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Benthic Respiration and Heavy Metal Benthic Fluxes in Artificial Shihwa Lake: Approaching In Situ Measurement

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Abstract: This study assessed the impact of intensive human activities on organic matter (OM) and heavy metal cycles in Shihwa Lake, South Korea. Sediment oxygen demand (SOD), benthic nutrient flux (BNF), and benthic heavy metal flux were estimated using in situ benthic chambers. The combined analysis of sediment trap and SOD showed that the vertical supply of OM was a major controlling factor for benthic respiration. The BNF accounted for 35–144% and 32–184% of the N and P required, respectively, for primary production (PP) in the water column. The higher SOD may have also accelerated the release of Mn, Fe, Co, and Ni from the sediment. Benthic fluxes of Cr, As, Cd, Pb, Cu, and Zn were highest near the industrial complex, with ranges of 1.3 ± 0.9, 6.4 ± 4.9, 0.2 ± 0.1, 0.5 ± 0.4, 7.7 ± 1.4, and 452 ± 133 μmol m^{-2} d^{-1}, respectively. Mn, Fe, Co, As, Pb, Ni, and Cu contributed more than 10% of the sediment to the current standing stock at Shihwa Lake.

Keywords: sediment oxygen demand; benthic nutrient flux; benthic–pelagic coupling; heavy metal benthic flux; artificial Shihwa Lake

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1. Introduction

Since the 1980s, the western coast of South Korea has been reclaimed for industrial and agricultural use, resulting in significant alterations to coastal ecosystems [1–3]. Over time, eutrophication, hypoxia, and the accumulation of pollutants in coastal lakes have become increasingly severe [4–6]. In particular, levels of organic matter (OM) and particle-reactive pollutants have become critically high via accumulation in artificial lakes or near artificial structures because of reduced tidal currents and hydrodynamic circulation. For example, reduced currents accelerate the deposition of suspended particles, and then deposition induces phytoplankton blooms in the water column because of increasing transparency, ultimately promoting the vertical flux of OM in the sediment [7–9].

Sediment oxygen demand (SOD) and benthic nutrient flux (BNF) are crucial parameters involved in understanding the impact of eutrophication in coastal waters [10,11]. Deposited OM is rapidly oxidized in the sediment via various electron acceptors, such as oxygen, nitrate, manganese oxide, iron oxide, and sulfate [12]. SOD can quantify the total oxidation rates of organic carbon (OC) because oxygen consumes the aerobic respiration of microorganisms and the reoxidation of reduced compounds via an anaerobic process [13,14]. Therefore, SOD has been used to assess the extent of OM enrichment in the sediment, which is an important proxy for determining the trophic state of the coastal ecosystem. Also, excess nutrient supply from terrestrial land and sediments can lead to

increased primary productivity via benthic–pelagic coupling, and this aggravates OM accumulation in the sediment, which can develop into hypoxic and anoxic conditions [8,15–17]. Thus, estimating SOD and BNF can provide insights into the severity of eutrophication and help in designing effective management strategies to mitigate its impacts.

Heavy metals discharged from industrial complexes rapidly bind to various substances and then deposit into the sediment, serving as the final sink for heavy metals [18]. Upon the occurrence of early diagenetic processes in the sediment, heavy metals can be released at the sediment–water interface (SWI), acting as a contaminant source [19]. Biogeochemical condition changes could affect heavy metal cycles in the sediments [20]. For example, under anoxic conditions, dissolved manganese and iron are released into the water, but hydrogen sulfide-produced sulfate reduction acts as a sink for iron through the precipitation of troilite (FeS) [12]. Cobalt, cadmium, nickel, and arsenic can be scavenged by particles and OM or adsorb onto Fe(III) and Mn(IV) under oxic conditions [21,22]. Furthermore, continual metal release from the sediment can be toxic to marine organisms, and such releases can accumulate in marine organisms, or eventually humans, posing a severe health threat [23,24].

Previous studies have examined the biological impacts of the artificial Shihwa Lake dike; however, benthic processes that significantly control water quality have received less attention [8]. In this study, we investigated the impacts of the artificial dike on the following aspects: (1) the sediment geochemistry and OC oxidation in lake sediment; (2) the benthic release of nutrients and heavy metals across the SWI; and (3) the potential impacts of (1) and (2) on Shihwa Lake's water quality.

