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Tungsten and other heavy metal contamination in aquatic environments receiving wastewater from semiconductor manufacturing

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ABSTRACT

Through analyses of water and sediments, we investigate tungsten and 14 other heavy metals in a stream receiving treated effluents from a semiconductor manufacturer-clustered science park in Taiwan. Treated effluents account for ~50% of total annual river discharge and <1% of total sediment discharge. Dissolved tungsten concentrations in the effluents abnormally reach 400 μg/L, as compared to the world river average concentration of <0.1 μg/L. Particulate tungsten concentrations are up to 300 μg/g in suspended and deposited sediments, and the corresponding enrichment factors are three orders of magnitude higher than average crust composition. Surprisingly, the estimated amount of tungsten exported to the adjacent ocean is 23.5 t/yr, which can approximate the amount from the Yangtze River should it be unpolluted. This study highlights the urgency of investigating the biological effect of such contamination.

1. Introduction

Heavy metals enter riverine, estuarine, and marine ecosystems via the discharge of treated or untreated industrial wastewater and municipal sewage, storm water runoff, acid mine drainage, and other diffuse sources. Most are toxic to aquatic biota at varying concentrations [1,2], although some, such as Cu and Zn, are essential to organisms. Living organisms accumulate heavy metals in tissues, a process called bioaccumulation, and concentrations of these elements may increase as they may move up the food chain because of slow breakdown in the environment, food chain energetics, and low degradation or excretion by organisms, termed biomagnification [3,4]. As a consequence, heavy metal pollution has become a serious, growing threat to aquatic environments across the world. More important, humans become especially vulnerable to this contamination when these contaminants enter aquatic food webs and accumulate in tolerant species, such as oysters, or reach groundwater used for drinking and irrigation.

Heavy metals/metalloids, including Hg, Cd, Pb, Cu, Zn, Cr, As, Mn, and Ni, are the most commonly discussed in literature [1,3]. However, with the rapid development of many state-of-the-art technologies, a few specific uncommon trace metals used in industries accumulate in wastes and wastewater are released into surrounding ecosystems, despite treatment before discharge [5,6].

Large quantities of tungsten are utilized in the production of wafers (http://en.wikipedia.org/wiki/Tungsten_hexafluoride), apart from being used in cemented carbide, mills, super alloys, lighting, steels, and chemicals ([7] and references therein). In addition to tungsten, other trace metals/metalloids, such as Cu, As, Ga, In, Mo, P, and B are also used in semiconductor manufacturing [8]. However, our current knowledge on these metals' respective biogeochemical characteristics and fates in receiving water bodies, which is in turn intensively related to their resultant effect on living biota and the routes linking the food chain [9], is substantially lacking. Tungsten is suspected to be potentially related to an acute lymphocytic leukemia cluster in three communities in the US (Fallon, Nevada; Sierrk Vista, AZ; Elk Grove, CA) and is also harmful to fish [10]. As reviewed by Koutsospyros et al. [7], the toxicological profile of tungsten, including its possible effects on living organisms and exposure pathways, remains rather sketchy, narrow, and fragmentary. They concluded that to this date, tungsten and its compounds remain among the least regulated and studied metal substance.

In the present study, we analyze tungsten and 14 other heavy metals (Ga, As, Cu, Sn, Mo, Zn, V, Cd, Ag, Ni, Cr, Fe, Al, and Mn) in water and sediment samples collected along the fluvial passage of effluents discharged from a wastewater treatment plant of

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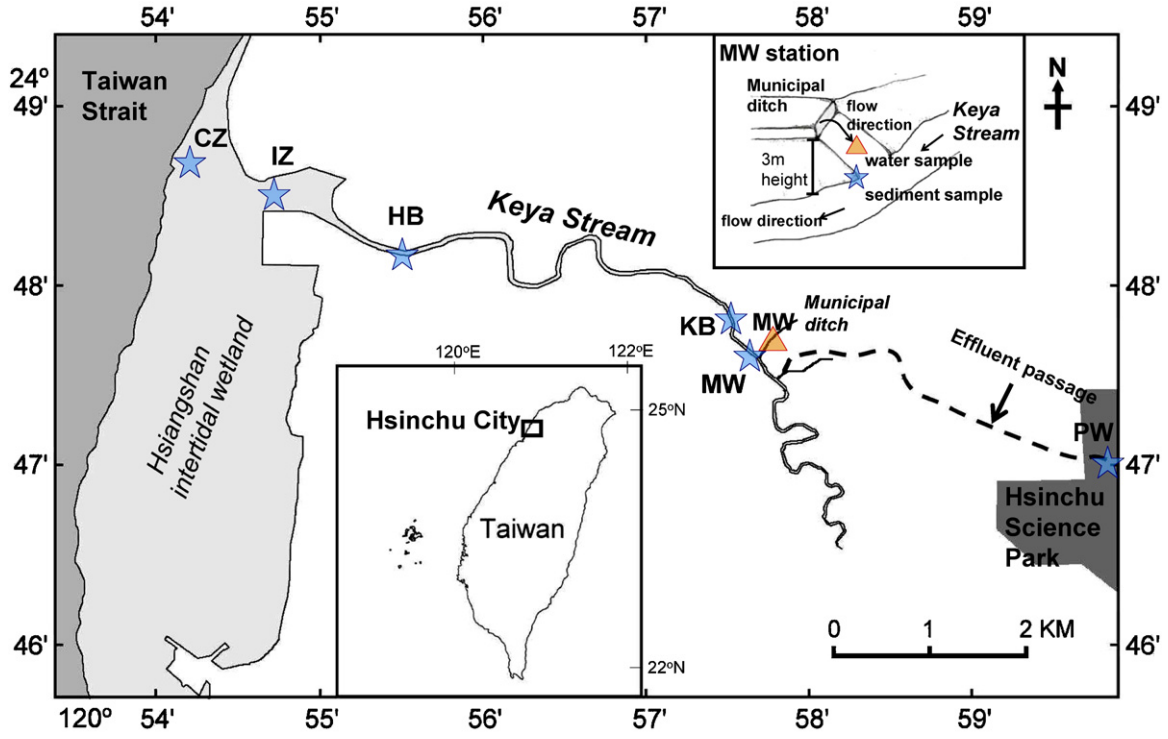

Fig. 1. Study area and sampling stations along the Keya Stream. Six stations from upstream to downstream reaches were PW, MW, KB, HB, IZ, and CZ and were described in details in the text. Sediments were collected at all six stations, but river water (and SPM) samples were collected at the first five stations.

a semiconductor manufacturer-clustered science park in Taiwan. Our study aims to assess the pollution degree of tungsten and other heavy metal/metalloids affected by the known strong point source, namely, high-tech electronic industrials; characterize their geochemical behaviors; clarify the primary controlling factors during transport; evaluate the fluvial flux of anthropogenic tungsten to the sea; examine their anomalies; and discuss the important implications for biological effects.

