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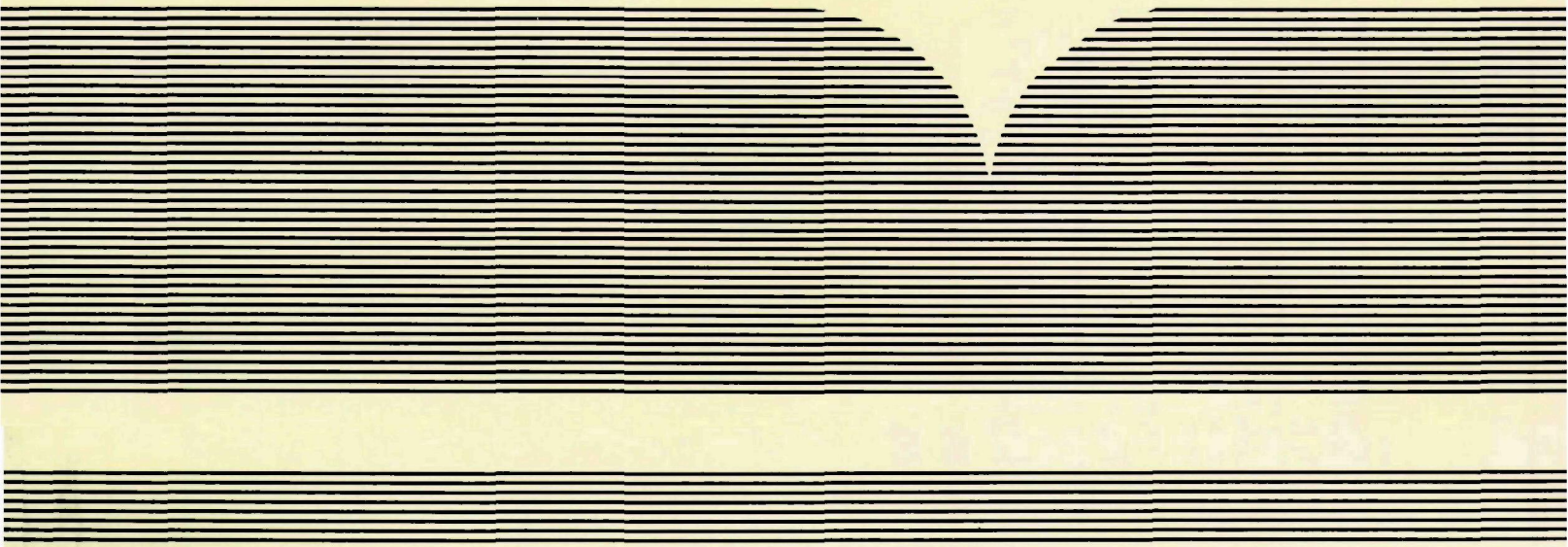

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REMOVAL OF METALS IN COMBINED TREATMENT SYSTEMS

by

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Eight pilot treatment plants, each consisting of primary clarifier, aeration basin, and secondary clarifier, were operated at varying influent metal levels to study the effect of significant variables indicated from the batch studies.

The results of this project indicate that the removal of metals in combined industrial-municipal treatment systems is influenced by a number of wastewater and treatment plant operation characteristics. The segregation of influent metals between the sludge (primary and secondary) phases and the plant effluent can be predicted, based upon the relationships presented in this report.

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Although the research described in this article has been funded in whole or in part by the United States Environmental Protection Agency through grant to Illinois Institute of Technology, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life. In partial response to these mandates, the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, is charged with the mission to manage research programs to investigate the nature, transport, fate, and management of pollutants in ground water and to develop and demonstrate technologies for treating wastewaters with soils and other natural systems for controlling pollution from irrigated crop and animal production agricultural activities; for developing and demonstrating cost-effective land treatment systems for the environmentally safe disposal of solid and hazardous wastes.

This report is a study of the mechanism of metals uptake by municipal treatment systems which receive a large amount of industrial wastes. Thus, the degree of "susceptibility" of heavy metals ions to municipal waste treatment process was determined. The results of this project indicate that the removal of metals in municipal systems is determined by a number of wastewater and treatment plant operation characteristics. The distribution of influent metals between the sludge phases on the plant effluent can be predicted, based upon the relationships presented.

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ABSTRACT

This project assessed the variables influencing the removal of eight metals through combined industrial-municipal treatment plants. The eight metals investigated were:

Aluminum	Iron
Cadmium	Lead
Chromium	Nickel
Copper	Zinc

The metals were studied at sub-toxic influent concentrations, and the interrelationships which influence metal removal were assessed.

The research was performed in two phases. Phase I involved batch studies on raw sewage and activated sludge to identify and define the impact of individual parameters or concentrations and of combinations of parameters on metals removal. These batch studies consisted of three parts. In Part I, metal solubility in filtered raw sewage and secondary effluent was determined as a function of pH. Part II investigated the equilibrium adsorption of the test metals onto primary sewage solids and onto activated sludge solids. In Part III, the effect of sewage variables such as detergent and ammonia concentration on metal adsorption was evaluated. In Phase II, eight pilot treatment plants, each consisting of primary clarifier, aeration basin, and secondary clarifier, were operated at varying influent metal levels to study the effect of significant variables indicated from the Phase I results.

The results of this project indicate that the removal of metals in combined industrial-municipal treatment systems is influenced by a number of wastewater and treatment plant operation characteristics. The segregation of influent metals between the sludge (primary and secondary) phases and the plant effluent can be predicted, based upon the relationships presented in this report.

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SECTION 1

INTRODUCTION

In recent years, increased emphasis has been placed on studies of the chemistry, biological effects, treatment, fate, and control of heavy metals in the environment. Findings include the discovery of heavy metals at high concentrations in surface waters receiving municipal and industrial waste discharges containing such metals; coupled with the recognition of potential health hazards and adverse environmental impacts associated with major disposal methods for metal-laden municipal and combined sludges. While the management of metals originating directly from industrial discharges has been implemented under effluent limitations guidelines and National Pollutant Discharge Elimination System (NPDES) permits, the control of industrial plus non-industrial metals entering combined municipal-industrial public-owned treatment works (POTWs) has been found to be much more difficult. As a result, heavy metals discharge into the municipal sewage treatment systems, and their fate during the sewage treatment processes, have become subjects of considerable interest in recent years.

Most of the studies to date concerning heavy metals in sewage treatment processes have represented attempts to perform mass balances of metals around a POTW, and determination of the per cent removal of each metal of concern across that POTW. However, there is a relative lack of information on the actual mechanisms affecting the distribution of heavy metals between liquid and solid phases through a municipal sewage treatment plant. There is a need for an understanding as to how the distribution of heavy metals is affected by variables such as the individual metal in total metals concentration, volatile suspended solids (VSS), soluble organic carbon (SOC), and inorganic ligands, such as carbonate, chloride, sulfate, and ammonia. Such an understanding is essential for developing criteria that can be used to predict the distribution of heavy metals through combined sewage treatment systems. Development of such criteria will be useful in different ways, including: 1) Given the influent and operational characteristics of a sewage treatment plant, the metals concentration in the sludge and the final effluent can be predicted. 2) Pretreatment standards necessary for heavy metals in the influent to the treatment plant can be predicted such that the metals will not

accumulate in the sludge to such levels that agricultural use will be restricted.

SECTION 2

CONCLUSIONS

METAL SOLUBILITY IN PROCESS LIQUIDS

The following conclusions have been drawn from the studies on metals solubility in filtered raw sewage and aeration basin mixed liquor.

1. At all pH values tested, equilibrium solubility conditions were achieved within six to 12 hours. Levels of metal solubility were equivalent at 24 hours to those observed at 12 hours.

2. High correlations were observed between metal solubility and process liquid pH, for all metals investigated.

3. Within the process liquids, over the 24-hour period of the solubility tests, the initial pH in each case shifted from the more extreme high or low pH values toward a final pH value of about 8.

This pH shift suggests that the process liquids are well buffered, and the occurrence of more extreme pH conditions in full-scale treatment systems would indicate the presence of strong acid or basic industrial wastes, which would influence metals solubility.

4. The effect of sulfide, at concentrations of 1 and 10 mg/l on metal solubility were tested. A comparison of the results where sulfide was added to those with no sulfide present revealed no difference in observed metals solubility. Sulfide effects may be significant at levels in excess of those tested, however.

5. A comparison of metals solubility in filtered process liquids with that in tap water revealed that in most instances the process liquids yielded higher metals solubility than did the tap water. This response is probably due to the complexation effects of organic and inorganic ligands in the process liquids.

6. The pH range of minimum metals solubility, for all metals tested and in both process liquids, was in the pH range of 8 to 9, except for aluminum in mixed liquor where a pH of minimum solubility of 6.8 was observed.

SORPTION OF METALS

The distribution of metals between the soluble and solids (sludge) phases in raw sewage and mixed liquor was studied, with metals added to the test liquids at concentrations below the metals solubility limits. The following results were observed.

1. A major portion of each added metal was removed from the soluble phase onto the solid phase in each test liquid. The sorption was essentially completed within a 15-minute contact time although some minor additional sorption continued for up to six hours.

2. Since the metals were added to the process liquids at concentrations below their solubility limits, removal from the liquid phase could not be by precipitation of metal salts, and therefore was due to accumulation by sorption onto the raw sewage and activated sludge solids.

3. The sorption behavior of each metal could be described by an adsorption isotherm relating µg of sludge metal sorbed per mg of total volatile suspended solids (TVSS) versus metal added in (mg/l) to the process liquids.

4. Although the sorption data generally followed the isotherm described in Item 3 above, the data for most metals did not fit a standard Freundlich isotherm based upon residual metal in solution.

5. Sorption of added metal in raw sewage ranged from 0 to 99%, with the following ranking of metals from least to most sorbed: iron, nickel, cadmium, copper, zinc, lead, chromium.

6. Sorption of added metal in activated sludge mixed liquor ranged from 8 to 98%, with the following ranking of metals from least to most sorbed: iron, nickel, zinc, cadmium, chromium, copper, and lead.

EFFECTS OF SEWAGE PARAMETERS ON METALS DISTRIBUTION

It has been suggested in the literature that a number of different waste constituents might influence the distribution of metals in raw sewage and mixed liquor between the soluble and solid phases.

This phase of the project investigated several domestic and industrial waste constituents, at low, normal, and high concentration, in replicate samples. The constituents evaluated were inorganics plus hardness, detergents, suspended solids concentration, SOC, pH, cyanide, and ammonia. The following conclusions were drawn, based upon statistical analysis of the experimental data.

1. Few of the waste constituents, at the levels tested had a statistically significant effect on metals distribution between the soluble and solid phases.

2. At the 99% confidence level, SOC influenced aluminum distribution in raw sewage; pH influenced iron and nickel distribution in raw sewage; and ammonia influenced aluminum in mixed liquor.

3. At the 95% confidence level, inorganics and hardness influenced the distribution of aluminum and lead in raw sewage, and cadmium and lead in mixed liquor.

4. At the 95% confidence level, detergent strength influenced the distribution of chromium and nickel in raw sewage. In mixed liquor, chromium, iron, lead, and nickel were indicated to be influenced.

5. At the 95% confidence level, pH influenced the distribution of aluminum in raw sewage and mixed liquor. Ammonia was indicated to influence the distribution of cadmium in raw sewage.

METALS DISTRIBUTION IN CONVENTIONAL ACTIVATED SLUDGE SYSTEMS

During this phase of the project, eight parallel continuous-flow pilot activated sludge systems were monitored around each unit process, during a total of 39 runs. Raw domestic sewage, spiked during each run with random levels of a mixture of test metals, was treated. Composite process liquid samples were collected several times weekly during each run, for raw sewage, primary clarifier effluent, mixed liquor, secondary clarifier effluent, and settled primary and secondary sludge. Total and filtered fractions of each metal were analyzed for metals plus other constitutents including SOC and VSS. Based upon the evaluation of this data, models were developed to predict the distribution of metals in each process liquid, and to predict the removal efficiency of each unit process and the full-treatment system in metals removal. The conclusions developed from this phase of the project are comprehensive, and are only briefly summarized here.

1. The removal of metals across the treatment system was directly related to the degree of distribution of each metal in the raw sewage and mixed liquor, and the efficiency of removal of the suspended solids (and associated metals) in the primary and secondary clarifiers. Thus, there are two principal classifications of variables which influence metals removal in combined treatment systems: those associated with the metals distribution in each process liquid; and those associated with the performance of the clarifiers solids separation.

2. In some experimental runs, negative removals of the metals were observed across the primary clarifiers, and/or the full-treatment systems. These negative metals removals always resulted from negative removals of suspended solids in the primary clarifier. Intermittent negative removals of suspended solids in primary clarifiers were observed in full-scale systems as well as pilot units. This negative performance of the primary clarifier in suspended solids removal explains why many short-term mass balance studies on full-scale systems have resulted in negative full-system removals of metals.

3. Over the course of the 39 experimental runs, a wide range of concentrations of influent SOC, VSS and metals were observed, reflecting the combination of natural fluctuations in the raw sewage composition, plus the spiking of the raw sewage with metals. Average performance of the system in solids removal was 76%, and removal of SOC averaged 61%.

4. Ranges of total effluent metals were also broad, although less so than the influent metals ranges. However, an evaluation of the soluble metals levels revealed that the average soluble concentration, for each metal, remained essentially constant across each unit process and the entire treatment system. Thus, the reduction of total metals across the unit processes was due to the sedimentation of solid-bound metal.

5. The lack of change in soluble metal concentration between raw sewage and primary clarifier effluent revealed that there was no redistribution of metals in that unit process.

6. The total metal concentrations in the activated sludge aeration basin were much higher than those observed in any other process liquid. However, the soluble metals levels in all process liquids were equivalent, and the higher total metals levels in the mixed liquor resulted due to higher levels of suspended solids and their associated metals.

7. Relatively wide variation in the total metals discharged in the secondary effluent resulted from variation in effluent suspended solids; the effluent soluble level of each

metal was comparable to the raw sewage soluble level of that metal.

8. The relative contribution of the soluble fraction of the effluent metals ranged from a low 2.9% for chromium up to 34.1% for nickel. Increased secondary clarifier efficiency in suspended solids removal would reduce only the non-soluble portion of the effluent metals.

9. The averaged removal of metals in the primary clarifier ranged from 14.0% for zinc to 41.1% for iron, and the metals ranked from lowest to highest removal in the primary clarifier were: zinc, copper, cadmium, aluminum, chromium, lead, iron, nickel.

10. The averaged removal of metals in the activated sludge process plus secondary clarifier ranged from 1.3 for aluminum to 38.9% for cadmium, and the metals ranked from lowest to highest as follows: aluminum, chromium, nickel, iron, zinc, copper, lead, cadmium.

11. The averaged overall removals of metal across the entire treatment system ranged from 27.6 for aluminum to 54.9% for lead, with the metals ranked from lowest to highest removal as follows: aluminum, zinc, chromium, copper, iron, nickel, cadmium, lead.

12. For the metals aluminum, chromium, iron, and nickel, the bulk of overall removal occurred in the primary clarifier. For the metals cadmium and copper, the secondary processes accounted for the majority of overall removal. Removals of lead and zinc were about equally distributed between the primary and secondary stages.

13. A number of models were assessed for their accuracy in predicting the distribution of metals in each process liquid, between the soluble and solid phases. An investigation of the influence for the total metal concentration of the parameters VSS, SOC, and pH revealed that a model which related total metal to sludge-bound metal per unit weight of VSS and to VSS solids in the process liquid provided an accurate prediction tool for metals distribution. This model has been designated as Metals Distribution Model 3 in this report, and model coefficients for each metal in each process liquid were derived. At moderate to high suspended solids levels, a simplified model (termed Model 4) which directly relates total metal to sludge-bound metal is equally accurate, and Models 3 and 4 have been utilized as the bases for a model of the full-treatment system.

14. Although the experimental data of the 39 runs can be fitted to adsorption isotherms in the manner described above in Part II, Item 3, a more striking and significant relationship was identified on the basis of the data generated from the continuous-run pilot units. This relationship reveals that the concentration of each metal sorbed on the solids of each process liquid was directly related to total metal, and was inversely related to total VSS present. In other words, at constant suspended solids, the metal per unit of solids increased with increasing total metal. However, at constant total metal, the metal per unit of solids increased with decreasing suspended solids concentration. Model 3, which incorporated all three variables, yielded high correlation coefficients with the experimental data on each process liquid and each metal, ranging from a squared coefficient of 0.80 for nickel to 0.99 for chromium in raw sewage, and coefficients of 0.99 for all metals in mixed liquor.

MODEL DEVELOPMENT

Section 8 of this report presents the development and application of the metals distribution and full-system metals removal models. The results of this activity are summarized below.

1. On the basis of the experimental data generated in the 39 continuous runs of the pilot treatment systems, an accurate metals distribution model, identified as Model 3, was developed. With this model, and known total metal and VSS concentrations, the distribution of soluble and solids bound metal in raw sewage and each other process liquid can be predicted.

2. A simplified version of Model 3, identified as Model 4, was developed for application where suspended solids concentrations are moderate to high. Model 4 can accurately predict solids bound metal, with only the total metal concentration given.

3. Models 3 and 4 have been used, together with suspended solids mass balance relationships, to develop a model, PW, for the performance of the primary clarifier. In addition to the constants of Model 3 or 4, the efficiency of the clarifier in suspended solids removal must be specified or estimated. The relative standard deviation of predicted against measured performance for Model PW (incorporating Model 4) was less than 10% for aluminum, chromium, copper, and zinc, and is near 15% for cadmium and iron. The relative standard deviation of predicted performance for lead and nickel was near 20%. The relative standard deviations, where Model PW incorporated Model 3, were somewhat higher.

Model 4 was thus indicated to be the preferred metals distribution base model for Model PW.

4. A predictive model, identified as Model FS, and incorporating Model PW, was developed to describe the full-treatment system including primary and secondary stages. This model also requires a solids mass balance, and this includes factors for activated sludge yield per unit of SOC removed, and secondary clarifier performance. Model FS has been used to predict the percentages of influent metals which will occur in the primary sludge, the secondary sludge, and the system effluent. Model FS, based upon Model 4, has the capability to predict effluent metal (and by difference sludge metal) within about 10% or less for all metals except nickel. For nickel, the difference between predicted and measured effluent metal was slightly below 20%.

5. Any full-system model, such as Model FS, must incorporate several submodels. These include metals distribution models, suspended solids removal models for the primary and secondary clarifier, and an excess sludge yield model for the activated sludge process. The metals distribution models resulting from this study were quite accurate. Prediction errors for the full-system model resulted primarily from the inability of existing clarifiers and activated sludge models to accurately predict solids balances around those unit processes, over short periods of performance. Thus, Model FS incorporates solids mass balance models with acknowledged inadequacies for short term performance. Until improved solids models are available, Model FS should only be applied to predict long-term (in excess of 60 days) performance on metals removal in combined treatment systems.

SECTION 3

RECOMMENDATIONS

This study has revealed that the distribution of metals in the individual process liquids of a combined treatment system follows patterns which can be accurately described by empirical relationships. Two such empirical relationships have been developed as one result of this project. The relationships, identified as Metals Distribution Models 3 and 4, reveal that the distribution of the metals between the soluble and solid phases of the process liquids are controlled, for each specific metal, by the total metal concentration and the VSS concentration. Model constants have been derived by statistically fitting these models to data collected during 39 runs on parallel continuous-flow activated sludge pilot systems. It is recommended that these two models, and the derived constants, be validated against full-scale treatment systems performance. Some preliminary validation has already been performed against one full-scale system and the results were promising.

In this study, the behavior of eight metals were investigated. Each metal demonstrated somewhat different behavior, and the study has revealed that different process liquid characteristics can influence the behavior of each metal to a variable extent. There is little basic information on the chemical and physical interactions of metals in process liquids such as investigated here which could provide for interpretation of these results as any basis other than an empirical one. In order to better understand the response patterns observed in this study and others of similar objective, fundamental research on the physical and chemical interactions of metals in raw sewage and activated sludge mixed liquor are necessary.

Finally, this project has resulted in the development of a full-system model to predict the removal of metals at each unit process across a combined treatment system. The full-system model relies upon submodels for (1) metals distribution, by process liquid, (2) primary clarifier performance in suspended solids removal, and (3) secondary treatment system performance in terms of sludge yield, and secondary clarifier performance.

A comparison of the full-system model to pilot-plant experimental data revealed that, where the full-system model was inaccurate, it failed through an inability to track the short-term solids balance around each unit process. These unit processes, while performing in a predictable fashion on a long-term average basis, perform in a more erratic fashion over short periods of days to weeks, sometimes exhibiting, for example, negative suspended solids removal in the primary clarifier or short-term interruptions in activated sludge yeild. Metals removals are closely tied to the solids balances around the unit processes of the treatment system, and improved models to predict the short-term behavior of the systems in terms of solids are necessary before more accurate short-term modeling of metals dynamics will be possible.

SECTION 4

HISTORICAL PERSPECTIVE

The large volumes of municipal and industrial wastewaters and treatment residues, coupled with increasing energy costs, reduced land availability, and enhanced public awareness of the potential environmental and health hazards associated with the toxic substances present in the effluents, have created a great deal of concern in recent years. Heavy metals pollution of surface waters, and the environmental hazards associated with their presence in sludges disposed on land, have received much attention beginning in the early 1970's. This concern is principally due to two factors: 1) There is increasing industrialization and growing awareness of the toxic effects of metals such as cadmium and lead. 2) Analytical techniques capable of measuring low metals concentrations found in the water bodies of the nation and the discharged effluents have increasingly become widely available.

Heavy metals loadings into surface waters arise from point sources as well as diffuse sources, and assessing the relative impact of the two sources is often difficult. Treated or untreated effluents from municipal and industrial activities are among the point sources, while atmospheric fall-out and surface runoff comprise the major portions of diffuse sources of heavy metals into the water bodies of the nation (Patterson and Kodukula, 1978).

HEAVY METALS IN POTW INFLUENTS AND EFFLUENTS

The metals found in municipal sewage originate from a variety of industrial, commercial, and residential activities, as well as from storm runoff. Several authors (Davis and Jacknow, 1975; Gurnham, et al., 1979; Kodukula and Obayashi, 1979; Olthof and Lancy, 1978) have published discussions on the sources of heavy metals in municipal sewage. The relative contribution of heavy metals from residential and industrial sources primarily depends upon the number and nature of the contributing industries, and the pretreatment regulations in the area under consideration. High influent metal concentrations, either due to domestic or industrial activities, interfere with the operation of treatment plants due to their toxic effects during the biological treatment.

Generally, in the United States, metals concentrations in the influents to POTWs are lower than the threshold toxic levels for biological treatment processes (U.S. Environmental Protection Agency, 1978). The concentrations may however be at environmentally unacceptable levels in the final effluent or the sludge, depending upon the metals removal efficiency within the treatment system. For example, Putnam and Paulus (1976) reported 2.3 tons/day of total heavy metals input from the sewage of the Twin Cities, entering the Minnesota Metropolitan Sewage Treatment Plant. Approximately 54% was removed by treatment processes prior to effluent discharge to the Mississippi River, while the remaining cadmium (55%), chromium (55%), copper (38%), manganese (72%), nickel (68%), lead (60%), and zinc (42%) were discharged with the plant effluent. The Metropolitan Sanitary District of Greater Chicago (MSDGC) was estimated to discharge 1,469 tons/year of combined copper, cadmium, lead, mercury, nickel, zinc, and chromium from its treatment plants (Patterson and Allen, 1975). Data presented by Patterson and Kodukula (1978) for the same metals indicate that about 6,000 tons of total metals from POTWs in the United States alone are discharged every year into the Great Lakes.

An extensive field survey was conducted by Sverdrup and Parcel, and Associates, on 103 POTWs across the United States. Table 1 shows the ranges and medians of influent and effluent metal concentrations reported in this study. Table 2 presents a partial summary of other published data on influent and effluent metal levels of several conventional sewage treatment plants. It is evident from these tables that there is extreme variation in removal efficiencies for each metal, and that while the metal removal efficiences are generally in the order of zinc>mercury>lead>copper>chromium>cadmium>nickel, there is variation in this order among plants.

HEAVY METALS IN SLUDGE

Heavy metals in sewage sludges emanating from biological treatment processes have received considerable attention in recent years, due to their potential as toxic agents in sludge treatment (e.g., anaerobic digestion) and disposal (e.g., land application, incineration) operations. The properties of sewage sludges and the agronomic and environmental considerations involved in the development of guidelines for land application of such sludges have been discussed in several reviews (Chaney, 1973; Dowdy et al., 1976; Jones and Lee, 1977; McCalla et al., 1977; Schmidtke and Cohen, 1977; Sommers and Sutton, 1977). Kodukula and Obayashi (1979), in their review paper, concluded that the heavy metals concentrations in sewage sludges are highly variable (Table 3). Similar variability has

TABLE 1. INFLUENT AND EFFLUENT METALS CONCENTRATIONS IN DIFFERENT POTWs (AFTER U.S. EPA, 1977)

Metal	Influent, µg/l[a]		Effluent, µg/l[b]		Percent Removal,
	Median	Range	Median	Range	Median
Cadmium	11	1-243	9	2-79	18
Chromium	100	5-14,000	18	3-246	82
Copper	120	10-1,968	33	10-352	73
Iron	2000	450-10,200	250	48-569	88
Lead	60	7-1,000	25	7-80	58
Mercury	1	0.2-240	0.6	0.2-2.9	40
Nickel	90	10-3,190	55	12-1240	39
Zinc	330	17-3,909	110	13,1039	67

a) Based on data available from 103 POTWs.
b) Based on data available from 22 POTWs meeting secondary treatment performance levels.

TABLE 2. SUMMARY OF INFLUENT AND EFFLUENT CONCENTRATIONS OF METALS IN SELECTED TREATMENT PLANTS*

Location		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc	Reference
Bryan, OH	Influent	-	0.8	0.2	-	-	0.05	2.2	Barth et al.,
	Effluent	-	0.2	0.1	-	-	0.05	0.2	1965
Dallas, TX	Influent	0.013	0.22	0.09	0.09	0.5	0.07	0.32	Esmond and
	Effluent	0.008	0.09	0.06	0.04	0.2	0.06	0.11	Petrasek, 1974
Grand Island, MI	Influent	0.018	0.059	0.17	0.16	0.6	-	0.353	Brown et al.,
	Effluent	0.016	0.013	0.067	0.092	0.5	-	0.182	1973
Grand Rapids, MI	Influent	-	3.6	1.4	-	-	2.0	1.5	Barth et al.,
	Effluent	-	2.5	1.6	-	-	1.8	0.8	1965
Hyperion, CA	Influent	0.028	0.3	0.13	0.11	0.5	0.2	0.43	Chen et al.,
	Effluent	0.028	0.21	0.13	0.10	0.5	0.14	0.26	1964
Joplin, MO	Influent	0.021	0.066	0.316	0.19	0.5	-	0.984	Brown et al.,
	Effluent	0.015	0.041	0.047	0.065	0.8	-	0.484	1973
Muncie, IN	Influent	-	0.26	0.26	0.93	-	0.13	0.97	Davis and
	Effluent	-	0.05	0.07	0.22	-	0.11	0.26	Jacknow, 1975
New York, NY	Influent	0.016	0.16	0.27	-	-	0.11	0.41	Klein et al.,
	Effluent	0.01	0.08	0.15	-	-	0.10	0.21	1974
Rockford, IL	Influent	0.25	-	1.17	-	-	0.37	2.8	Patterson,
	Effluent	0.05	-	0.19	-	-	0.32	0.45	1978
Burlington, CANADA	Influent	<0.01	0.04	0.10	<0.05	<1	0.04	0.11	Oliver and
	Effluent	<0.01	0.03	0.02	<0.05	<1	0.03	0.04	Cosgrove, 1975

*Metal concentrations expressed as mg/l except mercury, which is expressed as µg/l. (continued)

TABLE 2. (continued)

Location		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc	Reference
Clarkson, CANADA	Influent	0.02	0.14	0.26	0.37	6	0.08	0.34	Oliver and Cosgrove, 1975
	Effluent	0.01	0.06	0.10	0.08	1	0.07	0.09	
Oaksville, CANADA	Influent	0.006	0.29	0.31	0.23	7	0.33	2.4	Oliver and Cosgrove, 1975
	Effluent	0.001	0.06	0.08	0.15	1	0.27	0.56	
Oxford, ENGLAND	Influent	0.006	-	0.082	0.20	-	-	-	Perry et al., 1976
	Effluent	0.000	-	0.006	0.00	-	-	-	
Zurich, SWITZERLAND	Influent	0.006	0.08	0.09	0.27	-	0.07	0.6	Roberts et al., 1977
	Effluent	0.003	0.03	0.06	0.05	-	0.05	0.25	
Average Concentration:									
	Influent	0.031	0.459	0.290	0.229	2.02	0.267	0.919	
	Effluent	0.012	0.239	0.164	0.081	0.673	0.226	0.263	
Average Percent Removals		61.3	47.9	43.4	64.6	66.7	15.4	71.4	

*Metal concentrations expressed as mg/l except mercury, which is expressed as µg/l.

TABLE 3. SUMMARY OF DATA COLLECTED ON SELECTED METALS IN SEWAGE SLUDGES FROM VARIOUS MUNICIPAL WASTEWATER TREATMENT PLANTS (KODUKULA AND OBAYASHI, 1979)*

Location	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
United States:							
Indiana	163	3195	2846	--	993	2970	8107
Michigan	74	2031	1024	5.5	371	--	3315
Michigan	163	8086	2423	2.6	1040	2940	4900
Minnesota	131	931	1521	--	231	1190	2368
New Hampshire	10	6763	86	--	63	3347	121
New Jersey	29	1606	1400	--	156	327	2206
Ohio	198	1281	1392	4370	710	1634	4153
Pennsylvania	105	635	1091	--	172	784	3517
Wisconsin	64	--	1147	--	482	812	2982
Canada	--	75	19	28	6	63	181
England and Wales	<200	980	970	--	510	820	4100
Sweden	13	872	791	6.0	121	281	2055
Switzerland	30	500	800	--	300	800	3000

*All concentrations expressed as mg/kg.

also been demonstrated among the heavy metals concentrations in sludges from major cities in the United States (Furr et al., 1976).

HEAVY METALS IN SEWAGE TREATMENT PROCESSES

Conceptually, a typical municipal treatment plant can be divided into five major unit processes: primary sedimentation, secondary treatment (activated sludge for the purpose of this study), secondary clarification, anaerobic digestion and disinfection (Fig. 1). Similarly, the phases in which the heavy metals exist in the wastewater can be classified into three components: soluble, operationally defined as that portion passing through a 0.45-micron filter; settleable solids, characterized by being settleable within 30 minutes (Anon., 1973); and non-settleable solids. Heavy metals in each process stream exist in each of the above phases, as represented in Figure 1.

As shown in Figure 1, settleable solids and associated metals are removed via the primary and secondary clarifiers to the anaerobic digester. The effluent from the primary clarifier, containing soluble metals and metals associated with non-settleable solids, enters the aeration unit for secondary treatment. The settled secondary effluent undergoes chemical disinfection and is finally discharged. The supernatant from the sludge digestor is usually returned to the raw waste or primary clarified stream. This flow may or may not constitute a significant mass source of heavy metals to the process stream. Further, the complex organic and non-metal inorganic constituents of the digestor supernatant, when blended into the primary waste, may have a significant effect on metal distribution in subsequent treatment processes.

There is little information available on the heavy metals interactions in the disinfection process. It would, however, be expected that chlorination, a major disinfection process in the United States, could indirectly affect the heavy metals distribution in the secondary effluent by changing the pH of the medium and/or oxidizing some of the soluble and particulate organic ligands with which the metals are complexed. Prior to the point of disinfection however, the operational segregation of influent metals between POTW effluent phase and sludge phase is completed.

Sedimentation

In a typical sewage treatment plant, metals associated with settleable solids are removed during primary and secondary sedimentation. Metal removal efficiency in a primary clarifier

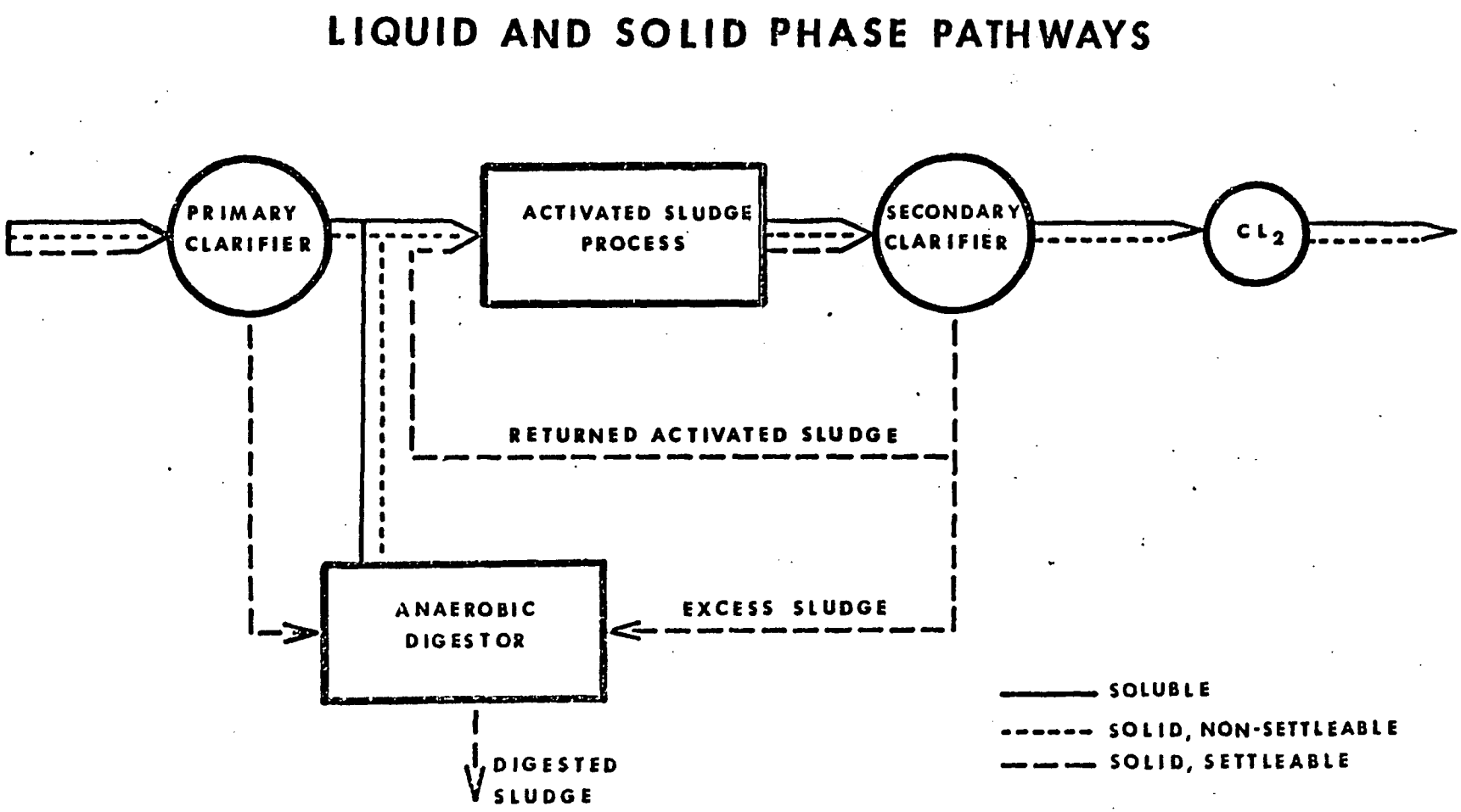


Figure 1. Schematic of a typical municipal sewage treatment plant illustrating the liquid and solid phase pathways.

has two important implications. When the metals are largely removed during primary sedimentation, problems might arise with regard to toxicity of metals if the primary sludge is disposed on land. Low metals removals in primary sedimentation due, for example, to the presence of complexing agents in the waste, which would render the metals soluble, or to ineffective solids separation lead to increased levels of metals input to the activated sludge system. The resulting high metals loading to the aeration basin may cause a decrease in the process performance efficiency of the activated sludge due to metals toxicity, and thereby result in a poor quality effluent in terms of organics and metals.

Table 4 presents data collected on removal of metals through ten primary treatment plants. According to this survey, cadmium and lead were the least removed metals, while iron, zinc, and copper exhibited the highest removals during primary treatment. Brown et al., (1973) reported average per cent removals for copper, cadmium, chromium, lead, mercury, and zinc at 42, 15, 27, 37, 32, and 46, respectively, during primary treatment. Except for lead, these results are comparable to those presented for primary plants in Table 4, and are similar to secondary plant data summarized in Table 2.

Activated Sludge Process

Removal of heavy metals by activated sludge has been a subject of interest since the 1950's (Rudolfs and Zuber, 1953), but has received considerable attention only during the last two decades (Adams et al., 1973; Cheng et al., 1975). Most early studies dealt with the percentage removal of metals by activated sludge, while information regarding the physical-chemical interactions between metal ions and the biomass has been reported only in recent years.

Rudolfs and Zuber (1953) studied the removal of copper and zinc by activated sludge, using laboratory-scale units. They reported removals of 33-100% and 31-90% for zinc and copper, respectively, for a contact period of 30 minutes, and concluded that the amount of metal removal was a function of two factors: the concentration of the activated sludge and the time of contact between the metal and the sludge. Stones (1955; 1956; 1958; 1959a; 1959b; 1959c) investigated the fate of iron, copper, nickel, and zinc in each treatment unit of a sewage treatment plant, and reported that activated sludge treatment removed about 80% of iron and copper, and 90, 60, and 30% of lead, zinc, and nickel, respectively, present in presettled sewage.

TABLE 4. REMOVALS OF SELECTED METALS DURING PRIMARY TREATMENT (U.S. EPA, 1977)

Metal	% Removal Efficiency	
	Range	Median
Cadmium	0-15	5
Chromium	0-71	31
Copper	14-60	37
Iron	19-66	42
Lead	0-25	11
Mercury	0-75	18
Nickel	8-21	14
Zinc	8-67	39

Barth et al. (1965), in their extensive pilot-plant investigations of heavy metal interactions in sewage treatment plants, demonstrated that activated sludge plays a major role in overall POTW metals removal during the sewage treatment process. This study found that removals of copper and zinc by activated sludge are very high compared to those of chromium, and especially nickel. Similar metals removals have been reported by Tarvin (1956) and Brown et al., (1973) in the United States, by Oliver and Cosgrove (1974; 1975) in Canada, and by investigators from England (Stones, 1955; 1956; 1958; 1959a; 1959b; 1959c), Germany (Anon., 1966), and Switzerland (Roberts et al., 1977). The information available in the literature on heavy metals removals indicates that copper and zinc show high removals by activated sludge, while nickel exhibits the least removal.

Extensive studies conducted at the Environmental Engineering laboratories of the Illinois Institute of Technology, Chicago, (Cheng, 1973) on heavy metal interactions in activated sludge have demonstrated that the sludge solids have a great ability to remove and accumulate metals from solution in a very rapid initial phase, followed by a slow phase. The removal achieved in the slow phase is relatively insignificant compared to that of the first phase. In these studies, the biofloc of the activated sludge process appeared to act as a chemisorption system, following a Langmuir adsorption isotherm. The efficiency of metal uptake by the sludge was found to follow the order of lead>copper>cadmium>nickel, based on the percentage removal of initial metal added. The total amount of metal taken up by the sludge floc was found to increase with the concentration of VSS. The removal of metal also increased with increasing metal concentration, for a constant VSS concentration. The amount of metal uptake increased with increasing pH up to a level where precipitation of metal hydroxide occurred. Cheng (1973) also studied the effect of added soluble ligands such as oxalate, and silicate on the metal uptake by activated sludge, and reported that high ligand concentration prevented metal sorption or precipitation, by formation of soluble metal-ligand complexes. Such reactions resulted in higher soluble metals concentrations in the final effluent.

In biological processes, the relative affinity of metal ion for the sludge depends upon the different metal ions present in the system. The Irving-Williams series (Irving and Williams, 1948; 1953) suggests that the stability complexes of bivalent metal ions, regardless of the nature of complexed ligand or of ligand molecules involved, follows the general sequence of zinc>copper>nickel>cobalt>cadmium>iron> manganese. However, Cheng et al., (1973) demonstrated that

under similar conditions of pH, VSS, and metal concentration, etc., the uptake of these metals by activated sludge is in the order of lead>copper>cadmium>nickel. Schnitzer and Skinner (1966; 1967), in their studies with metal-fulvic acid complexes, also reported the sequence of the stabilities of complexes as being different than that of the Irving-Williams series. It thus appears that guidelines derived from simple system behavior are not directly applicable to the complex systems of the POTW.

Anaerobic Digestion

Among the various process components of conventional wastewater treatment, including the various sludge treatment processes, anaerobic digestion appears to be particularly vulnerable to excessively high heavy metal loadings. Numerous investigators have attempted to study the heavy metal problems with respect to anaerobic digestion systems in recent years. However, most research performed thus far has focused on the toxic effects of heavy metals on anaerobic digestion systems (Moore et al., 1961; McDermott et al., 1963; English et al., 1964; Barth et al., 1967; Ghosh and Zugger, 1973), while only few studies have centered on the distribution and chemistry of metals within the digestor (Gould and Genetelli, 1975; Hayes and Theis, 1978; Lingle and Hermann, 1975; Patterson and Hao, 1979).

Adams et al., (1973) reviewed the effects and removal of heavy metals in biological systems including anaerobic digestion. Extensive studies conducted by Barth et al., (1967) over a period of ten years of continuous feeding of heavy metals demonstrated that a significant amount of heavy metals were removed from the bulk solution in anaerobic digestion. No effort was made in that study to investigate the chemistry and removal mechanisms of the metals. Gould and Genetelli (1975) examined the distribution of heavy metals in anaerobically digested sludge, and reported that more than 90% of the metals was found on the particulate fraction (>100 micron effective diameter).

More recently, Hayes and Theis (1978) investigated the distribution of heavy metals among the soluble, precipitated, and extracellular components of anaerobically digesting sludge. They concluded that the heavy metal chemistry is controlled not only by the stability of inorganic precipitates, but also by sorption onto and subsequent incorporation of metals into the digester biomass. Toxic effects were found to coincide with the near maximum uptake of metals by the biomass. Microbial uptake activity competed with precipitation in the removal of heavy metals from the digester supernatant. Depending upon the

metal, between 30 and 60% of the total metal was associated with the biomass.

Investigations by Patterson and Hao (1979) showed that in addition to the uptake by biomass and precipitation reactions, another important mechanism effecting heavy metal removal in anaerobic digesters is complexation of metals with the solids as well as the digester supernatant. By determining the stability constants of metal-sludge complexes, it was shown that the affinity of heavy metals toward anaerobically digesting sludge follows the order of lead>copper>iron>cadmium >nickel>zinc. A similar order of affinity was also observed for metal-digester supernatant complexes. It was reported in this investigation that in excess of 98% of each total metal in the digester was associated with the sludge phase. This corresponds to similar values reported by Gould and Genetelli (1975) and Hayes and Theis (1978).

HEAVY METAL DISTRIBUTION

Chen et al., (1974) measured the distribution of several metals in raw sewage at Los Angeles, California. For the four metals, copper, iron, lead, and zinc, the metal associated with the settleable solids fraction was 7, 46, 22, and 57%, respectively. For the same metals, the soluble fraction of the raw sewage contained 91, 42, 63, and 30% of the respective total influent metal. The remainder of the metals ranging from 2 (copper) to 13% (zinc) was associated with non-settleable suspended solids. Patterson (1978) reported that for a treatment plant in Illinois the soluble fractions of cadmium, copper, iron, nickel, and zinc in raw sewage were 24, 26, 4, 68, and 16, respectively.

In order to study the phase partitioning behavior of metals in raw sewage, Patterson et al., (1975) conducted batch experiments in which increments of stock metal solution was added dropwise to raw sewage, below a predetermined metal solubility limit. The pH of the sewage was maintained constant, and the reaction vessels were stirred for 24 hours, before the final soluble metal concentrations were measured. In this study, lead and zinc were most completely adsorbed to the raw sewage solids, while most of the added nickel stayed in solution. This distribution behavior partly explains the high removals of zinc and low removals of nickel observed in primary sedimentation. It was shown in these studies that for most metals, partitioning into the soluble phase followed a log-log function. However, the proportion of soluble copper appeared to be quite insensitive to total copper (1 - 40 mg/l) added, indicating that the soluble copper concentration in the primary effluent may remain relatively constant despite fluctuations in

the influent copper concentration over a limited range. The addition of lead resulted in considerable partitioning onto the solid phase, even at the highest lead concentration examined (only 2.7% soluble at a total lead dosage of 1.3 mg/l), while the data on cadmium, nickel, and zinc were found to be co-linear. For these four metals, effluent soluble metal concentrations from a primary clarifier would increase proportionally with increased influent metal concentration.

MECHANISMS EFFECTING HEAVY METALS DISTRIBUTION

Heavy metals in influent sewage undergo different physical, chemical, and biological interactions during each stage of the treatment process. The extent and affinity of such interactions is a complex function of intrinsic variables, such as the individual metal, its concentration, and the presence and concentrations of other metals; the physical-chemical characteristics of the aqueous medium such as solids content, pH, alkalinity, and its associated ions, the nature and variety of organic and inorganic complexing agents, and external factors such as plant operational procedures. The mechanisms which can affect the heavy metals distribution between soluble and solid phases are inorganic metal salt precipitation, sorption, biological uptake, and complexation. Of these mechanisms, sorption and complexation seem to be the most significant, as discussed below, while the other two are negligible.

Precipitation

Precipitation of a metal ion occurs when the salt with which it is in equilibrium reaches its solubility limit as defined by its solubility product. The values of the logarithm of the solubility products of different metal salts of interest have been compiled by several authors (Bard, 1966; Feitknecht and Schindler, 1963; Martell and Smith, 1974a; 1974b; 1974c; 1974d; Sillen and Martell, 1964; 1971). These constants may be used to plot the theoretical solubility diagrams for each metal. This information provides a representation of the theoretical concentrations of the metal salt and its solubility products in equilibrium with the specified precipitate solid phase in the aqueous solution, at the indicated pH conditions.

The solubility of metal salts in aqueous solutions is a function of factors such as pH, temperature, ionic strength, and the presence of anions or other complexing agents in the solution (Butler, 1964; Patterson and Minear, 1973). The values of solubility products determined by different authors for the same salts under similar conditions may vary. For instance, at the same temperature (25°C) and ionic strength (0), the solubility products of nickel hydroxide, $Ni(OH)_2$, are reported as $10^{-10.5}$, $10^{-15.5}$, $10^{-7.2}$ (Sillen and Martell, 1964).

Jenkins et al., (1964) conducted experiments to determine the effect of such factors as pH and concentration of metals upon the precipitation of heavy metal salts in water, sewage, and sewage sludge. They reported that for copper and nickel, precipitation occurred rapidly. The extent of precipitation for copper increased slightly over a period of six to eight hours, while for nickel it was very slight, and the fraction of that metal precipitated was not as high as with copper. Within the range of concentrations of copper used, 0.5 - 100 mg/l, the fraction of metal precipitated increased with increasing concentration of copper. Salts of zinc were precipitated up to 60 and 80% at initial zinc concentrations of 100 and 10 mg/l, respectively.

The solubility of metal salts in the filtered supernatant of activated sludge is generally somewhat higher than the value obtained from tap water experiments. For instance, it was shown that the solubility of lead in the supernatant of activated sludge at a contact period of four hours was at least 4 mg/l more than that observed in tap water, at the same pH (Cheng, 1973). In the same investigation, a similar higher soluble concentration of trivalent iron was also found.

Patterson and his co-workers (1975) determined the solubility of a number of metals in tap water, filtered raw sewage, and filtered secondary effluent. They reported that in all cases, metal solubility in tap water was less than that observed in filtered raw sewage or in filtered secondary effluent. Furthermore, raw sewage solubility was greater than could be accounted for by consideration of intrinsic carbonate, hydroxide, and chloride ligand effects. Increased solubility of cadmium in raw sewage and activated sludge mixed liquor (Patterson, 1979) and of copper in activated sludge effluent (Patterson et al., 1979) as compared to tap water was also observed in other recent studies. Metal solubility was also found to be higher in anaerobic digester supernatant than in tap water (Patterson and Hao, 1979).

The primary reason for the higher solubility of metals in different waste media than in tap water, explained by Patterson and his co-workers, is due to complexation of metals with inorganic and organic ligands in the waste. This important phenomenon of complex formation will be discussed subsequently in this chapter.

Sorption and Biological Uptake

The sorption phenomenon in an activated sludge system represents the association of a metal with the particulate matter, which is primarily raw sewage and floc particles,

microorganisms, or colloidal solids. Colloidal matter in sewage treatment process streams includes bacterial cell walls, other cellular debris, viruses, phages, detached flagella, clay and other inorganic particles, plus larger protein, carbohydrate, lipid, and acid molecules (Rickert and Hunter, 1972).

The biological floc of the activated sludge particles plays a key role in the adsorption of heavy metals to suspended matter. The microorganisms present in the biological floc are considered to be hydrophilic biocolloids, which are electronegative within the operational pH range of the activated sludge process (Baly, 1931; McKinney, 1956). The surface charge of the microorganisms is a result of the ionization of some of the anionic and non-ionic functional groups of the polymeric materials from which the flocs are built (Bush and Stumm, 1961; McKinney, 1962). The association of the functional groups depends upon the pH of the system, and, therefore, the sorbability of heavy metals also depends upon pH (Stumm and Morgan, 1970, Cheng, 1973).

The two major sorption processes that take place on the surface of the sludge solids during the interaction of metal and biomass are chemisorption and physical adsorption. In chemisorption, the adsorbed ion undergoes chemical interaction (for example, forming covalent bonds) with the adsorbent, while physical adsorption occurs as a result of weak van der Waals' forces, in which the adsorbed molecule is not fixed to a specific binding site (Weber, 1972). Experimentally, it is often difficult to distinguish between the two.

Various types of isotherm models, such as the Langmuir, Brunauer, Emmett, Teller (B.E.T.), and Freundlich formulations have been developed to describe sorption behavior (Weber, 1972). Among the three models, the Langmuir and Freundlich isotherms have been tested and shown to be applicable for the functional expression of metal association with the sludge (Cheng, 1973; Neufeld and Hermann, 1975). However, Rudolfs and Zuber (1953) reported the failure of copper to obey the Freundlich isotherm.

Neufeld and Herman (1975), in their studies of metal uptake by activated sludge, reported that metal equilibria relationships for cadmium and mercury were found to fit a Freundlich isotherm over a limited range of metal concentration. Since the sorption data in this study were collected from laboratory activated sludge units under steady state conditions, some of the metal believed to be sorbed to the biological floc was possibly taken up by the cells. However, Cheng (1973) used metal-sludge contact times of only 30 minutes

in his sorption studies and demonstrated that Langmuir and Freundlich isotherms were applicable for the functional expression of metal uptake by activated sludge.

Neufeld and Hermann (1975) observed a decrease in the per cent metal on biological floc at increased metal concentrations, and concluded that this may be due to a saturation effect of the floc surface by the metal and that the initial metal removal is probably more related to the physical and chemical properties of the biological mass than to biological phenomena. As was stated above, results from short-term metal uptake studies by Cheng et al., (1975) also seem to indicate that the initial phase of the metal uptake by activated sludge is due to sorption, a physical-chemical phenomenon.

Complexation

Complexation is the process whereby a positively charged metal ion attaches or bonds to a molecule or a charged ion called a ligand. Chelation is a special case of complexation, in which a ligand forms more than one bond with a metal ion (Cotton and Wilkinson, 1966). Of all the mechanisms that influence the heavy metals distribution in aquatic systems, complexation appears to play a relatively significant role.

Important inorganic ligands of environmental importance include hydroxide, carbonate, sulfate, chloride, phosphate, flouride, and ammonia. Significant concentrations of the above complexing agents exist in sewage treatment plant effluents. A wide variety of organic compounds exists which have chelating properties. A number of naturally occurring humic substances which act as chelators are found in natural waters and wastewaters (Schnitzer, 1971). These substances are usually classified into two groups: 1) humic acids, the portion of soil organic matter which is soluble in base and insoluble in mineral acid and alcohol, and 2) fulvic acids, material extracted with dilute base and soluble in mineral acid. Reuter and Perdue (1977) reviewed heavy metal-organic matter interactions in natural waters, while much of the literature concerning metal-fulvic acid interactions has been examined in extensive reviews by Flaig et al., (1975) and by Schnitzer and Khan (1972).

The organic matter in domestic sewage consists of carbohydrates, proteins, amino acids, fats, and other compounds, and its composition has been documented by Hunter and Heukelekian (1965) in the United States, by Painter (1959; 1971) in the United Kingdom, and by Rebhun and Manka (1971) in Israel. Pavoni (1970) extracted exocellular polymers from an activated sludge biomass of 1,200 mg/l for determination of its chemical

composition, and found that at least 28% of the extracted material possessed functional groups which can play a role in the formation of metal-sludge complexes.

The quantity of complexing agents present in sewage is considerable, and the existence of such compounds in sewage as well as other environmentally significant systems has been well established by electrochemical techniques (Allen et al., 1970; Bender et al., 1970; Chau et al., 1974; Chau and Lum-Shue-Chan, 1974) ion exchange methods (Cheng et al., 1975, Crosser and Allen, 1977; Patterson et al., 1979; Patterson and Hao, 1979; Van den Berg and Kramer, 1978) potentiometric techniques (Crosser, 1975), continuous variation methods (Haas, 1974; McBryde, 1974), and gel filtration (Mantoura and Riley, 1975).

Chau (1973) reported 1.8-2.5 micromoles of copper complexing capacity for sewage effluents, while Kunkel and Manahan (1973) reported 0.90 mg/l (or 14.16 micromoles/l) for the metal in sewage. The latter pair of investigators also found that raw sewage and primary effluent contained 3.39 and 3.01 mg/l of copper chelation capacity, respectively. Manahan and Smith (1973) found that the chelating capacity of tap water for copper was undetectable, while for raw sewage the capacity was 3.54 mg/l, and for activated sludge effluent, the capacity was 0.9 mg/l. These results suggest a reduction in quantity (but perhaps not strength) of ligands, as the sewage treatment process proceeds.

Bender et al., (1970) found that in an activated sludge effluent binding copper, ligands were associated with molecular weight fractions of 500-1000 and around 10,000 as determined by Sephadex G-50 medium. These fractions constitute a significant portion of the organics discharged from an activated sludge plant, as indicated by Rebhun and Manka (1971) and Manka et al., (1974). Such correlations would allow the use of a parameter like total organic carbon (TOC) or chemical oxygen demand (COD) as a substitute for the organic ligands concentrations, in studies of metal-organic interactions (Cheng et al., 1975).

From the above discussion, it is evident that complexation reactions could play an important role in heavy metal transformations in aqueous systems, by influencing the distribution of the metals between the soluble phase and particulate phases.

HEAVY METALS TRANSPORT

In order to gain preliminary insight into the nature of heavy metal transport through sewage treatment plants, Patterson et al., (1975) made a comparison between effluent metal levels and various influent and effluent wastewater parameters for several treatment plants in Chicago. They reported a strong

correlation between quarterly mean values for effluent five-day biochemical oxygen demand (BOD_5) versus effluent metals (Fig. 2) and for effluent suspended solids versus effluent metals (Fig. 3). These observations have been confirmed through subsequent assessments of 11 treatment plants, in California (Chen, 1976), Illinois (Cheng et al., 1975) and New York (Klein, 1974). Statistical evaluation of effluent BOD_5 versus total effluent metals yielded overall correlation coefficients for the 11 plants of 0.82 (range for individual plants 0.80 to 0.98) and for effluent suspended solids versus effluent metals of 0.87 (range 0.83 to 0.98) (Patterson, 1978).

In addressing these relationships between effluent metals, BOD_5, and suspended solids, alternate conclusions may be drawn. It is possible that the organic matter represented by BOD_5 serves to transport metals into the effluent via complexation; alternately, high levels of influent metals may cause lowered treatment efficiency resulting in higher effluent BOD_5. Suspended solids may likewise serve to transport metal into the effluent via sorption, as has been observed by Patterson et al., (1975). However, sewage with high influent metal content may cause effluent deterioration accompanied by high suspended solids concentrations. Whatever is responsible for the relationship between effluent metals and BOD_5 and suspended solids, the data reported by Patterson et al., (1975) confirm that effluent metals are strongly influenced through their association with effluent suspended solids. More interestingly, the soluble organics also appear to influence the metals removal in the treatment plant and thus the metals discharged from the treatment plant.

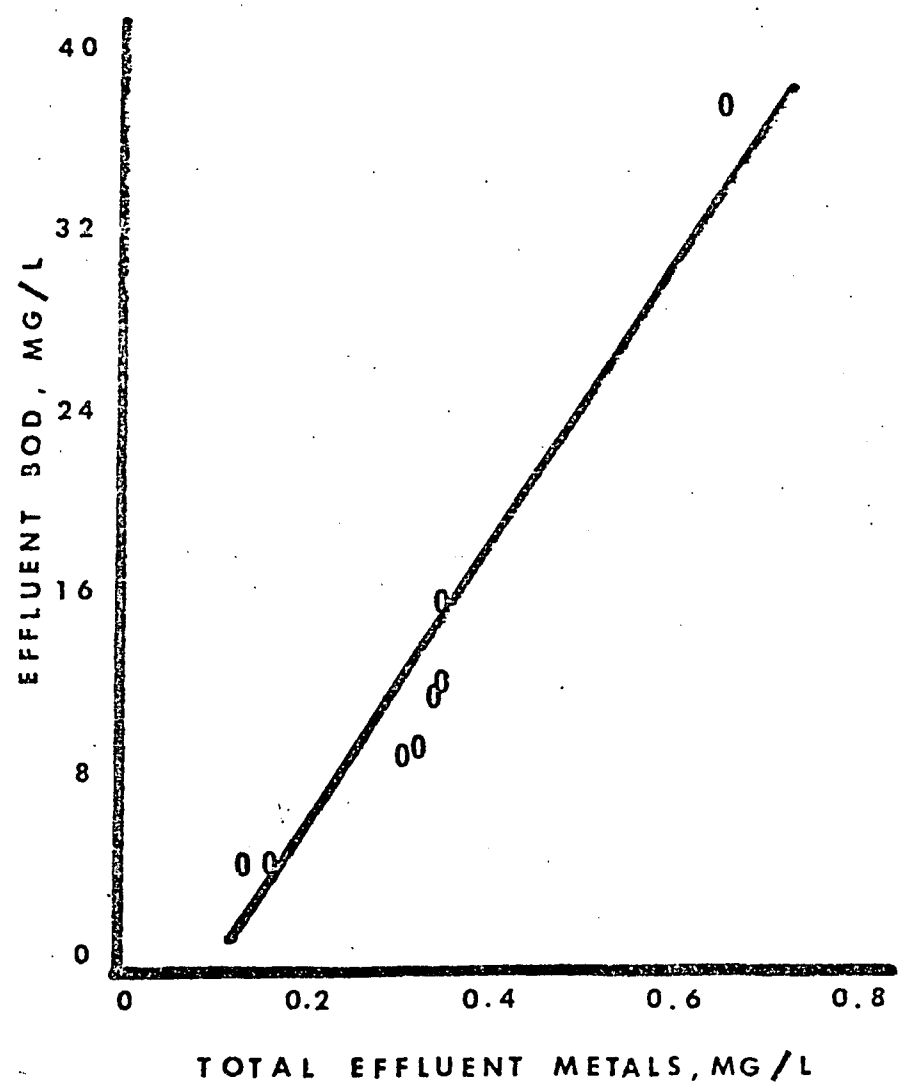


Figure 2. Correlation of effluent heavy metals and effluent BOD_5.

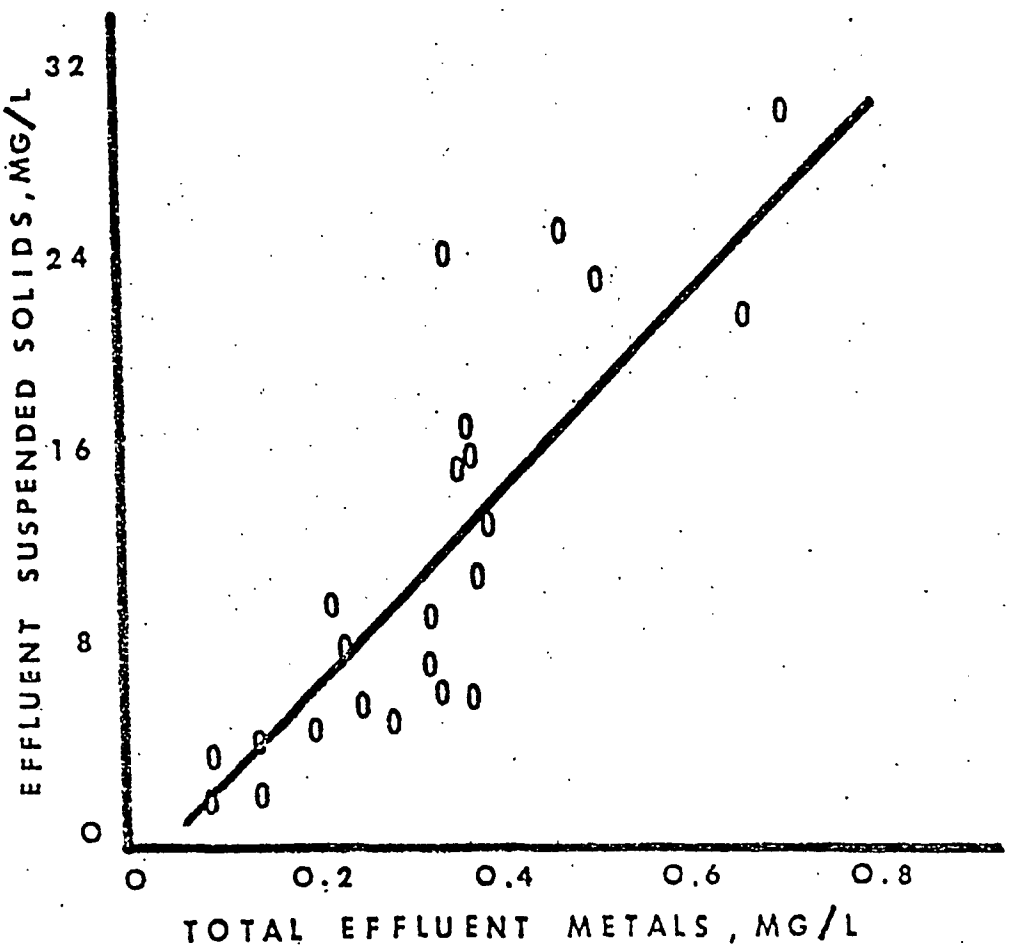


Figure 3. Correlation of effluent heavy metals and effluent suspended solids.

SECTION 5

OBJECTIVES

Goal of the Research Study

The primary goal of this investigation was to study the distribution of selected heavy metals between soluble and solid phases of different process liquids of a conventional activated sludge system. In order to achieve this goal, the investigation was divided into five parts and the specific objectives discussed below were established.

Specific Objectives

Solubility of Metals

1) to determine the solubility limits of heavy metals in tap water, raw sewage, and activated sludge mixed liquor for a range of initial pH levels and total sulfide concentrations;

Sorption of Metals

2) to develop heavy metal-solids sorption isotherms for raw sewage and activated sludge mixed liquor from batch experiments by relating total or soluble metal concentration to weight of metal adsorbed per unit weight of VSS;

Effect of Waste Parameters on Metals Distribution

3) to study the effect of individual natural waste characteristics, such as BOD_5 and suspended solids and industrial waste characteristics such as cyanide and ammonia on heavy metals distribution between soluble and solid phases of raw sewage and activated sludge mixed liquor;

Metals Distribution in Conventional Activated Sludge Systems

4) to develop heavy metal sorption isotherms for different process liquids of continuously-run pilot-scale conventional activated sludge systems, and to compare these isotherms to those developed in batch experiments under specific objective B-II;

5) to study the effect of total metal and VSS concentrations on the heavy metals distribution between the soluble and solid phases of raw sewage and activated sludge mixed liquor;

Model Development

6) to develop an empirical model, based on the results from the preceding four parts of the investigation, which would predict the heavy metals distribution between the soluble and solid phases of different process liquids of a conventional activated sludge plant, given the influent and operational characteristics of the system. A secondary part of this objective was to attempt to develop an overall POTW process model to describe metals distribution and removal through combined treatment systems;

7) to present an illustrative example dealing with heavy metals distribution through a conventional activated sludge system by using the POTW model developed under the above specific objective and to discuss the limitations of the model.

SECTION 6

METHODS AND PROCEDURES

The overall objective of this project was to develop technical information from laboratory studies which could be used to develop an empirical model for predicting metals distribution between soluble and solid phases through a conventional activated sludge system. This study focused upon the following eight metals:

Aluminum	Iron
Cadmium	Lead
Chromium	Nickel
Copper	Zinc

These metals were studied at sub-toxic influent concentrations, and the interrelationships which influence metal distribution in different process liquids of a conventional activated sludge system were assessed. The above metals were selected for study because of their environmental significance. The reason for selecting the trivalent form of chromium is that very little hexavalent chromium would be present in the influent raw sewage to most treatment plants, due to reducing conditions present in the sewers (Jan and Young, 1978).

As indicated in Section 5, this investigation was divided into five parts, and a brief description of each part of the project is given here:

I. Batch studies on tap water, filtered raw sewage, and filtered conventional activated sludge mixed liquor to determine the solubility limits of the eight metals.

II. Batch studies on raw sewage and activated sludge mixed liquor to develop sorption isotherms for selected metals.

III. Batch studies on raw sewage and conventional activated sludge mixed liquor to investigate the influence of both domestic and industrial waste constituents on metals distribution between the soluble and solid phases.

IV. Continuous-flow pilot-scale conventional activated sludge systems to study the effect of different variables, such as total metal concentration, TVSS, SOC, and major inorganic ligands, on heavy metals distribution in different process liquids.

V. Modelling techniques to predict the heavy metals distribution between soluble and solid phases of different process liquids of an activated sludge system.

A detailed discussion of the methods and procedures used under each part of the investigation is in order. Part V, which includes the model development, is, however, not included in this chapter, since it is more appropriate to discuss it after the experimental results are presented. Section 8 of this report presents the model development.

SOLUBILITY OF METALS

In this part of the study, solubility of metals at different pH levels and sulfide concentrations was determined for tap water, raw sewage, and activated sludge mixed liquor.

Tap water used in this study came from Chicago's city water distribution system, while the raw sewage and activated sludge mixed liquor were obtained from the West-Southwest Wastewater Treatment Plant operated by the Metropolitan Sanitary District of Greater Chicago. Batch experiments were performed for each test liquid (tap water, raw sewage, and mixed liquor) according to the following procedure.

