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Distribution of selenium in the plume of the Gediz River, Izmir Bay, Aegean Sea

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ABSTRACT

Selenium (Se) variations in the water column, suspended particulate matter, and sediment through the salinity gradient, together with water-quality parameters, were investigated over four different river conditions: lowest–highest runoff and high–low production period between November 2004 and August 2005 in the plume of the Gediz River, Aegean Sea, Turkey. The drainage basin of the Gediz delta is predominantly agricultural and industrial in character. Dissolved Se exceeded the water-quality standard of 5 μg L^{-1} during high flow and varied from 9.4 μg L^{-1} to 0.02 μg L^{-1} through the salinity gradient during the study period. Particulate Se ranged from 5.2 μg L^{-1} to 0.02 μg L^{-1}. Sediment in the river mouth was highly affected by Se contamination and reached a level greater than four times (7.6 μg g^{-1} dry wt) the background level. The results indicated that Se supplied by the river was removed rapidly from the water column before the salinity reached an average value of about 20 and accumulated within the delta.

Keywords: Selenium, particulates, sediment, river plume, Gediz River, Aegean Sea

1. Introduction

The importance of studying selenium (Se) in estuaries in order to understand the interactions of anthropogenic and natural processes on the distribution of Se and chemical changes of dissolved selenium (DSe) and particulate selenium (PSe) in the seawater has been increasing because of marked changes in major variables such as salinity during high and low river flow (Tetra Tech Inc. 2008), nutrient loading (Koike et al. 1993), and pH and temperature (U.S. Environmental Protection Agency 2004). The behavior of suspended particulate materials is much more difficult to interpret than that of dissolved materials mainly because of complicated patterns of sedimentation and resuspension mechanisms.

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Se in aquatic ecosystems exists in a broad range of oxidation states: (+VI) in selenate ($HSeO_4^-$, SeO_4^{2-}) and selenic acid (H_2SeO_4), (+IV) in selenite ($HSeO_3^-$, SeO_3^{2-}) and selenous acid (H_2SeO_3), (0) in elemental selenium, and (−II) in selenide (Se^{2-}, HSe^-), hydrogen selenide (H_2Se), and organic selenides. Se (VI) is usually the thermodynamically predicted stable and predominant form of Se in oxic waters; however, Se (IV) can also be an important species and may exist at concentrations higher than predicted levels (Luoma et al. 1992) because of its slow oxidation rate in natural waters (Cutter 1982). Moreover, Se (IV) is the most bioavailable of the dissolved phase inorganic species (Maier and Knight 1993; Skorupa 1998). The existence of multiple oxidation states of Se in natural waters complicates prediction of Se accumulation into plankton food webs because the different forms have different biological reactivity (Wrench and Measures 1982). It is well known that bacteria and algae can take up inorganic Se from solution. Some species are selective for Se (IV), whereas others take up both Se (IV) and (VI) (Robles et al. 1999). Se (IV) and Se (VI) are readily taken up by bacteria, wheres Se (IV) is preferred by phytoplankton (Price, Thompson, and Harrison 1987). Examples exist in nature where each of the three major species of Se is predominant: (1) Se (VI) predominates in most irrigation drainage inputs to wetlands (Presser and Ohlendorf 1987; Zhang and Moore 1996, 1997); (2) Se (IV) can predominate in systems affected by industrial wastes, especially those associated with wastes from fossil fuel products or consumption (Cutter and San Diego-McGlone 1990); and (3) organo-Se can predominate where Se is strongly recycled (Takayanagi and Wong 1984).

Among many trace elements, Se has a special place because of a narrow gap between essentiality and toxicity (Wilber 1983; Presser and Ohlendorf 1987), and hence, Se has received considerable attention from biologists and toxicologists (Harrison et al. 1988; Läuchli 1993; Lemly 1996, 1997). Uncertainty in developing toxicity criteria for aquatic life is also because of limited field data for Se.

Some selected cornerstone literature on the biogeochemical cycle of DSe in estuarine waters (Cutter 1989; Fan et al. 2002; Cutter and Cutter 2004; Doblin et al. 2006; Meseck and Cutter 2006) and sediments (Belzile and Lebel 1988; Velinsky and Cutter 1991) and on its bioavailability in the food web (Doblin, Blackburn, and Hallegraeff 1999) was reviewed. This review reveals the extreme complexity of Se biogeochemistry in aquatic environments. Once accumulated in aquatic primary and secondary producers, Se can be transferred through various aquatic consumers (e.g., zooplankton, insect larvae, larval fish, bivalves, etc.) into the top predators, including aquatic birds and piscivorous fish. The physical distribution of various Se species in surface waters is regulated by: (1) sorption to or incorporation in suspended particulate matter, and (2) complexation with inorganic and/or organic colloidal material and dissolved organic matter. Both sorption to suspended particulate matter and complexation with colloidal matter reduces the bioavailability of the DSe species.

There are limited studies on the biogeochemical cycle and ecological impacts of Se, as well as guidelines based on the results of those studies. In this respect, almost nothing has been done in coastal zones, particularly in the eastern Mediterranean and Aegean Sea. The

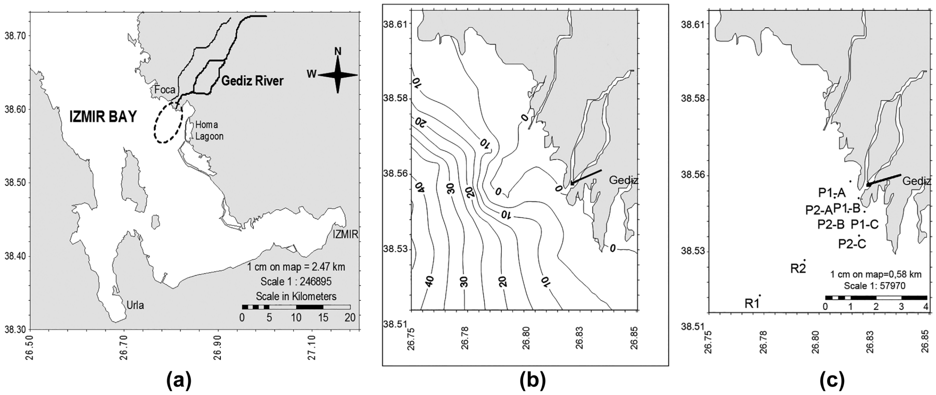

Figure 1. Maps of sampling areas (a), bathymetry (b), and stations in the study area (c) during the sampling period.

purpose of this study was to determine Se distribution in particles (PSe), dissolved (DSe) in the water column (Se IV + VI), and the loads and accumulation from these compartments to sediments in the polluted Gediz River delta. The Gediz River is highly contaminated with dissolved Cd, Co, Cr, and organic pollutants from domestic and industrial effluents (Bizsel et al. 2008). The water quality of Gediz River can be accepted only as third-grade irrigation water (Kayar and Çelik 2003). Adequate accuracy in forecasting the environmental fate of Se in the Gediz delta and Izmir Bay is crucial because its effect on reproduction in fish and aquatic birds has been suspected. Therefore, the distribution, amount, and speciation of Se are very important parameters for environmental monitoring and protecting aquatic life in the study area, where there is a bird paradise and where massive fish mortalities have been observed almost every year. The last mass mortalities of fish observed in Gediz delta were on 17 June 2014 and 26 September 2015 (Milliyet 2015, local press).

