

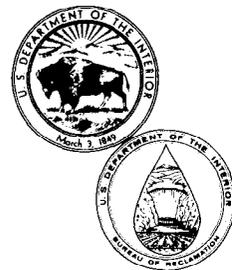
**REC-ERC-85-5**

# **SOLUTE-LOADING SOURCES IN THE DIRTY DEVIL RIVER BASIN, UTAH**

**May 1985**

**Engineering and Research Center**

**U. S. Department of the Interior  
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16. ABSTRACT Water management planning for salinity control is often based on the assumption that a reduction in the solute-loading level is conserved downstream. This assumption was tested using field data from the Dirty Devil River Basin, in southeastern Utah, and in a batch (laboratory) study of water and sediment samples. The study was designed to identify the sources of solute loading in the basin and to determine the differences in solute loading from channel sediments, in response to variations in initial water quality. A primary goal was to determine the present extent of gypsum dissolution from channel material and its potential change if agricultural salinity-control measures are instituted.  Synoptic sampling was conducted during the low-flow period, in October 1983. Contact-water samples for the batch study were collected from two locations. These samples were intended to represent the current, steady-state water quality below the irrigated area at Emery, Utah, and the best possible water quality after salinity control.  Field and laboratory data were analyzed using the geochemistry models WATEQF and BALANCE to postulate mineral reactions leading to solute loading. Three known sources of loading, involving two different geochemical mechanisms, were clearly discernible. Two additional areas of possible gypsum loading were identified.  Neither the field nor the laboratory results indicated much potential for increased solute loading from channel material after an improvement in upstream water quality. Although an upstream salinity reduction would not be totally conserved, it would not be significantly diminished by an additional dissolution of channel material.			
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DIRTY DEVIL RIVER BASIN, UTAH**

by

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**May 1985**

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## INTRODUCTION

Increasing salinity is one of the most serious water-quality problems in the Colorado River Basin. Since 1941, TDS (total dissolved solids) concentration at Imperial Dam, in the lower basin, has risen at an average rate of 3.9 mg/L per year [1]\*. The monthly average TDS at this location varied between 677 and 986 mg/L from 1978-81. At these levels, the economic damages to municipal, industrial, and agricultural water users in the lower basin are estimated to be \$113 million annually [2]. In response to this problem, the lower basin States adopted nondegradation standards for the lower Colorado River main stem in 1972. The Colorado River Basin Salinity Control Act of 1974 (Public Law 93-320) was designed to help maintain these standards by reducing solute loading in the upper basin. This act authorized 4 salinity-control units for construction and 12 for planning studies. One planning-study unit is located in the Dirty Devil River Basin, a tributary of the Colorado River in south-central Utah (fig. 1).

The Dirty Devil River annually contributes an average of 130 million kg of dissolved solids to the Colorado River [3], 65 percent of which comes from the Muddy Creek tributary area. Preliminary planning investigations identified three sources where solute loading might effectively be reduced. Two of these are point sources to Muddy Creek originating as saline springs and seeps in Salt Wash and South Salt Wash. The third is a diffuse source from agricultural return flows along Quichupah Creek and its tributaries in the Emery area. Salt Wash and South Salt Wash contribute predominantly sodium and chloride, indicating a halite (NaCl) source. Return flows from the Emery area are predominantly sodium and sulfate, probably resulting from gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) dissolution and subsequent cation exchange in the soil and aquifer material derived from Mancos Shale.

Gypsum, calcite ( $\text{CaCO}_3$ ), and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) are moderately soluble minerals commonly found in Mancos Shale. Salinity-control project planners generally assume return-flow solute concentrations from Mancos Shale areas are approximately in equilibrium with these minerals. Therefore, return-flow salinity concentrations are considered to be independent of return flow volumes, and reductions in volume due to irrigation system improvements should result in proportional reductions in solute loading. The improvement recommended for the Emery irrigation system involves removing winter stock water from the canal system to eliminate seepage during the nonirrigation season. A major uncertainty in this plan is whether the resultant reductions in solute loading

will be partially or completely offset by increased dissolution of downstream channel material. The subject study was performed to identify solute-loading sources along the Dirty Devil River and its major tributaries and to determine the occurrence of or potential for solute pickup within the channel. Two computer models, WATEQF [4] and BALANCE [5], were applied to aid in the interpretation of data from both the field and the laboratory batch studies.

The overall objectives of this investigation were to:

1. More completely define the sources of solute loading to Muddy Creek and the Dirty Devil River between Emery and the Poison Spring gauge;
2. Determine the potential magnitude of additional dissolution of channel materials following salinity-control activities in the Emery area;
3. Evaluate the use of chemical-equilibrium and mass-balance models in surface-water salinity studies.

## SUMMARY AND CONCLUSIONS

TDS concentrations in water samples collected along Muddy Creek increased from 245 mg/L above Emery to more than 2100 mg/L at Hanksville. Saturation with respect to halite and gypsum, computed by WATEQF, also increased along the flow path, indicating these two minerals were possible sources of solute loading. Mass transfer modeling, using BALANCE, showed significant loading from halite sources in two reaches. Both are below washes fed by saline springs and seeps from halite-bearing formations. The greatest loading from gypsum was computed for the reach affected by irrigation return flows from the Emery area. The mass transfer model indicated cation exchange was also an important loading source in this area. Mancos shale, underlying the irrigated land, contains both sodium-rich clays and gypsum, which provides a source of calcium and sulfate. As gypsum dissolves, calcium may be exchanged for sodium on the clays. The resultant return flow would have a large load of sodium and sulfate, and a smaller load of calcium. This would account for the change in solute concentrations between the sample sites above and below Emery. Similar changes were observed for Muddy Creek between Salt Wash and Hanksville and the Dirty Devil River between Hanksville and Poison Spring. Although no specific solute loading sources have been identified in these reaches, it is likely that a diffuse source exists where they cross exposures of gypsum-bearing rock.

The laboratory batch study demonstrated that channel sediments have essentially no impact on the sol-

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\* Numbers in brackets refer to entries in the bibliography.

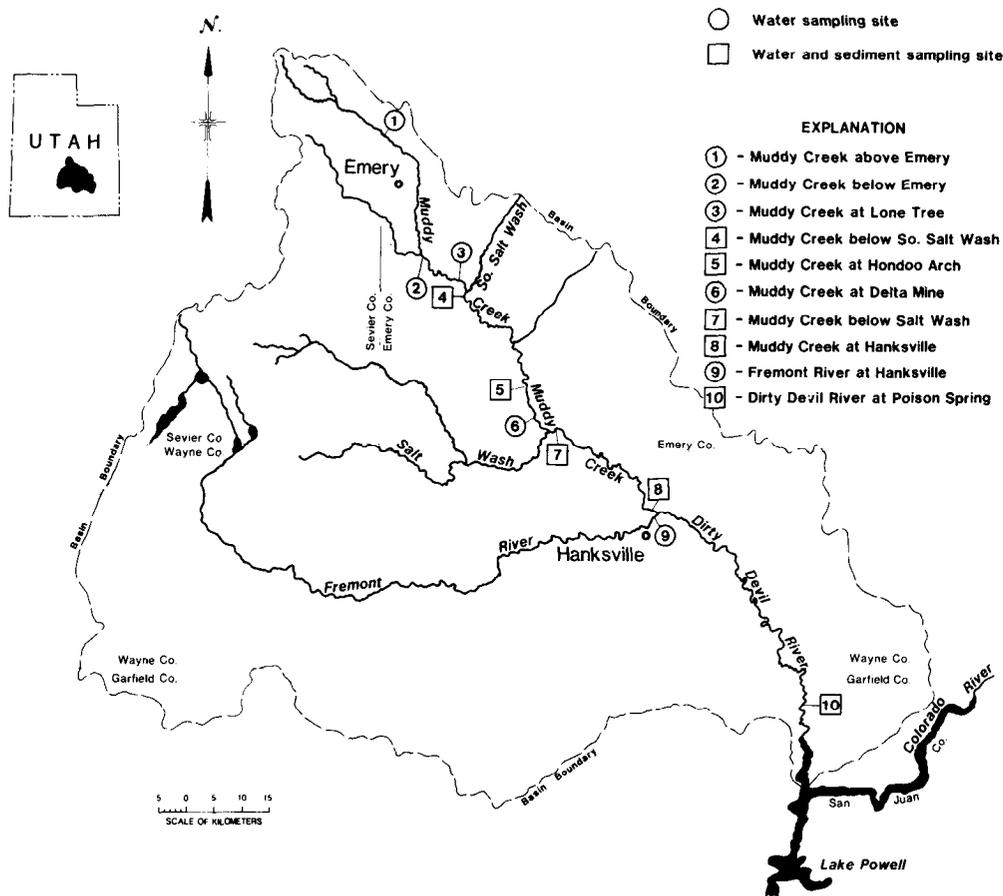


Figure 1. – Location map of the Dirty Devil River Basin, Utah.

ute load of the stream, regardless of the initial salinity of the stream. After initial contact with the sediment (0.5 h), the TDS of low-salinity water from Muddy Creek above Emery increased by 9 mg/L (3 percent) with 5 days additional contact. The TDS of high-salinity water from the Dirty Devil River at Poison Spring increased by 6 mg/L (1 percent). Neither increase is considered significant. According to WAT-EQF calculations, both contact solutions were undersaturated with respect to gypsum and were thus capable of dissolving gypsum in the channel sediments. BALANCE mass-transfer calculations indicated very slight dissolution of gypsum to account for solute changes in waters between 0.5 and 120 hours of contact. However, mineralogic analysis of sediments revealed that little or no gypsum was present. In general, the small solute increases observed between 0.5 and 120 hours were difficult to correlate with sediment analyses. Additional data would be required to determine the importance of reactions such as the dissolution of feldspars and the oxidation of sulfides and oxides.