2. Background of the study site

Hsinchu Science Park (HSP), hailed as "Taiwan's Silicon Valley," covers an area of 6.5 km^2 in northern Taiwan (Fig. 1) and houses the internationally important semiconductor, electronics, and optoelectronic manufacturing facilities of around 450 companies (http://eweb.sipa.gov.tw/en/dispatch.jsp?disp_to=10:38:24). Industrial and domestic wastewater generated within the park campus are treated by a wastewater treatment plant (WWTP) and subsequently discharged into the Keya Stream (Fig. 1). The daily volume of the effluent is 105,000 t, with an average of 7.1 mg/L suspended solids (http://venus.sipa.gov.tw/SPAEPI/wastewater/checkWaterQuality.jsp).

The Keya Stream, approximately 24 km long, is a major channel for removing wastewater from Hsinchu City, Taiwan. Aside from the HSP's effluent discharges and surface water runoff from rainfall, it also receives municipal wastewater produced by Hsinchu City. Its annual total river runoff discharge averages 78.3 Mm^3, and its annual sediment discharge is 0.19 Mt. In other words, the effluents (38.3 Mm^3/yr) from HSP account for nearly half of the total water discharge of the Keya Stream.

Elevated Cu (maxima 4750 μg/g dry weight) and Zn (5830 μg/g dry weight) concentrations in the oyster *Crassostrea angulata* [formerly misidentified as *Crassostrea gigas* [11,12], cultivated in the downstream coast of the Keya Stream, were reported [13,14]. It was suggested that the effluents of HSP are responsible for the green oyster problem observed in the coast [13]. Lin et al. [15] have detected extremely high concentrations of perfluorinated chemicals in the Keya Stream, even exceeding accepted safety thresholds and were also attributed to contamination from the effluents of HSP.

3. Materials and methods

3.1. Sampling

Water and sediments were collected along the effluent passage from the outlet (station PW) of HSP's WWTP to the Keya Stream main channel and coast (Fig. 1) in February 2006, the dry season in Taiwan, when there is little influence from rainfall. Stations from the upstream to the downstream reaches include PW, MW (the intersection between this stream and the municipal wastewater discharge ditch), KB (Keya Bridge; the area that the tides reach during flooding), HB (Hsiangya Bridge), IZ (the estuarine intertidal zone), and CZ (coastal zone). Because the municipal drainage ditch at station MW is located at an elevation higher than that of the Keya Stream channel, water collected in the ditch was not mixed with water from the Keya Stream, thus representing only municipal wastewater from Hsinchu City. However, sediment was not available in the ditch; hence, sediments were collected from a spot on the river bed of the Keya Stream beneath the ditch outlet (Fig. 1). As a result, sediments collected here could be contaminated more or less by HSP wastewater.

The water levels during the sampling time are mostly shallower than 30 cm. In order to avoid disturbing the bed sediments, river water was collected at each station using a stringing pre-cleaned 10-liter plastic bucket from river band or bridges by hand, with an exception for station CZ. Then the collected water was used for rinsing the pre-acid-cleaned 1-liter polyproylene (PP) wide-mouth bottle twice. Water samples were duplicated. The water-filled bottles were refrigerated in a cooler until transferring back laboratory

for subsequent filtration within 6 h. After water sampling, sediments on the river bed inside the river channel were collected using a stainless grab and from which only the most central part of the grabbed sediments were sampled by using a small PVC corer. The collected sediments were kept in PE ziploc and then refrigerated.

Because the investigated river is short (~24 km), together with the facts that precipitation in Taiwan is relatively episodic and the topography of Taiwan is considerably steep, therefore whiling raining the rainwater falling onto the watershed quickly flows out of the lands. In other words, the influencing time of rainfall is rather short. In most of time, the river water is mainly composed of background runoff and the discharged treated wastewater. Therefore our sampling and study can represent the typical case of the investigated Keya Stream even though the sampling was conducted once.

3.2. Chemical analysis

Water samples were operationally separated from suspended particulate matter (SPM) by filtering through pre-weighted, 0.45-μm pore sized, 47 mm diameter, polycarbonate filters (Millipore). The filtrate was acidified (1%) with ultra-pure, concentrated HNO_3 (Merck, Darmstadt, Germany) and analyzed for dissolved metals. After cryo-drying, the post-weighted SPM-laden filters were subjected to acid digestion for the determination of particulate metals. Sediments were wet-sieved with Milli-Q water, and particles of <62 μm in grain size (i.e., mud) were collected and placed into clean plastic beakers. Mud sediments were then cryo-dried and ground, and subjected to acid digestion.

SPM-laden filters and 0.05 g sediment powder were then digested in an acid mixture (5 mL HNO_3 + 2 mL HF) using an ultra-high throughput microwave digestion system (MARS Xpress, CEM Corporation, Matthews, NC, USA). Each type of sample was separately digested. In each run of microwave digestion, there were at least two blanks. The detailed procedures of microwave digestion of solid samples can be found elsewhere [16,17].

Acidified water samples and digested solutions were analyzed for 15 heavy metals/metalloids using inductively coupled plasma mass spectrometry (ICP-MS, Elan 6100, Perkin-Elmer TM SCIEX, Waltham, MA, USA). The instrument detection limits of the applied ICP-MS are less than 0.01 μg/L for most of the analyzed elements with exceptions for Mo (0.02 μg/L), Al (0.02 μg/L), Zn (0.1 μg/L), and Fe (0.1 μg/L). Indium was spiked to digest as an internal standard (10 μg/L). To guarantee analytical performance, we analyzed the standard reference sediment BCSS 1 (from National Research Council of Canada, Ontario, Canada). The recovered values for the elements with certified (Mn, Ni, Zn, Cu, Cd, Sn, Cr, As, and V) and non-certified (Al and Fe) concentrations fell within 10% ($n = 5$) of the reported values (i.e., the recoveries 100 ± 10%), except for Mo (15%), W (20%), Ag, and Ga, of which Mo has only information value; W, semiquantitative value; and Ag and Ga, no reported values. The details of ICP-MS analyses are provided elsewhere [16,18].

3.3. Enrichment factor and partition coefficient calculation

The degree to which element X in a solid sample is enriched or depleted relative to a specific source (e.g., average crust) is assessed using enrichment factor (EF) as follows [18]:

$$\mathrm{EF} = \frac{(C_X/C_{Al})_{sample}}{(C_X/C_{Al})_{crust}}$$

where $(C_X/C_{Al})_{sample}$ is the concentration ratio of a given metal X to Al in SPM or sediment samples, and $(C_X/C_{Al})_{crust}$ is the concentration ratio of a given element X to Al in the average crustal abundance [19].

The partition coefficient (K_d) is calculated to be the ratio of metal concentration in the particulate to the dissolved metal concentration [20], as follows:

$$K_d = \frac{C_{particulate}}{C_{dissolved}}$$

where $C_{particulate}$ is the concentration (mg/kg) of a given metal in SPM, and $C_{dissolved}$ is the concentration (mg/L) of a given metal in water.

