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Lagrangian Mass-Flow Investigations of Inorganic Contaminants in Wastewater-Impacted Streams

Larry B. Barber,[*,†] Ronald C. Antweiler,[†] Jennifer L. Flynn,[‡] Steffanie H. Keefe,[†] Dana W. Kolpin,[§] David A. Roth,[†] Douglas J. Schnoebelen,[§,⊥] Howard E. Taylor,[†] and Philip L. Verplanck[∥]

[†]U.S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303, United States

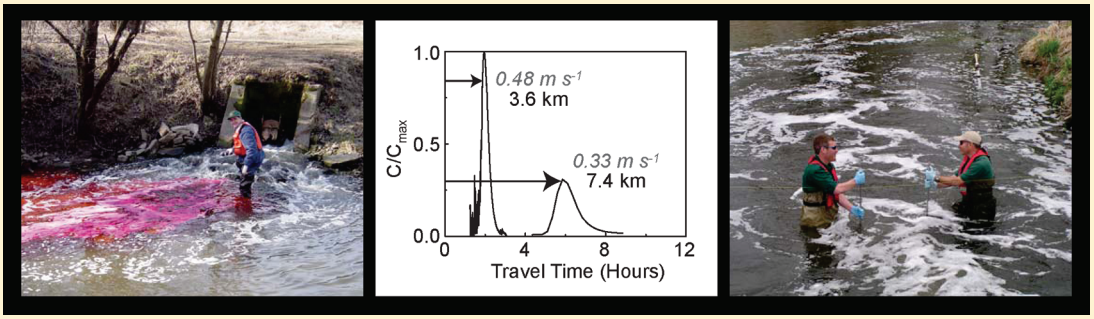
[‡]U.S. Geological Survey, P.O. Box 25046, MS 415, Denver, Colorado 80225, United States

[§]U.S. Geological Survey, 400 S. Clinton, Iowa City, Iowa 52244, United States

[∥]U.S. Geological Survey, P.O. Box 25046, MS 973, Denver, Colorado 80225, United States

S Supporting Information

ABSTRACT:



Understanding the potential effects of increased reliance on wastewater treatment plant (WWTP) effluents to meet municipal, agricultural, and environmental flow requires an understanding of the complex chemical loading characteristics of the WWTPs and the assimilative capacity of receiving waters. Stream ecosystem effects are linked to proportions of WWTP effluent under low-flow conditions as well as the nature of the effluent chemical mixtures. This study quantifies the loading of 58 inorganic constituents (nutrients to rare earth elements) from WWTP discharges relative to upstream landscape-based sources. Stream assimilation capacity was evaluated by Lagrangian sampling, using flow velocities determined from tracer experiments to track the same parcel of water as it moved downstream. Boulder Creek, Colorado and Fourmile Creek, Iowa, representing two different geologic and hydrologic landscapes, were sampled under low-flow conditions in the summer and spring. One-half of the constituents had greater loads from the WWTP effluents than the upstream drainages, and once introduced into the streams, dilution was the predominant assimilation mechanism. Only ammonium and bismuth had significant decreases in mass load downstream from the WWTPs during all samplings. The link between hydrology and water chemistry inherent in Lagrangian sampling allows quantitative assessment of chemical fate across different landscapes.

INTRODUCTION

With increasing stress on water resources due to climate change and population growth, reuse of municipal wastewater treatment plant (WWTP) effluents will play an important role in meeting demands for urban water supply, agricultural needs, and environmental flows. Considerable attention has focused on the occurrence and potential impacts of organic contaminants derived from WWTP sources,[1] but less attention has focused on the complex mixtures of inorganic contaminants in WWTP effluents and receiving waters.[2−4] WWTP effluents can be the primary source for chemical loading of many trace elements to surface water ecosystems and understanding the potential effects of the complex chemical mixtures in WWTP effluents requires consideration of as many constituents as possible because of the diversity of chemical behaviors and biological implications. In contrast to synthetic organic chemicals, which only come from anthropogenic sources, the inorganic chemistry of WWTP effluents is derived from both anthropogenic and geologic sources.[5−7] Much of the research on trace element contamination from WWTP discharges has focused on estuarine environments [8,9] and less is known about the impacts on streams. Likewise, many studies focus on toxic elements such as cadmium, copper, lead, and zinc,[10] but little is known about many of the

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other trace elements that co-occur. Synthetic-organic complexes of naturally occurring trace elements such as gadolinium can be indicators of contamination from WWTP effluents.[11,12] One of the limitations in understanding the potential impact of WWTP discharges is that few studies comprehensively investigate the underlying hydrology and broad suite of constituents (nutrients, major ions, and trace elements) that occur.

Quantitative evaluation of mass flow involves determining discharge and velocity in addition to measuring aqueous concentrations. Two approaches can be used to describe streamflow:[13] Lagrangian, which is fixed with respect to time, and Eulerian, which is fixed with respect to space. Experiments designed to fit Lagrangian or Eulerian constraints require a high degree of logistical coordination.[14,15] Lagrangian sampling, in which a specific parcel of water is tracked as it moves downstream under natural flow conditions, attempts to account for temporal and spatial variations in chemistry and discharge. Eulerian sampling requires constant flow conditions, which typically are not met in WWTP impacted systems because of diurnal fluctuations in flow.

This paper demonstrates the advantages of an integrated Lagrangian approach for quantifying the relative chemical loading from WWTP discharges with respect to landscape-based sources. Comprehensive chemical analysis to characterize the WWTPs and receiving streams combined with flow-based (velocity and discharge) Lagrangian sampling provides a direct link between hydrological and chemical processes. The development of contemporaneous data sets allows quantitative comparison of water quantity, water quality, and physical transport within and between streams, thus allowing determination of stream assimilative capacity. The Lagrangian approach was used to assess the stream assimilative capacity of 58 inorganic constituents with widely ranging chemical characteristics in two WWTP-impacted streams under differing flow conditions. By investigating the transition from upstream background conditions to impacted conditions below the first major WWTP discharge, relative contaminant loading from the WWTPs was evaluated with respect to landscape-based sources.

