

Estimation of Solute Transport and Storage Parameters in a Stream with Anthropogenically Produced Unsteady Flow and Industrial Bromide Input

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ABSTRACT

We used an anthropogenic tracer signal to evaluate downstream solute transport and storage in Valley Creek, a 60 km² watershed stream near Philadelphia, Pennsylvania that is subject to urbanization and anthropogenically induced unsteady flow. Bromide-bearing groundwater from an abandoned mineral processing plant enters the upstream reach of Valley Creek through a series of well-defined seeps and springs, producing a steady and significant concentration of bromide in Valley Creek. In addition, at the time of the study, a quarry located near the center of the watershed discharged accumulated groundwater seepage to the stream on a cyclical basis. The quarry discharge reduced the bromide concentration in the main stream and produced a periodicity in the in-stream bromide concentration downstream of the quarry. We used these variations in the ambient bromide concentration to assess solute mixing and transport in Valley Creek. We applied the USGS code OTIS to analyze solute advection, dispersion, transient storage, and groundwater inflow over a 7.5 km stream reach. To apply OTIS for unsteady flow

conditions, we independently modeled the variation of stream conditions during a flow cycle and then simulated solute transport using temporal- and reach-average values of the longitudinal dispersion coefficient (D), transient storage exchange rate (α), and transient storage area (A_s/A). Calibrated values of D ranged from $0.5 \text{ m}^2\text{s}^{-1}$ to $1.4 \text{ m}^2\text{s}^{-1}$, A_s/A ranged from 0.03 to 1.3, and α ranged from $8.7 \times 10^{-6} \text{ s}^{-1}$ to $1.0 \times 10^{-2} \text{ s}^{-1}$. Observed temporal variability in the in-stream bromide concentration was simulated well. The observed transient storage parameters reflect differences in the structure of the three test reaches. Solute storage in the middle reach was dominated by in-stream storage produced by relict hydraulic structures, while solute transport in the other two reaches reflected differences in bed sediment characteristics between upstream and downstream reaches. However, over-parameterization of the model and high sensitivity to the dispersion coefficient made it difficult to assess the magnitude of transient storage or hyporheic exchange.

1. Introduction

Solute transport processes, including downstream advection, in-stream mixing, and hyporheic exchange, are known to greatly influence water quality and stream ecology (Fisher et al., 1979; Rutherford, 1996; Jones and Mulholland, 2000). These processes can be significantly modified by anthropogenic activity, such as urbanization, which increases the volume and rate of surface runoff, increases soil erosion from the watershed and the corresponding sediment load to the stream, and reduces groundwater infiltration (Paul and Meyer, 2001). The connection between the hyporheic zone and the stream ecosystem has been examined in detail by many researchers over the past several years, but most of this work has focused on streams that are not affected by urbanization (Jones and Mulholland, 2000). New methods may be required to

analyze solute transport and hyporheic exchange in urbanized streams, which have significant anthropogenically induced perturbations in the magnitude and temporal variability of flow conditions, in the channel morphology and underlying sediment structure, and in localized or distributed inputs of contaminants, nutrients, and other chemicals.

As part of a larger project to study the effects of urbanization on watershed hydrology, subsurface chemical fluxes to the stream, and stream biota, we have developed estimates of dispersion, non-dispersive solute mixing, and groundwater inflows by measuring and analyzing known anthropogenic modifications of stream flow and composition. These estimates were obtained by applying the solute transport code OTIS to analyze variations in background bromide concentrations produced by a combination of an industrial bromide discharge and an anthropogenically produced periodic variation in stream flow. This analysis was not straightforward because OTIS was designed for steady flow conditions. The only previous application of OTIS to unsteady flows was in Huey Creek, a pristine Antarctic stream (Runkel et al., 1998). However, Valley Creek has significant surface storage capacity, surface and groundwater inflow, a higher flow variation frequency and more complex stream morphology and land use characteristics than Huey Creek. The methodology for analysis of this complex system should prove useful to others who are studying watersheds with high pollutant loads and unsteady flow conditions.