2. Materials and methods

a. Study area and sampling

With a 17,500 km^2 catchment basin and a length of 401 km, the Gediz River is located northwest of the Izmir Bay (Fig. 1a) and is the second largest river after the Menderes River, flowing from the Anatolian hinterland into the Aegean Sea and emptying into the outer Izmir Bay. There are more than 400 independent industrial establishments in the Gediz River basin that discharge their wastes into the river, and the total population was 1,700,000 in 2000 (Çetinkaya and Barbaros 2008). Consequently, the river has been identified as a significant pollution source for Izmir Bay according to several previous studies (Gundogdu et al. 2005; Bizsel et al. 2008; Bizsel and Sarıca, 2008). The Gediz River, where mass fish mortalities have been reported since 1989 (local press, Yeni Asir, 2015), is heavily polluted because of agricultural drainage waters, industrial wastewaters, and virtually all kinds of domestic wastewaters. Together with the areal intensification in agricultural activities, the qualitative diversification and quantitative fluctuations of agricultural pollutants carried by the river have also increased. According to archived flow data (State Water Administration 2004–2005), the recorded minimum and maximum values within the period 1962–2005 were 0.08 m^3 s^{-1} and 460 m^3 s^{-1}, respectively, with a mean value of 33 ± 51 m^3 s^{-1}. During the present study, the minimum runoff value was 5.2 m^3 s^{-1} in November 2004, and the maximum was 123 m^3 s^{-1} in February 2005 (data from State Water Works 2004–2005).

The concentrations of DSe and PSe in the water column under various river flow conditions in the mouth of the Gediz River and Izmir Bay were determined in samples collected in 2004–2005. The sampling runs were done during the dry season in November 2004 (no irrigation and lowest runoff), the extremely wet season in February 2005 (highest runoff), the productive season in April 2005 (base flow and high primary production), and the postproductive season in August 2005 (late summer, irrigation effects). The water samples (river and mixing zone) were collected 10–15 cm below the surface with a precleaned water sampler, and sampling depth in the water column was adjusted according to the conditions during the sampling period. The riverine samples were collected in the mouth of the estuary by Zodiac boat at the shallowest depth (Fig. 1b). The study area covered the river mouth and its surroundings, bordered by the end of the surface salinity gradient. There were nine stations, of which one was in the river (i.e., 50 m inward from the river mouth), six were along the river plume, and two were at the adjacent offshore as reference stations. The study area (Fig. 1c) was divided into four zones: the freshwater zone (river mouth), the plume 1 zone (stations P1-A, P1-B, and P1-C), the plume 2 zone (stations P2-A, P2-B, and P2-C), and the reference zone (R1 and R2). The station locations were determined via vertical salinity profiler by tracing the salinity gradients as a chemical gateway for export or retainment. The vertical profiles at the stations displayed that the river had a salt wedge property at all sampling periods. The distances between stations were kept as constant as possible. The transect in the plume 1 zone was on average 0.4 km, whereas it was 0.2 km in the plume 2 zone. The distance between the reference stations and the river mouth was about 5.5 km.

b. Analytic methods

Salinity and pH_{NBS} were measured in situ with a portable salinometer and a pH meter, respectively. Dissolved oxygen (DO) was measured with the modified Winkler titration (Strickland and Parsons 1968). In the laboratory, aliquots of water samples were filtered through acid-cleaned filters (Nuclepore, 0.4 μm) for the determination of Se and other metals. Another aliquot in each case was filtered through a precombusted (450°C, 4 h) GF/F filter for nutrients, particulate organic carbon (POC), and dissolved organic carbon (DOC) measurements. POC was measured by a CHN analyzer (Carlo ERBA NC2500; United Kingdom), whereas DOC and nutrients were determined by an Auto Analyzer (Skalar; Netherlands). Analyses of DSe and PSe were carried out by ICP-MS (Agilent 7500a Model;

USA) and AAS (Varian Spectra-300 Plus). Dissolved, particulate, and sedimentary forms of Se were determined after reducing Se (VI) to the lower oxidation state Se (IV). Because of the slower hydride formation kinetics of Se (VI), an isoformation procedure was applied to all samples in order to convert all Se into Se (IV), which has much faster hydride formation kinetics. This was achieved by heating the sample with 6 M HCl (1:1) at 85°C for 40 minutes (Anthemidis 2006). DSe was preconcentrated by percolating seawater through a Chelex-100 column. The column was then eluted with ultrapure acid (20 mL of 0.6 M HCl/0.2 M HNO_3 mixture). The particulate matter retained on the filter was digested with an acid mixture of HNO_3 (3 mL, 65%), HF (1 mL, 48%), $HClO_4$(0.7 mL, 60%), and HCl (0.8 mL, 37%) in a microwave oven (Milestone 1200 Mega). The sediment samples collected from the stations through the salinity gradient in August 2005 were also digested with the same acid mixture in a microwave oven for Se (IV + VI) determination (United Nations Environment Programme [UNEP] 1985). The determination of selenite was carried out using an AAS instrument (Perkin Elmer AAnalyst 800) equipped with flow injection (FIAS 100) and hydride generation units using validated analytic procedures according to International Organization for Standardization/International Electrotechnical Commision 17025 (developed/modified from Reference Methods for Marine Pollution Studies No. 10[E] 1984, UNEP/Food and Agriculture Organization of the United Nations/International Atomic Energy Agency, "Determination of total selenium in selected marine organisms by hydride generation atomic absorption spectrophotometry" [UNEP, International Atomic Energy Agency, and Intergovernmental Oceanographic Commission 1990]). The limit of detection (3σ) achieved for Se was 0.4 ng mL^{-1} using an EDL. The method was validated by analyzing certified reference materials (CRMs; LGC 6011 for water and GBW 07405 for soil). The accuracy of the method was also checked by analyzing spiked seawater samples using ICP-MS as an alternative method for confirmation/verification analysis (Fig. 2). The Se contents were determined in the CRMs with 2.8% and 8.3% standard errors for water and sediment, respectively, when compared with the certified values. Determination of Se performed via AAS was quite accurate (i.e., with relative error $<5\%$) and precise (i.e., with relative standard deviation $<3\%$) in real samples.