SITE DESCRIPTION

Boulder Creek, Colorado and Fourmile Creek, Iowa were selected to evaluate the occurrence and transport of WWTP-derived inorganic constituents and compare the effects of landscape and hydrology on stream chemistry. Although Boulder Creek and Fourmile Creek have different flow conditions and underlying geology, they are similar in that the upstream sites do not receive any major WWTP discharges and flow at the downstream sites consists of a large fraction of WWTP effluent.

The Boulder Creek watershed transects hydrological, geochemical, and land-use gradients from snowmelt to wastewater-impacted conditions and has a semiarid climate with an average precipitation of 55 cm yr^{-1}.[3,16] The upper watershed is underlain by Precambrian igneous and metamorphic rocks, and the lower watershed is underlain by Cretaceous marine shale and sandstone with a thin veneer of Quaternary alluvium.[17] The study reach was from 0.1 km upstream from the city of Boulder's WWTP to 7.4 km downstream from the WWTP outfall. The basin area upstream from the WWTP is 790 km^2 and population density was 220 people/km^2. Water supply for Boulder originated from Boulder Creek in the upper watershed underwent drinking water treatment prior to municipal use and discharge to the sewer system and provided an average annual WWTP inflow of 0.74 m^3 s^{-1}. The Boulder WWTP used primary clarification, trickling filter, solids contact, final clarification, chlorination, and dechlorination processes. There are three stream diversions and one tributary in the study reach.

The Fourmile Creek watershed has a temperate climate with 85 cm yr^{-1} precipitation.[18] The geology consists of Pennsylvanian marine sediments overlain by a thick sequence (55 m) of Pleistocene glacial deposits.[19] The study reach was from 0.1 km upstream from the city of Ankeny's WWTP to 8.4 km downstream from the outfall. The basin area upstream from the WWTP is 160 km^2 and population density was 170 people/km^2. Water supply for Ankeny was derived from groundwater and provided an average annual WWTP inflow of 0.21 m^3 s^{-1}. The Ankeny WWTP used primary clarification, fine bubble aeration, final clarification, and ultraviolet light disinfection processes. There are no tributaries or diversions in the study reach.

METHODS

Time of Travel Studies. Timing of the tracer experiments and Lagrangian samplings was coordinated to attempt to capture low-flow conditions on the falling limb of the hydrograph (August-September 2003) and the rising limb of the hydrograph (March-April 2005) when dilution of WWTP effluent by upstream water was at a minimum. The tracer experiments were conducted prior to the Lagrangian samplings to determine travel times to the downstream sites,[20] which were used to coordinate sampling the same approximate parcel of water as it moved downstream. Tracer experiments were conducted by adding rhodamine WT to the WWTP outfalls and measuring breakthrough curves at the downstream sites.[21] Travel times were estimated using temporal moment analysis.[22]

Water Sampling. Water samples were collected at sites upstream from the WWTPs (U), the WWTP effluents (E), and downstream (D) from the WWTP outfalls. The upstream sites represent the integrated flow and landscape-based chemical loads from the drainage basins, whereas the downstream sites represent combined landscape and WWTP-derived water and chemical loads. The downstream Boulder Creek sites were located 3.6 km (D1) and 7.4 km (D2) from the WWTP. The downstream Fourmile Creek sites were located 2.9 km (D1) and 8.4 km (D2) from the WWTP. Stream discharge was measured using depth-width-velocity methods.[23] Equal-width-integrated composite samples[24] were collected using clean protocols.[25] Replicate subsamples (summer $n = 3$ and spring $n = 4$) for multiple chemical analyses were obtained using a Teflon cone splitter. Water samples were filtered through 0.4-μm Nucleopore membranes. Samples for trace element and cation analysis were acidified with nitric acid and samples for anion and nutrient analysis were chilled.

Chemical Analysis. Nitrogen and phosphorus compounds were analyzed by photometry, major anions were analyzed by ion chromatography, and major cations were analyzed by inductively coupled plasma atomic-emission spectrophotometry at the U.S. Geological Survey (USGS) National Water Quality Laboratory, Denver, Colorado.[26−28] Trace elements were determined by inductively coupled plasma-mass spectrometry at the USGS National Research Program Laboratory, Boulder, Colorado.[29] Quality assurance consisted of field and laboratory blanks, analysis of standard reference samples, and replicate analysis of replicate field samples. Details on analytical methods and quality assurance are presented elsewhere.[21]

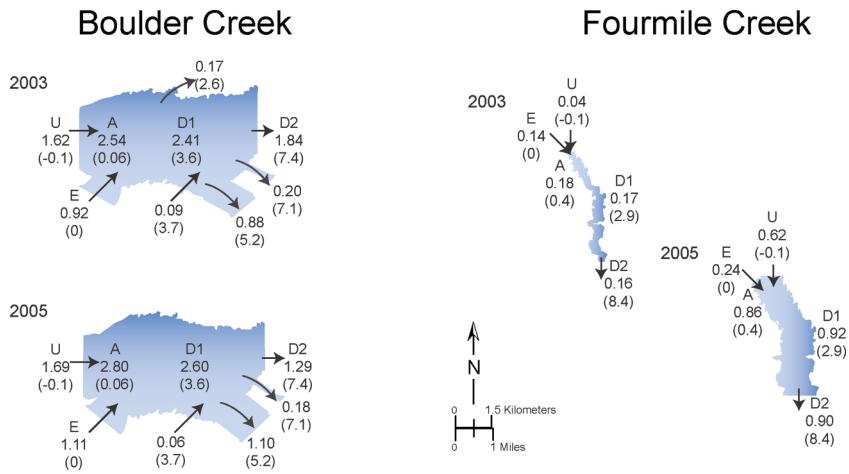

Figure 1. Flow characteristics of the study reaches in Boulder Creek, Colorado and Fourmile Creek, Iowa during the summer 2003 and spring 2005 Lagrangian samplings. [Boulder Creek summer sampling was conducted September 3, 2003 and spring sampling was conducted April 19, 2005; Fourmile Creek summer sampling was conducted August 5, 2003 and spring sampling was conducted March 8, 2005; U = upstream from wastewater treatment plant (WWTP); E = WWTP effluent; D1 and D2 = downstream from WWTP; size of flow diagram is proportional to stream discharge; discharge values in $m^3\ s^{-1}$; values in parentheses are distance from the WWTP in km; arrows show direction of flow (inflows and outflows)].

