of waste sludge to the primary clarifier.

The waste $AlCl_3$ added to the raw wastewater comes from Polysar in Sarnia, where it is a catalyst in converting benzene to ethyl-benzene [Faust, 1984]. This $AlCl_3$ contains several heavy metals. Consequently when this chemical is added to the wastewater for phosphorous removal, the heavy metals are also added. The City of Windsor has set upper limits for the amount of metals allowed in this chemical [Table 6.2]. With such a possible high concentration even a

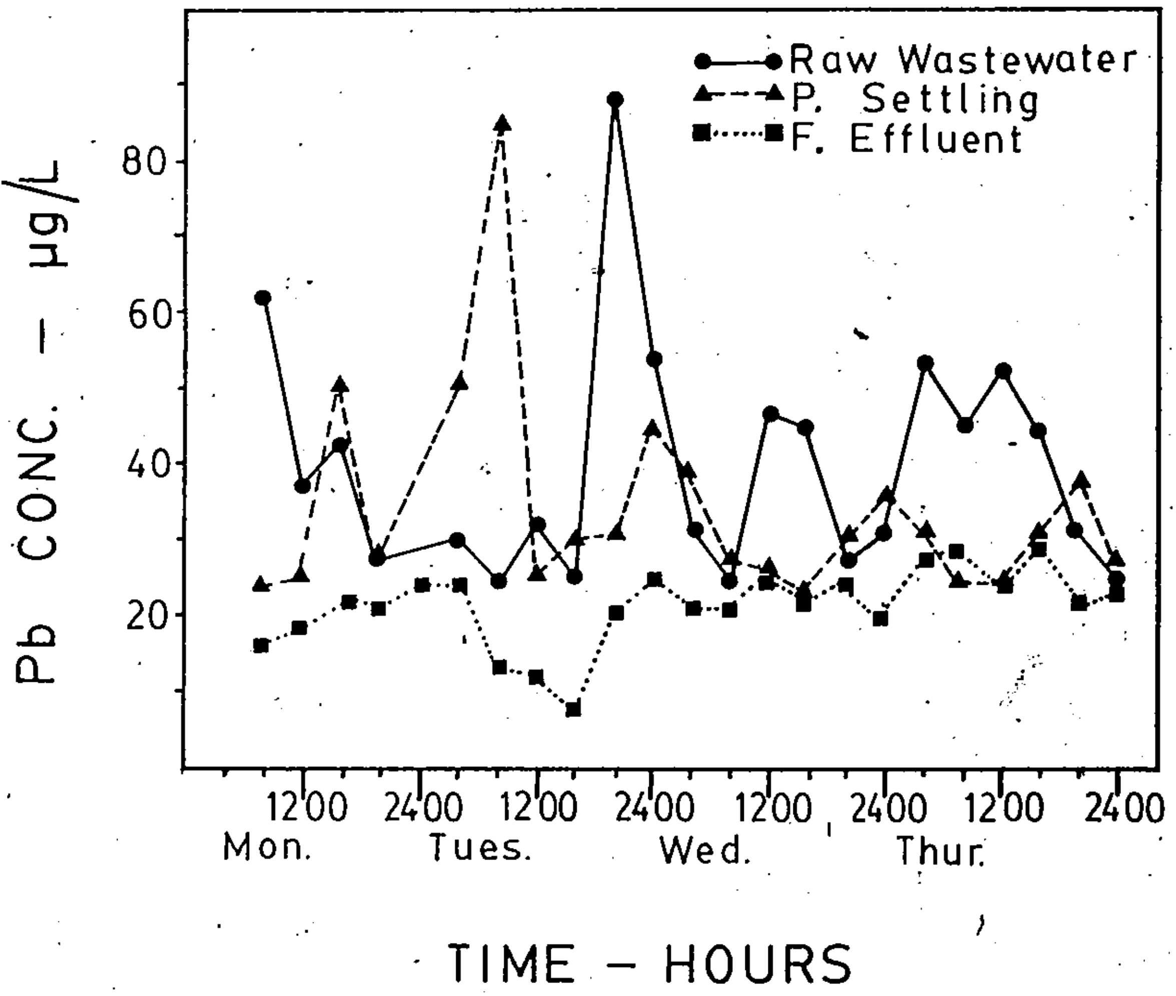

Figure 6.1: DIURNAL VARIATIONS FOR LEAD AT LITTLE RIVER

TABLE 6.1

Centrate Concentrations at Little River

Metal	Concentration of Centrate ug/L
Ni	71
Cd	15
Zn	335
Pb	111
Cu	178
Cr	42

dilution of one litre chemical per minute to eight million litres wastewater will give a noticeable increase in the metal concentration in the raw wastewater. In fact Black [1976] has even shown that manufactured chemicals contain metals which can contaminate the treatment process.

Adding to the problem of chemical contamination is the recycle of the waste activated sludge to the primary clarifiers. This sludge already contains metals previously entrapped and settled out. By reintroducing the sludge through recycling, some of these metals are released back into the wastewater.

As can be seen from Figure 6.1, the variations between raw and primary effluent metal concentrations are quite pronounced in two instances. These large variations are the

TABLE 6.2

Metal Limits set for $AlCl_3$ by the City of Windsor

Metal	mg/L
Cd	5
Cr	100
Cu	50
Ni	30
Pb	50
Zn	500

Ref: [Faust, 1983].

direct result of changes in metal concentrations in both the chemical and the recycled sludge. It is felt that if the influent metal concentrations were higher, the resulting influence of contamination would be minimized.

The metal concentrations in the final effluent at Little River were generally less than in the raw wastewater even after the contamination. On the average, the effluent lead concentration hovers around a lead removal threshold of 33 ug/L. The threshold value is defined as the minimum metal concentration consistently attained by the treatment process in question. This value varies for each metal.

6.2.1.2 Zinc

In Figure 6.2 similar patterns are observed for zinc as for lead. The major difference is the higher range of concentrations, 45 to 377 ug/L, in the raw wastewater.

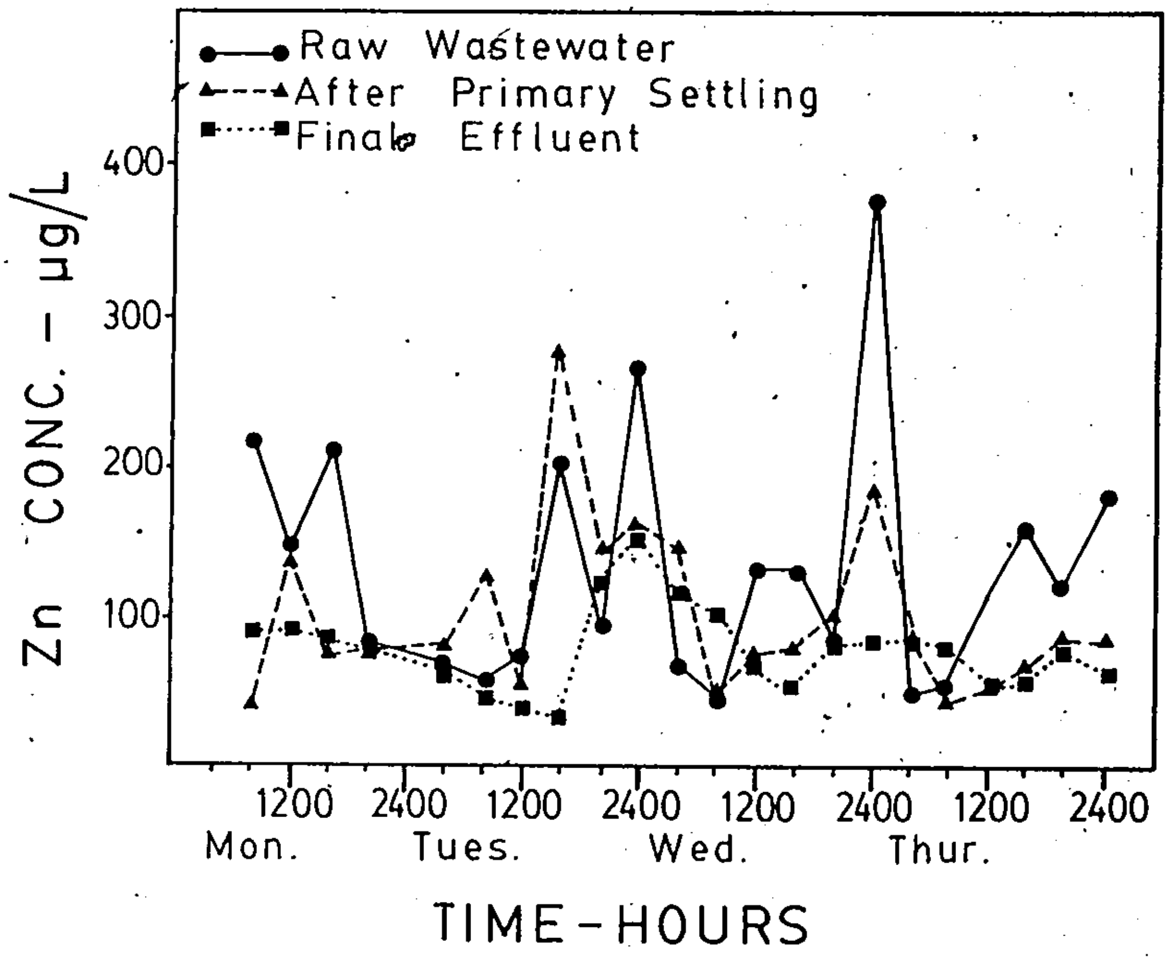

Figure 6.2: DIURNAL VARIATIONS FOR ZINC AT LITTLE RIVER

With the primary effluent ranging from 44 to 277 ug/L, these metal concentrations were in certain instances higher than in the raw wastewater. There also appears to be sufficient removal efficiency in the treatment process, since the final effluent has metal concentrations consistently less than in the raw wastewater.

However, one major difference exists with zinc. No removal threshold occurred. This fact is consistent with the low removals for zinc reported by Nielsen and Hrudey [1981].

6.2.1.3 Cadmium

From the cadmium diurnal variations shown in Figure 6.3, it is observed that the concentrations for all types of wastewater samples varied from 4 to 11 ug/L. As noted previously for lead, the primary effluent metal concentration exceeded the raw wastewater concentration on occassion. However, with the average cadmium contamination not as pronounced as with the other metals, the effluent concentration was generally less than influent concentration. Furthermore, with the effluent varying from 4 to 10 ug/L, it can be stated that a removal threshold exists.

6.2.1.4 Chromium

As can be seen in Figure 6.4, the diurnal variations for chromium were not as pronounced as with the other metals. The entire range of variations for the raw wastewater

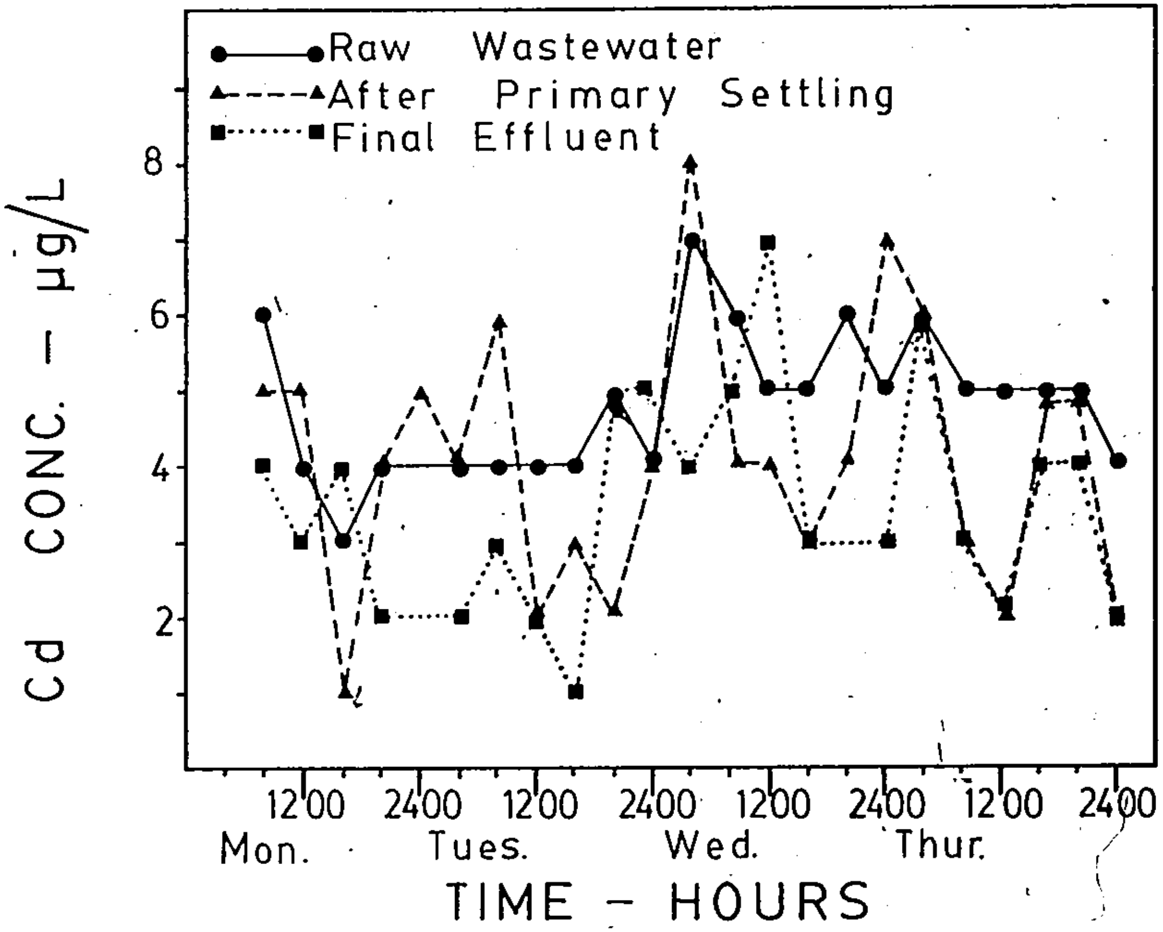

Figure 6.3: DIURNAL VARIATIONS FOR CADMIUM AT LITTLE RIVER

was quite small, 5 to 25 ug/L. All other patterns demonstrated by lead in raw wastewater were also exhibited by chromium.

With regards to the primary effluent, the occassional peaks higher than the raw occurred due to the contamination as discussed previously. However, for chromium there was one occassion when the primary effluent had an extremely high metal concentration. The reason for this sharp rise is most likely an extremely high concentration of metal in either the sludge or feed chemical added.

In studying the chromium effluent, it becomes apparent that a threshold value does exist. From the data presented in Figure 6.4, the lowest metal concentration hovers around 7 ug/L. Occassionally there are increases in the effluent, but these are related to the rapidly increased concentrations in both the raw wastewater and primary effluent.

6.2.1.5 Nickel

From the diurnal variations for nickel shown in Figure 6.5, it is apparent that the variations in concentrations ranged from 6 to 15 ug/L. Considering the fact that the influent has low metal concentrations, and the removal rate is low, it becomes clear why there are no major centrate peaks. If very little metal ends up in the sludge, very little metal can be transferred from the sludge to the centrate. There still exists the possibility of metal contamination of

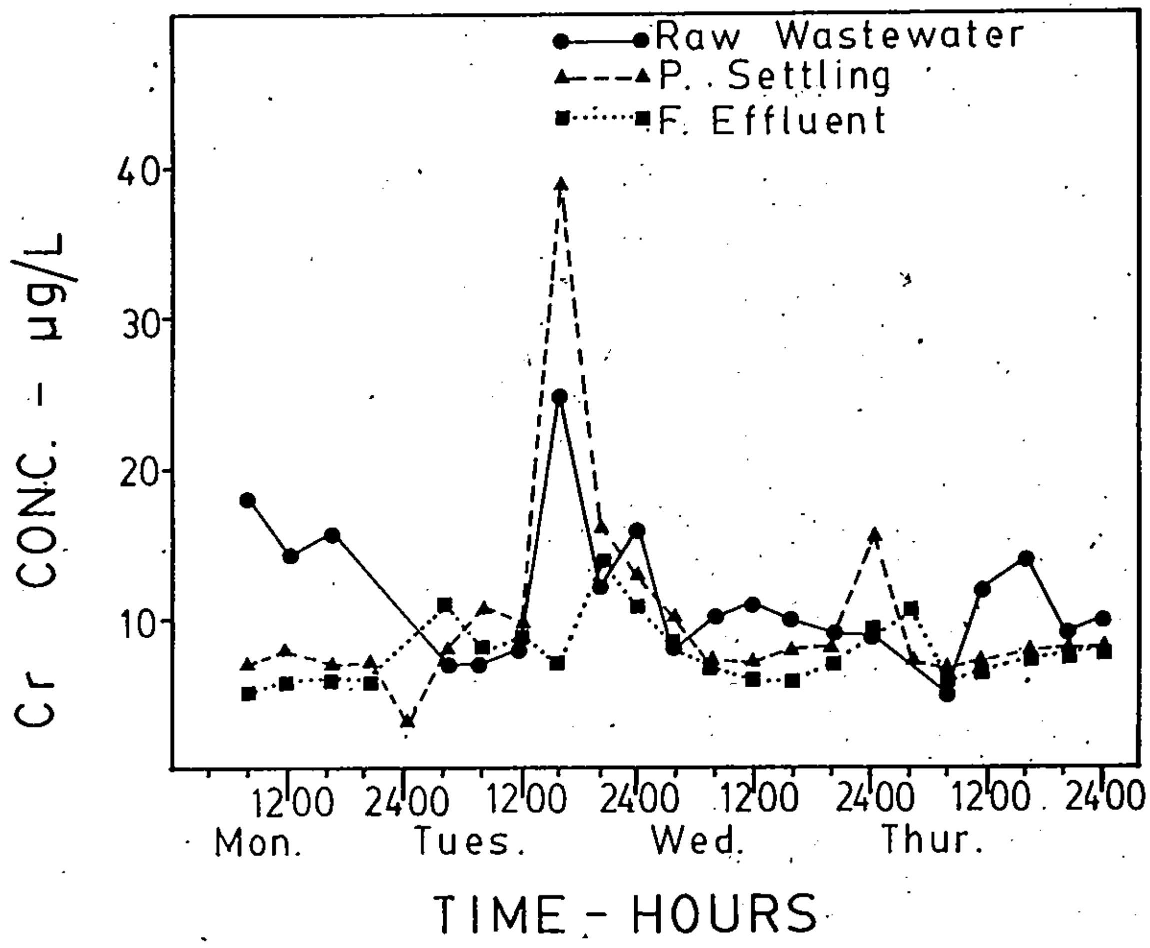

Figure 6.4: DIURNAL VARIATIONS FOR CHROMIUM AT LITTLE RIVER

the primary effluent, but considering the low range of values the problem was not severe. It can be seen that the final effluent generally has a concentration less than the raw, and the removal threshold hovers between 6 and 9 ug/L.

6.2.1.6 Copper

With regard to copper, it appears from Figure 6.6 that the raw wastewater concentrations vary from 19 to 91 ug/L, excluding the high peak observed in the first sample of the day due to centrate recycle.

It appears that the primary effluent is fairly consistent ranging from 20 to 60 ug/L, even with the metal contamination. The final effluent exceeds the raw wastewater only once, indicating consistent removal during the treatment process. The results show a removal threshold of 18 ug/L for copper.

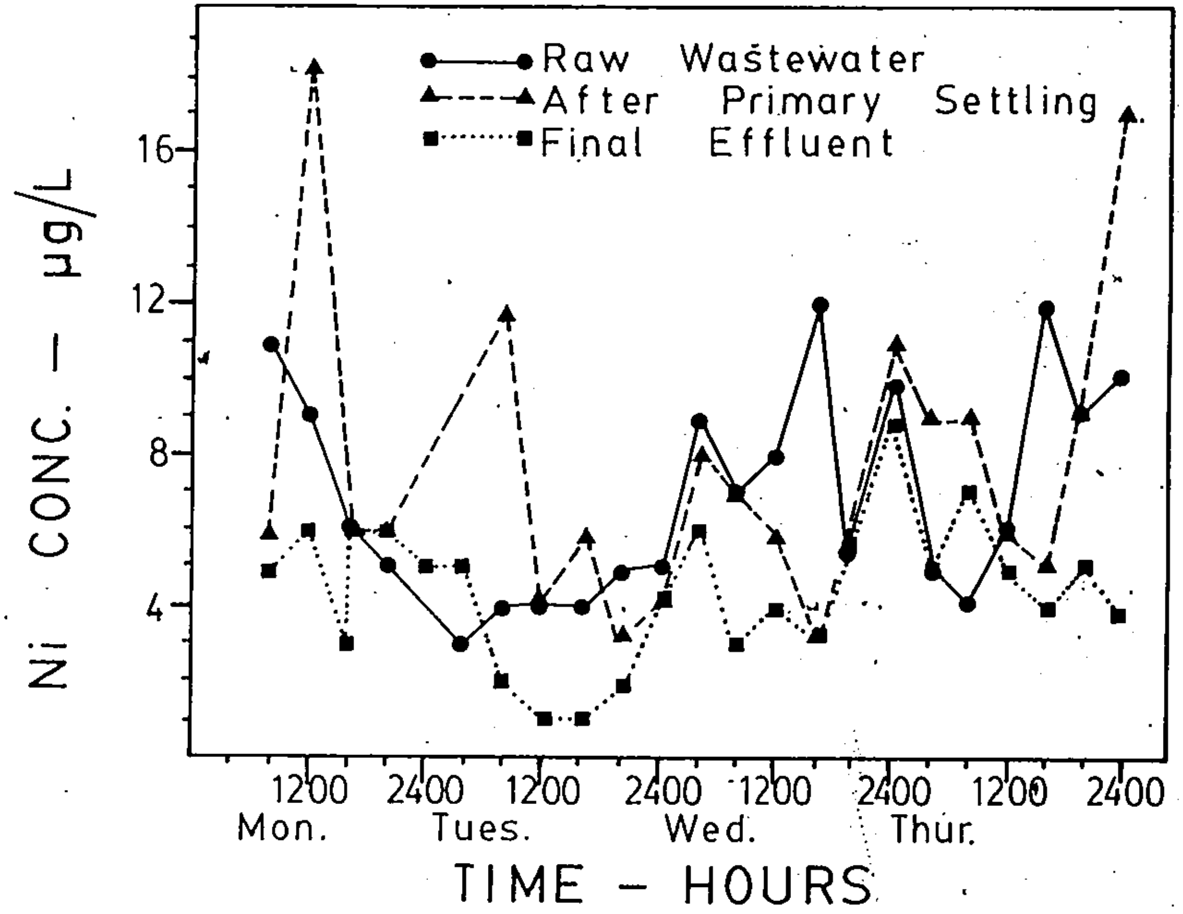

Figure 6.5: DIURNAL VARIATIONS FOR NICKEL AT LITTLE RIVER

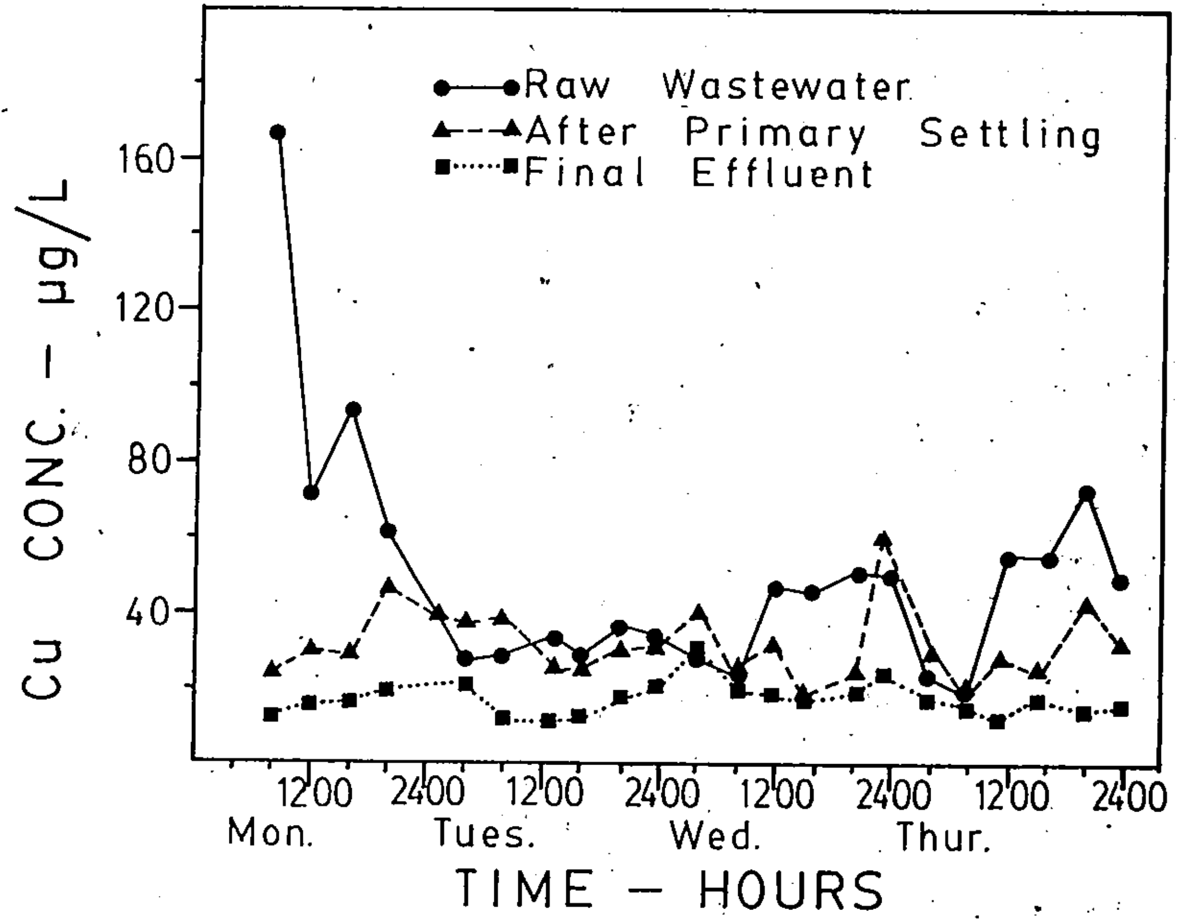

Figure 6.6: DIURNAL VARIATIONS FOR COPPER AT LITTLE RIVER

6.2.2 Daily Variations

6.2.2.1 Lead

Figure 6.7 shows, that lead was present in a fairly small range of concentrations varying from 33 to 55 ug/L. Like the diurnal variations, rapid increases occurred on the days of dewatering. Furthermore, the daily variations show a pattern related to the flowrate. It appears that when the flowrate increases due to heavy precipitation, as on Tuesday, the raw wastewater concentrations decrease due to dilution. While when the dryweather flowrate increases, as on Sunday, the metal concentrations increase.

