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## Using Mass Balances to Estimate Flow Rates from Mine Drainage Sources

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### ABSTRACT

At mine sites with multiple drainage sources, individual flow rates are often difficult and/or labor-intensive to measure in the field; however, water quality samples of all individual sources can often be obtained much more easily. When the individual discharges combine to form a single, measurable surface stream, the flow rates of the individual sources can be estimated via ion mass-balance methods. The accuracy of this estimation technique was evaluated at a field site where flow measurements of three individual mine drainage sources were available. For each sampling date, the median of the mass balance calculations was taken as the "best estimate" of the flow rate of each source. For the largest flow component at the site, the estimated flow was consistently less than the measured flow, but was generally within 15% of the measured value. The estimates for the two smaller flow components yielded much larger errors (often greater than 100%) when compared to the individual measured flows. However, these errors were also less than 15% when normalized with respect to total flow at the site. Therefore, while ion mass-balances can be a useful reconnaissance tool for estimating relative flow rates, they should not be relied upon for quantitative calculations, especially for small flow sources.

Key words: laboratory analyses, field sampling, flow measurement

### INTRODUCTION

Accurate measurements or estimates of mine drainage flow rates are extremely important in the evaluation of their environmental impacts. For discharges from underground mines, the flow rate is often the dominant factor affecting the contaminant load (Aljoe and Hawkins, 1991; Hawkins, 1994). Although the contaminant concentrations in a given surface stream will generally

determine the type and number of aquatic species which may be present, the contaminant loads (flow rate times concentration) often serve as better indicators of the severity of the pollution source or sources. For example, Pennsylvania's remining regulations require that contaminant loads must not exceed the baseline contaminant loads measured prior to remining (Smith, 1988). Additional water treatment operations are required only if the post-remining loads exceed the baseline.

At mine sites with multiple discharge sources (mine adits, toe-of-spoil seepages, etc.), both water quality samples and flow measurements must be obtained at each source in order to identify their relative contributions to the overall contaminant load. While flow measurement methods (weirs, flumes, bucket-and-watch, etc.) are straightforward, their implementation at AMD field sites is often difficult and labor-intensive. Abandoned mine sites are particularly problematic because discharges often emanate from steep slopes or marshy areas that can be reached only by foot. Unless a convenient natural channel happens to be present, routing the water to a flow measurement device often cannot be accomplished with hand tools alone, especially when flows exceed about 400 gpm. Flow measurement structures must be cleaned and reinforced regularly to remain accurate; they also may have to be moved periodically if the location of the discharge point changes, as often occurs with diffuse seepages. By contrast, water quality sampling involves fewer restrictions and considerably less field labor than flow measurements. The only requirements for valid sampling are that a free-flowing portion of the discharge stream be accessible, and that the flow stream accurately represent the water quality of the source of interest. In practice, almost all discharges can be sampled, even those for which direct flow measurements are impossible.

At many sites, two or more mine discharges eventually combine to form a single surface stream, or enter a natural stream within a short distance from their points of emanation. If water quality samples are obtained from the combined stream and all of its sources, ion mass-balances can be used to estimate the percentage of the total flow contributed by each source. Only one flow measurement, at either the combined stream or any of the source locations, would then be required to estimate the flow rates and contaminant loadings from all sources. If these estimates are reasonably accurate, considerable savings in field costs could be realized. The greatest benefit would occur at sites with many discharge points and sites where installation and maintenance of flow collection and measurement structures is a problem. However, the accuracy of such estimates compared to direct field measurements has not been documented.

## OBJECTIVES

The primary objective of this study was to use ion mass-balance methods to estimate the flow rates of three different mine drainage sources at a field site, and compare these estimates with flow measurements obtained for all three sources. A secondary objective was to determine how the accuracy of the estimate was affected by the combination of ions chosen for the mass-balance calculations. The results would indicate the expected degree of error if the technique were used at other field sites where direct flow measurements would be costly and difficult.