Hydraulic Analysis. Evaluating in-stream fate of contaminants requires quantitative mass-flow analysis.[7] Boulder Creek and Fourmile Creek had four sampling sites (U, E, D1, and D2) and a calculated mixing zone site (A). All Boulder Creek sites had measured discharges (Q_i ; $m^3\ s^{-1}$) and measured concentrations (C_i; $\mu g\ L^{-1}$ or $mg\ L^{-1}$). In Fourmile Creek, Q_i was measured at U, A, D1, and D2, and C_i was measured at U, E, D1, and D2. The outfall from the Ankeny WWTP cascades over limestone blocks before entering the stream, and Q_E could not be directly measured but rather was estimated by difference between measured discharge at U and A.

Mixing Zone (Site A). Calculated concentration ($C_{calculated}$), calculated discharge (Ω_i), and calculated mass flow (Θ_i; $g\ d^{-1}$ or $kg\ d^{-1}$) at mixing zone site A (located immediately downstream from the confluence of U and E before additional inflow, outflow, or chemical reactions) were used to compared against measured values for C_i, Q_i, and mass flow (M_i). At Boulder Creek, Ω_A and Θ_A were determined as

$$\Omega_A = Q_U + Q_E \tag{1}$$

and

$$\Theta_A = M_U + M_E = C_U Q_U + C_E Q_E \tag{2}$$

At Fourmile Creek, Q_E was not directly measured, therefore

$$\Theta_A = M_U + \Theta_E = C_U Q_U + C_E \Omega_E \tag{3}$$

Discharge was measured at site A so that

$$\Omega_E = Q_A - Q_U \tag{4}$$

and

$$C_{calculated,A} = \frac{\Theta_A}{\Omega_A} \tag{5}$$

Downstream Site 1. At downstream site D1, Ω_{D1} is defined as

$$\Omega_{D1} = \Omega_A + \sum_{i=1}^{n} Q_{in,i} - \sum_{j=1}^{m} Q_{out,j} \tag{6}$$

where $Q_{in,i}$ is inflow at location i, $Q_{out,j}$ is outflow at location j, and n and m are the number of inflows and outflows in the stream reach. Measured and calculated discharges are rarely equal, and a discharge discrepancy parameter (e_i) is introduced to correct Θ_i for variations in discharge along a stream segment

$$e_i = \frac{Q_i}{\Omega_i} \tag{7}$$

Thus, Θ_{D1} is defined as

$$\Theta_{D1} = (C_{calculated,A}\Omega_A + \sum_{i=1}^{n} C_{in,i}Q_{in,i} - \sum_{j=1}^{m} C_{out,j}Q_{out,j})e_{D1} \tag{8}$$

where $C_{in,i}$ is inflow concentration at location i, and $C_{out,j}$ is outflow concentration at location j. For the "conservative" element chloride, a mass flow discrepancy parameter ($\varepsilon_{i,Cl}$) similar to e_i is introduced

$$\varepsilon_{i,Cl} = \frac{M_{i,Cl}}{\Theta_{i,Cl}} \tag{9}$$

where $\varepsilon_{i,Cl}$ measures deviation from ideal chloride mass flow corrected for discharge discrepancies.

Downstream Site 2. At downstream site D2, Ω_{D2} and Θ_{D2} are

$$\Omega_{D2} = Q_{D1} + \sum_{i=1}^{n} Q_{in,i} - \sum_{j=1}^{m} Q_{out,j} \tag{10}$$

and

$$\Theta_{D2} = (C_{D1}Q_{D1} + \sum_{i=1}^{n} C_{in,i}Q_{in,i} - \sum_{j=1}^{m} C_{out,j}Q_{out,j})e_{D2} \tag{11}$$

In-Stream Gains and Losses. Error analysis was applied to assess the significance of mass loss or gain at the downstream sites.[30,31] Q_i was assumed to have an uncertainty of 8% (based on stream conditions and replicate cross-sectional measurements;[25]). C_i uncertainty was determined from analysis of replicate samples.

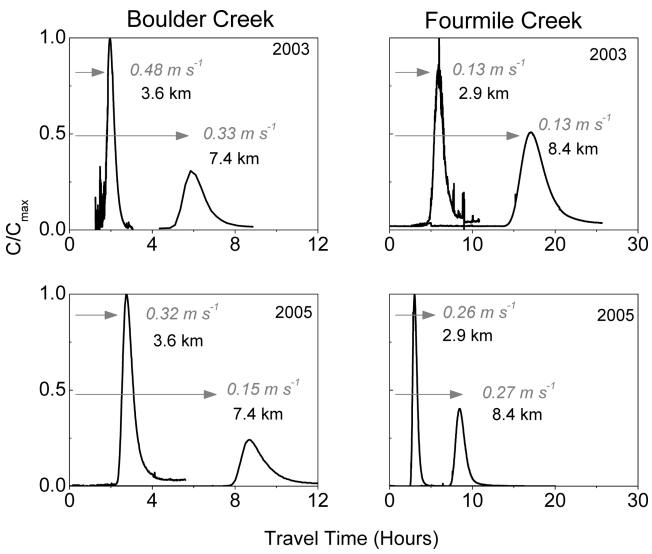

Figure 2. Rhodamine WT tracer experiment breakthrough curves for Boulder Creek, Colorado downstream sites D1 (3.6 km) and D2 (7.4 km), and Fourmile Creek, Iowa downstream sites D1 (2.9 km) and D2 (8.4 km) for summer 2003 and spring 2005 flow conditions. [Boulder Creek summer tracer experiment was conducted August 3, 2003 and the spring experiment was conducted April 16, 2005; Fourmile Creek summer tracer experiment was conducted July 30, 2003 and the spring experiment was conducted March 3, 2005; arrows show streamflow velocities; Boulder Creek hydraulic gradient between E and D1 is 0.0039 and between D1 and D2 is 0.0031; Fourmile Creek hydraulic gradient between E and D1 is 0.0007 and between D1 and D2 is 0.0013].