Initially, test liquid was filtered using a 0.45-micron membrane filter. Raw sewage and activated sludge mixed liquor were settled and prefiltered prior to membrane filtration, to enhance membrane filtration efficiency. Twelve batch units, each consisting of 500 ml of filtered sample in a 1000-ml Erlenmeyer flask, were set up for each test liquid and each of the eight metals. Each set of the 12 batch units was subdivided into three groups of four (see Figure 4). Two groups of each set received sulfide addition so as to result in initial sulfide concentrations of 1 and 10 mg/l in each group, while the third group acted as a control receiving no sulfide addition. pH levels of 6, 7, 8, and 9 ($\pm$ 0.3 units) were established in units of each group by pipetting sodium hydroxide or nitric acid into the test liquid, as required, with constant stirring. Prior to metal addition, two test liquids were adjusted to the required test sulfide levels. The background sulfide level was negligible, based upon analysis. Following sulfide adjustment, the appropriate concentrated metal solution was pipetted into the test liquid. Simultaneously, pH adjustment was made to maintain the target test pH

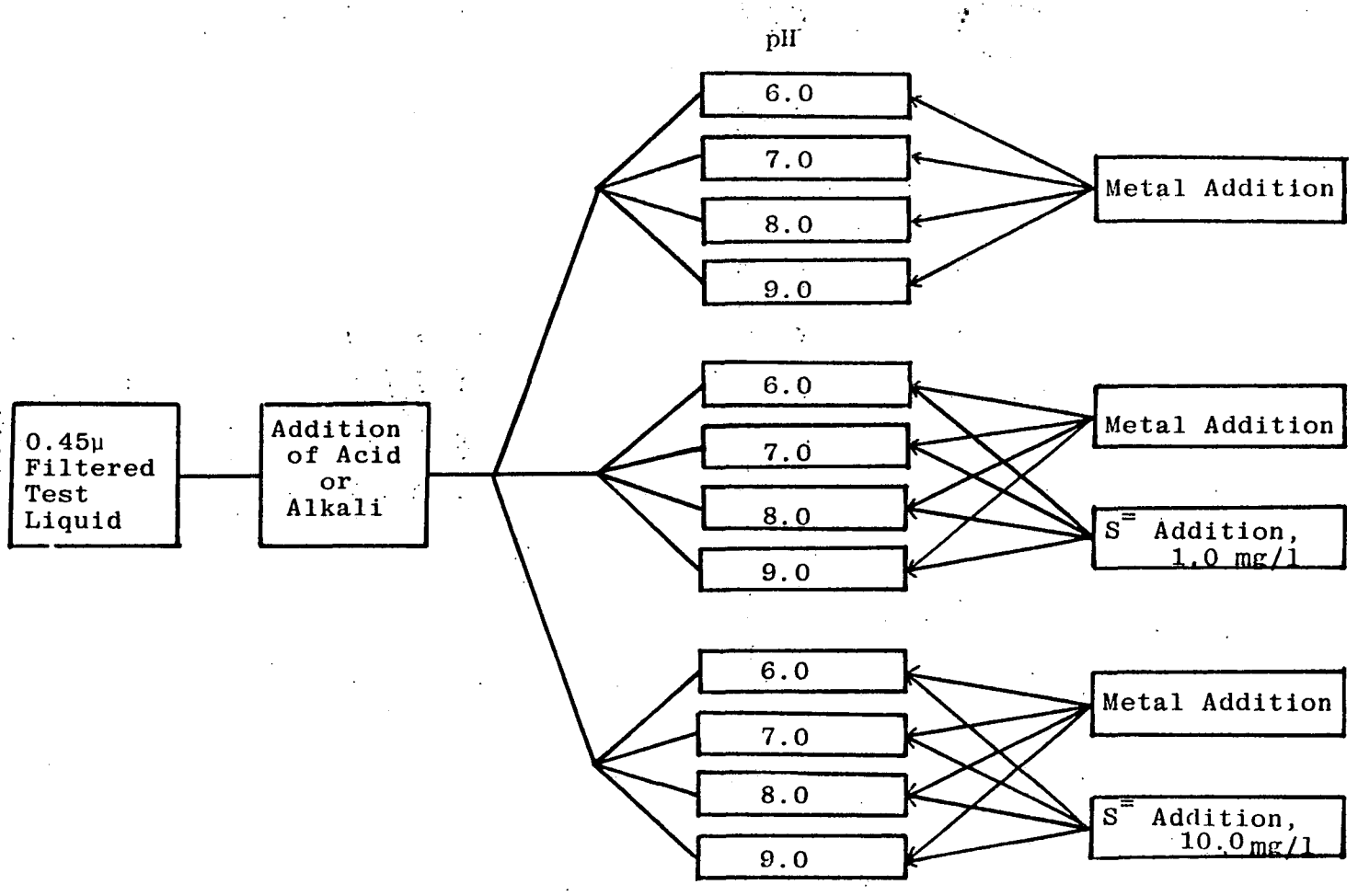


Figure 4. Schematic of batch experiments set up to study the minimum solubility of metals in tap water, raw sewage, and activated sludge mixed liquor.

level. Metal solution was added until a visible precipitate formed and remained after one minute of continuous stirring. The sample was continuously stirred during the metal addition step, and the pH was monitored.

The batch units were sealed with parafilm and placed on a shaker with continuous shaking at ambient temperature. After two hours, all batch units were readjusted to correct for any pH change. Aliquots of the test liquids were taken at six, 12, and 24 hours for measurement of pH, soluble metal, SOC, and sulfide. Background analyses on the test liquids included pH, total dissolved solids, total volatile dissolved solids, initial SOC, background metals, sulfide, sulfate, total phosphorus, orthophosphate, ammonia, hardness, and alkalinity.

SORPTION OF METALS

In this part of the project; sorption of metals to sludge was studied by measuring the amount of metal associated with the sludge fraction after the metal is added to the test liquid at a level below its solubility limit, as determined in Part I.

Batch experiments were set up in a similar fashion to that described in Part I, according to the scheme outlined in Figure 5. In this component of the project; unfiltered samples were taken, their pH was adjusted to the desired levels, and the selected metals added. The amount of metal added was below its solubility limit, to avoid precipitation. The minimum solubility of each metal for different pH levels was determined from the experiments in Part I. The initial sulfide concentration in all the samples was kept at the background level, which analysis showed to be negligible. After the metal addition, the samples were constantly stirred and aliquots of samples were taken at 0.25-, 0.50-, 1-, 3-, 6-, and 24-hour time intervals, to measure pH and soluble metal concentration. The samples from the 24-hour test period were also analyzed for total organic carbon (TOC), SOC, inorganic carbon, total suspended solids (TSS), VSS, total dissolved solids and total volatile dissolved solids, total phosphorus, orthophosphate, and alkalinity.

EFFECT OF WASTE PARAMETERS ON METALS DISTRIBUTION

Part III was designed to investigate, in depth, the influence of domestic and industrial waste constituents on the distribution of heavy metals between the soluble and solid phases of raw sewage and activated sludge mixed liquor. This objective was accomplished by spiking aliquots of test liquids with each selected waste constituent and determining how the distribution of metals was affected. In addition, for each

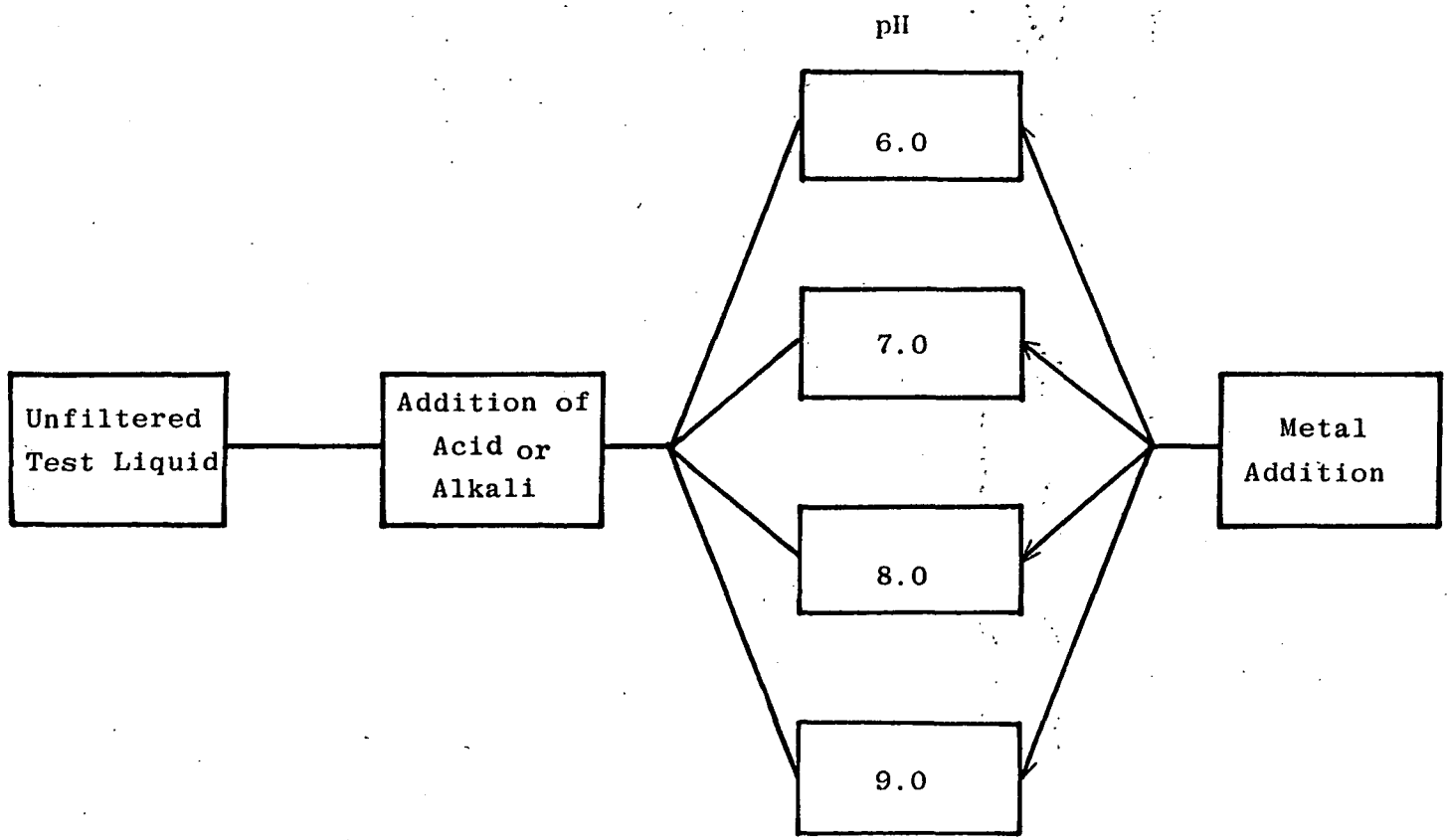


Figure 5. Schematic of batch experiments set up to study the adsorption of metals to solids in raw sewage and activated sludge mixed liquor.

domestic/industrial waste parameter tested, the metal distribution in test liquids with seven different metals compositions was studied. The factorial design of this series of experiments is explained in Table 5.

As presented in Table 6, seven different domestic/industrial waste parameters, with three levels for each parameter, were tested. For each parameter tested, a series of seven different metal combinations was evaluated (Table 7). Metal Combinations 1 through 4 consisted of mixtures of nine metals at low (Combination 1) to high (Combination 4) relative concentrations. Metal Combinations 5 and 6 were replicates of Combination 3, providing a statistical basis for the evaluation of experimental results. In Metal Combinations 7 and 8 the metal levels were varied randomly (i.e., some metals were at high and others at low concentrations). Random metal combinations were incorporated in the studies in order to determine whether interactive effects upon metal removal result from preferential removal of specific metals by the sludge phase. There was a control group (C_0) to which no metal was added. All metals concentrations fell within the range of influent values for POTWs reported in Table 1.

The waste parameters listed in Table 6 were also studied at multiple levels. Hardness, inorganic constituents, and detergents, the domestic waste variables, were varied by addition of the required constituent to the raw waste. The "as received" waste constituted the lowest level tested except for suspended solids. In the case of suspended solids, the lowest tested level was obtained by dilution of the raw sewage with filtered sewage, while the highest level was achieved by the addition of concentrated (settled) sludge to the raw sewage. The lowest BOD_5/TOC concentration was achieved by dilution of sewage with tap water, and the highest level by adding sewage which had been homogenized in a blender and subsequently filtered to remove remaining particulate matter. Suspended solids concentration was held constant for each BOD_5/TOC level tested. For the industrial waste parameters listed in Table 6, the levels tested were sub-toxic. The waste parameters listed in Table 6 simulated the varying characteristics of raw sewage, as might occur in the collection system.

Eight sets of three batch test units each were used for each test liquid and each waste parameter. All batch units consisted of 500 ml of test liquid (raw sewage or activated sludge mixed liquor) in 1000-ml Erlenmeyer flasks. Of the three units in each set, one unit was a control, while the other two were adjusted for the desired level (Table 6) of the waste parameter tested. One of the eight sets of the batch units served as the overall control group, while the remaining

TABLE 5. PART III EXPERIMENTAL DESIGN

Item	Explanation
2 Test liquids	Raw sewage and activated sludge mixed liquor
X	
7 Waste parameters	See Table 6
X	
3 Waste parameter levels	See Table 6
X	
7 Metal combinations	See Table 7
X	
2 Liquid samplings	Whole fraction and filtered sample

TABLE 6. LIST OF WASTE PARAMETERS AND THEIR LEVELS TESTED IN PART III

Waste parameter		Concentration, mg/l Level 1	Level 2	Level 3
Domestic Waste Variables:				
1 Inorganics and Hardness	Sodium	122.0*	600.0	1220.0
	Potassium	83.0*	415.0	830.0
	Sulfate	97.2*	194.4	388.8
	Phosphate	1.1*	11.2	22.4
	Chloride	125.0*	625.0	1250.0
	Calcium	33.0*	330.0	660.0
	Magnesium	10.0*	100.0	200.0
2 Detergents		40.0*	80.0	120.0
3 Suspended Solids		252.0	40.0	126.0*
4 BOD_5/TOC		5.5	15.8*	38.1
Industrial Variables:				
5 pH		5.0	7.0*	9.0
6 Cyanide		Trace*	0.1	0.5
7 Ammonia-N		30.0*	300.0	450.0

*"As is" Level and Control.

TABLE 7. METALS CONCENTRATION IN DIFFERENT METALS COMBINATIONS STUDIES IN PART III

Metal	Combinations of metal concentrations, mg/l					
	C_1	C_2	$C_{3,5,6}$	C_4	C_7	C_8
Aluminum	0.04	0.10	0.20	0.40	0.04	0.40
Cadmium	0.005	0.01	0.025	0.05	0.025	0.01
Chromium	0.02	0.04	0.10	0.20	0.02	0.04
Copper	0.04	0.10	0.20	0.40	0.10	0.40
Iron	0.20	0.40	1.00	2.0	2.0	1.0
mercury	0.001	0.002	0.005	0.01	0.005	0.001
Nickel	0.10	0.20	0.50	1.0	1.0	0.20
Lead	0.015	0.03	0.075	0.15	0.15	0.075
Zinc	0.08	0.20	0.40	0.80	0.20	0.80

seven sets of three units were dosed with six different combinations of heavy metals. These combinations, C_1 through C_8 (C_3, C_5, C_6 are replicates) were presented in Table 7.

Each group of 27 batch units was placed on a shaker table for four hours at ambient temperature. At the termination of the mixing period, an aliquot of the whole fraction of the batch unit samples was taken for analyses. An additional aliquot was filtered through a 0.45-micron filter to obtain soluble samples. The analyses performed on raw sewage and activated sludge mixed liquor are given in Table 8.

Since metals influent to activated sludge units have had extended contact periods with raw sewage, it is invalid to simulate metals distribution within the activated sludge process by direct addition of inorganic stock metal solutions. Therefore, in order to validly simulate the input of metals to the activated sludge process, it was necessary to precontact the metals with raw sewage. Therefore the settled supernatant resulting from the raw sewage experiments was utilized as the media for introduction of metals to the activated sludge process.

METALS DISTRIBUTION IN CONVENTIONAL ACTIVATED SLUDGE SYSTEMS

This part of this investigation was designed to study the distribution of heavy metals in different process liquids of continuous-flow pilot-scale conventional activated sludge systems receiving raw sewage and heavy metals at different concentrations.

The continuous-flow studies of Part IV were divided into six runs, each run consisting of eight separate parallel pilot-scale activated sludge treatment systems. Table 9 presents a summary of the schedule of operation of those treatment systems. As indicated in the table, there were 39 different activated sludge treatments contained in this phase. Table 10 presents the concentrations of different heavy metals in the raw sewage fed during the 39 different activated sludge runs. These individual metals concentrations and combinations were selected on a random basis to simulate low, high, and mixed levels of metals in raw sewage.

A flow schematic of each activated sludge system used in this study is presented in Figure 6. Municipal sewage was pumped from a City of Chicago sewer line to a laboratory grit chamber on a continuous basis. Settled grit was discharged. Raw sewage overflowed from the grit chamber into a 300-gallon stirred holding tank, having an average six-hour detention time. The holding tank was equipped with a low level alarm, to

TABLE 8. SAMPLE ANALYSES PERFORMED IN PART III

Test liquid	Parameters analyzed
Raw Sewage and Activated Sludge Mixed Liquor	Control Units at T=0 and T=4 hours
Whole Fraction	pH, D.O., TSS, TVSS, Temperature
Filtered Supernatant	Total dissolved solids, Total volatile dissolved solids, TOC, Alkalinity, Ammonia
	Ortho-Phosphate, Total Phosphorus, 9 test metals, calcium, magnesium
Raw Sewage and Activated Sludge Mixed Liquor	Test Units at T=4 hours
Whole Fraction	pH*, D.O.
	9 test metals, calcium, magnesium
Filtered Supernatant	9 test metals, calcium, magnesium

*At T=0 hrs. also.

TABLE 9. SUMMARY OF SCHEDULE OF OPERATION OF CONTINUOUSLY PILOT-SCALE ACTIVATED SLUDGE SYSTEMS

Run No.	Period of Operation, Daily	Treatment Number							
	Unit ID:	A	B	C	D	E	F	G	H
I	4/5 - 5/19	1	5	11	17	23	29	33	37
II	5/19 - 6/27	2	6	12	18	24	30	34	38
III	6/27 - 8/23	3	7	13	19	25	31	35	39
IV	8/23 - 9/26	3	8	14	20	26	32	36	
V	9/26 - 10/31	3	9	15	21	27			
VI	11/1 - 11/23	4	10	16	22	28			

TABLE 10. AVERAGE INFLUENT METALS CONCENTRATIONS (µg/l) IN RAW SEWAGE FED TO 39 DIFFERENT ACTIVATED SLUDGE SYSTEMS

Treatment No.	Aluminum	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Zinc
1	783	25	135	393	1265	81	672	482
2	433	42	143	359	1542	93	756	413
3	1003	140	174	274	1750	293	1629	1114
4	1310	80	630	280	1460	140	2740	826
5	678	12	113	90	1399	35	334	409
6	298	124	84	161	1247	37	369	383
7	375	63	150	177	1292	75	1780	481
8	372	143	128	530	1610	320	1220	830
10	932	60	600	150	2675	150	838	1583
11	383	28	155	429	1439	57	795	510
12	495	77	159	479	1641	88	1002	617
13	500	105	153	271	1521	158	869	643
14	295	154	122	460	2220	170	986	553
15	710	93	1062	338	3360	150	1220	1003
16	678	59	460	240	1534	90	1615	1575
17	678	12	113	90	1399	35	245	409
18	295	137	97	173	1576	154	352	450
19	677	88	183	453	636	267	2983	1114
20	520	138	144	625	1510	475	3263	694
21	661	146	500	425	3225	150	1678	1025
22	983	53	420	270	2510	140	1263	1860
23	655	24	106	308	1378	41	680	564
24	385	157	137	460	2243	75	653	477
25	785	135	109	367	2492	221	4008	514
26	240	128	124	325	1488	190	6075	766
27	834	77	513	363	3200	175	2050	1463
28	890	57	530	350	2350	180	2132	2160
29	669	11	113	90	1399	35	330	409
30	278	63	62	162	1527	100	366	440
31	567	69	90	213	936	143	490	429
32	216	98	128	180	650	120	2050	644
33	740	22	144	302	1385	66	603	520
34	778	222	253	756	2322	200	1522	536
35	1574	87	140	1071	2117	260	708	540
36	1193	102	100	210	1510	160	319	463
37	678	11	113	98	1399	35	245	409
38	337	87	84	170	1483	97	373	413
39	693	81	124	269	671	100	619	450

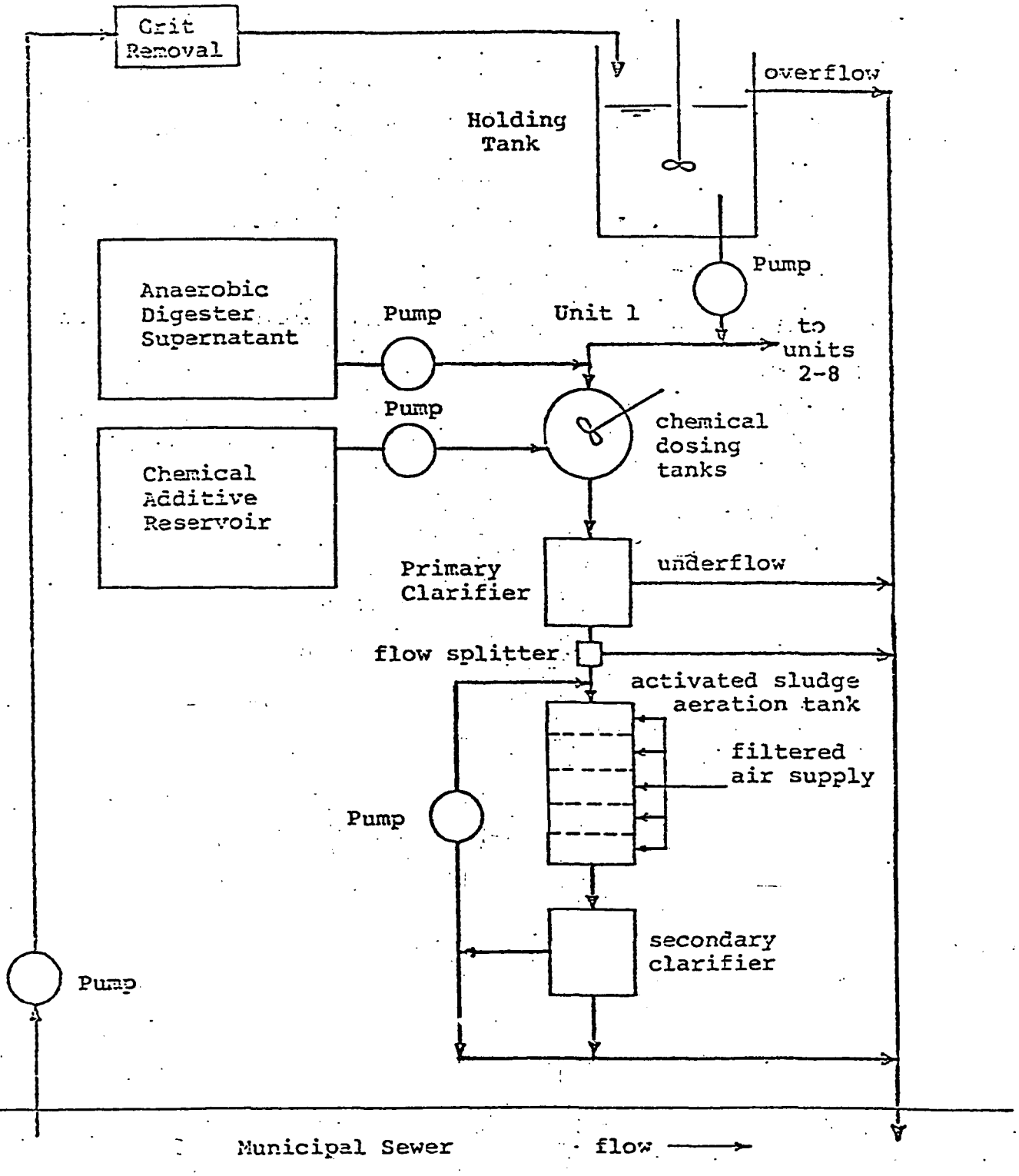


Figure 6. Flow schematic of continuously-run laboratory-scale unit.

cut off all downstream pumps and valves (except for return activated sludge pumps and excess sludge wastage valves), in the event that the raw sewage flow was interrupted. The raw sewage was pumped into a common header, and then into eight parallel dosing tanks of two-hour detention time each. Selected metals were metered into each chemical dosing tank, in accordance with the experiment underway for that particular treatment system.

Each dosing tank overflowed to the primary clarifier of the system. The flow rate was about 130 ml/mn. Clarifier (primary and secondary) design was based upon the design reported by Mulbarger and Castelli (1966), as modified by and in use at the U.S. EPA Municipal Environmental Research Laboratory. The design of the primary and secondary clarifiers was scaled for compatibility with the activated sludge units.

Primary clarifier overflow was through a flow splitter, to control hydraulic loading to the activated sludge unit. Each activated sludge unit was constructed as a five-chamber, 100-liter total capacity unit, with removable partitions to convert from a plug flow to complete mixed mode. Design criteria for the activated sludge units were based on the design of Mulbarger and Castelli (1966). Due to weak raw sewage, it was difficult to accurately monitor the solids retention time.

Activated sludge unit mixed liquor overflowed by gravity to the secondary clarifier, where settled sludge was returned by a peristaltic pump to the activated sludge unit. The recycle ratio used for all activated sludge units in this study was 0.5. Excess sludge was wasted directly from the secondary clarifier or by intermittent interval wasting of activated sludge unit overflow as was most appropriate for control of sludge age. Sampling from each unit was by timer activated solenoid switch flow diverters, to yield eight-hour composite samples.

Composite samples of the raw sewage, primary effluent, activated sludge mixed liquor, secondary effluent, primary sludge, and secondary sludge were collected several times each week. Total and soluble metal analyses were performed on all process liquid samples, while the sludge samples were analyzed for total metals. In addition, pH, suspended solids, and VSS were also measured on these samples. Soluble samples of the four process liquids were analyzed for TOC, SOC, inorganic carbon, phosphate, sulfate, chloride and ammonia nitrogen.

ANALYTICAL PROCEDURES

Metal analyses were performed by atomic absorption spectometry, using a Perkin Elmer Model 305B. The pH was measured using a Horizon (Ecology Company) Model 5998-10 pH meter. Total phosphorus, orthophosphate, sulfate, chloride, ammonia, calcium, hardness, and alkalinity determinations were performed according to procedures described in EPA Methods (U.S. EPA, 1974). TSS are reported as the weight of the dry solids per liter of sample retained by a 0.45-micron membrane filter. total dissolved solids represented the dry solids present in the filtrate of one liter of original sample. Volatile solids are reported as the weight of residue lost upon ignition at $600^{o}C$ of one liter of the original sample. Sulfide ion concentration was measured using a specific ion electrode, Orion-94-16.

SECTION 7

RESULTS AND DISCUSSION

SOLUBILITY OF METALS

In order to study the kinetics of metal solubility, soluble metal concentration was plotted with respect to time for each metal, for the four different pH levels, and for each initial sulfide concentration and test liquid. Since the number of such graphs is very large (3 test liquids x 3 sulfide levels x 8 metals = 72), only representative plots along with information on change in pH over the test period, for cadmium, are presented as examples, in Figures 7 through 12. From graphs such as those presented in Figures 7 - 12, the following observations were made:

1) Equilibrium solubility conditions seem to have been achieved within six to 12 hours after the addition of the metal in each test, since soluble metal concentration of most tests were found to be similar at t=12 hours and t=24 hours.

2) High correlation coefficients were found for soluble metal vs. pH (Table 11) indicating that variations in soluble metal within the test matrix are a reflection of changes in equilibria caused by fluctuations in pH. Changes in soluble metal concentration of a given sample over the test period also seem to be due to pH dependent variations of soluble metal species.

3) Generally, over the 24-hour period the pH of the samples with initial pH below 8 increased, while decreasing for samples with initial pH of 8 or higher. In other words, the pH of each sample shifted with time toward a pH value of 8, in most instances. This suggests that the test liquids were well buffered, probably by the carbonate-bicarbonate system.

4) A comparison of the results for samples at different initial sulfide concentration levels revealed that sulfide at all levels tested had no identifiable effect on the rate of precipitation or at the residual soluble level of metals, at any initial pH. In order to demonstrate the lack of effect of initial sulfide concentration on metal solubility, correlation coefficients were computed for the initial sulfide concentration

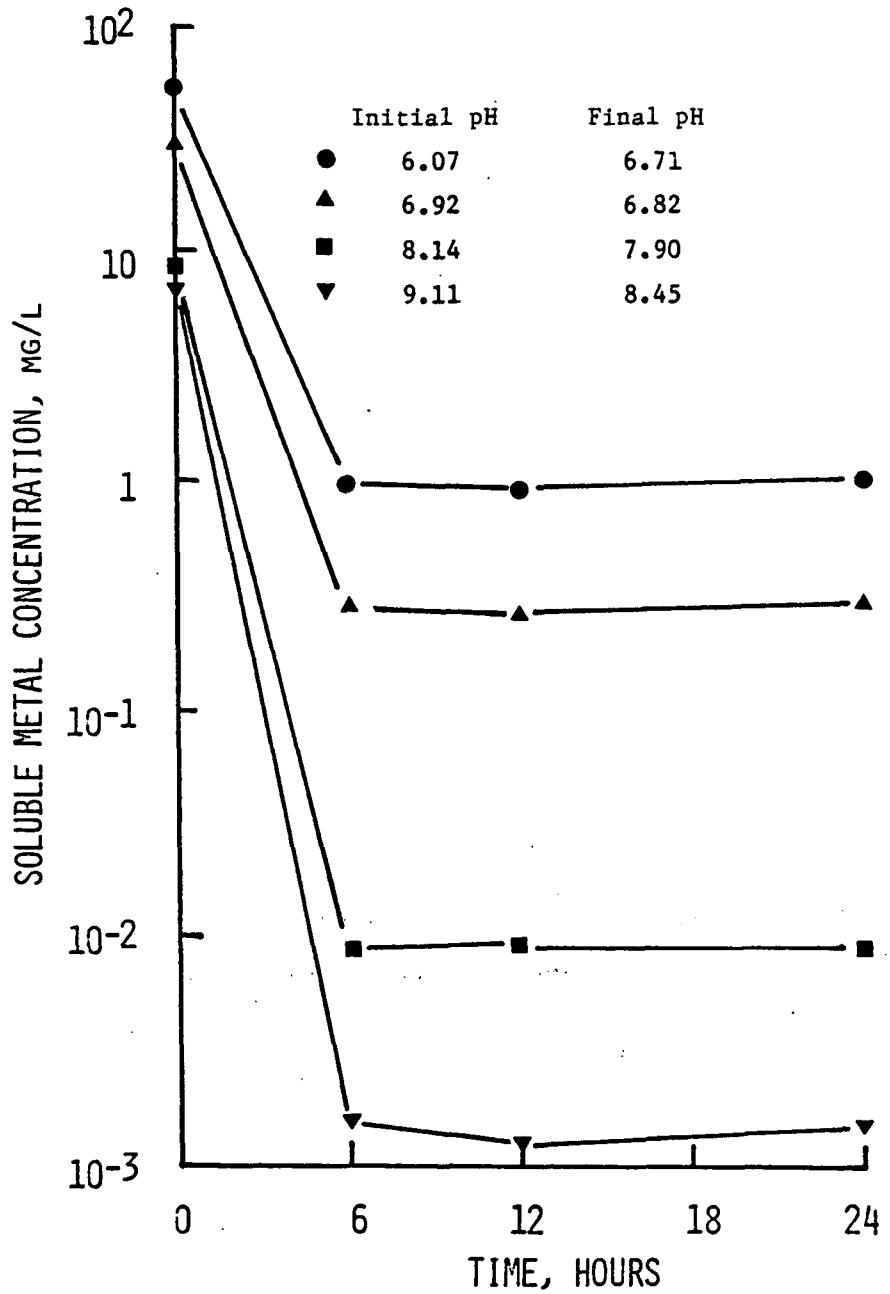


Figure 7. Change in soluble metal concentration with respect to time: Cadmium in raw sewage at negligible sulfide concentration.

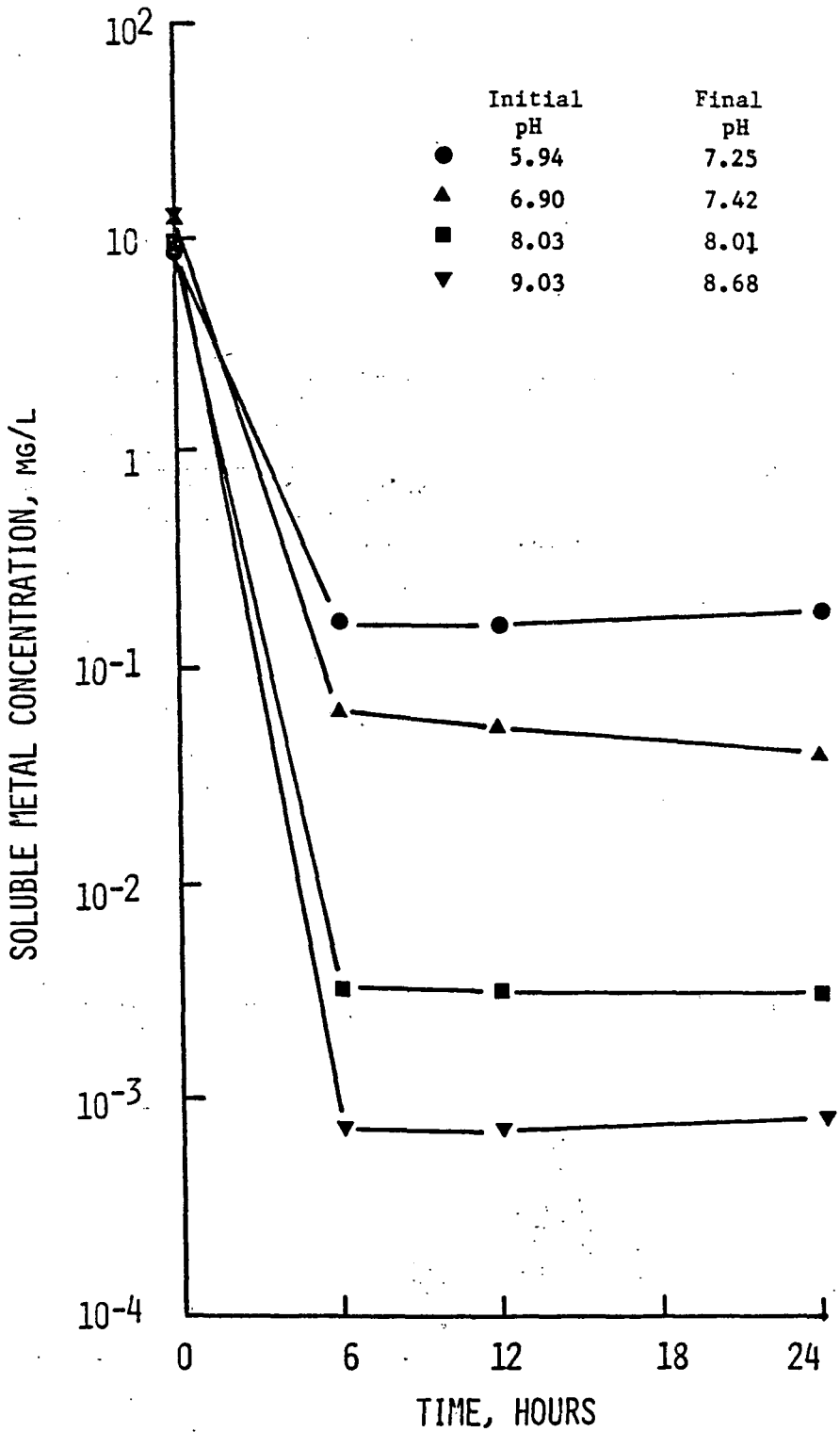


Figure 8. Change in soluble metal concentration with respect to time: Cadmium in raw sewage at sulfide = 1 mg/l.

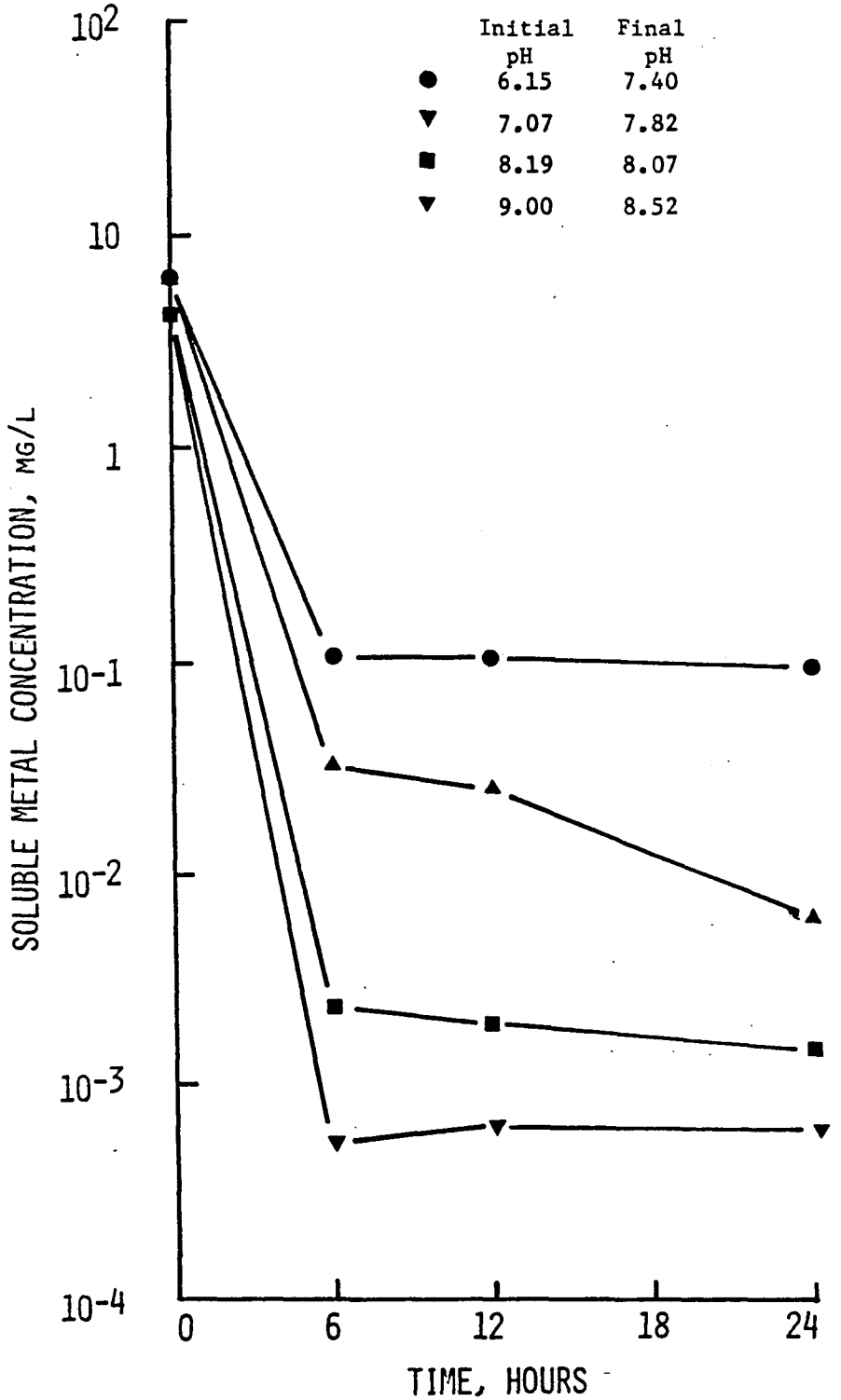


Figure 9. Change in soluble metal concentration with respect to time: Cadmium in raw sewage at sulfide = 10 mg/l.

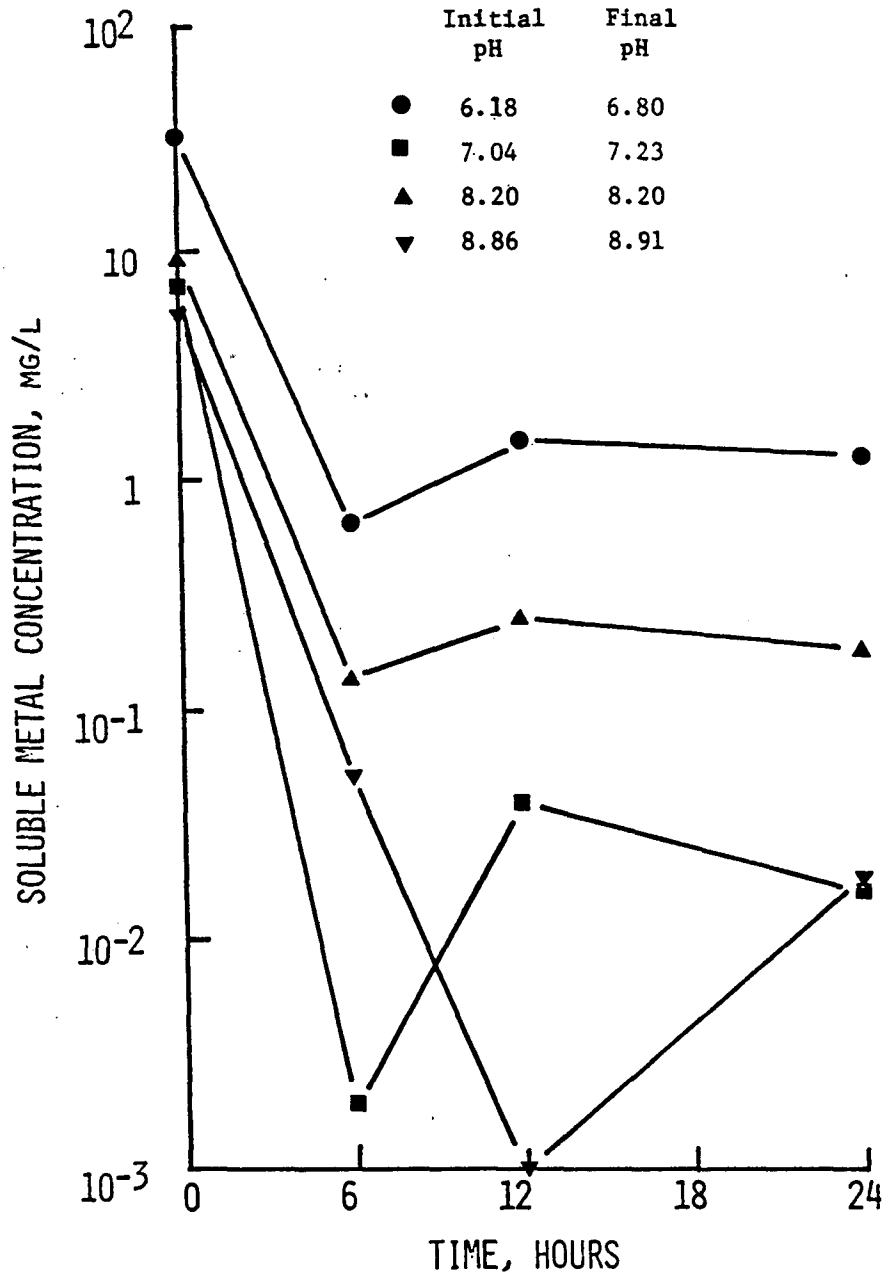


Figure 10. Change in soluble metal concentration with respect to time: Cadmium in activated sludge mixed liquor at negligible sulfide concehtration.

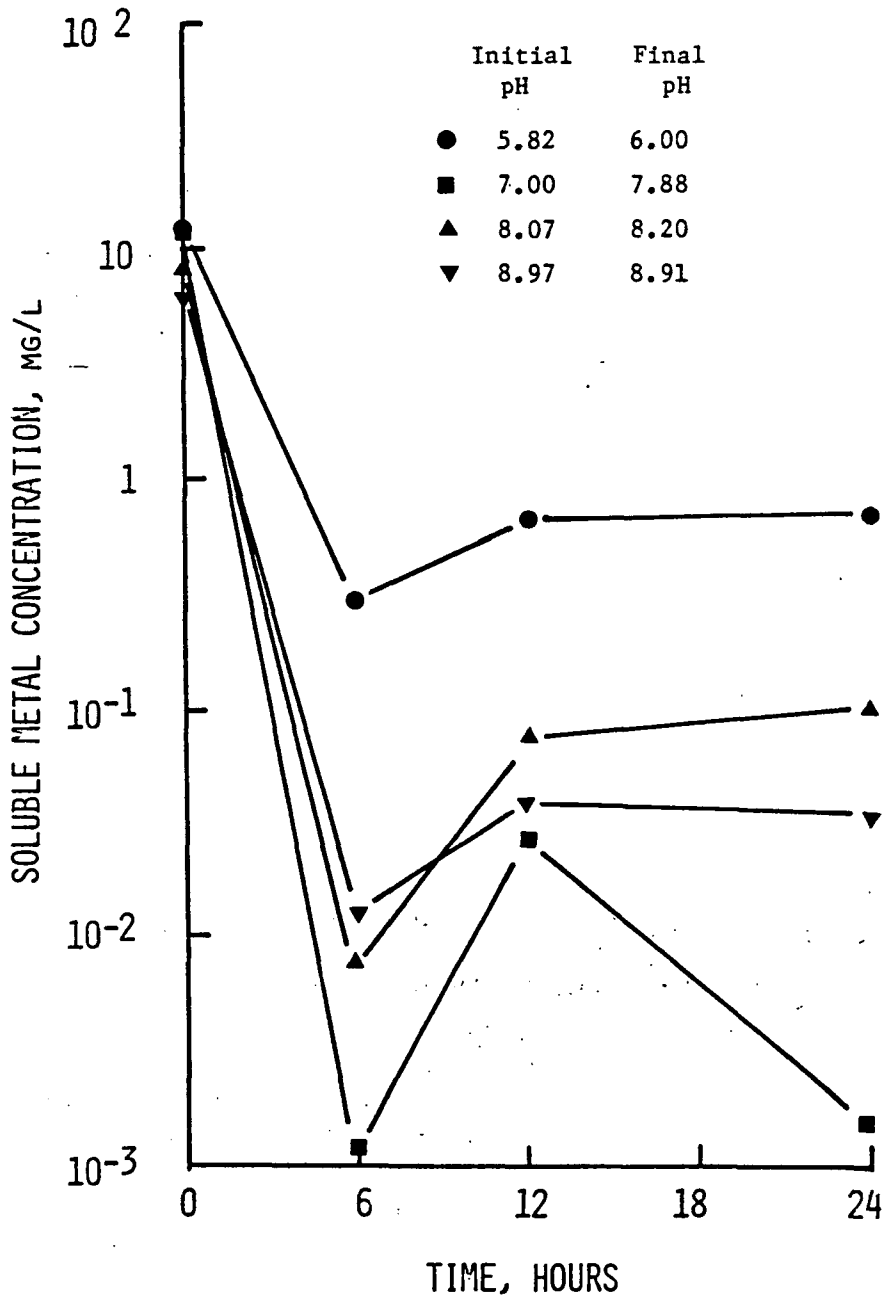


Figure 11. Change in soluble metal concentration with respect to time: Cadmium in activated sludge mixed liquor at sulfide = 1 mg/l.

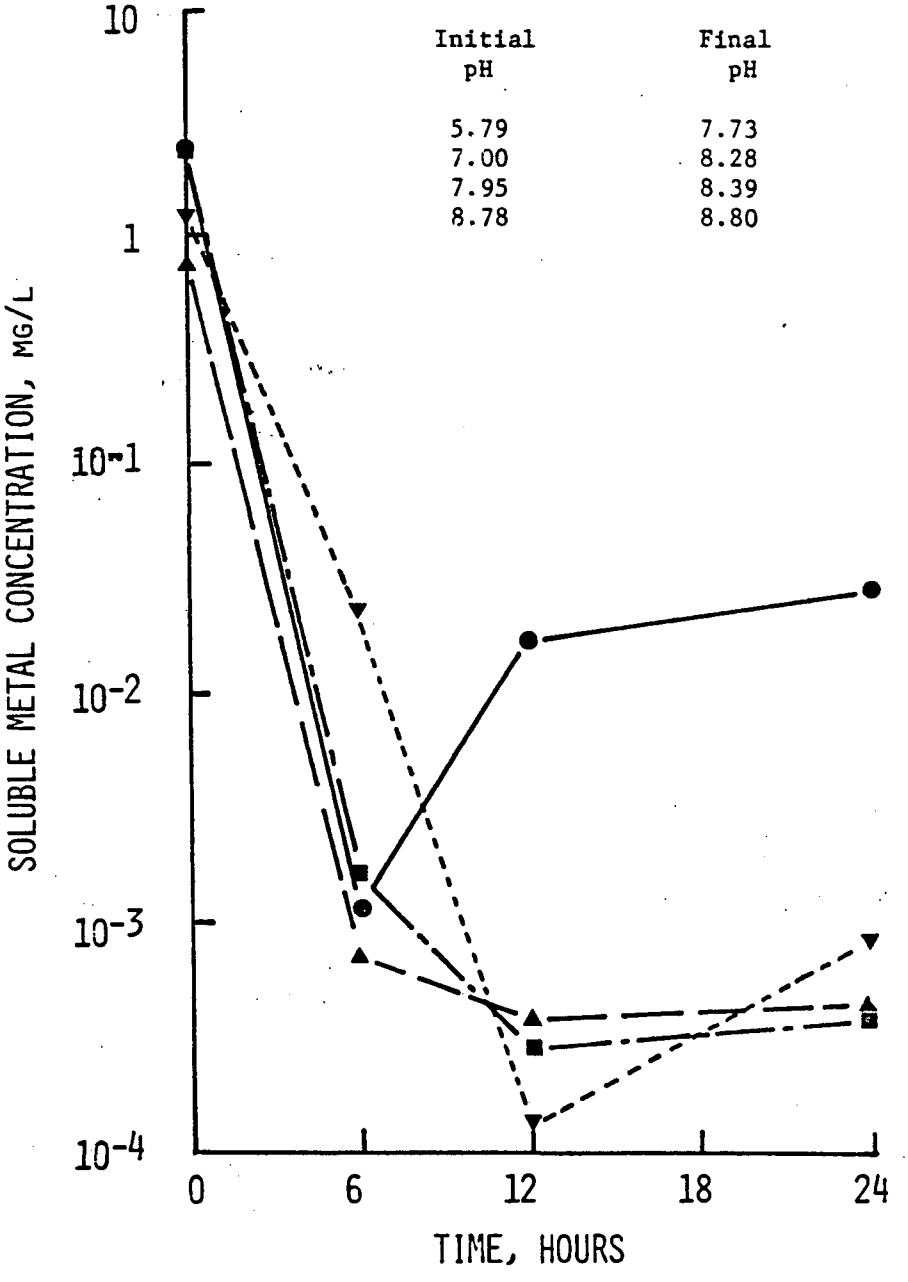


Figure 12. Change in soluble metal concentration with respect to time: Cadmium in activated sludge mixed liquor at sulfide = 10 mg/l.

TABLE 11. CORRELATION COEFFICIENTS: pH VS. SOLUBLE METAL CONCENTRATION

Test metal	Sulfide level	Tap water pH level 6	7	8	9
Aluminum	0	.829	.912	.988	.962
	1	.920	.875	.998	.970
	10	.804	.804	.835	.924
Cadmium	0	.928	.965	.785	.829
	1	.937	.955	.918	.628
	10	.909	.863	.605	.975
Chromium	0	.976	.814	.810	.911
	1	.845	.691	.949	.863
	10	.815	.859	.946	.984
Copper	0	.931	.959	.967	.968
	1	.887	.922	.943	.998
	10	.957	.932	.981	.991
Iron	0	.953	.860	.703	.874
	1	.926	.652	.832	.757
	10	.858	.706	.820	.853
Lead	0	.986	.916	.957	.865
	1	.998	.977	.992	.991
	10	.894	.996	.917	.937
Mercury	0	.999	.999	.999	1.000
	1	.998	.989	.993	.981
	10	.916	.999	.876	1.000
Nickel	0	.998	.999	1.000	.993
	1	.999	.999	.998	.861
	10	.995	.998	1.000	.971
Zinc	0	.999	.866	.738	.921
	1	.999	.907	.805	.986
	10	.991	.987	.808	.647

(continued)

TABLE 11. (continued)

Test metal	Sulfide level	Raw sewage pH level 6	7	8	9
	0	ND	ND	ND	.961
Aluminum	1	ND	ND	.937	.983
	10	ND	ND	.980	.995
	0	.999	.999	1.000	.994
Cadmium	1	.999	.977	1.000	.999
	10	.994	.858	.981	.997
	0	-	-	-	-
Chromium	1	-	-	-	-
	10	-	-	-	-
	0	.992	.852	.848	.890
Copper	1	.929	.929	.750	.904
	10	.998	.869	.934	.887
	0	.982	.903	.949	.910
Iron	1	.897	.965	.981	.909
	10	.983	.979	.981	.952
	0	.696	.818	.807	.876
Lead	1	.936	.814	.783	.843
	10	.991	.866	.949	.964
	0	.976	.967	.994	.998
Mercury	1	.851	.960	.988	.999
	10	.923	.947	1.000	.936
	0	.998	.999	.999	.988
Nickel	1	.999	1.000	1.000	.976
	10	.997	.996	1.000	.981
	0	.999	.999	.570	.675
Zinc	1	.996	.986	.830	.845
	10	.894	.974	.835	.784

ND = nondetectable

(continued)

TABLE 11. (continued)

Test metal	Sulfide level	Mixed Liquor pH level 6	7	8	9
	0	1.000	.937	.904	.986
Aluminum	1	.323	.826	.993	.996
	10	.972	.923	.997	.999
	0	.955	.973	.784	.754
Cadmium	1	.953	.862	.634	.924
	10	.862	.952	.762	.592
	0	.729	.654	.922	.688
Chromium	1	.835	.661	.943	.986
	10	.881	.883	.745	.820
	0	.796	.987	.998	.999
Copper	1	.797	.981	.999	.966
	10	.999	.957	.953	.932
	0	.914	.974	.998	.743
Iron	1	.782	.983	.967	.958
	10	.997	.801	.775	.983
	0	.944	.977	.995	.906
Lead	1	.909	.993	.981	.975
	10	.913	.957	.942	.753
	0	.992	.999	.988	.999
Mercury	1	1.000	.996	.999	.992
	10	.932	1.000	.907	.943
	0	.999	.999	.999	.982
Nickel	1	.999	.997	.996	.916
	10	.999	.999	.999	.902
	0	1.000	.983	.769	.891
Zinc	1	.991	.911	.939	.917
	10	.918	.954	.945	.664

vs. the soluble metal levels at 12 hours and 24 hours for each pH level and each test liquid (see Table 12). The low correlation coefficients in Table 12 confirm that there was no significant relationship between the initial sulfide concentrations at the levels tested, and metal solubility. This lack of effect of initial sulfide concentration is postulated to be due to the following reasons: a) much of the sulfide added escaped from the system during the incubation period, or b) the sulfide concentrations used in this study were too low to result in any noticeable changes in metal solubility.

5) In most cases, the soluble metal concentration was higher in samples of filtered raw sewage and mixed liquor than in their counterpart tap water samples. This is possibly due to the presence of organic and inorganic ligands in raw sewage and mixed liquor, which complex with the metals and increase their solubility.

6) In accordance with generalized hydroxide and carbonate solubility relations, the soluble metal concentration decreased for all test metals except aluminum as the pH increased, while the reverse pH relationship was observed for aluminum. No consistent relationship was observed between pH and soluble metal concentration in the case of lead.

Since it was demonstrated (Table 12) that initial sulfide concentration at the three sulfide levels tested had no effect on metal solubility, the data for all sulfide levels for each test liquid were composited into a single data base, thus making no distinction between the samples with different initial sulfide concentrations. In order to determine the minimum solubility of metal in each test liquid, equilibrium soluble metal concentration was plotted as a function of pH for each test liquid, as shown in Figures 13 through 21. The actual data points are not shown in these figures because of excessive overlapping of data points. In the case of mercury in activated sludge mixed liquor and lead in tap water, the data points were too scattered to establish a smooth curve. From these figures, pH values for minimum solubility limits were determined, and are presented in Table 13.

SORPTION OF METALS

In this investigation, metal was added below its solubility limit (Table 13) to the test liquids and the metal distribution between the soluble and solid phases was determined. In order to study the kinetics of metal distribution in raw sewage and activated sludge mixed liquor, the change in soluble metal concentration was monitored, and the results are plotted with respect to time for each metal and each test condition.

TABLE 12. CORRELATION COEFFICIENTS: INITIAL SULFIDE CONCENTRATION VS. SOLUBLE METAL CONCENTRATION UNDER EQUILIBRIUM CONDITIONS

Test metal	Sampling time	Tap water pH level 6	7	8	9
Aluminum	T=12 Hrs.	.285	.547	.663	.710
	T=24 Hrs.	.650	.553	.605	.580
Cadmium	T=12 Hrs.	.051	.153	.146	.035
	T=24 Hrs.	.047	.021	.083	.210
Chromium	T=12 Hrs.	.217	.305	.060	.280
	T=24 Hrs.	.036	.048	.238	.507
Copper	T=12 Hrs.	.217	.774	.647	.681
	T=24 Hrs.	.265	.786	.555	.598
Iron	T=12 Hrs.	.373	.983	.675	.957
	T=24 Hrs.	.195	.402	.115	.618
Lead	T=12 Hrs.	.260	.486	.283	.493
	T=24 Hrs.	.688	.646	.694	.821
Mercury	T=12 Hrs.	.076	.054	.016	.009
	T=24 Hrs.	.058	.050	.023	.012
Nickel	T=12 Hrs.	.123	.236	.408	.624
	T=24 Hrs.	.150	.231	.405	.570
Zinc	T=12 Hrs.	.079	.078	.184	.898
	T=24 Hrs.	.802	.292	.816	.148

(continued)

TABLE 12. (continued)

Test metal	Sampling time	Raw sewage pH level 6	7	8	9
Aluminum	T=12 Hrs.	ND	ND	.916	.594
	T=24 Hrs.	ND	ND	.897	.692
Cadmium	T=12 Hrs.	.123	.092	.221	.449
	T=24 Hrs.	.104	.032	.178	.378
Chromium	T=12 Hrs.	-	-	-	-
	T=24 Hrs.	.389	.222	.517	.522
Copper	T=12 Hrs.	.414	.762	.211	.265
	T=24 Hrs.	.433	.687	.930	.487
Iron	T=12 Hrs.	.947	.883	.511	.787
	T=24 Hrs.	.707	.893	.615	.465
Lead	T=12 Hrs.	.504	.259	.368	.813
	T=24 Hrs.	.336	.821	.197	.967
Mercury	T=12 Hrs.	.073	.186	.157	.167
	T=24 Hrs.	.031	.154	.171	.266
Nickel	T=12 Hrs.	.220	.180	.290	.571
	T=24 Hrs.	.215	.167	.283	.367
Zinc	T=12 Hrs.	.057	.110	.331	.812
	T=24 Hrs.	.022	.124	.047	.503

ND = nondetectable

(continued)

TABLE 12. (continued)

Test metal	Sampling time	Activated sludge pH level 6	7	8	9
Aluminum	T=12 Hrs.	.292	.686	.748	.640
	T=24 Hrs.	.278	.809	.660	.712
Cadmium	T=12 Hrs.	.052	.031	.064	.102
	T=24 Hrs.	.065	.051	.030	.097
Chromium	T=12 Hrs.	.772	.981	.955	.992
	T=24 Hrs.	.884	.919	.748	.239
Copper	T=12 Hrs.	.939	.687	.780	.796
	T=24 Hrs.	.985	.552	.557	.622
Iron	T=12 Hrs.	.996	.938	.993	.297
	T=24 Hrs.	.998	.294	.393	.490
Lead	T=12 Hrs.	.512	.630	.606	.818
	T=24 Hrs.	.482	.595	.519	.394
Mercury	T=12 Hrs.	.082	.068	.068	.045
	T=24 Hrs.	.058	.066	.080	.046
Nickel	T=12 Hrs.	.325	.317	.818	.598
	T=24 Hrs.	.321	.329	.813	.911
Zinc	T=12 Hrs.	.078	.008	.495	.788
	T=24 Hrs.	.073	.012	.334	.385

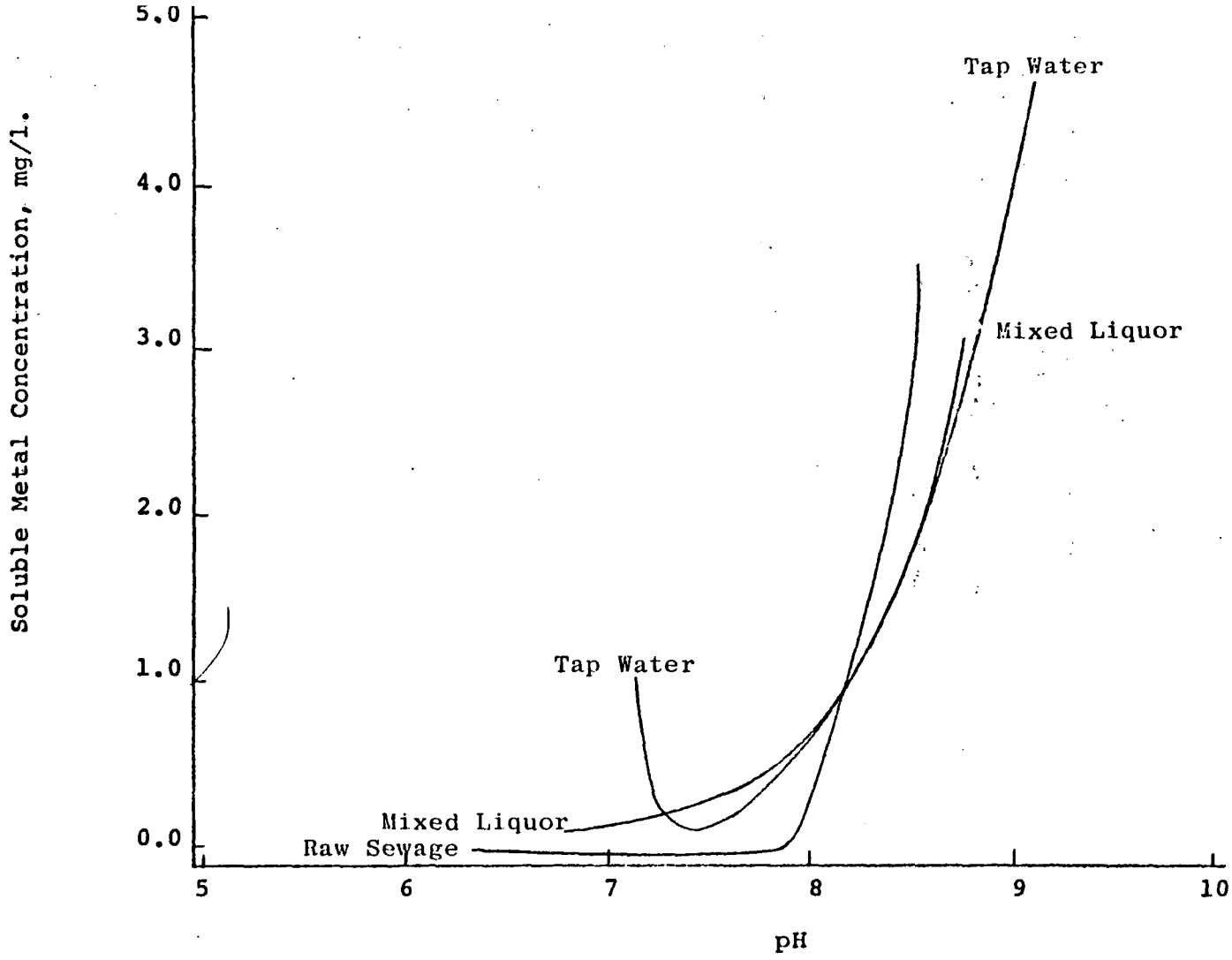


Figure 13. Solubility curves for aluminum in tap water, raw sewage, and activated sludge mixed liquor.

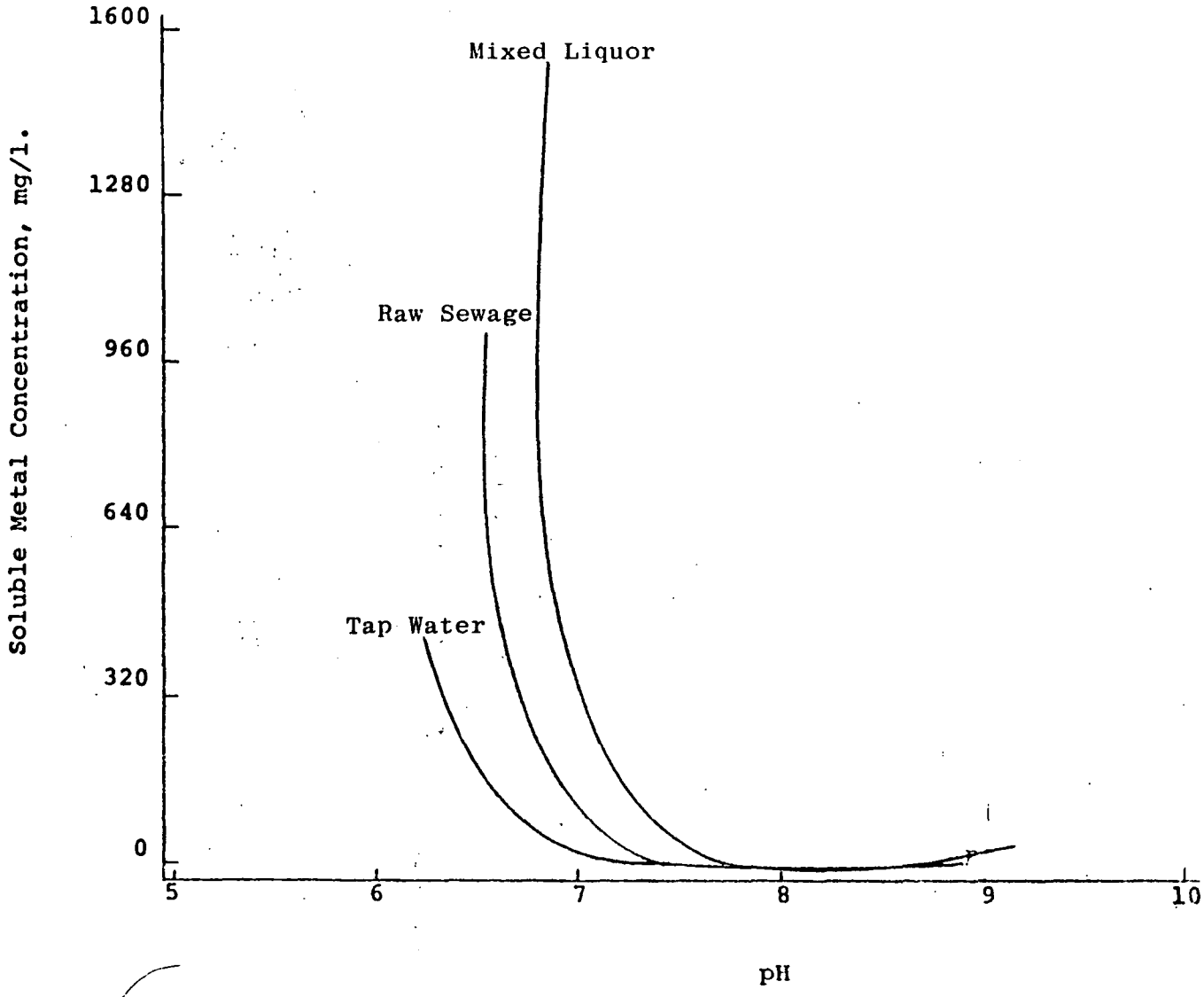


Figure 14. Solubility curves for cadmium in tap water, raw sewage, and activated sludge mixed liquor.