2. Site Description

Valley Creek watershed is located approximately 30 km northwest of Philadelphia, Pennsylvania. The 60 km² watershed drains Chester Valley, a carbonate formation bordered on the north by a quartzite ridge and on the south by a phyllite ridge (Sloto, 1990). The stream and

groundwater generally flow southwest to northeast, joining the Schuylkill River at Valley Forge National Historical Park. Impervious land cover constitutes approximately 17% of the watershed, which is indicative of the high degree of urbanization of the watershed. As of August 2001, the land use in the watershed included 36% residential, 19% commercial, 7% industrial, and 25% open/vacant lands.

A major limestone quarry operation in the watershed, though recently decommissioned, continues to pump accumulated groundwater out of the quarry pit and into a tributary of Valley Creek, as shown in Figure 1. During the period of the study, the quarry pumps operated in a cycle of (1) one pump operating, (2) two pumps operating, and (3) no pumping. The period of the cycle ranged from 5 to 7 hours. This cycle had a significant impact on the hydraulics of Valley Creek, as reflected by the stream stage record at a USGS gauge located 7.15 km downstream of the quarry tributary and 3.65 km upstream of the mouth of Valley Creek (Figure 1). During summer low-flow periods, when base flow was near $0.3 \text{ m}^3\text{s}^{-1}$, the gauge showed flow variations of up to 50% due to quarry cycling as shown in Figure 2.

A second anthropogenic impact occurs from an abandoned mineral processing plant located in the headwaters of Valley Creek, approximately 7 km upstream of the quarry tributary. Bromide-contaminated groundwater from this site is intercepted by a series of faults in the fractured limestone aquifer and is carried along these faults until they intercept Valley Creek in two locations as indicated in Figure 1. In each location, bromide-bearing groundwater enters the stream through several springs, producing high levels of bromide ($>1 \text{ mg L}^{-1}$) in Valley Creek. The quarry is located in an uncontaminated sub-watershed, and the bromide concentration of the quarry discharge is quite low (approximately 0.05 mg L^{-1}). The tributary inflow from the quarry dilutes the bromide in the main

stem of Valley Creek, and the downstream bromide concentrations vary over time because of the periodic nature of the quarry discharge.

3. Methods

Monitoring stations were limited to public lands and road crossings due to the highly urbanized nature of the watershed. A total of six sampling stations were established, as shown in Figure 1. Three stations were located on the main stem of Valley Creek downstream of the quarry tributary. Valley Creek Preserve (VC4) is located 1,950 m below the quarry tributary, Mill Rd (VC5) is located 5,200 m below the quarry tributary, and the USGS gauge (VC7) is located 7,150 m below the quarry tributary. Background monitoring stations were established in Valley Creek at Church Rd (VC1) 320 m upstream of the quarry tributary, in the quarry tributary (QT1), and in Little Valley Creek (LV1), which joins Valley Creek 5,350 m downstream of the quarry tributary and provides, on average, 29% of the flow measured at the USGS gauge.

Stream flow was determined at VC1 and LV1 twice during the experiment and at various times before and after the experiment using either a Gurley Pygmy Current Meter (Model #625) or a Sontek Flowtracker acoustic Doppler velocimeter.

Owing to the duration of the monitoring program and safety concerns, each of the downstream monitoring stations was equipped with an ISCO model 6700 automatic water sampler. Samples were collected hourly for 24 hours beginning at 2 pm on August 7, 2001. Additional samples were collected at 20-minute intervals beginning at 5 pm on August 8, 2001. The sampler installed at VC4 malfunctioned at 10:00 pm on August 8, 2001 resulting in a truncated data set. Each upstream (background) monitoring station was hand-sampled three times during the course of the study, and showed little variation in bromide concentration. All

sample bottles were acid-washed and triple-rinsed in deionized water. All samples were held on ice until they were returned to the laboratory and refrigerated at 4C. All samples were filtered through a 0.2- μm membrane just prior to bromide analysis using ion chromatography.

Calibration standards were run each day. Duplicates were run at an approximate ratio of 1 per 10 samples. A total of 110 samples were analyzed.

