Tracking the Fate of Mine Derived Sediments Using Chemical Fingerprinting and Statistical Analysis

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Abstract Geochemical fingerprinting can be a useful tool in tracing the fate of mine derived sediments. This generally involves identifying a unique set of elements within the mine-derived sediment to discriminate between mine- and non-mine derived sources downstream. The actual set of elements or other sediment properties used in the fingerprinting analysis will vary according to the in situ catchment characteristics. This paper uses three examples of sediment fingerprinting studies in remote environments; mines in Papua New Guinea, the Philippines and Indonesia. Using elemental composition and a range of multivariate statistical procedures, it was possible to distinguish between the mine and remaining catchment signatures and to identify specific elements that contributed to these differences. It was also possible to determine the ability of the a-priori site groupings to encapsulate the geochemical variation by comparing them to computer generated groupings determined with no prior assumptions.

Keywords sediment, fingerprint, signature, contaminant mapping

Introduction

Management of sediment runoff, including determining the source and fate of sediments, is one of the biggest issues currently faced in the mining industry. Sediment delivery to receiving waterbodies as a result of mine operations can have diverse environmental implications such as increased transport of nutrients and contaminants, changes to water quality, increased flooding, impacts to fisheries and deteriorating aesthetic values (Davis & Fox 2009, Hatfield & Maher 2009, Martinez-Carreras et al. 2010).

Traditionally, sediment movement and its impact within catchments has been assessed via a range (and usually a combination) of indirect (e.g. remote sensing/GIS, empirical equations, models) and direct measurements (field measurements – pins/surveys/traps, stratigraphic analysis, Cesium mass balance, fingerprinting). Fingerprinting is a direct sampling method that has become widely used in the last three to four decades to characterise sediments and to identify their source. The fundamental principle of fingerprinting is that one or more physical or chemical properties of sediment can be used to determine its provenance and estimate the amount of sediment delivered from all of its sources. Properties used for fingerprinting are diverse and catchment complexity often means composite signatures, where several different properties and ratios between some or all of those properties are used to distinguish between sediment sources.

This paper discusses the use of multivariate statistics to distinguish mine fingerprints in three tropical, remote mines – in Papua New Guinea (PNG), the Philippines and Indonesia.

Background

Hydrobiology was commissioned by the three different aforementioned mines to undertake separate fingerprinting studies to identify a 'signature' for each mine that could be used to trace mine-derived sediment within the receiving catchment. The name and absolute location of each of the mines is withheld for confidentiality reasons. However, a brief description of each is provided below.

Mine 1 is located in Papua New Guinea. The catchment containing the mine is an actively aggrading system subject to high sediment loading from its headwaters. The catchment headwaters are dominated by volcanic and volcaniclastic rocks and marine-origin carbonates. This differs greatly in structure, form and chemical composition from the saprolitic and limonitic laterite found at the mine site, which is situated on a plateau adjoining the floodplain of the main river about mid-catchment.

Mine 2 is located in the Philippines. This mining project is in the pre-operational phase and the data presented is related to sediments derived from a natural acid drainage and artisanal (illegal) mining activities in the vicinity of the proposed mine ore-body. The traced sediment source is derived from mineralized massive sulfide geology hosted within basaltic basement and andesite/volcanic overburden.

Mine 3 is located in Indonesia. The mine derived sediments are related to a quartz hosted ore-body and overburden of fragmental volcanics. The catchments surrounding the mine are a matrix of sandstone, mudstone, Quaternary Tuffs and andesite.

Analysis Methods

The concentrations of a wide range of elements from sediment samples were obtained through a semi-quantitative scan (ICP-MS) and XRF. Samples from each site were split in to *a-priori* groups, e.g. classifications such as mine, upstream/reference and downstream. The data were percent-standardised such that each sample, a given variable was expressed as percentages of the maximum value recorded for that variable. The data was square-root transformed and used to construct three separate Euclidean distance similarity matrices from the data forr each mine site.. The difference between groups of samples were quantified using the ANOSIM test's R-stat (Clarke and Gorely 2006).

