



Water Quality of the Upper Big Thompson Watershed

Big Thompson Watershed Forum
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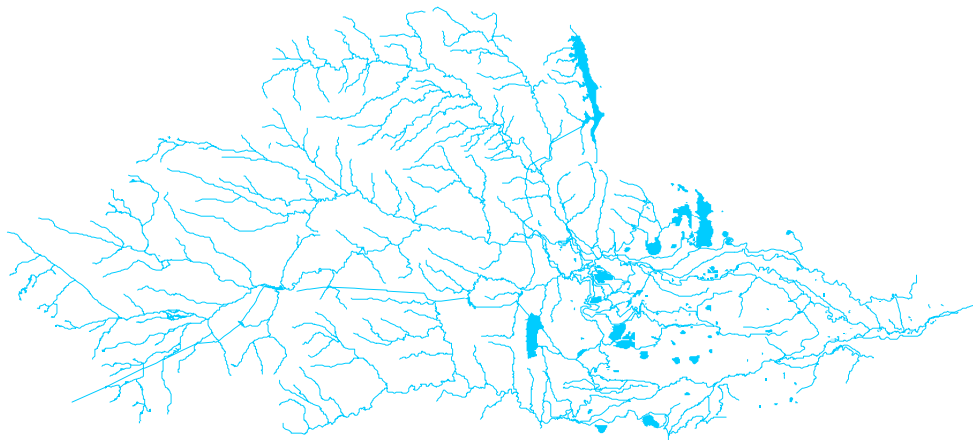


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Summary

The Big Thompson Watershed drains approximately 900 square miles of mountains and plains east of the continental divide. The headwaters of the Big Thompson River are in Rocky Mountain National Park, and water also enters the watershed from the Colorado River via a tunnel. Rapid population growth in the watershed has been accompanied by a slow decline in water quality of downstream reservoirs. The Big Thompson Watershed Forum was formed as a collaborative watershed management effort to address these water quality problems. As part of its mission, the Forum has sponsored a coordinated monitoring program since 2000.

The monitoring program measures a variety of water quality characteristics that are required to identify water quality problems and to develop a strategy for managing them:

Category	Water quality characteristics
General physical & chemical	temperature, turbidity, TDS (total dissolved solids), conductivity, pH, alkalinity, DO (dissolved oxygen), hardness
Major ions	calcium, magnesium, sodium, potassium, sulfate, chloride, bicarbonate
Major nutrients	ammonia, nitrate+nitrite, kjeldahl nitrogen, orthophosphate, dissolved and total phosphorus
Trace elements	silver, arsenic, copper, iron, mercury, manganese, nickel, lead
Organics	TOC (total organic carbon), BTEX (benzene, toluene, ethylbenzene, xylenes), MTBE (methyl tertiary butyl ether)
Bacteria	total coliforms, <i>E. coli</i>

Measurements are made at 19 flowing water stations, bimonthly in late spring and summer and monthly at other times. This report focuses on the 14 stations in the mountainous upstream portion of the watershed, from the inception of the program in fall 2000 to summer 2003.

Although average water quality conditions in the upper watershed show only slight human impact for most variables, there are frequent and significant excursions above existing criteria for humans and aquatic life for some of these variables. The main observations are summarized in the table below. Nutrients, TOC, copper, turbidity, and *E. coli* currently deserve the most consideration.

Nutrients foster phytoplankton growth and poor water quality in downstream reservoirs and canals. Nutrient reduction would be accomplished most efficiently by reducing phosphorus levels in wastewater effluent from the Upper Thompson and Estes Park Sanitation Districts.

The highest TOC concentrations are due to sources upstream of the current monitoring stations in spring. The sources appear to be natural organic matter. As the most

Property	Remark (% refers to the percentage of samples)
turbidity	8% exceed 5 NTU, the maximum allowed in unfiltered drinking water
TDS	typical of unpolluted watershed
conductivity	typical of unpolluted watershed
pH	5% exceed 8.5, the maximum recommended level for drinking water
alkalinity	low to moderate
DO	3% are less than 90% saturation, the recommended criterion for aquatic life at high altitudes
hardness	low
major ions	typical of pristine rivers, except for elevated sodium from road salt
nitrogen	significant enrichment compared with background conditions; ammonia high with respect to aquatic life criteria, but not in violation, near wastewater effluent
phosphorus	significant enrichment compared with background conditions
trace elements	silver, arsenic, iron, mercury, nickel, and lead low or undetectable
copper	10% (almost all in canals) exceed 0.0037 mg/L, an acute toxicity criterion for aquatic life
manganese	one sample exceeded 0.050 mg/L, the maximum recommended for drinking water
TOC	86% exceeded 2 mg/L, a level requiring reduction in treatment systems
BTEX	low or undetected, except isolated incident in which benzene approached standard
MTBE	undetected, but few data
total coliform	mostly typical of water with small anthropogenic impact
<i>E. coli</i>	9 of 13 stations occasionally exceeded the strictest water quality criteria for water contact activities

significant fecal contamination also originates in that area, it would be worthwhile to locate and identify these sources in order to consider possible remedial measures.

Copper is high in the canals because of copper algicide applications to reduce phytoplankton levels. Some phytoplankton species, however, contain toxins that are released from cells as a result of algicide application. Other problems include copper toxicity to nontarget organisms and locations such as the river, especially in cases of operational changes that may not be well-coordinated with algicide applications. If feasible, nutrient reduction is the preferred way to minimize these phytoplankton blooms.

Although definitive statements are hard to make at this early stage of the program, there is some evidence that turbidity is increasing in the lower canyon because of mineral suspensoid inputs, phytoplankton growth, or both. The increased turbidity

enters downstream reservoirs via the river mainstem and also the Hansen Feeder Canal through the Dille Diversion Tunnel. Higher turbidity increases the burden of treating reservoir water for drinking, and has food web effects by limiting the production of phytoplankton and attached algae.

E. coli concentrations, indicative of fecal contamination, occasionally exceed water quality criteria for single sample measurements. Measurements are generally highest at stations closest to headwaters and suggest that the sources are upstream of the current monitoring stations. Both animal such as elk and human sources may be contributing.

The remaining issues appear to be relatively minor. DO deficiency, excessive pH, and high manganese levels are all usually a by-product of phytoplankton activity, so nutrient reduction has the potential to eliminate these sporadic problems as well. Although road salt-enhanced sodium concentrations do not reach problem levels in the upper watershed, they do contribute to downstream excesses and may need to be managed in the future. Finally, benzene concentrations do indicate sporadic incidents of (perhaps fuel) spills and the continuing need for education in service of watershed protection.

Overall the monitoring program has succeeded at this early stage in characterizing the general water quality of the upper watershed and in identifying priority problems. Although the program is still too young to examine trends, the current picture will serve as a reference against which to compare changes in the coming years.

1 Introduction

1.1 Big Thompson Watershed Forum

The Big Thompson Watershed drains approximately 900 square miles of mixed mountainous and plains terrain east of the continental divide. The headwaters of the Big Thompson River are in Rocky Mountain National Park. Water also enters the watershed from the west slope of the divide via a tunnel. Together with precipitation, these waters provide drinking water to over 600,000 people and irrigation water to 630,000 acres. The water also generates electricity through six power plants in the watershed.

Rapid population growth is occurring in the watershed, which maintains ever-increasing demands on the water supply for drinking water, waste disposal, and recreation. A slow decline in water quality has been observed at certain locations, especially in downstream reservoirs such as Lake Loveland and Horsetooth Reservoir. Water quality problems need to be addressed on a watershed-wide basis in order to find problem sources and solutions. This geographic scope requires cooperation among localities within the watershed. They need to pool resources and coordinate the investigation of water quality conditions in a consistent and comprehensive manner.

In 1996, the North Front Range Water Quality Planning Association completed a preliminary watershed study, recommending the establishment of a collaborative watershed management effort to address a variety of needs.¹ A group of concerned people representing private citizens and government agencies responded by endorsing the formation of the Big Thompson Watershed Forum. The mission of the Big Thompson Watershed Forum (BTWF or the “Forum”) is to assess and protect the quality of water in the Big Thompson Watershed. Its goals are to foster stakeholder teamwork in watershed assessment, identify priority protection measures, educate affected interests, and promote voluntary practices that protect the watershed and its water quality. “In pursuit of its mission and goals the Big Thompson Watershed Forum will endeavor to:

1. build an effective voluntary watershed protection program that fosters open communication and cooperation among stakeholders, with strong public and financial support based on documented accomplishment of its objectives.
2. facilitate cooperative water quality assessment and the voluntary exchange of information in order to identify and address water quality concerns in a proactive manner.

1. This information is condensed from <http://www.btwatershed.org>.

3. reduce or eliminate existing and potential water quality problems in the Big Thompson Watershed by providing educational programs that increase awareness of water quality and related quantity issues; by developing and/or supporting voluntary operating practices that address existing and potential water quality problems; and by providing water quality and watershed related information to any party that has the potential to impact water quality within the Big Thompson Watershed.”

As part of its mission, the Forum has sponsored a coordinated water quality monitoring program since 2000. This program conducts measurements of a large variety of water quality parameters throughout the Big Thompson Watershed and a contiguous portion of the Cache La Poudre Watershed. The purpose of the present report is to summarize results for moving water (i.e., canals, mainstem, and tributaries) in the mountainous portion of the watershed, down to the mouth of the Big Thompson River Narrows. The report focuses on three themes:

1. general summary of water quality conditions.
2. compliance of water quality with existing standards.
3. sources of water quality constituents based on loading estimates.

An additional important theme—long-term trends and interannual variability—cannot be undertaken yet because of the relatively short length of the data set.

1.2 Site Description

The U.S. Bureau of Reclamation's Colorado-Big Thompson (C-BT) Project diverts water from the Colorado River on the western slope of the Rocky Mountains to a variety of conveyance and storage facilities on the eastern slope (Figure 1). On an average annual basis, more than half of the water flowing through the east slope portion of this project has been diverted from the upper Colorado River. The Big Thompson River, which is tributary to the South Platte, supplies water directly to the east slope. Major storage components of the C-BT water system, such as Horsetooth Reservoir and Carter Lake Reservoir, receive flows after hydroelectric power generation and hold the water in storage prior to distribution to municipal, agricultural, and industrial users along the foothills and plains of eastern Colorado. The Northern Colorado Water Conservancy District (NCWCD) is charged with operation of the collection, storage, conveyance, and distribution systems.

A central element of the Project is the Alva B. Adams Tunnel, which runs through the Continental Divide and carries water from Grand Lake on the western slope to Mary's Lake on the eastern slope. The Prospect Mountain Conduit and Tunnel carry water from the lake through Prospect Mountain to the Estes Park Power Plant penstock. Water then flows into Lake Estes, mixing with water from the Big Thompson River. Water exits Lake Estes into either the Olympus Tunnel or the south fork of

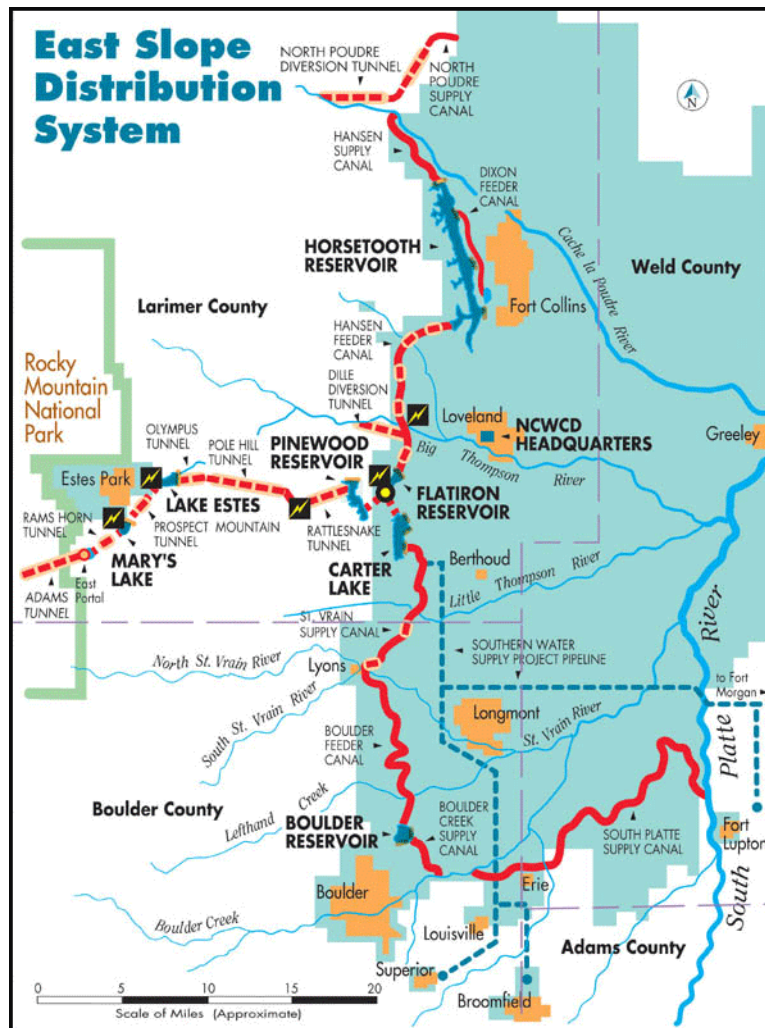


Figure 1: The Colorado-Big Thompson Project supplies water from the western slope and the Big Thompson River to a variety of conveyance and storage facilities on the eastern slope (http://www.ncwcd.org/project&features/cbt_maps.asp).

the Big Thompson River. The Olympus Tunnel feeds Pinewood Reservoir, which is the afterbay to Pole Hill Power Plant and the forebay for Flatiron Power Plant. Flatiron Reservoir, in turn, is a central distribution point for Colorado-Big Thompson Project water and serves as an afterbay for the Flatiron Power Plant. From Flatiron Reservoir, some water is pumped south to Carter Lake Reservoir, which is at a higher elevation and serves as the principal storage site for C-BT Project deliveries to municipal and agricultural water users to the south and east. The Charles Hansen Feeder Canal carries the remainder from Flatiron Reservoir north to Horsetooth Reservoir near Fort Collins. Water also enters the Canal from the Dille Tunnel,

which diverts water from the mainstem of the Big Thompson River. Just downstream of the Dille Tunnel outlet in the Canal is the Trifurcation. Here, the water flows (i) into a wasteway back to the Big Thompson River; (ii) through the Big Thompson Power Plant, which also discharges to the river; and (iii) downstream to Horsetooth Reservoir. Horsetooth Reservoir provides drinking water to the cities of Fort Collins and Greeley and numerous rural domestic suppliers, as well as water for regional industries, irrigation, and recreation. Water from both Flatiron Reservoir and the Dille Tunnel ultimately originates in Lake Estes, but the two supplies are subject to different watershed influences before joining in the Hansen Feeder Canal.

2 Data Sources and Analysis

2.1 Sampling program

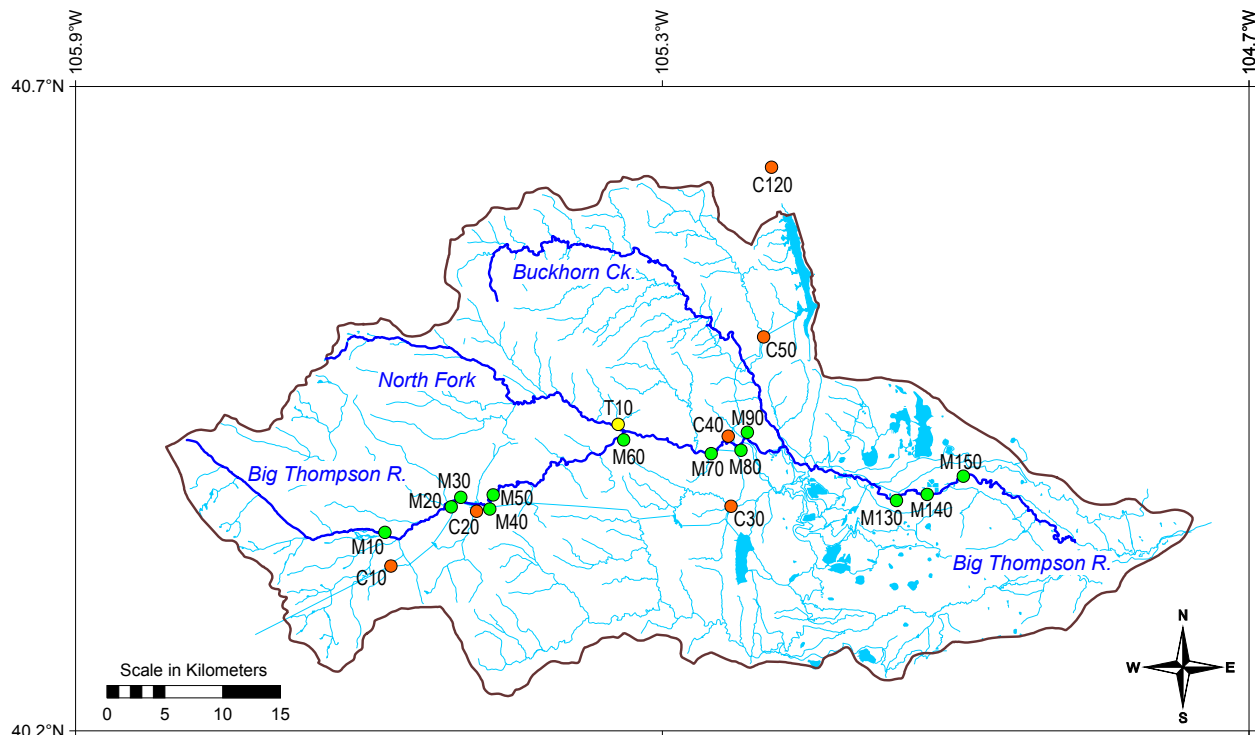


Figure 2: The BTWF monitoring program samples water quality at 19 flowing water stations. Canal stations are designated by a “C”, mainstem stations by an “M”, and tributary stations by a “T”. The outer curved line marks the boundary of the entire watershed area under investigation.

The BTWF monitoring program samples water quality at a variety of canal, river, and reservoir sites. Currently, there are six canal stations, twelve mainstem stations, and one tributary station (Figure 2, Figure 3, Table A-1). There are six additional gaging stations operated by the U. S. Bureau of Reclamation where daily cumulative discharge is estimated. The sampling stations not only provide information at their respective locations, but together allow us to infer conditions occurring between stations. The canal (designated Cxx), mainstem (Mxx), and tributary (Txx) stations in the upper watershed, which are the focus of this report, were chosen with the following rationale (BTWF 1999):

C10: C-BT background water quality

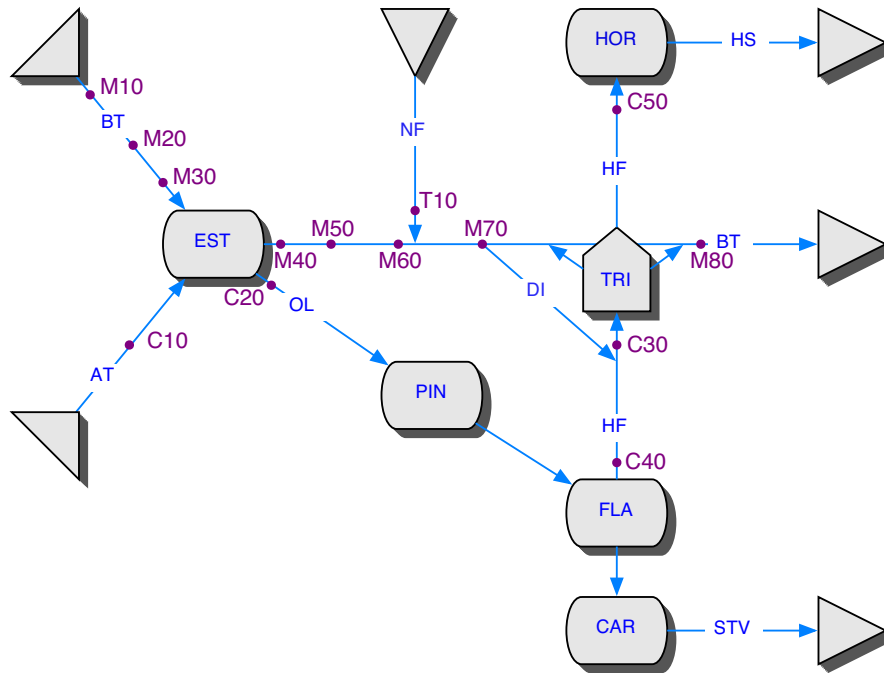


Figure 3: Schematic diagram of upper watershed monitoring stations and water flow. The spatial arrangement and relative distances are not intended to reflect actual geographical locations. EST, L. Estes; CAR, Carter L.; FLA, Flatiron Res.; HOR, Horsetooth Res.; PIN, Pinewood L.; AT, Adams Tunnel; BT, Big Thompson R.; HF, Hansen Feeder Canal; HS, Hansen Supply Canal; NF, North Fork; OL, Olympus Tunnel; STV, St. Vrain Supply Canal.