The models clearly identified the three known sources of solute loading in the basin, and provided

insight into the mechanism of irrigation return flow solute loading. Other potential loading sources could be discerned, as could areas from which loading is minimal.

The model results are also consistent with mineralogic analyses of channel sediment samples. Calcite and dolomite were present in all samples, as 2-10 percent by mass. WATEQF indicated supersaturation with respect to these minerals at all Muddy Creek sites, and BALANCE indicated the precipitation of calcite between sites. Supersaturation may be a steady-state condition. If so, it would limit dissolution of calcite, allowing calcite to accumulate in the channel sediments. Conversely, gypsum was not identified in any of the sediment samples. WATEQF showed that gypsum was below saturation at all sites, even below known gypsum sources. This could be due, in part, to cation exchange of sodium for calcium associated with the gypsum source, as discussed previously. Also, BALANCE showed that gypsum precipitation does not occur. Both models indicate that concentrations of calcium and sulfate are not limited by gypsum solubility, and that gypsum is unlikely to accumulate in the sediment.

Implementation of salinity control in the Emery area would reduce the loading of sodium, sulfate, and to a lesser extent, calcium into Muddy Creek. Based on interpretation of the laboratory and field data and the model results, these reductions would not cause increased mineral dissolution downstream. Of the three solutes, calcium is the only one that may be available in the channel sediments and the only one whose concentration may be limited by mineral solubility. However, it would require a large decrease in calcium concentration to reduce the calcite saturation sufficiently for dissolution to occur. The sampling period was selected to represent the most probable conditions for mineral saturation in the stream: low flow, high TDS concentration, and significant irrigation return flow. Other conditions should be even less favorable for solubility limitation.

In general, the WATEQF and BALANCE models were useful in identifying sources of solute loading in the basin. WATEQF provided necessary information on thermodynamic limitation of mineral dissolution in water from a given site. However, the comparison of results for more than one site could have been misleading without knowledge of the local lithology and mineralogy. For example, the large increase in the halite SI (saturation index) below Emery was probably caused by sodium loading from cation exchange rather than from halite dissolution. BALANCE was useful in evaluating the loading mechanisms, particularly when the computed mass transfer corresponded to the change in the SI from WATEQF. This was generally the case for gypsum and halite, which were undersaturated in all field and batch-study samples.

Mass-transfer values calculated for the carbonate minerals did not always correspond to changes in saturation indices. This may have been due to the inaccurate or oversimplified selection of reacting phases for the mass-transfer model. Knowledge of the local mineralogy is important in obtaining good model results. Equally important is an understanding of geochemistry, which is necessary not only in interpreting model results, but also in developing model input, particularly for BALANCE. Although WATEQF and BALANCE results are often qualitatively related, they are not quantitatively dependent. Nor does a good relationship ensure accurate representation of the system. The natural system is not normally in a state of chemical equilibrium. Therefore, the extent to which reactions occur depends greatly on kinetics. Calculations such as those performed by WATEQF and BALANCE provide guidelines and a framework for examining a system in light of known system characteristics and geochemical theory.

## DESCRIPTION OF THE STUDY AREA

### Hydrology

The Dirty Devil River Basin covers 11 000 km<sup>2</sup> in south-central Utah. Two principal tributaries, the Fremont River and Muddy Creek, join to form the Dirty Devil near the town of Hanksville. Average annual discharge from the Fremont subbasin is 50 million m<sup>3</sup>, 58 percent of the total discharge from the basin [3]. Muddy Creek provides 25 million m<sup>3</sup>/a (29 percent), and another 11 million m<sup>3</sup>/a comes from minor tributaries to the Dirty Devil River between Hanksville and the Poison Spring gauge.

The headwaters of both major tributaries are in the mountainous western part of the basin at elevations above 3000 m. Precipitation averages more than 75 cm/a, much of it as winter snowfall. Most of the discharge of the basin originates in this area. Generally, water is depleted as the streams flow through the central basin valleys. Here, average annual precipitation is less than 20 cm, and water is diverted for the irrigation of 5500 ha in the Fremont River subbasin and 2500 ha in the Emery area. High summer temperatures can cause evaporation of all remaining channel flow. The major sources contributing to streamflow in the lower basin are agricultural drains, low discharge springs and seeps, and summer thunderstorm runoff.

### Geology

The Fremont River originates in Tertiary igneous intrusive/extrusive complexes. Its lower reaches drain sedimentary formations that range in age from Permian to Tertiary. Muddy Creek originates in the Tertiary North Horn Formation, a variegated-colored shale and mudstone. Near its headwaters, Muddy Creek traverses the Cretaceous Mancos Shale, a dark gray to black shale, with interbeds of sandstone and limestone. Gypsum occurs in the Mancos both as crystalline precipitate along parting planes and as finely-disseminated material within the shale itself.

The primary structure in the Muddy Creek subbasin is the San Rafael Swell, an unsymmetrical anticline, which plunges toward the southwest. Muddy Creek trends normal to the axis near the nose of this anticline and subparallel to the local fracture zones. As it crosses the Swell, Muddy Creek receives drainage from gypsum-bearing Jurassic sandstones and mudstones. The Triassic, marine Moenkopi Formation, consisting of mudstone, siltstone, sandstone, and limestone, is exposed across the nose of the anticline. Thin layers and veinlets of gypsum are present in the upper and lower parts of this formation. Southeast of the anticlinal axis Muddy Creek again crosses the Jurassic and Cretaceous sediments described previously.

Near its mouth, Muddy Creek flows through Quaternary alluvium largely composed of debris from the surrounding older formations. Below the confluence of Muddy Creek and the Fremont River, the Dirty Devil River proceeds southeast through Triassic and Jurassic formations, with major exposures of Navajo and Wingate sandstones.

### Geochemistry

Runoff in the headwater areas of the Fremont River generally originates as snowmelt and contains less than 200-mg/L TDS [6]. Much of this subbasin is composed of volcanics with few highly-soluble minerals. TDS concentrations increase gradually downstream due to contributions from irrigation return flow and natural drainage. At Hanksville, the average TDS concentration exceeds 850 mg/L.

In contrast, TDS concentrations in Muddy Creek are high along most of its length. Near Emery, much of its flow is diverted for irrigation of Mancos-derived soils. The return flow is very saline due to the dissolution of gypsum and carbonate minerals and cation exchange with sodium-rich clays. Below Emery, TDS may be as high as 4000 mg/L, predominantly sodium, calcium, and sulfate. Additional solute load may be contributed downstream where the channel crosses formations containing gypsum. Suspended sediments derived from runoff and from the natural degradation of shaly units is another potential source of solute loading.

Minor structures and sandstone outcroppings yield small saline spring flows throughout the Muddy Creek subbasin. Caine Springs, in Salt Wash, is a perennial spring, which issues from the Carmel Formation. It is associated with a small anticline. The source of water for Caine Springs is postulated to be the underlying Navajo Sandstone [7]. However, its very saline (>9500-mg/L TDS) sodium-chloride character reflects the dissolution of halite, which has been identified in the Carmel Formation.

The average TDS of Muddy Creek at Hanksville exceeds 3400 mg/L. At Poison Spring, the average TDS concentration of the Dirty Devil River is approximately equivalent to a flow-weighted mixture of the Fremont River and Muddy Creek tributaries.

