

# COMPREHENSIVE FATE MODEL FOR METALS IN MUNICIPAL WASTEWATER TREATMENT

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**ABSTRACT:** A model was developed for predicting the fate of metals in municipal wastewater treatment. The model, which incorporates metal solubility and sorption onto solids, was calibrated with experimental data obtained by a titration technique. The calibrated model was evaluated using dynamic data collected in a separate study from three Ontario wastewater-treatment plants (WWTPs). A goodness-of-fit test was employed to determine if the model predictions were statistically different from the observed effluent concentrations. Predictions of copper and zinc effluent concentrations at two WWTPs were found to lie within the confidence limits defined by the variability of field replicates. Lack of fit of some model predictions was attributed to biasing of the data at low concentrations and lack of model calibration. The configuration of the model was concluded to be correct since the behavior of metals with significantly different physical properties were well predicted. It is concluded that the most accurate model predictions can be made if the model is calibrated at the specific WWTP.

## INTRODUCTION

Metals are among the most frequently detected contaminants in municipal wastewater (Fate 1982; Monteith 1987; *Thirty Seven* 1989). Metals discharged to treatment plants pose potential hazards to the receiving water body and may limit disposal options for sludges generated. Regulatory authorities in North America have responded by focusing legislation to limit the emissions of metals (U.S. Clean-Water Act; Ontario Municipal-Industrial Strategy for Abatements). To reduce the costs of implementing regulations, there is a need for reliable models that can predict the behavior of metals in treatment plants.

Metals enter wastewater-treatment plants in a variety of forms including soluble, organically complexed, precipitated and physically sorbed to organic matter (Nelson et al. 1981; Nielson 1984). While in the treatment plant, the distribution of forms of a given metal may be modified due to degradation of organic ligands, biomass uptake, and changes in both oxidation-reduction potential and pH (Sterritt and Lester 1981; Imai and Gloyna 1990). Models that incorporate all of these factors to predict the fate of metals would be cumbersome and require, as input, information that is not readily available to most researchers. Combined with the fact that conditions

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will change both temporally and from plant to plant, it is apparent that such detailed models would be of little use to either regulators or operators. The need for a simplified model that can adequately emulate the behavior of metals in wastewater-treatment plants is obvious.

A prior paper (Monteith et al. 1993) described a model (TOXCHEM) for predicting the fate of metals based upon soluble and sorbed fractions only. Although this model was satisfactory for some metals, it was apparent that the behavior of metals with low solubilities could not be represented. It was concluded that a mechanism that allowed for partitioning due to precipitation must be included in the model. This paper describes a revised version of the TOXCHEM model, experiments performed to calibrate the model, and a statistical evaluation of the model performance with dynamic data obtained from three Ontario wastewater-treatment plants.

### MODEL DEVELOPMENT

The TOXCHEM model simulates the removal of metals in grit removal; primary clarification; aeration; and secondary clarification by removal of metals sorbed to biological solids; and metal precipitates. Sorption coefficients for a given metal are separate for the primary and secondary systems to allow for differing solids and wastewater matrix characteristics. As well, two solubility limits for a given metal are employed to account for differences in the primary and secondary systems that result from changes in the wastewater matrix due to biodegradation of organic ligands. Instantaneous precipitation of metals is assumed while dissolution of precipitates is assumed to proceed at a negligible rate. Hence, separate mass balances are performed for soluble and precipitated metals in all cases except in the aeration basin where precipitate may form due to a reduction in the solubility limits.

It is necessary to partition the metals entering the wastewater-treatment plant into soluble, sorbed, and precipitated fractions. The influent metals concentration is partitioned into soluble, sorbed, and precipitate fractions by initially calculating

$$C_{\text{Test}} = \frac{C_o}{(1 + K_{p1}X_o)} \quad (1)$$

Notation employed in this equation and that to follow is appended. If  $C_{\text{Test}}$  is greater than the metal's primary solubility limit ( $C_{\text{Sol},1}$ ), the soluble concentration is set at  $C_{\text{Sol},1}$  and the concentration of metal present as precipitate is calculated as

$$C_{p_o} = C_o - (1 + K_{p1}X_o)C_{\text{Sol},1} \quad (2)$$

If  $C_{\text{Test}}$  is less than the metal's primary solubility limit, then the concentration of metal present as precipitate ( $C_{p_o}$ ) is zero and the soluble concentration ( $C_{s_o}$ ) is equal to  $C_{\text{Test}}$ . The total metal concentration at any point in the treatment process is calculated as the sum of the soluble, sorbed, and precipitate fractions.

Assumptions associated with modeling the fate of metals in the unit processes are as follow:

- The grit chamber and clarifiers are completely mixed continuous-flow stirred tank reactors (CSTRs).

- The aeration tank is a series of equal-volume CSTRs (the number of CSTRs is specified by the user).
- Sludge wasting occurs only from the clarifiers.
- The soluble contaminant concentration in the activated sludge waste and recycle streams is equal to the secondary clarifier-influent soluble contaminant concentration.
- The soluble contaminant concentration in the primary sludge waste stream is equal to the primary clarifier-influent soluble contaminant concentration.
- The equilibrium-sorbed contaminant concentration is a first-order function of the liquid-phase contaminant concentration.
- Sorption is reversible.
- Sorption and desorption occur instantaneously.
- Precipitates in the primary clarifier are removed to the same extent as the total suspended solids (TSS).
- Precipitates in the secondary clarifier are concentrated in the same ratio as the biomass.

