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Heavy Metals in Urban Dust

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Abstract

Urban dust is contaminated by pollutants from various diffused sources and is often difficult to be controlled. It elevates the background heavy metal exposure level to humans and ecosystems in and around urban area and may give an apparent or hidden impact. In this chapter, the recent studies on heavy metals in the urban dust are summarized. First, the heavy metal pollution of the dust in the atmosphere and on the road surface is described. Then, the process of road runoff and subsequent infiltration to the soil is discussed from the viewpoint of heavy metal mobility. Finally, the ecotoxicity of road dust is shown, and the causal pollutants in the dust are discussed.

Keywords: urban road dust, road runoff, infiltration, ecotoxicity, atmospheric particulate matter

1. Introduction

For the last few years, Global Environmental Goals (GEGs) agreed by a number of countries associated to the United Nations have shown commitments to address and improve air pollution and air quality, biodiversity, chemical and waste, energy, environmental governance, forests, freshwater, land, and oceans and seas. In the environmental issues, increasing metal concentration is one of the core issues [1]. There are a number of heavy metals of concerns that include arsenic (As), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and mercury (Hg).

Heavy metals usually occur in soil at low concentrations generated by the natural process such as weathering of rocks and minerals, volcanic eruption, etc. [2]. For the last few decades, because of human interference in the natural geochemical cycle, heavy metal input to our environment is speeding up [3]. Heavy metals become toxic and are regarded as contaminants in the environments when their rates of generation via man-made cycles are more rapid relative to natural

ones. The metal accumulation in both urban and rural environments above the background concentrations may affect ecosystems including plants and animals and has been causing a serious threat to human health. Some of the serious examples of metal toxicity include Minamata disease (methylmercury poisoning) [4] and itai-itai disease (cadmium poisoning) [5].

This chapter focuses on heavy metals in the urban dust. Urban dust contamination is caused by various diffused sources and is often difficult to be controlled. Although the degree of contamination is usually less than the direct industrial and mining pollution, it elevates the background heavy metal exposure level to humans and ecosystems in and around the urban area and may give an apparent or hidden impact. In this chapter, heavy metals in the urban dust, in the atmosphere, and on the road surface are summarized first. Then, the process of road runoff and subsequent infiltration to the soil is discussed from the viewpoint of heavy metal mobility. Finally, the recent research progress on the ecotoxicity of road dust is described.

2. Heavy metals in atmosphere and on road surface

2.1. Atmospheric particulate matter

The urban atmosphere is subjected to large inputs of anthropogenic contaminants arising from both stationary (power plants, industries, incinerators, and residential heating) and mobile sources (automobile- and transportation-related activities on road) [2] and natural surrounding sources (windblown dust, weathering of rocks and minerals, sea salt, volcanic eruptions, etc.). These pollutants are associated to particulate, liquid, and the vapor phases. They are subsequently transported to the Earth’s surface through dry and wet deposition. The air pollutants can be inorganic, organic, and/or microbiological. Among the pollutants, inorganic heavy metals such as copper, zinc, cadmium lead, arsenic, and chromium are a major concern due to their toxicity and potentially carcinogenic characteristics [6].

Aryal et al. studied the heavy metals (Ni, Cu, Zn, Pb, and Cd) in the particles (<10 μm) in the urban atmosphere in industrial city of Ulsan, South Korea [7]. **Figure 1** shows the concentration

