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TECHNICAL ARTICLE

Quantification of Changes in Metal Loading from Storm Runoff, Merse River (Tuscany, Italy)

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Abstract The Merse River in Tuscany is affected by mine drainage and the weathering of mine wastes along several kilometres of its catchment. The metal loading to the stream was quantified by defining detailed profiles of discharge and concentration, using tracer-dilution and synoptic-sampling techniques. During the course of a field experiment to evaluate metal loading to the Merse, such data were obtained for both storm and pre-storm conditions, providing a unique opportunity for comparison. Iron, Cu, and Mn were chosen to illustrate changes resulting from the storm. The total-recoverable load of Fe increased 21-fold, while loads of Cu and Mn increased by 8- and 7-fold, respectively, during the storm runoff. The increases most likely resulted from flushing particulates from near the stream, resuspension of colloidal material from the streambed, and increased ground-water inflow to the stream. The increases in Cu and Mn loads results from their association with colloids. It is possible that in-stream colloids had relatively more Cu than Mn, while near-stream colloids had relatively more Mn. Each of the metals also increased as a result of increased ground-water discharge during the storm. Despite great increases in load, the filterable concentrations of these metals did not increase substantially, remaining below chronic levels of toxicity.

Keywords Metal loading · Storm runoff · Colloids · Mine drainage · Tracer injection · Italy

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Introduction

The Merse River, located in southern Tuscany (Fig. 1), has been affected by centuries of mining. In September 2006, the mine drainage was being treated before being discharged to Fosso di Ribudelli, and was not a source of base metals to the Merse. However, mine wastes throughout the catchment contributed metals to the stream. These exposed mine wastes, including waste-rock dumps, flotation tailings, and metallurgical wastes, have been described by Benvenuti et al. (1997). The wastes are subject to erosion and, over time, have been flushed to the stream by storm runoff. In support of the Regione Toscana, a spatially detailed sampling of stream and inflow sites occurred before and during storm runoff in September 2006.

Studies of temporal variation from seasonal and storm runoff have documented changes in concentration of major ions and trace elements. The importance of changes during storm runoff was followed for major ions by Miller and Drever (1977) during a study of chemical weathering in the Absoroka Mountains, MT, USA. Like earlier studies of seasonal variation in the Matole River of California (Kennedy and Malcolm 1977), Miller and Drever (1977) found that hysteresis of concentrations over time was typical. In studies of seasonal change in streams affected by mine drainage, Nagorski et al. (2003a, b) found linear relations of major ions and discharge, but non-linear relations of trace elements and discharge. They also found that short-term