In order to calculate solute storage and dispersion parameters, the USGS code OTIS (One-dimensional Transport with Inflow and Storage) (Runkel, 1998) was fit to the measured bromide data. OTIS utilizes an advection-dispersion equation for the stream with added terms for lateral inflow and exchange with a stationary transient storage zone. This is coupled with an equation for mass accumulation in the storage zone as follows:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left(AD \frac{\partial C}{\partial x} \right) + \frac{q_l}{A} (C_l - C) + \alpha (C_s - C) \quad (1)$$

$$\frac{\partial C_s}{\partial t} = \alpha \frac{A}{A_s} (C - C_s) \quad (2)$$

where A and A_s are the cross sectional areas of the main channel and the storage area (m^2); C , C_s and C_l are the solute concentrations in the main channel, the storage area and the lateral inflow (mg L^{-1}); Q is the volumetric flow rate in the main channel (m^3s^{-1}); q_l is the lateral inflow rate ($\text{m}^3\text{s}^{-1}\text{m}^{-1}$); and α is the transient storage exchange rate (s^{-1}).

The required model inputs for the variable-flow case considered here are stream flow rate, cross sectional area, lateral inflow rate and lateral inflow concentration at each specified flow location at each time step. Based on field measurements, constant stream flow was specified at VC1. At the three sampling locations downstream of the quarry tributary, stream flow was estimated by mass balance using the measured bromide concentrations. This ‘dilution gauging method’ has been shown to provide better estimates of stream flow than standard velocity

gauging methods (Zellweger et al., 1989; Harvey and Wagner, 2000). The flow estimated by bromide dilution at VC7 was slightly higher than and slightly out of phase with that reported by the USGS gauge. Both the bromide-concentration-based flow estimates and the USGS gauge data were used as input for OTIS. A slightly better calibration was achieved using the USGS data.

Three additional flow locations were specified in OTIS to allow the quarry discharge and Little Valley Creek to be represented as localized inputs. As shown in Figure 2, location VC2 is just upstream of the quarry tributary, location VC3 is 100 m downstream of the quarry tributary, and location VC6 is just below the confluence with Little Valley Creek, 155 m downstream of sampling station VC5. Flow in Valley Creek at location VC2 was estimated as the flow at VC1 plus lateral inflow. Flow at location VC3 was estimated as the flow at VC4 minus lateral inflow. Lateral inflow was assumed constant from location VC1 to location VC4. These flow estimates were confirmed by comparison with measurements of quarry pumpage during and just before the experiment. Flow at VC6 was calculated by adding the flow measured at LV1 to the flow estimated at VC5.

For each of the flow locations analyzed in OTIS, cross-sectional areas were estimated at each time step from a calibrated model of Valley Creek which used the gradually varied flow equation (C. Emerson, Drexel University, written communication, 2002). In addition, net lateral inflow and outflow rates were estimated based on the change in average flow between flow locations using the method of Harvey and Wagner (2000).

The dispersion coefficient, transient storage area, exchange rate, and lateral inflow rate were used to calibrate OTIS to the measured bromide concentration data. The dispersion coefficient was initially estimated using the measured bromide data at VC4, VC5 and VC7. Initial estimates

of the transient storage area and exchange rate were obtained using the method of Harvey and Wagner (2000). Inflow was also used as a calibration parameter because of the unsteady stream flow. In steady flow applications, inflow is typically taken as a constant known value based on the change in stream flow between monitoring stations. However, for the cyclical flow conditions considered here, inflow could only be estimated from the change in the average flow between stations, and the inflow rate would be expected to vary over time as the stream flow rate changes. Thus inflow was used as a calibration parameter and the average inflow was used as the initial estimate.

In contrast to Huey Creek, the number of calibration parameters required to apply OTIS to a highly modified and complex watershed such as Valley Creek results in a model that is over parameterized. In our case, this resulted in STARPAC, the nonlinear least squares optimization package associated with OTIS, yielding unreasonable parameter estimates and flattened bromide response. Therefore, parameter estimates were first optimized by best-eye fitting the model output to the data to the best judgment of the modeler. Next, a spreadsheet-based least-squares analysis was conducted in which the error (the sum of the squares of the difference between the model estimated bromide concentration and the measured bromide concentration) was minimized by adjusting each parameter (A_s , α , D) individually and cumulatively. Model sensitivity was estimated by examining the change in error resulting from a two-fold change in the optimized parameter estimates.