- C20:** baseline for Olympus Canal downstream of lake
- C30:** changes in Hansen Canal due to Dille Tunnel
- C40:** baseline for Hansen Canal
- C50:** changes due to in-canal effects before Horsetooth
- M10:** Big Thompson R. background water quality
- M20:** changes due to runoff in Estes Park
- M30:** changes due to Estes Park Sanitation District effluent
- M40:** baseline for Big Thompson R. downstream of lake
- M50:** changes due to Upper Thompson Sanitation District effluent
- M60:** changes due to upper-canyon residents and businesses

M70: changes due to North Fork and lower-canyon effects

M80: changes due to Hansen Feeder water

T10: North Fork background water quality

Sampling began in August of 2000. Samples are collected approximately biweekly during late spring and early summer, and monthly at other times of year (Figure 4, Table A-2). The full suite of water quality variables was not sampled until early 2001. We therefore use the 12-month time period beginning with the spring quarter when averaging over years. As of this writing, two full annual periods are available for summary, namely, April 1, 2000-March 31, 2001 and April 1, 2001-March 31, 2003.

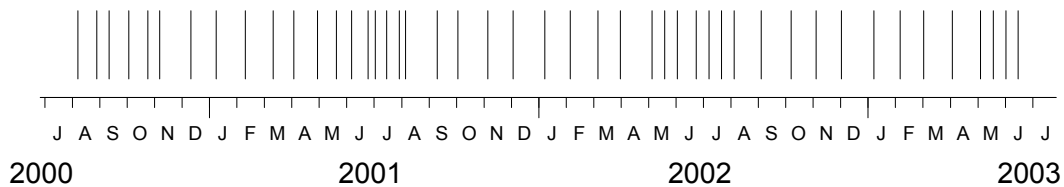


Figure 4: Vertical lines mark the beginning of each sampling event since the inception of the monitoring program considered in this report.

A large number of water quality variables are measured in this program, either in the field using electrode methods or in the laboratory with appropriately preserved samples and standard analytical methods (Table A-3). Variables include hydrological, physical, inorganic chemical, organic chemical, and microbial variables.

2.2 Data Analysis

Data files were downloaded from the Big Thompson Watershed Forum web site (<http://www.btwatershed.org>) on July 22 and August 27, 2003 (Table A-4). The data were processed to ensure consistency of parameter names, units, missing data codes, and designation of censored data (i.e., data beyond the reporting limit). A few physically impossible measurements were identified and excluded from further analysis.

Data analysis was carried out primarily in the S data analysis and graphics environment, using both the commercial version S-PLUS 6 (Insightful Corp. 2001) and the open software version R 1.7.1 (Ihaka and Gentleman 1996). Various S libraries that are not part of the base distribution of either S-PLUS or R were also used, especially `Hmisc` and `Design` (Harrell 2001).

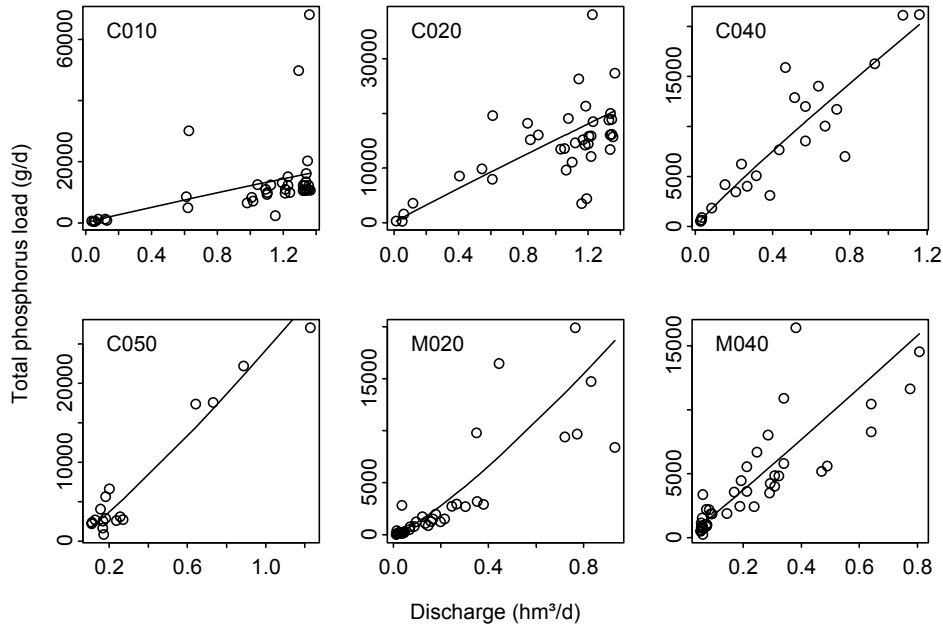


Figure 5: Daily rating curves for total phosphorus exhibit much scatter, especially at higher discharge values.

We analyzed annual loads (cumulative mass transport) for several water properties of interest at those stations with daily cumulative discharge data. *Regression* methods use the relation between constituent load and stream discharge (the constituent rating curve) to estimate missing daily concentrations (Crawford 1991). The regression is usually performed following logarithmic transformation of load or concentration and flow. In this report, we modeled the effect of daily discharge on load by:

$$\ln(L) = a_1 + a_2 \ln(Q) + a_3 \ln(Q)^2 \quad (1)$$

where L is daily load (g/d) and Q is cumulative daily discharge (m^3/d). The model was fit by maximum likelihood estimation using a parametric survival model, permitting the incorporation of censored data. An estimate of mean L was then obtained from $\ln(L)$ using Duan's smearing estimate (Duan 1983). This model was then compared with the simpler form in which $a_3 = 0$, and the model with the smaller *AIC* was selected. Because of the relatively small number of samples and years available at this early stage of the monitoring program, more elaborate formulations, such as models including seasonal terms, are not warranted. The daily loads were averaged over the period of interest, usually the two-year period 4/1/2001–3/31/2003. Confi-

dence limits were obtained by bootstrap sampling of the data used to estimate the rating-curve model. The confidence limits therefore reflect the variance introduced during model selection, as well as uncertainty in water quality measurements, but do not reflect uncertainty in cumulative discharge values. We used percentiles of the empirical distribution of replicates as confidence limits.

Daily rating curves typically show much scatter, which implies that estimates of daily load based on daily cumulative discharge are usually highly uncertain. For example, the rating curve for total phosphorus at M20 exhibits high variability when daily discharges exceed $0.2 \text{ hm}^3/\text{d}$ (Figure 5). However, when averaging these estimates over long periods, such as one or especially two years, the errors cancel somewhat and the estimates of these long-term averages can be reliable enough to draw interesting conclusions.

Regression methods are more suited to the biweekly to monthly sampling frequency in this program than *integration* methods, which depend on interpolation of concentration or load between sampling dates and generally require higher-frequency sampling. Nonetheless, we also estimated loads by integration to compare with the regression methods and because only instantaneous discharge data were available for most stations. Instantaneous loads were calculated for sampling days and then linearly interpolated for days between actual measurements. The daily loads were then averaged for the period of interest.

Data distributions are often shown using *standard* boxplots (e.g., Figure 20). An individual box extends from the lower to upper quartile (25th to 75th percentile) of the data. The point or line within the box represents the median. The straight lines perpendicular to the box (the *whiskers*) on each side extend to all points within 1.5 times the box length. Occasionally the *simple* boxplot is used, in which the whiskers extend to the maximum and minimum values (Figure 10). Because water chemistry data tends to be lognormally distributed, the boxplots will usually be displayed over a logarithmic axis. When it is illuminating to show the individual data points in the distribution, dotplots rather than boxplots will be used (e.g., Figure 16).

2.3 Water Quality Criteria

Several water quality criteria are used in this report for comparison with measurements. The National Primary Drinking Water Regulations (“primary standards”) are legally enforceable standards for public water supplies and are chosen to protect public health by limiting contaminants in drinking water. Contaminants include disinfectants and their by-products, inorganic and organic chemicals, radionuclides, and microorganisms. For most of these contaminants, a Maximum Contaminant Level Goal (MCLG) and Maximum Contaminant Level (MCL) have been set. The MCLG is the level below which there is no known or expected risk to health and it includes a margin of safety. The MCL, which is the enforceable standard, is the

Table 1: Nutrient reference conditions for Nutrient Ecoregion II, subcoregion 21.

Parameter	Reference	Units
TKN	0.04	mg/L
NO ₂ +NO ₃	0	mg/L
TN, calc. ^a	0.04	mg/L
TN	0.09	mg/L
TP	6.34	µg/L
Turbidity	1.65	NTU

a. Calculated from
TKN+NO₂+NO₃

highest level allowed in drinking water and is set as close as possible to the MCLG, taking into account available technology and costs.

The National Secondary Drinking Water Standards (“secondary standards”) are non-enforceable guidelines for drinking water contaminants that may cause cosmetic effects such as skin or tooth discoloration, or aesthetic effects such as taste, odor, or color. These secondary standards are recommended by the U.S. EPA for water systems, and individual states may adopt them as enforceable standards.

The U.S. EPA also recommends criteria for total phosphorus, total nitrogen, chlorophyll *a*, and turbidity for water bodies, including rivers and streams. EPA developed the National Strategy for the Development of Regional Nutrient Criteria in June 1998. Recommendations differ depending on the geographical region in question. For this purpose, the country is divided into a number of Nutrient Ecoregions and subcoregions, with separate criteria for each region based on historical conditions. These ecoregional nutrient criteria are intended to address *cultural eutrophication*, the adverse effects of excess nutrient inputs. The criteria are empirically derived to represent conditions of surface waters that are minimally impacted by human activities and protective of aquatic life and recreational uses. Criteria represent starting points for States and Tribes to develop more refined nutrient criteria with assistance from EPA. The relevant region for this report is Nutrient Ecoregion II (Western Forested Mountains), subcoregion 21 (Southern Rockies) (USEPA 2000). Reference conditions for this region are based on median values of 65 to 203 streams, depending on the parameter (Table 1).

3 Hydrology

3.1 Discharge

Table 2: Average water inputs (AF/d) for the watershed from the west slope (C10) plus the Big Thompson R. (M20) into L. Estes.

Year	Q1	Q2	Q3	Q4	Annual
2000	647	1230	1227	677	945
2001	876	943	1072	735	906
2002	969	1043	566	577	789
Mean	831	1072	955	663	880

Table 3: Percent of water inputs in Table 1 due to the Big Thompson R.

Year	Q1	Q2	Q3	Q4	Annual
2000	3.6	41.0	18.9	7.2	17.7
2001	1.8	45.4	20.0	5.2	18.1
2002	2.0	20.9	16.8	5.7	11.4
Mean	2.5	35.8	18.6	6.0	15.7

Hydrological factors, especially flow rates, play an important role in water quality. They affect loading rates of materials into reservoirs, flushing rates of materials from reservoirs, and water depth, which itself has a big effect on many ecological processes. The currents generated may also have effects on the thermal structure of reservoirs. Cumulative discharge estimates are available for 12 locations, although only 6 of them are also water quality sampling sites (Figure 6).

Note the strong variability of discharge during the year, which is a major factor in determining the seasonal cycle of reservoir water quality. In addition, there is significant year-to-year variability. These features are illustrated more clearly by averaging water flows into the system on a quarterly basis (Table 2). Water inputs are generally highest in spring and summer, lower in winter and especially in fall. Annual flow into the system from the west slope and the Big Thompson R. decreased from 2000 through 2002. Although the Big Thompson R. contributes relatively little of this water in fall and winter, it does provide a large percentage during spring and in summer, which is when most seasonal water quality problems have their origin (Table 3). Both sources of water are therefore instrumental in controlling water quality in the watershed.

The North Fork also contributes water but there is no continuous discharge record available. We can, however, examine the instantaneous discharges measured during monitoring events. Based on the events of Figure 4, the ratio of T10 to M20 dis-

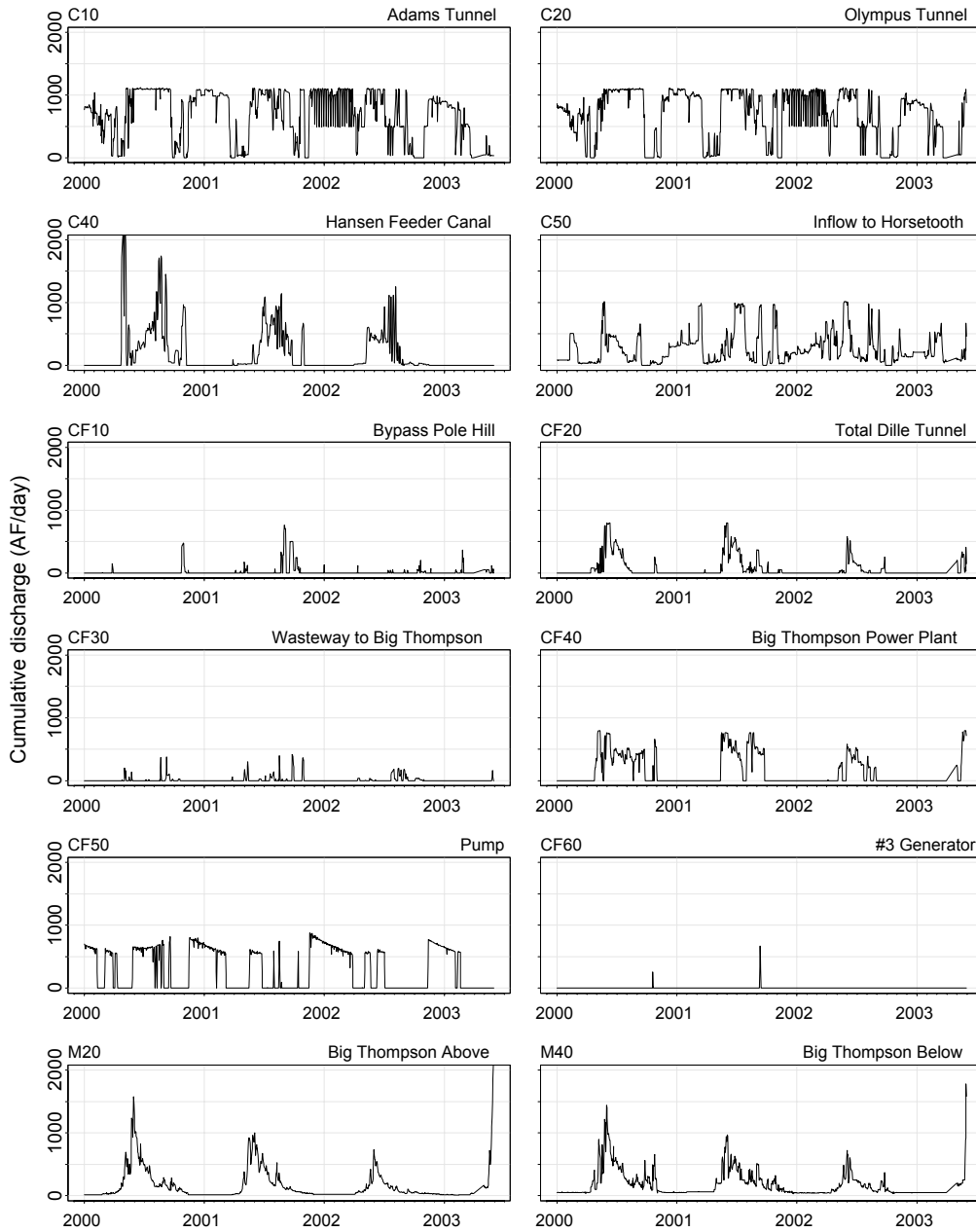


Figure 6: Daily discharge at key locations in the Big Thompson watershed.

Table 4: Summary statistics for instantaneous discharge (cfs).^a Num: number of samples; Censor: fraction censored, i.e., below the reporting limit; Min: minimum; lower: lower quartile; upper: upper quartile; Max: maximum.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	43	0	08/07/2000	07/08/2003	0.4	228	471	547	566
C20	42	0	08/30/2000	07/07/2003	7.6	278.2	482	532.5	570
C30	42	0	08/28/2000	07/09/2003	10.7	82.8	193	411.2	741
C40	43	0	08/28/2000	07/11/2003	0	49.5	83.7	232.5	514
C50	21	0	01/11/2002	07/11/2003	17	55	77	120	516
M10	26	0	02/09/2001	07/07/2003	2.1	4.4	15.5	34	230
M20	45	0	08/29/2000	07/07/2003	6.7	14	47.1	120	1060
M30	45	0	08/29/2000	07/07/2003	6.7	14	47	120	1060
M40	45	0	08/29/2000	07/07/2003	20	29.7	80	126	737
M50	45	0	08/30/2000	07/08/2003	21	30	78.2	130	571
M60	31	0	08/30/2000	07/08/2003	18	26.5	66	125	695
M70	44	0	08/31/2000	07/09/2003	13	43.3	94.4	161.2	803
M80	37	0	03/13/2001	07/09/2003	18.8	47.8	142	267	1030
T10	45	0	08/31/2000	07/08/2003	3.1	7.1	14	28	277.2

a. Numbers are rounded to 1 decimal place, with decimal 0's omitted.

charge had a median value 0.29, i.e., the North Fork contributed a median of 29% additional water to the watershed compared to the Big Thompson R. flow at M20 (Table 4). The range was 0.082 to 4.4, so the North Fork instantaneous contribution can occasionally exceed flows into L. Estes from the Big Thompson R. Without a continuous record for the North Fork, however, we cannot extrapolate this result reliably to the annual time scale.

A substantial amount of water also enters the watershed through precipitation. The NCWCD experienced an annual average of 14.43 inches during the period 1957-2001 (http://www.ncwcd.org/WeatherData/net_prec.txt). Assuming a watershed area of 800 square miles, this is equivalent to almost 1700 acre-feet per day, more than the total from the Colorado and Big Thompson rivers (Table 2). Most precipitation falls on land, however, and part will be lost through evapotranspiration before entering waterways, depending on the runoff ratio. Moreover, the precipitation is spread throughout the watershed, so that the proportion actually entering waterways decreases to zero as we move upstream.

The main use of daily cumulative discharge values in this report is to estimate loading of certain key water quality constituents. In principle, seasonal or annual loading estimates can be done only for the six stations where cumulative discharge can

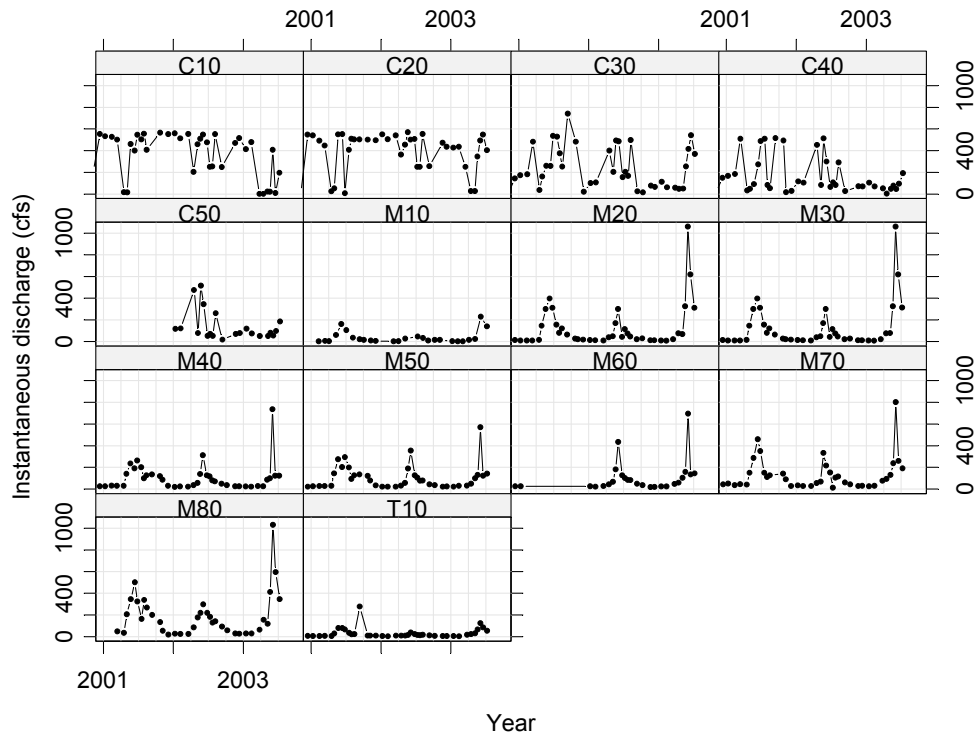


Figure 7: Instantaneous discharges at each sampling station in the upper watershed.

be estimated and samples are also taken periodically for water quality analysis. In practice, though, instantaneous discharges at river stations exhibit a regular seasonal cycle and we will use these discharge data to compare instantaneous loads among stations (Figure 7).