## PREVIOUS INVESTIGATIONS

Solute loading in the Upper Colorado River Basin has been studied extensively in two areas: the Price River Basin in Utah and the Grand Valley in western Colorado. Jurinak et al. [8] examined the kinetics of solute release from saline sediment in the Price River Basin. In a 1:1 suspension of sediment and distilled

water, EC (specific electrical conductivity) was measured for contact times ranging from 2 seconds to 72 hours. Three rates of diffusion that controlled dissolution were defined by these measurements. It was postulated that the three dissolution stages were controlled by the following reactions: (1) dissolution of finely divided, highly-soluble salts, such as NaCl and Na<sub>2</sub>SO<sub>4</sub>, (2) dissolution of moderately-soluble minerals, such as gypsum and calcite, and (3) hydrolysis of silicates.

Riley et al. [9] summarized several additional years of study in the Price River Basin. Their goal was to develop a hydrosalinity model of surface discharge from the Basin. One laboratory study involved mixing unweathered Mancos Shale from the channel bed with deionized water in a 1:1 mass ratio. The EC was measured periodically for 45 days. Dissolution rates declined exponentially with time: approximately 80 percent of the 45-day total EC increase occurred in the first 3 days. Unconsolidated bed material was not tested, and complete chemical analyses were not made. However, based on the small overall increase in EC and correspondingly small EC changes measured down channel reaches in the field, Riley et al. concluded that mineral weathering of channel material was not an important source of solute loading.

Bowles et al. [10] expanded on this work by investigating solute release from suspended sediment. Mixing studies were again used to determine solute-release rates. The sources of suspended sediment were assumed to be unconsolidated materials from the channel bottom, channel bank, and valley floor. Samples of these materials from the Price River near Woodside were mixed with deionized water at mass ratios ranging from 1:5 through 1:100. To determine the impact of ionic strength on dissolution, several tests were made with initial solutions containing various amounts of reagent grade NaCl or Na<sub>2</sub>SO<sub>4</sub>. All mixtures were continuously stirred to keep the sediment suspended. The EC was measured periodically until apparent equilibrium was attained. This varied from 1 to 4 hours for solutions with channel-bank and valley-floor materials, depending on the dilution and the initial ionic strength of the solution. Solute release from the channel-bed material was essentially complete a few minutes after mixing. Like the previous investigators, Bowles et al. concluded that solute loading from channel material is relatively minor. They postulated that, of the sediment source materials, soil washed into the channel provides the most significant salinity contribution. However, most of the solute release from this material occurs during overland flow. They found that solution ionic strength affected solute release, but not significantly at ionic strengths less than 0.019 molar. They did not consider the effect of saturation with respect to minerals commonly found in the basin.

Shen et al. [11] also studied solute release from sediments, although they limited their investigation to erosion and sediment transport during storm events. They measured solute release from weathered and unweathered hillslope shale samples in 1:4 to 1:20 dilutions. The mixtures were agitated for 30 seconds and EC was measured periodically. When EC became constant, the mixture was reagitated. If reagitation did not produce a significant shift in EC, 75 percent of the solution was replaced with fresh water. This cycle was repeated through two replacements. In the most dilute mixture, solute release continued for more than 16 days. In less dilute mixtures, the constant EC of each water replacement approached the same value, indicating that mineral saturation had inhibited further dissolution. Field data from the Grand Valley area indicated gypsum saturation in storm runoff water. Shen et al. concluded that dissolution of erosional sediments is incomplete and additional solute release is possible after dilution, such as might occur at a confluence. Therefore, salinity contribution from in-channel solute loading may be more significant than indicated by the Price River Basin studies.

Evangelou et al. [12] hypothesized chemical mechanisms for solute release from Mancos Shale. They duplicated the extract studies reported by Shen et al. After 3 hours of continuous agitation and 30 minutes of settling, they found that the low dilution extracts of partially weathered shale were at or near gypsum saturation. High dilution extracts and unweathered shale solutions were undersaturated. Evangelou et al. concluded that solute loading from Mancos Shale is primarily a result of dissolution of dispersed gypsum in partially weathered shale. Additional sodium, potassium, and magnesium loading was attributed to exchange with calcium on clays.

## METHODS

### Experimental Design

The subject study geochemically characterized sediment and water samples in the Dirty Devil River Basin and evaluated potential impacts to the system caused by changes in water management. A batch study was designed using surface water from the Dirty Devil Basin. Complete chemical analyses were conducted on all field and laboratory samples, and thermodynamic concepts were applied in data analysis to evaluate the effects of specific minerals on in-channel solute loading.

The batch study was performed to evaluate whether a water of low salinity would dissolve more material from channel sediments than a water of high salinity. The low-salinity water was taken from Muddy Creek above Emery, upstream of the irrigated area. This

water was considered representative of the Muddy Creek water downstream of the irrigated area without diversions and saline return flows. Water from the Dirty Devil River at Poison Spring was used for the high-salinity water. The solute concentrations in this water were assumed to be in steady-state equilibrium with minerals in the channel material and were not expected to change significantly with additional contact during the batch study. An increase in solute concentrations in the low-salinity water upon contact with channel sediment would indicate the potential for increased mineral dissolution from this material after the implementation of salinity control upstream. The amount of solute release was used to determine whether the effectiveness of salinity control in the irrigated area would be reduced by additional solute loading along the channel between Emery and Poison Spring.

Water samples from gauge sites along Muddy Creek and the Dirty Devil River were also analyzed to quantify chemical changes along the flow path. The conditions observed in the field were compared with the results of the batch study to distinguish loading from sources other than channel sediments.

### Field Sampling

Field sampling was conducted from October 17-21, 1983. This period was selected as representative of the low-flow, nonirrigation season, when the effects on water quality due to evaporation are minimal. Water samples were collected at eight locations along Muddy Creek, at the mouth of the Fremont River, and at the Poison Spring gauge site on the Dirty Devil River (fig. 1). A portion of each sample was filtered in the field through a 0.45- $\mu$ m nitro-cellulose filter. The filtered sample was then split, and half was preserved at pH < 2 with 8 N nitric acid. All samples were transported on ice to the USBR (Bureau of Reclamation) Water Quality Laboratory in Salt Lake City for analysis.

The temperature, EC, and pH of the samples were measured in the field. Celsius temperature was measured with a mercury thermometer. EC was measured using a YSI (Yellow Springs Instruments) Model 33 conductivity meter; pH was measured using a Radiometer Model PHM80 meter with a gel combination electrode. Calibrations were made using pH 7.0 and 10.0 standards. Additional EC and pH measurements were made with a Presto-Tek Poly-Pram multiparameter meter. Discharge at the time of sampling was measured using a Marsh-McBirney current meter.

Channel-bottom sediment samples were collected at five of the water-sampling sites downstream from the Emery irrigation area. Two samples were collected from each site, one in midchannel and one near the bank. These were packed in airtight Nalgene bot-

tles and transported on ice to the USBR Soil Laboratory in Denver for use in the batch study. Bulk water samples for the batch study were taken from Muddy Creek above Emery and from the Dirty Devil River at Poison Spring. These samples were filtered in the field through a glass-fiber filter to remove suspended sediment. They were transported on ice with the sediment samples to the USBR Soil Laboratory.

### Batch Study

The sediment samples were air dried in the laboratory. Two samples from each site were then combined, gently pulverized to break up the aggregates, and passed through a No. 10 (2-mm) standard sieve. Equal masses of sieved material from each of the five sites were combined to form a composite sample. This composite sediment sample was mixed thoroughly and split into four equal parts. Three of these parts were used to produce triplicate sediment-water extracts for the batch study, and the fourth part was set aside for physical and chemical analysis.

Batch mixtures consisted of 30 g of the composite sediment combined with 200 mL of sample water in a 250-mL glass Erlenmeyer flask. Separate mixtures were made from every combination of the three sediment splits and the two source water samples (from Emery and from Poison Spring). After each specified contact time, the solutions from six mixtures (three with water from above Emery and three with water from Poison Spring) were removed for analysis. In this way, three replicate analyses were generated for each combination of contact time and source water.

The flasks were sealed and agitated on a reciprocating shaker for 20 minutes. The samples with 0.5-hour contact time were then decanted and centrifuged for 10 minutes at 1000 r/min. The remaining mixtures were allowed to settle and then agitated another 20 minutes. This process was repeated on each of the next 5 days. Samples were decanted and centrifuged at 24, 48, 72, 96, and 120 hours after initial mixing. Blank samples of both source waters were taken at 0.5 and 120 hours.