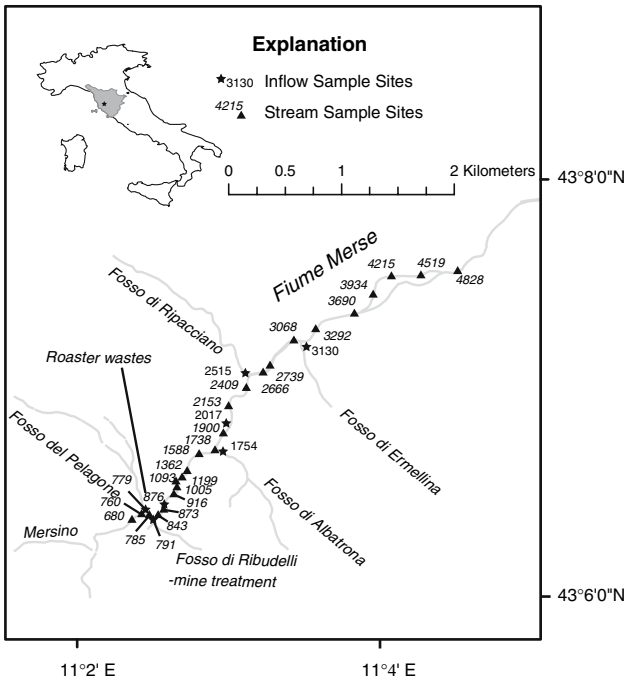

Fig. 1 Study area with location of the sampling points

storm runoff caused important temporal variability within the scheme of seasonal variation. Sampling during a snowmelt runoff in an acidic, metal-rich stream, Kimball (1999) found snowmelt, which typically is acidic in comparison to stream water, actually increased the pH of the stream, causing greater sorption of metals onto iron colloids during the seasonal runoff. Al and Blowes (1996) observed the contribution of tailings pore waters to stream runoff near a Cu–Zn sulphide mine, and found that the storm mobilized pore-water metals to the stream, but in proportions lower than originally reported by others. Sandén et al. (1997) followed variations in trace-metal chemistry through a storm event, noting decreases in Cu and Zn as concentrations of other elements increased with the storm wave. The different behavior was attributed to different sources for the elements. Our study differs from each of these studies because of the hydrologic framework established by using an injected tracer to quantify the hydrologic context before and during storm runoff. Results of this study not only provide baseline information to facilitate remediation planning for Regione Toscana, but also provide an opportunity for a detailed quantification of changes that occurred in the stream as a result of the storm runoff.

The Merse River begins more than 1 km upstream from the study reach indicated in Fig. 1. The storm comparison addressed here includes samples beginning at 680 m and ending at 4,828 m. Samples upstream and downstream from that reach were part of a companion study (Biochemielab and Bianchi 2006). The injection of Br tracer was at 680 m. Downstream, at 791 m, the mine-treatment inflow, which was combined with the Fosso di Ribudelli, enters the Merse. From 873 m to about 1,200 m, substantial ground-water inflow occurred, contributing water that was affected by weathering of sulphide minerals in roaster-waste piles along the left bank (downstream orientation). Three additional tributaries included the Fosso di Albatrona at 1,754 m, Fosso di Ripacciano at 2,515 m, and Fosso di Ermellina at 3,130 m.

Methods

Quantification of metal loading to streams supports the process of making decisions about stream remediation because sources are best compared in terms of their loading. Our approach to quantification of metal load relies on detailed spatial sampling of stream and inflow sites (synoptic sampling) and tracer injection to quantify discharge along a study reach (Kimball et al. 2002; Miller and Miller 2007). Traditionally, loading of solutes from a catchment has been quantified at the outlet of the catchment (Fig. 2a), a successful approach for many applications. However, when many possible sources of metal loading occur in a catchment, a detailed approach that extends up into the catchment is needed to allow the identification and comparison of the various sources. Our approach is to identify all the visible inflows that may represent sources of loading during a reconnaissance of the study reach. We then choose stream sampling sites to bracket the inflows to allow for mass balance calculations (Fig. 2b). Additional stream sampling sites at regular intervals help quantify inflow of ground water and supplement the necessary spatial detail of synoptic sampling. Combining a longitudinal profile of discharge, calculated by tracer dilution, with spatially detailed samples of stream and inflow chemistry allows the calculation of mass-loading profiles to detect and compare

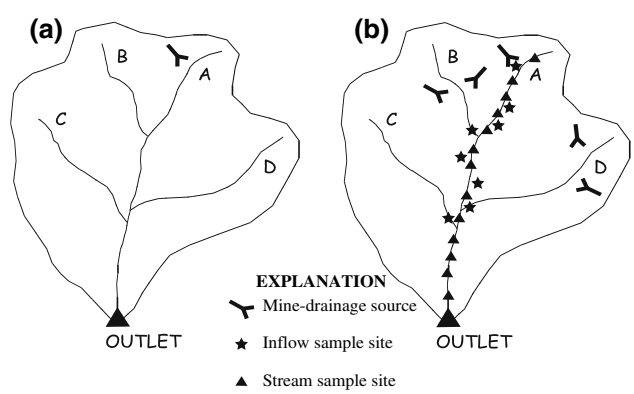

Fig. 2 Sampling design for **a** a single-sample approach at the outlet of a catchment versus, **b** detailed multiple-sample, synoptic sampling to quantify loading from multiple sources of metals in a catchment

metal sources and to quantify the mass transfer of processes affecting metal transport. This is accomplished by designing a field-scale experiment (Kimball et al. 2003). Figure 1 indicates the 49 stream sites and 9 inflows sampled along this 4,148 m study reach of the Merse.

