

# USE OF THE BIOTIC LIGAND MODEL TO PREDICT METAL TOXICITY TO AQUATIC BIOTA IN AREAS OF DIFFERING GEOLOGY<sup>1</sup>

Kathleen S. Smith<sup>2</sup>

**Abstract.** This work evaluates the use of the biotic ligand model (BLM), an aquatic toxicity model, to predict toxic effects of metals on aquatic biota in areas underlain by different rock types. The chemical composition of water, soil, and sediment is largely derived from the composition of the underlying rock. Geologic source materials control key attributes of water chemistry that affect metal toxicity to aquatic biota, including: 1) potentially toxic elements, 2) alkalinity, 3) total dissolved solids, and 4) soluble major elements, such as Ca and Mg, which contribute to water hardness. Miller (2002) compiled chemical data for water samples collected in watersheds underlain by ten different rock types, and in a mineralized area in western Colorado. He found that each rock type has a unique range of water chemistry. In this study, the ten rock types were grouped into two general categories, igneous and sedimentary. Water collected in watersheds underlain by sedimentary rock has higher mean pH, alkalinity, and calcium concentrations than water collected in watersheds underlain by igneous rock. Water collected in the mineralized area had elevated concentrations of calcium and sulfate in addition to other chemical constituents. Miller's water-chemistry data were used in the BLM (computer program) to determine copper and zinc toxicity to *Daphnia magna*. Modeling results show that waters from watersheds underlain by different rock types have characteristic ranges of predicted LC<sub>50</sub> values (a measurement of aquatic toxicity) for copper and zinc, with watersheds underlain by igneous rock having lower predicted LC<sub>50</sub> values than watersheds underlain by sedimentary rock. Lower predicted LC<sub>50</sub> values suggest that aquatic biota in watersheds underlain by igneous rock may be more vulnerable to copper and zinc inputs than aquatic biota in watersheds underlain by sedimentary rock. For both copper and zinc, there is a trend of increasing predicted LC<sub>50</sub> values with increasing dissolved organic carbon (DOC) concentrations. Predicted copper LC<sub>50</sub> values are extremely sensitive to DOC concentrations, whereas alkalinity appears to have an influence on zinc toxicity at alkalinities in excess of about 100 mg/L CaCO<sub>3</sub>. These findings show promise for coupling the BLM (computer program) with measured water-chemistry data to predict metal toxicity to aquatic biota in different geologic settings and under different scenarios. This approach may ultimately be a useful tool for mine-site planning, mitigation and remediation strategies, and ecological risk assessment.

Additional Key Words: bioavailability, toxicological testing, copper, zinc, *Daphnia magna*, ecological risk assessment, water chemistry

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Kathleen S. Smith, Research Geologist, U.S. Geological Survey, Box 25046, M.S. 964, Denver Federal Center, Denver, CO 80225-0046 303-236-5788 [ksmith@usgs.gov](mailto:ksmith@usgs.gov)  
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## **Introduction**

The goal of this work was to evaluate the use and sensitivity of the biotic ligand model (BLM, an aquatic toxicity computer model) to predict toxic effects of metals on aquatic biota in areas underlain by different rock types. The bedrock, soil, and sediment are the source of chemical constituents that ultimately enter hydrological and biological systems, so different rock types give rise to different water compositions. In this work, the chemical compositions of water collected from areas with different underlying geology were entered into the BLM to compute the aquatic toxicity of a given metal to a given organism for a given water composition. Linking knowledge of bedrock geology with resulting water composition, and differences in water composition with commensurate differences in predicted aquatic toxicity may provide a valuable planning tool for mine sites, mitigation and remediation design, and risk-assessment efforts.

## **Background Discussion**

### **The Biotic Ligand Model**

The biotic ligand model (BLM) quantitatively predicts the effects of water chemistry on the speciation of metals and their bioavailability to aquatic biota (Di Toro et al., 2001; Santore et al., 2001; Gorsuch et al., 2002; Niyogi and Wood, 2004). It is being used to develop site-specific water-quality criteria and in aquatic risk assessment for metals. The BLM has been incorporated into the 2003 draft update of ambient water quality criteria for copper (U.S. Environmental Protection Agency, 2003), and is being used to determine regulatory site-specific concentration criteria for copper. Given site-specific water chemistry, a chosen metal, and a chosen organism, the BLM predicts the LC<sub>50</sub> for the metal and organism. The LC<sub>50</sub> is the metal concentration that results in the death of 50% of a group of test organisms.

The BLM is an interface between the fields of aqueous geochemistry, the physiology of aquatic biota, and aquatic toxicology (Paquin et al., 2002). Fig. 1 illustrates the relationships between chemistry, physiology, and toxicology in the BLM. The BLM is based on the assumption that toxicity is related to the amount of metal bound to a biochemical site (the biotic ligand), which is the site of toxic action on the organism. Based on toxicity data from research on fish gills, the biotic ligand appears to approximate the active ion-uptake pathways that can be quantified with in-vivo gill-binding tests (Niyogi and Wood, 2004). The amount of metal bound to the biotic ligand depends on the speciation of the dissolved metal and the resulting concentration of the free ion of the metal (Pagenkopf, 1983). The speciation of the dissolved metal depends on the amount and kinds of complexing ligands (i.e., molecules that can bind to the metal, both inorganic and organic) in the water. In the model, the complexing ligands compete with the biotic ligand for the metal and other cations (e.g., Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>) present in the water. Therefore, the BLM can account for site-specific water-quality parameters that influence metal bioavailability and toxicity to aquatic biota. Consequently, any parameter that decreases the free-metal concentration would, in turn, decrease the metal bioavailability. For example, increases in alkalinity or dissolved organic matter would tend to decrease metal bioavailability and result in a higher predicted LC<sub>50</sub> concentration. The BLM assumes that the extent of short-term metal-gill binding is predictive of mortality in the organisms; hence, the greater the binding affinity of a metal for the biotic ligand, the greater the toxicity of that metal.

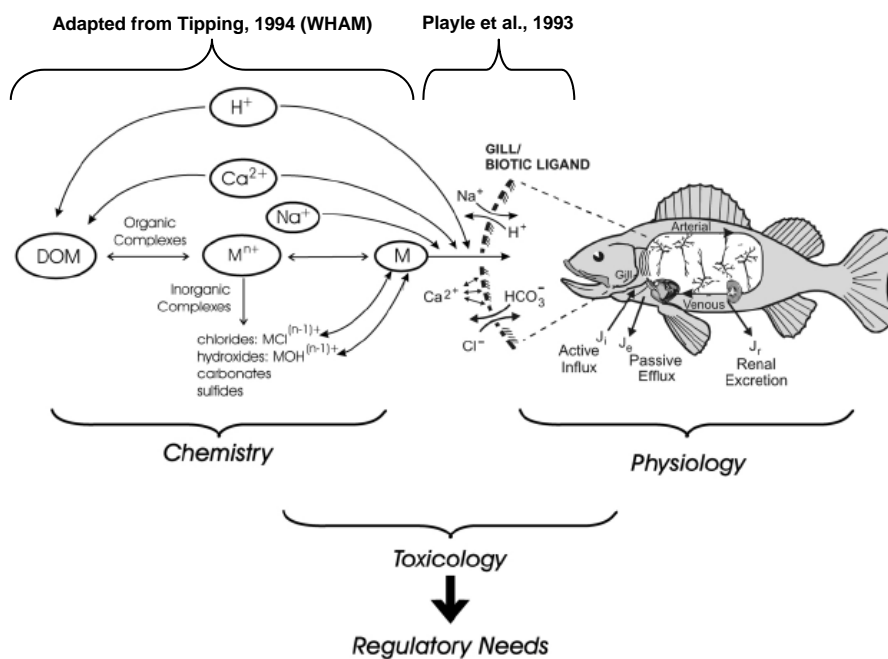


Figure 1. Diagram showing the relationships between chemistry, physiology, and toxicology in the biotic ligand model (BLM). The BLM assumes that (1) metals form various inorganic and organic complexes, (2) the free cationic form of metals is the source of acute toxicity, (3) metal toxicity is produced by binding on the gill surface, and (4) the extent of short-term metal-gill binding is predictive of longer term mortality (e.g., at 96 hours). (After Paquin et al., 2002.)