Each sample was immediately analyzed for resistivity, temperature, pH, and alkalinity. Resistivity was measured with an Industrial Instruments meter and a Beckman probe. The EC was calculated using measured resistivity [13]. Temperature was measured with a mercury-filled, Celsius thermometer. Measurements of pH and alkalinity were made using an Orion digital ionalyzer (Model 601A) with an Orion combination electrode. Alkalinity was determined by acid titration to an endpoint of pH 4.5 [13].

The remaining sample was vacuum filtered through a 0.45- $\mu\text{m}$  nitrocellulose filter. For analysis of cat-

ions, half of the filtrate was preserved at  $\text{pH} < 2$  with 8 N nitric acid. The remaining filtrate was used for analysis of sulfate, chloride, and the carbonate species. Samples were refrigerated until completion of the batch study and then shipped on ice to the USBR Water Quality Laboratory, Salt Lake City, Utah, for analysis.

### Sample Analysis

Water samples collected in the field and generated in the batch study were analyzed in the USBR Water Quality Laboratory. Calcium, magnesium, sodium, and potassium concentrations were determined by atomic absorption spectrophotometry [14]. Chloride and sulfate were analyzed by ion chromatography. Carbonate and bicarbonate concentrations were determined by fixed-point acid titration [13]. The USBR Water Quality Laboratory is certified by the State of Utah to meet EPA standards for all these analyses.

Site-specific and composite sediment samples were analyzed in the USBR Chemistry and Petrography Laboratory, Denver, Colorado. Mineralogy was determined by X-ray diffraction, by petrographic microscopy, and by qualitative chemical and physical tests.

### Model Application

The results of chemical analyses of field and laboratory water samples were evaluated using two computer models. The WATEQF model provides a thermodynamic mass-balance evaluation of a water sample by calculating the distribution of aqueous species and the degree of mineral saturation, which is the ratio of the ion activity product and the theoretical mineral solubility. The common logarithm of this ratio is referred to as the SI (Saturation Index) in this report. SI values of zero indicate equilibrium saturation with respect to the given mineral. Values greater than zero indicate supersaturation; and values less than zero, undersaturation. Calculations were performed using thermodynamic constants in the USGS (U.S. Geological Survey) WATEQF mineral data set, as of April 1983. WATEQF was used to answer the following questions:

1. Did mineral saturation change with time in the batch study or with distance along the flow path in field sampling?
2. Did the waters attain equilibrium with respect to any minerals that may act as solubility control?
3. Based on the lithology and the mineralogy of the study area, which minerals were identified as major contributors to salinity?

BALANCE examines hypothesized reactions between water samples and mineral phases by calculating mass transfer, the amount of dissolution or precipitation that must occur to account for chemical changes between samples. This program is not based on thermodynamics. The validity of its calculations is determined by the accuracy of laboratory analyses and by the user's ability to define the phases participating in the chemical reaction in the waters. The mass-transfer model was used to answer the following questions:

1. Were the mass-transfer calculations consistent with the thermodynamic (WATEQF) evaluation of the system?
2. Regarding the batch study, what were the quantitative differences in dissolution or precipitation between samples in contact with low-salinity and high-salinity waters?
3. How were the model results affected by changes in the set of mineral phases considered?
4. What can be concluded regarding the application of the model to surface-water systems?

## RESULTS AND DISCUSSION

### Batch Study

Table 1 summarizes mineral compositions of individual and composite sediment samples analyzed before and after a distilled-water leach. Leaching was intended to remove soluble residues deposited during drying of the sediment. Quartz was the major mineral phase in the sediments, with varying quantities of feldspars, calcite, and dolomite. Minor amounts of illite and smectite clays corroborated a low cation exchange capacity measurement of 3.22 meq/100 g. Sulfide and sulfate minerals were observed in only a few samples in very low quantities. Relatively soluble minerals, such as calcite, dolomite, and gypsum, measurably decreased in some leached samples. Complete mineral data for individual sediment samples are presented in the appendix.

Analyses of sample filtrates from the batch study are presented in table 2. Solute concentrations increased in both the Emery and Poison Spring source waters after 0.5-hour contact with the composite sediment. The increases were attributed to the resolubilization of chloride and sulfate salt residues that had precipitated when the samples were dried and were qualitatively identified in the sediments. After initial contact, filtrates collected at 24-hour intervals showed only minor changes in their major chemical constituents. The pH decreased with time in both

sets, possibly due to hydrolysis of iron oxide minerals. The sulfate concentration increased steadily with time in the filtrates and reflected the slower rate of dissolution of trace amounts of gypsum or sulfide minerals. Complete analyses of replicate samples are presented in the appendix.

SI values computed by WATEQF for the raw contact solutions (blanks) and for 0.5- and 120-hour contact times are summarized in table 3. WATEQF calculations on the Emery and Poison Spring blanks indicate that neither contact solution was initially in equilibrium with calcite, dolomite, gypsum, or halite. Both were supersaturated ( $\log SI > 0$ ) with respect to calcite and dolomite, and undersaturated ( $\log SI < 0$ ) with respect to gypsum and halite. SI values were generally higher for the Poison Spring blank than for the Emery blank. SI values of halite and gypsum increased in both source waters after 0.5-hour contact. This reflected increased concentrations of sodium, chloride, and sulfate. Bicarbonate concentrations did not vary significantly during the experiment. However, the activity of carbonate ( $CO_3^{2-}$ ) decreased with time in both source waters due to the increasing acidity of the systems. This caused the SI values for calcite and dolomite to decline.

After 0.5-hour contact, chloride, sulfate, and sodium concentrations increased by approximately equal amounts in the Emery and Poison Spring waters. However, the SI values for no mineral increased equally in the two waters. The Poison Spring water had an initially higher solute content and was more capable than the Emery water of forming aqueous complexes and ion pairs when additional ions entered the system. For example, sulfate concentrations increased by 34 and 35 mg/L in the Poison Spring and Emery contact solutions, respectively; however, the activity of free sulfate in the Poison Spring water increased approximately half the amount of that in the Emery water. This reflected the greater extent to which sulfate was complexed in the Poison Spring water. Because saturation indices are calculated using activities rather than concentrations, and because activities are a function of the total solution composition, a change in SI could not be simply related to changes in constituent concentrations.

BALANCE was used to quantify the mass transfer between minerals and the contact solution as a function of time (table 4). Mineral phases participating in mass-transfer reactions were postulated using X-ray diffraction data from sediment samples (table 1) and mineralogic descriptions from the literature.  $CO_2$  gas was used as a phase to serve as a sink, or source of carbonate in the system. Calculated mass transfers between blank and 0.5-hour samples for Emery and Poison Spring were essentially the same for the gypsum, halite, and thenardite phases, and together

Table 1. – Summary of sediment analyses.

Mineral	Composition of sample (percent)					
	Site 4	Site 5	Site 7	Site 8	Site 10	Composite
Unleached Samples						
Quartz	55-75	55-70	55-70	55-75	60-80	55-65
Feldspar	5-10	2-10	2-10	5-10	5-10	5-10
Calcite	5-10	5-10	5-10	5-10	2-10	5-10
Dolomite	5-10	5-10	5-10	2-10	2-10	5-10
Mica/Illite	2- 5	2- 5	2- 5	2- 5	tr- 5	5
Smectite	2-10	2-10	2- 5	2-10	tr- 3	tr- 3
Kaolinite	tr- 5	tr- 5	tr- 3	tr- 5	tr- 5	tr- 3
Gypsum	tr	0- tr	0- tr	0- tr	0	–
Other**	5-10	5-10	5-10	5-10	5-10	10
Water-leached Samples						
Quartz	60-75	60-70	55-70	55-75	60-80	55-75
Feldspar	5-10	2-10	2-10	5-10	5-10	5-10
Calcite	5-10	5-10	5-10	5-10	2-10	2-10
Dolomite	5-10	5-10	5-10	2-10	2-10	2-10
Mica/Illite	2- 5	2- 5	2- 5	2- 5	tr- 5	2- 5
Smectite	2-10	2-10	2- 5	2-10	tr- 3	tr- 3
Kaolinite	tr- 5	tr- 5	tr- 3	tr- 5	tr- 5	tr- 3
Gypsum	0- tr	0- tr	0- tr	0- tr	0	–
Other**	5-10	5-10	5-10	5-10	5-10	10

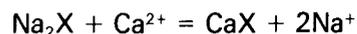
\*See figure 1 for sample site locations.