## SITE BACKGROUND AND DATA COLLECTION

Figure 1(a) is a cross-section of the field study site, which is located in western Pennsylvania. The overall hydrology and water quality characteristics of this site have been described previously (Aljoe, 1992; 1994). The mine portals were sealed in a deliberate attempt to flood the mine; however, the hydrostatic pressure of the mine pool eventually caused a surface "blowout" about 45 m behind the portal seals. The borehole shown in Figure 1(a) was installed to collect the mine discharge at this point. The two other mine discharge sources at this site are two french drains, shown in Figure 1 (b), that collect mine water seepage in the portal seal area. The flows from the french drains and the borehole are routed to a manhole, and the combined discharge is sent to a nearby surface stream.

The flow rate of the combined mine discharge was measured with an H-type flume from December 1992 through June 1994. Flow rates of the french drains were measured by bucket-and-stopwatch methods. The terminus of the borehole discharge pipe at the manhole was inaccessible for similar flow measurement, so the borehole flow rate was calculated by subtracting the sum of the french drain flows from the total flow. Borehole flow rates calculated in this manner are referred to as "measured" rather than "calculated" in this paper, to avoid confusion with flows that are calculated from ion mass-balances. Total flow at the site ranged from 25 to 550 L/min; for most of the year, the borehole was the dominant flow source, comprising about 80% of the total flow. During the fall, the borehole flow rate slowed and sometimes ceased, and the west french drain was the major flow source. Flow from the west french drain was consistently 3 to 4 times greater than flow from the east french drain. The combined flow rate of the french drains did not exhibit significant seasonal fluctuations, remaining at about 30 L/min throughout the year.

Water quality samples were obtained at the locations shown in Figure 1 (c); samples were collected at least monthly, with a few exceptions, throughout the study period. A total of 19 samples were used in the subsequent analysis. All samples were analyzed for pH, acidity, alkalinity, total iron, ferrous iron, aluminum, calcium, magnesium, sodium, potassium, manganese, sulfate, and chloride. Ion chromatography was used for chloride analyses; all other ion analyses were by inductively-coupled plasma atomic emission spectroscopy (ICP). The water quality variations among the three discharge sources were discussed previously by Aljoe (1994), and the median concentrations are listed in Table 1. Note that the borehole discharge was the most contaminated (acid) source, followed by the west french drain. The east french drain discharge came primarily from the mine (high sulfate), but had a relatively high pH and was net alkaline. Because of the dominance of the borehole flow source for most of the study, the median values of the water quality parameters at the manhole outlet were very similar to those of the borehole.

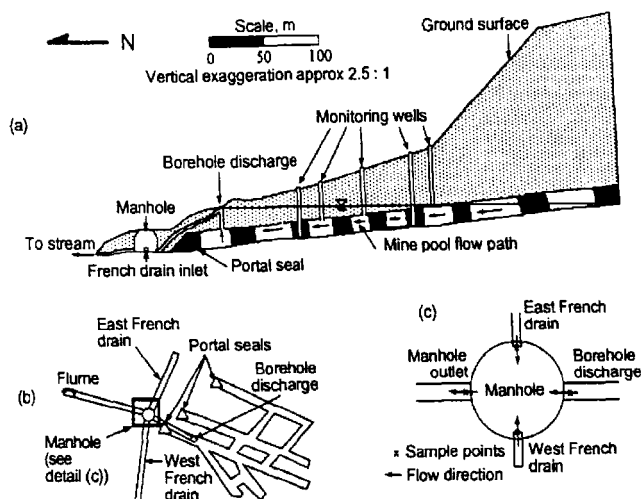


FIGURE 1. Schematic representation of study site: (a) Cross-section of mine pool; (b) Plan view of discharge area; (c) Manhole sampling points.

TABLE 1. Median water quality parameters in mine discharges.