2. Sampling and Methods

2.1. Study Area

Shihwa Lake is one of the artificial saltwater lakes typical of South Korea's west coast, covering 56.5 km^2, with a drainage basin of 476.5 km^2 that introduces excessive inflows and continuous discharges of various nonpoint pollutants into the lake (Figure 1) [2]. The cites of Shiheung and Ansan, with a combined total population exceeding 1 million, have expanded near the lake, which also poses a potential risk of eutrophication. The northern part of the lake is adjacent to the Shihwa–Banweol industrial complex, where more than 13,000 are companies present—largely steel, electrical/electronic, mechanical, petrochemical, and textile companies—accounting for 32.7% of South Korea's total industrial facilities [25]. The southern lake edge features a thriving urban center that features the Daesong agricultural complex (36.36 km^2) and Songsan Green City (55.59 km^2), which were built through reclamation efforts over the past decades [26]. Pollutants from the industrial complexes, e.g., heavy metals, organic compounds, and nutrients, have been found to affect Shihwa Lake's ecosystem [27,28]. To solve Shihwa Lake's serious problems, a tidal power plant was installed in 2011. Despite efforts to prevent environmental pollution, the rapid growth of the population and industrial development in the region has led to a deterioration in water quality and biodiversity [5,29,30].

2.2. Field Surveys and Sampling

In the central part of the Korean Peninsula, approximately 60% of annual precipitation occurs during the summer monsoon, lasting from July to September (https://data.kma.go.kr/resources/html/en/aowdp.html, accessed on 1 November 2023). To avoid disturbance by heavy rainfall, our sampling was conducted from 9 to 14 June 2022 on the inside of the Shihwa Lake dike (stations SH1, 2, 3, and 4) and the outside (station GB) of the Shihwa Lake dike (Figure 1; Table 1). Sampling stations SH1 and SH2 were located in close proximity to the wastewater discharge pathways from the Shihwa–Banweol industrial complex, while SH4 was situated near the freshwater reservoir gate used for the Daesong agricultural complex. SH3, on the other hand, was located in a transitional zone between the industrial complex and the water gate.

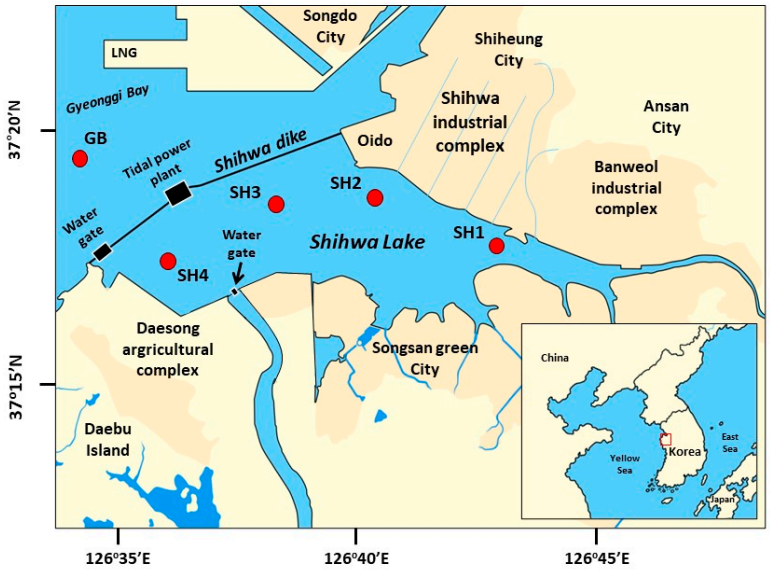

Figure 1. Sampling stations at Shihwa Lake.

Table 1. Latitude and longitude.

