Data Collection and Analysis Methods for Two-Zone Temperature and Solute Model Parameter Estimation and Corroboration

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DATA COLLECTION AND ANALYSIS METHODS FOR TWO-ZONE TEMPERATURE AND SOLUTE MODEL PARAMETER ESTIMATION AND CORROBORATION

by

Quinten G. Bingham

A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Civil and Environmental Engineering

Approved:

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UTAH STATE UNIVERSITY
Logan, Utah

2010
ABSTRACT

Data Collection and Analysis Methods for Two-Zone Temperature and Solute Model Parameter Estimation and Corroboration

by

Quinten G. Bingham, Master of Science
Utah State University, 2010

Major Professor: Bethany T. Neilson
Department: Civil and Environmental Engineering

Water temperature directly affects biological and chemical processes of fresh water ecosystems. Elevated instream temperatures are commonplace in the Virgin River of southwestern Utah during summer due to a hot desert climate and high water demands that result in low stream flows. This is of concern since the Virgin River is home to two endangered species, the Virgin River Chub (Gila seminuda) and Woundfin (Plagopterus argentissimus). Efforts to model instream temperatures within the Virgin River have been undertaken to help mitigate elevated instream temperatures including the development of a two-zone temperature and solute (TZTS) model. This model was developed to approximate the dominant processes that influence instream temperatures and used both temperature and solute data in parameter estimation. Past model applications highlighted two concerns: (1) how to confidently estimate the high number of parameters and (2) whether Rhodamine WT (RhWT) could be used as a conservative solute tracer within the Virgin River. To begin addressing these issues, spatially...
representative data were collected to facilitate the physical estimation of two previously calibrated parameters: total average channel width ($B_{TOT}$) and the fraction of channel width associated with dead zones ($\beta$). Methods for analyzing multispectral and thermal infrared imagery were developed to provide estimates of these parameters at different resolutions. Three different TZTS model calibration cases were then evaluated to determine how decreasing the calibrated parameters and increasing the resolution and frequency at which these parameters are estimated improved model predictions and/or decreased parameter uncertainty. While temperature predictions did not change significantly in each of the calibrations, parameter uncertainty was reduced. The concern regarding the use of RhWT resulted in a series of studies to quantify the potential losses of RhWT within this system. A batch sorption study resulted in distribution coefficient values lower than those found in literature. A photodegradation study suggested possible photolysis; however, a dual tracer study conducted within the Virgin River comparing Br$^-$ (conservative tracer) with RhWT confirmed that there was insignificant RhWT loss within this system.
ACKNOWLEDGMENTS

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Thanks to Noah Schmadel, Jonathan D. Bingham, Andrew Hobson, Dr. Enrique Rosero, Dr. Lindsey Goulden, and Ian Gowing for the valuable help with data collection efforts and discussions. What an immeasurable learning experience it has been to have been surrounded by, learned from, and able to work with such amazing people.

Thanks to the USGS for affording a grant that funded multiple data collection efforts. Thanks to Washington County Water Conservancy District for awarding a grant that funded the acquisition of the thermal infrared and multispectral imagery. Additionally, thanks to the Washington County Water Conservancy District for the willingness to permit multiple data collection efforts to be conducted within their district.
I want to give special acknowledgment and thanks to my parents. It is true that we are products of our environment and the examples that surround us; therefore, an immeasurable thanks to my parents is necessary for providing a great environment in which to grow and learn, as well as invaluable examples.

All of this would not have been possible without the support, patience, and love of my amazing wife, Bryn. She truly is an extraordinary person, full of kindness and love. I am a much better person due to her influence.

Above all, thanks to God for blessing me with this opportunity, the numerous answered prayers, support, and patience He has offered me throughout, not only this program and research, but most of all throughout my life.

Quinten Glen Bingham
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CHAPTER 1
INTRODUCTION

Water temperature is one of the most influential physical properties of freshwater ecosystems. Chemical and biological characteristics of freshwater ecosystems are directly influenced by water temperature [Benson and Krause, 1980; Stoneman and Jones, 2000]. If instream temperature is permanently altered, this may render formerly suitable habitat unsuitable for native species assemblages [Holtby, 1988; Wissmar et al., 1994; Quigley and Arbelbide, 1997]. Due to the semiarid to arid climate and rapid population growth of southwestern Utah, low stream flows are commonplace. Therefore, heightened demands for water in Washington County, Utah, primarily due to population increases, have directly reduced already low flows. These flow conditions adversely affect the instream temperature regime of the Virgin River where two endangered species, the Virgin River Chub (Gila seminuda) and the Woundfin (Plagopterus argentissimus), exist and are of chief management concern. In efforts to improve impaired water bodies such as the Virgin River, the Clean Water Act (CWA) was passed and instituted in 1972. The CWA requires that standards for temperature and other water constituents are established in order to meet the designated beneficial use, which may include sustaining sensitive species. Once these standards are set, states must understand when these limiting conditions occur, what is causing the impairment, and which management options will remedy the impairment. Temperature impairments are not only a concern in southern Utah, nationally EPA has placed temperature at #9 on the list of Top 100 water quality impairments [EPA, 2004].
In an attempt to mitigate elevated instream temperatures of the Virgin River, a previous temperature modeling effort was conducted on a reach that spans from Hurricane to Washington City, Utah [Addley et al., 2005]. They found that various influential heat fluxes were potentially missing in the temperature model that were necessary to capture the temperature response in the Virgin River. Based on this finding, a separate and additional effort to improve temperature predictions for this reach was undertaken [Neilson, 2006]. This included collecting numerous types of data that were direct and indirect measures of heat and mass exchange. These were used to assist in more fully identifying and characterizing heat sources and sinks within this system through the development and testing of a two-zone temperature and solute (TZTS) model [Neilson et al., 2009, 2010a, 2010b].

In addition to estimating the dominant water surface heat fluxes, similar to other instream temperature models, the TZTS estimates the heat and mass exchange associated with the surface (dead zones) and subsurface (hyporheic zone) storage zones with the main channel. Prior to this research, surface and subsurface storage modeling efforts primarily used a lumped one-zone representation to quantify the effects of storage processes in rivers [Bencala and Walters, 1983; Runkel, 1998]. Tracer studies using data collected only in the main channel are typically used to estimate the associated storage zone parameters (i.e., storage zone volume and the rate of exchange between main channel and storage zone) [Laenen and Bencala, 2001].

In developing this TZTS modeling approach, the number of parameters requiring estimation increased from conventional instream temperature models and one zone solute models. These included: $A_{c,DZ} = \text{cross-sectional area of dead zone} \ (m^2)$; $\alpha_{DZ} = \text{exchange
between the main channel and the dead zone \( (m^2 \text{ d}^{-1}) \); \( Q_{HS} \) = hyporheic storage
advection transport coefficient \( (m^3 \text{ d}^{-1}) \); \( Y_{HS} \) = depth of hyporheic zone (m); \( Y_{gr} \) = depth of ground conduction layer (m); \( B_{TOT} \) = total channel width (m); and \( \beta \) = the dead zone fraction of the total channel width. To support parameter estimation, a multi-objective optimization algorithm known as MOSCEM (Multi-Objective Shuffled Complex Evolution Metropolis) \cite{Vrugt2003} was used to estimate objectively indistinguishable parameter sets for many 2-objective calibrations. \cite{Neilson2010a, Neilson2010b} used both temperature and solute collected in various locations within the Virgin River during parameter calibration and found that the TZTS model reproduced better temperatures and solute in the main channel and storage zones.

In this past research, however, two concerns were highlighted: (1) the total number of parameters requiring calibration and the associated uncertainty was high; and (2) conflicting views exist regarding the use of RhWT as a conservative solute tracer in surface water systems was in question \cite{Smart1977, Bencala1983, Dharni2001, Dierberg2005}. Based on these two concerns, the following two research objectives were developed.

1. Collect and analyze high spatial resolution remotely sensed data to provide physical estimates of two previously calibrated TZTS model parameters in order to improve model parameter calibration.

2. Determine if RhWT behaves as a conservative solute tracer within the Virgin through a batch sorption study, photodegradation study, and a dual tracer study.

Therefore, this thesis is composed of two individual papers: Chapter 2 – Model Calibration using Thermal Infrared and Multispectral Imagery for Physical Estimation of Two Model Parameters and Chapter 3 – Analysis of Rhodamine WT Behavior.
CHAPTER 2
MODEL CALIBRATION USING AIRBORNE THERMAL INFRARED AND MULTISPECTRAL IMAGERY FOR PHYSICAL ESTIMATION OF TWO MODEL PARAMETERS

Abstract

This paper presents the evaluation and results of a thermal infrared imagery data analysis method used to estimate two model parameters within the two-zone temperature and solute (TZTS) model. Previous TZTS modeling efforts provided accurate instream temperature predictions; however, model parameter ranges resulting from the multi-objective calibrations were quite large. In addition to the data types previously required to populate and calibrate the TZTS model, high resolution remotely sensed thermal infrared (TIR) and near infrared, red, and green (multispectral) band imagery were collected to aid in the physical estimation of 2 previously calibrated parameters. These parameters were (1) average total channel width ($B_{TOT}$) and (2) the fraction of the channel width associated with surface dead zones ($\beta$). Instream temperature distributions provided by the TIR imagery enabled the calculation of temperature thresholds at which main channel temperatures could be delineated from dead zones permitting the estimation of $\beta$. Multispectral imagery in combination with the TIR imagery provides high resolution estimates of $B_{TOT}$. It was found that an increase in the resolution and frequency at which $B_{TOT}$ and $\beta$ were physically estimated resulted in similar objective functions, but the uncertainty associated with the estimated parameters decreased.
Introduction

Remotely sensed emitted thermal infrared radiation (TIR) ($\lambda = 8 – 12$ $\mu$m) is a well-established method for monitoring the “skin” temperature (top 100 $\mu$m) of streams [Torgersen et al., 2001]. This procedure of TIR remote sensing has also been used to monitor ocean surface temperatures [Wick et al., 1992; Lillisand and Kiefer, 1994; Emery and Yu, 1997], as well as lake surface temperatures [LeDrew and Franklin, 1985; Garrett et al., 2001]. Additionally, a growing body of literature supports the use of TIR remote sensing for mapping spatial temperature patterns in streams and rivers [Atwell et al., 1971; Belknap and Naiman, 1998; Kay et al., 2001; Loheide and Gorelick, 2006].

These spatial stream temperature data can provide numerous types of information such as: mapping sources of thermal heterogeneity at the watershed scale; identifying biologically important areas such as thermal refugia [Torgersen et al., 1999]; mapping of thermal conditions that provide an understanding of non-point sources of thermal pollution [Torgersen et al., 1999]; understanding mechanisms of anthropogenic thermal degradation by alleviating problems of access to private lands and providing a spatial context for evaluating relationships between land use and water quality [Torgersen et al., 2001]; understanding the effects of land management practices on stream temperature [Norton et al., 1996; Chen et al., 1998a, 1998b]; and facilitating model validation by integrating the spatial data into instream temperature models [Faux et al., 2001].

In order to accurately model instream temperatures, an understanding and approximation of the dominant heat fluxes is essential. The most common heat fluxes approximated within temperature models are surface fluxes, which include: atmospheric
longwave radiation, solar shortwave radiation, water emitted longwave radiation, conduction/convexion, evaporation/condensation, and at times bed conduction [Boyd and Kasper, 2003; Hauser and Schohl, 2003; Neilson et al., 2009]. Past these, additional fluxes associated with the surface storage zone or dead zone (DZ) (i.e., slower moving waters in relation to main channel velocities caused by riverbanks and large debris) and the subsurface storage zone or hyporheic zone have been shown to have differing influences on main channel temperatures [Loheide and Gorelick, 2006; Arrigoni et al., 2008; Neilson et al., 2009]. Past efforts to describe the mass fluxes associated with these two storage zones (DZ and HS) combined them into one zone, often referred to as transient storage [Bencala et al., 1983]. However, the combination of these storage zones may not be representative of all the processes and characteristics of each individual zone [Harvey and Wagner, 2000; Runkel and McKnight, 2003; Runkel et al., 2003; Briggs et al., 2008].

Briggs et al. [2008] recently split a one-zone solute model into a two-zone solute model that represented surface and subsurface storage and used solute tracer data collected in various zones for model calibration. Neilson et al. [2010a, 2010b] further showed the utility of using temperature data, in addition to solute data, to assist in estimating parameters associated with a two zone representation of the surface and subsurface storage zones. This two-zone temperature and (conservative) solute (TZTS) model developed by Neilson et al. [2010a, 2010b] describes many of the typical heat fluxes (surface fluxes and bed conduction), but additionally approximates the heat fluxes between the main channel and surface storage (DZ) and the subsurface storage (HS). While previous modeling efforts estimated surface fluxes over the entire surface area of a
river, if the effects of DZ storage are to be accounted for, the portion of the surface area associated with these stagnant areas has to be approximated to calculate the surface fluxes occurring individually within these zones.