With regard to the primary effluent, it again becomes evident that chemical usage and sludge wastage are contaminating the primary effluent. This is particularly noticed by the significant rise in concentration on Tuesday. However, even after the addition of metals, the final effluent is consistently lower than the raw, with concentrations varying from 24 to 46 ug/L. Therefore, it can be stated that an overall lead removal efficiency exists. However, it should be noted that when the raw and primary effluent concentrations are high, the final effluent also tends to increase.

6.2.2.2 Zinc

When comparing the daily variations in zinc concentrations, Figure 6.8, to lead, it can be seen that the same

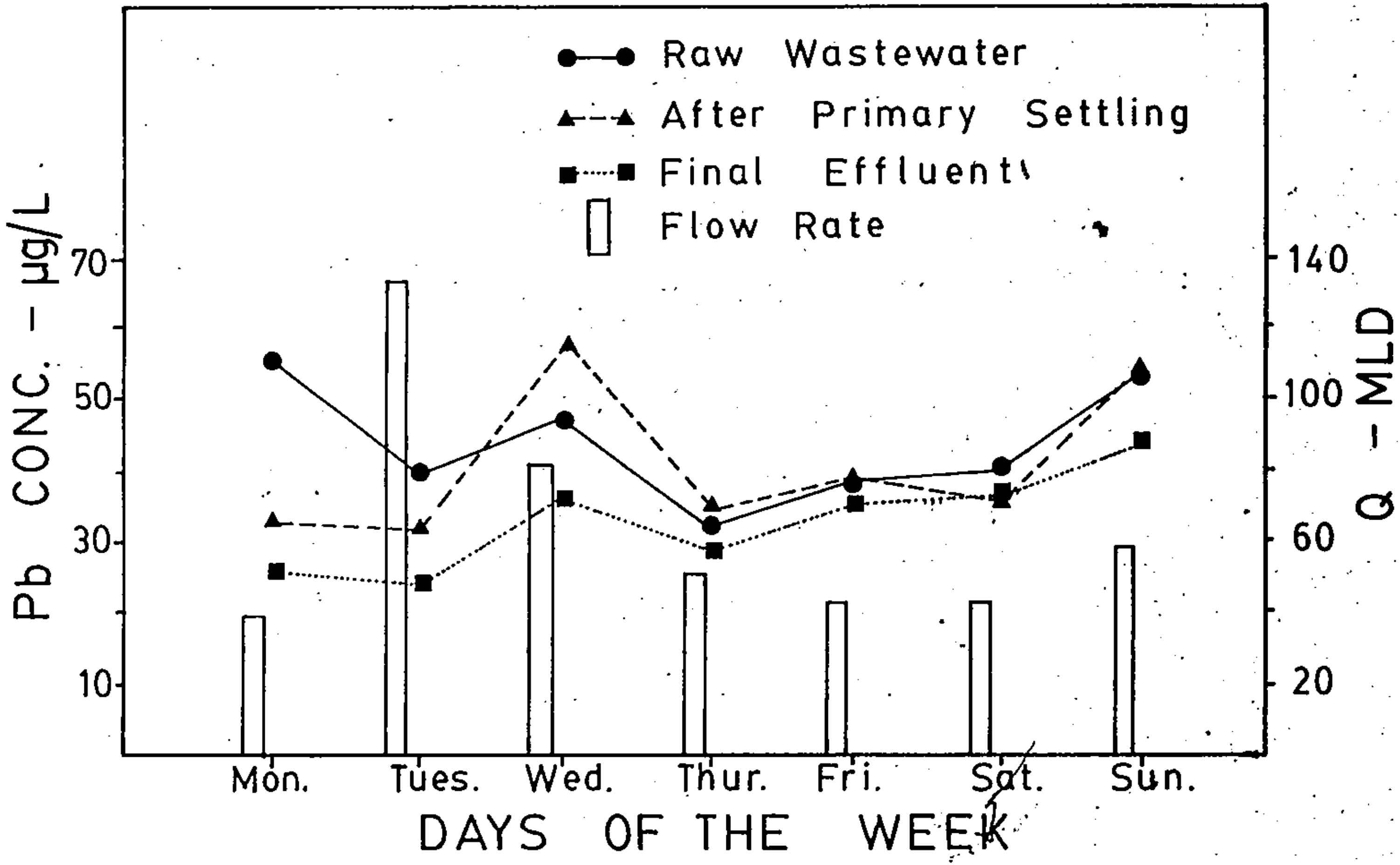

Figure 6.7: DAILY VARIATIONS FOR LEAD AT LITTLE RIVER

overall pattern exists. The only major difference is in the range of concentrations. The zinc values range from 68 to 430 ug/L, which is quite large.

With respect to the final effluent, the daily variations confirm that no removal threshold exists as the concentrations vary from 69 to 156 ug/L. However, it should be noted that initally a threshold appeared, which was at a concentration of 120 ug/L. The change in final effluent can be attributed to the fluctuating removal efficiencies noted elsewhere.

6.2.2.3 Cadmium

From Figure 6.9, it appears that the daily variations in cadmium concentrations are irregular, and range from 2 to 12 ug/L. All other patterns exhibited by Little River composites previously mentioned are repeated for cadmium.

With the final effluent varying from 2 to 9 ug/L, it can be stated that a removal threshold exists as observed in the diurnal variations. Furthermore, on the average the final effluent was less than the raw and primary effluent, indicating that certain removal does occur.

6.2.2.4 Chromium

The daily concentrations for chromium, shown in Figure 6.10, demonstrate the same patterns as lead with respect to flowrates, centrate recycle and contamination from chemi-

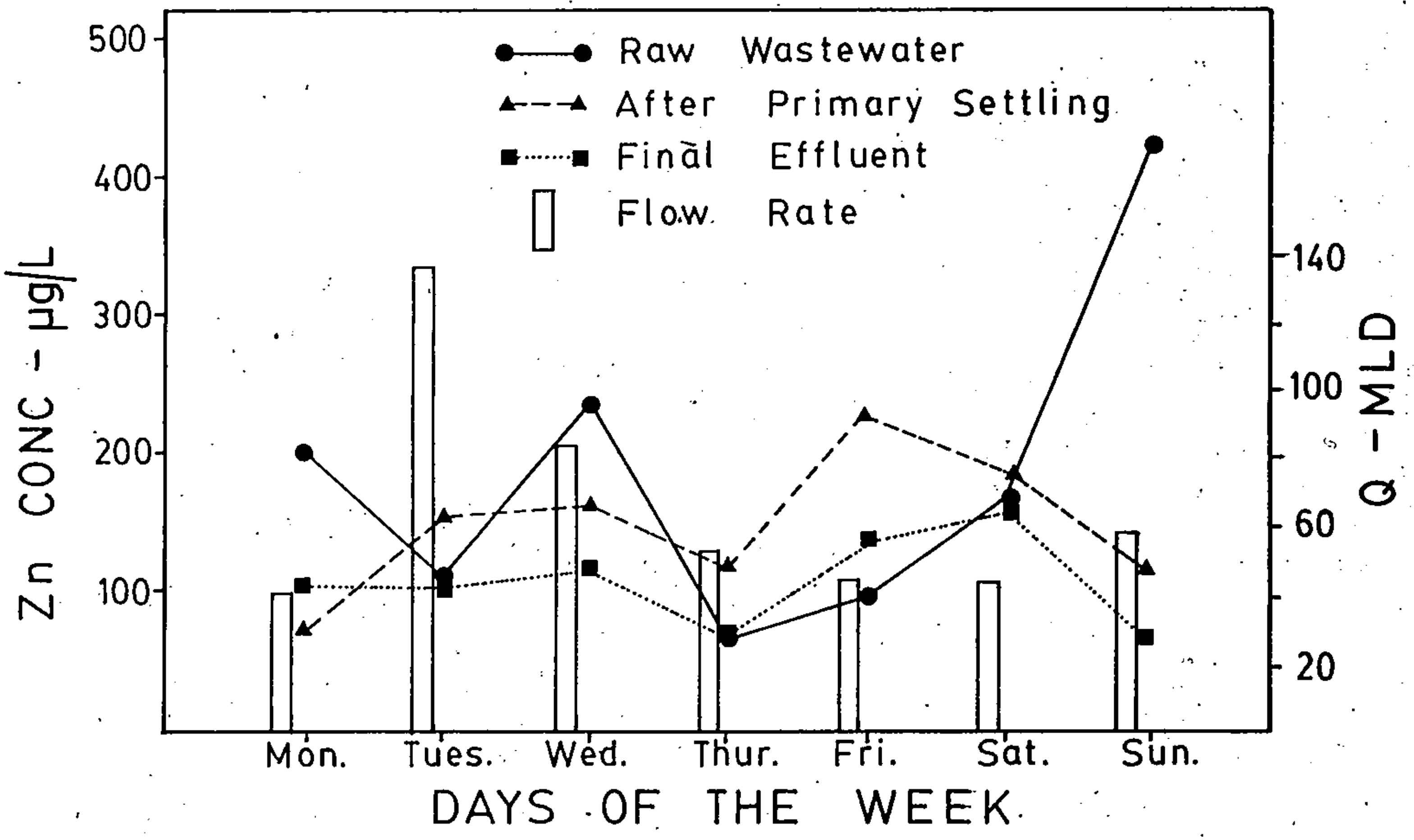

Figure 6.8: DAILY VARIATIONS FOR ZINC AT LITTLE RIVER

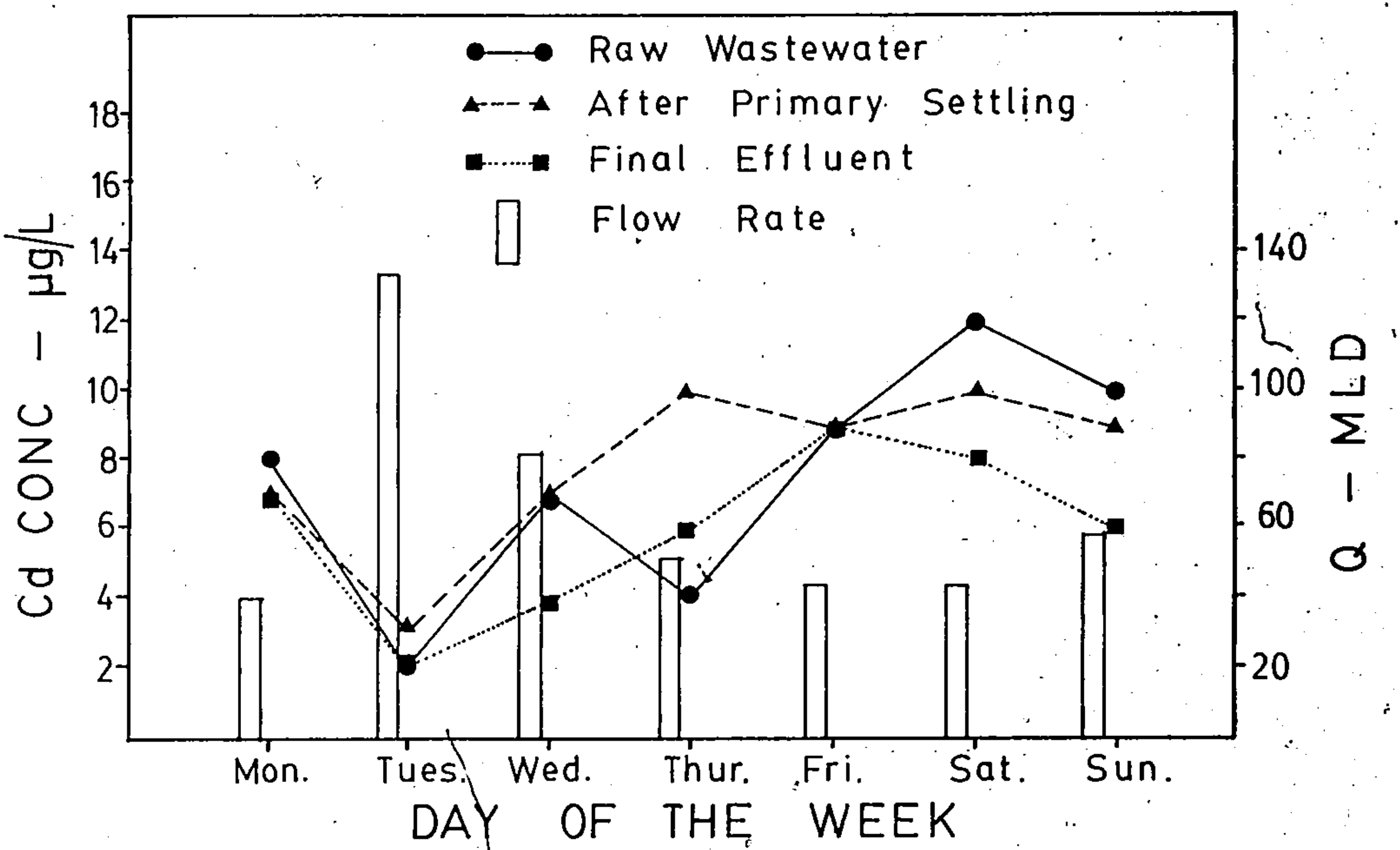

Figure 6.9: DAILY VARIATIONS FOR CADMIUM AT LITTLE RIVER

cals. The raw concentrations maintain a small range, varying from 7 to 18 ug/L. However small, the graph still exhibits the decreased concentration on Tuesday due to dilution and the increased concentration on Sunday from the increased dry weather flow.

Also, one large contamination of the primary effluent appears on Tuesday. Most likely the metal concentration in the feed chemical reached the high end of the set limit, easily increasing the chromium concentration even after diluted. Less likely is the situation where an abnormally high amount of waste sludge is added to the primary clarifier, containing high amounts of chromium.

As the daily variations indicate, the final effluent was almost always less than the raw. The only deviation occurred when the primary effluent was exceedingly high in chromium on Tuesday. Still the concentration in the final effluent approached the normal level exhibited for the remainder of the week, indicating a removal threshold. This removal threshold appears to be 6 ug/L, which is quite low.

6.2.2.5 Nickel

Figure 6.11 shows that the nickel variations ranged from 5 to 23 ug/L. These variations show that on Friday either the centrate recycle concentrations for nickel was higher than the other metals, or an abnormally high industrial discharge of nickel was released. Also, the pattern

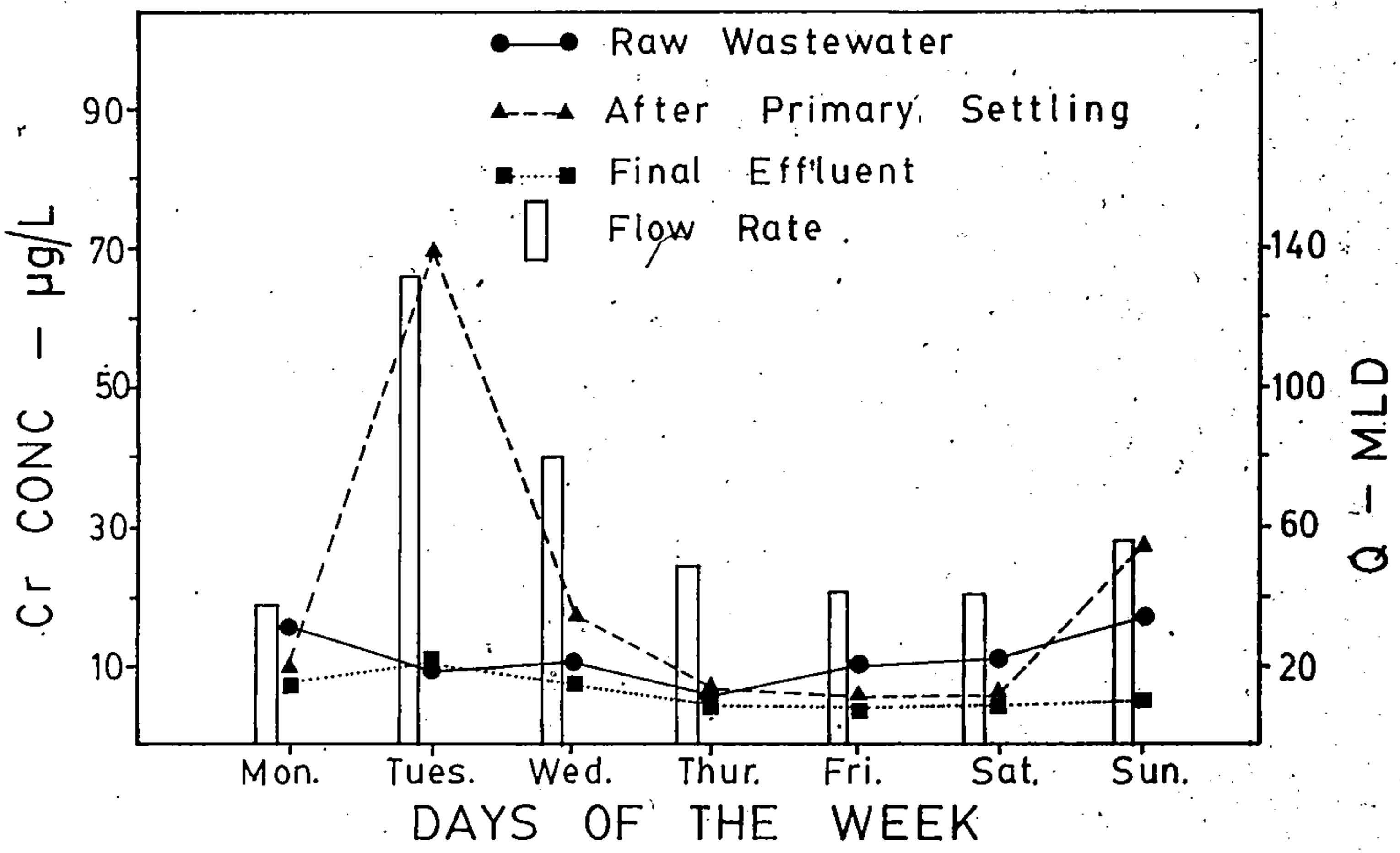

Figure. 6.10: DAILY VARIATIONS FOR CHROMIUM AT LITTLE RIVER

in fluctuations in nickel concentration due to flowrate is different from the other metals. The concentrations still decreased due to dilution on Tuesday but the concentration rise due to an increase in dry weather flow was not as large as for the other metals.

It can be seen that the impact of contamination from chemicals and sludge recycle still occurs. In fact the contamination occurs all week except for Friday and Saturday. Since the raw concentrations were high, it makes the contamination impact negligible.

On the average, the final effluent had a removal threshold of 8 ug/L with the effluent generally less than the raw. When the effluent level does exceed the raw, it was due to the highly contaminated primary effluent.

6.2.2.6 Copper

As Figure 6.12 indicates, the pattern demonstrated by the majority of metals at Little River was also repeated by copper. There was an increase in concentrations due to contamination from chemicals and recycled sludge and also due to an increase in dry weather flow. The raw wastewater exhibited a large range of concentrations, varying from 24 to 83 ug/L.

However, even with the large fluctuations in the raw wastewater concentrations, the final effluent was consistent and shows a removal threshold of 18 ug/L, consistent with the diurnal variations.

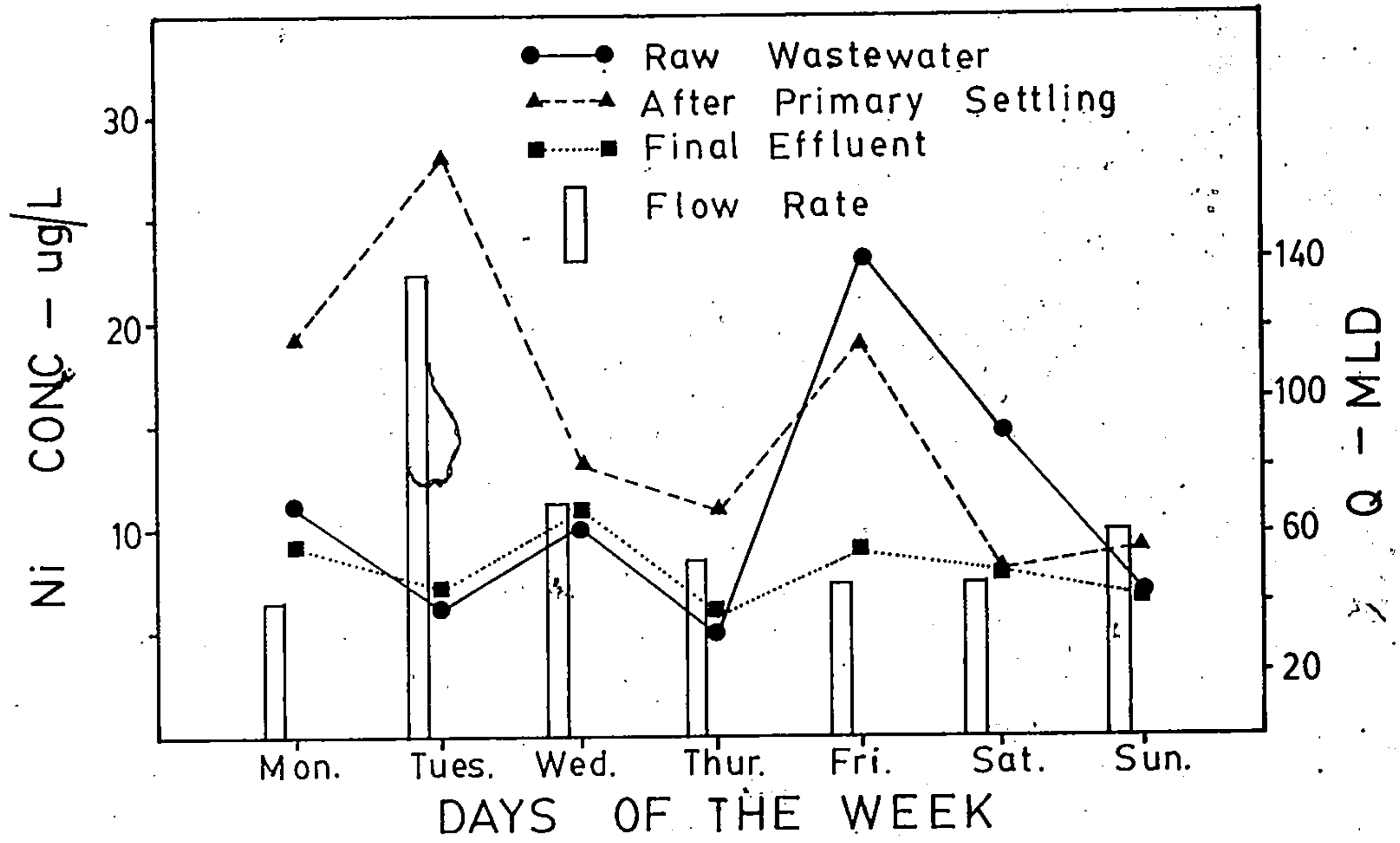

Figure 6.11: DAILY VARIATIONS FOR NICKEL AT LITTLE RIVER

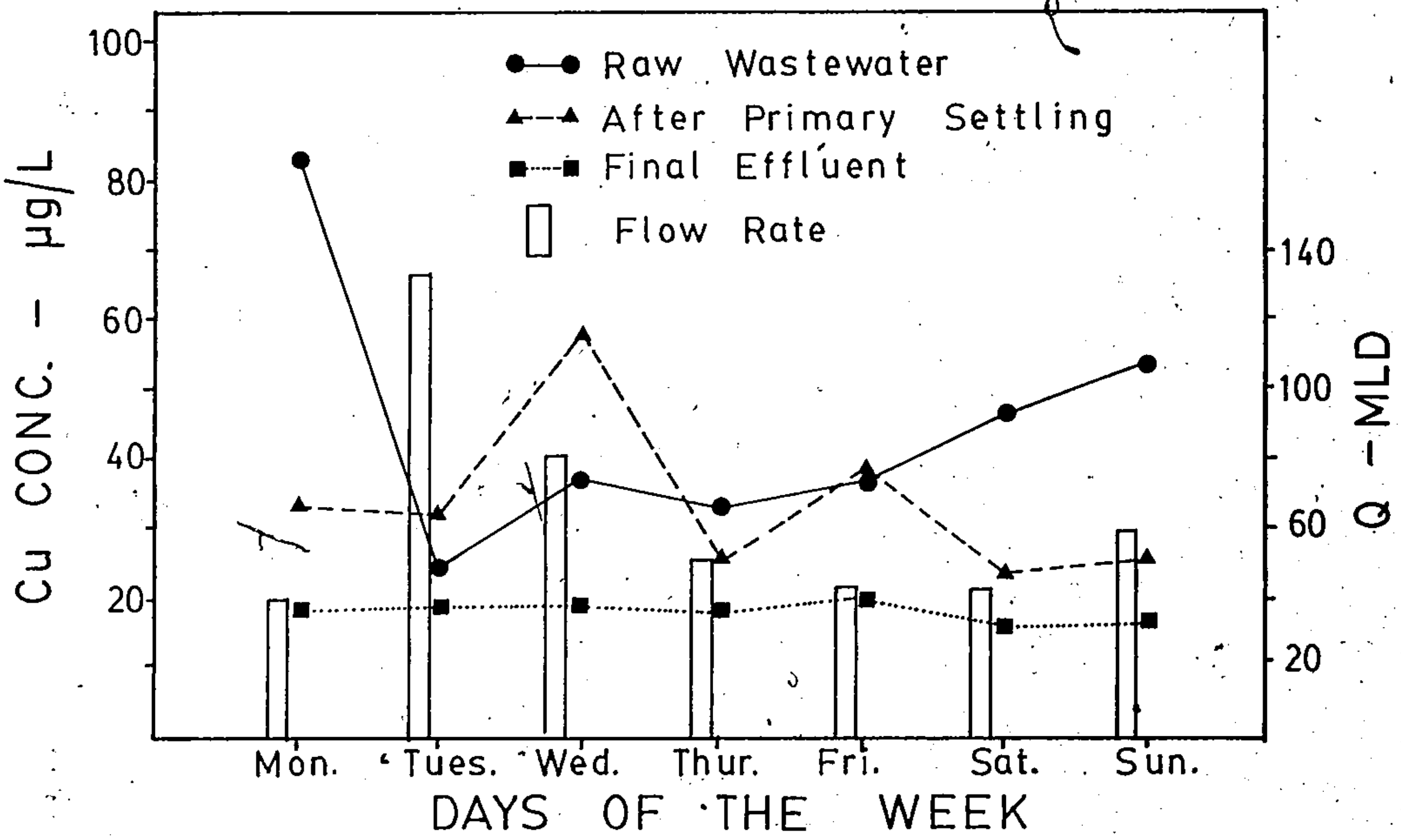

Figure 6.12: DAILY VARIATIONS FOR COPPER AT LITTLE RIVER

6.2.3 Phase Distributions of Metals

6.2.3.1 Copper

Figure 6.13 indicates that the distribution of different phases, suspended and dissolved, for copper were quite variable. This large variation coincides with a similar behaviour observed by Patterson [1978], who also reported that each metal acted randomly and independently according to the nature of the wastewater.