3. Results and discussion

As a basis of the subsequent discussion of Se data, seasonal distributions of salinity, temperature, pH, DO, total suspended solid (TSS), POC, and DOC in the study area are shown in Table 1.

a. Dissolved and particulate Se in the water column

The total Se concentration in water samples from the mouth of Gediz River is 5.4 ± 2.6 μg L^{-1} as an annual average value, which means that the level of concern (2 μg L^{-1}) as defined by Shaul et al. (2008) was consistently exceeded during the study period. Such a state indicates an unignorable potential for bioaccumulation of Se from the water

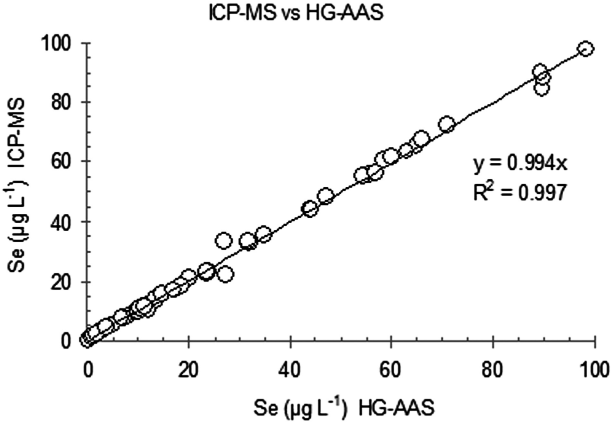

Figure 2. Comparing data obtained by inductively coupled plasma mass spectrometry (ICP-MS) and hydride generation atomic absorption spectrometry (HG-AAS).

through the planktonic food chain in this river system. According to Hamilton (2004), typical background levels of Se in the marine environment are <2 μg L^{-1} in water and <2 μg g^{-1} in sediment. If these levels increase to 2–5 μg L^{-1} and 4 μg g^{-1}, respectively, there is a concern for toxicological effects and effects on the reproductive physiology of organisms such as mollusks, crustaceans, fishes, and thereby birds, and when levels rise further, such effects are very likely. Lemly (2002) defined a "hazard profile" with five categories for Se accumulation from water into the planktonic food chain with resultant toxicity to fish and aquatic birds: high, >5 μg L^{-1}; moderate, 3–5 μg L^{-1}; low, 2–3 μg L^{-1}; minimal, 1–2 μg L^{-1}; none, <1 μg L^{-1}. The 2 μg L^{-1}, which is a guideline for the water column, will protect aquatic life both from direct toxic effects and from accumulating undesirable levels of Se via the food chain (Beatty and Russoi 2044). Meanwhile, a typical open-ocean water concentration of Se was reported to be 0.1 μg L^{-1} (1.27 nM) in the form of selenite and selenate ions (Raymont 1980).

The concentration of total Se (TSe = DSe + PSe) ranged from 5.2 to 14.5 μg L^{-1} (mean 8.5 μg L^{-1}) in the mouth of the Gediz River, apparently resulting from the influence of river basin runoff and anthropogenic inputs (Table 2). The range slightly narrowed in the plume 1 area (0.83 to 7.25 μg L^{-1}) and the plume 2 area (0.05 to 6.01 μg L^{-1}), and the values of minimum and maximum decreased abruptly. For the reference area, the decrease was both in terms of range and minimum/maximum limits. In Figure 3, the declining values of DSe and PSe from Gediz to the reference area show that the Gediz River has a remarkable potential to act as an important source of Se for the study area as well as for the whole Izmir Bay. Another remarkable point is that the values of both Se fractions steadily decreased through the salinity gradient. The concentrations measured were 5.41 ± 0.41, 1.67 ± 0.10, 1.03 ± 0.09, and 0.24 ± 0.09 μg L^{-1} for DSe and 3.11 ± 0.36, 1.98 ± 0.13, 1.13 ± 0.09, and

Table 1. Surface distribution of minimum-maximum ranges and means (in parentheses) values of physicochemical parameters. Chl *a*, chlorophyll *a*; DO, dissolved oxygen; DOC, dissolved organic carbon; POC, particulate organic carbon; Ref., reference; TSS, total suspended solid.

Date	Debi ($m^3\ sn^{-1}$)	Zone	Salinity	Temperature (°C)	DO ($mg\ L^{-1}$)	pH	TSS ($mg\ L^{-1}$)	Chl *a* ($\mu g\ L^{-1}$)	POC (μM)	DOC (μM)
Nov 2004	5	Ref.	39.31	20.2	6.72	8.85	2	0.19	14	67
		P2	12.78–13.12 *(12.93)*	19.0–19.1 *(19.1)*	6.85–6.98 *(6.90)*	–	5.20–13.53 *(10.35)*	0.83–1.19 *(0.96)*	21–46 *(30)*	94–126 *(113)*
		P1	10.63–13.16 *(11.63)*	17.3–18.5 *(17.7)*	5.34–6.77 *(5.99)*	–	6.10–17.73 *(13.14)*	0.14–2.71 *(1.84)*	16–85 *(58)*	78–196 *(149)*
		Gediz	4.96	12.8	8.84	7.58	6.67	0.80	52	2,327
Feb 2005	123	Ref.	30.26–36.66 *(33.46)*	13.0–13.4 *(13.2)*	7.79–7.9 *(7.85)*	–	0.85–5.80 *(3.33)*	0.08–0.32 *(0.20)*	7–21 *(14)*	71–84 *(77)*
		P2	1.45–4.09 *(2.7)*	12.4–13.6 *(13.0)*	1.52–2.9 *(2.21)*	7.09–7.8 *(7.36)*	64–144 *(115)*	0.43–4.28 *(2.81)*	114–273 *(206)*	513–1,126 *(863)*
		P1	2.70–3.02 *(2.85)*	11.1–12.5 *(11.7)*	2.22–3.4 *(2.99)*	6.95–7.28 *(7.08)*	199–526 *(378)*	0.36–2.00 *(1.21)*	275–361 *(308)*	1,736–1,928 (1, 827)
		Gediz	0.29	9.9	3.31	6.52	349	2.43	340	1,521
Apr 2005	19	Ref.	38.75–38.86 *(38.80)*	15.6–15.9 *(15.7)*	6.95–7.55 *(7.25)*	–	1.30–1.45 *(1.38)*	0.13–0.16 *(0.15)*	1–17 *(9)*	87–75 *(81)*
		P2	15.00–34.20 *(23.38)*	17.0–19.2 *(17.8)*	5.17–8.13 *(6.78)*	7.07–8.37 *(7.91)*	11.14–18.00 *(15.05)*	2.02–4.60 *(3.44)*	110–126 *(116)*	332–634 *(507)*
		P1	14.40–18.20 *(16.70)*	16.7–18.2 *(17.7)*	6.65–8.37 *(7.46)*	8.25–8.57 *(8.38)*	12.67–18.00 *(15.78)*	4.51–6.08 *(5.37)*	198–246 *(216)*	574–782 *(650)*
		Gediz	2.07	17.5	9.63	7.42	22.67	8.51	432	688
Aug 2005	31	Ref.	39.40–39.41 *(39.40)*	24.7–25.0 *(25.1)*	–	–	0.80–2.40 *(1.60)*	0.01 *(44)*	39–49 *(77)*	67–101
		P2	23.15–37.67 *(32.44)*	26.6–27.2 *(26.9)*	6.35–8.33 *(7.53)*	8.33–8.54 *(8.47)*	6.00–21.43 *(13.37)*	0.01–0.05 *(0.03)*	30–36 *(32)*	618–1,569 (1, 205)
		P1	18.36–25.34 *(20.85)*	27.5–27.9 *(27.7)*	7.65–9.13 *(8.17)*	7.98–8.44 *(8.26)*	6.00–15.33 *(10.22)*	0.03–0.07 *(0.06)*	58–120 *(90)*	344–1,391 *(801)*
		Gediz	8.54	28.74	8.75	7.39	5.71	0.12	82	618

Table 2. Water and sediment average concentrations of selenium in reference station and exposure sites during the study period.