The BLM combines several different types of models with several different binding constants. The binding constants for biotic ligand-cation complexes are adopted from the work of Playle et al. (1993) and Playle (1998). Binding constants for metal-organic matter interactions are determined using the Windermere Humic Aqueous Model (WHAM; Tipping, 1994), and inorganic binding constants are determined using the CHESS model (Santore and Driscoll, 1995).

#### Some Key Water Parameters Used in the Biotic Ligand Model

The pH of water is one of the main controls on the speciation of metals in aqueous systems. Generally, water with higher pH values ( $\text{pH} > 8$ ) contains more ligands that can bind free-metal cations, which results in lower toxicity of the metal to aquatic organisms. In lower-pH water ( $\text{pH} < 6$ ), it is likely that there is a higher proportion of free-metal cations in solution, which results in higher toxicity of the metal to aquatic organisms. At pH values below about 5, aquatic toxicity can be a result of the low pH itself.

Alkalinity is the capacity of water to resist acidification (Hem, 1989). Alkalinity is determined by titrating water with a strong acid, and is commonly referred to as the buffering capacity of the water. The principal sources of alkalinity in most natural waters are the dissolved

carbon dioxide species bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ). Generally, atmospheric carbon dioxide and biologically mediated reactions in soil are the principal sources of the dissolved carbon dioxide species in water, but significant amounts of bicarbonate and carbonate concentrations in water can be acquired through water-rock interactions with carbonate minerals, especially calcium carbonate (limestone,  $\text{CaCO}_3$ ). Carbonate minerals are common in many different types of geological settings. High alkalinity values tend to reduce the free-metal cations and, in turn, decrease toxicity.

The property of water hardness is difficult to define, and several procedures have been used to determine hardness. Generally speaking, hardness is determined by the amount of dissolved calcium and magnesium in the water. Although the concept of hardness is of limited geochemical value, it has been incorporated into regulations (e.g., hardness-based water-quality criteria for metals) because of the roles of calcium and magnesium in mediating metal toxicity to aquatic biota (e.g., Pagenkopf, 1983). With current chemical techniques that separately analyze calcium and magnesium in water, a preferable approach is to directly measure calcium and magnesium concentrations in water. This approach is incorporated into the BLM to determine site-specific water-quality criteria for metals. Both calcium and magnesium concentrations are required parameters for the BLM.

Dissolved organic matter (DOM) or natural organic matter (NOM) in water may be an important ligand for most metals, and is likely to play a major role in metal transport (Macalady and Ranville, 1998). NOM is chemically complex and can be derived from a variety of sources (Thurman, 1985). The dissolved organic carbon (DOC) content of water is determined by converting all carbon species present to carbon dioxide and correcting for the dissolved inorganic carbon dioxide species initially present. Meybeck (1981; 1982) reviewed the DOC concentrations of river water and calculated an average DOC value of 5.75 mg/L for all rivers, with temperate, arid, and semiarid zones having an average DOC of approximately 3 mg/L. Although DOC can be an important constituent in water, commonly it is not reported in routine water analyses. Because DOC can strongly bind many metals, higher DOC concentrations tend to reduce metal toxicity. The BLM uses the Windermere Humic Aqueous Model (WHAM) of Tipping (1994) to determine metal binding with NOM. WHAM has been calibrated for a large number of samples of NOM from a wide variety of locations.

### Geoavailability

Geoavailability is the ease with which a chemical element is released into the environment from an earth material. It is defined as that portion of the total content of an element or compound, present in an earth material that can be liberated to the surficial or near-surface environment (or biosphere) through mechanical, chemical, or biological processes (Smith and Huyck, 1999). The geoavailability of a chemical element is determined by the susceptibility and availability of its resident mineral phase(s) to alteration and weathering reactions. Release of chemical elements contained within the structure of minerals in rock depends on the composition and properties of the resident mineral phase(s) because different mineral phases and different mineral textures weather differently in the presence of water.

Once geoavailable elements are released from the geologic source material, they persist and become available for exposure to aquatic biota (Fig. 2). Hence, determining the concentration and speciation of geoavailable elements is an important initial step in predicting toxicity and risk

to ecosystems. As an element moves through the environment, it may be altered by physical, chemical, or biological processes. Each stage, from total metal content through toxicity, in Figure 2 is a reservoir with a distinct “half-life.” As an element moves through each stage, generally less than 100% is transferred to the next stage; the grey scale on the left side of Figure 2 portrays this concept. Total metal content and geoavailability represent source terms, dispersivity and mobility represent transport terms, and intake, bioavailability, and toxicity represent fate terms (Smith and Huyck, 1999).

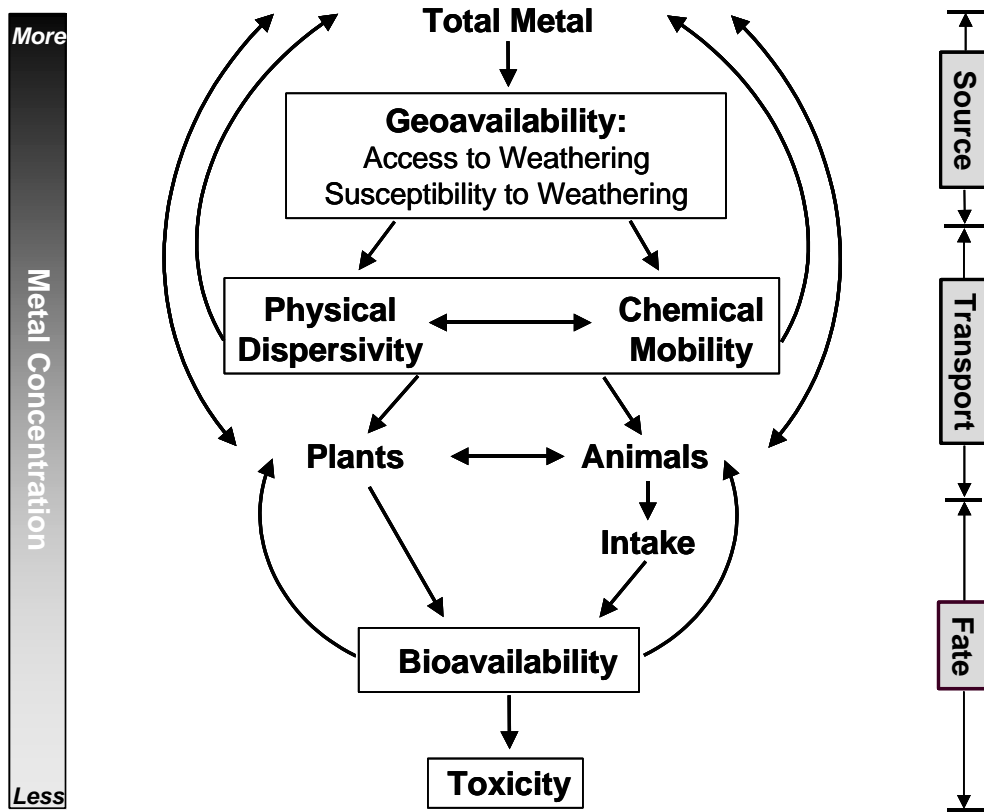


Figure 2. Diagram illustrating the pathways and relationships between total metal, geoavailability, bioavailability, and toxicity. (After Smith and Huyck, 1999.)