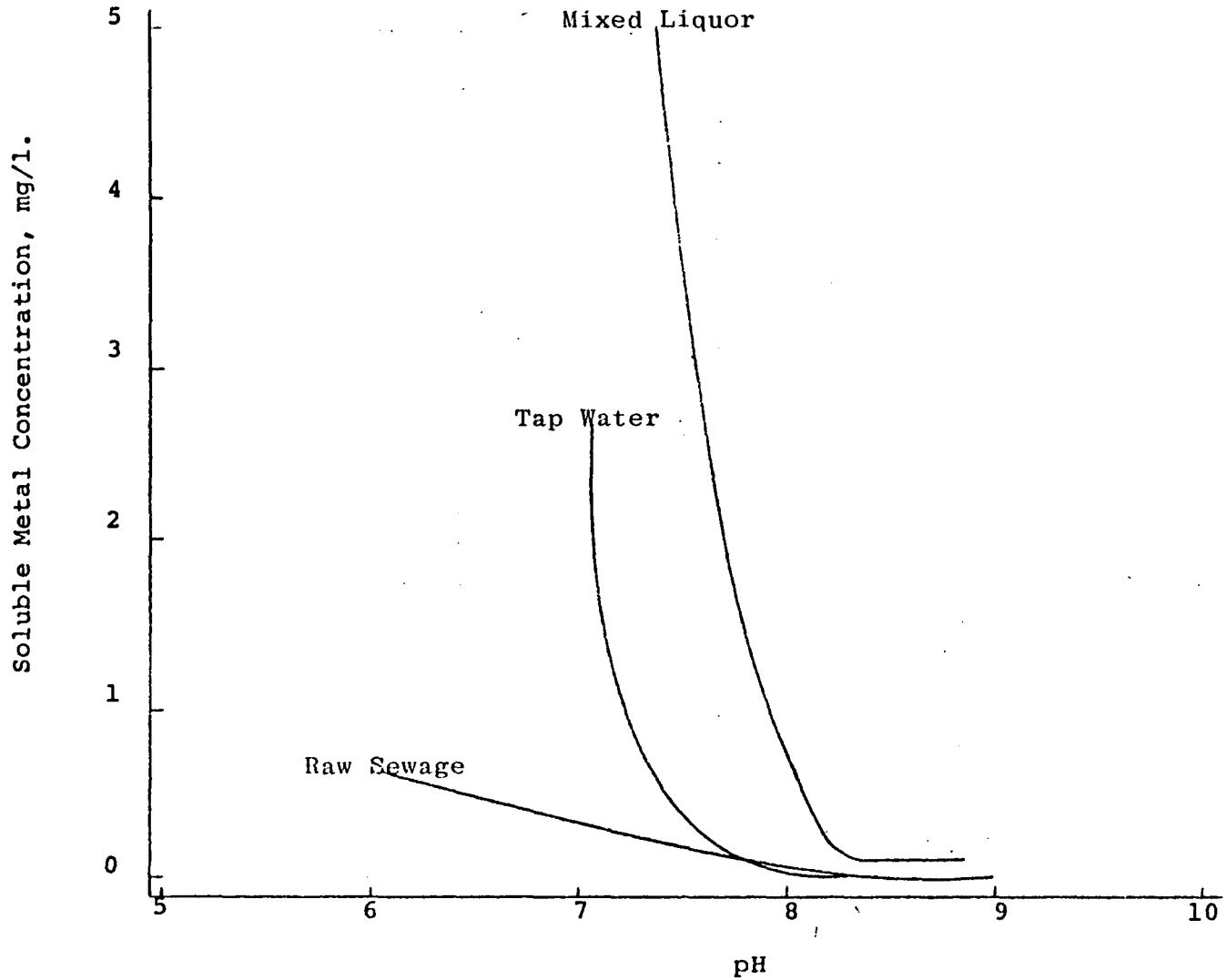


Figure 15. Solubility curves for chromium in tap water, raw sewage, and activated sludge mixed liquor.

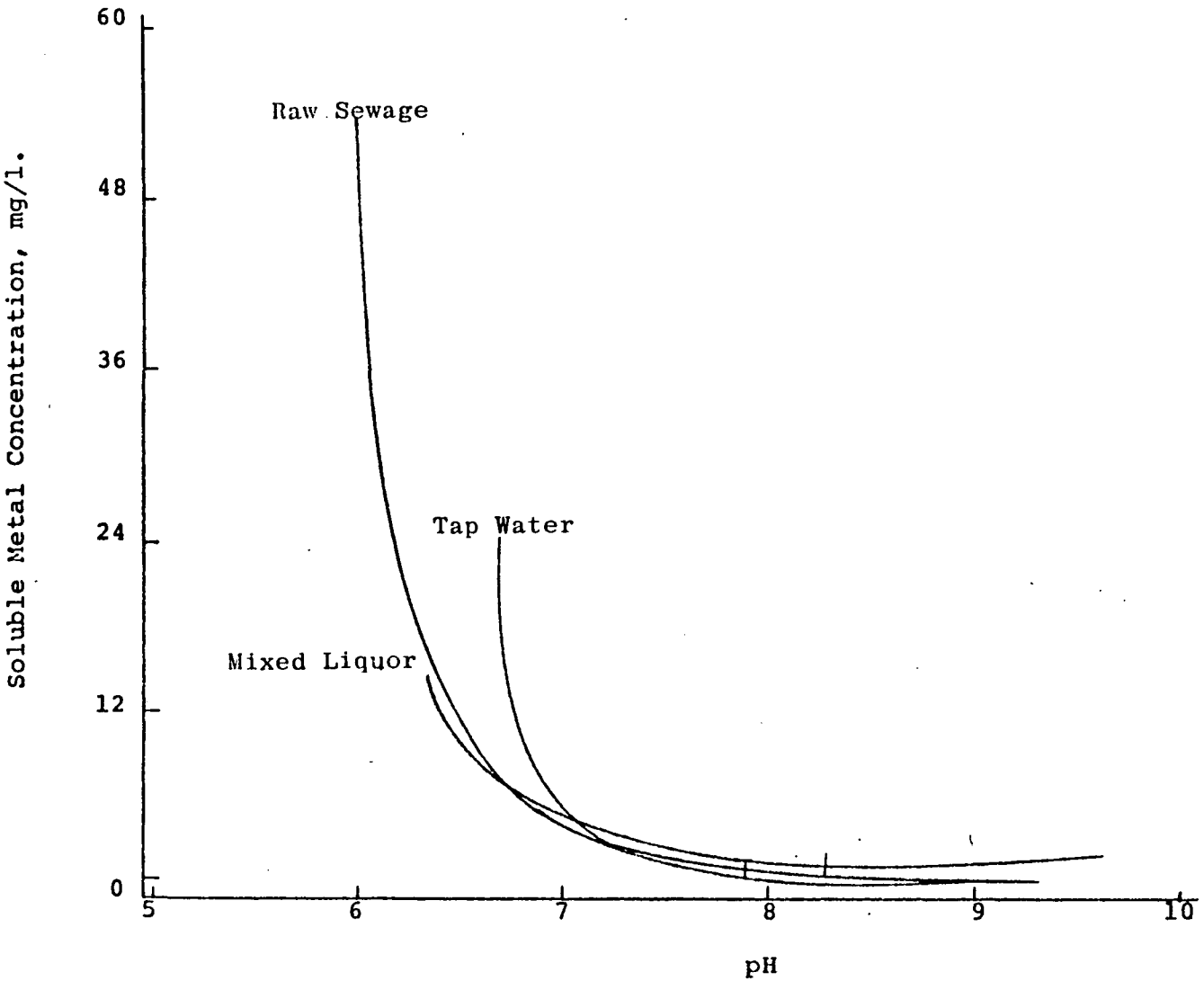


Figure 16. Solubility curves for copper in tap water, raw sewage, and activated sludge mixed liquor.

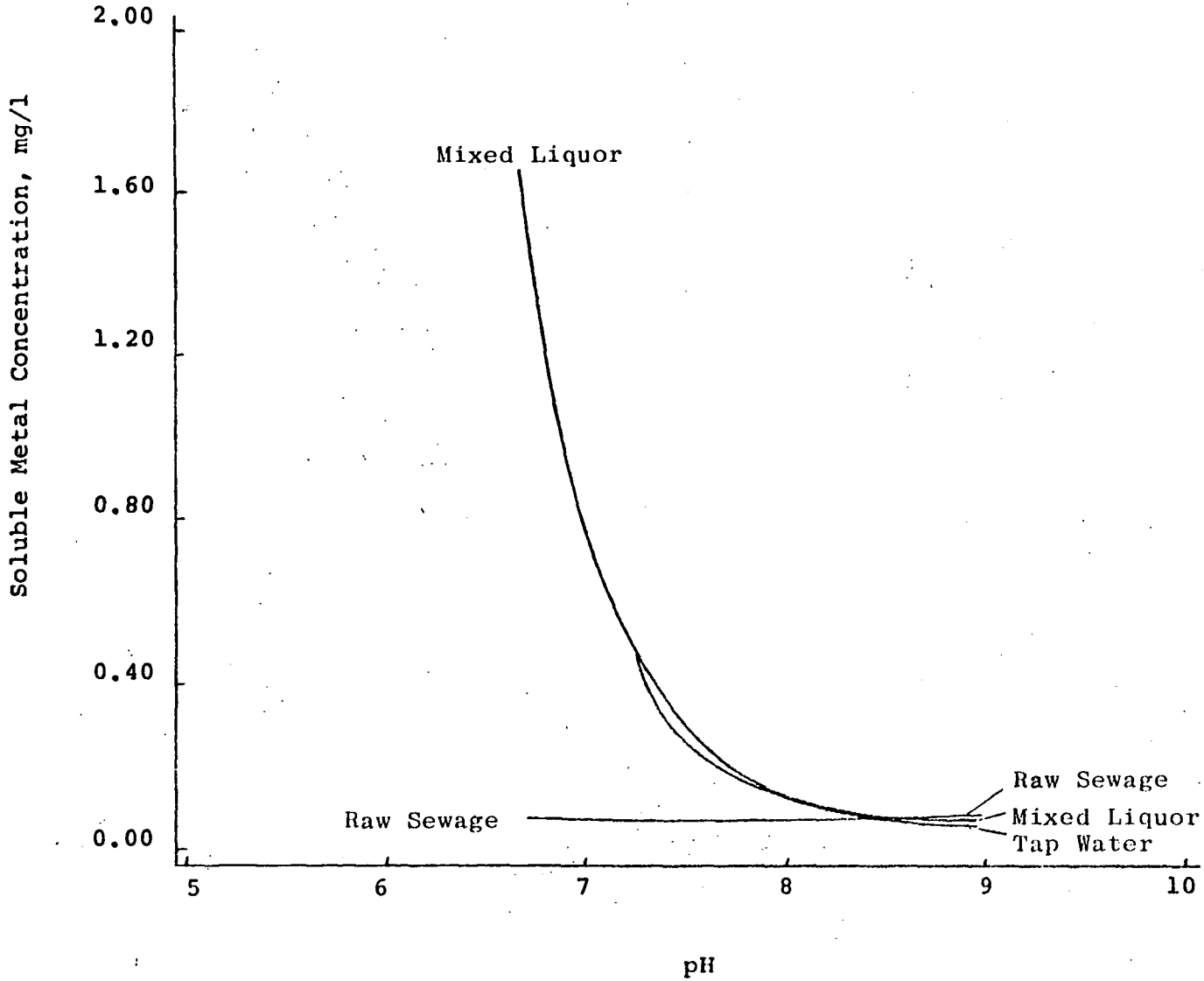


Figure 17. Solubility curves for iron in tap water, raw sewage, activated sludge mixed liquor.

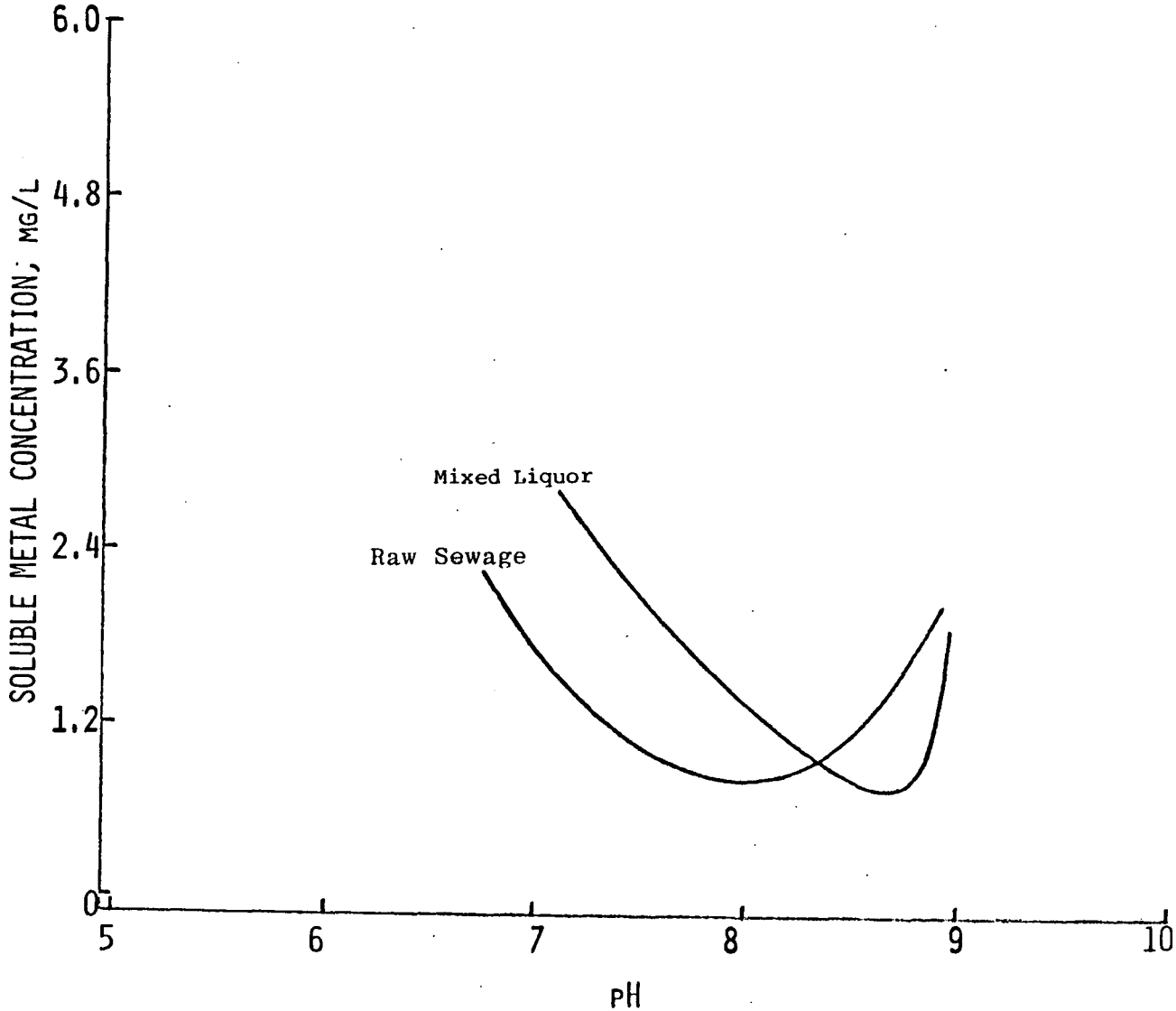


Figure 18. Solubility curves for lead in raw sewage, and activated sludge mixed liquor.

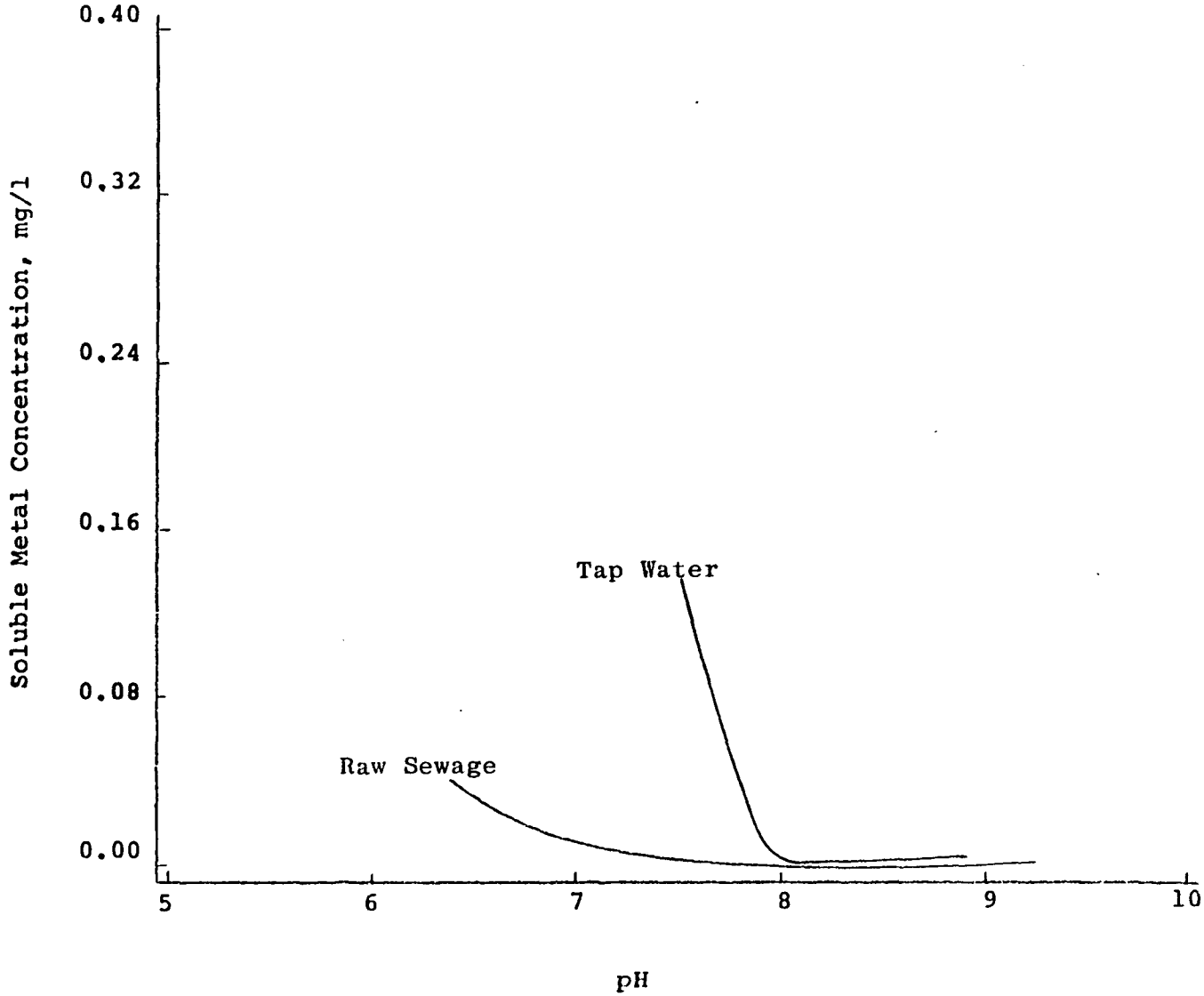


Figure 19. Solubility curves for mercury in tap water and raw sewage

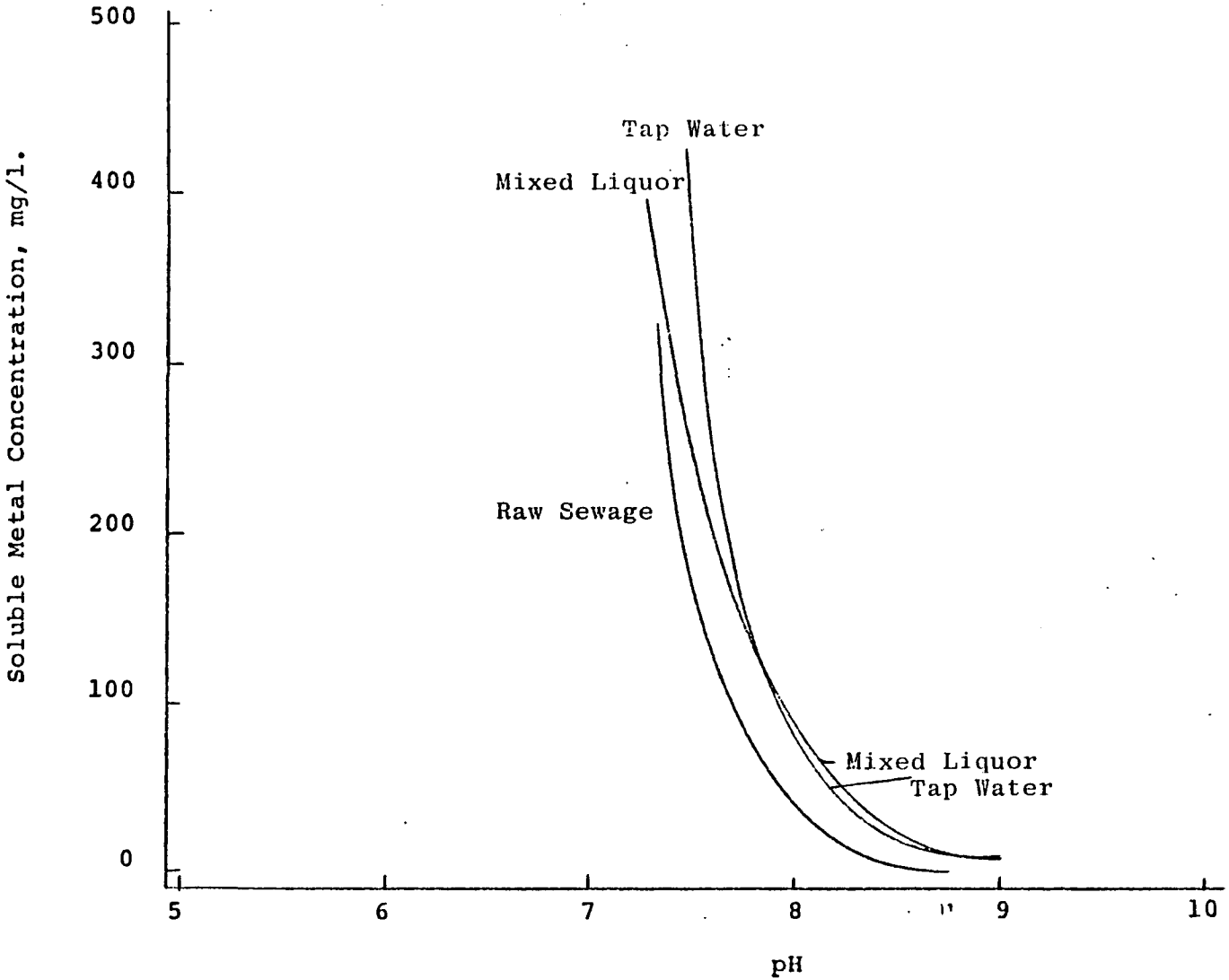


Figure 20. Solubility curves for nickel in tap water, raw sewage, and activated sludge mixed liquor.

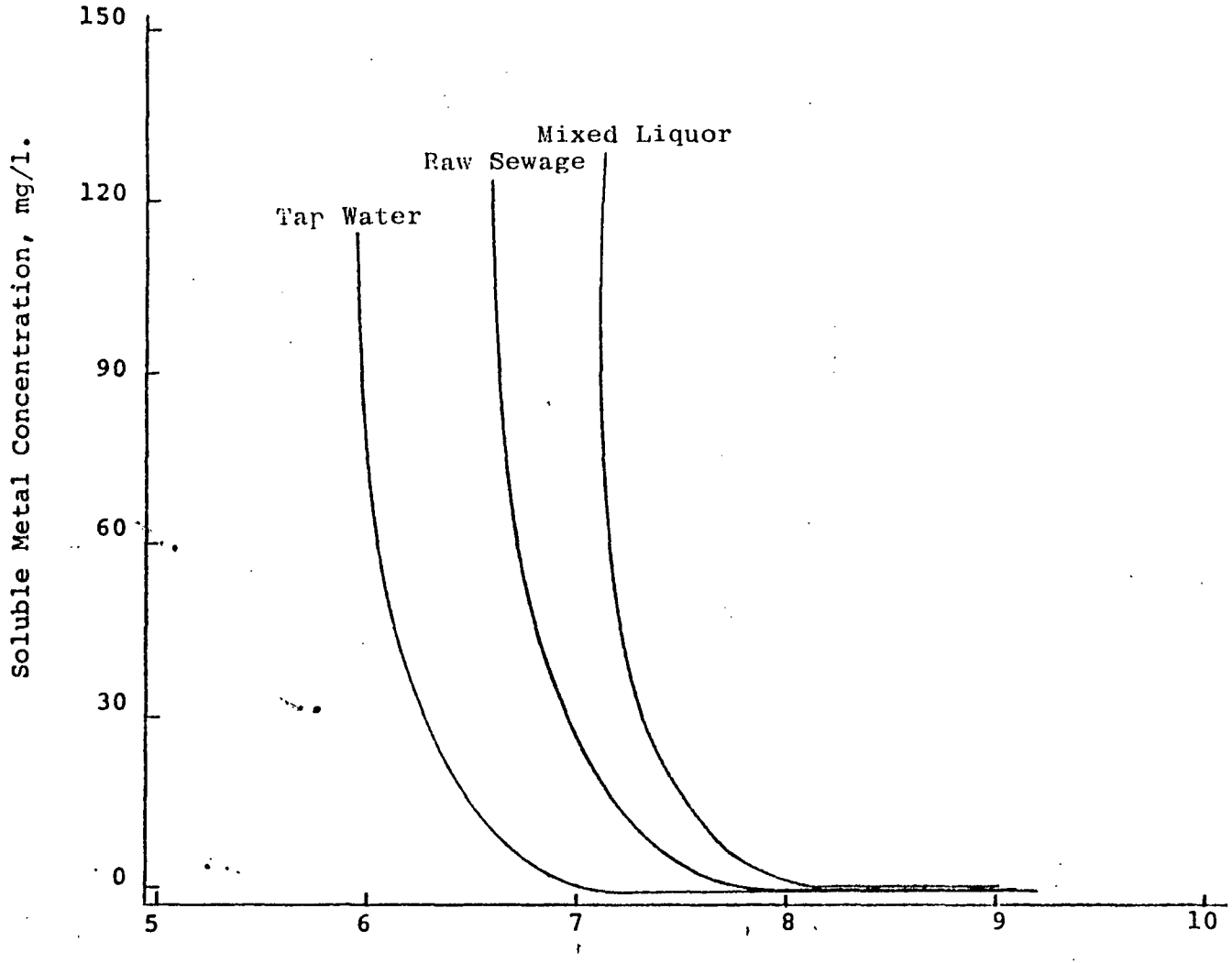


Figure 21. Solubility curves for zinc in tap water, raw sewage, and activated sludge mixed liquor.

TABLE 13. pH OF MINIMUM SOLUBILITIES OF METALS

Metal	Tap Water	Raw Sewage	Mixed Liquor
Aluminum	7.4	7.9	6.8
Cadmium	7.3-9.0	7.4-8.9	7.8-8.7
Chromium	8.1-8.3	8.3-9.0	8.3-8.8
Copper	8.0-9.3	9.5-9.3	8.6-8.8
Iron	8.7-9.0	6.8-9.0	8.7-9.0
Mercury	8.1-8.3	8.0-9.0	-
Nickel	8.7	8.5-9.0	8.7-9.0
Zinc	7.0-9.2	7.8-9.1	8.1-9.0

Figure 22 presents data for cadmium in raw sewage while Figure 23 is for cadmium in activated sludge mixed liquor. Due to the large number of graphs involved, plots for other test systems are not included in this report.

The following observations were made from the kinetic studies on metal distribution:

1) A major portion of each metal was removed within 15 minutes after the addition of the metal. The metal removal appeared to follow a two-phase reaction, as previously reported by Cheng et al. (1975); an initial rapid phase in which the metal was rapidly removed followed by a long-term slow-phase uptake process proceeding for many hours. In most instances, near-equilibrium conditions seem to have been reached approximately six hours after metal addition, with the soluble metal concentration remaining relatively constant thereafter.

2) Since the amount of metal added was below the solubility limit of the metal for the pH of each unit, the decrease in soluble metal concentration of samples cannot be attributed to precipitation reactions. Thus the decrease in soluble metal concentration must be due to metal removal by sludge mass through sorption and/or biological uptake. However, considering the biological uptake of metal to be slow, especially during the relatively short test periods used in this study, it can be assumed that the metal removal was due primarily to sorption phenomena.

3) The change in pH of a given sample was generally found to be toward the neutral side. Despite initial pH values established for a given set of samples ranging from pH of 5.7 to 9.3, the final values were within a pH range of $\pm$ 0.5 units.

Adsorption isotherms for the test metals in raw sewage and mixed liquor were developed, as shown in Figures 24 and 25, respectively. These isotherms demonstrate the relationship between the amount of metal added to the test liquid and the amount adsorbed to the solids in the liquid under equilibrium conditions. The data points on each curve represent samples with different equilibrium pH values; the difference being only within $\pm$ 0.5 units, in most instances.

The relationships shown in Figures 24 and 25 indicate that the metal adsorbed per unit weight of volatile suspended matter increases as the metal added to the test solution increases, until the solubility limit of the metal is reached. Such relationship did not appear to exist for iron and mercury, however. In the case of iron, the added metal remained in solution with no adsorption taking place, within the range of

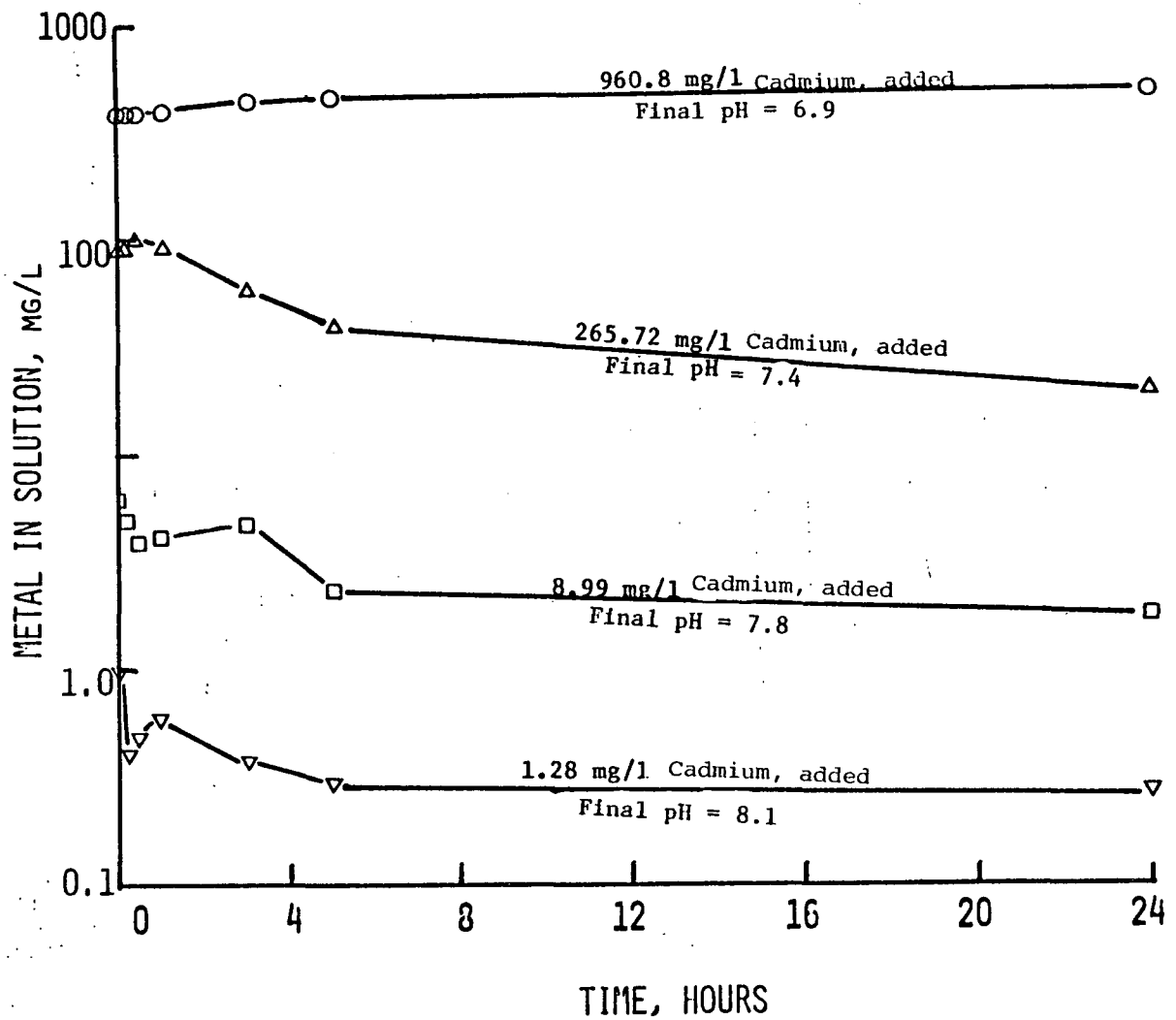


Figure 22. Change in soluble cadmium concentration in raw sewage after the addition of the metal below its solubility limit.

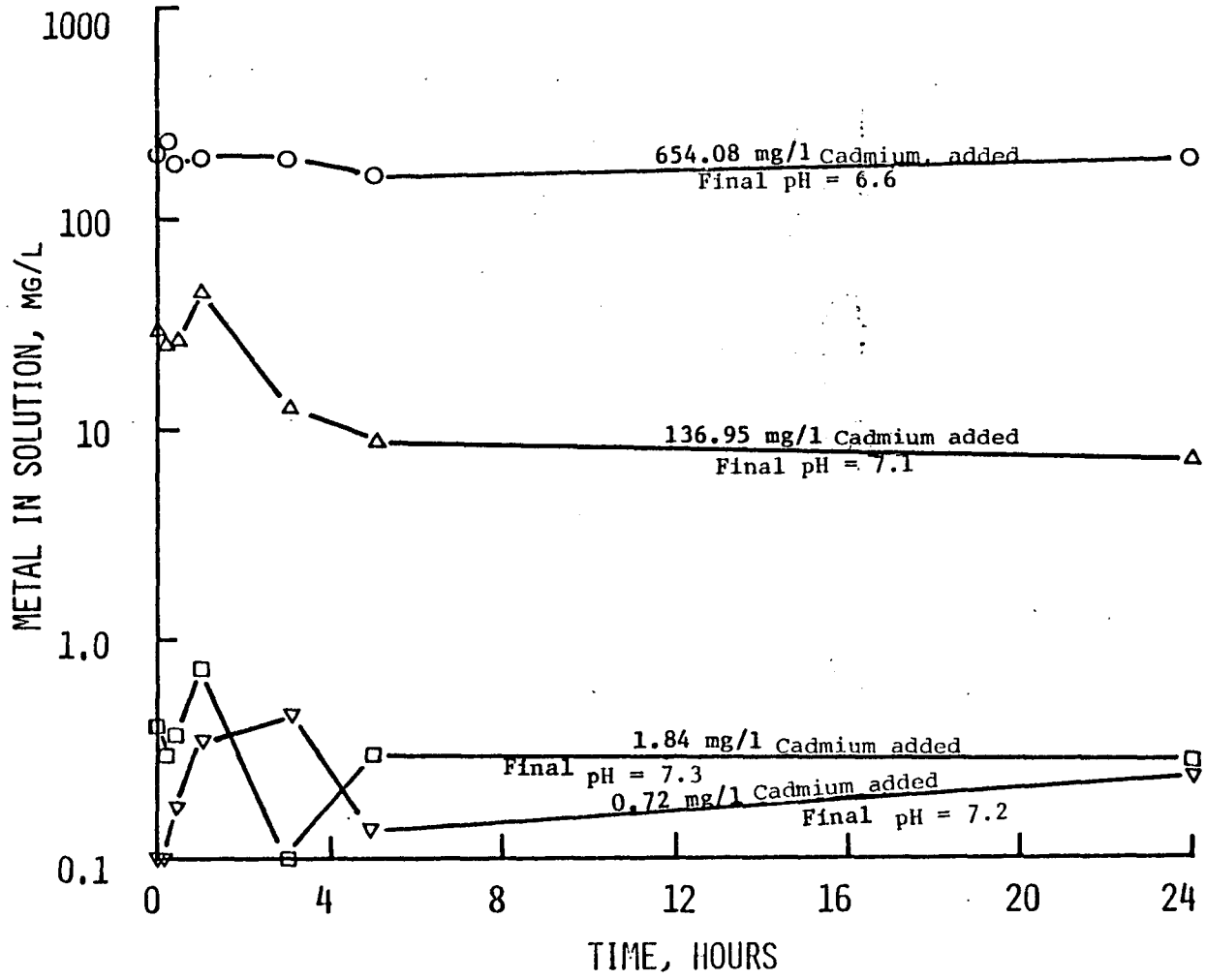


Figure 23. Change in soluble cadmium concentration in activated sludge mixed liquor after the addition of the metal below its solubility limit.

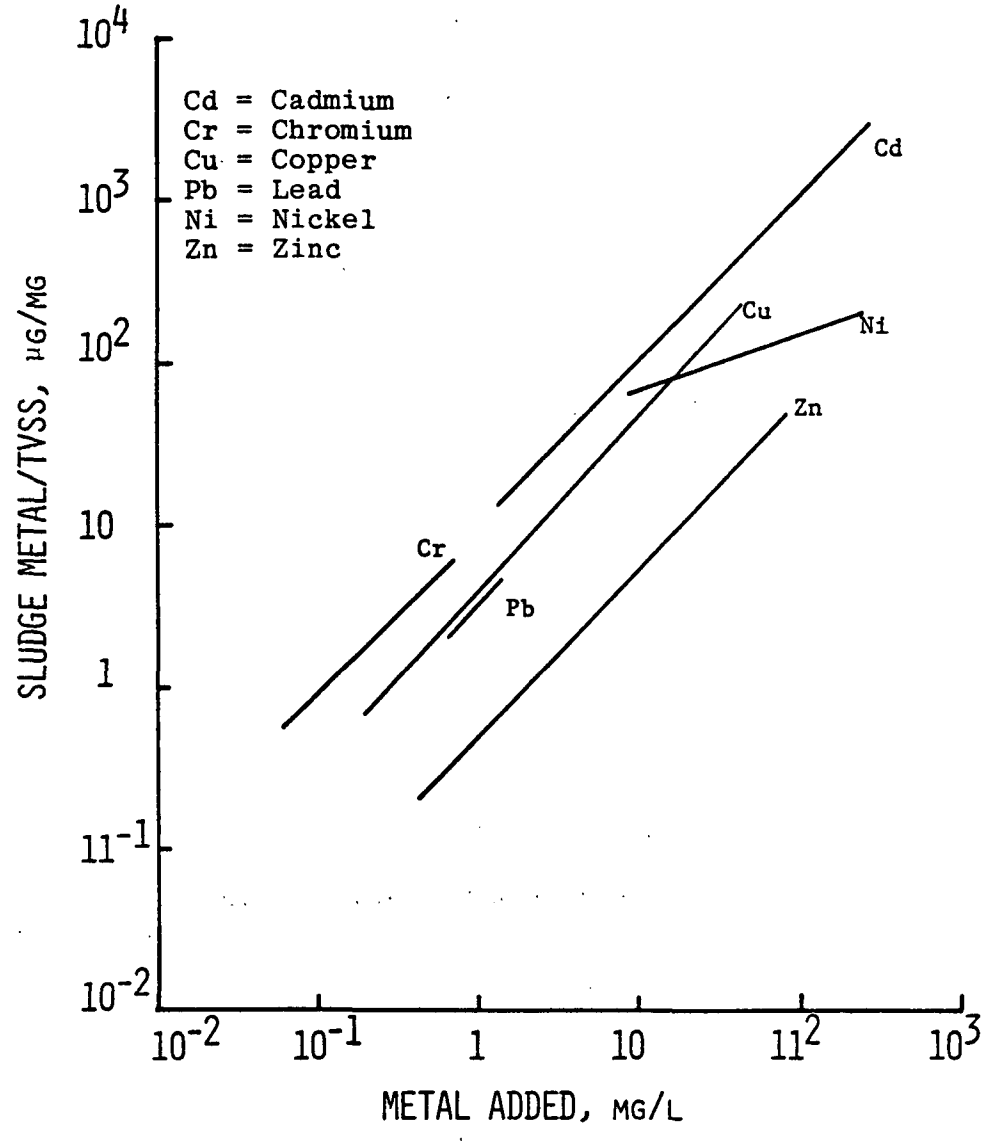


Figure 24. Adsorption isotherms for metals in raw sewage.

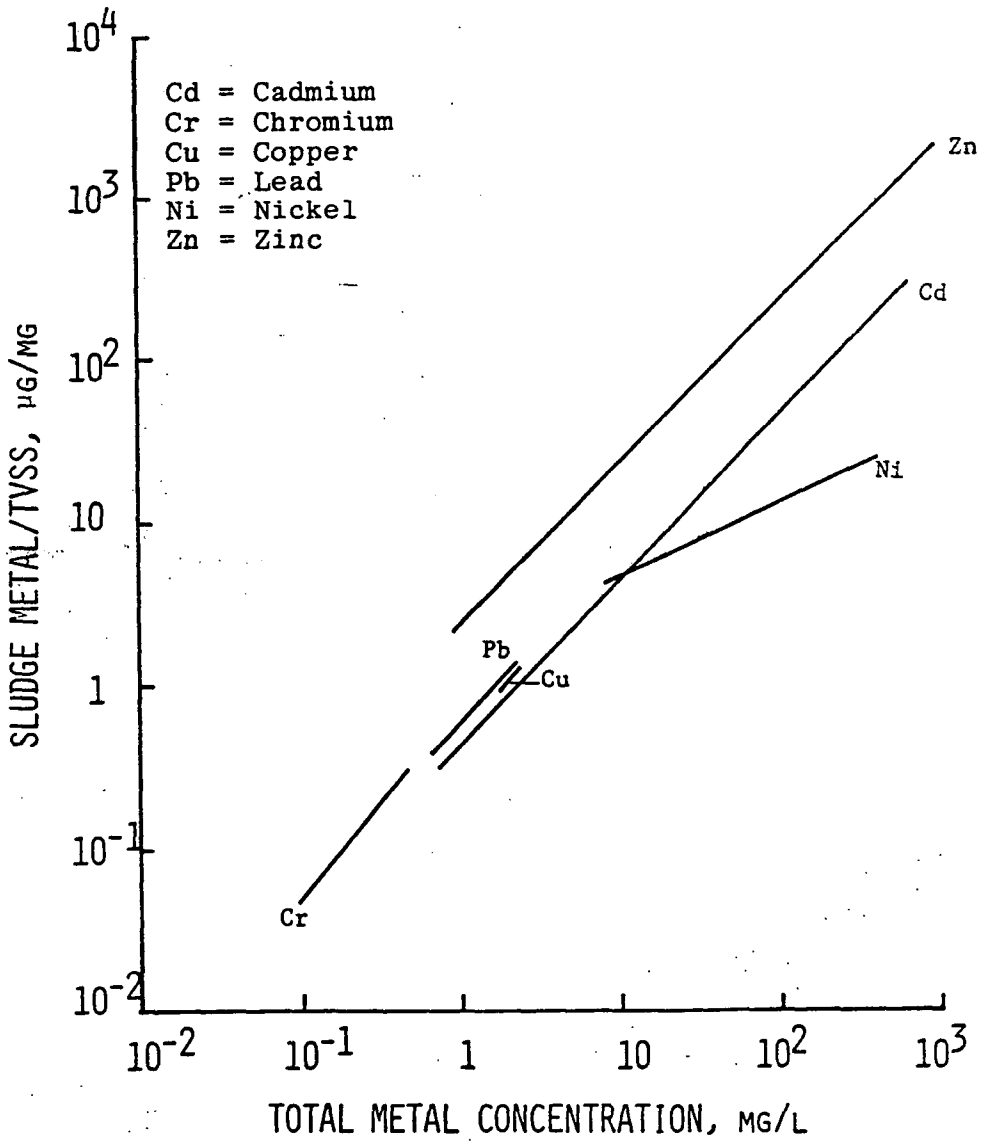


Figure 25. Adsorption isotherms for metals in activated sludge mixed liquor.

iron added. For mercury, a portion of the metal added was adsorbed but no relationship was observed between the total metal concentration in the system and the metal adsorbed per unit weight of VSS.

The relative placement of the isotherms in Figure 24 indicates that cadmium is most highly adsorbed per unit weight of volatile suspended solids in raw sewage, followed by chromium, copper, lead, zinc and nickel, in that order (Table 14). However, if the isotherm for nickel is extended toward lower total nickel concentration, it can be seen that the concentration of sludge-bound nickel per unit weight of TVSS will be higher for nickel than for other metals at any total metal concentration in the lower range. This indicates that nickel sorption will be higher compared to other metals, when nickel concentration is relatively lower. A similar pattern is also observed for nickel in activated sludge mixed liquor (Figure 25). From Figure 25, it can be seen that zinc is adsorbed to the greatest extent to the activated sludge solids, followed by chromium, lead, copper, cadmium and nickel. This order of removal is similar to that reported by Cheng et al., (1975) for activated sludge solids.

A comparison of the ranked order of metals sorption onto the two sludges, from Table 14, indicates that for all metals except cadmium and zinc, the relative sorption ranks are similar. Cadmium sorbed most in raw sewage solids and much less in mixed liquor solids, while zinc demonstrated the reverse pattern.

An attempt was made to determine if the results of the adsorption experiments would fit a standard Freundlich isotherm. As shown in Figures 26 and 27, adsorption of cadmium and copper in the case of raw sewage, and of cadmium, copper and nickel in the case of activated sludge seems to follow a Freundlich isotherm model. The rest of the metals did not fit the Freundlich model. As noted in Section 4, there have been conflicting results reported in the literature (Rudolfs and Zuber, 1953; Cheng, 1973) on the question of metal adsorption by activated sludge according to Freundlich isotherms.

Table 15 lists the average per cent removals of metals by the solids portion of raw sewage and mixed liquor, and as can be seen from the data, the magnitude of metals removals are generally similar for raw sewage and mixed liquor, except in the case of mercury. These per cent removal values are higher than the corresponding values for full-scale treatment plants reported in the literature. (See Section 4.) However, the metals removals reported in Table 14 are based on laboratory-scale filtration through 0.45-micron filters, while the data

TABLE 14. ORDER OF CONCENTRATION OF METALS IN RAW SEWAGE AND ACTIVATED SLUDGE AT 10 mg/l METAL ADDED

Metal Added	Rank Order of Concentration	
	Raw Sewage	Mixed Liquor
Cadmium	1	5
Chromium	2	2
Copper	3	4
Iron	7	7
Lead	4	3
Nickel	6	6
Zinc	5	1

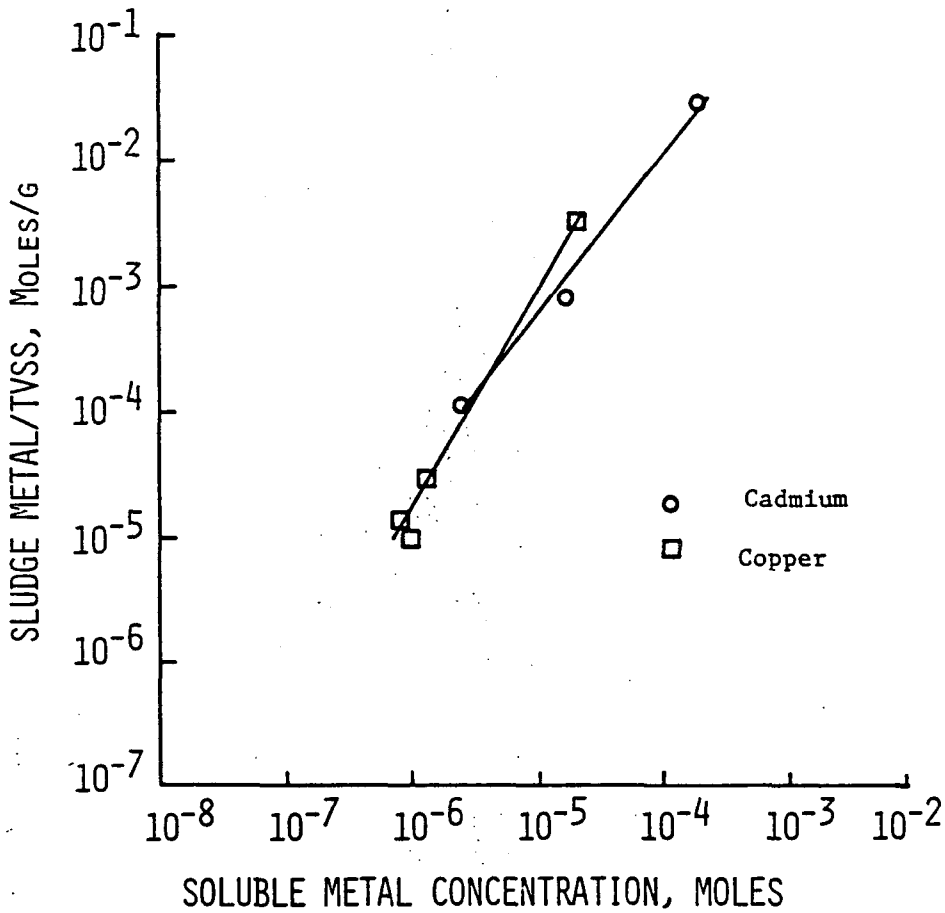


Figure 26. Freundlich adsorption isotherms for metals in raw sewage.

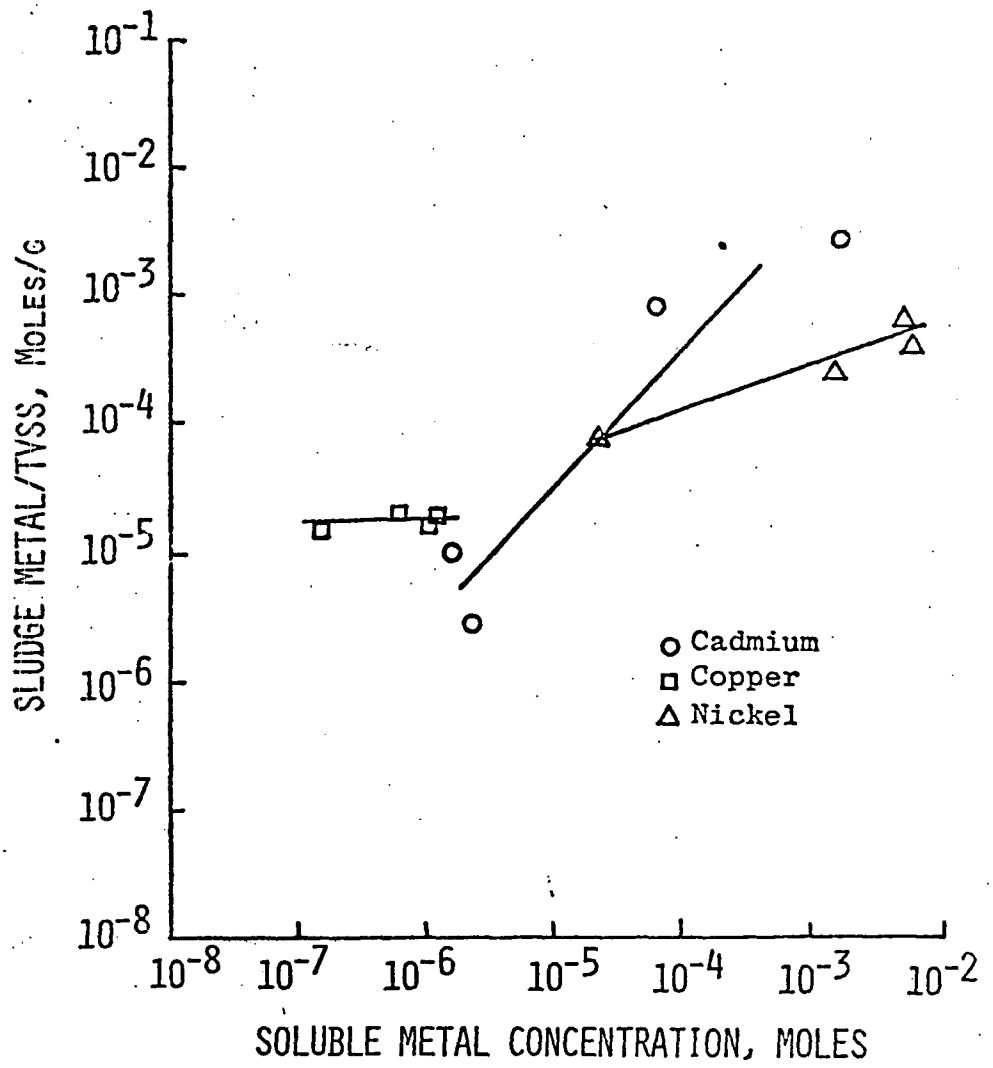


Figure 27. Freundlich adsorption isotherms for metals in activated sludge mixed liquor.

TABLE 15. AVERAGE PER CENT METAL REMOVALS DUE TO ADSORPTION TO SLUDGE MASS

Metal	Test liquid	
	Raw sewage	Activated sludge
Cadmium	75	80
Chromium	99	93
Copper	82	98
Iron	0	8
Lead	97	98
Mercury	20	93
Nickel	29	34
Zinc	89	76

in Tables 1 and 2 are based on full-scale primary and activated sludge clarifier units.

EFFECT OF WASTE PARAMETERS ON METALS DISTRIBUTION

This part of the investigation dealt with batch studies in which the effects of domestic/industrial waste parameters and the metals combinations on the metals distribution in raw sewage and activated sludge mixed liquor were studied. The discussion concerns the analysis of data on filtered samples of raw sewage and activated sludge mixed liquor for replicate metal combinations. As discussed earlier, these three treatments have identical metals combinations.

In order to assess the variability in the residual soluble metal concentrations in the replicates, and the effect of different waste parameters on the final individual metal concentration in the filtered fractions of the test liquids, statistical evaluations were performed using the technique of analysis of variance (AOV).

The results of the AOV calculations for the three replicate treatments are presented in Tables 16 through 31. Refer to Table 6 for the identification of treatment levels. The notation used in the AOV tables is described below:

df	degrees of freedom
SS	sum of squares
MS	mean square
F	mean square/error square
REPS	replicates
TRMTS	treatments (waste parameters)
*	F test significant at 0.01
**	F test significant at 0.05

The statistical analysis indicates that few of the waste parameters evaluated in this component of the project had a significant affect on the final metal concentration of the filtered test liquids, at the parameter concentrations tested. However, there were certain waste parameters for which the AOV indicated an effect on the final soluble concentration, for some of the metals. These effects are summarized in Table 32. Among the waste parameters tested, the levels of pH, inorganics plus hardness, and detergents seem to affect most metals. The detergent concentration had a significant influence on the final soluble concentrations of chromium and nickel in both test liquids, and on those of iron and lead in mixed liquor.

TABLE 16. AOV FOR ALUMINUM IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	498262		
MEAN		1	350424.01		
REPS		2	13.87	6.94	0.01
TRMTS		7	65701.88	9385.98	10.13
LEVELS	1	2	15466.89	7733.45	8.35**
	2	2	852.67	426.34	0.46
	3	2	709.56	354.78	0.38
	4	2	6574.22	3287.11	3.55*
	5	2	11552	5776	6.23**
	6	2	1666.67	833.34	0.90
	7	2	2429.56	1214.78	1.31
ERROR		46	42613.78	926.39	

TABLE 17. AOV FOR ALUMINUM IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	334975		
MEAN		1	184528.13		
REPS		2	1341.08	670.54	2.65
TRMTS		7	124201.76	17743.11	70.2**
LEVELS	1	2	53.56	26.78	0.11
	2	2	1350.02	675.01	2.67
	3	2	50.0	25.0	0.10
	4	2	304.89	152.45	0.60
	5	2	9602.89	4801.45	19.0**
	6	2	50.0	25.0	0.10
	7	2	1814	907	3.59*
ERROR		46	11621.78	252.65	

TABLE 18. AOV FOR CADMIUM IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	7305		
MEAN		1	4528.35		
REPS		2	0.192	0.1	<0.01
TRMTS		7	1267.98	181.14	8.25**
LEVELS	1	2	66.67	33.34	1.52
	2	2	0.22	0.11	0.01
	3	2	16.89	8.45	0.38
	4	2	4.22	2.11	0.10
	5	2	44.22	22.11	1.01
	6	2	44.67	22.34	1.02
	7	2	317.56	158.78	7.23**
ERROR		46	1009.8	21.95	

TABLE 19. AOV FOR CADMIUM IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	1748		
MEAN		1	1283.56		
REPS		2	13.52	6.76	4.72*
TRMTS		7	258	37	25.8**
LEVELS	1	2	111	56	39.1**
	2	2	8	4	2.8
	3	2	0.2	0.1	0.07
	4	2	0.7	0.4	0.29
	5	2	5	2.5	1.75
	6	2	0.2	0.1	0.07
	7	2	2	1	0.7
ERROR		46	65.85	1.43	

TABLE 20. AOV FOR CHROMIUM IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	3940		
MEAN		1	2862.72		
REPS		2	8.45	4.23	1.86
TRMTS		7	721.72	103.10	45.42**
LEVELS	1	2	1.56	0.78	0.34
	2	2	213.56	106.78	47.04**
	3	2	8.67	4.34	1.91
	4	2	5.56	2.78	1.22
	5	2	8.00	4.00	1.76
	6	2	0.00	0.00	0.00
	7	2	5.56	2.78	1.22
ERROR		46	104.2	2.27	

TABLE 21. AOV FOR CHROMIUM IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	20447		
MEAN		1	9964.01		
REPS		2	93.53	46.77	0.94
TRMTS		7	6803.66	971.95	19.58**
LEVELS	1	2	0.00	0.00	0.00
	2	2	856.89	428.45	8.63**
	3	2	2.89	1.45	0.03
	4	2	268.67	134.34	2.71
	5	2	46.22	23.11	0.47
	6	2	0.00	0.00	0.00
	7	2	128.00	64.00	1.29
ERROR		46	2283.13	49.63	

TABLE 22. AOV FOR COPPER IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	241204		
MEAN		1	118584.5		
REPS		2	2997.25	1498.63	1.31
TRMTS		7	52205.28	7457.90	6.51**
LEVELS	1	2	3902.89	1951.45	1.70
	2	2	37.56	18.78	0.20
	3	2	2689.56	1344.78	1.17
	4	2	2810.89	1405.45	1.23
	5	2	134.89	67.45	0.06
	6	2	120.67	60.34	0.05
	7	2	4934.22	2467.11	2.15
ERROR		46	52690.07	1145.44	

TABLE 23. AOV FOR COPPER IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	34688		
MEAN		1	16867		
REPS		2	212	106	0.75
TRMTS		7	10684	1526	10.8**
LEVELS	1	2	246	123	0.87
	2	2	48	24	0.17
	3	2	10	5	0.04
	4	2	28	14	0.10
	5	2	22	11	0.08
	6	2	4	2	0.01
	7	2	96	48	0.34
ERROR		46	6471	140.7	

TABLE 24. AOV FOR IRON IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	1690906		
MEAN		1	1024834.7		
REPS		2	18718.05	9359.03	1.67
TRMTS		7	263035.3	37576.47	6.71**
LEVELS	1	2	281.56	140.78	0.03
	2	2	20200.67	10100.34	1.80
	3	2	8321.56	4160.78	0.74
	4	2	9100.22	4550.11	0.81
	5	2	49355.56	24677.78	4.41*
	6	2	34738.89	17369.45	3.10
	7	2	688.89	344.45	0.06
ERROR		46	257430.6	5596.32	

TABLE 25. AOV FOR IRON IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	2310910		
MEAN		1	1382785		
REPS		2	9617	4809	3.0
TRMTS		7	706830	100976	62.8**
LEVELS	1	2	3545	1773	1.1
	2	2	118084	59042	37.0**
	3	2	140	70	0.04
	4	2	793	397	0.25
	5	2	6022	3011	1.90
	6	2	4381	2191	1.40
	7	2	3200	1600	0.99
ERROR		46	74024	1609	

TABLE 26. AOV FOR LEAD IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	94741		
MEAN		1	15283.35		
REPS		2	1022.19	511.10	1.57
TRMTS		7	56353.88	8050.55	24.66**
LEVELS	1	2	6852.67	3426.3	10.50**
	2	2	0.22	0.11	<0.01
	3	2	8.22	4.11	0.01
	4	2	26.89	13.45	0.04
	5	2	2.0	1.0	<0.01
	6	2	8.22	4.11	0.01
	7	2	168.22	84.11	0.28
ERROR		46	15015.14	326.4	

TABLE 27. AOV FOR LEAD IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	44682		
MEAN		1	9248		
REPS		2	7	3.5	0.78
TRMTS		7	26839	3834	828.1**
LEVELS	1	2	8047	4024	869.0**
	2	2	313	157	33.8**
	3	2	10	5	1.08
	4	2	2	1	0.22
	5	2	0.2	0.04	0.01
	6	2	2	1	0.22
	7	2	0.9	0.45	0.10
ERROR		46	213	4.63	

TABLE 28. AOV FOR NICKEL IN RAW SEWAGE

		df	SS	MS	F
TOTAL		72	11978474		
MEAN		1	11127403		
REPS		2	38740.21	19370.11	6.49**
TRMTS		7	429608.11	61372.59	20.58**
LEVELS	1	2	8963.56	4481.78	1.50
	2	2	175664.67	87832.34	29.45**
	3	2	6560.89	3280.45	1.10
	4	2	1134	567	0.19
	5	2	27234.89	13617.45	4.57*
	6	2	10040.22	5020.11	1.68
	7	2	14177.56	7088.78	2.38
ERROR		46	137206.22	2982.74	

TABLE 29. AOV FOR NICKEL IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		72	2068632		
MEAN		1	1696482		
REPS		2	15426	7713	9.0**
TRMTS		7	132043	18863	22.0**
LEVELS	1	2	451	226	0.3
	2	2	175665	87833	103.0**
	3	2	1408	704	0.8
	4	2	38	19	0.02
	5	2	3654	1827	2.10
	6	2	488	244	0.28
	7	2	2839	1420	1.70
ERROR		46	39385	856.2	

TABLE 30. AOV FOR ZINC IN RAW SEWAGE

		df	SS	MS	F
TOTAL		63	2179688		
MEAN		1	1288859		
REPS		2	4078	20354	0.10
TRMTS		6	582520	97087	0.47
LEVELS	1	2	81	40.5	<0.01
	2	2	2443	1221.5	0.01
	3	2	1784	892	<0.01
	4	2	28620	14310	0.07
	5	2	2231	1116	0.01
	6	2	12872	6436	0.03
ERROR		40	206609	5165.23	

TABLE 31. AOV FOR ZINC IN MIXED LIQUOR

		df	SS	MS	F
TOTAL		63	2077686		
MEAN		1	904561.92		
REPS		2	5566.13	2783.07	0.13
TRMTS		6	198545.52	33090.92	1.54
LEVELS	1	2	1652.67	826.34	0.04
	2	2	14126	7063	0.33
	3	2	2082.89	1041.45	0.05
	4	2	26456	13228	0.61
	5	2	9302.89	4651.45	0.22
	6	2	436.22	218.11	0.01
ERROR		40	861737.87	21543.45	

TABLE 32. WASTE PARAMETERS WHOSE TREATMENT LEVELS HAD A SIGNIFICANT EFFECT ON FINAL SOLUBLE METAL CONCENTRATION

Treatment Level	Aluminum	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Zinc
1. Inorganics and Hardness	RS*	ML**				RS,ML		
2. Detergents			RS,ML		ML	ML	RS,ML	
3. Suspended Solids								
4. SOC	RS							
5. pH	RS,ML				ML		RS	
6. Cyanide								
7. Ammonia	ML	RS						

*RS = raw sewage
**ML = mixed liquor

From the tables of AOV, it can be seen that the F-test is significant for every metal in each test liquid (except for aluminum in raw sewage and zinc in mixed liquor) with regard to the waste parameters (treatments). This indicates that the final metal concentrations in the filtered fractions of the test liquids did differ significantly in samples receiving different treatments although, as demonstrated by the AOV, there was little significant difference when each sample was tested against the mean value for that group. A Studentized Range Test was conducted, with the results shown in Tables 33 and 34, to determine which treatments resulted in higher residual soluble metal concentrations. The results from this statistical analysis are summarized in Table 35. The numbers given in this table represent the treatment (waste parameters) applied, and their position in the table indicates if they result in low, normal, or high concentrations of metals (on a relative scale) in the filtered fractions of the test liquids, at the end of the equilibration period.

The studentized range test indicates the following impacts of the waste parameters on the distribution of metals between the liquid and solid phases.

1. Higher inorganic and hardness levels induce higher soluble levels of cadmium, copper and lead, in raw sewage and mixed liquor.

2. Detergents induce higher soluble raw sewage and mixed liquor chromium, and mixed liquor iron, lead, and nickel.

3. For cadmium (raw sewage and mixed liquor) and raw sewage nickel, a direct relationship is indicated between increased suspended solids and increased soluble metal. This result is unexpected since data reported by Cheng (1973) indicated reduced soluble metal with increased mixed liquor suspended solids.

4. Higher levels of SOC resulted in higher soluble levels of mixed liquor chromium and raw sewage iron, only.

5. Cyanide, at the levels tested, influenced the solubility of raw sewage cadmium, and mixed liquor iron, only.

6. Higher ammonia levels induced higher soluble concentrations of mixed liquor aluminum, raw sewage cadmium and chromium, and raw sewage and mixed liquor copper.

TABLE 33. STUDENTIZED TEST FOR TREATMENTS OF RAW SEWAGE

Studentized Range Test:

CADMIUM $q_{0.5} = 4.5$ (from statistical tables)

$S_x = \left(\frac{21.95}{9}\right)^{\frac{1}{2}} = 1.56$

$(q_{0.5})S_x = 4.5 \times 1.56 = 7.03$

1.56*	3.44	8.22	9.78	11.89	12.30	12.67
T_2	T_4	T_5	T_3	T_7	T_6	T_1

CHROMIUM $S_x = \left(\frac{2.27}{9}\right)^{\frac{1}{2}} = 0.50$

$(q_{0.5})S_x = 4.5 \times 0.50 = 2.26$

2.33	3.33	4.56	5.56	6.00	10.56	12.11
T_5	T_3	T_1	T_4	T_6	T_7	T_2

COPPER $S_x = \left(\frac{1145.44}{9}\right)^{\frac{1}{2}} = 11.28$

$(q_{0.5})S_x = 4.5 \times 11.28 = 50.77$

12.00	12.78	16.22	34.56	45.89	73.56	90.22
T_6	T_2	T_5	T_3	T_4	T_1	T_7

*Metal Concentration in µg/l, ranked

(continued)

TABLE 33. (continued)

IRON $S_x = \left(\frac{5596.32}{9}\right)^{\frac{1}{2}} = 24.94$

$(q_{0.5})S_x = 4.5 \times 24.94 = 112.23$

43.56	77.00	81.56	118.89	191.11	239.44	318.67
T_1	T_2	T_3	T_5	T_7	T_6	T_4

LEAD $S_x = \left(\frac{326.4}{9}\right)^{\frac{1}{2}} = 6.02$

$(q_{0.5})S_x = 4.5 \times 6.02 = 27.10$

1.33	2.44	3.78	4.78	7.11	7.78	88.3
T_5	T_6	T_2	T_3	T_4	T_7	T_1

NICKEL $S_x = \left(\frac{2982.74}{9}\right)^{\frac{1}{2}} = 18.20$

$(q_{0.5})S_x = 4.5 \times 18.20 = 81.92$

249.33	327.11	361.00	381.44	424.78	440.89	519.44
T_2	T_1	T_4	T_7	T_6	T_5	T_3

(continued)

TABLE 33. (continued)

ZINC

$S_x = \left(\frac{5165.23}{9}\right)^{\frac{1}{2}} = 23.96$

$(q_{0.5})S_x = 4.5 \times 23.96 = 107.8$

58.67	59.22	89.4	97	272.78	310.1
T_2	T_1	T_5	T_3	T_6	T_4

TABLE 34. STUDENTIZED TEST FOR TREATMENTS OF MIXED LIQUOR

Studentized Range Test:

ALUMINUM $q_{0.5} = 4.5$

$S_x = \left(\frac{252.65}{9}\right)^{\frac{1}{2}} = 5.30$

$(q_{0.5})\ (S_x) = 4.5 \times 5.30 = 23.84$

15.67*	17.33	22.4	44.56	55.44	70.67	149.44
T_3	T_6	T_1	T_2	T_4	T_7	T_5

CADMIUM $S_x = \left(\frac{1.43}{9}\right)^{\frac{1}{2}} = 0.40$

$(q_{0.5})S_x = 4.5 \times 0.40 = 1.79$

2.11	3.00	3.67	4.33	4.56	6.22	7.89
T_6	T_4	T_2	T_5	T_7	T_3	T_1

CHROMIUM $S_x = \left(\frac{49.63}{9}\right)^{\frac{1}{2}} = 2.35$

$(q_{0.5})S_x = 4.5 \times 2.35 = 10.57$

2.11	4.11	6.00	7.67	8.00	27.0	29.22
T_3	T_5	T_6	T_7	T_1	T_4	T_2

*Metal Concentration in µg/l, ranked

(continued)

TABLE 34. (continued)

COPPER	$S_x = (\frac{140.7}{9})^{\frac{1}{2}} = 3.95$						
	$(q_{0.5})(S_x) = 4.5 \times 3.95 = 17.79$						
	3.89	5.11	6.89	17.89	22.56	24.11	39.44
	T_6	T_2	T_3	T_4	T_1	T_5	T_7
IRON	$S_x = (\frac{1609}{9})^{\frac{1}{2}} = 13.37$						
	$(q_{0.5})S_x = 4.5 \times 13.37 = 60.17$						
	43.89	64.78	81.44	128.89	146.67	700.22	368.53
	T_4	T_1	T_3	T_5	T_7	T_2	T_6
LEAD	$S_x = (\frac{4.63}{9})^{\frac{1}{2}} = 0.72$						
	$(q_{0.5})S_x = 4.5 \times 0.72 = 3.23$						
	1.11	1.56	3.33	3.44	4.33	14.67	61.22
	T_5	T_7	T_6	T_3	T_4	T_2	T_1

(continued)

TABLE 34. (continued)

NICKEL	$S_x = (\frac{856.2}{9})^{\frac{1}{2}} = 9.75$						
	$(q_{0.5})S_x = 4.5 \times 9.75 = 43.89$						
	102.22	110.11	137.33	139.56	154.78	175.56	249.33
	T_4	T_3	T_1	T_5	T_7	T_6	T_2
ZINC	The test was found not to be significant for any treatment of zinc in mixed liquor.						