From analyzing the data, it can be seen that natural precipitation in the sewers due to hydrogen sulfide did not have a significant effect on the metals. This contradicts the trend observed by Black [1976], where by the time wastewater reaches the plant, the majority of the metals are insoluble. The low insolubility is especially apparent on Wednesday and Friday. It should be mentioned that Maruyama _et al._ [1975] observed that when the concentrations are low, natural precipitation was not great. This fact can then be taken as the contributing factor at Little River where the metal concentrations were low. However, there appears to be some contradiction to this statement when observing the Sunday values. On Sunday there appears to be a greater percentage of suspended metals. The reason for the change can be attributed to the increased dry weather flowrate, where the increase consisted of a higher proportion of suspended metals. Most likely an industrial discharge occurred.

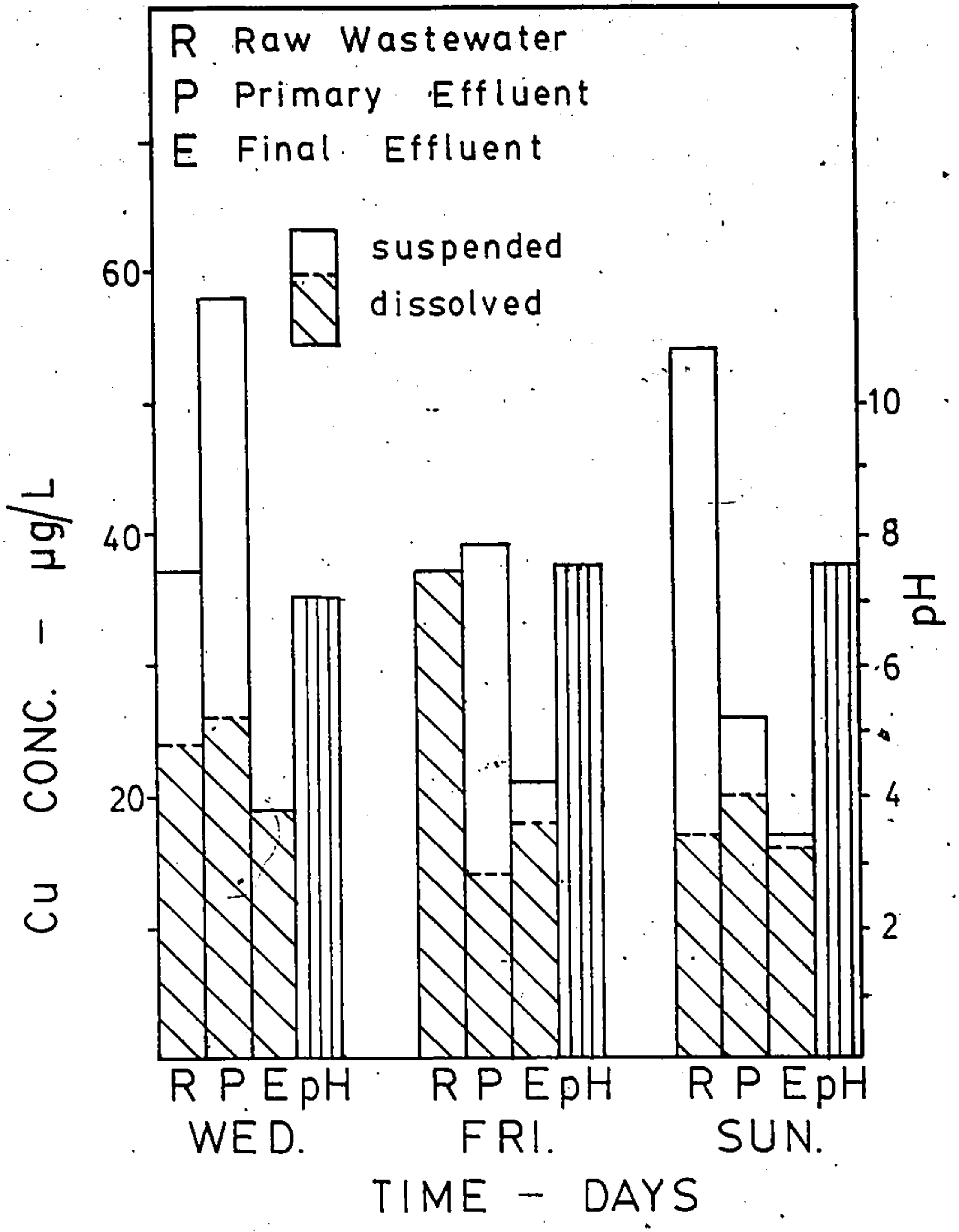

Figure 6.13: COPPER PHASE FRACTIONS AT LITTLE RIVER

Another observation, differing from those reported in the literature, concerns the increase in the dissolved to total ratios in the primary effluent. Studies have shown that as treatment progresses, the ratio of dissolved to total metal increases, since the suspended metals are removed, leaving only the dissolved metals [Aulenbach et al., 1983, Chen et al., 1974, Oliver and Cosgrove, 1974 and Barth et al., 1965]. This general pattern can be seen in Table 6.3 However, Table 6.4 indicates that the opposite occurred at Little River where the ratio of dissolved to total metal decreases after the primary treatment and then increased in the effluent. By examining the phase fraction figure the following reasons can be given.

First, when the metal contamination occurs by sludge recycle and feed chemical, the majority of metals must be in suspended form, thereby decreasing the ratios as shown by Wednesday's data. Second, as demonstrated by Fridays results, some complexation of copper does occur due to the addition of the $AlCl_3$ Similar observations have been shown by [Argaman and Weddle, 1973 and Kodukula et al., 1983]. Further, it becomes apparent that when the raw wastewater has a dissolved concentration below 25 ug/L, as on Wednesday and Sunday, no reduction in dissolved metals occurs. While when the concentration is higher, as on Friday, some reduction is obtained. This type of pattern indicates that a complexing limit for copper exists which is dependent on the nature of wastewater and the chemicals added. This complexing limit is defined as the concentration where no more change from soluble to insoluble will occur due to chemical reaction with the phosphorous chemical. Each type of metal has its own limit. Examination of data for the other metals indicates a similar behaviour. From the Sunday data, it is observed that the normal removal patterns exist with the higher percentages of suspended metals. This pattern evolves due to the reduction of suspended metals through settling in the primary clarifier.

With respect to the effluent phase fractions, it is seen that the effluent fractions are consistent with those of other plants, as shown in Table 6.5 This consistent effluent is due to the biological action in the aeration tank, followed by successful settling in the secondary clarifier.

6.2.3.2 Zinc

As Figure 6.14 indicates, all the patterns exhibited by copper are also repeated for zinc. The only difference is the concentration at which complexation occurs. For zinc, the metals complex only when the dissolved metals are in excess of 50 ug/L, as on Wednesday and Friday.

Table 6.5 shows that the zinc levels in the Little River effluent are still lower than those reported elsewhere. Furthermore, it is seen that the aeration tank can resolubi-

TABLE 6.3

General Pattern of Dissolved to Total Metal Ratios

Metal	Sewage Type	Ratio
Ni	Raw	67
	P. Eff.	79
	Eff.	81
Cd	Raw	17
	P. Eff.	33
	Eff.	100
Zn	Raw	24
	P. Eff.	51
	Eff.	71
Pb	Raw	5
	P. Eff.	13
	Eff.	40
Cu	Raw	55
	P. Eff.	76
	Eff.	88
Cr	Raw	7
	P. Eff.	8
	Eff.	17

Ref: [Oliver and Cosgrove, 1974].

TABLE 6.4

Dissolved to Total Metal Ratios for Little River

Metal	Sewage Type	Range for Wed.,Fri.,Sun.	Average
	Raw	70-88	79
Ni	P. Eff.	54-100	71
	Eff.	73-100	91
	Raw	40-100	70
Cd	P. Eff.	44-100	57
	Eff.	44-100	76
	Raw	8-79	55
Zn	P. Eff.	16-47	32
	Eff.	16-81	73
	Raw	50-100	74
Pb	P. Eff.	46-87	67
	Eff.	46-100	70
	Raw	32-100	66
Cu	P. Eff.	24-45	35
	Eff.	86-100	93
	Raw	33-82	66
Cr	P. Eff.	28-83	63
	Eff.	63-100	82

TABLE 6.5

Comparison of Metal Ratios for Little River

Metal	Sewage Type	Little River Concentration ug/L		[Oliver and Cosgrove, 1974] Concentration ug/L	
		Tot.	Dis.	Tot.	Dis.
Cu	Raw	43	20	310	170
	P. Eff.	41	20	210	160
	Eff.	19	18	80	70
Cd	Raw	9	6	6	1
	P. Eff.	8	5	3	1
	Eff.	7	4	1	1
Pb	Raw	47	34	230	12
	P. Eff.	47	15	90	12
	Eff.	39	28	15	6
Ni	Raw	14	10	330	220
	P. Eff.	14	8	280	220
	Eff.	9	8	270	220
Zn	Raw	256	101	2400	570
	P. Eff.	123	49	1130	580
	Eff.	106	70	560	400
Cr	Raw	13	8	290	20
	P. Eff.	18	7	130	10
	Eff.	7	6	60	9

Ref: [Oliver and Cosgrove, 1974].

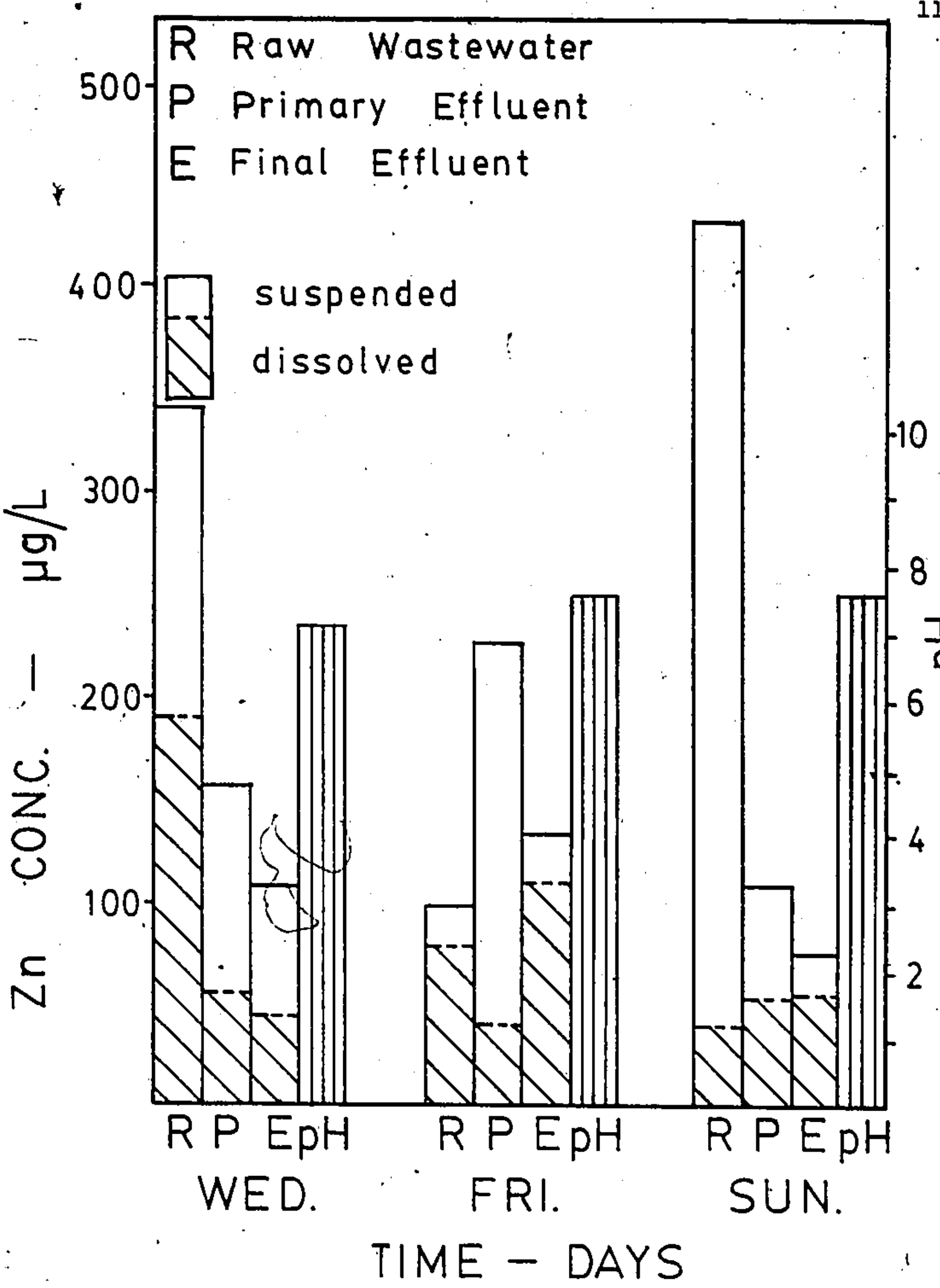

Figure 6.14: ZINC PHASE FRACTIONS AT LITTLE RIVER

lize the suspended metals. This pattern was also was observed by Kiang and Metry [1982].

6.2.3.3 Chromium

Figure 6.15 indicates that chromium demonstrates most of the same patterns exhibited by copper. However, the significant difference was the large increase of metals on Sunday, with the majority of it in dissolved form. This can be attributed to the changing band of complexation. Lanouette [1977] has shown that chromium can precipitate over a large range of pH, 5 to 10, depending on the concentration. With 7.5 being the optimum pH, at a concentration of 200 ug/L, it becomes evident that the wastewater was in a condition where precipitation and/or solubilization could occur. These actions can then explain why some complexation occurred on Wednesday and Friday, and while solubilization occurred on Sunday.

For the effluent no major difference occurred. Apparently the biological floc can adsorb only metal ions when the concentrations are higher than 5 ug/L. This was seen on Wednesday and Friday when no reduction in dissolved concentration occurred, while on Sunday significant reduction had occurred, since the dissolved concentration had exceeded 5 ug/L. As with the other metals, dissolved chromium concentrations are less than in the other wastewater plants [Table 6.5].

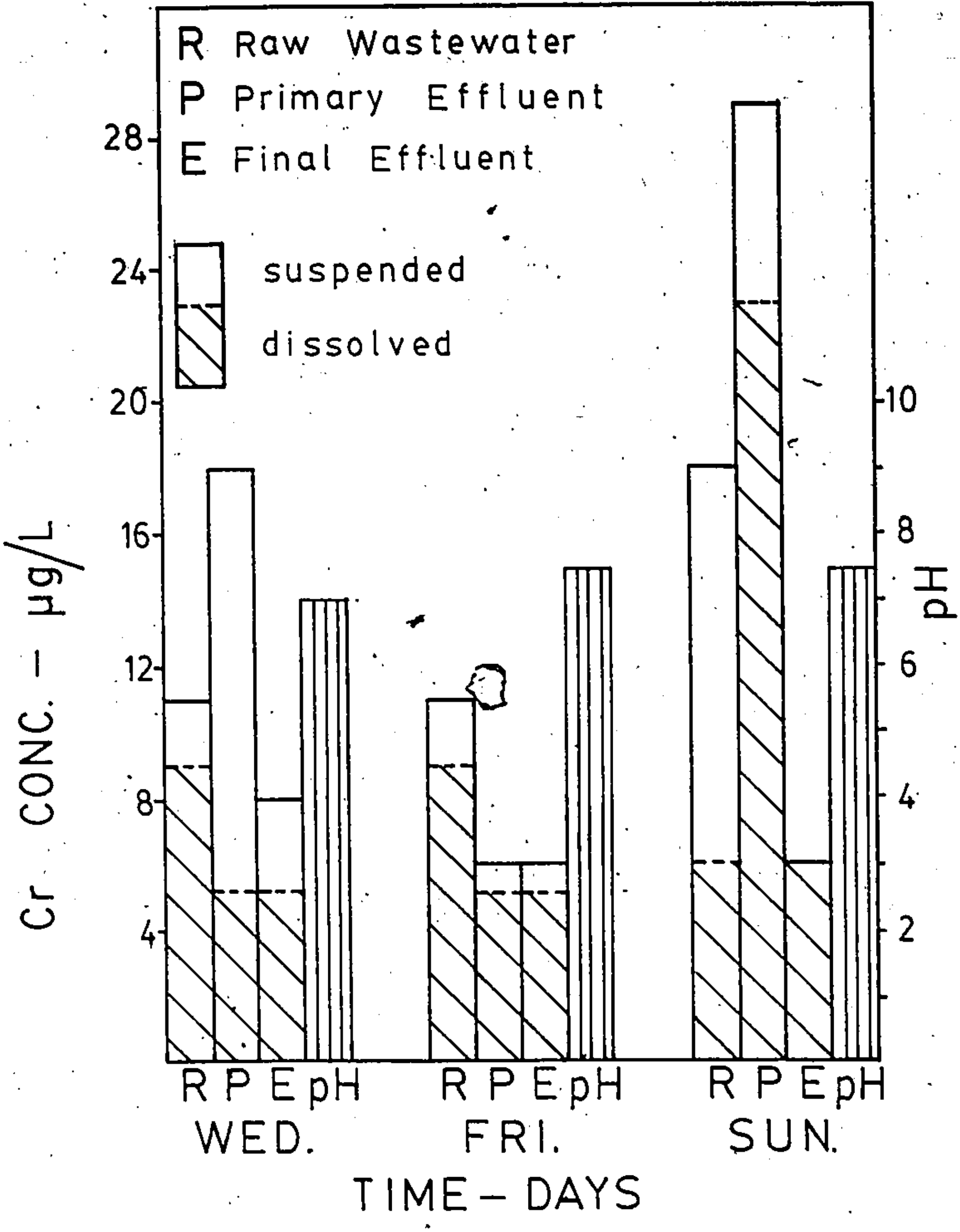

Figure 6.15: CHROMIUM PHASE FRACTIONS AT LITTLE RIVER

6.2.3.4 Cadmium

Figure 6.16 shows that the low suspended concentrations in the raw wastewater were maintained throughout the week. However, the primary effluent showed one difference. There was no apparent increase in the metal levels which indicates that the contamination was just enough to maintain a constant level. Even so, the data still show that when the dissolved concentrations are above a certain value, 5 ug/L, complexation will occur.

For the final effluent, there was reduction in suspended form for two of the three days. Finally one observation that differed when compared to the values presented in Table 6.5, was the final dissolved concentration of cadmium. As can be seen, Little River has higher cadmium concentrations in the effluent due to the difference in source of the wastewater.

6.2.3.5 Lead

Figure 6.17 indicates that the basic pattern exhibited by cadmium was repeated by lead. No major removal occurred, with only minor changes in the phase distributions, where the dissolved fraction hovers around 35 ug/L.

With regard to the effluent, Table 6.5 shows that lead also existed with higher dissolved concentrations. This pattern indicates that the biological floc at Little River can not handle lead as well as other plants. A possible

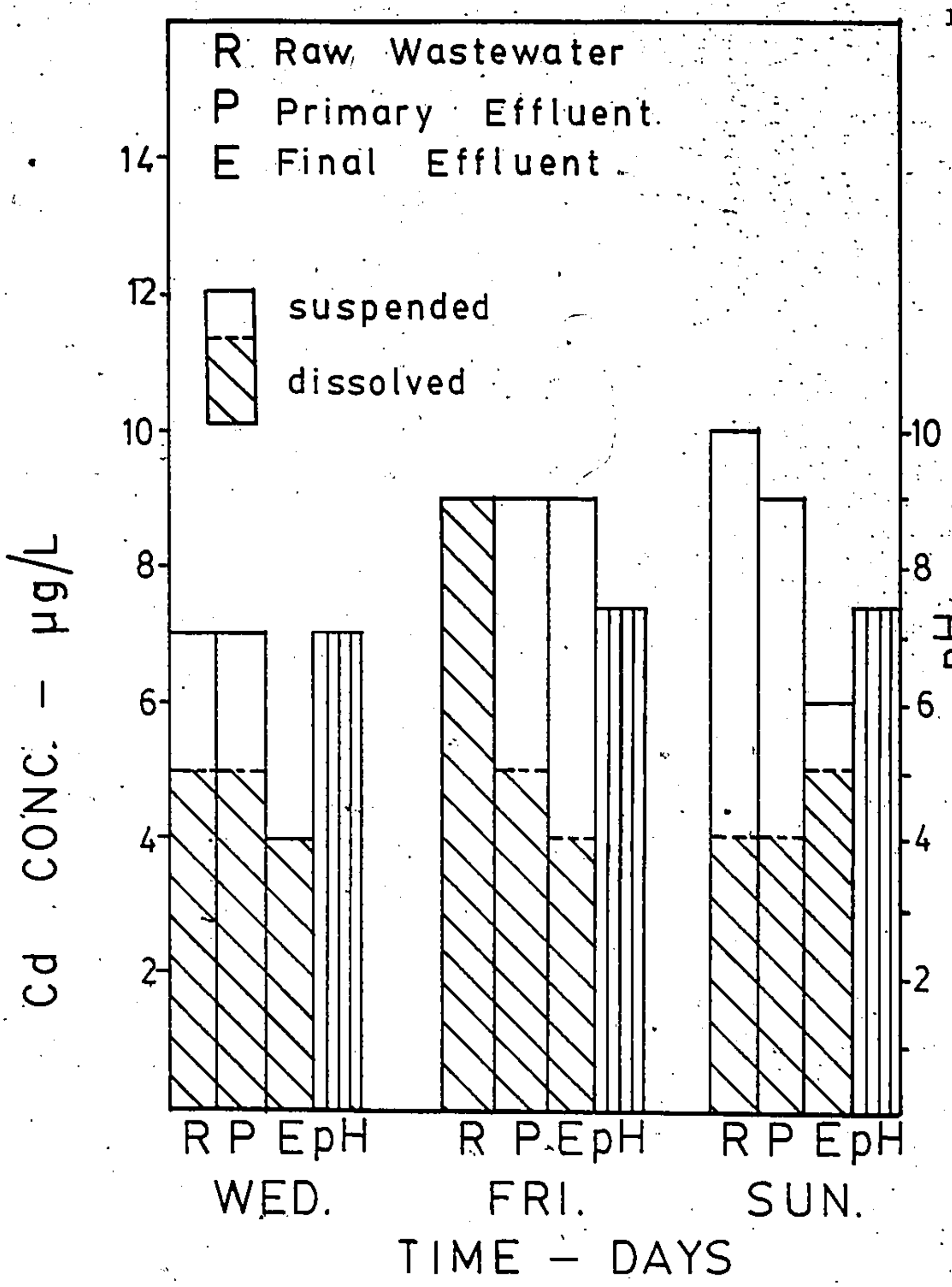

Figure 6.16: CADMIUM PHASE FRACTIONS AT LITTLE RIVER

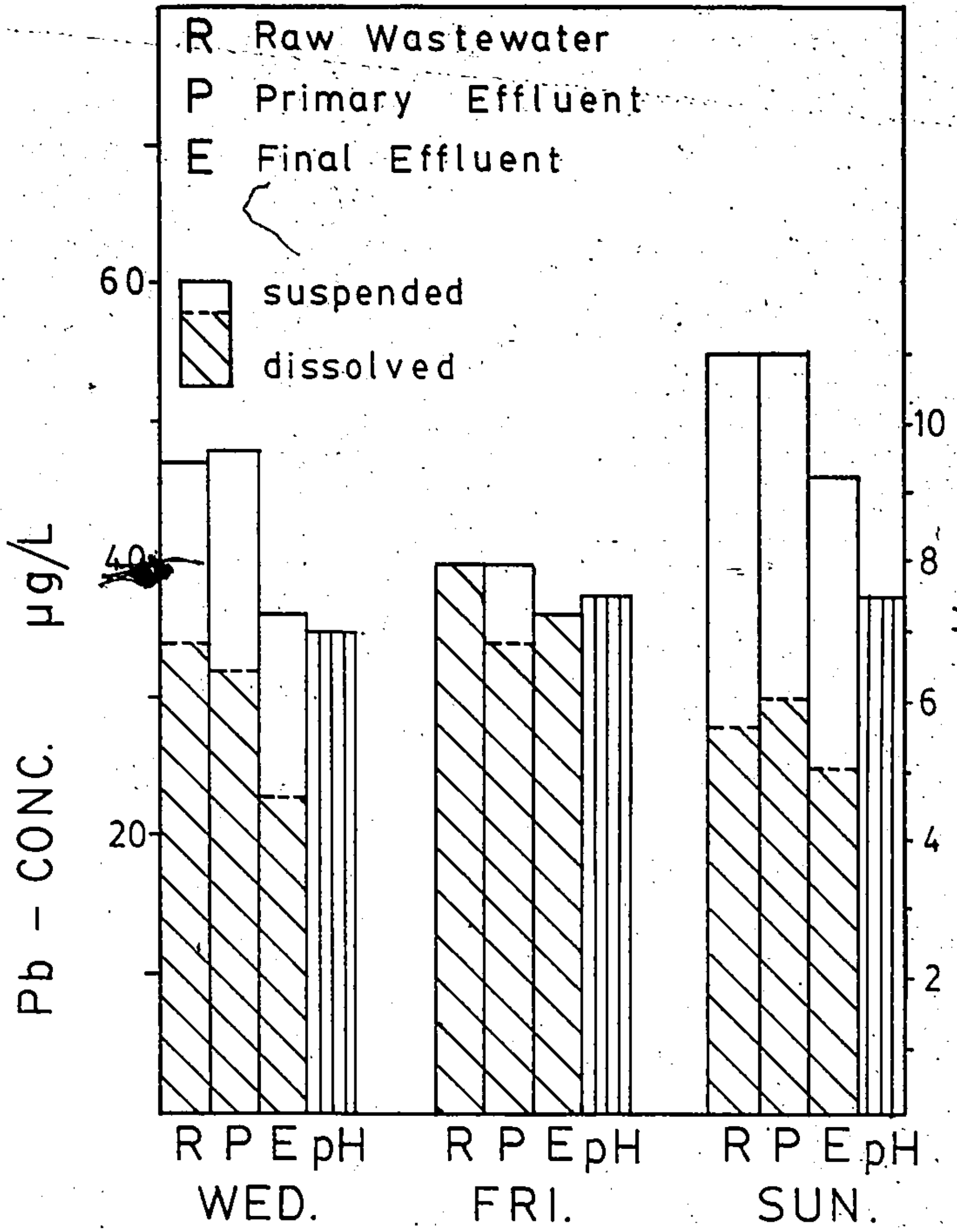

Figure 6.17: LEAD PHASE FRACTIONS AT LITTLE RIVER

reason could be that Little River had lower concentrations than the comparison wastewater.