3.2 Temperature

Water temperature is controlled primarily by climate and flow rates, so it is closely tied to the hydrology of the watershed. Temperature has wide-ranging effects on solubility of oxygen and other materials, activity of bacteria and other aquatic biota, taste and odor of drinking water, and corrosion. Water flow may, in some cases, be regulated to affect temperatures, especially to protect aquatic organisms downstream of dams. Temperature is not, however, subject to public health standards because of its insignificant direct effects on human health.

Flowing water temperatures at different locations in the watershed tend to follow the same pattern, but they are shifted higher as we move downstream (Figure 8, Table 5). Upstream river water is generally colder than upstream canal water (compare C10 and M10), but the differences in summer decrease as the water moves

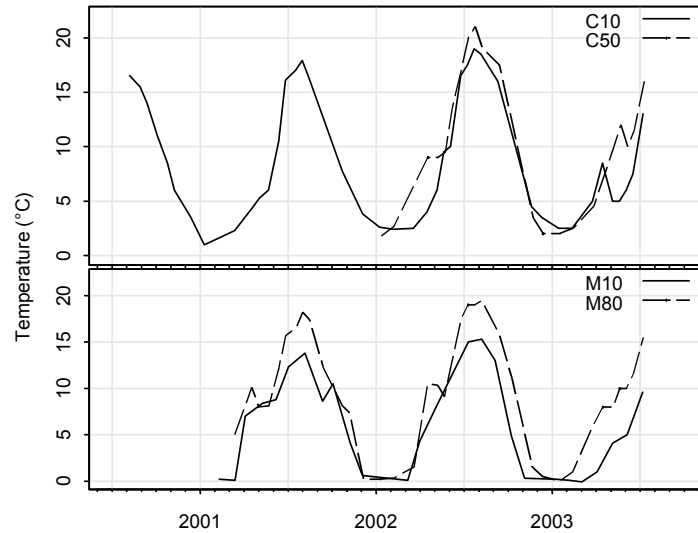


Figure 8: Water temperature at upstream and downstream locations for the C-BT canal system (top) and the Big Thompson R. (bottom).

Table 5: Summary statistics for temperature (°C).

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	43	0	08/07/2000	07/08/2003	1	3.9	6	14.8	19
C20	42	0	08/30/2000	07/07/2003	1.2	2.6	8.2	14.2	19
C30	42	0	08/28/2000	07/09/2003	1.5	4.2	10.5	16	20.5
C40	43	0	08/28/2000	07/11/2003	1.5	4.7	10.5	15.8	21
C50	21	0	01/11/2002	07/11/2003	1.8	3.5	10	16	21
M10	33	0	02/09/2001	07/07/2003	-0.1	0.3	4.9	9	16.6
M20	46	0	08/29/2000	07/07/2003	0	0.6	5	10.2	16.6
M30	45	0	08/29/2000	07/07/2003	0	1.5	5.1	10.5	17
M40	45	0	08/29/2000	07/07/2003	1.4	3.5	8.5	14.5	19
M50	45	0	08/30/2000	07/08/2003	0.1	4.3	8.5	14.2	19.5 ^a
M60	31	0	08/30/2000	07/08/2003	0	0.5	8.9	13.2	19.5
M70	45	0	08/31/2000	07/09/2003	0	4	8.5	14.5	20
M80	37	0	03/13/2001	07/09/2003	0	6	10	15.5	19.5
T10	45	0	08/31/2000	07/08/2003	0	3	9.5	13.7	20 ^b

a. One value of 28 omitted.

b. One value of 32.5 omitted.

downstream (compare C50 and M80). Note also the slight increase in temperatures in later years, which corresponds with the lower discharges in those years.

4 Water Quality

4.1 General or Physical Parameters

4.1.1 Turbidity

Turbidity results from the scattering and absorption of light by particles in the water, including silt, clay, detritus, and phytoplankton. It is a measure of the overall concentration of these fine suspended particles. Turbidity is important because it affects the growth rates of phytoplankton, transport of contaminants, and the effectiveness of disinfection. It usually varies seasonally in response to runoff from the watershed and biological cycles within the water itself. Turbidity can also vary on very short time scales in response to heavy rainfall, which is why instantaneous measurements, as opposed to continuous monitoring, often cannot be extrapolated reliably to the seasonal or annual time scales. Turbidity is usually measured in terms of the amount of light scattering in Nephelometric Turbidity Units (NTUs).

Table 6: Summary statistics for turbidity (NTU).

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	31	0.16	04/17/2001	07/08/2003	0.2	1	1.1	1.5	4.7
C20	31	0.06	04/16/2001	07/07/2003	0.2	1.1	1.5	2.5	6.3
C30	32	0	04/19/2001	07/09/2003	1	1.7	2	3.3	6.5
C40	31	0.03	04/19/2001	07/11/2003	0.7	1.5	2	3	5.4
C50	30	0	04/19/2001	07/11/2003	0.6	1.5	2	2.9	5
M10	6	0	05/10/2001	04/01/2002	0.3	0.6	0.8	1.4	3.8
M20	32	0.12	04/16/2001	07/07/2003	0.2	1	1.5	2.5	11
M30	32	0.06	04/16/2001	07/07/2003	0.2	1.1	1.6	2.5	14
M40	32	0.03	04/16/2001	07/07/2003	0.2	1	1.6	2.1	6.5
M50	32	0	04/16/2001	07/08/2003	0.2	1	1.8	2.9	8.5
M60	32	0.09	04/17/2001	07/08/2003	0.2	1	1.9	3.5	12
M70	33	0.06	04/17/2001	07/09/2003	0.2	1.1	2.4	3.5	11
M80	32	0.12	04/17/2001	07/09/2003	0.2	1	2.1	3.9	11
T10	32	0.09	04/17/2001	07/08/2003	0.2	1	1.7	3	5.1

A summary of the turbidity is displayed in Table 6. Very few of these data are censored. Except for M10, measurements are available regularly since spring 2001. Turbidity in this upstream portion of the watershed is relatively low, with a maximum value of 14 observed at M30. The overall median is 1.9, very close to the regional nutrient criterion of 1.65 NTU (Table 1). There is no fixed MCL for turbid-

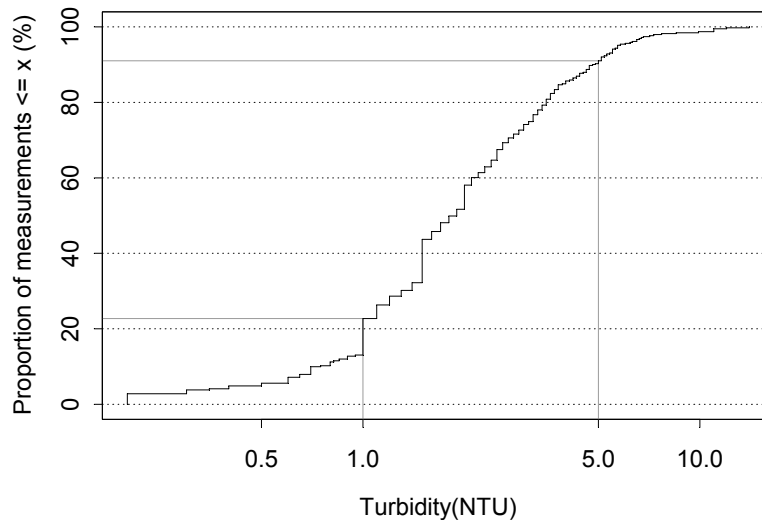


Figure 9: Empirical cumulative distribution plot for turbidity. Light grey lines show the percentage of measurements less than 1 and 5 NTU, respectively.

ity in drinking water regulations, but nonetheless there are primary standards that must be met to protect public health, depending on the source of the water and how it is treated. Key turbidity levels with regard to these primary standards are values of 1 and 5 NTU. The 5 NTU value in particular is interesting because it is the level at which a consumer usually notices sediment and finds water to be impaired aesthetically, and the standards stipulate that no drinking water should exceed 5 NTU in turbidity. As shown by the cumulative distribution plot, most values in the upper watershed are well below that level (Figure 9). Overall, only about 10% of the values exceed 5. The greatest frequency of exceedances is in spring and fall, and at the downstream river stations M60-M80.

The boxplots of the distribution of data at each station suggest an almost monotonic increase as water moves downstream in either the canal system or mainstem (Figure 10). Recall that M10 data are limited and therefore not directly comparable to the others in a boxplot. The canal data show largest turbidity increases from C10 to C20, and C20 to C30, but they do not give very high spatial resolution between the latter two (Lake Estes outflow and the Hansen Supply Canal; Figure 2, Figure 3). Notable turbidity increases occur in the Narrows (from M60 to M80), and these cannot be explained by the North Fork inflow (T10), which has generally smaller turbidity values than M60. Just as these spatial plots combine all time data for each station, we can examine time plots that combine all canal or river station data for each time. Rather than a separate boxplot for each sampling event, however, it is more informative to plot the lower, median, and upper quantiles of the data over time based on equal amounts of data for each point defining the lines (Figure 11).

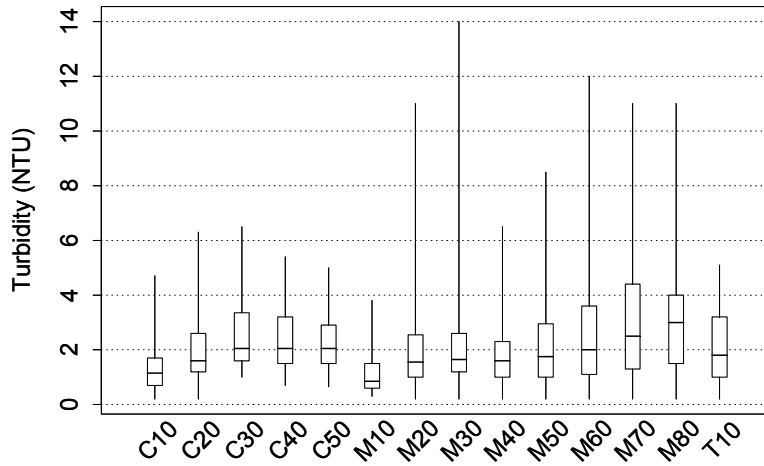


Figure 10: Distribution of turbidity values for each station, as indicated by simple boxplots. The horizontal line within the box marks the median value, the boxes enclose the middle two quartiles, and the vertical lines extend to the full range of the data.

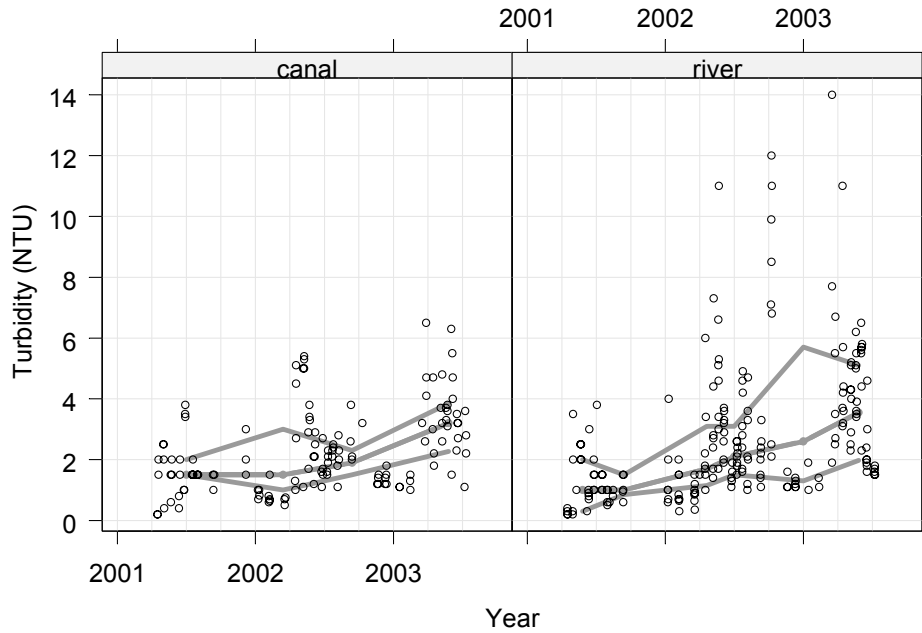


Figure 11: Turbidity values combined for all canal and all river stations, respectively. Lines represent lower, median, and upper quartiles of the data.

The turbidity range tends to be higher in the river than in the canal system, but both show increasing turbidity since sampling began and both show high values during

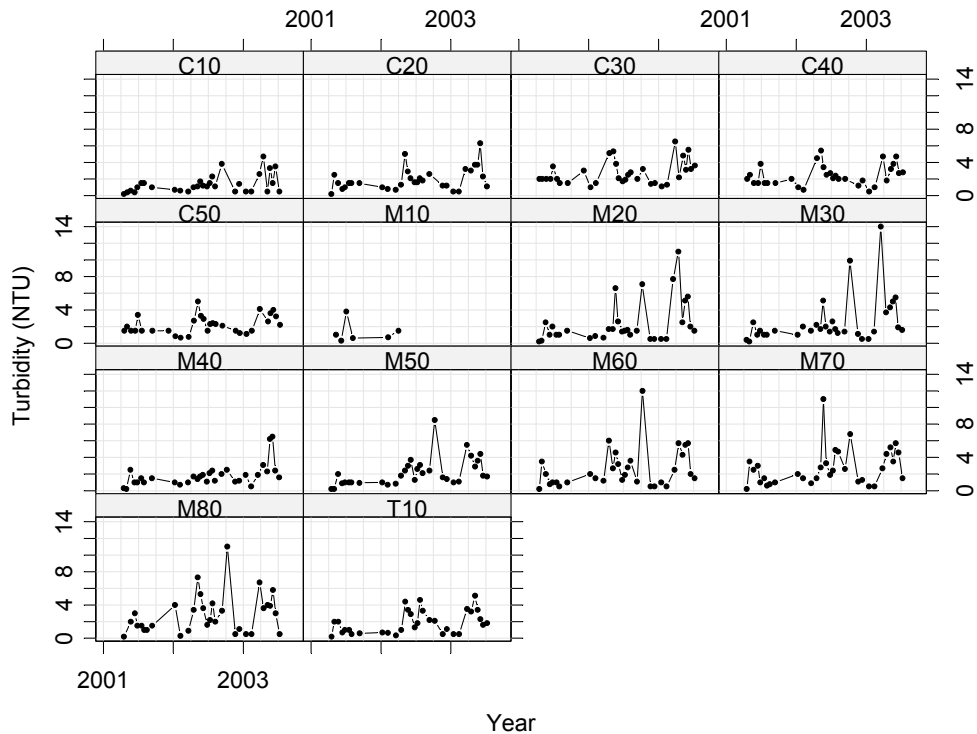


Figure 12: Time plot of turbidity at each station. Note that identical axes are used for each plot.

spring. The mainstem also exhibits high values during fall 2002. River discharge peaks in the spring and at least some of the higher turbidity at this time could be due to higher flows. Canal discharge, on the other hand, does not peak in spring, yet certain canal stations still exhibit high turbidity at this time. Some of the turbidity increase could therefore be due to phytoplankton growth, which could also account for the high mainstem values in fall 2002. Without actual phytoplankton biomass data, however, the reasons will remain speculative.

Turbidity loads were estimated for the two-year period beginning with spring 2001 (Table 7). Insufficient data were available for M10. The units are unusual because turbidity is not expressed in terms of mass concentration; only the relative values, however, are important. The first estimate uses the integration method and can be calculated for every station except M10. It is difficult to know the uncertainty of these estimates because they are based on instantaneous discharge and subject to error insofar as the load does not change smoothly between sampling events. The second estimate uses the regression method and can be calculated only for those stations with continuous discharge estimates. Also shown are 95% confidence limits for the latter. The biggest discrepancy between the methods occurs for C40, where the integration estimate is more than double the regression estimate and does not lie

Table 7: Turbidity loads ($kNTU\cdot m^3/d$) for the two-year period 4/1/2001–3/31/2003. Integration-method loads are based on load interpolation between instantaneous measurements. Regression-method loads are based on rating curves and daily cumulative discharge. Bootstrapped estimates of the lower and upper 95% confidence limits are also shown for the regression-method loads.

Station	Integration	Regression	Lower	Upper
C10	1140	1070	882	1950
C20	1520	1520	1250	1970
C30	1400	-	-	-
C40	1040	508	363	697
C50	853	777	638	951
M20	353	476	290	751
M30	348	-	-	-
M40	297	331	250	416
M50	380	-	-	-
M60	473	-	-	-
M70	676	-	-	-
M80	808	-	-	-
T10	106	-	-	-

within its confidence limits. Such discrepancies occur because extrapolation of instantaneous discharge measurements can be distorted by large spikes in discharge (compare C40 in Figure 6 and Figure 7). They are more likely to occur for channel than river stations, because discharge changes much more smoothly in the latter (M20 and M40 in Figure 6).

The Olympus Canal carries a much larger load of turbidity than the C-BT inflow, and the difference cannot be explained by the slight drop in the mainstem (although the confidence limits are too large to allow definitive statements). Lake Estes therefore apparently acts as a source of turbidity, although how much is in the form of phytoplankton and how much as mineral suspensoid remains unknown. The load in the canal system then decreases downstream until the Hansen Feeder Canal, but increases again by the time it reaches Horsetooth. The mainstem load increases downstream after Lake Estes. The largest increase occurs between M60 and M70, but about half of this can be accounted for by North Fork inflow. Because the load from Flatiron Reservoir is lower than at Horsetooth, the increase between M70 and M80 could have its source in the canyon and may contribute to the load increase between Flatiron and Horsetooth. The conclusions would be opposite if the instantaneous loads were used, showing the importance of basing canal load estimates on continuous discharge records. Again, it is worth repeating that these increases in turbidity could be due, in principle, to either mineral suspensoid or phytoplankton

Table 8: Summary statistics for total dissolved solids (mg/L) in the upper watershed. All samples are well below the secondary standard of 500 mg/L.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	28	0	04/17/2001	05/20/2003	12	36	41	46.2	79
C20	28	0	04/16/2001	05/19/2003	26	35.2	40	44.5	70
C30	29	0	04/19/2001	05/23/2003	24	34	35	44	65
C40	28	0	04/19/2001	05/23/2003	16	34	38	43.5	67
C50	27	0	04/19/2001	05/23/2003	18	31.5	37	43	74
M20	28	0.04	04/16/2001	05/19/2003	10	21.8	28.5	40.5	66
M30	29	0.03	04/16/2001	05/19/2003	10	22	34	46	68
M40	29	0	04/16/2001	05/19/2003	18	33	38	44	73
M50	29	0	04/16/2001	05/20/2003	20	34	44	49	80
M60	29	0	04/17/2001	05/20/2003	22	38	44	53	112
M70	30	0	04/17/2001	05/21/2003	26	36.5	45	51	101
M80	29	0	04/17/2001	05/21/2003	12	34	42	51	93
T10	29	0	04/17/2001	05/20/2003	11	29	34	42	77

increases. The record is too short to deduce the answer from turbidity data alone, and no corresponding phytoplankton biomass data are available yet.