\*\*See table 1 of the appendix for a complete list.

accounted for most of the increases in TDS. This is consistent with the hypothesis that residual chloride and sulfate salts in the sediments were dissolved upon initial contact with either solution. The mass transfer involving the carbon phases (calcite, dolomite, CO<sub>2</sub> gas) was more variable. This was due to the stability of the magnesium concentration in the Emery sample, and the increase in the magnesium concentration of the Poison Spring contact solution. Dissolution of dolomite is not thermodynamically favored because of its supersaturated condition in both solutions. Contrary to thermodynamic principals, the lesser state of supersaturation in the Poison Spring may have allowed a small amount of dissolution to occur. However, due to the speed at which the magnesium entered the solution, its source may have been ion exchange with calcium on clay particles. The activity ratio of calcium to magnesium in the Poison Spring water is more than double that in the Emery sample. Thus, this exchange reaction is favored in the Poison Spring solution.

In place of thenardite, calcium-sodium exchange was used for mass-transfer calculations between the 0.5-

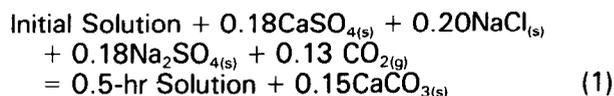
and 120-hour samples. The exchange phase was postulated due to the presence of smectite and illite clays in the sediment sample. It is represented by the reaction:



where X represents the clay substrate. Mass-transfer calculations indicated little change in solute concentrations from this reaction.

In general, the mass-transfer equations can be written as follows:

Emery: 0.5-h contact



Emery: 120-h contact

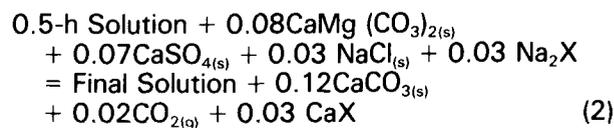


Table 2. – Average composition of leachate samples from the batch study.

Hours of contact	pH	Concentration (mg/L)							
		Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Chloride	Sulfate	TDS
Composite sediment sample contacted with water from Muddy Creek above Emery									
0 (blank)	8.1	45	26	11	0.3	279	6	18	243
0.5	8.1	46	26	24	2.4	274	13	53	299
24	7.6	44	25	24	2.6	265	13	55	294
48	7.6	44	26	25	2.5	266	14	57	299
72	7.7	45	26	26	2.7	269	13	57	302
96	7.6	45	27	25	2.6	269	14	59	305
120	7.7	46	28	26	2.3	268	14	60	308
120 (blank)	7.8	45	26	11	0.3	266	6	17	236
Composite sediment sample contacted with water from Dirty Devil River at Poison Spring									
0 (blank)	7.9	151	36	112	5.3	177	88	494	973
0.5	7.8	149	47	127	6.1	178	96	528	1041
24	7.6	141	44	124	6.1	176	95	529	1026
48	7.7	145	47	126	5.9	177	96	529	1036
72	7.6	143	44	127	5.9	179	96	525	1029
96	7.5	144	45	127	6.0	179	97	530	1037
120	7.6	142	44	125	5.9	181	96	534	1036
120 (blank)	7.8	151	36	113	5.4	176	87	487	966

Table 3. – Saturation indices, calculated by WATEQF, for samples from the batch study.\*.

Source water	Saturation index				
	pH	Calcite	Dolomite	Halite	Gypsum
<u>Muddy Creek above Emery</u>					
Blank	8.1	0.627	1.27	-8.74	-2.31
0.5-h contact	8.0	.556	1.13	-8.07	-1.86
120-h contact	7.7	.261	0.58	-8.01	-1.82
<u>Dirty Devil River at Poison Spring</u>					
Blank	7.9	.597	.85	-6.62	-0.641
0.5-h contact	7.8	.490	.75	-6.53	-.642
120-h contact	7.6	.295	.37	-6.54	-.650

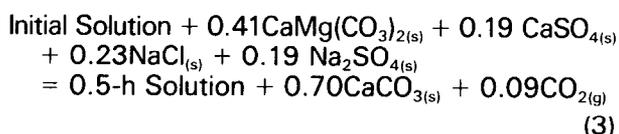
\*Saturation index is  $\log(IAP/KT)$ , where IAP is the ion activity product, and KT is the thermodynamic, temperature-dependent solubility constant of the mineral of interest. Thus, a negative number indicates undersaturation, and a positive number indicates supersaturation with respect to a particular mineral species. Input data are presented in table 3 of the appendix.

Table 4. – Changes in dissolved mass in batch study samples, computed by BALANCE.

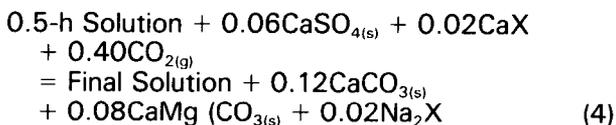
Sample	ΔpH	Mass transfer* (mmol/L)						
		Calcite	Dolomite	Gypsum	Halite	Thenardite	Ca-Na Exchange	CO <sub>2</sub>
<b>Emery</b>								
Blank to 0.5 h	-0.1	-0.15	0.0	0.18	0.20	0.18		0.13
0.5 h to 120 h	-.3	-.12	.08	.07	.03		0.03	-.02
<b>Poison Spring</b>								
Blank to 0.5 h	-.1	-.70	.41	.19	.23	.19		-.09
0.5 h to 120 h	-.2	-.12	-.08	.06	.00		-.02	.40

\*Positive values indicate dissolution of phase; negative values indicate precipitation.

Poison Spring: 0.5-h contact



Poison Spring: 120-h contact



The relatively large coefficients of reactant minerals in reactions (1) and (3) demonstrate that the greatest interaction of solution and sediment occurred upon initial contact. Qualitative mineralogic analyses and thermodynamics support the calculated dissolution of highly-soluble residue minerals, such as thenardite and halite. Smaller coefficients of reactant and product phases in reactions (2) and (4) reflect slower solute release from the sediments after initial contact. The mineral specification used to describe mass transfer after 0.5-hour contact indicates that the dissolution of moderately soluble gypsum or dolomite drives the reactions to precipitate calcite.

Changes in the SI values with time for minerals in the two batch sets showed general thermodynamic consistency with mass-transfer calculations. WATEQF calculations for the solutions indicated undersaturation with respect to gypsum, halite, and thenardite, and BALANCE indicated the additional dissolution of those phases. Computed mass transfer among carbon phases was not as clearly related to changes in SI values. BALANCE computed dissolution of dolomite in the Emery contact solution between 0.5 and 120 hours of contact. However, the SI for dolomite

was greater than zero in the 0.5-hour sample. This indicated a supersaturated condition, in which additional dolomite should not dissolve. For both contact solutions, decreases in calcite SI throughout the contact period corresponded with the calculated precipitation of calcite. This is consistent with calcite supersaturation of the source water, which should thermodynamically favor mineral precipitation. The general decrease in the SI of calcite in both contact solutions corresponded well to calculations of precipitation in the mass-transfer model.

### Field Study

Field measurements and laboratory analyses from nine sampling locations in the Dirty Devil Basin are presented in table 5. Tributaries in the agricultural area near Emery accounted for the increased streamflow at the gauging station below Emery, and seeps identified in Salt and South Salt Washes contributed to the solute load of Muddy Creek, but had little impact on its discharge. The apparent increase in streamflow below South Salt Wash is questionable due to measurement inaccuracy. However, flow through the surrounding alluvium could account for some gain. The differences in discharge measurements for Muddy Creek from Hondoo Arch to Hanksville are insignificant. The Fremont River and Muddy Creek join near Hanksville and form the Dirty Devil River. Discharge measurements indicated that flow was conserved from the confluence down to the final gauging station at Poison Spring.

In general, the concentrations of most constituents increased along the Muddy Creek flow path from above Emery to the station at Hanksville. Increases in sodium and sulfate at the station below Emery were attributed to saline irrigation return flow. Sub-surface inflow originating from seeps and springs in South Salt Wash probably contributed to the in-

Table 5. – Data for water samples from the field study.