Parameter	East French Drain	West French Drain	Borehole Discharge	Manhole Outlet
pH	6.37	4.31	3.07	3.10
Net Acidity	-47.1	174	285	263
Total Iron	25.6	61.6	80.0	73.9
Aluminum	3.5	12.0	16.0	15.2
Manganese	11.8	11.4	11.7	11.8
Calcium	233	215	175	186
Magnesium	51.1	66.9	68.9	68.1
Sodium	12.3	8.6	7.4	7.8
Potassium	4.6	3.12	2.75	2.8
Sulfate	769	970	996	985
Chloride	8.7	9.1	9.5	9.6

pH in standard units; all other data in mg/L

## DATA ANALYSIS

The basic mass-balance equation used to estimate flow was:

$$C_{j,t}Q_t = \sum_{i=1}^n C_{j,i}Q_i \quad (1)$$

where  $C_j$  is the concentration of ion  $j$ ;  $Q$  is the flow rate;  $n$  is the number of individual flow sources (in this case,  $n=3$ ); the subscript  $t$  denotes the total flow stream (manhole outlet); and the subscript  $i$  ( $i=1-3$ ) denotes an individual flow source (borehole, east french drain, or west french drain). The assumptions implicit in equation 1 include: (1) the measured concentrations accurately represent the total chemical compositions of the flow streams from which they were taken (this is a reasonable assumption, since cation/anion ratios of all samples were within 3% of unity); (2) the sources were completely mixed prior to sampling at the manhole outlet; (3) no leakage occurred either into or out of the manhole other than through the source inlet and main outlet pipes; and (4) all ions behaved conservatively (no precipitation or other chemical reaction) throughout the sampling domain. Since iron and aluminum were observed to precipitate in the manhole, these two ions were eliminated from the mass-balance analyses. Other field conditions which could have caused violations of these assumptions are discussed in this paper after the results are presented.

For computation purposes, equation 1 was divided by the total flow  $Q_t$  to yield:

$$C_{j,t} = \sum_{i=1}^n C_{j,i}Q'_i \quad (2)$$

and

$$Q'_i = Q_i/Q_t \quad (3)$$

where  $Q'_i$  is the fraction of the total flow originating from flow source  $i$ . For this analysis, the measured concentrations  $C_{j,t}$  and  $C_{j,i}$  were used in equation 2 to estimate the flow fractions  $Q'_i$  of the three individual flow sources. Since there were three unknown flow fractions, equation 2 was formulated for three different ions, and the three resulting equations were solved simultaneously. A spreadsheet program for a personal computer was used to perform the matrix inversion and multiplication functions required to achieve this solution. The estimated flow fractions  $Q'_i$  and the total measured flow rate  $Q_t$  were then used in equation 3 to estimate the flow rates of the sources.

Since only three ions were needed to perform the mass-balance analyses, there was some question as to which ions were the "best" ones to use; no physical or chemical justification for relying on a particular ion set or sets could be found *a priori*. For each of the 19 sampling dates, there were seven ions (Ca, Mg, Na, Mn, K,  $SO_4$ , and Cl) that appeared to be suitable for formulating mass-balance equations. In addition, the mass-balance of water:

$$Q_t = \sum_{i=1}^n Q_i \quad \text{or} \quad \sum_{i=1}^n Q'_i = 1 \quad (4)$$

is identical in form to equations 1 and 2; the only difference is that the coefficients  $C_{j,t}$  and  $C_{j,i}$  are unity. Inclusion of the water balance equation provided an eighth "ion" (water) for use in the analysis. This allowed a total of 56 different three-ion sets of equations to be formulated for each sampling date. The computer spreadsheet mentioned above was expanded to facilitate these calculations and to compute the mean and median estimated flow rates for each source on each sampling date. These estimates were then compared to the measured flow rates for each source and date, and errors (measured minus estimated flows) were computed. The results of the 56 individual mass-balance calculations for each sampling date were also examined to determine whether one or more ion sets consistently yielded more accurate flow estimates than others.