6.2.3.6 Nickel

For nickel, the consistent high dissolved percentages in the raw wastewater can be seen in Figure 6.18 This percentage occurs even on Sunday. With nickel being different than the other metals, a strong case industrial discharge can be made. If it were not an industrial discharge, the pattern would be more consistent and similar to that shown by five of six metals.

With respect to the other patterns, the same ones described for copper were repeated. There does exist a maximum complexation value of 8 ug/L, combined with the effluent dissolved values less than those tabulated in Table 6.5.

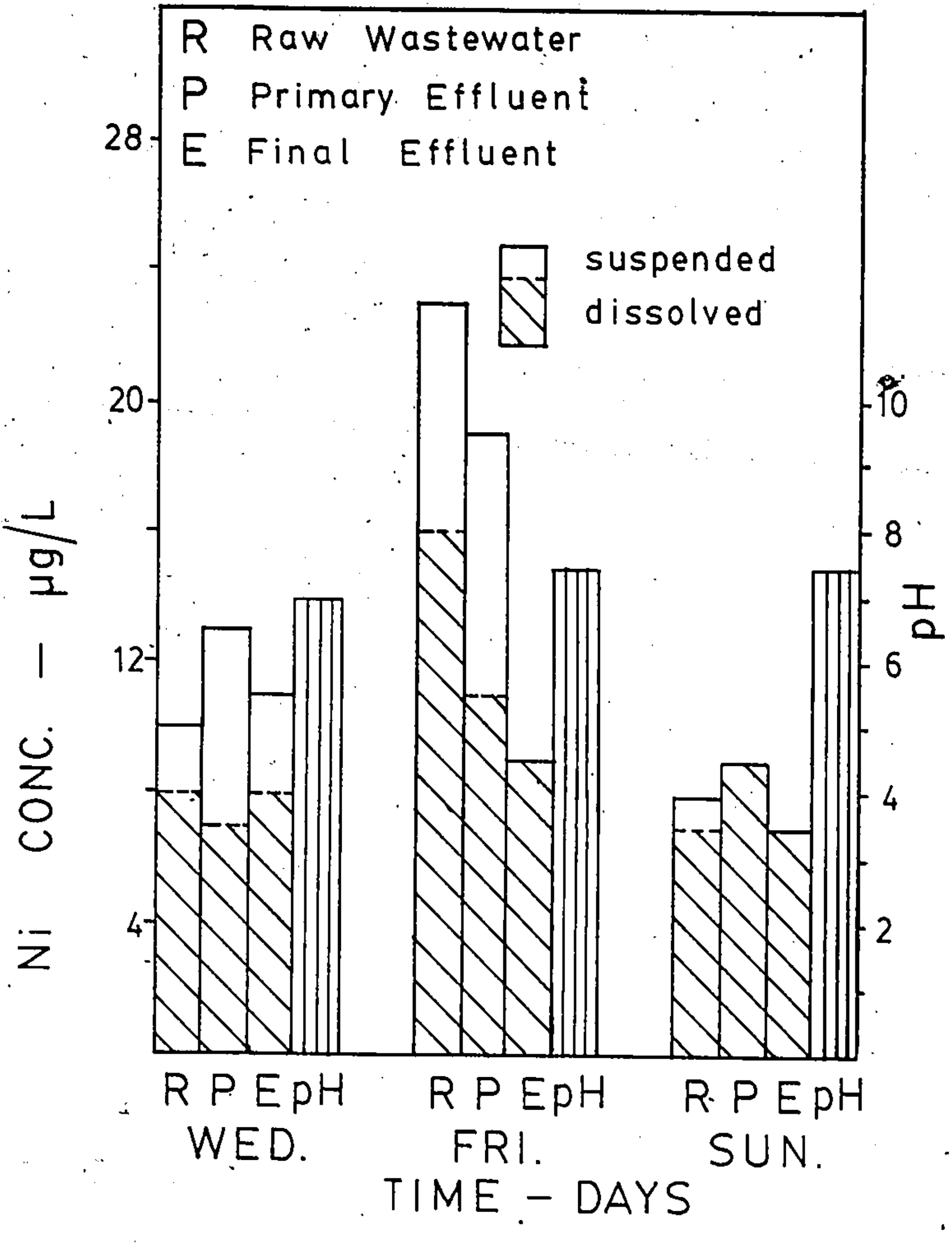

Figure 6.18: NICKEL PHASE FRACTIONS AT LITTLE RIVER

6.2.4 Removal Efficiencies

As Table 6.6 indicates, there is a wide range for the overall removal efficiencies of all the metals. The values ranged from the high removal of 84% for zinc, to the high addition of 600% for chromium.

In analyzing the primary removal it becomes quite clear that for all the metals the removal efficiencies are erratic. For certain days high removals occur while on other days high amounts of addition occur. These jumps can all be attributed to contamination from the $AlCl_3$ and the wasted activated sludge. Again it can be observed that the contamination occurs randomly, with no means of applying a correction.

The same randomness occurrs when the biological removals are studied. However, the phase figures indicated that the biological treatment was successful in removing the suspended metals while only slightly removing some dissolved metals.

When comparing the average 7-day overall removal rates to those of other plants in Table 6.7, it quickly becomes clear that Little River has low removal efficiencies. However it should be remembered that Little River has low metal concentrations in raw wastewater which results in lower removal percentages. In general the removal trends for each metal are similar to patterns noted elsewhere. Furthermore,

TABLE 6.6

Removal Efficiencies for Little River

Day	Type of Removal	Metal Concentration in ug/L					
		Ni	Cd	Zn	Pb	Cu	Cr
Mon.	P	-73	13	62	36	60	38
Dec. 5	S	53	0	-37	26	46	20
1983	O	18	13	48	53	78	50
Tues.	P	-367	-50	-38	15	-33	-600
Dec. 6	S	75	33	33	29	41	84
1983	O	-17	0	7	40	21	-10
Wed.	P	-30	0	34	-2	-57	-64
Dec. 7	S	15	43	27	25	67	56
1983	O	-10	43	52	19	49	27
Thur.	P	-120	-150	-74	-6	24	-14
Dec. 9	S	46	40	43	17	28	38
1983	O	-20	-50	3	12	45	29
Fri.	P	17	0	-133	0	-5	46
Dec. 9	S	53	0	41	8	46	0
1983	O	61	0	-38	8	43	46
Sat.	P	47	17	-10	10	49	33
Dec. 10	S	0	20	18	0	33	25
1983	O	47	33	9	10	66	50
Sun.	P	-13	10	74	0	52	-61
Dec. 11	S	22	33	40	16	35	79
1983	O	13	40	84	16	69	67
Average 7-Day Removal		13	11	24	23	53	37
Standard Deviation		32	32	40	17	19	25

P=Primary removal thru settling.
S=Secondary removal thru biological action.
O=Overall removal.

it is important to remember that even with the low removals, Little River has effluents comparable to similar plants reported by Nielsen and Hrudey [1981].

Table 6.7: Average Overall Metal Removal Efficiencies in Various Municipal Activated Sludge Treatment Systems

Location	Average Overall Percent Removal						Remarks
	Ni	Cd	Zn	Pb	Cu	Cr	
Little River Treatment Plant	18	11	24	24	51	37	
Ontario Average	16	80	77	93	73	79	Oliver and Cosgrove, 1974
New York, USA	17	38	36	--	45	48	Klein et al, 1974
Zurich, Switzerland	45	35	60	65	55	70	Roberts et al, 1977
Honolulu, Hawaii	54	55	73	76	83	35	Nomura and Young, 1974
United Kingdom	70	89	94	92	96	67	Lester et al, 1979

6.2.5 Mass Balance

6.2.5.1 General

The mass balance at Little River was used to determine three phenomena:

1. the metal contribution from the phosphorous removal chemical, $AlCl_3$
2. the effect of recycled centrate on the raw wastewater.
3. the metal concentrations that exist in the sludge cake.

The calculations used to analyze the data have been placed in Appendix A. Before the results of these three investigations are disccussed, it should first be explained how the mass balance was performed.

With composite samples being collected for one week, it was decided to do a single day average based on the entire weeks' samples. This in fact was necessary since the sludge samples were obtainable only three times in the week. However, they contain the metals removed for the entire week. For averaging results over the week, the metal concentrations were weighted by flow to give equal representation.

As indicated earlier, there were periods of overflow in the plant due to the limited capacity of the plant. Thus certain amounts of metals are removed from the system through overflowing. Now if the overflow would occur occasionally, both the concentrations of the overflow and wastewater would fluctuate due to dilution by the surface runoff. However, during this study at Little River, the overflow occurred consistently for the entire week, allowing for the concentrations in the overflow to be set equal, to the concentrations in the influent.

The mass balance was completed by comparing all the 'mass in' to all the 'mass out'. The difference was then attributed to the $AlCl_3$ chemical.

6.2.5.2 Metals Added Through $AlCl_3$

In Table 6.8, the metals added through $AlCl_3$ are listed. The values vary from the lowest of 82 g for cadmium, to the highest of 10396 g for zinc. When the percentage of metals by mass in $AlCl_3$ solution are observed, it can be seen that the values range from 0.001% to 0.141%. Even though these values seem low, one must not forget the relativly large amounts of wastewater treated at the plant, giving significant amounts of metal added to the wastewater.

From the mass of metal added, the concentrations of metals existing in the $AlCl_3$ solution were calculated. As the results indicate, the metal concentrations in the chemicals exceed the limits set by the City of Windsor. Thus, with this waste chemical being so contaminated, it justifies the explanation of chemical contamination of the primary effluent.

TABLE 6.8

Metals Added Through $AlCl_3$ Solution

Metal	Mass g	% of Metal in $AlCl_3$ Solution as received (by mass)	Concentration in $AlCl_3$ Solution as received mg/L
Ni	310	.003	31
Cd	82	.001	11
Zn	10396	.141	1410
Pb	2170	.029	294
Cu	5442	.074	738
Cr	898	.012	122

6.2.5.3 Effect of Recycled Centrate on Raw Wastewater

In order to compare the centrate contributions to the influent on a weekly basis, the concentrations were broken down into hourly rates. This breakdown was necessary since Little River dewatered for only 113.5 hrs in December. The hourly comparisons were done by assumming that the centrate and influent concentrations were constant for the whole month. As Table 6.9 indicates, the ratio of centrate to influent varied from 1.1% to 4.3%. These percentages help explain the jumps observed in the raw wastewater metal concentrations. This becomes especially true for the diurnal variations, which measured the increases in concentration as dewatering was taking place. Furthermore, the recycle of the centrate can affect the efficiency of the plant. As noted by Brown et al. [1973], the high concentrations of metals pumped back to the head of the plant hinder the metal removal efficiency.

TABLE 6.9

Centrate Recycle Ratios

Metal	Mass in Influent Min per month g/h	Mass in Centrate Mcent per month g/h	Mmcent/Mmin %
Ni	26	1	4.3
Cd	16	0.3	1.5
Zn	477	5	1.1
Pb	116	2	1.7
Cu	105	3	2.9
Cr	32	1	2.0

Since the majority of dissolved metals pass through the treatment plant, the majority of metals in the sludge are suspended metals. With the centrate being the water from the dewatered sludge, it can be stated that of the metals present in the centrate are also suspended. This would then indicate that a fair amount of metals are loosely enmeshed in the sludge floc, and not adsorbed chemically; then on dewatering pass through the centrifuge.

One final comment concerning the centrate is the toxicity of the centrate. If the influent metal concentrations would have been higher, the centrate metal concentration would also have been higher, causing toxicity for the bacteria. This toxicity would be along the same lines as the observed toxicity from recycled digester supernatant [Barth et al., 1965 and Olver et al., 1975].

6.2.5.4 Metal Concentrations in the Sludge Cake

After determining the effect the metals in the centrate had on the influent, it was decided to calculate the ratio of metals in sludge that were recycled in the treatment process through the centrate. The recycled ratio was calculated from the (mass of metal in sludge - mass of metal in cake)/(mass of metals in sludge). As Table 6.10 indicates, the recycle ratios were all less than 1.3%, pointing to the fact that the majority of metals were leaving the treatment plant. These ratios can be related to removal efficiencies, where lower the removal efficiency, higher the ratio as seen for nickel and cadmium.

Furthermore, Table 6.10 also gives the comparisons of the sludge cake to the guidelines set by the Ontario Government for land disposal. The values indicate that the Little River sludge cake was less than the government guidelines, except for one metal, cadmium. This indicates that under the present conditions, Little River sludge cake could not

TABLE 6.10

Metal Concentrations in Sludge Cake Plus Recycle Ratios

Metal	Conc.* in sludge mg/kg	Conc.** in sludge mg/kg	cake mg/L	Conc.# in sludge cake mg/kg	Govern.+ Limits mg/L	Recycle % Cent/Sludge
Ni	104	19	20	8	160	1.3
Cd	28	5	5	.3	1	1.2
Zn	4520	823	97	720	1650	0.1
Pb	880	160	174	150	450	0.2
Cu	2128	387	422	190	750	0.2
Cr	370	67	73	153	1000	0.3

* Little River sludge Dec. 1983 (dry basis)

** Little River sludge cake Dec. 1983 (wet basis)

\# Little River sludge cake samples analyzed May 1983 by the City of Windsor Wastewater Laboratory (wet basis)

\+ [Ontario Ministry of Agriculture, 1981] (wet basis)

be disposed on land for agriculture uses until improvements are made with respect to the cadmium concentration.

Finally Table 6.10 shows that the sludge metal concentration values varied from May to Dec., proving that the metal concentrations in wastewater vary in time.

6.3 WEST WINDSOR TREATMENT FACILITY

6.3.1 Diurnal Variations

6.3.1.1 Lead

As can be seen from Figure 6.19, there were significant variations in the lead concentrations, ranging from 40 to 385 ug/L. With West Windsor recycling the centrate as Little River, similar influent peaks due to centrate occur. An early morning concentration decrease similar to the one observed at Little River was also observed here. The main difference between the two plants is the higher overall concentrations during the week days and the low concentrations observed on the weekend at West Windsor. The lower concentrations on the weekends can be attributed to the fact that metal industries have irregular discharges as was found by Nielsen and Hrudey [1983].

In observing the effluent concentrations, it becomes apparent that lead has a removal threshold. This threshold hovers around 35 ug/L. However, a significant rise in raw wastewater concentrations due to diurnal variations can lead to an increased lead concentrations in the effluent. This pattern is especially noticed on Monday at 1900 hr when the effluent rose to 125 ug/L.

6.3.1.2 Zinc

By observing Figure 6.20, it becomes apparent that the same general pattern exists as exhibited by lead. The only

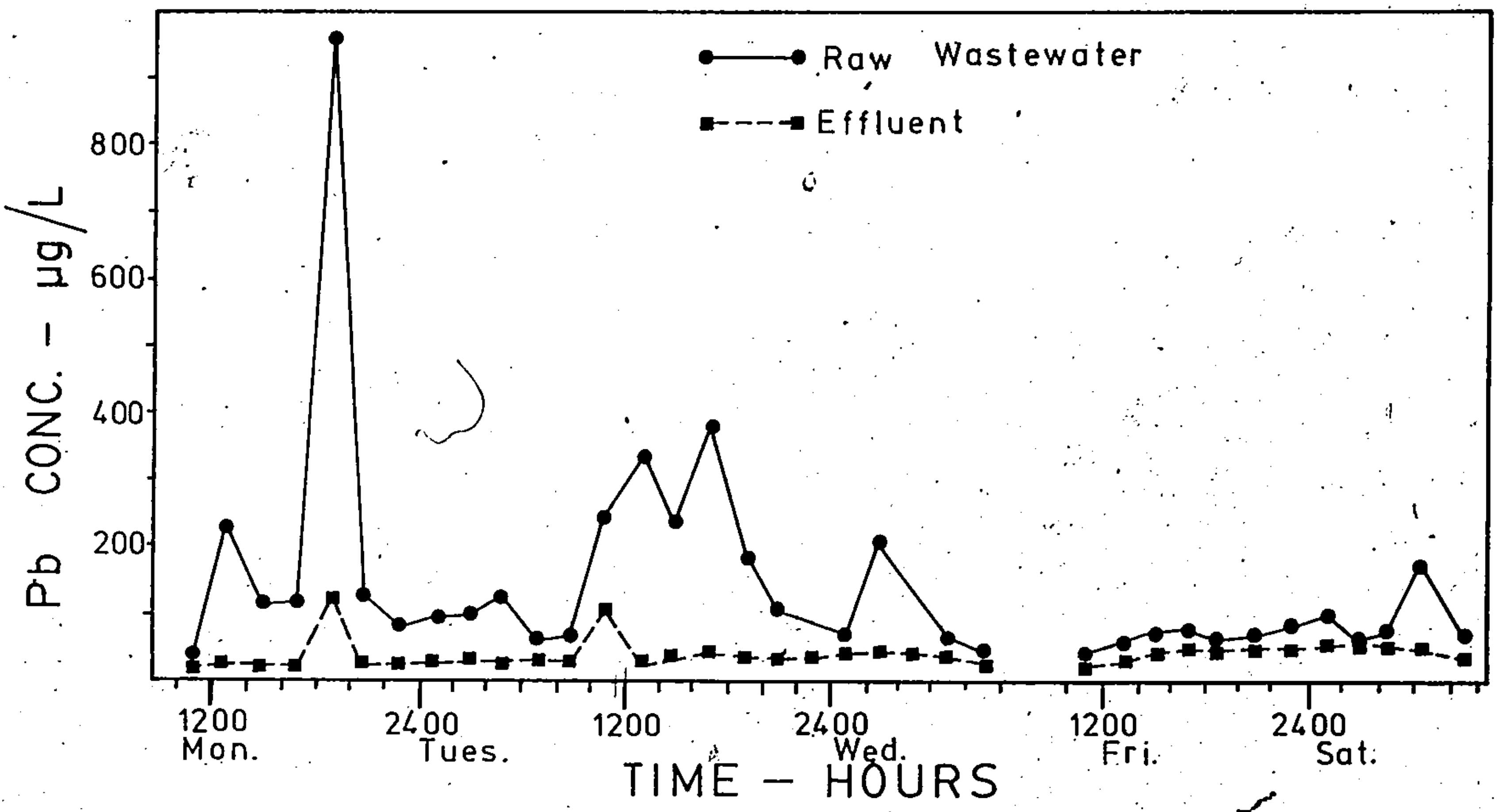

Figure 6.19: DIURNAL VARIATIONS FOR LEAD AT WEST WINDSOR

difference is the concentration range which has increased to 93 to 210 ug/L, excluding the centrate peak. Even with the higher concentrations for zinc, the concentration drops in the early morning are still observed.

For the effluent, it appears that a removal threshold exists, around 450 ug/L. This value is consistent with the removal efficiencies summarized by Nielsen and Hrudey [1981]. Furthermore, as indicated by the plot, there is a decrease in effluent quality as the raw wastewater concentrations increase.

There appears some type of contamination for the sampling done on Friday and Saturday. With the low zinc wastewater concentrations reappearing as exhibited by lead, the increased metal levels must be attributed to the metals contained in the chemicals. The waste chemical used at West Windsor is $FeCl_3$, with the corresponding metal limits shown in Table 6.11 This chemical originates from pickling liquor discharged by a steel mill. It is first filtered to remove large particles, and then oxidized with chlorine to convert the ferrous into ferric. With the dilution factor being one litre $FeCl_3$ per minute to eleven million litres of wastewater, it can be seen that a significant rise will occur in the metal levels on addition. Another source would be the Alkapam 3000 polymer added to improve settling.

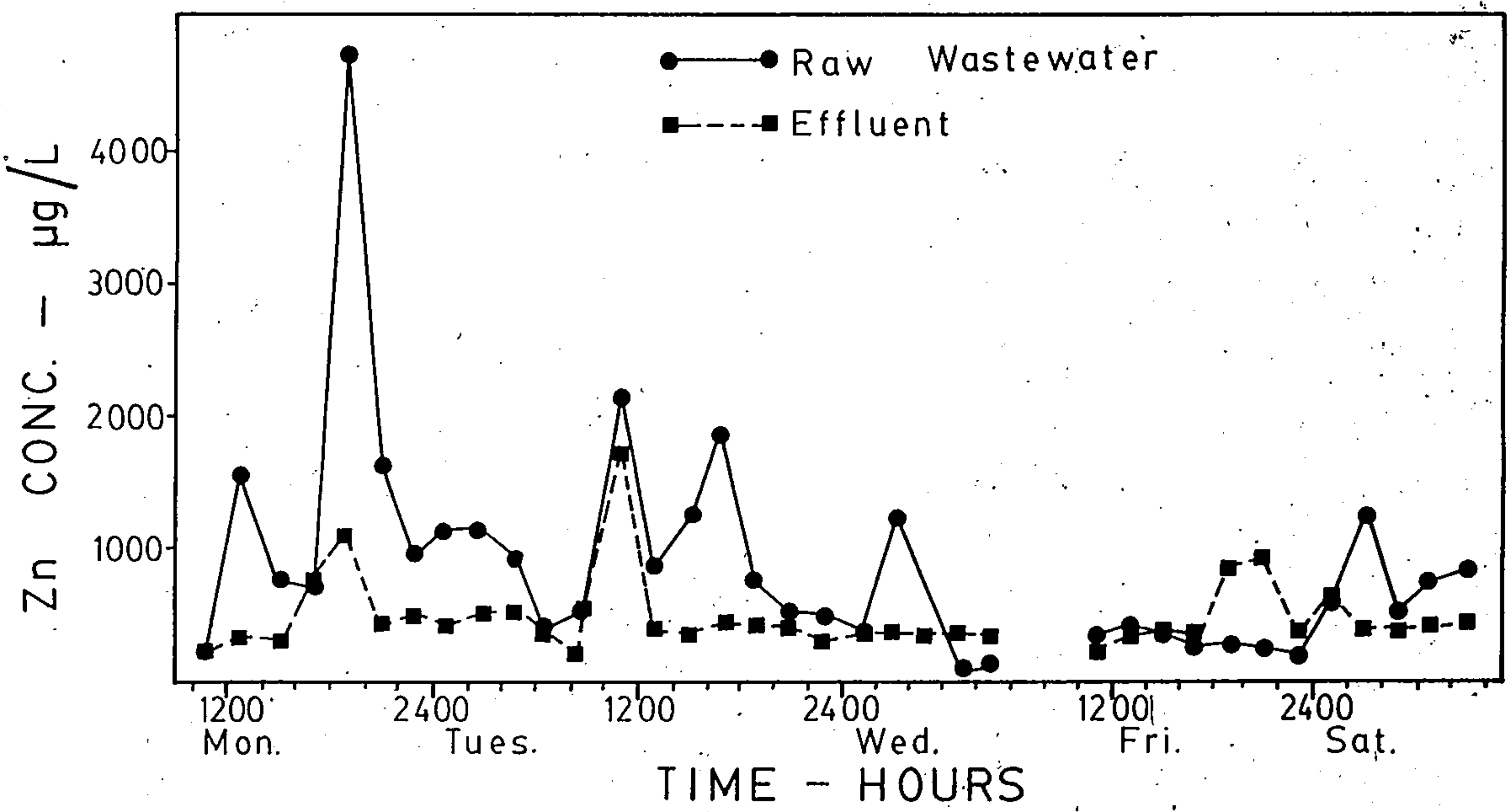

Figure 6.20: DIURNAL VARIATIONS FOR ZINC AT WEST WINDSOR

TABLE 6.11

Metal Limits Set for $FeCl_3$ By the City of Windsor

Metal	$FeCl_3$ mg/L
Cd	5
Cr	100
Cu	200
Ni	30
Pb	50
Zn	500

Ref: [Faust, 1983].