Station	Latitude	Longitude
SH1	37°17.961′ N	126°43.901′ E
SH2	37°18.656′ N	126°40.984′ E
SH3	37°18.319′ N	126°38.588′ E
SH4	37°17.643′ N	126°36.044′ E
GB	37°19.165′ N	126°33.406′ E

Surface and bottom water samples were collected using a Niskin water sampler. The water temperature, salinity, and dissolved oxygen (DO) of the water were measured using a water quality meter (6200; YSI, Yellow Springs, OH, USA). For the analysis of dissolved inorganic nutrients, water samples were immediately filtered through a membrane filter (pore size, 0.45 μm; Advantec, Tokyo, Japan), and then the samples were stored in a freezer (−20 °C) until analysis. Chlorophyll-a (Chl-a) in the water was filtered using a glass fiber filter (pore size, 0.7 μm; Whatman, Maidstone, UK), and then Chl-a was stored in the dark at −20 °C until analysis. Duplicate, or mostly triplicate, cores (8 cm in diameter and 30 cm in length) were collected by a SCUBA diver for geochemical analysis. Sediment samples of total reduced sulfur (TRS) were sectioned at 2 cm intervals up to 20 cm, and porewater samples were extracted through pre-drilled holes at 2 cm intervals up to 20 cm using a soil moisture sampler (Rhizon SMS, Rhizosphere Research Products, Wageningen, The Netherlands) under an N2-gas-filled glove box; porewater samples were then stored in a deep freezer (−20 °C) until analysis.

2.3. In Situ Chamber Experiment

A benthic lander (KIOST Belc*II*, Busan, Republic of Korea) was lowered carefully using a ship's crane with the assistance of a SCUBA diver to minimize surface sediment disturbance [31,32]. In situ incubations were conducted for over 6 h to estimate SOD, benthic nutrients, and heavy metal benthic fluxes. The Belc*II* consists of a Teflon-coated incubation chamber, which can prevent contamination during incubation, and an automatic syringe water sampler [32]. The lid of the chamber contains an optode oxygen sensor (4330F, Aanderaa Data Instruments, Bergen, Norway) that measures O_2 evolution during in situ incubation. The automatic syringe water sampler collects water samples from the benthic chamber at 40 min intervals.

All syringes, tubing, and plastic wares were rinsed with 5% alkaline surfactant (Extran MA 05, Merck, Rahway, NJ, USA) and 10% HCl (Ultra-100, Kanto, Tokyo, Japan) to prevent

metal contamination, and onboard works were performed in a plastic vinyl chamber. Water samples for the nutrient analysis were filtered immediately using membrane syringe filter paper (pore size, 0.45 µm; Advantec, Tokyo, Japan) and then stored in a freezer (−20 °C) until further processing in the laboratory. Samples for heavy metal analysis were filtered through an acid-cleaned membrane syringe filter (0.45 µm; Advantec, Tokyo, Japan) and acidified to a pH of ~1.8 using 12 N HCl (Ultrapure, Merck) under a custom-made portable clean-bench system equipped with a clean HEPA filter (Class 100). The samples were stored in the refrigerator (<4 °C) until analysis.

2.4. Sediment Trap

Four acrylic cylinder traps with diameters of 7 cm, lengths of 60 cm, and aspect ratios of 8.6 were deployed at each site. After the benthic chamber was installed on the sediment, the sediment traps were gently placed on the top frame of the benthic chamber by a SCUBA diver [33]. About 2 h later, the trap cups (filled with high-density salt brine solution [>50‰], which can prevent washout and preserve the collected particles in the trap) were loaded to the bottom of the sediment trap. After retrieving the sediment trap and bringing it back on board the ship, it was left to stand for ~1 h to allow the particulate matter to settle. The overlying water was then carefully siphoned off, and the samples were stored in a dark refrigerator for further processing in the laboratory.

2.5. Laboratory Analysis

Dissolved inorganic nutrients (nitrate, ammonium, phosphate, and silicate) were measured using standard colorimetry methods [34] on a flow injection autoanalyzer (Bran + Luebbe, QuAAtro39 AutoAnalyzer, Delavan, WI, USA). The Chl-a in the water and sediment were spectrophotometrically determined according to the methodology of Parsons et al. [35]. The dissolved Fe^{2+} in porewater was determined via the colorimetric method using a ferrozine solution [36]. The heavy metals (Mn, Fe, Cr, Co, As, Cd, Pb, Ni, Cu, and Zn) of in situ incubated samples were measured using the Element-2 high-resolution ICP-MS (iCAP-RQ, Thermo Fisher Scientific, Waltham, CA, USA) coupled with a seaFAST (seaFAST-SP3, ESI, Omaha, NE, USA) automated sample introduction system. Measurement quality was assured using certified reference materials for CASS-6 (National Institute Standard and Technology, Gaithersburg, MD, USA) and nearshore seawater certified reference material for heavy metals. The results indicated a recovery rate of 96–108% (Table S1).