### Chemical Characteristics of Water Originating from Different Rock Types

There is a general relationship between the chemical composition of a water and the mineralogical composition and weathering characteristics of the rocks with which the water is in contact (e.g., the underlying geology). Of course, water-rock interactions entail a wide variety of complex weathering and rate-dependent reactions, and factors such as grain size, crystallinity, contact time, climate, relief, erosion rate, soil biota, and surrounding vegetation also play a role. Even so, some generalizations can be made about rock type and resulting water composition.

Igneous rocks. Igneous rocks tend to be relatively impermeable; therefore, they do not provide abundant surface areas of exposed minerals for water-rock interactions (Hem, 1989). Consequently, water draining igneous and metamorphic rocks tends to be relatively dilute and does not contain high concentrations of solutes. Generally, the water has bicarbonate as the major anion, and sodium and calcium as the major cations (Drever, 1997). Fine-grained igneous rocks tend to weather more quickly and produce more solutes than do coarse-grained rocks, and mafic rocks, such as basalt, tend to produce water containing more solutes with higher  $\text{Ca}^{2+}/\text{Na}^{+}$  and  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios than do felsic rocks, such as granite (Drever, 1997).

Sedimentary rocks. Sedimentary rocks can be classified into three groups (Rankama and Sahama, 1950): (1) resistates, such as sandstones, which are made up of relatively unaltered detrital rock fragments, (2) hydrolyzates, which are fine-grained materials consisting primarily of clay minerals, and (3) precipitates, which are primarily carbonate rocks. Water in contact with resistate rocks tends to contain fewer solutes than that in contact with hydrolyzate or precipitate rocks. Shale is a very complex rock type, and water in contact with shale is variable in composition. Water in contact with carbonate rocks commonly has calcium, magnesium, and bicarbonate as the only significant solutes (Drever, 1997). Sedimentary rocks, especially hydrolyzate and precipitate rocks, tend to produce more solutes than do igneous or metamorphic rocks.

Origin of solutes. Because most rocks consist of minerals that are not readily water soluble, minor components of a rock may control the composition of the associated water (Hem, 1989). This is especially true for igneous and metamorphic rocks, and for resistate sedimentary rocks. As a result, the more easily weathered minerals in a rock contribute disproportionately to the composition of surface and ground waters (Drever, 1997). Consequently, it is useful to determine the geoavailability of elements in a given rock or soil to be able to predict the solutes that the rock or soil will contribute to water that flows through them.

Calcium and magnesium concentrations in water are important because both calcium and magnesium have been shown to protect aquatic biota from metal toxicity. The source of dissolved calcium and magnesium in most water is most likely carbonate minerals, although gypsum ( $\text{CaSO}_4$ ) can be an important source of calcium, particularly in some environments. Commonly, calcium and bicarbonate are the predominant cation and anion present in natural waters (Hem, 1989). This association links the parameters of alkalinity (which is related to the bicarbonate concentration) and hardness (which is related to the calcium and magnesium concentrations). Generally, there is a positive correlation between alkalinity and hardness in natural waters.

Mineralized areas. The chemical composition of water originating from mineralized areas can be quite different from that of water originating from non-mineralized areas. Water originating from areas underlain by mineralized rock commonly has lower pH and alkalinity values, and has higher sulfate concentrations resulting from the chemical breakdown and oxidation of sulfide minerals. As mentioned above, in many natural waters it is common to observe a positive correlation between alkalinity and hardness. However, in water originating from mineralized areas, it is common to observe proportionately higher concentrations of calcium (and magnesium) resulting from acid dissolution of rock-forming minerals that contain calcium (and magnesium). Because this calcium does not necessarily originate from carbonate minerals, the

result is increased calcium concentration (and hardness) without increased alkalinity. This has implications for the toxicity of dissolved metals to aquatic biota since calcium (and magnesium) has been shown to be protective in the presence of many dissolved metals, and current water-quality criteria for metals are calculated based on water hardness.

#### Geoenvironmental Models of Mineral Deposits

Plumlee (1999) and Plumlee et al. (1999) discuss how mineral deposits are classified according to similarities in their geologic characteristics and geologic setting, and how this classification system may be extended to incorporate potential environmental impacts of mineral deposits. This extended classification is termed “geoenvironmental models of mineral deposits” (du Bray, 1995). Geoenvironmental models can distinguish characteristics of various mineral deposits that may affect the geochemistry of aquatic systems. Coupling the BLM with geoenvironmental models may allow broad-spectrum prediction of the potential effects on aquatic toxicity of a particular mineral deposit with a particular regional bedrock.

### Methods

#### Data Source

Miller (2002) conducted a geochemical baseline study to determine water composition, acid-neutralizing capacity, and potential release of total dissolved solids for stream and spring waters in watersheds predominantly underlain by each of ten different rock-composition types in the Gunnison, Uncompahgre, and Grand Mesa National Forests in western Colorado. He collected water samples in montane headwater watersheds that have comparatively high precipitation and low evapotranspiration rates, and that have minimal ground-water capacity. Miller also collected water from the mineralized (but unmined) Redcloud Peak area near Lake City, Colorado, to compare the geochemistry of water from the relatively unmineralized watersheds with water from a mineralized area. Data from Miller’s study are listed in Tables 1 and 2. The data in Table 2 represent mean values for stream and spring water collected in watersheds underlain by a particular rock type.

#### Modeling Approach

For the purposes of this study, each rock type has been classified as either igneous, sedimentary, or mineralized (see Table 1). The water-chemistry data in Table 2 were used by the BLM to compute copper and zinc toxicity to *Daphnia magna* (water flea), which is a sensitive fresh-water invertebrate commonly used in toxicity testing of contaminants. Miller’s data set did not include DOC determinations; hence, a DOC value of 1 mg/L was used for BLM computations unless otherwise stated.

Table 1. Classification and location information for water samples collected from small streams and springs in headwater watersheds underlain by different rock types in western Colorado. Information is from Miller (2002).