6.3.1.3 Cadmium

Cadmium appears in a significantly wide range of values, from 7 to 87 ug/L, as shown in Figure 6.21 . As with the other metals, the centrate peaks coincide properly with dewatering periods. However, several peaks appear on non-dewatering days, indicating the inconsistencies in industrial discharges.

The quality of effluent is inconsistent. The range of values vary from 5 to 41ug/L, with no apparent removal threshold. As previously observed for zinc, the effluent concentration exceeds the raw wastewater on Friday and Saturday. It can be concluded that metal contamination from $FeCl_3$ occurred. Furthermore, the effluent maintains the same general pattern during the earlier part of the week,

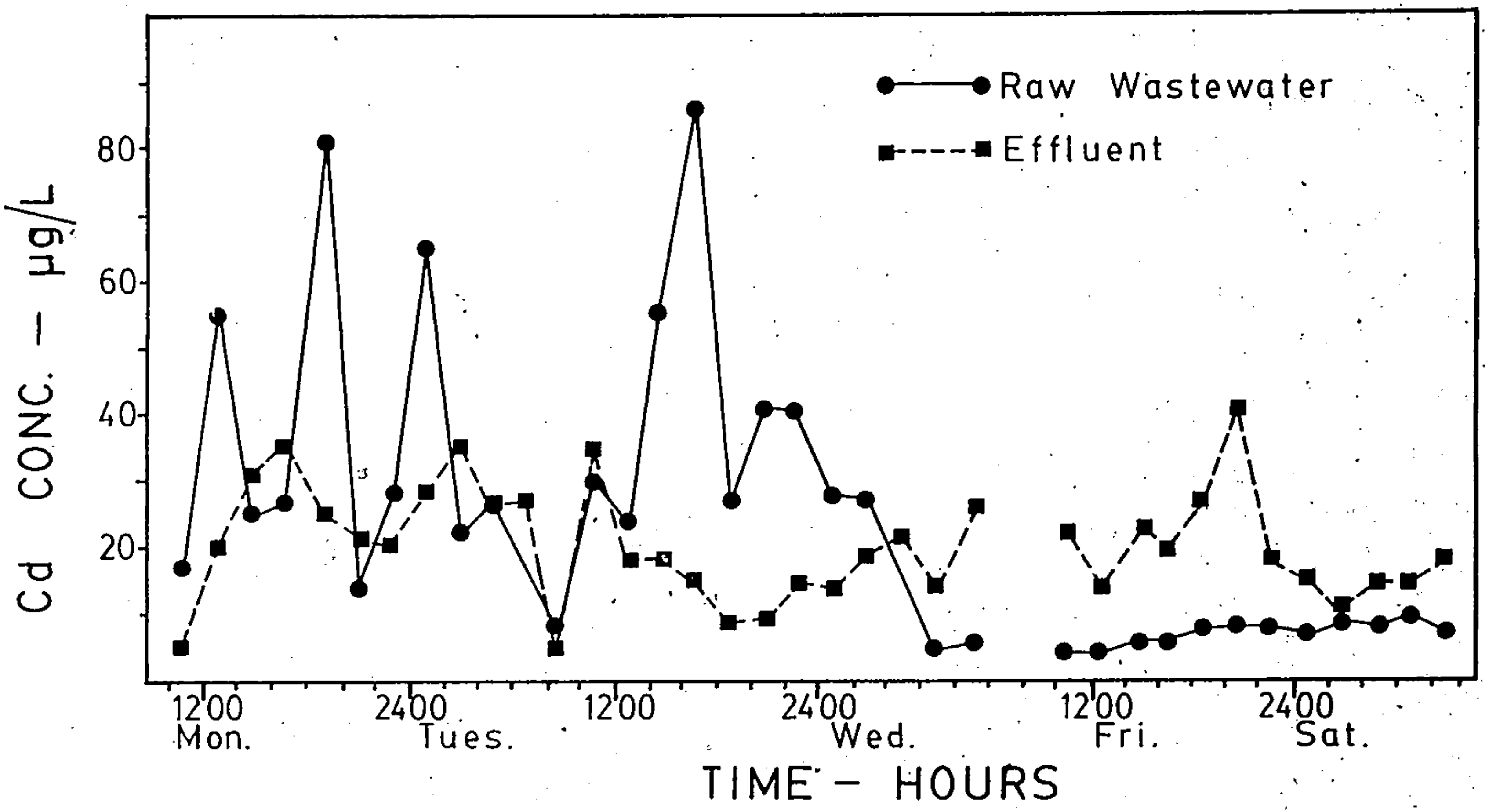

Figure 6.21: DIURNAL VARIATIONS FOR CADMIUM AT WEST WINDSOR

even when raw wastewater concentrations were high. This confirms the chemical contamination.

6.3.1.4 Chromium

In studying the chromium variations, shown in Figure 6.22, the same patterns as exhibited by lead are generally observed. The raw wastewater concentration fluctuates from 20 to 230 ug/L. However, the centrate peak for 1900 hrs on Monday is missing. Most likely the metal concentrations in the collected sludge were lower, reducing the chromium concentration recycled in the centrate.

With respect to the effluent, observations show the existence of a removal threshold of approximately 25 ug/L, indicating good removal.

6.3.1.5 Nickel

As Figure 6.23 shows, the diurnal variations are quite extensive. The values range from 27 to 678 ug/L, indicating that metal discharges are not consistent. All other patterns previously observed have been repeated. In studying the effluent concentrations, it becomes apparent that no real removal threshold exists. Instead there is a general removal range, varying from 40 to 200 ug/L.

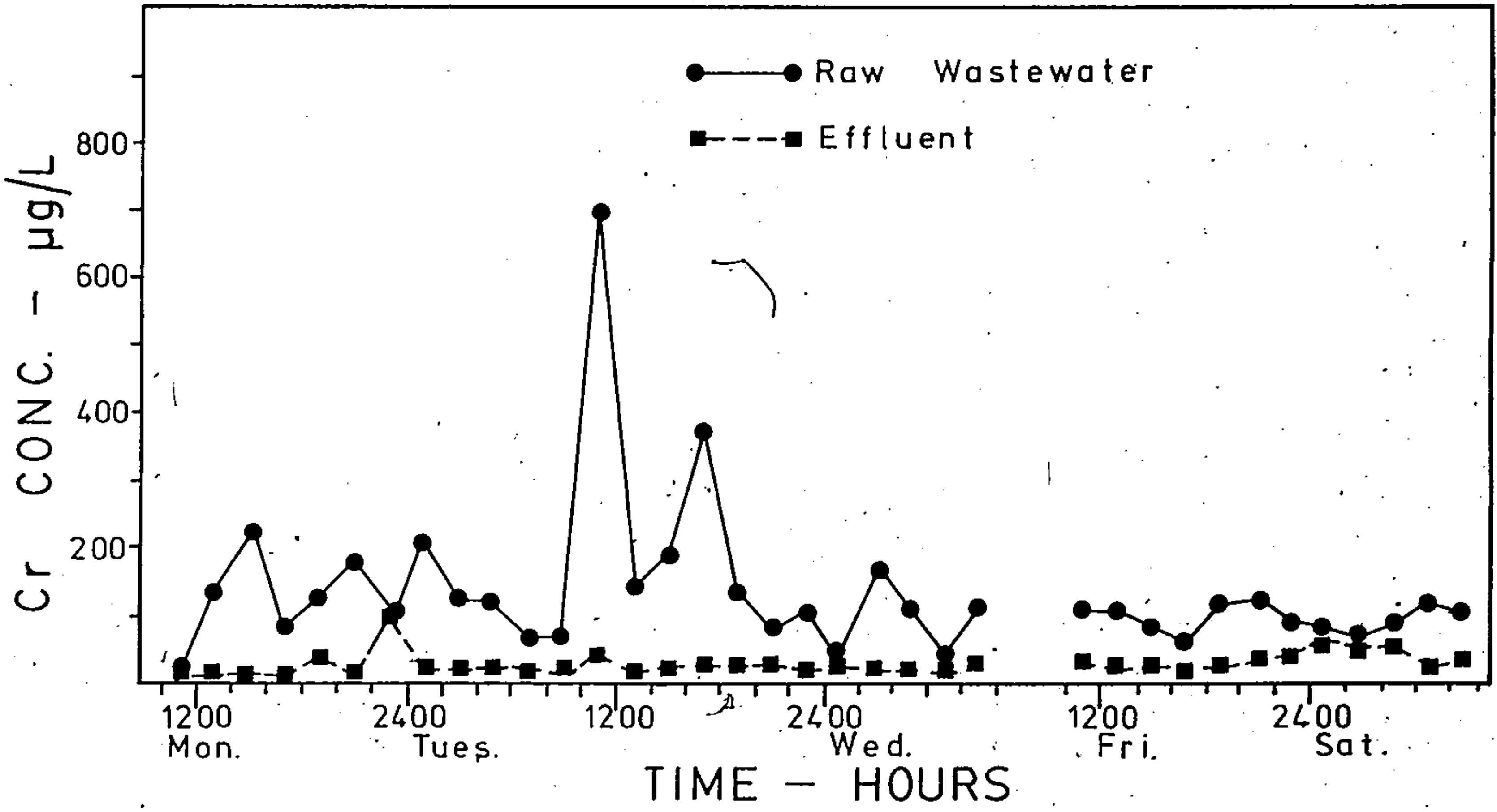

Figure 6.22: DIURNAL VARIATIONS FOR CHROMIUM AT WEST WINDSOR

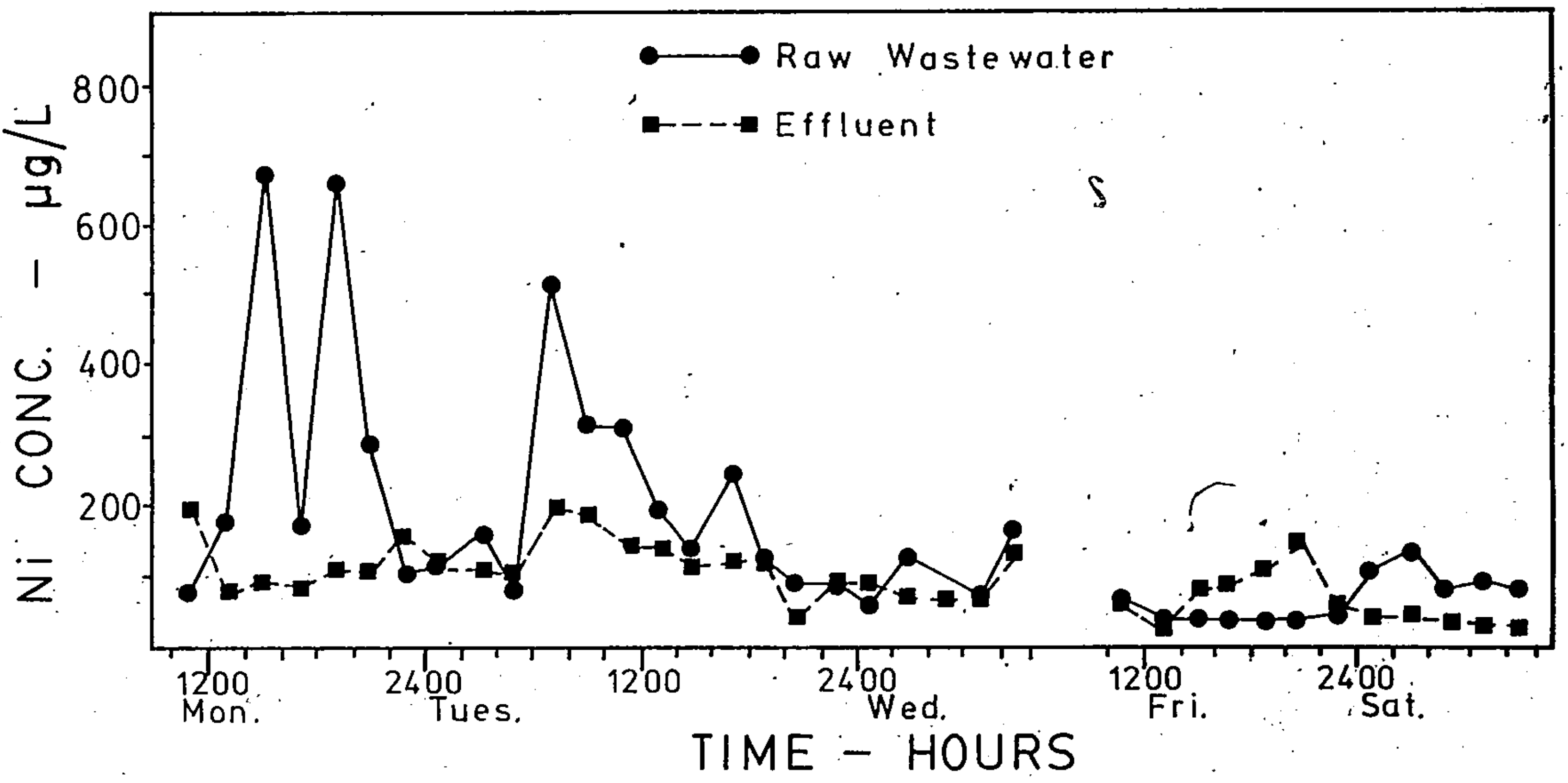

Figure 6.23: DIURNAL VARIATIONS FOR NICKEL AT WEST WINDSOR

6.3.1.6 Copper

Figure 6.24 shows that the raw wastewater concentration ranged from 25 to 350 ug/L, excluding the two high centrate peaks. All other influent patterns are similar to those disscussed for lead.

With regard to the effluent, it becomes apparent that a removal threshold does exist. This level is approximately 35 ug/L, and is maintained even when the raw wastewater concentration drops during the weekend sampling period. The only severe deviation from the threshold value was the increase which occurred during the high centrate peak on Monday at 1900 hrs.

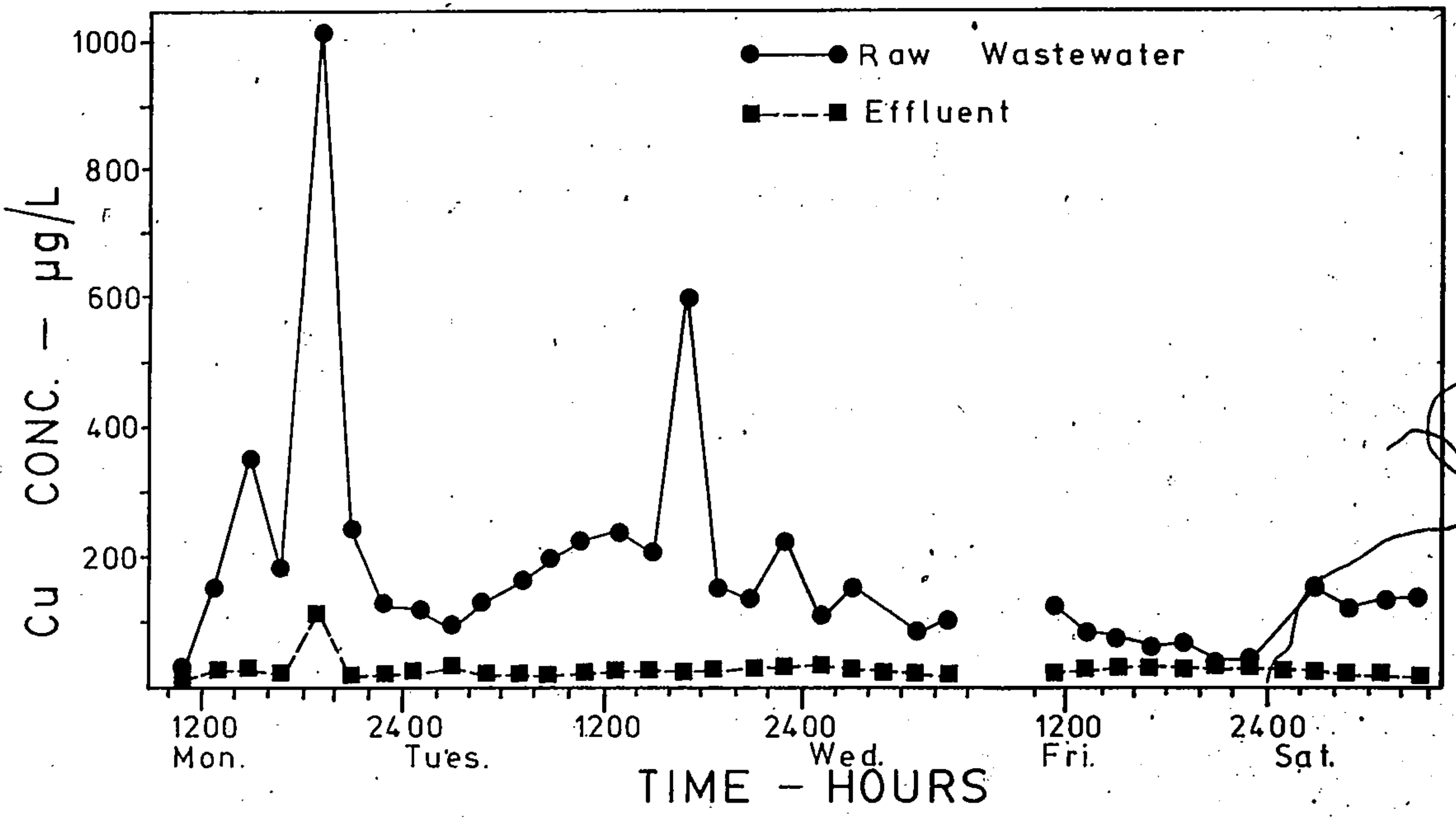

Figure 6.24: DIURNAL VARIATIONS FOR COPPER AT WEST WINDSOR

6.3.2 Daily Variations

6.3.2.1 Lead

As Figure 6.25 shows, there ~~are considerable~~ fluctuations in the metal concentrations, varying from 55 to 134 ug/L. Among these fluctuations there are three relatively large increases occurring on Tuesday, Thursday, and Saturday. The Tuesday and Thursday increases can be attributed to centrate recycle and increased industrial discharges. However, with no regular work force at the plant on Saturday, no dewatering took place, pointing to another cause for the large concentration increases.

A study by Barkdoll [1976] has shown that in areas of relatively high air pollution, large amounts of metals can accumulate on the ground due to the dustfall. Then when a storm occurs, the metals are flushed into the sewers and the combined wastewater can enter the treatment plant. Since West Windsor has both high air pollution and combined sewers in its catchment area, both conditions apply. The fact that a storm event occurred on Saturday confirms the source of this increase in lead level. However, when the high flowrate for Sunday is taken into consideration, it can be seen that dilution rather than flushing became a factor. The reason is that when the metals are flushed after one storm event, no metals are left for the second storm to flush that follows quickly after the first storm. Since certain time

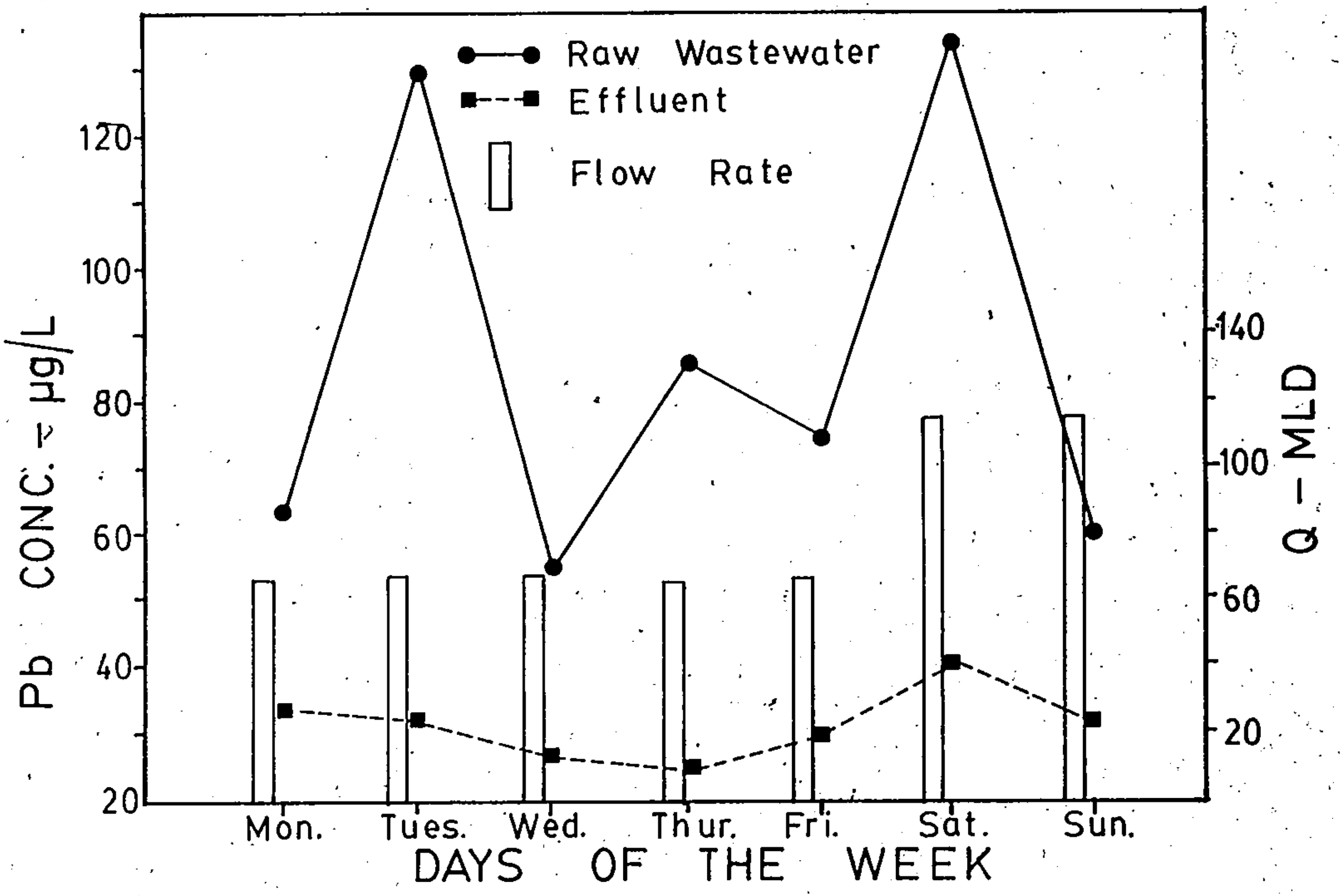

Figure 6.25: DAILY VARIATIONS FOR LEAD AT WEST WINDSOR

is required for the dustfall accumulation to reach the asymptote value.

Even though the raw wastewater concentrations are fairly erratic, the final effluent approaches a removal threshold of 32 ug/L. The final effluent is fairly constant. Any deviations are attributed to the extremely high influent concentrations and the contaminated chemicals used for phosphorous removal.

6.3.2.2 Zinc

As Figure 6.26 shows, all the patterns displayed by zinc are similar to those demonstrated by lead. However, the raw concentrations for zinc are considerably greater, varying from 124 to 952 ug/L, indicating that zinc predominates in West Windsor wastewater. Even with these large raw concentrations, and relatively high removal threshold of 175 ug/L, the effluent was comparable to other industrialized cities reported by Nielsen and Hrudey [1981].

6.3.2.3 Cadmium

As Figure 6.27 indicates, the raw influent concentration for cadmium is fairly consistent, ranging from 5 to 10 ug/L. The patterns for centrate recycle and storm-event dilution remain the same as for lead. However, there is no flushing of cadmium on Saturday. It appears that cadmium is not as predominant in the dustfall as the other metals.

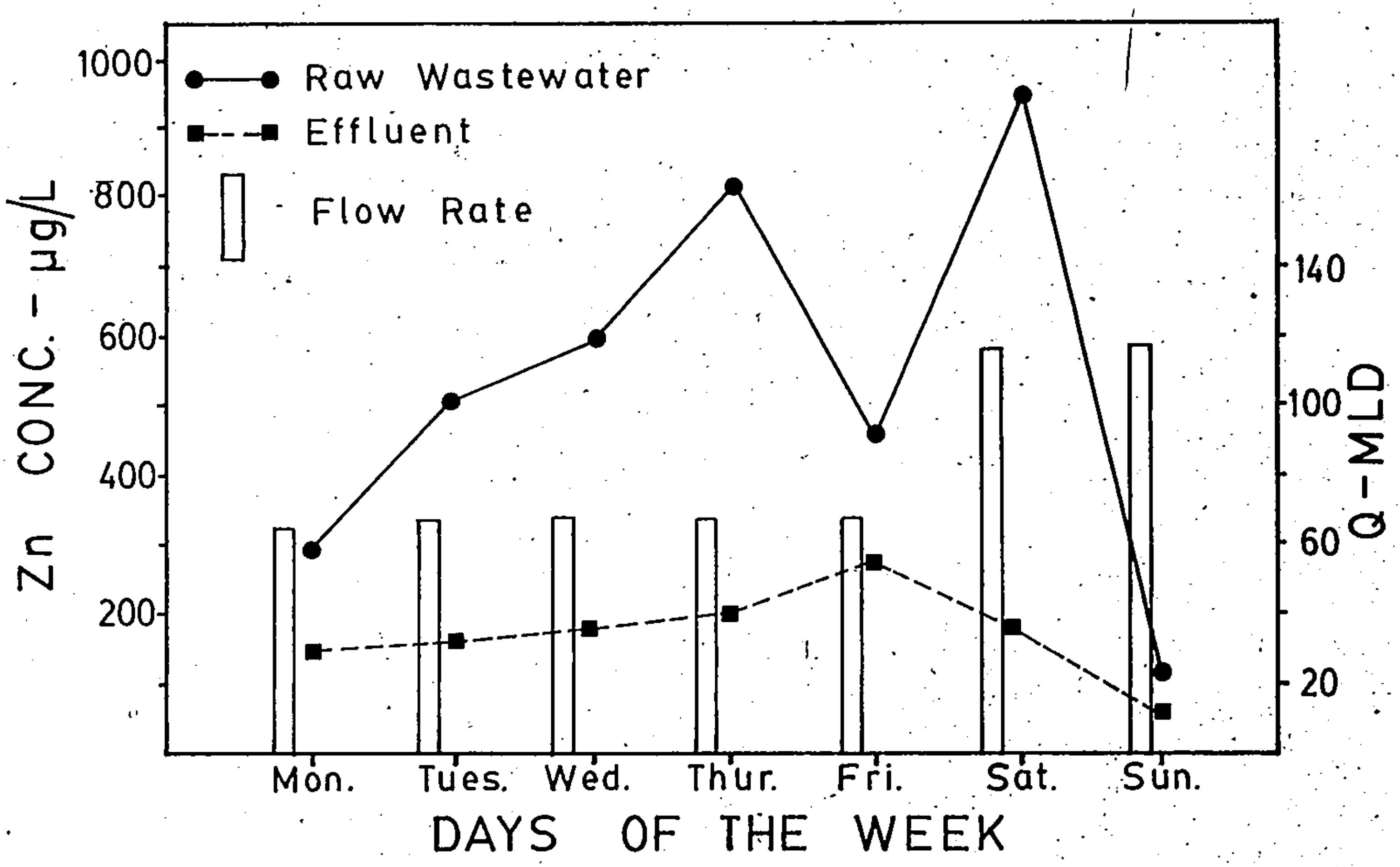

Figure 6.26: DAILY VARIATIONS FOR ZINC AT WEST WINDSOR

This fact is benefical considering the severe toxicity of cadmium.