TABLE 35. COMPARISON OF RESULTS FROM STUDENTIZED RANGE TEST[1]

	LOW[3]	MEDIUM	HIGH
ALUMINUM			
raw sewage[2]			
mixed liquor	3,6,1	2,4	7,5
CADMIUM			
raw sewage	2,4,5		3,7,6,1
mixed liquor	6,4,2	5,7	3,1
CHROMIUM			
raw sewage	5,3,1	4,6	7,2
mixed liquor	3,5,6,7,1		4,2
COPPER			
raw sewage	6,2,5,3,4		1,7
mixed liquor	6,2,3,4		1,5,7
IRON			
raw sewage	1,2,3,5	7,6	4
mixed liquor	4,1,3	5,7	2,6
LEAD			
raw sewage	5,6,2,3,4,7		1
mixed liquor	5,7,6,3	4	2,1
NICKEL			
raw sewage	2,1	7,6	2
mixed liquor	4,3,1,5	4,7,6,5	3
ZINC			
raw sewage	2,1,5,3	6,4	
mixed liquor[2]			

1) The numbers in the columns indicate the number of the waste parameter tested. See Table 6 for the waste parameter corresponding to the number.
2) F-test not found to be significant.
3) Low means that the waste parameter given under this column has the least effect compared to other waste parameters on the distribution of metal between solid and soluble phases; medium means an intermediate effect; high means relatively significant effect.

These results indicate that no single waste parameter influences the metals distribution of all metals tested, and that different parameters affect different metals. The affect may be observed in one or both of the raw sewage and mixed liquor process streams. Further, the affect may be rather slight, since AOV failed to identify many of these factors.

METALS DISTRIBUTION IN CONVENTIONAL ACTIVATED SLUDGE SYSTEMS

This part of the investigation dealt with the 39 separate continuously run pilot-scale activated sludge units. The overall range and average values of different parameters (including metals) for raw sewage, primary effluent, mixed liquor, and secondary effluent for these 39 units are summarized in Table 36. As is evident from Table 36, a wide range of values for each parameter was observed in the raw sewage feed. As may be expected, the range of values of different parameters of other process liquids is also wide. However, the per cent soluble metal for any given metal seems to be relatively constant for all the process liquids, despite large variations in the total metal concentration. Tables A.1 through A.39 in Appendix A summarize the average equilibrium values of various parameters analyzed in each treatment for the four different process liquids (raw sewage, primary effluent, mixed liquor and secondary effluent.

Overall System Characteristics

As demonstrated in Table 36, the influent sewage to the pilot treatment systems was relatively weak, averaging 62 mg/l VSS and 28 mg/l SOC. The primary clarifier effluent VSS averaged 36 mg/l, representing on the basis of average influent and effluent a 42% removal efficiency of VSS. Overall VSS removal efficiency, from raw sewage to secondary effluent, was 76%. The clarifiers sometimes performed erratically, with negative efficiencies of VSS removal occurring in the primary clarifier. Settled sludge bridging was also a problem, and would result in floating sludge in the primary and secondary clarifiers, plus interruption of sludge return from the secondary clarifier to the aeration basin. Mechanical rakes were eventually installed in the secondary clarifiers, and were at least partially effective in solving the operational problems of that unit process.

As indicated by the reduction in SOC across the primary clarifier, there appeared to be significant biological activity in that process. SOC was reduced from an average of 28 mg/l in the raw sewage, to 19 mg/l in the primary effluent. Thus, biological growth in the primary clarifier may have contributed to the erratic VSS removal efficiencies observed in

TABLE 36. OVERALL AVERAGES AND RANGES FOR DIFFERENT PARAMETERS IN DIFFERENT TEST LIQUIDS*

Parameter			Raw sewage	Primary Effluent	Mixed liquor	Secondary Effluent
VSS		Ave.	62	36	1307	15
		Range	2-460	1-196	150-8106	1-220
SOC		Ave.	28	19	14	11
		Range	3-294	1-106	1-200	1-38
Aluminum	Total	Ave.	652	478	7179	472
		Range	63-5100	24-3032	526-21000	67-2732
	Soluble	Ave.	81	79	61	83
		Range	11-425	8-375	0-325	5-350
	% Soluble	Ave.	12.4	16.5	0.8	17.6
Cadmium	Total	Ave.	85	72	411	44
		Range	3-650	2-514	4-810	2-382
	Soluble	Ave.	16	14	15	13
		Range	1-305	1-295	1-98	1-67
	% Soluble	Ave.	18.8	19.4	3.6	29.5
Chromium	Total	Ave.	241	170	1292	162
		Range	18-1700	5-650	10-3150	31-1600
	Soluble	Ave.	4.2	4.0	4.0	3.9
		Range	2-17	2-9	2-9	2-5
	% Soluble	Ave.	1.7	2.4	0.3	2.4
Copper	Total	Ave.	330	281	3215	210
		Range	11-2900	3-913	4-8500	11-1866
	Soluble	Ave.	17	12	14	14
		Range	1-157	1-100	1-96	1-50
	% Soluble	Ave.	5.2	4.3	0.4	6.9

*VSS and SOC expressed as mg/l, metals concentrations as µg/l.

(continued)

TABLE 36. (continued)

Parameter			Raw sewage	Primary Effluent	Mixed liquor	Secondary Effluent
Iron	Total	Ave.	1778	1247	28184	1089
		Range	200-7000	200-3500	1048-8400	100-5800
	Soluble	Ave.	118	97	70	52
		Range	5-783	5-842	3-885	3-580
	% Soluble	Ave.	6.6	7.8	0.2	4.7
Lead	Total	Ave.	142	100	1971	64
		Range	0-1069	0-600	11-9000	0-1200
	Soluble	Ave.	24	27	24	18
		Range	2-197	2-248	2-474	2-211
	% Soluble	Ave.	16.9	27.1	1.2	28.3
Nickel	Total	Ave.	1349	794	6602	733
		Range	22-8500	5-15000	77-23000	10-5000
	Soluble	Ave.	319	297	290	250
		Range	8-1168	9-1479	5-975	3-849
	% Soluble	Ave.	23.6	37.4	4.4	34.1
Zinc	Total	Ave.	741	637	11589	514
		Range	100-5000	80-3400	1000-36000	100-4100
	Soluble	Ave.	90	74	79	65
		Range	2-1000	1-430	2-900	1-900
	% Soluble	Ave.	12.1	11.6	0.7	12.6

*VSS and SOC expressed as mg/l,
metals concentrations as µg/l.

that unit. Overall SOC reduction across the treatment systems averaged 61%, yielding an average secondary effluent SOC value of 11 mg/l.

As would be expected, there was a strong correlation between VSS and TSS for all process liquids. The ratio VSS:TSS, and the squared correlation coefficients (r^2) are listed below:

Process liquid	VSS:TSS	r^2
Raw sewage	0.73	0.95
Primary effluent	0.68	0.89
Mixed liquor	0.68	0.92
Secondary effluent	0.65	0.96
Primary sludge	0.69	0.90
Secondary sludge	0.68	0.94

There was no correlation between VSS and SOC, in any process liquid. For raw sewage, this indicates that VSS and SOC varied in strength independently.

The patterns of metals transported across the treatment systems are extremely interesting. The range of raw sewage concentrations for each metal were quite broad, reflecting the combination of material fluctuations in the influent raw sewage, plus the spiking of the raw sewage with metals within the laboratory. For each metal, there was a reduction in the average total metal concentration across the primary clarifier. However, there was no significant reduction in the average soluble metal across that process. This indicates that the reduction in total metal is due to sedimentation of solids-bound metal. The lack of change in soluble metal concentration from raw sewage to primary effluent indicates that there was no redistribution of metals between the soluble and solid phases within the primary clarifier.

The total concentrations of metals in the mixed liquor are much higher than in the raw sewage, typically by 5- to 10-fold. For iron, lead, and zinc the concentration factor is closer to 15-fold. However, the soluble metal levels in the mixed liquor are equivalent to those in the raw sewage and primary effluent, revealing that the higher metal concentrations in the mixed liquor are the result of the higher mixed liquor VSS concentrations. The mixed liquor VSS are about 10-fold greater on the average then the raw sewage VSS. Comparing this to the data for metals suggests that iron, lead, and zinc are disproportionately overconcentrated

(compared to the concentration of VSS) in the mixed liquor, while cadmium, chromium, and nickel (at a 5-fold concentration from primary effluent to mixed liquor) are disproportionately underconcentrated. In other words, for these six metals the concentrations effect of VSS (with which the major fraction of each of the metals is associated) in the mixed liquor does not fully account for the concentration factor observed for those metals.

An evaluation of the composite of secondary clarifier effluent (secondary effluent) reveals that the soluble metals levels are essentially unchanged from the raw sewage soluble metals levels, except for iron and perhaps nickel and zinc. Thus, from the data base of Table 36, there is either no, or only slight change in the soluble levels of the test metals through the full-treatment system. Any removal of metals in the unit processes therefore results only from removal of influent solids-bound metals. The implication of this finding is that in combined treatment systems, metals removal efficiency is directly tied to the efficiency of removal of suspended solids. Table 37 summarizes the average metals removal efficiencies across the primary clarifier activated sludge aeration basin plus secondary clarifier, and overall treatment system.

Although the soluble metals levels in the secondary effluent were equivalent to those in the influent sewage, the relative contribution of the soluble metals to the total secondary effluent metals discharge varied. On the average, soluble chromium and iron constituted less than 5% of the total secondary effluent levels of these metals, while soluble cadmium, lead, and nickel contributed close to 30% of the total second effluent values of these latter metals. This indicates that enhanced VSS removal in the secondary clarifier would reduce total secondary effluent metals such as chromium and iron (which are predominantly solid-bound in the secondary effluent) to a much greater extent than for cadmium, lead, or copper.

Relationship Across the Primary Clarifier

Since the primary clarifier represents the first step in solids, and associated solids-bound metal removal, the performance of that process unit is discussed in this section. Figures 28 through 35 present relationships between the metals concentrations of raw sewage and primary effluent. These graphs clearly demonstrate that the metal concentration in the primary effluent is a function of the metal concentration in the influent to the primary sedimentation tank. Metal removal in the primary clarification stage is due to suspended

TABLE 37. AVERAGE PERFORMANCE OF TREATMENT SYSTEM IN METALS REMOVAL

Metal	% Removal Across P. Clarifier	% Removal Across A. Sludge	Overall % Removal
Aluminum	26.6	1.3	27.6
Cadmium	15.3	38.9	48.2
Chromium	29.5	4.7	32.8
Copper	14.8	25.3	36.4
Iron	29.9	12.7	38.8
Lead	29.6	36.0	54.9
Nickel	41.1	7.7	45.7
Zinc	14.0	19.3	30.6

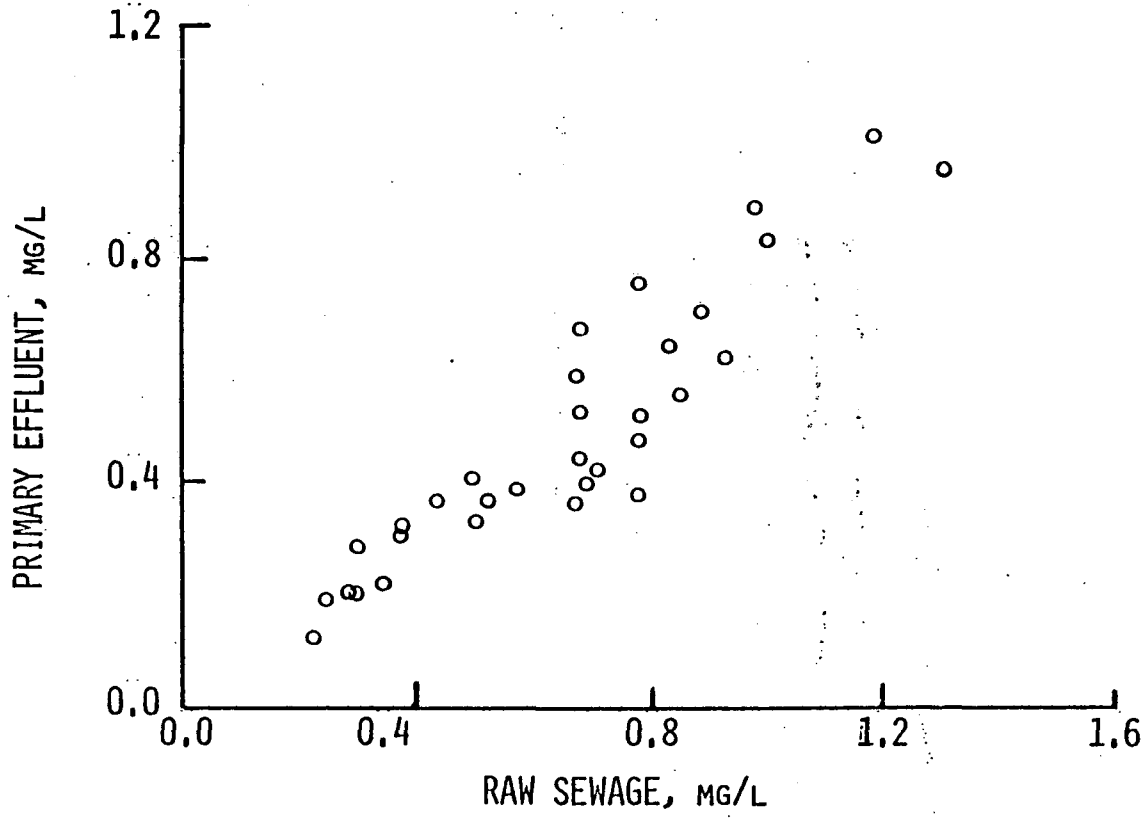


Figure 28. Relationship between total aluminum concentrations in raw sewage and primary effluent.

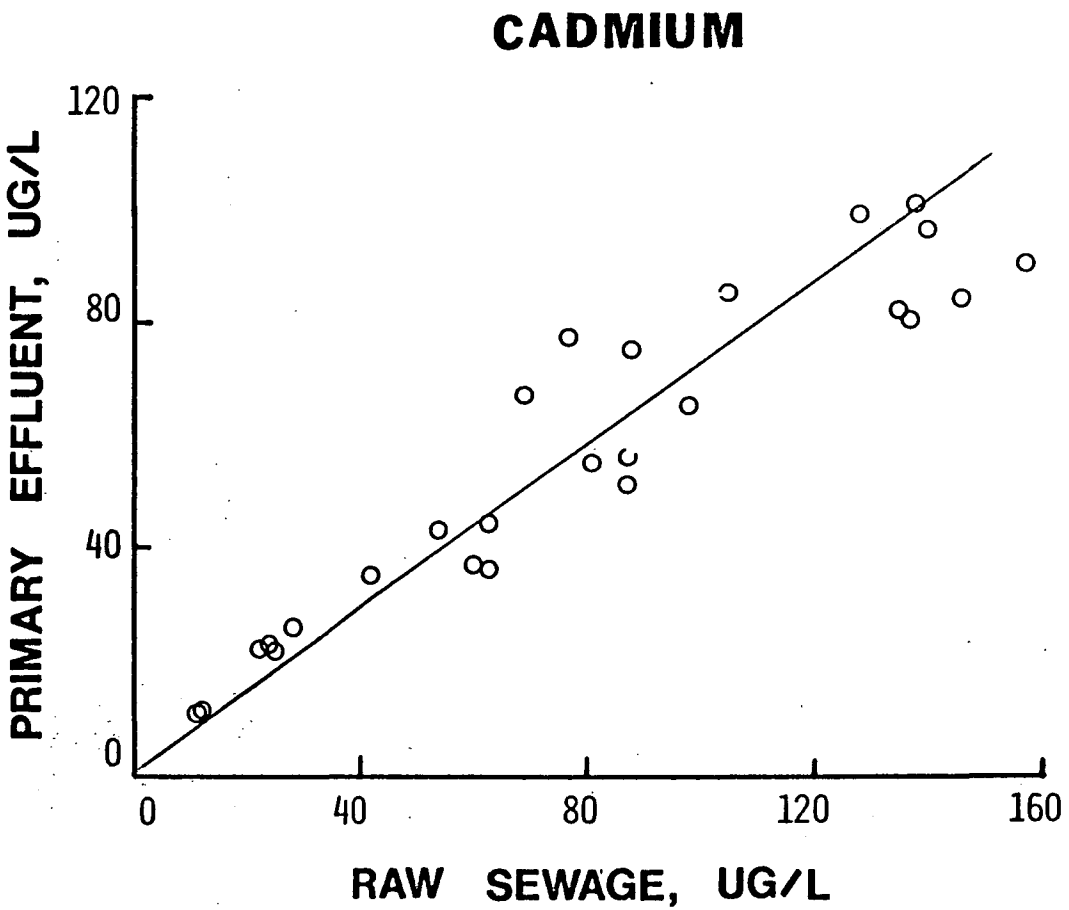


Figure 29. Relationship between total cadmium concentrations in raw sewage and primary effluent.

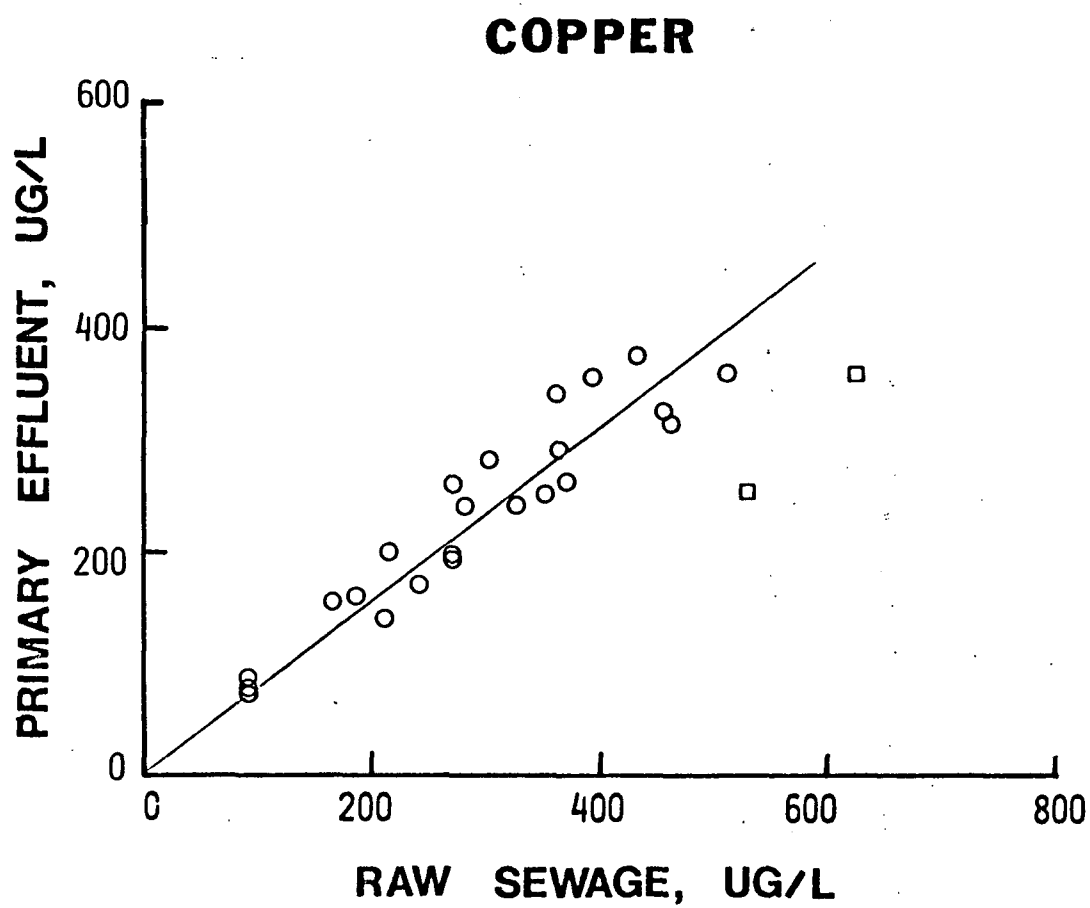


Figure 30. Relationship between total copper concentrations in raw sewage and primary effluent.

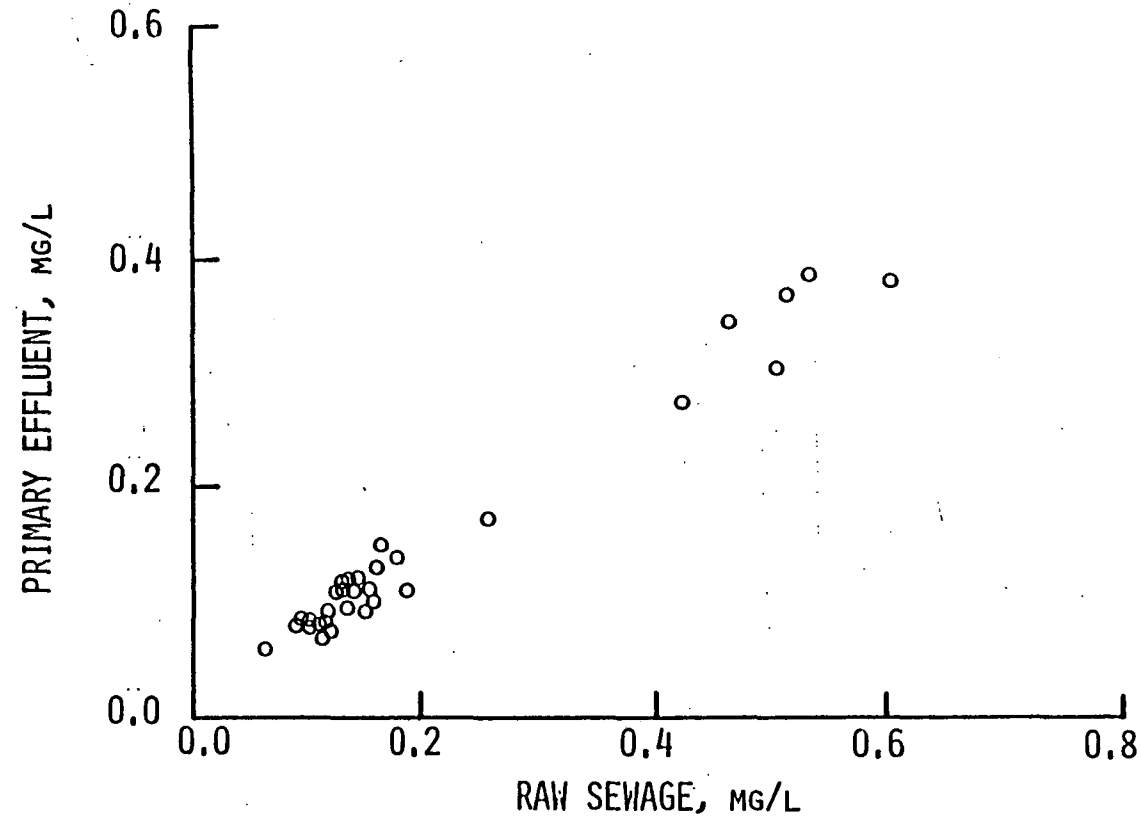


Figure 31. Relationship between total chromium concentrations in raw sewage and primary effluent.

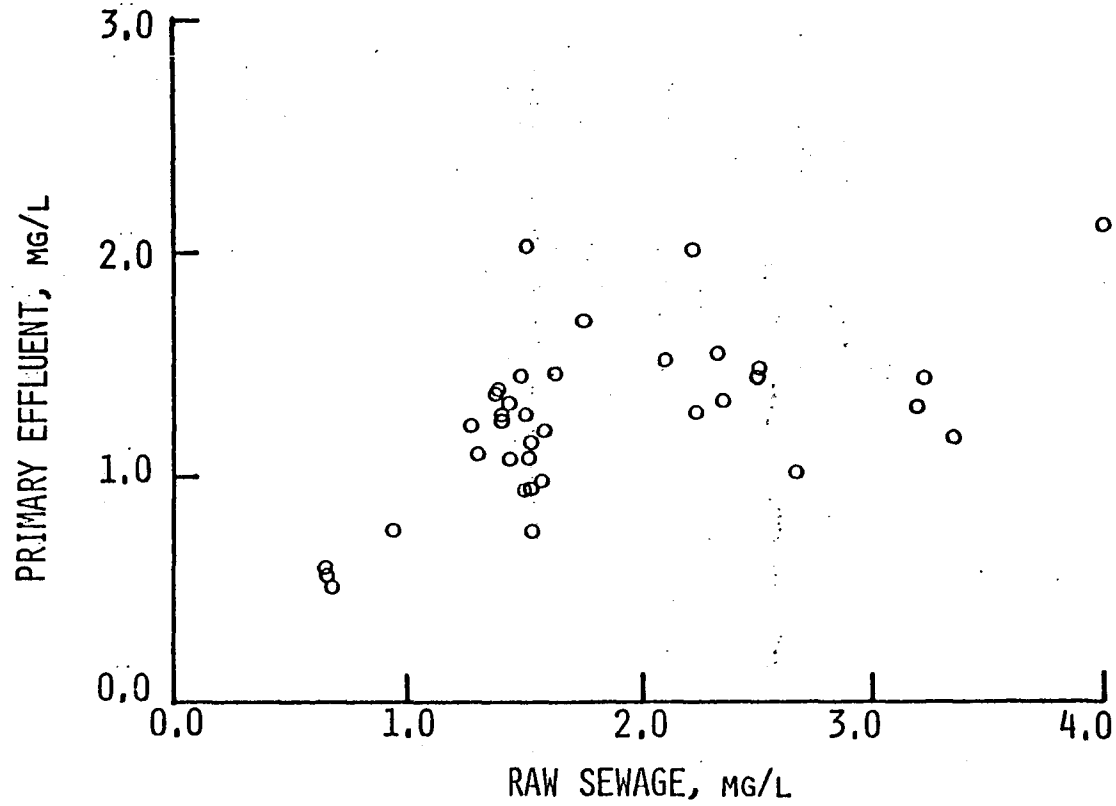


Figure 32. Relationship between total iron concentrations in raw sewage and primary effluent.

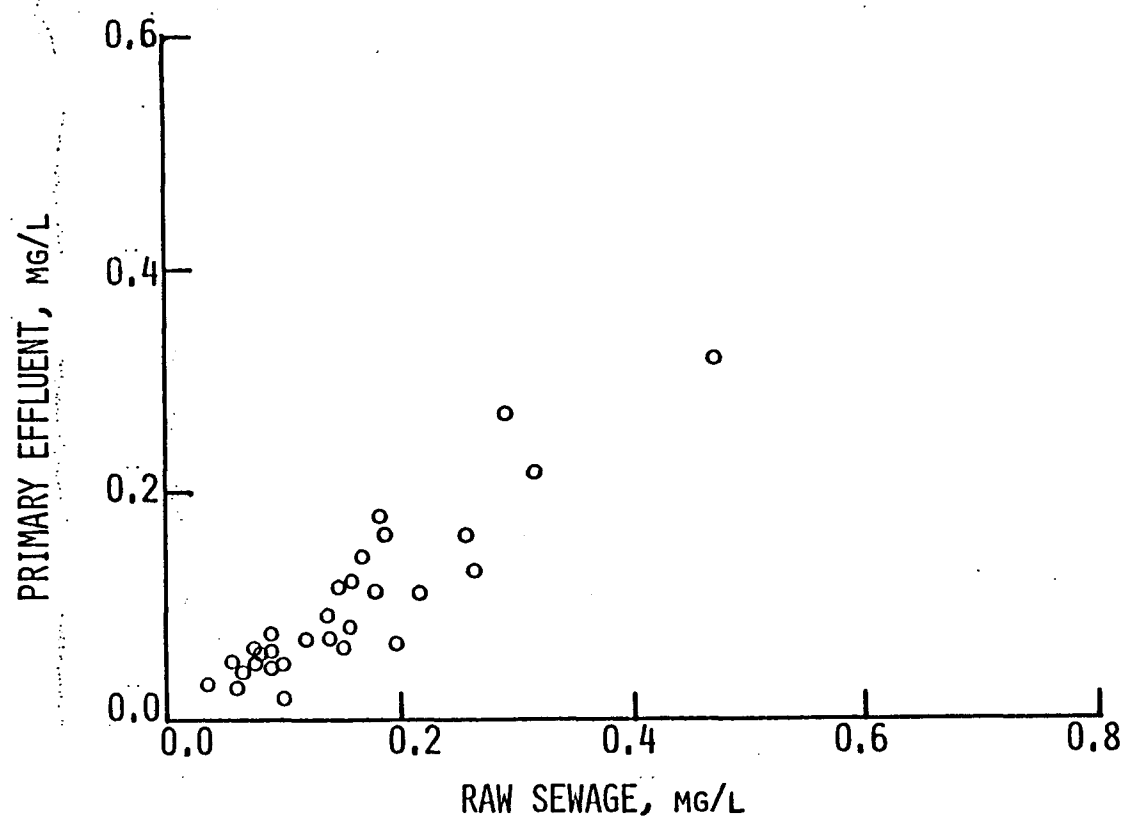


Figure 33. Relationship between total lead concentrations in raw sewage and primary effluent.

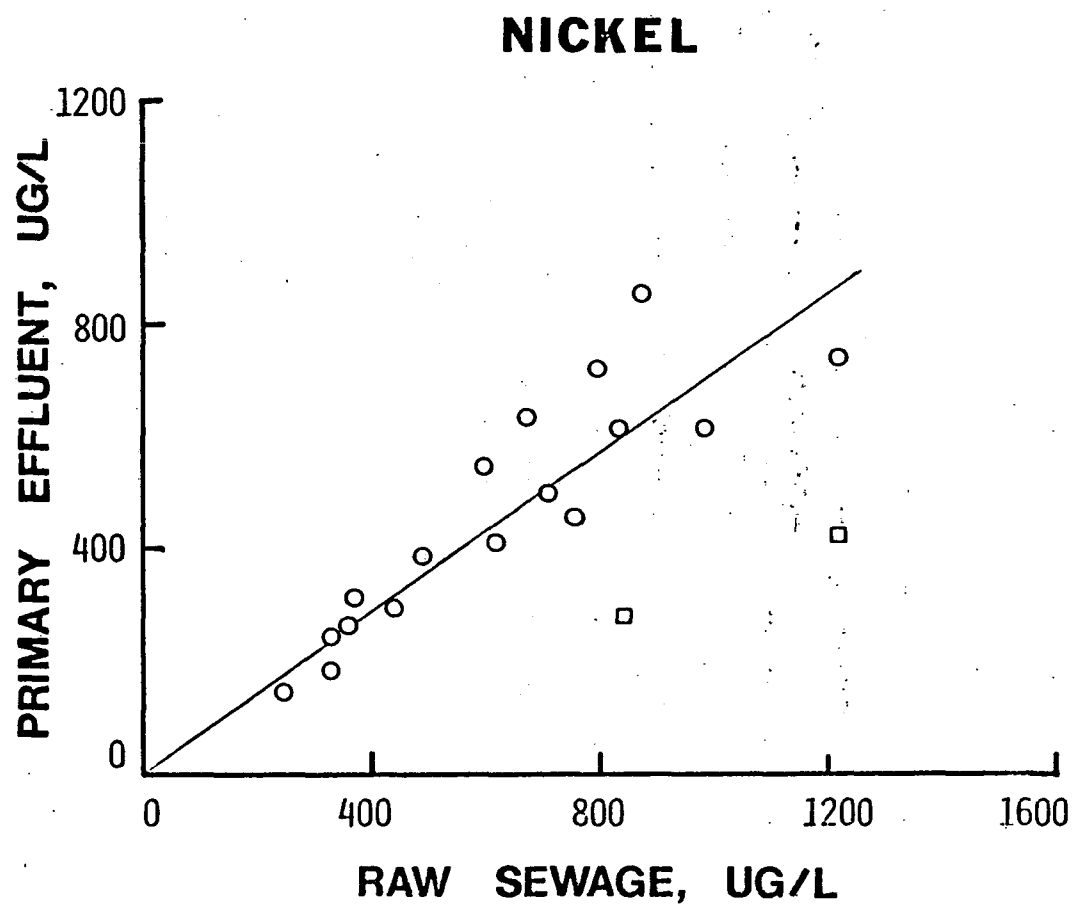


Figure 34. Relationship between total nickel concentrations in raw sewage and primary effluent.

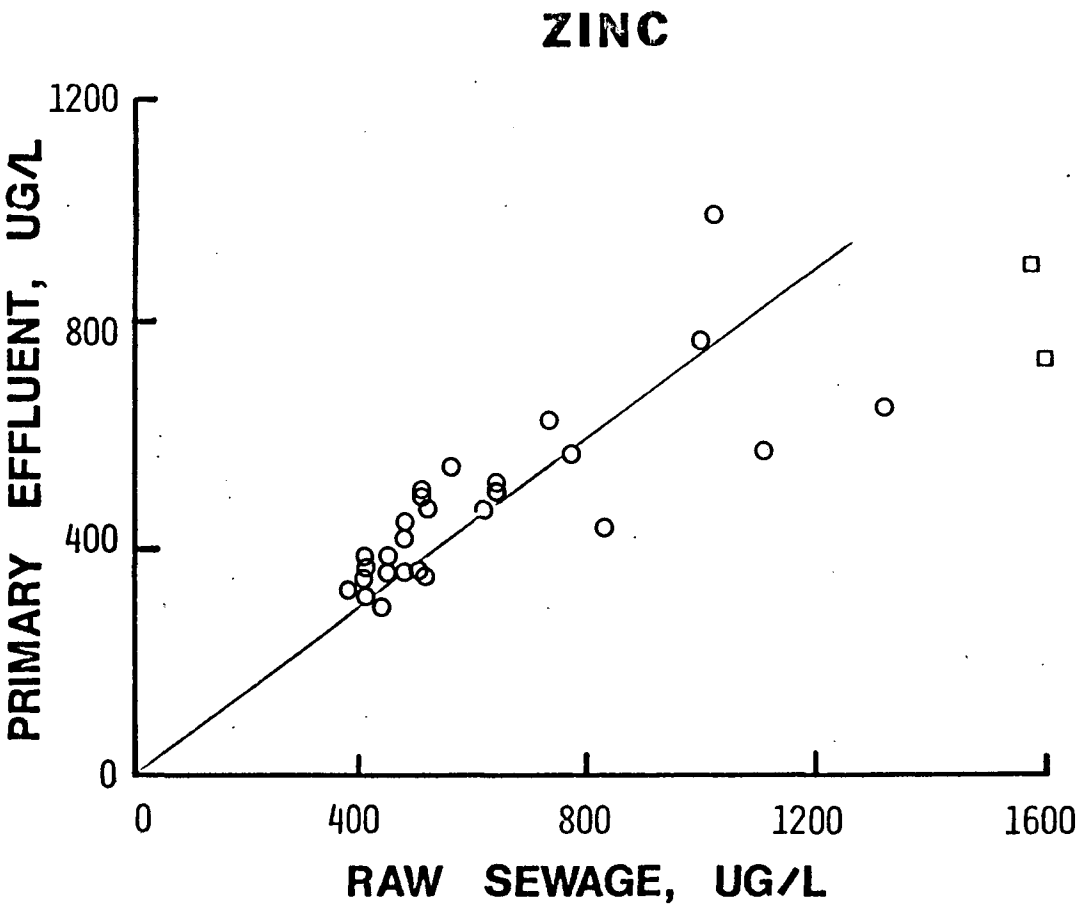


Figure 35. Relationship between total zinc concentrations in raw sewage and primary effluent.

solids removal, and the scatter of data in Figures 28 through 35 reflects variations in suspended solids removal performance by the primary clarifier.

Figures 36 through 39 present the relationship between the per cent removal of suspended solids and per cent removal of sludge-bound metal in the primary clarifier. These figures indicate a linear relationship between the solids removal and sludge-bound metal removal, and confirm that sedimentation of solids-bound metal is the major removal mechanism for metals during primary sedimentation. The lines on Figures 36 through 39 have about 1:1 slopes. If sludge bound metal is equally distributed per unit of VSS mass among particules over the full spectrum of settleability, the data points should be fit by that line. Although there is scatter in the data, for at least copper and zinc, the points fall below the line, suggesting that these two metals are disproportionately distributed onto the non-settleable fraction of the VSS. Similar results were observed for chromium and iron. The data for the remaining four metals generally followed the line of about 1:1 slope, although with some scatter, indicating uniform distribution of metal per unit of VSS among all solids particles irrespective of their settling characteristics.

An attempt was made to relate the metal concentrations in the primary effluent and mixed liquor, as shown for cadmium in Figure 40. The mixed liquor cadmium concentration seems to increase with increasing cadmium concentration in the primary effluent, but the data are too scattered to draw firm conclusions based upon this preliminary data analysis. One reason for this scatter could be variation in the amount of metals sent back to the aeration tank through the sludge recycle line. The slope of the line of Figure 40, which is equivalent to a concentration factor of mixed liquor to primary effluent cadmium, is about 6. This is equivalent to the mixed liquor to primary effluent concentration factor indicated for average performance in Table 36.

Figure 41 presents the relationship between the cadmium concentrations in mixed liquor and secondary effluent. This figure does not indicate a strong relationship between the metal concentrations of the two process liquids. Similar observations were also made in the case of other metals studied. This lack of correlation is probably principally due to variations in the efficiency of suspended solids (and associated solids-bound metals) removal in the secondary clarifier.

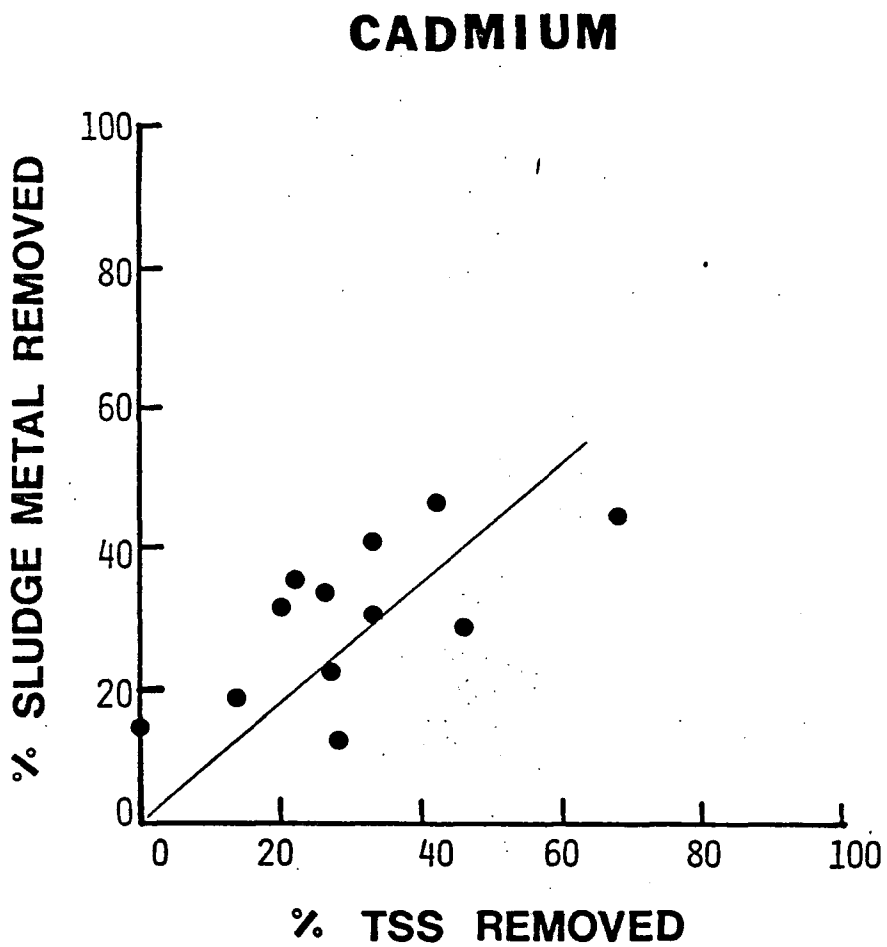


Figure 36. Relationship between the removals of TSS and sludge bound cadmium.

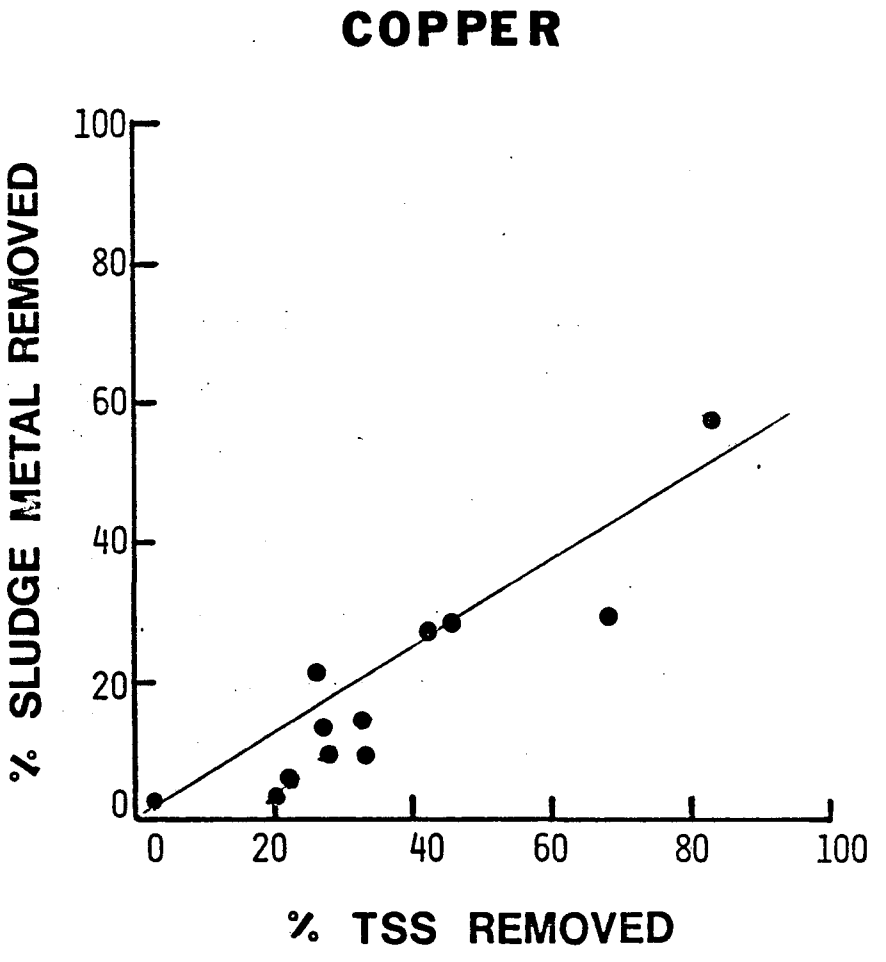


Figure 37. Relationship between the removals of TSS and sludge bound copper.

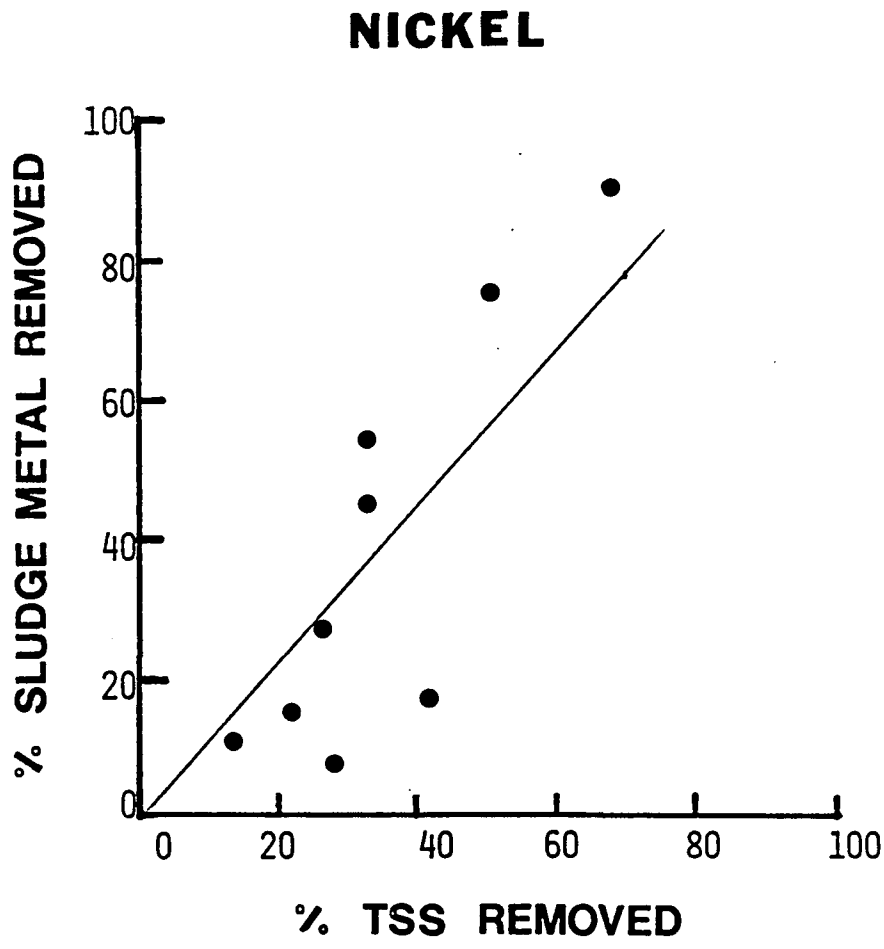


Figure 38. Relationship between the removals of TSS and sludge bound nickel.

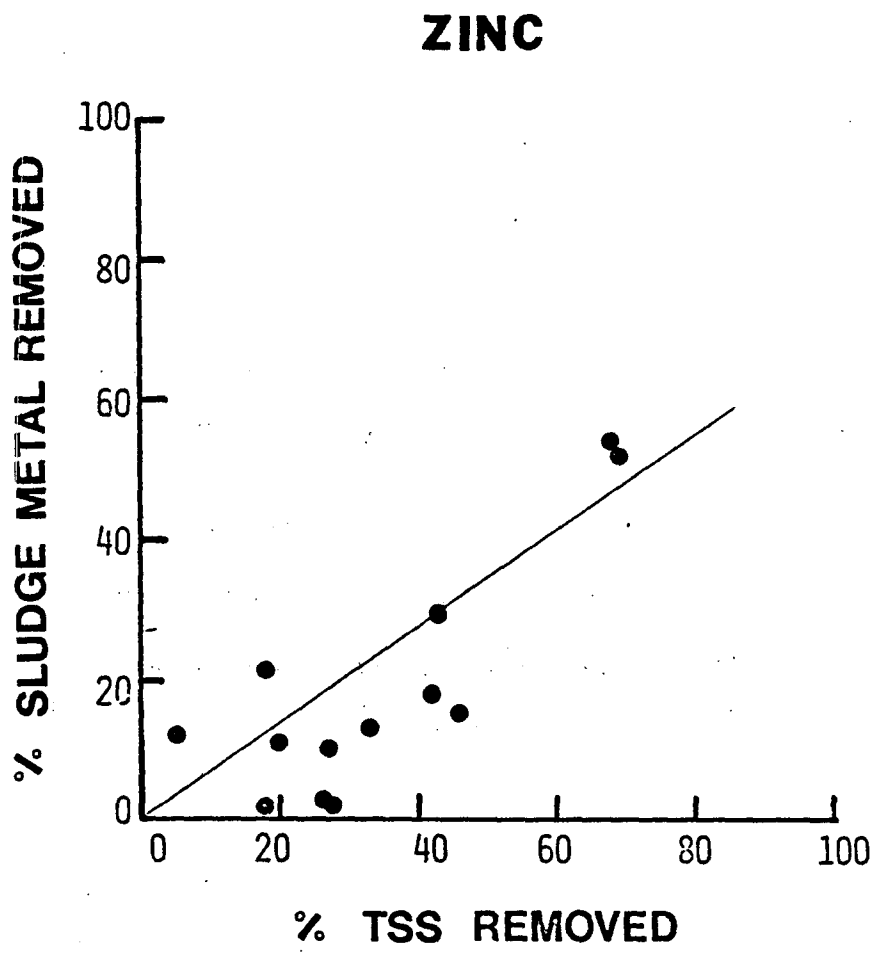


Figure 39. Relationship between the removals of TSS and sludge bound zinc.

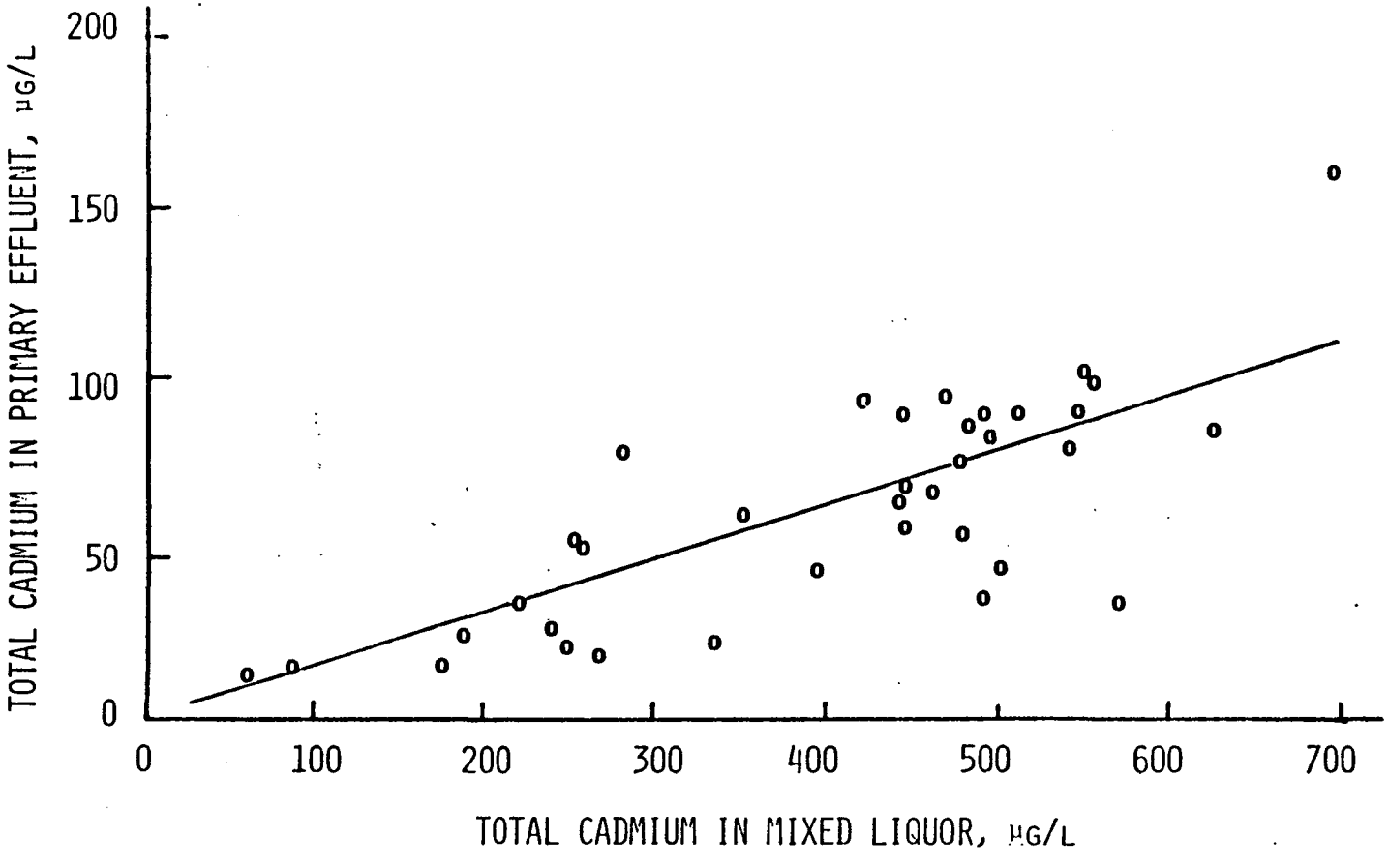


Figure 40. Relationship between total cadmium concentrations in primary effluent and mixed liquor.

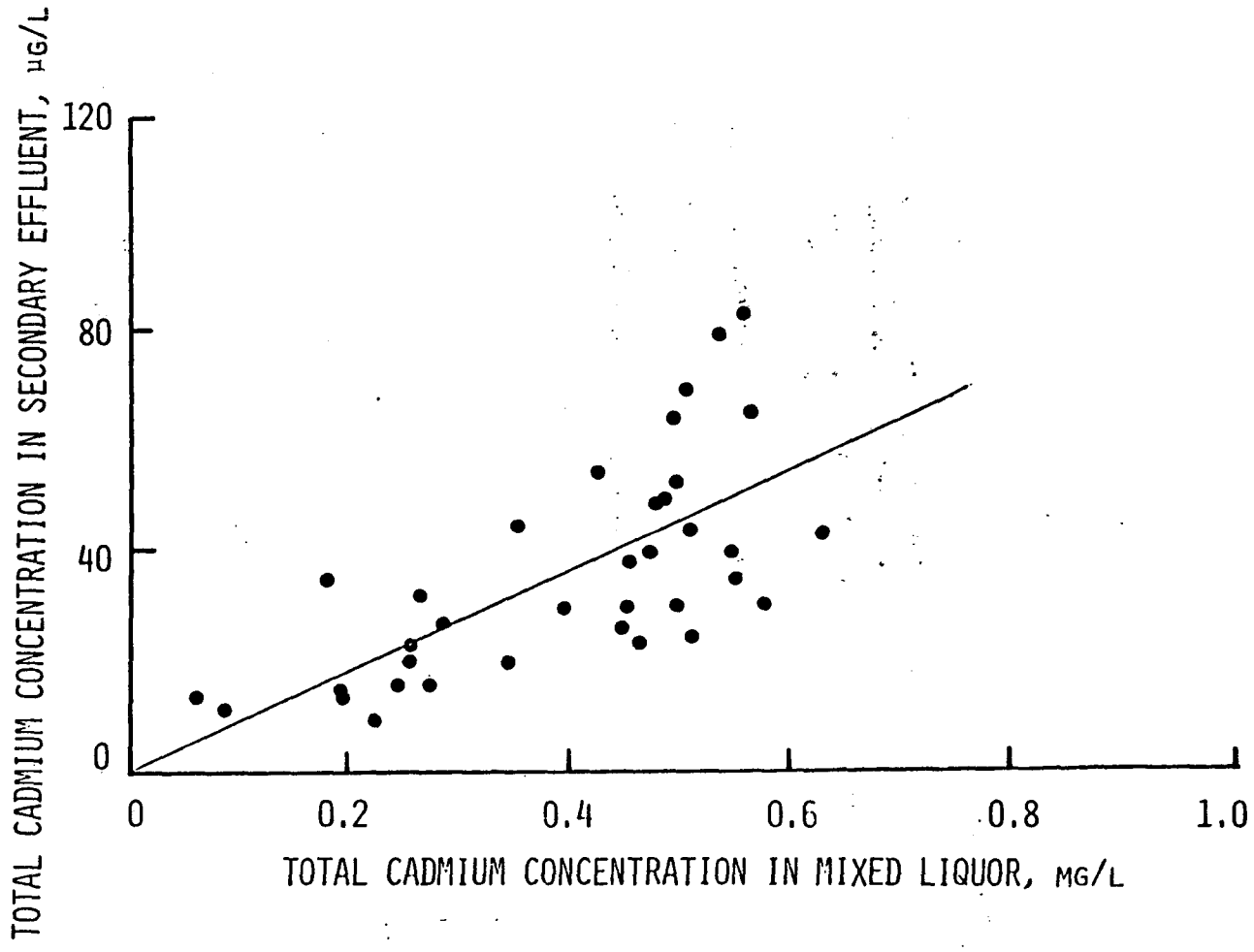


Figure 41. Relationship between the total cadmium concentrations in mixed liquor and secondary effluent.

Adsorption Characteristics of Process Liquids

In order to study the adsorption characteristics of sludge solids of different process liquids, different types of adsorption isotherms were attempted. Efforts to relate the soluble metal concentration to the concentration of metal on the sludge solids, using either Freundlich and Langmuir isotherm models, were futile.

Figures 42 through 45 present best fit adsorption isotherms for the four process liquids and the eight metals studied in this investigation. These isotherms relate the concentration of total metal present in the process liquid to the amount of metal associated with a unit weight of VSS in that process liquid. There seems to be a log-log relationship between the two variables, although there is quite a bit of scatter in the data points for most of the metals. The actual data points from which the lines in Figures 42 through 45 were developed are not presented, because of excessive overlapping of too many data points. However, the 'goodness of fit' of each line in the figures representing the adsorption behavior of the metals can be evaluated by examination of the regression analysis data presented in Tables 38 through 41. Figure 46 presents the adsorption isotherm for nickel in mixed liquor, which had the best regression coefficient of 0.98, while Figure 47 is the isotherm for aluminum in raw sewage which had the poorest regression coefficient of 0.36. These figures give an idea of the relative scatter of data, with respect to the regression coefficients.

Among the four process liquids studied, more significant log-log relationship (higher regression coefficient) between the sludge metal and total metal in the system was obtained in the case of mixed liquor than in other process liquids. This may directly result from the fact that in mixed liquor, the soluble metal fraction of the total metal is extremely low and typically below 1%. In the other process liquids, the soluble fraction is much greater, and therefore constitutes a higher portion of the total metal in raw sewage, primary effluent, and secondary effluent.

The adsorption isotherms presented in Figures 42 through 45 demonstrate that the amount of metal bound per unit of VSS generally increases with increasing total metal concentration, over the range studied. It may be that at very high metal concentrations, the sludge solids would reach a maximum adsorption capacity, where the isotherm would level off. However, precipitation of metals might occur before

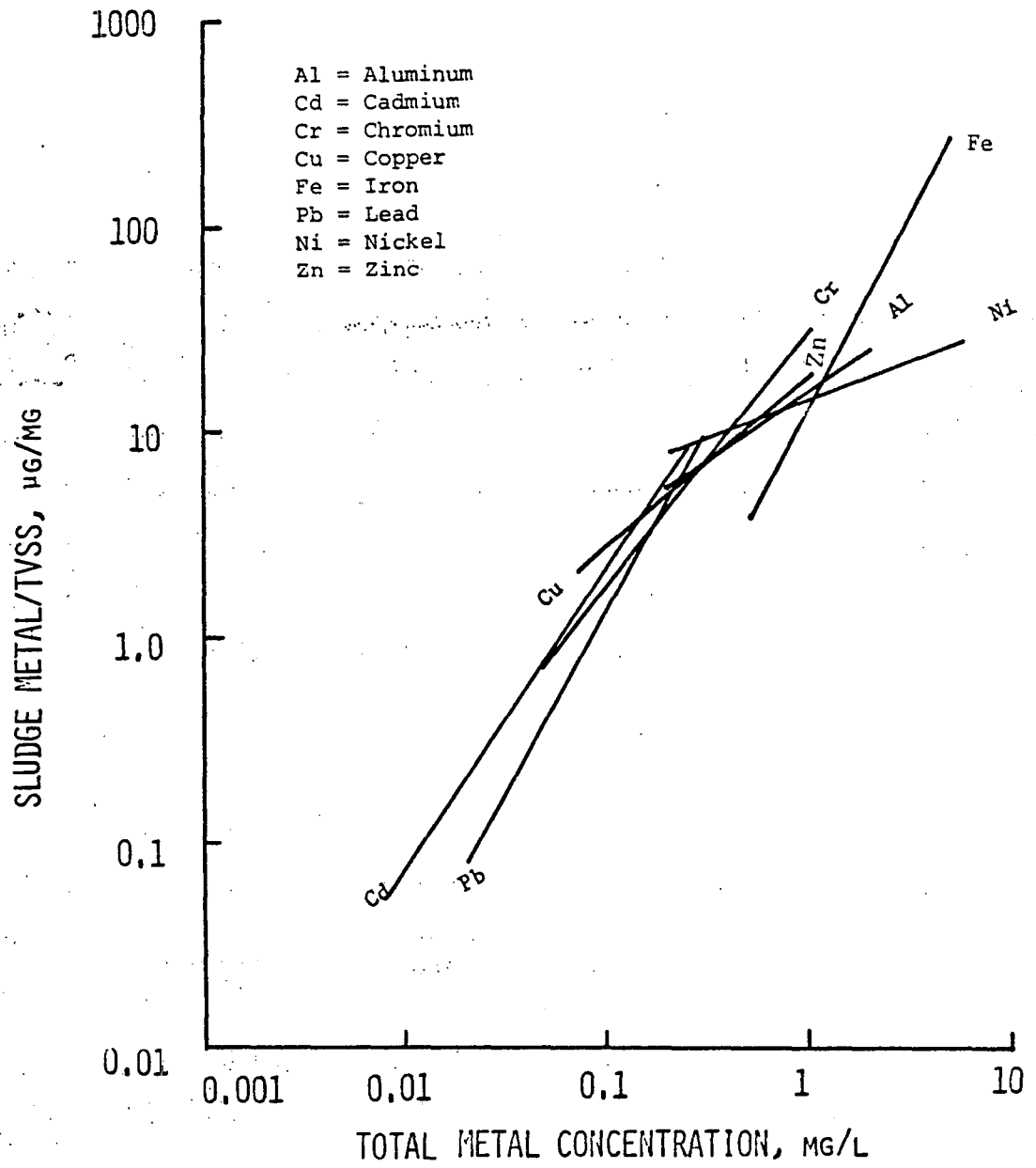


Figure 42. Metal adsorption isotherms for raw sewage.

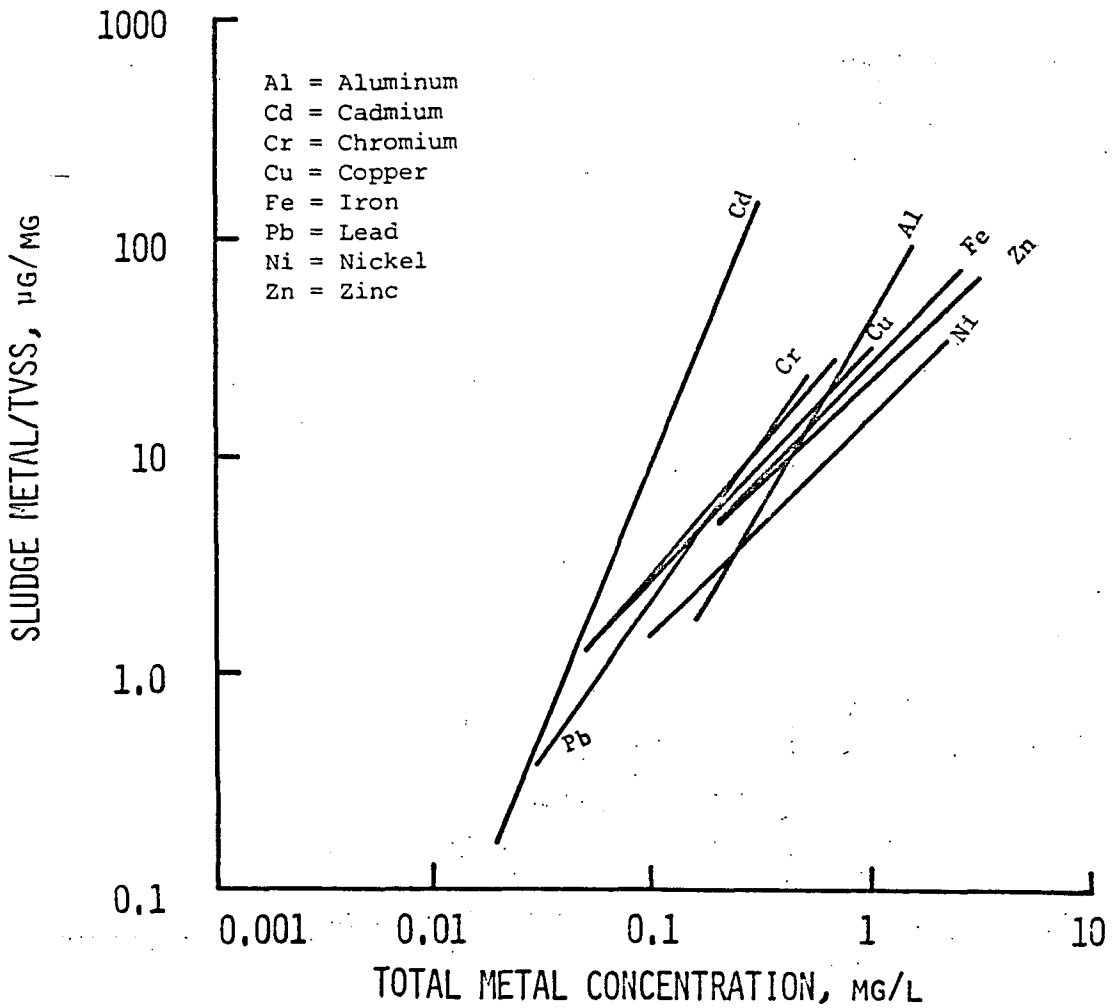


Figure 43. Metal adsorption isotherms for primary effluent.