To estimate the vertical flux of total mass (TM), particulate organic carbon (POC), total nitrogen (TN), and stable carbon isotope, four aliquots of samples in the sediment trap cup were filtered through precombusted GF/F glass microfiber filters (6827-1315, Whatman, Maidstone, UK) and freeze-dried until reaching a constant weight. The POC and TN content, as well as the stable carbon isotopic composition (δ13C), were analyzed using an elemental analyzer (EA; Vario PYROcube, Elementar, Langenselbold, Germany) in conjunction with an isotope ratio mass spectrometer (IRMS; Isoprime 100, Isoprime, Cheadle Hulme, UK) after acidification with 1N HCl fumes. The isotopic composition was expressed in the δ notation as $\delta^{13}C\ (‰) = ((R_{sample}/R_{reference}) - 1) \times 1000$, where R is the corresponding ratio $^{13}C/^{12}C$. The isotopic reference for carbon was Vienna PeeDee Belemnite (VPDB).

TRS in the sediment, including acid-volatile sulfide (AVS = FeS + H_2S) and chromium-reducible sulfur (CRS = S^0 + FeS_2), was determined using the methylene blue method [37] after the single-step distillation of sediment with cold 12 N HCl in boiling 0.5 M Cr^{2+} solution [38].

2.6. Calculation

Benthic fluxes of oxygen, nutrients, and heavy metals across the SWI were calculated as follows:

$$BF = (dC/dt) \times (V/A), \quad (1)$$

where BF is the benthic flux (mmol m^{-2} d^{-1}), dC/dt is the slope of the linear regression line derived from the relationship between the concentration and increasing time (mmol L^{-1} d^{-1}), V is the chamber volume (m^3), and A is the chamber area (m^2). A negative slope denotes sinking into the sediment, and a positive slope denotes release from the sediment.

The contribution of heavy metal benthic flux to the total amount was calculated as follows [39]:

$$\text{Contribution } (\%) = \frac{\text{mean BF} \times \text{RT} \times \text{A}}{\text{BC} \times \text{A} \times \text{WD}} \times 100 \quad (2)$$

where mean BF is the mean benthic flux of each metal (μmol m^{-2} d^{-1}), RT is the residence time (d), A is the area (m^2), BC is the bottom concentration (μmol L^{-1}), and WD is the mean water depth (m).

2.7. Statistical Analysis

Principal components analysis (PCA) was used to evaluate the benthic fluxes and classify the local characteristics of the station by human impacts. The PCA was conducted on the correlation matrix of the variables with varimax rotation [40] using PASW Statistics 19 (SPSS Inc., Chicago, IL, USA).

3. Results

3.1. Physicochemical Characteristics of Water and Vertical Fluxes

The water depth, temperature, salinity, DO, Chl-a, and nutrient values of the water samples are listed in Table 2. Water depth and temperature ranged from 4.4 to 7.9 m and from 16.1 to 21.2 °C, respectively. The DO was generally well saturated (94–135%), except for SH2 (79%) in the bottom water. The Chl-a concentrations in the water ranged from 2.7 ± 0.0 to 15.3 ± 0.9 μg L^{-1}. The lower salinity and higher nutrient concentrations in the surface water of SH1 indicated freshwater inputs from the streams located near the industrial complex and Ansan City. Compared to other stations, all the nutrients in the surface water of SH1 were higher, with ammonium (NH_4^+) being 6–33 times as high, nitrate (NO_3^-) being 2–34 times as high, phosphate (PO_4^{3-}) being 6–11 times as high, and silicate ($Si(OH)_4$) being 2–13 times as high.

Table 2. Environmental parameters of the surface (S) and bottom (B) water.