4. Results

4.1. Dissolved and particulate metals in wastewater effluents and stream water

The analyzed dissolved and particulate metals in wastewater effluents and stream water (Figs. 2 and 3) were classified into three groups based on their levels and spatial distribution of concentrations. The first group included W, Cu, Cd, Sn, Ag, and Ga. The main feature was that their dissolved and particulate concentrations at station PW (W, 430 μg/L and 274 μg/g; Cu, 15 μg/L and 1380 μg/g; Sn, 0.17 μg/L and 68 μg/g; Ga, 1.3 μg/L and 47 μg/g; Ag, 0.025 μg/L and 16 μg/g; Cd, 0.054 μg/L and 1.4 μg/g) were the highest among the sampled stations, except for dissolved Ag and particulate Ga. They also showed a nearly decreased trend from PW downstream to IZ/CZ. Dissolved W concentrations remained at a noticeably abnormal level of ~300 μg/L or higher throughout the stream's section affected by the effluents from the WWTP, although the dissolved concentrations of other heavy metals appeared to be relatively low (Cu: ~10 μg/L; Ga: ~1 μg/L; Cd, Sn, and Ag: ~0.1 μg/L or lower). Moreover, their particulate concentrations at PW were much higher than those at MW, and the corresponding EF values were ~10^3 for W and Ag, ~10^2 for Cu and Sn, and >10 for Cd and Ga, revealing at least moderate pollution from these heavy metals. This group is related to wastewater from high-technology facilities.

The second group included Mo, Ni, Zn, and As, which displayed a pattern similar to that of the first group. Their dissolved concentrations minimized at station MW and peaked at station PW, except for As; they remained at a relatively constant level (Mo, Ni, Zn, and As: ~10–20 μg/L) in the downstream beyond PW. By contrast, their particulate concentrations showed a somewhat contrasting pattern, tending to increase downstream with peak concentrations (Zn, 413 μg/g; Ni, 84 μg/g; Mo, 15 μg/g and As, 15 μg/g) at intertidal (for Mo, Ni, and Zn) and coastal (for As) zones. Nevertheless, the spatial trends of EF values peaked at stations MW and/or PW. This group essentially originated from the effluents of the WWTP, whereas the contribution of other sources, such as municipal wastewater and geochemical processes regulating the interactions, and in turn the partitioning between dissolved and particulate species, was also important to their spatial distribution. Note that the dissolved concentrations of the first and second groups of elements decreased by a factor of only ~2 from PW to the inter-tidal zone.

The third group included V, Mn, Cr, Fe, and Al. Their dissolved concentrations at station MW could be comparable to (for V) and even higher (for Mn, Cr, and Al) than those at station PW. Their particulate concentrations tended to increase downstream; the corresponding EF values were all at low levels of <5, indicative of being less polluted to unpolluted for these metals. This suggests that the effluents of the WWTP were not the primary source for this group of metals, whereas municipal wastewater input might be relatively important (particularly

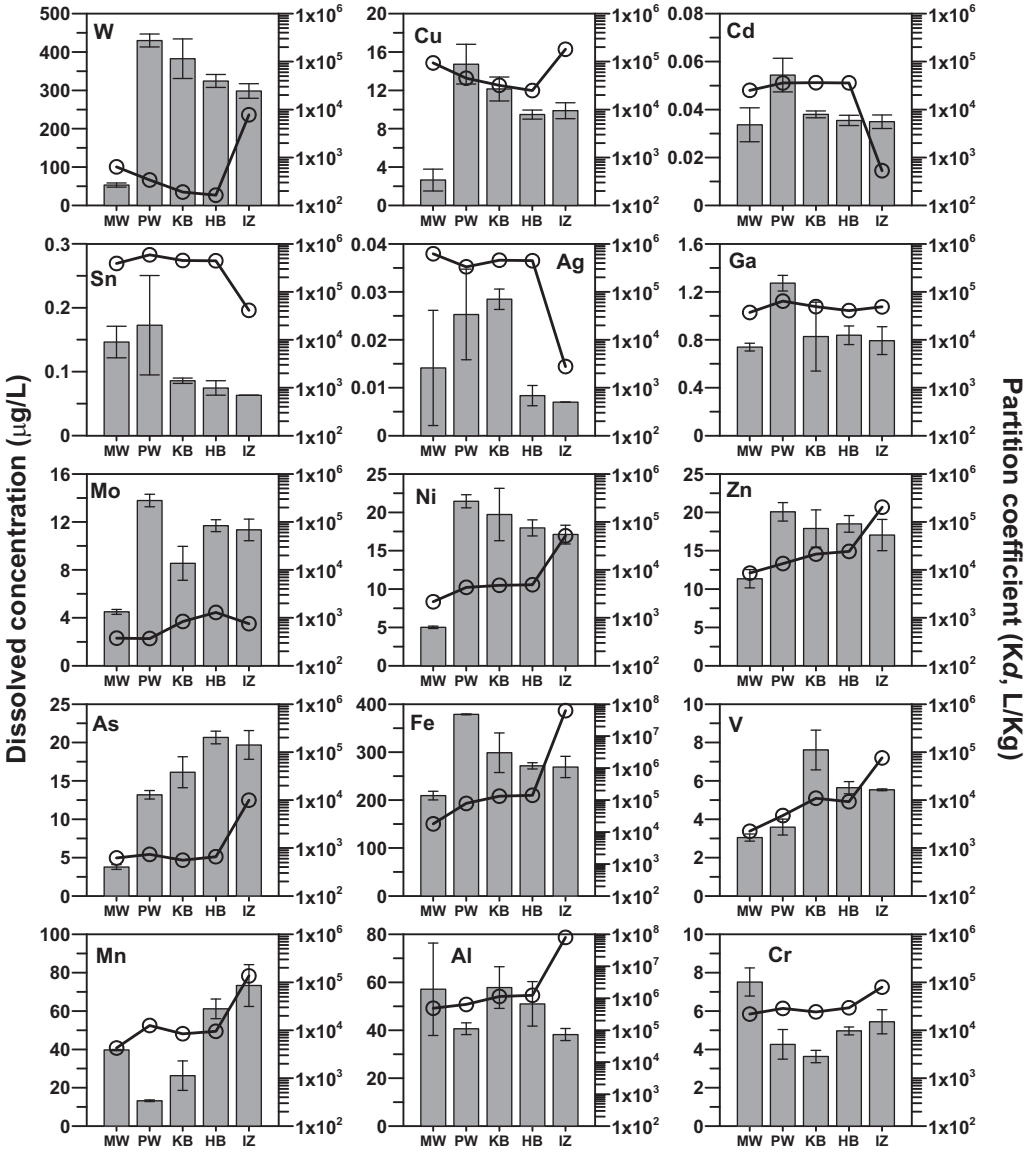

Fig. 2. Spatial distribution of dissolved concentrations (μg/L; bar charts) and partition coefficients (K_d, in unit L/kg; symbols and lines) of the heavy metals in the Keya Stream. Error bars (standard deviations) are indicated for dissolved concentrations of trace metals.

for Cr). Besides, the intrinsic geochemical natures of the metals and the changes of geochemical conditions in water bodies determined their corresponding fates in the studied stream and adjacent estuary.

4.2. Sedimentary heavy metals

The levels and spatial distribution of the concentrations and EF values of the analyzed sedimentary metals (Fig. 4) were generally consistent with those observed in the suspended particulate matter (Fig. 3), especially for the first and third groups of metals. However, several distinct features can still be identified: (1) the first group of metals showed a pronounced concentration and EF value at PW, sharply decreasing downstream; (2) the third group of elements exhibited their lowest concentrations at PW, which is clearly lower than those at MW; the increased tendencies beyond PW were also not as evident as those of particulate metals and (3) the second group of elements showed distinguishable patterns. Concentrations of Mo, Zn, and As were highest at PW, decreasing downstream, a pattern somewhat similar to that of the first group. Ni seemed to show a combined pattern of the first and second groups.