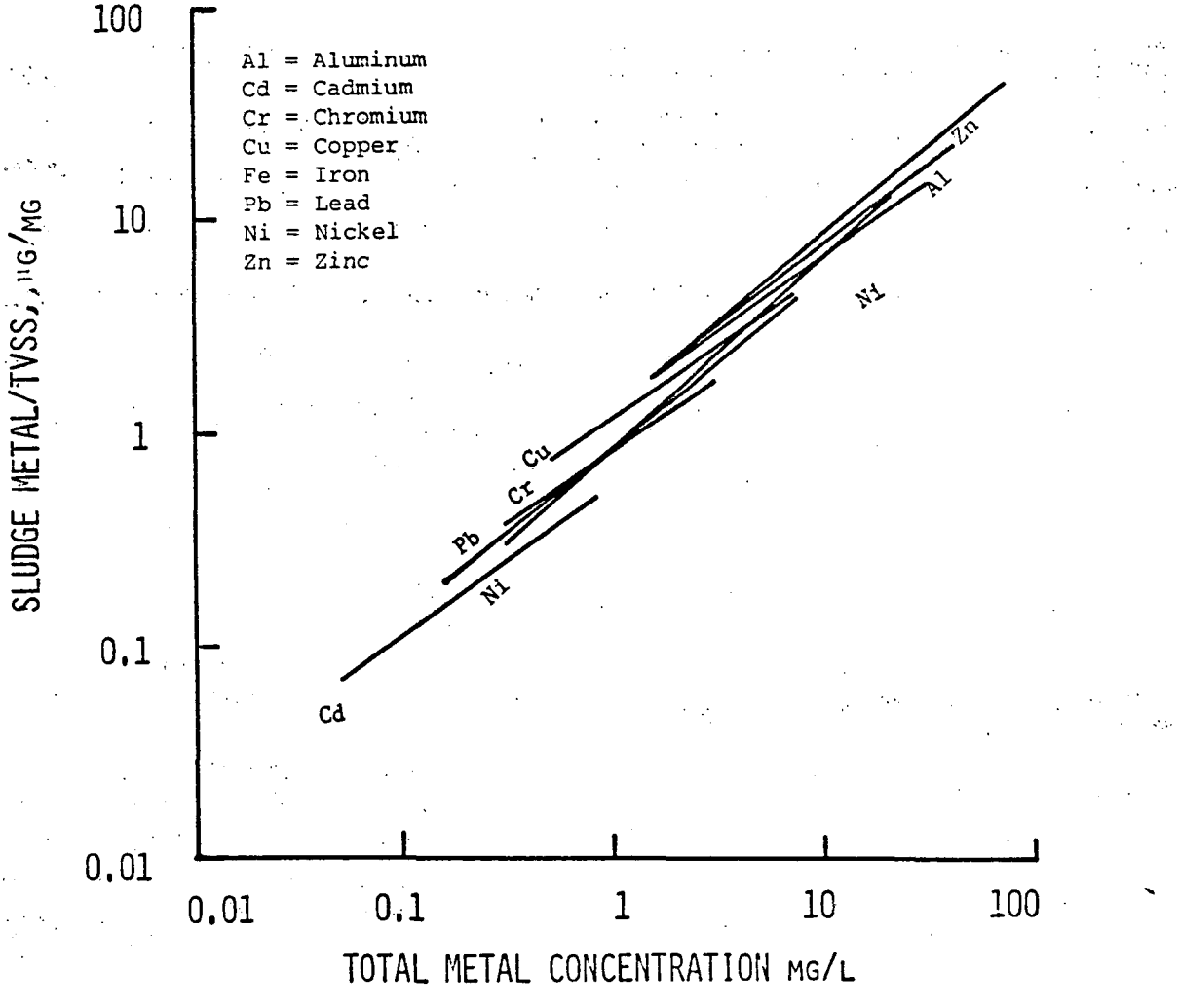


Figure 44. Metal adsorption isotherms for mixed liquor.

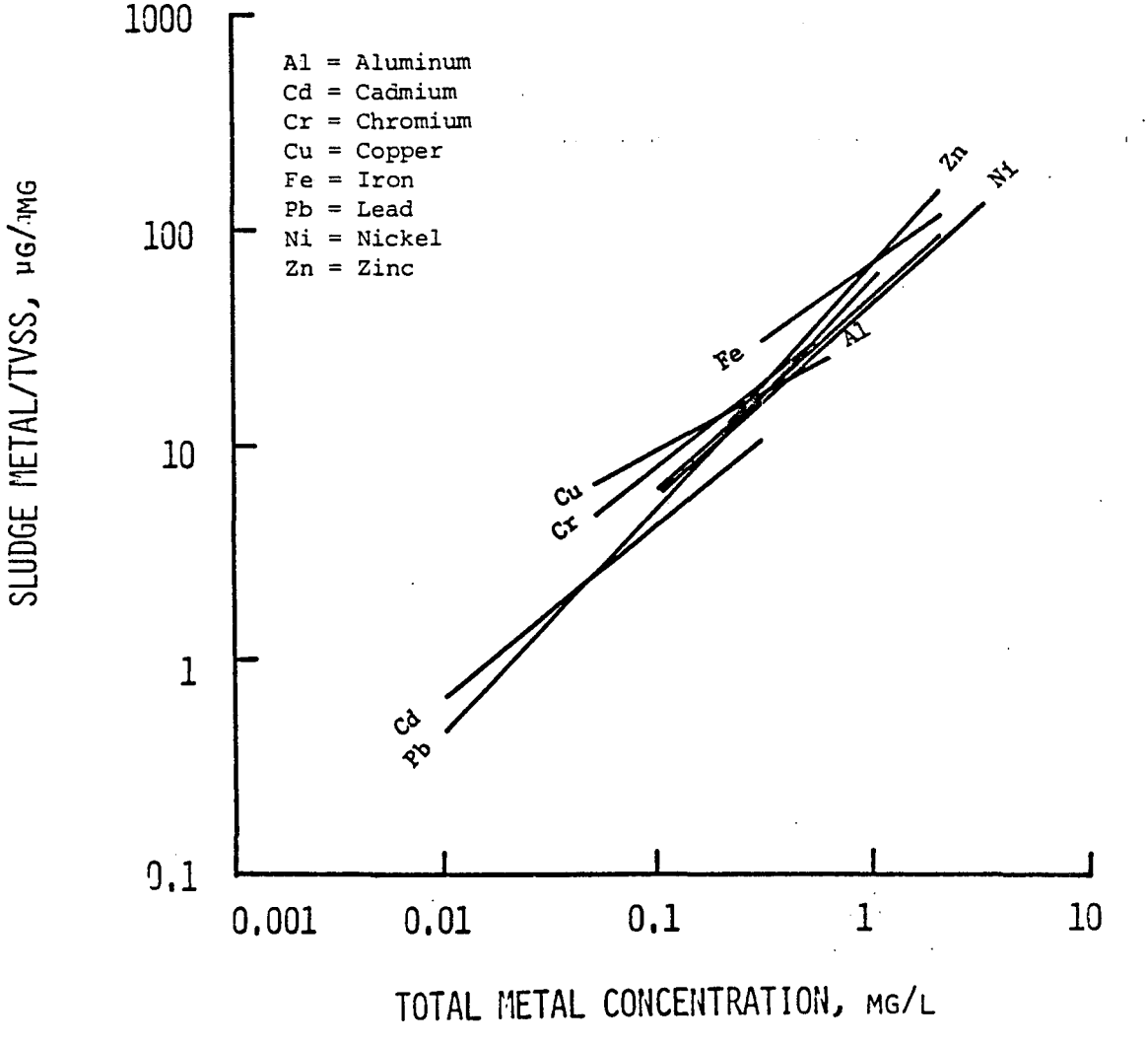


Figure 45. Metal adsorption isotherms for secondary effluent.

TABLE 38. REGRESSION ANALYSIS DATA FOR FIGURE 42 - RAW SEWAGE

Metal	Regression Equation	r^2
Aluminum	log Y = 0.68 (log X) - 0.83	0.36
Cadmium	log Y = 1.46 (log X) - 2.57	0.82
Chromium	log Y = 1.25 (log X) - 2.26	0.71
Copper	log Y = 0.83 (log X) - 1.23	0.47
Iron	log Y = 1.88 (log X) - 4.50	0.69
Lead	log Y = 1.78 (log X) - 3.42	0.75
Nickel	log Y = 0.37 (log X) + 0.05	0.36
Zinc	log Y = 0.55 (log X) - 1.89	0.50

TABLE 39. REGRESSION ANALYSIS DATA FOR FIGURE 43 - PRIMARY EFFLUENT

Metal	Regression Equation	r^2
Aluminum	log Y = 1.58 (log X) - 3.21	0.76
Cadmium	log Y = 1.60 (log X) - 2.70	0.92
Chromium	log Y = 1.18 (log X) - 1.91	0.83
Copper	log Y = 1.08 (log X) - 1.74	0.73
Iron	log Y = 1.05 (log X) - 1.72	0.55
Lead	log Y = 1.47 (log X) - 2.61	0.82
Nickel	log Y = 1.00 (log X) - 1.81	0.71
Zinc	log Y = 0.45 (log X) - 1.48	0.75

TABLE 40. REGRESSION ANALYSIS DATA FOR FIGURE 44 - MIXED LIQUOR

Metal	Regression Equation	r^2
Aluminum	log Y = 0.69 (log X) - 1.93	0.84
Cadmium	log Y = 0.71 (log X) - 2.36	0.81
Chromium	log Y = 0.68 (log X) - 2.11	0.71
Copper	log Y = 0.66 (log X) - 1.89	0.90
Iron	log Y = 0.82 (log X) - 2.35	0.91
Lead	log Y = 0.80 (log X) - 2.44	0.89
Nickel	log Y = 0.89 (log X) - 2.71	0.98
Zinc	log Y = 0.75 (log X) - 2.11	0.86

TABLE 41. REGRESSION ANALYSIS DATA FOR FIGURE 45 - SECONDARY EFFLUENT

Metal	Regression Equation	r^2
Aluminum	log Y = 0.89 (log X) - 0.97	0.69
Cadmium	log Y = 0.80 (log X) - 0.96	0.84
Chromium	log Y = 0.77 (log X) - 0.62	0.82
Copper	log Y = 0.53 (log X) - 0.08	0.71
Iron	log Y = 0.70 (log X) - 0.25	0.64
Lead	log Y = 1.05 (log X) - 1.37	0.88
Nickel	log Y = 0.87 (log X) - 0.94	0.83
Zinc	log Y = 1.08 (log X) - 1.43	0.86

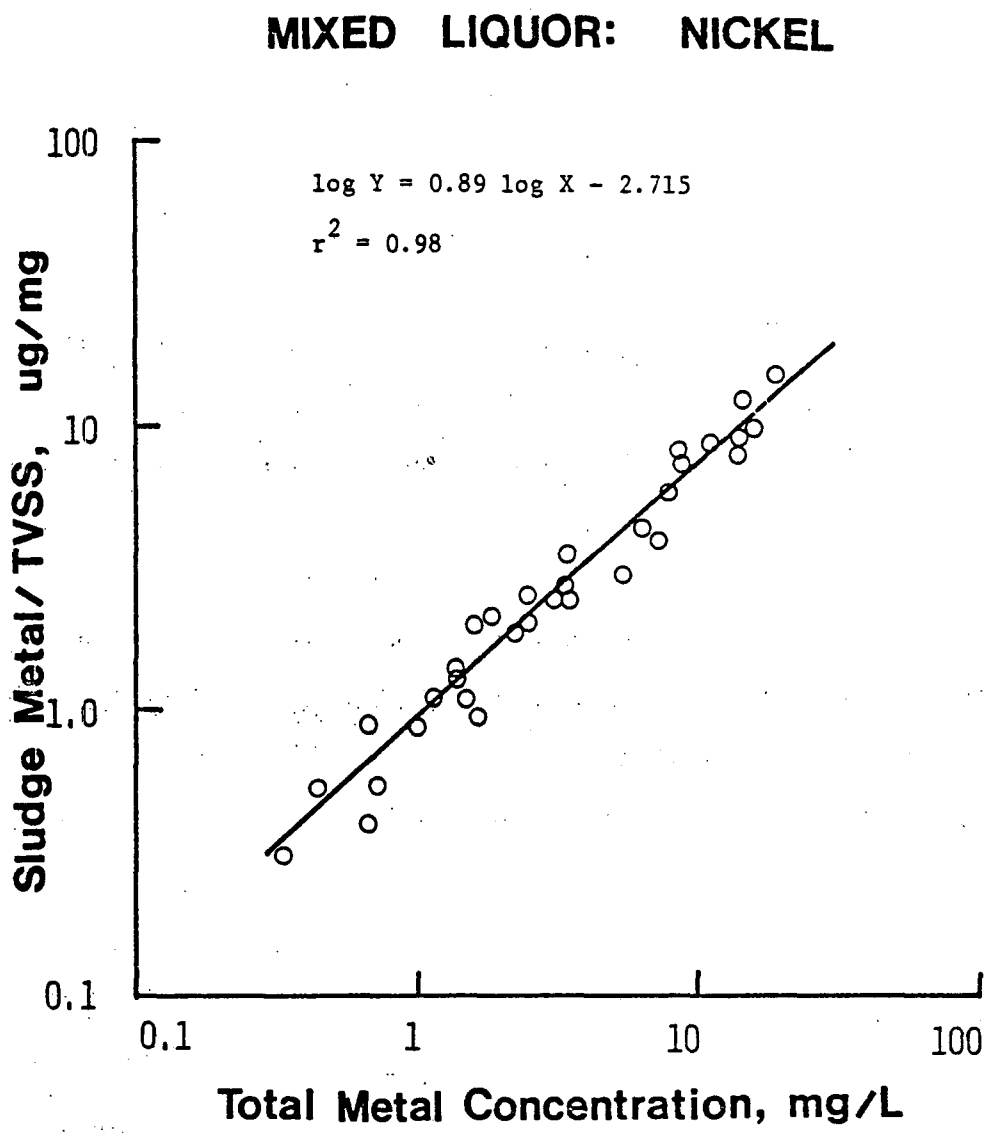


Figure 46. Adsorption isotherm for nickel in mixed liquor.

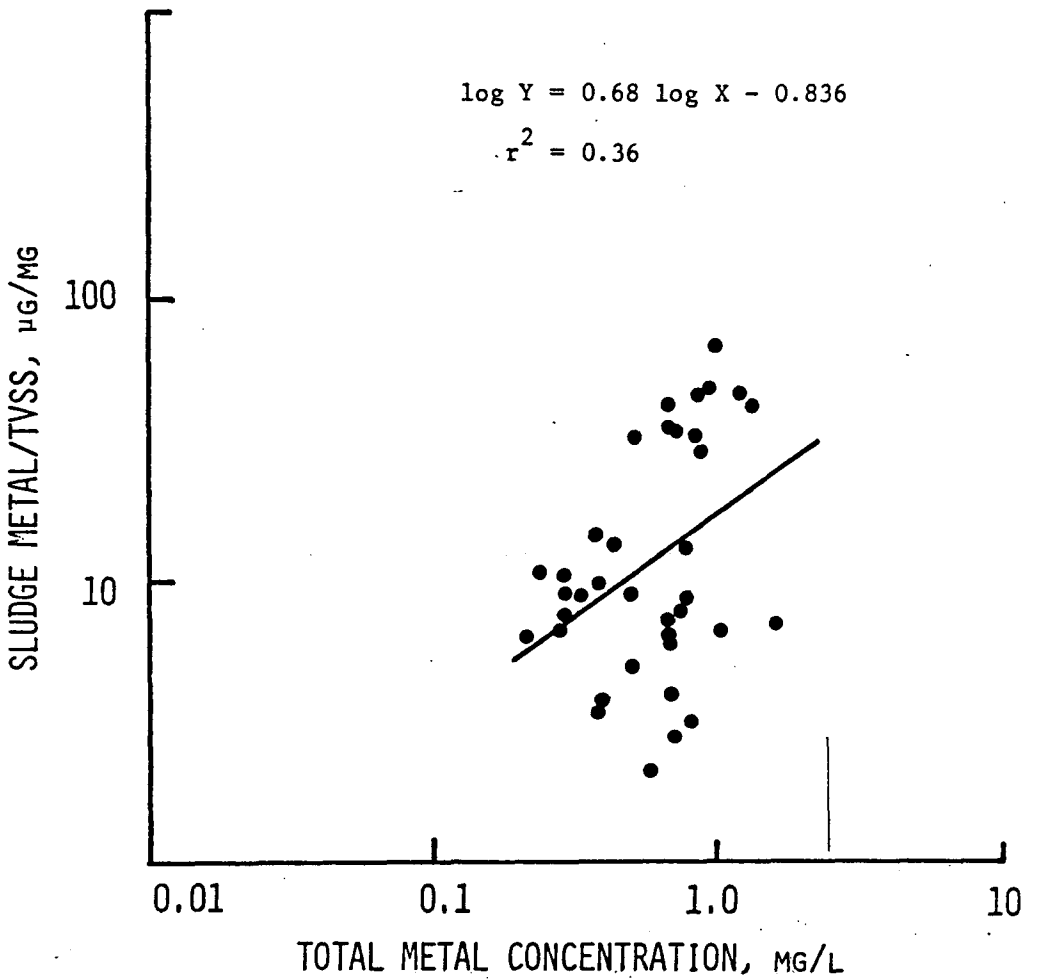


Figure 47. Adsorption isotherm for aluminum in raw sewage.

the maximum adsorption capacity of the sludge is reached. If precipitation of metals occurred, it would be difficult to develop valid adsorption isotherms of sludge solids due to the presence of another solid phase, the metal precipitate.

Figures 42 through 45 are indicative of general trends, but can not be used for predictive purposes such as estimating the amount of metal present in the solid phase for a given total metal and VSS concentrations. This is due to the degree of scatter of the data points around the isotherm lines for most of the metals. This scatter results in the generally poor correlation coefficients seen in Tables 38 through 41.

The reason for this poor fit is that the isotherms presented in Figures 42 through 45 can not account for differences in VSS concentrations. This problem is, however, overcome by plotting isotherms for total metal concentration vs. sludge metal/VSS, for constant VSS concentrations, as shown in Figure 48. This figure presents adsorption isotherms for cadmium in raw sewage at VSS concentrations of 25, 50, and 100 mg/l. Since the experiments were not originally designed to keep the VSS concentrations constant at given levels, the VSS concentration is noted next to each data point on Figure 48, and isotherms for the three VSS levels were interpolated.

Figures 48 through 51 are the adsorption isotherms for cadmium in raw sewage, primary effluent, mixed liquor, and secondary effluent, respectively. Similar isotherms are presented in Figures 52 through 75 for the other seven metals investigated. The figures for all metals in all process liquids follow similar patterns, and illustrate the following:

1) As the total metal concentration increases, the amount of sludge bound metal per unit weight of VSS also increases, at each constant level of VSS.

2) At any given total metal concentration, the sludge-bound metal per unit weight of VSS decreases as the VSS concentration increases.

3) At low total metal concentrations, the effect of VSS on sludge-bound metal is slight.

These relationships hold for all eight metals, and for all four process liquids.

The relationships represented in Figures 48 through 75 can be described mathematically, and therefore can provide a

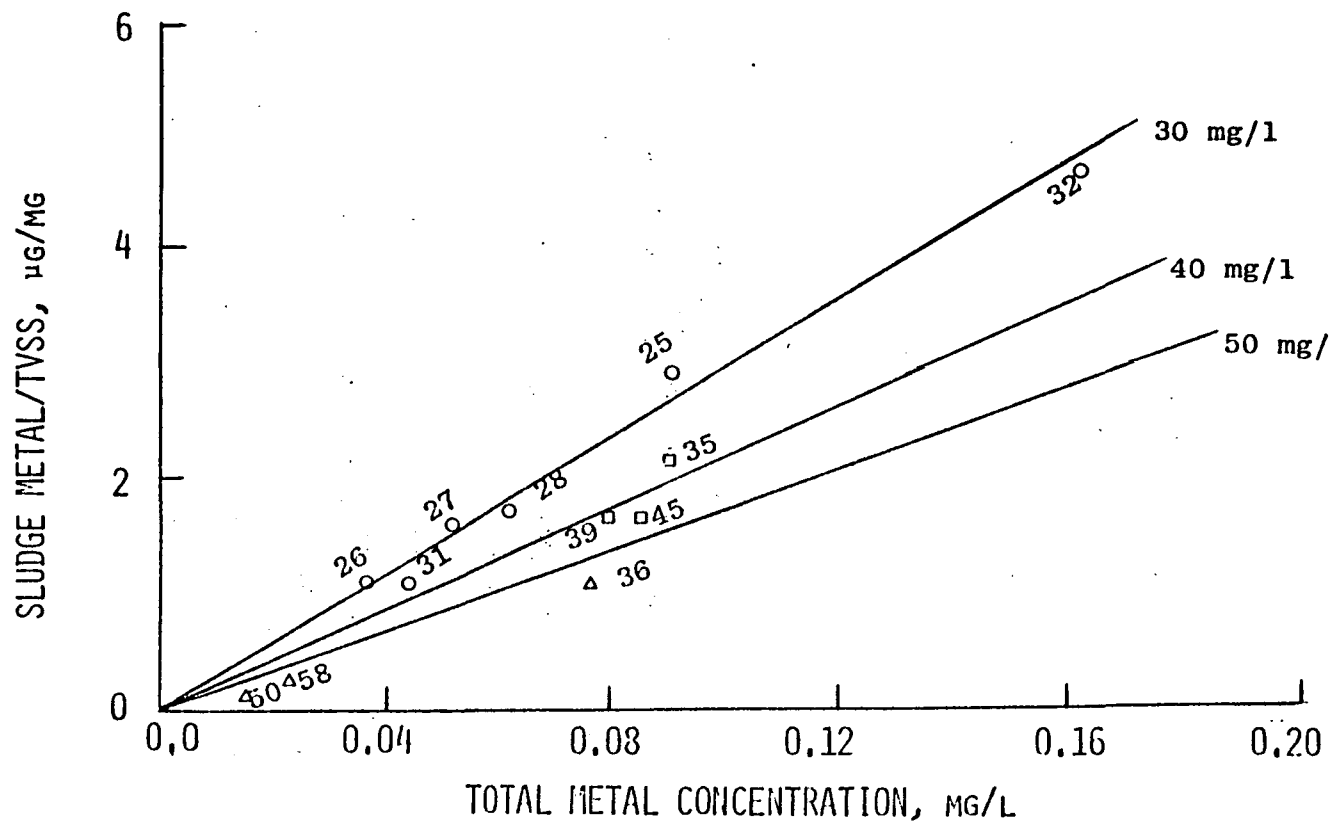


Figure 48. Adsorption isotherms of cadmium in raw sewage at different VSS concentrations.

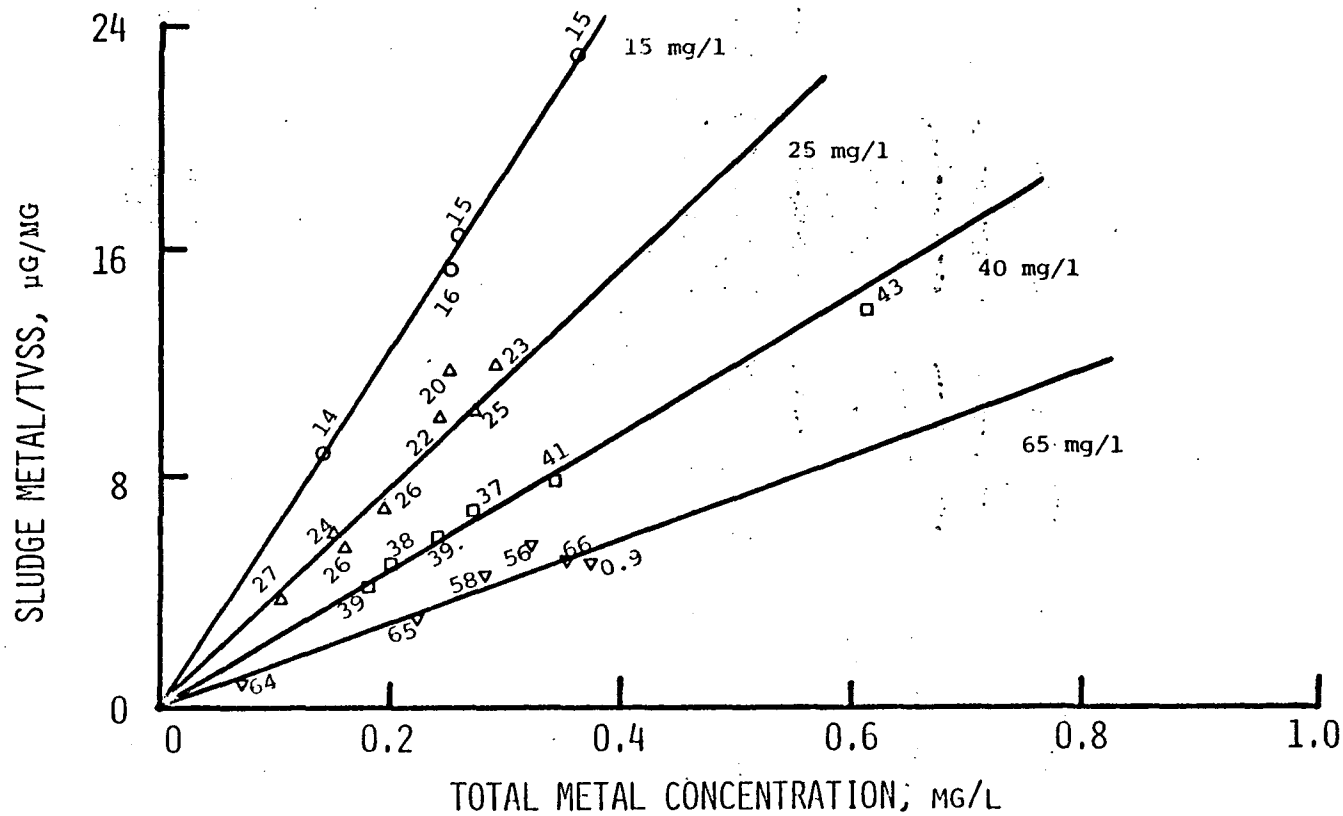


Figure 49. Adsorption isotherms of cadmium in primary effluent at different TVSS concentrations.

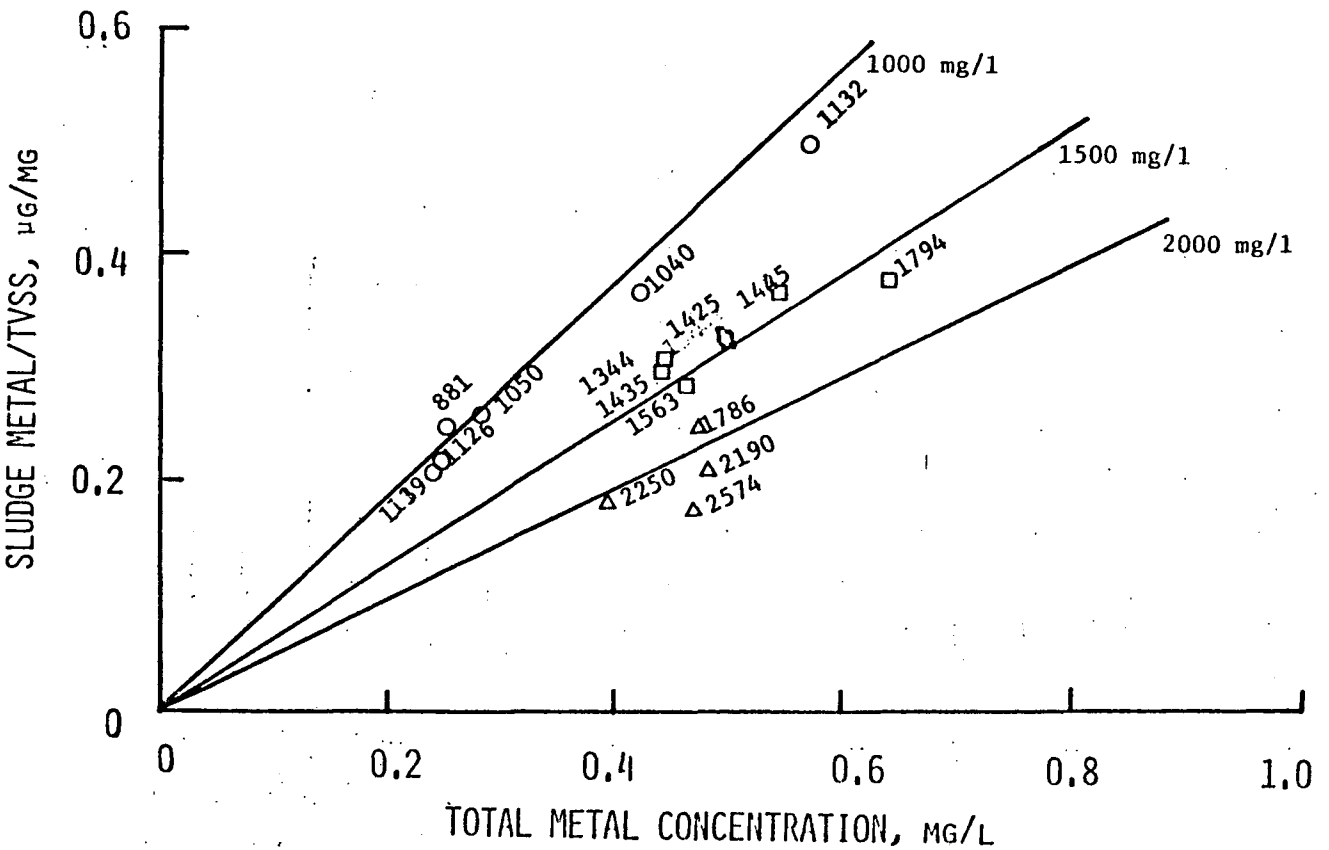


Figure 50. Adsorption isotherms of cadmium in mixed liquor at different TVSS concentrations.

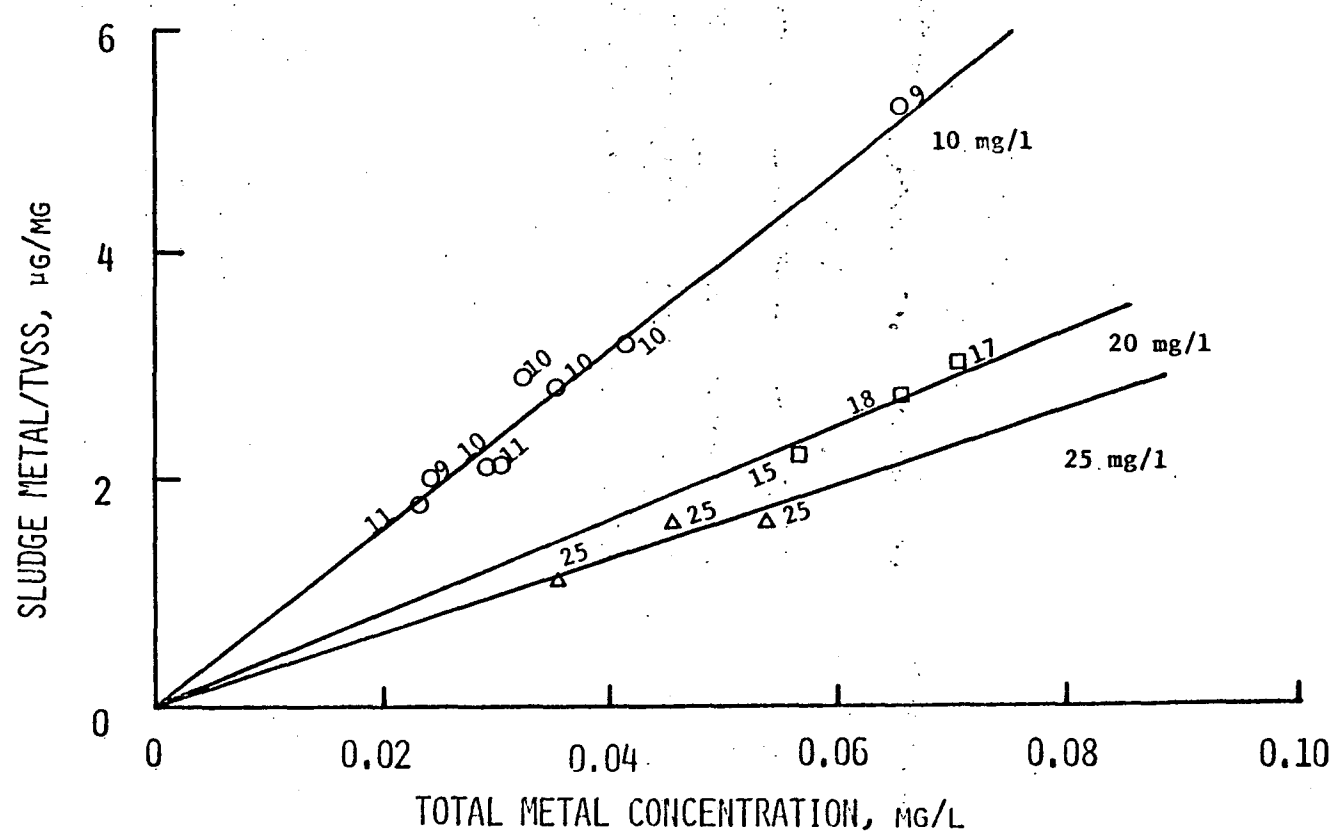


Figure 51. Adsorption isotherms of cadmium in secondary effluent at different TVSS concentrations.

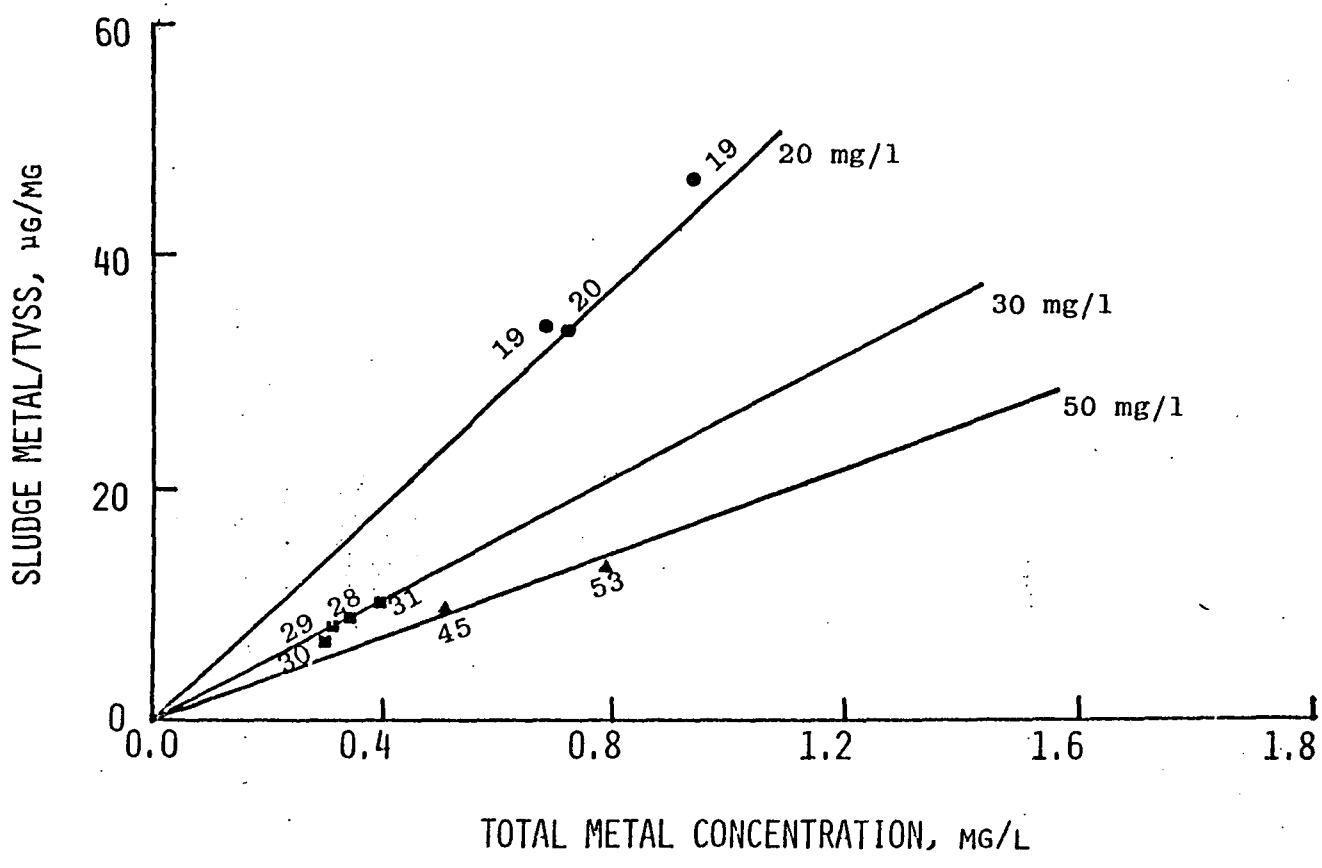


Figure 52. Adsorption isotherms for aluminum in raw sewage at different VSS concentrations.

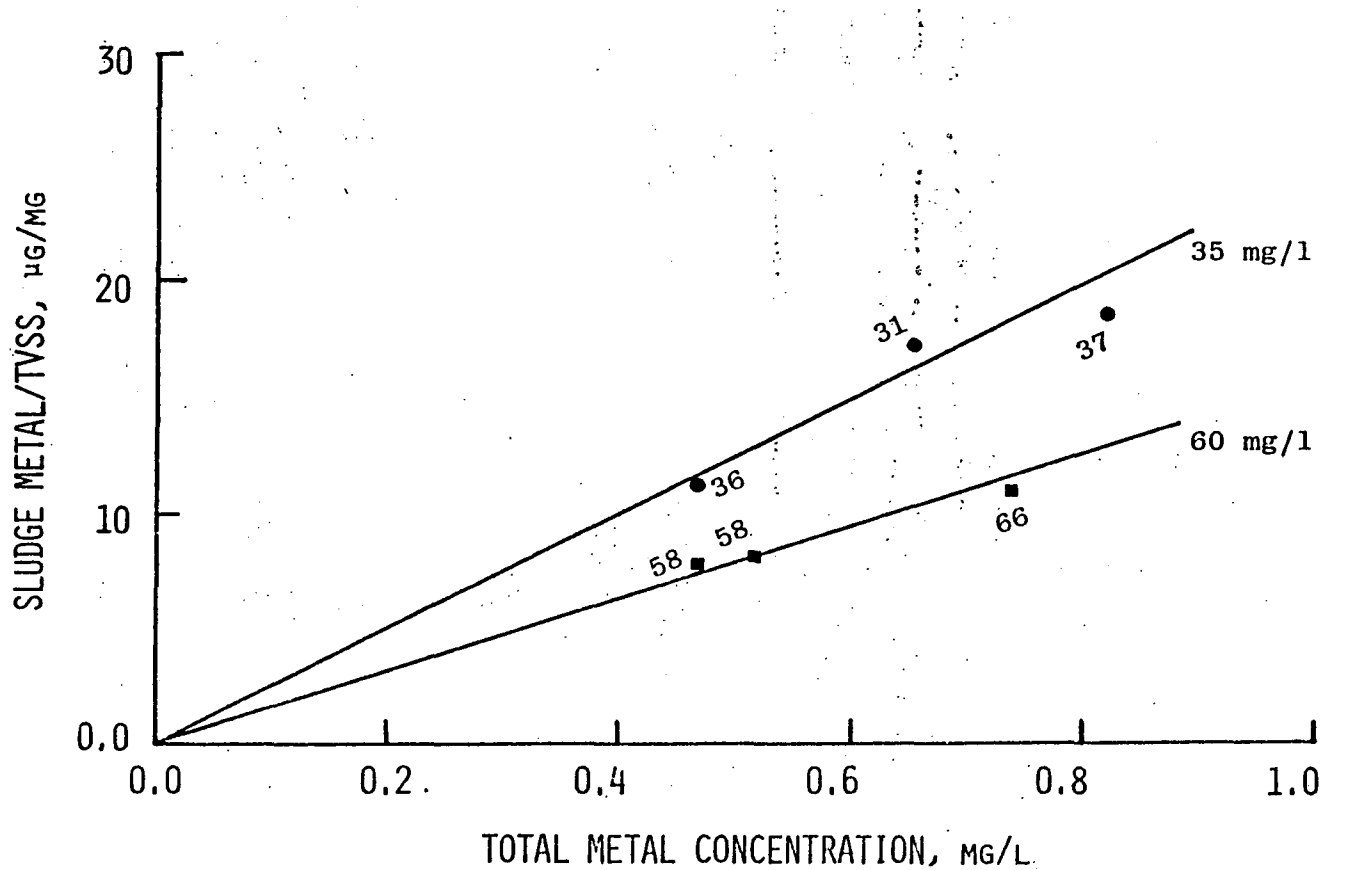


Figure 53. Adsorption isotherms for aluminum in primary effluent at different VSS concentrations.

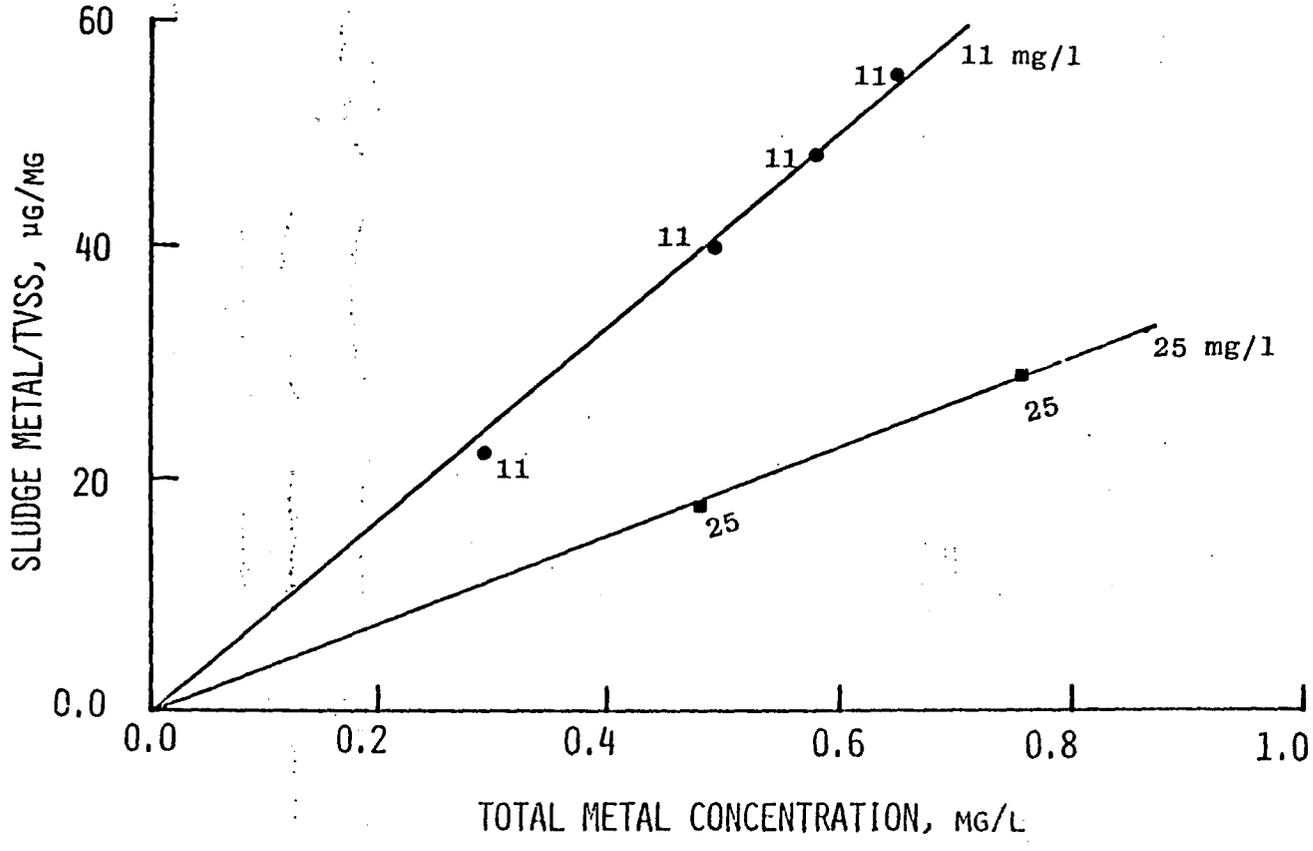


Figure 54. Adsorption isotherms of aluminum in secondary effluent at different VSS concentrations.

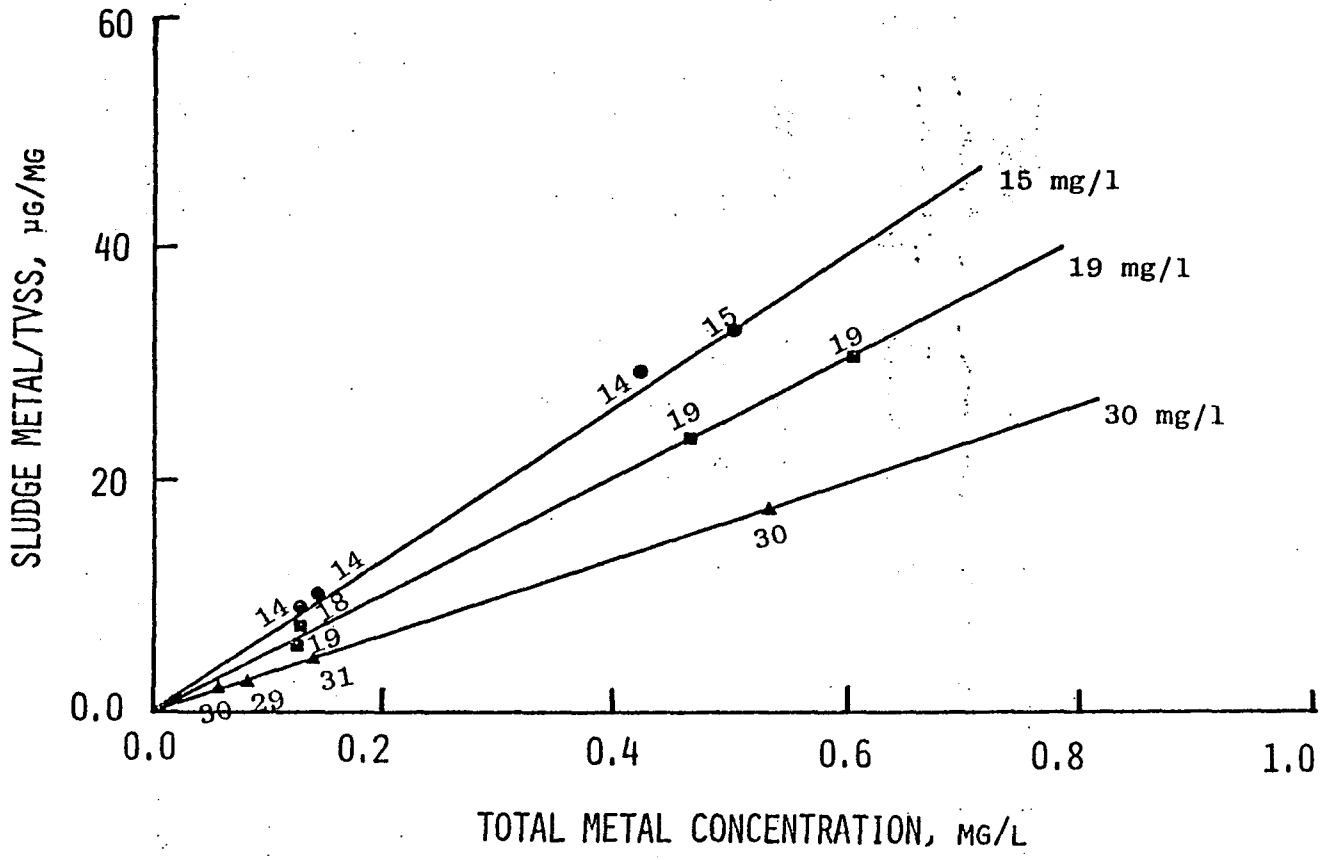


Figure 55. Adsorption isotherms for chromium in raw sewage at different VSS concentrations.

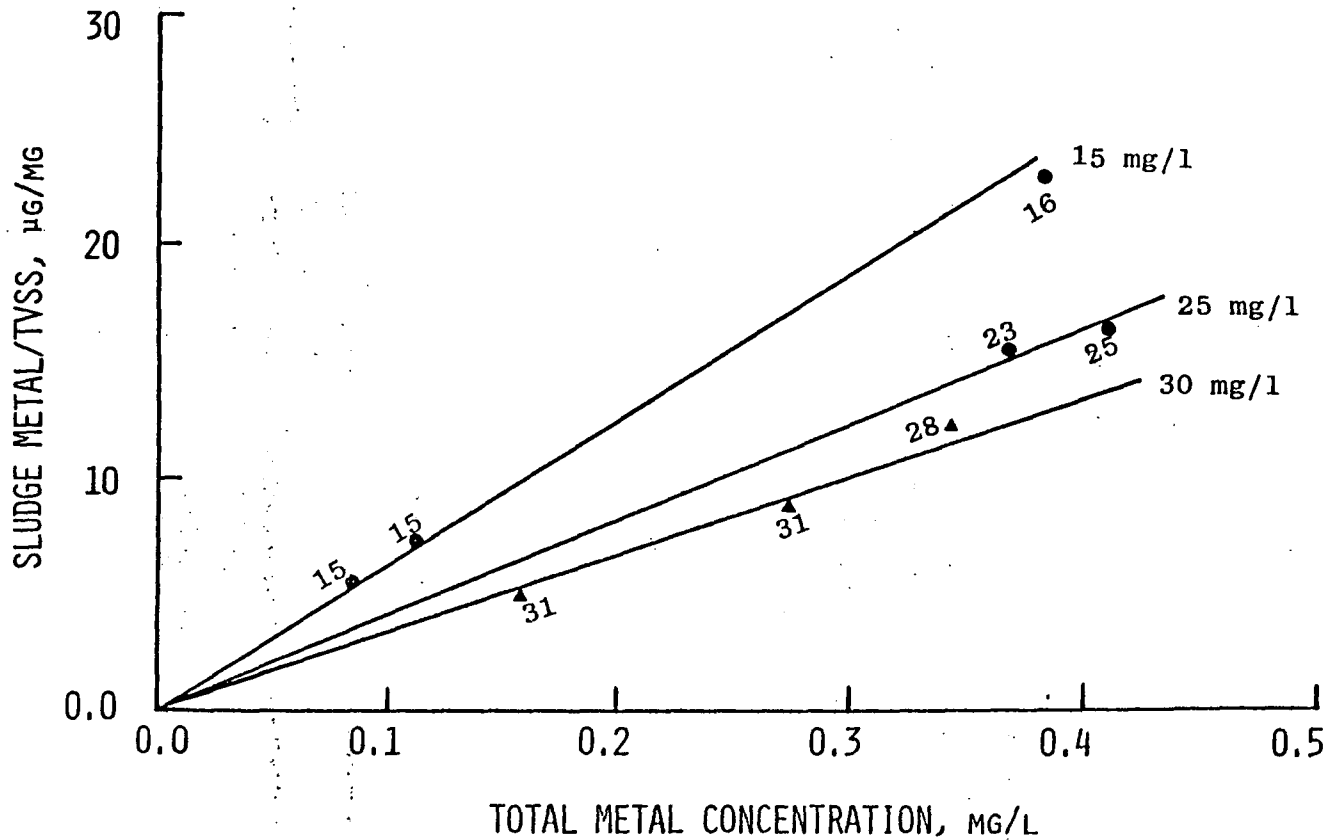


Figure 56. Adsorption isotherms for chromium in primary effluent at different VSS concentrations.

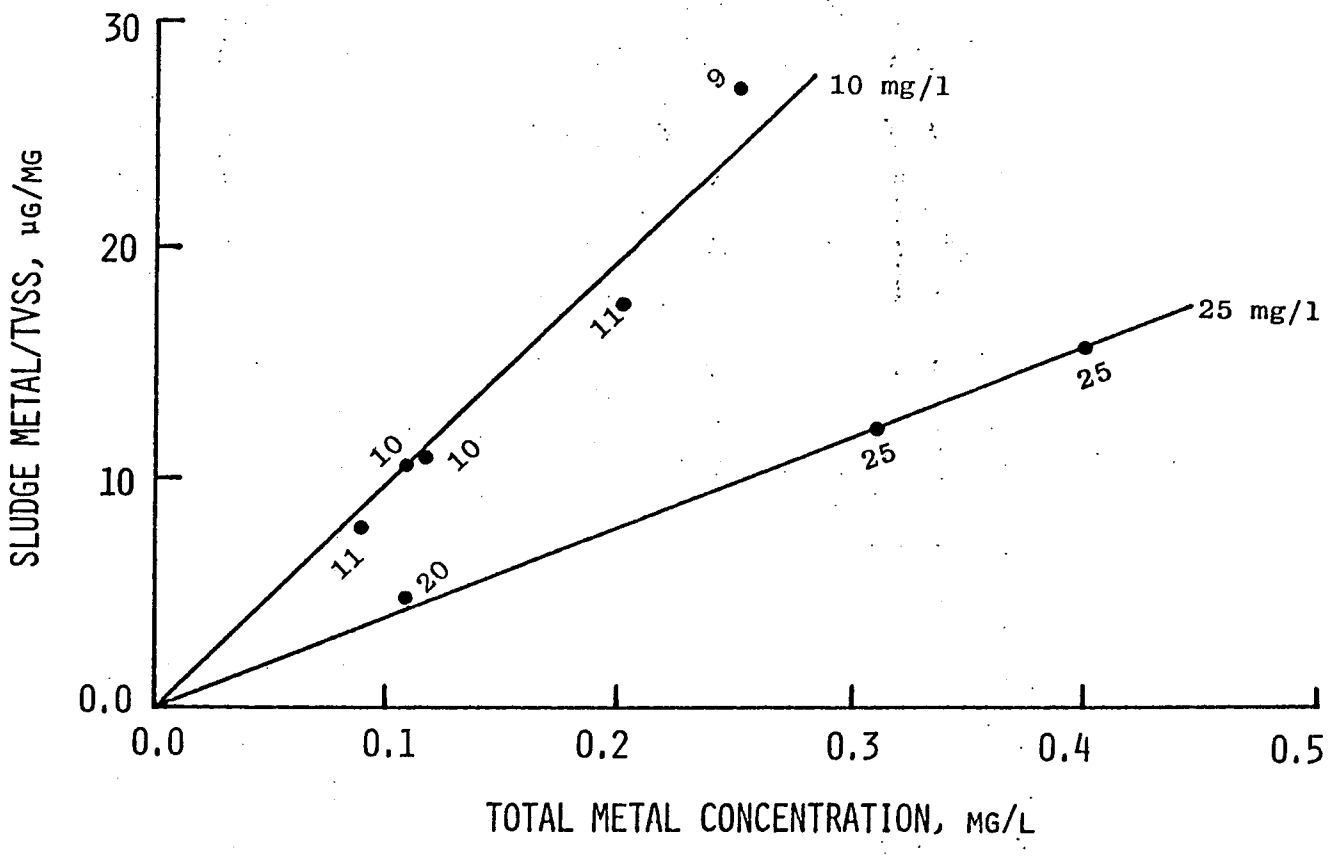


Figure 57. Adsorption isotherms for chromium in secondary effluent at different VSS concentrations.

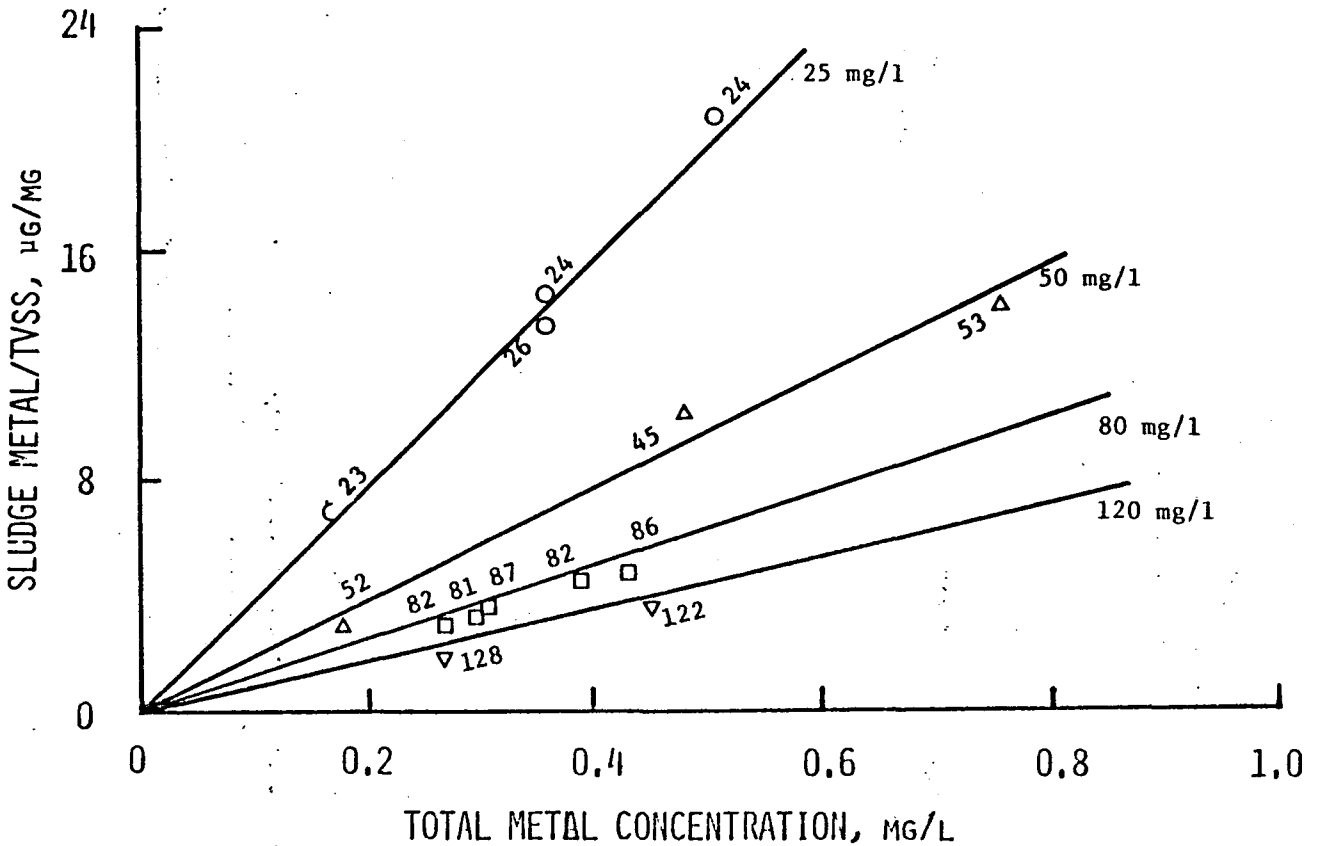


Figure 58. Adsorption isotherms of copper in raw sewage at different VSS concentrations.

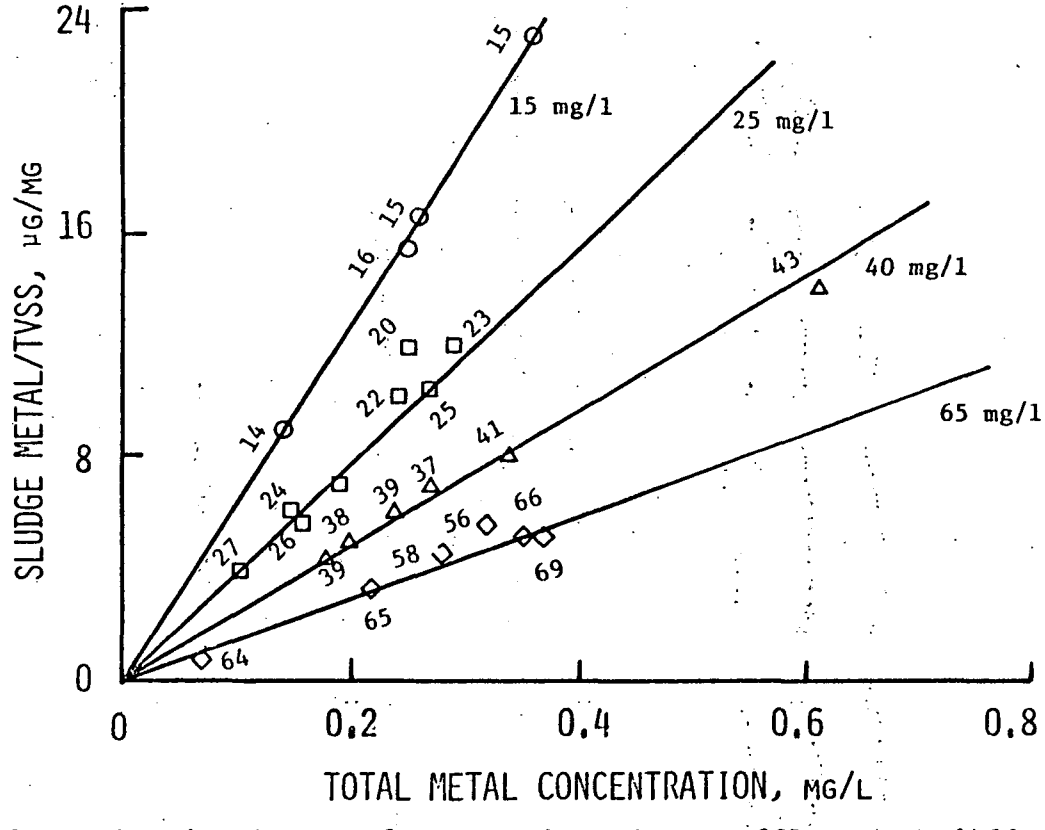


Figure 59. Adsorption isotherms of copper in primary effluent at different VSS concentrations.

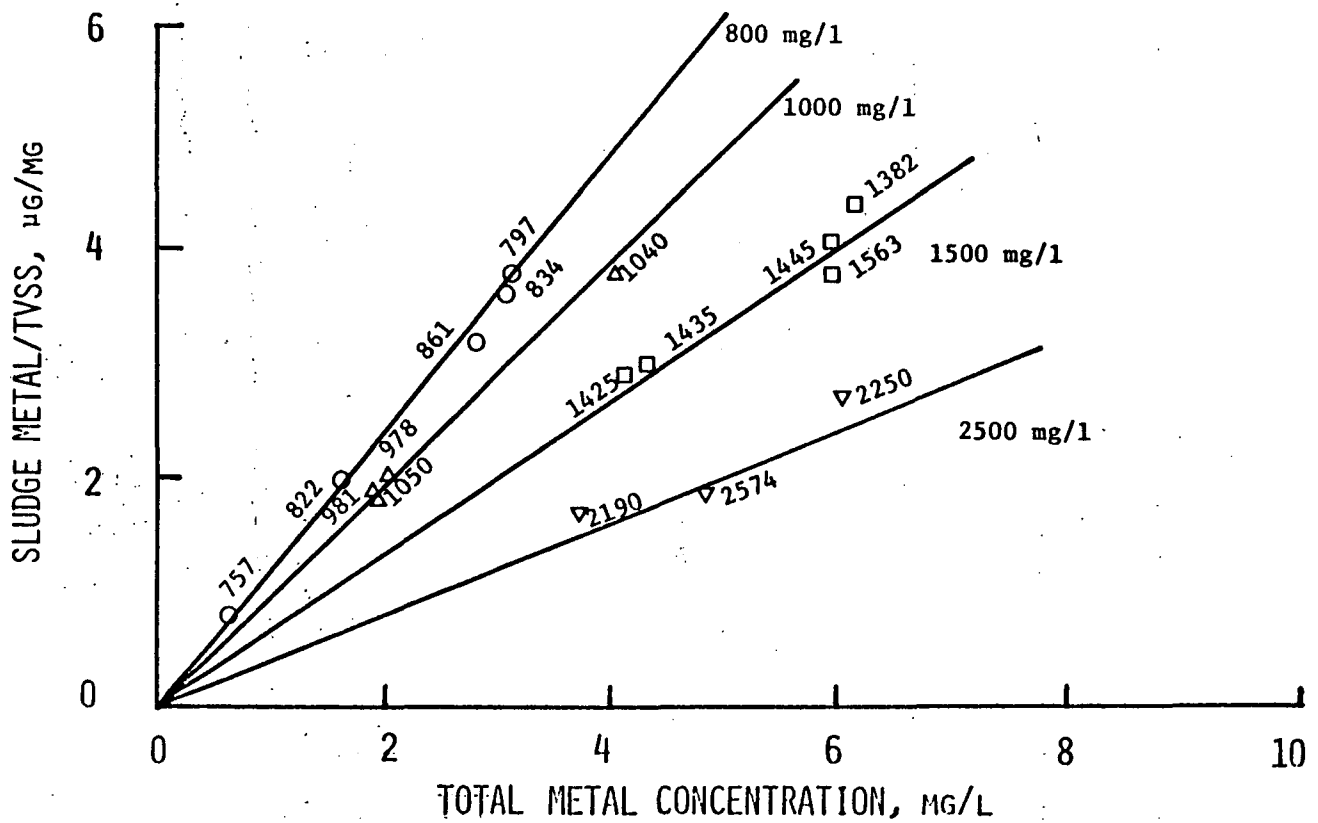


Figure 60. Adsorption isotherms of copper in mixed liquor at different VSS concentrations.

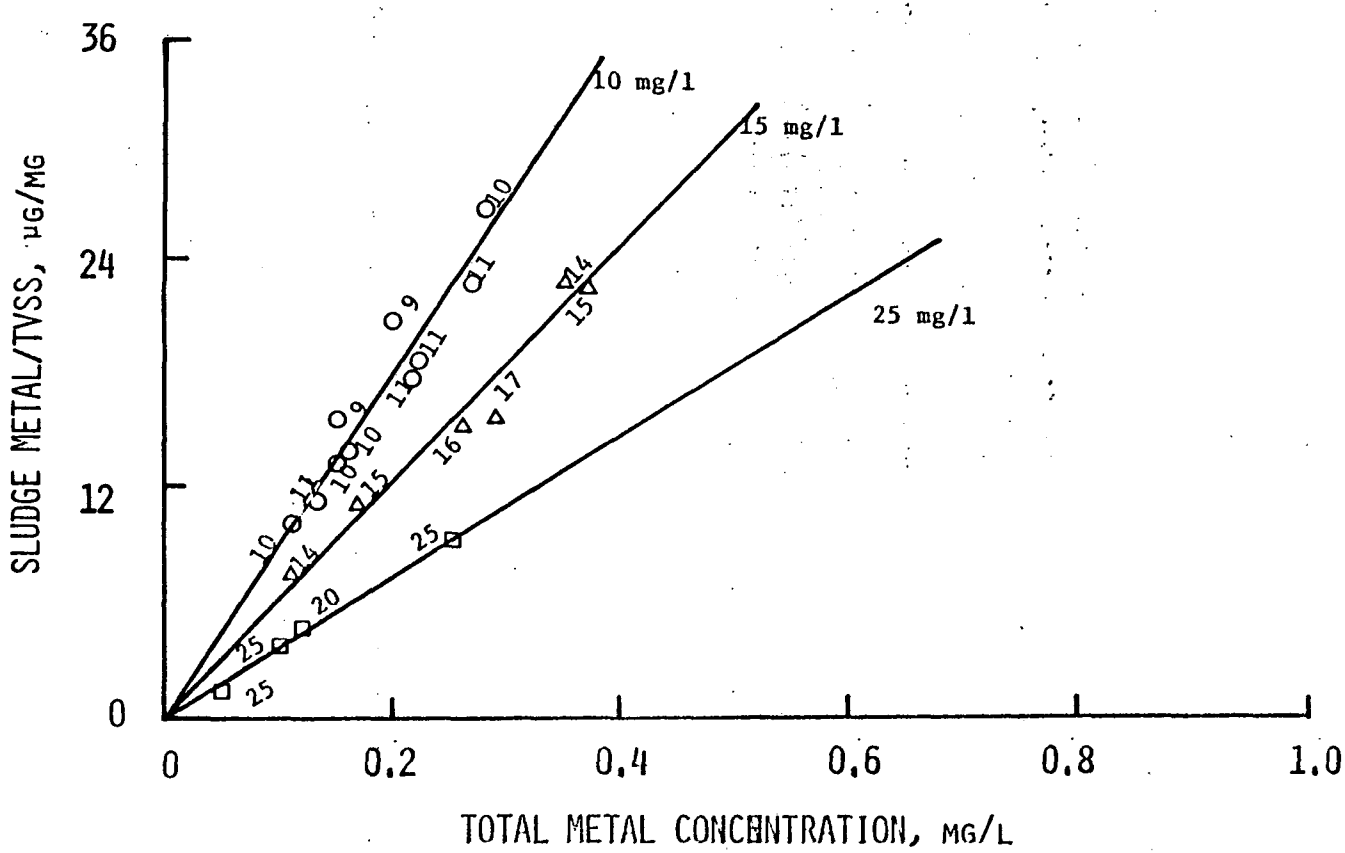


Figure 61. Adsorption isotherms of copper in secondary effluent at different VSS concentrations.