Samples were obtained using standard USGS methods (Ward and Harr 1990) and methods previously described by Kimball et al. (2002). Only three filtered (0.45-µm filtration) samples were obtained during the pre-storm sampling; all the rest of the pre-storm samples were total-recoverable samples, which are unfiltered, acidified samples. Acidification of an unfiltered sample results in the dissolution of Al, Fe, and Mn colloids and release of any metals that might be sorbed to them. Both filtered and total-recoverable samples were obtained during the storm sampling. During the storm, additional samples were obtained from an auto sampler at 2,409 m, covering a period from 06:00 to 16:00. These samples indicate the variation of concentrations at a single site over time. The suspended colloids during the storm resulted in the formation of a filter cake on the in-line capsule filters; the effective pore size for the filtered sample most likely was much less than 0.45 µm. Concentrations of many metals were determined, but this discussion will be limited to changes in discharge, Cu, Fe, and Mn. A more comprehensive, companion evaluation was prepared for Regione Toscana (Biochemielab and Bianchi 2006).

Results and Discussion

A continuous injection of 300 L of NaBr solution at 66 mL/min was initiated at 15:41 on 9/22/06, 2 days prior to synoptic sampling. The injection of Br caused a substantial increase over the background Br concentration of ≈0.04 mg/L upstream from the injection. The concentration of the injectate was 127,700 mg/L Br. Conditions for the pre-storm sampling on 9/24/06 were stable, indicated by a steady Br concentration at two auto-sampler locations. Sampling on 9/24/06 represented a near steady state profile of discharge and stream chemistry, and the pre-storm profile of Br indicates the locations where both ground and surface inflows caused increases in discharge (Fig. 3a). The corresponding discharge was calculated from the Br dilution, using to an equation modified from Kilpatrick and Cobb (1985):

$$Q_s = \frac{Q_{inj} C_{inj}}{C_s - C_{bg}} \quad (1)$$

where: Q_s is the downstream discharge, in L/s, Q_{inf} is the injection rate, in L/s, C_{inf} is the injectate concentration of Br, in mg/L, C_s is the concentration of Br at the downstream site, in mg/L, and C_{bg} is the background, pre-injection concentration of Br in the stream, in mg/L.

The Br concentration profile indicates the steadily increasing discharge downstream during pre-storm conditions (Fig. 3b). The storm started about 07:00 hours the day of synoptic sampling on 9/25/06, with heavy rainfall that continued until past 12:00. Synoptic sampling started at 10:00 and ended about 14:30, so the storm runoff was decreasing at the most upstream sampling sites. The resulting variation of bromide was very different from the pre-storm variation. Downstream from 2,739 m, the pre-storm and storm Br concentrations were similar, indicating that the storm wave had not arrived downstream when those samples were collected during the storm. However, the small difference in Br concentrations downstream from 2,739 m indicates a small increase in discharge before the

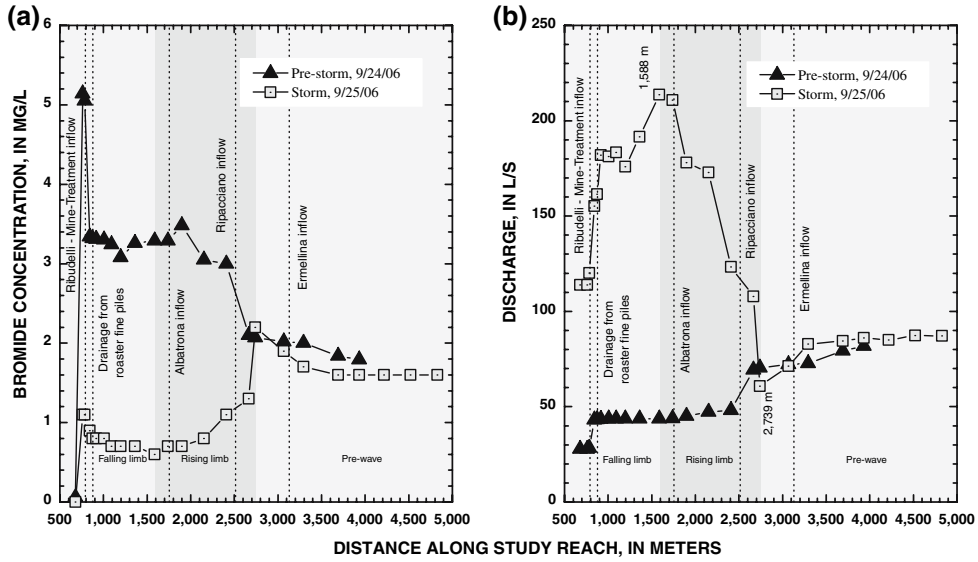

Fig. 3 Variation of **a** bromide concentration and **b** calculated discharge with distance along the study reach, Merse River, Tuscany, September 2006. *Shaded areas* represent temporal aspects of the spatial storm profile: Pre-wave, downstream from the storm wave; Rising limb, the time of increasing discharge from the storm wave; Falling limb, the time of decreasing discharge