5. Discussion

5.1. Comparison with water and sediment metal quality guidelines and other studies

To further assess heavy metal pollution in the Keya Stream, we compared the measured heavy metal concentrations in the water and sediments affected by wastewater effluents with national (Taiwan, ROC) river water quality and soil (Taiwan has no guidelines for sediment metals) regulation standards and international sediment quality guidelines (SQGs). These standards, however, pertain to only a few metals, as compiled in Table 1 (for dissolved metals) and Table 2 (for particulate and sedimentary metals). Note that in this study, we did not rely on a specific value of a given SQG; instead, certain ranges were considered [21,22]. We also compared the measurements with average world river and global seawater concentrations [23] and average crust composition [19], the latter

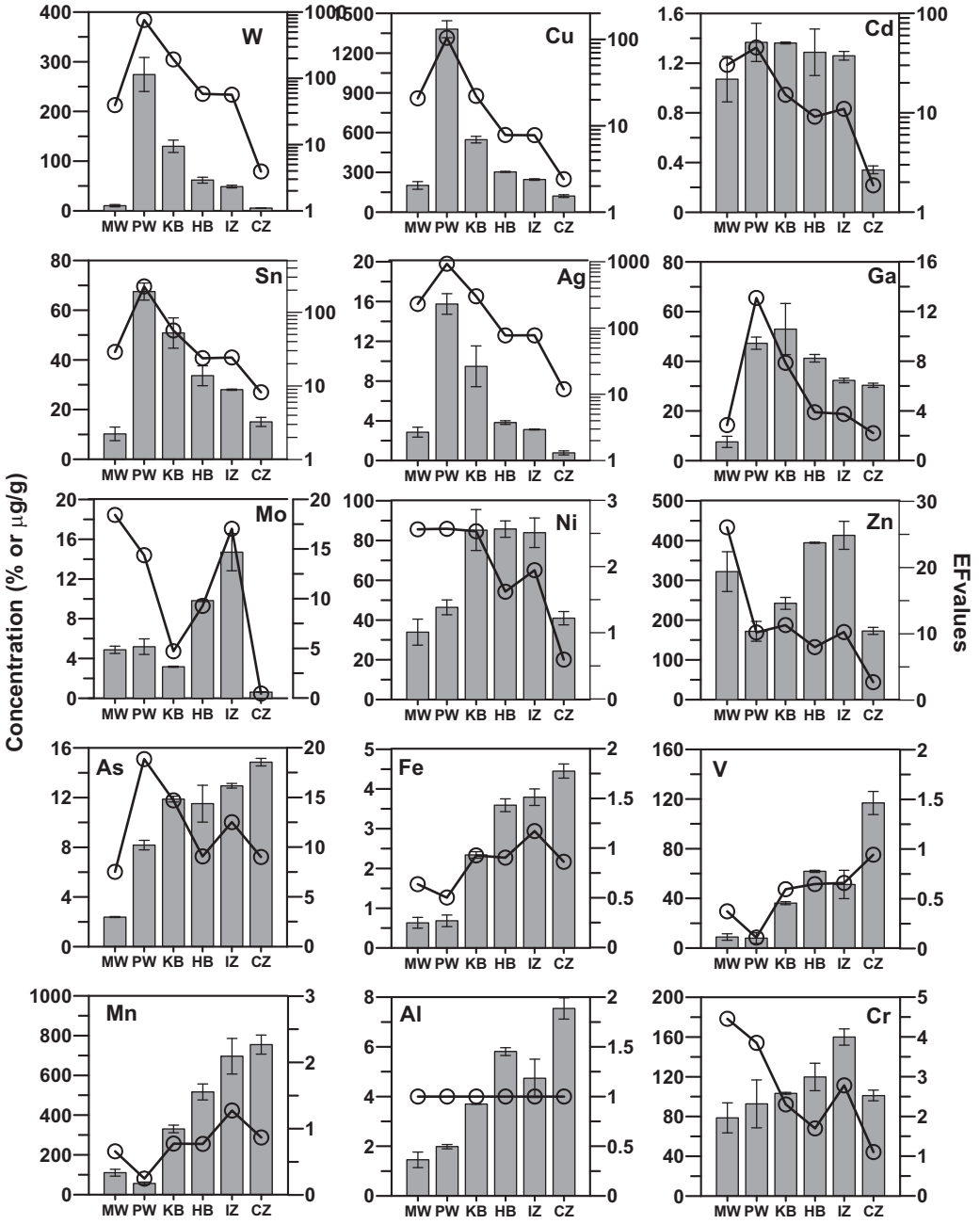

Fig. 3. Spatial distribution of particulate concentrations (% for Al and Fe, and μg/g for other elements; bar charts) of the heavy metals in the Keya Stream. Enrichment factors are also shown (symbols and lines). Error bars (standard deviations) are indicated for particulate concentrations of trace metals.

adopted as the most common reference for assessing anomalies of heavy metals in solid particles.

The dissolved concentrations for some heavy metals (e.g., Cu, Zn, and Ni) were two to ten times higher than those previously observed in 1992 since the early stage of HSP operation [24], indicating the deterioration of heavy metal pollution. However, the concentrations of the analyzed heavy metals mostly fell within national water quality and soil regulation standards, with dissolved Mn at IZ as the only exception; however, there were several particulate and sedimentary metals, such as Ag, Zn, Cu, As, and Ni, which were found at concentrations close to or higher than the SQGs at certain or even all stations (Tables 1 and 2). Compared with average world river and global ocean average concentrations, the concentrations of the analyzed heavy metals, particularly tungsten, were much higher. The world river average concentration is only 0.03 [25] to 0.09 μg/L [23] (Table 1); the dissolved tungsten concentrations measured in this study were up to three to four orders of magnitude higher. The maximum allowable concentrations for tungsten in drinking water and fishing water reservoirs are 50 and 0.8 μg/L, respectively ([26] and references therein). Furthermore, the concentrations of particulate and sedimentary tungsten were much higher than that (1.5 μg/g) of the average crust composition (Table 2), which is further confirmed by the pronounced EF values. The excessive anomalies for many other heavy metals were particularly highlighted when compared with unpolluted (or slightly polluted) natural water bodies. For instance, our particulate Ag concentrations were measured to be higher than those (0.04–0.28) in Japanese rivers and Tokyo Bay, indicative of Ag pollution in the Keya Stream.

