Chapter 4
How to Assess Ecological Risks of Trace Metals in Environment

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Abstract Ecological risk assessments for chemicals are fundamental to understand and manage their adverse impacts on the environment. In this chapter, we introduce methods to assess the ecological risks of chemicals with a particular focus on trace metals such as zinc and copper. In freshwater ecosystems which are most threatened than other ecosystems at a global scale, trace metal contamination is a long-standing concern worldwide. A typical source of the trace metal contamination is active/inactive (legacy) mines, and many of those mines have been causing different levels of environmental impacts. Here, we introduce three types of methods to assessing ecological risks and impacts of trace metals, and their advantages and limitations. First, comparing the measured concentrations of metals with environmental quality benchmarks such as water quality standards is a useful screening-level approach. Second, by performing toxicity tests with field-collected water samples, the whole toxicity to aquatic organisms (e.g., algae, crustaceans, or fishes) is directly examined. Third, field surveys of biological groups can directly capture the ecological consequences of metal exposure to aquatic populations and communities. Typical biological groups used for biological assessment in streams and rivers are periphyton, benthic macroinvertebrates, and fishes. The simplest study design for the field survey is comparing aquatic populations and communities at two river sites upstream and downstream the inflow of mine discharge. If ecological risks of a chemical are highly concerned, the countermeasures to reduce the environmental concentrations are ideally required. In Japan, the environmental water quality standard for zinc in freshwater was established to be 30 μg/L to protect aquatic populations and was derived based on a chronic toxicity value for a macroinvertebrate (mayfly) species. However, the results of field surveys in multiple rivers suggest that dissolved zinc concentrations of more than twice the standard (70–115 μg/L) has little effect on macroinvertebrate richness and thereby that the Japanese water quality standard is somewhat overprotective for the protection of the macroinvertebrate richness.

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Accumulated findings clearly indicate that field survey can be used to reasonably infer "safe" concentrations in the natural environment.

4.1   Ecological Risk Assessment for Chemicals in General

The number of chemicals registered in the Chemical Abstracts Service (CAS) is over 140 million and a recent study estimated that over 350 thousand chemicals have been globally registered for production and use (Wang et al. 2020). Chemicals are essential and beneficial for our life, but the historical experience clearly indicates that their impacts on ecosystems as well as human health (see Chap. 1) can be critical. To avoid and minimize such adverse impacts, we need risk assessments to examine, e.g., if new chemicals entering the market are safe (e.g., the Toxic Substances Control Act (TSCA) in the United States and Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) in the European Union), if there is a risk of concern for any chemical in the natural environment, and if the discharge from a given point source (e.g., manufacturing plant) is affecting aquatic organisms inhabiting in the downstream river.

Tiered approaches are commonly used for ecological risk assessment (ERA) for chemicals. As a screening-level (first) assessment, ecological risks are examined by a simple and generally conservative (or safe-side) way with a minimum (available) toxicity dataset. Such screening-level ERA is typically performed by dividing predicted environmental concentration (PEC) by predicted no-effect concentration (PNEC; Fig. 4.1):

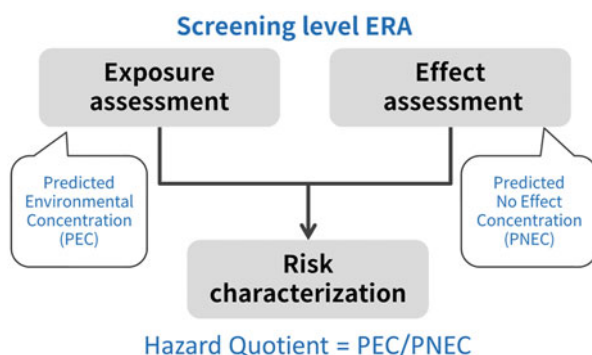**Fig. 4.1** Screening-level ecological risk assessment (ERA)

Screening level ERA

Exposure assessment

Effect assessment

Predicted Environmental Concentration (PEC)

Predicted No Effect Concentration (PNEC)