Classification	Rock Type	Location
Igneous-1	Tertiary basalt flows and associated rocks	Grand Mesa National Forest, Colorado
Igneous-2	Tertiary felsic ash-flow tuff	Gunnison National Forest, Colorado (San Juan volcanic field)
Igneous-3	Tertiary quartz latitic lava and breccia	Gunnison National Forest, Colorado (San Juan volcanic field)
Igneous-4	Tertiary andesitic lava and breccia	Gunnison National Forest, Colorado (West Elk volcanic field)
Igneous-5	Tertiary and Proterozoic intrusive rocks and Proterozoic metamorphic rocks (granite, granodiorite, quartz monzonite, diorite, gneiss, gabbro)	Gunnison National Forest, Colorado (Sawatch Range)
Sedimentary-1	Tertiary sedimentary rocks (oil shale, sandstone, marlstone, claystone, lignite)	Grand Mesa National Forest, Colorado (Battlement and Grand Mesa)
Sedimentary-2	Cretaceous Mesaverde Formation (sandstone, shale, coal, claystone, minor intrusive rock)	Gunnison National Forest, Colorado (Piceance Basin, Elk Mountains)
Sedimentary-3	Cretaceous Mancos Shale (marine shale, sandstone, calcareous sandstone)	Gunnison and Uncompahgre National Forest, Colorado (San Juan volcanic field, Paradox Basin)
Sedimentary-4	Mesozoic sedimentary rocks (sandstone, siltstone, shale, limestone, conglomerate, mudstone)	Uncompahgre National Forest, Colorado (Uncompahgre uplift)
Sedimentary-5	Paleozoic sedimentary rocks (sandstone, conglomerate, carbonate, quartzite, shale, mudstone, grit)	Gunnison National Forest, Colorado (west flank of Sawatch Range)
Mineralized	Mineralized Sunshine Peak Tuff (silicic alkalic rhyolite tuff with propylitic alteration)	Redcloud Peak area, Colorado (Lake City caldera)



Table 2. Chemical data for water samples collected from small streams and springs in headwater watersheds underlain by ten different rock types and from a mineralized area in western Colorado. Data are geometric means, except pH, which is an arithmetic mean, with the number of samples listed under the classification column. Samples were filtered through a 0.45  $\mu\text{m}$  membrane filter. Alkalinity measurements were performed on unfiltered samples using Gran's plot technique. Data are from Miller (2002).

Classification	pH	Alkalinity (mg/L CaCO <sub>3</sub> )	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO <sub>4</sub> (mg/L)	Cl (mg/L)	Cu ( $\mu\text{g/L}$ )	Zn ( $\mu\text{g/L}$ )
Igneous-1 (n=4)	7.4	23	5.4	2.1	1.8	0.37	0.65	0.29	<1	0.40
Igneous-2 (n=5)	7.4	38	11	1.7	4.4	1.3	2.7	0.88	<1	0.24
Igneous-3 (n=4)	7.5	30	13	1.8	6.9	1.1	17	0.56	0.56	0.50
Igneous-4 (n=8)	8.0	59	16	3.0	7.7	1.7	3.5	0.70	<1	0.22
Igneous-5 (n=8)	7.8	28	8.0	1.7	3.1	0.55	3.5	0.39	<1	0.64
Sedimentary-1 (n=7)	8.5	157	39	12	15	1.4	8.1	1.4	<1	0.22
Sedimentary-2 (n=8)	8.3	44	13	3.0	5.4	0.49	5.3	0.49	<1	0.24
Sedimentary-3 (n=10)	8.2	83	32	7.5	4.7	0.36	18	0.60	<1	0.21
Sedimentary-4 (n=5)	7.9	168	59	10	5.2	1.8	4.7	3.5	<1	0.23
Sedimentary-5 (n=15)	8.3	117	53	11	1.3	0.47	14	<0.25	<0.5	0.60
Mineralized (n=19)	6.1	3	12	1.6	1.0	1.0	30	0.12	1.2	11

## **Results and Discussion**

Miller (2002) found that each rock type had an associated unique range of water chemistry. The relationships between alkalinity and pH (Fig. 3), and between alkalinity and calcium concentration (Fig. 4) indicate that water from watersheds underlain by igneous rock has a relatively consistent composition, whereas water from watersheds underlain by sedimentary rock tends to have a more variable composition. Water from sedimentary-rock watersheds (SRW) has a narrow pH range (pH 7.9 to 8.5), a wide alkalinity range (44 to 168 mg/L CaCO<sub>3</sub>), and calcium concentrations ranging from 13 to 59 mg/L. Water from igneous-rock watersheds (IRW) has somewhat lower pH (pH 7.4 to 8.0), notably lower alkalinity (23 to 59 mg/L CaCO<sub>3</sub>), and lower calcium concentrations (5.4 to 16 mg/L) than water from SRW. Water having the highest alkalinity is from areas underlain by Mesozoic and Tertiary sedimentary rock, and water with the lowest alkalinity is from areas underlain by Tertiary basaltic rock (classified as igneous rock). Miller (2002) calculated a normalized alkalinity to account for duration of contact differences and evaporation effects. Although normalized alkalinity was not used in this study, it is an important concept in considering the ability of rocks within a watershed to neutralize introduced acidity. In general, calcium concentrations are lower in water from IRW (5 to 16 mg/L). In fact, solutes are generally lower in water from IRW. Compared with the other water from SRW, the Cretaceous Mesaverde Formation (Sedimentary-2) water is an outlier due to its lower alkalinity and calcium concentration. Miller (2002) performed chemical modeling on mean compositions of water underlain by the different rock types and found that water underlain by Tertiary sedimentary rocks, the Mancos Shale, Mesozoic sedimentary rocks, and Paleozoic sedimentary rocks is supersaturated with respect to calcite and dolomite. This indicates that carbonate minerals have a large influence on the composition of water from SRW, except that from watersheds underlain by the Mesaverde Formation. The Mesaverde Formation is mostly sandstone, with some shale and coal beds. The sediments were deposited in beach, river delta, and swamp environments (Miller, 2002). Miller (2002) observed a wide range in alkalinity in the eight water samples from watersheds underlain by this rock type and suggested that there may be an effect from the weathering of pyrite associated with coal beds, which would result in consumption of some of the alkalinity.

As shown in Figures 3 and 4, water collected from watersheds underlain by mineralized rock has lower mean pH and alkalinity than does water from watersheds underlain by the ten predominantly unmineralized rock types. For water collected from the mineralized area, it is likely that most of the alkalinity is neutralized or consumed by acidity released from the weathering of pyrite. Further evidence for the weathering of pyrite is the higher concentration of sulfate, a weathering product of pyrite, in the water collected from the mineralized area compared with water collected from the predominantly unmineralized areas (see Table 2). Water collected from the mineralized area deviates from the trend in Figure 4 in that it has a proportionately higher calcium concentration, which is most likely due to acid dissolution of rock-forming minerals.