In the original efforts, seven TZTS model parameters were estimated including: $A_{c,DZ}$ = cross-sectional area of dead zone ($m^2$); $a_{DZ}$ = exchange between the main channel and the dead zone ($m^2 d^{-1}$); $Q_{HS}$ = hyporheic storage advection transport coefficient ($m^3 d^{-1}$); $Y_{HS}$ = depth of hyporheic zone (m); $Y_{gr}$ = depth of ground conduction layer (m); $B_{TOT}$ = total channel width (m); and $\beta$ = the dead zone fraction of the total channel width [Neilson, 2006; Neilson et al., 2010a, 2010b]. The parameter calibration was conducted using the MOSCEM (MultiObjective Shuffled Complex Evolution Metropolis) algorithm [Vrugt et al., 2003] and used both solute and temperature data at different locations. It was found that the TZTS model reproduced temperatures and solute in the main channel and storage zones when considered independently. This past research, however, highlighted the concern that the total number of parameters requiring calibration was high and resulted in a large range of objectively indistinguishable parameter sets.

This paper will present a data analysis method that uses high resolution airborne remotely sensed thermal infrared (TIR) and multispectral imagery to assist in the physical estimation of $B_{TOT}$ and $\beta$, which are necessary to more accurately predict instream temperatures and to further understand the influence of surface storage on instream temperatures. To test whether these parameters provide more confident estimates of instream temperatures, a series of 2-objective function model calibrations are presented that incorporate various resolutions of parameter estimates and a decrease in the parameters estimated.
Site Description

The focus area of this study was an 11.94 km reach of the Virgin River in southwestern Utah near the city of Hurricane (Figure 2-1). Management of this segment of river is requisite since it is heavily influenced by diversions and impoundments that supply water for urban and agriculture purposes and experiences consistent ambient air temperatures of >38°C throughout the summer months of July and August [Neilson et al., 2009]. Concern exists regarding the loss of habitat for native aquatic biota unique to this system, which include two endangered species (Virgin River Chub (Gila seminuda) and Woundfin (Plagopterus argentissimus)). Consequently, improved water management strategies (e.g., required instream flow rates) were and are necessary to mitigate instream temperature extremes in order to maintain sustainable fish habitat while at the same time, meeting water demands of agriculture and growing urban use requirements.

The major lateral inflow, Stratton Pond (average flow rate of 0.62 m³ s⁻¹), significantly cools the instream Virgin River temperatures even though this impoundment provides a means to warm waters released from the hypolimnion of Quail Creek reservoir prior to its return to the Virgin River. The study area was divided into two main sections (section 1 and 2) with section 2 beginning at the confluence of Stratton Pond and the Virgin River (Figure 2-1). This portion of the Virgin River was selected partially due to limited groundwater influence [Herbert, 1995].

Three data acquisition sites were located along this study reach (Figure 2-1). Site 1 (S1) was located at the start of the study reach and was deemed the headwater or boundary condition of the study. S2 is located 6.47 km downstream from S1 and S3 is
4.47 km downstream from S2. The average bed slope between S1 and S2 is 0.0039 and 0.0012 between S2 and S3. S1 bed substrate consisted of 56% sand, 26% gravel, and 14% cobble. While S2 and S3 consisted of 72% sand, 15% gravel, and 10% cobble [Neilson et al., 2010a].

Figure 2-1. Study reach layout including data collection locations and Stratton pond inflow.
**Methods**

Several data types were collected to support model population, calibration, and testing. These data include: instream temperature data collected at various locations within the water column; weather data (i.e., relative humidity, ambient air temperature, wind speed and direction, and insolation); solute tracer data; remotely sensed thermal infrared (TIR) stream temperatures; and multispectral imagery of the study reach. These data types and their application in this study are shown in Table 2-1.

**Table 2-1. Collected Data Types and Their Application to the Study**

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Data Purpose</th>
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<tbody>
<tr>
<td><strong>Weather Data</strong></td>
<td>• Estimate surface heat fluxes for model calibration.</td>
</tr>
<tr>
<td>(i.e., insolation, wind speed and direction, relative humidity, ambient air temperature)</td>
<td>• Aided in TIR imagery calibration.</td>
</tr>
<tr>
<td><strong>In situ Temperature</strong></td>
<td>• Ground-truthing data for TIR Imagery calibration.</td>
</tr>
<tr>
<td></td>
<td>• Time series data for TZTS model calibration and corroboration.</td>
</tr>
<tr>
<td><strong>Solute Tracer Data</strong></td>
<td>• Aided in calculating transport times and dispersion rates.</td>
</tr>
<tr>
<td></td>
<td>• Facilitated the calibration of Manning’s roughness coefficient ($n$) for modeling purposes.</td>
</tr>
<tr>
<td><strong>Multispectral Imagery</strong></td>
<td>• Aided in TIR imagery analysis and processing.</td>
</tr>
<tr>
<td><strong>TIR Imagery</strong></td>
<td>• Estimate model calibration parameters $B_{TOT}$ and $\beta$.</td>
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Imagery Collection and Analysis Methods

TIR Image Collection and Processing

TIR imagery was acquired by remote sensing for the entire 11.94 km study reach using a forward-looking infrared (FLIR) camera, which was deployed via the USU remote sensing laboratory research aircraft. In using TIR remote sensing of streams and rivers, there are three major concerns that require consideration. These include: (1) influence of stream and river bank thermal emissions; (2) ability to use TIR imagery to measure actual water temperature versus water skin temperature; and (3) correcting for atmospheric interferences [Torgersen et al., 2001].

In addressing the influence of bank thermal emissions, it has been concluded that the pixel frequency distribution in thermal imagery of narrow stream channels indicates that temperature accuracy is compromised at stream widths less than 10 pixels due to the emitted long-wave radiation of banks and bank vegetation [Torgersen et al., 2001]. Therefore, the TIR pixels of narrow streams may be highly influenced by their surroundings, resulting in the misrepresentation of pixel temperatures. Bank thermal emissions were not expected to influence remotely sensed instream TIR temperatures of the Virgin River since the mean channel width was 15 m and TIR pixel resolution was 0.7 m x 0.7 m.

To address the issues associated with water skin temperature versus actual water temperature, Robinson et al. [1984] found that in the top millimeters of a calm water body, energy exchange between air and water surface resulted in evaporative heat loss. This creates an aqueous thermal boundary layer 0.1 – 0.5°C cooler than underlying water.
However, according to Torgerson et al. [2001] the formation and persistence of this thermal boundary layer is directly dependent on heat flux, wind speed, and current stresses that may perturb the water surface. In rivers and streams, turbulent flow is more common than laminar flow [Selby, 1985; Narigasawa et al., 1988]; therefore, thermal stratification is relatively uncommon. This suggests that by remote sensing TIR water temperatures are appropriate for rivers and streams that predominantly experience turbulent flows. For the case of the Virgin River, the Reynolds number is $3 \times 10^5$ for the study reach, therefore is considered turbulent. Neilson et al. [2009] additionally collected instream temperature data near the benthic zone and within the center of the water column of our study reach to affirm that water temperatures are homogeneous throughout the water column in the Virgin River. To further justify the use of TIR imagery, Torgerson et al. [2001] compared radiant temperatures from TIR images to instream temperatures collected with in situ data loggers and found that both consistently agree within $\pm 0.5^\circ$C.

For remotely sensed thermal infrared stream temperature data to provide representative stream temperatures, it is necessary to correct for atmospheric conditions present during the survey. The primary factor is the atmospheric transmission and absorption of long-wave radiation by water vapor between the sensor and the stream surface that influences remote measurements of water temperature [Kay et al., 2001]. These errors can be further reduced if thermal surveys are conducted from early to mid-afternoon when relative humidity is low and relatively constant [Torgersen et al., 2001; Cherkauer et al., 2005].

In the Virgin River, the TIR imagery of the study reach was collected during mid-
afternoon, the mean air temperature was 40°C and the mean relative humidity was 7.3%. Although the collection of TIR imagery during this time of day reduced the effects of atmospheric interference, there was still need to correct for the atmospheric interference that occurred. The MODtran model (MODerate resolution atmospheric TRANsmission) and ground-truthing data were both used to estimate the necessary corrections [Kay et al., 2001]. Ground-truthing data was provided by HOBO® U22 Water Temp Pro v2 (Bourne, MA) instream temperature data loggers (accuracy of ±0.2°C) which were installed within the Virgin River and logged during TIR collection efforts. Temperature probe installation coordinates were recorded using a handheld GPS unit. In situ measured temperatures were compared to associated resulting calibrated TIR pixels to evaluate the quality of TIR image calibration and ensure that the TIR temperatures were representative of actual instream temperatures.

Multispectral imagery was collected simultaneously with the TIR imagery as an additional data type to facilitate the analysis of the TIR imagery. This imagery enabled the separation of land and water pixels in the TIR imagery. The image processing resulted in a calibrated and rectified mosaic for both the multispectral and TIR imagery.

**TIR and Multispectral Imagery Analysis**

Using the multispectral mosaic, a mask of water pixels was generated using ERDAS IMAGINE (Norcross, GA) by performing a supervised classification (i.e., classifying water pixels). The resulting polygon was then edited to exclude any water bodies that were not within the study reach, ultimately producing a polygon of the river within our study reach.
The TIR imagery was then clipped to the generated river polygon to produce a raster of only river temperature pixels. Close examination of the resulting river temperature raster indicated that the clip not only provided a raster of river temperature pixels, but also some bank temperature pixels and instream sandbars that were significantly warmer than those of the river. A simple raster calculation excluded these warmer temperature pixels, which resulted in a raster representing water pixels as validated with the multispectral imagery.

With both a river polygon and representative river temperature raster generated, the river polygon was then sub-divided into sub-polygons representing 1 km reaches. These sub-polygons were then used to generate sub-rasters of the river temperature raster. This multiple raster clip and conversion of the sub-rasters to ASCII files was automated using Python (refer to Appendix A for Python code).

B and β Calculation and Analysis

Analyzing each ASCII file associated with the sub-rasters, the average $B_{TOT}$ could be calculated using Equation 2-1. This analysis was automated with a MATLAB script (refer to Appendix A for MATLAB script).

$$B_{TOT} = \frac{(\text{Total # of Water Pixels})}{(\text{Total # of Rows})} \times 0.7 \text{ meters}$$

(2-1)

where:

0.7 meters = TIR imagery pixel resolution

Dead zone areas in the Virgin River have been shown to have greater temperatures during the late afternoon than those of the main channel due to their
relatively slow velocities, which limits advective heat transfer and permits greater exposure time to solar radiation warming [Neilson et al., 2009]. With this information, it was hypothesized that a temperature threshold that distinguishes between MC and DZ temperatures could be established to calculate the dead zone fraction of total channel width ($\beta$) using the TIR imagery. Since Stratton Pond influences the downstream temperature regime of the Virgin River (i.e., net cooling effect confirmed by the TIR imagery), a threshold had to be established for each of the two study sections (Figure 2-1).

With the TIR imagery divided into two study sections, the temperature distribution of each section was evaluated using three methods: (1) a statistical analysis using $k$-means cluster analysis, histograms and probability plots (QQ plots); (2) an unsupervised classification via ERDAS IMAGINE, and (3) a natural break classification via ESRI ArcGIS. The ERDAS IMAGINE approach uses the ISODATA algorithm to perform the classification. The ISODATA cluster method uses the minimal spectral distance formula to form clusters. Based on the number of classes that are designated in the analysis, the algorithm may determine whether or not there is a distinct break in temperature distribution. The Natural Break Classification distinguishes where natural breaks occur in the distribution based on the number of classifications assigned. In both cases (IMAGINE and ArcGIS), 2 classes were assigned (DZ and MC), thus resulting in one break or one temperature threshold, per method, at which these two zones may be divided.