Risk characterization

Hazard Quotient = PEC/PNEC

Table 4.1 Test durations and endpoints in acute and chronic ecotoxicity tests

Biological groups	Type	Time	Endpoints
Algae	Acute	$\leq$72 h	Growth Inhibition
	Chronic	$\geq$72 h	Growth Inhibition
Crustacean (cladocerans)	Acute	48 h	Immobilization (mortality)
	Chronic	21 days	Fecundity, growth, immobilization (mortality)
Fish	Acute	96 h	Survival
	Chronic	>7 days	Hatchability, fecundity, growth, survival

Durations and endpoints shown here are some examples based on, e.g., OECD guidelines for testing chemicals, and they can vary depending on test species, life stages of species tested, and regulatory jurisdictions

$$\text{Hazard quotient} = \frac{\text{PEC}}{\text{PNEC}}$$

If the hazard quotient (HQ; Suter 2007) is well below than 1, the risk is *not* at the level of concern and further testing or risk reduction measure is not required. If the HQ is close to or higher than 1, the risk may be at the level of concern and further detailed assessment is required. Although those are typical examples, how we interpret the HQs may change depending on, e.g., regulatory jurisdictions, methods used, and empirical evidence available.

Here, let us pretend that we are performing the nationwide ERA for a chemical in freshwaters. In the exposure assessment (Fig. 4.1), the maximum concentration of a chemical observed in the nationwide water quality monitoring may be used as the "safe-side" PEC. However, given that the maximum value is not a statistically robust estimate (if the sample size increases, the maximum value can increase), use of quantiles such as the 0.95 quantile (95th percentile) is a better alternative. If the water quality monitoring data is lacking, exposure models that simulate watershed hydrology and water quality are often used to derive the PEC.

In the effect assessment (Fig. 4.1), the PNEC is derived from the results of ecotoxicity tests. In toxicity tests, by exposing a given biological species (typically, an algal, crustacean, or fish species) to a range of concentrations of a chemical of concern, individual-level effects (endpoints) such as those on survival, growth, and fecundity (e.g., number of spawned eggs) are investigated. Although a tremendous number of biological species are present in freshwaters, a limited number of species such as *Raphidocelis subcapitata* (a microalgal species), *Daphnia magna* (a planktonic crustacean), and *Pimephales promelas* (fathead minnow; a cyprinid fish species) are commonly used in ecotoxicity data. Acute (short-term) or/and chronic (long-term) toxicity are examined in toxicity tests, in which the testing periods and endpoints vary depending on the species tested (Table 4.1). Median lethal concentration (LC50) and 50% effective concentration (EC50) are usually estimated in acute toxicity tests, while no observed effect concentration (NOEC; the maximum concentration at which no statistically significant effect is observed), and EC10 (or EC20) are derived as "safe" concentrations in chronic toxicity tests.

Table 4.2 Hypothetical examples of the derivation of predicted no-effect concentration (PNECs) for a chemical by applying different uncertainty factors (Forbes and Calow 2002)

Case	Toxicity values (mg/L)			Uncertainty factor	PNEC (mg/L)
	Algae	Crustacean	Fish		
Case 1		100 (acute)		1000	0.1
Case 2		10 (chronic)		100	0.1
Case 3	15 (chronic)	10 (chronic)	50 (chronic)	10	1

PNEC is the concentration below which any unacceptable impacts on ecosystems will most likely not occur and is rather loosely defined. To derive a PNEC, there are two major sources of uncertainty, lack of understanding, and natural variability, the latter of which cannot be avoided because it is the inherent property of ecosystems (Forbes and Calow 2002). Generally, we need to derive a PNEC based on very limited toxicity data (say, only a single acute toxicity data). In other words, we need to extrapolate the results of limited toxicity tests performed in the laboratory to ecological impacts in actual environments. Do you think it is really possible? To address this uncertainty, in ERAs, the minimum toxicity value is commonly divided by the uncertainty (so-called, application, assessment, or safety) factors (UFs). Although scientific evidence supporting the use of such factors has not been fully gained, there is a long history of the use in ERAs. For instance,

1. If you have only a single acute toxicity value (e.g., LC50), a UF of 1000 is applied to take into account the acute to chronic ratio, variation in interspecies sensitivity, and lab-to-field extrapolation.
2. If you have only a single chronic toxicity value (e.g., NOEC), a UF of 100 is applied to take into account variation in interspecies sensitivity and lab-to-field extrapolation.
3. If you have at least three chronic toxicity values from each of the three biological groups (see Table 4.1), a UF of 10 for lab-to-field extrapolation is applied to the minimum toxicity value.