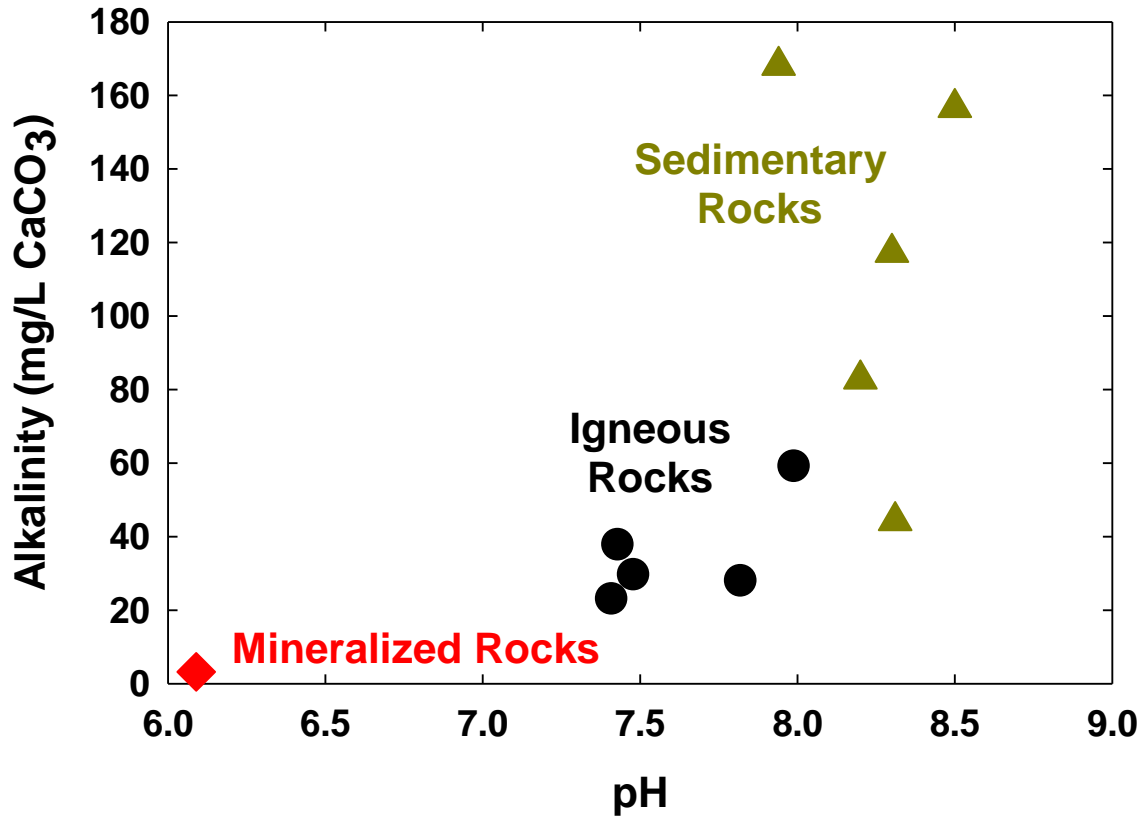


Figure 3. Graph showing mean pH and alkalinity of water collected from watersheds underlain by different rock types, and of water collected from watersheds underlain by mineralized rock.

#### Differences in Predicted LC<sub>50</sub> Values

Mean water compositions (Table 2) were entered into the BLM, with DOC values of 1 mg/L. The predicted LC<sub>50</sub> values for copper and zinc toxicity to *Daphnia magna* are shown relative to mean alkalinity (Figures 5 and 6) and mean calcium concentration (Figures 7 and 8). There is a positive correlation between the predicted LC<sub>50</sub> values and alkalinity and calcium concentration. One of the most significant observations to be made from these data is that water from watersheds underlain by the different rock types has characteristic ranges of predicted LC<sub>50</sub> values, with water from IRW having lower predicted LC<sub>50</sub> values than water from SRW. The characteristic range for predicted copper LC<sub>50</sub> values is between 9 and 22 µg/L in water collected from watersheds underlain by igneous rock, and between 25 and 42 µg/L in water collected from watersheds underlain by sedimentary rock. The characteristic range for predicted zinc LC<sub>50</sub> values is between 400 and 1,100 µg/L in water from IRW, and between 1,100 and 4,700 µg/L in water from SRW. For water collected from a mineralized area, the predicted copper LC<sub>50</sub> value is very low (1 µg/L) and the predicted zinc LC<sub>50</sub> value is within the range of water from IRW (900 µg/L). With the exception of the LC<sub>50</sub> for water collected from the mineralized area, the

predicted copper LC<sub>50</sub> values calculated in this study are within the range of the Colorado hardness-based surface water-quality standards for acute copper toxicity, which range from 3.6 to 50 µg/L for hardness ranging from 25 to 400 mg/L CaCO<sub>3</sub>. However, the predicted zinc LC<sub>50</sub> values calculated in this study are significantly higher than the Colorado hardness-based surface water-quality standards for acute zinc toxicity, which range from 36 to 379 µg/L for hardness ranging from 25 to 400 mg/L CaCO<sub>3</sub>. This difference between copper and zinc may be due to the fact that species more sensitive to zinc than *Daphnia magna* were used to determine the water-quality criteria for zinc.

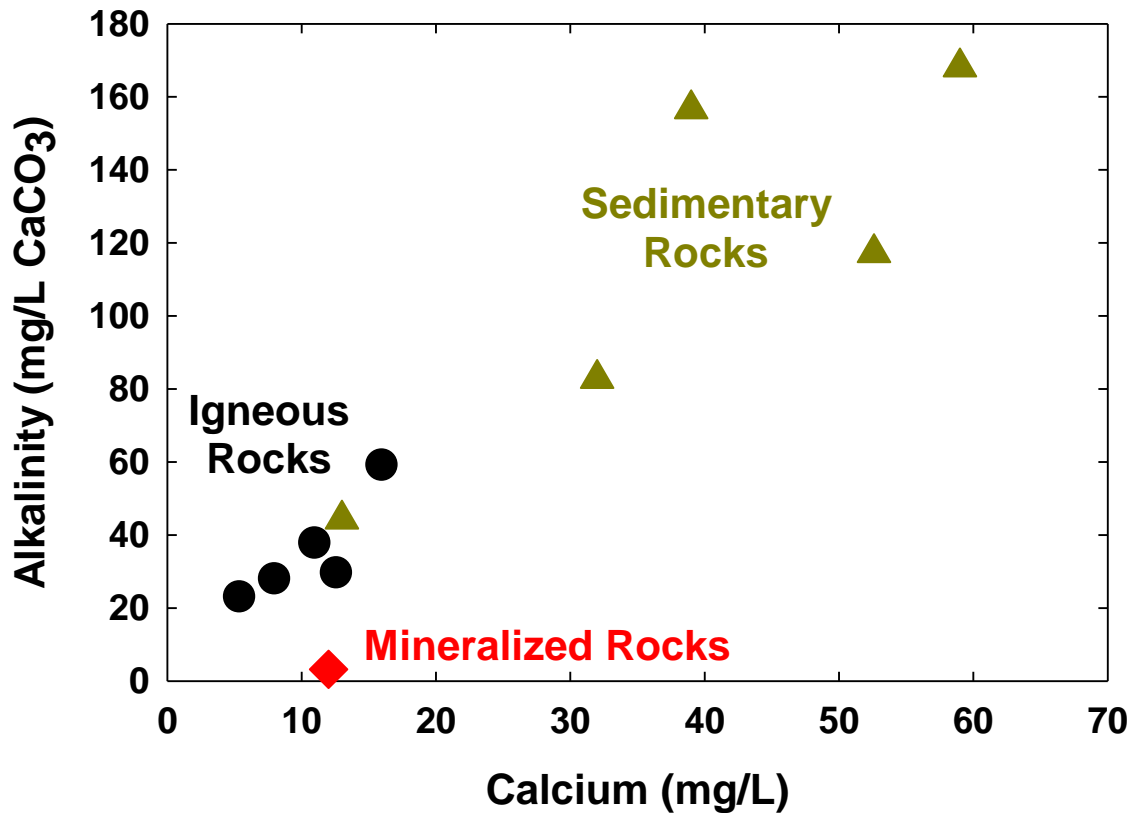


Figure 4. Graph showing the relationship between mean calcium concentration and alkalinity in water collected from watersheds underlain by different rock types, and of water collected from watersheds underlain by mineralized rock.