The calculation of these temperature thresholds for both sections enabled the calculation of the average $\beta$ for all 1 km sub-sections. This was completed by converting
the sub-rasters into ASCII files, which were then analyzed via MATLAB to provide estimated \( \beta \) for each sub-raster based on the set threshold. This was a simple calculation using Equation 3-2. Refer to Appendix A for MATLAB script.

\[
\beta = \left( \frac{\text{Total # of DZ Pixels}}{\text{Total # of Water Pixels}} \right) \times 100
\]

(3-2)

Modeling Methods

Calibration Data

*In situ* temperature time series data was the primary data type collected for TZTS model calibration purposes and were collected at all three study reach sites (S1, S2, and S3) (Figure 2-1) using Onset HOBO® U22 Water Temp Pro v2 (Bourne, MA) temperature data loggers (instrument accuracy is ±0.2°C). These data loggers were installed at various locations within the river’s water column and substrate of each site. Figure 2-2 depicts the specific installation locations for each temperature probe per site. Based on previous efforts of Neilson et al. [2009], probe (1) and (3) recorded instream temperatures in dead zone regions, probe (2) recorded temperatures in the main channel, and probes (4-6) were buried at 3, 9, and 20 cm in the bed substrate (Figure 2-2). The main channel data were used for model calibration purposes and the other temperature time series were used for corroboration of the predicted temperatures in the surface and subsurface zones.

Additional forcing data collected and used for modeling included: boundary condition flow and temperature data collected at S1 (headwater location); weather data including insolation magnitude, ambient air temperature, wind speed, and relative
humidity; and lateral inflow and temperatures along the study reach.

**Model Calibration using MOSCEM**

The TZTS model predictions in Neilson et al. [2010a, 2010b] provided reasonable estimates of instream temperatures in the main channel, surface storage zones, and subsurface storage zones. However, the concerns with parameter uncertainty suggested that additional investigation into parameter estimation is necessary.

Using the parameter estimates from the TIR imagery, three different 2-objective calibrations were completed in this study. These used the Nash-Sutcliffe Efficiency (NSE) as the objective function for the main channel temperature at S2 and S3 and the calibration cases were:

**Case I)** $(B_{TOT, set, section})$ $B_{TOT}$ was set to the calculated overall average width for both study sections based on estimates from TIR imagery. Calibrated parameters included: $\beta$, $A_{c,DZ}$, $a_{DZ}$, $Q_{HS}$, $Y_{HS}$, and $Y_{gr}$.

**Case II)** $(B_{TOT, set, 1km})$ $B_{TOT}$ was set to average channel width calculated from TIR for 1 km sections within the model. Calibrated parameters included: $\beta$, $A_{c,DZ}$, $a_{DZ}$, $Q_{HS}$, $Y_{HS}$, and $Y_{gr}$. This calibration did not vary in the total number of parameters being calibrated, but incorporated higher resolution data to represent the parameter $B_{TOT}$.

**Case III)** $(B_{TOT, set 1km} \text{ and } \beta_{set, 1km})$ $B_{TOT}$ and $\beta$ were set to average channel width and average dead zone fraction calculated from TIR imagery for 1 km sections. This calibration set two parameters and represented these values at a higher resolution. The result was fewer parameters to calibrate, which were: $A_{c,DZ}$, $a_{DZ}$, $Q_{HS}$, $Y_{HS}$, and $Y_{gr}$.

It was hypothesized that by reducing the number of parameters requiring calibration and establishing two parameters at a higher spatial resolution based on physical data, uncertainty in the other model parameters would be reduced.
Figure 2-2. Locations of temperature probes at sites #1 - #3 within the study reach (adapted from Neilson et al. [2009]).

Results

TIR and Multispectral Image Processing and Analysis

Figure 2-3 is the linear regression of in situ measured temperatures versus TIR image temperatures used to assess the TIR image calibration quality. This analysis ensured that TIR imagery temperatures were representative of actual instream temperatures.

Figure 2-4 shows the generated mosaics of the TIR and multispectral imagery, respectively, for the entire 11.94 km study reach. The combination of these images was necessary to decipher water from land pixels within the TIR imagery. Figure 2-5 provides a visual aid to demonstrate the need for the river temperature raster correction in order for it to only represent and contain water temperature pixels. In Figure 2-5(a), sandbars are visible within the main channel of the Virgin River (note red rectangles). Figure 2-5(b) is the uncorrected river temperature raster superimposed upon the multispectral image and demonstrates how prior to raster correction, land pixels (sandbars) were included with water pixels; therefore, confirming the necessity of further raster corrections. Figure 2-5(c) shows the final result of the raster correction, which
resulted in only water pixels within the river temperature raster.

Figure 2-6 shows two diel fluctuations of MC and DZ temperatures measured \textit{in situ} of S2 using the HOBO\textsuperscript{®} temperature data loggers. From this figure it is apparent that DZ temperatures, on average, are greater than MC temperatures during the day and are less during the night. The rectangle in Figure 2-6 shows that there was a significant difference in DZ and MC temperatures when the TIR imagery was collected and suggests that the DZ and MC could be delineated based on water temperature pixel distribution. Additionally, Neilson et al. [2009] showed that DZs are heat sources during the day and heat sinks during the night.

\textbf{Figure 2-3.} Linear regression of \textit{in situ} measured temperatures versus remotely sensed TIR temperatures used to assess the calibration quality of the TIR imagery.
Figure 2.4. TIR (a) and multispectral (b) imagery mosaic of the Virgin River.
Figure 2-5. Before and after results of river temperature raster correction process. (a) Multispectral image of a segment of the study reach indicating sandbars (note red rectangles) with the Virgin River. (b) River temperature raster superimposed on multispectral image demonstrates the importance of raster correction since sandbars are included in the river temperature raster (note red rectangles) which is to only include water pixels/temperatures. (c) The corrected river temperature raster (note red rectangles).
Figure 2-6. Instream temperature time series of MC and DZ at S2. Rectangle indicates time of date when TIR and multispectral imagery was collected.

Figure 2-7 shows the results of the statistical analysis of temperature distributions of both section 1 and 2. Analyzed temperature distributions were provided by the TIR imagery. The distinct breaks in temperature pixel frequency at 32°C in Figures 2-7(a) and (c), as well as at 30°C in Figure 2-7(b) or 30.33°C in (d) confirms that the majority of water temperature pixels ranged from 28 to 32°C and 24 to 30.33°C for section 1 and 2, respectively.

The other two methods used to estimate temperature thresholds (i.e., ERDAS IMAGINE and ESRI ArcGIS) provided similar values as the statistical analysis (Table 2-2). Therefore, any water temperature pixel with a temperature < 32°C in the section 1 and < 30.33°C in section 2 were classified as main channel and any water pixels greater than these temperature thresholds were classified as a dead zone. Refer to Appendix B for R script used to perform $k$-mean cluster analysis.
Figure 2-7. Statistical analysis results of the distribution of water temperature pixels of both section 1 and 2. Histogram of the temperature distribution of section 1 (a) and section 2 (b). Note the distinct change in frequencies at 32 and 30°C for section 1(a) and section 2 (b), respectively. *K*-means cluster analysis results of the distribution of the water temperature pixels of section 1 (c) and section 2 (d) reaches. Note the abrupt change in water temperature frequency at 32 and 30.33°C for section 1 (c) and section 2 (d), respectively.
Figure 2-8 shows an example of the dead zone and main channel delineation resulting from the calculated temperature threshold values. Black indicates DZ and gray MC.

Table 2-2. Calculated Temperature Thresholds of All Three Analysis Methods. Temperature Values Were Provided by the TIR Imagery

<table>
<thead>
<tr>
<th>Threshold Analysis Method</th>
<th>Calculated Temperature Thresholds</th>
</tr>
</thead>
</table>
| Statistical Analysis      | Section 1 = 32°C  
Section 2 = 30.33°C           |
| ERDAS IMAGINE             | Section 1 = 32.15°C  
Section 2 = 30.23°C           |
| ESRI ArcGIS               | Section 1 = 32.17°C  
Section 2 = 30.30°C           |

Figure 2-8. Delineated dead zone from main channel based on calculated temperature threshold. Red indicates DZ and yellow MC.
Using these temperature thresholds, $\beta$ values were estimated for each section at 1 km reach lengths. The average $\beta$ values of the entire section 1 and 2 were 15.5 and 20.7 percent, respectively. The calculated average $B_{TOT}$ of the entire section 1 and 2 were 15.6 m and 12.9 m, respectively. Additionally, this delineation permitted the calculation of the average MC and DZ temperatures of section 1 and 2, which were 30.7 and 28.3°C and 34.1 and 32.7°C, respectively. These averages further attest that the lateral inflow, Stratton Pond, does have an overall net cooling effect on section 2.

**Model Calibration**

The model calibrations for case I through III resulted in a tradeoff between the two objectives. Represented by the diamonds (Figure 2-9), this tradeoff results in a number of parameter sets that give objectively indistinguishable, but most likely variable, predictions. With this tradeoff, a best parameter set can be identified that results in a compromise solution. Assuming that the Euclidean distance is an appropriate compromise, the best parameter set is shown as the black dot in Figure 2-9. The squares represent other inferior parameter sets.

Model calibrations for cases I through III provided information to evaluate the visual fit achieved for each calibration in the MC, DZ, and subsurface zones. Figures 2-10 through 2-12 shows the predicted temperature results provided by the best parameter set from the three calibration cases. Figure 2-10 shows the results of case I ($B_{TOT, set, section}$), in which parameter $B_{TOT}$ was set to the average of the entire section for both sections. Figure 2-10(a) and (b) show the observed MC temperature versus the predicted MC temperatures at S2 and S3, respectively. These were the time series used in
calibration, and while they match the diel temperature trend of the observed data, both miss the maximum and minimum temperatures in each location. The same is true for predicted DZ temperatures at these locations (Figure 2-10(c) and (d)). Additionally, there was a slight lag in the predicted DZ temperatures of day two at S2. As for predicted subsurface or hyporheic zone (HS) temperatures, given the simple representation of the hyporheic zone in the TZTS model, the predicted temperatures should represent some sort of average of the observed HS temperature time series at the three depths (Figure 2-10(e) and (f)) [Neilson et al., 2010a], however, the predicted temperatures most closely mimic the temperatures at 3 cm.

**Figure 2-9.** Example of a tradeoff resulting from of a 2-objective calibration.
Figure 2-11 shows the results of case II \((B_{TOT, \text{set, } 1km})\), in which the parameter \(B_{TOT}\) was set to 1 km averages for both sections. Figure 2-11(a) indicates that by increasing the spatial resolution of \(B_{TOT}\), the predicted MC temperatures at S2 were improved. This was also the case at S3, but was not as dramatic of an improvement. Predicted DZ temperature from case II did not improve from case I. Figure 2-11(e) and (f) affirm that the goodness of fit for HS temperatures was similar to that of case I.

Figure 2-12 shows the results of case III \((B_{TOT, \text{set, } 1km \text{ and } \beta_{set, \text{1km}}}\)), in which parameters \(B_{TOT}\) and \(\beta\) were set to 1 km averages for both sections. Case III calibrations for MC, DZ, and HS temperatures did not show much improvement from case II, but were better than the results from case I.

Figure 2-13 through 2-15 show the uncertainty bounds plots based on the parameter sets that were objectively indistinguishable for the three calibration cases. Figure 2-13(a) and (b) confirm that these parameter sets result in predicted temperatures that bracket most of the observed data in the MC at S2 and S3. Parameter sets for section 1 provide more representative uncertainty bounds for the observed temperature time series data of S2 (Figure 2-13(a)) than those parameter sets for section 2 (Figure 2-13(b)) as represented by S3. The same is true for the DZ uncertainty bounds of S3 (Figure 2-13(c) and (d)). The DZ for S2 resulted in a lag. Figure 2-13(e) show that the predicted HS minimum and maximum uncertainty bounds of S2 are over predicted and do not represent the average of the three observed temperature time series. Figure 2-13(f) shows that the parameter ranges represent the average HS temperatures of S3, but the uncertainty in these parameters are large.

Figure 2-14 shows the uncertainty bounds produced by the parameter sets for case
II. MC uncertainty bounds are reduced in case II from case I and bounds associated with S2 have a smaller spread than those of S3 (Figure 2-14(a) and (b)). Figure 2-14(c) and (d) indicate that once again bounds are reduced for the DZ; however, a lag is still present in case II for S2 DZ (Figure 2-14(c)). The predicted HS bounds for S2 are again over predicted and do not represent the average of the three observed temperature time series (Figure 2-14(e)), the bounds for S3 represent more of an average, but the upper bound in day two is high (Figure 2-14(f)).

Figure 2-15 shows the uncertainty bounds of the parameter sets produced by case III. The uncertainty bounds of the MC and DZ in case III are similar if not a slightly larger spread than those of case II (Figure 2-15(a) through (d)). Moreover, the HS uncertainty bounds experienced the most visible spread increase in case III from case II.

To provide more information regarding these calibrations, the root mean squared error (RMSE) was calculated to quantitatively evaluate the goodness of fit of predicted temperatures for each best parameter set versus observed temperatures (Table 2-3) for each calibration case (Figures 2-10 through 2-12). Furthermore, the RMSE was also calculated for the upper and lower bounds of the uncertainty plots (Figures 2-13 through 15).