By assuming that a crustacean species is most sensitive among the three biological groups, Table 4.2 shows some hypothetical examples for the derivation of PNECs. Although those are simple examples, the derived PNECs depend on the data availability. Compared to Case 3 in Table 4.2, PNECs for Cases 1 and 2 are underestimated (i.e., indicating overprotection). Thus, the interpretation of PEC exceedance of PNEC should be assessed based on the availability of information (i.e., how reliable a PNEC or PEC is; Chapman 2018).

When the screening-level ERA suggests that the risk may be at the level of concern, more ecotoxicity data or environmental monitoring data are needed to be acquired to more accurately estimate the PNEC or PEC. For instance, once ecotoxicity data are obtained for many biological species (say, 5–10 species or more), species sensitivity distribution (SSD) may be used to estimate a PNEC (Posthuma et al. 2002). The SSD expresses a set of toxicity values such as EC10 and NOEC, as a statistical distribution (e.g., log-normal distribution) and has been

used to estimate the hazardous concentration for 5% of the species (HC5) that can be used to derive a PNEC by applying a smaller UF (usually, 1–5). SSDs are now commonly used to derive water quality benchmarks such as environmental water quality standards/criteria in many regulatory jurisdictions.

Importantly, the exceedance of a chronic toxicity value such as NOEC or EC10 for a chemical does not necessarily mean that the corresponding species will disappear at a site or area of concern. Even if the concentration for a chemical exceeds the chronic toxicity value for a species, it does not mean that no individual of the species reproduces or survives at all. As explained in the theory of sustainable fisheries, many organisms become resilient in their attempts to maintain population persistence when the population size decreases. Even if the survival and reproductive rates decrease, the species are not so fragile that their populations continue to decrease before the extinction. However, if there is the effect of a chemical beyond the resilience of the population, the population will not recover and will continue to decline. The chronic toxicity values such as EC10 and NOEC, at which almost no or small effects on survival or/and reproduction are expected, should be somewhat protective to guarantee the population persistence.

To address such issue of unclear ecological consequences based on the chronic toxicity values, Kamo and Naito (2008) developed a population-level SSD approach. In the approach, first, threshold concentrations leading population extinction for individual species are generally estimated by incorporating concentration-effect relationships into life-history parameters. In the case of zinc, the concentration that guarantees the persistence of 95% of the species population (called the population-level hazardous concentration of 5% of species) was estimated to be 107 μg/L, while HC5 based on a conventional (individual-level) SSD based on NOECs was 27 μg/L (Fig. 4.2).