4.1.2 Total dissolved solids and conductivity

Total dissolved solids (TDS) is composed mainly of inorganic salts, especially calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, and silicate. Organic matter usually contributes relatively small amounts. The major source of total dissolved solids is contact with rock and soils, with minor contributions from urban runoff, but road salt applied for snow and ice control can be an important component at times. Physiological effects (“saltiness”) may appear with TDS values over 500 mg/L, but more likely over 1000 mg/L. TDS levels also affect corrosion, depending on the actual constituents of TDS. TDS is regulated under the National Secondary Drinking Water Standards (secondary standards), which are EPA recommendations for contaminants that cause cosmetic or aesthetic effects. The TDS secondary standard is 500 mg/L.

The TDS data are summarized in Table 8. All measurements are well below the secondary standard in the upper watershed, although they do increase downstream in the river mainstem. The values are typical of unpolluted watersheds around the world (Meybeck and Helmer 1989). Conductivity is closely related to TDS and major ion (see below) concentrations. TDS (mg/L) can usually be estimated from conductivity ($\mu\text{S}/\text{cm}$) by a factor of 0.55-0.75, with the higher values characteristic

of waters containing more sulfate. For the data collected in the upper watershed to date, the best multiplier is 0.747 ± 0.002 standard error (SE).

Table 9: Summary statistics for field-measured pH in the upper watershed.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	43	0	08/07/2000	07/08/2003	6.6	7.5	7.8	8	9.3
C20	42	0	08/30/2000	07/07/2003	7	7.5	7.9	8.1	9.1
C30	42	0	08/28/2000	07/09/2003	7.1	7.5	7.8	8.1	8.6
C40	43	0	08/28/2000	07/11/2003	6.9	7.4	7.8	8	9.1
C50	21	0	01/11/2002	07/11/2003	7.1	7.6	7.9	8	9
M20	46	0	08/29/2000	07/07/2003	6.9	7.4	7.7	7.8	8.5
M30	45	0	08/29/2000	07/07/2003	7	7.3	7.8	7.9	8.9
M40	45	0	08/29/2000	07/07/2003	7.1	7.4	7.8	8	9.1
M50	44	0	08/30/2000	07/08/2003	7.2	7.8	8.1	8.4	9.5
M60	30	0	08/30/2000	07/08/2003	7	7.7	8.1	8.3	8.8
M70	45	0	08/31/2000	07/09/2003	7.1	7.4	7.7	7.9	8.8
M80	37	0	03/13/2001	07/09/2003	7	7.5	7.7	8	8.6
T10	45	0	08/31/2000	07/08/2003	7.1	7.5	7.7	7.9	8.3

4.1.3 pH and alkalinity

pH, which measures the hydrogen ion activity of water, is associated with many other water quality variables such as alkalinity and acidity, as well as many aspects of drinking water treatment, including corrosivity, chlorination, and coagulation. It has important effects on the composition of biological communities such as the phytoplankton, as well as on the toxicity of contaminants such as ammonia. The pH of natural waters usually averages between 6 and 8.5, although lower values can occur in dilute waters with high organic matter content or subject to acid rain, and higher values are frequently seen in waters with high algae concentrations. The normal range of pH has no immediate direct effect on human health, but there is a secondary standard of pH 6.5-8.5 for drinking water. Values above 8.5 favor the formation of trihalomethanes (THMs), which are carcinogenic disinfection by-products.

Measured pH levels in the upper watershed range from 6.6 in M10 up to 9.5 in M50 (Table 9). The range is considerably less for the samples measured in the laboratory (not shown) because of water chemistry changes during storage. In all, five percent of pH measurements in the upper watershed were above the 8.5 criterion (Figure 13). Although median concentrations do not differ much among stations, maximum values increase markedly in the mainstem from M10 through M50, and all mainstem stations downstream of M20, as well as all canal stations, have some values exceeding 8.5 (Figure 14). Downstream of M60, the North Fork inflow (T10)

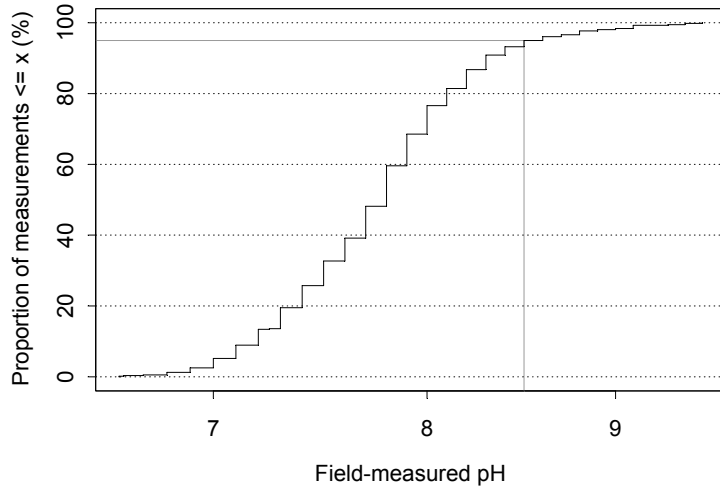


Figure 13: Empirical cumulative distribution plot for pH in the upper watershed. About 5% of samples are above the secondary standard of 8.5 for pH.

returns pH to lower values and may also be responsible via the Dille Tunnel for the slightly lower pH range at C30 compared to C40. High pH values are usually found in conjunction with high phytoplankton populations, because phytoplankton photosynthesis is one of the main reasons for high pH. This is probably behind the high value for C10 in late summer of 2001 (Figure 15). But there are also high values at some stations in early spring (e.g., M50) and it remains to be determined if phytoplankton photosynthesis is the explanation.

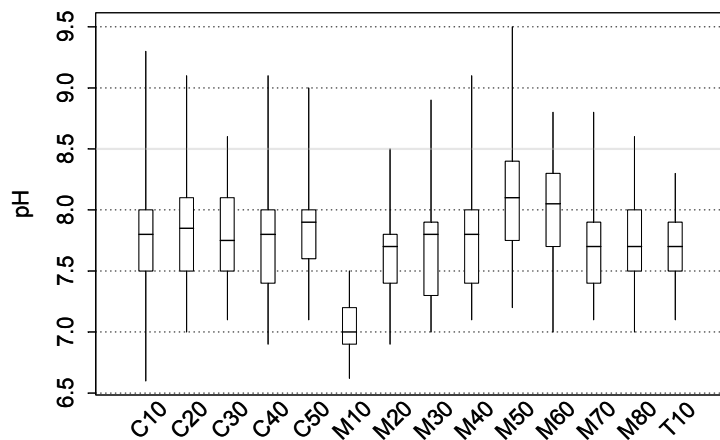


Figure 14: Distribution of pH values at each station.

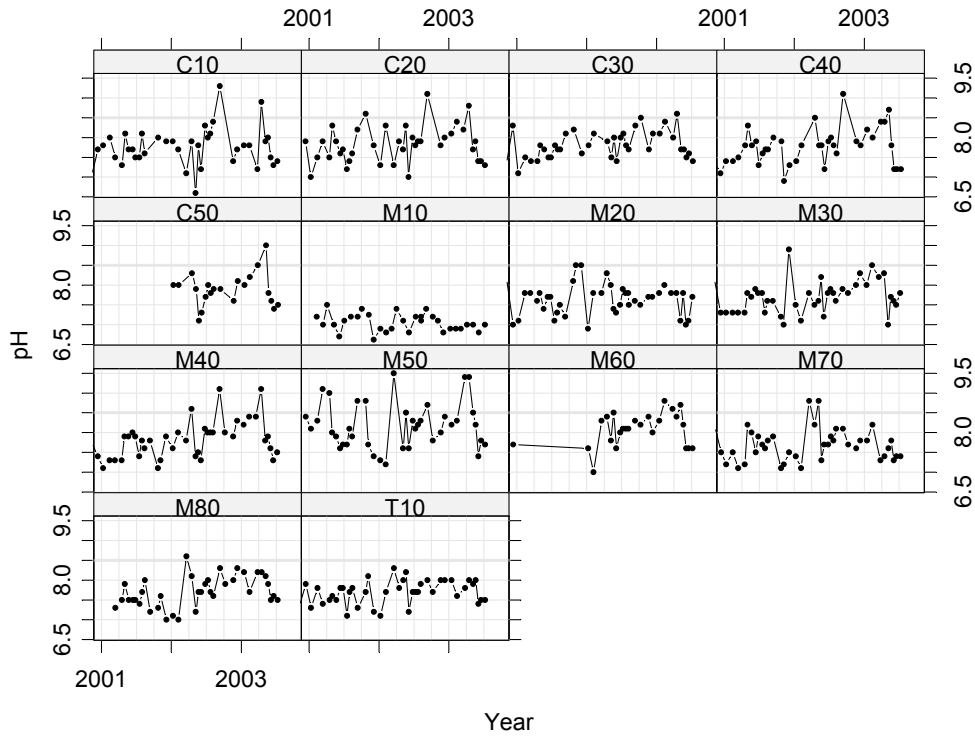


Figure 15: Time plots of pH at each station in the upper watershed.

Table 10: Summary of total alkalinity (mg/L) for stations in the upper watershed.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	28	0	04/17/2001	05/20/2003	8	21.5	24	25.2	59
C20	28	0	04/16/2001	05/19/2003	5	16	22	25.2	30
C30	29	0	04/19/2001	05/23/2003	8	18	23	27	31
C40	28	0	04/19/2001	05/23/2003	8	18	23	26	31
C50	27	0	04/19/2001	05/23/2003	5	20	23	26	31
M20	29	0	04/16/2001	05/19/2003	5	8	11	17	24
M30	29	0	04/16/2001	05/19/2003	5	8	13	19	30
M40	29	0	04/16/2001	05/19/2003	8	18	22	25	30
M50	29	0.03	04/16/2001	05/20/2003	5	17	22	25	48
M60	29	0	04/17/2001	05/20/2003	6	19	23	27	41
M70	30	0	04/17/2001	05/21/2003	8	18.2	21.5	25	47
M80	29	0	04/17/2001	05/21/2003	10	17	22	26	29
T10	29	0	04/17/2001	05/20/2003	7	13	15	18	21

Alkalinity is closely related to pH and measures the capacity of water to neutralize acids that may enter a water body from the atmosphere or watershed, or may be added during treatment processes. Alkalinity in natural waters is due mostly to the presence of carbonate, bicarbonate, and hydroxide ions, although borates, silicates, phosphates, and organic ions may also contribute. Alkalinity is not significant from the viewpoint of potability and has no direct correlation with health, so there are no primary or secondary standards. But low alkalinity does indicate more susceptibility to pH changes from acid rain and other contaminants, as well as from photosynthesis and respiration, and thereby has profound effects on many aspects of water quality and biological communities. Generally speaking, most natural waters fall in the range of 5-125 mg/L total alkalinity (as CaCO_3). A minimum of 15 mg/L is desirable if coagulation is used in drinking water treatment and a maximum of about 100 mg/L is acceptable for domestic use. In comparison, values in the upper watershed range from 5-59 mg/L, with median values of 11-24, depending on the station (Table 10). The lower values (<10 mg/L) indicate sensitivity to acid rain.

4.1.4 Dissolved oxygen

Dissolved oxygen is essential for aquatic life. It is produced by plant photosynthesis, consumed by bacterial and animal respiration, and exchanged with the atmosphere, so it can be quite variable in waters with high biological activity. Wastewater effluent with high levels of organic matter or ammonia can create low dissolved oxygen (DO) conditions downstream. Similarly, phytoplankton blooms in reservoir surface waters eventually die and sink to deeper waters where their decomposition results in low or no DO near bottom waters. Low DO conditions affect not only fish and other aquatic life but also drinking water quality in direct and indirect ways. A bad taste is usually associated with $\text{DO} < 2\text{-}3$ mg/L, and anaerobic decomposition results in sulfides that produce problem odors. As sometimes experienced in Horsetooth Reservoir, low DO promotes solubilization of manganese from reservoir sediments, which subsequently can enter the water supply and form precipitates on laundry or food.

Low DO is not a direct human health threat and there are no drinking water standards. Water quality criteria for DO are sometimes established locally in response to impairment of a water body and as a target to guide the establishment of a Total Maximum Daily Load (TMDL) for oxygen-demanding substances. These criteria depend on local conditions and the biological resources in question. Saturation concentrations are needed to ensure maximum production of desirable species such as salmonids at critical stages of life, but many non-game fish species experience no problems at even much lower concentrations. The U.S. EPA has recommended ambient water quality criteria for DO for protection of “coldwater” fish communities (i.e., communities including salmonids) (USEPA 1986): a 30-day mean of 6.5 mg/L, a 7-day mean minimum of 5 mg/L, and a 1-day minimum of 4 mg/L. Criteria for early life stages are higher: a 7-day mean of 9.5 mg/L and a 1-day minimum of 8

Table 11: Summary statistics for dissolved oxygen (mg/L) in the upper watershed.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	43	0	08/07/2000	07/08/2003	7	7.9	8.6	9.2	11.6
C20	41	0	08/30/2000	07/07/2003	6.4	8.7	9.4	10.2	12.7
C30	38	0	08/28/2000	07/09/2003	7.2	8.7	9.8	11.2	14.1
C40	43	0	08/28/2000	07/11/2003	6.6	8.6	9.8	11.1	14.5
C50	21	0	01/11/2002	07/11/2003	7.4	8.3	9.7	11.3	13.7
M10	31	0	02/09/2001	07/07/2003	7.4	9.5	10.1	10.4	11.4
M20	44	0	08/29/2000	07/07/2003	7	8.8	10.2	11	14.2
M30	43	0	08/29/2000	07/07/2003	7.8	9	10.1	11.7	13.9
M40	43	0	08/29/2000	07/07/2003	7.4	8.7	9.7	10.4	12
M50	44	0	08/30/2000	07/08/2003	7.2	8.2	9.2	11	13
M60	30	0	08/30/2000	07/08/2003	7.4	8.3	9.6	11.9	14
M70	44	0	08/31/2000	07/09/2003	7.5	8.6	9.8	11.7	13.9
M80	36	0	03/13/2001	07/09/2003	7.5	8.4	9.8	12.3	13.5
T10	44	0	08/31/2000	07/08/2003	7.1	8.2	9.3	11.4	14.6

mg/L. These criteria were established for water bodies at sea level, however, and saturation concentrations of DO decrease with altitude. At the elevation of Estes Park (2293 m), for example, the saturation DO level is only 7.7 mg/L at 15 °C, compared to 10.1 mg/L at sea level. When natural conditions alone create DO concentrations less than the applicable criteria, the minimal acceptable concentration is 90% of the natural concentration (USEPA 1986).

DO levels in the canals and river stations of the upper watershed always remain above 6.4, at least at those times of day when measurements are made. Measurements were performed between 0800 and 1700, with a median of about 1100. DO is generally highest in the afternoon and lowest before sunrise in waters with biological activity, so actual daily minimum levels are probably lower than the values recorded. Fish likely respond to the minimum daily DO rather than the daily average, so the values reported here may be an optimistic picture of conditions for fish.

The complete set of DO data in terms of percent saturation is plotted in Figure 16. Very few measurements fall below 90% and most of these are above Lake Estes. The imported C-BT water had the highest incidence of these values, while the lowest value occurred after the Estes Park runoff enters the mainstem. The same data are plotted in Figure 17 to show variation with time of year. Most of the values below 90% occur during the cold season. Although measurements are still few at this point, almost all values are well above criteria to protect aquatic life.

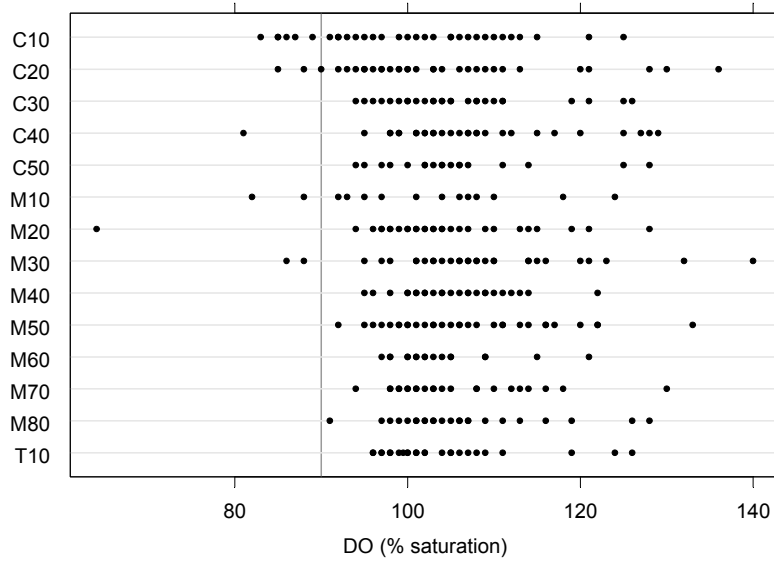


Figure 16: Dotplot of percent DO saturation in the upper watershed. The vertical line is at the 90% saturation level.

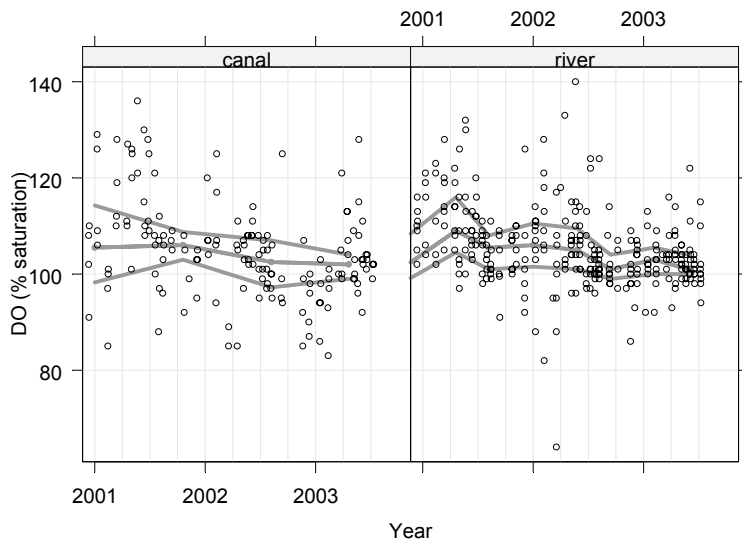


Figure 17: Percent DO saturation measurements combined for all canal and all river stations, respectively. Lines represent lower, median, and upper quartiles of the data.

4.2 Major Ions

4.2.1 Hardness

Originally, hardness was used as a measure of the ability to destroy the lather of soap. Calcium and magnesium are major factors, but other polyvalent cations such as iron, aluminum, and manganese may also precipitate soap lather. As calcium and magnesium are normally the only significant precipitating ions, hardness is equated with total calcium and magnesium, usually reported in equivalent units of calcium carbonate. However, it should be noted that in waters of low DO, such as the bottom waters of Horsetooth Reservoir in summer and fall of some years, manganese can become a major factor in precipitation (and resulting consumer problems with laundry and cooked food). There are no primary or secondary standards associated with hardness, although hardness levels are significant for health and other matters.

Water that is too soft (< 50 mg/L) enhances corrosion of copper and lead pipes, whereas excessively hard water (> 150-200 mg/L) promotes scaling. Water begins to taste unpleasant at very high hardness and the World Health Organization (WHO) has set a criterion of 500 mg/L on aesthetic grounds. Hardness has a major effect on metal solubility and therefore on the toxicity of harmful trace elements, as well as the availability of essential trace elements, to plants and animals. Mortality from cardiovascular disease has been found to decrease as hardness increases, up to about 170 mg/L.