In the case of the RMSE for the best parameter sets for section 1, a reduction in the RMSE occurs across the board from case I to III in all three zones (Table 2-3). The most notable improvement in predicted temperature fit was found to have occurred in the HS zone. Minimal improvement was found in the DZ. As for the RMSE for the best parameter set of section 2, no significant improvement resulted from the three calibration cases (Table 2-3).
Figure 2-10. Model temperature predictions (dashed lines) for case I versus observed data (solid black lines) for both S2 and S3. Observed data included main channel, dead zone, and hyporheic storage temperatures. Plots (a) and (b) are observed main channel temperatures for both S2 and S3 versus model predicted main channel temperatures. Plot (c) and (d) are observed dead zone temperatures of both S2 and S3 versus model predicted dead zone temperatures. Plots (e) and (f) are observed hyporheic storage temperatures at 3 depths (3, 9, and 20 cm) within the river substrate versus model predicted temperatures.
Figure 2-11. Model temperature predictions (dashed lines) for case II versus observed data (solid black lines) for both S2 and S3. Observed data included main channel, dead zone, and hyporheic storage temperatures. Plots (a) and (b) are observed main channel temperatures for both S2 and S3 versus model predicted main channel temperatures. Plot (c) and (d) are observed dead zone temperatures of both S2 and S3 versus model predicted dead zone temperatures. Plots (e) and (f) are observed hyporheic storage temperatures at 3 depths (3, 9, and 20 cm) within the river substrate versus model predicted temperatures.
Figure 2-12. Model temperature predictions (dashed lines) for case III versus observed data (solid black lines) for both S2 and S3. Observed data included main channel, dead zone, and hyporheic storage temperatures. Plots (a) and (b) are observed main channel temperatures for both S2 and S3 versus model predicted main channel temperatures. Plot (c) and (d) are observed dead zone temperatures of both S2 and S3 versus model predicted dead zone temperatures. Plots (e) and (f) are observed hyporheic storage temperatures at 3 depths (3, 9, and 20 cm) within the river substrate versus model predicted temperatures.
Figure 2-13. Model uncertainty bounds based on objectively indistinguishable parameter sets as criteria of 2-objective functions for case I. Black line indicates observed temperatures and gray bounds depict parameter uncertainty bounds. Plots (a) and (b) are observed main channel temperatures plotted with uncertainty bounds for S2 and S3, respectively. Plot (c) and (d) are observed dead zone temperatures plotted with uncertainty bounds for S2 and S3, respectively. Plots (e) and (f) are observed hyporheic storage temperatures at 3 depths (3, 9, and 20 cm) within the river substrate plotted with uncertainty bounds for S2 and S3, respectively.
**Figure 2-14.** Model uncertainty bounds based on objectively indistinguishable parameter sets as criteria of 2-objective functions for case II. Black line indicates observed temperatures and gray bounds depict parameter uncertainty bounds. Plots (a) and (b) are observed main channel temperatures plotted with uncertainty bounds for S2 and S3, respectively. Plot (c) and (d) are observed dead zone temperatures plotted with uncertainty bounds for S2 and S3, respectively. Plots (e) and (f) are observed hyporheic storage temperatures at 3 depths (3, 9, and 20 cm) within the river substrate plotted with uncertainty bounds for S2 and S3, respectively.
Figure 2-15. Model uncertainty bounds based on objectively indistinguishable parameter sets as criteria of 2-objective functions for case III. Black line indicates observed temperatures and gray bounds depict parameter uncertainty bounds. Plots (a) and (b) are observed main channel temperatures plotted with uncertainty bounds for S2 and S3, respectively. Plot (c) and (d) are observed dead zone temperatures plotted with uncertainty bounds for S2 and S3, respectively. Plots (e) and (f) are observed hyporheic storage temperatures at 3 depths (3, 9, and 20 cm) within the river substrate plotted with uncertainty bounds for S2 and S3, respectively.
In the case of the RMSE of the upper and lower uncertainty bounds some tightening from case I to III is noted, especially in the MC of section 1 and the HS of section 2. As for the other zones of each section, tightening of the lower bounds of the DZ and HS of section 1 and the MC and DZ of section 2 were noted. However, the upper bounds seemed to increase in the DZ and HS of section 1 and in the MC and DZ of section 2.

Table 2-3. RMSE Values. RMSE Calculated from Predicted versus Observed Temperature and Upper and Lower Bounds of the Uncertainty Bounds of All Sampling Zones and Calibration Cases for Section 1 and 2

<table>
<thead>
<tr>
<th>CASE</th>
<th>SECTION 1</th>
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<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
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<tr>
<td>MC</td>
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<tr>
<td></td>
<td>Upper</td>
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<td></td>
<td>Lower</td>
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<tr>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
Discussion

The analysis of the multispectral and TIR imagery resulted in higher spatial resolution data with which the two model parameters $B_{TOT}$ and $\beta$ were estimated. However, in calculating these parameters, careful attention should be taken during analysis of TIR imagery due to possible negative thermal influences that may prove detrimental. Some examples of these thermal influences from this study that resulted in erroneously high remotely sensed instream temperatures were: large growths of woody riparian vegetation (e.g., Tamarisk or Salt Cedar) and/or rock embankments and cliffs near the riverbank. These influences produced larger than normal quantities of bank thermal emissions. Additionally, semi submerged algal mats within the river may interfere with remote sensing thermal infrared emissions. These stationary algal mats become thermally stratified (i.e., very warm on the surface and cooler below the surface); thus, TIR measured skin temperatures of these mats are not representative of the true water temperatures below the mats and may be mistaken as water temperatures. These thermal influences generally increase pixel temperatures erroneously, which may result in misrepresentative parameter estimates. For example, $\beta$ estimates are based on a calculated temperature threshold and if a section of river is highly influenced by algal mat accumulation, resulting in abnormally high remotely sensed instream temperatures, then the $\beta$ value of this section will be abnormally high as well. Therefore, in processing TIR imagery for the purpose of estimating these model parameters, care should be taken to identify and account for erroneous thermal influences.

Results from the three calibration cases generated qualitative representations of
how well the model results matched the observations for each calibration (Figures 2-10 through 2-15). These figures show that even though the number of parameters calibrated was reduced and the resolution of two parameter estimates was increased, the improvement in prediction of instream temperatures were notable, but small. However, the uncertainty bounds generated from the parameter sets produced by these three cases suggest that the increase in parameter resolution and the decrease in parameter space may decrease the uncertainty associated with parameter estimates. Additionally, these conclusions were confirmed by the RMSE analysis (Table 2-3).

Figure 2-16 shows the scatter of the normalized parameter sets associated with the objectively indistinguishable parameter sets for each of the three calibration cases. The best parameter set is indicated by the black line. The parameter spread of case I (Figure 2-16(a)) shows that for many parameters, the best parameter values are near their maximum, particularly for section 1. In general, many calibrated parameter values are scattered or noisy. Additionally, it should be noted that $\beta$ values were estimated in case I and are fairly confidently estimated for section 1. Figure 2-16(b) is the parameter spread generated by case II. Similar to case I, many of the calibrated best parameter values are near their maximum values; however, the spread of the other parameter values appear to be less noisy and repeatedly approximates some parameter values (e.g., $A_{DZ,1&2}$, $\beta_{1&2}$, $Y_{HS,1&2}$, and $Q_{HS,i}$). Parameter spread results of case III (Figure 2-16(c)) are much improved from case I and case II. The best parameter values are not close to their maximums and the parameter spread is less noisy, indicating that calibrated parameter values are more consistently estimated.
Figure 2-16. Normalized scatter plots of objectively indistinguishable parameter sets produced by the three calibration cases. Objectively indistinguishable parameter sets are represented by gray lines and the best parameter set is depicted by solid black line. Case I (a), Case II (b), and Case III (c). The subscript on each parameter denotes section 1 or 2.
A more quantitative analysis of the parameter sets generated from each case provided more conclusive information regarding the three tested calibration cases (Figure 2-17 and 2-18). Since each calibration case afforded multiple indistinguishable parameter sets, box plots were generated to further understand the changes in the parameter distributions for each case.

Figures 2-17(a) through (e) are the box plots of the calibrated model parameters of section 1. The ranges of all parameters were reduced in case II or III (Figure 2-17(a), (c), and (e)) and often both (Figure 2-17(b) and (d)). Figure 2-18(a) through (d) are the box plots of the calibrated model parameters of section 2. As was the case with section 1, the combined quantile ranges of each parameter was reduced from case I to II and/or III. The most notable improvements occurred with parameters $A_{DZ}$, $\alpha_{DZ}$, and $Y_{HS}$ (Figures 2-18(a), (b), and (d), respectively). This information affords more evidence that by increasing the resolution of $\beta$ and $B_{TOT}$, a direct positive influence on calibrated model parameters is the result.

**Conclusions**

This study has elucidated the utility of high resolution TIR and multispectral imagery to improve parameter estimation for the TZTS model. Analysis of these high resolution data enabled the calculation of a temperature threshold at which the MC may be delineated from the DZ within this particular system by way of a temperature distribution analysis. Three different analysis methods resulted in similar temperature
Figure 2-17. Box plots of each calibrated model parameter ((a) $A_{DZ}$, (b) $\alpha_{DZ}$, (c) $Y_{HS}$, (d) $Q_{HS}$, and (e) $Y_{GR}$) for section 1 based on calibration case. $Y_{GR}$ was calibrated once to represent both section 1 and 2; therefore, only one box plot was generated for $Y_{GR}$. 
Figure 2-18. Box plots of each calibrated model parameter ((a) $A_{DZ}$, (b) $a_{DZ}$, (c) $Y_{HS}$, and (d) $Q_{HS}$) for section 2 based on calibration case.

thresholds. The temperature threshold allowed the physical estimation of two previously calibrated TZTS model parameters, which were the fraction of channel width associated with the DZ ($\beta$) and average channel width ($B_{TOT}$).

Based on three different calibration cases, the uncertainty in calibrated TZTS model parameters was found to be reduced by decreasing the total number of parameters calibrated and increasing the resolution at which $\beta$ and $B_{TOT}$ were represented.
Additionally, the three different cases reproduced reasonable predicted instream temperatures where observations were present. However, by increasing the resolution of the model parameter $B_{TOT}$ (case II), minimal improvement of prediction occurred, but the ranges of many estimated parameters were reduced. Moreover, by increasing the resolution of both model parameters $B_{TOT}$ and $\beta$, which reduced the number of model parameters requiring calibration (case III), parameter calibration improved again. Ranges of calibrated parameter values were reduced even more than those of case II. The most notable parameter calibration improvement was $Y_{HS}$ due to setting $\beta$. Therefore, it may be concluded that increasing the resolution of $B_{TOT}$ and $\beta$ based on physical estimates and reducing the overall number of calibrated parameters can be an effective method to reduce uncertainty in estimates.
CHAPTER 3

ANALYSIS OF RHODAMINE WT BEHAVIOR WITHIN THE VIRGIN RIVER

Abstract

The anionic fluorescent dye tracer, Rhodamine WT (RhWT), was used as a tracer to aid in determining the extent of transient storage and solute transport within a reach of the Virgin River near Hurricane, Utah. Contradicting views and results exist within the current research literature regarding the use of RhWT as a conservative tracer. While some have found it to be nearly conservative, others have found it to be non-conservative. Photodegradation, sorption to sediments and aquatic plants, and biodegradation are the major processes influencing mass loss in surface water applications. These mass loss sources, however, are dependent on the particular system in which it is used. To determine, its behavior within the Virgin River, three independent mass loss studies were conducted: (1) a batch sorption study, (2) a photodegradation study, and (3) a dual tracer study. The mean distribution coefficient ($K_d$) of RhWT resulting from the batch sorption study (1.5 mL g$^{-1}$) was less than others found in literature for similar studies. Photodegradation was found to occur in one liter clear sample vials exposed to direct solar radiation, further photodegradation studies are recommended to more fully represent site specific water characteristics such as turbidity, turbulence, and water column depth. The combined effects of sorption and photodegradation, as well as any other potential loss mechanism were evaluated at one time using a dual tracer study. The simultaneous injection of the conservative solute tracer, NaBr, and RhWT enabled the calculation of the percent mass recoveries of both (102% and 100%, respectively). Based
on such high RhWT recovery, *in situ* sorption and photodegradation were found to be negligible. Site specific evidence further supporting the high recovery of RhWT included: the low organic carbon content of the river sediment (0.067%); sandy loam sediment; and low observed $K_d$ values.