Even with the low raw wastewater concentrations, the effluent still had a removal threshold hovering around 5 ug/L. Slight fluctuations in the effluent are related to the raw wastewater concentrations. Furthermore, equal values for raw and effluent concentrations on Sunday can be attributed to the chemical additions for phosphorous removal.

6.3.2.4 Chromium

For chromium, it appears from Figure 6.28 that the metal range varied from 35 to 110 ug/L. Even though the total metal concentrations occur at higher levels than for cadmium, the same patterns are repeated. In fact the same low contribution from the storm event on Saturday occur, indicating that the air pollution contains minimal ammounts of chromium.

The effluent exhibits a removal threshold of 20 ug/L, even though certain fluctuations occur. The small changes can be directly tied to the $FeCl_3$ additions.

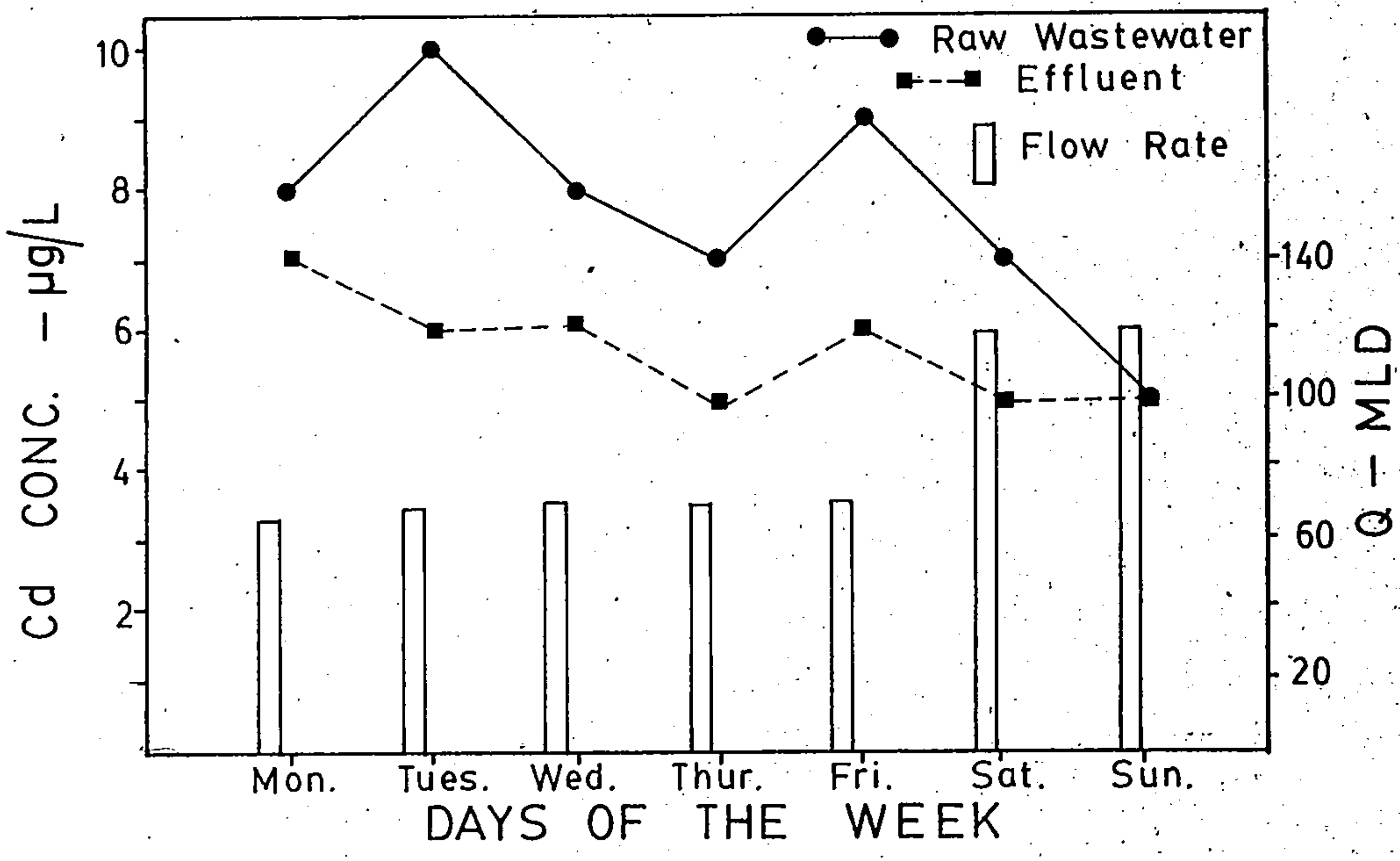

Figure 6.27: DAILY VARIATIONS FOR CADMIUM AT WEST WINDSOR

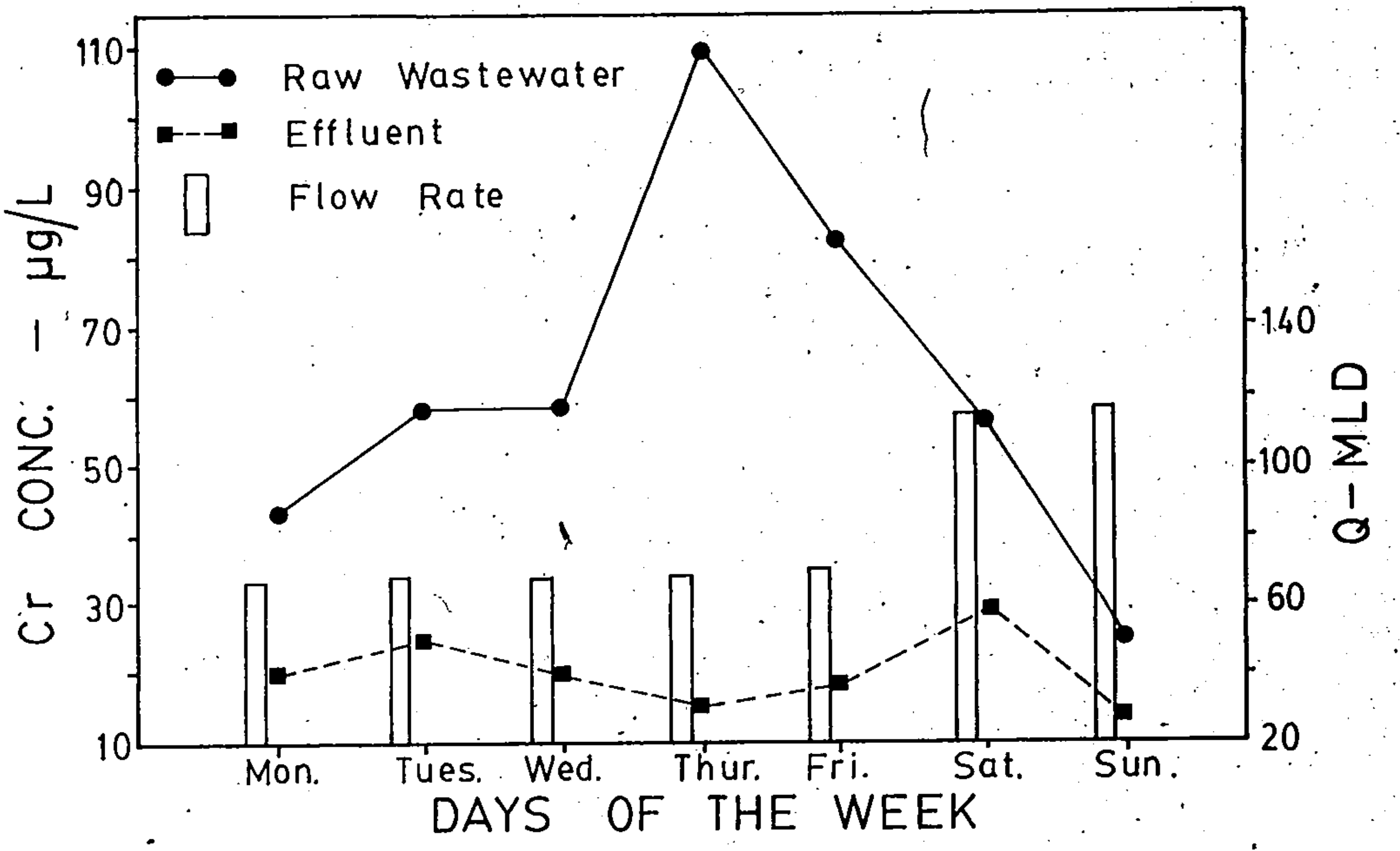

Figure 6.28: DAILY VARIATIONS FOR CHROMIUM AT WEST WINDSOR

6.3.2.5 Nickel

In Figure 6.29 it can be seen that the raw concentrations varied from 42 to 184 ug/L. The raw wastewater shows the same pattern as described for lead, with respect to storm events and centrate recycle. However, it should be noted that the difference which occurs with final effluent is quite erratic. In fact in two instances, on Sunday and Monday, the effluent exceeds the raw wastewater. The high effluent values can be directly related to the possible high contamination by the $FeCl_3$ It is felt that on these two consecutive sampling days, the contamination approached or exceeded the maximum limit set for nickel. For example, if the contamination was 50% of the maximum limit, then with the existing dilution at West Windsor, 25 ug/L could easily be added to the wastewater. Such a contamination can be difficult to remove in the treatment processes used at West Windsor.

6.3.2.6 Copper

Unlike nickel, Figure 6.30 shows that copper behaves exactly as described for cadmium. With the raw concentrations varying from 35 to 119 ug/L, it can be seen that, during the constant dry weather conditions, fluctuations occurred due to the centrate recycle and changes in metal discharges. Then on Saturday there occurred a slight decrease in the metal concentration due to the storm event.

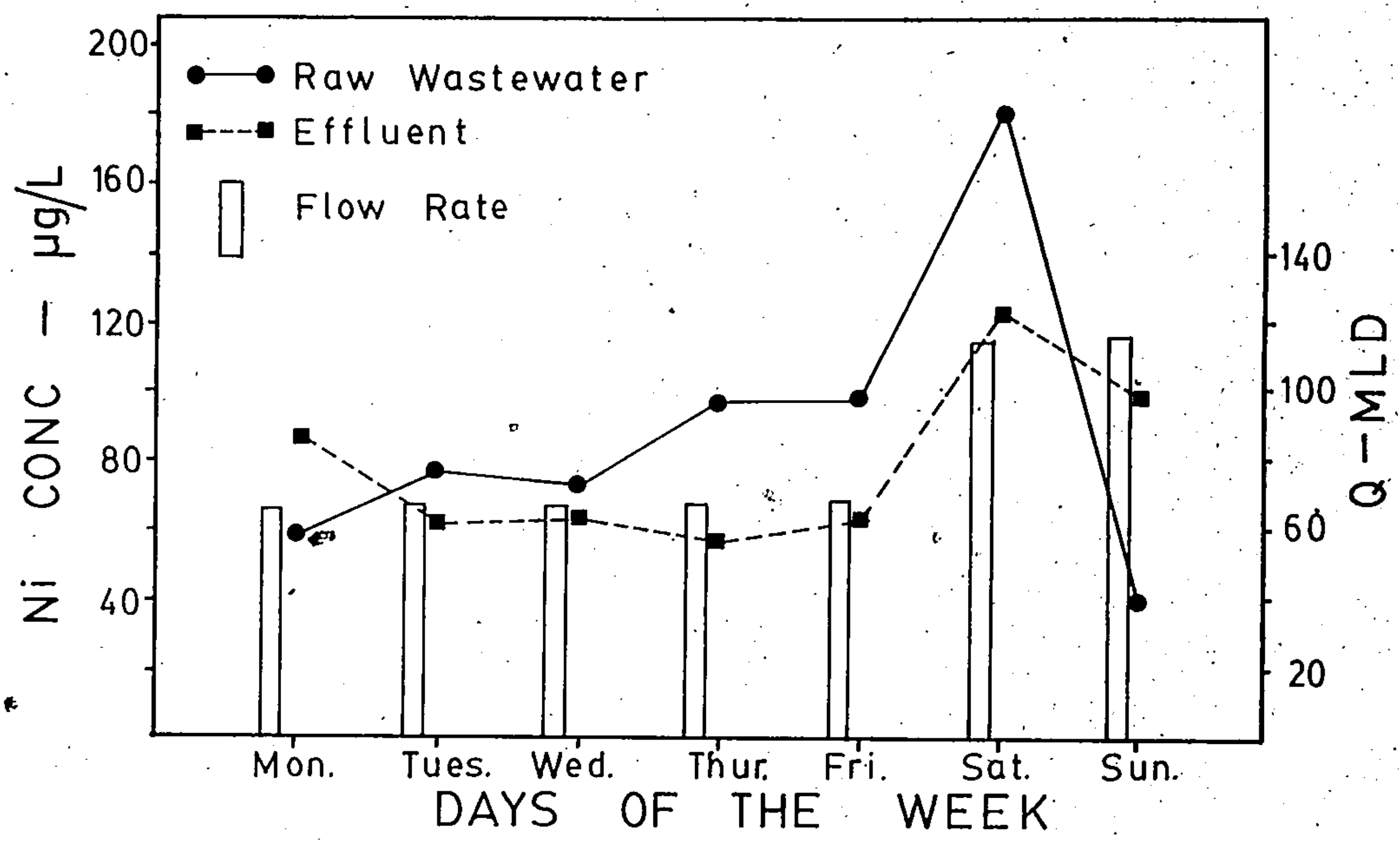

Figure 6.29: DAILY VARIATIONS FOR NICKEL AT WEST WINDSOR

Comparing this to Sunday, a significant dilution of the dry weather flow occurred, since the majority of metals were already flushed away.

For the effluent, it can be concluded that the range 22 to 51 ug/L, is the removal threshold for the daily variations.

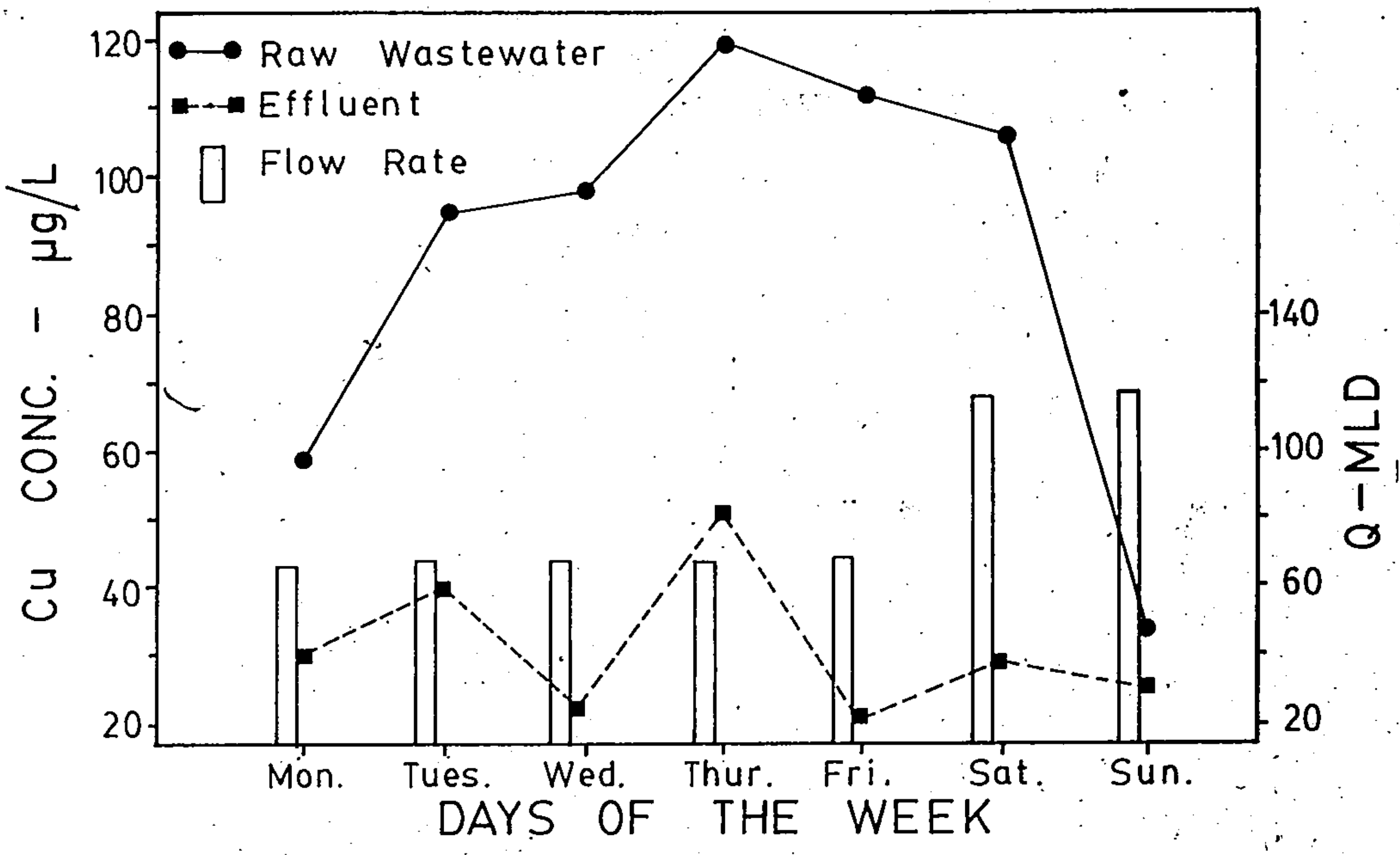

Figure 6.30: DAILY VARIATIONS FOR COPPER AT WEST WINDSOR

6.3.3 Phase Distributions of Metals

6.3.3.1 Copper

As Figure 6.31 indicates, there existed good removal of the suspended metals during the study period. In fact West Windsor has the dissolved to total metal ratios increasing as the treatment progresses, as shown in Table 6.12 .

Also, no dissolved metals are removed during the week. In fact, on the average the dissolved concentration increased in the effluent. This occurrance can be attributed to the low concentration of metals and the low pH. With the pH being lower than the optimum shown by Lanouette [1977] for precipitation, the metals can easily go back into solution.

It is also observed for copper that there existed a a minimum concentration of dissolved copper in solution, similar to that at Little River. This is seen through the increase in the dissolved concentration of copper in the effluent to 20 ug/L. Even though the dissolved concentrations increased in the effluent they approached a consistent level. This complexing level for copper appears to be 20 ug/L.

6.3.3.2 Zinc

As Figure 6.32 indicates, zinc has patterns slightly different to those for copper. There is a major removal of suspended metals, with minor reduction in the dissolved

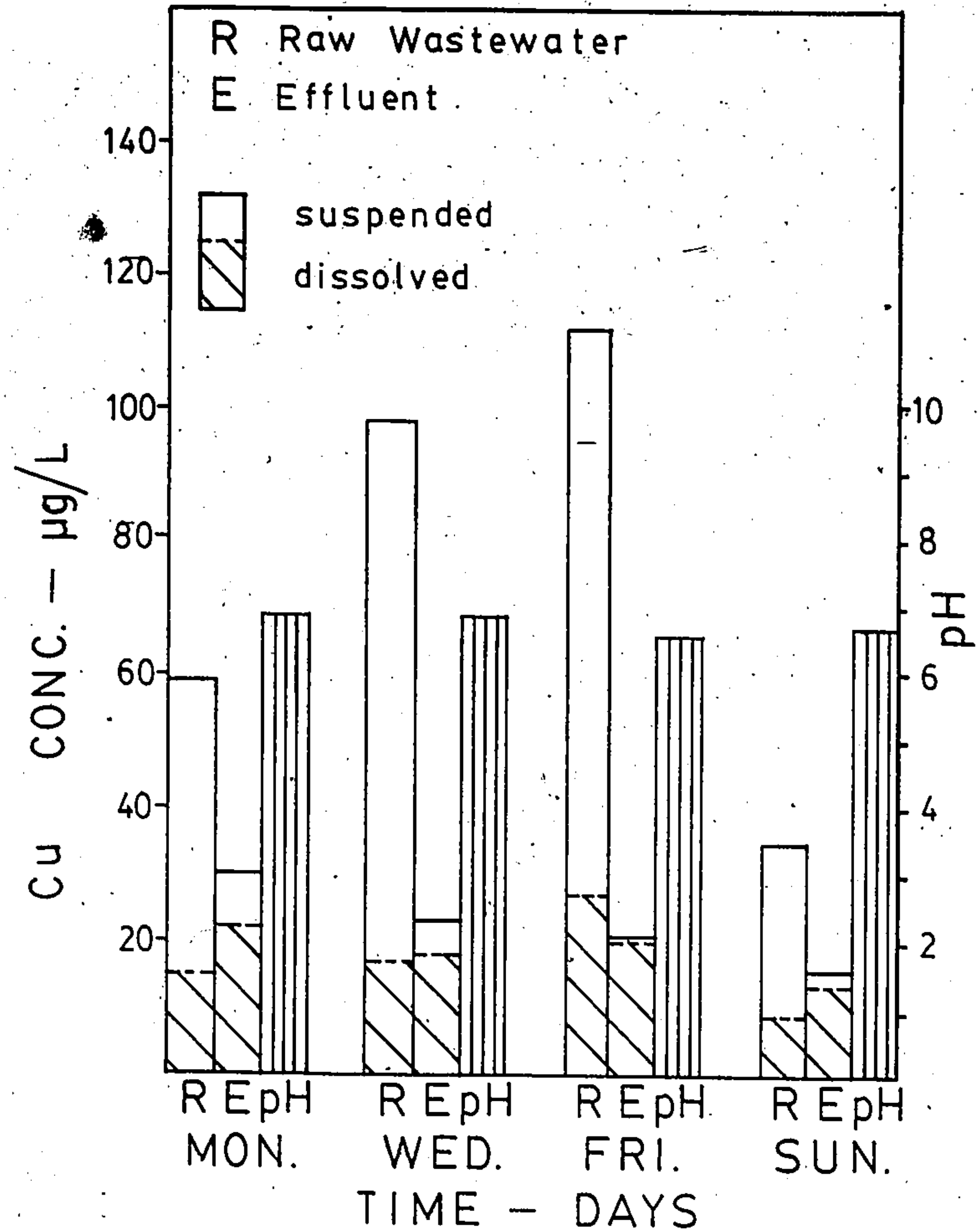

Figure 6.31: COPPER PHASE FRACTIONS AT WEST WINDSOR

TABLE 6.12

Dissolved to Total Metal Ratios for West Windsor

Metal	Sewage Type	Range for Mon., Wed., Fri., Sun.	Average
Ni	Raw	71-89	81
	Eff.	89-97	94
Cd	Raw	56-63	61
	Eff.	60-83	70
Zn	Raw	26-75	44
	Eff.	50-93	77
Pb	Raw	36-51	43
	Eff.	73-100	86
Cu	Raw	17-26	23
	Eff.	73-95	86
Cr	Raw	20-43	32
	Eff.	79-83	72

part. The overall zinc concentration is five times higher than copper, but the dissolved concentration in the effluent is still low when compared to the final effluent in Table 6.5. The complexing level of 130 ug/L is also roughly five times greater.

6.3.3.3 Chromium

Chromium exhibits the same patterns as explained previously for zinc, with respect to suspended metal removal and reduction in dissolved fractions. As Figure 6.33 indicates, the reduction in dissolved fractions are greater and more consistent, with the complexing level hovering around 16 ug/L. This consistent removal is due mainly to the fact that the existing pH was closer to the optimum pH described by Lanouette [1977], reducing the amount of resolubilization.

6.3.3.4 Cadmium

Figure 6.34 shows that the cadmium removal was not as large as for the other metals mainly due to the low suspended concentrations in the raw wastewater. Furthermore, no dissolved removal occurs due to the low pH of the wastewater, keeping the dissolved concentration at 4 ug/L. However, it appears that the dissolved metal concentrations are slightly higher than the final effluent in Table 6.5. This behaviour of cadmium is similar to that noticed for the Little River treatment plant.