A value of 5% was assumed for parameters without measured uncertainty. Measurement uncertainty in mass flow at site i (m_i) is defined as

$$m_i = \sqrt{q_i^2 C_i^2 + c_i^2 Q_i^2 + c_i^2 q_i^2} \quad (12)$$

where q_i is uncertainty in Q_i, and c_i is uncertainty in C_i. Uncertainty also can be expressed as a ratio

$$\mu_i = m_i / M_i \quad (13)$$

where μ_i is similar to the relative standard deviation and allows uncertainties to be compared on an equal basis.

It is important to attempt to account for stream physical characteristics such as dispersion and travel time when conducting error analysis. Three measures were used to estimate the effects of stream characteristics: Ω_i/Ω_i (=1), Q_i/Ω_i (=e_i), and M_i/Θ_i (=$\varepsilon_{i,Cl}$). The overall uncertainty (E_i) combines measurement uncertainties with estimates of physical uncertainties and is defined by

$$E_i = \sqrt{\mu_i^2 + \mathrm{var}(1, e_i, \varepsilon_{i,Cl})} \quad (14)$$

where var is variance. The mass flow discrepancy ratio (R_i) is defined as

$$R_i = \frac{M_i/\Theta_i}{(1 + e_i + \varepsilon_{i,Cl})/3} \quad (15)$$

If $|R_i\text{-}1| > 2E_i$, in-stream gain or loss between sites is considered to be significant (similar to standard deviation analysis; [30]).

RESULTS AND DISCUSSION

Hydrology. Measured discharges at the upstream Boulder Creek site (Figure 1) did not differ substantially between the summer 2003 and spring 2005 Lagrangian samplings, whereas the Boulder WWTP discharge was 17% greater during the spring sampling. Sewage inflow is not constant throughout the day and during mid-August, 2005, the Boulder WWTP minimum average daily inflow occurred at approximately 05:00 and the maximum average inflow occurred around 10:00. Hydraulic mixing ratios determined using Q_U and Q_E, indicate that 36% of the flow in Boulder Creek at downstream site A was WWTP effluent during the summer sampling and 40% was effluent during the spring sampling. These results are consistent with reported values of 15−20% of Boulder Creek flow consisting of WWTP effluent during high-flow and 50−65% during low-flow.[16]

Tracer experiments conducted in Boulder Creek (Figure 2) indicate that it took 6.2 h for water to travel from E to D2 (7.4 km) during the summer experiment and 9.3 h during the spring experiment. The decrease in velocity is likely due to flow diversions during the spring, which removed water (Figure 1). Mass flow investigations in engineered streams such as Boulder Creek are complicated by intermittent removal of water (controlled by water rights, growing conditions, and reservoir storage capacity).

Although there were differences in Fourmile Creek discharge and velocity between the summer and spring samplings, values were relatively constant along the study reach within each sampling (Figures 1 and 2). Hydraulic mixing ratios at Fourmile Creek downstream site A indicate that 81% of the flow was WWTP effluent during the summer sampling and 28% was effluent during the spring sampling. Fourmile Creek flow velocities during the summer tracer experiment were considerably lower than the Boulder Creek velocities, whereas during the spring experiment velocities in Fourmile Creek were greater than in the summer and similar to Boulder Creek.

Concentration Trends and Loads. Stream chemistry is controlled by underlying geology, climate, and anthropogenic influences, and response to a WWTP discharge is dependent on the volume and concentrations relative to background stream conditions. In addition to physical mixing and transport, the fate of contaminants introduced into a stream by WWTP effluent is controlled by geochemical processes such as precipitation/dissolution, sorption, and oxidation/reduction reactions which are controlled by solution characteristics such as pH, redox, ionic strength, and organic carbon content.[5] Chloride is a tracer that undergoes limited chemical and biological reactions, and the chloride mixing ratios $[(C_{D1}\text{-}C_U)/(C_E\text{-}C_U)]$ indicate that 30% of the flow in Boulder Creek at site D1 was effluent during the summer sampling and 36% was effluent during the spring sampling (corresponding to 83% and 90% of the site A hydraulic mixing ratios, respectively). Fourmile Creek chloride mixing ratios indicate that 73% of streamflow at site D1 was effluent during the summer sampling and 20% during the spring sampling (90% and 71% of the site A hydraulic mixing ratios). Plotting the concentrations of individual constituents against chloride concentrations (Figure 3) provides a simple mixing model approach (U and E as end members) for comparing results from the two streams. The full data sets for all constituents are presented elsewhere (ref 21, Supporting Information).