### Introduction

Rhodamine WT (RhWT) has been used for a myriad of purposes in many environments, including: identifying phosphorous treatment areas in a constructed wetland [Dierberg et al., 2005]; dye dilution gauging for calibrating structures [Zellweger, 1994]; determining zones of effluent mixing in limonitic environments [Lull et al., 1997]; mapping karst groundwater [Smart and Smith, 1976]; mapping the conveyance of bacteria through preferential flow paths in an aquifer [Pang et al., 1998]; studying tracer movement in tidally active waters [Upstill-Goddard et al., 2001]; and determining small-scale turbulent diffusion in lakes [Suijlen and Buyse, 1994]. More customary uses include the determination of flow velocities and preferential flow paths for surface [Bencala, 1983; Stern et al., 2001] and groundwater [Bencala, 1983; Sabatini and Austin, 1991; Pang et al., 1998; Sutton et al., 2001] systems; groundwater/surface water interactions [Nishikawa et al., 1999]; dispersion and hydraulic residence time of wetlands [Werner and Kadlec, 2000; Lin et al., 2003]; and estimation of various processes affecting solute transport in lotic systems [Bencala, 1983; Bencala and Walters, 1983; Tate et al., 1995; Laenen and Bencala, 2001; Neilson et al., 2009].

In the applications associated with solute transport, RhWT tracer studies may provide information necessary to estimate transient storage zone parameters, longitudinal
dispersion, and travel times. In many stream tracer study applications, the anionic fluorescent dye-tracer RhWT (Table 3-1) has commonly been selected as the most reasonable and practical dye-tracer. The reasoning includes: detectable at low concentrations (0.01 μg L⁻¹) by portable fluorescence detectors [Smart and Laidlaw, 1977; Kilpatrick and Wilson, 1982; Turner Designs, 1998]; biological and chemical inertness; relatively low cost; and high solubility [Turner Designs, 1998]. Additionally, background RhWT concentrations are negligible in most lotic systems [Smart and Laidlaw, 1977] and it is not considered to be a toxic dye-tracer in the dosage necessary to achieve the desired results [Parker, 1973]. Smart and Laidlaw [1977] suggests RhWT as the preferred dye-tracer for single injection studies due to other fluorescing dye-tracers behaving less conservatively. Pang et al. [1998] and Pang and Close [1999] concluded that RhWT behaved conservatively in their respective studies.

Table 3-1. Physical and Chemical Properties of Rhodamine WT

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generic namea</td>
<td>C.I. Acid Red 388</td>
</tr>
<tr>
<td>Dye typea,b</td>
<td>Xanthene</td>
</tr>
<tr>
<td>Molecular weighta,b</td>
<td>567 g mole⁻¹</td>
</tr>
<tr>
<td>Compositional formulaa,b</td>
<td>C₂₉H₂₉N₂O₅Na₂Cl</td>
</tr>
<tr>
<td>Octanol/Water partitioning coefficient K₀wᵃ</td>
<td>0.047</td>
</tr>
<tr>
<td>Toxicity (rat LD₅₀ oral)ᵃ</td>
<td>&gt; 25.0 g kg⁻¹</td>
</tr>
<tr>
<td>Excitation wavelength (maximum adsorption)b</td>
<td>555 nm</td>
</tr>
<tr>
<td>Emission wavelength(maximum)b</td>
<td>580 nm</td>
</tr>
</tbody>
</table>

[a] Smart, 1984
[b] Smart and Laidlaw, 1977
In contrast to the above findings, concerns exist regarding the use of RhWT as a conservative dye-tracer. Some studies have shown that it does not behave as a conservatively in various systems due to sorption to stream sediments [Bencala et al., 1983; Dharni et al., 2001], photodegradation [Tai and Rathbun, 1988; Dierberg and DeBusk, 2005], and biological decay [Smart and Laidlaw, 1977]. Biological decay, however, is considered inconsequential due to relatively low microbial populations in natural surface water systems [Smart and Laidlaw, 1977]. In the case of sorption to vegetation, it was found to be negligible [Smart and Laidlaw, 1977; Turner et al., 1997; Stern et al., 2001]. However, sorption to sediment is still a concern and photodegradation may need to be considered for tracer studies lasting longer than a week [Smart and Laidlaw, 1977].

The literature surrounding RhWT provides possible remedies to account for RhWT loss during solute tracer studies if study results are going to be used to estimate transient storage parameters. Laenen and Bencala [2001] and Suijlen and Buyse [1994] used a first order decay coefficient, in modeling, to compensate for dye loss during their study. Bencala et al. [1983] calculated the distribution coefficient of RhWT within their studied system. Thus, there are tried and proven methods to account for mass loss during solute tracer studies.

Based on a review of the literature regarding RhWT, it is apparent that conflicting views, opinions, and results surround the use of RhWT as a conservative dye-tracer. In this paper, three different studies were conducted to quantify the behavior of RhWT in a sandy system to account for potential losses of the tracer for use in transient storage modeling applications. To provide multiple lines of evidence, these studies consisted
of a batch sorption study, photodegradation study, and a dual tracer study.

The batch sorption study consisted of two parts: (1) a kinetic (sorption equilibrium) study and (2) distribution coefficient (K_d) study. These two studies provide an understanding of the sorptive properties of the studied systems’ sediment. A photodegradation study was used to understand the influence of solar radiation (insolation) on instream RhWT concentrations through photolysis. The third study, the dual tracer study, was an all encompassing study in that all possible instream RhWT sinks were represented by the resulting percent mass recovery.

Site Description

An 11.94 km reach of the Virgin River in southwestern Utah near the city of Hurricane was studied. The original tracer study effort for estimation of transient storage parameters was conducted during June of 2007. During the summer months ambient air temperatures of this area often exceed 38°C and there is little precipitation. Due to a combination of low flow rates caused by river management and high solar radiation and air temperatures, the risk of elevated instream temperature regimes is high and a reduced amount of thermal refugia for two endangered species (Virgin River Chub (Gila seminuda) and woundfin (Palgopterus argentissimus)) becomes heightened. Three data acquisition sites were located along this study reach (Figure 3-1). Site 1 (S1) was located at the start of the study reach and used as the headwater or boundary condition of the study. S2 is located 6.47 km downstream from S1 and S3 is 4.47 km downstream from S2. The average bed slope between S1 and S2 is 0.0039 and is 0.0012 between S2 and S3. S1 bed substrate consisted of substrate consisting of 56% sand, 26% gravel, and
14% cobble. Bed substrate of S2 and S3 consisted of 72% sand, 15% gravel, and 10% cobble [Neilson et al., 2010a]. Stratton Pond outflow was the largest lateral inflow along this study reach and had the most significant influence on the downstream temperature regime of the Virgin River. Stratton Pond is a warming impoundment used to permit the warming of hypolimnetic water release from Quail Creek Reservoir. Additionally, it should be noted that this reach experiences minimal groundwater influence [Herbert, 1995].

Figure 3-1. Layout and description of study reach.
Methods

Batch Sorption Study Methods

Studies have shown that in natural environments, RhWT sorption is dependent on initial dye concentrations, sediment type, and sediment organic carbon content [Smart and Laidlaw, 1977; Everts and Kanwar, 1994]. Therefore, a batch sorption study was conducted using different RhWT concentrations to estimate a distribution coefficient (Kd) of RhWT for sediments collected at different locations within the studied reach. Similar studies have been conducted to determine Kd’s of various sediment types and locations [Trudgill et al., 1983; Trudgill, 1987; Sabatini and Austin, 1997; Laenen and Bencala, 2001; Lin et al., 2003]. Equation 3-1 was used to calculate the distribution coefficients.

\[ K_d = \frac{m_s \cdot V_o}{m_{aq} \cdot m_{soil}} \]  

\[ (3-1) \]

where:
- \( m_s \) = mass RhWT adsorbed to soil at equilibrium (M)
- \( m_{aq} \) = mass RhWT remaining in solution (M)
- \( m_{soil} \) = initial mass of soil (M)
- \( V_o \) = initial volume of solution (V) 
[OECD, 2000]

A Kd is defined as the concentration ratio of a chemical in the sorbed phase to that remaining in the equilibrated solution and are soil specific since the organic carbon present in soils greatly influences this ratio [Smart and Laidlaw, 1977; Bohn et al., 1985]. In order to determine the ability of the Virgin River sediment to act as an irreversible sink, a batch sorption study was conducted using sediment from S1, S2, and S3.
As for desorption, Smart and Laidlaw [1977] state that the sorption of RhWT to sediment particle surfaces is essentially irreversible in natural systems, therefore a desorption study was not conducted. Another factor considered was that desorption of RhWT occurs relatively slowly and is consequently assumed to not affect pulse RhWT tracer studies negatively [Smart and Laidlaw, 1977].

**Field Methods**

Approximately 0.3 meter vertical sediment samples were collected from S1 through S3 within the study reach in August 2008 and were kept cool (~4°C) once collected [Gavlak et al., 2003]. Each sample was air dried and thoroughly mixed to ensure a representative sediment distribution. Sediment samples were analyzed for various parameters of which two that largely influence adsorptive properties of sediments: organic carbon content (expressed as organic carbon fraction, $f_{oc}$) and soil texture [OECD, 2000]. Organic carbon content is typically the most influential sorption parameter [Smart and Laidlaw, 1977; Bohn et al., 1985].

Water samples were also collected and kept cool (~4°C) [Menzel and Vaccaro, 1964; APHA, 2005] to be used in the batch sorption study by providing the liquid medium with which RhWT solutions were prepared. The presence of DOC may increase background fluorescence [Sabatini and Austin, 1997]. Therefore, water samples were also analyzed for total organic carbon (TOC) and dissolved organic carbon (DOC).

**Laboratory Methods**

To determine a distribution coefficient ($K_d$) for each of the three sediment samples, a sorption kinetic study was conducted to estimate the required agitation time
for samples to reach sorption equilibrium. The required agitation time (or equilibrium agitation time), was calculated to ensure that the future samples achieved full sorption equilibrium prior to analysis of $K_d$ values. Additionally, the sorption kinetic study provided information regarding the appropriate soil to solution ratio necessary to conduct the actual distribution coefficient study. To determine the distribution of RhWT on each of the three sediments sampled, specific $K_d$ values were established using OECD Methods [2000].

**Sorption Kinetic Study**

To establish the appropriate sample agitation time, two solution concentrations (10 and 60 μg L$^{-1}$ RhWT) were tested by preparing sixteen glass centrifuge test tubes with PTFE caps per solution concentration. Solution concentrations were based on the range of concentrations observed during the solute tracer study conducted in June 2007. Each tube was filled with 40 mL of solution and 8 grams of sediment from the Virgin River. This 1:5 soil-to-solution ratio was recommended as the initial ratio [OECD, 2000].

RhWT solutions for this study were prepared with river water to maintain any variables introduced by river water matrix. Test tubes were agitated for the following times; 0.5, 1, 1.5, 2, 4, 8, 12, and 24 hours. Two test tubes were allotted to each agitation time to create duplicate samples. All samples and standards were wrapped in aluminum foil and stored in the dark to eliminate any potential mass loss due to photodegradation caused by ambient lighting.

Using a Sequoia-Turner Model 450 Fluorometer (Block Scientific, Inc., Holbrook, NY), RhWT concentrations were measured to determine representative
concentrations for each of the two solutions used to prepare each test sample. Additionally, calibration standards (0, 5, 20, 40, 100 μg L⁻¹ RhWT) were prepared with river water for the generation of calibration curves.

Six concentration control (CC) samples (test tubes filled only with 10 or 60 μg L⁻¹ RhWT solution and no sediment) were prepared, as well as six blank samples (test tubes filled with 8 grams of river substrate and strictly river water without RhWT). The CCs permitted the affirmation of any mass loss resulting from sorption to the glass test tubes. Blanks indicated any matrix problems induced by the river water and/or sediment used in this study. Therefore, both the CCs and blanks were subjected to the same study procedural methods as the test samples. The mean of the blank concentrations was calculated and subtracted from all test sample concentrations.

Once an allotted agitation time passed, the respective two sample tubes for that time were removed from the agitator and centrifuged for twenty minutes to ensure the removal of any particulate matter that may induce error in the fluorescence measurements [OECD, 2000]. Samples were centrifuged due to RhWT sorption to the recommended 0.2 μm filters [OECD, 2000]. Upon completion of centrifugation of each sample agitation time, a new calibration curve was generated using the previously prepared calibration standards. This resulted in a total of eight calibration curves.

As mentioned previously, the sorption kinetic study provided two valuable pieces of information requisite for the completion of the distribution coefficient study: (1) the time required to achieve sorption equilibration and (2) a preliminary Kₐ. The sorption equilibration time ensured that the samples were permitted adequate time to obtain sorption equilibrium prior to analysis. The preliminary Kₐ (Eqn. 3-1) facilitated the
determination of the appropriate soil to solution ratio necessary for the distribution coefficient study samples to provide the desired 20% - 50% sorption of RhWT [OECD, 2000].