### RESULTS

Probably the most notable result of the analysis was the large number of mass-balance calculations that yielded "invalid" flow rates. A result was considered invalid when one or more of the flow fractions  $Q'_i$  computed from equation 2 was negative. Figure 2 shows that on most sampling dates, less than 50% of the mass-balance calculations yielded "valid" results. Figure 3 shows that no single ion set could be relied upon throughout the analysis; the two sets that yielded valid results most often (Ca-Mn-SO<sub>4</sub> and Na-SO<sub>4</sub>-H<sub>2</sub>O) still failed on more than 30% of the sampling dates. Factors which may have been responsible for the high percentage of invalid mass-balance calculations at this field site are discussed later in this paper.

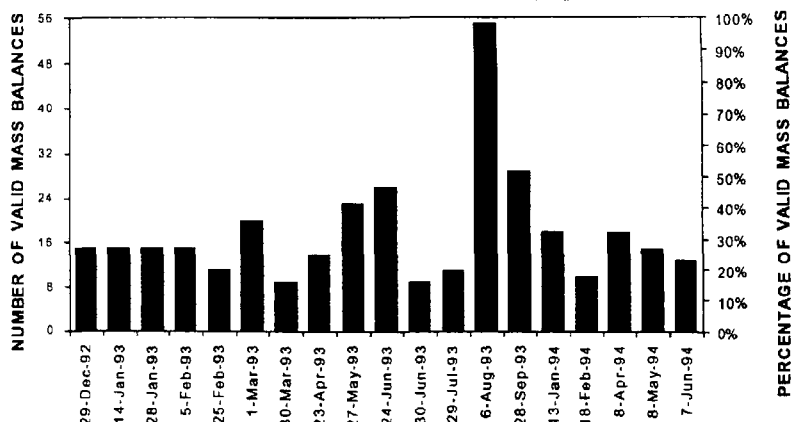
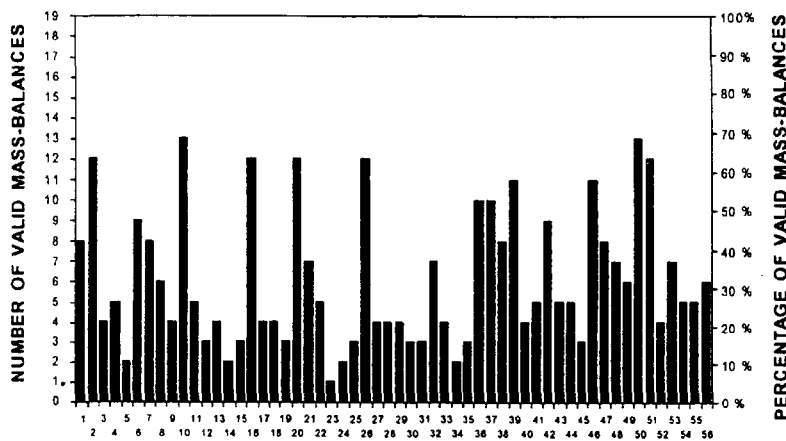


FIGURE 2. Summary of validity of mass-balance calculations, by date.



I.D.#	Ion Set	I.D.#	Ion Set	I.D.#	Ion Set	I.D.#	Ion Set
1	Ca, Mg, Na	15	Ca, K, Cl	29	Na, SO4, K	43	Mg, SO4, H2O
2	Ca, Mg, Mn	16	Mg, Na, Mn	30	Na, SO4, Cl	44	Mg, K, H2O
3	Ca, Mg, SO4	17	Mg, Na, SO4	31	Na, K, Cl	45	Mg, Cl, H2O
4	Ca, Mg, K	18	Mg, Na, K	32	Mn, SO4, K	46	Mg, Mn, H2O
5	Ca, Mg, Cl	19	Mg, Na, Cl	33	Mn, SO4, Cl	47	Na, Mn, H2O
6	Ca, Na, Mn	20	Mg, Mn, SO4	34	Mn, K, Cl	48	Na, K, H2O
7	Ca, Na, SO4	21	Mg, Mn, K	35	SO4, K, Cl	49	Na, Cl, H2O
8	Ca, Na, K	22	Mg, Mn, Cl	36	Ca, Mg, H2O	50	Na, SO4, H2O
9	Ca, Na, Cl	23	Mg, SO4, K	37	Ca, Na, H2O	51	Mn, SO4, H2O
10	Ca, Mn, SO4	24	Mg, SO4, Cl	38	Ca, Mn, H2O	52	Mn, Cl, H2O
11	Ca, Mn, K	25	Mg, K, Cl	39	Ca, SO4, H2O	53	Mn, K, H2O
12	Ca, Mn, Cl	26	Na, Mn, SO4	40	Ca, K, H2O	54	SO4, K, H2O
13	Ca, SO4, K	27	Na, Mn, K	41	Ca, Cl, H2O	55	SO4, Cl, H2O
14	Ca, SO4, Cl	28	Na, Mn, Cl	42	Mg, Na, H2O	56	K, Cl, H2O