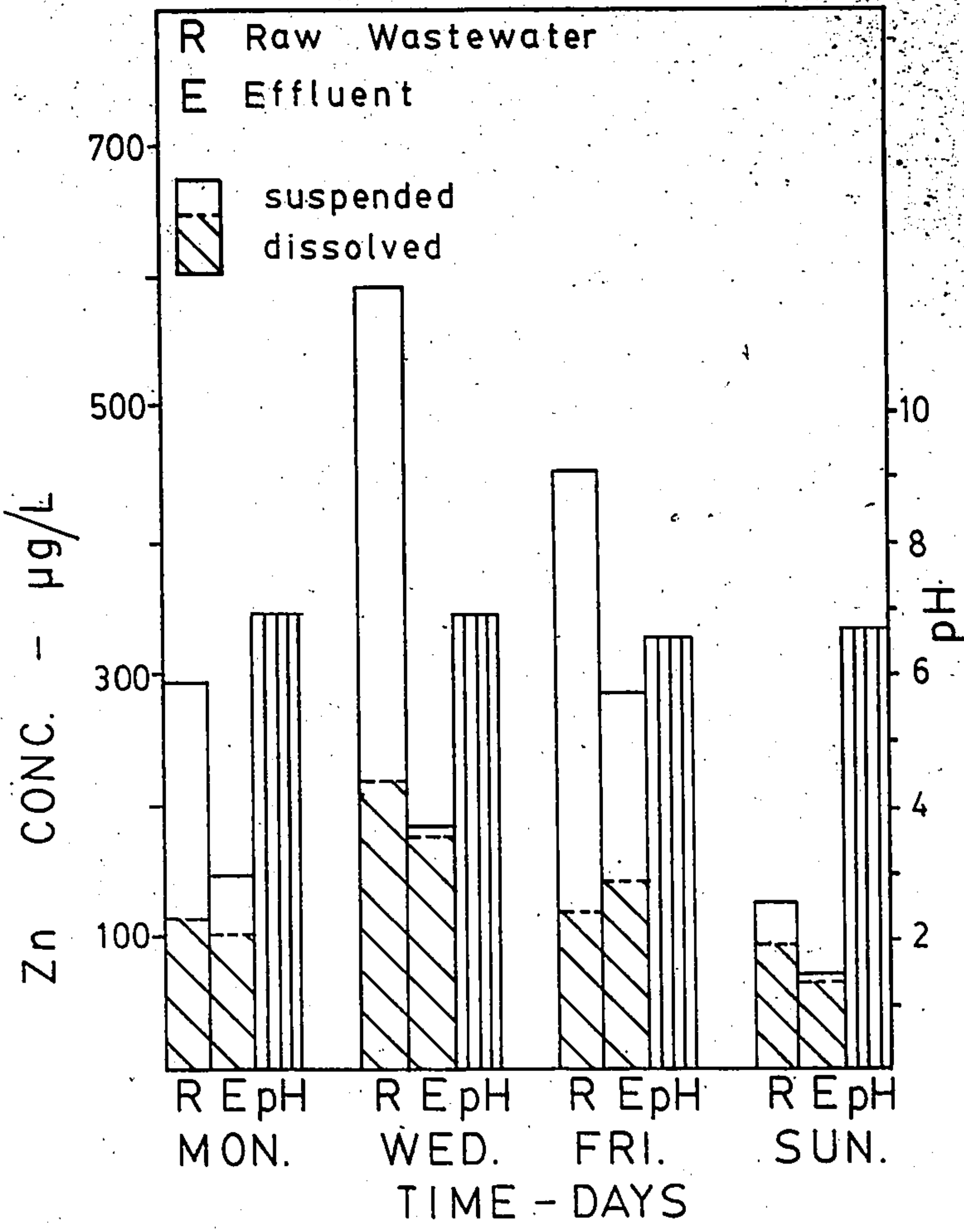

Figure 6.32: ZINC PHASE FRACTIONS AT WEST WINDSOR

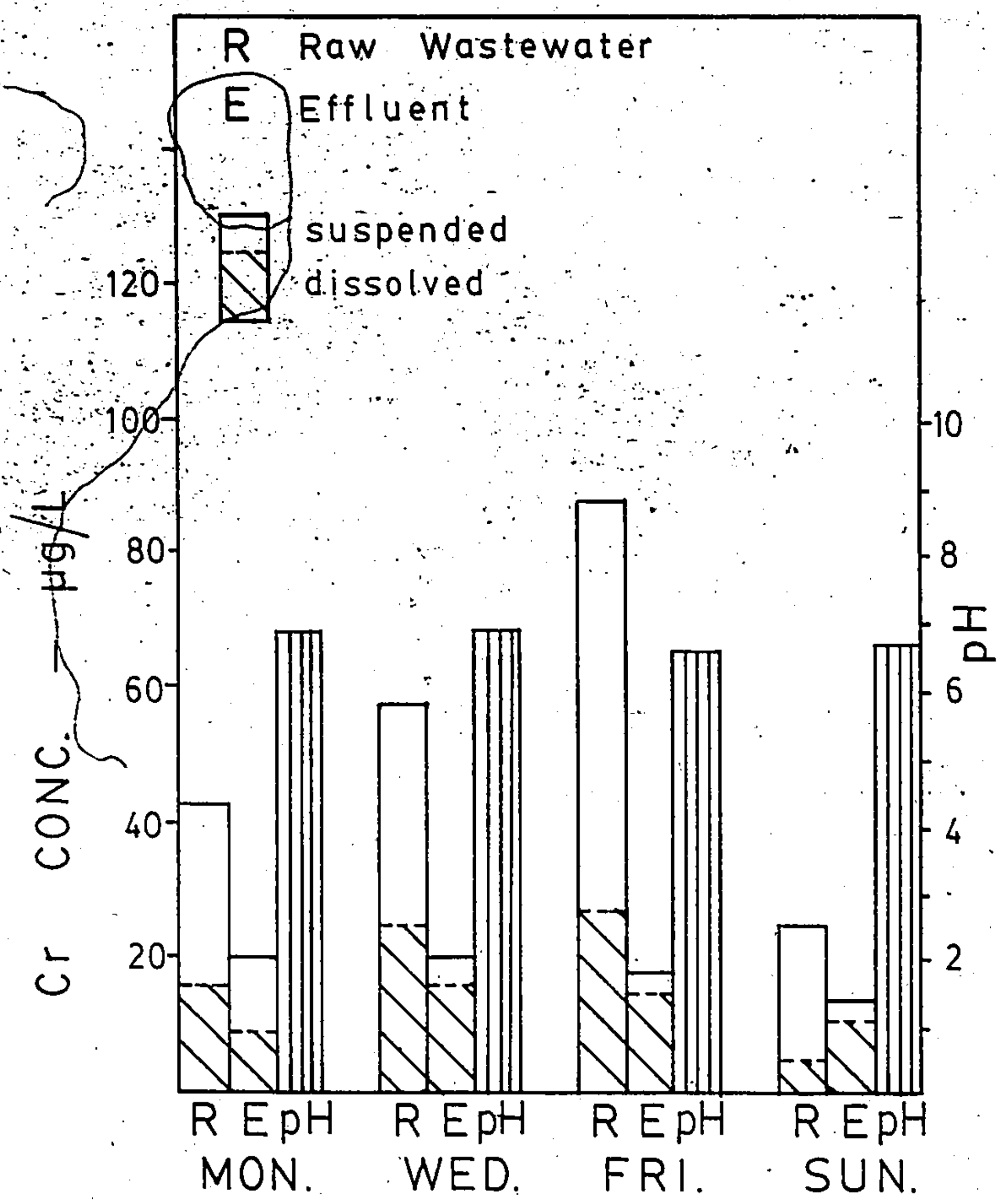

Figure 6.33: CHROMIUM PHASE FRACTIONS AT WEST WINDSOR

6.3.3.5 Lead

Lead exhibits all the patterns described previously for the other metals, ie., satisfactory suspended metal removal along with inconsistent dissolved removal. As Figure 6.35 shows, there exists a complexing level varying from 22 to 34 ug/L. This is expected due to the pH being lower than the optimum values as reported by Lanouette [1977]. In comparing the West Windsor effluent to the final effluent in Table 6.5, it can be seen that the treatment plant was inefficient in removinq lead.

6.3.3.6 Nickel

It becomes apparent from Figure 6.36 that nickel behaves differently as compared to the other metals. The percentage of the dissolved metals in the raw are similar but the removal efficiencies differ. On Sunday and Monday, the effluent had hiqher dissolved concentrations. This can be attributted to the metals added through the chemical contamination, and lower pH levels. With the pH of the wastewater varying form 6.9 to 7.2, the metals have a tendency to go back into the solution since the optimum pH for nickel precipitation is 8 to 10.

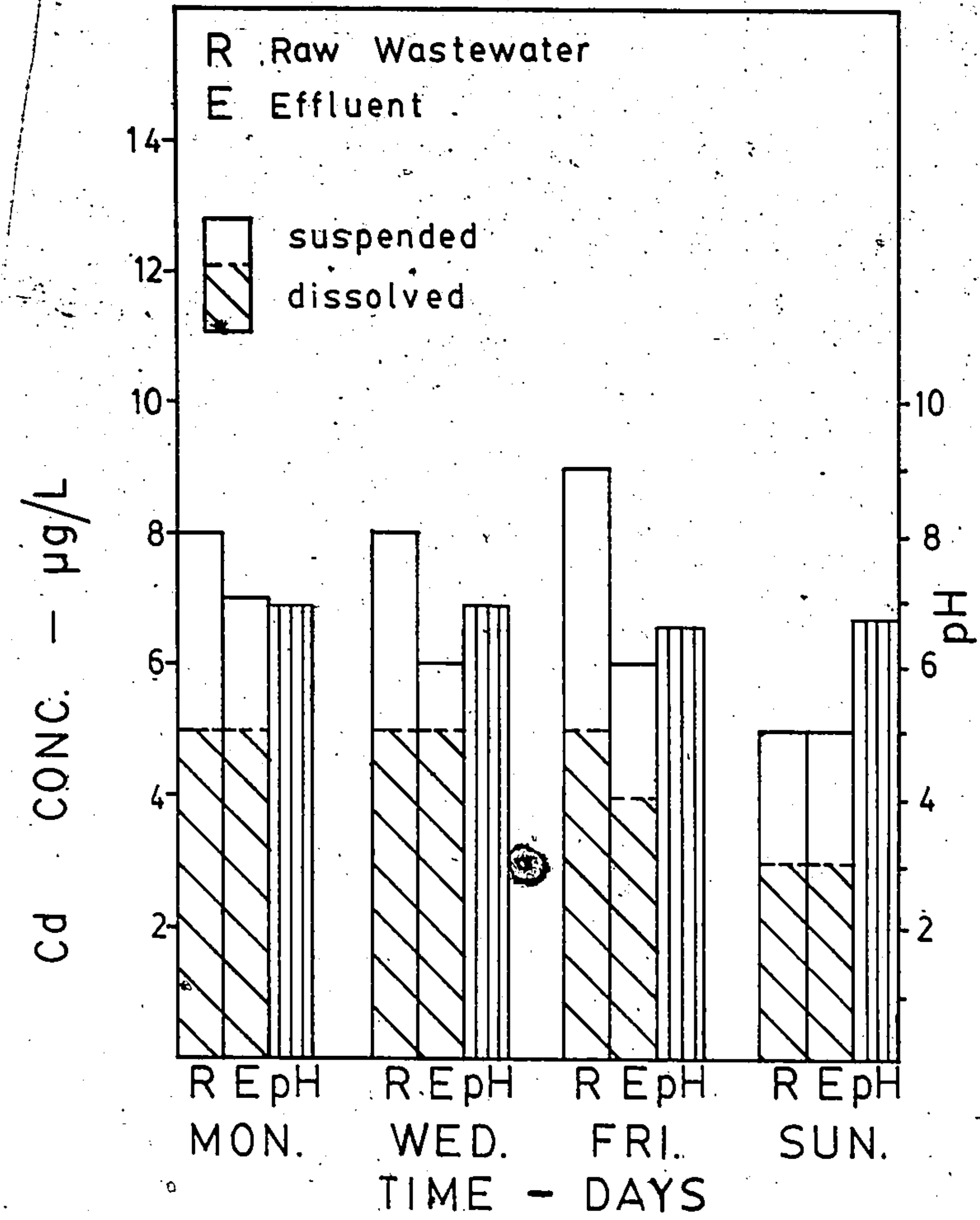

Figure 6.34: CADMIUM PHASE FRACTIONS AT WEST WINDSOR

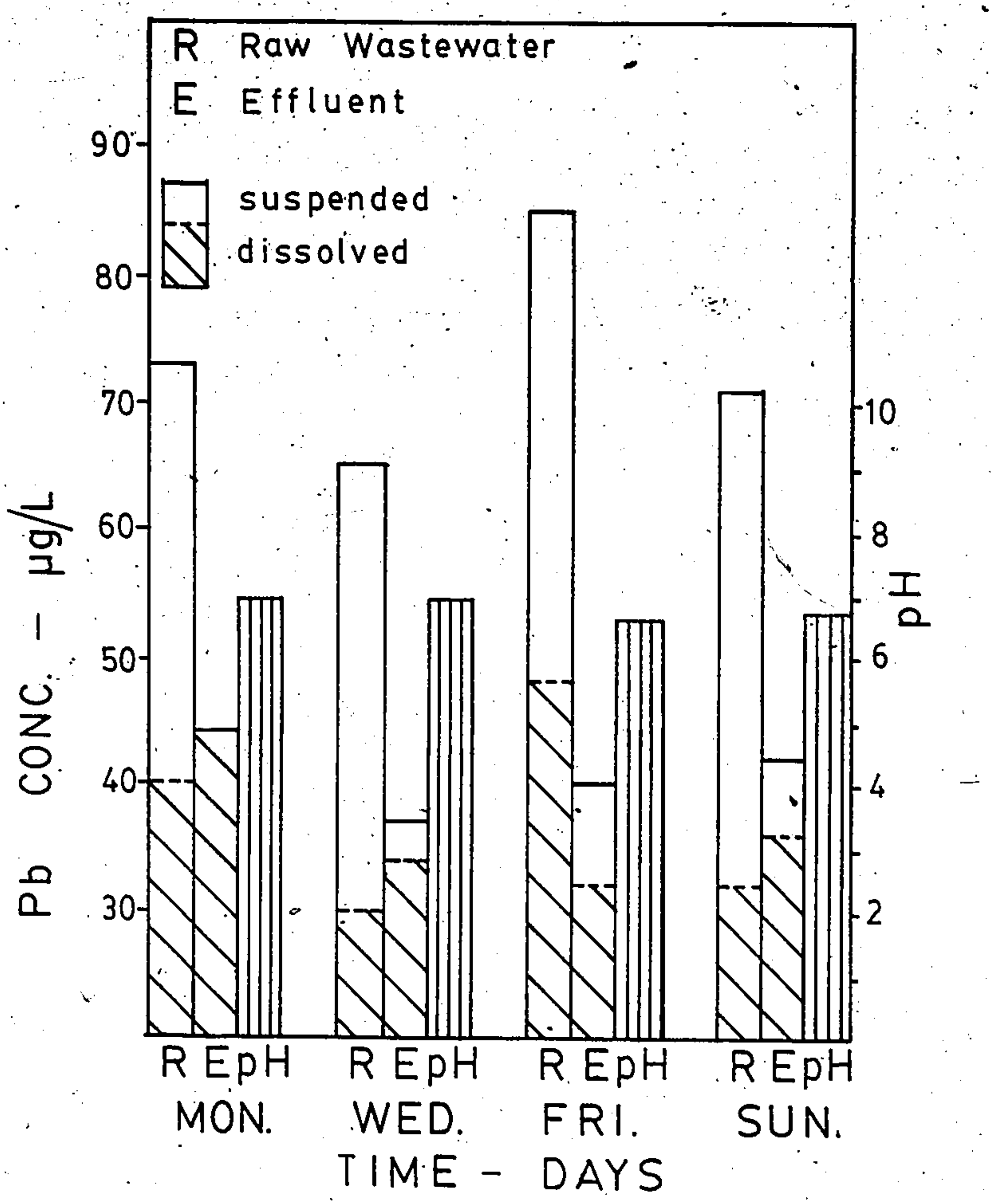

Figure 6.35: LEAD PHASE FRACTIONS AT WEST WINDSOR

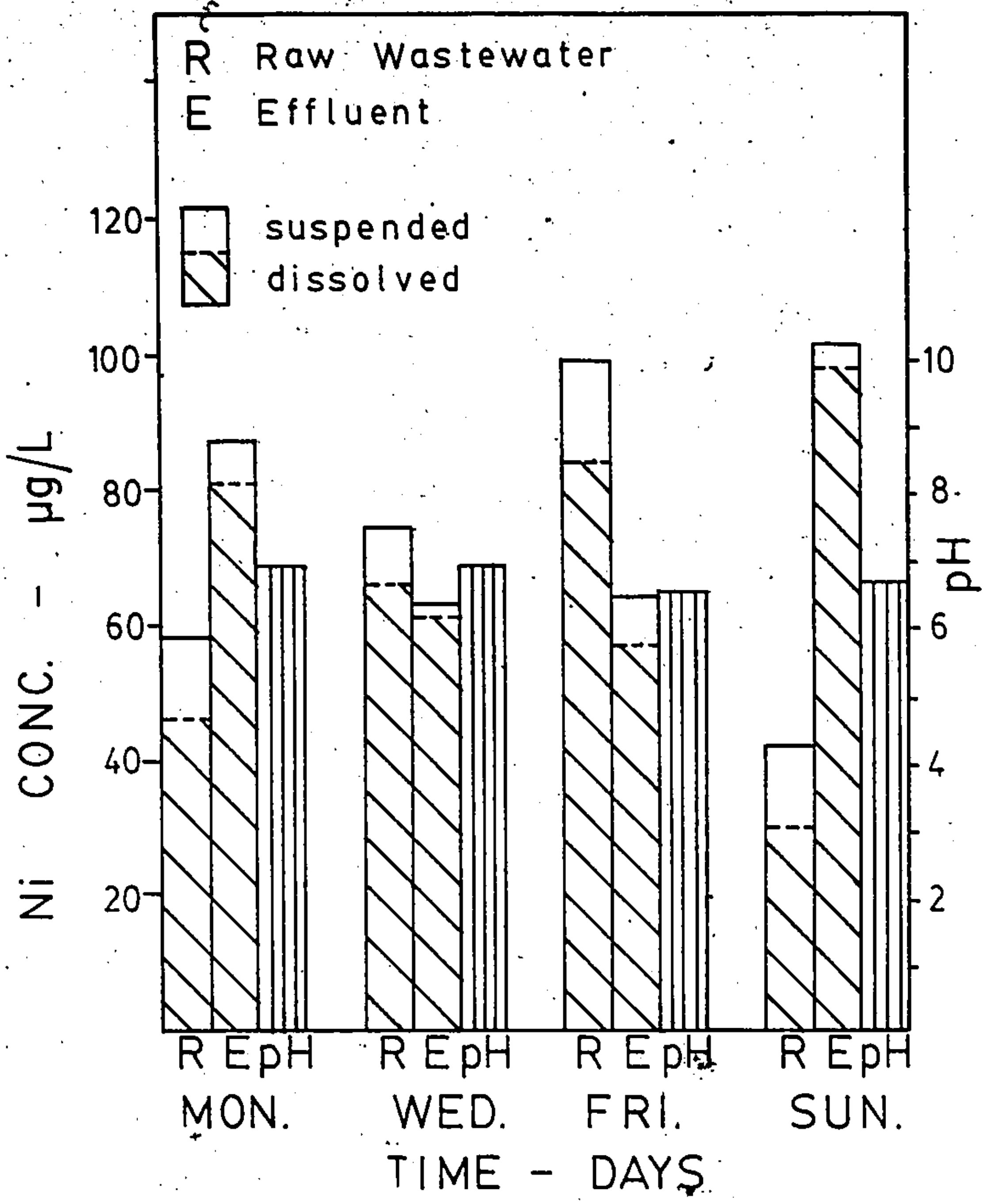

Figure 6.36: NICKEL PHASE FRACTIONS AT WEST WINDSOR

Taking the above information into consideration, it becomes apparent that nickel has a high complexing level, hovering between 57 and 98 ug/L. However, even with this behaviour, the dissolved nickel in the effluent is still lower than the final effluent values reported in Table 6.5.

6.3.4 Removal Efficiencies

When the removal rates are analyzed in Table 6.13, it becomes apparent that the contamination does effect the efficiencies. Even though the effluent exceeded the raw only twice, it is felt that on the other days, the efficiencies are reduced because of the chemical contamination. The removal rates are fairly consistent as evidenced by the low standard deviations.

When comparing the removal efficiencies to the other plants listed in Table 6.14, it becomes obvious that the West Windsor treatment plant is similar to Kansas City, but lower that the other two plants. It should be remembered that Kansas City has the same basic treatment as West Windsor while the other two plants have complete physical-chemical treatment, including lime addition and activated carbon. Since West Windsor uses chemical only for phosphorous removal, very little removal of dissolved metals can be expected thru complexing, as compared to complete physical-chemical treatment. However, Table 6.14 does indicate that West Windsor has sufficient metal removal for the type of treatment provided.

TABLE 6.13

Removal Efficiencies for West Windsor

Day	Removal Percentage for Various Metals					
	Ni	Cd	Zn	Pb	Cu	Cr
Tues. Oct. 18 1983	22	40	68	75	58	60
Wed. Oct. 19 1983	15	25	69	51	77	66
Thur. Oct. 20 1983	41	29	75	71	57	86
Fri. Oct. 21 1983	35	33	37	60	81	80
Sat. Oct. 22 1983	31	29	81	69	73	50
Sun. Oct. 23 1983	-140*	0	44	48	54	44
Mon. Oct. 24 1983	-50	13	50	46	49	54
Average 7-Day	16	24	61	60	64	63
Standard Deviation	31	14	17	12	13	16

* Omitted from average calculation

Table 6.14: Average Overall Metal Removal Efficiencies in Physical-Chemical Treatment Systems

Location	Average Overall Percent Removal						Remarks
	Ni	Cd	Zn	Pb	Cu	Cr	
West Windsor Pollution Control Plant	30	24	61	53	64	63	
Kansas City, Mo.	--	25	68	59	70	36	Brown et al, 1973
Cincinnati, Ohio*	99.3	99.7	88	99	90	99	Maruyama et al, 1975
Pilot Plant*	86	50	60	90	92	93	Argaman and Weddle, 1973

*Complete Physical-Chemical Treatment which includes Lime and Activated Carbon.

6.3.5 Mass Balance

6.3.5.1 General

As at Little River, the mass balance was carried out for the West Windsor Treatment Plant to determine the same important phenomena. Calculations were done according to the procedure described previously with one modification. With West Windsor having no overflow, the only metals removed from the system are those contained in the sludge cake after dewatering.

6.3.5.2 Metal Addition Through $FeCl_3$

Table 6.15 lists the percentage of metals added through the chemical. The same patterns exist as at Little River, ie., cadmium the lowest percentage, zinc the largest percentage, and concentrations higher than the set limits., However, the West Windsor percentages added by mass are higher than those exhibited by Little River. These higher percentages by mass translate into higher contamination through the usage of $FeCl_3$ as the phosphorous precipitant. These occurrences justify the occasional higher metal concentrations in the effluent when compared to the raw wastewater metal concentations.

TABLE 6.15

Metal Addition Through $FeCl_3$

Metal	Mass g	% of Metal (by mass) in $FeCl_3$ Solution as received	Concentration in $FeCl_3$ as received mg/L
Ni	3686	.034	341
Cd	181	.002	17
Zn	50577	.468	4680
Pb	5924	.055	548
Cu	11314	.105	1047
Cr	16319	.151	1510

6.3.5.3 Metals Added Through Centrate Recycle

The hourly ratios of centrate to influent are given in Table 6.16 These are higher than the values calculated for Little River. The reason for the large ratios can be attributed to the fact that West Windsor has higher metal concentrations in the influent, plus the fact they dewatered only for a total of 76.75 hours per month as compared to Little River's 113.5 hours per month.

These increased ratios can explain the large rises in raw wastewater metal concentrations, especially those seen during the diurnal sampling. Furthermore, with the high ratios, the possibility of toxicity could become a problem with the present centrate if biological treatment were implemented.

TABLE 6.16

Centrate to Influent Ratios For West Windsor

Metal	Mass in Influent Min per month g/h	Mass in Centrate Mcent per month g/h	Ratio Mcent/Min %
Ni	323	22	6.7
Cd	24	1	5.2
Zn	1824	53	2.9
Pb	302	19	6.3
Cu	292	24	8.2
Cr	199	25	12.3

6.3.5.4 Metals in Sludge Cake

As Table 6.17 indicates, the recycling of metals occurs at West Windsor at slightly higher concentrations than at Little River. Possibly when dewatering, the centrifuges at West Windsor pass more metals thru, due to the different type of sludge being dewatered.

Furthermore, as expected due to the higher influent concentrations, West Windsor sludge cake has higher concentrations as compared to Little River. In comparing to the Ontario Guidelines [Ontario Ministry of Agriculture, 1981], the cake at West Windsor exceeds the limits for two metals, zinc and cadmium. Therefore, before the cake is used for land application, these two metal concentrations must be reduced.

TABLE 6.17

Metal Concentrations in Sludge Cake Plus Recycle Ratios

Metal	Conc.* sludge mg/kg	Conc.** sludge mg/kg	cake mg/L	Conc.# sludge cake mg/kg	Govern.+ Limits mg/L	Recycle Cent/Sludge %
Ni	346	113	123	260	160	1.2
Cd	21	7	7	7	1	1.1
Zn	6404	2107	2303	1500	1650	0.2
Pb	837	275	300	270	450	0.5
Cu	1271	417	456	640	750	0.4
Cr	1550	509	557	480	1000	0.3

* West Windsor sludge Oct. 1983 (dry basis)

** West Windsor sludge cake Oct. 1983 (wet basis)

\# West Windsor sludge cake analyzed by the City of Windsor Wastewater Laboratory Sept. 1983 (wet basis)

\+ [Ontario Minstry of Agriculture, 1981] (wet basis)

Chapter VII

CONCLUSIONS

Based on the field investigations at both treatment plants in Windsor for their efficiency in metal removal, the following conclusions are drawn:

1. In terms of heavy metals, the raw wastewater at Windsor is significantly different in characteristics from others reported in the literature. While generally the raw wastewaters are reported to consist mainly of insoluble metals on reaching the treatment plant, the raw wastewater at both plants in Windsor had a higher proportion of soluble metals.
2. Both plants showed significant diurnal variations in metal concentrations. Observations indicate that as dry weather flow rate increased, so did the metal concentrations. However, after a storm event dilution of metal concentrations occurred. This dilution becomes more evident after the initial flushing takes place.
3. From the studies of composite samples, it can be stated that the West Windsor plant receives higher metal concentrations than Little River. It ranges from almost no difference in cadmium levels, to 1.5

times for lead and zinc, twice for copper, three times for chromium and four times for nickel. These increases are attributed to the higher industrial contributions on the west side of Windsor.