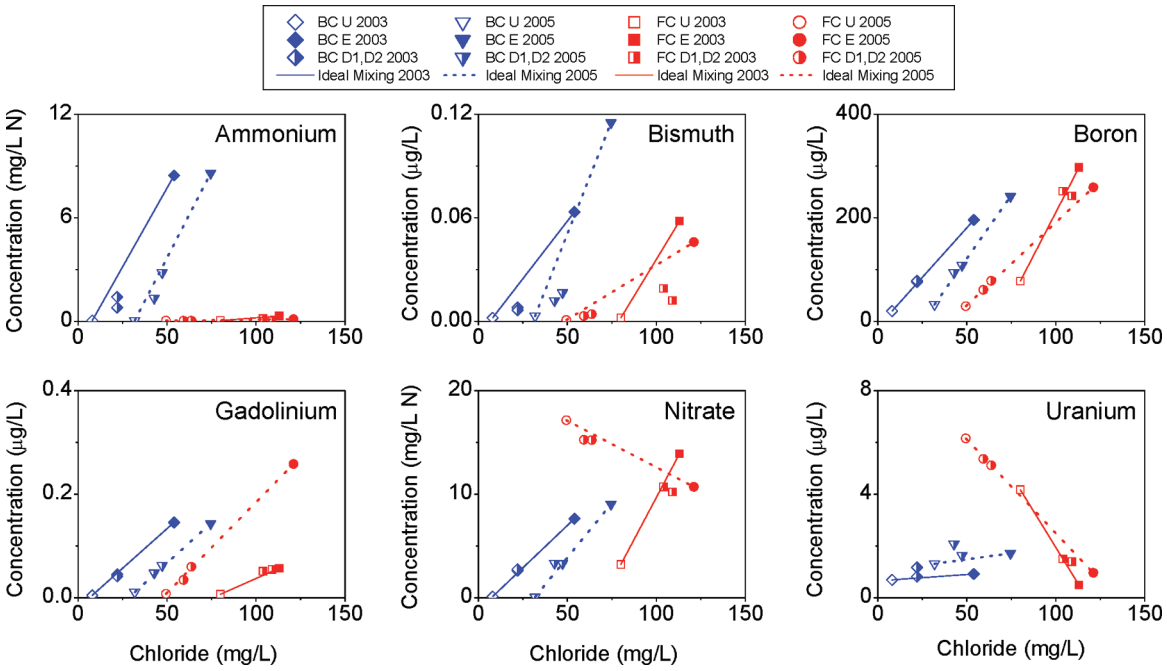

Figure 3. Concentrations of select inorganic constituents plotted against chloride concentrations for the summer 2003 and spring 2005 Lagrangian samplings in Boulder Creek, Colorado (BC) and Fourmile Creek, Iowa (FC). [*U* = upstream from wastewater treatment plant (WWTP); *E* = WWTP effluent; D1 and D2=downstream from WWTP].

There were several distinct geochemical differences between Boulder Creek and Fourmile Creek reflecting the underlying landscape. Fourmile Creek had higher concentrations of uranium (Figure 3), consistent with the water chemistry being influenced by the underlying marine sediments.[5,19] Nutrient status also differed between Boulder Creek and Fourmile Creek (Figure 3) and was influenced by both WWTP and landscape sources. For example, concentrations of ammonium and nitrite (produced during nitrification of ammonium, data not shown) were greater in the Boulder WWTP effluent than in the Ankeny WWTP effluent resulting in higher concentrations at downstream sites in Boulder Creek sites than in Fourmile Creek. Ammonium concentrations in Boulder Creek plot below the mixing lines, suggesting in-stream loss due to biological transformations, whereas nitrite concentrations plot above the mixing lines suggesting in-stream production. Nitrate concentrations were higher in the Ankeny WWTP effluent than in the Boulder effluent, suggesting more nitrifying conditions. During the spring sampling, the nitrate concentration at the upstream Fourmile Creek site was higher than in the Ankeny WWTP effluent, suggesting inputs from the agricultural landscape.[32]

Many of the inorganic constituents investigated in this study have landscape-derived sources other than WWTP discharges, and it is important to consider the relative natural and anthropogenic mass fluxes. Although environmental relationships were complex, 29 of the 58 constituents typically had greater concentrations and loads in the WWTP effluents than in the upstream water during all samplings (Table 1). Ten constituents typically had greater concentrations at the upstream sites than in the WWTP effluents during all samplings. Nineteen constituents had less clear relationships between the upstream and WWTP effluent sites with equivalent upstream and effluent concentrations, higher upstream concentrations in one stream but lower upstream concentrations in the other, or higher upstream concentrations during one sampling but lower upstream concentrations during the other. Dissolved concentrations of many of the constituents were similar to values reported for the Montreal WWTP effluent and St. Lawrence River,[2] where bismuth, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, and zinc were 5−10 times higher in the effluent than the river water.

The spatial and temporal relations were complex, but most constituents had little mass loss or gain downstream from the WWTPs (Table 1). The correlation between chloride and boron (Figure 3; average r^2 for the four individual sampling events was 0.9884) is consistent with boron's use as a tracer of WWTP effluent.[3,4,33] Boron mixing ratios indicate that Boulder Creek was 32% effluent during the summer sampling and 36% during the spring sampling (89% and 80% of the site A hydraulic mixing ratios). Boron mixing ratios indicate that Fourmile Creek was 79% effluent during the summer sampling and 21% during the spring sampling (98% and 75% of the hydraulic mixing ratios). Although the boron load in Boulder Creek primarily comes from the WWTP effluent, there are other potential upstream sources such as a coal-fired power plant[3] and marine sediments.[17] Elevated upstream antimony concentrations in Boulder Creek and Fourmile Creek could be attributed to anthropogenic sources such as break-pad dust from the transportation networks that surround the streams.[34] The rare earth element gadolinium is naturally occurring in surface waters but had greater concentrations in the WWTP effluents (Figure 3) due to its use as a contrast agent in magnetic resonance imaging.[11,12] Lithium is another element with a potential pharmaceutically derived source (treatment of bipolar disorder[3]) that was elevated in the WWTP effluents, although it also has other natural and anthropogenic sources.