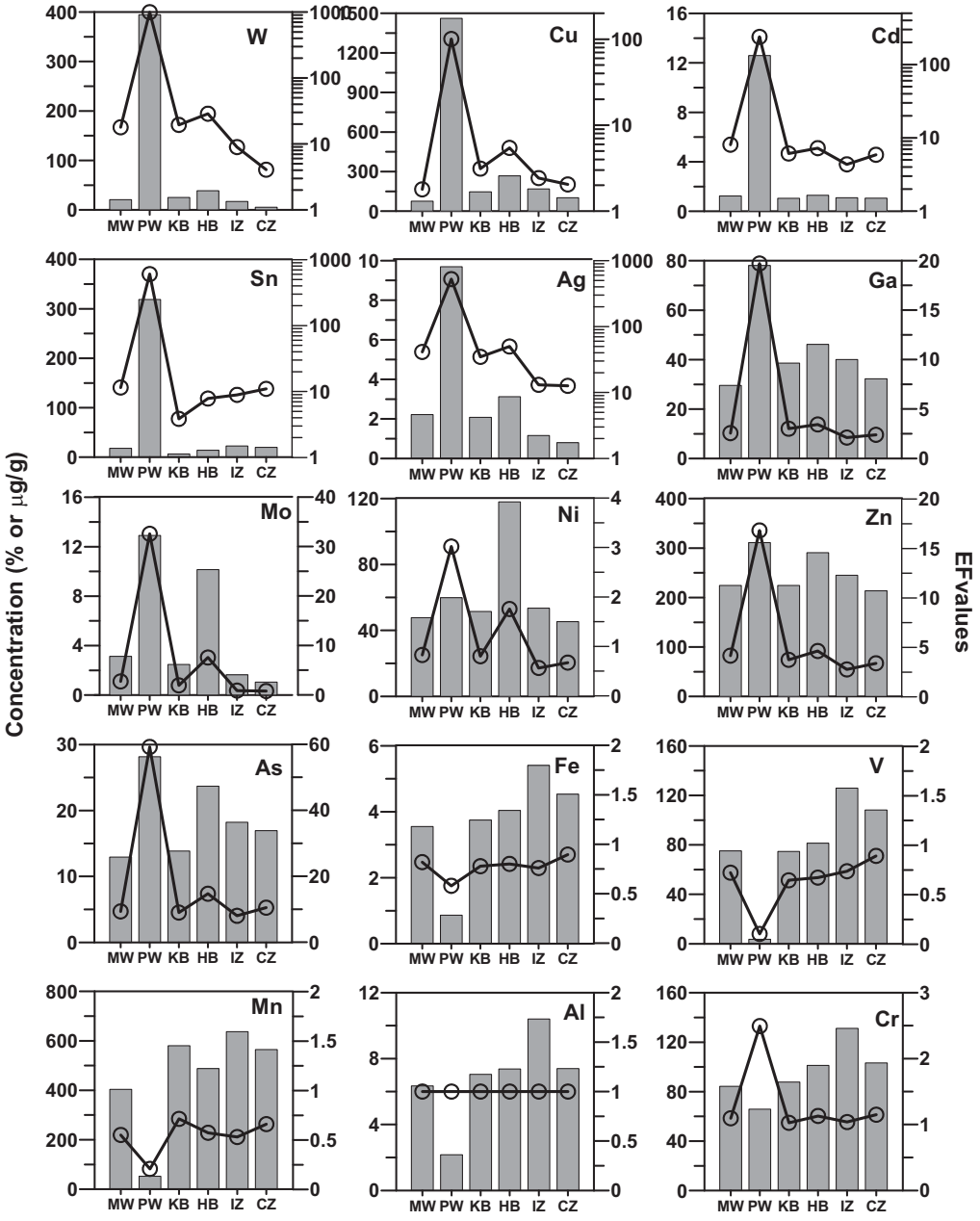

Fig. 4. Same as Fig. 3, but for sedimentary metals.

5.2. Tungsten and other metal pollutants related to semiconductor industrials

For the first group of elements (W, Cu, Cd, Sn, Ag, and Ga), both dissolved and particulate concentrations were considerably higher in the treated effluents from the WWTP of HSP than in the untreated municipal wastewater (station MW) (Figs. 2 and 3). The elevated EF values for the particulate metals again noticeably revealed suspended particulates to be highly contaminated by tungsten and other metals in the first group. The results suggest that the treated effluents are the most important source not only of dissolved metals, but also of particulate metals. They are related to semiconductor manufacturing and likely to other unidentified high-tech industrials. An elevated level of fluorite ion in the treated effluents, reaching a mean concentration of ~8 mg/L, was consistently measured during the regular monitoring (http://venus.sipa.gov.tw/SPAEPI/wastewater/checkWaterQuality.jsp), showing good accordance with the observed high tungsten because tungsten is utilized in the production of wafers (http://en.wikipedia.org/wiki/Tungsten_hexafluoride). Nevertheless, the facilities which acted as sources for certain other heavy metals (e.g., Ga and As) could not be readily identified, although both As and Ga in water and sediments were high. This is because the effluents comprise of mixed wastewater from all facilities located within the entire science park. Relevant fundamental information on the specific heavy metal pollutants is lacking.

The second group of elements may have partly originated from the same effluents because their dissolved concentrations followed a pattern similar to that of the first-group elements. In addition, a portion of the particulate forms of these elements may have accumulated from the dissolved metals in the water via adsorption onto the newly formed and originally existing Fe and Mn oxides/hydroxides as pH increased from nearly neutral to slightly basic and redox conditions changed from slightly reduced to oxidized in surface water downstream of the intertidal estuary and coastal ocean [27]. This suggestion can be supported by the result

Table 1
Dissolved concentrations (μg/L) of heavy metals/metalloids in the Keya Stream. For comparison, Taiwan's national water quality standard, world average river composition, and global average seawater composition are also given.

	This work	Taiwan's national water quality standard[a]	World average river [23]	Global average seawater [40]
W	298–430	–	0.1[b]	0.001[c]
Cu	9.5–15	30	1.5	0.1
Cd	0.035–0.054	10	0.02	0.01
Sn	0.063–0.17	–	–	–
Ag	0.007–0.028	50	0.3	0.04
Ga	0.79–1.3	–	0.09	0.03
Ni	17–21	–	0.5	0.2
As	13–21	50	1.7	1.5
Mo	8.6–14	–	0.5	10
Zn	17–20	500	30	0.1
Fe	269–379	–	40	2
V	3.6–7.6	–	1	2.5
Mn	13–73	50	8.2	0.2
Cr	3.6–5.4	50[d]	1	0.3
Al	38–58	–	50	0.5

[a] Refer to: http://ivy5.epa.gov.tw/epalaw/docfile/060190a.doc.
[b] This value is taken from Gaillardet et al. [41], but according to Turekian [25], the concentration as low as 0.03 μg/L was reported.
[c] This is taken from Turekian [42].
[d] For Cr (VI), not total Cr.

in which the particulate concentrations for this and the third group gradually increased from stations PW to IZ/CZ (Figs. 3 and 4).

The benthic supply from reduced sediments in the estuary could serve as an additional, internal source for dissolved and particulate Mn in stream waters, as confirmed by the fact that the concentrations and EF values of sedimentary Mn remained at a relatively low (Fig. 4), constant level, apparently lower than those of particulate Mn (Fig. 3). This may reveal that dissolved Mn migrates from reduced sediments somewhere when approaching the estuary [28]. Consequently, the concentrations and EF values of particulate Mn increased downstream. In the Keya Stream, municipal wastewater discharge could likely be an important source of certain metals such as Al and Cr; however, it may consist of a mixture of both untreated domestic and industrial wastewater.