larger storm wave reached that section of the stream. Upstream from 2,739 m, however, Br concentration was lower, indicating greater discharge upstream (Fig. 3a). The corresponding discharge shows that the peak in discharge for the storm synoptic sampling occurred at 1,588 m (Fig. 3b). The storm wave, as sampled by the synoptic profile, was not instantaneous; the wave was moving downstream as we sampled downstream to upstream. Thus, the discharge and subsequent loading profiles during the storm represent a wave with a rising limb from 2,739 m to the peak at 1,588 m and then a falling limb from the peak upstream to 680 m. Thus, both spatial and temporal aspects of the data set are illustrated in Fig. 3 and subsequent figures. For pre-storm samples, the ordinate indicates the spatial changes along the study reach. For storm samples, the shaded areas from right to left represent the pre-wave period, then the rising limb, and finally the falling limb of the storm wave.

The greatest visual difference between pre-storm and storm conditions for the Merse was the increased abundance of suspended colloidal Fe, which created a dark ochre color during the storm. The increase in total Fe concentration is quantified by the comparison between the 2 days (Fig. 4a). Those points representing total Fe concentrations along the study reach for pre-storm conditions represent a near steady-state Fe profile, but the broad peak in total Fe concentration during the storm represents non-steady state, temporal variation resulting from the storm wave. Pre-storm increases like those upstream from Fosso di Albatrona and Fosso di Ermalina were related to spatial variation along the study reach. On the other hand, the total Fe concentration at the peak of the storm wave was more than 20 times greater than the pre-storm concentration. At 3,934 m, the storm concentration was still more than 25 times higher than the pre-storm concentration. This site was the most downstream sample of the pre-storm conditions and a location where the storm wave had not reached full impact. Total Fe concentrations downstream from Fosso di Emilina were much lower than in the storm wave, but the relative increase in total Fe concentration indicates some initial flushing.

Pre-storm Fe concentrations indicated a decrease at the site just downstream from Fosso di Ribudelli, followed by a substantial increase as the stream passed the roaster-waste piles (Fig. 4a). Because the mine discharge was treated before entering Fosso di Rubidelli and the Merse, its addition caused a decrease rather than an increase in concentration at 843 m. During the storm, the decrease in concentration was mostly overwhelmed by the increase in concentration from upstream sources. Essentially all of this increase in total Fe concentration during the storm was a result of increased colloidal iron. For example, at 2,409 m the filtered pre-storm Fe concentration for temporal samples was 6.3 μg/L, and the colloidal concentration was 2,930 μg/L, more than 450 times greater (Fig. 4a). Near the peak of the storm wave at 2,409 m, the filtered Fe concentration decreased to 4.7 μg/L, but the colloidal concentration was 16,400 μg/L, more than 3,000 times greater than filtered Fe. The maximum total Fe concentration during the storm, at 1,739 m, preceded the peak of the discharge at 1,588 m (Fig. 3b). This separation suggests the importance of the flushing of colloidal material. Even the small increase in discharge during the pre-wave period initiated an increase in total Fe concentration. This initial flushing could have suspended colloidal material from the streambed, where colloidal Fe had been deposited in every pooled area. Additional flushing with substantial rainfall from mine-waste materials away from the stream could have caused the higher peak in total Fe concentration at 1,738 m. These changes in Fe are important because colloidal Fe can have substantial effects on the physical habitat and can adversely affect aquatic organisms (Besser et al. 2001). Colloidal Fe also increases trace-element transport (Church et al. 1997; Kimball et al. 1995).