Table 12: Summary statistics for calcium hardness (mg/L CaCO₃) in the upper watershed.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	11	0	04/17/2001	03/19/2002	9.5	14.5	17	18	19
C20	11	0	04/16/2001	03/18/2002	8.2	13.5	16	17.5	19
C30	11	0	04/19/2001	02/07/2002	9.4	12.5	16	17.5	22
C40	11	0	04/19/2001	02/07/2002	9.5	13	16	17.5	22
C50	11	0	04/19/2001	03/21/2002	9.8	13	16	18	22
M20	11	0	04/16/2001	03/18/2002	5.8	6.5	8.1	12.5	15
M30	11	0	04/16/2001	03/18/2002	5.7	6.9	8.4	13.5	16
M40	11	0	04/16/2001	03/18/2002	8.2	13.5	17	17.5	20
M50	11	0	04/16/2001	03/18/2002	8.8	13.5	17	18.5	20
M60	11	0	04/17/2001	03/19/2002	9.3	14	18	19.5	23
M70	12	0	04/17/2001	03/19/2002	9.8	13.8	16	18.2	23
M80	11	0	04/17/2001	03/20/2002	9.5	13	15	18	23
T10	11	0	04/17/2001	03/19/2002	7.5	8.4	9.7	10	16

Total hardness in the upper watershed is quite low, and varies over a small range. The median values range from 14 to 24 mg/L, and the entire range is only 9.6-25. As there are only four sampling events over a period of about seven months for total hardness, we show the summary statistics for calcium hardness instead (Table 12). Calcium hardness accounts for 66-79% of the total hardness for the samples in which they were both measured. Mainstem values above Lake Estes are a median of 8.1-10 (including the North Fork). Median values in the canal and downstream of the lake are almost double, but still signify soft water. In most rivers, hardness typically shows seasonal variation with highest values during low flow conditions, and this appears to be true for the upper Big Thompson and canal water as well (compare Figure 18 and Figure 6).

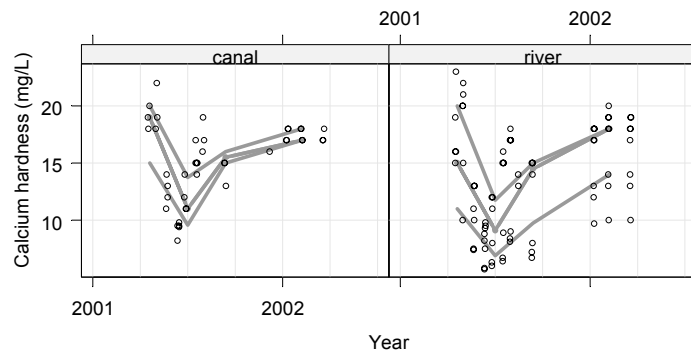


Figure 18: Calcium hardness measurements combined for all canal and all river stations, respectively. Lines represent lower, median, and upper quartiles of the data.

4.2.2 Major cations and anions

The major cations of most natural waters are calcium, magnesium, sodium, and potassium, and the major anions are chloride, sulfate, and bicarbonate (and carbonate at high pH). Together they constitute most of the total dissolved solids, and subgroups account for most of the hardness (calcium and magnesium) and alkalinity (bicarbonate and carbonate). We treat them together and briefly because they are rarely of much concern for either human health or aquatic life in relatively unpolluted mountain waters, although they can influence exactly which plant and animal species are able to flourish and form the biological community of a water body. The median concentrations in the upper watershed (Table 13) are typical of unpolluted streams draining common rock types. The sum of the median cation values is equivalent to 480 $\mu\text{eq/L}$, also typical of pristine rivers (the median of the sum is preferred, but there are not enough sampling days in which all cations were measured simultaneously). In comparison, the global “most common natural concentration” is 800 $\mu\text{eq/L}$ (Meybeck and Helmer 1989).

Table 13: Summary statistics (mg/L) for dissolved major ions in the upper watershed.

Ion	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
calcium	359	0	04/16/2001	05/23/2003	1.5	4.2	5.6	6.9	13
magnesium	339	0	04/16/2001	05/23/2003	0.005	0.55	1.0	1.3	3.2
sodium	365	0	04/16/2001	05/23/2003	0.7	1.9	2.3	3.5	15
potassium	231	0	04/15/2002	05/23/2003	0.24	0.54	0.69	0.85	2.4
sulfate	287	0	01/07/2002	06/05/2003	0.18	2.4	2.9	4	12
chloride	285	0.01	01/07/2002	06/05/2003	0.16	0.7	1.3	2.7	22
bicarbonate	89	0	04/16/2001	08/02/2001	5	11	17	24	39

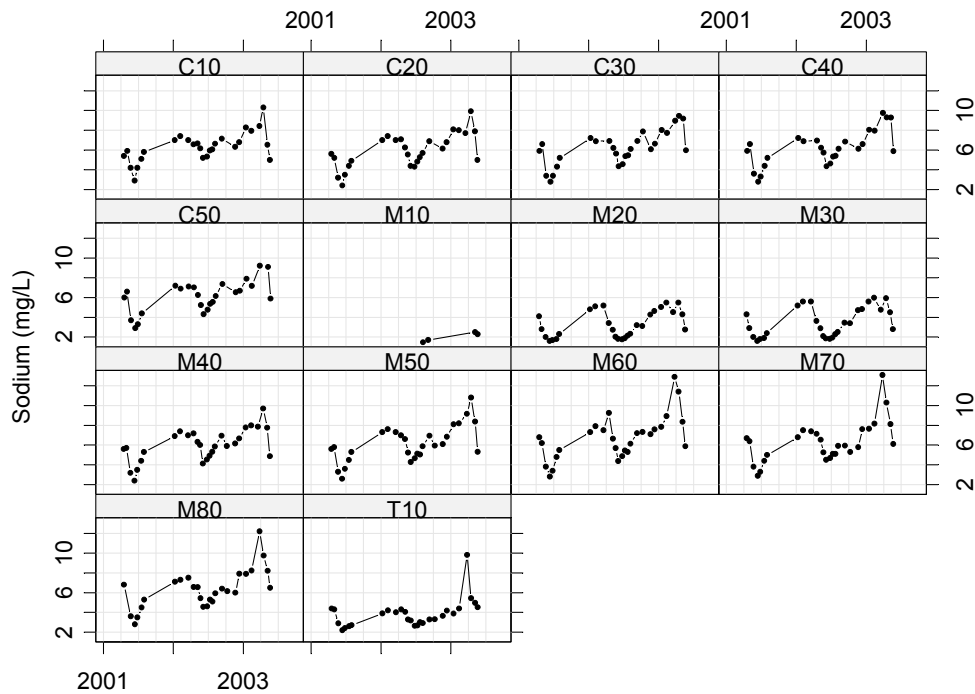


Figure 19: Sodium concentrations in the upper watershed. Note the regular peaks during late winter or early spring.

There are no national standards for calcium, magnesium, or potassium in drinking water. WHO and the European Community (EC) have set acceptable limits for all of these substances, but the limits are well above the highest values measured in the upper watershed. Secondary standards of 250 mg/L exist for both sulfate and chloride because of effects on taste, but clearly the standards are also far above concentrations of these ions.

Although there is no national standard for sodium, the EC has a guide level of 20 mg/L for vulnerable individuals because of the relation between sodium intake and blood pressure. The highest values in the upper watershed are close to that level, and downstream values reach 135 mg/L (not shown). Sodium concentrations peak in late winter or early spring, indicating that the source is probably salt applied to roads in winter and eventually released into waterways, especially when warming begins (Figure 19). The highest values are approximately equimolar with chloride concentrations—for example, the maximum sodium is 0.65 mmol/L and the maximum chloride is 0.62 mmol/L—confirming that the source of the high values is sodium chloride. Concentrations tend to increase downstream and there is a notable jump between M50 and M60, indicating sources in the upper canyon. M80 is somewhat lower because of dilution from the canals.

4.3 Major Nutrients

The macronutrients or major plant nutrients of most interest in the water quality context are nitrogen (N) and phosphorus (P). These are typically the elements that are depleted first during excessive growth of phytoplankton and attached algae. In some situations, silica (SiO_2) depletion below 0.5 mg/L may limit growth of diatoms, which require silica as a component of their cellular casings. We know, however, that silica concentrations in Horsetooth and Carter reservoirs are above 3 mg/L, even in surface waters during summer when we would expect the most depletion (Jassby and Goldman 1999). River concentrations in general are almost always above 2 mg/L. N and P are therefore the main nutrients of interest in the upper watershed.

Aside from natural sources, inorganic N concentrations can be enhanced as nitrate (NO_3), nitrite (NO_2), or ionized ammonia (NH_4) from wastewater and fertilizer, as well as from atmospheric deposition. These same sources contribute to P enrichment of natural waters in the form of orthophosphate (o-PO_4). There is a primary standard for nitrate of 10 mg/L and nitrite of 1 mg/L: infants drinking water in excess of these concentrations can become seriously ill and die. Such concentrations are rare in surface waters except when grossly polluted by wastewater effluent or agricultural drainage (these concentrations have been measured in the lower watershed). Excessive ammonium can also become a problem because, at high pH, a substantial portion is in the form of unionized ammonia, which is toxic to fish and other organisms. The nutrient reference condition for the southern Rockies subcoregion is 0.04 mg/L total N (TN) (for the method used here, which estimates TN indirectly from other measurements), and 6.43 $\mu\text{g/L}$ total P (TP).

The summary statistics for N and P measurements indicate a large fraction of censored values (with multiple censoring levels) for both ammonia—by which we mean unionized plus ionized forms—and orthophosphate (Table 14). In the latter case, even the median is an overestimate. This implies that estimates of ammonia, dis-

Table 14: Summary statistics for measured N and P fractions (mg/L) in the upper watershed.

Nutrient	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
NH ₄	561	0.42	08/07/2000	07/11/2003	0.002	0.009	0.015	0.015	0.68
NO ₃ +NO ₂	561	0.07	08/07/2000	07/11/2003	0.005	0.031	0.085	0.17	1.8
TKN ^a	559	0.01	08/07/2000	07/11/2003	0.057	0.18	0.23	0.29	1.2
o-PO ₄	557	0.59	08/07/2000	07/11/2003	0.001	0.007	0.007	0.01	0.62
DP ^b	546	0.11	08/07/2000	07/11/2003	0.002	0.004	0.006	0.018	0.66
TP	557	0.01	08/07/2000	07/11/2003	0.002	0.011	0.019	0.038	0.69

a. total kjeldahl N

b. dissolved phosphorus

Table 15: Measured and derived quantities describing N and P in the upper watershed.

Quantity	Min	Lower	Median	Upper	Max
DIN (mg/L)	0.004	0.043	0.096	0.193	1.780
TN (mg/L)	0.100	0.237	0.297	0.462	2.210
DIP (mg/L)	0.000	0.004	0.004	0.010	0.625
TP (mg/L)	0.002	0.011	0.019	0.038	0.690
NH ₄ :DIN	0.00	0.05	0.12	0.31	0.82
DIN:TN	0.01	0.17	0.32	0.54	0.93
DIP:TP	0.020	0.19	0.31	0.51	1.00 ^a
DIN:DIP	0.90	6.7	15	31	270
TN:TP	1.2	11	16	22	240

a. 12 ratios (out of 537) had impossible values > 1.

solved inorganic N (DIN = NH₄ + NO₃ + NO₂) and dissolved inorganic P (DIP = o-PO₄, approximately) will be subject to considerable uncertainty, especially for some stations where censoring levels can exceed 70% (C10, M10, M20, and T10). For that reason, and also in order not to provide a redundant examination of the processes at work (because the inorganic and total fractions often demonstrate the same phenomena), we focus primarily on TN (here calculated as TN = TKN + NO₃ + NO₂) and TP when discussing N:P ratios. All of these quantities and related ratios are summarized in Table 15. Censored values were replaced by one-half of the corresponding reporting limit for the calculations in this table. Median TN exceeded nutrient reference values by almost a factor of 6 and median TP values exceeded reference values by a factor of 3. These measurements indicate significant N and P enrichment in the upper watershed compared with values for pristine environments

in this subcoregion. A median of one-third of the total is in inorganic form, in the case of both N and P. Only about 10% of the inorganic N is from ammonia, the rest from nitrate + nitrite. Nitrate + nitrite are always below the primary standards for drinking water and should not pose any health problem in these surface waters.

Ammonia toxicity for aquatic life depends on pH, temperature, and life stage, as well as on the concentration of ammonia itself. We calculated the aquatic life acute and chronic criteria (USEPA 2002a) for each combination of pH and temperature, and compared with measured ammonia levels. We used the more demanding criteria that apply when salmonids and fish early life stages are present. No measurements exceeded the acute or chronic toxicity levels. The stations below wastewater effluent, M30 and M50, approached closest to these levels in late fall and winter. The pH was high at these times (about 8.5-9.5), elevating the fraction present as unionized ammonia, and the temperature was low (1-6 °C), inhibiting consumption of ammonia by bacteria and algae. Still, levels remained below about 25% of the acute criterion and 44% of the chronic criterion. Recall that these are the maximum *observed* levels based on sparse measurements; the true maxima are probably much higher and could exceed criteria.

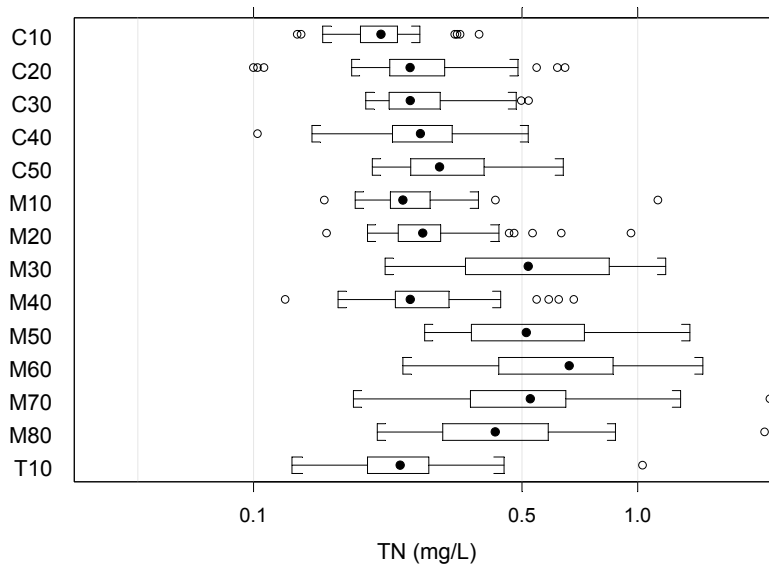


Figure 20: Standard boxplots of total nitrogen distributions at each station in the upper watershed. The nutrient reference condition of 0.04 for this subcoregion is located at the y-axis.

TN is lowest at C10, M10, and T10, although values at all stations are enriched to at least twice reference conditions (Figure 20). The level jumps at M30, representing the impact of EPSD effluent, and then declines again due to dilution with canal water in Lake Estes. It jumps again at M50 in response to UTSD effluent, and then

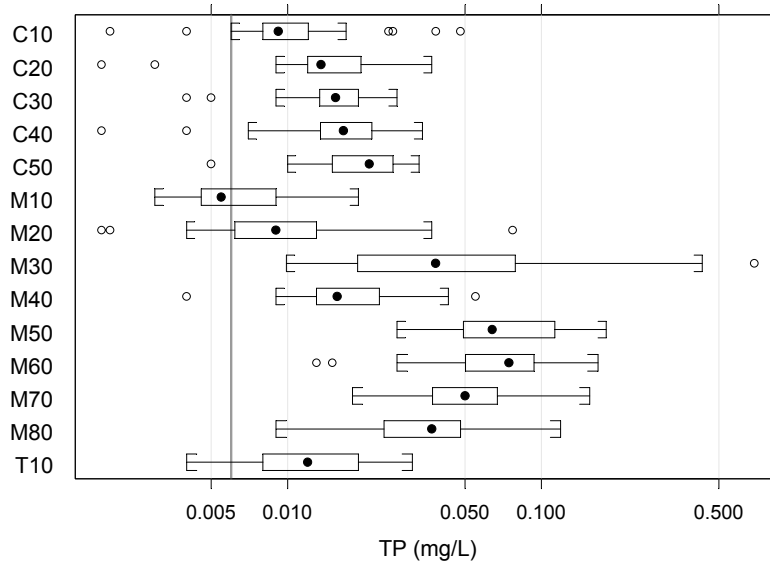


Figure 21: Standard boxplots of total phosphorus distributions at each station in the upper watershed. The heavier vertical line represents the nutrient reference condition of 0.006 for this subcoregion.

again to a smaller extent as it passes through the upper canyon. Finally it decreases as it is diluted first by the North Fork inflows and eventually canal water.

TP shows much the same patterns as for TN, except that the most upstream stations are much closer to background conditions. Levels undergo the largest increases once again after the EPSD and the UTSD effluents. The upper canyon inputs (M60) have a smaller effect than they do for TN, while Estes Park runoff (M20) has a larger effect on TP than TN. As in the case of TN, there is a gradual increase in the canal system on the way to Horsetooth.

The ratio of N to P in phytoplankton cells typically averages about 7.2 on a weight basis (16 on a molar basis), and so this number is often taken as the dividing line between N- and P-limited water bodies, i.e., water with TN:TP < 7.2 should be N-limited. The threshold is not so clear cut in practice, however, and there is a region of ambiguity about this threshold. It is probably best to consider ratios in the range 4-14 (at least) as ambiguous, with N:P < 4 indicating probable N limitation and N:P > 14 indicating probable P limitation. The results of Table 15 therefore suggest cases of both N and P limitation in the upper watershed, although there is clear P limitation in about half the cases and clear N limitation very infrequently. Also, if phosphorus in mineral suspensoids makes a large contribution to TP, which it can do in flowing waters, then the true bioavailable TN:TP is much higher than measured and P limitation is much more frequent than indicated by the data summary. The

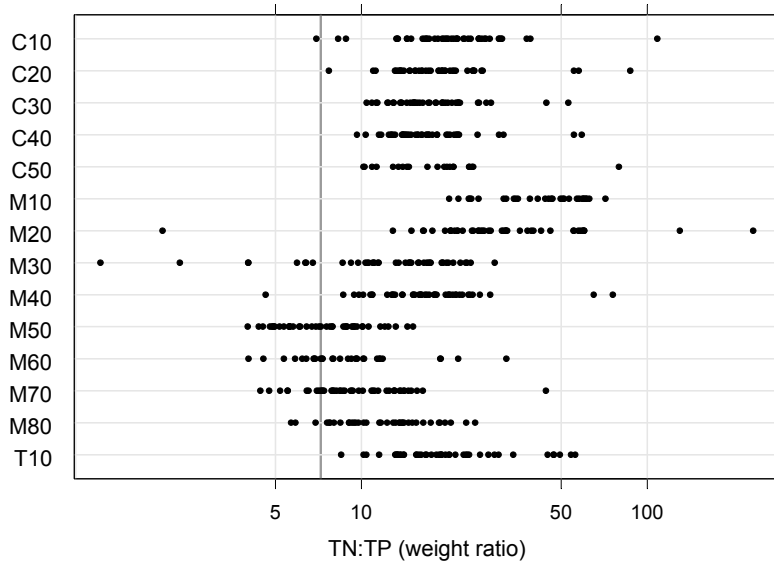


Figure 22: TN:TP ratios for the upper watershed stations. The heavy vertical line is placed at 7.2, the characteristic ratio of N:P in phytoplankton cells.

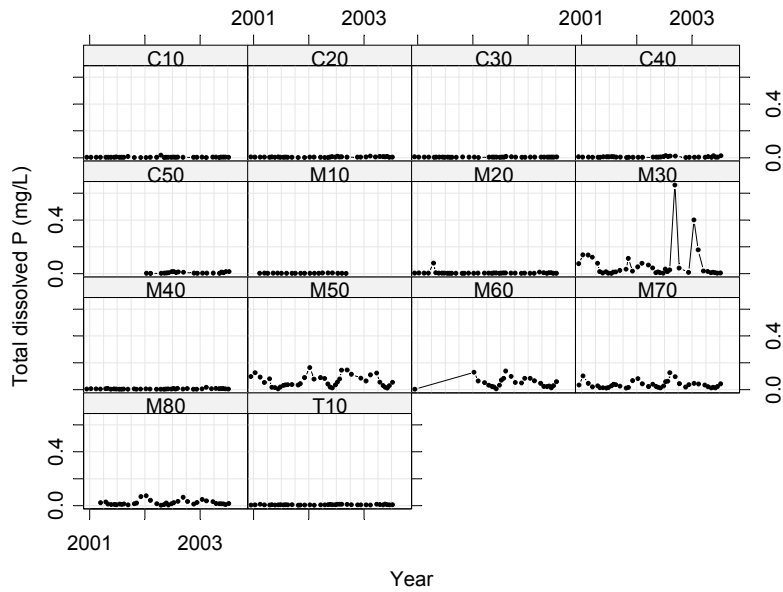


Figure 23: Time series for total dissolved P at each station.

weight of evidence therefore favors P limitation as the common condition in the upper watershed.