5.3. Dilution effects and other controlling factors during transport

The Keya Stream annually discharges a total water runoff of $78.3 \times 10^6\ m^3$ into the estuary, of which nearly half of the amount ($0.105 \times 10^6\ m^3$/day, equivalent to $38.3 \times 10^6\ m^3$/yr) comes from the effluents of the HSP's WWTP (http://venus.sipa.gov.tw/SPAEPI/wastewater/page7-2-1.jsp). In other words, the contaminants discharged from the WWTP, especially dissolved tungsten and other dissolved first group elements, are gradually diluted by the imported surface runoff water [29] by a factor of approximately two, in the absence of a considerable additional supply and/or effective removal processes (e.g., adsorption/desorption, oxidation/reduction, biological uptake/regeneration), which appear to be important for the other two groups. This inference is quite consistent with what was found for the first-group elements that decreased by a factor of around two from the effluent's outlet to the estuary. That is, dissolved tungsten and other first-group elements essentially followed a conservative behavior, which can be further demonstrated by their nearly constant partitioning coefficients in the stream water till running into the saline water at station IZ (Fig. 2), as discussed later.

On the other hand, the annual sediment discharge of the Keya Stream was 0.19 Mt. According to the report of HSP (http://venus.sipa.gov.tw/SPAEPI/wastewater/page7-2-1.jsp), the

Table 2
Concentrations of heavy metals in suspended particulate matter (SPM) and sediments in the Keya Stream. Also given are the ranges of various sediment quality guidelines (SQGs), Taiwan's soil guideline (http://www.epa.gov.tw/), and average crust composition for evaluating pollution degree.

	SPM (this work)	Sediment (this work)	Midrange effect SQGs[a] [21]	TEL/PEL-based SQGs[b] [22]	Taiwan's soil guidelines[c]	Average crust composition [19]
W (μg/g)	5.4–274	5.5–394	–	–	–	1.5
Cu (μg/g)	121–1380	76–1462	36–390	18.7–110	400	55
Cd (μg/g)	0.3–1.4	1.0–12.6	1–9.6	0.67–4.21	20	0.2
Sn (μg/g)	10–68	6.6–319	–	0.048[d]	–	2
Ag (μg/g)	0.8–15.8	0.8–9.7	–	0.73–1.77	–	0.07
Ga (μg/g)	7.6–53	30–78	–	–	–	15
Ni (μg/g)	34–86	45–118	33–150	15.9–42.8	200	75
As (μg/g)	2.4–15	13–28	11–85	7.2–42	50	1.8
Mo (μg/g)	0.6–15	1.1–13	–	–	–	1.5
Zn (μg/g)	172–413	214–311	100–700	120–271	1000	70
Fe (%)	0.6–4.5	0.9–5.4	–	–	–	5.63
V (μg/g)	8.0–117	3.7–126	–	–	–	135
Mn (μg/g)	56–755	52–637	–	–	–	950
Cr (μg/g)	79–160	66–131	23–370	52–160	250	100
Al (%)	1.5–7.5	2.2–10.4	–	–	–	8.23

[a] These guidelines are valid for freshwater sediments.
[b] TEL is referred to threshold effect level, and PEL, probable effect level. Here shown are the values of ranges of TEL and PEL from four sets of SQGs for marine sediments [22].
[c] Refer to http://ivy5.epa.gov.tw/epalaw/docfile/140120.pdf.
[d] Only TEL is available for tin.

average concentration of suspended solids in the effluents from the WWTP was 7.1 mg/L; this value corresponds to the annual amount of suspended particulate discharges, that is, only 0.00027 Mt. This amount therefore represents only 0.14% of the annual sediment discharge of the Keya Stream to the sea. This finding is also consistent with the spatial patterns of the first-group particulates and sedimentary elements, in which their concentrations gradually (for particulate metals) or sharply (for sedimentary metals) decreased beyond the effluent outlet (Figs. 3 and 4). These aforementioned observations enable us to assume that the fluvial-eroded sediments are able to substantially dilute the particulate and sedimentary metals carried by the effluents. However, the relatively higher (or close) concentrations of certain elements (such as Al, Fe, Mn, Cr, and V) in eroded sediments do not support this assumption. Conversely, the third-group elements showed an increasing pattern downstream. In addition, aside from mixing with background sediments, grain size effect and adsorptive enhancement appeared to be partly responsible for the observed spatial distribution [13,29].

Aluminum, typically used as an indicator of terrigeneous sediments, increased downstream and reached ~7% or higher in SPM and sediments at intertidal and coastal zones, demonstrating the predominance (~85%) of terrigeneous sediments [30,31]. Therefore, the sharp decrease in particulate and sedimentary concentrations in the intertidal or coastal zones of certain heavy metals, such as W, Cd, Sn, Ag, Ni, Mo, and Zn, could be attributed to the dilution effect of relatively huge amounts of discharged fluvial and coastal terrigeneous sediments.

5.4. Partition between dissolved and particulate metals

In addition to the dilution effect, a variety of geochemical processes are involved in the transport and fate of the investigated elements. As concluded by Shafer et al. [32], the short-term fate of metals in natural waters from effluents released by a WWTP can behave conservatively (controlled by dilution) and non-conservatively (controlled by particle scavenging, sorption to streambed sediments, particle settling, and uptake into biota). We calculated their K_d values to specify their environmental behaviors.

Based on the spatial variation of the computed K_d for the studied heavy metals, as shown in Fig. 2, we found that distinctly different values were often observed somewhere between the inland stations and the intertidal zone station, suggesting that the salinity (ionic strength) could be a crucial factor of partitioning [20,33]. We therefore treated them separately on the basis of the levels and spatial patterns of K_d values. First, at the inland stations, they ranked in the following order: W, Mo, As (10^2–10^3) < Ni, V, Mn (10^3–10^4) < Zn, Cr, Cd, Cu, Ga, Fe (10^4–10^5) < Ag, Sn, Al (10^5–10^6). At the intertidal station, the coefficients followed a different order as follows: Cd, Mo (10^2–10^3) < Ag, W, As (10^3–10^4) < Sn, Ga, Ni, V, Cr (10^4–10^5) < Mn, Cu, Zn (10^5–10^6) < Fe, Al (10^7–10^8). The K_d values for almost all analyzed elements in the inland stream water remained at a nearly steady level. However, the changes in K_d between the inland and estuarine stations showed three distinguishable patterns, including: (1) a clear increase at the intertidal station for W, Cu, Ni, Zn, As, Fe, V, Mn, and Al; (2) a decrease at the intertidal station for Cd, Sn, and Ag; and (3) nearly no change at the intertidal zone for Ga, Mo, and Cr.

The relatively constant K_d at inland stations might indicate conservative behavior in freshwater and less saline waters, but different processes accounted for these three different spatial patterns at the mixing zone [33]. The increased K_d at the intertidal station suggests that these dissolved elements would be favorably removed by suspended particles while entering the estuary because they (e.g., Fe, Al, Mn, Zn, V, and Ni) mostly have strong particle affinities [23]. For this type of behavior, Mn is a representative element; because it has a high particle-reactive nature, its K_d is also relatively high in general [34]. Consequently, the estuarine and coastal sediments could serve not only as a sink and but also as a source of certain metals such as Mn.