By subjecting the data to Cluster analysis with SIMPROF (Clarke et al. 2008), the samples were separated into groups in such a way such as to maximize the between group differences based on their geochemical signature and with no a-priori knowledge of whether they were, for example, mine site or reference site samples. A measure of the degree of difference or separation of these groups was again achieved by subjecting them to an ANOSIM test (Clarke and Gorely 2006). The resultant R-stat computed during an ANOSIM tests provides a comparison of the similarity of samples within the same groups compared to those between samples of different groups. When the R-stat nears 1, groupings are discrete with samples in the same group very similar but very different from those of different groups. When R is nearing 0 samples are no more similar to other samples in the same group than those in different groups. It was assumed that as these groupings were defined using the iterative similarity profiling routine (SIMPROF), that they represent groupings that would provide the maximum R value possible for that data set. The first R-stat value (calculated using the a-priori groupings) expressed as a percentage of the second R-stat value (assumed to be the maximum possible for that data set) provided a measure of the extent to which the geochemical signature of the samples can be explained by the separation of those samples into a-priori groupings, which infers the extent to which the effects of mining determine the geochemical signature of those samples.

MDS ordination plots were used to visualize the relative differences between samples and their pre-defined groupings. When groups were identifies as being significantly different from each other through ANOSIM tests, the variables driving the difference between those groups were identified using SIMPER analysis (Clarke and Gorely 2006). This routine was used to identify which variables contributed to the differences between groups where ANOSIM had identified significant differences.

Results

Mine 1 - MDS ordination demonstrates a marked difference in the composition of samples from the mine compared to all other samples which were all relatively more similar to each other (fig. 1). The samples from the remaining sites are also clearly separated according to site but to a lesser extent, with some degree of overlap. Cluster/SIMPROF analysis also identified the user-defined groups and identified many discrete sub-groups within those. The ANOSIM results further confirmed these observations showing high R-values for pairwise comparisons between the mine site samples and all others ($P<5\%$, $R>0.8$ in all cases). The SIMPER analysis showed that these differences were largely driven by the presence of nickel (Ni) and chromium (Cr) at the mine site and higher levels of selenium and rubidium at ORWB1. These results suggest that the presence of Ni and Cr represent a strong mine signature that could be used to identify downstream impacts. The absence of these metals in the downstream sites also suggests that mine impact is currently either minimal or masked by natural sediment load. The R-stat values derived from a-priori groupings was 0.7 whereas the R-stat calculated from the groupings derived from the SIMPROF and cluster analysis was 0.95. The resulting ratio of 0.72 indicated that the geochemical signatures of the samples depended considerably on the a-priori groupings. This implies that mining activities were a driving factor in determining the geochemical signature of a sample and depended largely on site location.

Mine 2 - MDS analysis demonstrated somewhat less discrete clustering among impact, upstream and downstream sites compared with Mine 1 however a clear separation of the impact sites from the others was evident (fig. 1). Again, downstream samples were more similar to upstream samples than the impact samples indicating that mine derived sediments were not being transported downstream in significant amounts. Groups identified by cluster analysis with SIMPROF were largely different from a-priori groupings. The ANOSIM test among the a-priori defined groups showed a reasonable degree of separation ($R=0.45$, $P<5\%$) and pairwise tests show that the impact sites were clearly different from the other sites ($R>0.7$ in all cases) as was observed in the MDS ordination plot, however, the differences between up and downstream sites was weak ($R<0.3$). SIMPER analysis identified higher levels of antimony, mercury (Hg), molybdenum (Mo) and arsenic as the variables separating the impact sites from the other sites. The R stat of 0.8 calculated for groups defined by cluster analysis with SIMPROF was much larger than that calculated for the a-priori groups ($R=0.45$) and the resulting ratio of 0.52 indicated that the a-priori groupings were less effective at explaining the geochemical signatures of samples in this instance compared with mine site 1. This implies that some other effect was influencing their geochemical signature such as, for example, catchment height, flow velocity, or sediment characteristics.

Mine 3 - The MDS ordination shows three distinct groupings; samples from impact, reference and mine sites. The clusters of impact sites are positioned between the reference and mine site clusters on the MDS plot indicating that they bare some similarities to both reference and mine site conditions (fig. 1). This indicated that mine derived sediments were to some extent reaching the impact area. The ANOSIM results quantified the extensive and significant difference between the mine site samples and both the impact and reference sites ($P<5\%$, $R>0.8$) while the difference between the impact and reference sites is significant and of medium strength ($P<5\%$, $R>0.5$). This suggests that, although the downstream sites are receiving mine derived sediments, they still retain geochemical signatures that resemble most closely those of the reference sites. Similarity percentage (SIMPER) analysis has demonstrated that the difference between the mine sites, reference sites and impact sites is driven by elevated levels of Cd, silver, sulphur and Mo in the mine site samples. The difference between reference and impact sites is driven by higher levels of sodium, Hg,

uranium and zirconium at the reference sites and higher levels of sulphur at the impact sites. This indicates that the difference between the impact and reference sites is not only due to mine derived sediments but also due to differences in the geochemical/elemental signature between catchments.