Variable	Gediz River	Plume 1	Plume 2	Reference stations
Water				
Dissolved selenium (DSe) (Se IV + Se VI) ($\mu g\ L^{-1}$)[a]	5.41 ± 0.41	1.67 ± 0.10	1.03 ± 0.09	0.24 ± 0.09
Particulate selenium (PSe) (Se IV + Se VI) ($\mu g\ L^{-1}$)[b]	3.11 ± 0.36	1.98 ± 0.13	1.13 ± 0.09	0.40 ± 0.13
Total selenium (DSe + PSe) ($\mu g\ L^{-1}$)	8.52 ± 0.52	3.50 ± 0.16	2.24 ± 0.13	0.64 ± 0.15
Sediment				
($\mu g\ g^{-1}$)	7.64	3.18	4.17 ± 0.73	N/S[c]

Notes: [a,b] Samples represent the mean (± standard error) of surface water samples during the sampling period. [c] Not sampled.

0.40 ± 0.13 for PSe along the same gradient (Table 2). Apparently, DSe was the dominant Se fraction in the river mouth, except in November 2004 (Fig. 3). The same data also demonstrated that PSe could be the dominant form in the plume zones, even at reference station R2, in August 2005. The reason for such variability might be the effects of prevailing physical driving forces, which can originate sediment resuspension and/or rapid dispersion of suspended particulate matter. Such physical forces were prevailing via stronger winds (19 km h^{-1}), and the waves generated by these winds during this period and their driving effects for sediment resuspension and dispersion could be strengthened or diminished by interacting forces such as precipitation and river flow intensity when the shallowness of the estuarine zone and plume zones are considered.

With reference to Hibbs and Andrus (2003), the Se levels observed in water and sediment at the Gediz River mouth may cause toxicological and reproductive effects. The TSe in water samples collected from the Gediz River mouth always exceeded the high hazard profile level of 5.0 $\mu g\ L^{-1}$ during the study period and reached the level of threefold (14.5 $\mu g\ L^{-1}$) during the maximum flow season (i.e., February 2005; Fig. 3). The DSe and PSe concentrations then decreased at the reference stations to 0.56 $\mu g\ L^{-1}$ and 0.92 $\mu g\ L^{-1}$, respectively, where the average surface salinity reached 37.5. It is assumed that the composite Se input is removed from surface water through the delta, as freshwaters move toward the sea. The concentration of DSe among rivers and estuaries in England (Measures and Burton 1978) and several rivers in eastern North America (Takayanagi and Cossa 1985) range from 0.049 μg Se L^{-1} to 0.39 μg Se L^{-1}. The lowest DSe and PSe concentrations at the R2 station have been measured at 0.02 $\mu g\ L^{-1}$, whereas the values increased at the R1 station (0.2 $\mu g\ L^{-1}$ for DSe and approximately 0.1 $\mu g\ L^{-1}$ for PSe) in August 2005. In Gediz delta, Izmir Bay, DSe, which amounted to approximately 40% of TSe (Fig. 4a), and PSe varied

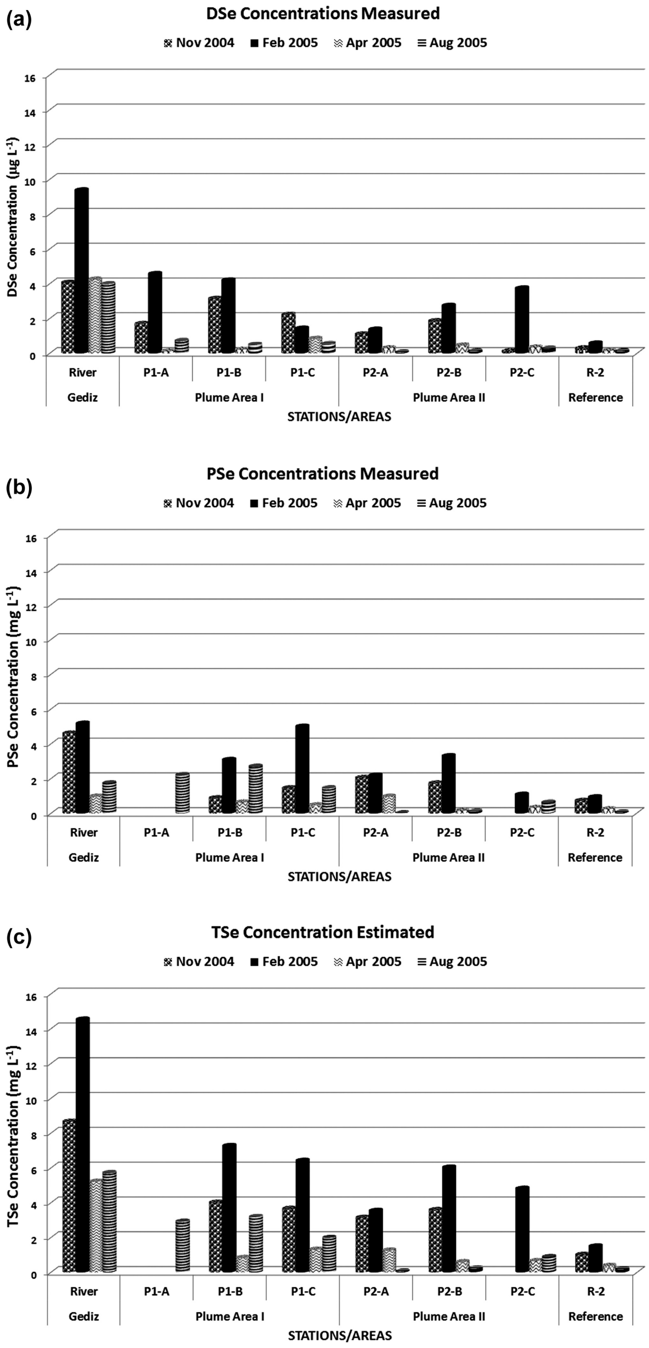

Figure 3. Distribution of DSe (a), PSe (b), and TSe (c) in the study area in Gediz delta, Izmir Bay. DSe, dissolved selenium; PSe, particulate selenium; TSe, total selenium.