5.5. Significant inputs of tungsten from the studied small stream into the adjacent coastal ocean

Tungsten concentrations observed in the Keya Stream reached ~300 μg/L, up to nearly four orders of magnitude higher than the average world river concentration (0.03–0.1 μg/L) (Table 1) [23,25]. By assuming that the average concentrations measured at stations HB and IZ could represent the discharged concentration of dissolved tungsten into the sea, the Keya Stream would annually discharge dissolved tungsten at an approximate amount of $300\,mg/m^3 \times (80 \times 10^6)\ m^3/yr$. This amount is equivalent to that discharged by a much larger unpolluted river, whose tungsten concentration is assumed to be similar to the average world river concentration (0.03–0.1 μg/L) and annual water discharge of $0.24–0.8 \times 10^{12}\ m^3/yr$. Surprisingly, this assumed water discharge is quite close to those of the 5–14th largest rivers worldwide ($0.9 \times 10^{12}\ m^3/yr$ for the Yangtze River and $0.25 \times 10^{12}\ m^3/yr$ the Columbia River). This simple estimation highlights the fact that even a small river, such as the Keya Stream, can supply a considerable quantity of tungsten (i.e., 23.5 t/yr) into the adjacent ocean, even as high as that by a large river, such as the Yangtze, if its dissolved tungsten concentration is only 0.03 μg/L, similar to that of the global river average. This estimate excludes the input of particulate tungsten. This is the first estimation ever documented for the riverine discharge of anthropogenic tungsten into the ocean. This may also imply that the anthropogenic input of certain trace elements (e.g., tungsten) increasingly used in high-tech industrials might disturb the inherent biogeochemical cycles of elements in natural aquatic ecosystems, which should be of considerable concern.

5.6. Implications for potential effects on the aquatic organisms

Substantial accumulation of heavy metals, such as Cu, Zn, Cd, Pb, and As, were found in the oyster *C. angulata* cultivated in the Hsiangshan intertidal flat adjacent to the Keya Stream estuary [13,14,24,35]. Recently, Yurchenko et al. [36] observed a higher incidence of reproductive impairment in the oyster *C. angulata* collected from the same intertidal area than that from a remote, uncontaminated offshore island, Penghu, in Taiwan Strait. These impairments include sperm with abnormal acrosomes and lacking mitochondria and flagella (26.6% spermatozoan damage in Hsiangshan oysters vs. 0.4% in Penghu oysters). Besides, female gonads exhibited prominent oocyte degeneration, hemocytic infiltration, and parasitic infections (e.g., 100% oocyte alterations at Hsiangshan vs. 28.6% at Penghu, personal communication with M Vaschenko). Yang and Chen [37] also found the toxic effects of Ga from semiconductor facilities on common carp (*Cyprinus carpio*). In addition, high levels of heavy metals, such as Ga, As, Cd, In, and Tl related to semiconductor manufacturing, were found in Formosan squirrels captured around HSP [38]. These authors attributed the pollution to HSP. In the present study, we have observed abnormal levels of tungsten and other heavy metals in the Keya Stream. However, even around the world, field studies on the effects of tungsten on aquatic organisms are extremely inadequate, although a few studies have concluded that tungsten may act as a toxin to aquatic biota ([39] and references therein). Strigul et al. [10] observed the acute toxicity of tungsten to fish in terms of not only its concentration level but also its chemical speciation. Although the toxic mechanism is not known well, the authors further hypothesized to be related to the damage of gill epithelium. We strongly urge that the unusual high loading in the aquatic ecosystems is worthy of more compre-

hensive field and laboratory investigations on the biogeochemistry and biological effects of these metals.

6. Concluding remarks

The studied dissolved and particulate heavy metals mostly displayed an evident spatial variation decreasing downstream from the outlet of the science park's WWTP to the estuary. They originated from the treated effluents from semiconductor manufacturing, particularly for W, Cu, Ga, and Ag. Dissolved W concentrations remained at an abnormally pronounced level of up to ~300 μg/L or higher throughout the entire river. Also, high W was observed in suspended particles and sediments, and enrichment factors reached ~10^3. This is the first study to provide evidence on the influence of semiconductor industrials on tungsten concentration in the receiving river. Our results suggest that the spatial distribution of the studied metals in the stream water appears to be regulated primarily by the dilution effect of natural river runoff and background-eroded sediments and their respective geochemical characteristics, apart from the strength of pollution sources. These sources include effluents from the HSP's WWTP and municipal wastewater discharge from Hsinchu City. This study also highlights potentially substantial effects on the aquatic ecosystem, especially on the adjacent estuarine and coastal zones, which serve as oyster farms. Consequently, establishing fundamental data on the specific heavy metal pollution profiles of each type of high-tech manufacturing facility is an urgent endeavor [5]. This enables identification of pollution sources for the formulation of management strategies.