Station	Depth (m)		Temperature (°C)	Salinity	DO (%)	Chl-a (μg L^{-1})	NH_4+	NO_3^- (μmol L^{-1})	PO_4^{3-} (μmol L^{-1})	$Si(OH)_4$ (μmol L^{-1})
SH1	4.4	S	21.2	30.67	97	4.0 (±1.0)	18.1 (±0.2)	6.7 (±0.1)	1.80 (±0.02)	41.9 (±0.0)
		B	19.9	31.16	94	6.6 (±0.7)	2.0 (±0.1)	1.4 (±0.1)	0.76 (±0.00)	35.8 (±0.1)
SH2	6.1	S	20.3	31.20	113	6.2 (±0.0)	0.6 (±0.1)	0.3 (±0.1)	0.28 (±0.00)	27.3 (±0.7)
		B	17.9	31.28	79	7.9 (±0.2)	1.1 (±0.0)	0.7 (±0.0)	0.44 (±0.07)	28.8 (±3.7)
SH3	7.9	S	17.7	31.28	105	5.9 (±0.2)	2.9 (±0.4)	2.8 (±0.5)	0.30 (±0.03)	6.1 (±0.5)
		B	17.0	31.26	98	2.7 (±0.0)	4.0 (±0.5)	3.7 (±0.6)	0.30 (±0.01)	7.7 (±0.3)
SH4	6.0	S	17.7	31.23	103	7.4 (±0.3)	1.8 (±0.5)	1.9 (±0.4)	0.16 (±0.02)	10.4 (±1.2)
		B	17.0	31.24	97	5.0 (±0.6)	4.0 (±0.4)	2.6 (±0.4)	0.37 (±0.08)	8.3 (±2.0)

Table 2. *Cont.*

Station	Depth (m)		Temperature (°C)	Salinity	DO (%)	Chl-a (μg L^{-1})	NH_4+	NO_3^-	PO_4^{3-}	$Si(OH)_4$
						(μmol L^{-1})				
GB	7.1	S	18.1	31.17	135	15.3 (±0.9)	0.6 (±0.1)	0.2 (±0.0)	BDL [a]	3.3 (±0.0)
		B	16.7	31.27	109	3.8 (±0.4)	2.0 (±0.0)	1.7 (±0.0)	0.10 (±0.00)	4.1 (±0.0)

Values represent averages ± 1 SD (n = 3). [a] BDL indicates below the detection limit.

The vertical fluxes are listed in Table 3. The vertical fluxes of TM, POC, and TN varied from 100 ± 10 to 142 ± 10 g m^{-2} d^{-1}, from 87 ± 9 to 157 ± 11 mmol m^{-2} d^{-1}, and from 8.4 ± 0.8 to 12.4 ± 0.9 mmol m^{-2} d^{-1}, respectively, with the highest fluxes found at SH4, which is located near the freshwater reservoir gate servicing the Daesong agricultural complex. The POC and TN content in the sediment trap ranged from 1.00 ± 0.04 to 1.33 ± 0.17% and from 0.108 ± 0.005 to 0.122 ± 0.009%, respectively. SH4 also yielded the highest POC and TN values. The stable carbon isotopic compositions (δ13C) and C/N molar ratio were less different between the stations in this study.

Table 3. Vertical particle flux of total mass (TM), particulate organic carbon (POC), total nitrogen (TN), and stable carbon isotope composition of particulate matter collected via the sediment trap.

Station	TM Flux	δ13C	POC	TN	POC Flux	TN Flux	C/N Ratio
	(g m^{-2} d^{-1})	(‰)	(%, dry wt.)		(mmol m^{-2} d^{-1})		
SH1	100 (±10)	−24.5 (±0.8)	1.05 (±0.07)	0.118 (±0.019)	87 (±9)	8.4 (±0.8)	10.4
SH2	130 (±12)	−24.2 (±0.1)	1.00 (±0.04)	0.117 (±0.005)	109 (±10)	10.9 (±1.0)	10.0
SH3	117 (±4)	−23.4 (±0.1)	1.04 (±0.04)	0.108 (±0.005)	101 (±4)	9.0 (±0.3)	11.2
SH4	142 (±10)	−23.3 (±0.3)	1.33 (±0.17)	0.122 (±0.009)	157 (±11)	12.4 (±0.9)	12.7

Values represent averages ± 1 SD (n = 3).