4. Results

Upstream bromide levels in Valley Creek at VC1 were measured several times during the experiment and found to be 1.19 mgL^{-1} , 1.24 mgL^{-1} and 1.37 mgL^{-1} . Measured bromide

concentrations at QT1 were 0.054 mgL^{-1} , 0.040 mgL^{-1} and 0.052 mgL^{-1} . Bromide concentrations at LV1 were 0.100 mgL^{-1} , 0.093 mgL^{-1} and 0.082 mgL^{-1} . Analytical precision, determined through replicate analysis, was $\pm 4.6\%$. Flow upstream of the quarry at VC1 was measured two times during the experiment and found to be $0.071 \text{ m}^3 \text{ s}^{-1}$ and $0.067 \text{ m}^3 \text{ s}^{-1}$. In February 2002, flow was again measured at VC1 ($0.068 \text{ m}^3 \text{ s}^{-1}$) and then measured at VC2 ($0.077 \text{ m}^3 \text{ s}^{-1}$). The estimated discharge of the quarry tributary ranged from $0.118 \text{ m}^3 \text{ s}^{-1}$ to $0.247 \text{ m}^3 \text{ s}^{-1}$ over each pump cycle. This is not exactly the same as the flow pumped out of the quarry due to losses to groundwater between the quarry discharge point and the confluence of the quarry tributary with Valley Creek. There were also losses to groundwater at some locations within the main stem of Valley Creek. We calculated a net water efflux from the stream of $0.062 \text{ m}^3 \text{ s}^{-1}$ between stations VC6 and VC7. Independent flow measurements made using a Gurley Pygmy Current Meter (Model #625) in June 2002 under steady state flow conditions showed a loss of $0.04 \text{ m}^3 \text{ s}^{-1}$ in this location.

The bromide concentration data and OTIS simulations for the breakthrough curves at stations VC4, VC5 and VC7 are shown in Figure 3. It is apparent that there is a periodic variation in the in-stream bromide concentration downstream of the quarry inflow, and that this wave is attenuated as it travels downstream due to dispersion and other mixing processes. We were able to simulate the periodicity and the magnitude of the bromide variation quite well at all three stations. The simulation at the USGS gauge (VC7) is based on the stream discharge data reported by USGS because these values provided a better fit of the bromide data. The total bromide mass from the model simulation was within 3% of the mass measured at each station, as given in Table 1. The calibration at VC4 is better than at either VC5 or VC7. There appears to be a phase shift in the early model output relative to the measured bromide data at VC5. At VC7

there appears to be a change in the lateral inflow that was not captured by the model. Both of these discrepancies may be explained in part by an additional variation in the quarry pumping cycle before the start of monitoring. Note that the early bromide cycles recorded at the downstream sampling stations reflect quarry input flows that occurred before the upstream monitoring had begun. The reach from VC1 to VC2 has a steady flow rate and constant bromide concentration making parameter estimation in this reach trivial. The reach from VC2 to VC3 is a very short reach (100 m) to allow for an approximate point source input of the quarry discharge. Parameter estimates for this reach have little impact on the model output at VC4, 1850 m downstream of VC3. Therefore, longitudinal dispersion, storage area, and exchange rate for the two most upstream reaches (VC1 to VC2 and VC2 to VC3) were assumed to be similar to the values for the reach from VC3 to VC4.

The final reach-average estimates of longitudinal dispersion (D), transient storage area (A_s/A) and exchange rate (α) for three reaches are given in Table 2. The reach between VC4 and VC5 has a much greater transient storage area and faster exchange rate than the other reaches of Valley Creek, most likely due to the presence of two dams (one 2.1 m high and one 0.9 m high), a small riparian wetland, and an active millrace that diverts as much as 50% of stream flow through a channel with a slower velocity than Valley Creek. All of these surface water impoundments represent ‘dead zones’ or off-channel pools in which surface water enters and is slowly released back to the main channel. These conclusions are somewhat obscured by the fact that the period of the quarry variation was rather short so that long tailing of each solute pulse could not be observed, and the model was very sensitive to the dispersion coefficient.

As shown in Table 3, adjusting D by a factor of two increased error by at least 13% in the upper reach, 58% in the middle reach and 286% in the lower reach. The model appears to have

limited sensitivity to α in the upper and lower reaches, where adjusting α by a factor of two increased the error by no more than 2.7%. In the middle reach the error estimate increased by at least 36% when α was adjusted by a factor of two. The model also has limited sensitivity to A_s in the lower reach where a factor of two adjustment increases the error by no more than 1.2%. However, in the upper reach, increasing the value of A_s by a factor of two increases the error by 253%, while decreasing A_s by a factor of two increases the error by only 3.3%. The middle reach is the most sensitive to adjustment of A_s where a factor of two adjustment increases the error by at least 1300%.