## MASS BALANCES FOR UNIT PROCESSES

### Grit Chamber

#### *Soluble and Sorbed Fractions*

$$Q_o(C_{S_o} - C_{S1})(1 + X_o K_{P1}) = V_g(1 + X_o K_{P1}) \frac{dC_{S1}}{dt} \quad (3)$$

#### *Precipitate Fraction (If Applicable)*

$$Q_o(C_{P_o} - C_{P1}) = V_g \frac{dC_{P1}}{dt} \quad (4)$$

### Primary Clarifier

#### *Soluble and Sorbed Fractions*

$$\begin{aligned} Q_o(1 + X_o K_{P1})C_{S1} - Q_{PC}(1 + X_{PC} K_{P1})C_{S1} - Q_1(1 + X_1 K_{P1})C_{S2} \\ = V_P(1 + X_1 K_{P1}) \frac{dC_{S2}}{dt} \end{aligned} \quad (5)$$

#### *Precipitate Fraction (If Applicable)*

$$Q_o C_{P1} - Q_{PC} C_{P1} \left( \frac{X_{PC}}{X_o} \right) - Q_1 C_{P2} = V_P \frac{dC_{P2}}{dt} \quad (6)$$

## Aeration Basin

### Soluble and Sorbed Fractions

First CSTR is

$$Q_1(1 + K_{P1}X_1)C_{S2} + Q_r(1 + K_{P2}X_r)C_{S,N+2} - (Q_1 + Q_r)(1 + K_{P2}X_m)C_{S3} = V_{a,1}(1 + K_{P2}X_m) \frac{dC_{S3}}{dt} \quad (7)$$

subsequent CSTRs are

$$(Q_1 + Q_r)(1 + K_{P2}X_m)(C_{S,n+1} - C_{S,n+2}) = V_{a,n}(1 + K_{P2}X_m) \frac{dC_{S,n+2}}{dt} \quad (8)$$

### Precipitate Fraction (If Applicable)

First CSTR [no precipitate formation in aeration basin ( $C_{S3} < C_{Sol,2}$ )] is

$$Q_1C_{P2} + Q_r \left( \frac{X_r}{X_m} \right) C_{P,N+2} - (Q_1 + Q_r)C_{P3} = V_{a,1} \frac{dC_{P3}}{dt} \quad (9)$$

and [with precipitate formation in aeration basin ( $C_{S3} > C_{Sol,2}$ )] is

$$Q_1(C_{P2} + (1 + K_{P1}X_1)C_{S2}) + Q_r \left( C_{P,N+2} \left( \frac{X_r}{X_m} \right) + (1 + K_{P2}X_r)C_{S,N+2} \right) - (Q_1 + Q_r)(C_{P3} + (1 + K_{P2}X_m)C_{Sol,2}) = V_{a,n} \frac{dC_{P3}}{dt} \quad (10)$$

Subsequent CSTRs are

$$(Q_1 + Q_r)(C_{P,n+1} - C_{P,n+2}) = V_a \frac{dC_{P,n+2}}{dt} \quad (11)$$

## Secondary Clarifier

### Soluble and Sorbed Fractions

$$[(Q_1 + Q_r)(1 + X_m K_{P2}) - (Q_r + Q_w)(1 + X_r K_{P2})]C_{S,N+2} - (Q_1 - Q_w)(1 + X_e K_{P2})C_{S,N+3} = V_s(1 + X_e K_{P2}) \frac{dC_{S,N+3}}{dt} \quad (12)$$

### Precipitate Fraction (If Applicable)

$$\left[ (Q_1 + Q_r) - (Q_r + Q_w) \left( \frac{X_r}{X_m} \right) \right] C_{P,N+2} - (Q_1 - Q_w)C_{P,N+3} = V_s \frac{dC_{P,N+3}}{dt} \quad (13)$$

## MODEL CALIBRATION

The previously described model requires solubility limits and sorption coefficients for metals in both primary and secondary systems. Determining the two factors is complicated by the fact that it is very difficult to differentiate between sorbed and precipitated metals in the solid phase. The following experiments were performed to systematically estimate the coefficients for seven metals in dewatered wastewater and aeration-basin mixed liquor.

### Experimental Program

Two separate batch experiments were conducted to investigate the sorption and precipitation of metals in municipal sewage. Dewatered wastewater and aeration-basin mixed liquor were obtained from the Burlington Skyway publicly owned treatment works (POTW) and studied in separate experiments. The Burlington POTW receives 93,000 m<sup>3</sup>/d, of which 18% is from industrial contributors.

For each experiment, approximately 40 L of sample were collected in a 50-L glass carboy, and subsequently split into two 20-L glass carboys. Solids were removed from the contents of one of the 20-L portions by centrifugation at a relative centrifugal force (RCF) of 5,700 for 10 min. The wastewater temperature was maintained at approximately 4°C in the time between collection and experimentation. Immediately prior to experimentation, the samples were warmed to a temperature between 20° and 24°C. The sample pH remained relatively constant during the experimentation with values ranging from 7.2 to 7.4.

A spike solution containing aluminum, cadmium, chromium (III), copper, lead, nickel, and zinc at concentrations of 100 mg/L each was prepared in distilled water from chloride salts. Incremental volumes of this solution were added to each of the carboys in a series of doses such that the total concentration of each metal increased by approximately 40 µg/L for the first six doses and by approximately 80 µg/L for the final three doses. The target final concentration, above the background concentration, was 480 µg/L for each metal. Dosing was performed in 1 h intervals. The two carboys were mixed continuously by magnetic stir bars. A schematic depicting the dosing and solids separation procedure is presented in Fig. 1.

Each carboy was sampled for metal concentrations prior to dosing to determine background metals concentrations. The carboys were sampled a period of 1 h after each dosing, which allowed for sample equilibration. Samples from each of the carboys were split, with one portion analyzed whole, and the other centrifuged at an RCF of 5,700 for 15 min and filtered through a 1.2 µm membrane filter prior to analysis. The spike solution was also analyzed for metals.

Suspended-solids analyses were performed on samples collected from both centrifuged and uncentrifuged wastewater portions. Total suspended

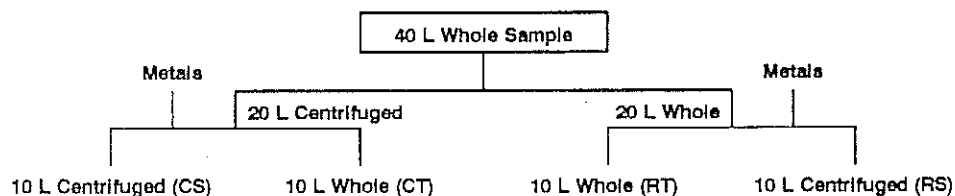


FIG. 1. Preparation of Metals Samples

solids determined in primary influent samples collected at 4, 6, and 8 h averaged 13 mg/L for the centrifuged portion and 217 mg/L for the uncentrifuged portion. Total suspended solids determined in mixed-liquor samples collected at 0, 4, and 8 h averaged 6 mg/L for the centrifuged portion and 3,707 mg/L for the uncentrifuged portion. Total-suspended-solids concentrations did not change significantly over the time of either experiment.