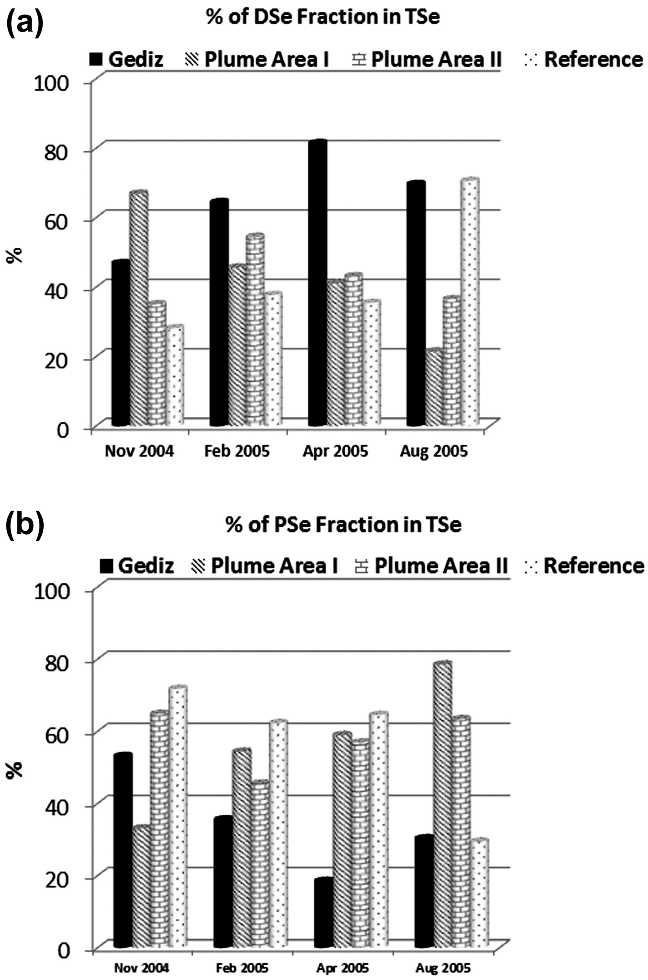

Figure 4. Percent distributions of DSe (a) and PSe (b) in the study area in Gediz delta, Izmir Bay. DSe, dissolved selenium; PSe, particulate selenium.

in the plume region (Fig. 4b). More than 80% of riverine Se (both PSe and DSe) has been removed before reaching the salinity zone of 15–20 (Fig. 5a and b). The removal of PSe seems to occur more rapidly when river water meets with the saline water at the mouth of the river (Fig. 5b); however, some riverine PSe or autochthonous PSe is still present in the surface water at about the 1 μg L^{-1} level.

Dividing the observed PSe by the total suspended material concentration, the particle-associated Se (μg g^{-1}) can be calculated. During high flow in February 2005 (123 m^3 s^{-1}), the particle-associated Se in the mouth of the river was the lowest (15 μg g^{-1}), which is almost 45 times lower than at low flow in November 2004 (4.9 m^3 s^{-1}, 689

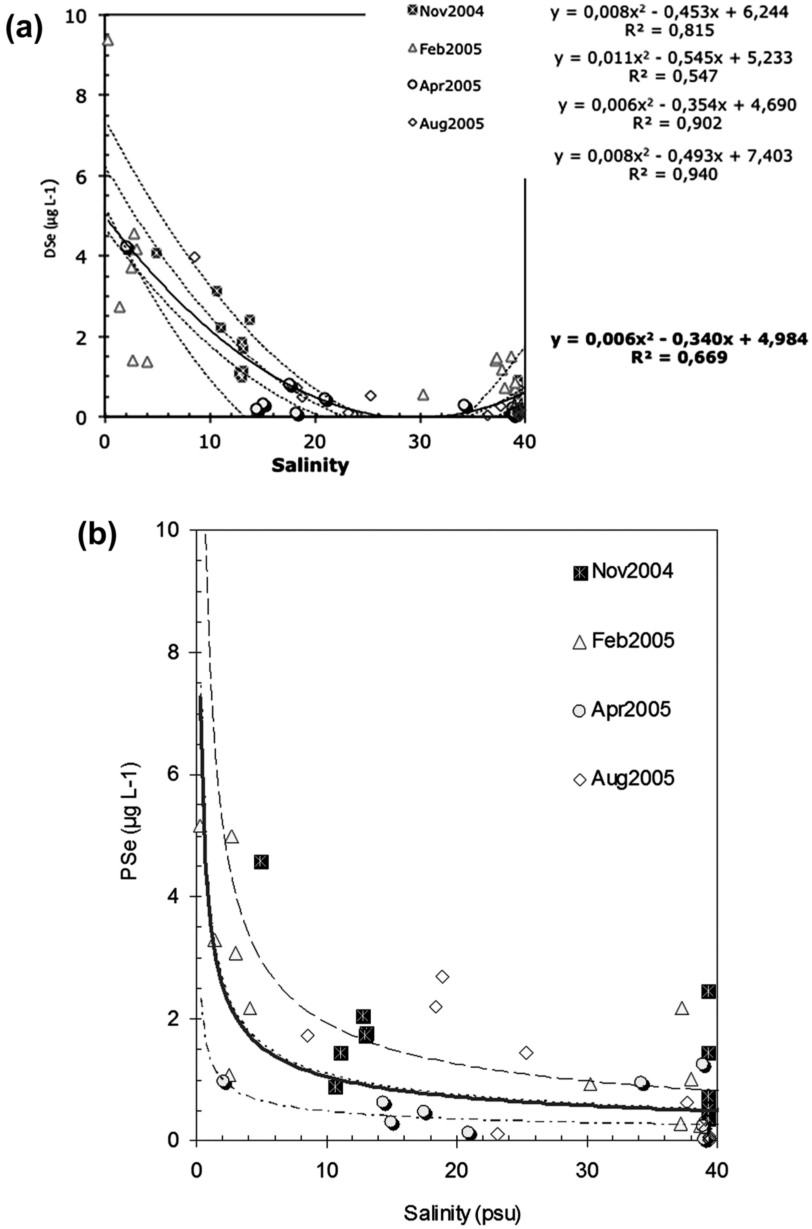

Figure 5. DSe (a) and PSe (b) values throughout the salinity gradient. DSe, dissolved selenium; PSe, particulate selenium; psu, practical salinity unit.