FIGURE 3. Summary of validity of mass-balance calculations, by ion set.

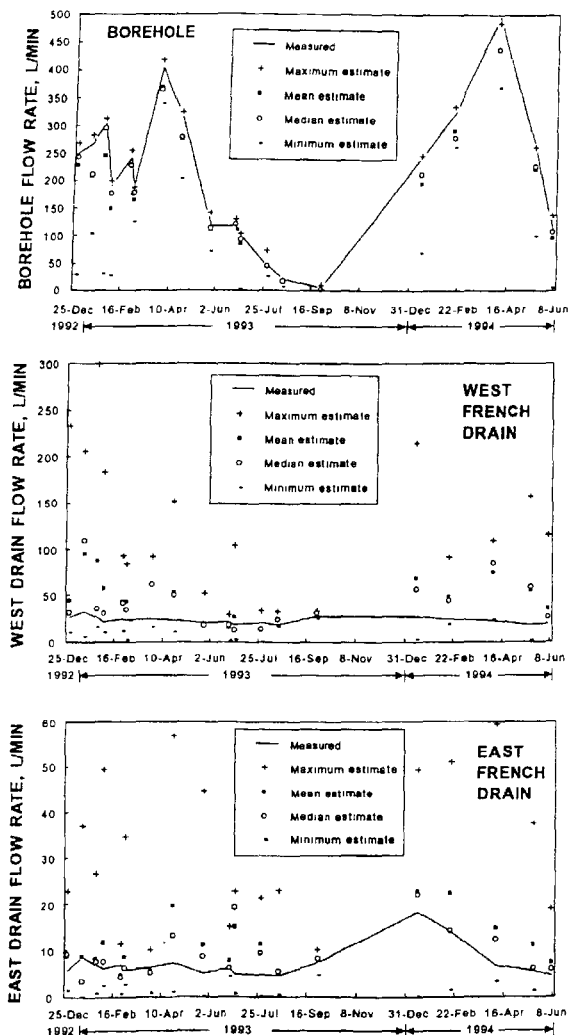


FIGURE 4. Measured and estimated flow rates at mine discharge sources.

The data in figures 2 and 3 reflect only the validity, not the accuracy, of the mass-balance calculations. Figure 4 shows that many of the flow estimates obtained from individual "valid" mass-balances were vastly different than the flow rates measured in the field. To establish a consistent standard for comparison to measured flows, the median of the mass-balance calculations was used as the "best estimate" for each source on each sampling date. Comparison of errors showed that the median rather than the mean was the more accurate estimator, probably because the median is not as severely influenced by very high or low individual mass-balance estimates.

In order to evaluate errors in the median estimates for each flow source and date, the errors were normalized in terms of both the flow rate at the source the total flow at the site (figure 5). Since the french drains generally had low flow rates, estimation errors that were rather small in terms of total flow at the site (errors on the order of 5-10 L/min) appeared to be relatively large when expressed as a percentage of the individual french drain flows. Median errors for the west french drain ranged from about -50% to 300% of the measured flows (Figure 5); errors for the east french drain typically ranged from -50% to 100% of the measured flows. However, figure 5 also shows that the errors in estimating the french drain flows were far less significant (almost always 15% or less) when expressed as a percentage of the total flow at the site.