All samples were collected in 120 mL polyethylene sample bottles and preserved with HNO<sub>3</sub>. Ten-mL sample aliquots were digested with AquaRegia (10 mL HCL, 3 mL HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>). Metals were analyzed by atomic emission (D.C. Plasma) using a Spectrometric Spectrospan VI spectrophotometer. The resulting detection limit for both liquid and sludge samples was approximately 0.05 mg/L.

## Results

Titration-type curves for each metal were generated for the four sample streams generated in the experimental program. These curves describe metal concentrations in the raw-total (RT), raw-soluble (RS), centrifuged-total (CT), and centrifuged-soluble samples (CS) (see Fig. 1). Figs. 2–5 describe typical results obtained for chromium and copper in degrittled wastewater and mixed liquor, respectively. Recovery of the dosed metals was generally excellent, as indicated by the linear relationship between the raw and centrifuged total sample concentrations and the dosing concentrations. The differences between concentrations measured in the total raw wastewater and the total centrifuged wastewater were generally consistent and equal to the concentration of particulate metal present in the initial sample prior to dosing. The metals present in the original degrittled wastewater at the highest concentrations included aluminum, copper, lead, and zinc, all of which contained some particulate form of these metals. Only nickel and cadmium had identical RT and CT values. With the exception of cadmium, all of the metals were present in the initial mixed-liquor sample at total concentrations greater than 50 µg/L. Aluminum was present in this sample at a concentration of 16 mg/L, probably as a result of dosing at the plant with alum for