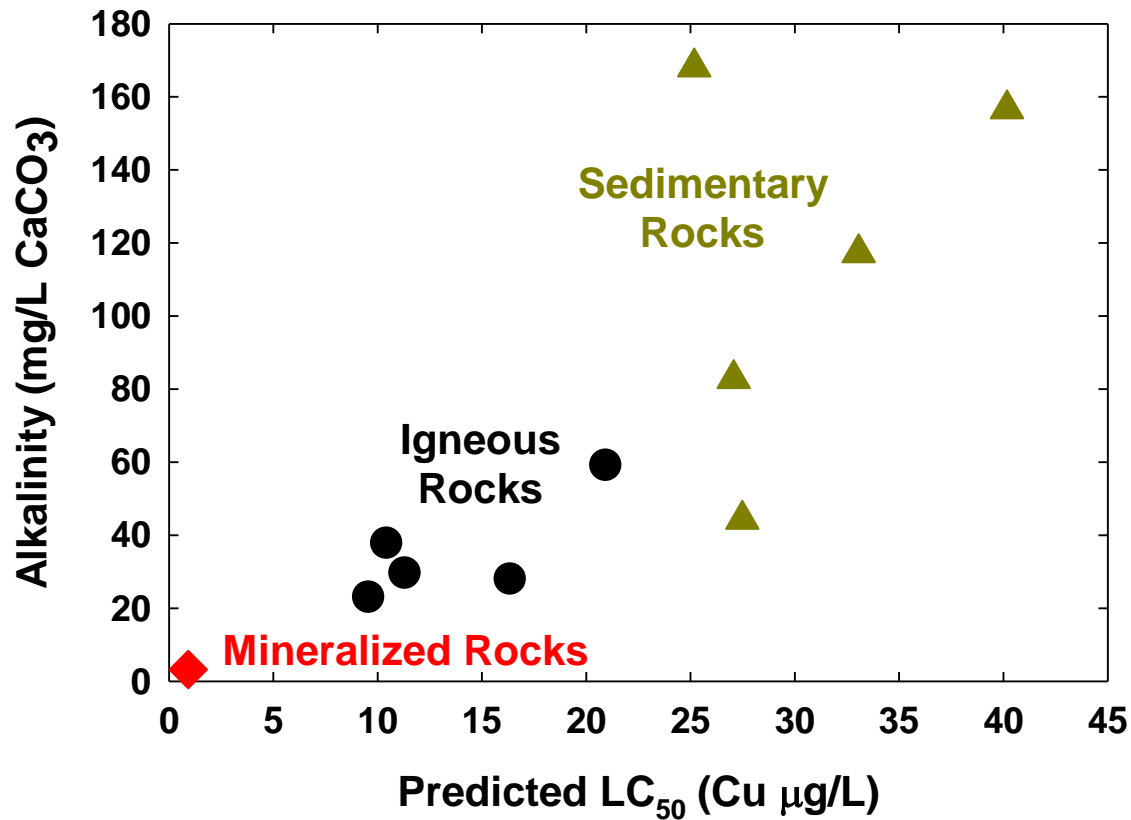


Figure 5. Graph showing mean alkalinity and predicted copper LC<sub>50</sub> values for *Daphnia magna*, using 1 mg/L DOC concentration, for water collected from watersheds underlain by different rock types, and for water collected from watersheds underlain by mineralized rock. Note that data from the different underlying rock types fall within particular ranges of predicted LC<sub>50</sub> values.

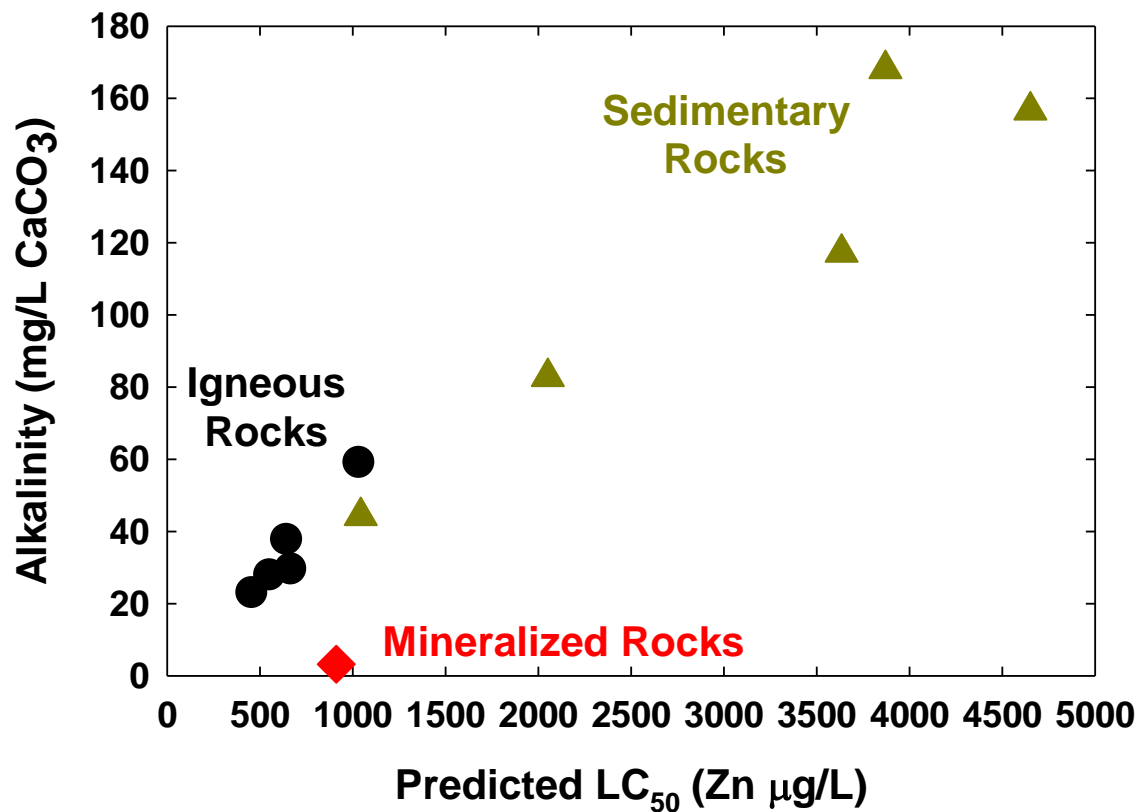


Figure 6. Graph showing mean alkalinity and predicted zinc LC<sub>50</sub> values for *Daphnia magna*, using 1 mg/L DOC concentration, for water collected from watersheds underlain by different rock types, and for water collected from watersheds underlain by mineralized rock. Note that data from the different underlying rock types fall within particular ranges of predicted LC<sub>50</sub> values.