To determine when significant changes in concentration were no longer occurring due to sorption an instrumental error analysis of sample fluorescence during the sorption kinetic study was calculated using the statistical method known as Working-Hotelling confidence bands [Berthouex and Brown, 2002]. The method produces a 95% confidence bands based on the linear regression line generated from all eight calibration curves (Equations 3-2 and 3-3). This confidence limit represents the error in instrumental analysis manifested in calculated sample concentrations.

\[ b_o + b_1x \pm \sqrt{2F_{s,v,a} s^2 \left( \frac{1}{n} + \frac{(x-x)^2}{\sum{(x_i-x)^2}} \right)} \]  

(3-2)

where:
- \( b_o + b_1x \) = linear model of calibration curve
- \( s^2 \) = variance of fluorescence observations
- \( F_{s,v,a} \) = F distribution
- \( n \) = number of points on calibration curve
- \( x \) = calibration standard concentration (M/V)
- \( \bar{x} \) = calibration standard concentration mean (M/V)
- \( x_i \) = calibration standard concentration (M/V)  
[Berthouex and Brown, 2002]

\[ s^2 = \frac{\sum(y_i-\hat{y})^2}{n-2} \]  

(3-3)

where:
- \( s^2 \) = variance of fluorescence observations
- \( y_i \) = calibration standard concentration (M/V)
- \( \hat{y} \) = Predicted concentration based on linear model equation (M/V)
- \( n \) = number of observations  
[Berthouex and Brown, 2002]
**Distribution Coefficient Study**

K_d values established within the literature are generally derived using batch sorption studies [Shiau et al., 1993; Everts and Kanwar, 1994; Lin et al., 2003]. Any loss of analyte from solution is presumed to be due to sorption on to solids. To generate a K_d value for each of the three sediments collected from various sites and evaluate any differences between sites, K_d values were established using Equation 3-1 and a 1:3 soil to solution ratio based on the results from the sorption kinetic study. Study samples were prepared in duplicate for each sediment sampling location (S1, S2, or S3) and solution concentration (10, 30, and 60 μg L^{-1} RhWT solution). This meant that each sample contained 13.3 grams of river substrate from S1, S2, or S3 and 40 mL of 10, 30, or 60 μg L^{-1} RhWT solution, which equated to be six test tubes for each sediment sampling site. An average initial concentration for all three sample solutions was determined based on triplicate measurements. With this initial concentration the calculation of the mass lost due to sorption to sediment was possible.

In addition to the six test samples, duplicate blanks were made from river water and river substrate from each site to determine if there were any interferences caused by the substrate or water of each location. Duplicate concentration controls were not made since the sorption kinetic study determined that no measurable mass loss was occurring as a result of adsorption to the glass test tubes. Once all test samples and blanks were prepared, they were subjected to the appropriate agitation time (1.5 hr) to ensure complete sorption equilibrium.

After sample agitation the samples were centrifuged for 20 minutes [OECD, 2000] and then the fluorescence of each sample was measured. Four fluorescence
measurements were recorded from each test tube, thus generating a total of eight fluorescence measurements for each concentration at each location. With a total of eight recorded measurements, a representative mean concentration was calculated. This mean concentration was then used to calculate a representative $K_d$ value for each site. Prior to the calculation of $K_d$ values, the average blank concentration for each sampling site was subtracted from the respective test sample concentrations.

**Outdoor Photodegradation Study**

While Smart and Laidlaw [1977] found that the effect of photodegradation on mass loss of RhWT is only significant in studies of the duration greater than one week, an outdoor photodegradation study was conducted to validate this statement for the Virgin River and/or elucidate the effect of insolation on RhWT concentrations. This study was based on similar solar radiation intensities, exposure time, and RhWT concentrations observed during the June 2007 tracer study. In the case that photodegradation occurs, a first order decay coefficient may be calculated to represent the mass loss due to exposure to solar radiation [Tai and Rathbun, 1988; Suijlen and Buyse, 1994; Lin et al., 2003].

The outdoor photodegradation study was conducted using three clear one liter glass vials filled with solution of three different known RhWT concentrations (10, 30, and 60 μg L$^{-1}$) representative of the range of concentrations experienced and recorded during the June 2007 solute tracer study. Solutions were prepared with distilled-deionized water. In addition to the three test solutions, calibration standards were also prepared.
Three 5 mL samples were withdrawn from each vial on an hourly basis to provide triplicate measurements. Once withdrawn, these samples were then stored in a lab cabinet, out of light exposure, for one hour prior to analysis. One hour storage period permitted samples to equilibrate to the same ambient temperature of the calibration standards. This temperature equilibration period was necessary since the fluorescence of RhWT is directly influenced by temperature [Bencala et al., 1983; Turner Designs, 1998].

Once the temperature equilibration period was complete and a calibration curve generated, samples were analyzed for any changes in RhWT concentrations due to photodegradation. As in the case of both the sorption kinetic study and the distribution coefficient study, a calibration curve was produced for each sampling period.

In conjunction with recording changes in RhWT concentrations over time, solar radiation intensity was also recorded to verify that a similar insolation magnitude to that of the June 2007 study was experienced during this study. A Davis Vantage Pro2™ Weather Station (Davis Instruments Corp., Hayward, CA) was used to measure and record solar radiation during the outdoor photodegradation study.

The results of this study were then analyzed to determine the most representative reaction kinetic order (i.e., zero, first, and second) based on changes in sample concentrations. Since the same sample analysis method was used as that of the sorption study, measurement uncertainty of this study was addressed with the Working-Hotelling confidence bands.
Indoor Photodegradation Study

To ensure that no mass loss due to photodegradation was occurring during the batch sorption study, an in-lab photodegradation study was conducted. This study revealed whether or not prolonged exposure of study samples to ambient lab lighting had any significant effect on the RhWT concentrations of the study samples. It should be noted however, that during the sorption study that all study samples were wrapped in aluminum foil and stored in a box within a drawer while not in use.

Samples for this study were prepared based on two RhWT concentrations (10 and 60 μg L\(^{-1}\) RhWT) and light or no light, as well as specific analysis times (2, 5, 12, 21, and 24 hr). Each specific analysis time had two 10 and two 60 μg L\(^{-1}\) RhWT (one exposed to light and one guarded from light) resulting in a total of 20 samples (four per each specified analysis time).

The “light” samples were exposed to the ambient lighting of the lab and the “no light” samples were wrapped in aluminum foil, placed in a box, and stored within a drawer. Once the designated analysis time passed for each sample, each sample was measured in triplicate and calibration curve was generated for each sampling time interval. Measurement uncertainty was calculated using Working-Hotelling confidence bands.

Other Laboratory Analyses

Collected water samples were frozen and analyzed for total organic carbon (TOC) and dissolved organic carbon (DOC) using wet persulfate oxidation [Menzel and Vaccaro, 1964], which is the same method as described in the APHA Standard Methods
for the Analysis of Water and Wastewater [APHA, 2005]. The analytical variability of DOC/TOC samples was calculated by dividing the standard deviation of measured concentrations of samples with a known concentration by their average.

Collected sediment samples were kept cool (~4°C) and analyzed for organic carbon, texture, and cation exchange capacity (CEC) using standard methods [Gavlak et al., 2003]. The texture was determined by feel. Individual method numbers were as follows: Organic matter was by Walkley-Black, S-9.10, CEC (ammonium acetate), S-10.10, Saturation % (saturated paste extraction), S-1.00 (paste %), S-1.60 (analyze B, Ca, Mg, Na, K, S).

Dual Tracer Study

The objective of the dual tracer study was to compare the conservativeness of RhWT to that of a well-known conservative ionic tracer, sodium bromide (NaBr). The anion bromide (Br⁻) was selected as the conservative solute tracer since it is widely accepted and used as such [Tanner et al., 1998; Kimball et al., 2002; Constantz et al., 2003; Lin et al., 2003; Gooseff and McGlynn, 2005], as well as background concentrations being relatively low within the Virgin River. By simultaneously injecting one liter of concentrated RhWT (2x10⁸ μg L⁻¹ RhWT) and 8 kg of sodium bromide (NaBr), their percent mass recoveries may be compared to deduce whether or not RhWT behaved conservatively. Additionally, a flow rate was measured before and after tracer injection to ensure a steady flow rate was experienced during the study. Lin et al. [2003] conducted a similar study in a wetland. It should be noted that this dual tracer study was conducted in January 2009; therefore, solar radiation magnitudes experienced during this
study were less than those of the June 2007 tracer study and therefore, may not fully account for photodegradation. In the case that RhWT is found to not be conservative, then a first order decay coefficient may be calculated, which represents the lumped effects of all the processes contributing to mass loss of RhWT within this particular system. This decay coefficient could also be incorporated into any model to account for RhWT mass loss.

In order to measure and record each tracer response curve, a SCUFA® (Self Contained Underwater Fluorescence Apparatus) (Turner Designs, Sunnyvale, CA) was deployed in the main channel which recorded RhWT concentrations every 10 seconds. This apparatus internally-adjusts measured concentration for changes in water temperature. Instream grab samples were collected at three minute sampling intervals, near the SCUFA installation location, for future analysis of Br⁻ concentrations. Sample collection and concentration measurements were taken at S3, approximately 3 km downstream from the injection site (approximately 1 km downstream from S2). Background water was also collected prior to tracer injections for analysis of background concentrations of both tracers. All grab and background water samples were kept cool at ~4°C prior to analysis [Pfaff, 1993]. Analyses of background and grab samples were completed using anion chromatography following EPA Method 300.0 [Pfaff, 1993] using a Dionex ICS 3000 ion chromatographer (Dionex, Sunnyvale, CA).

The variance in Br⁻ sample analysis was calculated and pooled to determine the uncertainty in the ion chromatographic analysis. This method provides an upper and lower bound based on the calculated variance for the bromide tracer response curve generated by the analyzed bromide grab samples.
Additionally, the upper and lower PMRs were also calculated based on the calculated 95% confidence limits of each tracer using Working-Hotelling confidence bands method and variance pooling [Berthouex and Brown, 2002].

Results

Sorption Kinetic Study

The results of the sorption kinetic study using the 1:5 soil-to-solution ratio and the two solution concentrations of 10 and 60 μg L\textsuperscript{-1} RhWT are presented in Figure 2-2. Instrumental analysis error was calculated using Working-Hotelling confidence bands method and was found to be ±0.96 and ±1.16 μg L\textsuperscript{-1} for solution concentrations 10 and 60 μg L\textsuperscript{-1} RhWT, respectively. From these results it is clear that sorption equilibrium is occurring within 30 minutes of agitation.

Table 3-2 contains the mean concentration of the concentration controls (CC) for each designated sampling time and the mean blank concentration. These results show that there was insignificant mass loss due to sorption to lab materials, as well as, minimal background influence. This background fluorescence is hypothesized to be the result of colloidal or dissolved organics [Sabatini and Austin, 1997].

These results provided the necessary data to calculate an average distribution coefficient of 1.6 mL g\textsuperscript{-1} based on Equation 3-1 and Figure 1 of OECD Guideline [2000]. This distribution coefficient permitted the determination of the appropriate soil-to-solution ratio of 1:3 to be used in the distribution coefficient study.
**Distribution Coefficient Study**

Using the 1:3 ratio, a distribution coefficient was calculated for the three different tested solution concentrations for all 3 sampled sediments (Table 3-3). Distribution coefficients were found to be similar from site to site.

**Outdoor Photodegradation Study**

Figure 3-3 contains the results of the RhWT concentration changes versus time of the three different concentrations (10, 30, and 60 μg L⁻¹ RhWT) tested in the outdoor photodegradation study. Furthermore, these figures also contain the recorded solar radiation magnitudes experienced throughout the study. Figure 3-3(a-c) shows that photodegradation most likely occurred during this study. However, the statistical analysis of measurement uncertainty indicates that concentration loss may have been statically insignificant for sample concentration 10 μg L⁻¹ RhWT even though there was a negative slope in concentration over time. Using Working-Hotelling confidence bands method the measurement uncertainties were calculated to be ±0.90, ±0.82, and ±0.92 μg L⁻¹ RhWT for sample concentrations 10, 30, and 60 μg L⁻¹ RhWT, respectively.