Figure 22 shows the TN:TP ratios by station for the entire sampling period. The canal stations are P-limited almost all of the time, as are stations closest to Big Thompson headwaters. The ratio declines as water flows toward Lake Estes, presumably reflecting the lower N:P ratio in Estes Park runoff and EPSSD effluent. The ratio then increases downstream of the lake because of mixing with canal waters, again decreasing at M50 due to the UTSD effluent, after which it slowly drifts back toward P limitation as the waters flow downstream. The wastewater effluent is apparently the main force driving the watershed from clear P limitation into an ambiguous zone. Nonetheless, it is clear that canal water entering reservoirs in the upper watershed is essentially P-limited, and that water passing out of the canyon downstream to the lower watershed is mostly P-limited. Because of the importance of P, we examine the individual time series more closely. DIP is not so informative because of the very high percentage of censored values, and TP can be ambiguous because it potentially includes P in mineral suspensoids that may not be readily available for biological uptake. As an alternative, we plot the dissolved P data, which include inorganic and organic fractions, both of which are probably bioavailable. The unusually high contributions at M30 and M50 stand out. Although M30 is higher in P, these waters are soon diluted in Lake Estes by canal water. The inputs at M50, however, are still visible at M80 after dilution by canal water. High values occur in both summer and winter, and do not appear to be related to seasonal flow patterns. Rather, these nutrient patterns seem to be driven largely by wastewater effluent.

Although it is the concentration (mass/volume) of a substance that is important for river water quality, it is the loading (mass/time) of the same substance that is important for downstream reservoirs. For that reason, one needs to assess how N and P loading—in addition to concentration—changes at different locations in order to determine whether N and P control at a specific location has significant value. TP loading estimates for the period 4/1/2001–3/31/2003 using both the integration and regression methods are listed in Table 16. The values for C50 and M60 cover a shorter period from the beginning of 2002, and therefore are not exactly comparable with the others. The integration and regression methods show excellent agreement except for station C40, as was the case for turbidity loads (Table 7). These TP loading estimates show a loading increase of 6.7 kg/d (M30 - M10) due to Estes Park runoff and (primarily) wastewater. Therefore, Estes Park runoff and wastewater contribute about 39% of the combined TP loading (C10 + M30) to Lake Estes from the Big Thompson River and C-BT project water. The contribution of the UTSD effluent is even larger, about 10 kg/d (M50 - M40), more than tripling the TP load in the mainstem at this point.

Nitrogen loading estimates are shown in Table 17. In the case of $\text{NO}_3 + \text{NO}_2$, the rating curves had too much scatter to obtain reliable estimates for C10 and C20, and the uncertainty was unusually large for C50 and M40. We therefore estimated loading separately for the two components of TN, namely, TKN and $\text{NO}_3 + \text{NO}_2$. Like

Table 16: Total phosphorus loads (kg/d) for the two-year period 4/1/2001–3/31/2003.

Station	Integration	Regression	Lower	Upper
C10	9.9	10	7.4	13
C20	14	13	11	14
C30	9.6	-	-	-
C40	7.8	3.6	3.0	3.9
C50 ^a	7.5	8.1	6.6	10
M10	0.49	-	-	-
M20	2.3	2.7	1.9	3.6
M30	7.2	-	-	-
M40	3.2	3.5	3.0	4.0
M50	13	-	-	-
M60 ^b	9.2	-	-	-
M70	13	-	-	-
M80	11	-	-	-
T10	0.79	-	-	-

a. Measurements began in 2002

b. Measurements began in 2002, except for one prior sampling event.

TP loading, TKN loading decreases in the canal system downstream of the lake, but the declines for N are much stronger than for P. $\text{NO}_3 + \text{NO}_2$ loading does not decline, but TKN constitutes most of the TN loading in the canals. In the mainstem, there are large increases in TKN loading after Estes Park runoff and EPSD effluent (M30 - M10). Estes Park runoff and EPSD effluent also contribute significant inorganic N loading. Of the 69 kg/d TN loading at M30, 76% is contributed by Estes Park runoff and wastewater. Most of this enters before the wastewater effluent (compare M30 - M20 with M20 - M10). Lake Estes is a sink for the inorganic N but has little effect on TKN (M30 versus M40). The UTSD effluent increases TN loading by 73%, the larger share due to inorganic inputs. TN loading increases another 35% between M50 and M70, almost half of which comes from North Fork inflows and the rest presumably from local inputs in the canyon.

4.4 Trace Elements

Trace elements measured in this program include arsenic, copper, lead, mercury, nickel, and silver. They are important because of toxicity to humans and aquatic life, and they occur naturally and in industrial and municipal wastewaters, urban runoff, mine drainage, and atmospheric deposition. Copper is used as an algicide,

Table 17: Nitrogen loads (kg/d) in the form of total kjeldahl nitrogen (left) and nitrate + nitrate (right) for the two-year period 4/1/2001–3/31/2003. Together these constitute total nitrogen.^a

Station	Integration	Regression	Lower	Upper	Station	Integration	Regression	Lower	Upper
C10	200	170	160	180	C10	21	-	-	-
C20	220	190	170	200	C20	34	-	-	-
C30	130	-	-	-	C30	15	-	-	-
C40	100	47	40	54	C40	13	11	7	15
C50 ^b	94	96	84	110	C50 ^b	12	15	10	26
M10	9.6	-	-	-	M10	7.0			
M20	29	30	25	39	M20	20	20	18	24
M30	46	-	-	-	M30	23	-	-	-
M40	47	45	41	50	M40	7.8	10	7	21
M50	61	-	-	-	M50	34	-	-	-
M60 ^c	41	-	-	-	M60 ^c	35	-	-	-
M70	81	-	-	-	M70	47	-	-	-
M80	80	-	-	-	M80	36	-	-	-
T10	9.4	-	-	-	T10	5.3	-	-	-

a. Values have two significant digits.

b. Measurements began in 2002.

c. Measurements began in 2002, except for one prior sampling event.

which can greatly elevate its concentration in surface waters. Iron and manganese are also measured. Their main impact is on the aesthetic properties of drinking water, and they occur naturally in greater abundance than the others. Iron is also a major concern to breweries because of its toxicity to yeast; brewing processes are sensitive to any significant variation in the iron content of their water supply.

Table 18: Summary of total trace element concentrations (mg/L).

Element	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
silver	59	0.98	06/07/2001	04/01/2002	0.0001	0.0001	0.0001	0.0001	0.0001
arsenic	230	0.17	06/07/2001	05/23/2003	0.0001	0.0002	0.0002	0.0002	0.001
copper	59	0.98	06/07/2001	04/01/2002	0.001	0.002	0.002	0.002	0.0054
iron	59	0.90	06/07/2001	04/01/2002	0.1	0.1	0.1	0.1	0.5
mercury	58	0.98	06/07/2001	03/21/2002	0.0001	0.0001	0.0001	0.0001	0.0001
manganese	59	0.69	06/07/2001	04/01/2002	0.003	0.003	0.003	0.0036	0.020
nickel	59	0.98	06/07/2001	04/01/2002	0.003	0.003	0.003	0.003	0.005
lead	59	0.98	06/07/2001	04/01/2002	0.001	0.001	0.001	0.001	0.001

Table 19: Summary of dissolved trace element measurements.

Element	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
silver	321	0.84	04/16/2001	05/23/2003	0.0001	0.0001	0.0002	0.001	0.001
arsenic	110	0.53	04/16/2001	04/01/2002	0.001	0.001	0.005	0.005	0.005
copper	322	0.12	04/16/2001	05/23/2003	0.0004	0.0008	0.001	0.002	0.0133
iron	324	0.15	04/16/2001	05/23/2003	0.006	0.03	0.06	0.1	0.260 ^a
mercury	321	0.83	04/16/2001	05/23/2003	0	0	0	0.0001	0.0001
manganese	231	0	04/15/2002	05/23/2003	0.0002	0.0019	0.0032	0.006	0.0598
nickel	321	0.14	04/16/2001	05/23/2003	0	0.0002	0.0004	0.005	0.005
lead	321	0.44	04/16/2001	05/23/2003	0	0.0001	0.0001	0.001	0.001

a. one anomalous value of 1.39 at C10 ignored—misplaced decimal point?

Primary standards exist for arsenic (0.01 mg/L), copper (1.3 mg/L), inorganic mercury (0.002 mg/L), and lead (0.015 mg/L). In the case of copper and lead, these standards represent action levels for addressing corrosion problems in the water delivery system. Copper also has a secondary standard of 1.0 mg/L because of the undesirable metallic taste it imparts to water in high concentrations. Secondary standards also exist for iron (0.3 mg/L) and manganese (0.05 mg/L). All of these standards refer to total, as opposed to dissolved, element concentrations. There are also aquatic life criteria for each element except iron and manganese. These latter criteria are set in terms of dissolved concentrations, because the acute toxic effect of heavy metals on fish is due more to the dissolved ionic form than to other complexes. Dissolved metal concentrations are very difficult to measure accurately, however, because of low concentrations and possible contamination during sampling, pretreatment, and storage. As a result, the aquatic life criteria are meant to be applied to total concentrations converted to dissolved concentrations by a factor that depends on the element and—for copper, lead, nickel, and silver—water hardness. For chronic effects due to accumulation in body tissues, the concentrations of organically-complexed, non-ionic forms of these elements can be most important (such as in the case of methylmercury).

Total and dissolved trace element measurements are summarized in Table 18 and Table 19, respectively. The percentage of censored data is very high, especially in the case of total concentrations. Also, because of different methods used, longer time periods, and possible contamination during processing, dissolved measurements are sometimes higher than total measurements. Nonetheless, the information is sufficient to see that several of these elements do not require further attention. Maximum arsenic is less than the primary standard, and much less than the acute and chronic freshwater criteria of 340 and 150 $\mu\text{g/L}$, respectively. Similarly, mercury is less than the primary standard, and the acute and chronic criteria of 1.4 and 0.77 $\mu\text{g/L}$, respectively.

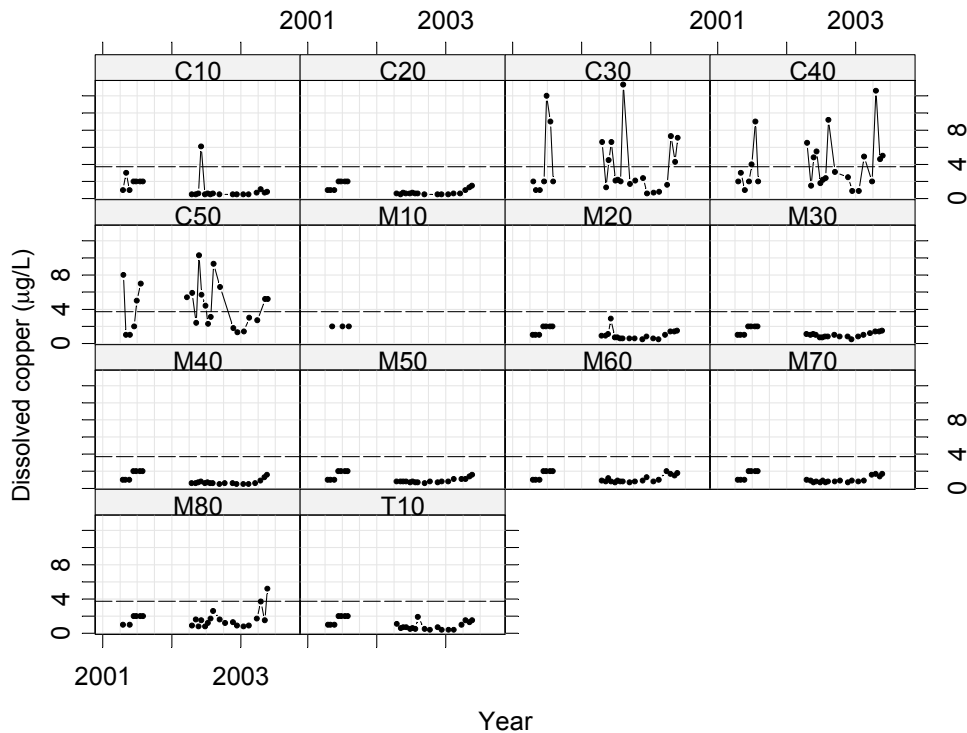


Figure 24: Dissolved copper concentrations. The horizontal dashed line is the acute criterion for aquatic life when hardness = 25 mg/L.

As pointed out above, the criteria for copper, lead, nickel, and silver are hardness-dependent, and so measurements have to be assessed on a sample-by-sample basis according to the corresponding hardness. Calcium and magnesium, the components of hardness, compete with toxic metals for binding sites at the gill surface and reduce their toxicity. So toxicity increases as hardness decreases. There are not sufficient hardness data to go with every trace element sample, so we used the minimum observed hardness of 9.6 mg/L CaCO_3 to derive a conservative estimate of toxicity. The corresponding acute and chronic criteria for copper are 1.51 and 1.21 $\mu\text{g/L}$; for lead, 3.97 and 1.55 $\mu\text{g/L}$; for nickel, 64.2 and 7.13 $\mu\text{g/L}$; and for silver, 0.0671 $\mu\text{g/L}$ (there is no chronic criterion for silver). A comparison of these criteria with the maximum observed values in Table 19 shows that lead and nickel are probably not at toxic levels in the upper watershed, even by conservative estimates. Although the maximum reported silver of 1 $\mu\text{g/L}$ exceeds the acute criterion, the maximum uncensored value above the criterion is only 0.1 $\mu\text{g/L}$, i.e., just slightly above the acute criterion (and it is possible that these were incorrectly registered as uncensored).

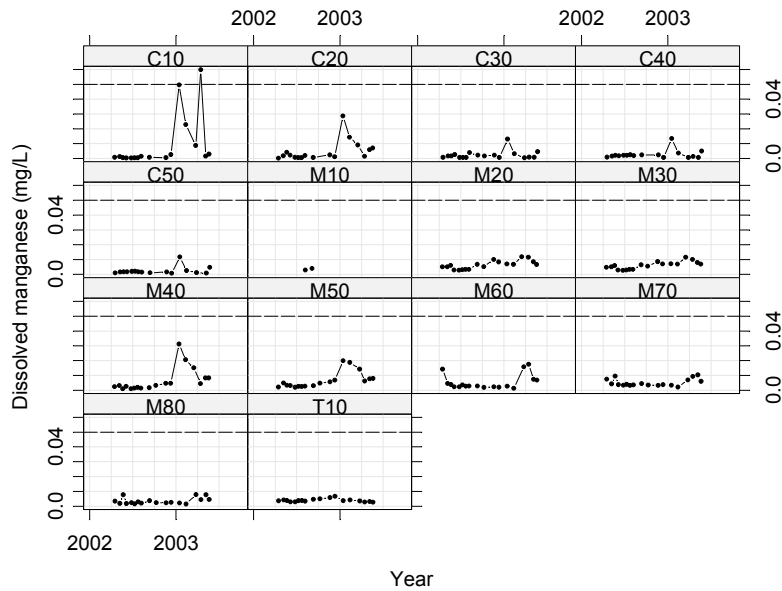


Figure 25: Dissolved manganese concentrations. The horizontal dashed line is the secondary standard for manganese in drinking water.

The maximum copper level, on the other hand, is well above the acute criterion. In fact, even when we use a liberal hardness estimate of 25 mg/L, maximum copper still exceeds the corresponding criteria of 3.72 $\mu\text{g/L}$, respectively. Where are these higher copper concentrations occurring? Plots of the dissolved copper time series for each station show clearly that these maxima are occurring in the canal system during spring and summer, a result of copper algicide applications to control algae blooms. Although the mainstem remains free of high copper levels, the canals eventually transport this copper into drinking water reservoirs where it can also influence water quality.

Although maximum total iron is listed as 0.5 mg/L, the highest uncensored value measured is actually 0.19 (lower than maximum dissolved because of the shorter time period). So iron is well within the secondary standard. The dissolved manganese concentrations, on the other hand, have exceeded the secondary standard of 0.05 mg/L (only a single time, although other values are close to the standard). The undesirable effects of manganese—taste, staining of laundry, discoloration of water—actually start at about 0.15 mg/L, but it is worthwhile to look at the manganese data more closely because of difficulties with manganese in downstream drinking water reservoirs. The dissolved manganese time series are plotted in Figure 25. Highest values occur at C10 during the winter of 2003. These levels then decrease downstream in the canal system. Similarly, in the mainstem, highest values occur at M40 in the winter and then gradually decrease downstream. The high values at C10 probably originated upstream in Grand Lake, when low-oxygen conditions during

winter favor the conversion of manganese in bottom sediments to a more soluble, reduced form. The manganese concentration then increases in the overlying water, where it can be captured by outflows and transported downstream. As it flows downstream under oxygen conditions close to saturation, it is oxidized back to a less soluble form and precipitates to the channel bottom. The increase at M40 could be due simply to the canal inputs into Lake Estes, or there could be further contributions from the lake itself if it were to become anoxic in winter.

Because Horsetooth Reservoir has occasionally experienced excessive manganese concentrations, it is of interest to estimate the load into the reservoir. For the period of record, 4/15/2002–5/23/2003, the average load of dissolved manganese at C50 was 0.75 kg/d. In comparison, each 0.001 mg/L increment in average concentration in the reservoir is equivalent to a whole-reservoir content of 2.1 kg. When reservoir concentrations reach their peak in fall, and concentrations near Soldier Canyon Dam can exceed 0.050 mg/L, the average reservoir concentration is probably order-of-magnitude 0.010 mg/L, equivalent to a whole-reservoir content of about 21 kg. In other words, the manganese load is very large compared to typical whole-reservoir manganese content. Although the immediate source of the dissolved manganese is bottom sediments, the constant high load may provide a surficial sediment layer high in manganese that becomes readily available under anoxic conditions.

4.5 Organic Compounds

4.5.1 TOC

Table 20: Total organic carbon concentrations (mg/L) at stations of the upper watershed.

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	24	0	04/17/2001	05/20/2003	2.0	3.0	3.0	3.3	4.0
C20	24	0	04/16/2001	05/19/2003	2.5	3.0	3.0	3.3	8.0
C30	25	0	04/19/2001	05/23/2003	2.0	3.0	3.1	3.4	7.5
C40	24	0	04/19/2001	05/23/2003	2.0	3.0	3.1	3.6	8.1
C50	23	0	04/19/2001	05/23/2003	2.5	3.0	3.1	3.7	8.1
M20	25	0	04/16/2001	05/19/2003	1.0	1.5	1.9	3.0	8.6
M30	25	0	04/16/2001	05/19/2003	1.5	2.0	2.2	3.0	9.2
M40	25	0	04/16/2001	05/19/2003	2.6	3.0	3.0	3.4	8.5
M50	25	0	04/16/2001	05/20/2003	2.8	3.0	3.3	4.0	8.5
M60	25	0	04/17/2001	05/20/2003	2.6	3.0	3.4	3.8	9.2
M70	26	0	04/17/2001	05/21/2003	2.0	2.9	3.2	3.6	9.1
M80	25	0	04/17/2001	05/21/2003	2.0	3.0	3.1	3.3	8.2
T10	25	0	04/17/2001	05/20/2003	1.3	1.7	2.0	3.0	8.4

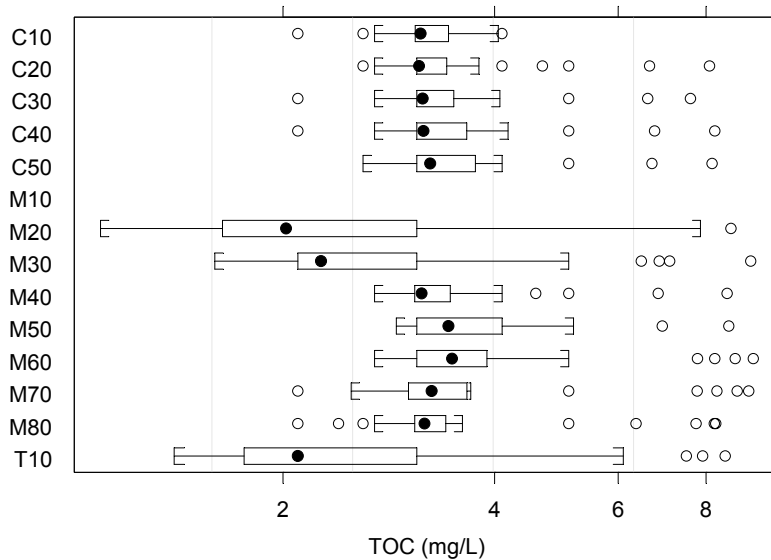


Figure 26: TOC distributions at each station in the upper watershed.