μg g^{-1}). The high content of Se-containing particles is probably attributable to a change of character of the source. At the same time, phytoplankton play a key role in the biotransformation of Se in aquatic ecosystems (Reunova et al. 2007). We also observed the lowest DSe during maximum phytoplankton abundance (>4.5 μg L^{-1} chlorophyll *a*) in April 2005, which may be attributed mainly to the uptake of DSe by phytoplankton (Table 1).

b. Se in the sediment

Sediment samples taken from stations P2-A, P2-B, and P1-A and Gediz River in August 2005 showed higher values than the toxic effect threshold (TET), which is 2 μg g^{-1} (Table 2). There is no clear trend in spatial distribution of sediment Se concentration. Se in sediment was 7.64 μg g^{-1} in the mouth of the Gediz River, 3.18 μg g^{-1} at station P1-A, 2.65 μg g^{-1} at station P2-A, and 5.69 μg g^{-1} at station P2-B (Table 2). Unfortunately, the samples collected from the reference station could not be preserved because of a technical problem. Applying Lemly's (1995, 2002) protocol for Se hazard profile assessment, sediment from the Gediz River basin receives a high hazard rating and implies bioaccumulation of the element from this matrix into the benthic food chain. At the mouth of the Gediz River, the Se content in bottom sediments (7.64 μg g^{-1} dry wt) was about four times greater than the background level (<2 μg g^{-1} dry wt). In the plume 2 area, it was 4.17 μg g^{-1} dry wt, which was equal to two times greater than the background value. In the water column overlying the high Se sediment zone, we observed high PSe. This high value of PSe in the water column during the nonproductive period (November 2004 and February 2005 in Fig. 6a and b) suggests that sediment resuspension is more effective than in situ production of PSe by phytoplankton. In sediments, PSe can undergo a variety of oxidation-reduction reactions that may cause Se to become mobile or permanently buried (Velinsky and Cutter 1991).

c. Load

The results show that seasonal variations of Se depend on the flow rate of the Gediz River and biological activity. DSe and PSe reached their maximum values during the high inflow period (February 2005; Figs. 3 and 6). Estimates of fluxes indicated that the export of TSe from the Gediz River was within the range of 3.6 kg day^{-1} (1.7 kg day^{-1} DSe, 1.9 kg day^{-1} PSe) in November 2004 and 154 kg day^{-1} (99 kg day^{-1} DSe, 55 kg day^{-1} PSe) in February 2005. PSe in the mouth of the Gediz delta was relatively constant between low (November 2004) and high (February 2005) flow periods, 4.59 μg L^{-1} and 5.16 μg L^{-1}, respectively, and comprising 53% and 36% of the TSe inventory. However, it varied with river flow, with higher DSe content during high flow (9.36 μg L^{-1}) compared with low flow (4.06 μg L^{-1}). This result demonstrates that increased flow accesses additional sources rather than simply diluting Se. Silicate results also support this situation with maximum Si values (249 μM in February 2005).

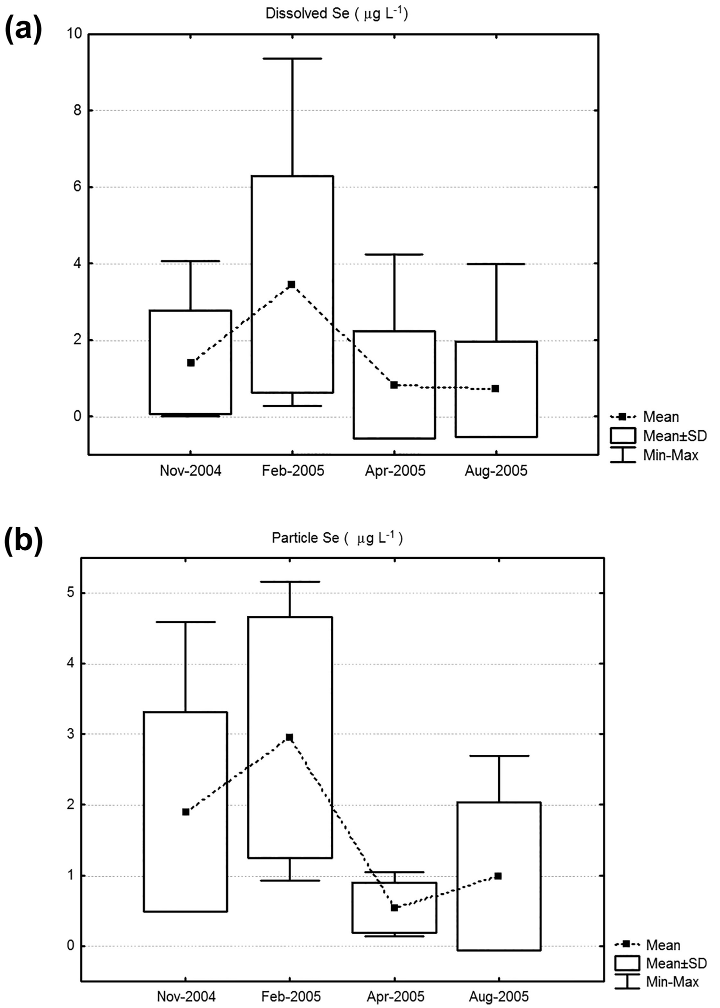

Figure 6. Spatiotemporal distribution of DSe (a) and PSe (b) in the study area. DSe, dissolved selenium; Max, maximum; Min, minimum; PSe, particulate selenium; SD, standard deviation.

d. Range of distribution coefficients

The distribution coefficient (K_d) is a way to quantitatively describe the partitioning of total Se between dissolved and particulate states. The K_d is the ratio of Se per unit mass particulate material versus Se per unit volume water, in equivalent units. The K_d's in various field studies have ranged from 0.3×10^3 to 2×10^4, reflecting the complicated transformation reactions and processes (Cutter 1989). Se in sediment is high in the study area because it contains schist with clay and organic matter (Malisa 2001). K_d values in this work are consistently $> 1 \times 10^4$ L kg^{-1} in the plume area, except for the high-flow period in February 2005 where the low K_d values might be explained by the low DO and high organic carbon values observed (Table 1). The roles of different factors such as organic content and particle size and different transformation processes need to be better understood to resolve causes of the differences between suspended and sedimentary Se.

e. Other environmental parameters and their correlation with Se

In a follow-up study, the same sediment samples used for Se analyses were additionally analyzed for particulate Cu, Zn, Pb, Mn, Fe, Hg, Ni, and Cr and dissolved Mn, Fe, Cr, Ni, Co, Cu, Zn, Cd, Hg, and Pb. In this augmented data set, correlation analysis showed that there is significant correlation among all metals, but there is a particularly high correlation coefficient between DSe and dissolved Mn (DMn) ($r^2 = 0.82, n = 57, P < 0.05$). The distribution of DMn can also be used as an indicator of the redox condition of riverine and estuarine waters. The maximum concentration of DMn was 940 μg L^{-1} during the lowest DO level (<3 mg L^{-1}) in February 2005. This was probably because of an enhanced reductive dissolution of naturally occurring Mn oxides in the sediment with organically enriched materials by the Gediz River. It seems that Se adsorbed on the surface of the Mn oxides may be released because of dissolution of Mn oxides, part of the early diagenesis. The inverse relation between DMn and K_d for Se also supports this possible release mechanism of PSe because of reduction of redox potential with the onset of suboxic conditions in the sediment. High organic matter content may be the reason for the development of suboxic conditions in the sediment.