From this data, zero, first, and second order reaction kinetics were evaluated for each of the three solution concentrations (Table 3-4). The results of this analysis indicated that reaction kinetics may be dependent on RhWT concentrations. For example, based on the calculated R² values of sample concentration 10 μg L⁻¹ RhWT a 2nd order reaction kinetic best represents the decay kinetics of this concentration. However, a zero order reaction kinetic best represents the results of sample concentrations 30 and 60 μg L⁻¹ RhWT.
Figure 3-2. Sorption kinetics of two RhWT solution concentrations and river sediment with organic carbon content of 0.067%. RhWT solution concentrations over time for sample concentration 10 μg L\(^{-1}\), which had an instrumental analysis error of ±0.96 μg L\(^{-1}\) (a). RhWT solution concentrations over time for sample concentration 60 μg L\(^{-1}\), which had an instrumental analysis error of ±1.16 μg L\(^{-1}\) (b).
Additionally, based on the calculated measurement uncertainties (Figure 3-3) it may be assumed that higher RhWT concentrations may be more heavily altered by photodegradation than lower concentrations. Net changes in solution concentrations 10, 30, and 60 μg L\(^{-1}\) RhWT were 1.95, 7.01, and 14.94 μg L\(^{-1}\) RhWT, respectively. Since sample solutions for this study were prepared with distilled-deionized water, and not river water, photodegradation rates found in this study are expected to be greater than those occurring in a natural system. Natural systems have greater turbidity levels and greater depths, of which directly influences the amount of exposure and the solar radiation entering and attenuating within the water column. A more representative study is recommended to provide more conclusive data regarding photodegradation of RhWT within this system.

**Indoor Photodegradation Study**

Figure 3-4 is the results of the indoor photodegradation study with error bars representing the error in instrumental analysis from the Working-Hotelling confidence bands method. Instrumental analysis errors for solution concentrations 10 and 60 μg L\(^{-1}\) RhWT were determined to be ±1.0 and ±1.20 μg L\(^{-1}\) RhWT, respectively. Based on Figure 3-4(a,b, and c), it may be concluded that no photodegradation occurred from test

<table>
<thead>
<tr>
<th>Sampling Time (hr)</th>
<th>10 μg L(^{-1})</th>
<th>60 μg L(^{-1})</th>
<th>Blanks (μg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10.9</td>
<td>60.4</td>
<td>0.33</td>
</tr>
<tr>
<td>12</td>
<td>12.2</td>
<td>62.6</td>
<td>0.34</td>
</tr>
<tr>
<td>24</td>
<td>11.1</td>
<td>59.9</td>
<td>0.37</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>11.4</strong></td>
<td><strong>60.9</strong></td>
<td><strong>0.35</strong></td>
</tr>
</tbody>
</table>
sample exposure to lab lighting. Although, it should be noted that a statistically significant change in concentration occurred over time with the 60 μg L$^{-1}$ no light sample (Figure 3-4d). This may be due to sorption to lab material, but is not likely since multiple CC samples showed no statistically significant changes in concentration.

**Dual Tracer Study**

The RhWT and bromide tracer response curves generated and recorded during the dual tracer study are shown in Figures 3-5(a) and (b), respectively. The shaded regions of (a) and (b) are the 95% confidence regions calculated by the Working-Hotelling confidence bands and the Dunnett’s method [Dunnett, 1964; Berthouex and Brown, 2002], respectively. Percent mass recoveries (PMR) of each response curve were calculated based on the trapezoidal rule and were found to be 102% and 100% for Br$^-$ and RhWT, respectively. Additionally, the 95% confidence limits for each tracer response curve permitted the calculation of a minimum and maximum PMR for each tracer. The upper PMR values were 107% and 120% and the lower PMR values were 92% and 85% for RhWT and Br$^-$, respectively. Refer to Appendix B for R script used to generate Figure 3-5.
Figure 3-3. RhWT concentrations and insolation magnitude versus exposure time for various solutions. (a) initial concentration 10 μg L\(^{-1}\) RhWT (Measurement uncertainty ± 0.90 μg L\(^{-1}\) RhWT), (b) 30 μg L\(^{-1}\) RhWT (Measurement uncertainty ± 0.82 μg L\(^{-1}\) RhWT), (c) and 60 μg L\(^{-1}\) RhWT (Measurement uncertainty ± 0.92 μg L\(^{-1}\) RhWT).
Table 3-4. $R^2$ Values of Reaction Kinetics of the Outdoor Photodegradation Study

<table>
<thead>
<tr>
<th>Solution Sample</th>
<th>Zero</th>
<th>1st</th>
<th>2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μg L$^{-1}$</td>
<td>0.904</td>
<td>0.907</td>
<td>0.908</td>
</tr>
<tr>
<td>30 μg L$^{-1}$</td>
<td>0.986</td>
<td>0.982</td>
<td>0.973</td>
</tr>
<tr>
<td>60 μg L$^{-1}$</td>
<td>0.983</td>
<td>0.975</td>
<td>0.963</td>
</tr>
</tbody>
</table>

TOC/DOC Analysis

The TOC and DOC analysis results conducted on the sample water collected at S1 and S2 (Figure 3-6) had an analytical variability of 3.01%. These results indicate low DOC concentrations and that the organic carbon within the water column is primarily in the form of DOC.

Sediment Analysis

The results of the analyzed sediment samples are contained in Table 3-5. The sediment parameters of concern regarding the sorption of RhWT are organic matter percentage and texture. These parameters are found to have the greatest influence on sorption capacity of sediments [Smart and Laidlaw, 1977; Bohn et al., 1985]. The organic matter percentage was found to be very low and other studies have shown that sandy soils have little sorptive capacity for RhWT [Smart and Laidlaw, 1977; Everts and Kanwar, 1994]. Based on these results, it is expected that minimal RhWT mass loss should occur. This was confirmed by the results of the dual tracer study and calculated $K_d$ values.
Figure 3-4. Recorded concentrations versus time of the 10 and 60 μg L⁻¹ RhWT sample. 10 μg L⁻¹ RhWT samples exposed to the ambient lighting (a) and no light exposure (b). Instrumental analysis error of solution concentration 10 μg L⁻¹ RhWT was determined to be ±1.00 μg L⁻¹ RhWT. 60 μg L⁻¹ RhWT samples exposed to the ambient lighting (c) and no light exposure (d). Instrumental analysis error of solution concentration 60 μg L⁻¹ RhWT was determined to be ±1.20 μg L⁻¹ RhWT.
Figure 3-5. Measured solute tracer response curves of RhWT (a) and Br- (b). Gray shaded regions represent the 95% confidence regions. (Refer to Appendix B for R script)
Table 3-5. Results of Tested Sediments of S1 Through S3

<table>
<thead>
<tr>
<th>Sampling Site #</th>
<th>Organic Matter %</th>
<th>Texture</th>
<th>CEC cmol/kg</th>
<th>Calcium mg/kg</th>
<th>Potassium mg/kg</th>
<th>Magnesium mg/kg</th>
<th>Sodium mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>Sandy Loam</td>
<td>0.9</td>
<td>2172</td>
<td>29.5</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>Sandy Loam</td>
<td>1.2</td>
<td>2478</td>
<td>29.2</td>
<td>156</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>Sandy Loam</td>
<td>1.2</td>
<td>2726</td>
<td>30.6</td>
<td>166</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sampling Site #</th>
<th>Saturation Percentage %</th>
<th>Calcium mg/kg</th>
<th>Magnesium mg/kg</th>
<th>Sodium mg/kg</th>
<th>Potassium mg/kg</th>
<th>Boron mg/kg</th>
<th>Sulfur mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.4</td>
<td>28.1</td>
<td>7.76</td>
<td>42.4</td>
<td>4.16</td>
<td>0.07</td>
<td>33.5</td>
</tr>
<tr>
<td>2</td>
<td>26.5</td>
<td>35.6</td>
<td>8.39</td>
<td>69.6</td>
<td>4.88</td>
<td>0.10</td>
<td>44.5</td>
</tr>
<tr>
<td>3</td>
<td>25.4</td>
<td>27.7</td>
<td>8.67</td>
<td>51.7</td>
<td>4.12</td>
<td>0.08</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Figure 3-5. Analytical results of TOC and DOC samples from S1 and S2. Analytical variability was 3.01%.

Discussion

This study has shown that the behavior of RhWT is relatively conservative within this particular reach of the Virgin River. The resulting calculated $K_d$ values (Table 3-3) provided by the batch sorption study were low (1.5 mL g$^{-1}$) in relation to values cited for similar studies. Other $K_d$ values found for RhWT were: 4.5 mL g$^{-1}$ in alluvium sands.
[Sabatini and Austin, 1997]; 5.6 mL g⁻¹ in a mountain stream [Bencala et al., 1983]; 54 mL g⁻¹ in silty-loam soil [Trudgill, 1987]; and 850 mL g⁻¹ in aggregated soil [Trudgill et al., 1983]. Therefore, comparison of these values affirms that the sorptive properties of sediments from this study reach of the Virgin River are less than those of other systems studied. The analysis of the Virgin River sediment provided more evidence as to why these K_d values are so low. These results (Table 3-5) showed that sediments from this particular reach of the Virgin River have very low organic carbon content (0.067%) and that the soil texture is sandy loam.

In addition to the above, analysis results of TOC and DOC in the water (Figure 3-6) reveal that the organic carbon within this lotic system, at the time of year samples were collected, is predominately in the form of DOC. This is important because its sorptive ability is less than that of TOC resulting in mass loss due to sorption to TOC/DOC being negligible in this specific system [Smart and Laidlaw, 1977]. This may not be the case other times of the year. For example, spring runoff events can drastically increase TOC/DOC concentrations, which in turn may directly affect RhWT solute tracer studies conducted during such events.

Further investigation of possible causes of RhWT mass loss during dye-tracer studies with in the study system included the indoor and outdoor photodegradation study. The indoor photodegradation study confirmed that no mass was lost due to sample exposure to ambient lighting (Figure 3-4). The result of the outdoor photodegradation study (Figure 3-3), however, suggests that more detailed and comprehensive studies are necessary to comprehend the effects of insolation on instream RhWT concentrations during solute tracer studies.
The final and most conclusive study was the dual tracer study. The resulting concentration response curves (Figure 3-5) show that the PMR of RhWT and Br⁻ were both quite high. While these confidence bounds account for error in the tracer analyses, there is also error associated with flow measurements. However, the same flow measurement was used to calculate both PMR values since simultaneously injected and therefore does not create variability between the values. These results corroborate that over a 3 km reach of the Virgin River, RhWT is behaving as a conservative dye-tracer. Moreover, this study is quite conclusive since it captures all the effects of all possible irreversible RhWT sinks. It should be noted that the dual tracer study was conducted in January of 2009 when turbidity is slightly higher and insolation magnitudes are slightly lower than those experienced during the main study of June 2007. Additional dual tracer studies are recommended during low turbidity flows and during summer months when insolation magnitudes are greater to ensure that the potential for photolysis is captured.

Overall, from the results of these studies it is conclusive that the sediments within this study reach have little sorptive capabilities, DOC concentrations are minimal, and most importantly RhWT behaved as a conservative dye-tracer in comparison to Br⁻.

**Conclusions**

RhWT has been used a conservative dye-tracer for the purpose of estimating volumes and exchange rates associated with transient storage. Conflicting views, opinions, and results surround the use of RhWT as a conservative dye-tracer in surface waters. In an effort to evaluate the parameters that influence the conservativeness of RhWT within a lotic system a batch sorption study, a photodegradation study, and a
dual tracer study were completed.

The first of the three studies conducted, the batch sorption study, consisted of a sorption kinetic and a distribution coefficient study. The kinetic study indicated that sorption equilibrium was achieved within 30 minutes of sample agitation. The overall results of the batch sorption study enabled the calculation of an overall reach specific distribution coefficient of 1.5 mL g⁻¹. This $K_d$ is low relative to literature and indicated low sorptive capacity of sediments within the study reach for RhWT.

The indoor photodegradation study confirmed that test samples from the batch sorption study experienced no mass loss due to photolysis caused by ambient lighting. However, additional and more extensive investigations of the effects of insolation on instream RhWT concentrations are recommended based on the results of the outdoor photodegradation study conducted.

The dual tracer study using RhWT and NaBr afforded evidence affirming that RhWT behaves as a conservative solute tracer within a 3 km reach in relation to NaBr. Additionally, this study encompassed all possible parameters that may result in RhWT mass loss during solute tracer study and therefore, suggests that RhWT behaves as a conservative tracer within this reach of the Virgin River.
CHAPTER 4
CONCLUSIONS

This research has addressed two concerns regarding parameter calibration of the TZTS model. These two concerns were the high number of parameters requiring calibration and the use of RhWT as a conservative solute tracer. In general, this study has shown the utility of a new data collection (TIR and multispectral imagery) and analysis method for improving parameter estimation for TZTS model. By increasing the data resolution from which the two model parameters $B_{TOT}$ and $\beta$ are estimated, uncertainty associated with other model parameters is decreased. These high resolution data (TIR and multispectral) enabled the calculation of a temperature threshold at which the MC may be delineated from the DZ within this particular system by way of temperature distribution analysis. This then allowed for the estimation of the fraction of channel width associated with the DZ. Using three different analysis methods (a statistical analysis, unsupervised classification with ERDAS IMAGINE, and a natural break classification with ERSI ArcGIS), similar thresholds were established.