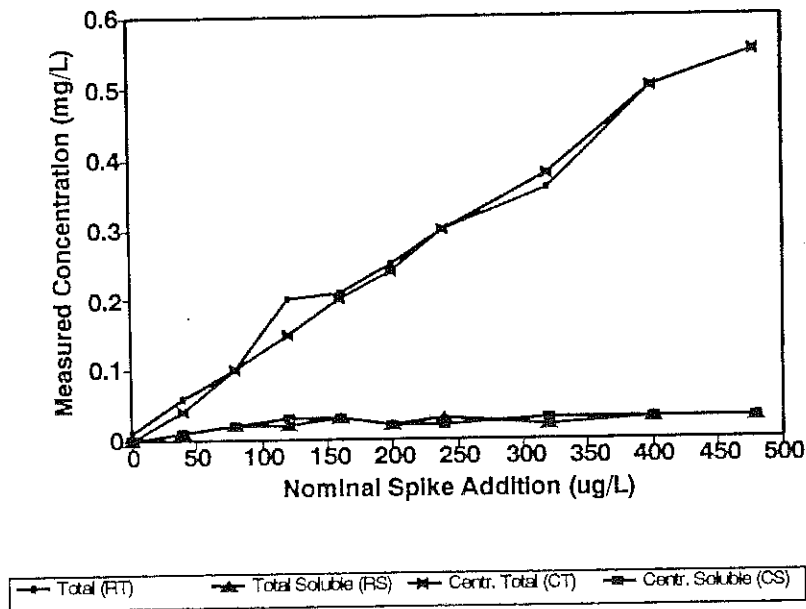


FIG. 2. Concentrations of Chromium in Degrittled Wastewater

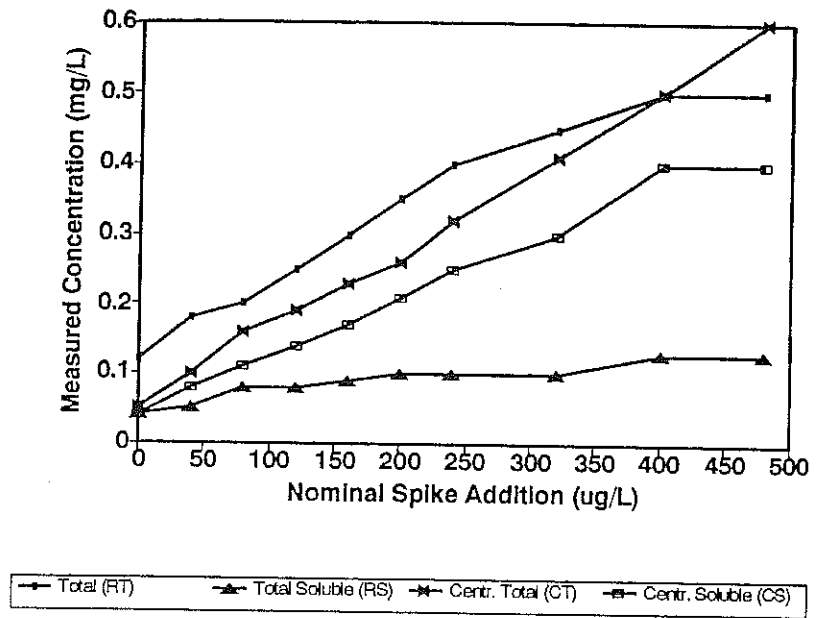


FIG. 3. Concentrations of Copper in Degrittied Wastewater

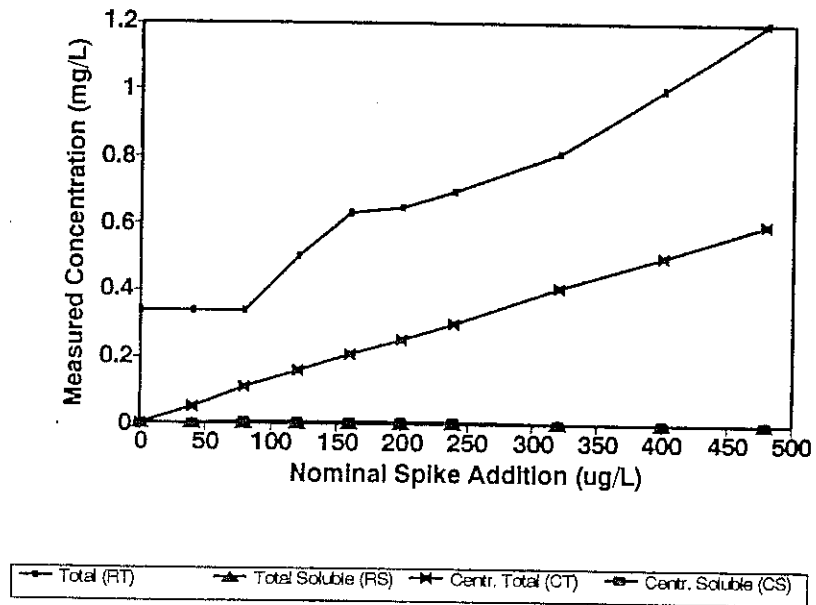


FIG. 4. Concentrations of Chromium in Mixed Liquor

phosphorous removal. Almost all of the metals present in the initial mixed-liquor samples were associated with the particulate phase.

Two trends of solubility and sorption are apparent in Figs. 2-5 and one or both of these trends was typically observed with all of the metals. Soluble concentrations of chromium in both the degrittied wastewater and the mixed-liquor samples did not differ between the raw samples and the centrifuged samples (Figs. 2 and 4). Therefore, sorption of chromium onto the solids in the raw wastewater, which had a higher concentration of solids as compared to the centrifuged wastewater, did not significantly increase the removal by centrifugation. This indicates that the solubility limit of this chromium was exceeded at the concentrations studied and that all of the incremental

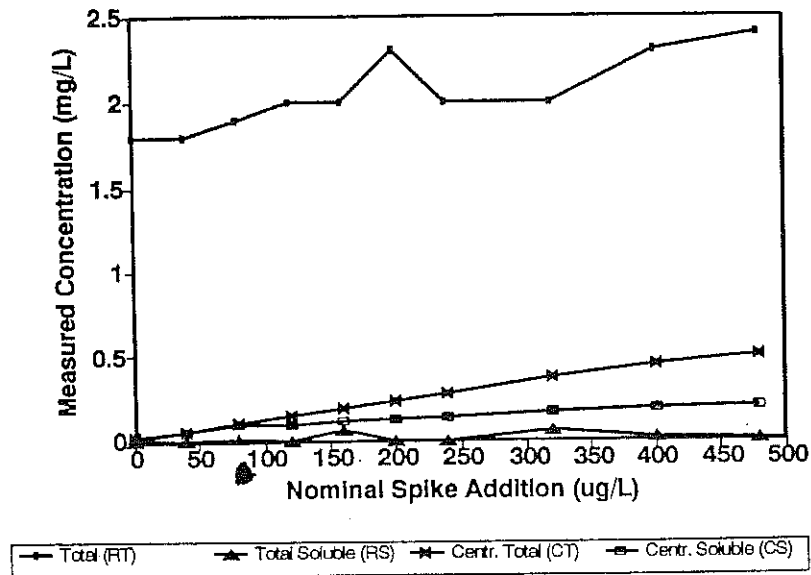


FIG. 5. Concentrations of Copper in Mixed Liquor

chromium, which was added to the samples, was removed by precipitation and subsequent centrifugation. These results suggest a relatively low capacity for sorption and a low solubility limit for chromium.

Conversely soluble concentrations of copper were less in the raw wastewater as compared to the centrifuged wastewater. This is apparent in both the degrittled wastewater and the mixed liquor. It is apparent that the removal of copper, during centrifugation, was enhanced by sorption onto the solids present in the raw wastewater. These results suggest a relatively high partitioning coefficient for copper, which maintained a concentration of copper in the liquid phase, which was below the solubility limit.

#### Solubility Limits

Solubility limits for the seven metals in the two wastewater streams were determined by assessing the data resulting from the soluble fraction of the sample with the solids removed by centrifugation. This fraction of the stream contained any ligands that would influence solubility but did not contain solids, which would remove metals from solution by sorption. The solubility limits were determined by either of the following:

- Averaging the concentrations of the CS sample after the apparent solubility limit had been achieved. This was indicated by a negligible increase in concentration of the CS sample as the level of dosing increased.
- Nonlinear-regression fitting of the CS curve to the following equation:

$$C_s = C_{Sol}(1 - e^{-kd})$$

where  $C_s$  = measured CS curve;  $C_{Sol}$  = solubility limit;  $k$  = fitting parameter; and  $d$  = nominal dosing concentration.

This latter method was employed when the CS curve had not completely flattened at the highest level of dosing and was required for copper and cadmium in the mixed-liquor samples. The average solubility limits along



TABLE 1. Estimated Solubility Limits

Metal (1)	SOLUBILITY LIMIT ( $\mu\text{g/L}$ )			
	Degrittied Influent		Mixed Liquor	
	Average (2)	Standard deviation (3)	Average (4)	Standard deviation (5)
Aluminium	264	66.2	177	64.4
Cadmium	360	NA <sup>1</sup>	3,340	4,461
Chromium	25	7.1	5	5
Copper	400	0 <sup>2</sup>	218	16
Nickel	>500	NA <sup>1</sup>	>500	NA <sup>1</sup>
Lead	110	42.4	58	19.8
Zinc	252	4.0	117	35.3

<sup>1</sup>No estimate of average value.

<sup>2</sup>Average based upon two equal values.

with the standard deviations are presented in Table 1. A considerable degree of uncertainty was associated with the estimate for cadmium in the mixed liquor. This uncertainty resulted from a high degree of correlation between the fitted parameters in this case.