Total organic carbon (TOC) refers to the sum of all forms of dissolved and particulate carbon. The components of TOC play many important roles: reacting with and modifying trace element concentrations; serving as an energy source for bacteria; and producing taste, color, and odor in drinking water. Some individual organic carbon compounds may be toxic to humans or aquatic life (see below). TOC itself also has health significance because it is correlated with the formation of harmful disinfection by-products (DBPs) such as chloroform that occur after water has been treated with disinfectants such as chlorine. These DBPs have been shown to cause cancer and reproductive effects in lab animals. In order to improve public health protection by improving protection from DBPs, the U.S. EPA has established treatment and monitoring procedures that include TOC. Briefly, if the TOC average exceeds 2 mg/L, then TOC must be reduced before water treatment. The percent reduction depends on the TOC concentration and the alkalinity of source water. For example, for typical conditions in this watershed of 3 mg/L TOC and 25 mg/L alkalinity as CaCO_3 , TOC would need to be reduced by 35% or about 1 mg/L.

TOC measurements are summarized in Table 20. The range of TOC is 1-9.2 mg/L, which is quite typical of surface waters not receiving industrial or municipal waste, and not colored due to natural humic materials. The only stations below the 2 mg/L threshold are the river stations nearest headwaters, namely, M20, M30, and T10.

The TOC boxplot distributions are quite revealing (Figure 26). The median values downstream of Lake Estes are largely determined by C-BT inflow, because the median values at M20, M30, and T10 are so much lower. The C-BT inflow raises median TOC about 50%, from 2 to 3 mg/L, and thereby pushing many samples above the threshold at which TOC reduction is required. On the other hand, the peak values must originate within the Big Thompson watershed, because the peak values at C10 are so much lower. The Big Thompson inflows are therefore responsible for less frequent but much more challenging TOC burdens.

It is of interest to examine the higher values in more detail because of the potential treatment burden they represent. The main feature of the TOC time series is the peak in spring of 2001 and 2003 (Figure 27). The peak is quite narrow and it is possible that the gap in sampling in 2002 simply missed the peak that year, i.e., high spring values may occur every year. Note that the C10 peaks are quite small and canal stations do not show large peaks until downstream of Lake Estes. Also, the headwater stations—despite having the lowest values at times—have the largest peaks. These clues suggest that the TOC peaks are arising in the mainstem upstream of Estes Park. Given their anomalous values and the impact that they have on annual averages for downstream stations, it would be worthwhile to identify their source.

Various organic compounds strongly absorb ultraviolet radiation, and a correlation therefore exists between the measurement of UV absorption at 254 nm (UV254) and measurement of TOC. The measurement of UV254 offers certain advantages such as ease and low expense, and it has sometimes been proposed as an inexpensive surro-

gate for TOC. UV254 was measured during only two sampling events in the spring of 2001, and so the data are few. The UV254 data for the upper watershed are plotted against corresponding TOC values in Figure 28. Although the relationship may look reliable at first glance, it is actually determined by the few highest values. Below 4 mg/L TOC, where most of the data occur, the relationship is highly uncertain. The real value of UV254 is in indicating differences in TOC characteristics. For example, the sulfonated aromatic rings in synthetic detergents absorb less UV light than the phenol-substituted rings in naturally-occurring humic materials. This implies that the ratio of UV254 to TOC, sometimes called the *specific ultraviolet absorbance* (SUVA), can sometimes distinguish among different sources of TOC. The SUVA of samples originating from detergent-containing septic systems, for example, should be much lower than for samples influenced only by natural plant and animal matter.

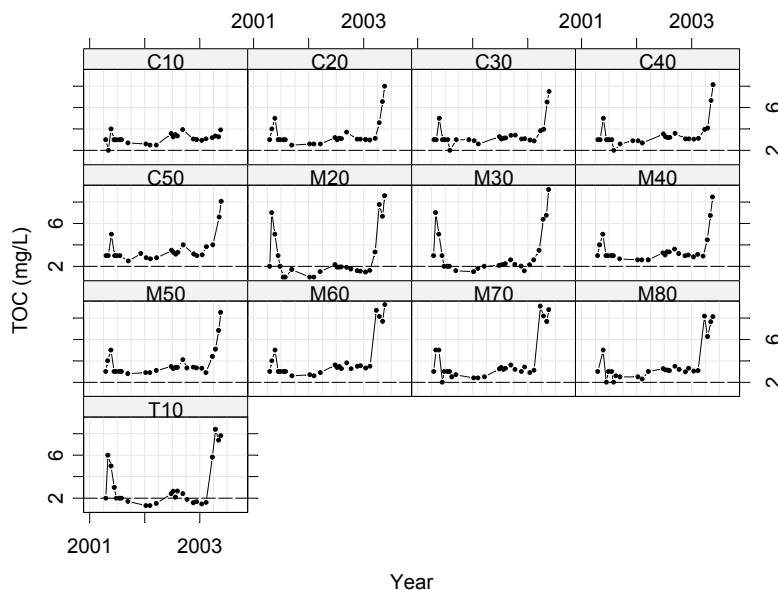


Figure 27: Total organic carbon concentrations at each station of the upper watershed.

The stations nearest the headwaters, where the highest TOC occurs, indeed all have the highest river SUVA (M20, M30, and T10 in Figure 29) and are clearly separated from downstream river stations. As these data were collected during the period of high TOC in spring (Figure 27), this supports the notion that the high TOC levels at these stations originate from natural organic matter and not from anthropogenic sources. The temporal pattern probably represents an annual flush that occurs with spring snow melt. The highest levels come after a few years of drought during which spring flush events have been relatively small. During wetter climate cycles

ral TOC curve follows the turbidity curve closely on the rising limb of the hydrograph, but sometimes it remains at high levels longer than turbidity. After the runoff event TOC levels drop to 2 mg/L or less in the free flowing tributaries.¹

4.5.2 BTEX

The BTEX chemicals (**b**enzene, **t**oluene, **e**thylbenzene, and **x**ylenes) are volatile hydrocarbons commonly found together in crude petroleum and petroleum products such as gasoline. They are also produced on a large scale as bulk chemicals for industrial use as solvents and starting materials for the manufacture of pesticides, plastics, and synthetic fibers. They are considered a major cause of environmental pollution because of widespread leakage from underground petroleum storage tanks and spills at petroleum production wells, refineries, pipelines, and distribution terminals. Some estimate that 35% of the gasoline storage tanks in the U.S. are leaking. The BTEX compounds can cause blood, neurological, kidney, or liver problems. There is evidence from both human and animal studies that benzene is a human carcinogen. Exposure to BTEX in water can occur by ingestion or absorption through the skin, although acute toxicity is more likely from occupational exposure and inhalation.

Table 21: Number of samples in which at least one of the BTEX compounds could be detected.

	Winter	Spring	Summer	Fall
T10	0	0	2	2
M80	0	0	2	2
M70	0	0	1	2
M60	0	0	1	2
M50	0	0	2	2
M40	0	0	2	2
M30	0	0	1	2
M20	0	0	1	1
C50	1	4	3	6
C40	0	0	2	2
C30	1	0	3	1
C20	0	0	2	1
C10	0	1	2	1

1. Ben Alexander, personal communication, 29 October 2003, based largely on experience with the Cache La Poudre watershed.

Primary drinking water standards have been set for benzene, 0.005 mg/L; toluene, 1 mg/L; ethylbenzene, 0.7 mg/L; and total xylenes, 10 mg/L. In comparison, the maximum observed values in the upper watershed were 0.0042 mg/L benzene, 0.0025 mg/L toluene, 0.0047 mg/L ethylbenzene, and 0.012 mg/L total xylenes. All of these maxima occurred in February 2002 at C30 and probably relate to a single incident of contamination. Except for benzene, these values were far below the primary standards. Although the benzene level was close to the primary standard, this was the only sample where benzene exceeded the detection level of 0.0004 mg/L and so is an isolated case. In all, there are only 57 samples in which at least one of the BTEX compounds could be detected, and always far below the primary standard. The pattern of detection is summarized in Table 21. Most of the incidents occurred in summer and fall, and BTEX was most frequently detected at C50. Because the number of detections at C30 is smaller, the BTEX at C50 is likely due to local sources.

4.5.3 MTBE

Methyl tertiary butyl ether (MTBE) is an oxygenate that makes gasoline burn cleaner, reducing air pollution. Beginning in the early 1990s, the U.S. EPA required some smog-prone metropolitan areas—particularly in California and on the East Coast—to require the sale of gasoline blended with an oxygenate. MTBE quickly became the oil companies' oxygenate of choice. The EPA now lists MTBE as a potential human carcinogen because it has been shown to cause cancer in laboratory animals. The biggest problem with the fuel additive, however, is its extraordinarily foul taste and smell, which can render water supplies undrinkable even when present in minute amounts. In a recent study, the U.S. Geological Survey found widespread occurrence of MTBE in wells. Another oxygenate, ethanol, is now expected to replace MTBE in many parts of the country.

Only two flowing water measurements have been made so far of MTBE in the upper watershed, at T10 and C10 in May and June 2001. Both were below the detection limit of 0.0004 mg/L, as were 27 measurements made in Horsetooth Reservoir about the same time.

4.6 Microorganisms

Total coliform bacteria and *E. coli* bacteria are measured in this program. The coliform group consists of many types, some of which are natural residents of soil, water, wood, and industrial wastes, as opposed to sewage contamination. The presence of large concentrations of total coliforms is therefore not specific to fecal contamination. In contrast, although the presence of *E. coli* does not distinguish between human and other warm-blooded animals as sources, it is generally accepted as an indicator of fecal contamination. Illnesses associated with water contact activities have been shown to be correlated with the level of *E. coli* in the water.

Table 22: Summary of total coliform bacteria (cfu/100 ml).

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	42	0	08/29/2000	07/22/2003	0	0	6	64.5	7250
C20	42	0	08/30/2000	07/21/2003	0	0	28	308	1000
C30	42	0	08/28/2000	07/24/2003	0	0	35	208	4800
C40	42	0	08/28/2000	07/24/2003	0	0	40	268	1330
C50	42	0	08/28/2000	07/25/2003	0	9	94	430	3800
M20	43	0	09/12/2000	07/21/2003	0	30	140	660	2000
M30	46	0	08/29/2000	07/21/2003	0	61	145	602	2880
M40	44	0	08/29/2000	07/21/2003	0	1	30	220	1020
M50	44	0	08/30/2000	07/22/2003	0	8	106	446	2240
M60	43	0	08/30/2000	07/22/2003	0	40	220	715	3280
M70	43	0	09/13/2000	07/23/2003	0	65	255	628	5500
M80	38	0	03/13/2001	07/23/2003	0	70	265	986	2100
T10	42	0	09/13/2000	07/22/2003	0	28	145	778	2800

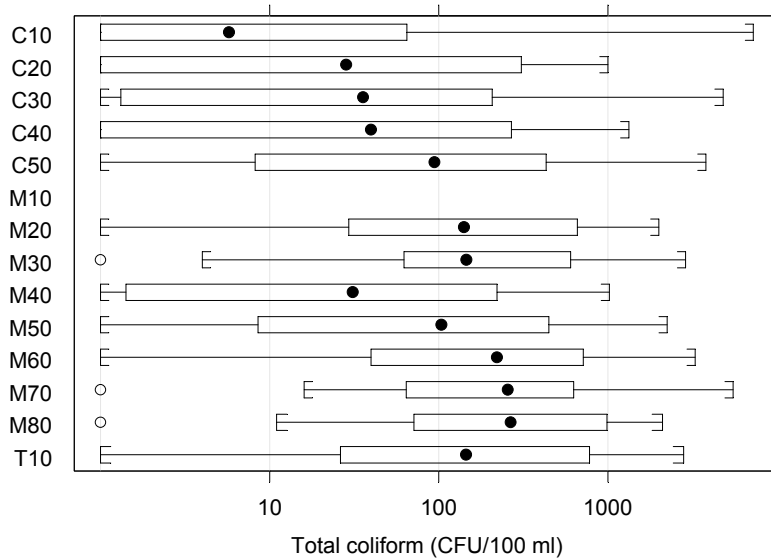


Figure 30: Total coliform distributions at stations in the upper watershed.

The primary drinking water standards for microorganisms apply to water after treatment and disinfection, which usually eliminates almost all bacteria, and therefore are not useful for comparison with natural levels of bacteria. It is not uncommon for surface waters with little human impact to have coliform concentrations of several

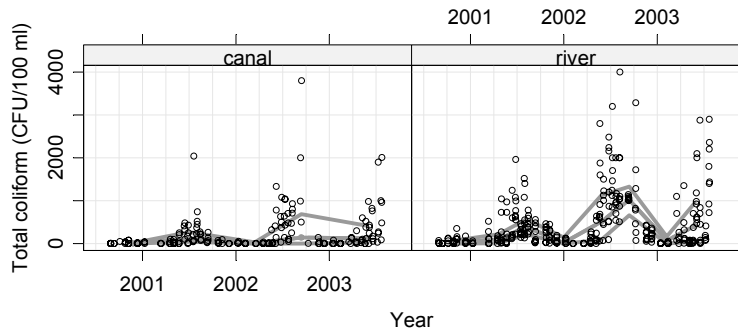


Figure 31: Total coliform measurements combined for all canal and all river stations, respectively. Lines represent lower, median, and upper quartiles of the data.

thousand colony forming units (cfu) per 100 ml, although the remotest mountain areas are usually below 100 cfu/100 ml. The main purpose of measurement on raw water is to identify any extreme values, which can help pinpoint dangerous sources of fecal contamination. For a given source of contamination, levels of these indicator bacteria will decrease with time and distance.

Table 23: Summary statistics for *E. coli* (cfu/100 ml).

Station	Num	Censor	Start	End	Min	Lower	Median	Upper	Max
C10	43	0	08/29/2000	07/22/2003	0	0	0	0	270
C20	42	0	08/30/2000	07/21/2003	0	0	0	10	100
C30	42	0	08/28/2000	07/24/2003	0	0	0	10	1900
C40	42	0	08/28/2000	07/24/2003	0	0	0	8	80
C50	42	0	08/28/2000	07/25/2003	0	0	0	3	210
M20	45	0	08/29/2000	07/21/2003	0	0	30	72	620
M30	46	0	08/29/2000	07/21/2003	0	0	22	88	500
M40	45	0	08/29/2000	07/21/2003	0	0	0	10	140
M50	45	0	08/30/2000	07/22/2003	0	0	0	17	130
M60	44	0	08/30/2000	07/22/2003	0	0	0	10	105
M70	44	0	08/31/2000	07/23/2003	0	0	0	30	170
M80	38	0	03/13/2001	07/23/2003	0	0	8	59	190
T10	44	0	08/31/2000	07/22/2003	0	0	10	32	620

Total coliform data are summarized in Table 22. Although the maximum value at C10 is over 7000 cfu/100 ml, most measurements are typical for surface waters with minor anthropogenic impact. Despite the high value, C10 has the lowest median of all stations (Figure 30). Total coliform tends to increase downstream, both in the

canal system and in the mainstem below Lake Estes. The jump at M50 probably represents the influence of UTSD effluent. Total coliform tends to be highest in warm summer weather, as illustrated in Figure 31, which also makes clear the generally higher values in the river compared with the canals.

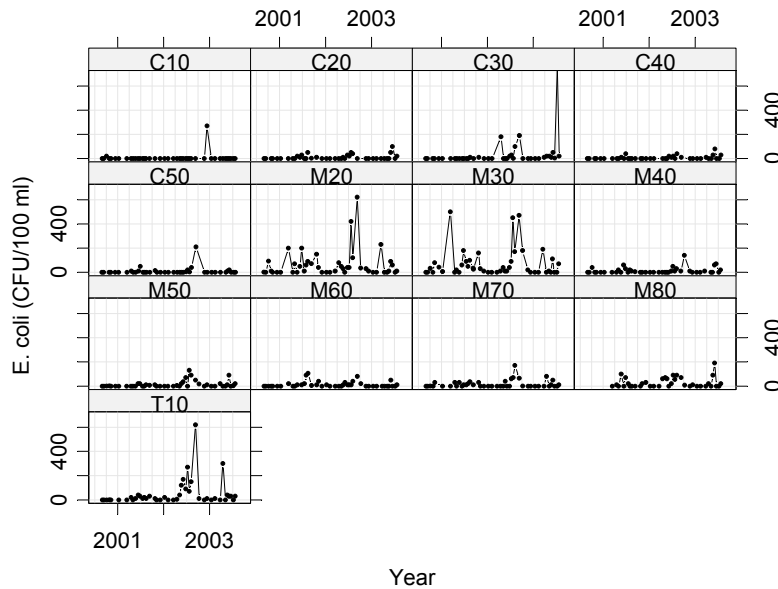


Figure 32: *E. coli* measurements at stations of the upper watershed. The high value of 1900 at C30 is off-scale.

As for total coliforms, *E. coli* data show no evidence of gross contamination in the upper watershed, although there is evidence for low-level fecal contamination. Depending on the season and type of recreational activity, Colorado *E. coli* criteria range from 126 to 630 cfu/100 ml, calculated as the geometric mean (USEPA 2002b). The USEPA's recommended 1986 freshwater quality criteria for bacteria specified a single-sample maximum allowable *E. coli* density of 235 to 576 cfu/100 ml, again depending on the type of water contact (swimming, fishing, etc.). M20 and T10 at times exceeded even the highest criterion value, and 9 of 13 stations exceeded the lowest criterion value (Table 23). M20 and M30 generally have the highest levels (Figure 32). Although one would have expected these two to stand out because of Estes Park runoff and wastewater, a similar pattern and magnitude can be observed at T10. It is also interesting to note the absence of a jump in *E. coli* at M50, despite inflows of UTSD effluent. The source, therefore, is probably above the monitored watershed. In the case of T10, possible sources include a pasture with some cattle in the upper watershed and individual septic disposal systems from the few scattered homes and one very small community in that sub-watershed. M20 has a huge elk population upstream, as well as two livery stables, quite a few homes and

residential developments, and some Park-associated facilities like the visitor center, although many of the human sources may be sewerred. The very high value at C30 is anomalous and appears to be an isolated case.

5 Concluding Remarks

Careful recording and management of data is essential to a monitoring program, because it leads to both cost-effective and accurate data analysis. When several monitoring entities are contributing data to a single database, there are problems arising from inconsistent designations for methods, units, and other features of the data. In addition, even when a single entity is collecting data, data entry errors are always a problem. In this study, we encountered examples of both problems, which necessitated much initial data processing activity that could be avoided in future. These problems always occur in the early stages of monitoring programs, but they do not disappear without a conscious effort. Even a single word spelled incorrectly can cause problems.

Accordingly, we recommend the implementation of a single data entry and verification system for all data input. Such an interface would require choosing analyte names, units, methods, and codes for censored values and other special cases from predefined lists. Even remarks or comments should be selected from a predefined coded list. Such restrictions built into a data entry interface will eliminate inconsistencies among monitoring entities. In addition, values should be checked automatically on entry for consistency with the plausible range for the corresponding water quality variable. We came across several cases where the value was implausible and seemed to arise because of a misplaced decimal point. Restrictions on the ranges of values will decrease these kinds of input errors.

In the longer term there will be a need for a database management system. There are many choices available and the entire field is changing quickly, such as with the implementation of XML for managing data. It is all too easy to waste time and resources on database management, either by over- or underestimating the needs. Although the current amount and complexity of data does not require much more than the existing text files, it would be worthwhile to begin considering this issue. A competent graduate student in computer science with good professional guidance should suffice.

The comparison of loading estimates using both the regression and the integration method shows that the latter method should not be used when flows are highly variable. There is no substitute for continuous discharge estimates when flows are highly variable, and any loading estimates made under those conditions cannot be trusted. In the context of the BTWF monitoring program, the integration method cannot be used reliably for canal stations. Fortunately, continuous discharge data are available for most of these stations. Although the integration method appears to give reliable results for river stations, direct comparison of methods was possible only for M20 and M40.