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References

[1] P.S. Rainbow, Trace metal concentrations in aquatic invertebrates: why and so what? Environ. Pollut. 120 (2002) 497–507.
[2] M.S. Islam, M. Tanaka, Impacts of pollution on coastal and marine ecosystems including coastal and marine fisheries and approach for management: a review and synthesis, Mar. Pollut. Bull. 48 (2004) 624–649.
[3] G.W. Bryan, W.J. Langston, Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review, Environ. Pollut. 76 (1992) 89–131.
[4] M.G. Vijver, C.A.M. van Gestel, R.P. Lanno, N.M. van Straalen, W.J.G.M. Peijnenburg, Internal metal sequestration and its ecotoxicological relevance: a review, Environ. Sci. Technol. 38 (2004) 4705–4712.
[5] P. Edelman, Environmental and workplace contamination in the semiconductor industry: implications for future health of the workforce and community, Environ. Health Perspect. 86 (1990) 291–295.
[6] G. Agoramoorthy, M.J. Hsu, Taiwan pays the price for growth, in toxic pollution, Nature 408 (2000) 905–1905.
[7] A. Koutsospyros, W. Braida, C. Christodoulatos, D. Dermatas, N. Strigul, A review of tungst: from environmental obscurity to scrutiny, J. Hazard. Mater. 136 (2006) 1–19.
[8] K. Schischke, M. Stutz, J.-P. Ruelle, H. Griese, H. Reichl, Life cycle inventory analysis and identification of environmentally significant aspects in semiconductor manufacturing, in: Proceedings of the 2001 IEEE International Symposium on Electronics and the Environment, 7–9 May 2001, Denver, CO, 2001, pp. 145–150.
[9] M.I. Castro-Gonzáleza, M. Méndez-Armenta, Heavy metals: implications associated to fish consumption, Environ. Toxicol. Pharmacol. 26 (2008) 263–271.
[10] N. Strigul, A. Koutsospyros, C. Christodoulatos, Tungsten speciation and toxicity: acute toxicity of mono- and poly tungstates to fish, Ecotoxicol. Environ. Saf. 73 (2010) 164–171.
[11] K. Lam, B. Morton, P. Boudry, S. Heurtebise, Morphological and mitochondrial DNA characteristics of two cultured species of cupped-oysters (Bivalvia: Ostreidae) in Hong Kong: toward a significant taxonomic name change, in: B. Morton (Ed.), Perspectives on Marine Environment Change in Hong Kong and Southern China, 1977–2001, Hong Kong University Press, Hong Kong, 2003, pp. 229–344, Proceedings of an International Workshop Reunion Conference, Hong Kong 21–26 October 2001.
[12] S. Lapegue, F.M. Batista, S. Heurtebise, Z. Yu, P. Boudry, Evidence for the presence of the Portuguese oyster, *Crassostrea angulata*, in northern China, J. Shellfish Res. 23 (2004) 759–763.
[13] S. Lin, I.J. Hsieh, Occurrences of green oyster and heavy metals contaminant levels in the Sien-San area, Taiwan, Mar. Pollut. Bull. 38 (1999) 960–965.
[14] M.S. Jeng, W.L. Jeng, T.C. Hung, C.Y. Yeh, R.J. Tseng, P.J. Meng, B.C. Han, Mussel watch: a review of Cu and other metals in various marine organisms in Taiwan, 1991–98, Environ. Pollut. 110 (2000) 207–215.
[15] A.Y.C. Lin, S.C. Panchangam, C.C. Lo, The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers, Environ. Pollut. 157 (2009) 1365–1372.
[16] S.C. Hsu, S.C. Liu, Y.T. Huang, S.C.C. Lung, F. Tsai, J.Y. Tu, S.J. Kao, A criterion for identifying Asian dust events based on Al concentration data collected from northern Taiwan between 2002 and early 2007, J. Geophys. Res. 113 (2008) D18306, doi:10.1029/2007JD009574.
[17] S.C. Hsu, T.F.G. Wong, G.C. Gong, F.K. Shiah, Y.T. Huang, S.J. Kao, F. Tsai, C.S.C. Lung, F.J. Lin, I.I. Lin, C.C. Hung, C.M. Tseng, Source, solubility and dry deposition of aerosol trace elements over the East China Sea, Mar. Chem. 120 (2010) 116–127.
[18] S.C. Hsu, F.J. Lin, Elemental characteristics of surface suspended particulates off the Changjiang estuary during the 1998 flood, J. Mar. Syst. 81 (2010) 323–334.
[19] S.R. Taylor, Abundance of chemical elements in the continental crust: a new table, Geochim. Cosmochim. Acta 28 (1964) 1273–1285.
[20] A. Turner, M. Martino, S.M. Le Roux, Trace metal distribution coefficients in the Mersey Estuary, UK: evidence for salting out of metal complexes, Environ. Sci. Technol. 36 (2002) 4578–4584.
[21] G.A. Burton Jr., Sediment quality criteria in use around the world, Limnology 3 (2002) 65–75.
[22] R. Hübner, K.B. Astin, R.J.H. Herbert, Comparison of sediment quality guidelines (SQGs) for the assessment of metal contamination in marine and estuarine environments, J. Environ. Monit. 11 (2009) 713–722.
[23] R. Chester, Marine Geochemistry, Unwin Hyman, London, 1990.
[24] C.M. Tseng, C.L. Wei, P.C. Mao, Heavy metals in oysters from Shangshan (Taiwan) in relation to environmental levels, Acta Oceanogr. Taiwan 31 (1993) 101–116.
[25] K.K. Turekian, The oceans, streams and atmosphere, in: K.H. Wedepohl (Ed.), Handbook of Geochemistry, vol. 6, Springer-Verlag, Heidelberg, 1969, pp. 297–323.
[26] N.S. Strigul, A. Koutsospyros, C. Christodoulatos, Tungsten in the former Soviet Union: review of environmental regulations and related research, J. Land Contam. Reclam. 17 (2009) 189–215.
[27] D. Colbert, J. McManus, Importance of seasonal variability and coastal processes on estuarine manganese and barium cycling in a Pacific Northwest estuary, Cont. Shelf Res. 25 (2005) 1395–1414.
[28] K.M. Huang, S. Lin, Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan, Chemosphere 53 (2003), 1113-1121.
[29] T.F. Rozana, K.S. Hunter, Effects of discharge on silver loading and transport in the Quinnipiac River, Connecticut, Sci. Total Environ. 279 (2001) 195–205.
[30] S.C. Hsu, F.J. Lin, W.L. Jeng, T.Y. Tang, The effect of a cyclonic eddy on the distribution of lithogenic particles in the southern East China Sea, J. Mar. Res. 56 (1998) 813–832.
[31] S.C. Hsu, F.J. Lin, W.L. Jeng, Y. Chung, L.M. Shaw, K.W. Hung, Observed sediment fluxes of the southwestern most Okinawa Trough enhanced by episodic events: flood runoff from northeastern Taiwan river and great earthquakes, Deep-Sea Res. 51 (2004) 979–997.
[32] M.M. Shafer, J.T. Overdier, D.E. Armstong, Removal, partitioning, and fate of silver and other metals in wastewater treatment plants and effluent-receiving streams, Environ. Toxicol. Chem. 17 (1998) 630–641.
[33] A. Turner, G.E. Millward, Partitioning of trace metals in a macrotidal estuary, Implications for contaminant transport models, Estuar. Coast. Shelf Sci. 39 (1994) 45–58.
[34] Y.H. Li, Distribution patterns of the elements in the ocean: a synthesis, Geochim. Cosmochim. Acta 55 (1991) 3223–3240.
[35] P.C. Han, T.C. Hung, Green oysters caused by copper pollution on the Taiwan coast, Environ. Pollut. 65 (1990) 347–362.
[36] O.V. Yurchenko, V.I. Radashevsky, H.L. Hsieh, A.A. Reunov, Ultrastructural comparison of the spermatozoa of the Pacific oyster *Crassostrea gigas* inhabiting polluted and relatively clean areas in Taiwan, Aqua. Ecol. 43 (2009) 513–519.
[37] J.L. Yang, H.C. Chen, Toxic effects of the semiconductor metal gallium on common carp (*Cyprinus carpio*), Acta Zool. Taiwan 13 (2002) 63–72.
[38] Y. Suzuki, I. Watanabe, T. Oshida, Y.J. Chen, L.K. Lin, Y.H. Wang, K.C. Yang, K. Kuno, Accumulation of trace elements used in semiconductor industry in Formosan squirrel, as a bioindicator of their exposure, living in Taiwan, Chemosphere 68 (2007) 1270–1279.

[39] F. Malekzadeh, S.G. Mashkani, H. Ghafourian, M.R. Soudi, Biosorption of tungstate by a *Bacillus* sp. isolated from Anzali lagoon, World J. Microbiol. Biotechnol. 23 (2007) 905–910.
[40] J.M. Martin, M. Whitfield, The significance of the fiver inputs to the ocean, in: C.H. Wong, E. Boyle, K.W. Bruland, J.D. Burton, E.D. Goldberg (Eds.), Trace Metals in Seawater, Plenum, New York, 1983, pp. 265–296.
[41] J. Gaillardet, J. Viers, B. Dupré, Trace elements in river waters, in: J.I. Drever (Ed.), Surface and Ground water, Weathering, and Soils, Treatise on Geochemistry, vol. 5, Elsevier Ltd., Oxford, 2003, pp. 225–272.
[42] K.K. Turekian, Oceans, Prentice Hall, Englewood Cliffs, New Jersey, 1968.