Whatever the case, the DMn data support the DO distributions and suggest that the conditions were significantly more reducing in the Gediz system during the high-flow period in February 2005 (123 m^3 s^{-1}). Furthermore, the significant correlations among TSe and POC (r^2 = 0.78, n = 20), total organic carbon (TOC; r^2 = 0.75, n = 20), total inorganic nitrogen (r^2 = 0.49, n = 20), 2–5 μm and 5–10 μm particles (r^2 = 0.67 and 0.68, n = 20, respectively), and TSS (r^2 = 0.72, n = 20) indicate the importance of organic matter, nitrogen, and particle size on the Se dynamics in the plume area. Another significant correlation with Si (r^2 = 0.52, n = 12) shows that the source is same through natural weathering process such as leaching and runoff and anthropogenic sources. The distribution of different forms of Se, DOC, and DO in the Gediz delta during the present sampling periods showed that there is a significant inverse relationship between DO and DSe (r^2 = −0.43, n = 52), PSe (r^2 = −0.45, n = 39), and DOC (r^2 = −0.39, n = 61). Se is strongly correlated with organic matter, with which it is known to form complexes (Cohen et al. 1992). In the present study, there is significant correlation between TOC and DSe (r^2 = 0.53, n = 60) and PSe (r^2 = 0.57, n = 47).

f. Conclusions

There is still considerable uncertainty and debate surrounding the TET of Se (see Section 3b). In this study, Se concentrations were higher than water-quality guidelines in the plume area but not in the bay (as an average 0.38 μg L^{-1} in the water column). However, the risk of Se accumulation in the food web was sufficiently high to be considered as a threat to ecosystem and human health because the Gediz River delta is one of the most important nursery grounds for several marine species and breeding grounds for birds. Considering there are no relevant natural sources containing Se throughout the river's basin, the extensive agricultural and industrial activities in the drainage basin are the usual suspects for Se levels above pristine conditions and for the highest Se levels observed during the winter period when the basin was flushed most effectively.

To forecast the fate of Se and to understand its bioavailability and toxicity, the need for further studies is apparent. A special emphasis on monitoring studies with higher spatiotemporal resolution is critical in order to be able to continue the assessment efforts of the highest source(s) of Se concentrations transported via suspended material to the bay through the Gediz delta. Furthermore, a series of tissue-based studies are essential for understanding the distribution of Se in species inhabiting the Gediz River and its plume area, considering that fish mortality incidents have been observed almost every year. The strong relationship that we observed between DSe, PSe, and DMn concentrations during high flow, together with the likely dependence of Se K_d on Mn-oxide associations, suggests that Se cycling may be closely coupled to redox conditions affecting Mn. This potential coupling, which could be affected by diagenetic reactions in bottom sediments and benthic fluxes, as well as water column reactions, should be considered in future study designs.

Consequently, future studies based on continuous environmental monitoring efforts including tissue analyses of a series of organisms representing each trophic level could provide an improved understanding of the potential impacts of Se on estuarine and coastal marine systems because understanding the fate and bioavailability of Se is especially challenging in the areas where estuaries and bays are interconnected and a complex cycling dynamics of Se prevails.

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REFERENCES

Anthemidis, A. N. 2006. Determination of selenium (IV) in natural waters by HG-AAS using an integrated reaction chamber gas–liquid separator. Spectrosc. Lett., *39*(6), 699–711.

Beatty, J. M., and G. A. Russoi. 2104. Ambient water quality guidelines for Selenium Technical Report Update, Water Protection and Sustainability Branch, Environmental Sustainability and Strategic Policy Division, British Columbia Ministry of Environment, CANADA, ISBN 978-0-7726-6740-3.

Belzile, N., and J. Lebel. 1988. Selenium profiles in the sediments of the Laurentian Trough (northwest North Atlantic). Chem. Geol., *68*, 99–103.

Bizsel, K. C., N. Bizsel, A. Süzal, A. Demirdağ, and M. Ozturk. 2008. Gediz Nehri ağzinda (İzmir Körfezi, Ege Denizi) tuzluluk değişimi boyunca partikül ve çözünmüş formdaki organik ve inorganik madde düzeylerinin belirlenmesi. Final Report TÜBİTAK ÇAYDAG 104Y037, TÜBİTAK, ANKARA.

Bizsel, N., and Y. D. Sarıca. 2008. Gediz Nehri ağzında selenyum dağılımı. Final Report TÜBİTAK ÇAYDAG 107Y228, TÜBİTAK, ANKARA.

Çetinkaya, C. P., and F. Barbaros. 2008. Su Yönetimi senaryoları ile Gediz Nehri yıllık su bütçesi performansının değerlendirilmesi, *in* TMMOB 2 Su Politikaları Kongresi, 20–22 March 2008, TMMOB, ANKARA, pp. 323–334.

Cohen, R., D. Schuhmann, F. Sinan, and P. Vanel. 1992. The role of organic coatings in the enrichment of marine particles with selenium. The fixation of selenite on an adsorbed amino acid. Mar. Chem., *40*, 249–271.

Cutter, G. A. 1982. Selenium in reducing waters. Science, *217*, 829–831.

Cutter, G. A. 1989. The estuarine behaviour of selenium in San Francisco Bay. Estuarine, Coastal Shelf Sci., *28*, 13–34.

Cutter, G. A., and L. S. Cutter. 2004. Selenium biogeochemistry in the San Francisco Bay estuary: Changes in water column behavior. Estuarine, Coastal Shelf Sci., *61*, 463–476.

Cutter, G. A., and M. L. C. San Diego-McGlone. 1990. Temporal variability of selenium fluxes in San Francisco Bay. Sci. Total Environ., *97–98*, 235–250.

Doblin, M. A., S. B. Baines, S. L. Cutter, and G. A. Cutter. 2006. Sources and biogeochemical cycling of particulate selenium in the San Francisco Bay estuary. Estuarine, Coastal Shelf Sci., *67*(4), 681–694.

Doblin, M. A., S. I. Blackburn, and G. M. Hallegraeff. 1999. Comparative study of selenium requirements of three phytoplankton species: *Gymnodinium catenatum*, *Alexandrium minutum* (Dinophyta), and *Chaetoceros* cf. *tenuissimus* (Bacillariophyta). J. Plankton Res., *21*, 1153–1169.

Fan, T. W.-M., S. J. Teh, D. E. Hinton, and R. M. Higashi. 2002. Selenium biotransformations into proteinaceous forms by foodweb organisms of selenium-laden drainage waters in California. Aquat. Toxicol., *57*, 65–84.

Gundogdu, V., E. Torusdag, and D. Sarikaya. 2005. İzmir kus cenneti sulak alaninin ekolojik yapısı ve su kirliliği izleme çalışması. Ekoloji, *50*(14), 31–36.

Hamilton, S. J. 2004. Review of selenium toxicity in the aquatic food chain. Sci. Total Environ., *326*, 1–31.

Harrison, P. J., P. W. Yu, P. A. Thompson, N. M. Price, and D. J. Phillips. 1988. Survey of selenium requirements in marine phytoplankton. Mar. Ecol. Prog. Ser., *47*, 89–96.

Kayar, V. N., and A. Çelik. 2003. Gediz Nehri Kimi Kirlilik Parametrelerinin Tayini ve Su Kalitesinin Belirlenmesi. Ekoloji Çevre Dergisi, *12*(47), 17–22.

