Effluent Characterization, Water Quality Monitoring and Sediment Monitoring in the Metal Mining EEM Program

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The metal mining Environmental Effects Monitoring (EEM) program will require mines to conduct effluent characterization and water quality monitoring on an ongoing basis. Samples will be collected four times a year, and will be analyzed for a range of parameters. This information will be used to aid in the design and interpretation of fish surveys and benthic invertebrate community surveys. There are also a number of water quality monitoring methods that may be used to help determine the cause of any effects identified by the EEM program. Mines will also be required to collect sediment samples for determination of particle size distribution and total organic carbon. This information will be used in the design and interpretation of benthic invertebrate community surveys. A range of sediment monitoring techniques are available to aid in the determination of the causes of effects on the benthic invertebrate community.

Key words: water quality, effluent quality, sediment, metal mining, monitoring

Introduction

An understanding of the physical and chemical characteristics of aquatic ecosystems is important to the design and interpretation of biological monitoring studies conducted as part of EEM. Some physical characteristics, such as hydrological properties, will be described during site characterization, which is completed as part of the study designs for biological monitoring. Water and effluent quality will be monitored on an ongoing basis, as part of the effluent and water monitoring requirements of the metal mining EEM program. Sediment monitoring requirements are limited to the determination of sediment particle size distribution and total organic carbon in conjunction with benthic invertebrate community surveys.
Selection of Parameters for Analysis in Effluent and Water

A multistakeholder committee, the Water and Sediment Subgroup, was established to formulate requirements and guidance for effluent, water and sediment monitoring. One of the key issues for this subgroup, co-chaired by representatives of Environment Canada and the Mining Association of Canada, was the selection of the parameters to be required for measurement in samples of effluent and water.

In determining the list of recommended monitoring parameters, the subgroup considered a number of factors including: recommendations of the AQUAMIN Final Report (AQUAMIN Steering Group 1996), national relevance and occurrence of parameters, significance of parameters as potential contaminants, importance of parameters to provide supporting information, and overlap with monitoring requirements of other jurisdictions. The parameters which the subgroup recommended for effluent characterization and water quality monitoring are presented in Table 1. This list has been reviewed as part of the legal review of the EEM requirements, and will be finalized before the requirements come into force.

A key recommendation of the subgroup is that metals be measured as total metals, not dissolved metals. This recommendation was based on the conclusions of the Natural Resources Canada-led Aquatic Effects Technology Evaluation (AETE) program.

Some water quality monitoring programs require the measurement of dissolved metals, defined as that fraction that passes through a 45-µm filter. However, there is ongoing debate about the validity of the methods

<table>
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<tr>
<th>Key parameters</th>
<th>Supporting parameters</th>
<th>Additional supporting parameters for water quality</th>
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<tbody>
<tr>
<td>Metals: aluminum, arsenic, cadmium, copper, iron, lead, manganese, mercury, molybdenum, nickel, selenium, uranium, zinc</td>
<td>Major ions: calcium, chloride, magnesium, potassium, sodium, sulphate</td>
<td>• dissolved oxygen</td>
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<td>Other: ammonia-nitrogen, fluoride, nitrate/nitrite, pH, radium 226, total cyanide, total phosphorus, total thiosalts, total suspended solids</td>
<td>Other: conductivity, total hardness, alkalinity or acidity, effluent discharge rate</td>
<td>• temperature</td>
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<td>• dissolved and total organic carbon</td>
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<td>• salinity (marine and estuarine)</td>
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and assumptions associated with measurement of dissolved metals. To examine these issues the AETE program compared total and dissolved metal concentrations with respect to their ability to indicate exposure of aquatic ecosystems to metals in mine effluent. This comparison was completed using samples from several mines across Canada, and the results indicated that, at the sites examined, a very high proportion of the total metals occurred in dissolved form. Consequently, it was concluded that total and dissolved metals measurements would be equally effective in indicating exposure of aquatic ecosystems to effluent (ESG 1999).

The AETE program also examined quality assurance and quality control issues associated with the filtration of water samples (Hall 1998). This work illustrated the considerable risks of sample contamination during filtration, unless strict protocols are followed.

Given the results of the field sampling, and the risks of sample contamination during filtration, the AETE program recommended the measurement of total metal concentrations for routine water quality monitoring (ESG 1999). AETE did however acknowledge that the measurement of dissolved metals may be useful in detailed site-specific studies.