Variations of Cu and Mn concentrations (Fig. 4c, e) indicate similarities and differences before and during the storm, demonstrating the effects of colloidal transport and reactive processes. Both Cu and Mn principally occurred in the colloidal phase (Fig. 4c, e). The strong affinity of Cu for transport in the colloidal Fe phase at near-neutral pH, which occurred both before and during the storm, is evident in the difference between filtered and total Cu concentrations (Runkel et al. 1999; Schemel et al. 2000; Smith 1999). Colloidal Mn has been observed in other streams affected by mining that have high pH (Harvey and Fuller 1998; Kimball et al. 2001). During the storm, transport of both Cu and Mn was dominated even more by the colloidal phase. Before the storm, Cu and Mn concentrations decreased substantially downstream from the mine-treatment inflow at 843 m, similar to the variation of Fe concentration (Fig. 4a, c, e). Downstream between 916 and 1,199 m, both metal concentrations increased substantially. The highest inflow concentrations of both Cu and Mn were in samples of drainage from the roaster-fine piles at 876 m, in the area where the roaster-waste pile influenced stream concentrations, but the increases continued downstream from this visible inflow. Increases also occurred between 1,362 and 1,738 m. Although there were no visible inflows in this section of the stream, a small, dark-red pool of acidic water was found downstream from 1,362 m that may indicate where dispersed roaster-waste material was contributing metals to the stream. A second area of dispersed inflow that caused an increase in Fe and Cu concentrations, but not Mn concentrations, occurred between 2,739 and 3,068 m.