3.2. Porewater and Solid-Phase Geochemistry

Figure 2a shows the vertical profiles of the nutrients and dissolved iron (Fe^{2+}) in the porewater. The NH_4^+, PO_4^{3-}, and $Si(OH)_4$ concentrations in the porewater ranged from 94 ± 8 to 879 ± 0 μmol L^{-1}, from 0.7 ± 0.0 to 94 ± 77 μmol L^{-1}, and from 97 ± 3 to 420 ± 56 μmol L^{-1}, respectively. At stations SH1 and SH2, the vertical profiles of NH_4^+ and PO_4^{3-}, as well as nd $Si(OH)_4$ in the porewater, exhibited rapid increases with depth, whereas values at stations SH3, SH4, and GB were relatively constant with depth. The NO_3^- concentrations in the porewater ranged from 0.8 ± 0.1 to 3.4 ± 1.1 μmol L^{-1}. Measured vertically, a higher concentration of NO_3^- was evident at depths of 0–2 cm, but NO_3^- was depleted at lower depths, suggesting denitrification and/or anammox in the sediment layer. In particular, high NO_3^- concentrations in the surface sediment were evident at sites (SH1 and SH2) nearest the industrial complexes. The Fe^{2+} concentrations in lake sediment ranged from 381 ± 139 to 0.7 ± 0.6 μmol L^{-1} and showed a sharp increase at a depth of 4–6 cm, but thereafter, Fe^{2+}decreased with increased depth at all stations. Figure 2b shows the vertical profiles of lake sediment TRS, with concentrations ranging from 4.3 ± 0.1 to 94.2 ± 0.1 μmol cm^{-3}, which increased rapidly with increasing depth at SH1, SH2, and SH3.

Table 4 presents depth-integrated nutrient, Fe^{2+}, and TRS values down to a 10 cm depth. The depth-integrated inventory of SH1 and SH2 averaged values for NH_4^+, PO_4^{3-}, and $Si(OH)_2$ were ~2, 4–14, and ~2 times higher, respectively, than those of other stations (Table 4). Little difference in depth-integrated NO_3^- was observed across stations. Depth-integrated inventories of Fe^{2+} ranged from 6.62 to 15.45 mmol m^{-2}, with the highest value evident at station SH1. The depth-integrated inventories of TRS at SH1 and SH2 (2.54–2.67 mol m^{-2}) were comparable to or higher than those measured at other stations (1.19–2.56 mol m^{-2}).