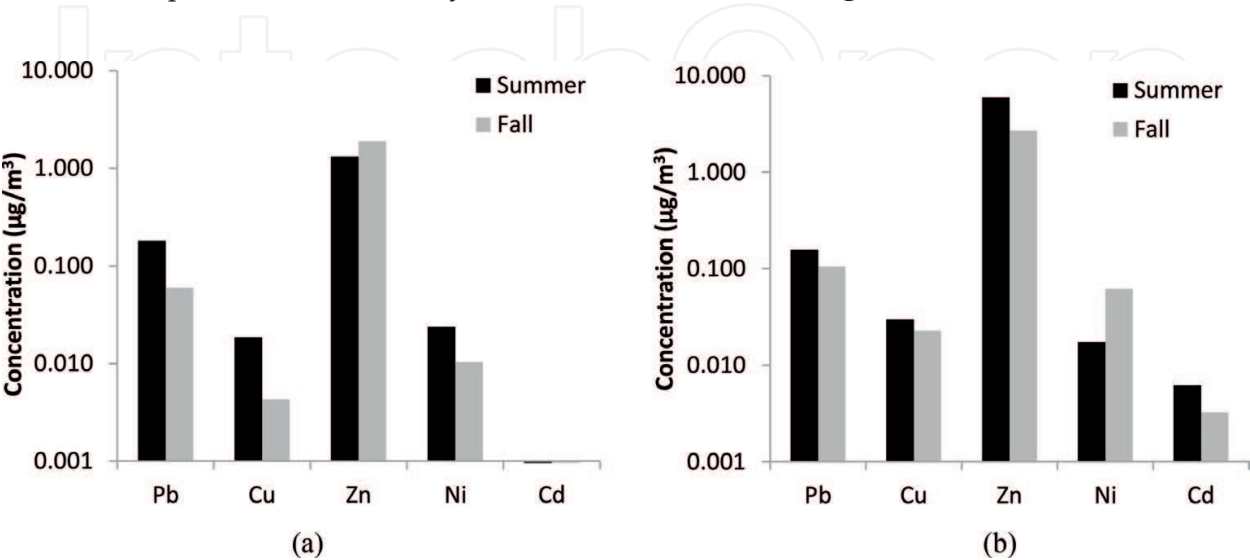


Figure 1. Metal concentrations ($\mu\text{g}/\text{m}^3$) in the atmospheric particulate matter (<10 μm) in (a) petrochemical area and (b) nonferrous metal industry area [6].

of heavy metals in atmospheric particulate in summer and fall seasons at the two sampling sites. The result indicated the highest Zn content among the five elements and higher heavy metal concentrations in summer except for Ni in the nonferrous metal industry area (likely due to the input from the surrounding area). Their detailed analysis of the size-fractionated dust particles showed that the particles were in bimodal distribution with one peak corresponding to the particle size range of 1.1–4.7 μm and the other to the range of 4.7–10 μm . Among the metals measured, Pb was found size dependent, whereas Zn was homogeneously mixed in all sizes.

Many cities are frequently impacted by dust storms traveling from a long distance. Examples include yellow sand-dust storms in Asia and Sahara dust storms in Northern Europe, etc. Since the dust storm travels a long distance, they may pick up many hazardous pollutants available on the path. The composition of such dust particles is of a great concern. Aryal et al. investigated physical and chemical properties of particles in the dust storm that hit east coast cities of Australia including Sydney on 23 September 2009 and blanketed for a number of hours [8]. The dust storm was the worst since 1942 for Sydney dwellers. The dust particle analysis by a wide-angle X-ray scattering (WAXS) and electron diffraction X-ray showed that it contained mostly crustal elemental oxides such as SiO_2 , Al_2O_3 , and Fe_2O_3 . **Figure 2** shows the elemental composition obtained from electron diffraction X-ray spectra and morphology of the dust particle using scanning image microscopy (**Figure 2**). The ratio of Al/Si in the Sydney dust storm was ~ 0.39 which indicated desert origin. They also analyzed the organic matter in the dust and concluded that the dust was unlikely to contain the biohazardous compounds to human health.

2.2. Road dust

Heavy metal deposit on the urban and rural road surface can cause significant and serious contamination. The vehicular fuel exhaust, abrasion of vehicle parts including tire and body, and industrial emissions are the sources of toxic metals [9, 10]. Road dust scatters to the atmosphere, causing air pollution and transported to wider areas [11]. Such resuspended road dust can enter the human body through direct ingestion of dust, inhalation of dust particles through the mouth and nose, and dermal absorption, threatening people's health [12]. Road dust is transported also to water environment by atmospheric deposition and by