Nickel was the most soluble metal in this study, with no apparent flattening of the CS curve and chromium was the least soluble with solubility limits of 25  $\mu\text{g/L}$  and 5  $\mu\text{g/L}$  for the degrittied influent and mixed liquor, respectively. Aluminum and chromium were present at the solubility limit for all the samples in both the degrittied wastewater and in the mixed liquor.

Five of the seven metals demonstrated lower solubility limits in the mixed liquor as compared to the degrittied influent. Only cadmium had a higher solubility limit in the mixed liquor than in the degrittied influent, while a solubility limit for nickel was not obtained in either the degrittied influent or the mixed liquor. The lower solubilities in the aeration tank are likely due to biodegradation of organic complexing ligands, which act to maintain metals in solution (Stoveland and Lester 1980).

#### Partitioning Coefficients

The analysis of sorption of metals onto biosolids depended upon the solubility limits of the metals and whether or not precipitate was present. In cases where the concentration of a metal in the soluble fraction of the raw sample was less than the solubility limit, the concentration of precipitate was assumed to be zero. In this case the linear sorption partitioning coefficient ( $K_p$ ) was determined by regressing  $C_T$  against  $C_S$  in the following model:

$$C_T = C_S(1 + K_p X) \quad (14)$$

In the regression, the RT samples were used as the  $C_T$  values while the RS samples were used as  $C_S$  values. The slope of the regression line was taken as  $(1 + K_p X)$  from which  $K_p$  was determined. The regression line was forced through the origin for this analysis.

In cases where the solubility was exceeded during titration, this approach was employed for the samples where the RS concentrations of the metal were less than the solubility limit. After the solubility limits were exceeded,

**TABLE 2. Sorption Partitioning Coefficients**

Metal (1)	SORPTION PARTITIONING COEFFICIENT (L/g)			
	Degrittied Wastewater		Mixed Liquor	
	$K_p$ (2)	Standard error (3)	$K_p$ (4)	Standard error (5)
Cadmium	11.90	2.60	>19.9	NA <sup>1</sup>
Copper	17.64	0.80	13.9	6.50
Lead	5.85	0.20	5.65	1.10
Nickel	0.40	0.01	3.94	0.30
Zinc	4.30	0.20	6.27	2.60

<sup>1</sup>All soluble concentrations below detection limit.

it was assumed that the sorption capacity of the biosolids had been exhausted, and therefore, any incremental increase in the total concentration was due to precipitation. For each of the dosage levels where RS was at the solubility limit, the calculated precipitate concentration was deducted from the total concentration and the solubility limit was employed for  $C_s$ . The  $K_p$  value was then calculated for each dose level and an average value over all of the dose levels was obtained. The value obtained for the cases where precipitate was absent was then averaged with that obtained for when precipitate was present.

For metals where the soluble concentration in the raw wastewater was at the solubility limit for all dosage levels, it was impossible to determine the  $K_p$  coefficient as there was no available information to indicate the portion of the particulate metal that was associated with the biosolids and was precipitate. This occurred for aluminum and chromium in the degrittied wastewater and the mixed liquor. For these metals, the low solubility limits relative to the background concentrations of metal present indicate that a majority of the removal of these compounds would be due to removal of precipitate. A conservative estimate of effluent quality could be obtained by employing zero for the sorption partitioning coefficients for these compounds. The estimated values for the sorption partitioning coefficients along with their standard deviations are presented in Table 2.

Copper, with a partitioning coefficient of 17.64 L/g in the degrittied wastewater and 13.9 L/g in the mixed-liquor samples, was the most strongly partitioned metal. Nickel partitioned the least with coefficient values of 0.4 and 3.94 L/g in the degrittied wastewater and the mixed liquor, respectively. No trend to indicate higher or lower partitioning in the primary or secondary systems was apparent. Of the five metals for which partitioning coefficients could be estimated, two had higher values in the degrittied wastewater while three had higher values in the mixed liquor.

### MODEL ASSESSMENT

Testing of the TOXCHEM model was performed to verify the model configuration and to assess the validity of the model parameters estimated in the previously described experiments. The results from a study of three municipal wastewater-treatment plants in Southern Ontario (*Fluctuations* 1991) were employed for this purpose. The study documents the influent and effluent concentrations of five metals, taken at 2-h intervals for a period of 196 h. Plant design and operating data for input to the model were taken

TABLE 3. Summary of Wastewater-Treatment Plant Characteristics

Parameter (1)	Wastewater Treatment Plant		
	Galt (2)	Waterloo (3)	Welland (4)
Wastewater flow rate (m <sup>3</sup> /d)	30,912	39,674	34,974
Influent total suspended solids concentration (mg/L)	102	136	74
Grit-chamber surface area (m <sup>2</sup> )	100	99.4	62.4
Grit-chamber depth (m)	3	0.62	0.9
Primary-clarifier surface area (m <sup>2</sup> )	1,052	1,662	1,120
Primary-clarifier depth (m)	2.9	3.5	2.7
Suspended solids removal in primary clarifier (%)	50	50	50
Aeration-basin surface area (m <sup>2</sup> )	1,571	2,722	923
Aeration-basin depth (m)	4.2	4.94	4.6
Mixed-liquor suspended solids concentration (mg/L)	1,300	3,050	2,380
Return activated sludge suspended solids concentration (mg/L)	2,600	6,000	5,000
Secondary-clarifier surface area (m <sup>2</sup> )	1,648	2,990	4,242
Secondary-clarifier depth (m)	3	3.1	3.9
Final-effluent suspended solids conc., mg/L	34	5.8	4