4.2   Metal Pollution and Ecological Impacts

Environmental pollution with trace metals such as copper, zinc, cadmium, and lead is a worldwide concern in terms of the protection of human health and ecosystems (Luoma and Rainbow 2008). Before getting down to the point, the two terms are to be discussed. First, although the discrimination between "contamination" and "pollution" is not often done even in scientific literature, contamination is the presence of a pollutant and pollution is "contamination that causes adverse biological effects in the natural environment" (Chapman 2007). Also, the term "heavy metal" is very commonly used in the field of environmental science but is surprisingly ill-defined (surprisingly many definitions are available; Duffus 2002). Because of this, the use of heavy metal has been occasionally but severely criticized (Duffus 2002; Hodson 2004); We like the title of Hodson's paper, "Heavy metals - geochemical bogey men?"). There are several alternatives such as a classification of metallic elements based on the periodic table (s-, p-, d-, or f-block; see Duffus 2002 for more details). Those alternatives are unfamiliar, but this should not be a reason not to use them and
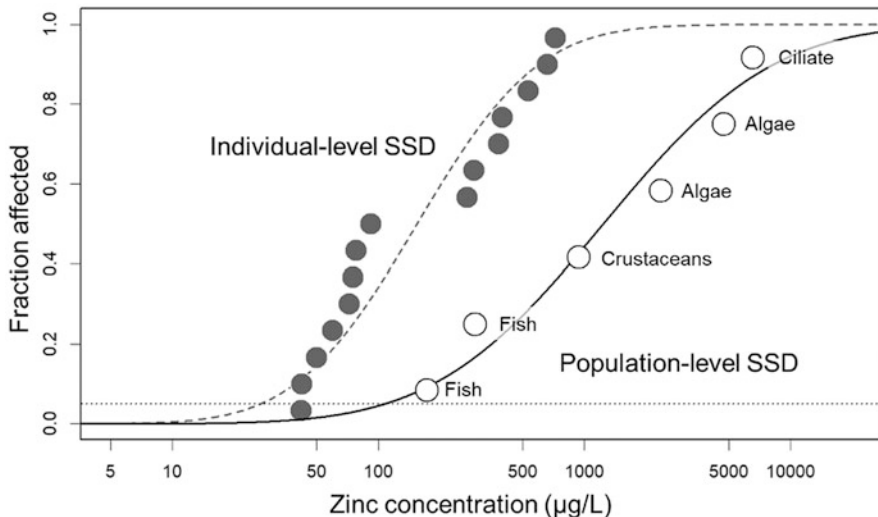
Fig. 4.2 Individual-level (broken line) and population-level (solid line) species sensibility distributions (SSDs). Filled and open circles indicate NOECs for 15 biological species and the threshold concentrations leading to population extinction for 6 biological species, respectively. A horizontal dotted line indicates the fraction affected of 5%

it is important to recognize that "heavy metal" is not scientifically valid term. In this chapter, the term "metal" or "trace metal (metal generally found in low concentration)" is used to express those such as copper, zinc, cadmium, and lead.

Numerous studies have demonstrated aquatic (freshwater, marine) and terrestrial ecosystems affected by trace metal pollution (Adriano 2001; Luoma and Rainbow 2008). Among the different ecosystems, freshwater ecosystems such as streams, rivers, and lakes harbor diverse species and provide important ecosystem services, but these ecosystems are currently being stressed by various anthropogenic impacts (Flitcroft et al. 2019; Reid et al. 2019). Freshwater ecosystems are the most threatened at a global scale based on the Living Planet Index—that is, the average rate of change over time across a set of species populations (WWF 2018). The freshwater Living Planet Index, representing over 3000 populations of 880 species, showed an 83% decline. Water pollution is one of the significant causes, and others include habitat modification including instream flow modification, fragmentation, climate change, invasive species, and so on.

In freshwater ecosystems, a typical source of metal pollution is mining. There are many inactive (legacy) mines worldwide, as well as active mines, and many of those mines have been causing different levels of environmental impacts. Historic disasters caused by active/inactive mines sometimes occurred and recent examples include the Gold King Mine spill, Colorado, USA (US Environmental Protection Agency 2018) and the collapse of the Fundão tailings dam, Minas Gerais, Brazil (do Carmo et al. 2017), both of which occurred in 2015. Particularly, the collapse of Fundão dam was "the biggest environmental disaster of the world mining industry,

Fig. 4.3 Photo of an acidic river downstream a closed mine in Japan. Even though the riverbed was covered by the orange-colored iron deposition, a few species of macroinvertebrates such as nemourid stonefly larvae (Plecoptera) were present

both in terms of the volume of tailings dumped and the magnitude of the damage" (do Carmo et al. 2017). In contrast, interestingly, the clear ecological effects of the Gold King Mine spill, that is, those on fish populations and macroinvertebrate communities in rivers, were not found despite the devastating fact that the Animas river temporally turned yellow likely due to the chemical reaction of iron and aluminum with the river (US Environmental Protection Agency 2018). In addition to such extreme events, acidic mine drainages (AMDs) are perennially released from individual mines and often contain high levels of trace metals such as cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) (Fig. 4.3). Regardless of whether AMDs are treated or not, ecological impacts of trace metal contamination in freshwaters caused by mine drainages are a long-standing concern worldwide and have been extensively studied (Luoma and Rainbow 2008; Namba et al. 2020). In this regard, ecological risk assessments have a crucial role to provide fundamental information about the predicted or observed impacts and thereby how the metal contamination should be managed.