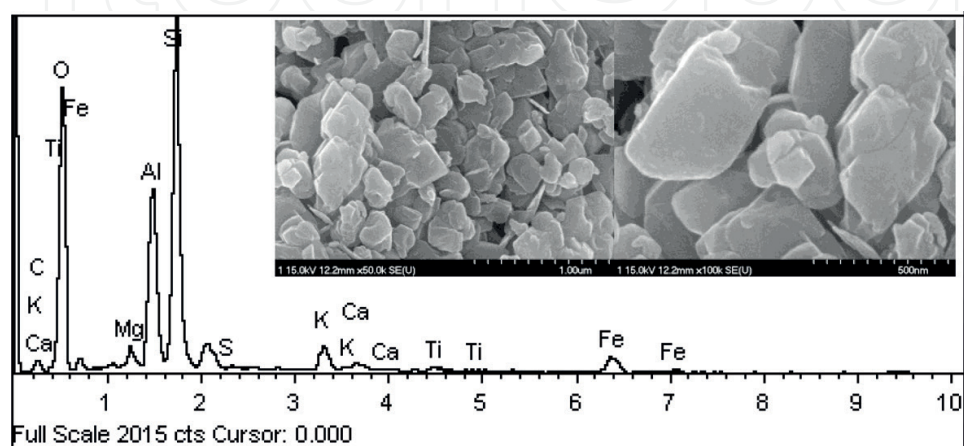


Figure 2. X-ray spectrum of the Sydney dust storm particles [7].

surface runoff of rainwater. The contaminated dust may deteriorate the ecological health in the receiving waterbodies. Therefore, to protect the human and ecological health, attention should be paid to the heavy metals in road dust in large cities.

There are a number of studies of road dust and heavy metals. A study on road dust and heavy metals in Winterthur, Switzerland, revealed that heavy metals are accumulated in various dust sizes [13]. Another study reported heavy metal concentrations in road dust in Ulsan, South Korea, in various particle sizes (<75, 75–180, 180–800, and 800–2000 μm) [1]. The heavy metal contents overall ranged from 0.4 to 21 $\mu\text{g/g}$ for Cd, 25 to 204 $\mu\text{g/g}$ for Cu, 6 to 58 $\mu\text{g/g}$ for Ni, 43 to 343 $\mu\text{g/g}$ for Pb, and 79 to 326 $\mu\text{g/g}$ for Zn. The heavy metal concentration was found in the order of: industrial complex > industrial vicinity > heavy traffic > residential > background.

3. Heavy metals in road runoff and infiltration

3.1. Road runoff

Urban runoff, especially from the roadways (road runoff), often contains significant loads of dissolved and particulate metals along with other pollutants such as hydrocarbons and nutrients [14–19]. Unlike organic compounds, metal elements are not degraded in the environment and constitute an important class of constituents generated by traffic activities due to their non-degradability.

During wet weather period, the surface-deposited metals are washed off to the pipe network and finally to the receiving waterbodies including rivers, lakes, ponds, reservoirs, etc. The deposited pollutants are washed off mostly at the early stage of the runoff, called first flush [20]. Under heavy traffic conditions, the depositions of toxic pollutants are usually more concerned rather than those of other nonpoint pollutants such as nitrogen and phosphorus.

A monitoring on highway runoff in Winterthur, Switzerland, was conducted from September to December 2000 [13, 21]. The study covered nine runoff events, and samples were collected first 3 mm rainfall in order to capture the first flush. Furumai et al. reported that the runoff samples with higher SS concentrations had higher heavy metal concentrations [13]. The particle-bound Zn, Cu, and Pb concentrations were 155–524, 29–69, and 13–46 $\mu\text{g/L}$, respectively. The heavy metal concentrations were close to other studies [22–27]. Aryal et al. reported the fractionated samples in this monitoring campaign [21]. The collected serial total suspended solid (TSS) samples were fractionated into five size fractions (<20, 20–45, 45–106, 106–250, and >250 μm) to understand the runoff behavior of the particles. The wash-off behavior of fine and coarse fractions was quite different. With respect to the TSS, a coarse fraction (>106 μm) showed power growth relationship, whereas the finer fractions (<106 μm) showed clustering at lower range TSS and almost saturated at higher TSS region (**Figure 3**). This result indicated that particle sizes were very important in metal transport in runoff.