Bismuth concentrations were elevated in the Boulder and Ankeny WWTP effluents, and concentrations and loads significantly decreased at the downstream Boulder Creek and Fourmile Creek sites (Figure 3, Table 1). Bismuth occurs in WWTP

Table 1. Mass Flow Discrepancy Ratios (R_i) and Overall Uncertainty (E_i) between Measured and Calculated Values for Boulder Creek, Colorado (BC) and Fourmile Creek, Iowa (FC) Downstream Sites D1 and D2 during the Summer 2003 and Spring 2005 Lagrangian Samplings*

	BC 2003 D1		BC 2003 D2		BC 2005 D1		BC 2005 D2		FC 2003 D1		FC 2003 D2		FC 2005 D1		FC 2005 D2	
Constituent	R_i	E_i	R_i	E_i	R_i	E_i	R_i	E_i	R_i	E_i	R_i	E_i	R_i	E_i	R_i	E_i
Alkalinity[c]	0.92	0.11	0.84	0.21	0.99	0.08	1.05	0.16	1.05	0.08	1.08	0.11	1.07	0.11	1.06	0.10
Aluminum[a]	0.88	0.25	0.76	0.48	0.82	0.08	0.76	0.18	0.38	0.09	0.37	0.20	0.55	0.11	na	na
Ammonium[a]	0.48	0.13	0.44	0.37	0.86	0.10	0.41	0.19	0.61	0.10	0.20	0.11	0.00	na	na	na
Antimony[a]	0.97	0.11	0.98	0.21	1.03	0.07	1.01	0.14	1.03	0.08	0.96	0.09	0.90	0.10	0.88	0.10
Arsenic[c]	1.24	0.11	1.26	0.20	1.19	0.07	1.31	0.14	1.45	0.07	1.38	0.09	1.01	0.10	1.08	0.12
Barium[b]	1.13	0.11	1.01	0.20	1.04	0.07	1.08	0.15	1.20	0.06	1.24	0.09	1.07	0.11	1.03	0.09
Bismuth[a]	0.36	0.14	na	na	0.38	0.10	na	na	0.42	0.09	0.60	0.11	0.31	0.11	na	na
Boron[a]	0.94	0.11	0.89	0.22	0.98	0.08	0.86	0.16	1.01	0.08	0.96	0.09	0.84	0.10	0.80	0.09
Cadmium[a]	1.00	0.13	1.40	0.30	0.95	0.09	1.24	0.22	1.42	0.09	1.25	0.10	1.15	0.12	1.15	0.10
Calcium[c]	0.98	0.11	0.88	0.21	1.06	0.08	1.05	0.15	1.02	0.08	1.07	0.11	0.97	0.10	1.07	0.10
Cerium[b]	1.49	0.15	1.43	0.28	1.17	0.09	1.11	0.16	2.55	0.08	0.90	0.09	0.94	0.11	1.00	0.10
Cesium[a]	1.05	0.14	0.81	0.25	1.12	0.09	1.27	0.18	0.31	0.09	0.47	0.10	0.00	na	na	na
Chloride[a]	0.90	0.12	0.93	0.24	1.01	0.08	0.94	0.16	1.00	0.09	1.05	0.11	0.92	0.10	0.96	0.10
Cobalt[a]	1.04	0.12	1.13	0.25	1.14	0.08	1.23	0.15	1.88	0.07	1.38	0.10	1.28	0.09	1.09	0.09
Copper[a]	0.72	0.12	0.86	0.26	0.81	0.08	0.80	0.18	1.14	0.08	1.03	0.09	0.88	0.10	1.06	0.10
Dysprosium[b]	1.24	0.15	1.36	0.27	1.08	0.14	1.00	0.26	2.16	0.08	1.24	0.11	0.93	0.11	1.22	0.12
Erbium[c]	1.12	0.16	1.10	0.29	1.18	0.12	0.70	0.19	1.80	0.09	1.39	0.10	1.07	0.15	1.15	0.10
Fluoride[a]	0.85	0.12	1.15	0.24	0.90	0.08	1.02	0.17	0.93	0.09	1.00	0.11	0.91	0.10	0.85	0.10
Gadolinium[a]	0.83	0.12	0.84	0.25	1.02	0.09	0.76	0.16	1.11	0.09	1.07	0.10	0.77	0.11	0.59	0.10
Holmium[c]	1.11	0.11	1.10	0.22	1.18	0.10	1.18	0.28	1.83	0.09	1.65	0.09	0.98	0.12	1.26	0.20
Iron[a]	0.98	0.11	0.75	0.21	1.03	0.08	0.95	0.16	0.35	0.10	0.64	0.11	1.33	0.10	0.93	0.10
Lanthanum[b]	1.34	0.16	1.21	0.28	1.08	0.09	1.05	0.17	2.24	0.07	0.93	0.10	0.98	0.11	1.05	0.12
Lead[a]	1.41	0.46	na	na	1.00	0.08	1.08	0.17	0.86	0.10	0.90	0.09	0.83	0.11	0.64	0.09
Lithium[a]	0.97	0.11	0.91	0.20	1.01	0.07	1.03	0.14	1.02	0.08	0.97	0.09	1.01	0.10	1.00	0.09
Lutetium[c]	1.09	0.13	1.21	0.25	1.18	0.10	0.86	0.17	1.22	0.10	1.28	0.10	0.90	0.14	1.22	0.18
Magnesium[c]	0.96	0.11	0.99	0.20	1.01	0.08	1.10	0.15	1.01	0.08	1.04	0.11	0.98	0.10	1.07	0.10
Manganese[a]	0.96	0.11	0.65	0.20	1.19	0.07	0.88	0.13	1.15	0.08	0.32	0.09	1.23	0.09	1.08	0.09
Molybdenum[a]	0.93	0.11	0.92	0.21	0.96	0.08	0.98	0.17	1.04	0.08	0.98	0.10	0.89	0.09	0.96	0.09
Neodymium[b]	1.40	0.14	1.26	0.24	1.19	0.10	1.23	0.19	2.31	0.07	1.12	0.11	1.05	0.11	1.02	0.09
Nickel[a]	0.93	0.11	0.99	0.23	1.01	0.07	0.97	0.15	1.20	0.08	1.22	0.10	0.84	0.12	0.83	0.12
Nitrate[c]	0.95	0.13	0.99	0.26	0.96	0.10	1.10	0.22	0.92	0.09	0.95	0.11	1.00	0.11	1.03	0.10
Nitrite[a]	1.46	0.13	1.17	0.22	1.72	0.11	2.10	0.20	0.95	0.09	1.12	0.11	0.84	0.11	0.95	0.10
Orthophosphate[a]	0.74	0.13	0.67	0.29	0.89	0.10	0.79	0.21	0.93	0.10	1.04	0.11	0.62	0.12	0.73	0.10
Potassium[a]	0.89	0.12	0.89	0.24	1.00	0.09	0.85	0.17	0.96	0.09	0.92	0.11	1.17	0.10	0.82	0.10
Praseodymium[b]	1.41	0.15	1.24	0.26	1.18	0.11	1.05	0.19	2.38	0.07	1.10	0.12	0.97	0.11	1.13	0.10
Rhenium[a]	0.99	0.11	0.91	0.21	1.05	0.08	1.04	0.15	1.01	0.08	1.01	0.09	1.00	0.09	0.98	0.09
Rubidium[a]	0.93	0.11	0.88	0.22	0.98	0.08	0.88	0.16	0.91	0.08	0.88	0.10	0.69	0.10	0.66	0.09
Samarium[b]	1.44	0.18	1.16	0.29	1.20	0.09	1.11	0.19	2.16	0.10	1.26	0.14	0.93	0.12	1.17	0.15
Selenium[c]	na	na	na	na	na	na	na	na	1.06	0.09	0.93	0.09	1.06	0.10	1.06	0.10
Silica[c]	0.97	0.11	0.87	0.21	1.00	0.08	0.88	0.15	0.87	0.09	1.02	0.11	1.03	0.10	1.01	0.10
Sodium[a]	0.91	0.12	0.87	0.23	1.00	0.08	0.94	0.16	0.99	0.09	0.97	0.11	1.19	0.10	0.82	0.10
Strontium[c]	1.02	0.10	1.15	0.21	1.02	0.07	1.33	0.15	1.05	0.07	0.99	0.10	1.04	0.10	1.06	0.09
Sulfate[a]	0.92	0.11	0.82	0.21	1.02	0.08	1.11	0.16	1.00	0.09	1.03	0.11	0.93	0.10	0.92	0.10
Terbium[b]	1.47	0.13	1.19	0.22	0.93	0.11	1.54	0.29	2.12	0.08	1.27	0.13	0.97	0.12	1.37	0.10
Thorium[c]	1.14	0.13	1.55	0.27	1.06	0.31	1.19	0.61	0.67	0.32	0.60	0.19	na	na	na	na
Thulium[c]	1.31	0.16	1.23	0.29	1.08	0.17	0.88	0.32	1.31	0.10	1.63	0.14	1.13	0.17	1.28	0.18
Tungsten[c]	1.14	0.10	1.02	0.20	1.28	0.08	1.48	0.18	na	na	na	na	na	na	na	na
Uranium[c]	1.11	0.10	0.88	0.19	1.15	0.07	1.27	0.13	1.29	0.06	0.93	0.09	1.10	0.11	1.08	0.09
Vanadium[c]	na	na	na	na	1.44	0.10	1.60	0.20	2.34	0.06	1.32	0.09	1.15	0.18	1.00	0.21
Ytterbium[c]	1.07	0.11	1.22	0.22	1.28	0.10	0.86	0.16	1.46	0.09	1.38	0.13	1.00	0.12	1.07	0.10
Yttrium[b]	1.23	0.11	1.08	0.21	1.07	0.08	1.02	0.16	1.88	0.07	1.38	0.09	1.04	0.11	1.21	0.09
Zinc[a]	0.83	0.14	0.85	0.29	0.93	0.09	0.75	0.17	0.98	0.09	0.85	0.10	0.73	0.11	0.60	0.09
Zirconium[a]	0.59	0.16	na	na	0.63	0.26	na	na	0.77	0.08	0.97	0.10	1.16	0.16	1.15	0.18