Using this threshold and the resulting parameters estimates, three different model calibration cases reproduced reasonable instream temperatures where observations were present. By increasing the resolution of the model parameter $B_{TOT}$ (case II), minimal improvement of predicted instream temperatures occurred, but the range of many estimated parameters were reduced. Moreover, by increasing the resolution of both model parameters $B_{TOT}$ and $\beta$, which reduced the number of model parameters requiring
calibration (case III), parameter calibration improved again. Ranges of calibrated parameter values were again reduced. Perhaps the most notable parameter calibration improvement was $Y_{HS}$. By setting $\beta$, the confidence at which this parameter was calibrated was significantly increased. Therefore, it may be concluded that increasing the resolution of $B_{TOT}$ and $\beta$ based on physical estimates and reducing the overall number of calibrated parameters can be an effective method to assist in model parameter calibration.

In studying the behavior of RhWT, conclusive data was collected regarding how conservative this solute tracer is within the Virgin River system. This study was conducted since RhWT had been used a conservative dye-tracer for the purpose of estimating volumes and exchange rates associated with transient storage; however, conflicting views, opinions, and results surround the use of RhWT as a conservative dye-tracer in surface waters. In effort to evaluate the parameters that influence the conservativeness of RhWT within a lotic system a batch sorption study, a photodegradation study, and a dual tracer study were completed.

The first of the three studies conducted, the batch sorption study, consisted of a sorption kinetic and a distribution coefficient study. The kinetic study indicated that sorption equilibrium was achieved within 30 minutes of sample agitation. The overall results of the batch sorption study enabled the calculation of an overall reach specific distribution coefficient ($Kd$) of $1.5 \text{ mL g}^{-1}$. This $Kd$ is low relative to literature and indicated low sorptive capacity of sediments within the study reach for RhWT.

The indoor photodegradation study confirmed that test samples from the batch sorption study experienced no mass loss due to photolysis caused by ambient lighting. However, additional and more extensive investigations of the effects of insolation on
instream RhWT concentrations are recommended based on the results of the outdoor photodegradation study conducted.

The dual tracer study using RhWT and NaBr afforded evidence affirming that RhWT behaves as a conservative solute tracer within a 3 km reach in relation to NaBr. Additionally, this study encompassed all possible parameters that may result in RhWT mass loss during solute tracer study and therefore, provided conclusive results that RhWT behaves as a conservative tracer within this reach of the Virgin River.
CHAPTER 5
ENGINEERING SIGNIFICANCE

This research represents advances in the field of Environmental Engineering by providing a new analysis method of high spatial resolution data to physically estimate two model parameters within a two-zone temperature and solute (TZTS model). This model was developed to predict more accurate instream temperatures of the Virgin River since it is home to two endangered fish species. Physical estimation of the two parameters reduced the uncertainty in TZTS parameter estimates. These advances improve our understanding of and the ability to quantify dominant heat fluxes that influence elevated instream Virgin River temperature regimes.

Given the limited number of conservative tracers that can be used in the Virgin River due to very high background salinity, this research additionally provided advancements by addressing the validity of using Rhodamine WT (RhWT) as a conservative solute tracer within the Virgin River. Solute tracer information aids in the calibration of transient storage and TZTS model parameters; therefore, it was paramount to determine if RhWT behaves conservatively within this system. Since it was found to be conservative, this validates its use in parameter estimation. Additionally, it confirms the credibility of past TZTS modeling efforts that used RhWT solute data for calibration.

Overall, the significance of this research has improved the calibration of the TZTS model for instream Virgin River temperature predictions which will facilitate future management decisions. For example, the TZTS model may aid in the cost benefit
analysis of possible remedies to decrease elevated instream temperatures including increased dam releases or changes in riparian shading.
CHAPTER 6
RECOMMENDATIONS FOR FUTURE RESEARCH

This research has provided a greater understanding of how more spatially representative data collected in the form of remotely sensed thermal infrared instream temperatures and MULTISPECTRAL imagery of the Virgin River may facilitate the physical estimation of specific model parameters. Additionally, this research has afforded a better comprehension about the behavior of RhWT within this section of the Virgin River. However, based on the results, some future research recommendations can be made.

Evaluation of the uncertainty in the thermal infrared imagery is recommended. Comprehension of the uncertainty associated with image calibration would afford additional confidence in calculated temperature thresholds used to delineate the main channel from dead zones. The resulting imagery could also be extremely useful in model calibration at a higher spatial resolution.

In future TIR studies, it is recommended that a larger quantity of in situ temperature data loggers be installed throughout the study reach and other nearby water bodies to provide a greater range of measured temperatures (e.g., near the water surface of Stratton Pond and perhaps Pah Tempe hot springs). This larger range of measured temperatures would supply a more confident image calibration.

From the three calibration cases presented in Chapter 2, it is now understood that physically estimating $B_{TOT}$ and $\beta$ at a higher spatial resolution data does improve
parameter calibration of the TZTS model. An additional calibration case is recommended to be conducted and the results compared to those of case III from this study. The recommended calibration case would set both $B_{TOT}$ and $\beta$ to section average for each section, similar to case I. This comparison would evaluate how increasing the frequency at which the $B_{TOT}$ and $\beta$ are physically estimated may influence the estimation of other model parameters. Furthermore, the use of the solute tracer data collected for parameter calibration is also recommended followed by a comparison of temperature versus solute calibrated parameters. This would provide an understanding of the utility of using both temperature and solute data in conjunction with high spatial resolution data for improved parameter estimations.

The collection of an additional data type is also recommended to improve model calibration. If temperature data is collected in the river substrate at approximately 1 meter depth, this would eliminate the need to calibrate model parameter $Y_{gr}$. This further reduction of the number of calibrated parameters could reduce parameter uncertainty.

Future studies on the behavior of RhWT within the Virgin River may further corroborate its utility as a conservative solute tracer. Additional dual tracer studies, using Br$^-$ as the conservative comparison tracer, should be conducted during the month of June. These studies would provide more conclusive information about the behavior of RhWT within this system if insolation magnitudes, water clarity, and flows were the same as those experienced during the data collection effort of June 2007. If any losses are found, decay coefficients would need to be established for use in the model applications.
REFERENCES

Addley, C., B. T. Neilson, L. Basdekas, and T. Hardy (2005), Virgin river temperature model validation, Utah Water Research Laboratory, Utah State University.


EPA (2004), Top 100 Impairments List, edited, United States Environmental Protection Agency.


Herbert, L. R. (1995), Seepage study of the Virgin River from Ash Creek to Harrisburg Dome, Washington County, Utah, United States Geological Survey/State of Utah Department of Natural Resources.


APPENDICES
APPENDIX A

Supporting Python and MATLAB Code for TIR Imagery Analysis
Python code for a batch clip of TIR raster:

```python
##Script Name: Multiple Clip
##Description: Multiple clips using sub-polygons
##Created By: Quin Bingham
##Date: 05/26/2009

#Import standard library modules
import arcgisscripting,sys,os

# Create the Geoprocessor object
gp=arcgisscripting.create(9.3)# Create the Geoprocessor object
gp.overwriteoutput=1

#Check out the spatial analyst extension
gp.checkoutextension("spatial")

# Set the workspace
#GP.workspace = ("C:\Documents and Settings\Administrator\Desktop\VR_Subpoly")
#Set workspace
gp.workspace = sys.argv[1]

#input polygon feature with subtiles
#polygon = gp.GetParameterAsText("gwwfd_polygon.shp")
polygon = sys.argv[2]

#input raster
#InRaster = gp.GetParameterAsText("VR_361.img")
InRaster = sys.argv[3]

#output workspace for save derived subrasters
#outWorkspace = gp.GetParameterAsText("C:\Documents and Settings\Administrator\Desktop\VR_Subpoly\TestResults")

#Set up cursor object
rows = gp.SearchCursor(polygon)
row = rows.Next()
try:
    while rows:
        id = str(row.FID)#FID only for shapefile
        #OutRaster=outWorkspace+os.sep+"raster_"+id
        gp.AddMessage("processing polygon "+id)
        gp.select_analysis(polygon, polygon[:-4]+"tmp"+id+.shp", "FID" = '+id)
```
# gp.MakeFeatureLayer(polygon,"lyr"+id)
# gp.SelectLayerByAttribute("lyr","NEW_SELECTION","FID" + "=" + id)
gp.ExtractByMask_sa(InRaster, polygon[:-4]+"tmp"+id+".shp", "outras"+id)
gp.delete_management(polygon[:-4]+"tmp"+id+".shp")

    row = rows.Next()
except:
gp.AddMessage(gp.GetMessages(2)) # show geoprocessing error messages

# message when script is done
gp.AddMessage("Script done")

Python code for batch conversion of raster files to ASCII files:

# RasterToASCII
# Description: Convert multiple rasters into ASCII files
# Author: Quin Bingham
# Date: June 26, 2009

# Import system modules
import arcgisscripting,sys,os

# Create the Geoprocessor object
gp = arcgisscripting.create(9.3)
gp.overwriteoutput=1

#Set the input workspace
gp.workspace = sys.argv[1]

#Set the output workspace
OutAscii = sys.argv[2]

try:
    #Get list of InRasters in the input folder

    irs = gp.ListRasters()
    for rs in irs:
        #Validate the new feature class name for the output workspace
        OutAsciiFile = OutAscii + os.sep + rs+".txt"
        #Convert each raster in the list to ASCII
        gp.RasterToASCII_conversion(rs, OutAsciiFile)
except:
gp.AddMessage(gp.GetMessage(2)) #show geoprocessing error messages
gp.AddMessage("Script don") #message when script is done

MATLAB script used to estimate $B_{TOT}$ and $\beta$: 
APPENDIX B

Supporting R Script
require(psych)

CalibL = read.clipboard()
Timex = (CalibL$Time); My = matrix(nrow=length(Timex),ncol=3)

My[,1] = (CalibL$PRED)
My[,2] = (CalibL$UCB)
My[,3] = (CalibL$LCB)

plot(My[,1]~Timex,xlim=c(0,165),ylim=c(-0.2,2),type='l',col='black',tcl=.4,
    xlab='Time (min)',ylab='Br- Concentration (mg/L) error +/- 0.067 mg/L',
    font.axis='6',font.lab='6',cex.axis='1.5',cex.lab='1.5')
px = c(Timex,rev(Timex))
py = c(My[,2],rev(My[,3]))
polygon(px,py,col='gray70',border=NA)
lines(My[,1]~Timex,lwd=1,col='gray0')
lines(My[,2]~Timex,lwd=1,col='gray56',lty="dashed")
lines(My[,3]~Timex,lwd=1,col='gray56',lty="dashed")
points(My[,1]~Timex,ps=0.1,pch=21)

Cdata = read.clipboard()
points(My[,1]~Timex,pch=19,ps=1)

Data = read.clipboard()
Timex = (Data$Time); My = matrix(nrow=length(Timex),ncol=3)

My[,1] = (Data$PRED)
My[,2] = (Data$UCB)
My[,3] = (Data$LCB)

plot(My[,1]~Timex,xlim=c(0,10000),ylim=c(0,90),type='l',col='black',tcl=.4,
    xlab='Time (sec)',ylab='RhWT Concentration (ug/L) error +/- 0.925 ug/L',
    font.axis='6',font.lab='6',cex.axis='1.5',cex.lab='1.5')
px = c(Timex,rev(Timex))
py = c(My[,2],rev(My[,3]))
polygon(px,py,col='gray70',border=NA)
lines(My[,1]~Timex,lwd=1,col='gray0')
lines(My[,2]~Timex,lwd=1,col='gray56', lty="dashed")
lines(My[,3]~Timex,lwd=1,col='gray56',lty="dashed")
points(My[,1]~Timex,ps=0.1,pch=21)

Cdata = read.clipboard()
points(My[,1]~Timex,pch=19,ps=1)

#########################################################################
###Kmeans Cluster Analysis###
#########################################################################
require(graphics)
require(psych)
Temp = read.clipboard()
TempDist = (Temp$C); x = matrix(nrow=length(TempDist),ncol=1)
x[,1] = (Temp$C)

(cl <- kmeans(x, 2))
plot(x, col = cl$cluster, xlab='Sample #',ylab='Degrees C',font.lab='6',font.axis='6')