Aryal and Lee also studied the relationship between heavy metal content in particles and SS concentrations in urban runoff [28]. They found that all the runoff samples had low heavy metal content in particles at the beginning of the rainfall with higher SS concentration. As the time elapsed, the heavy metal content increased with lower SS concentration. The content of heavy

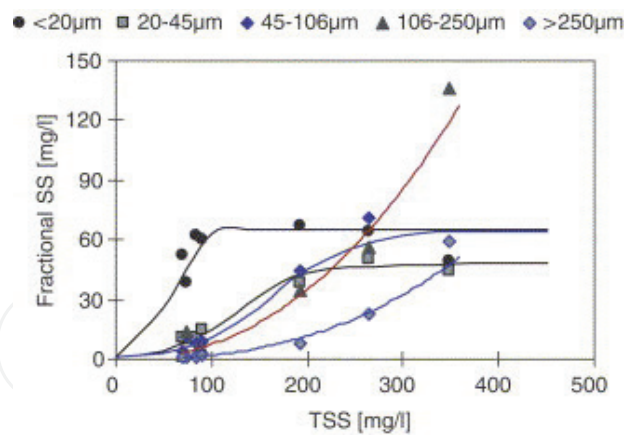


Figure 3. Relationship between total suspended solid (TSS) concentrations and size-fractionated SS concentrations in highway runoff [20].

metals reached the lowest level when SS concentration reached the highest value. The high contents of heavy metals at low SS concentration were believed to be due to higher contribution of fine particles to the total suspended solids (Figure 4).

3.2. Stormwater infiltration

The urban runoff is managed in the city via different means. Among the stormwater management system, stormwater infiltration facilities are one of them for flood control, designed to reduce the peak flow by infiltrating water to the subsurface [29]. However, there is a considerable concern of groundwater contamination by heavy metals since these infiltration system structures are usually not designed with any consideration for pollutant retention [30]. The environment in the facilities including pH, oxidation reduction potential (oxygen availability), minerals, and organic matter defines the mobility of deposited metals [31–35]. Within the sediment, different particle sizes have different heavy metals accumulating behavior [36].

Aryal et al. surveyed more than 200 infiltration inlets for road runoff in Tokyo [37]. They measured sediment depth, collected sediment samples, and measured heavy metals in total,

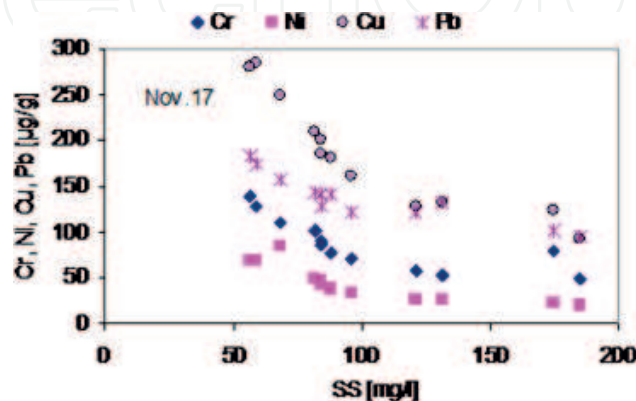


Figure 4. Relationship between SS concentrations in the runoff samples and heavy metal content in SS (adopted from [28]).

in different particle sizes as well as speciation of heavy metals. The sediment accumulation depth varied from almost few centimeters to more than 14 cm. The particle size analysis of the sediment showed a heterogeneous distribution of size at the different depth. The heavy metal contents in the inlet sediment ranged from Cr 7 to 143 µg/g, Mn 383 to 1009 µg/g, Co 9 to 31 µg/g, Ni 10 to 84 µg/g, Cu 51 to 316 µg/g, Zn 288 to 1974 µg/g, and Pb 24 to 230 µg/g. The heavy metal contents in the sediment were mostly close to the road dust but in some cases lower than the background soils. **Table 1** shows the heavy metal contents in the sediments at two inlets. The study in the inlet sediment showed lower in content at the bottom sediment than the top. This reflects that heavy metals may have leached to subsurface soil [37, 38].