5. Discussion and Conclusions

We successfully calibrated OTIS to represent downstream solute transport and storage in a highly urbanized stream system characterized by multiple anthropogenic impacts including a highly variable, cyclical flow rate driven by the periodic input of water from a large quarry and background bromide contamination in the main stem of the stream emanating from groundwater contamination. Transient storage appears to have a major effect on solute transport. OTIS model output indicates that the size of the transient storage zone in the middle reach is much greater than in any other reach, most likely due to surface storage. Hyporheic exchange also appears important in some reaches. Valley Creek has a varied substratum with areas of exposed fractured bedrock as well as areas of cobble, gravel and sand, sometimes covered with fine silt and clay. For example, grain size mass analysis at a location downstream of the USGS gauge indicates that while 65% - 84% of the bed sediment is coarse sediment ($> 2000 \mu\text{m}$), the fine sediment ($< 2000 \mu\text{m}$) is approximately 92% sand ($> 75 \mu\text{m}$) and 8% fine sand, silt and clay.

These types of sediment are consistent with observed transient storage exchange rates of $8.7 \times 10^{-6} \text{ s}^{-1}$ to $1.0 \times 10^{-2} \text{ s}^{-1}$.

We found that both transient storage area (A_s/A) and exchange rate (α) appear to decrease in the downstream direction. In contrast to these results, Morrice et. al. (1997) found A_s/A decreased with flow while α increased with flow, and suggested that sediment grain size and hydraulic conductivity strongly influence transient storage. D'Angelo et al. (1993) indicated that transient storage decreased with stream size and velocity while exchange rate increased with flow and velocity. Wörman et al. (2002) and Packman and Salehin (2003) have found that the exchange rate varies with the square of the stream velocity, and that stream morphology and sediment characteristics are also important controls on transient storage. In Valley Creek, the temporal velocity variation is quite large (39% increase in velocity associated with a 54% increase in flow over a 3.25 hour period) while the spatial velocity variation is quite small (6.5% increase in average velocity associated with a 50% increase in average flow from the upper reach to the lower reach). It appears, therefore, that surface water impoundments and sediment characteristics have a greater influence on solute transport than does the downstream increase in velocity in Valley Creek. However, these conclusions must be tempered due to the model's lack of sensitivity to changes in A_s and α . Large variations in these two parameters result in only minor increases in the total error. In addition to the sensitivity analysis shown in Table 3, we evaluated model sensitivity to an increase in α in the upper reach of two orders of magnitude to approximate the value of α in the lower reach. The result was an increase in the total error of only 79%. This lack of sensitivity reflects the use of a natural tracer in a highly urbanized system. While this is a convenient method to obtain useful data, the reliability of the results may be limited because the researcher has only limited control over important design criteria, such as

reach length and the temporal variation in the tracer concentration signal (Harvey and Wagner, 2000).

Several assumptions used in OTIS, including the requirement that dispersion, transient storage area, and exchange rate be taken as steady input parameters over a given reach, hindered calibration and contributed to the model's lack of sensitivity. In a system such as Valley Creek, each of these parameters will vary with time due to the unsteady stream flow. The importance of the variable exchange rate can be seen in an examination of the calibration curves. Where bromide concentration is at a maximum, the stream flow rate is at a minimum, and vice versa. The calibration curve is most influenced by exchange rate in these two areas (Harvey and Wagner, 2000), indicating that the calibration curve is more influenced by the upper and lower limits of the exchange rate than the average value of exchange rate. Because of the nonlinear variation of exchange rate with stream velocity, the average α over a flow cycle would not be expected to be the same as the α obtained from the average velocity. In addition, velocity is not a fitting parameter in OTIS. Instead, the model utilizes the flow rate and cross sectional area specified at each flow location.