Figure 5 also shows that the median estimation error for the borehole source was usually less than 15% of the measured borehole flow; these errors were consistently lower than those of the french drains because the borehole was almost always the dominant source. For the same reason, the decrease in percentage error was less marked when the borehole estimation errors were normalized as a percentage of the total flow. The relative importance of these types of estimation errors, in terms of overall utility of the mass-balance estimation technique, is discussed below.

Figure 5 also illustrates several other general trends with respect to flow estimation errors at this site. For example, the median of the mass-balance calculations usually overestimated the flow rate of the two french drains (positive errors), with larger and more consistent positive errors in the case of the west french drain. For the borehole source, errors were almost always negative, indicating that the median mass-balance calculation consistently underestimated the borehole flow. Also, the largest percentage errors in the borehole flow estimates occurred at the lowest borehole flows; no such trend was observed in the french drain errors.

### DISCUSSION

The surprisingly large number and high percentage of "invalid" mass-balance calculations cited above is the first problem that must be addressed if the technique is to be used to facilitate flow estimation. The problem was traced to two principal factors: (1) the concentrations of many of the ions in the sources and the manhole outlet were very similar to each other; and (2) the mass-balance calculations are very sensitive to very small differences in ion concentrations. Random errors introduced through sampling and analytical procedures were apparently sufficient to cause both a large number of invalid calculations (figures 2 and 3) and a wide range of flow estimates for those calculations which were valid (figure 4). Perhaps the best way to illustrate these effects is to consider an example mass-balance calculation using the median ion concentrations listed in Table 1. Although these exact parameter values were not measured on any given date, their absolute and relative magnitudes are typical of what was measured during the course of the study.

First, the concentrations of the ions in the three sources listed in Table 1 and the median measured flow fractions for each source (0.8699, 0.1019, and 0.0282) for the borehole, west french drain, and east french drain, respectively), can be used in equation 2 to calculate the "expected" concentrations of all ions in the manhole outlet. Table 2 shows that these expected ("Calculated") ion concentrations at the manhole outlet are very close to the actual median ("Measured") concentrations taken from Table 1 -- all are within 3 percent of each other. However, when mass-balances are performed with the source concentrations in Table 1 and the "Measured" outlet concentrations in Table 2, 42 of the 56 calculations yield invalid results. It is therefore apparent that even slight variations in ion concentrations can cause the mass-balance calculations to produce many invalid results. In fact, laboratory error alone could cause such results; while the ICP and ion chromatography analytical techniques are generally considered to be very accurate (within 3 percent of actual concentration), this can be sufficient to substantially affect the results of the mass-balance calculations.

Sampling variability is often more difficult to quantify than analytical variability, and could cause the assumptions inherent in the mass-balance equation to be violated. For example, residence time within the manhole was only about 0.5 to 5 minutes, which may not have allowed complete mixing to