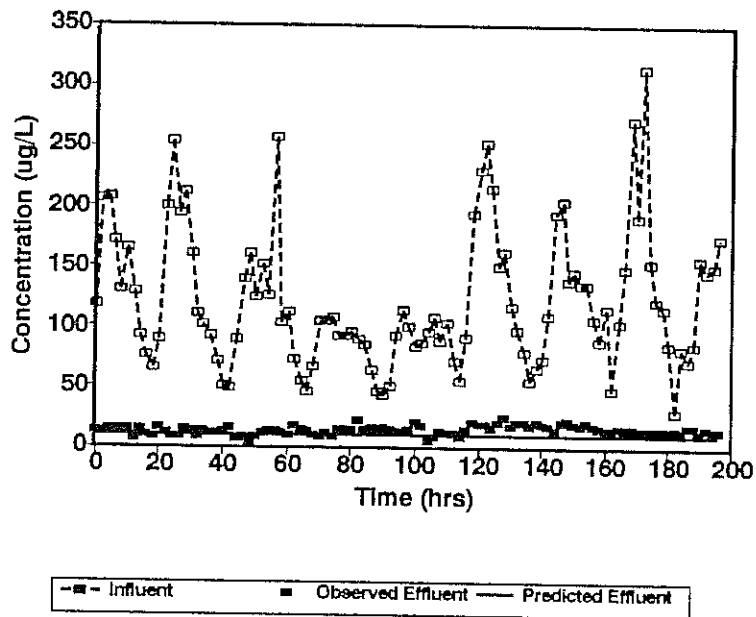


FIG. 6. Observed and Predicted Copper Concentrations at Waterloo WWTP

from the project report and are summarized in Table 3. Effluent suspended-solids concentrations from the Galt plant were abnormally high due to a period of excessive wet weather during the monitoring program.

Measured influent concentrations for each metal were employed as input to the model and the model predictions were compared to those measured in the treatment-plant effluent. Figs. 6-8 demonstrate the results of this modeling exercise for copper and zinc in the Waterloo plant and nickel in the Galt plant, respectively. A large peak in the influent nickel concentration in the latter case masked the effluent concentrations; therefore, Fig. 8 presents only observed and predicted effluent concentrations.

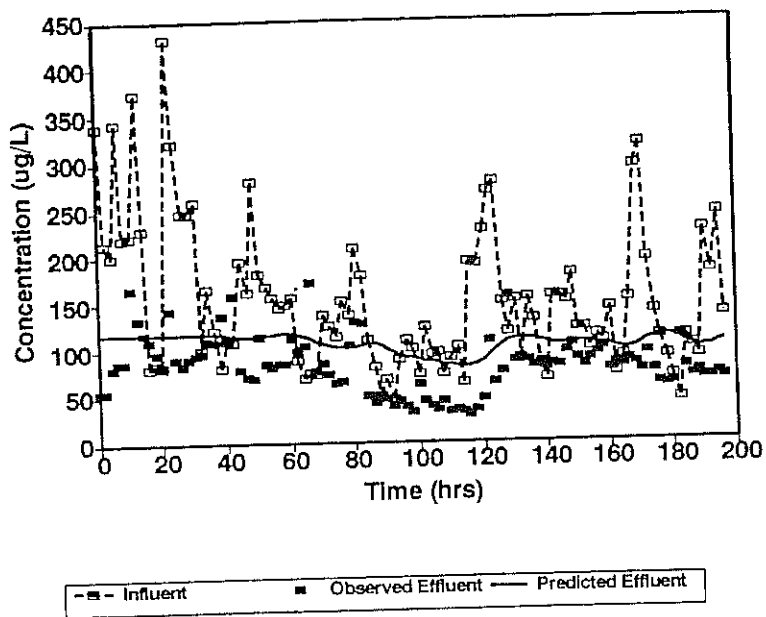


FIG. 7. Observed and Predicted Zinc Concentrations at Waterloo WWTP

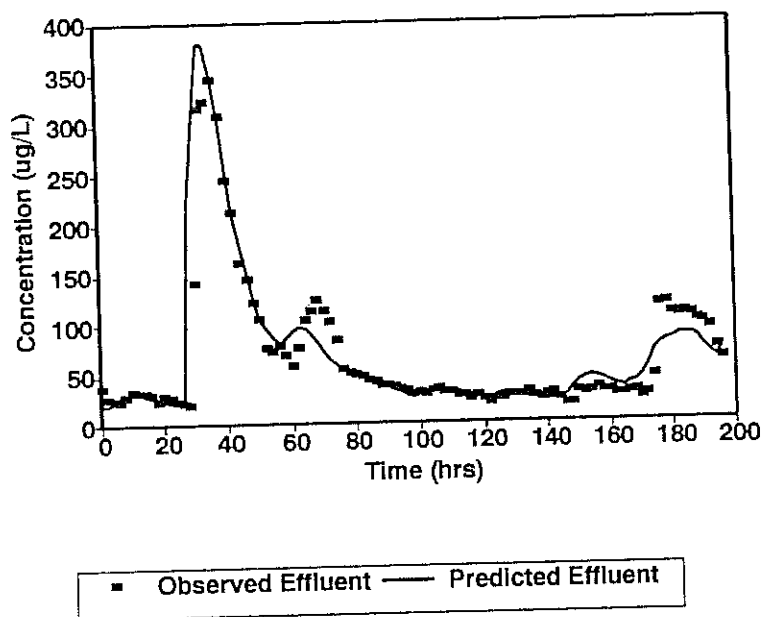


FIG. 8. Observed and Predicted Nickel Concentrations at Galt WWTP

The model assessment was performed to appraise the validity of the experimentally determined solubility and sorption partitioning coefficients and to determine if these coefficients were transferable from plant to plant. It is apparent from Fig. 7 that although the model predicted the general trend in behavior of zinc, the predicted effluent concentrations varied at some times from the observed values. To ascertain whether or not the model adequately reflected the measured effluent concentrations with the associated experimental error, a statistical goodness-of-fit test was employed.

Values of field duplicates were obtained from the original researchers. Approximately 5% of the samples had been submitted as field duplicates. The variance of these duplicates was assumed to represent the pure error

variance resulting from variability in the sampling and analytical procedures. The variance was calculated as

$$\sigma^2 = \frac{\sum^{0.5}(d1 - d2)^2}{n - 1} \quad (15)$$

where  $\sigma^2$  = variance of duplicates;  $d1, d2$  = duplicate values; and  $n$  = number of duplicates.