In the only other published use of OTIS with unsteady flow, Runkel et al. (1998) indicate that variation of storage parameters with flow or velocity is not an issue in Huey Creek, an Antarctic stream with coarse alluvial substrata. In the Huey Creek system, transient storage is dominated by rapid hyporheic exchange down to a depth constrained by permafrost and therefore, parameter estimates obtained from OTIS may not be sensitive to the velocity variation observed in Huey Creek. In contrast, the temporal velocity variations we observed in Valley Creek were quite large, and Valley Creek also has high spatial heterogeneity in both stream and subsurface conditions so that solute transport behavior was apparently controlled by different processes in

different stream reaches. Thus, flow variation in Valley Creek may have a greater impact on transient storage and a model that allows for time-varying dispersion and transient storage may provide a better estimate of solute transport. This analysis would be complicated by the fact that relatively little is known about mixing and transport processes in unsteady flows, so that it might be difficult to even obtain adequate estimates of the variation of in-stream dispersion and dead-zone storage over the variable flow cycle.

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Figure 2 Flow in Valley Creek recorded by USGS gauge

Figure 3 OTIS Calibration Curves: A—VC4; B – VC5; C – VC7. Dots indicate measured bromide concentration data; solid lines indicate model runs

Table 1 Measured and Simulated Mass

Station	Bromide, kg		
	Meas.	Sim.	% Difference
VC4	8.34	8.28	0.72
VC5	8.36	8.14	2.66
VC7	8.67	8.82	1.73

Table 2 Reach Average Parameters for Valley Creek

Reach	D, m ² /s	A _s /A	α, s ⁻¹
VC3 - VC4	1.4	0.07	2.7E-04
VC4 - VC5	0.5	1.3	1.0E-02
VC5 - VC7	0.7	0.03	8.7E-06

Table 3 Sensitivity Analysis Results. Values are the percent increase in error associated with increasing (decreasing) the parameter estimate by a factor of 2

Reach	D	A _s	α
VC3 - VC4	21 (13)	153 (3.3)	0.6 (1.5)
VC4 - VC5	58 (64)	1300 (2800)	36 (42)
VC5 - VC7	676 (186)	1.2 (0.2)	2.5 (2.7)

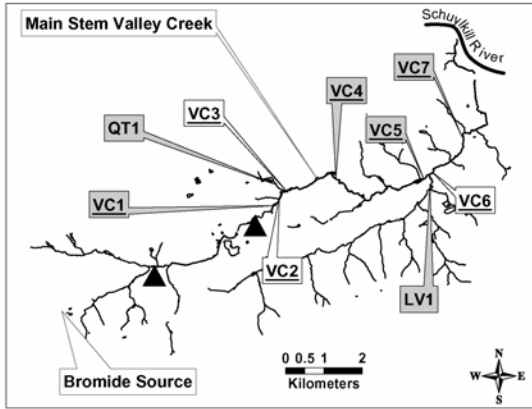


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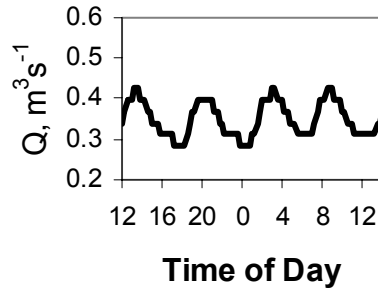


Figure 2 Flow in Valley Creek recorded by USGS Gage

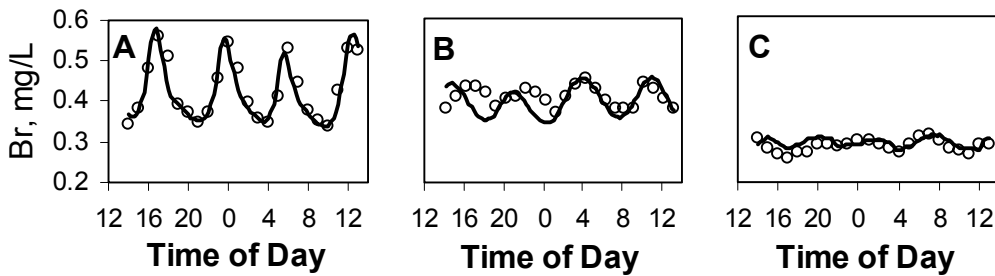


Figure 3 OTIS Calibration Curves: A—VC4; B – VC5; C – VC7. Dots indicate measured bromide concentration data; solid lines indicate model runs