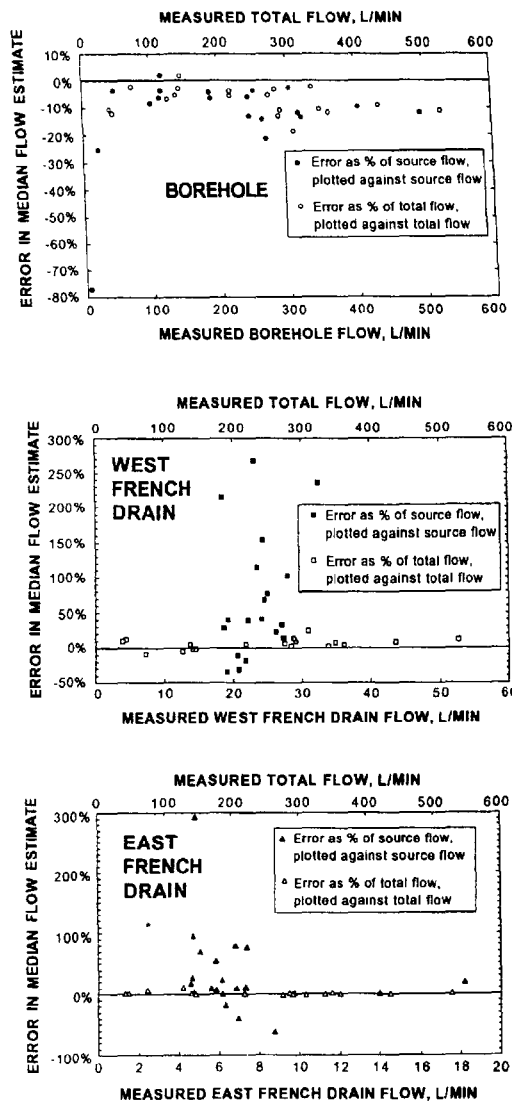


FIGURE 5. Normalized errors in mass-balance flow estimates.

TABLE 2. Effect of minor concentration differences on mass-balance calculations.

Parameter	Concentrations at manhole outlet, mg/L		Percentage difference in concentration
	Calculated	Measured	
Calcium	180.42	185.98	-2.99%
Magnesium	68.15	68.05	0.14%
Sodium	7.66	7.82	-1.93%
Manganese	11.66	11.80	-1.19%
Sulfate	986.85	985.00	0.19%
Potassium	2.84	2.80	1.43%
Chloride	9.44	9.60	-1.70%
<b>Number of invalid mass balances</b>	<b>0</b>	<b>42</b>	

occur. Slight changes in source concentrations, on the order of those shown in table 2, could have occurred within the time lapse (about 5 min.) between the first and last sample taken on each day. Chemical reactions such as the co-precipitation of manganese with iron or loss of sulfate with aluminum precipitation, while negligible from a pollution loading standpoint, may also have been sufficient to cause concentration discrepancies of this magnitude. The minor seepage of shallow groundwater into the sides of the manhole (too diffuse to sample) was observed during rainy periods; again, this effect could easily be neglected for most purposes, but perhaps not for mass-balance calculations.

Surprisingly, the presence of a high percentage of valid mass-balances on a given date did not greatly improve the accuracy of the estimates obtained by selecting the medians of the mass-balance calculations. If this were the case, a strong negative correlation would exist between the percentage of valid calculations and the absolute errors of the median flow estimates. However, the correlation coefficient between the percentage of valid estimates and the percentage error in the borehole flow estimate was weakly positive (0.220), opposite of what would be expected. Only weak negative correlations were found between the percentage of valid mass-balances and the percentage errors of the median flow estimates of the east and west french drains (coefficients of -0.459 and -0.339, respectively). These findings suggest that the small inaccuracies in sampling and analysis caused "invalidity" to occur in a high percentage of cases at this study site simply because the source and outlet concentrations were so similar. If the concentrations of the sources and outlet had been less similar, more of the results may have been "valid", but the errors in the flow estimates may not have been greatly reduced.

While the inherent sensitivity of the mass-balance calculations can explain much of the error in the flow estimates at this site, it cannot explain why the french drain flow rates were overestimated and the borehole flow rate was underestimated in a disproportionate number of cases (figure 5). One factor that could produce these trends is the incomplete mixing of water within the manhole. Water sampling at the manhole outlet (figure 1 (c)) consisted of slightly submerging a 125 mL or 250 mL sample bottle into the center of the outlet flow stream, about 10 cm downstream from the entrance to the outlet pipe. This procedure was chosen because it minimized the amount of iron hydroxide particulate in the samples and consequently obviated the need to filter the samples in the field. However, if water quality of the outlet flow stream were stratified such that the slightly less-contaminated water from the french drains were near the surface, the french drains would be over-represented and the borehole would be under-represented in the water quality of the manhole outlet sample. Another systematic error that would yield the trends in figure 5 is related to the flow measurement procedure. The ends of the french drain pipes were submerged in standing water within the manhole; in order to measure flow, 45° PVC elbows were force-fit onto the submerged pipes, and turned upward such that a small bucket could be placed beneath their spillover. Leakage at the submerged joints, if present, would not have been detected; this would mean that the "measured" french drain flow rates would have been less than the actual flow rates. Since the french drain flows were subsequently subtracted from the total flow to calculate the borehole flow rate, the error resulting from leakage would have been exacerbated by an overestimation of the "measured" borehole flow.