The number of duplicate values in the effluent data set were relatively few in number. This reduced the power of any statistical test, and therefore, to obtain more information on the variability resulting from the sampling and analysis, the duplicates in the influent data set were also examined. The variance was estimated using the available duplicates on each metal for both the influent and effluent measurements. These were compared for each plant using an  $F$  test at the 95% level of confidence. This test showed that the influent and effluent variances could be considered equal. This result was obtained for each metal at each plant. Therefore, the estimated influent and effluent variances could be pooled to obtain a more precise estimate of the pure error variance.

The mean residual sum of squares was calculated employing

$$\text{mean RSS} = \frac{\sum \{\text{predicted } y_i - \text{observed } y_i\}^2}{\text{degrees of freedom}} \quad (16)$$

Since the model parameters were not fit to the data, the number of degrees of freedom associated with this estimate was assumed to be  $n - 1$  where  $n$  is the number of observations.

If the model predictions were to fit the observed data, then the mean RSS should have the same value as the pure measurement error, within a margin of error. The ratio of the mean RSS to the pure measurement error was therefore compared to the appropriate  $F$  statistic to determine the statistical significance of any differences. Table 4 summarizes the calculations for each of the metals at each of the three wastewater-treatment plants.

It is apparent from Table 4 that the model fit is specific to metals and wastewater-treatment plants. The model predicted the behavior of two metals, copper and zinc, with an accuracy that was within the variability observed in field replicates in two of the three plants. The predictions for the remaining compounds did not fit the requirements of the goodness-of-fit test at any of the plants. The apparent lack of fit in these latter cases may be attributed to one or more of the following sources:

- A flaw in the model configuration.
- Measured concentrations do not adequately reflect the true variability in response of the metals.
- The model is not calibrated properly for the given metal and wastewater-treatment plant.

The validity of the model configuration can be evaluated by examining the model predictions for metals with differing chemical properties. Fig. 6 demonstrates that the concentrations of copper in the effluent were consistently low, despite substantial fluctuations in the influent concentration and the model accurately simulated this behavior. In this case, the model predictions were within the goodness-of-fit criteria. In contrast, Fig. 8 dem-

TABLE 4. Summary of Goodness-of-Fit Testing

Statistical parameter (1)	Chromium			Copper			Lead			Nickel			Zinc		
	GALT (2)	WAT (3)	WELL (4)	GALT (5)	WAT (6)	WELL (7)	GALT (8)	WAT (9)	GALT (10)	WAT (11)	WELL (12)	GALT (13)	WAT (14)	WELL (15)	
Error variance	5.0	9.4	6.9	57.6	17.2	13.0	3.1	35.9	15.2	8.5	0.6	1,370.5	993.6	41.1	
Mean RSS	652.3	826.8	60.3	713.5	38.1	24.1	45.8	419.5	1,185.7	75.1	8.8	2,579.3	1,234.7	1,086.2	
F Statistic	130.5	88.1	8.7	12.4	2.2	1.9	14.6	11.7	78.0	8.8	15.4	1.9	1.2	26.5	
Conclusion	Different <sup>1</sup>	Different	Different	Different	Same <sup>2</sup>	Same	Different	Different	Different	Different	Different	Same	Same	Different	

Note: GALT = Galt, Ontario POTW; WAT = Waterloo, Ontario POTW; and WELL = Welland, Ontario POTW. RSS = residual sum of squares.

<sup>1</sup>Different indicates failed goodness-of-fit test.

<sup>2</sup>Same indicates passed goodness-of-fit test.

onstrates that the model essentially simulated the response of nickel to a large influent concentration spike. In spite of the apparently accurate response of the model, the model predictions did not meet the goodness-of-fit criteria. The sources of error between the observed and predicted responses in the latter case are primarily due to differences during the rapid response to the large influent spike and also due to a predicted increase at run time of 140 h, which was not observed in the plant effluent. The former variation likely resulted from nonideal mixing in the aeration basin, while the latter was likely a predicted response to an erroneous influent measurement. In spite of these concerns, it is apparent that the model accurately predicted the behavior of two metals with divergent chemical properties. These results suggest that the configuration of the model is valid.

The nature of the data set, and any biases in it that do not reflect the actual behavior of the metals, can also be responsible for an apparent lack of fit of the model predictions. An example of such a bias is when the concentrations of the metals are at or near the analytical detection limit. For the purposes of this study, the data were reported as the analytical detection limit when concentrations were less than this value. Variability in the data, which would provide an error sum of squares, is therefore attenuated by the use of this substitution. Consequently, relatively small deviations of the model predictions from the observed data would result in a statistical difference. In this study all of the metals, with exception of zinc, were consistently present at concentrations less than 5  $\mu\text{g/L}$  in the effluents of at least one plant. A total of six cases were identified where these conditions prevailed. It is quite apparent that in at least some of the cases that the data were being biased by the use of detection limits. Chromium at the Welland plant and lead at the Galt plant in particular had low effluent concentrations and as a result extremely small error variances. It is probable that some of the lack-of-fit conclusions obtained were as a result of this phenomenon, which would make the test excessively rigorous.

Model calibration is a concern when employing models that utilize macroscopic properties such as experimentally defined solubility limits and sorption partitioning coefficients of metals in complex matrices, such as degrittled wastewater and aeration-basin mixed liquor. These parameters can be influenced by factors such as alkalinity, hardness, pH, and the presence of organic complexing ligands. The results of this study suggest that the model should be calibrated for each metal at a given wastewater-treatment plant. The goodness-of-fit test demonstrated that copper and zinc were accurately predicted in two out of three plants, yet the plants that fit the test were not the same for both metals. For other metals, the model did not meet the test criteria for any of the plants, suggesting that parameters determined for the Burlington plant were not representative of those at other plants. Since the model configuration is apparently correct, it would appear that the most accurate predictions would result from a model that is calibrated for each metal at a specific plant. Calibration could be performed by regression of the model predictions against data measured at the plant influent, the primary clarifier effluent and the final clarifier effluent. The influent solubility limits and the partitioning coefficients would be calibrated separately from the effluent coefficients. Unfortunately, the data collected in the three-plant study did not include measurements of the primary clarifier effluent and without this information, calibration of the model parameters with this data set is not possible.