Parameter	Units	Sampling location*								
		Muddy Creek above Emery	Muddy Creek below Emery	Muddy Creek below South Salt Wash	Muddy Creek at Hondoo Arch	Muddy Creek at Delta Mine	Muddy Creek below Salt Wash	Muddy Creek at Hanksville	Fremont River at Hanksville	Dirty Devil River at Poison Spring
<b>Field</b>										
Date		10/17/83	10/17/18	10/18/83	10/19/83	10/19/83	10/20/83	10/19/83	10/19/83	10/20/83
Discharge	m <sup>3</sup> /s	0.79	0.93	1.08	0.85	0.82	0.76	0.79	3.37	4.16
Temperature	°C	13.0	11	11	10	16	18	20	18	16
pH	Standard units	8.6	8.6	8.2	8.5	8.5	8.4	8.3	8.3	8.3
Specific conductance	µS/cm at 25 °C	370.0	1630	1665	1970	1970	2570	2885	800	1290
<b>Laboratory**</b>										
pH	Standard units	8.7	8.4	8.4	8.3	8.3	8.2	8.2	8.4	8.3
Calcium	mg/L	46	99	101	121	115	141	207	105	151
Magnesium	mg/L	26	73	76	79	78	79	80	25	36
Sodium	mg/L	11	173	209	254	258	371	384	33	110
Potassium	mg/L	1.6	3.4	3.8	5.1	5.1	5.6	7.5	5.6	6.4
Carbonate	mg/L CO <sub>3</sub> <sup>2-</sup>	22.2	33.4	15.6	10.5	10.8	0	0	0	0
Bicarbonate	mg/L HCO <sub>3</sub> <sup>-</sup>	234	267	271	255	227	224	203	180	179
Chloride	mg/L	6	33	60	129	136	339	340	18	86
Sulfate	mg/L	17	602	632	724	748	764	988	261	480
TDS	mg/L	245	1148	1231	1448	1463	1810	2106	536	957

\*See figure 1.

\*\*Some values represent the average of replicate samples.

crease in sodium and chloride observed between the South Salt Wash and Hondoo Arch gauge sites. The sample collected below Salt Wash reflected the saline spring flow from Caine Springs, a perennial spring located in Salt Wash. Decreases in concentrations of all chemical constituents from Muddy Creek at Hanksville to the Dirty Devil River at Poison Spring were due to dilution by the Fremont River. However, dilution ratios varied for individual constituents. This indicated that the water at Poison Spring was not strictly the result of conservative mixing of the two streams.

SI values calculated by WATEQF for minerals believed to be major contributors to salinity in the system did not indicate that solubility controlled the concentration of most chemical constituents (table 6). At the station above Emery, upstream of the irrigated area, calcite was more than 10 times saturated, and dolomite was almost 100 times saturated. Below Emery, the SI values for these carbonate minerals were even higher. Such supersaturation in irrigation return flow has been reported by Suarez [15]. He found that short residence time, multiple sources of ions, and crystal surface inhibitors limited calcite precipitation, despite the availability of mineral surfaces for precipitation in the soil-aquifer system.

The SI values for calcite and dolomite decreased along Muddy Creek from below Emery to Hanksville

due to decreases in pH and the activity of carbonate. The decreasing trend indicated a tendency toward a steady-state concentration of bicarbonate. However, thermodynamic equilibrium with carbonate minerals did not appear to strictly control cation concentrations.

Gypsum and halite were undersaturated in all samples. Below the Emery agricultural area, the SI values for both these minerals increased, reflecting the high concentrations of sulfate and sodium in irrigation return flows. However, the increase in ionic strength of the water between these stations tempered the approach to saturation with respect to gypsum. The total concentrations of SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> increased by factors of 35 and 2.2, respectively; and activities of SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> increased by factors of 27 and 1.4, respectively. The smaller increases for activities reflected the decreasing activity coefficients of SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> due to ion-pair formation. Without considering the increase in ionic strength and ion pairing, the water below Emery would have been near gypsum saturation. The SI of gypsum continued to increase downstream, primarily because of the increasing sulfate concentration. Throughout the system, the increase in ionic strength was a significant factor in the increase in the solubility of gypsum.

The halite SI increased along Muddy Creek to Hanksville. However, this parameter was not useful in iden-

Table 6. – Saturation indices, computed by WATEQF, for water samples used in the field study.\*

Sample location**	Calcite	Dolomite	Gypsum	Halite	Thenardite
Muddy Creek above Emery	1.03	1.97	-2.32	-8.72	-10.5
Muddy Creek below Emery	1.18	2.38	-.76	-6.84	-6.77
Muddy Creek at Hondoo Arch	1.06	2.09	-.64	-6.09	-6.40
Muddy Creek below Salt Wash	1.01	2.02	-.61	-5.54	-5.98
Muddy Creek at Hanksville	1.04	1.95	-.40	-5.54	-5.98
Fremont River at Hanksville	0.88	1.37	-.94	-7.81	-8.47
Dirty Devil River at Poison Spring	.92	1.44	-.64	-6.62	-7.24

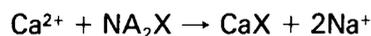
\* Saturation index is  $\log(IAP/KT)$ , where IAP is the ion activity product, and KT is the thermodynamic solubility constant. Negative values indicate undersaturation; positive values indicate supersaturation.

\*\*See figure 1 for sample locations.

tifying halite sources. For example, the greatest increase in the halite SI occurred between the Muddy Creek stations above and below Emery. The chloride concentration increased by more than a factor of 5, and sodium increased by a factor of 16. Assuming that chloride and sodium behaved conservatively and that halite was the sole source of chloride, only 10 percent of the sodium increase can be attributed to halite dissolution. Most of the increase in sodium had some other source, possibly cation exchange of calcium for sodium on clay derived from the Mancos Shale.

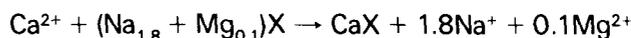
The SI of both gypsum and halite decreased from Muddy Creek at Hanksville to the Dirty Devil River at Poison Spring due to dilution by the Fremont River.

BALANCE was used to quantify dissolution, precipitation, and cation exchange reactions to account for water-quality changes along the channel (table 7). Precipitation of calcite and dissolution of dolomite, gypsum, and halite were calculated to occur between the Muddy Creek sampling sites above and below Emery. Calcium-sodium exchange was represented by the reaction:



A second exchange reaction was also tested, based on Evangelou's [16] finding that magnesium also entered the system by exchange reactions on clays. This second exchange reaction considered the exchangeable cations to be 90 percent sodium and 10 percent magnesium. The exchange with calcium is

then written as:



BALANCE calculated that significant cation exchange occurred for both proposed exchange reactions. The addition of magnesium to the reaction decreased the computed precipitation of calcite and dissolution of dolomite.

For BALANCE calculations downstream of the sampling site below Emery, thenardite (sodium sulfate) was substituted for cation exchange as a source of sodium. Although sodium sulfate minerals were not identified as primary minerals in the surrounding strata, they have been identified in efflorescent salts [16] and represent a diffuse source of salinity. Dissolution of thenardite was calculated to occur along the entire Muddy Creek channel except the reach between Hondoo Arch and Salt Wash.

BALANCE was also used to calculate the mixing ratio of two waters based on the resultant water analysis. Samples from the Muddy Creek and Fremont River tributaries above Hanksville were used to represent end-member water chemistry. The sample collected at Poison Spring represented the resultant water from the mix of the end-member waters. Chloride was assumed to behave conservatively upon mixing below Hanksville and was used to calculate the mixing ratio of the tributaries. BALANCE calculated that the water quality of the Dirty Devil River at Poison Spring resulted from a mixture of 79 percent Fremont River water and 21 percent Muddy Creek water. This closely agrees with the discharge measurements,

Table 7. – Change in saturation index (dimensionless) and computed mass transfer (mmol/L) for selected stream segments.

Flow-path <sup>1</sup> segment	Phase <sup>2</sup> set	Calcite		Dolomite		Gypsum		Halite		Thenardite		Cation exchange MT	CO <sub>2</sub> MT
		ΔSI	MT	ΔSI	MT	ΔSI	MT	ΔSI	MT	ΔSI	MT		
1	1	0.15	-3.57	0.41	1.94	1.56	6.10	1.88	0.76	3.73	-	3.15	0.53
	2	.15	-2.87	.41	1.59	1.56	6.10	1.88	.76	3.73	-	3.50	.53
2	3	-.12	-0.54	-.29	0.24	0.12	0.85	0.75	2.71	0.37	0.43	-	-.83
3	3	-.05	-.34	-.07	.01	.03	.83	.55	5.94	.32	-.41	-	-.49
4	3	.03	-.49	-.07	.04	.21	2.11	.0	0.03	.10	.21	-	.06
<sup>3</sup> 5a	4	-.12	.02	-.51	-.03	-.24	.62	-1.08	-	-1.26	.07	-	-
5b	-	.04	-	.07	-	.30	-	1.18	-	1.23	-	-	-.05

<sup>1</sup>Flowpath segments are as follows (see figure 1 for locations): 1 = Muddy Creek, above to below Emery; 2 = Muddy Creek, below Emery to Hondo Arch; 3 = Muddy Creek, Hondo Arch to below Salt Wash; 4 = Muddy Creek, below Salt Wash to Hanksville; 5a = Muddy Creek at Hanksville to Dirty Devil River at Poison Spring; 5b = Fremont River at Hanksville to Dirty Devil at Poison Spring.