4. Both wastewater treatment plants recycle metals through the centrifuge centrate. This process reduces the plants efficiency for metal removal since suspended metals once removed are being reintroduced into the plant. At Little River, the metal concentrations were below the toxicity level for the bacteria in activated sludge system.

5. The chemicals used for phosphorous removal and coagulation contribute noticable amounts of metals. This becomes particularly obvious at Little River, where the primary effluent showed higher metal concentrations than the raw wastewater.

6. Both treatment plants show a significant removal of the suspended metals, where the average removal for West Windsor approaches 75%. Unfortunately, there is no major reduction in the dissolved metal concentrations. However, the metal concentrations in the effluents at both plants indicate satisfactory removal performance, with each plant having a removal threshold for each metal.

7. With respect to sludge disposal, the Zn and Cd concentrations in the sludge cake presently exceed the

guidelines set by the Ontario Minsitry of Agriculture for sludge application on land. In fact cadmium, one to the most toxic metals exceeds the limits five to seven times.

8. Even with different sample preparation techniques, the metal concentrations determined by DCP and AA were within reasonable agreement.

Chapter VIII

RECOMMENDATIONS

1. Further investigation should be carried out on the metal content of chemicals used for phosphorous removal, eq., $FeCl_3$ and $AlCl_3$ The possibility of reducing the metal levels contained in these chemicals should be investigated. Other plants should also investigate such chemicals to ensure that no severe contamination is taking place. Furthermore, the biological removal of phosphorous, an alternative being considered by the City of Windsor should always be given a serious consideration. By implementing biological treatment, the metal contamination by chemicals can be eliminated.
2. An investigation of metal sources in Windsor should be carried out. By taking samples directly from the sewer system, the points of origin can be indentified. This way the large contibutions for heavy metals can be continuously monitored, and if necessary improvements can be implemented at the source. It is easier to treat metals in the concentrated state than when diluted. Also, a study can be carried out to determine why Windsor's sewage behaves differently in terms of solubility metal fractions.

3. The City of Windsor may wish to investigate the possibilty of pretreating the centrate before recycling to the head of the plant. By doing so, the metals can be removed while still relatively concentrated, before being diluted by the raw wastewater. This treatment can improve plant efficiency since the metals would be removed from the system.
4. More comprehensive studies on the sludge cake should be performed, since the City of Windsor uses composted sludge cake form West Windsor as landfill. With two metals exceeding the government limits, a more detailed study concerning the sludge cake could possibly determine a way to reduce the metal concentrations in the sludge cake to allow this practice to continue.

Appendix A

MASS BALANCE CALCULATIONS

A.1 LITTLE RIVER

A.1.1 Calculation of Specific Gravity of Sludge

The calculations of sludge specific gravity was based on the following average values of the 7-day data:

Percentage of solids, Ps = 4.14

Percentage of volatile solids, Pvs = 50.47

Assuming,

Specific gravity of fixed solids, Sfs = 2.65

Specific gravity of volatile solids, Svs = 1.0

The specific gravity for all the solids, Ss is given by:

$$1/Ss = Mfs / Sfs + Mvs / Svs$$

$$= Pfs / Sfs + Pvs / Svs$$

$$= .4953/2.65 + .5047/1.0$$

$$= .6916$$

Therefore, Ss = 1.445.

The specific gravity of the sludge, Ssl is given by:

$$1/Ssl = Ms / Ss + Mw / Sw$$

$$= Ps / Ss + Pw / Sw$$

$$= .0414/1.445 + .9586/1.0$$

$$= .9873$$

Therefore, Ssl = 1.013.

The volume of wet sludge collected per day, Qsl is given by,

$$Qsl = Msl / \rho wsl$$

where:

Msl = total mass of wet sludge pumped for December, (averaged for 31 days of pumping), kg

ρw = density of water, 1000 kg/m .

Calculating gives:

$$Qsl = [(2245/31)1000]/1000(1.013)$$

$$= 71.54\ m^3/d$$

$$= 0.072\ ML/d$$

Therefore, 0.072 ML of wet sludge are pumped to the dewatering room per day.

In order to determine the volume of wet sludge cake disposed of per day, Qsc the specific gravity of the sludge cake, Ssc must be determined. Where, it has been determined that the:

Percentage of solids, Pscs = 19.6.

Therefore,

$$1/Ssc = Pscs / Ss + Pscw / Sw$$

$$= .196/1.445 + .804/1.0$$

$$= .9392$$

Therefore, Ssc = 1.065.

By taking the mass of wet sludge cake, Msc as the daily average for the entire month, Qsc is given by:

$$Qsc = Msc / Ssc \rho w$$

$$= [(507/31)1000]/1000(1.065)$$

$= 15.357\ m^3/d$

$= 0.015\ ML/d.$

The volume of centrate recycled per day, Qcent is the difference in volume of sludge and volume of sludge cake per day. This gives:

$$Qcent = Qsl - Qsc$$
$$= 0.072 - 0.015$$
$$= 0.057\ ML/d.$$

A.1.2 Metals Added From $AlCl_3$

For calculating the mass of metals added through the chemical addition, the mass flow diagram in Figure A.1 was used. All the mass of metal is the product of the flowrate and the concentration. Balancing the 'mass of metals in', with 'mass of metal out', gives:

$$Ma + Mchem = Mov + Msl + Mc$$

Therefore,

$$Mchem = Mov + Msl + Mc - Ma$$

The rate of chemical addition by the city was 1L of chemical per minute for each 8 ML/d flow. Therefore, quantity of chemical, Qchem is:

$$Qchem = Qtreat\ [(1L/m)/8MLD]$$
$$= (Qa - Qov)[(1L/m)/8MLD]$$
$$= (40.95/8) x 60 x 24$$
$$= 7371\ L/d$$

Assuming the specific gravity of the chemical, to be equal to 1, the mass of chemical added per day as received is:

Qchem = 7371 L/d x 1000 kg/m³

= 7371 kg/d.

Finally, the percentage of metals added was calculated by dividing the mass of metal determined, by the mass of chemical added. The calculation for zinc is below.

Mass of zinc added through chemical treatment, from mass balance is:

Mchem = 10396 g

Therefore,

% of zinc added = (10396/1000) x (100/7371)

in chemicals = 0.14 % by mass as received

The concentration of metal in chemical is:

Cchem = Mchem / QChem

= 10396/7371

= 1410 mg/L as received.

All the values have been summarized in Table A.3

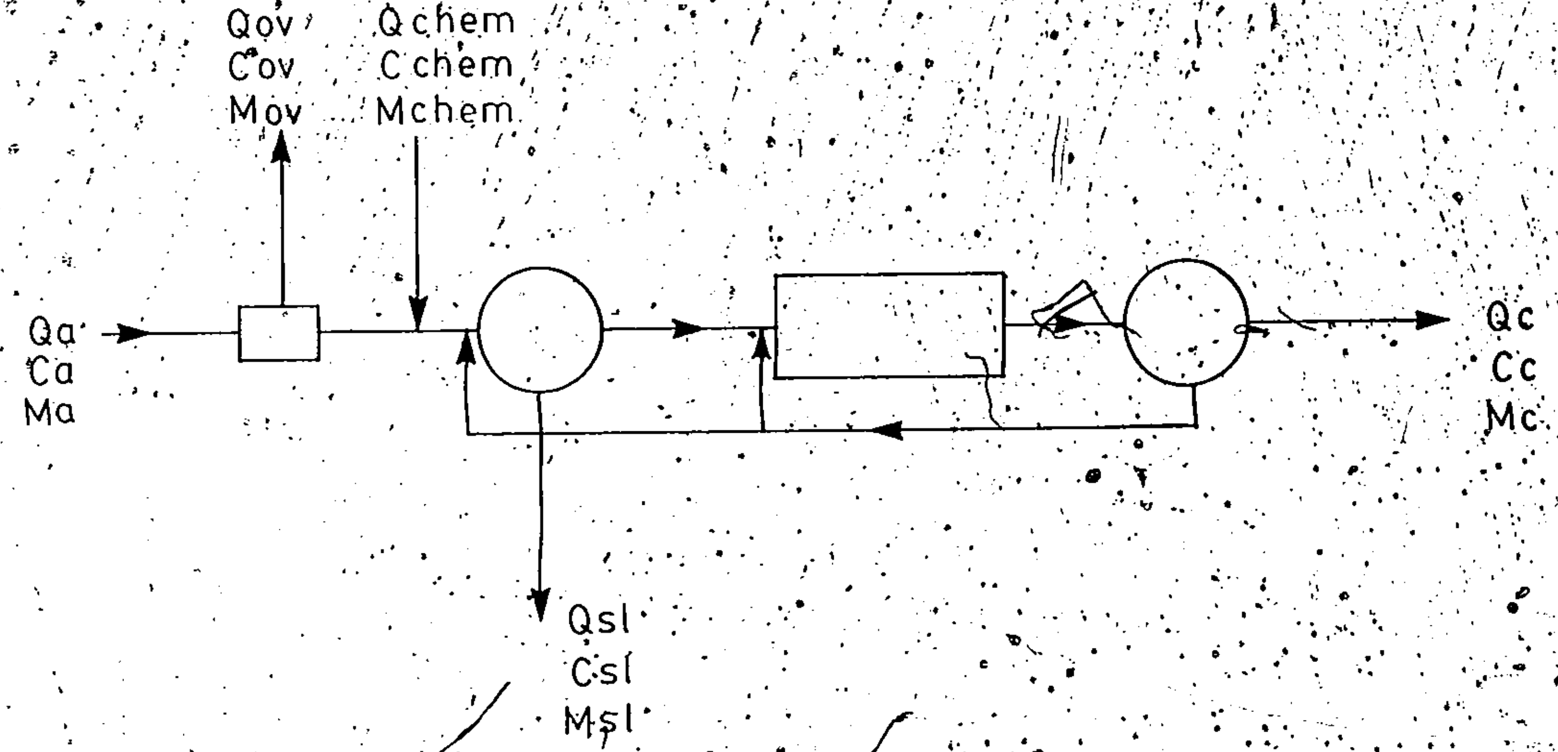

Figure A.1: MASS MOVEMENT OF METALS AT LITTLE RIVER

Table A.1: Summary of Metals Added Through $AlCl_3$

Metal	Q A MLD	Conc. A ug/L	Mass A	Q OV MLD	Conc. OV ug/L	Mass OV g	Q Sludge (dry basis) kg/d	Conc. Sludge (dry basis) mg/kg	Mass Sludge g	Q C MLD	Conc. C ug/L	Mass C g	Mass Chem. g	% of metal added by mass through $AlCl_3$ as received	Conc. of metal in $AlCl_3$ as received ug/L
Ni	63.27	10	633	22.320	10	223	2998	104	310	40.885	8	327	227	.003	31
Cd	63.27	6	380	22.320	6	134	2998	28	83	40.885	6	245	82	.001	11
Zn	63.27	182	11515	22.320	182	4062	2998	4520	13474	40.885	107	4375	10396	.141	1410
Pb	63.27	44	2784	22.320	44	982	2998	880	2623	40.885	33	1349	21708	.029	294
Cu	63.27	40	2531	22.320	40	893	2998	2128	6344	40.885	18	736	5442	.074	738
Cr	63.27	12	759	22.320	12	268	2998	370	1103	40.885	7	286	898	.012	122

Note: A is sample point, C is sample point, OV is overflow, and Sludge is sludge before dewatering.

A.1.3 Effect of Centrate Recycle on Raw Wastewater

The following calculation for zinc show how the ratio of centrate mass per hour, Mmcen to influent mass per hour, Mmin was determined.

Total volume of influent in December is:

Vin = Qin ML/d x 31 d
= 63.213 x 31
= 1960 ML.

Total mass of zinc in influent per hour is:

Mmin = Vin x Cin / hours in December
= 1960 ML x 181 ug/L x (24 x 31)
= 477 g/h.

Total mass of zinc per hour in centrate for 113.5 hours of dewatering during December is calculated below:

Vcen = Qcen x 31 d
= .057 ML/d x 31 d
= 1.767 ML

Total mass of zinc in centrate per hour,

Mmcen = Vcent x Ccent / hours dewatered in Dec.
= 1.767 ML x 335 ug/L / 113.5 h
= 5 g/h

Where, the percentage ratio of centrate to influent is:

Ratio = Mmcen / Mmin x 100
= 5 / 474 x 100
= 1.1%

The complete results for all the metals have been placed in Table A.2

Table A.2: Calculation of Centrate to Influent Mass Ratio per Hour at Little River Treatment Plant

Metal	Mass A g	Q Cent. MLD	Conc. Cent. ug/L	Mass Cent. g	Mass Infl g	Q Infl MLD	Conc. Infl. ug/L	Infl. Mass g/h per mon.	Cent. Mass g/h per mon.	Recycle Percentage M_{cent}/M_{infl}
Ni	633	.057	71	4	629	63.213	10	26	1	4.3
Cd	380	.057	15	1	379	63.213	6	16	.3	1.5
Zn	11515	.057	335	19	11496	63.213	181	477	5	1.1
Pb	2784	.057	111	6	2778	63.213	44	116	2	1.7
Cu	2531	.057	178	10	2521	63.213	40	105	3	2.9
Cr	759	.057	42	3	756	62.213	12	32	1	2.0

Note: Cent. = Centrate recycled
Infl. = Raw wastewater entering the plant

A.1.4 Metal Concentration in Sludge Cake

To determine the metals in the sludge cake, the mass balance in Figure A.2 was done. Note, the concentration of metals in the sludge cake is based on a wet basis, ie., as the sludge cake leaves the dewatering room. The concentration in the sludge cake, Csc has been calculated in both mg/kg and mg/L. The results have been placed in Table A.3

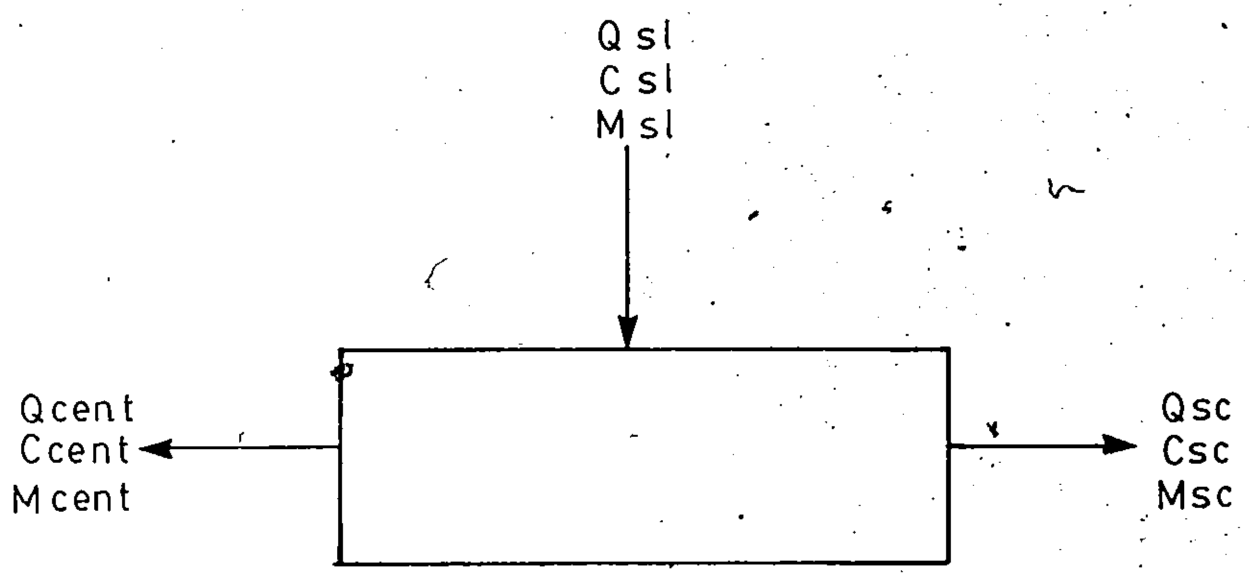

Figure A.2: MASS BALANCE FOR LITTLE RIVER DEWATERING ROOM

Table A.3: Summary of Metals in Little River Sludge Cake

Metal	Mass Sludge g	Mass Cent. g	Mass Cake g	Q Cake (wet basis) kg/d	Q Cake MLD	Conc. Cake (wet basis) mg/kg	Conc. Cake mg/L	Recycle Percentage Cent./Sludge
Ni	310	4	306	16355	.015	19	20	1.3
Cd	83	1	82	16355	.015	5	5	1.2
Zn	13474	19	13455	16355	.015	823	897	0.1
Pb	2623	6	2617	16355	.015	160	174	0.2
Cu	6344	10	6334	16355	.015	387	422	0.2
Cr	1103	3	1100	16355	.015	67	73	0.3

Note: Sludge = Sludge before dewatering
Cake = Sludge after dewatering

A.2 WEST WINDSOR

For West Windsor, the same procedure was followed as outlined for Little River, with the exception that no overflow occured. Listed below are the values used for West Windsor calculations.

Percent solids, Ps = 7.29

Percent volatile solids, Pvs = 47.23

Sfs = 2.65

Svs = 1.0

From calculations, Ss = 1.49 and Ssl = 1.025. With Msl = 5361.7 tonnes for October, Qsl = 0.169 ML/d.

With, Ssc = 1.103, Psc = 28.38 and Msc = 1186.1 tonnes for October, Qsc = 0.035 ML/d.

From the above values, the centrate flowrate, Qcent = 0.134 ML/d. With this information, and the mass flow diagram in Figure A.3, the percent metals added through $FeCl_3$ addition, can be calculated as shown in Table A.4 However, for West Windsor a different dilution rate is used, where, 1 L of chemical per minute/ 11 ML/d of flow.

Further calculating in Table A.5 shows the centrate to influent ratios, where the dewatering duration is 76.75 hours, while Table A.6 shows the metal levels in the sludge cake on a wet basis.

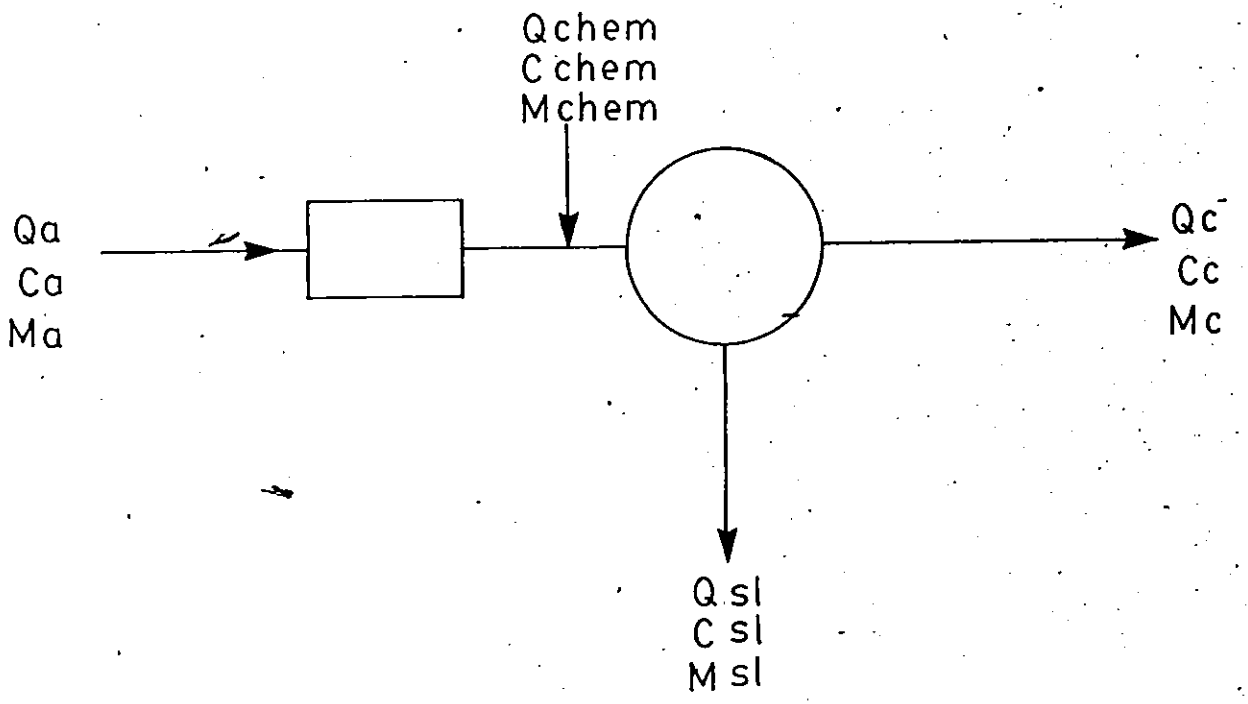

Figure A.3: MASS MOVEMENT OF METALS AT WEST WINDSOR

Table A.4: Summary of Metals Added Through $FeCl_3$

Metal	Q_A MLD	Conc. A ug/L	Mass A g	Q_{Sludge} (dry basis) kg	Conc. Sludge (dry basis) mg/kg	Mass Sludge g	Q_C MLD	Conc. C ug/L	Mass C g	Mass Chem. g	% of metal added by mass through $FeCl_3$ as received	Conc. of metal in $FeCl_3$ as received ug/L
Ni	82.56	94	7761	12608	346	4362	82.380	86	7085	3686	.034	341
Cd	82.56	7	578	12608	21	265	82.380	6	494	181	.002	17
Zn	82.56	532	43922	12608	6404	80742	82.380	167	13757	50577	.468	4680
Pb	82.56	88	7265	12608	837	10553	82.380	32	2636	5924	.055	548
Cu	82,56	86	7100	12608	1271	16025	82.380	29	2389	11314	.105	1047
Cr	82.56	59	4871	12608	1550	19542	82.380	20	1648	16319	.151	1510

Note: Sludge = Sludge before dewatering
Cake = Sludge after dewatering

Table A.5: Calculation of Centrate to Influent Mass Ratio per Hour at West Windsor Treatment Plant

Metal	Mass A g	Q Cent. MLD	Conc. Cent. ug/L	Mass Cent. g	Mass Infl. g	Q Infl. MLD	Conc. Infl. ug/L	Infl. Mass per month g/h	Cent. Mass per month g/h	Recycle Percentage M_{cent}/M_{infl}
Ni	7761	.134	406	54	7707	82.426	94	323	22	6.7
Cd	578	.134	23	3	575	82.426	7	24	1	5.2
Zn	43922	.134	983	132	43790	82.426	531	1824	53	2.9
Pb	7265	.134	350	47	7218	82.426	88	302	19	6.3
Cu	7100	.134	445	60	7040	82.426	85	292	24	8.2
Cr	4871	.134	453	61	4810	82.426	58	199	25	12.3

Note: Cent. = Centrate recycled
Infl. = Raw wastewater entering the plant

Table A.6: Summary of Metal Concentrations in West Windsor Sludge Cake

Metal	Mass Sludge g	Mass Cent. g	Mass Cake g	Q Cake (wet basis) kg/d	Q Cake MLD	Conc. Cake (wet basis) mg/kg	Conc. Cake mg/L	Recycle Percentage Cent./Sludge
Ni	4362	54	4308	38261	.035	113	123	1.2
Cd	265	3	262	38261	.035	7	7	1.1
Zn	80742	132	80610	38261	.035	2107	2303	.2
Pb	10553	47	10506	38261	.035	275	300	.5
Cu	16025	60	15965	38261	.035	417	456	.4
Cr	19542	61	19481	38261	.035	509	557	.3

Note: Sludge = Sludge before dewatering
Cake = Sludge after dewatering

NOMENCLATURE

A =maximum level of heavy metal that can be associated with the biological solids, mg metal/g biomass

C =liquid phase metal concentration in intimate contact with biomass, mg/L

Ce =equilbrium concentration of metals in the liquid phase, mg/L

Ccent =concentration of metal in centrate, mg/L

Cchem =concentration of metal in feed chemical, mg/L

K1 =forward rate constant

K2 =reverse rate constant

Ksp =solubility product

Ma =mass of metal at sample point A, g

Mc =mass of metal at sample point C, g

Mchem =mass of metal in feed chemical, g

Mfs =mass of fixed solids in sludge, %

Mmcent =monthly average of metals in centrate, g/h

Mmin =monthly average of metals in influent, g/h

Mov =mass of metals leaving thru overflow, g/h

Ms =mass of solids in sludge before

dewatering, %

Msc =mass of sludge cake hauled to disposal, wet basis, kg

Msl =mass of sludge before dewatering, wet basis, kg

Mvs =mass of volatile solids in sludge, %

Mw =mass of water in sludge before dewatering, %

Mx =metal concentration in solution, mg/L

OH =hydroxyl concentration, mg/L

pH =negative log of the hydrogen ion concentration

Ps =percentage of solids in sludge before dewatering

Psc =percentage of solids in sludge cake

Pvs =percentage of volatile solids in sludge

Q =quantity of metal already associated with biomass, mg metal/g biomass

Qcent =quantity of centrate recycled, MLD

Qchem =quantity of feed chemical added, kg/d, MLD

Qin =quantity of influent, MLD

Qtreat =quantity of wastewater treated after overflow, MLD

Qsc =quantity of sludge cake, MLD

Qsl =quantity of sludge before dewatering, MLD

Sfs =specfic gravity of fixed solids

Ss =specific gravity of solids in sludge

Ssc =specific gravity of sludge cake

Ssl =specific gravity of sludge

Svs =specific gravity of volatile solids

Sw =specific gravity of water

T =temperature, C

Vcent =total volume of centrate during dewatering, ML

Vin =total volume of influent during sample month, ML

a =exponent

b =exponent

r =overall rate of metal accumulation on biomass, mg metal/g biomass-min

γ =measure of physical resistance to mass transfer

ρ_w =density of water, kg/m^3

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