Organic matter is one of the most important factors in heavy metal mobility in soil and sediment. Organic matter associated with the particulate matter may contain wide ranges of organics with potentially different sources. Humic substances are often the dominant organic fraction in soils and sediments [39]. They consist of heterogeneous mixtures of molecules having molecular weights ranging from a few hundred to several hundred thousand Daltons and are polyfunctional (each molecule may have a large number of different complexing sites, e.g., carboxylic, phenolic, phthalic, salicylic, and amine functional groups) [40–42]. Due to the large variation in structural properties, different organic matters can possess different strengths in terms of metal bonding. Also, the competitiveness among metals to bind to organic matter may vary [32, 43, 44]. It is reported that the general order of affinity of metal cations complexed by organic matter is Cu > Cd > Fe > Pb > Ni > Co > Mn > Zn [45]. Organic matter with a different functional group shows different affinities to the same heavy metals. This means that a single metal may show different affinities to different organic substances and may attach to the site where it is attracted more.

Aryal et al. studied road dust organic matter in different particle sizes and the organics’ possible role in binding heavy metals [46]. The road dust was collected from industrial, business, and commercial districts and residential areas in the city of Ulsan, South Korea. Their study used fluorescent spectroscopy in combination with parallel factor analysis (PARAFAC). The study found that the finest fraction contained more microbial humic-like substances, whereas the coarse fraction was enriched with fulvic acid. The organic matter in two fractions (75–180 and 180–800 µm) showed dual characteristics. It was also observed that Zn had high affinity with aromatic protein, humic substances, and microbial by-products, whereas Cd showed a negative correlation with fulvic acids.

Inlet	Cr		Mn		Co		Ni		Cu		Zn		Pb	
	T	B	T	B	T	B	T	B	T	B	T	B	T	B
#4	31	94	842	765	31	25	80	62	259	214	1827	1350	271	220
#172	74	67	965	699	33	28	67	66	221	201	1071	791	96	85

Note: T, top (0–3 cm) and B, bottom (12–15 cm).

Table 1. Heavy metal content (µg/g) in the top and bottom sediment of two infiltration inlets of road runoff in Tokyo (#4 and #172) [36].

The fate of heavy metals in infiltration systems is highly dependent upon the sorptive and desorptive behavior of organic matter received from various sources such as road surfaces, parks, and agricultural areas. The organic matter found in the infiltration inlet sediment seemed changed with time due to prolonged deposition. Aryal et al. investigated the potential role of organic matter in binding and mobilizing heavy metals in the deposited sediment of infiltration facilities in Tokyo by using fluorescent spectroscopy combined with parallel factor analysis [47]. The surface sediment (few cm deep) showed a variation in organic matter and heavy metal content place by place. The sediment samples in lower layers had been relatively similar in different infiltration facilities. The result suggested that the sediment surface was used to be disturbed by scouring and mixing while receiving the runoff. The heavy metal content was found lower at the higher depth indicating possible release to the subsurface soil. The study also found that Cu and Zn had a positive linear relationship in the sediment samples which reflected that both of them had a common source. The PARAFAC analysis identified three major components with different spectral shapes and volumes in different excitation emission locations. The components reflected UV A humic-like substances (defined in [48]) and fresh organic matter [49], UV C-like organic matter having higher molecular weight humic substances [50, 51], and commercial humic acid [52]. While correlating organic components with heavy metals, they observed that UV A-type substances had a negative relationship with all metals, whereas commercial humic-type substances had a positive relationship with heavy metals.

4. Ecotoxicity of urban dust

As described above, urban road dust contains toxic heavy metals as well as other various toxic chemicals such as polycyclic aromatic hydrocarbons (PAHs), perfluorinated surfactants (PFSs), etc. [53–55]. Stormwater runoff brings the road dust to the receiving waterbody and poses the harmful effect to the aquatic lives. In this section, recent studies on ecotoxicity of urban road dust are reviewed, and the heavy metal contribution to the effect is discussed.