<sup>2</sup>Phase set used in BALANCE mass-transfer calculations:

1 = Calcite, dolomite, gypsum, halite, sodium-calcium exchange, CO<sub>2</sub>

2 = Calcite, dolomite, gypsum, halite, (90% sodium + 10% magnesium) – calcium exchange, CO<sub>2</sub>

3 = Calcite, dolomite, gypsum, halite, thenardite, CO<sub>2</sub>

4 = Calcite, dolomite, gypsum, thenardite, CO<sub>2</sub>

<sup>3</sup>MT values are based on the mixing of the Fremont River and Muddy Creek at Hanksville, using chloride as the mixing parameter; thus, no MT value is presented for the chloride-bearing phase halite.

which indicated contributions of 81 percent and 19 percent from the Fremont River and Muddy Creek, respectively. Minor quantities of dolomite precipitation and calcite and thenardite dissolution were predicted. Relatively significant dissolution of gypsum was calculated to occur below the confluence of the tributaries along the flow path to Poison Spring.

BALANCE calculations were evaluated by examining whether SI or changes in SI for a mineral can be qualitatively correlated with predicted mass transfer. Bar graphs display the results for the minerals gypsum, halite, calcite, and dolomite (fig. 2). Sample site numbers refer to sites shown on figure 1. Changes in the saturation index (ΔSI) were calculated by subtracting the SI at the upstream station from the SI at the downstream site. Positive values for MT (mass transfer) between sites represent dissolution, and negative values indicate precipitation.

In general, one would expect an increase in SI between sample sites (ΔSI positive) to be accompanied by dissolution (MT positive). This should occur until the water reaches mineral saturation. Downstream from a site where saturation is exceeded, ΔSI and MT should both be negative, indicating mineral precipitation. If the water at a site is in approximate equilibrium with a mineral, downstream ΔSI should be zero, but MT may be negative or positive, depending upon whether the solution must precipitate or dissolve mineral mass to maintain equilibrium.

For the flow-path segment from above to below Emery, sample sites 1 and 2, there was considerable variability between ΔSI and mass-transfer values.

Waters above Emery were undersaturated with respect to gypsum and halite. Although the waters below Emery remained undersaturated, the SI values of both minerals increased, and mass-transfer calculations indicated gypsum and halite dissolution. However, the relationship between the ΔSI value and amount of dissolution was very different for the two minerals. The ΔSI of gypsum reflected a very large increase in the sulfate concentration. Because gypsum was designated as the only source of sulfate, BALANCE calculated a substantial amount of gypsum dissolution. In contrast, the calculated dissolution of halite was less than 15 percent that of gypsum, although the ΔSI of halite exceeded that of gypsum. The ΔSI for halite was caused by the large increase in sodium concentration. However, halite was not the sole source of sodium. The amount of dissolution of halite actually reflected the much smaller increase in chloride concentration.

Water above Emery was greater than 10 times supersaturated with respect to calcite and dolomite, and SI values further increased along the reach to below Emery. In contrast to the results observed for gypsum and halite, a positive ΔSI did not necessarily correspond to dissolution. On the one hand, dissolution of dolomite was calculated although it contradicts the thermodynamics of the system. On the other hand, precipitation of calcite was predicted and was consistent with its state of supersaturation in the system. Mass transfer among the carbonate phases decreased when the postulated cation exchange reaction included magnesium. This second source of magnesium input to the system decreased the amount of dolomite dissolution required to ac-

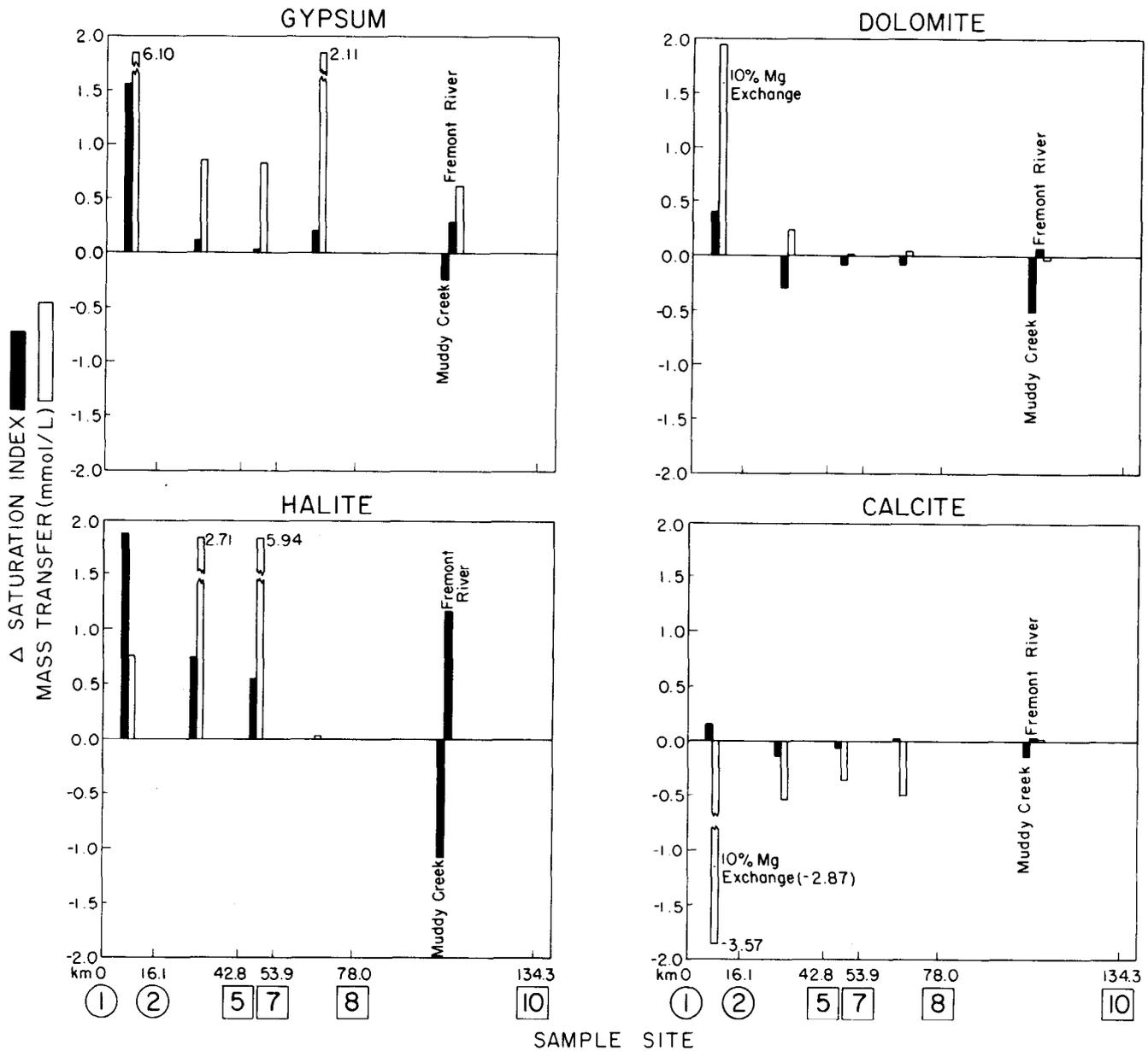
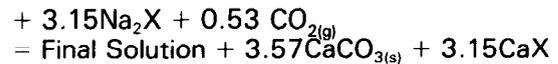
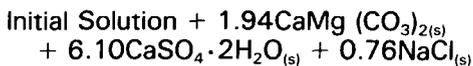


Figure 2. – Change in saturation index and mass transfer for selected minerals between sampling sites (see fig. 1 for location).

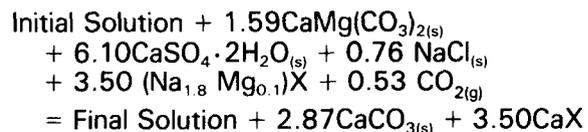
count for the observed increase of magnesium. In turn, the amount of calcite predicted to precipitate decreased because less carbonate was transferred to solution from dolomite dissolution.

In general, for the flow path from above to below Emery, changes in SI values were consistent with the predicted mass transfer. The reactions can be written as follows:

1. Reaction including calcium exchange with sodium only:



2. Reaction including calcium exchange with sodium and magnesium:



In both cases, the dissolution of gypsum made the greatest contribution to observed increases in solute concentrations. Assuming that sulfate did not precipitate or sorb to clay-size particles in surface water,

gypsum dissolution added 585 mg/L of sulfate to Muddy Creek between the two gauges near Emery.