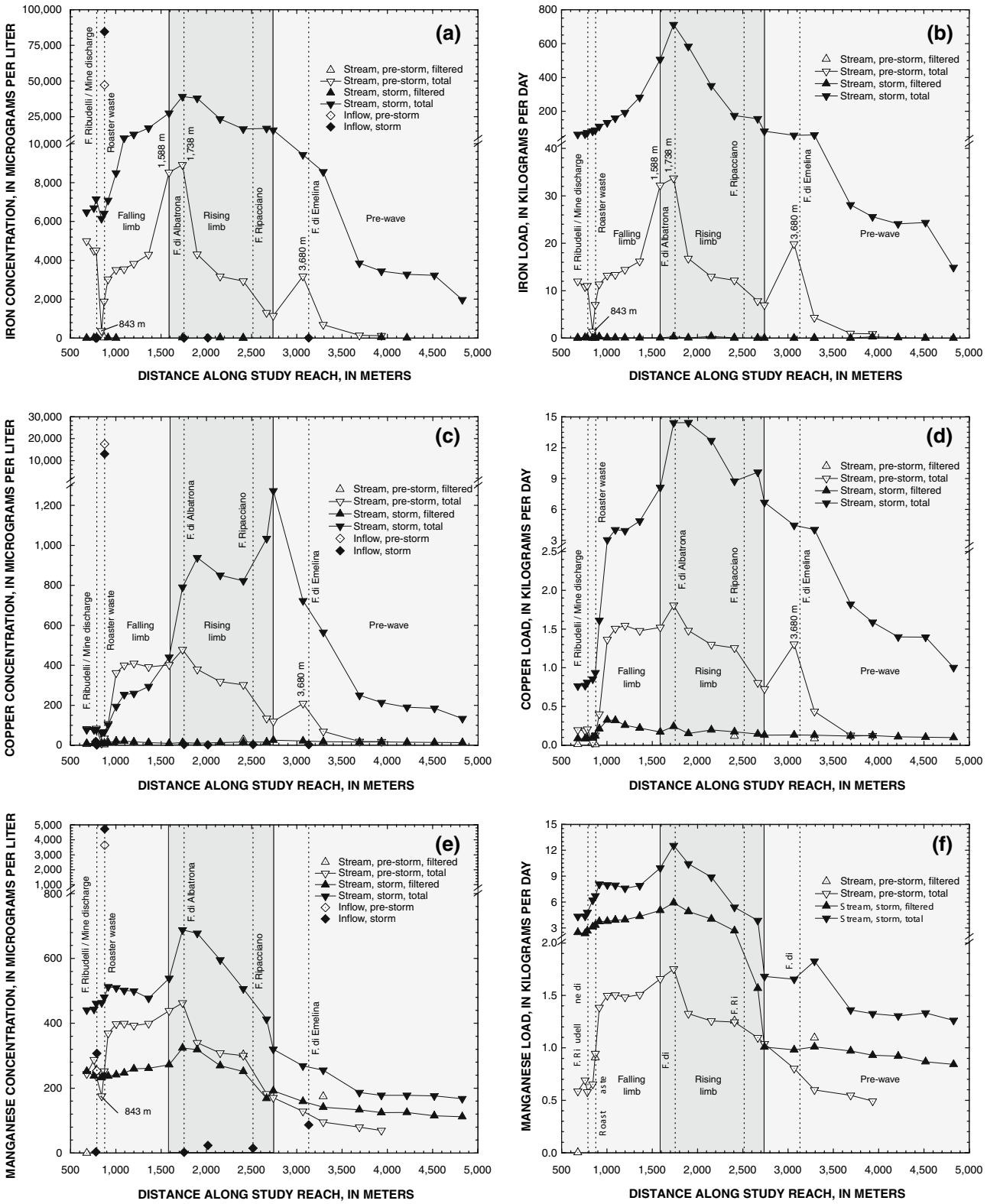

Fig. 4 Variation of concentrations and loads for **a** and **b** iron, **c** and **d** copper, and **e** and **f** manganese with distance along the study reach, Merse river, Tuscany, September 2006

During the storm, most of the increase in total-recoverable Cu and Mn concentrations was from the increase in the colloidal phase, similar to what was observed for the Fe concentrations (Fig. 4a, c, e). For total-recoverable Mn concentration, however, a small amount of the increase was from filterable Mn (Fig. 4e). Filterable Cu concentrations remained low during the storm and did not exceed chronic toxicity levels before or during the storm. In the period ahead of the storm wave, both Cu and Mn total-recoverable concentrations were greater than before the storm (downstream from 2,739 m). Concentrations of total Cu increased much more than Mn concentrations, reaching a maximum at 2,739 m. If this pre-wave increase is a result of resuspension of streambed colloids, then this would suggest a difference in composition of the colloidal material in the streambed as opposed to colloidal material washed in from near the stream. The maximum total Mn concentration essentially coincided with total Fe concentration, near 1,739 m, and could represent such a second source of colloidal material. It is also plausible that the Fe and Mn peaks represent surges from different sub-catchments. High copper concentrations also have been found during flushing as a result of the dissolution of efflorescent salts in mine settings (Alpers et al. 1994). If the earlier peak in total Cu concentration were a result of efflorescent dissolution, however, it would mean that such dissolved Cu had been very rapidly sorbed to colloidal Fe (Runkel et al. 1999). Concentrations of total Mn increased on the rising limb of the flood wave, between 2,739 to 1,738 m, similar to total Fe. All three metal concentrations decreased on the falling limb of the storm wave between 1,738 and 680 m. On the most upstream end of the storm wave, at 680 m, both Fe and Mn concentrations were higher than the pre-storm concentrations; the total Cu concentration was essentially the same. This difference could also suggest that the storm wave carried more near-stream colloidal material, which had a relatively higher concentration of Mn. The changes in concentration are quantified by the load profiles for Fe, Cu, and Mn.

Pre-storm loading profiles give the baseline conditions for evaluating changes that resulted from the storm. Such a summary of loading for principal source areas can help one evaluate remediation options (Kimball et al. 2003; Runkel and Kimball 2002). Copper loading at the beginning of the study reach was 8% of the cumulative total loading that was measured along the study reach (Fig. 5). Loading of both Fe and Mn was greater, with 21% of the Fe and 31% of the Mn coming from upstream sources. Loading profiles indicate that the decrease in concentration for Fe, Cu, and Mn at 843 m (Fig. 4a, c, e) was a result of dilution for Mn, but resulted from net removal of Fe and Cu from the stream through chemical or physical processes (Fig. 4b, d, f). This removal most likely was a result of sorption of Cu to the hydrous Fe oxides that were formed as the pH 8.1 water from the mine treatment entered the Merse. Any contribution of Fe and Cu from Fosso di Ribudeli and the mine treatment was masked by the net removal that occurred between 785 and 843 m (Fig. 4b, d); only a small portion of the total Mn load to the study reach was contributed there (Fig. 5). Loads of Fe, Cu, and Mn increased substantially between 843 and 1,199 m, reflecting the contribution from drainage affected by the roaster-waste piles (Fig. 5). Because the drainage of the inflow at 876 m had a small discharge compared to the total increase in discharge between 843 and 1,199 m (Fig. 3b), the loading contribution principally resulted from dispersed ground-water inflow to the stream. Downstream from this principal loading, each metal load increased between 1,362 and 1,738 m. Again, because of the absence of visible inflows in that segment, the increased load most likely came from dispersed ground-water inflow. An additional area of dispersed loading for Fe and Cu occurred at 3,068 m (Figs. 4b, d, 5). Downstream from 3,068 m, all the loads decreased, most likely as Fe colloidal material settled from the stream. The five areas summarized in Fig. 5 accounted for essentially all the loading of these metals in the pre-storm profile.