The *R* stat derived from the a-priori classifications was *R*=0.65 whereas the R-stat was 0.73 for the groupings defined by cluster analysis with similarity profiling (fig. 1). This gave a ratio of 0.9 indicating that the geochemical signatures of those samples can be predicted largely by which a-priori grouping a given sample belongs to; mine, impact or reference sites.
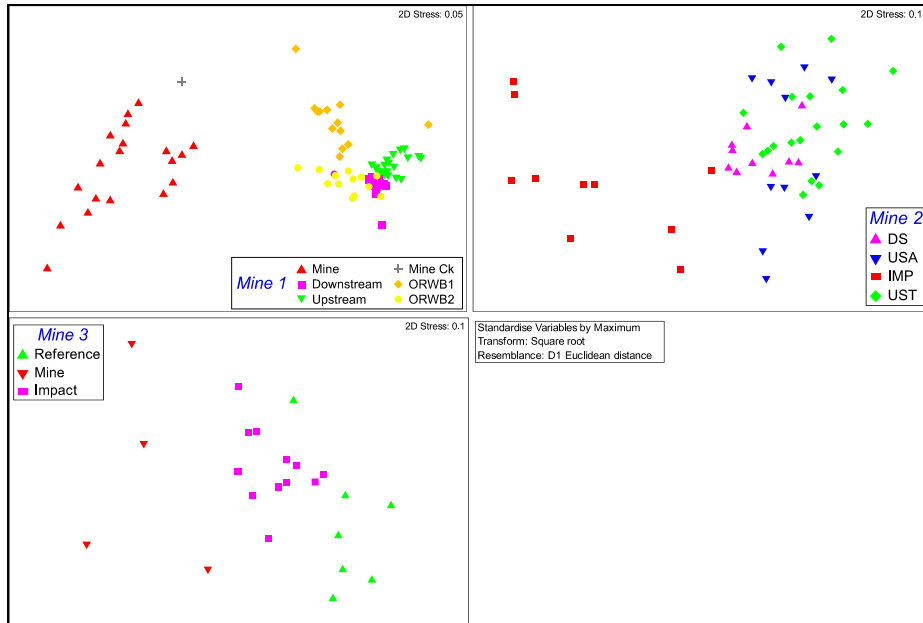

Fig. 1 *MDS ordinations of a-priori sample groups from Mine 1 (top left), Mine 2 (top right) and Mine 3 (centre) based on standardised concentrations of various trace elements.*

Conclusions

The described method for exploring sediment geochemical signatures provides an approach able to detect subtle similarities and differences between a-priori groupings such as mine site, reference and impact sites in a quantitative manner. The use of SIMPER analysis provides an objective method for identifying which variables contributed to the observed differences and similarities between sites and therefore which sites were typify by variables that also typified mine site locations and were thus probably receiving mine derived sediments. By comparing R-values derived from a-priori groupings and those from cluster analysis/SIMPROF derived groupings, a measure of how well those predefined groupings are able to explain the differences in geochemical signatures between samples can be calculated and thus infer if mining impacts are the main driving factor in differences in geochemical signatures.

The results from the first two mine sites suggest that the mine derived sediments do not propagate into the downstream catchments to a significant extent however in the third case the impact sites (downstream) are clearly more similar to the mine site samples than the reference site samples are. This similarity is potentially as a result of the sediments from the mine area having been transported into the "impact" area. It should be noted that, as mine sites are located in specifically targeted geochemically unique areas (ore-bodies), that this pattern could also be from pre-mining natural erosion. Further testing of sediment vertical

profiles (stratigraphy), including dating methods, can be used to identify the historical lineage of sediment deposition if required.

At mine sites 1 and 3 the R-values were similar for both predefined and cluster/SIMPROF defined groupings suggesting that the sampling design and classification of samples largely encapsulated the geochemical variation in the sediment. However, at mine site 2, there was some discontinuity between the two values. This could be due to, for example, catchment height, grain size, river flow rate or combinations thereof and thus if the samples were regrouped according to one or more of those factors, the discontinuity between R values could be decreased.

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