4.3   Factors Affecting Toxicity of Metals

Elevated metal concentrations in environmental media such as surface waters in rivers can cause direct and indirect ecological impacts. Although the comprehensive and detailed mechanical understanding of metal toxicity is still lacking, it has been well demonstrated that waterborne metal toxicity depends on the metal bioavailability that is affected by several water quality parameters including major ions (e.g., Ca and Mg), pH, and dissolved organic matter (Adams et al. 2020). For instance, major ions such as Ca and Mg compete with trace metals at biotic ligands and thereby increased those concentrations mitigate the toxicity of trace metals. US EPA chronic water quality criteria for zinc depend on water hardness ($2.497 \times$ Ca (mg/L) + $4.118 \times$ Mg (mg/L)) and those at water hardness of 20 and 100 mg/L, are 30 and 120 μg/L, respectively (US Environmental Protection Agency 2002). Also, the binding of trace metals to dissolved organic matter can reduce the metal toxicity (i.e., reduced toxicity with increased dissolved organic matter).

   Historically, the influence of major ions, pH, and dissolved organic matter on the metal toxicity was a critical issue when assessing ecological risks of trace metals because results of toxicity tests were too variable to derive a reliable PNEC and also because the total, dissolved (filtered), or free-ion concentration of metals measured is not necessarily a good predictor of toxicity. To address this issue, the biotic ligand models (as known as BLMs), which assume that toxicity occurs by the accumulation of metals on biotic ligands (e.g., gills of fish), have been developed and tested extensively for many trace metals. An excellent example is that the acute toxicity measures (LC50s) based on the estimated concentrations of Ni and Cu bound to gills of a fish species (fathead minnow) were constant when Ca concentrations increased, whereas those based on the total and free-ion concentration were not (Meyer et al. 1999). Note that, in BLMs, the influences of those water quality parameters on the metal bioavailability vary among trace metals (OECD 2017) and often among biological species of concern.

   Although empirical evidence has been accumulated for use of BLMs, there are several issues to conclude that BLMs should be used to predict trace metal exposure and environmental impacts on diverse aquatic species in general. First, in environments, aquatic organisms can accumulate metals from their food and often sediment in addition to water, and the relative importance of the individual exposure routes to the overall bioaccumulation and resulting toxicity is often uncertain. Cation may be required particularly when the concentrations of trace metals in water, sediment, and food are not correlated. Second, the accumulated evidence is largely based on laboratory testing with a very limited number of species. Based on the state-of-the-art knowledge, ease of sampling and analyzing, and the circumstance of study sites of concern (e.g., little variation in water quality parameters), use of simple exposure predictors such as total and dissolved concentrations of metals can be adequate.

4.4   Methods to Assessing Ecological Risks of Metals Caused by Mine Discharge

In this section, we discuss three types of methods to assessing ecological risks and impacts of trace metals caused by mine discharge as well as their advantages and limitations. To this end, we focus on the trace metal pollution in freshwater, particularly, streams and rivers. Given that many active/inactive mines are located in mountainous areas, the streams and rivers are the typical environmental media receiving the mine discharges. Also, such location characteristic can lead to negligible impacts of other anthropogenic factors such as agricultural/urban pollution and land-use changes, and thereby causal inference based on field surveys should be more straightforward. For the simplicity and reasons explained in the previous section, we will use dissolved concentrations of trace metals as a predictor for effects.