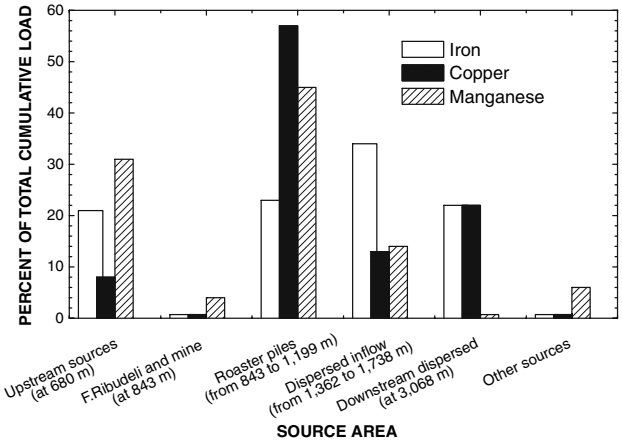

Fig. 5 Comparison of pre-storm loads for iron, copper, and manganese from principal sources

As noted, storm runoff greatly increased the total-recoverable load at the beginning of the study reach. The comparison between the pre-storm and storm loads near the storm-wave peak (1,738 m) indicates a factor of 21 increase for total Fe, an eightfold increase for Cu, and a sevenfold increase for Mn. These increases resulted from increased colloidal concentrations. Sources of the increased load most likely include metal-bearing particulate matter washed from stream banks, remobilization of particulates (mostly colloids) from the streambed, and increased discharge from ground-water inflows. The individual

contributions of these three sources cannot be quantified separately from the load profiles. Downstream from the storm wave, which started at 2,739 m, each metal load was greater than pre-storm loads (Fig. 4b, d, f), even though the increase in discharge was small (Fig. 3b). Total-recoverable Cu load increased more than Mn load, most likely because it was a more substantial part of the colloid material stirred up from the streambed by the small increase in discharge. Total and filtered Mn loads increased substantially within the storm wave, comparable to Fe load, and the loads reached a maximum at 1,738 m. The most notable case of resuspension occurred at 843 m. Pre-storm removal of Fe and Cu loads downstream from the mine-treatment inflow were less pronounced during the falling limb of the wave (Fig. 4b, d). Almost no loss of Cu load occurred at 843 m in the falling limb.

Only three filtered samples were obtained during the pre-storm synoptic sampling. In comparison to corresponding storm samples, the increase in filtered load of Cu was much less than the increase in total-recoverable Cu load. At 843 m, the increase was from 0.01 to 0.12 kg/day; the small load before the storm resulted from the removal of Cu at that site. At 2,409 m, the increase was from 0.12 to 0.17 kg/day and at 3,292 m, the increase was from 0.09 to 0.13 kg/day.

Conclusions

Having detailed synoptic-sampling and tracer-injection experiments on consecutive days before and then during a storm provided a unique opportunity to quantify the effects of storm runoff in a catchment affected by mining. The Br tracer, injected at a constant rate on both days, provided quantification of discharge while the detailed synoptic sampling provided the chemistry to quantify the loading profiles. The synoptic sampling during the storm defined a storm wave moving downstream. Iron, Cu, and Mn total-recoverable loads increased in advance of the storm wave as a result of a small increase in discharge that may have stirred up colloidal material from the streambed. This caused a relatively greater increase in the Cu load than the Mn load, suggesting a compositional difference of the in-stream colloids. The rising limb of the storm wave brought a large increase in total-recoverable loads of all the metals, which reached their greatest quantity near the peak of the storm wave. The falling limb of the storm wave caused dilution of Cu and Mn concentrations, but their total-recoverable loads were still much greater than the pre-storm loads. Although these metal loads increase substantially during the storm, the in-stream concentrations of Cu and Mn did not increase to toxic levels. The substantial concentrations of Fe colloidal material transported by the storm would likely have a greater impact on organisms through sediment overload on the streambed than would the slight increase in filtered concentrations of Cu and Mn.

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