Finally, it should be noted that the water flow and quality data discussed above were collected under a broad program to remediate the acidic drainage at this site; determination of source flow rates via mass-balances and minimization of sampling errors were not the primary purposes of the sampling program. If the primary goal were to make the mass-balance flow estimates as accurate as possible, greater efforts to reduce or quantify the degree of sampling and analytical variability (field blanks, duplicate samples, field filtering, concurrent sample collection, more rigorous flow measurement, etc.) would have to be undertaken. However, this would increase the cost of the effort and reduce its desirability compared to direct flow measurement. More importantly, the sampling and analytical procedures used here were similar to those which would be employed in a typical mine drainage site investigation. The purpose of the foregoing analysis was to determine whether reasonable estimates of flow rates could be obtained in cases where water quality data were collected but flows were not measured directly.



## CONCLUSIONS

The errors associated with using ion mass-balances to estimate flow rates at this mine site typically ranged from 2% to -15% of the measured flow at the largest flow source. For two smaller sources, however, estimation errors typically ranged from -50% to as much as 300% of the measured flows. Thus, it can be concluded that the mass-balance technique should not be relied upon to accurately quantify the flow rates of small flow sources, especially if the small sources are believed to be major contributors to the overall pollution load coming from the mine site. In such cases, direct measurement of the flow rates of all sources would be essential. However, if the dominant flow source at the site is at least as contaminated as the smaller sources, it will almost certainly be the greatest contributor to the pollution load. At such a site, if an error of approximately 15% in the measurement of pollution load is acceptable, and if the direct measurement of the source flows is difficult, mass-balance estimation of individual source flow rates coupled with direct flow measurement at any convenient location in the flow stream may prove to be useful. Initial reconnaissance studies at remote mine sites often fall into this category.

Mass-balance techniques may also be useful in obtaining initial order-of-magnitude approximations of the flow rates of mine drainage sources which enter a larger surface stream. Flow measurements may already be available at a downstream gaging station, and mass-balance studies similar to the one described in this paper could be performed to determine the relative contribution of each mine source to the stream of concern. In such cases, inaccuracies in flow measurement on the order of 100% or more may be acceptable, as long as the relative magnitudes of the sources are correct and the estimation errors are only a small percentage of the total flow of the surface stream. Remediation efforts could then be focused on the sources with the greatest pollutant loads.

The sensitivity of mass-balance calculations to very small differences in ion concentrations can result in a wide variation of flow estimates for a given sampling date. This suggests that a comparatively unbiased parameter (e.g., the median of the mass-balance calculations) be used as the best estimate of the flow rate for that source and date. If the concentrations of several ions at two or more of the sampling points are very similar to each other, this sensitivity can cause a large number of "invalid" results (negative flow estimates) to occur; however, the accuracy of the flow estimate obtained by using the median of the mass-balance calculations is not greatly reduced in such cases. Analysis of all possible combinations of seven ions typically present in mine drainage showed that there is no single "preferred" ion set whose mass-balance will yield more accurate flow estimates than the median of all ion mass-balances.

Consistent error trends in the mass-balance estimates at this study site could not be attributed solely to inherent variation in the mass-balance calculations. Possible systematic errors in water quality sampling and flow measurement were identified; these errors may have resulted in the french drains being consistently over-represented in the final water quality sampling and/or under-represented in the direct flow measurements, and vice versa for the borehole discharge.

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