4.4.1   Ecological Risk Assessment Based on Measured Concentrations of Metals

Let us pretend that we are interested in assessing the ecological impacts of mine discharge in a river. A likely first step is to assess whether or not ecological risks are of concern in the river by performing a screening-level ERA. By collecting and analyzing water samples (preferably multiple times) at several study sites in the river, dissolved concentrations of trace metals of concern (e.g., Cd, Cu, Pb, Zn) and other relevant water quality parameters such as water hardness are measured. Water samples for dissolved metals analysis are filtered (0.45-µm mesh size) at the field sampling and analyzed in the laboratory. Then, the hazard quotient (HQ; see Sect. 4.1) can be calculated by the measured concentration of a metal divided by a PNEC or relevant water quality benchmark. The measured concentration may be the averaged or maximum concentration of multiple samples collected, e.g., at different times of the year. For example, if the long-term effects of mine discharge, which perennially flows into the river and has relatively constant concentrations of metals, are of concern, comparing the averaged concentration of metals with chronic water quality benchmarks such as USEPA chronic water quality criteria (U.S. Environmental Protection Agency 2002) would be appropriate. If episodic effects are of concern (e.g., historic disasters mentioned above), comparing the maximum concentration with acute water quality benchmarks may be more relevant.

The ecological risks can be assessed by examining the magnitudes of HQ values calculated for individual metals (see Sect. 4.1 for the typical interpretation). Importantly, even though all the HQs calculated for individual metals are below 1, the effects of metal mixtures may be of concern. Examining if the sum of HQs exceeds 1 is a potentially useful way to assess the ecological risks of metal mixtures but the threshold of 1 may be too protective (Iwasaki et al. 2020). In either way of

assessment, the limitations should be paid attention. Because water quality benchmarks are typically conservative and not absolute, the final decision-making should not be made based only on those benchmarks (Chapman 2018). If ecological risks are concerned, performing further detailed assessments are recommended (see Sects. 4.4.2 and 4.4.3).

4.4.2 Toxicity Testing with Field-collected Waters

By performing toxicity tests with field-collected water samples, the whole toxicity to aquatic organisms (e.g., algae, crustaceans, or fishes) is directly examined. This type of toxicity testing is more commonly applied to facilities' effluents and is called whole effluent toxicity (WET) testing (Grothe et al. 1996). Test durations and endpoints in Table 4.1 may be used. An advantage of this approach is to directly examine the whole toxicity of a water sample, while the HQ approach needs to predict the overall toxicity by summing up HQ values of individual metals or chemical substances. If an unmeasured metal or chemical substance significantly contributes to the overall toxicity, the HQ approach cannot take it into account but the toxicity testing approach can do. Another advantage is to be capable of identifying the water sample characteristics causing toxicity and the procedure is called toxicity identification evaluation (TIE; Grothe et al. 1996). However, it is uncertain how the observed toxicity links to effects in the field.

4.4.3 Field Surveys of Biological Groups

In contrast to the other two methods described above, an appealing advantage of field surveys of biological groups is to directly capture the ecological consequences of metal exposure to aquatic populations and communities. Typical biological groups used for biological assessment in streams and rivers are periphyton, benthic macroinvertebrates, and fishes, which have different advantages (Barbour et al. 1999). Periphyton primarily consists of algae, supporting riverine food webs as primary producers. Their life cycles are relatively short, are easy to sample, and are often highly sensitive to short-term physical and chemical disturbances. Benthic macroinvertebrates are relatively sedentary, have variable life cycles, and comprise diverse sets of species with a wide range of sensitivities to trace metals (Iwasaki et al. 2018; Rosenberg et al. 2008), being useful for assessing relatively local-scale and long-term cumulative effects. Fishes are relatively long-lived and mobile, being good indicators of longer term and broad-scale effects. In addition, because fishes are important resources for our food and recreational and commercial fishing, they are more valued than other biological groups by many local human communities.

Which biological groups (periphyton, benthic macroinvertebrates, and fish) are better to be surveyed in assessing metal impacts on aquatic populations and

communities in rivers? A recent systematic review of a total of about 200 published studies worldwide concluded that (1) benthic macroinvertebrates have been most frequently used (>60% of studies), that (2) correlations between responses of the different biological groups were often low, and that (3) abundance (number of individuals) and richness (number of taxa or species) metrics of macroinvertebrates were generally more responsive to changes in metal contamination level than those of periphyton or fishes (Namba et al. 2020). These results suggest that, although it is important to survey multiple biological groups for comprehensively understanding the responses of aquatic populations and communities to metal contamination in rivers, benthic macroinvertebrates (mainly aquatic insects) could be a reasonable first choice to detect the ecological impacts of metal contamination. In this systematic review, studies only investigating the accumulation of metal in aquatic organisms were not included. In addition to the ecological impacts, if you are interested in metal accumulation in, e.g., fishes, for human health, the investigation on such aspect is further required.