*R_i calculated according to eq 15; E_i calculated according to eq 14; superscripts associated with the constituents indicate relative loading from the wastewater treatment plants with respect to the receiving streams; cells shaded tan have significantly lower ($\pm$ two E_i) mass flows; cells shaded pink have significantly higher ($\pm$ two E_i) mass flows; beryllium[a], chromium[a], europium[b], tellurium[c], and thallium[c] were measured but not detected in sufficient samples or at concentrations five times the detection limit for inclusion in table; na, not applicable due to detection limits; 0.00, indicates mass removal to below detection limit. [a] Twenty-nine of the 58 constituents typically had greater concentrations and loads in the WWTP effluent than in the upstream water in both streams during both sampling events. [b] Ten of the constituents typically had greater concentrations at the upstream sites than in the WWTP effluent in both streams during both samplings. [c] Nineteen of the constituents had less clear relationships between the upstream and WWTP effluent sites - equivalent upstream and effluent concentrations, higher upstream concentrations in one stream but lower upstream concentrations in the other, or higher upstream concentrations during one sampling but lower upstream concentrations during the other.

effluents[2−4] because of its use in pharmaceuticals and as a lead replacement in solder in copper plumbing.[35] Bismuth occurs in the nitrogen group of the periodic table (metallic character increases going down the group; nitrogen and phosphorus are nonmetals, arsenic is a metalloid, and antimony and bismuth are metals) and undergoes oxidation/reduction and hydrolysis reactions to form insoluble hydroxide and oxide species.[36] Removal of bismuth by precipitation is suggested by its enrichment in suspended matter in the Montreal WWTP effluent relative to the St. Lawrence River.[2]

Mass-Flow Analysis and In-Stream Fate. The two Boulder Creek samplings were conducted under low-flow conditions (Figure 1) with no recent precipitation events, resulting in relatively stable hydrology. However, many of the constituents had greater concentrations (and loads) in the spring sampling (Figure 3) suggesting longer groundwater residence times, allowing water/rock interactions to occur. Measured discharge at Boulder Creek site D1 (Q_{D1}) during the summer sampling was nearly equal to calculated discharge (Ω_{D1}), and Q_{D2} increased relative to Ω_{D2} (Supporting Information). During the spring sampling, there was a small discharge discrepancy (loss) at Boulder Creek sites D1 and D2. During the Fourmile Creek summer sampling, measured discharge at D1 and D2 were slightly less than calculated discharge. Several possible factors can account for $\Omega_i \neq Q_i$, including measurement errors, unmeasured water gains or losses, and daily variability in WWTP and streamflow.