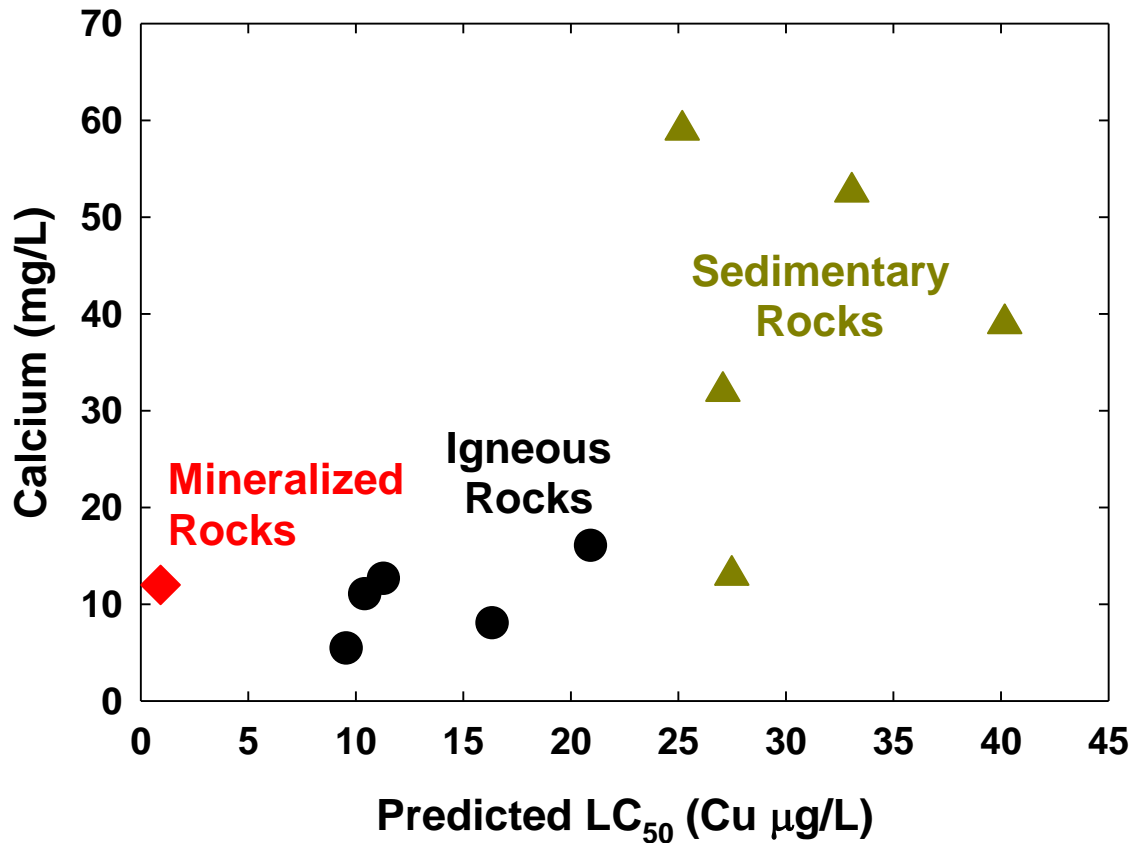


Figure 7. Graph showing mean calcium and predicted copper LC<sub>50</sub> values for *Daphnia magna*, using 1 mg/L DOC concentration, for water collected from watersheds underlain by different rock types, and for water collected from watersheds underlain by mineralized rock. Note that data from the different underlying rock types fall within particular ranges of predicted LC<sub>50</sub> values.

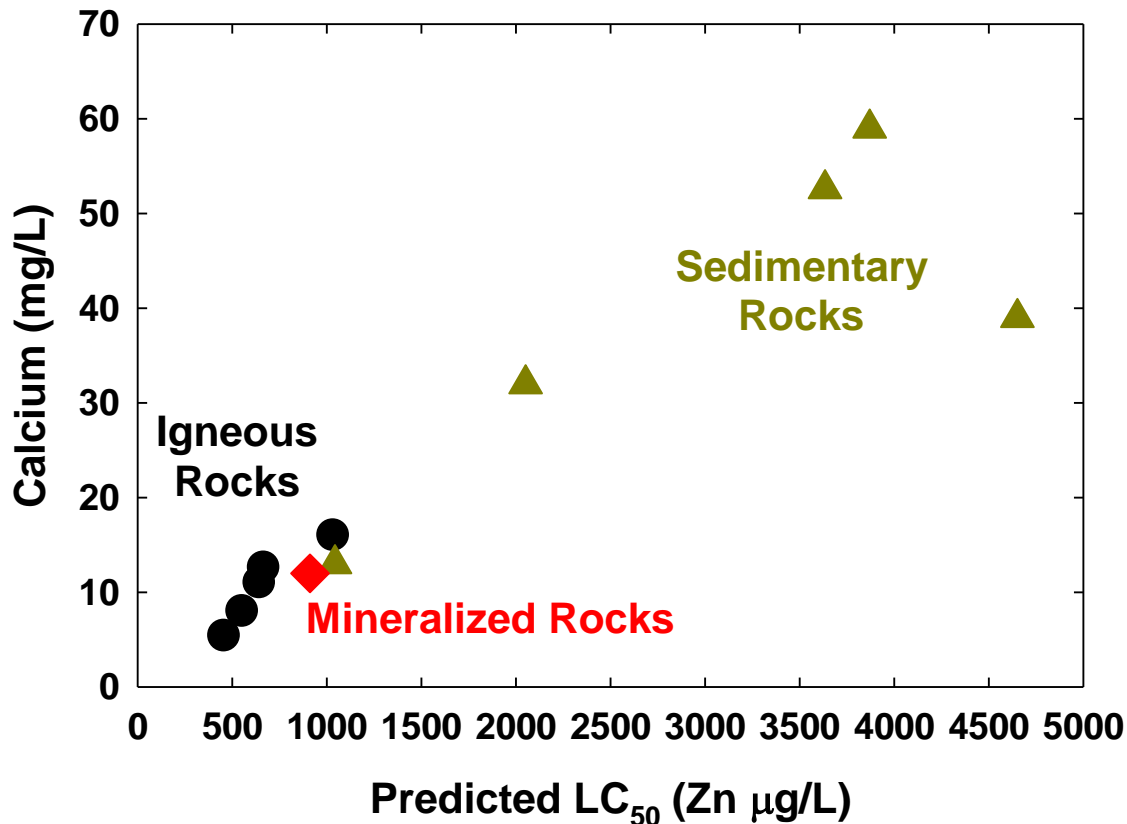


Figure 8. Graph showing mean calcium and predicted zinc LC<sub>50</sub> values for *Daphnia magna*, using 1 mg/L DOC concentration, for water collected from watersheds underlain by different rock types, and for water collected from watersheds underlain by mineralized rock. Note that data from the different underlying rock types fall within particular ranges of predicted LC<sub>50</sub> values.

Characteristic ranges of predicted LC<sub>50</sub> values that correspond to different underlying rock types have some significant implications. Lower predicted LC<sub>50</sub> values for watersheds underlain by igneous rock means that aquatic biota in these waters may be more sensitive to inputs of copper and zinc than are aquatic biota in watersheds underlain by sedimentary rock. This suggests that copper or zinc contaminants in a watershed underlain by igneous rock pose a greater potential threat to aquatic biota than in a watershed underlain by sedimentary rock. This type of information could be very valuable in risk assessments for metals and mining, mine-site planning, and remediation strategies, and could be a useful extension to existing geoenvironmental models of mineral deposits.

#### Effect of DOC Concentration

Because Miller (2002) did not report DOC concentrations, a value of 1 mg/L was used in the BLM computations previously discussed. Additional model simulations were performed for a range of DOC concentrations (0.5 to 4 mg/L) to test the influence of DOC concentration on the



predicted LC<sub>50</sub> values. The BLM results are in Figure 9a for copper and Fig. 9b for zinc. For both copper and zinc, there is a trend of increasing predicted LC<sub>50</sub> values with increasing DOC concentration. Fig. 9c and 9d present the same data recalculated to display the percent differences in predicted LC<sub>50</sub> values between the different DOC concentrations. Compared with zinc, copper shows much higher percent differences in predicted LC<sub>50</sub> values between the different DOC concentrations. This indicates that predicted copper LC<sub>50</sub> values are extremely sensitive to DOC concentration. This is consistent with the fact that copper-organic binding constants generally are significantly greater than zinc-organic binding constants (Smith and Huyck, 1999). Fig. 9e and 9f show the percent differences in predicted LC<sub>50</sub> values between the different DOC concentrations as a function of alkalinity. In the case of copper, there does not appear to be much of an influence from alkalinity. However, in the case of zinc, alkalinity appears to have an influence at alkalinities in excess of about 100 mg/L CaCO<sub>3</sub>. Because alkalinity in water from watersheds underlain by sedimentary rock tends to be higher than alkalinity in water from watersheds underlain by igneous rock, it appears that alkalinity may have more of a protective influence on zinc toxicity to aquatic biota in watersheds underlain by sedimentary rock.