The dissolution of gypsum and dolomite provided available calcium to drive the exchange reaction. In the case of sodium-calcium exchange, 3.15 mmol/L (126 mg/L) of calcium exchanged onto clays, releasing to solution 6.30 mmol/L (145 mg/L) of sodium. For sodium magnesium-calcium exchange, 3.50 mmol/L (122 mg/L) of calcium exchanged for 6.30 mmol/L (145 mg/L) of sodium and 0.35 mmol/L (9 mg/L) magnesium. The net results are relatively minor TDS increases of 19 mg/L for the first reaction and 32 mg/L for the second. The significance of the influx is that sodium is unlikely to precipitate or exchange back onto clays along the flow path to the Dirty Devil River.

Supersaturation of calcite can be the result of kinetic competition between gypsum, dolomite, and calcite [17]. Hydrodynamic dispersion of solutes in the irrigation drainage system and in surface receiving waters exceeds the rate at which solutes react and precipitate. This theory is consistent with the increasing supersaturation of Muddy Creek waters with respect to calcite and dolomite.

For the Muddy Creek flow path segments below Emery to Hanksville, there was little quantitative correlation between  $\Delta SI$  and mass transfer values (table 7). However, except for the carbonates, increases in SI ( $\Delta SI$  positive) generally corresponded with dissolution calculated by the mass-transfer model. This indicated that the proposed dissolution reactions were within the defined thermochemical constraints of the system. Changes in SI for calcite and dolomite were not dramatic. The decreasing trend was partially attributed to decreases in pH along the flow path. However, mass-transfer calculations indicated calcite precipitation, which was not consistent with calculated calcite supersaturation of the water.

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**APPENDIX**  
**CHEMICAL DATA FOR SEDIMENT**  
**AND BATCH STUDY SAMPLES**

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Table 1. – Composition of sediment samples by size fraction.

Mineral	Composition (percent) of Unleached/Water-leached Sample <sup>1</sup>								
	Muddy Creek below South Salt Wash			Muddy Creek at Hondoo Arch			Muddy Creek below Salt Wash		
	Sand	Silt	Clay <sup>2</sup>	Sand	Silt	Clay	Sand	Silt	Clay
Quartz	70-75/70-75	60-65/60-65	55-60/60	70/70	65/65	55/60	70/70	65/65	55-60/55-60
Feldspar	5/5	5-10/5-10	5/5	5/5	5-10/5-10	2-3/2-3	2-3/2-3	10/10	
Calcite	5-10/5-10	5-10/5-10	5-10/5-10	5/5-10	5/5	5-10/5	5-10/5-10	5/5	5/5
Dolomite	5-10/5-10	5-10/5-10	10/5-10	5/5	5-10/5-10	10/5-10	5/5	5-10/5-10	10/10
Mica/Illite	5/2-3	2-3/2-3	5/5	5/2-3	2-3/2-3	5/5	5/5	2-3/2-3	5/5
Smectite	2-3/2-3	2-3/2-3	5-10/5-10	2-3/2-3	2-3/2-3	5-10/5-10	2-3/2-3	2-3/2-3	5/5
Kaolinite	tr/tr	2-3/2-3	5/5	tr/tr	2-3/2-3	5/5	tr/tr	tr/tr	2-3/2-3
Gypsum	tr/0	tr/0	tr/tr	0/0	0/0	tr/tr	tr/0	0/0	tr/tr
Other <sup>3</sup>	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10
	Muddy Creek near Hanksville			Dirty Devil River at Poison Spring			Composite		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Quartz	70-75/70-75	55/55	55/55	80/80	60-65/60-65	60/60	65/75	65/60-65	55/55
Feldspar	5-10/5-10	10/10	5/5	5-10/5-10	10/10	5/5	5-10/5-10	5-10/10	5-10/10
Calcite	5/5	5-10/5-10	5-10/5-10	2-3/2-3	5/5	5-10/5-10	5-10/2-3	5/5-10	5-10/5-10
Dolomite	2-3/2-3	5-10/5-10	5-10/5-10	2-3/2-3	5-10/5-10	5-10/5-10	5/2-3	5-10/5-10	10/5-10
Mica/Illite	2-3/2-3	5/5	5/5	tr/tr	2-3/2-3	5/5	5/2-3	5/2-3	5/5
Smectite	2-3/2-3	5/5	5-10/5-10	tr/tr	2-3/2-3	2-3/2-3	tr/tr	tr/tr	2-3/2-3
Kaolinite	tr/tr	2-3/2-3	5/5	tr/tr	2-3/2-3	5/5	tr/tr	tr/tr	2-3/2-3
Gypsum	0/0	tr/0	tr/tr	0/0	0/0	0/0	–	–	–
Other <sup>3</sup>	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	5-10/5-10	10/10	10/10	10/10
Particle – size distribution							63.3	31.6	5.1

<sup>1</sup>See figure 1 for sampling locations. Approximate mineral proportions are estimated volume percentages based on megascopic, microscopic, X-ray diffraction, and qualitative analyses.

<sup>2</sup>Sand = retained on No. 200 sieve (0.075 mm); silt = passing No. 200 sieve and retained on No. 400 sieve (0.038 mm); clay = passing No. 400 sieve.

<sup>3</sup>Includes trace amounts of above-listed minerals, magnetite, ilmenite, hematitic iron oxides, chlorite, hornblende, epidote, pyroxene, tourmaline, zircon, carbonaceous organic material, and trace amounts of unidentified chloride and sulfate salts.

Table 2. – Composition of 3:20 distilled water extracts of sediment samples.

Sample location	Concentration (mg/L)							
	pH	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Chloride	Sulfate
Muddy Creek below South Salt Wash	8.1	9	4	17	0.9	44	4	37
Muddy Creek at Hondoo Arch	8.1	9	4	22	0.9	39	8	44
Muddy Creek below Salt Wash	7.8	8	3	14	0.5	28	9	25
Muddy Creek at Hanksville	8.1	13	4	25	1.0	33	15	55
Dirty Devil River at Poison Spring	8.0	11	2	8	1.1	28	4	26
Composite	8.3	9	4	17	1.0	35	8	36

Table 3. – Composition of batch study replicate samples with water from Muddy Creek above Emery.

Contact time, h	Concentration (mg/L)							
	pH	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Chloride	Sulfate
0 (blank)	8.1	45	26	11	0.3	279	6	18
0.5	8.0	46	26	25	3.0	271	13	53
	8.1	47	26	24	2.5	275	13	53
	8.1	45	26	23	1.8	276	13	53
24	7.5	44	25	25	2.3	262	13	55
	7.7	43	25	24	2.4	264	13	55
	7.8	44	26	24	3.2	268	13	55
48	7.4	45	26	26	2.0	268	14	58
	7.6	44	25	25	2.6	265	14	57
	7.7	44	26	24	2.9	265	13	56
72	7.6	45	26	25	3.0	268	13	57
	7.7	44	26	24	3.0	268	13	56
	7.7	46	26	28	2.2	271	14	59
96	7.6	45	26	24	3.0	271	13	58
	7.7	45	28	25	3.3	268	14	57
	7.6	45	28	25	1.6	268	14	61
120	7.6	46	28	26	1.8	268	13	58
	7.7	45	28	24	2.9	268	14	56
	7.7	48	28	29	2.3	268	14	66
120 (blank)	7.8	45	26	11	0.3	266	6	17

Table 4. – Composition of batch study replicate samples with water from the Dirty Devil River at Poison Spring.

Contact time, h	Concentration (mg/L)							
	pH	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Chloride	Sulfate
0 (blank)	7.9	151	36	112	5.3	177	88	494
0.5	7.7	144	44	124	6.2	174	97	525
	7.9	151	47	130	6.2	180	96	531
	7.9	151	50	128	5.9	180	96	529
24	7.5	140	43	124	6.0	174	95	523
	7.6	141	44	124	6.0	177	95	529
	7.7	141	44	125	6.2	178	95	534
48	7.7	142	45	124	5.9	177	97	520
	7.6	152	53	129	5.8	177	96	533
	7.7	140	43	125	5.9	177	96	534
72	7.6	145	45	127	6.0	180	95	514
	7.7	141	43	125	5.9	180	97	535
	7.6	142	44	128	5.9	177	97	527
96	7.5	144	45	124	5.9	177	96	515
	7.5	146	47	129	6.2	180	97	539
	7.5	142	44	127	5.9	180	98	535
120	7.6	142	44	124	6.0	182	97	536
	7.6	143	45	127	5.8	180	97	538
	7.6	141	44	125	5.9	181	94	529
120 (blank)	7.8	151	36	113	5.4	176	87	487



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