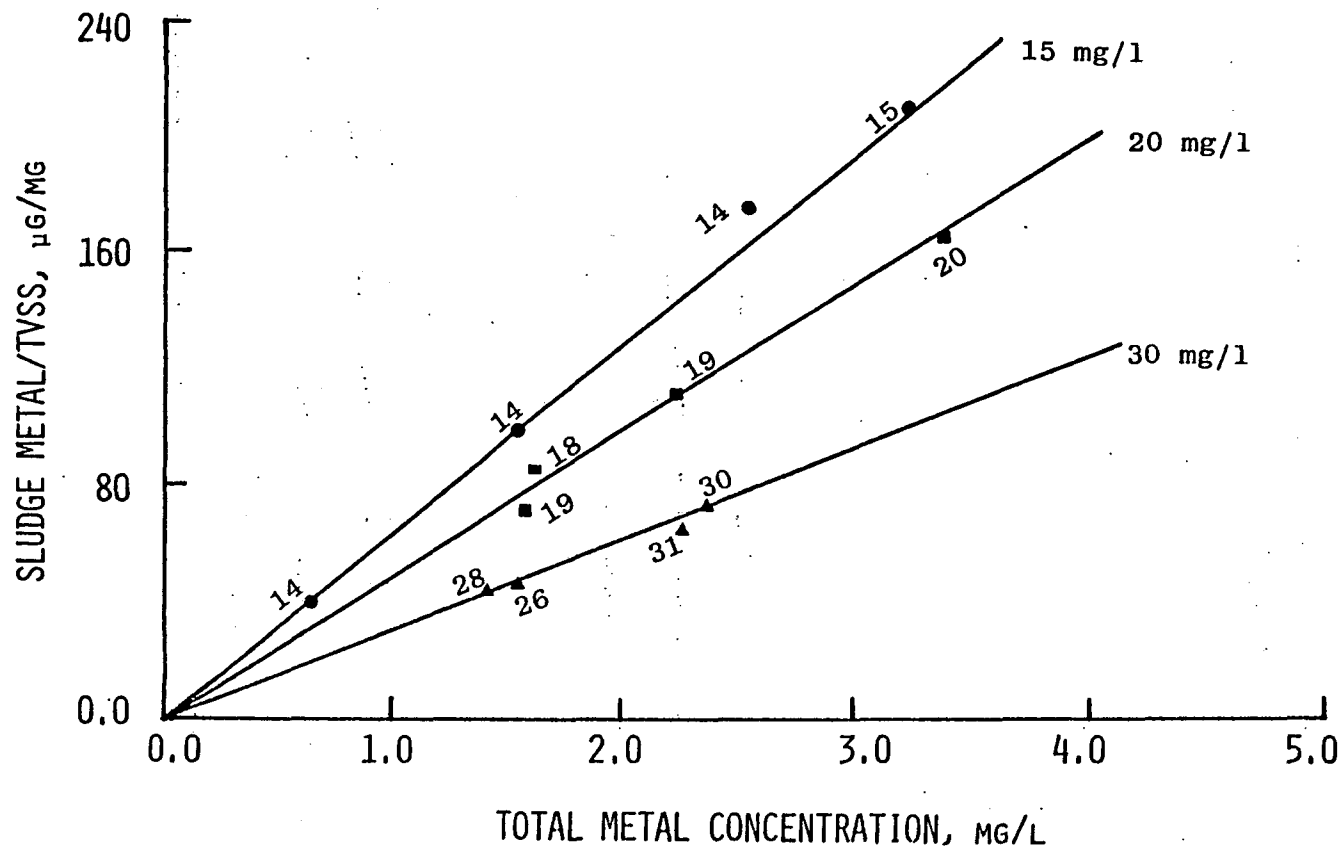


Figure 62. Adsorption isotherms of iron in raw sewage at different VSS concentrations.

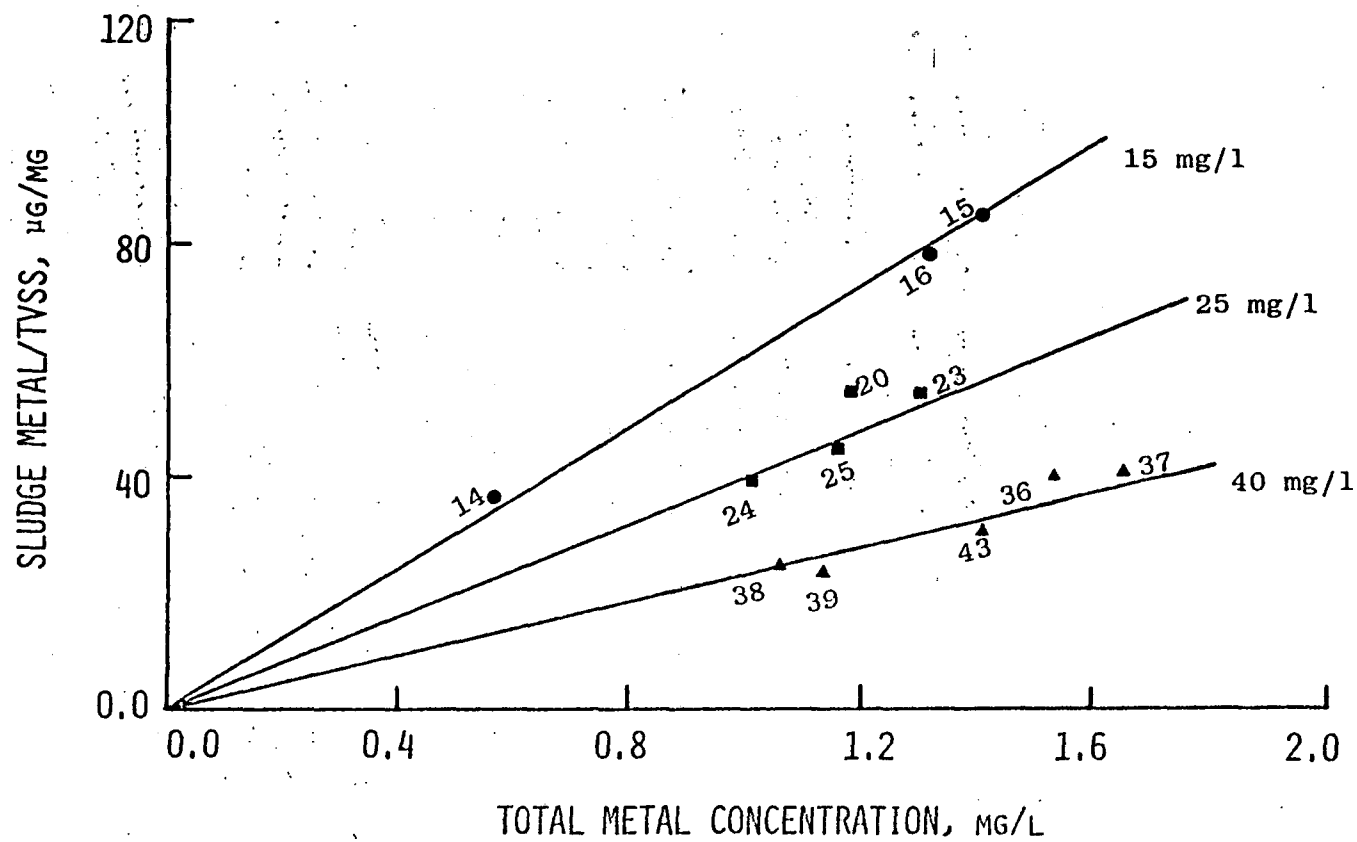


Figure 63. Adsorption isotherms for iron in primary effluent at different VSS concentrations.

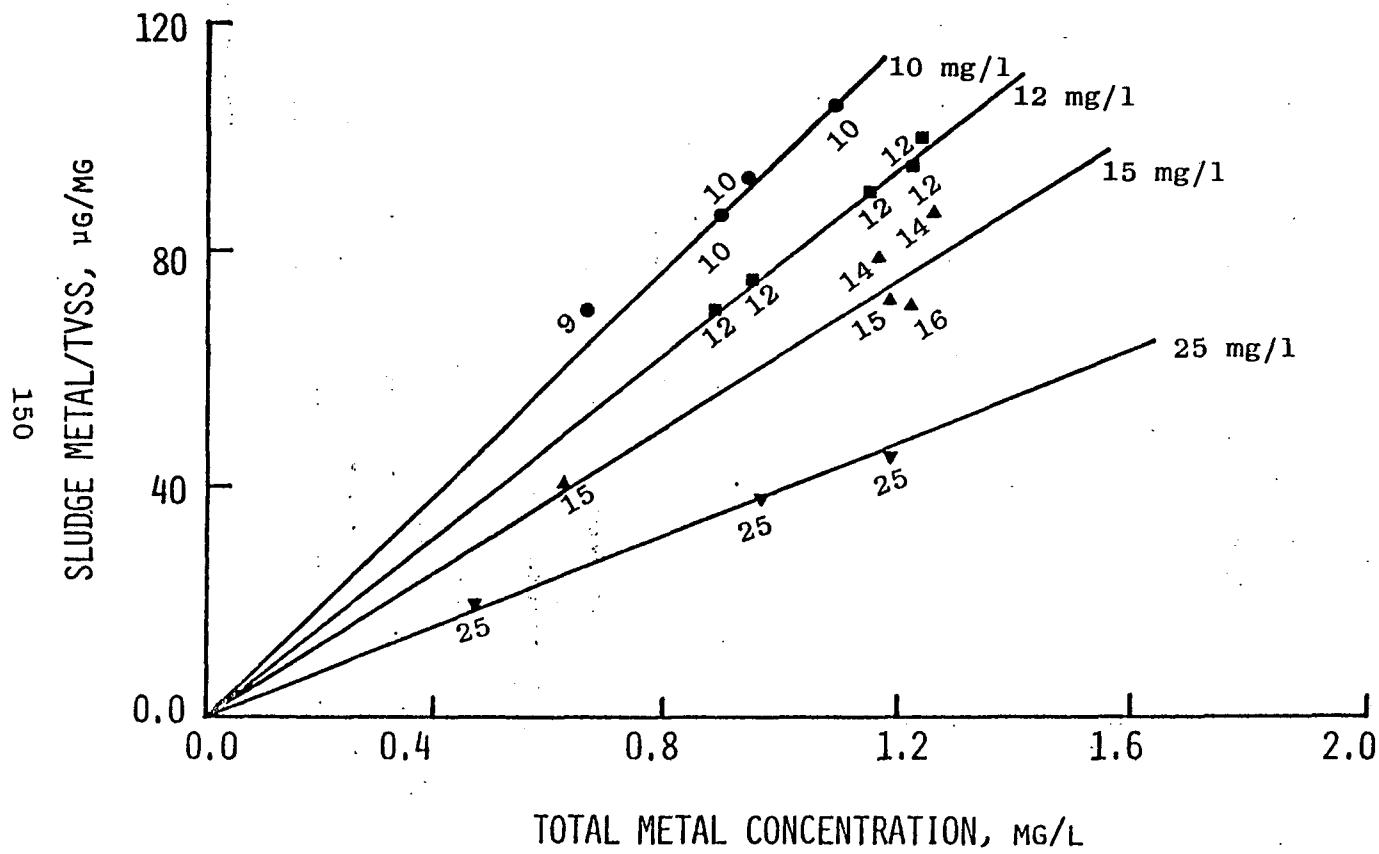


Figure 64. Adsorption isotherms of iron in secondary effluent at different VSS concentrations.

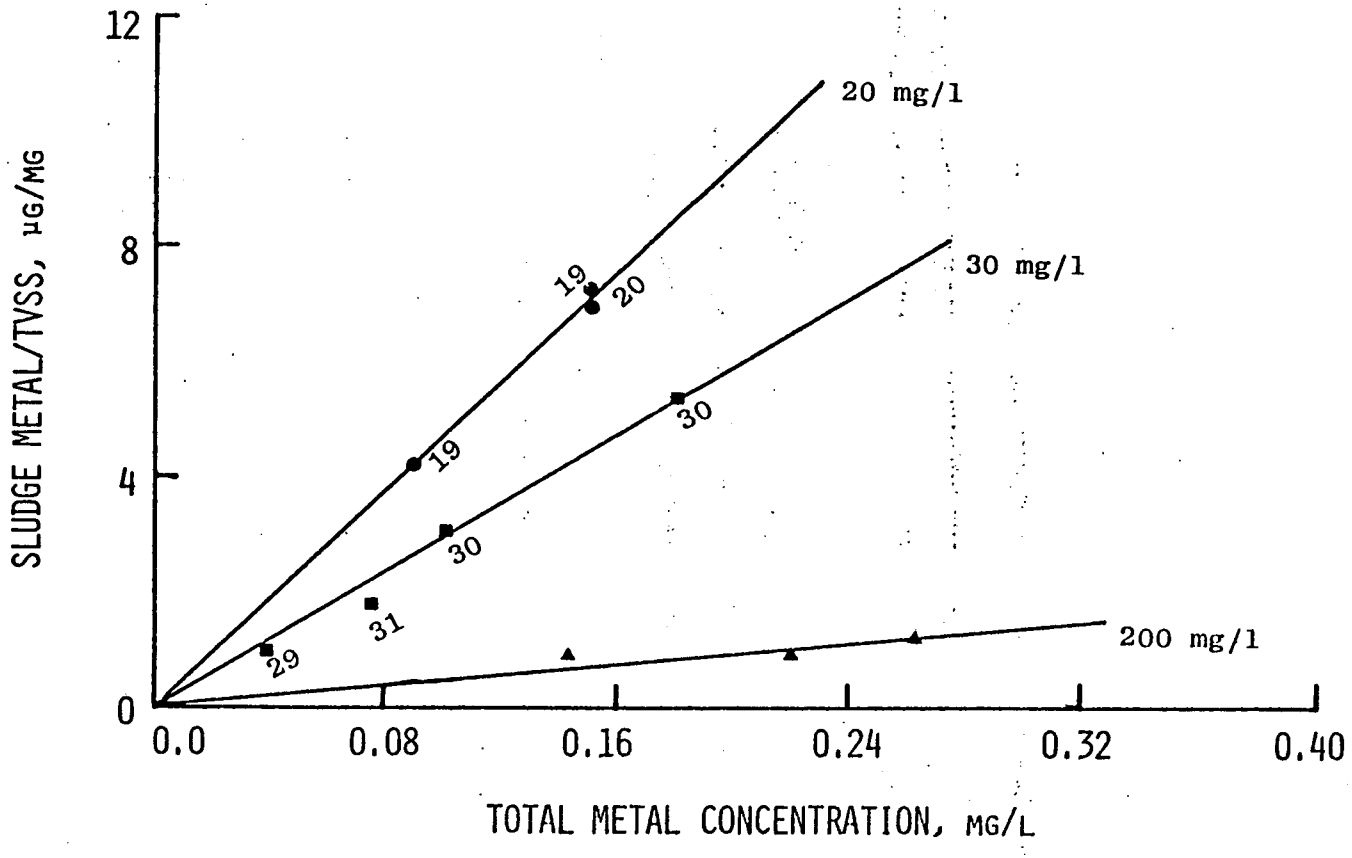


Figure 65. Adsorption isotherms for lead in raw sewage at different VSS concentrations.

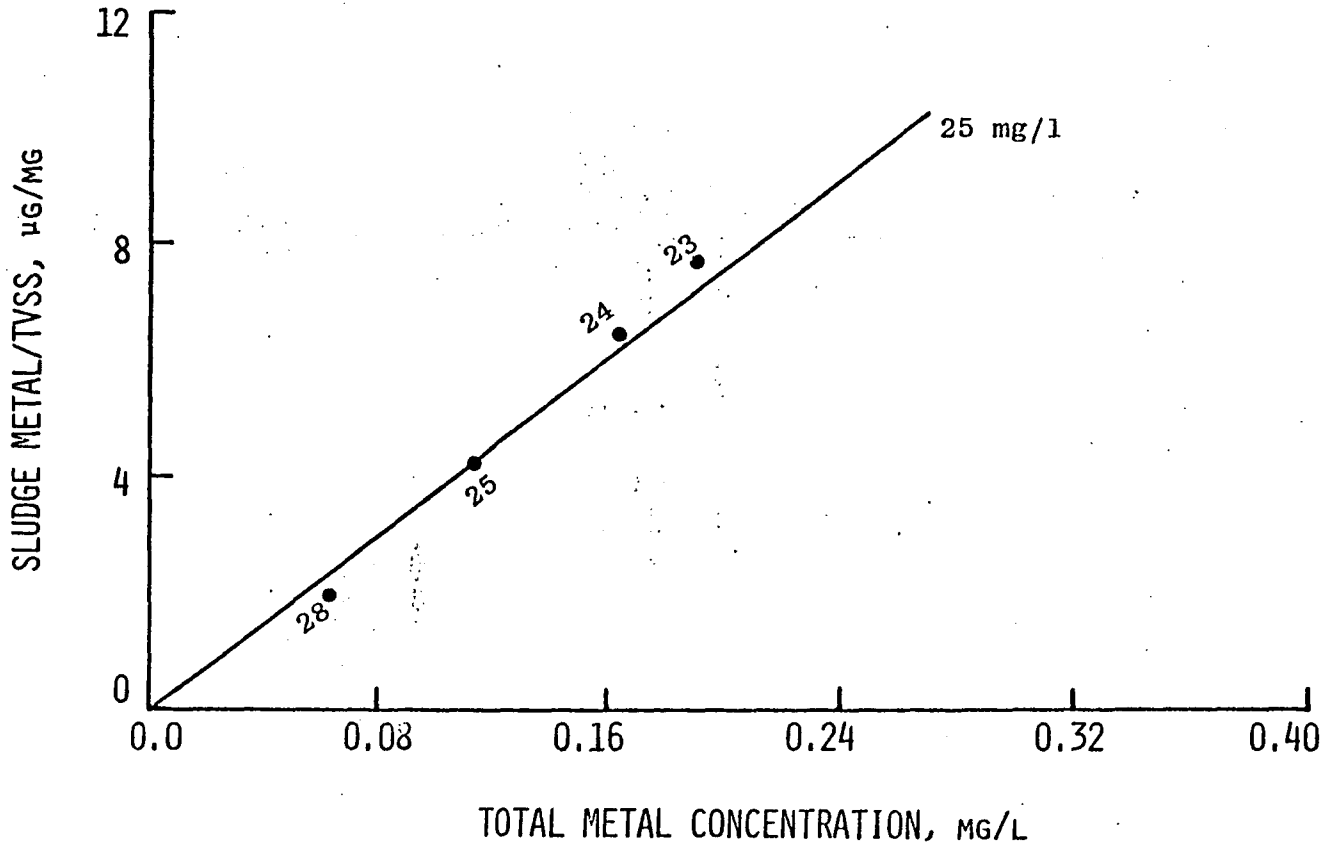


Figure 66. Adsorption isotherms for lead in primary effluent at 25 mg/l VSS concentration.

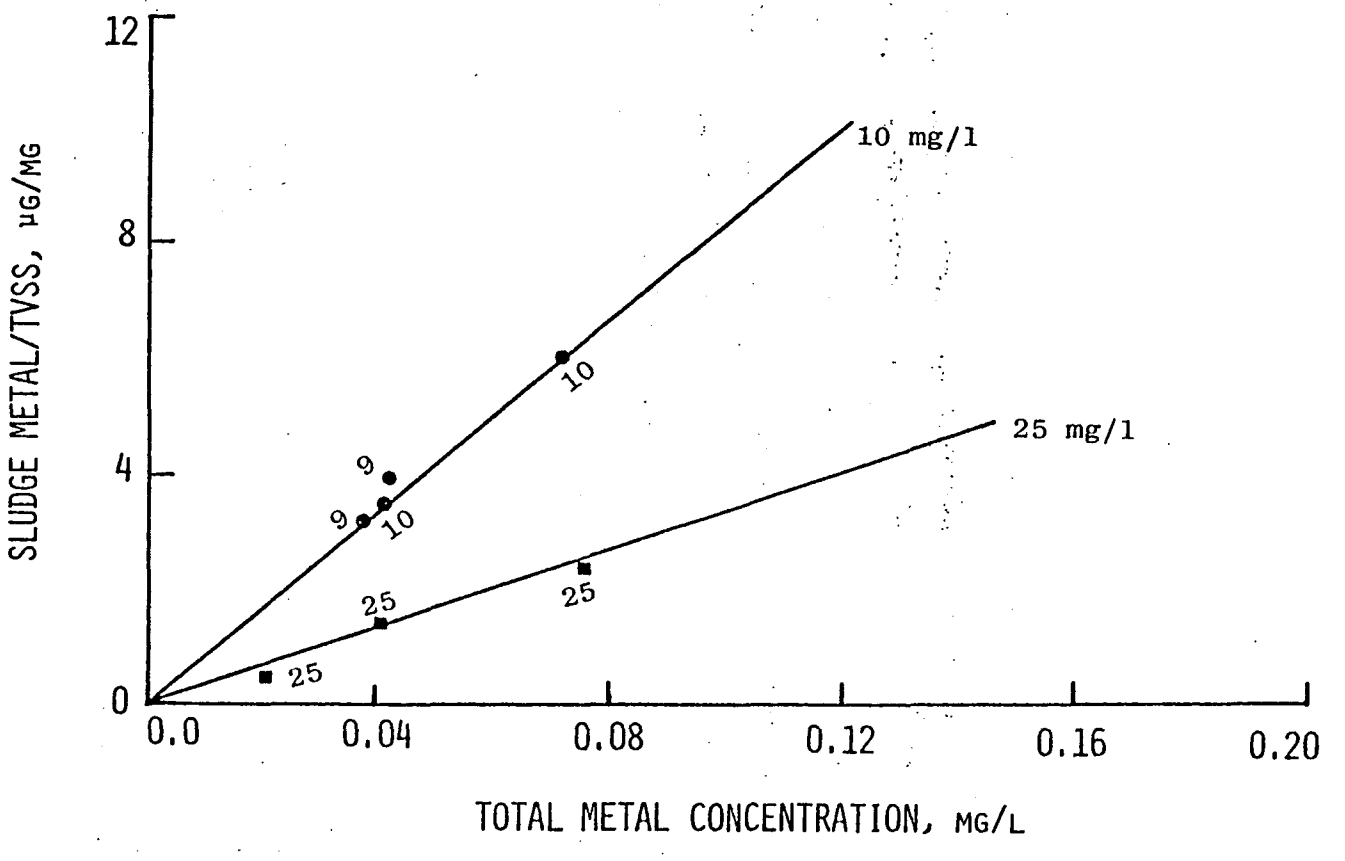


Figure 67. Adsorption isotherms for lead in secondary effluent at different VSS concentrations.

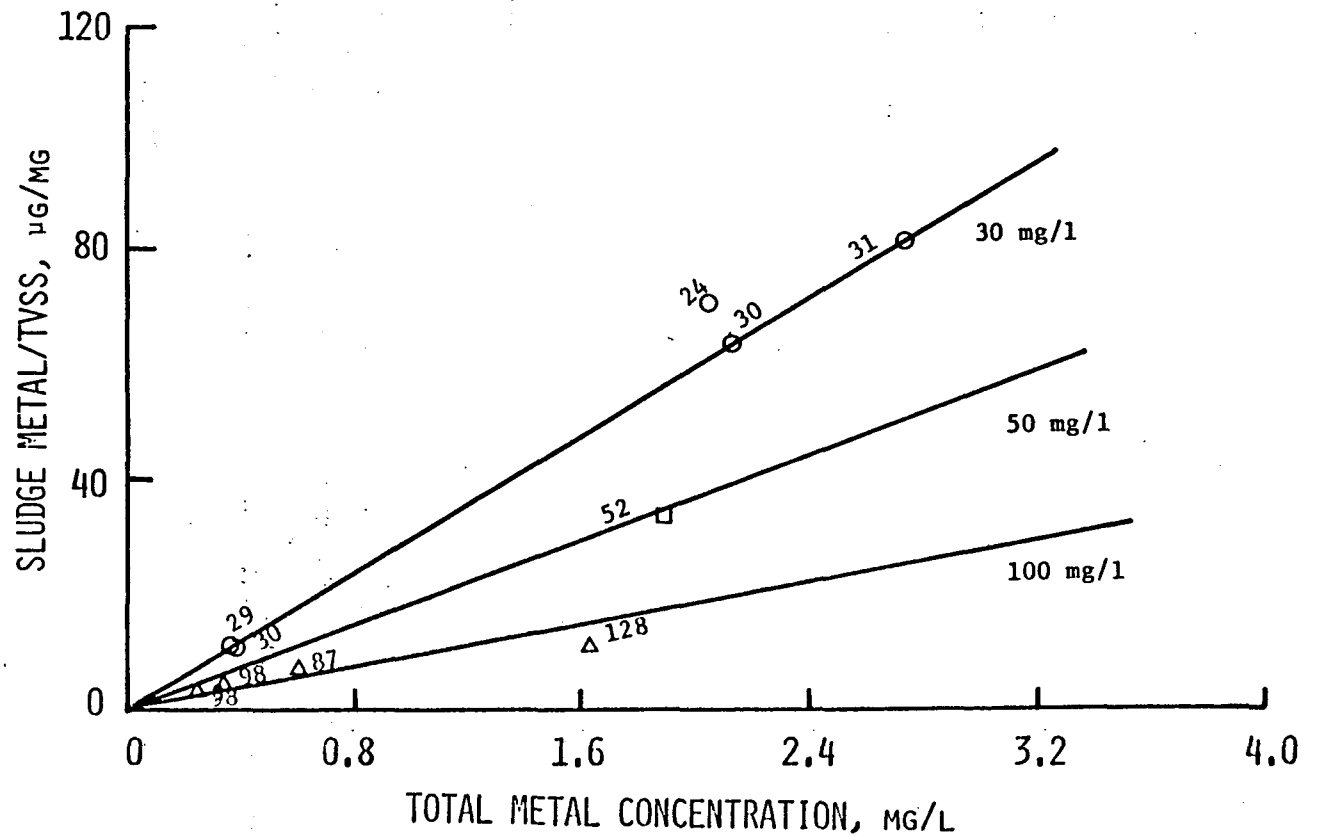


Figure 68. Adsorption isotherms of nickel in raw sewage at different VSS concentrations.

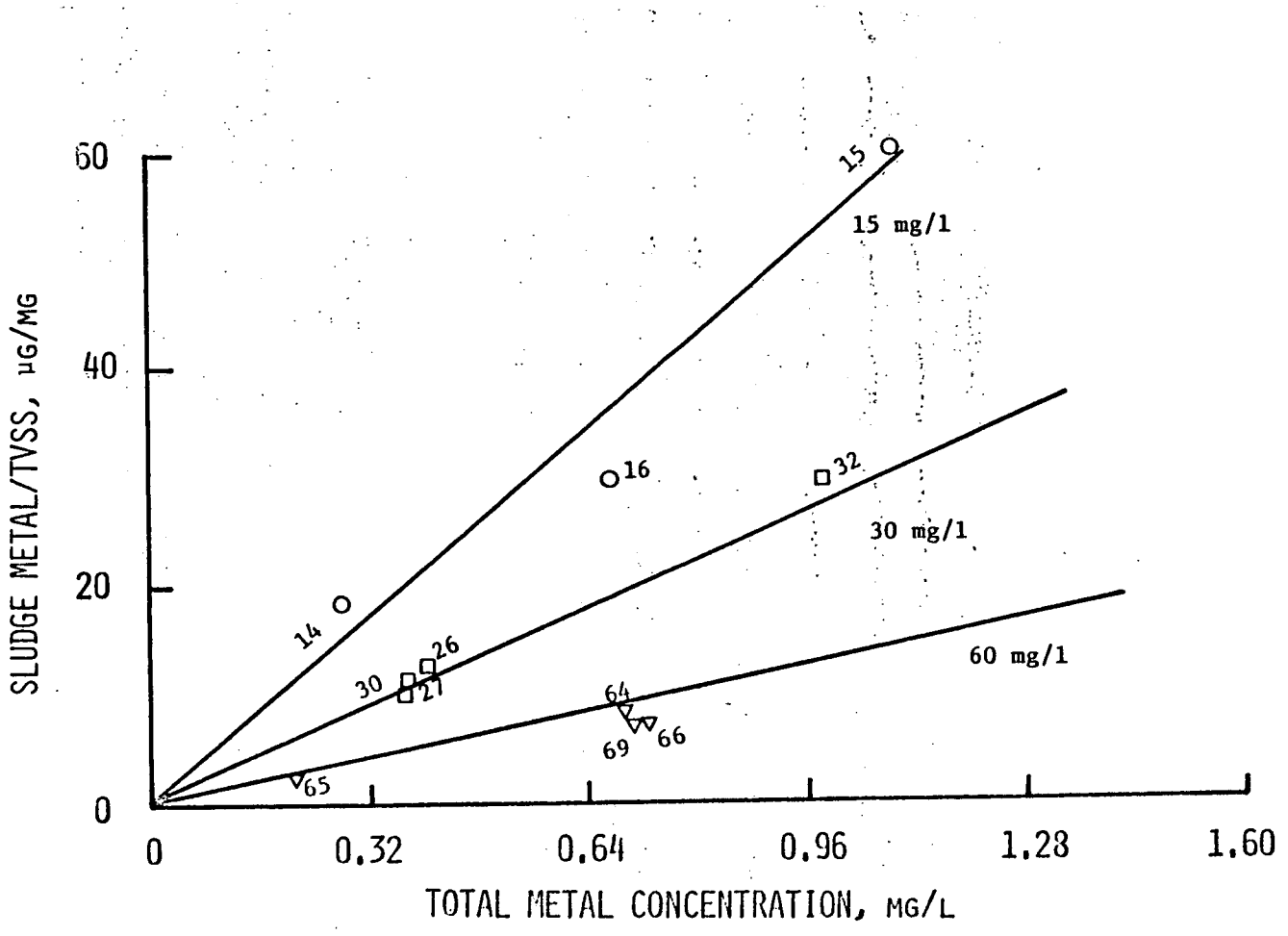


Figure 69. Adsorption isotherms of nickel in primary effluent at different VSS concentrations.

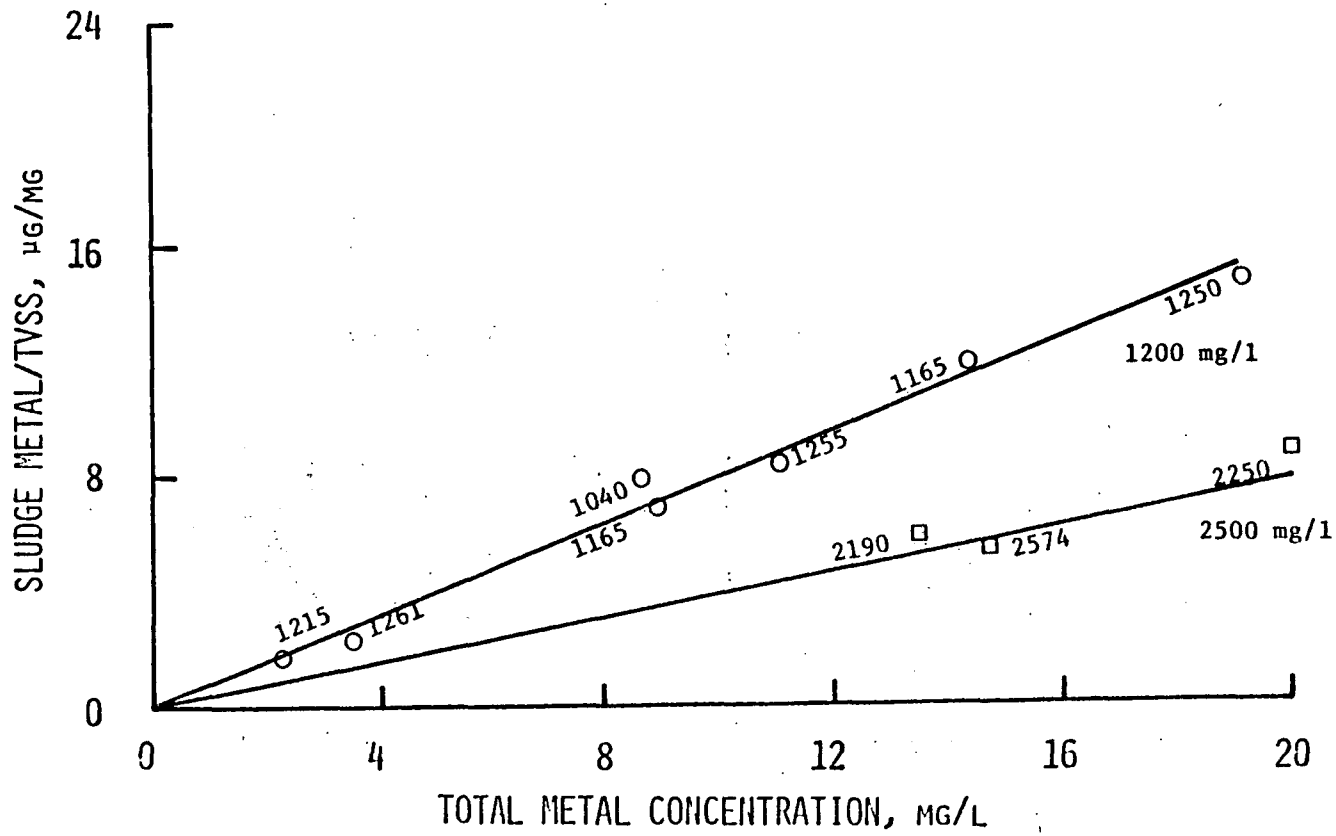


Figure 70. Adsorption isotherms of nickel in mixed liquor at different VSS concentrations.

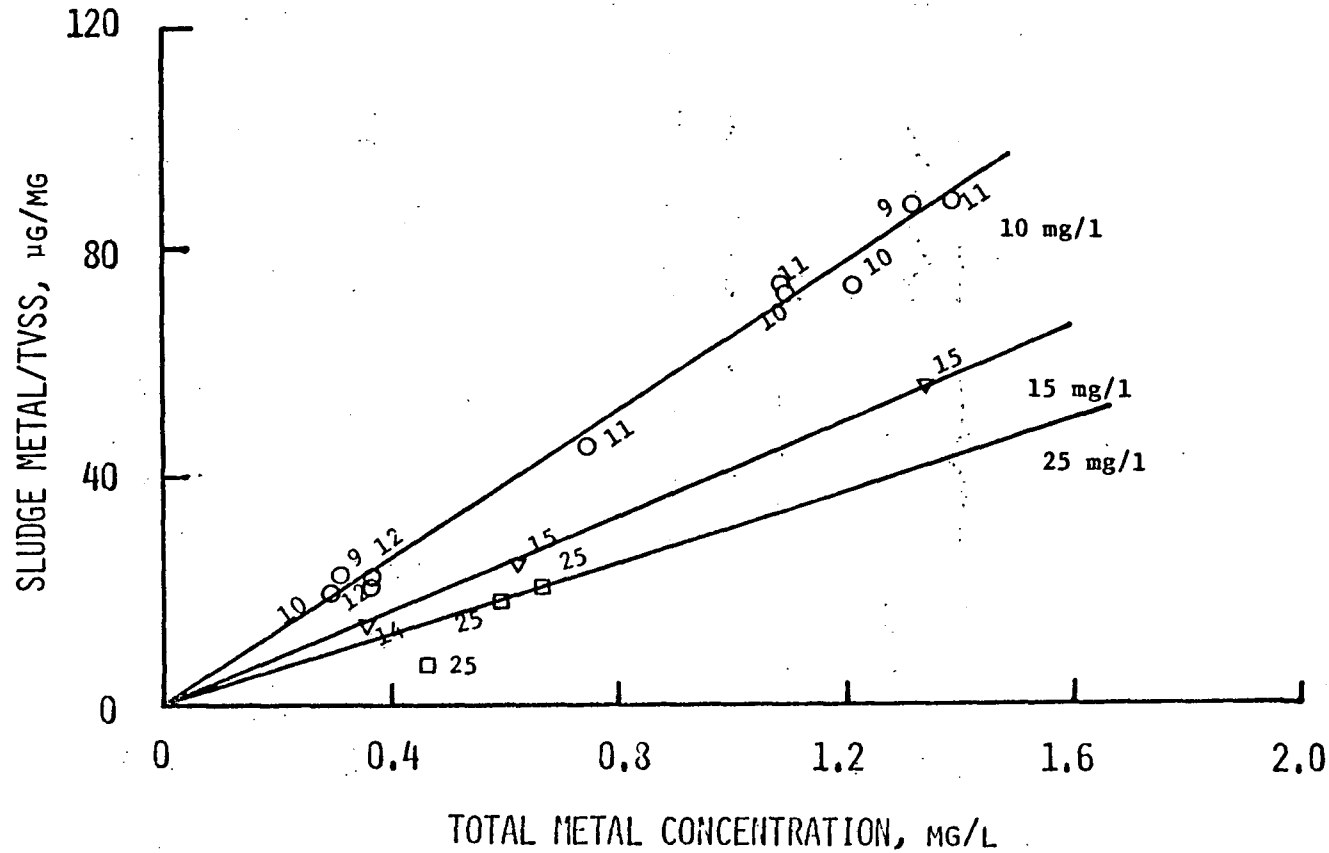


Figure 71. Adsorption isotherms of nickel in secondary effluent at different VSS concentrations.

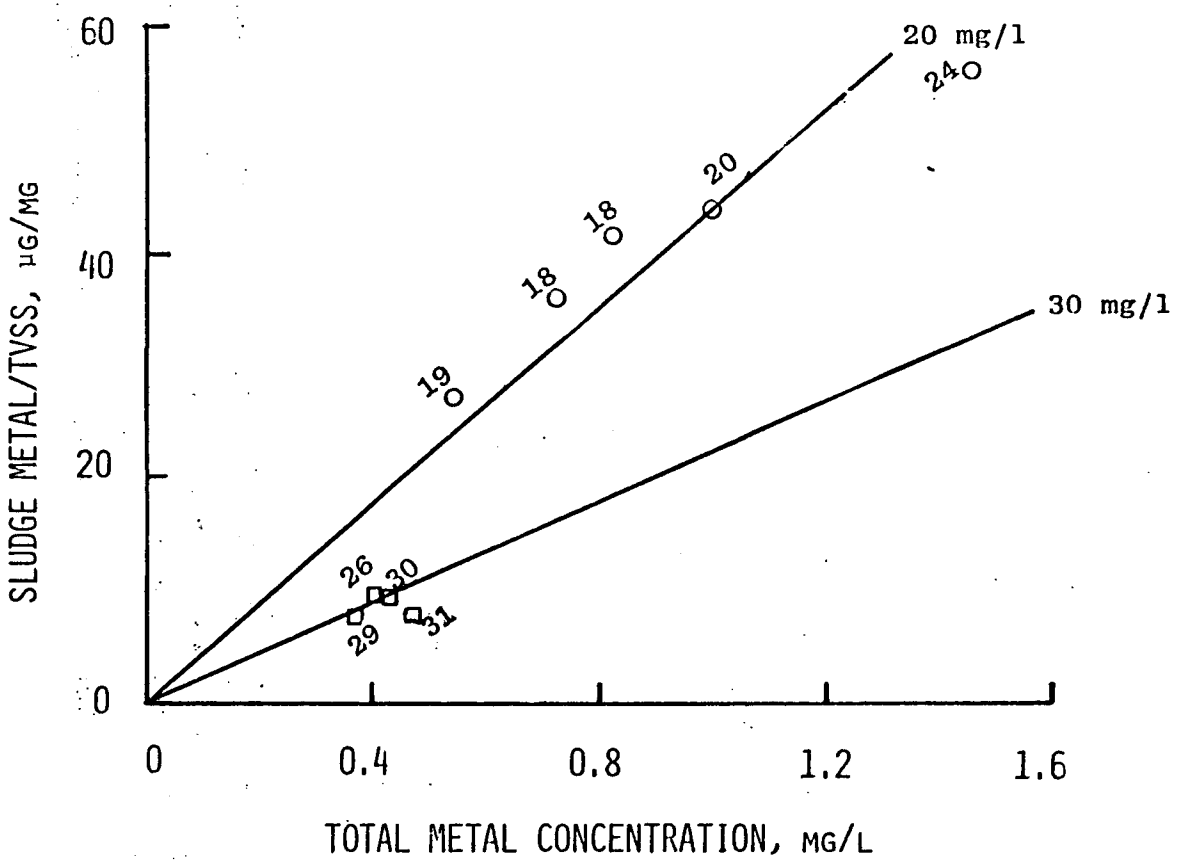


Figure 72. Adsorption isotherms of zinc in raw sewage at different VSS concentrations.

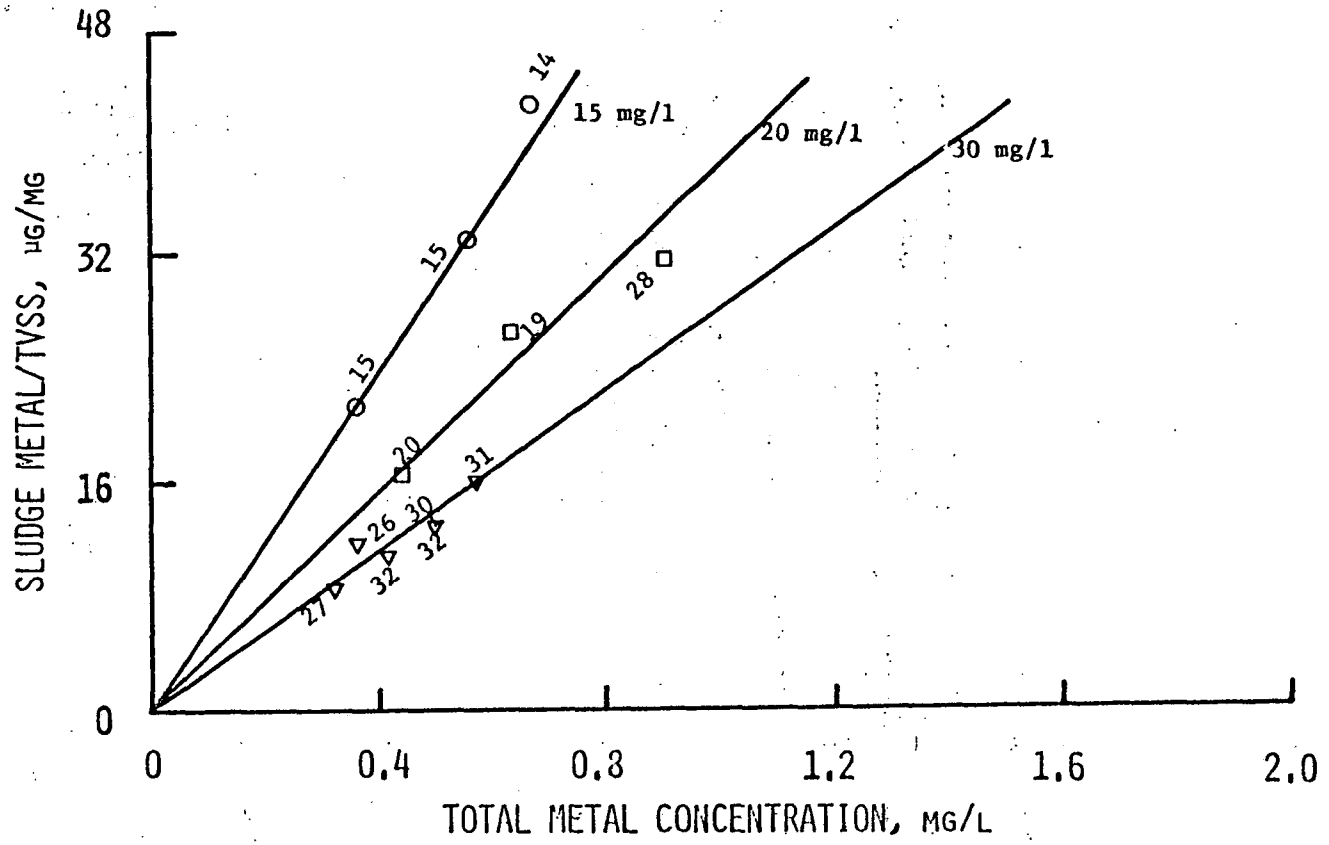


Figure 73. Adsorption isotherms of zinc in primary effluent at different VSS concentrations.

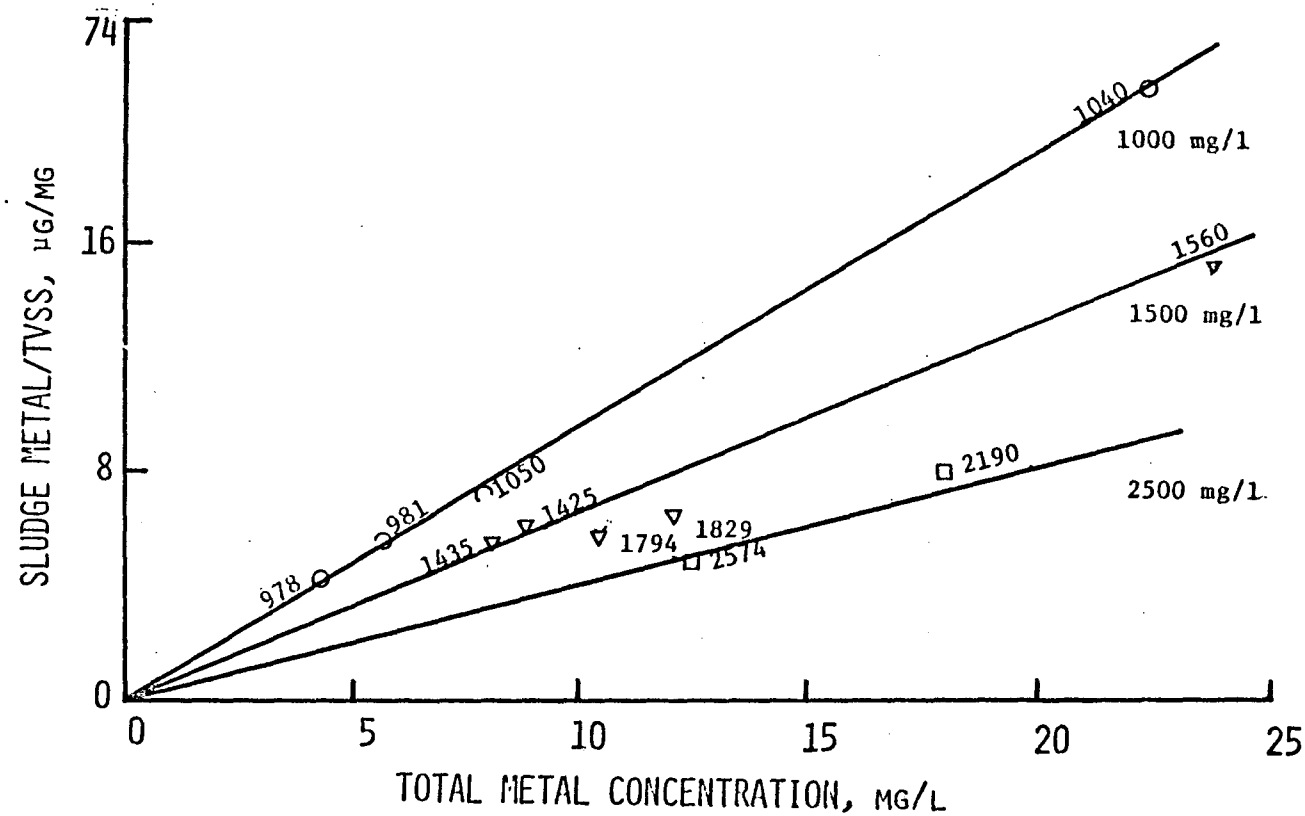


Figure 74. Adsorption isotherms of zinc in mixed liquor at different VSS concentrations.

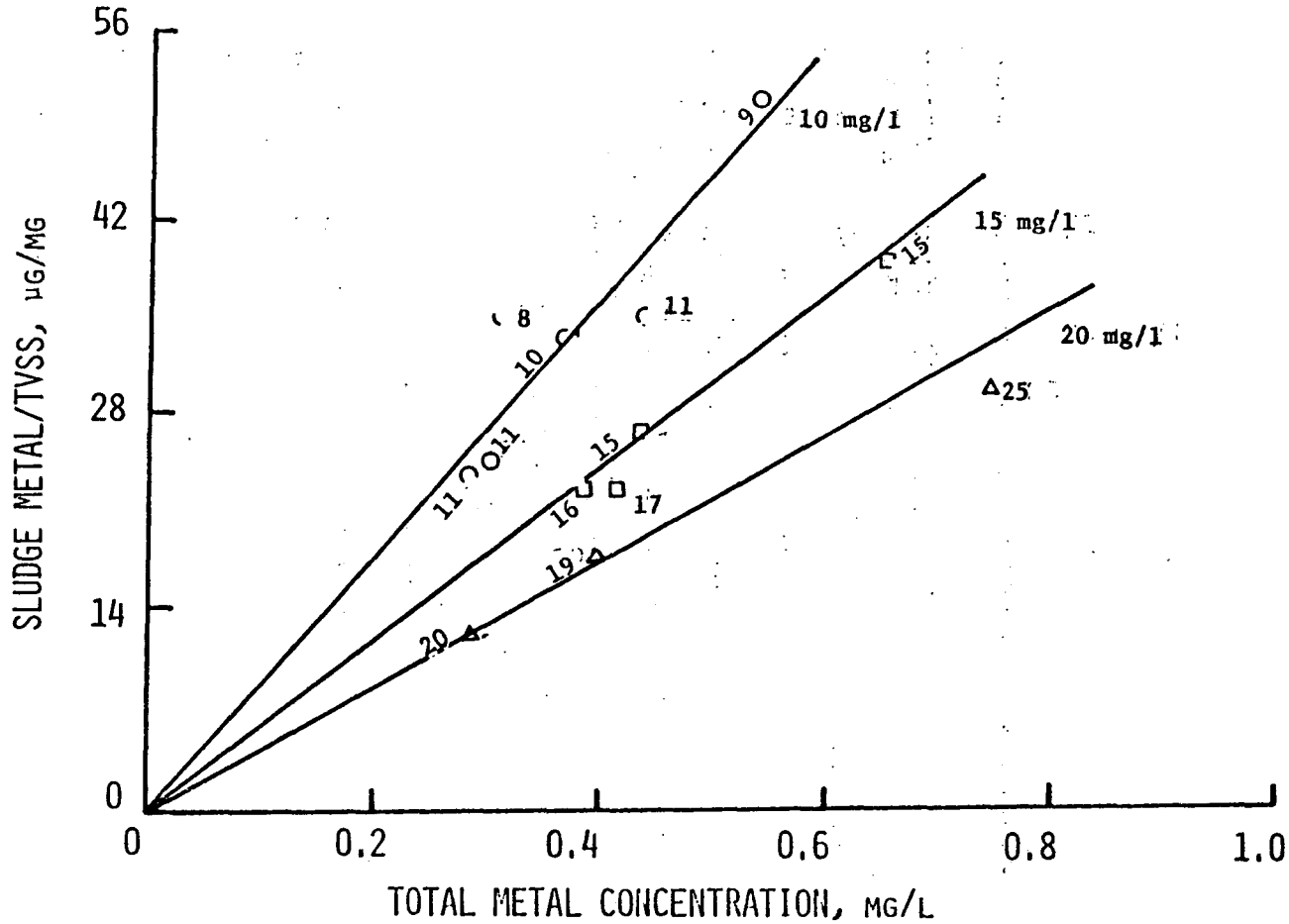


Figure 75. Adsorption isotherms of zinc in secondary effluent at different VSS concentrations.

basis to predict the distribution of any of the eight metals, within any of the four process streams, as a function of total metal concentration and VSS concentration. The general equation of any of the lines shown in these figures is,

$$C_{SM}/VSS = m \times C_{TM}$$

Where, C_{SM}/VSS is sludge metal/VSS, µg/mg C_{TM} is total metal concentration, mg/l m is the slope of the line.

The slope of each isotherm is an inverse function of VSS, since slope increases as VSS decreases. Analysis of the slopes, for each metal and each process liquid, revealed that the relationship between m and VSS is linear, and takes the form

$$m = 1/(A \times VSS + B)$$

Where A and B are constants for each metal and process liquid.

These relationships have not heretofore been presented in the published literature in metals distribution in combined treatment systems, and are a unique contribution of this study. These relationships provide the basis for the development of a predictive model on metals distribution, as described in Section 8 of this report.

SECTION 8

MODEL DEVELOPMENT

This section of the report describes two predictive models for distribution of metals in the process streams, and presents a model for metals removal through the combined treatment plant. The process models, built up from material balance equations through the plant, predict the effluent heavy metals concentrations, based upon influent metals concentrations and the operating conditions of the plant, such as per cent VSS removal and per cent SOC biodegradation. The predictive process models are checked against the measured data of the 39 continuously run pilot-scale units.

In Part I, the distribution relationship between solid and liquid phases for the heavy metals is reviewed, and models based upon regression equations obtained describing the correlation of the heavy metals concentrations between the liquid and solid phases, with the sampled liquors taken from the process stream of the pilot-scale units. The regression models can predict metal concentration of either the solid or liquid phase.

In Part II, a predictive process model for metals removal through the primary clarifier is first developed. Two regression models developed in Part I are used to predict the solid bound metal concentration from the total metal concentration. Part II also demonstrates a predictive process model for the continuously run pilot systems. For the process model, both of the predictive regression models of Part I were tested. The final section of Part II concerns the heavy metal removal percentage, predicted by the process model developed in Part II.

PREDICTION OF METALS DISTRIBUTION

In order to develop a predictive process model, it is necessary first to predict the metals distribution between the solid and liquid phases for the process streams. After evaluation of the experimental data on metals distribution, regression models are developed to predict the metals

distribution. The predictive models have been checked for their prediction errors, against the data collected from the pilot-scale system.

The distribution is described in terms of the correlation, among the total metals concentration (C_{TM}), the solid (or sludge) bound metal concentration (C_{SM}), and the soluble metal concentration (C_{SO}). The distribution may be influenced by soluble ligands, such as SOC, or proton concentration (C_H). Proton concentration was measured as pH, where

$$pH = - \log C_H$$

Freundlich type isotherms do not incorporate information about soluble metal-ligand complexation effects, since the isotherm is the correlation between C_{SM}/VSS and C_{SO}. As is seen in Figures 42 through 45, most of the isotherms show low correlation coefficients. This may be due in part to the existence of soluble ligands, which affect the metal distribution.

To describe the ligand effect, Cheng (1973) proposed a chemical equilibrium absorption model. His model was based upon the liquid phase chemical equilibrium between the soluble ligands (he used COD and pH, and successfully correlated the liquid phase data) concentration and the metal concentration in the soluble phase. Using his model, the researchers tested for a correlation between

$$C_{SO} \times (VSS/C_{SM}) \text{ and SOC.}$$

That is $C_{SO} \times (VSS/C_{SM}) = 1/K_S + (K_L/K_S) \times SOC$

where $K_S = C_{SM}/(VSS \times C_M)$

$K_L = C_{ML}/(SOC \times C_M)$

C_M is noncomplexed soluble metal concentration, and C_{ML} is the soluble complexed metal concentration. This predictive model for the metals distribution was tested by the linear regression technique against the 39 runs of data. The results of the regression analysis are listed in Table 42.

Very low squared correlation coefficients were obtained, implying poor prediction of any impact of soluble ligands by Cheng's model. Therefore, different equilibrium models were tested, some of which also incorporated soluble and solid phase ligands (SOC, C_H and VSS). The investigators assumed a linear combination, and tested three separate models of increasing simplicity as follows:

TABLE 42. RESULTS OF REGRESSION ANALYSIS FOR EFFECT OF SOC ON METALS DISTRIBUTION

Metal	Squared Correlation Coefficient			
	Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	0.31	0.13	0.01	0.02
Cadmium	0.25	0.26	0.00	0.17
Chromium	0.33	0.44	0.07	0.00
Copper	0.18	0.21	0.23	0.18
Iron	0.43	0.40	0.43	0.01
Lead	0.14	0.40	0.28	0.04
Nickel	0.17	0.05	0.06	0.11
Zinc	0.48	0.29	0.24	0.00

$$C_{TM} \times (VSS/C_{SM}) = A \times VSS + B \times SOC + C \times C_H + D \qquad \text{Model 1}$$

$$C_{TM} \times (VSS/C_{SM}) = A \times VSS + B \times SOC + C \qquad \text{Model 2}$$

$$C_{TM} \times (VSS/C_{SM}) = A \times VSS + B \qquad \text{Model 3}$$

The latter, Model 3, was that postulated on the basis of the data presented in Section 7, Figures 52 through 75, and represents the most simple form of a model to predict the distribution of C_{TM} between the soluble and solid phases. Model 3 results through a rearrangement of the equations presented at the end of Section 7, which described the relationship of Figures 52 through 75.

$$C_{SM}/VSS = m \times C_{TM}$$

$$m = 1/(A \times VSS + B)$$

For Model 3, only C_{TM} and VSS would be required, to determine C_{SM}/VSS, the sludge bound metal concentration per unit weight of VSS. Since, in the model calculation VSS is given, then C_{SM} can be determined and by difference between C_{SM} and C_{TM}, C_{SO} is also determined. The model parameters; A, B, C and D were computed by multivariant linear regression and the computed models then tested against the performance data for the 39 pilot runs . For each model, and each metal in each of the four process liquids, the means of the relative errors and the mean relative standard deviations for each model were calculated. The means of the relative errors are summarized in Table 43, and the mean relative standard deviations of the predicted from the measured conditions are presented in Table 44. As demonstrated in Table 43, there is surprisingly good fit by all three models, with little difference in mean relative error among any of the models for any metal in any process liquid, except that for zinc in raw sewage the simple Model 3 gave a greater prediction error than did Models 1 or 2. Table 44 reveals that, again except for zinc in raw sewage, the best model for fit to the experimental data is Model 3, the most simple model. For Model 3, the relative standard deviations are all below 20%, and next are below 10%. This indicates extremely good fit, and Model 3 was therefore selected as the model of choice among the three tested, in predicting metals distribution within the process liquids.

A fourth model, incorporating only SOC was also tested. This model takes the form $C_{TM} \times (VSS/C_{SM}) = A \times SOC + B$. There was essentially no correlation between $C_{TM} \times (VSS/C_{SM})$

TABLE 43. MEAN RELATIVE ERRORS OF PREDICTION OF MODELS 1, 2 AND 3 AGAINST MEASURED DATA, %

Metal	Process Liquid			
	Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	12.0	14.2	0.6	16.8
Cadmium	12.6	12.6	1.8	18.6
Chromium	1.3	1.0	0.0	1.0
Copper	4.0	2.1	0.2	3.3
Iron	6.3	3.7	1.1	7.1
Lead	24.8	14.3	1.5	20.1
Nickel	21.5	27.3	2.9	24.6
Zinc	9.8	10.5	0.5	15.3
	Model 2			
Aluminum	11.4	13.5	0.6	17.9
Cadmium	12.3	15.0	2.0	24.0
Chromium	1.4	1.1	0.0	1.0
Copper	3.7	2.2	0.2	3.6
Iron	6.6	3.7	1.1	7.1
Lead	23.2	13.1	1.5	20.1
Nickel	20.7	29.2	3.0	22.2
Zinc	9.6	9.9	0.6	18.7
	Model 3			
Aluminum	13.6	16.0	0.6	17.2
Cadmium	12.4	15.0	2.0	24.7
Chromium	1.3	1.3	0.1	1.2
Copper	4.0	2.9	0.2	4.5
Iron	4.2	4.0	1.6	6.9
Lead	26.5	16.7	2.0	25.8
Nickel	20.9	30.8	3.4	22.6
Zinc	21.5	10.6	0.7	19.1

TABLE 44. MEAN RELATIVE STANDARD DEVIATIONS OF PREDICTIONS OF MODELS 1, 2 AND 3 AGAINST MEASURED DATA, %

Metal	Process Liquid			
	Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	22.3	21.6	0.9	22.7
Cadmium	17.6	18.3	3.1	28.7
Chromium	2.4	1.7	0.2	1.1
Copper	6.2	3.6	0.3	5.2
Iron	11.7	6.1	1.9	11.7
Lead	36.7	20.9	2.6	31.4
Nickel	36.0	38.3	5.1	37.1
Zinc	15.8	15.7	0.8	21.9
	Model 2			
Aluminum	20.5	20.8	1.0	23.8
Cadmium	16.9	21.2	3.3	32.9
Chromium	2.4	1.7	0.2	1.6
Copper	5.6	3.7	0.3	5.4
Iron	11.7	6.0	1.9	11.5
Lead	24.9	20.5	2.6	31.4
Nickel	30.9	37.6	5.3	35.4
Zinc	15.4	14.5	1.0	26.0
	Model 3			
Aluminum	9.9	14.3	0.5	10.5
Cadmium	9.2	9.8	1.5	15.0
Chromium	1.3	0.8	0.0	0.8
Copper	3.1	2.2	0.3	3.8
Iron	3.3	3.7	1.6	8.0
Lead	13.4	8.3	1.9	16.3
Nickel	13.7	20.2	3.5	19.1
Zinc	18.3	7.5	0.6	12.6

and SOC. The distribution of metals is therefore indicated to be primarily influenced by the solid phase, VSS. Metals equilibrium distribution through the plant is controlled by the solid or sludge phase, rather than by the liquid phase. The liquid phase ligands SOC and pH have scant effect on the metals distribution. VSS, the solid phase ligand, is revealed to be the dominant factor.

As reported in Section 7, the slopes of Figures 52 through 75 are obviously inversely proportional to the VSS values. Model 3, $C_{TM} \times (VSS/C_{SM}) = A \times VSS + B$ corresponds to the relationships observed in Figures 52 through 75. Table 45 presents the Model 3 parameters A and B, and Table 46 the squared correlation coefficients of the simplified linear Model 3. The high squared correlation coefficients of Table 46 indicate that Model 3 is extremely accurate, particularly in predicting the metals distribution in raw sewage and mixed liquor. Poorest correlation in raw sewage, although still quite good, is observed for nickel and zinc. Raw sewage correlation coefficients for all other metals exceed 0.95. Correlation coefficients for all metals in mixed liquor exceed 0.98, reflecting the predominance of the sludge bound metal in that process liquid.

As would be expected, the correlation coefficients for primary effluent and secondary effluent are somewhat lower than for raw sewage, since in these two effluents, the distribution is at least in part influenced by the efficiency of clarifier suspended solids (and associated solids-bound metals) removal.

The results of these evaluations, for the several models considered, are that the simple Model 3 provides best prediction of the distribution of all metals in all process streams, and the fit of Model 3 to the observed data is excellent, as indicated by the regression analysis correlation coefficients. The fit of data to Model 3 is also illustrated in the computer-generated graphs contained in Figures B.1 through B.8 of Appendix B.

One aspect of the distribution behavior pattern described by Model 3, and demonstrated in Figures 52 through 75, is that at any fixed value of C_{TM}, metal concentration per unit weight of sludge increases as total VSS decreases. For example, considering cadmium in raw sewage at a C_{TM} of 0.2 mg/l, the values of C_{SM}/VSS at VSS levels of 25, 15 and 5 mg/l are 7, 11 and 38 µg/mg, respectively. This pattern suggests that same factor controls or establishes the maximum possible soluble metal level, and the excess metal above that maximum is "driven" onto the VSS present.

TABLE 45. REGRESSION CONSTANTS FOR METALS DISTRIBUTION MODEL 3

Metal	Constant	Process Liquid: Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	A	1.23	0.96	1.00	1.09
	B	-0.58	11.23	11.19	3.26
Cadmium	A	1.34	1.24	1.05	1.08
	B	-1.37	2.50	-17.02	6.45
Chromium	A	1.05	1.03	1.00	1.02
	B	-0.70	0.01	-0.01	0.15
Copper	A	1.06	1.08	1.00	1.02
	B	0.67	-0.71	4.88	1.02
Iron	A	1.17	1.11	0.99	1.02
	B	-2.59	-0.28	24.07	0.84
Lead	A	1.34	1.50	1.00	1.70
	B	2.93	-6.13	21.19	-1.18
Nickel	A	1.52	1.94	1.00	2.69
	B	-2.15	-1.37	92.69	-13.77
Zinc	A	1.09	1.16	1.00	0.90
	B	7.34	1.42	16.62	5.06

TABLE 46. SQUARED CORRELATION COEFFICIENTS FOR METALS DISTRIBUTION MODEL 3

Metal	Process Liquid			
	Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	0.959	0.749	0.999	0.852
Cadmium	0.970	0.837	0.997	0.720
Chromium	0.999	0.999	0.999	0.999
Copper	0.996	0.989	0.999	0.992
Iron	0.989	0.984	0.998	0.949
Lead	0.877	0.840	0.997	0.826
Nickel	0.803	0.560	0.986	0.909
Zinc	0.953	0.914	0.999	0.814

Model 3 correlates C_{TM} and C_{SM} as a function of VSS concentration. At high values of VSS, the term (A x VSS + B)/VSS is essentially constant, and another correlation is feasible. That is the direct correlation between C_{TM} and C_{SM}, without VSS.

$$(C_{TM} = pC_{SM} + q)$$

The relationships between C_{TM} and C_{SM} as described in Model 4 are shown in Figures B.9 through B.16 of Appendix B. At high VSS values, where C_{TM} or C_{SM} also have high values, the plots demonstrate good linear relationships. In lower C_{TM} or C_{SM} domains, particularly where VSS is also low, there is more scattering, with nonlinear aspects. The slope, p, and intersection, q, of the linear regression for Model 4 are listed in Table 47. The intercept value, q, represents the residual solubility of the metal in the system, and at C_{TM} values below this intercept value, all metal present is predicted to be in solution. At C_{TM} value in excess of the intercept value, the slope, p, represents the distribution of the increment in total metal between the sludge and soluble phases. The intercept value for each metal across all four process liquids remains essentially constant, indicating little or no change in the soluble concentration of each metal from raw sewage to secondary effluent. These patterns were also noted in the averaged performance of the 39 runs as summarized in Table 36, and in fact the q values are extremely close to the average soluble metals concentrations noted in Table 36.

Table 48 lists the squared correlation coefficients for Model 4, as tested against the pilot data. The squared correlation coefficients, r^2, are all very close to a value of unity. The lowest value, obtained for nickel in primary effluent is $r^2 = 0.90885$ ($r = 0.95334$). The highest value is $r^2 = 0.99999$, for chromium in mixed liquor. This simplified model must be employed with caution, and only within the range of C_{TM} and VSS values for which the experimental data apply. At C_{TM} values exceeding the maximum values indicated on Figures B.9 through B.16 of Appendix B, the metals for which the slope, p, in Table 47 is less than 1.0 could be predicted to have values of C_{SM} exceeding C_{TM}. This condition obviously cannot occur.

In applying Model 4, for the overall process model development, it is necessary to calculate C_{SM} from given values of C_{TM}. Therefore, Model 4 has been rearranged as shown below, and Table 49 presents the calculated values of p′ and q′ for Model 4′.

TABLE 47. REGRESSION CONSTANTS FOR METALS DISTRIBUTION MODEL 4

Metal	Constant	Process Liquid: Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	p	0.953	0.890	1.003	0.955
	q	0.107	0.122	0.038	0.100
Cadmium	p	1.045	1.089	1.035	1.022
	q	0.011	0.009	0.001	0.012
Chromium	p	1.002	1.004	1.001	1.007
	q	0.004	0.003	0.002	0.003
Copper	p	1.016	1.018	1.001	1.001
	q	0.012	0.007	0.009	0.012
Iron	p	0.997	0.992	0.999	0.945
	q	0.173	0.107	0.106	0.108
Lead	p	1.036	1.024	1.007	1.137
	q	0.015	0.013	0.010	0.011
Nickel	p	1.033	1.090	1.019	1.300
	q	0.276	0.245	0.172	0.106
Zinc	p	0.928	0.961	0.997	0.943
	q	0.137	0.096	0.108	0.090

Units of q are mg/l.