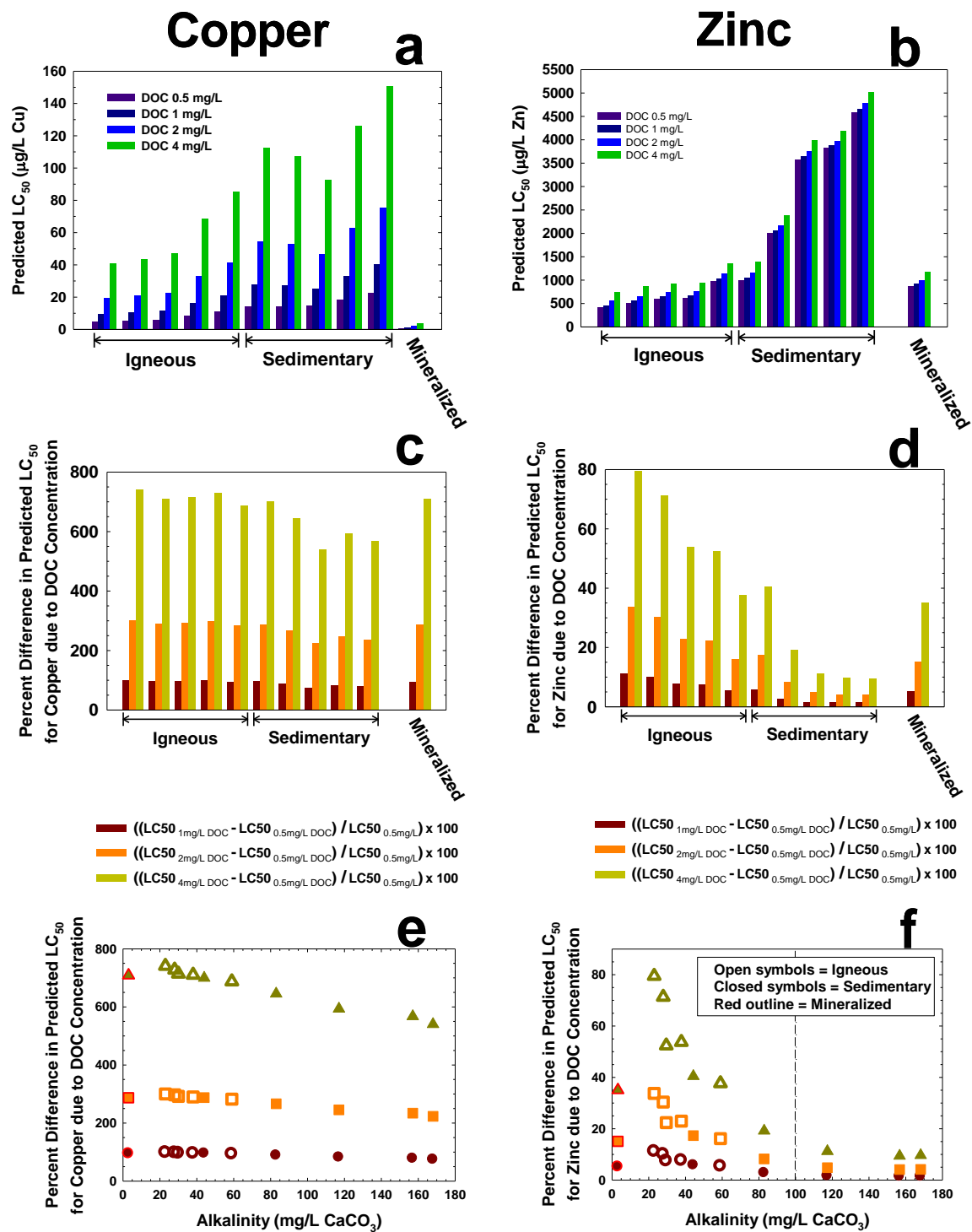


Figure 9. Graphs showing copper (left side) and zinc (right side) predicted LC<sub>50</sub> values for *Daphnia magna* at different DOC concentrations for water collected from watersheds underlain by different rock types, and for water collected from watersheds underlain by mineralized rock. Graphs c-f present differences in predicted LC<sub>50</sub> values for the different DOC concentrations, and e and f show the data as a function of mean alkalinity.

## Summary and Conclusions

Several conclusions may be drawn from this study.

- 1) The chemistry of stream and spring waters collected from montane watersheds is controlled primarily by the chemical composition of the underlying bedrock (Miller, 2002).
- 2) Unique ranges in water chemistry correspond to each underlying rock type examined in this study (Miller, 2002).
- 3) Water collected from watersheds underlain by sedimentary rock has higher mean pH, alkalinity, and calcium concentrations than water collected from watersheds underlain by igneous rock.
- 4) Predicted LC<sub>50</sub> values for copper and zinc toxicity to *Daphnia magna* calculated from water-chemistry data for the different underlying rock types fall within distinct ranges.
- 5) The characteristic range for predicted copper LC<sub>50</sub> values for *Daphnia magna* is between 9 and 22 µg/L in water collected from watersheds underlain by igneous rock, and between 25 and 42 µg/L in water collected from watersheds underlain by sedimentary rock.
- 6) The characteristic range for predicted zinc LC<sub>50</sub> values for *Daphnia magna* is between 400 and 1,100 µg/L in water collected from watersheds underlain by igneous rock, and between 1,100 and 4,700 µg/L in water collected from watersheds underlain by sedimentary rock.
- 7) For water collected from a mineralized area, the predicted copper LC<sub>50</sub> value for *Daphnia magna* is 1 µg/L, and the predicted zinc LC<sub>50</sub> value for *Daphnia magna* is 900 µg/L.
- 8) Aquatic biota in watersheds underlain by igneous rock are likely to be more vulnerable to copper and zinc contamination than are aquatic biota in watersheds underlain by sedimentary rock.
- 9) Predicted LC<sub>50</sub> values for copper and zinc toxicity to *Daphnia magna* increase with increasing DOC concentrations.
- 10) Predicted LC<sub>50</sub> values for copper are extremely sensitive to the DOC concentration.
- 11) Predicted LC<sub>50</sub> values for zinc are dependent on DOC concentration, but alkalinity appears to have an influence on zinc toxicity when alkalinity exceeds about 100 mg/L CaCO<sub>3</sub>.
- 12) The BLM appears to be sensitive enough to predict metal toxicity to aquatic biota in different geologic settings, however these predictions should be verified by toxicity tests to fully validate the BLM approach for water from varied geological settings. In future work, coupling the BLM with geologic and water-quality information may prove to be a useful planning tool in ecological risk assessments for metals and mining, mine-site planning and remediation, and mitigation strategies, and could be an effective extension to existing geoenvironmental models of mineral deposits.

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