**Effluent Characterization**

An understanding of mine effluent quality is necessary to an overall understanding of environmental quality, since mine effluent discharges are the primary source of contaminants in aquatic ecosystems affected by mining activities. All mines subject to the amended Metal Mining Effluent Regulations (MMER) will be required to collect effluent samples weekly and analyze samples for pH, arsenic, copper, cyanide, lead, nickel, zinc, total suspended solids, and radium 226. This is termed “compliance monitoring.” Effluent characterization will provide additional information to that provided by compliance monitoring, since it will require the analysis of additional parameters. The Water and Sediment Subgroup recommended that mines be required to collect samples for effluent characterization at least four times a year from each final discharge point required by the MMER. The results of effluent characterization and compliance monitoring will allow for the determination of temporal trends in effluent quality, and provide a mechanism for detecting any changes in effluent quality which may be relevant to the design or interpretation of biological monitoring studies conducted as part of the EEM program.

The results of effluent characterization, as well as the locations and dates of sample collection, and QA/QC data will have to be reported to Environment Canada annually.

**Water Quality Monitoring**

Data from water quality monitoring are required for the design and interpretation of biological monitoring studies conducted as part of the
EEM program. The objective of water quality monitoring is to answer the following:

1. What are the measured concentrations (of effluent contaminants) in the study area?
2. What is the estimated mine-related change in contaminant concentrations in the exposure area?

Water quality monitoring will allow for the determination of temporal trends in receiving water quality as a result of the input of contaminants from a mining operation. It will also provide a mechanism for detecting any changes in effluent quality which may be relevant to the design or interpretation of biological monitoring studies.

The Water and Sediment Subgroup recommended that mines be required to collect water samples for water quality monitoring at least four times a year. Sampling will be conducted at a minimum of one representative sampling station in the reference area and a minimum of one representative sampling station in the mine effluent exposure area. It is recommended that at least two to three samples be collected within each sampling station to get an estimation of the variability and to determine if concentrations of the contaminants are homogeneous within the sampling station. In addition, water samples for water quality monitoring will be collected in each fish sampling area and each benthic invertebrate community sampling area, concurrently with the biological monitoring. Water samples will be analyzed for the same parameters as for effluent characterization, including any parameters analyzed on a site-specific basis.

The results of water quality monitoring will be reported to Environment Canada annually, and this report will include a determination of whether there have been any changes in water quality in the exposure area that may be caused by the effluent.

When there is more than a factor of two difference between measurements taken in the exposure and reference areas, the mine is encouraged to estimate and report the geographical extent for which this condition exists, based on expanded water quality monitoring or modelling.

When effects on fish, fish tissue or the benthic invertebrate community have been identified, and the magnitude and geographic extent of these effects have been determined, then mines will be required to conduct additional monitoring studies to try to determine the cause of the observed biological effects. The metal mining EEM Guidance Document (Environment Canada In press) describes numerous water quality monitoring methods that may be used at this stage to assist with the determination of the cause of any observed biological effects. These methods go beyond those required for routine water quality monitoring and can include dissolved metals and metal speciation and modelling as follows.

**Dissolved Metals**

When more detailed monitoring is required to determine the cause of biological effects, and total concentrations of certain metals in the exposure
area are elevated, then measurement of dissolved metals may be warrant-
ed as part of investigation-of-cause monitoring studies. The measurement
of both total and dissolved metals in effluent and exposure area samples in
an investigation-of-cause monitoring study would assist in determining
which metals might be causing or contributing to the observed biological
effects. The rationale for measuring dissolved metals is based on the theo-
ry that it is the metals in the dissolved fraction, particularly the free metal
ions, that are the most bioavailable to aquatic organisms. There is qualita-
tive evidence to support this theory, especially in defined synthetic media
(i.e., laboratory bioassays). However, this relationship appears to break
down in natural waters, particularly in the presence of natural dissolved
organic matter (EVS Environmental Consultants 1997).

The normal procedure for measuring dissolved metal concentrations
involves the immediate filtration of the raw water sample through a 0.45-
µm filter and then preserving the filtered sample with nitric acid to a pH
of less than 2.0 to keep the dissolved metals in solution until analysis.