TABLE 48. SQUARED CORRELATION COEFFICIENTS FOR METALS DISTRIBUTION MODEL 4

Metal	Process Liquid			
	Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	0.975	0.961	0.999	0.961
Cadmium	0.963	0.944	0.994	0.947
Chromium	0.999	0.999	0.999	0.999
Copper	0.998	0.998	0.999	0.998
Iron	0.993	0.985	0.999	0.983
Lead	0.976	0.981	0.999	0.953
Nickel	0.964	0.909	0.999	0.913
Zinc	0.981	0.992	0.999	0.988

TABLE 49. REGRESSION CONSTANTS FOR METALS DISTRIBUTION MODEL 4

Metal	Constant	Process Liquid: Raw Sewage	Primary Effluent	Mixed Liquor	Secondary Effluent
Aluminum	p'	1.023	1.079	0.997	1.006
	q'	-0.096	-0.117	-0.037	-0.086
Cadmium	p'	0.921	0.875	0.961	0.926
	q'	-0.007	-0.005	0.001	-0.009
Chromium	p'	0.998	0.996	0.998	0.993
	q'	-0.004	-0.003	-0.002	-0.003
Copper	p'	0.982	0.980	0.999	0.987
	q'	-0.011	-0.007	-0.009	-0.012
Iron	p'	1.027	0.993	1.001	1.040
	q'	-0.166	-0.088	-0.106	-0.095
Lead	p'	0.942	0.959	0.993	0.838
	q'	-0.012	-0.011	-0.009	-0.007
Nickel	p'	0.934	0.834	0.981	0.705
	q'	-0.220	-0.157	-0.164	-0.033
Zinc	p'	1.057	1.032	1.002	1.048
	q'	-0.132	-0.094	-0.107	-0.089

$$C_{SM} = p' \times C_{TM} + q' \qquad \text{Model 4'}$$

In summary, the correlation of Model 3, between $C_{TM} \times (VSS/C_{SM})$ and VSS, though simple, is a good predictive model for metals distribution between the solid and liquid phases in the process liquors. The relative prediction error of the model ranges from 1 to 26% and averages 13% for raw sewage, 0 to 7% and averages 1% for mixed liquor, 1 to 30% and averages 12% for primary effluent and 1 to 25% and averages 15% for secondary effluent. Good prediction is also possible using Model 4, involving a direct correlation between C_{TM} and C_{SM}, as long as conditions fall within the range of the experimental data base, and high values of VSS are present.

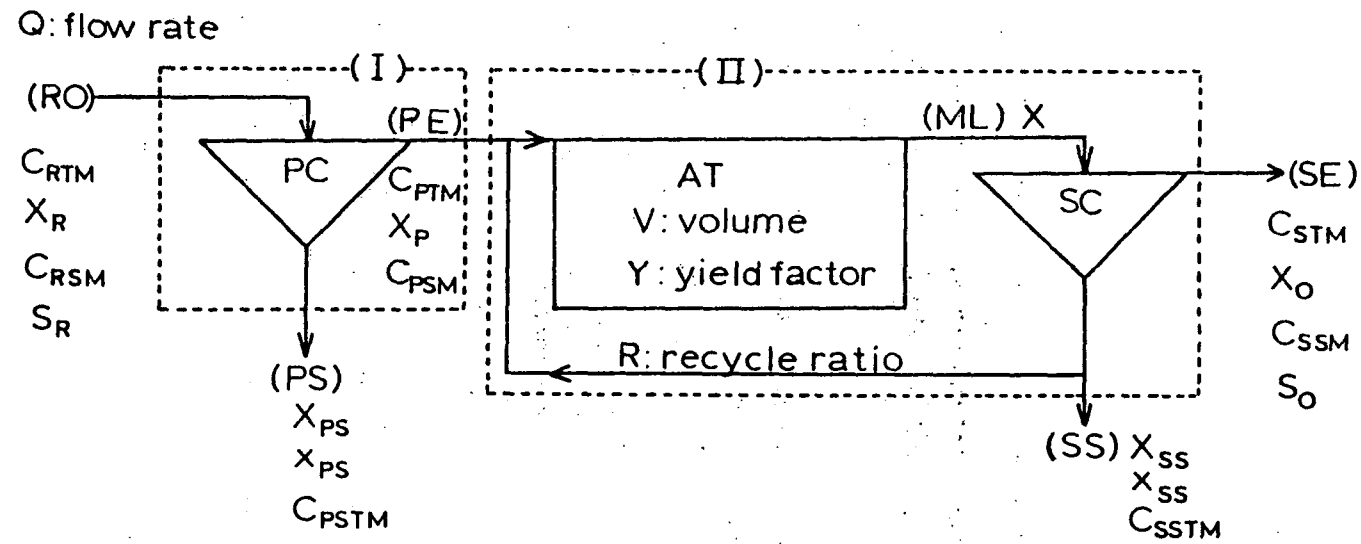
PROCESS MODELS

Process models are developed here to predict the removal of heavy metals through the complete combined treatment system. The predictive process models are checked against the measured data of the 39 continuously run pilot-scale plants. The process models, built upon material balance equations through the plant, are intended to predict the effluent heavy metals concentrations from the given inflow heavy metal concentration and from the operating conditions of the plant. A prediction of the percentages of influent heavy metals contained in the primary clarifier sludge and the secondary clarifier sludge can also be performed, as part of the application of the predictive process model.

The model continuous treatment plant is illustrated in Figure 76. Symbolic codes and nomenclature are also included in Figure 76.

Predictive Process Model for Primary Effluent Metal Concentra- Based Upon the Raw Sewage Condition

Based on the metals and TSS balances around the primary clarifier, a predictive process model, Model PW, has been developed. Model PW predicts the total metals concentration, C_{pTM}, of the primary effluent, from the influent total metal concentration (C_{RTM}), and the operating condition of the primary clarifier. The operating condition utilized is the efficiency, Z_p, of VSS removed through the primary clarifier.



PC = Primary Clarifier
AT = Aeration Tank
SC = Secondary Clarifier
RO = Raw Sewage
ML = Mixed Liquor
PS = Primary Sludge
PE = Primary Effluent
SE = Secondary Effluent
SS = Secondary Sludge

Figure 76. Schematic of continuous flow combined treatment system.

$$Z_p \simeq (\chi_R - \chi_p)/\chi_R$$

where χ_R and χ_p are the VSS values for raw sewage and primary effluent, respectively. One assumption of Model PW is that the metal content in the primary sludge phase, χ_p (mg metal/mg VSS), is a weighted mean value, with weight W, between the influent metal content in that solid phase, C_{RSM}/χ_R, and the primary effluent metal content in that solid phase, C_{PSM}/χ_p, C_{RSM} and C_{PSM} are the solids bound metals concentrations for raw sewage and primary effluent, respectively. Where W = 1.0, the value of C_{RSM}/VSS is used, and where W = 0.0, the value of C_{PSM}/VSS is used. A W value of 0.5 represents an arithmetic averaged between influent and effluent metal per unit VSS levels.

The equation to describe this assumption is

$$\chi_p = W\ (C_{RSM}/\chi_R) + (1 - W)\ (C_{PSM}/\chi_p)$$

Appendix C presents the derivation of Model PW. Tables 50 and 51 present the mean predicted errors and relative standard deviations of Model PW, as based upon Models 3 and 4', respectively.

Model PW develops a mass balance for influent, effluent, and settled sludge components of the primary clarifier. A more simple approach is possible if only the effluent conditions are to be predicted, based upon the influent conditions. The steps in performing this mass balance prediction around the primary clarifier are as follows:

1. For a given C_{RTM} and Z_p if using Model 4', or C_{RTM}, Z_p, and raw sewage VSS for Model 3, calculate the concentration of C_{RSM}. By difference between C_{RTM} and C_{RSM}, determine C_{SOL}, the soluble metal level.

2. For C_{RSM}, calculate C_{PSM} as a function of Z_p

$$C_{PSM} = (1 - Z_p)\ C_{RSM}$$

The predicted total metal in the primary effluent is then C_{PSM} plus C_{SOL}, equals C_{PTM}.

TABLE 50. MEAN PREDICTION ERROR AND RELATIVE STANDARD DEVIATION OF MODEL PW AT W = 1.0, BASED ON MODEL 3

Metal	Prediction Error	Standard Deviation
Aluminum	0.214	0.139
Cadmium	0.288	0.193
Chromium	0.179	0.071
Copper	0.241	0.114
Iron	0.248	0.195
Lead	0.301	0.346
Nickel	0.229	0.168
Zinc	0.184	0.065

$Z_p = 0.277$

TABLE 51. MEAN PREDICTION ERROR AND RELATIVE STANDARD DEVIATION OF MODEL PW AT W = 1.0, BASED ON MODEL 4´

Metal	Prediction Error	Standard Deviation
Aluminum	0.196	0.093
Cadmium	0.261	0.134
Chromium	0.185	0.056
Copper	0.250	0.090
Iron	0.238	0.153
Lead	0.255	0.205
Nickel	0.254	0.240
Zinc	0.197	0.044

$Z_p = 0.314$

Table 52 presents the results of this prediction around the primary clarifier, using Model 4´. The input data are the average values of C_{RTM} and Z_p, from Table 36. The predicted values of C_{PTM} are compared with the actual averaged values and for most of the metals are quite close. Even for copper and nickel, the predicted values of C_{PTM} were only in error by about 20%.

Predictive Process Model for Secondary Effluent Metal Concentration from the Raw Sewage Condition

By performing a material balance of VSS and metal around Domain II in Figure 76, including SOC biodegradation associated with sludge yield in the aeration tank, the predictive process model for the full-process system, Model FS, is developed. This model is fully derived in Appendix C. When the researchers utilize the semi-empirical correlation of Model 4´, as demonstrated in Appendix C, then,

$$C_{STM}^{pred.} = (C_{PTM}^{pred.} - q_S^1 \times J)/(1 + p_S^1 \times J)$$

is the derived predictive equation of the process model. $C_{STM}^{pred.}$, the secondary effluent total metal, is the target of the prediction. $C_{PTM}^{pred.}$ is the predicted C_{PTM} for the given C_{RTM} through Model PW, developed above. J is defined as,

$$J = (\chi_p - \chi_o + Y\ (1 + R)(S_R - S_o) - k_d \times \chi \times V/s)/\chi_o$$

J is related to the sludge generation in the aeration tanks, where χ_p, χ_o and χ are VSS values for primary effluent, secondary effluent and mixed liquor (see Figure 76). S_R and S_o are the SOC values for raw sewage and secondary effluent. V and Q are the volume of the aeration tank, and the influent flow rate. The constant, k_d, is the endogenous reaction constant. Y is the yield factor, with substrate expressed as SOC.

The computed means of the relative prediction errors, and the relative standard deviations on C_{STM} with Model FS are shown in Table 53 for Model 3, and Table 54 for Model 4´. The fit of the Model FS, based upon Models 3 and 4´, is quite good.

TABLE 52. APPLICATION OF MODEL PW TO AVERAGED PRIMARY CLARIFIER PERFORMANCE FOR 39 RUNS

Metal	Measured C_{RTM} (1)	Calculated Values (3) C_{RSM}	C_{SOL}	C_{PTM} (2)	Measured C_{PTM} (1)	Present Error
Aluminum	0.652	0.571	0.081	0.471	0.478	- 1.5
Cadmium	0.080	0.067	0.013	0.059	0.062	- 4.8
Chromium	0.241	0.236	0.004	0.165	0.170	- 2.9
Copper	0.303	0.287	0.016	0.212	0.268	-20.9
Iron	1.778	1.660	0.118	1.332	1.247	6.8
Lead	0.142	0.122	0.020	0.117	0.100	17.0
Nickel	1.064	0.774	0.290	0.819	0.674	21.5
Zinc	0.657	0.562	0.095	0.479	0.548	-12.6

(1) Values taken from Table 36
(2) Based upon average per cent VSS removal in primary clarifier of 31.7%
(3) Calculations based upon Model 4

Prediction of Heavy Metal Removal Through the Combined Treatment System

As the final objective of this investigation, the metal removal percentage from the primary and secondary sludge is predicted by the process Model FS, and compared with the measured removal percentage, based on the pilot-scale data.

By utilizing the PW model, the heavy metal removal rate, $H_{PS} = \chi_{PS} \times Q \times (\chi_R - \chi_p)$, in mg of metal/hour is determined for the primary sludge. Regarding the secondary sludge, the following relationship is used.

$$H_{SS} = \chi_{SS}(Q\{(\chi_p - \chi_o) + Y(1 + R)\ (S_R - S_o)\} - k_d\chi V)$$

The secondary effluent rate is $H_O = C_{STM}^{pred.} \times Q$.

χ_{PS} and χ_{SS} are predicted as

$$\chi_{PS} = W(C_{RSM}/\chi_R) + (1-W)\ (C_{PSM}/\chi_p)$$

$$\chi_{SS} = C_{SSM}/\chi_o$$

C_{RSM}, C_{PSM} and C_{SSM} are predicted by C_{RTM}, $C_{PTM}^{pred.}$ and $C_{STM}^{pred.}$ through either Model 3 or 4[1].

From the predicted values of heavy metal content in the sludge χ_{PS} and χ_{SS}, H_{PS}, H_{SS} and H_O can be calculated, and therefore, the percentages:

$$\% \text{ PS} = (H_{PS}/H_T) \times 100$$
$$\% \text{ SS} = (H_{SS}/H_T) \times 100$$
$$\% \text{ SE} = (H_O/H_T) \times 100$$

where $H_T = H_{PS} + H_{SS} + H_O$

Tables 55 and 56 present the predicted and measured performance, for $W = 1.0$, $k_d = 0.0$, based upon Model 3 and Model 4, respectively. Further, as shown in Tables 55 and 56, the predicted performance is quite close to the measured performance, for most of the metals.

TABLE 53. MEAN PREDICTION ERROR AND RELATIVE STANDARD DEVIATION OF MODEL FS AT W = 1.0, BASED ON MODEL 3

Metal	Prediction Error	Standard Deviation
Aluminum	0.340	0.167
Cadmium	0.310	0.195
Chromium	0.400	0.195
Copper	0.346	0.239
Iron	0.402	0.175
Lead	0.337	0.275
Nickel	0.375	0.243
Zinc	0.261	0.172

Note: $k_d = 0.0$, $Y = 0.438$, $Z_{SOC} = 0.485$

TABLE 54. MEAN PREDICTION ERROR AND RELATIVE STANDARD DEVIATION OF MODEL FS AT W = 1.0, BASED ON MODEL 4

Metal	Prediction Error	Standard Deviation
Aluminum	0.303	0.178
Cadmium	0.272	0.201
Chromium	0.412	0.192
Copper	0.326	0.244
Iron	0.365	0.177
Lead	0.309	0.295
Nickel	0.382	0.240
Zinc	0.231	0.160

Note: $k_d = 0.0$, $Y = 0.238$, $Z_{SOC} = 0.485$

TABLE 55. FULL SYSTEM PREDICTED AND MEASURED METALS DISTRIBUTION, BASED UPON DISTRIBUTION MODEL 3

Metal		Per Cent Metal In Primary Sludge	Secondary Sludge	Secondary Effluent
Aluminum	Measured	18.1	22.2	59.7
	Predicted	22.9	21.6	55.5
Cadmium	Measured	16.7	40.8	42.5
	Predicted	21.5	21.5	37.0
Chromium	Measured	32.2	14.5	52.2
	Predicted	27.3	22.9	49.8
Copper	Measured	11.1	37.1	48.8
	Predicted	25.7	24.7	49.7
Iron	Measured	32.3	16.1	51.6
	Predicted	26.0	24.3	49.7
Lead	Measured	29.5	30.5	40.0
	Predicted	19.2	21.0	59.7
Nickel	Measured	38.2	27.7	34.1
	Predicted	19.6	20.4	60.0
Zinc	Measured	14.5	24.0	61.4
	Predicted	21.0	22.7	56.3

Note: Results for all metals based only upon runs yielding net metals removals from PE to SE.

TABLE 56. FULL SYSTEM PREDICTED AND MEASURED METALS DISTRIBUTION, BASED UPON DISTRIBUTION MODEL 4

Metal		Per Cent Metal In Primary Sludge	Secondary Sludge	Secondary Effluent
Aluminum	Measured	18.1	22.2	59.7
	Predicted	27.4	21.7	50.9
Cadmium	Measured	16.7	40.8	42.5
	Predicted	26.4	23.4	50.1
Chromium	Measured	33.2	14.5	52.2
	Predicted	31.0	24.0	45.0
Copper	Measured	14.1	37.1	48.8
	Predicted	29.8	24.8	45.4
Iron	Measured	32.3	16.1	51.6
	Predicted	29.6	24.9	45.5
Lead	Measured	29.5	30.5	40.0
	Predicted	24.0	22.5	50.5
Nickel	Measured	38.2	27.7	34.1
	Predicted	25.1	21.7	53.2
Zinc	Measured	14.5	24.0	61.4
	Predicted	24.3	23.0	49.8

Note: Results for all metals based only upon runs yielding net metals removals from PE to SE.

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APPENDIX A

SUMMARY TABLES OF AVERAGE OPERATIONAL CHARACTERISTICS OF PILOT ACTIVATED SLUDGE SYSTEMS--TREATMENT NOS. 1 THROUGH 39.

TABLE A-1. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-1

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.58	7.61	7.88	8.28	7.12	7.71
TSS, mg/l		116	84	1581	20	11045	8599
TVSS, mg/l		82	66	1176	12	9467	6389
SOC, mg/l		35.7	28.3	17.7	11.7		
Chloride, mg/l		336			355		
Sulfate, mg/l		154			162		
Phosphate, mg/l		2.5			2.4		
Ammonia-N, mg/l		-			-		
Aluminum	Total	783	737	4704	340	7.89	17.68
	Soluble	49	32	30	55		
Cadmium	Total	25	22	336	20	0.60	0.52
	Soluble	3	3	3	5		
Chromium	Total	135	118	1005	99	1.07	2.33
	Soluble	3	2	2	2		
Copper	Total	393	353	3621	165	4.89	6.88
	Soluble	19	12	16	22		
Iron	Total	1265	1192	2047	1229	39.17	57.20
	Soluble	135	134	74	32		
Lead	Total	81	58	497	36	1.51	2.58
	Soluble	9	30	14	11		
Nickel	Total	672	633	3072	595	16.78	18.93
	Soluble	173	176	258	241		
Zinc	Total	482	450	5510	370	48.22	22.46
	Soluble	80	56	87	89		

All metal concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-2. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-2

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.20	7.62	7.99	8.23	7.06	7.98
TSS, mg/l		36	54	1762	17	2156	5802
TVSS, mg/l		26	41	1132	11	1513	3825
SOC, mg/l		39.1	22.6	13.4	8.7		
Chloride, mg/l		222			203		
Sulfate, mg/l		145			132		
Phosphate, mg/l		0.8			0.9		
Ammonia-N, mg/l		4.5			0.3		
Aluminum	Total	433	360	3537	357	25.82	17.88
	Soluble	87	75	69	120		
Cadmium	Total	42	35	572	30	1.52	1.36
	Soluble	6	5	6	7		
Chromium	Total	143	122	1526	131	1.75	1.33
	Soluble	2	2	2	2		
Copper	Total	359	337	2820	268	5.14	5.06
	Soluble	9	7	11	11		
Iron	Total	1542	1126	32170	1489	53.80	36.70
	Soluble	221	125	46	21		
Lead	Total	93	44	1702	23	3.05	2.80
	Soluble	11	8	15	9		
Nickel	Total	756	454	3403	1089	11.84	7.15
	Soluble	341	263	316	278		
Zinc	Total	413	367	11075	312	29.92	18.09
	Soluble	118	161	153	162		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-3. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-3

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.09	7.44	7.77	8.27	6.89	7.90
TSS, mg/l		178	56	2540	16	811	5292
TVSS, mg/l		128	37	1786	10	18	3695
SOC, mg/l		75.3	28.9	20.6	15.3		
Chloride, mg/l		169			142		
Sulfate, mg/l		133			128		
Phosphate, mg/l		0.4			0.4		
Ammonia-N, mg/l		3.9			0.2		
Aluminum	Total	1003	819	19339	425	27.61	1.32
	Soluble	155	131	125	178		
Cadmium	Total	140	96	468	41	0.58	0.70
	Soluble	23	30	25	28		
Chromium	Total	174	137	1514	116	1.69	1.55
	Soluble	5	5	5	5		
Copper	Total	274	268	4586	164	5.36	2.97
	Soluble	26	10	16	21		
Iron	Total	1750	1650	50214	886	59.79	6.60
	Soluble	244	129	62	23		
Lead	Total	293	264	2814	79	3.89	1.16
	Soluble	47	62	37	22		
Nickel	Total	1629	1413	7307	1337	7.88	1.48
	Soluble	315	332	333	260		
Zinc	Total	1114	571	18983	375	19.71	2.14
	Soluble	66	63	52	39		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-4. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-4

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.26	7.39	7.81	7.93	6.86	7.43
TSS, mg/l		44	55	2175	51	21765	11110
TVSS, mg/l		31	39	1445	25	8610	7075
SOC, mg/l		5.0	6.3	5.4	3.4		
Chloride, mg/l		-			50		
Sulfate, mg/l		-			69		
Phosphate, mg/l		-			0.4		
Ammonia-N, mg/l		-			0.5		
Aluminum	Total	1310	938	15440	890	23.60	24.44
	Soluble	19	28	26	28		
Cadmium	Total	80	78	544	35	0.68	0.62
	Soluble	6	12	5	8		
Chromium	Total	630	490	2720	400	3.35	3.16
	Soluble	5	5	5	5		
Copper	Total	280	240	5860	250	5.84	5.72
	Soluble	7	7	10	12		
Iron	Total	1460	1050	56000	1175	104.80	77.10
	Soluble	51	64	17	37		
Lead	Total	140	90	2960	40	6.64	5.78
	Soluble	10	7	8	5		
Nickel	Total	2740	596	16780	666	22.18	19.28
	Soluble	226	196	174	146		
Zinc	Total	826	744	27750	754	66.17	43.96
	Soluble	15	14	9	5		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-5. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-5

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.65	7.63	7.94	8.31	6.87	7.86
TSS, mg/l		111	81	1315	18	12561	5599
TVSS, mg/l		98	58	934	12	10745	4299
SOC, mg/l		29.2	28.1	18.4	12.8		
Chloride, mg/l		336			352		
Sulfate, mg/l		154			155		
Phosphate, mg/l		2.5			2.6		
Ammonia-N, mg/l		-			-		
Aluminum	Total	678	515	2455	334	6.90	12.31
	Soluble	39	39	31	35		
Cadmium	Total	12	12	58	10	0.45	0.39
	Soluble	3	3	4	3		
Chromium	Total	113	88	433	97	0.29	0.97
	Soluble	3	2	2	2		
Copper	Total	90	78	624	73	1.94	2.36
	Soluble	12	10	10	11		
Iron	Total	1399	1231	1934	1223	45.17	46.83
	Soluble	114	111	114	81		
Lead	Total	35	32	233	29	0.98	1.19
	Soluble	27	20	22	9		
Nickel	Total	334	244	314	151	1.61	0.88
	Soluble	52	38	26	22		
Zinc	Total	409	350	2145	282	16.20	13.95
	Soluble	62	38	39	51		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-6. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-6

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.46	7.60	7.92	8.34	7.01	7.96
TSS, mg/l		42	46	1460	19	3045	5782
TVSS, mg/l		29	34	981	12	2279	4194
SOC, mg/l		33.7	28.6	14.5	10.4		
Chloride, mg/l		222			206		
Sulfate, mg/l		145			140		
Phosphate, mg/l		0.8			1.1		
Ammonia-N, mg/l		4.5			0.3		
Aluminum	Total	298	279	5828	287	21.09	17.19
	Soluble	76	68	62	74		
Cadmium	Total	124	53	249	19	0.65	0.45
	Soluble	6	6	6	5		
Chromium	Total	84	82	719	78	1.39	0.82
	Soluble	2	2	2	2		
Copper	Total	161	235	1859	161	5.17	4.64
	Soluble	10	9	10	10		
Iron	Total	1247	1207	24348	1138	53.06	34.15
	Soluble	103	107	56	55		
Lead	Total	37	52	1013	27	3.21	3.49
	Soluble	8	18	6	8		
Nickel	Total	369	308	1150	368	6.98	4.99
	Soluble	81	143	98	97		
Zinc	Total	383	332	5600	264	16.25	19.53
	Soluble	153	159	149	122		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-7. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-7

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.27	7.42	7.82	8.28	6.47	7.97
TSS, mg/l		61	41	1943	16	605	4268
TVSS, mg/l		52	32	1215	11	12	2695
SOC, mg/l		36.0	30.1	21.1	18.1		
Chloride, mg/l		169			158		
Sulfate, mg/l		133			133		
Phosphate, mg/l		0.4			0.4		
Ammonia-N, mg/l		3.9			0.2		
Aluminum	Total	375	311	12215	657	26.12	10.04
	Soluble	194	176	110	162		
Cadmium	Total	63	44	500	44	0.51	1.10
	Soluble	34	32	30	23		
Chromium	Total	150	112	1392	130	1.60	1.49
	Soluble	5	5	5	5		
Copper	Total	177	159	2300	92	2.69	1.64
	Soluble	16	13	14	12		
Iron	Total	1292	1080	28667	1208	31.00	4.75
	Soluble	98	125	109	55		
Lead	Total	75	50	1675	50	1.50	0.64
	Soluble	37	33	55	30		
Nickel	Total	1780	970	2263	366	1.20	0.68
	Soluble	79	26	22	11		
Zinc	Total	481	420	5875	292	9.88	3.60
	Soluble	64	59	39	31		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-8. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-8

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.32	7.64	7.68	8.23	6.80	7.73
TSS, mg/l		30	31	2086	23	3748	1899
TVSS, mg/l		18	20	1425	17	2510	1224
SOC, mg/l		14.3	9.6	11.8	10.5		
Chloride, mg/l		110			94		
Sulfate, mg/l		108			123		
Phosphate, mg/l		0.2			0.5		
Ammonia-N, mg/l		1.8			0.3		
Aluminum	Total	372	303	3037	327	26.08	16.74
	Soluble	105	106	80	147		
Cadmium	Total	143	132	502	70	0.58	0.59
	Soluble	25	11	15	19		
Chromium	Total	128	122	1250	110	1.31	1.67
	Soluble	5	5	5	5		
Copper	Total	530	254	4100	290	3.89	5.58
	Soluble	46	18	14	15		
Iron	Total	1610	1170	20000	850	20.10	43.20
	Soluble	52	70	52	79		
Lead	Total	320	210	3440	140	3.02	4.76
	Soluble	16	16	18	10		
Nickel	Total	1220	420	1663	472	7.06	10.71
	Soluble	497	420	331	236		
Zinc	Total	830	440	8675	420	8.39	6.10
	Soluble	85	100	65	32		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-9. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-9

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.20	7.34	7.72	8.01	6.91	7.68
TSS, mg/l		40	33	1153	27	8160	4430
TVSS, mg/l		18	19	473	14	5020	2605
SOC, mg/l		9.1	9.2	7.2	6.6		
Chloride, mg/l		-			80		
Sulfate, mg/l		-			90		
Phosphate, mg/l		-			0.5		
Ammonia-N, mg/l		-			0.6		
Aluminum	Total	851	548	5725	393	23.10	46.13
	Soluble	25	23	35	45		
Cadmium	Total	94	173	528	80	0.69	0.79
	Soluble	39	54	57	50		
Chromium	Total	838	488	2475	375	3.25	3.81
	Soluble	5	5	5	5		
Copper	Total	463	588	4775	350	5.52	5.55
	Soluble	29	43	32	32		
Iron	Total	4000	2058	27875	1155	76.25	106.63
	Soluble	44	237	164	53		
Lead	Total	186	175	1525	100	4.52	6.65
	Soluble	9	20	5	35		
Nickel	Total	2788	850	13375	875	17.50	15.85
	Soluble	607	595	535	457		
Zinc	Total	733	633	21775	713	65.00	56.00
	Soluble	91	124	68	46		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-10. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-10

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.37	7.81	7.76	8.03	10.29	7.77
TSS, mg/l		34	37	2603	37	21894	6635
TVSS, mg/l		19	24	1650	25	15430	4055
SOC, mg/l		5.3	4.4	4.2	5.1		
Chloride, mg/l		-			451		
Sulfate, mg/l		-			261		
Phosphate, mg/l		-			0.4		
Ammonia-N, mg/l		-			0.5		
Aluminum	Total	932	612	8250	754	26.75	18.63
	Soluble	42	61	14	24		
Cadmium	Total	60	37	488	53	0.60	0.59
	Soluble	9	34	40	13		
Chromium	Total	600	375	2600	413	3.12	2.55
	Soluble	5	5	5	5		
Copper	Total	150	150	5825	50	5.80	5.65
	Soluble	12	9	12	12		
Iron	Total	2675	1000	41875	963	87.88	45.00
	Soluble	13	60	39	6		
Lead	Total	150	163	1450	75	4.02	3.72
	Soluble	6	7	9	7		
Nickel	Total	838	275	16000	593	21.10	20.17
	Soluble	240	150	175	147		
Zinc	Total	1583	744	19525	1205	53.07	25.12
	Soluble	9	5	6	7		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-11. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-11

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.63	7.65	7.91	8.32	6.94	7.87
TSS, mg/l		101	101	1546	16	14201	7487
TVSS, mg/l		86	69	1134	11	11922	5515
SOC, mg/l		34.7	29.4	19.6	13.5		
Chloride, mg/l		336			358		
Sulfate, mg/l		154			162		
Phosphate, mg/l		2.5			2.5		
Ammonia-N, mg/l		-			-		
Aluminum	Total	383	367	4348	289	11.66	20.34
	Soluble	52	37	32	43		
Cadmium	Total	28	26	238	16	0.63	0.49
	Soluble	4	3	3	4		
Chromium	Total	155	131	1003	87	1.23	1.61
	Soluble	4	4	3	2		
Copper	Total	429	373	2960	108	4.41	3.53
	Soluble	18	14	12	14		
Iron	Total	1439	1303	1873	1287	39.25	39.33
	Soluble	134	98	69	35		
Lead	Total	57	51	383	29	2.12	1.98
	Soluble	21	14	40	32		
Nickel	Total	795	719	2477	436	11.15	5.70
	Soluble	187	220	205	231		
Zinc	Total	510	489	5067	320	34.44	27.60
	Soluble	58	58	75	107		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-12. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-12

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.22	7.57	7.91	8.32	6.92	7.90
TSS, mg/l		59	47	1969	20	4069	4503
TVSS, mg/l		45	46	1261	10	2819	2978
SOC, mg/l		47.0	24.1	12.4	9.7		
Chloride, mg/l		222			211		
Sulfate, mg/l		145			143		
Phosphate, mg/l		0.8			0.6		
Ammonia-N, mg/l		4.5			0.3		
Aluminum	Total	495	397	3709	273	21.40	30.14
	Soluble	81	65	79	91		
Cadmium	Total	77	66	541	41	1.14	1.20
	Soluble	12	7	6	9		
Chromium	Total	159	150	1356	117	1.86	1.65
	Soluble	2	2	2	2		
Copper	Total	479	437	2942	279	5.17	4.99
	Soluble	18	11	10	11		
Iron	Total	1641	1429	32482	1317	67.36	50.28
	Soluble	225	162	38	27		
Lead	Total	88	73	2056	30	3.65	2.30
	Soluble	16	7	6	12		
Nickel	Total	1002	938	3531	1215	12.68	8.70
	Soluble	531	515	473	475		
Zinc	Total	617	466	10100	336	22.12	8.84
	Soluble	253	245	211	204		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-13. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-13

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.07	7.44	7.74	8.24	7.07	7.93
TSS, mg/l		60	57	3133	17	1562	2528
TVSS, mg/l		82	38	2190	11	64	1761
SOC, mg/l		43.6	27.9	18.6	17.4		
Chloride, mg/l		169			145		
Sulfate, mg/l		133			129		
Phosphate, mg/l		0.4			0.2		
Ammonia-N, mg/l		3.9			0.2		
Aluminum	Total	500	323	17856	709	16.67	17.25
	Soluble	84	138	81	120		
Cadmium	Total	105	85	479	49	0.53	0.57
	Soluble	22	33	23	22		
Chromium	Total	153	103	1571	117	1.58	1.53
	Soluble	5	5	5	5		
Copper	Total	271	197	3743	176	4.56	3.17
	Soluble	14	10	7	16		
Iron	Total	1521	936	62786	779	60.67	24.60
	Soluble	246	127	37	34		
Lead	Total	158	79	2886	86	3.01	1.14
	Soluble	105	44	30	40		
Nickel	Total	869	854	13467	2183	14.56	8.74
	Soluble	537	577	536	579		
Zinc	Total	643	521	17833	314	12.67	10.62
	Soluble	67	49	56	39		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-14. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-14

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.29	7.63	7.83	8.25	6.84	7.80
TSS, mg/l		28	23	1685	22	8770	2486
TVSS, mg/l		19	15	1165	16	5367	1711
SOC, mg/l		12.6	9.0	9.0	9.3		
Chloride, mg/l		110			108		
Sulfate, mg/l		108			124		
Phosphate, mg/l		0.2			0.4		
Ammonia-N, mg/l		1.8			0.5		
Aluminum	Total	295	202	2604	215	5.38	19.32
	Soluble	90	77	47	91		
Cadmium	Total	154	197	578	120	0.61	1.02
	Soluble	31	22	24	14		
Chromium	Total	122	112	840	120	1.12	1.63
	Soluble	5	5	5	5		
Copper	Total	625	360	3740	260	5.58	6.80
	Soluble	25	17	13	11		
Iron	Total	2220	1962	28200	1210	50.80	112.38
	Soluble	70	55	56	67		
Lead	Total	170	140	2980	90	3.72	5.68
	Soluble	75	45	18	28		
Nickel	Total	986	613	8900	710	12.48	16.80
	Soluble	718	659	661	532		
Zinc	Total	553	563	12440	390	25.30	9.75
	Soluble	44	62	42	28		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-15. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-15

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.29	7.37	7.78	8.04	6.80	7.72
TSS, mg/l		40	70	610	15	8980	4508
TVSS, mg/l		20	25	378	9	5920	2833
SOC, mg/l		9.6	8.3	5.2	5.5		
Chloride, mg/l		-			88		
Sulfate, mg/l		-			94		
Phosphate, mg/l		-			0.4		
Ammonia-N, mg/l		-			0.8		
Aluminum	Total	710	416	2782	477	14.97	28.13
	Soluble	30	26	37	33		
Cadmium	Total	93	89	491	65	0.75	0.74
	Soluble	16	17	17	17		
Chromium	Total	1062	413	1425	250	2.92	3.14
	Soluble	5	5	5	5		
Copper	Total	338	267	2875	200	5.75	5.70
	Soluble	9	6	9	7		
Iron	Total	3360	1153	25875	660	78.00	114.00
	Soluble	34	35	81	31		
Lead	Total	150	113	933	88	2.85	3.25
	Soluble	5	7	5	11		
Nickel	Total	1220	740	7375	965	17.20	16.20
	Soluble	595	607	610	532		
Zinc	Total	1002	765	10425	553	59.25	56.00
	Soluble	132	133	103	92		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-16. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-16

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.38	7.41	7.59	8.08	7.04	7.78
TSS, mg/l		30	43	1408	100	18543	5970
TVSS, mg/l		19	28	1255	25	13085	3770
SOC, mg/l		4.9	5.7	3.9	3.0		
Chloride, mg/l		-			46		
Sulfate, mg/l		-			64		
Phosphate, mg/l		-			0.3		
Ammonia-N, mg/l		-			0.5		
Aluminum	Total	678	662	4480	479	14.32	24.10
	Soluble	25	45	19	29		
Cadmium	Total	55	46	348	45	0.58	0.58
	Soluble	30	12	12	6		
Chromium	Total	460	340	1600	310	2.78	2.90
	Soluble	5	5	5	5		
Copper	Total	240	170	1960	100	4.76	6.00
	Soluble	5	4	5	2		
Iron	Total	1534	744	31600	470	92.70	110.30
	Soluble	127	62	21	9		
Lead	Total	90	60	1040	20	2.58	4.18
	Soluble	6	5	7	9		
Nickel	Total	1615	626	11080	470	20.42	20.78
	Soluble	354	336	376	292		
Zinc	Total	1575	903	7020	2480	32.49	43.32
	Soluble	6	9	6	4		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrationa are in mg/l.

TABLE A-17. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-17

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		-	7.72	7.92	8.38	6.92	7.87
TSS, mg/l		111	89	1409	18	12254	10321
TVSS, mg/l		104	64	903	12	10258	7896
SOC, mg/l		29.2	29.3	34.8	14.3		
Chloride, mg/l		336			358		
Sulfate, mg/l		154			161		
Phosphate, mg/l		2.5			2.5		
Ammonia-N, mg/l		-			-		
Aluminum	Total	678	372	3807	684	11.54	17.22
	Soluble	39	39	29	43		
Cadmium	Total	12	12	265	11	0.16	0.59
	Soluble	3	4	3	3		
Chromium	Total	113	79	519	100	0.33	1.59
	Soluble	3	3	2	2		
Copper	Total	90	66	2536	77	2.68	7.07
	Soluble	12	14	16	19		
Iron	Total	1399	1251	1851	1222	38.40	57.22
	Soluble	121	106	136	67		
Lead	Total	35	27	520	25	0.96	2.11
	Soluble	29	33	13	18		
Nickel	Total	245	138	1522	207	5.01	2.12
	Soluble	52	84	123	92		
Zinc	Total	409	367	3413	310	34.56	13.70
	Soluble	62	58	71	107		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-18. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-18

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.28	7.69	7.96	8.35	6.98	7.89
TSS, mg/l		31	53	1481	14	2231	7698
TVSS, mg/l		23	39	1050	9	1561	5602
SOC, mg/l		40.8	23.3	11.8	10.5		
Chloride, mg/l		222			201		
Sulfate, mg/l		145			139		
Phosphate, mg/l		0.8			1.0		
Ammonia-N, mg/l		4.5			0.3		
Aluminum	Total	295	283	2311	197	15.89	16.18
	Soluble	84	77	60	72		
Cadmium	Total	137	80	280	27	0.53	0.35
	Soluble	7	5	6	5		
Chromium	Total	97	80	750	91	1.34	0.89
	Soluble	2	2	2	2		
Copper	Total	173	176	1914	153	5.40	5.36
	Soluble	12	10	13	12		
Iron	Total	1576	944	22189	1196	53.05	28.45
	Soluble	131	117	69	42		
Lead	Total	154	63	960	37	3.50	3.02
	Soluble	14	6	7	8		
Nickel	Total	352	418	1063	316	7.64	6.07
	Soluble	117	192	156	113		
Zinc	Total	450	388	7800	294	21.25	17.73
	Soluble	231	176	185	192		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-19. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-19

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		6.98	7.51	7.70	8.26	6.77	7.81
TSS, mg/l		230	74	3428	18	1451	6605
TVSS, mg/l		122	56	2574	11	29	4833
SOC, mg/l		40.9	25.3	19.7	14.8		
Chloride, mg/l		169			154		
Sulfate, mg/l		133			127		
Phosphate, mg/l		0.4			0.3		
Ammonia-N, mg/l		3.9			0.2		
Aluminum	Total	677	579	16562	643	26.99	6.76
	Soluble	172	133	116	164		
Cadmium	Total	88	75	472	33	0.52	0.63
	Soluble	22	12	22	15		
Chromium	Total	183	111	1400	141	1.62	1.38
	Soluble	5	5	5	5		
Copper	Total	453	322	4786	186	5.89	4.97
	Soluble	16	10	17	12		
Iron	Total	636	580	43429	574	70.93	24.54
	Soluble	113	139	65	27		
Lead	Total	267	129	2650	114	3.66	2.56
	Soluble	37	222	69	47		
Nickel	Total	2983	880	14657	2093	12.19	12.49
	Soluble	895	666	513	528		
Zinc	Total	1114	571	12367	350	17.76	4.42
	Soluble	59	80	52	42		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-20. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-20

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.21	7.68	7.76	8.23	6.45	7.72
TSS, mg/l		26	38	1765	23	6314	6053
TVSS, mg/l		14	22	1250	15	3668	4224
SOC, mg/l		14.2	10.2	6.9	8.6		
Chloride, mg/		110			93		
Sulfate, mg/l		108			121		
Phosphate, mg/l		0.2			0.4		
Ammonia-N, mg/l		1.8			0.3		
Aluminum	Total	520	357	11163	232	14.30	32.25
	Soluble	78	108	50	90		
Cadmium	Total	138	101	548	84	0.63	0.84
	Soluble	25	18	12	14		
Chromium	Total	144	93	1124	96	1.39	1.67
	Soluble	5	5	5	5		
Copper	Total	625	240	7060	370	7.52	7.08
	Soluble	46	16	25	29		
Iron	Total	1510	1980	45600	1180	68.00	103.13
	Soluble	67	38	46	105		
Lead	Total	475	310	5340	160	7.52	7.74
	Soluble	40	27	15	31		
Nickel	Total	-	590	19200	1340	19.60	20.9
	Soluble	810	808	639	503		
Zinc	Total	694	700	21250	440	33.70	14.38
	Soluble	28	59	42	35		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-21. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-21

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.29	7.44	7.80	8.04	6.86	7.67
TSS, mg/l		32	78	1880	17	7370	11058
TVSS, mg/l		15	43	1165	11	4870	6753
SOC, mg/l		8.2	12.2	6.0	5.2		
Chloride, mg/l		-			85		
Sulfate, mg/l		-			92		
Phosphate, mg/l		-			0.3		
Ammonia-N, mg/l		-			0.5		
Aluminum	Total	661	630	10033	576	52.82	38.25
	Soluble	30	29	38	50		
Cadmium	Total	146	84	625	45	0.72	0.65
	Soluble	13	13	20	18		
Chromium	Total	500	300	1638	200	3.41	3.00
	Soluble	5	5	5	5		
Copper	Total	425	610	4675	215	4.88	5.60
	Soluble	14	7	17	16		
Iron	Total	3225	1395	38333	1060	103.38	86.00
	Soluble	32	66	40	77		
Lead	Total	150	200	1725	100	5.57	5.2
	Soluble	183	5	17	7		
Nickel	Total	1678	1165	14375	1388	18.52	16.47
	Soluble	632	630	482	410		
Zinc	Total	1025	988	23200	800	44.60	54.50
	Soluble	94	97	77	84		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-22. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-22

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.39	7.47	7.67	8.08	7.03	7.67
TSS, mg/l		24	48	3938	16	11160	12225
TVSS, mg/l		14	31	2250	10	7625	7100
SOC, mg/l		5.1	6.0	3.9	3.6		
Chloride, mg/l		-			44		
Sulfate, mg/l		-			71		
Phosphate, mg/l		-			0.3		-
Ammonia-N, mg/l		-			0.5		
Aluminum	Total	983	871	9940	1091	51.30	37.96
	Soluble	35	24	12	33		
Cadmium	Total	54	43	391	29	0.59	0.57
	Soluble	5	9	7	8		
Chromium	Total	420	270	1960	330	3.18	2.88
	Soluble	5	5	5	5		
Copper	Total	270	260	6040	110	5.90	5.88
	Soluble	12	8	5	5		
Iron	Total	2510	1450	53100	940	102.40	95.80
	Soluble	16	16	7	12		
Lead	Total	140	90	2920	40	6.28	6.48
	Soluble	6	5	5	5		
Nickel	Total	1263	1212	20260	1090	23.94	21.8
	Soluble	422	407	424	364		
Zinc	Total	1860	1970	37960	1594	67.24	63.74
	Soluble	7	25	6	6		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-23. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-23

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.60	7.73	7.84	8.34	6.90	7.79
TSS, mg/l		95	93	1597	20	10339	8896
TVSS, mg/l		81	64	1126	11	8622	6635
SOC, mg/l		33.1	28.8	25.8	14.5		
Chloride, mg/l		336			339		
Sulfate, mg/l		154			166		
Phosphate, mg/l		2.5			2.3		
Ammonia-N, mg/l		-			-		
Aluminum	Total	655	801	3201	647	11.04	19.98
	Soluble	54	45	37	42		
Cadmium	Total	24	23	247	23	0.44	0.58
	Soluble	4	3	4	3		
Chromium	Total	106	111	582	100	0.80	2.00
	Soluble	4	3	2	2		
Copper	Total	308	356	2759	224	5.42	8.26
	Soluble	15	15	16	15		
Iron	Total	1378	1336	1936	1373	47.80	69.94
	Soluble	141	107	132	40		
Lead	Total	41	63	502	36	1.48	2.03
	Soluble	14	10	19	8		
Nickel	Total	680	699	2560	747	18.19	9.77
	Soluble	161	159	266	237		
Zinc	Total	564	550	4430	445	41.30	21.30
	Soluble	120	67	74	56		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-24. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-24

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.35	7.78	7.89	8.33	7.00	7.85
TSS, mg/l		42	43	1328	15	4065	5201
TVSS, mg/l		31	35	861	8	2898	3530
SOC, mg/l		42.5	19.8	12.5	9.7		
Chloride, mg/l		222			208		
Sulfate, mg/l		145			135		
Phosphate, mg/l		0.8			1.0		
Ammonia-N, mg/l		4.5			0.3		
Aluminum	Total	385	310	3288	332	18.34	21.83
	Soluble	75	78	54	82		
Cadmium	Total	157	90	442	26	0.97	0.94
	Soluble	9	5	6	7		
Chromium	Total	137	110	1116	111	1.78	1.49
	Soluble	2	2	2	2		
Copper	Total	460	313	2772	225	4.82	4.74
	Soluble	16	9	9	9		
Iron	Total	2243	1261	32738	1205	60.50	43.10
	Soluble	200	86	36	37		
Lead	Total	75	62	1564	29	3.86	3.61
	Soluble	21	9	18	18		
Nickel	Total	653	589	2519	834	12.38	8.88
	Soluble	366	333	347	318		
Zinc	Total	477	363	8575	295	29.09	15.26
	Soluble	203	134	184	129		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-25. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-25

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.13	7.60	7.70	8.29	7.25	7.85
TSS, mg/l		258	23	2925	20	395	7172
TVSS, mg/l		198	15	18.29	12	30	4611
SOC, mg/l		43.6	23.2	20.1	17.3		
Chloride, mg/l		169			151		
Sulfate, mg/l		133			128		
Phosphate, mg/l		0.4			0.5		
Ammonia-N, mg/l		3.9			0.2		
Aluminum	Total	785	515	16693	618	23.30	6.82
	Soluble	140	152	112	163		
Cadmium	Total	135	82	493	27	0.51	0.51
	Soluble	18	23	20	31		
Chromium	Total	109	83	1357	106	1.54	1.37
	Soluble	5	5	5	5		
Copper	Total	367	259	5571	173	5.84	4.58
	Soluble	9	8	23	25		
Iron	Total	2492	1400	41286	936	49.00	6.80
	Soluble	199	117	72	22		
Lead	Total	221	108	2679	43	3.54	1.47
	Soluble	47	140	58	19		
Nickel	Total	4008	1099	5533	777	6.58	2.61
	Soluble	242	195	214	142		
Zinc	Total	514	357	11950	350	22.36	3.67
	Soluble	44	35	31	19		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-26. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-26

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.45	7.69	7.73	8.20	7.03	7.79
TSS, mg/l		28	16	1843	24	4395	3167
TVSS, mg/l		12	9	1382	18	3128	2362
SOC, mg/l		12.2	11.5	8.6	8.5		
Chloride, mg/l		110			98		
Sulfate, mg/l		108			129		
Phosphate, mg/l		0.2			0.3		
Ammonia-N, mg/l		1.8			0.3		
Aluminum	Total	240	191	7212	182	8.56	17.07
	Soluble	110	126	73	139		
Cadmium	Total	128	99	553	65	0.51	0.63
	Soluble	10	9	14	17		
Chromium	Total	124	108	1070	93	1.37	1.58
	Soluble	5	5	5	5		
Copper	Total	180	270	6100	213	6.28	6.64
	Soluble	17	15	14	20		
Iron	Total	1488	920	35100	675	39.10	56.75
	Soluble	74	53	61	65		
Lead	Total	190	160	4880	75	4.70	5.20
	Soluble	11	22	46	19		
Nickel	Total	-	160	8040	613	7.32	5.25
	Soluble	232	199	176	145		
Zinc	Total	766	570	12480	400	22.74	13.82
	Soluble	62	69	79	26		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-27. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-27

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.32	7.46	7.83	8.03	6.77	7.75
TSS, mg/l		51	38	1518	19	9430	6888
TVSS, mg/l		24	23	1040	15	6180	4593
SOC, mg/l		9.0	7.7	6.0	4.4		
Chloride, mg/l		-			84		
Sulfate, mg/l		-			93		
Phosphate, mg/l		-			0.6		
Ammonia-N, mg/l		-			0.4		
Aluminum	Total	834	633	3641	301	21.25	33.50
	Soluble	52	38	42	54		
Cadmium	Total	77	68	419	56	0.74	0.46
	Soluble	84	81	34	23		
Chromium	Total	513	363	1963	288	3.24	3.42
	Soluble	5	5	5	5		
Copper	Total	363	288	4000	168	5.32	5.87
	Soluble	12	9	11	8		
Iron	Total	3200	1285	27250	625	72.50	84.25
	Soluble	49	25	52	23		
Lead	Total	175	188	2250	100	4.25	4.42
	Soluble	6	12	7	5		
Nickel	Total	2050	630	8650	620	14.00	9.67
	Soluble	377	347	302	242		
Zinc	Total	1462	1425	22375	663	63.50	59.88
	Soluble	133	141	112	73		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-28. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-28

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.35	7.44	7.76	8.04	7.08	7.63
TSS, mg/l		44	24	2455	23	6480	8870
TVSS, mg/l		30	16	1563	14	4927	5995
SOC, mg/l		5.3	6.6	3.3	3.5		
Chloride, mg/l		-			44		
Sulfate, mg/l		-			66		
Phosphate, mg/l		-			0.6		
Ammonia-N, mg/l		-			0.5		
Aluminum	Total	890	692	11600	471	32.00	16.10
	Soluble	28	53	23	38		
Cadmium	Total	37	67	462	23	0.58	0.43
	Soluble	5	8	13	4		
Chromium	Total	530	380	2340	310	3.14	2.63
	Soluble	5	5	5	5		
Copper	Total	350	250	5920	110	5.84	6.04
	Soluble	9	4	3	5		
Iron	Total	2350	1310	48500	1250	105.60	76.40
	Soluble	53	41	6	36		
Lead	Total	180	110	2720	60	5.78	6.10
	Soluble	6	5	7	7		
Nickel	Total	2132	664	13960	360	21.26	17.28
	Soluble	232	192	190	156		
Zinc	Total	2160	1830	23810	980	63.40	47.72
	Soluble	8	5	6	6		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-29. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-29

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.68	7.70	7.99	8.27	6.87	7.81
TSS, mg/l		111	74	1154	18	16318	7344
TVSS, mg/l		98	50	757	12	13781	5626
SOC, mg/l		29.2	30.2	18.2	14.8		
Chloride, mg/l		336			352		
Sulfate, mg/l		154			161		
Phosphate, mg/l		2.5			2.7		
Ammonia-N, mg/l		-			-		
Aluminum	Total	669	352	2354	338	9.37	11.88
	Soluble	39	34	56	39		
Cadmium	Total	11	11	83	9	0.18	0.35
	Soluble	3	4	3	3		
Chromium	Total	113	69	421	107	0.55	1.11
	Soluble	3	2	2	2		
Copper	Total	90	75	623	61	2.80	2.65
	Soluble	12	8	10	8		
Iron	Total	1399	1231	1885	1233	49.22	64.20
	Soluble	114	108	135	36		
Lead	Total	35	27	214	20	0.89	1.32
	Soluble	27	13	15	11		
Nickel	Total	330	179	440	186	0.93	0.58
	Soluble	52	52	42	29		
Zinc	Total	409	390	2282	290	16.60	14.68
	Soluble	62	88	61	50		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-30. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-30

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		6.68	7.67	7.90	8.31	7.08	7.85
TSS, mg/l		40	39	1141	18	2681	5257
TVSS, mg/l		30	26	686	11	2103	3924
SOC, mg/l		34.8	28.0	13.5	11.8		
Chloride, mg/l		222			208		
Sulfate, mg/l		145			138		
Phosphate, mg/l		0.8			1.1		
Ammonia-N, mg/l		4.5			0.4		
Aluminum	Total	278	197	2098	250	10.76	22.37
	Soluble	77	72	53	73		
Cadmium	Total	63	36	219	10	0.35	0.29
	Soluble	6	6	6	4		
Chromium	Total	62	63	591	116	0.98	0.92
	Soluble	2	2	2	2		
Copper	Total	162	157	1577	134	5.02	4.97
	Soluble	10	10	10	8		
Iron	Total	1527	1060	26655	1361	51.77	26.25
	Soluble	102	104	100	42		
Lead	Total	100	20	1004	16	2.81	2.09
	Soluble	8	9	9	4		
Nickel	Total	366	262	672	231	6.28	6.14
	Soluble	79	111	66	45		
Zinc	Total	440	300	7242	305	19.26	10.95
	Soluble	153	116	77	59		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-31. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-31

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.16	7.55	7.70	8.29	6.50	7.86
TSS, mg/l		240	37	3972	12	237	4316
TVSS, mg/l		185	30	1285	8	17	3441
SOC, mg/l		41.8	23.3	26.6	17.5		
Chloride, mg/l		169			153		
Sulfate, mg/l		133			128		
Phosphate, mg/l		0.4			0.6		
Ammonia-N, mg/l		3.9			0.3		
Aluminum	Total	567	385	11466	738	14.57	4.55
	Soluble	163	186	97	138		
Cadmium	Total	69	67	445	29	0.53	0.53
	Soluble	19	24	24	22		
Chromium	Total	90	86	1200	78	1.45	1.36
	Soluble	5	5	5	5		
Copper	Total	213	200	2757	113	3.95	2.73
	Soluble	16	10	7	14		
Iron	Total	936	743	26571	525	33.58	6.17
	Soluble	145	159	140	40		
Lead	Total	143	71	2043	71	2.02	0.84
	Soluble	19	58	19	22		
Nickel	Total	490	383	721	274	0.88	0.55
	Soluble	175	42	19	14		
Zinc	Total	429	486	6814	321	12.25	3.87
	Soluble	24	77	49	25		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-32. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-32

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.45	7.68	7.64	8.23	7.06	7.63
TSS, mg/l		22	22	1987	18	3511	3224
TVSS, mg/l		14	14	1435	13	2281	4140
SOC, mg/l		12.0	11.6	9.9	9.0		
Chloride, mg/l		110			97		
Sulfate, mg/l		108			127		
Phosphate, mg/l		0.2			0.3		
Ammonia-N, mg/l		1.8			0.3		
Aluminum	Total	216	121	2533	210	9.10	6.04
	Soluble	126	120	70	136		
Cadmium	Total	98	65	442	94	0.61	0.45
	Soluble	9	9	7	7		
Chromium	Total	128	96	1320	100	1.39	1.29
	Soluble	5	5	5	5		
Copper	Total	210	140	4280	130	4.34	5.16
	Soluble	46	13	15	17		
Iron	Total	650	560	19100	400	49.38	56.75
	Soluble	95	48	187	210		
Lead	Total	120	70	3280	70	5.82	5.54
	Soluble	13	10	11	11		
Nickel	Total	438	288	658	148	2.15	0.56
	Soluble	66	45	36	34		
Zinc	Total	644	672	7960	440	21.48	6.63
	Soluble	92	72	60	39		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-33. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-33

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.66	7.79	7.92	8.32	6.90	7.84
TSS, mg/l		107	84	1235	18	16010	10645
TVSS, mg/l		87	58	822	12	9334	8019
SOC, mg/l		34.2	26.4	17.6	13.7		
Chloride, mg/l		336			347		
Sulfate, mg/l		154			162		
Phosphate, mg/l		2.5			2.6		
Ammonia-N, mg/l		-			-		
Aluminum	Total	740	464	3516	450	14.00	17.23
	Soluble	40	31	44	50		
Cadmium	Total	15	19	187	15	0.48	0.65
	Soluble	4	6	4	3		
Chromium	Total	114	77	491	79	0.90	2.24
	Soluble	3	2	2	2		
Copper	Total	302	282	1631	80	4.32	3.72
	Soluble	10	7	13	12		
Iron	Total	1384	1352	2007	1234	33.70	53.22
	Soluble	80	68	42	33		
Lead	Total	66	43	365	28	1.62	1.84
	Soluble	20	9	31	9		
Nickel	Total	603	546	1874	367	14.24	7.61
	Soluble	93	112	130	111		
Zinc	Total	520	473	4282	336	38.89	23.30
	Soluble	114	55	126	38		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-34. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-34

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.17	7.72	7.91	8.32	6.91	7.86
TSS, mg/l		47	52	1337	16	3629	6809
TVSS, mg/l		53	36	834	9	2371	4443
SOC, mg/l		46.0	20.7	12.3	8.1		
Chloride, mg/l		222			202		
Sulfate, mg/l		145			145		
Phosphate, mg/l		0.8			0.7		
Ammonia-N, mg/l		4.5			0.3		
Aluminum	Total	778	464	3465	311	26.65	25.91
	Soluble	83	66	56	92		
Cadmium	Total	222	89	507	24	1.81	1.60
	Soluble	9	6	6	6		
Chromium	Total	253	169	1343	132	2.06	1.88
	Soluble	2	2	2	2		
Copper	Total	756	503	3050	300	5.45	4.88
	Soluble	18	6	11	8		
Iron	Total	2322	1526	24328	1373	73.32	58.50
	Soluble	279	104	37	15		
Lead	Total	200	64	1926	41	4.16	3.44
	Soluble	17	26	14	6		
Nickel	Total	1522	1179	3514	1318	16.49	8.70
	Soluble	570	661	586	525		
Zinc	Total	536	532	6859	436	24.91	18.41
	Soluble	315	139	247	171		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-35. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-35

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.00	7.52	7.83	8.27	7.12	7.85
TSS, mg/l		302	51	2248	19	1525	3873
TVSS, mg/l		197	31	1344	12	40	2259
SOC, mg/l		45.8	26.6	21.2	18.7		
Chloride, mg/l		169			149		
Sulfate, mg/l		133			132		
Phosphate, mg/l		0.4			0.3		
Ammonia-N, mg/l		3.9			0.2		
Aluminum	Total	1574	652	21084	855	32.45	12.46
	Soluble	140	118	149	188		
Cadmium	Total	87	56	446	38	0.45	0.49
	Soluble	23	34	28	34		
Chromium	Total	140	155	1536	127	1.81	1.52
	Soluble	5	5	5	5		
Copper	Total	1071	475	4586	135	4.60	5.02
	Soluble	18	24	9	15		
Iron	Total	2117	1490	36750	883	56.25	23.50
	Soluble	174	192	79	39		
Lead	Total	260	160	2717	75	3.33	3.31
	Soluble	22	137	50	47		
Nickel	Total	708	496	6388	775	12.35	1.62
	Soluble	420	523	550	436		
Zinc	Total	540	570	8600	350	15.95	6.97
	Soluble	61	63	30	15		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-36. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-36

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.31	7.60	7.77	8.22	6.89	7.71
TSS, mg/l		39	21	3025	47	6564	5858
TVSS, mg/l		24	32	1794	19	4528	3645
SOC, mg/l		10.7	10.7	9.8	8.9		
Chloride, mg/l		110			102		
Sulfate, mg/l		108			123		
Phosphate, mg/l		0.2			0.4		
Ammonia-N, mg/l		1.8			0.5		
Aluminum	Total	1193	1004	3736	407	16.50	21.82
	Soluble	96	97	85	120		
Cadmium	Total	102	160	692	224	0.73	1.02
	Soluble	13	13	12	14		
Chromium	Total	100	85	1500	97	1.83	1.49
	Soluble	5	5	5	5		
Copper	Total	510	360	6660	750	6.98	6.64
	Soluble	11	17	25	20		
Iron	Total	1510	1250	55500	833	80.00	22.50
	Soluble	60	80	57	69		
Lead	Total	160	140	5640	330	6.72	6.60
	Soluble	35	43	116	61		
Nickel	Total	319	288	14275	780	17.70	19.25
	Soluble	609	501	555	454		
Zinc	Total	463	488	10410	400	23.08	8.47
	Soluble	47	53	81	50		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-37. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-37

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.79	7.76	8.03	8.31	6.90	7.89
TSS, mg/l		111	96	1392	16	12787	9415
TVSS, mg/l		98	65	978	11	10773	7086
SOC, mg/l		29.2	25.1	18.3	15.9		
Chloride, mg/l		336			353		
Sulfate, mg/l		154			160		
Phosphate, mg/l		2.5			2.5		
Ammonia-N, mg/l		-			-		
Aluminum	Total	678	435	3006	486	12.88	13.40
	Soluble	39	41	44	42		
Cadmium	Total	11	11	174	11	0.49	0.52
	Soluble	3	4	4	4		
Chromium	Total	113	93	702	86	0.62	2.14
	Soluble	3	3	3	2		
Copper	Total	98	220	2000	82	2.04	3.02
	Soluble	12	11	12	12		
Iron	Total	1399	1344	1945	1311	40.95	54.89
	Soluble	114	89	62	62		
Lead	Total	35	50	417	26	0.71	2.23
	Soluble	27	17	18	14		
Nickel	Total	245	216	1388	122	8.25	0.76
	Soluble	52	96	128	122		
Zinc	Total	409	464	4179	355	40.00	15.05
	Soluble	62	39	81	49		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-38. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-38

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.26	7.66	7.98	8.36	6.95	7.90
TSS, mg/l		38	36	1261	14	3367	4899
TVSS, mg/l		28	27	887	10	2642	3478
SOC, mg/l		42.7	22.0	11.8	9.8		
Chloride, mg/l		222			211		
Sulfate, mg/l		145			141		
Phosphate, mg/l		0.8			1.0		
Ammonia-N, mg/l		4.5			0.2		
Aluminum	Total	337	218	2727	217	12.87	19.10
	Soluble	84	67	60	84		
Cadmium	Total	87	51	258	32	0.43	0.32
	Soluble	9	5	5	5		
Chromium	Total	84	79	832	107	1.22	1.30
	Soluble	2	2	2	2		
Copper	Total	170	113	2009	150	5.41	5.30
	Soluble	14	7	12	13		
Iron	Total	1483	1415	19996	1090	44.10	33.09
	Soluble	126	93	59	31		
Lead	Total	97	50	1007	23	3.08	2.67
	Soluble	10	6	7	6		
Nickel	Total	373	469	1409	300	7.57	6.20
	Soluble	123	196	135	102		
Zinc	Total	413	316	7654	229	23.31	11.69
	Soluble	145	80	119	143		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

TABLE A-39. SUMMARY OF AVERAGE OPERATIONAL CHARACTERISTICS
TREATMENT NO: A-39

Parameter		Raw Sewage	Primary Effluent	Mixed Liquor	Second. Effluent	Primary Sludge	Second. Sludge
pH		7.05	7.52	7.80	8.20	6.74	7.63
TSS, mg/l		209	33	1052	29	173	3028
TVSS, mg/l		171	26	797	20	44	2236
SOC, mg/l		60.4	23.0	21.9	20.1		
Chloride, mg/l		169			146		
Sulfate, mg/l		133			131		
Phosphate, mg/l		0.4			0.5		
Ammonia-N, mg/l		3.9			0.4		
Aluminum	Total	693	391	8232	309	21.44	1.88
	Soluble	209	196	121	166		
Cadmium	Total	81	55	476	49	0.42	0.39
	Soluble	22	25	29	29		
Chromium	Total	124	119	1193	107	1.69	1.49
	Soluble	5	5	5	5		
Copper	Total	269	193	3071	117	4.37	4.08
	Soluble	16	13	16	24		
Iron	Total	671	508	25186	458	30.83	5.80
	Soluble	170	125	71	72		
Lead	Total	100	50	1943	50	2.76	0.76
	Soluble	69	133	47	30		
Nickel	Total	619	406	1624	403	3.58	0.78
	Soluble	110	78	68	59		
Zinc	Total	450	364	6271	286	10.43	2.88
	Soluble	62	52	44	33		

All metals concentrations in micrograms/l except for primary and secondary sludges where concentrations are in mg/l.

APPENDIX B

CORRELATION OF METALS DISTRIBUTION DATA WITH PREDICTIVE MODELS

I. Correlation of Data with Model 3

II. Correlation of Data with Model 4

PART I. FIT OF EXPERIMENTAL DATA TO MODEL 3

Model 3 is expressed, from Section 8, in the form

$$C_{TM} (VSS/C_{SM}) = A (VSS) + B \qquad \text{Model 3}$$

In Figures B.1 through B.8, each figure presents a computer generator plot for one metal in the form process liquids. The data points plotted are numbers, which correspond to the Runs (1-6) of the 39 treatments tested in the pilot studies. Abbreviations are as follows:

AL - Aluminum	FE - Iron
CD - Cadmium	PB - Lead
CR - Chromium	NI - Nickel
CU - Copper	ZN - Zinc

RO - Raw Sewage
PE - Primary Effluent
ML - Mixed Liquor
SE - Secondary Effluent
TVSS - Volatile Suspended Solids

On the plots, YY is the Y-axis, corresponding to the left hand side of the Model 3 equation. Maximum values of YY and TVSS plotted are indicated on the axes, for scale. Units of both axes are mg/l.

PART II. FIT OF EXPERIMENTAL DATA TO MODEL 4

Model 4 is expressed, from Section 8, in the form

$$C_{TM} = pC_{SM} + q \qquad \text{Model 4}$$

In Figures B.9 through B.16, each figure represents a computer generated plot for one metal in the form process liquids. The data points plotted are numbers, which correspond to the Runs (1-6) of the 39 treatments tested in the pilot studies. Abbreviations are identical to those used on Figures B.1 through B.8. Units of both the X- and Y-axes are mg/l.