Watanabe et al. and Khanal et al. reported the toxicity of the dilution series of road dust in Tokyo to calculate LC20 and LC50 by direct contact test with a benthic crustacean (ostracod, *Heterocypris incongruens*) (ISO 14371) [56, 57]. Those results are summarized in **Table 2**. Watanabe et al. showed the apparent lethal toxicity in six out of seven road dust samples tested although the dose-response relationship was shown only for the St. 6 in **Table 2** [56]. Six out of 10 samples in [57] were toxic as shown in **Table 2**, and the rest of the four samples had <50% mortality (so that LC20 and LC50 were not calculated).

Niyommaneerat et al. recently developed a new method of sediment chronic toxicity evaluation using ostracod reproduction and applied the method to urban road dust [58]. The road dust sample in [58] caused delayed egg production in 6.25% (v/v) dilution although LC20 for 6-day mortality test was 14% (v/v). Acute chronic ratio (ACR) was calculated as 6.8, and the authors estimated that 179 times of dilution was necessary to make the most toxic road dust (St.8 in [57]; see **Table 2**) nontoxic in the reproduction endpoint. Such dilution is not always achieved in the cities as the road dust contaminated the sediment in 3.7% in a river receiving road runoff in Tokyo [59].

Road dust sample name in reference	Toxicity to benthic ostracod <i>H. incongruens</i>		Ref.
	LC20 (% (v/v))*	LC50 (% (v/v))*	
St. 6	20	30	[56]
St. 1	13	31	[57]
St. 2	9	41	
St. 3	10	13	
St. 4	49	67	
St. 7	13	24	
St. 8	1.6	3.8	

*The unit is a volumetric percentage of road dust in the tested sediment. The sediment was composed of road dust and nontoxic reference sediment (quartz sand [56] and commercially available reference soil [57]).

Table 2. Toxicity of urban road dust to benthic ostracod *Heterocypris incongruens*.

Urban road dust, originally in dry form, is likely to change its toxic nature by wetting process. Watanabe et al. showed the toxicity of water-soluble (easily desorbable) components and remaining solids (particle-bound components), separately [56]. As a result, the primary toxic compounds of road dust existed mainly in the water-soluble form rather than the particle-bound form. Interestingly, after 7 days of incubation in water, the solid part also showed significant lethal toxicity. The similar phenomena of toxicity change in solid phase were also confirmed in other road dust samples [60]. The causal substances of the toxicity observed after several days are still unknown.

Toxicity change was also observed in seawater [61]. Road dust toxicity was tested in different salinities with the estuarine amphipod *Grandidierella japonica*. For three road dust samples, the toxicity in 3.5% salinity was significantly higher than in 0.5 and 2.0% salinity. The toxicity change may be caused by the change of bioavailability and/or toxicity of chemicals in the road dust.

In most of the cases, it is generally difficult to identify the causal substances of toxic environmental samples. Watanabe et al. and Khanal et al. applied toxicity identification evaluation (TIE) approach to the road dust toxicity assessment by benthic ostracod *H. incongruens* [62, 63]. In both of the studies, the two different types of adsorbents were used to manipulate the toxic substances in road dust, namely, Ambersorb/XAD for hydrophobic organic matter and Chelex/SIR-300 for cationic metals. Watanabe et al. showed that the adsorbent for hydrophobic organic matter was effective to reduce the toxicity of all the three road dust tested and concluded that the heavy metals were not considered to be major toxicants in the dust sample [62]. In contrast, Khanal et al. indicated that the adsorbent effectiveness depended on the dust samples (**Figure 5**) and one of the dust samples (St. 7 in **Figure 5**) became less toxic only by the adsorbent for cationic metals [63].

One of the limitations in the TIE approach is that the adsorbent mainly removes the dissolved toxicant and may not reduce the dietary exposure through the ingestion of contaminated particles in the sediment tests. To assess the dietary exposure pathway, we should have dose-response relationship for the contaminated solids. However, such information is very limited