Metal Speciation and Modelling

The chemical form in which a metal or metalloid occurs (i.e., the spe-
ciation of the metal) can have a significant effect on the bioavailability and
toxicity of that metal to aquatic organisms (Tessier and Turner 1995;
Stumm and Morgan 1996). As a result, understanding the speciation of
contaminants of concern can be important to understanding the nature
and causes of biological effects.

Metal speciation can be measured through direct analysis, or esti-
mated with modelling tools. Measurement techniques for the speciation
of metals in aqueous solutions have been comprehensively reviewed by
Tessier and Turner (1995). For more information on measurement tech-
niques, see EVS Environmental Consultants (1997).

A number of computer programs are available for the modelling of
chemical speciation of metals in water. These programs can be used to
predict the forms and concentrations of metals in effluent or water, and
can be used to predict toxicity (EVS Environmental Consultants 1997).

Sediment Monitoring

As part of the requirements for conducting benthic invertebrate com-
mmunity surveys, mines will be required to collect sediment samples for
determination of particle size distribution and total organic carbon.

Knowledge of the particle size distribution of a sediment is impor-
tant in the interpretation of the results of chemical or biological analyses.
In particular, sediment particle size has a significant impact on the struc-
ture of benthic invertebrate communities. Further, with the results of par-
ticle size analysis, the specific surface area of sediment can be determined
and used to assess the adsorptive capacity of the sediment for metals and
organic substances.

Determination of the total organic carbon concentration is important
since carbon is present in sediment in several organic forms such as humic
matter, chemical, plant and animal matter as well as inorganic carbonate forms. Organic carbon in sediment and the water column causes a decrease in dissolved oxygen, hence creating a more eutrophic environment. Also, at certain pH levels, humic substances form complexes with metals, increasing metal solubility in the water column. Given the influence of organic carbon on habitat characteristics, information on total organic carbon concentrations is important in ensuring that reference areas for benthic invertebrate community surveys are as similar as possible to the exposure areas. Differences in organic content between the exposure and reference areas may make the interpretation of the results of benthic invertebrate surveys more difficult.

When investigation-of-cause monitoring studies of the benthic invertebrate community are to be conducted, sediment monitoring can contribute important information, particularly with respect to sediment characteristics that may contribute to effects on benthic invertebrate communities. Therefore, there is guidance in the metal mining EEM Guidance Document (Environment Canada In press) on the use of a range of sediment monitoring tools and methodologies.

Chemical analyses of sediment can be one of the most important sediment monitoring tools to help identify the cause of biological effects and they are strongly recommended as part of investigation-of-cause monitoring studies for the benthic invertebrate community. Such analyses would include the measurement of the concentrations of metals in sediment samples collected from the exposure and reference areas. The selection of parameters for sediment chemistry analyses will be determined on a site-specific basis. Sediment chemistry analyses may identify elevated concentrations of certain metals in the exposure area that are contributing to the observed effects.

In addition to the use of sediment chemistry analyses, there are a number of other sediment monitoring methods that may be used during investigation-of-cause monitoring studies of the benthic invertebrate community including, but not necessarily limited to, the following.

**Sediment Profiles**

Core samplers are often used to collect sediment profiles for the determination of the vertical distribution of sediment characteristics. Core samplers should be used where it is important to maintain an oxygen-free environment below the surficial sediment, since there is less chance for oxidation to occur. Core samplers have the advantage of collecting intact sediment samples from both surficial sediments (upper 15–30 cm) and deep sediments (>30 cm deep), but their main limitation is that the sample volumes are relatively small. Chemical and other analyses can be done on samples taken from sediment cores, allowing for the identification of any long-term trends in sediment quality (Environment Canada 1994).
Partial Metal Concentrations in Sediment and SEM/AVS

Although total metal concentrations may not be directly related to biological availability and toxicity, many sediment quality guidelines are based on total metal concentrations. A variety of methods have been used to predict the biological effects of metals from metal-contaminated sediments. These include the normalization of sediments for particle size, organic content, or extractable fraction of metals using acid volatile sulphides (AVS) and simultaneously extracted metals (SEM) methods.

It is generally thought that a particular chemical form of an element determines its behaviour, biological availability and potential toxicity, rather than the total concentration in sediments. Specific chemical forms can be measured: a) by direct instrument techniques, b) directly by sequential digestion of sediments, or can be predicted by c) predicting levels through thermodynamic modelling.