Koike, Y., Y. Nakaguchi, K. Hiraki, T. Takeuchi, T. Kokubo, and T. Ishimaru. 1993. Species and concentrations of selenium and nutrients in Tanabe Bay during red tide due to *Gymnodinium nagasakiense*. J. Oceanogr., *49*, 641–656.

Läuchli, A. 1993. Selenium in plants: uptake, functions, and environmental toxicity. Bot. Acta, *106*, 455–468.

Lemly, A. D. 1995. A protocol for aquatic hazard assessment of selenium. Ecotoxicol. Environ. Saf., *32*, 280–288.

Lemly, A. D. 1996. Assessing the toxic threat of selenium to fish and aquatic birds. Environ. Monit. Assess., *43*, 19–35.

Lemly, A. D. 1997. Ecosystem recovery following selenium contamination in a freshwater reservoir. Ecotoxicol. Environ. Saf., *36*, 275–281.

Lemly, A. D. 1999. Selenium transport and bioaccumulation in aquatic systems: A proposal for water quality criteria based on hydrological units. Ecotoxicol. Environ. Saf., *42*, 150–156.

Lemly, A. D. 2002. Interpreting selenium concentrations, *in* Selenium Assessment in Aquatic Ecosystems: A Guide for Hazard Evaluation and Water Quality Criteria, D. E. Alexander, ed. New York: Springer, 18–38.

Luoma, S. N., C. Johns, N. S. Fisher, N. A. Steinberg, R. S. Oremland, and J. R. Reinfelder. 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. Environ. Sci. Technol., *26*(3), 485–491.

Maier, K. J., and A. W. Knight. 1993. Comparative acute toxicity and bioconcentration of selenium by the midge *Chironomus decorus* exposed to selenate, selenite, and seleno-DL-methionine. Arch. Environ. Contam. Toxicol., *25*(3), 365–370.

Malisa, E. P. 2001. The behaviour of selenium in geological processes. Environ. Geochem. Health, *23*, 137–158.

Measures, C. I., and J. D. Burton. 1978. Behavior and speciation of dissolved selenium in estuarine waters. Nature, *273*, 293–295.

Meseck, S. L., and G. A. Cutter. 2006. Evaluating the biogeochemical cycle of selenium in San Francisco Bay through modeling. Limnol. Oceanogr., *51*(5), 2018–2032.

Milliyet 2015. http://www.milliyet.com.tr/olu-yayin-ve-sazanlar-kiyiya-vurdu-gundem-2122998/, Milliyet Gazetecilik ve Yaımcılık A.Ş., İstanbul, Turkey.

Presser, T. S., and H. M. Ohlendorf. 1987. Biogeochemical cycling of selenium in the San Joaquin Valley, California, USA. Environ. Manage., *11*(6), 804–821.

Price, N. M., P. A. Thompson, and P. J. Harrison. 1987. Selenium: An essential element for growth of the coastal marine diatom *Thalassiosir*a *pseudonana* (Bacillariophyceae). J. Phycol., *23*, 1–9.

Raymont, J. E. G. 1980. Plankton and Productivity in the Oceans, Vol. 1, Phytoplankton, 2nd ed. Oxford, UK: Pergamon Press.

Reunova, Y. A., N. A. Aizdaicher, N. K. Khristoforova, and A. A. Reunov. 2007. Effects of selenium on growth and ultrastructure of the marine unicellular alga *Dunaliella salina* (Chlorophyta). Russ. J. Mar. Biol., *33*(2), 125–132.

Robles, L. C., J. C. Feo, B. de Celis, J. M. Lumberas, C. García-Olalla, and A. J. Aller. 1999. Speciation of selenite and selenate using living bacteria. Talanta, *50*, 307–325.

Shaul, S., Andrus, R., and Hibbs, B. 2008. Time Series Analysis of Nitrate and Selenium in Upper Newport Bay; in Selenium, Nitrate, and Other Constituents in San Diego Creek and Newport Bay Watersheds, 2004–2008: California State University, Los Angeles. Technical contract report prepared for the Santa Ana Regional Water Quality Control Board.

Skorupa, J. P. 1998. Selenium poisoning of fish and wildlife in nature: Lessons from twelve real-world examples, *in* Environmental chemistry of selenium, W. T. Frankenberger Jr. and R. A. Engberg, eds. New York: Marcel Dekker, 315–354.

State Water Administration. 2004–2005. Periodic Reports on Flow Observations of Gediz River from the Measurement Stations at Menemen and Muradiye Bridges, data obtained from http://rasatlar.dsi.gov.tr/#, Ankara, Turkey.

Strickland, J. D. H., and T. R. Parsons. 1968. Determination of dissolved oxygen, *in* A Practical Handbook of Seawater Analysis. Bulletin 167. Ottawa: Fisheries Research Board of Canada, 71–75.

Takayanagi, K., and D. Cossa. 1985. Speciation of dissolved selenium in the upper St. Lawrence estuary, *in* Marine and Estuarine Geochemistry, A. C. Sigleo and A. Hattori, eds. Chelsea, MI: Lewis, 275–284.

Takayanagi, K., and G. T. F. Wong. 1984. Total selenium and selenium (IV) in the James River estuary and southern Chesapeake Bay. Estuarine, Coastal Shelf Sci., *18*, 113–119.

Tetra Tech Inc. 2008. North San Francisco Bay Selenium Data Summary and Source Analysis. Oakland, CA: Regional Water Quality Control Board, San Francisco Bay Region.

United Nations Environment Programme (UNEP). 1985. GESAMP: Cadmium, Lead and Tin in the Marine Environment. UNEP Regional Seas Reports and Studies 56. Nairobi: UNEP.

United Nations Environment Programme (UNEP), International Atomic Energy Agency, and Intergovernmetnal Oceanographic Commission. 1990. Reference Methods and Materials: A Programme of Support for Regional and Global Marine Pollution Assessments. Nairobi: UNEP.

U.S. Environmental Protection Agency (EPA). 2004. Aquatic Life Water Quality Criteria for Selenium. Washington, DC: EPA, Office of Water, Office of Science and Technology.

Velinsky, D. J., and G. A. Cutter. 1991. Geochemistry of selenium in a coastal salt marsh. Geochim. Cosmochim. Acta, *55*, 179–191.

Wilber, C. G. 1983. Selenium: A Potential Environmental Poison and a Necessary Food Constituent. Springfield, IL: C. C. Thomas.

Yeni Asır 2015. http://www.yeniasir.com.tr/yasam/2015/09/27/gediz-nehrinde-toplu-balik-olumleri. Turkuaz Haberleşme ve Yayıncılık A.S., İzmir Turkey.

Wrench, J. J., and C. Measures. 1982. Temporal variations in dissolved selenium in a coastal ecosystem. Nature, *293*, 413–433.

Zhang, Y., and J. N. Moore. 1996. Selenium fractionation and speciation in a wetland system. Environ. Sci. Technol., *30*, 2613–2619.

Zhang, Y., and J. N. Moore. 1997. Environmental conditions controlling selenium volatilization from a wetland system. Environ. Sci. Technol., *31*(2), 511–517.

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