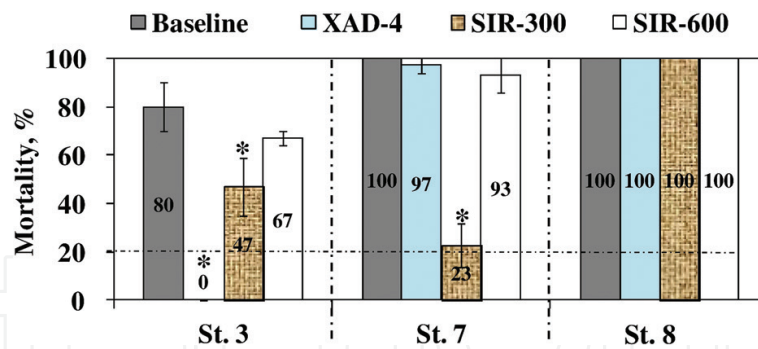


Figure 5. Toxicity reduction by adsorbent addition to urban road dust [63]. Baseline indicates toxicity of urban road dust without adsorbent addition. XAD-4, SIR-300, and SIR-600 are adsorbents for hydrophobic organic matter, cationic metals, and ammonia, respectively. The toxicity was evaluated in a 6-day ostracod test.

even for the sediment toxicity test species. Sevilla et al. showed such dose-response relationship for a benthic ostracod to heavy metal-contaminated food algae (**Figure 6**) [64, 65]. This will be useful to interpret the toxicity test result. For example, Watanabe et al. showed the overall toxicity of urban road dust but could not discuss the dietary pathway of heavy metal exposure [56]. The toxic urban road dust contained heavy metals in 1300–2980 $\mu\text{g Zn/g}$, 279–1200 $\mu\text{g Cu/g}$, and 0.64–2.0 $\mu\text{g Cd/g}$. Assuming that the heavy metal bioavailability of the dust and algae is similar (probably it is a safer side assessment), zinc and copper may cause the mortality of the ostracod species.

Biomarker is a promising tool to identify the heavy metal exposure from the road dust. But for relatively small-sized benthic organisms used in sediment toxicity tests, it is technically difficult to obtain the sufficient amount of tissues to quantify the conventional biomarker such as metallothionein. Recent development of molecular technique enables us to detect the biological response to toxic substances more comprehensively as gene expression. Hiki et al. reported a challenge in exploring biomarker genes of benthic amphipod *G. japonica* to zinc, copper, and nicotine [66]. They applied a technique of cDNA-amplified fragment length polymorphism (AFLP) to the non-model species whose genome sequence information was not available. The unique loci to each exposure treatment were identified, and they considered

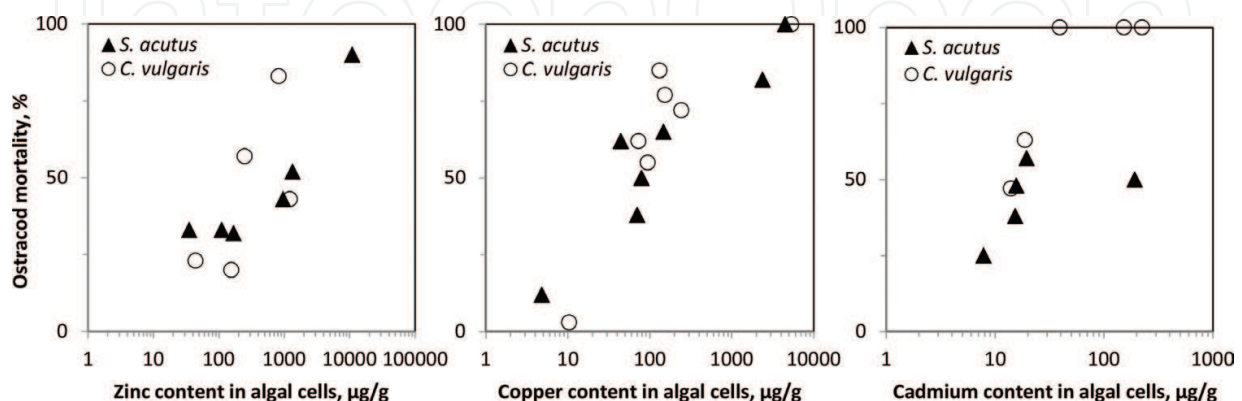


Figure 6. Dose-response relationship for benthic ostracod *Heterocypris incongruens* to heavy metal-contaminated food algae (*Scenedesmus acutus* and *Chlorella vulgaris*) (adopted from [64]).

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