By establishing the appropriate reference sites with similar physicochemical characteristics other than concentrations of trace metals and comparing the populations and communities at the contaminated and reference sites, we can infer the field impacts caused by the mine discharge. The simplest approach is comparing aquatic populations and communities at two river sites upstream and downstream the inflow of mine discharge (called, the upstream-downstream comparison). If the inflow of mine discharge is relatively low compared to the river discharge and thereby the physicochemical characteristics are similar between the two sites, the upstream-downstream comparison is probably the best to directly examine the ecological impacts of the mine discharge. For instance, if effects of concern are not observed by the upstream-downstream comparison, it is probably not necessary to examine the impact at further downstream river sites.

Further, to investigate the ecological impacts of mine discharge at multiple downstream sites or in a certain section of the river, a useful approach is to establish multiple study sites in the river and reference sites with similar physicochemical characteristics in a nearby uncontaminated river (e.g., a similar-sized river within the same basin) with low or background-level concentrations of metals. The reference sites may be established in different river basins as long as physicochemical characteristics other than concentrations of trace metals are similar. Then, aquatic communities are compared between multiple contaminated and reference sites. As an example of such a study design, the results of the macroinvertebrate survey performed in a northern Japanese river (Iwasaki et al. 2020) are shown in Fig. 4.4. Even though the sum of HQs based on US EPA criteria for Cd, Pb, Cu, and Zn exceeded 1 at the contaminated sites (1.7–7.4; particularly the exceedance of dissolved concentrations of Cd and Pb were apparent), the number of taxa and individuals of metal-sensitive mayflies (Fig. 4.4), as well as other macroinvertebrate metrics, were similar between contaminated and reference sites. These results have demonstrated that the assessment based on the sum of HQs can be overprotective in terms of the prediction of the impacts on aquatic communities in the field, and also
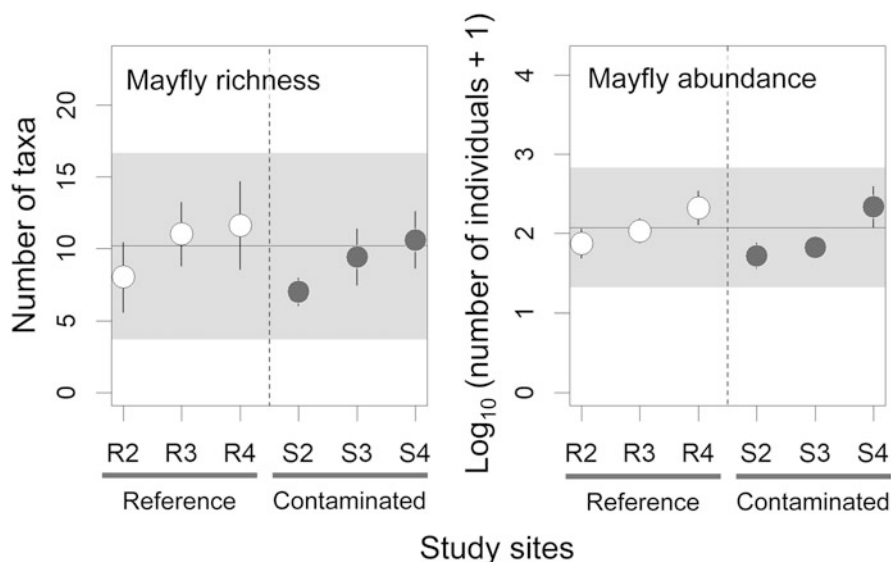
Fig. 4.4 Mayfly (Ephemeroptera) richness and abundance at reference (R2 to R4) and contaminated (S2 to S4) sites. Error bars indicate 90% confidence intervals calculated from 5 samples collected at individual sites. Gray areas are 90% prediction intervals calculated from means for the three reference sites. Data are from Iwasaki et al. (2020)

highlighted the importance of performing field surveys to better understand ecological impacts.