The relative strength of association between metals and particles can be assessed by single or sequential extraction or sediment digestion methods. Weak acids or chelating agents and reducing agents may be used to differentiate between different chemical forms. Sediment fractions can be operationally defined (e.g., ferromanganese oxyhydrides) depending on the digestion method used. The acid volatile sulphide (AVS) concept assumes that metal concentrations in pore water of anoxic sediments are controlled by sulphides. AVS are extracted by the cold-acid purge and trap technique. Simultaneously extracted metals (SEM) represent the portion of total metals released during AVS dissolution. The SEM/AVS ratio is sometimes used to characterize metal availability. When the SEM fraction exceeds the AVS fraction (e.g., SEM:AVS ratio >1) then the free metal may be present in the pore water at levels adequate to cause acute toxicity (ESG 1999). However, toxicity cannot be predicted—only non-toxicity can be predicted (SEM:AVS ratio <1). A major limitation of these analyses is that anoxic sediment samples must be carefully collected and stored to prevent oxidation.

Whole Sediment Toxicity Testing

Sediment toxicity tests may be used to evaluate potential contamination in aquatic environments. These tests provide a direct method to determine chemical availability of contaminants in sediment by evaluating the effects of sediment on test organisms, and they can be used as an evaluation tool in conjunction with chemical data. Whole sediment toxicity testing can be used to verify that changes seen in benthic invertebrate communities are due to toxicity of sediments and not other physical or biological factors. These tests also provide important information for interpretation of observed effects in situations where benthic invertebrate community data are inconclusive, or where only pollution-tolerant species are present in both exposure and reference areas.

The limitation of whole sediment toxicity tests is that they are laboratory tests that do not determine in situ toxicity directly. Further, if a
standard overlying water is used, instead of water collected from the study site, then the effects of differences in overlying water quality on sediment toxicity, if present, are not taken into account.

**Sediment Quality Triad**

The sediment quality triad (SQT) approach integrates sediment chemistry, toxicity and resident biota (the community structure of benthic invertebrates), making the data more powerful than if each component were interpreted individually (Chapman 1992). The use of the sediment quality triad approach is strongly recommended during any investigation of causes of effects on benthic invertebrate communities.

The three corners of the triad can be designated as chemical (C), biological (B), and toxicity (T) (see Fig. 1). Results from each “arm” of the triad can be statistically examined to determine if any significant correlation exists. The results from the various components of the SQT can be integrated into a weight-of-evidence analysis which can be presented both qualitatively and quantitatively in a number of different interpretation and presentation formats (see Chapman 1992, 1996; Warwick and Clarke 1991).

**Sediment Pore Water Monitoring or Pore Water Toxicity**

The water that occupies the space between sediment particles is referred to as pore or interstitial water. The association of this water with the surface of sediment particles results in reactions between the particles and the water that approach equilibrium. The partitioning of contaminants in sediments between the particulate and water phases depends to a large extent on the amount of organic carbon, sediment particle size, the chemical form of the contaminants, and the physiochemical environment (e.g., pH, temperature, redox potential, sorption/desorption properties of sediments, or the equilibrium between the solid and liquid phases). The dynamics of these processes are not well understood; however, it is generally assumed that concentrations of most substances in the pore water approach equilibrium with the solid phase and its associated contami-

![Fig. 1. Schematic representation of the axes of the sediment quality triad.](image-url)
nants, and that metals in pore water largely represent the biologically available fraction in sediments. Consequently, pore water has been collected for toxicity testing to approximate the relative toxicity of contaminated sediment, and/or to assess contaminant levels (Environment Canada 1994). There is substantial literature describing toxicity testing with pore water (Burton 1998); however, there are few standardized methods for toxicity testing of aquatic organisms with pore water.

Conclusions

The ongoing collection of samples of effluent and water, and the measurement in these samples of a range of potential contaminants, will provide important information to the EEM program regarding the releases of contaminants to the environment, and the concentrations of these contaminants in the environment. This information will be very helpful to the design and interpretation of biological monitoring studies conducted as part of the EEM program. When environment effects have been identified through biological monitoring, additional effluent and water monitoring tools can be used to help determine the cause of those effects.

The measurement of sediment particle size distribution and total organic carbon will contribute to the design and interpretation of benthic invertebrate community surveys, and when these surveys identify effects, there are a range of sediment tools that may be invaluable in determining the cause of these effects.

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