Table 24: General summary of water quality conditions in the upper Big Thompson watershed. When exceedances are given, their significance can be found in the corresponding section of this report.

Variable	Remark
turbidity	8% exceed 5 NTU, the maximum allowed in unfiltered drinking water
TDS	typical of unpolluted watershed
conductivity	typical of unpolluted watershed
pH	5% exceed 8.5, the maximum recommended level for drinking water
alkalinity	low to moderate
DO	3% are less than 90% saturation, the recommended criterion for aquatic life at high altitudes
hardness	low
major ions	typical of pristine rivers, except for elevated sodium from road salt
nitrogen	significant enrichment compared with background conditions; ammonia high with respect to aquatic life criteria, but not in violation, near wastewater effluent
phosphorus	significant enrichment compared with background conditions
trace elements	silver, arsenic, iron, mercury, nickel, and lead low or undetectable
copper	10% (almost all in canals) exceed 0.0037 mg/L, an acute toxicity criterion for aquatic life
manganese	one sample exceeded 0.050 mg/L, the maximum recommended for drinking water
TOC	86% exceeded 2 mg/L, a level requiring reduction in treatment systems
BTEX	low or undetected, except isolated incident in which benzene approached standard
MTBE	undetected, but few data
total coliform	mostly typical of water with small anthropogenic impact
<i>E. coli</i>	9 of 13 stations occasionally exceeded the strictest water quality criteria for water contact activities

A brief summary of the situation for all monitored variables is contained in Table 24. Values exceeding water quality criteria occurred for turbidity, pH, copper, (rarely) manganese, TOC, and *E. coli*. In addition, DO can sometimes be deficient above Lake Estes in winter; phosphorus and especially nitrogen are both well above background conditions for this ecoregion; and benzene approached the primary drinking water standard on one occasion. Finally, ammonia is high near wastewater effluent and, given the frequency of measurement, could easily exceed criteria at times.

The TN:TP nutrient ratios indicate that Big Thompson headwaters are phosphorus-limited. C-BT water also appears to be primarily phosphorus-limited, although less

so. The impact of wastewater effluent from both the EPSD and UTSD is to add a lower ratio of TN:TP and push the system toward nitrogen limitation, but downstream of each effluent the ratios drift back toward phosphorus limitation. This implies that controlling phosphorus should be the primary focus of any nutrient control strategy.

The TP loading estimates indicate that the EPSD and UTSD effluents have strong effects on the mass transport of phosphorus downstream, and Estes Park runoff also plays a significant, although secondary, role. Assuming that the canal and river deliver most of the TP load (as opposed to atmospheric deposition and nonpoint sources to the system), Estes Park runoff and wastewater account for about 40% of the TP entering Lake Estes and therefore continuing on into the canal and mainstem downstream of the lake. While canal water loses some of its load on its way to the Hansen Feeder Canal, the mainstem load is increased 300% by UTSD effluent and remains elevated in transit to the Dille Tunnel Diversion and beyond. The load in the mainstem is about 3.6 times the load in the Hansen Feeder Canal near the point where they mix. This implies that decreasing TP load from the UTSD effluent is probably the single, most cost-effective way to decrease TP loads exiting the canyon. Moreover, decreasing TP load from the EPSD effluent (and secondarily from Estes Park runoff) is probably the most direct way—from within the Big Thompson Watershed—to decrease TP concentrations in Lake Estes and TP loads carried by the canal system up to the Hansen Feeder Canal. For the Feeder Canal itself and for the subsequent load into Horsetooth Reservoir, the relative importance of UTSD and EPSD will be determined by the extent to which Dille Diversion water dilutes canal water. This will require reliable discharge estimates at C30, which were not available for this report. Phosphate from sewage can be controlled in a number of ways in wastewater treatment works. Secondary treatment may remove about 30-40% of phosphate present. However, more stringent control is provided by tertiary treatment, either biological (70-85% removal depending on conditions), chemical (up to 95% removal), or some combination of the two. The European Community experience in phosphate removal and recovery is well-documented and instructive (IEEP 1999).

The TN loading behaves qualitatively like the TP loading, but there are some notable differences. Estes Park runoff and wastewater contribute only about 20% of the TN to Lake Estes, and UTSD effluent increases the mainstem load about 70%. As a result, a given percent decrease in TN and TP from wastewater effluent has a smaller impact on TN than on TP load. Although in principle one can limit phytoplankton growth by controlling either TN or TP, pushing the system toward nitrogen limitation by eliminating much more of the nitrogen than the phosphorus load carries the risk of favoring cyanobacteria (“blue-green algae”) growth. Many of these organisms can fix nitrogen from the atmosphere, which means they are at an advantage in nitrogen-limited waters. They are especially undesirable because some species carry toxins that can affect public health, and many are filamentous and

gelatinous and can interfere with the water treatment process, water transport, and aquatic communities.

The TOC data point to the overwhelming influence of natural sources upstream of the monitoring stations. TOC concentrations reaching the most upstream stations in the watershed increase more than four-fold over background values in the spring. The resulting TOC concentrations of over 8 mg/L (in 2003) remain elevated as the water moves downstream through both the canal system and the mainstem. These levels present a significant treatment burden for downstream drinking water facilities. Moreover, they may be contributing to the DO deficit that develops in these reservoirs, quite apart from their effects on DBP formation (Jassby and Goldman 1999). Nonpoint sources of TOC are often the most significant inputs of THM precursors in drinking water supplies. Their control is challenging, however, as it requires persistent institutional arrangements and cost-effective options for landowners. Nonetheless, it would be desirable to investigate the area upstream of M10 and M20, pinpoint the source, and consider possible remedial options such as diversions, barriers, and riverbank filtration.

The investigation of upstream sources of TOC could be combined with a similar investigation of fecal contamination from this area. The concentrations of *E. coli* are sometimes high above Lake Estes, which means that contact with river water carries a potential health risk.

The use of copper sulfate to control phytoplankton blooms in the canals has led to numerous exceedances of aquatic life criteria. Of course, that is the whole point of these applications—to exceed the tolerance of nuisance, bloom-forming algae. There are some drawbacks, however, in taking this course to control algae, related to the above points regarding cyanobacteria. Copper algicide applications can lyse cells, resulting in the solubilization of any toxins they contain. These toxins—such as the liver toxin microcystin carried by *Microcystis aeruginosa*—are currently candidates for national water quality regulation, and the WHO and certain countries have already established guidelines. Once released from the cells, the toxins are much more difficult to remove during the drinking water treatment process. In view of possible public health effects and the upcoming guidelines, it would be prudent to examine other strategies for coping with these blooms, such as preventing them in the first place with nutrient control. Also, copper algicide applications can actually promote blooms by killing zooplankton and other organisms that consume phytoplankton and prevent their proliferation. Moreover, there is always the risk of spills to the river. As summarized by Cooke and Carlson (1989): “Copper can be highly effective in some cases, but its effects are always temporary, annual costs can be high, and there are major negative impacts through effects on nontarget organisms and through long-term contamination of sediments with this heavy metal. Most, if not all other management and restoration methods for algae control have

less negative environmental impact and provide the possibility of longer term control.”

The increasing turbidity load in the lower canyon is of potential importance to downstream users (Table 7). Turbidity in Horsetooth Reservoir, for example, can reflect the turbidity of inflowing water in spring (Jassby and Goldman 1999). This implies that increases in the lower canyon can affect Horsetooth water quality in spring via the Dille Diversion Tunnel. Note how the (regression) loading estimates appear to increase between C40 and C50 after inputs from the Dille Tunnel. We have not yet determined, though, that the increase in the canyon contributes a significant fraction of the reservoir turbidity. Moreover, the estimates are uncertain at this early stage and many features are barely statistically significant. Finally, we cannot tell from existing data whether increases in the canyon are due to mineral suspended inputs or phytoplankton growth (or both). Understanding turbidity sources is an essential part of this program, however, and it would be useful to include estimates of phytoplankton biomass (as chlorophyll *a* concentration) in the future to sort out the various contributions.

It is difficult to say whether or not the high manganese levels coming in with the C-BT water have practical significance for reservoirs in the Big Thompson watershed. As we have seen, the manganese loading to Horsetooth is high compared to the amount of manganese in the reservoir water column. The reservoir sediments, however, are the proximate source of this manganese, and it remains to be seen whether or not the inflowing manganese actually promotes higher levels of manganese in the raw water intake. Regardless, manganese is a problem only when reservoir waters become anoxic due to the growth and decomposition of phytoplankton. As high levels of phytoplankton and phytoplankton-derived detritus also cause other problems in the water treatment process, it is most efficient to focus on reducing phosphorus and nitrogen loads to these reservoirs.

Overall the monitoring program has succeeded at this early stage in illustrating the general water quality of the upper watershed. This picture will serve as a reference against which to compare short- and longer-term changes in the coming years. Although average water quality conditions in the upper watershed show only slight anthropogenic impact for most variables, there are frequent and significant excursions above existing human and aquatic life criteria for some of these variables. Nutrients, TOC, copper, turbidity, and *E. coli* currently deserve the most consideration.

6 Acknowledgements

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7 References

- [BTWF] Big Thompson Watershed Forum. 1999. Big Thompson Watershed Monitoring Program, Preliminary Design. Big Thompson Watershed Forum, Loveland, CO.
- Cooke, G. D., and R. E. Carlson. 1989. Reservoir management for water quality and THM precursor control. AWWA Research Foundation, Denver.
- Crawford, C. G. 1991. Estimation of suspended-sediment rating curves and mean suspended-sediment loads. *Journal of Hydrology* **129**:331-348.
- Duan, N. 1983. Smearing estimate—a nonparametric retransformation method. *Journal of the American Statistical Association* **78**:605-610.
- Harrell Jr., F. E. 2001. Regression modeling strategies: with applications to linear models, logistic regression, and survival analysis. Springer, New York.
- [IEEP] Institute for European Environmental Policy. 1999. Implementation of the 1991 EU urban waste water treatment directive and its role in reducing phosphate discharges. Centre Europeen d'Etudes des Polyphosphates, Brussels.
- Ihaka, R., and R. Gentleman. 1996. R: a language for data analysis and graphics. *Journal of Computational and Graphical Statistics* **5**:299-314.
- Insightful Corporation. 2001. S-PLUS 6 for Windows programmer's guide. Insightful Corp., Seattle, WA.
- Jassby, A. D., and C. R. Goldman. 1999. Horsetooth and Carter Lake reservoirs: water quality comparisons. City of Fort Collins Water Utility, Fort Collins, CO.
- Meybeck, M., and R. Helmer. 1989. The quality of rivers: from pristine stage to global pollution. *Paleogeography, paleoclimatology, and paleoecology* **75**:283-309.
- [USEPA] U.S. Environmental Protection Agency. 1986. Ambient water quality criteria for dissolved oxygen. EPA 440/5-86-003. National Technical Information Service, Springfield, VA.
- [USEPA] U.S. Environmental Protection Agency. 2000. Ambient water quality criteria recommendations: Information supporting the development of state and tribal nutrient criteria for rivers and streams in Nutrient Ecoregion II. EPA 822-B-00-015. National Technical Information Service, Springfield, VA.
- [USEPA] U.S. Environmental Protection Agency. 2002a. National recommended water quality criteria: 2002. EPA-822-R-02-047. National Technical Information Service, Springfield, VA.

[USEPA] U.S. Environmental Protection Agency. 2002b. DRAFT implementation guidance for ambient water quality criteria for bacteria. EPA-823-B-02-003. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

Appendix A Sampling Program

Table A-1: Sampling sites for the BTWF monitoring program, plus additional sites (CF10-CF60) where only discharge is measured.

ID	Site Name	USGS ID	Type
C10	Alva B Adams Tunnel at E Portal nr Estes Pk	9013000	canal
C20	Olympus Tunnel at Lk Estes	6734900	canal
C30	Hansen Canal blw Flatiron Reservoir nr Loveland	402227105134700	canal
C40	Hansen Canal blw Trifurcation nr Loveland	402524105133300	canal
C50	Hansen Canal abv Tunnel No. 5 nr Loveland	403020105114700	canal
C120	Hansen Canal abv Greeley Filtration Plant nr Laporte	403814105111800	canal
M10	Big Thompson abv Estes Pk	402114105350101	mainstem
M20	Big Thompson at Estes Pk	6733000	mainstem
M30	Big Thompson blw Sanitation Outflow abv Lk Estes	402245105302300	mainstem
M40	Big Thompson nr Estes Pk	6735500	mainstem
M50	Big Thompson at Whispering Pines nr Estes Pk	402249105282000	mainstem
M60	Big Thompson abv Nf Big Thompson at Drake	402554105202100	mainstem
M70	Big Thompson abv Dille Tunnel nr Drake	6736700	mainstem
M80	Big Thompson blw Big Thompson Power Plant	402518105131300	mainstem
M90	Big Thompson blw Sulzer Gulch nr Loveland	402533105124300	mainstem
M130	Big Thompson at Loveland	6741510	mainstem
M140	Big Thompson blw Loveland	6741520	mainstem
M150	Big Thompson at I-25	6741530	mainstem
T10	North Fork Big Thompson at Drake	6736000	tributary
CF10	Bypass Pole Hill		canal flow
CF20	Total Dille Tunnel		canal flow
CF30	Wasteway to Big Thompson		canal flow
CF40	Big Thompson Power Plant		canal flow
CF50	Pump		canal flow
CF60	#3 Generator		canal flow

Table A-2: Sampling times for the BTWF monitoring stations considered in this report.

	2000	2001	2002	2003
1	8/7/00	1/8/01	1/7/02	1/7/03
2	8/28/00	2/9/01	2/4/02	2/5/03
3	9/11/00	3/12/01	3/7/02	3/3/03
4	10/3/00	4/4/01	4/1/02	4/4/03
5	10/24/00	4/30/01	5/6/02	5/5/03
6	11/6/00	5/21/01	5/20/02	5/19/03
7	12/11/00	6/7/01	6/3/02	6/2/03
8		6/25/01	6/24/02	6/16/03
9		7/3/01	7/8/02	
10		7/16/01	7/22/02	
11		7/30/01	8/5/02	
12		8/6/01	9/4/02	
13		9/10/01	10/7/02	
14		10/3/01	11/4/02	
15		11/5/01	12/2/02	
16		12/3/01		

Table A-3: Water quality variables and corresponding sampling methods used in the BTWF monitoring program.

Description	Method
Alkalinity, bicarbonate	SM2320B
Alkalinity, carbonate	SM2320B
Alkalinity, hydroxide	SM2320B
Alkalinity, phenolphthalein	SM2320B
Alkalinity, total	SM2320B, TWRI I203085
Arsenic, dissolved	E200.8, TWRI I247792
Arsenic, total	E200.8
Barometric pressure	gage
Benzene	E502.2
Bicarbonate	E310.1, E310.2
Calcium, dissolved	E200.7, TWRI I147287
Carbonate	E310.1, E310.2
Chloride, dissolved	E300.1, TWRI I205785
Copper, dissolved	E200.8, TWRI I247792
Copper, total	E200.8
E.coli	m-ColiBlue24
Ethylbenzene	E502.2
Gage height	gage
Hardness	E200.7
Hardness, calcium	SM2340B
Hardness, magnesium	SM2340B
Hardness, total by calculation	SM2340B
Hydroxide	E310.1
Iron dissolved	E200.7, TWRI I147287
Iron, total	E200.7
Lead dissolved	E200.8, TWRI I247792
Lead, total	E200.8
Magnesium, dissolved	E200.7, TWRI I147287
Manganese, dissolved	E200.8, TWRI I247792
Manganese, total	E200.8
Mercury, dissolved	EPA 1631
Mercury, total	E245.1
MTBE	E502.2

Table A-3: Water quality variables and corresponding sampling methods used in the BTWF monitoring program.

Description	Method
Nickel, dissolved	E200.8, TWRI I247792
Nickel, total	E200.8
Nitrogen, ammonia + organic total	TWRI I451591
Nitrogen, ammonia, dissolved	TWRI I252589, TWRI I252290
Nitrogen, NO ₂ + NO ₃ , dissolved	TWRI I254590, TWRI I254691
Oxygen, dissolved	electrode
pH, laboratory	E150.1, TWRI I258785
Phosphorus, dissolved	E365.1, TWRI I261099
Phosphorus, ortho, dissolved	TWRI I260190, TWRI I260689
Phosphorus, total	E365.1, TWRI I461091
Potassium, dissolved	TWRI I163085, SM3120-ICP
Residue, 180 C	E160.1, TWRI I175085
Silver dissolved	E200.8, TWRI I247792
Silver, total	E200.8
Sodium, dissolved	E200.7, TWRI I147287
Sodium, total	E200.7
Specific conductance	electrode
Specific conductance, laboratory	TWRI I278185
Sulfate, dissolved	E300.1, TWRI I205785
Sulfate, total	E300.1
Temperature, water	electrode
Toluene	E502.2
Total coliform	m-ColiBlue24
Total dissolved solids	E160.1
Total organic carbon	E415.1, SM5310C
Turbidity	E180.1, TWRI I386085
UV254	SM5910B
Xylenes	E502.2

Table A-4: BTWF monitoring program data files used in this report. Water quality data were downloaded on August 27, 2003, and hydrological data were downloaded on July 22, 2003.

Name	Description	Size (KB)
alltodateAugust03.txt	flowing water quality data	2189
alltodateJuly'03-bacti.txt	bacteriological assays	164
alltodateMay'03-btex.txt	BTEX measurements	312
CBTFlowData-BTWFFormat.txt	CBT hydro data in BTWF format	2551

Appendix B Conversion Factors

Multiply numbers in these units	by	this factor	to obtain	numbers in these units
feet	x	0.3048	=	meters
acres	x	4047	=	square meters
square miles	x	2.590	=	square kilometers
acre-feet	x	1233	=	cubic meters
cubic feet second ⁻¹	x	0.02832	=	cubic meters second ⁻¹

Appendix C Glossary of Water Quality Terms

algae: Primitive plants usually living in water and occurring as single cells, filaments, colonies and irregular aggregations. Distinguished from aquatic vascular plants.

censored: Data that are below a lower detection or reporting limit, or above an upper detection or reporting limit, for a particular method.

chlorophyll: A green pigment present in most plants and essential for the process of photosynthesis by which these plants obtain most if not all of their energy. Chlorophyll *a* is one form of chlorophyll that is often assumed to be an approximate index of algal mass.

detritus: Nonliving particulate and dissolved organic matter.

photosynthesis: The set of reactions in plant cells by which solar energy is used to produce organic matter and oxygen from inorganic nutrients, carbon dioxide, and water. Usually measured in terms of primary productivity.

phytoplankton: Microscopic algae that live suspended in a water body, unattached to any substrate.

primary productivity: The rate at which algae and higher plants incorporate inorganic carbon into organic matter. Usually measured on a volumetric (e.g., $\text{mg C m}^{-3} \text{d}^{-1}$) or areal ($\text{mg C m}^{-2} \text{yr}^{-1}$) basis. Primary production is often used to refer separately to the amount of organic carbon produced in a particular time interval (i.e., mg C m^{-3} or mg C m^{-2}).

primary standards: More formally known as the National Primary Drinking Water Regulations (NPDWRs), legally enforceable standards applying to public water systems. Intended to protect public health by limiting contaminants in drinking water.

quartile: In a group of data, the 1st quartile is the value for which 25% of the data are smaller; the 2nd quartile is the value for which 50% of the data are smaller (i.e., the same as the median); and the 3rd quartile is the value for which 75% of the data are smaller. These are equivalent to the 25th, 50th, and 75th percentile.

respiration: Metabolic processes of organisms that consume oxygen and break down organic materials into inorganic nutrients and carbon dioxide.

secondary standards: More formally known as the National Secondary Drinking Water Regulations (NSDWRs), non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects in drinking water. The EPA recommends secondary standards and some states may choose to enforce them.

suspended sediments: Small mineral (mostly clay) particles suspended in waters.

turbidity: Cloudiness of water due to the scattering of light by colloidal and suspended matter.

watershed: Defined here as the entire area (land plus water) that supplies a central collecting water body through drainage or direct precipitation.