4.5 Summary with Some Management Perspectives

If ecological risks of a chemical are highly concerned, the countermeasures to reduce the environmental concentrations are ideally required. In Japan, environmental water quality standards are used as PNECs to evaluate the individual-level ecological risks, and the nationwide effluent standards are typically established or strengthened to reduce the environmental concentrations if the major sources of the chemicals are industries. However, because the water quality standards are established largely based on the laboratory toxicity data, interpretation of the exceedance needs some caution. For example, in Japan, the environmental water quality standard for zinc in freshwater was established to be 30 µg/L in 2003 to protect aquatic populations and derived based on the minimum toxicity value, that is, chronic toxicity to a macroinvertebrate species. However, results of the macroinvertebrate surveys in multiple Japanese rivers suggest that zinc concentrations of more than twice the standard (70–115 µg/L) has little effect on six macroinvertebrate taxon richness (mayfly richness is shown as an example in Fig. 4.5) and thereby the water quality

Fig. 4.5 Relationship between dissolved zinc concentrations in river water and mayfly richness (number of taxa) in Japan (Data are from Iwasaki et al. 2011). The solid line is the estimated threshold response. Different colored dots indicated different sampling rivers. Mayflies (Ephemeroptera) are often reported to be sensitive to metal contamination
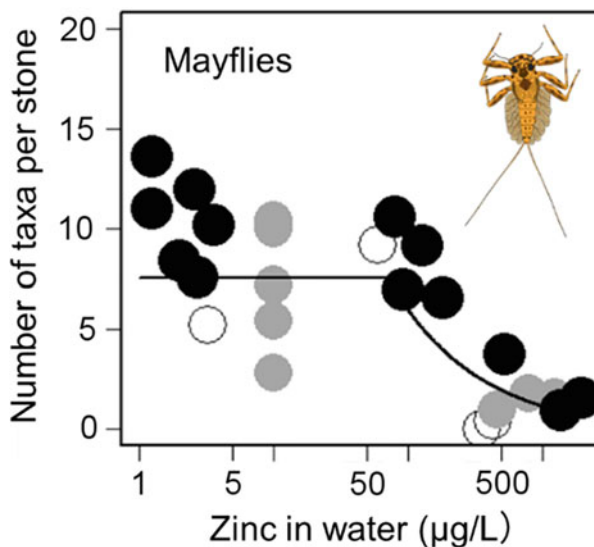
standard is somewhat overprotective for protection of the macroinvertebrate richness. Furthermore, these results indicate that field survey can be used to reasonably infer "safe" concentrations in the natural environment. Interestingly, the "safe" concentrations estimated from the macroinvertebrate data are close to the population-level HC5 of 107 µg/L (Fig. 4.2).

The nationwide effluent standard was lowered from 5 to 2 mg/L in 2006 to maintain and reduce the environmental concentrations of zinc in Japan. The primary zinc sources for river sites with elevated zinc concentrations were estimated to be legacy mines (17%), and industrial point source and/or municipal wastewater treatment plants (58%; Naito et al. 2010). The latter sources indicate that many zinc-elevated sites are located in urban areas where other physical, chemical, and biological factors such as flow alternation, organic pollution, and invasive species likely affect aquatic communities. In such environment, controlling a single factor (e.g., zinc concentration) may be ineffective. Based on field survey data on macroinvertebrates, Iwasaki et al. (2018) provide empirical evidence that, because macroinvertebrate communities are severely affected and macroinvertebrate species susceptible to metal pollution should be sparse or absent in organic-contaminated rivers (5-day biochemical oxygen demand (BOD) of >3 mg/L), the reduction in zinc concentration by the effluent regulation may not be a first choice in such rivers for the recovery of lotic macroinvertebrates. A similar issue can occur at zinc-elevated sites affected by mine discharge because the mine discharges generally have elevated concentrations of multiple metals. Therefore, it would be essential to perform more integrated management rather than the regulation of individual chemicals to effectively restore aquatic ecosystems as well as employing multiple assessment approaches including water quality measurements, toxicity testing, and field surveys to better understand the ecological impacts and their causes.

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