Table 1 summarizes R_i and E_i results from the error analysis for dissolved mass loads at the Boulder Creek and Fourmile Creek downstream sites. These data provide a measure of the overall uncertainty in observed mass gains and losses. For example, during the Boulder Creek summer sampling, ammonium significantly decreased at D1, whereas during the spring sampling, the decrease was only significant at D2. There was significant loss of bismuth and copper in Boulder Creek during both samplings. In Fourmile Creek, ammonium and bismuth also significantly decreased at D1. Other elements, such as arsenic and barium, had significant increases during the Fourmile Creek summer sampling.

The combined Lagrangian sampling data provide a matrix for assessing in-stream contaminant fate. During three of the four sampling events (Boulder Creek summer and spring; Fourmile Creek summer) the hydrological and chemical results were relatively consistent. The spring Fourmile Creek hydrological and chemical results deviated from the other samplings, and some "conservative" elements such as gadolinium showed significant downstream mass loss (Table 1). When the fraction of mass flow from effluent at site A ($M_{i,E}/\Theta_{i,A}$) is plotted against $M_i/\Theta_{i,A}$ for the spring Fourmile Creek sampling (Figure 4) there is a linear relationship for select compounds suggesting that the greater the fraction of mass flow derived from WWTP effluent the greater the loss along the flow path. This apparent mass loss illustrates the complexity of conducting field experiments with inherently uncontrolled variables. The Fourmile Creek spring sampling deviated most from "base-flow" conditions, and flow at the upstream site was 10-fold greater than during the summer (Figure 1). Because discharge from the Ankeny WWTP was not directly measured and was much less than streamflow, there was increased uncertainty in the estimated Q_E value. In Figure 1, Q_U = 0.62 and Q_A = 0.86 so Q_E = 0.24. If Q_A is 5% high then "true" Q_A = 0.82 and Q_E = 0.20, which translates to a 17% decrease in the load from the WWTP. In addition, transient recharge events can influence surface water/groundwater interactions[32] and increase experimental uncertainty.

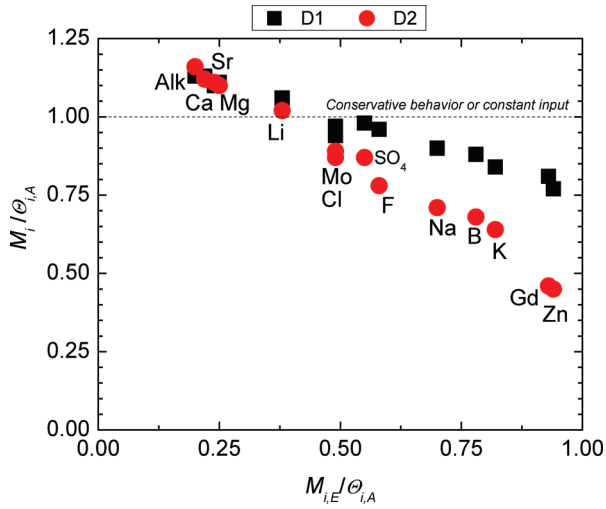

Figure 4. Fractional load of select constituents derived from the Ankeny wastewater treatment plant (WWTP) effluent input at mixing site A ($M_{i,E}/\Theta_{i,A}$) plotted against the ratio of the measured and calculated mass flows ($M_i/\Theta_{i,A}$) for Fourmile Creek downstream sites D1 and D2 during the spring 2005 Lagrangian sampling. [$M_{i,E}$ = measured load at effluent site; M_i = measured load at site i; $\Theta_{i,A}$ = calculated mass flow at site A; Alk = alkalinity, B = boron, Ca = calcium, Cl = chloride, F = fluoride, Gd = gadolinium, Li = lithium, Mg = magnesium, Mo = molybdenum, K = potassium, Na = sodium, Sr = strontium, SO_4 = sulfate, Zn = zinc].

The Lagrangian sampling approach helps minimize the temporal and spatial complexity of in-stream transport, and directly links chemical and hydrological processes. This study incorporated integrated cross-sectional stream sampling, contemporaneous discharge measurements, and comprehensive chemical analyses. These results allow internally consistent mass flux comparisons to be made. Despite efforts to conduct truly "Lagrangian" sampling, logistical limitations and unpredictable hydrological and anthropogenic variables add uncertainty to tracking the same exact parcel of water (which is continuously evolving). The broad range of inorganic constituents measured had a diversity of behaviors, and biological and chemical processes controlled in-stream fate. The ability to quantitatively compare sources and transport behavior between different streams under different flow conditions illustrates the utility of the holistic Lagrangian approach for investigating chemical fate in the environment.

■ ASSOCIATED CONTENT

Supporting Information. The summer 2003 and spring 2005 Lagrangian samplings in Boulder Creek, Colorado and Fourmile Creek, Iowa includes two tables on concentrations and loads, one table on discharge and chloride mass flow discrepancies, three figures showing streamflow, meteorological conditions, and daily variability of sewage inflow, one figure showing concentrations and loads, and one figure showing rare earth element concentrations normalized to the North American Shale Composite. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (303)541-3039. Fax: (303)541-3084. E-mail: lbbarber@usgs.gov.

Present Addresses
⊥IIHR-Hydroscience and Engineering, University of Iowa, Iowa City, Iowa 52242, US.

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