## CONCLUSIONS

Solubility limits and sorption partitioning coefficients in degrittled wastewater and activated-sludge mixed liquor were experimentally determined for seven metals commonly found in municipal wastewaters. Nickel was the most soluble metal, and chromium was the least soluble with solubility limits of 25  $\mu\text{g/L}$  and 5  $\mu\text{g/L}$  for the degrittled influent and mixed liquor, respectively. Five of the seven metals demonstrated lower solubility limits in the mixed liquor as compared to the degrittled influent. Only cadmium had a higher solubility limit in the mixed liquor than in the degrittled influent; a solubility limit for nickel was not obtained in either the degrittled influent or the mixed liquor.

Copper, with a partitioning coefficient of 17.64 L/g in the degrittled wastewater and 13.9 L/g in the mixed-liquor samples, was the most strongly partitioned metal. Nickel partitioned the least with coefficient values of 0.4 and 3.94 L/g in the degrittled wastewater and the mixed liquor, respectively. No trend to indicate higher or lower partitioning in the primary or secondary systems was apparent.

Predictions of the calibrated model were compared to dynamic data, which were obtained from three municipal wastewater-treatment plants in a separate study. A goodness-of-fit test was employed to determine whether or not the model predictions were significantly different from the observed effluent concentrations if experimental variability was accounted for. This test compared the difference between the model predictions and the observed concentrations to an error variance, which was calculated from variability determined in field replicates. The test demonstrated that copper and zinc were accurately predicted within the data-set variability. The model form is apparently correct as the behavior of copper and nickel, metals with substantially different chemical properties, was well predicted. In some cases, the experimental data were biased by a proximity of most of the measured concentrations to the analytical detection limit. This resulted in an attenuation of the error variance term and, hence, made the goodness-of-fit test excessively rigorous. It would appear that the most accurate prediction of the behavior of metals would be obtained by calibrating the model specifically for each wastewater-treatment plant.

## APPENDIX I. REFERENCES

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## APPENDIX II. NOTATION

*The following symbols are used in this paper:*

- $C_o$  = total metal concentration in plant influent,  $\mu\text{g/L}$ ;
- $C_{P_o}$  = concentration of metal in plant influent in precipitate form,  $\mu\text{g/L}$ ;
- $C_{P_1}$  = concentration of metal in degritter effluent in precipitate form,  $\mu\text{g/L}$ ;
- $C_{P_2}$  = concentration of metal in primary clarifier overflow in precipitate form,  $\mu\text{g/L}$ ;
- $C_{P_3}$  = concentration of metal in first aeration-basin effluent in precipitate form,  $\mu\text{g/L}$ ;
- $C_{P,n+1}$  = concentration of metal in  $n$ th aeration-basin influent in precipitate form,  $\mu\text{g/L}$ ;
- $C_{P,n+2}$  = concentration of metal in  $n$ th aeration-basin effluent in precipitate form,  $\mu\text{g/L}$ ;
- $C_{P,N+3}$  = concentration of metal in secondary clarifier overflow in precipitate form,  $\mu\text{g/L}$ ;
- $C_{S_o}$  = concentration of metal in plant influent in soluble form,  $\mu\text{g/L}$ ;
- $C_{S_1}$  = concentration of metal in degritter effluent in soluble form,  $\mu\text{g/L}$ ;
- $C_{S_2}$  = concentration of metal in primary clarifier overflow in soluble form,  $\mu\text{g/L}$ ;
- $C_{S_3}$  = concentration of metal in first aeration-basin effluent in soluble form,  $\mu\text{g/L}$ ;
- $C_{S,n+1}$  = concentration of metal in  $n$ th aeration-basin influent in soluble form,  $\mu\text{g/L}$ ;
- $C_{S,n+2}$  = concentration of metal in  $n$ th aeration-basin effluent in soluble form,  $\mu\text{g/L}$ ;
- $C_{S,N+3}$  = concentration of metal in secondary clarifier overflow in soluble form,  $\mu\text{g/L}$ ;
- $C_{\text{Sol},1}$  = solubility limit of metal in degritting and primary clarification,  $\mu\text{g/L}$ ;
- $C_{\text{Sol},2}$  = solubility limit of metal in aeration basin and secondary clarification,  $\mu\text{g/L}$ ;
- $K_{P_1}$  = sorption partitioning coefficient in degritting and primary clarification,  $\text{L/g}$ ;
- $K_{P_2}$  = sorption partitioning coefficient in aeration basin and secondary clarification,  $\text{L/g}$ ;
- $Q_o$  = plant influent flow rate,  $\text{m}^3/\text{d}$ ;
- $Q_1$  = primary clarifier overflow rate,  $\text{m}^3/\text{d}$ ;
- $Q_{PC}$  = primary clarifier underflow rate,  $\text{m}^3/\text{d}$ ;
- $Q_r$  = activated sludge recycle flow rate,  $\text{m}^3/\text{d}$ ;

- $Q_w$  = activated sludge wasting flow rate,  $m^3/d$ ;  
 $V_{a,1}$  = first aeration-basin volume,  $m^3$ ;  
 $V_{a,n}$  =  $n$ th aeration-basin volume,  $m^3$ ;  
 $V_g$  = grit-chamber volume,  $m^3$ ;  
 $V_p$  = primary-clarifier volume,  $m^3$ ;  
 $V_s$  = secondary-clarifier volume,  $m^3$ ;  
 $X_o$  = volatile suspended-solids concentration in plant influent,  $g/L$ ;  
 $X_1$  = volatile suspended-solids concentration in primary-clarifier overflow,  $g/L$ ;  
 $X_e$  = volatile suspended-solids concentration in primary-clarifier overflow,  $g/L$ ;  
 $X_m$  = volatile suspended-solids concentration in aeration basin,  $g/L$ ;  
 $X_{PC}$  = volatile suspended-solids concentration in primary clarifier underflow,  $g/L$ ; and  
 $X_r$  = volatile suspended-solids concentration in activated sludge recycle,  $g/L$ .