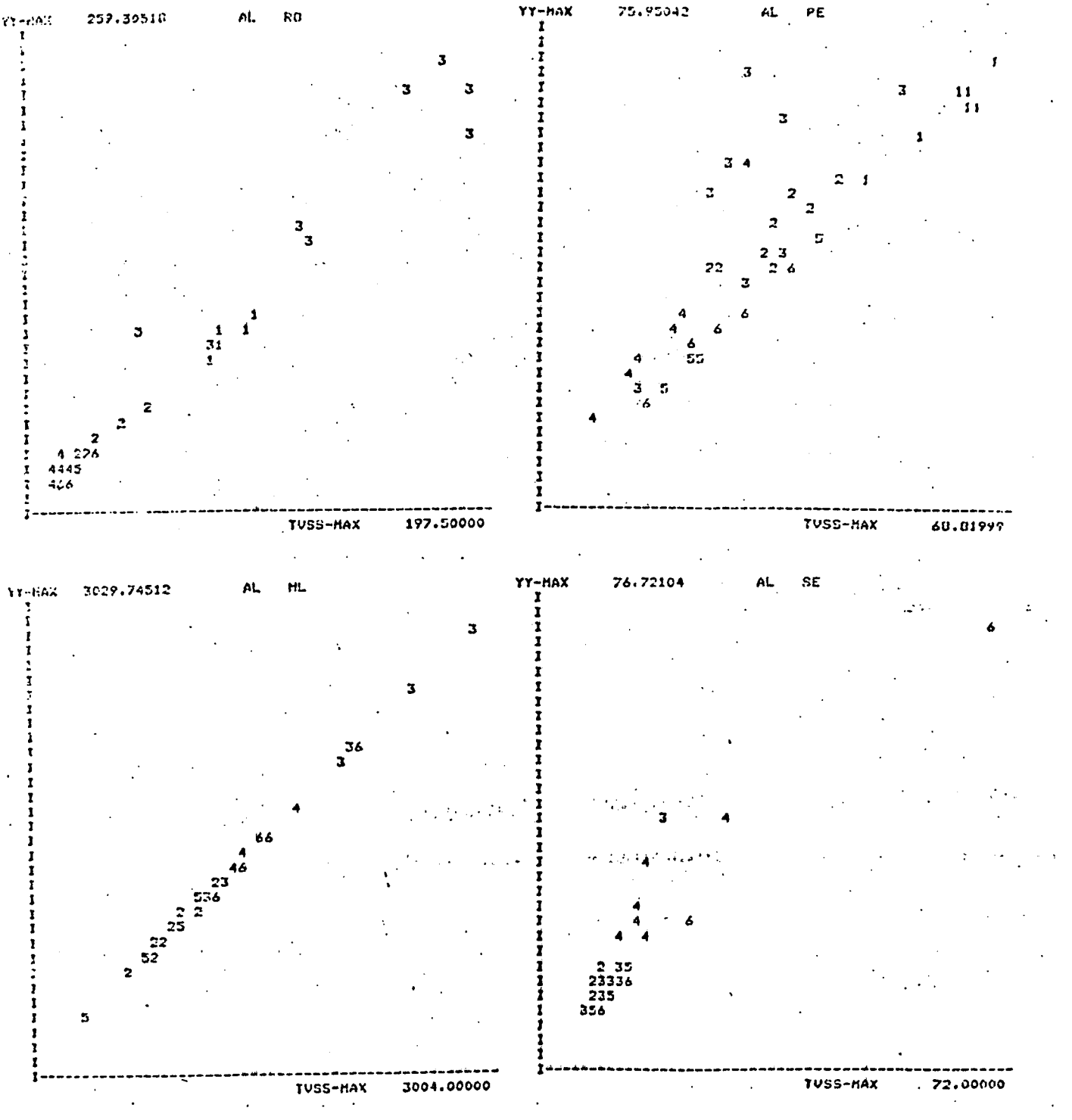

Figure B-1. Correlation of Model 3 in four process liquids for aluminum.

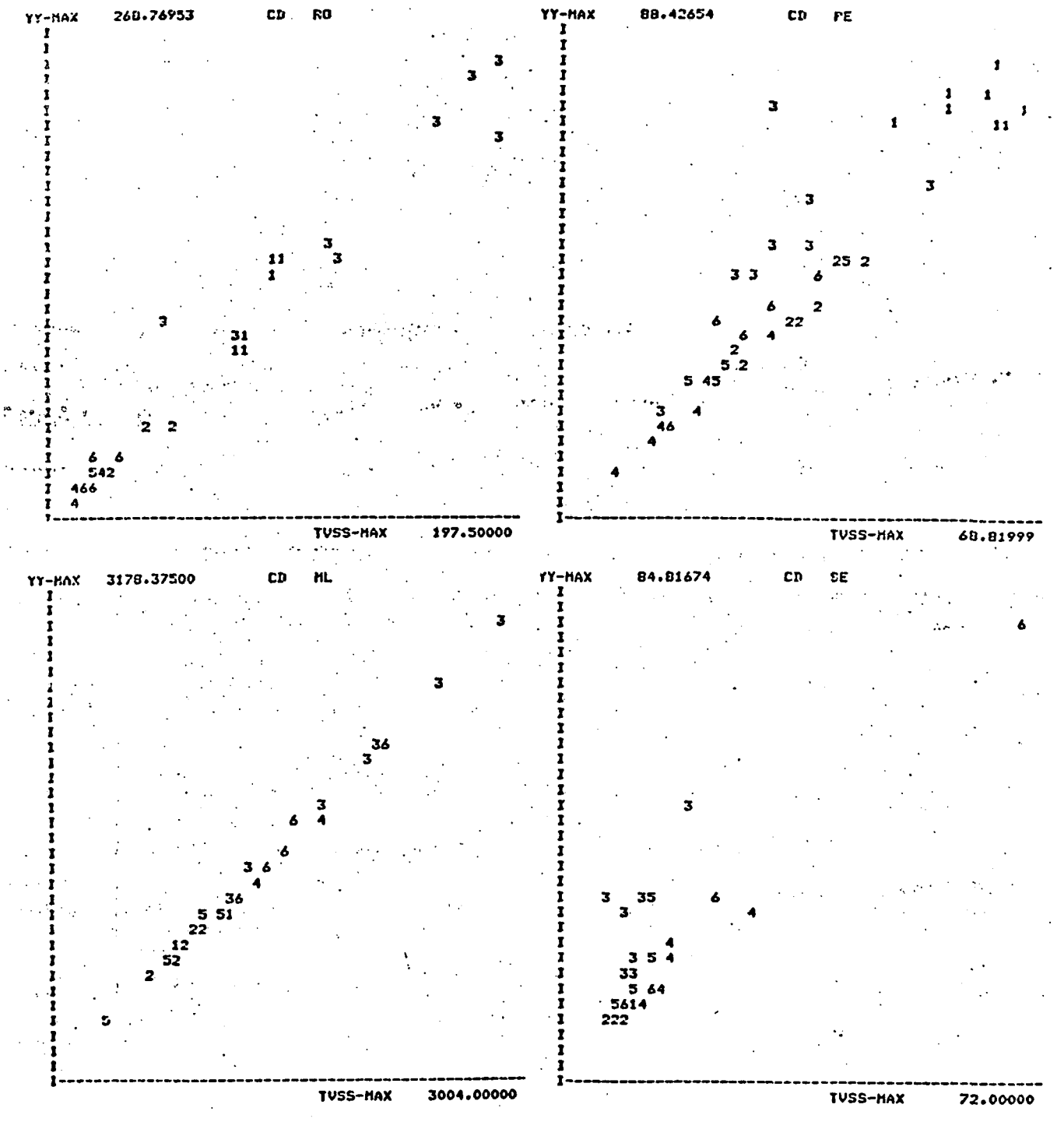

Figure B-2. Correlation of Model 3 in four process liquids for cadmium.

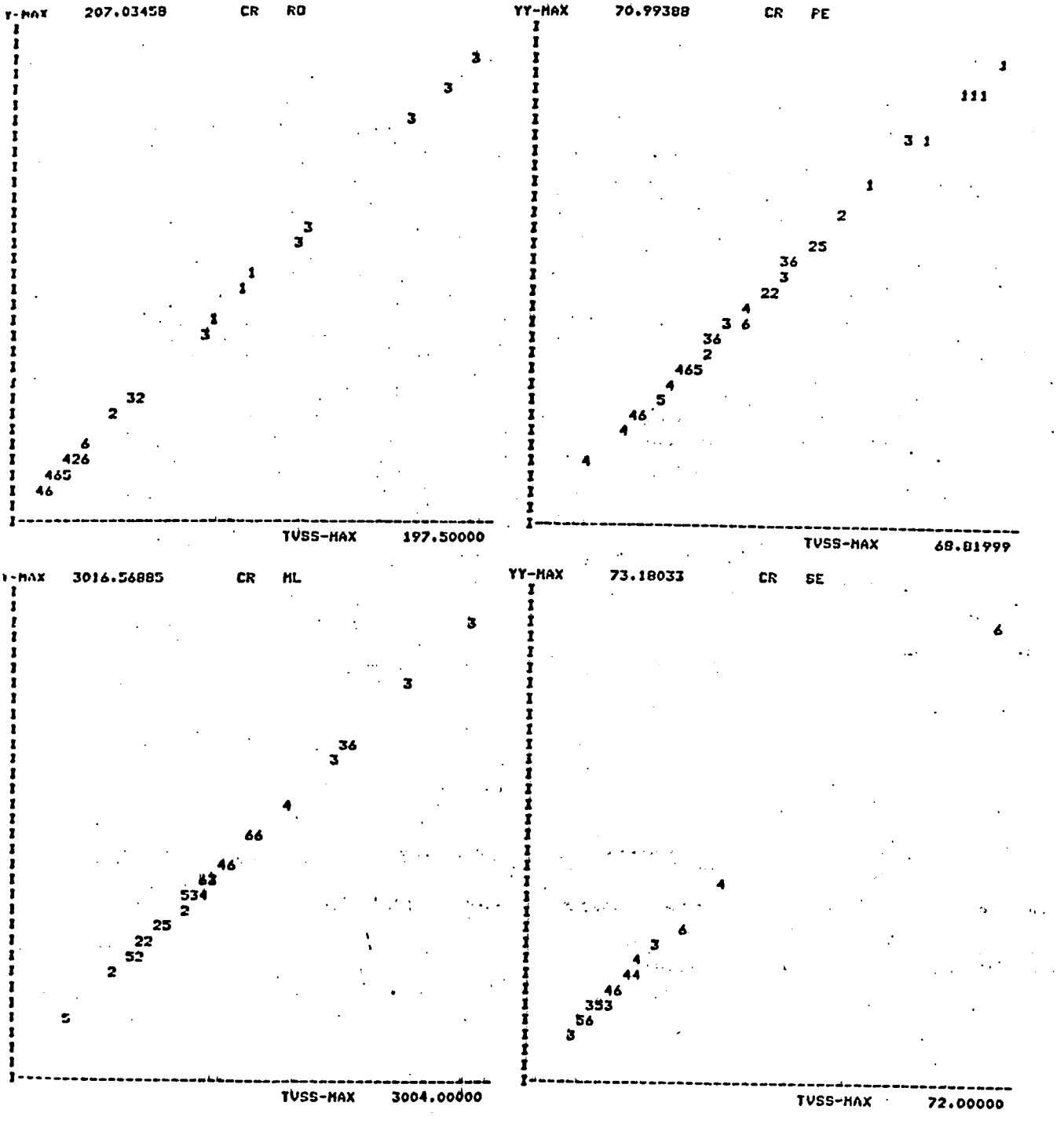

Figure B-3. Correlation of Model 3 in four process liquids for chromium.

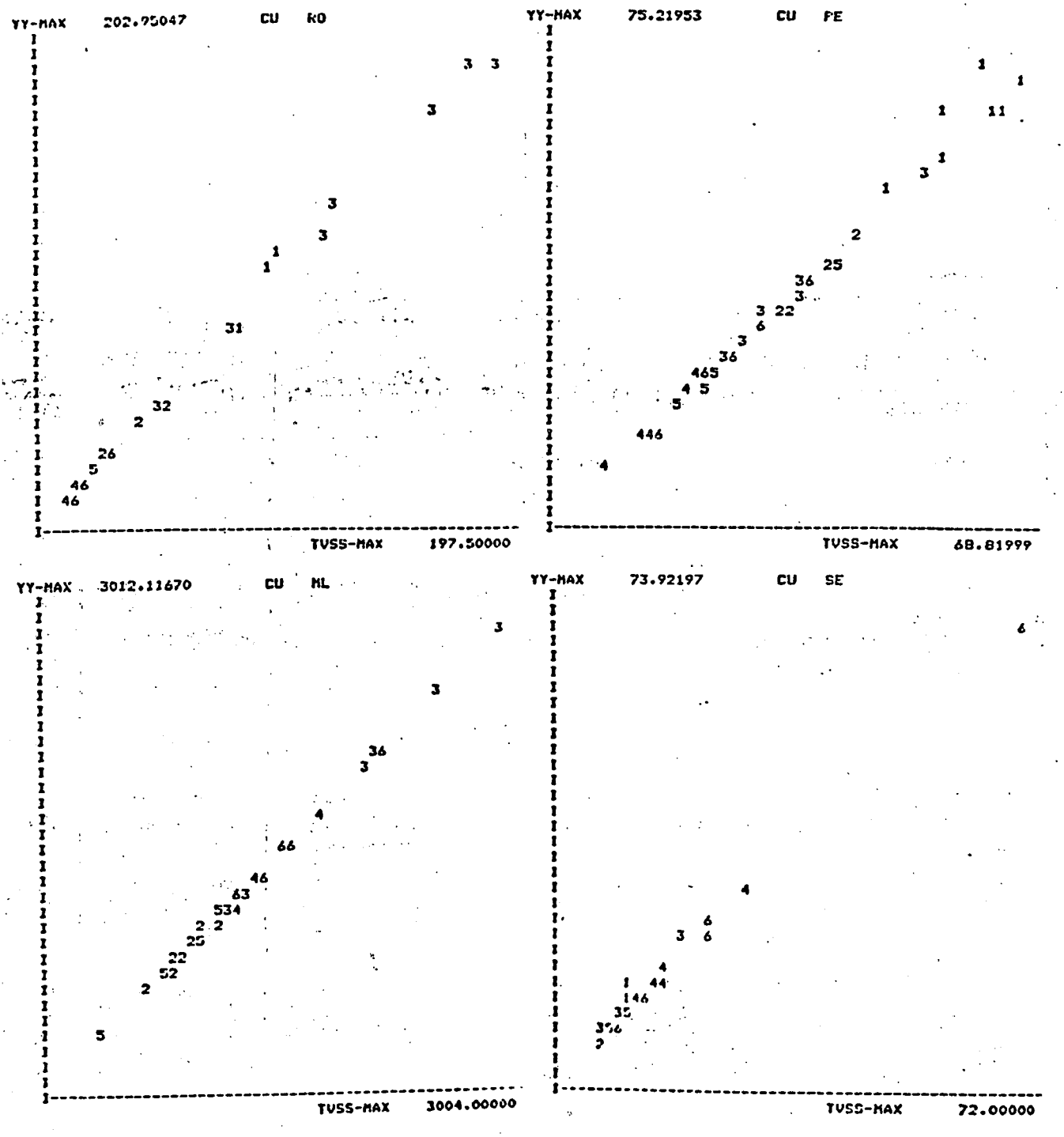

Figure B-4. Correlation of Model 3 in four process liquids for copper.

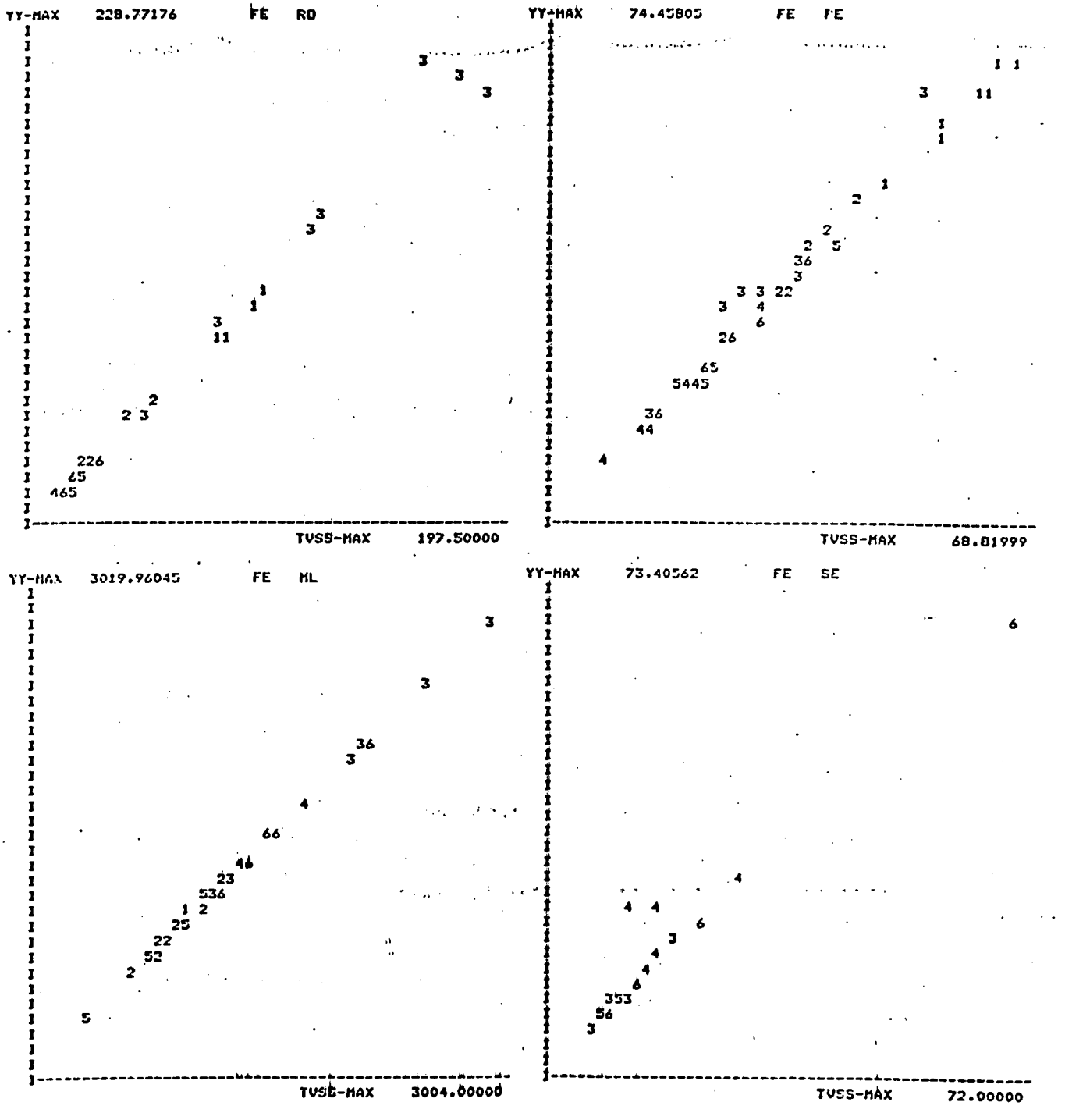

Figure B-5. Correlation of Model 3 in four process liquids for iron.

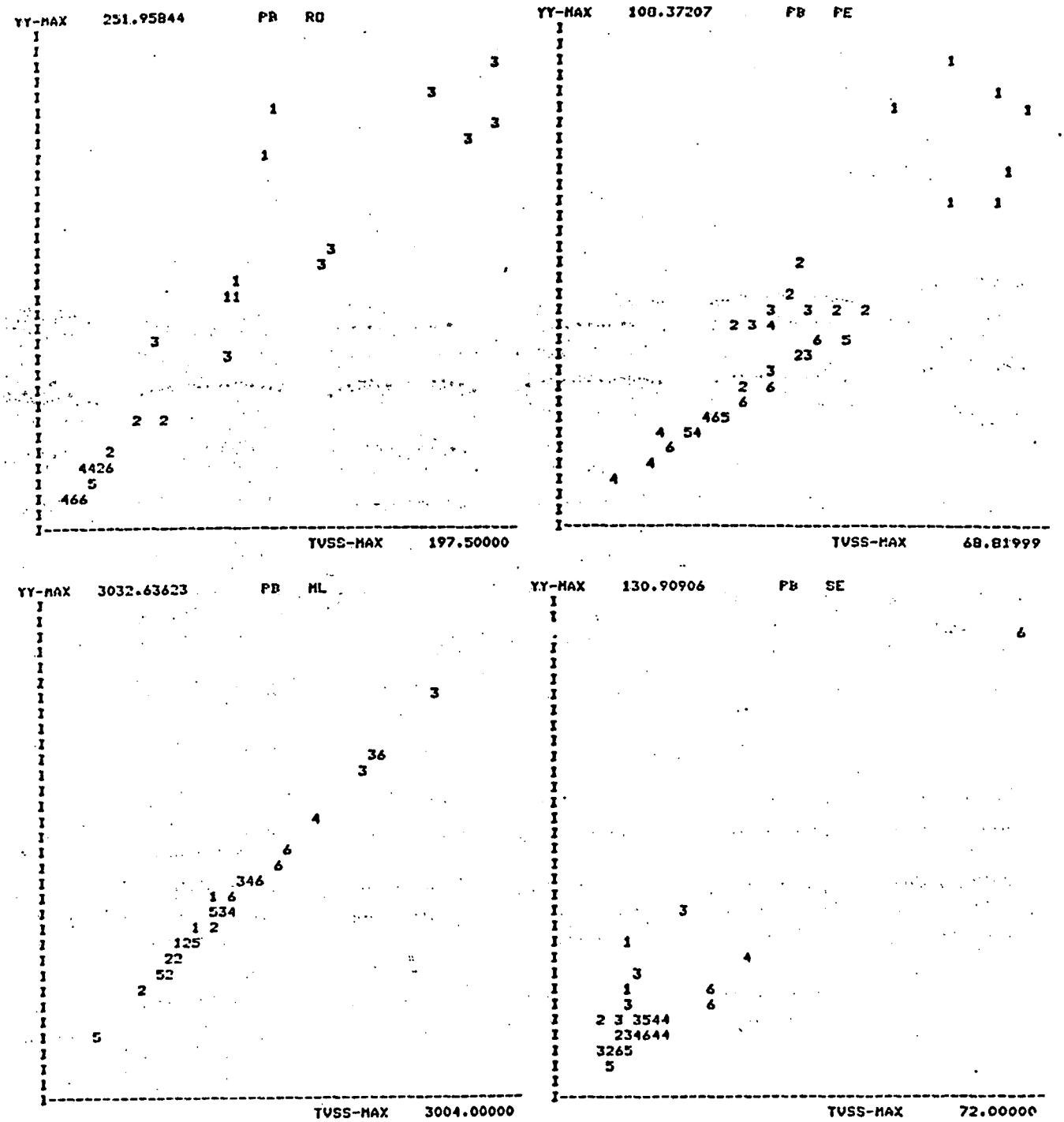

Figure B-6. Correlation of Model 3 in four process liquids for lead.

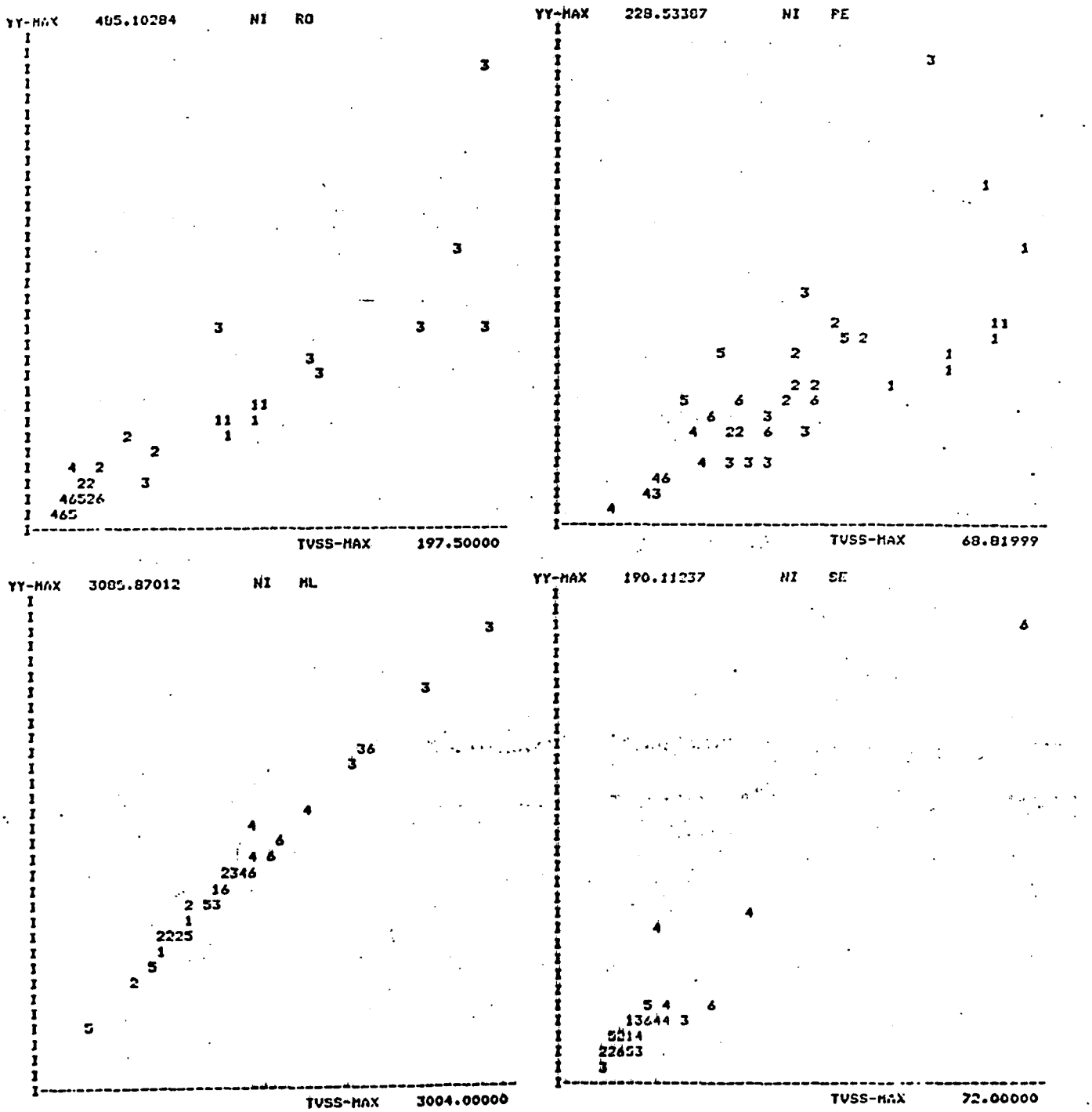

Figure B-7. Correlation of Model 3 in four process liquids for nickel.

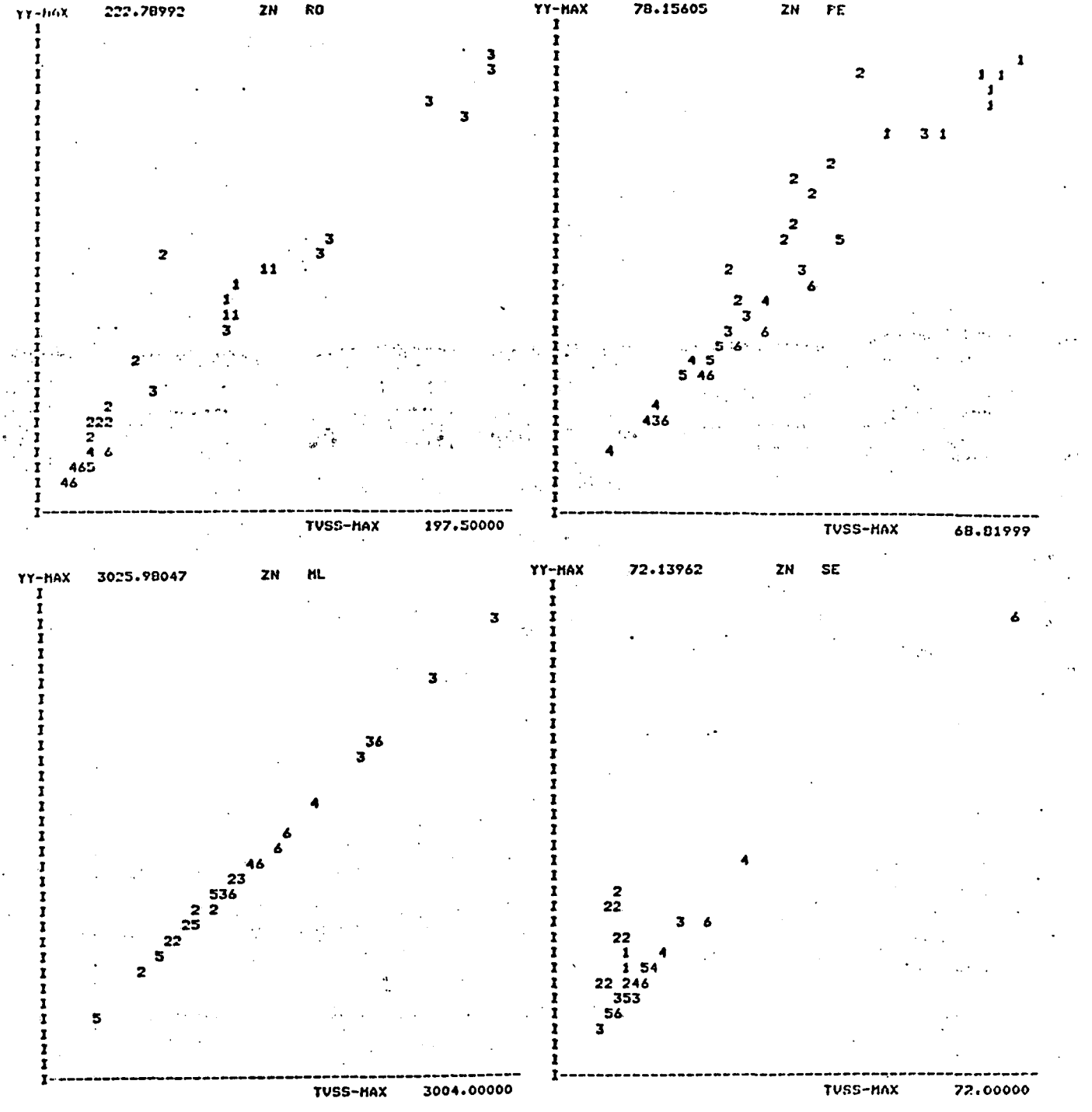

Figure B-8. Correlation of Model 3 in four process liquids for zinc.

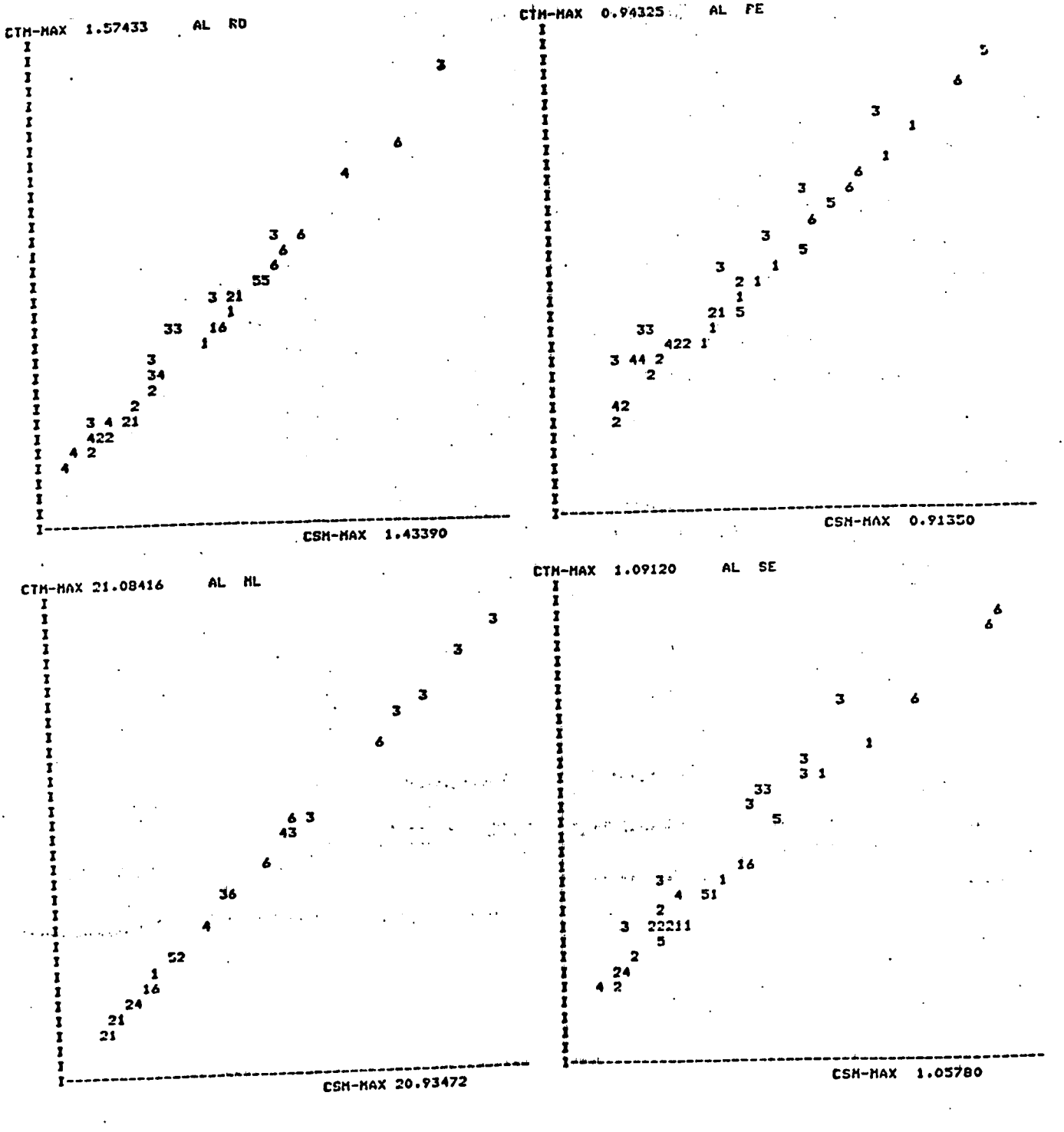

Figure B-9. Correlation of Model 4 in four process liquids for aluminum.

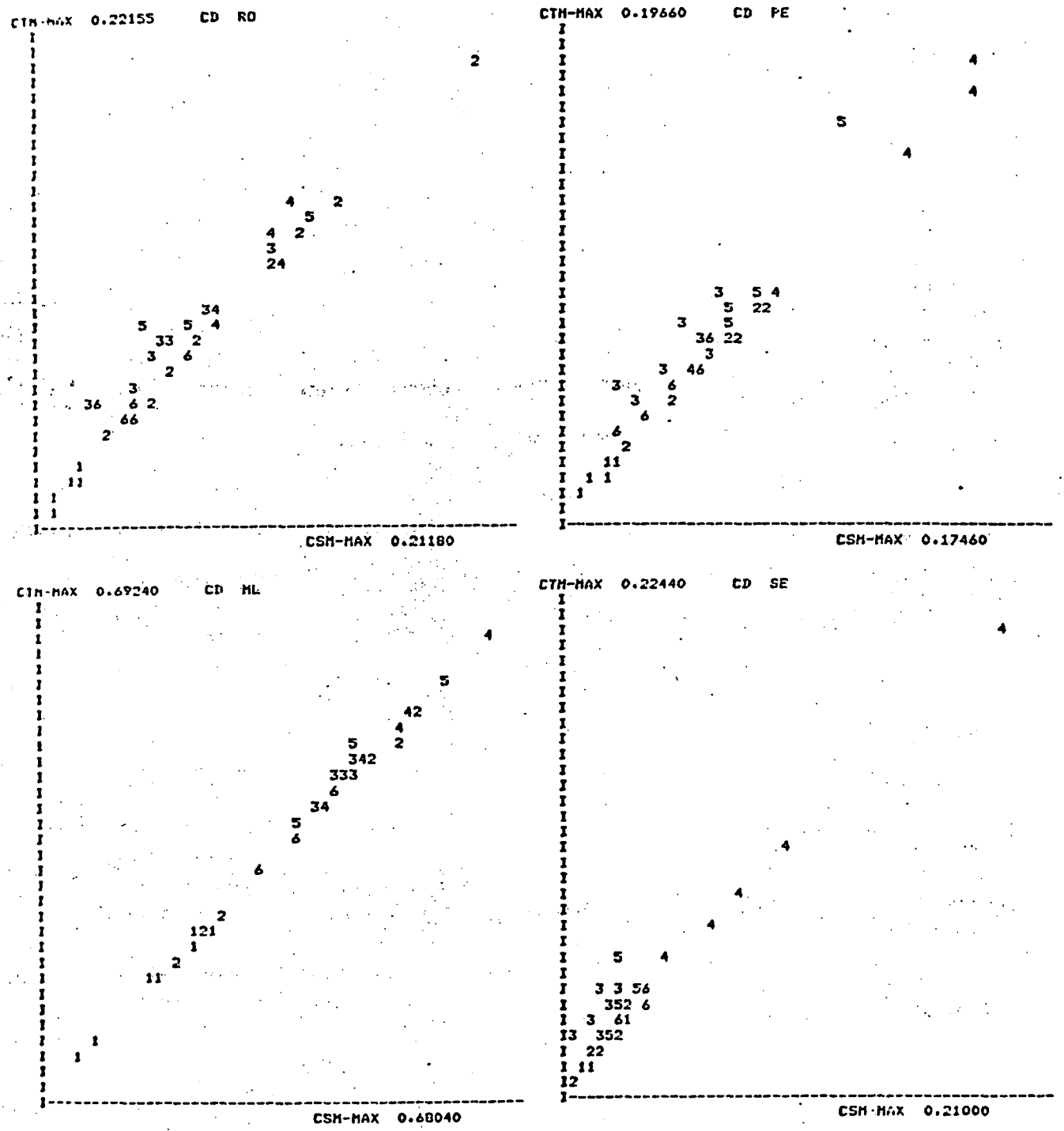

Figure B-10. Correlation of Model 4 in four process liquids for cadmium.

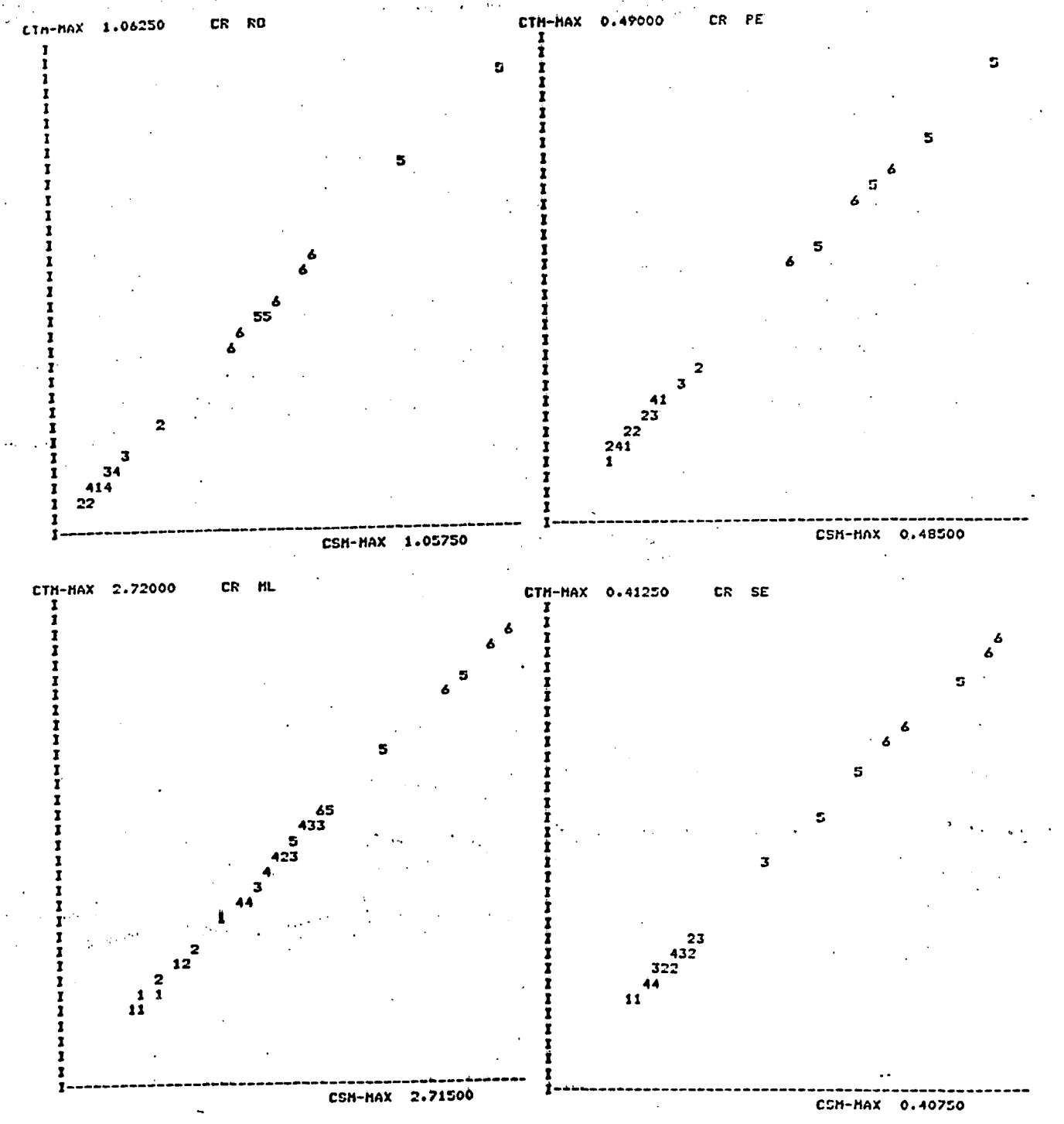

Figure B-11. Correlation of Model 4 in four process liquids for chromiu

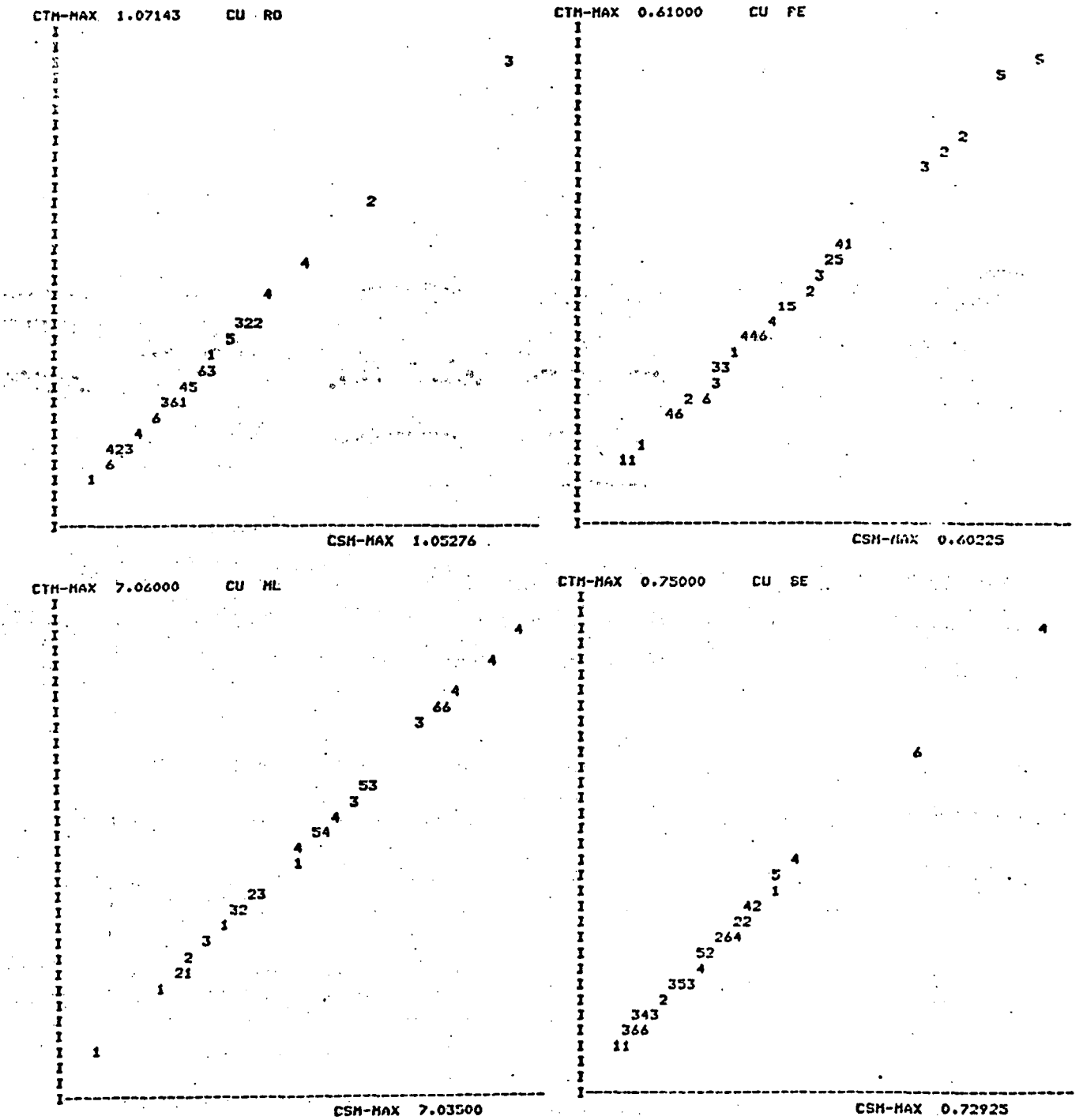

Figure B-12. Correlation of Model 4 in four process liquids for copper.

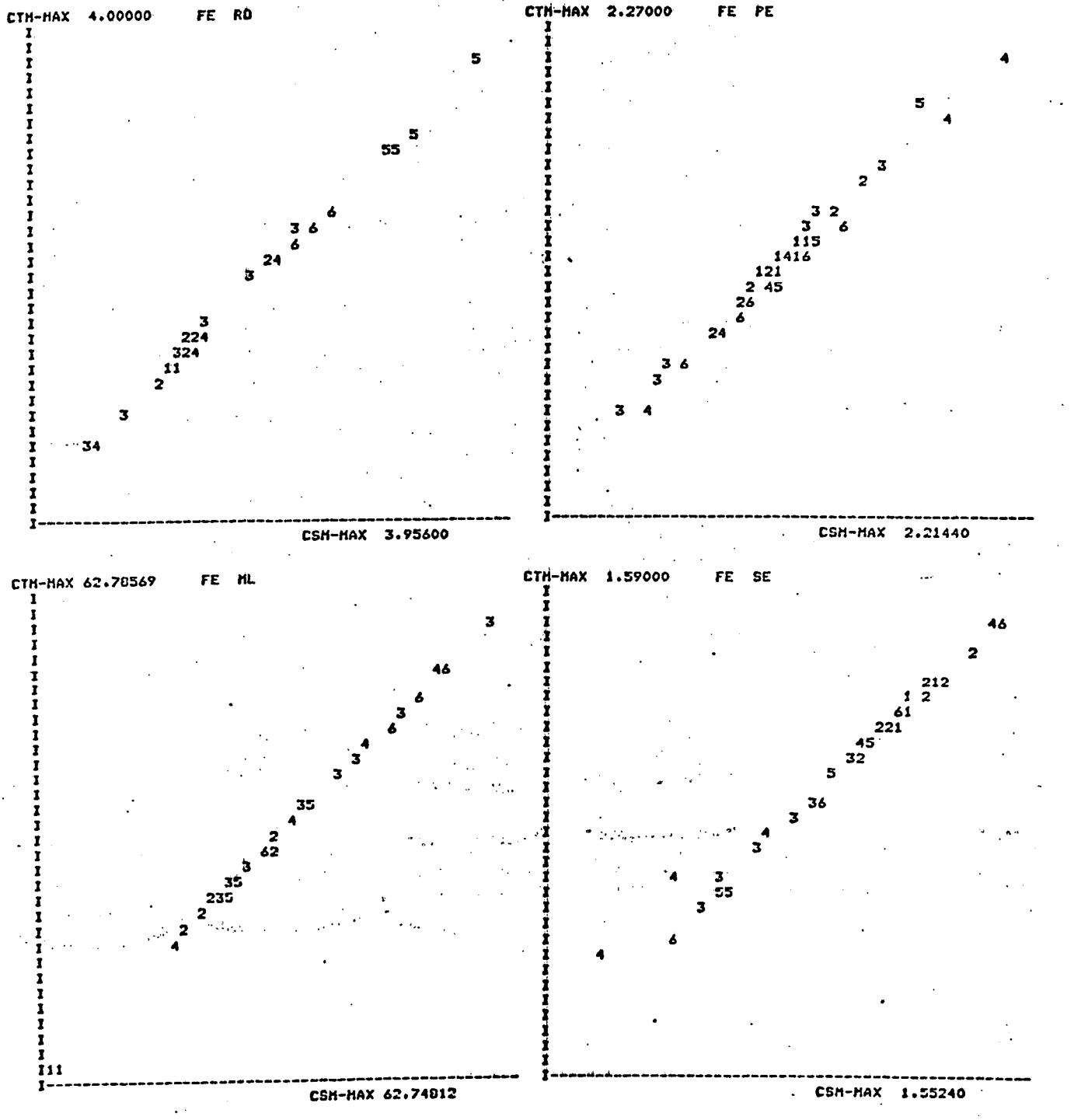

Figure B-13. Correlation of Model 4 in four process liquids for iron.

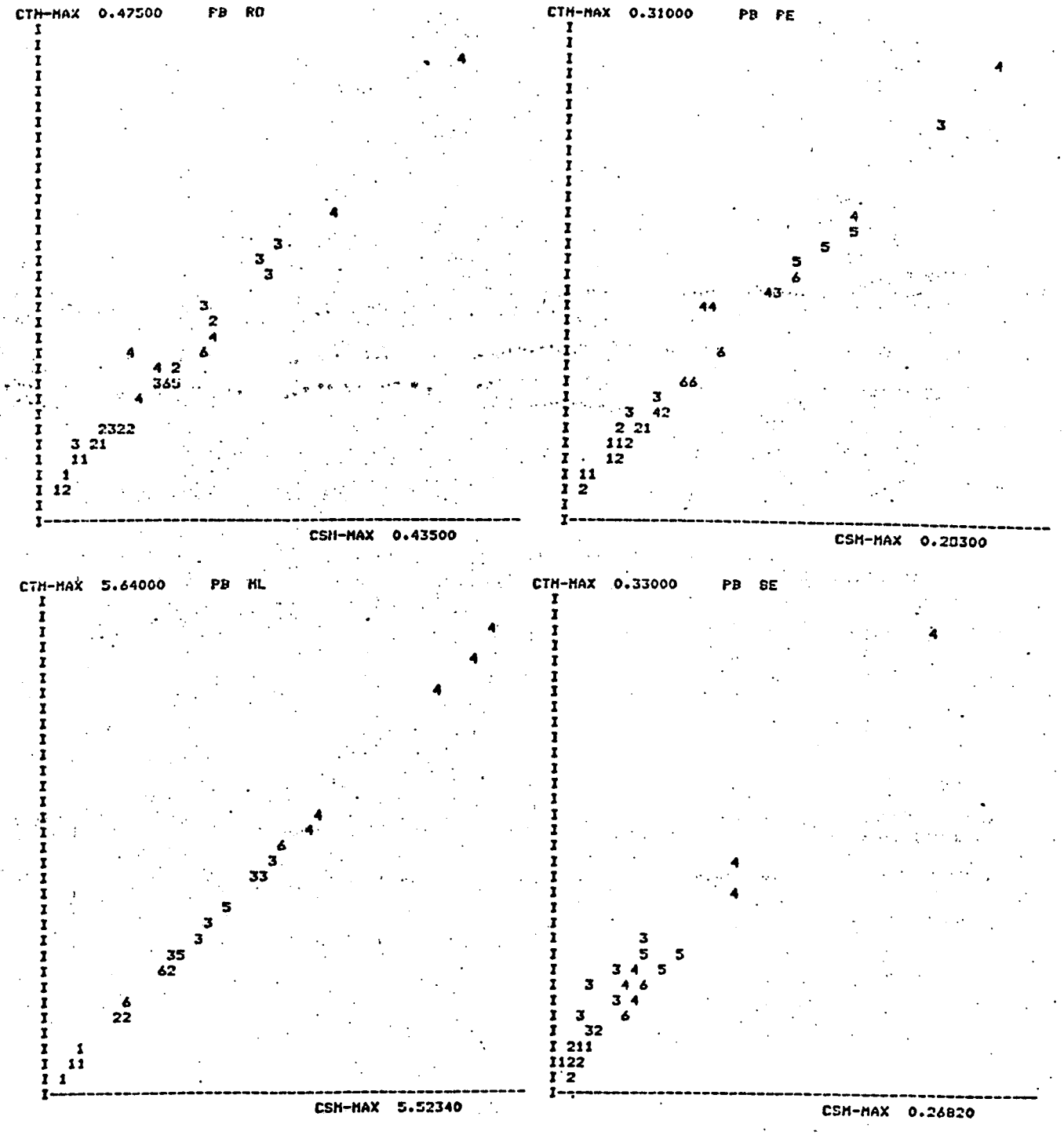

Figure B-14. Correlation of Model 4 in four process liquids for lead.

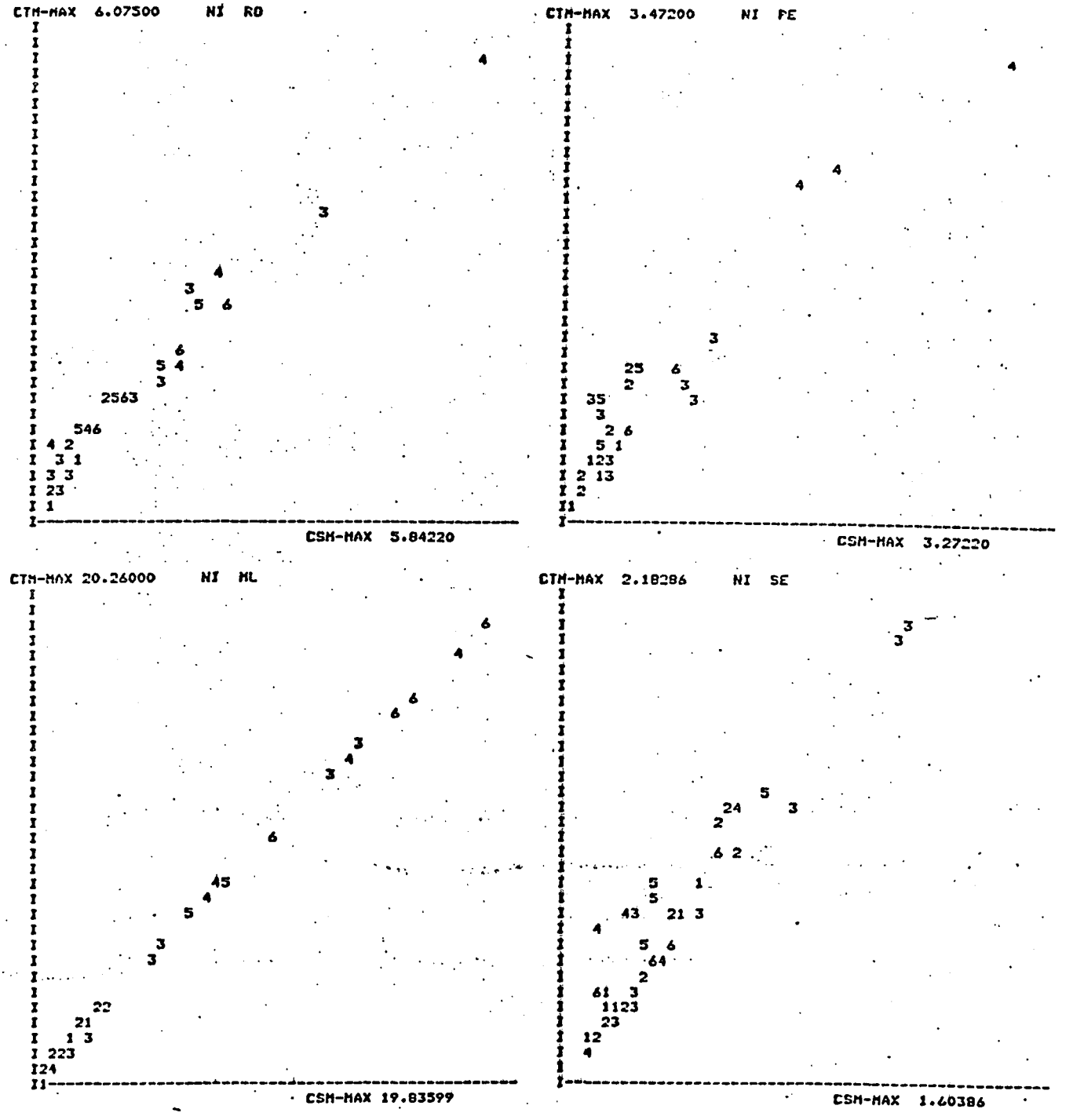

Figure B-15. Correlation of Model 4 in four process liquids for nickel.

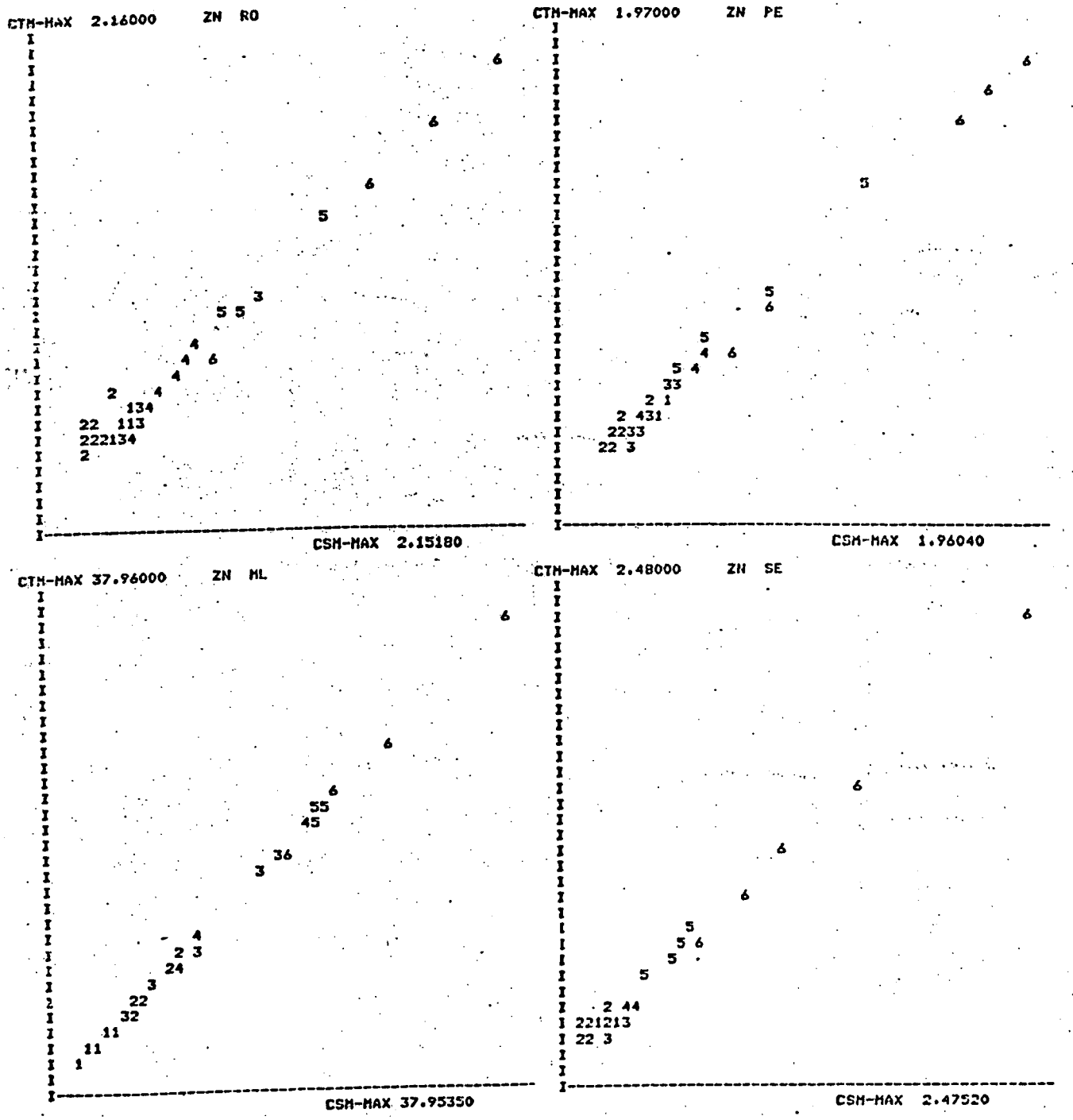

Figure B-16. Correlation of Model 4 in four process liquids for zinc.

APPENDIX C

DEVELOPMENT OF PREDICTIVE MODELS

I. Model PW

II. Model FS

I. PROCESS MODEL FOR THE PREDICTION OF METAL REMOVAL THROUGH THE PRIMARY CLARIFIER--MODEL PW

This process model is intended to simulate the heavy metal removal through the primary clarifier. The effluent heavy metal concentration is predicted from the influent raw sewage metal concentration and the removal efficiency of VSS in the primary clarifier.

In the primary clarifier, the draw-out of the sludge is often intermittent, while the influent and effluent flow is continuous. Therefore the exact measurement of sludge mass flux is difficult. Thus, Model PW assumes continuous steady-state draw-out of the sludge in the process model. The measurement of heavy metal content in the sludge is also difficult. The Model PW incorporates an assumption for the heavy metal content, χp in mg metal/mg VSS, of the draw-out sludge, as a weighted mean of the influent level C_{RSM}/X_R and effluent level C_{PSM}/Xp, where X_R and X_p are the VSS concentrations in the raw sewage and in the primary effluent, respectively. A W value of 1.0 represents the influent condition, and a W value of 0.0 the effluent condition.

VSS and metals balances give Equations (1) and (2).

$$Q\chi_R = Q\chi_p + D_p \qquad (1),$$

$$QC_{RTM} = QC_{PTM} + Dp \times \chi p \qquad (2),$$

where, Q = flow rate
D = flux

and the removal efficiency of VSS in the primary clarifier, Zp, is defined by Equation (3),

$$Zp = 1 - X_p/X_R \qquad (3).$$

The expression to calculate χp is described by Equation (4),

$$\chi_p = W\ (C_{RSM}/X_R) + (1 - W)\ (C_{PSM}/Xp) \qquad (4).$$

From Equation (2), one obtains Equation (5)

$$C_{PTM} = C_{RTM} - D_p \times \chi_p/Q \qquad (5)$$

Equation (1) rearranged is, $Dp/Q = (X_R - Xp)$. Thus, we obtain Equation (6).

$$C_{PTM} = C_{RTM} - \chi_p \times (X_R - X_p) \qquad (6)$$

Introducing the expression for χp in Equation (4), one obtains Equation (7),

$$C_{PTM} = C_{RTM} - \{W(C_{RSM}/X_R) + (1 - W)\ (C_{PSM}/X_p)\}\ (X_R - X_p) \qquad (7)$$

Introducing $Zp = 1 - Xp/X_R$, and as a rearrangement $Z_R = X_R/Xp - 1$ into Equation (7), one develops Equation (8),

$$C_{PTM} = C_{RTM} - \{W\ C_{RSM}\ Z_p + (1 - W)\ C_{PSM}\ Z_R\} \qquad (8)$$

We have from Model 4′ the correlations between C_{RSM} and C_{RTM}, and C_{PSM} and C_{PTM}, i.e., $C_{RSM} = p'_R\ C_{RTM} + q'_R$ and $C_{PSM} = p'_p\ C_{PTM} + q'_p$. Replacing C_{RSM} and C_{PSM} by these correlations, we have Equation (9),

$$C_{PTM}^{predicted.} = \{1 - Z_p W p'_R)\ C_{RTM} - Z_p W q'_R - Z_R\ (1 - W) q'_p\}/\{1 + Z_R (1 - W) p'_p\} \qquad (9)$$

Equation (9) predicts the effluent total metal concentration, C_{PTM}, from the primary clarifier, based upon the influent total metal concentration, C_{RTM}, the removal efficiency of VSS, Z_p, and the coefficients of the Model 4′ correlation p'_R, p'_p, q'_R and q'_p. Z_R is calculated from Z_p, i.e., $Z_p = X_R/Xp - 1 = 1/(1 - Z_p) - 1$.

We also predict the heavy metal concentration in the primary sludge, as follows. Based upon volume flow rate, Q_{ps}, for the sludge draw-out, we can predict the metal concentration in the sludge by Equation (10),

$$C_{PSTM} = Q(C_{RTM} - C_{PTM}/Q_{ps} \qquad (10)$$

Alternately, if we have VSS data for the sludge, X_{ps}, we get a prediction C_{PSTM} by Equation (11).

$$C_{PSTM} = \chi_p \times X_{ps} \qquad (11)$$

The accurate measurement of X_{ps} is often difficult. Equation (10) is recommended rather than Equation (11).

II. PROCESS MODEL FOR THE PREDICTION OF METAL REMOVAL THROUGH THE SEWAGE TREATMENT PLANT--MODEL FS

The full system model (Model FS) is devised to simulate the heavy metal removal through the plant. The secondary effluent total metal concentration, C_{STM} is predicted from the raw sewage total metal concentration, C_{RTM}, and the removal efficiencies of VSS and SOC through the plant. The operational characteristic constants of the process are also needed, including yield factor, Y, recycle ratio, R, VSS values in the aeration tank, X, and the endogenous constant, k_d. VSS, SOC and metal balances are presented in Equations (12), (13), and (14).

$$QX_p + \chi_R - k_d XV = QX_O + D_s \qquad (12)$$

$$(1 + R)\, Q\, (S_R - S_O) = \chi_R / Y \qquad (13)$$

$$QC_{PTM} = QC_{STM} + \chi_{SS}\, D_s \qquad (14)$$

D_s and χ_{SS} are VSS draw-out rate (mg VSS/hr) and metal content in the secondary sludge (mg metal/mg VSS), respectively. Xp, X_O, and X are VSS concentrations of primary effluent, secondary effluent, and mixed liquor, respectively. S_R and S_O are SOC subtrate concentrations, for raw sewage and secondary effluent. χ_R is the VSS generation rate through biodegradation (mg VSS/hr). Y and R are yield factor and recycle ratio, respectively.

From Equations (12) and (13), we obtain Equation (15) for D_s.

$$D_s = Q(X_p - X_O) + Y(1 + R)\, Q\, (S_r - S_O) - k_d XV \qquad (15)$$

We assume $\chi_{SS} = C_{SSM}/X_O$, and substitute for χ_{SS} in Equation (14). Then, replacing D_s and χ_{SS} in Equation (14) by D_s from Equation (15), we obtain Equation (16).

$$C_{STM} = C_{PTM} - (C_{SSM}/X_O)\, \{Xp - X_O + Y(1 + R)\, (S_R - S_O) - k_d XV/Q\} \qquad (16)$$

We also have the Model 4′ correlation between C_{SSM} and C_{STM}, represented by Equation (17).

$$C_{SSM} = p'_S C_{STM} - q'_S \qquad (17)$$

Equation (16) is rewritten as Equation (18).

$$C_{STM} = C_{PTM} - C_{SSM} \times J \qquad (18)$$

where, $J = \{Xp - X_O + Y(1 + R)(S_R - S_O) - k_d XV/Q\}/X_O$ (19)

By combining Equations (17) and (18), one gets Equation (20).

$$C_{STM}^{predicted} = (C_{PTM}^{predicted} - q'_S \times J)/(1 + p'_s \times J) \quad (20)$$

C_{PTM} in Equation (20) is predicted by Model PW. Equation (20) is the prediction equation of C_{STM}, for the process Model FS. J of Equation (19) can be rewritten by using removal efficiencies, Z_{VSS} and Z_{SOC}, as Equation (19a),

$$J = \{XpZ_{VSS} + Y(1 + R)S_R Z_{SOC} - k_d XV/Q\}/\{Xp(1 - Z_{VSS})\} \quad (19a)$$

where, $Z_{VSS} = 1 - XO/Xp$ and Z_{SOC} $1 - S_O/S_R$.
Xp is related to X_R by $Z_p (= 1 - Xp/X_R)$, and so $Xp = X_R (1 - Zp)$.

We can predict C_{STM} by Equation (20), knowing C_{RTM}, SOC, and VSS of raw sewage, VSS of mixed liquor, X, and Zp, Z_{VSS}, and Z_{SOC}.

The removal rates (metal fluxes) as primary sludge, secondary sludge and secondary effluent are calculated by Equations (21), (22), and (23) respectively.

$$HMPS = Q \times (C_{RTM} - C_{PTM}) \quad (21)$$

$$HMSS = Q \times (C_{PTM} - C_{STM}) \quad (22)$$

$$HMSE = Q \times C_{STM} \quad (23)$$

Then, percentage removals are given by Equations (24), (25), and (26).

$$\%PS = HMPS \times 100/HOUT \quad (24)$$

$$\%SS = HMSS \times 100/HOUT \quad (25)$$

$$\%SE = HMSE \times 100/HOUT \quad (26)$$

where HOUT = HMPS + HMSS + HMSE.