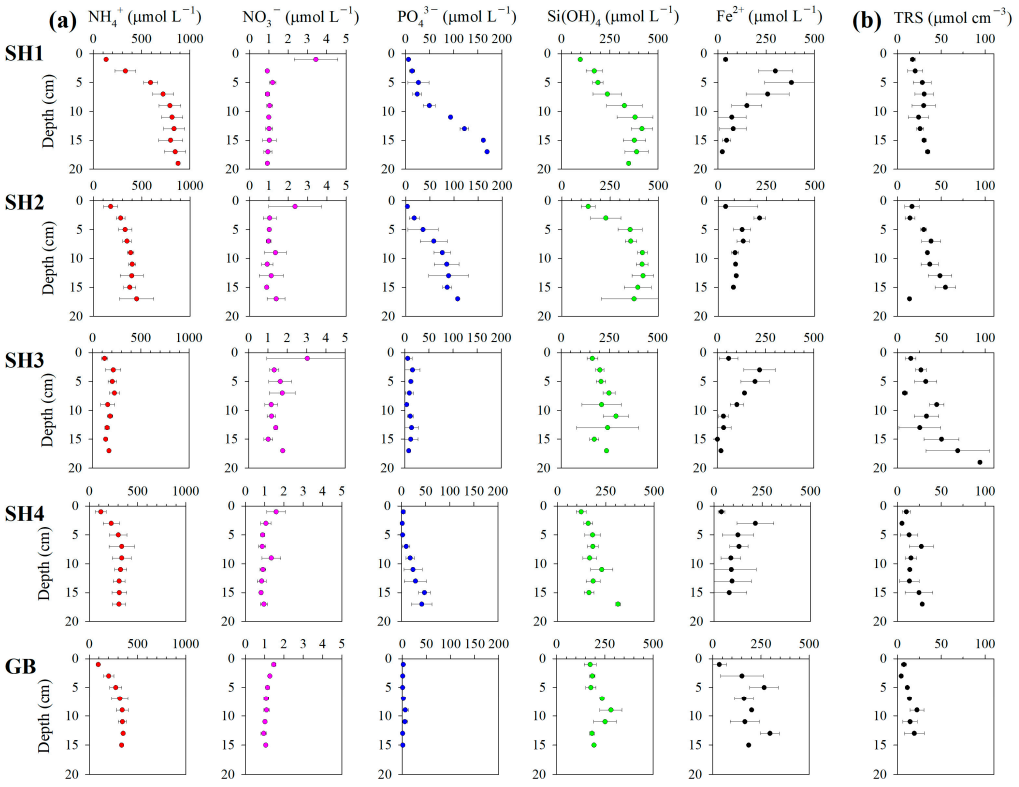

Figure 2. Vertical profiles of (**a**) nutrients (NH_4^+, NO_3^-, PO_4^{3-}, $Si(OH)_4$) and Fe^{2+} in the porewater, as well as (**b**) total reduced sulfur (TRS) in the sediment.

Table 4. Depth-integrated (0–10 cm) inventories of porewater and solid-phase inventories.

Station	Porewater (mmol m^{-2})					Solid Phase (mol m^{-2})
	NH_4^+	NO_3^-	PO_4^{3-}	$Si(OH)_4$	Fe^{2+}	TRS
SH1	36.38	0.106	1.72	14.25	15.45	2.54
SH2	23.95	0.108	3.00	23.51	6.62	2.67
SH3	12.19	0.117	0.64	13.45	9.50	2.56
SH4	17.90	0.078	0.46	10.98	8.19	1.43
GB	17.07	0.084	0.17	14.54	12.70	1.19

3.3. Sediment Oxygen Demand and Benthic Nutrient Flux

Figures 3 and 4 show oxygen and nutrient variations yielded during in situ incubation, respectively. The SOD and BNF measurements are listed in Table 5. Oxygen concentrations in the benthic chamber decreased linearly over time at all stations. Unfortunately, the SOD measurement taken at the GB station is not included in our dataset because of a failure of the optode sensor. The SOD results ranged from 30.6 ± 0.0 to 83.3 ± 0.2 mmol m^{-2} d^{-1}, with the highest value estimated at SH4. Overall, nutrient concentrations gradually increased over time, but the decreases in NO_3^- at stations SH1 and SH4 imply that denitrification and/or anammox may be more prominent than nitrification in lake sediment. The BNF across the SWI ranged from 7.36 ± 2.69 to 12.50 ± 3.72 mmol m^{-2} d^{-1} for NH_4^+, –from 1.99 ± 0.45 to 1.31 ± 0.17 mmol m^{-2} d^{-1} for NO_3^-, from 0.19 ± 0.02 to 1.18 ± 0.12 mmol m^{-2} d^{-1} for PO_4^{3-}, and from 3.56 ± 0.36 to 29.00 ± 3.71 mmol m^{-2} d^{-1} for $Si(OH)_4$.

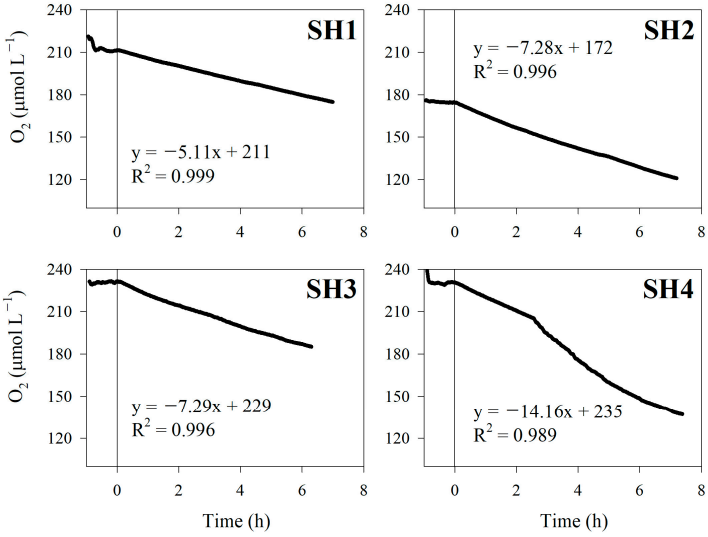

Figure 3. Evolution of dissolved oxygen (DO) concentration with time in the benthic chamber on the inside of Shihwa Lake.

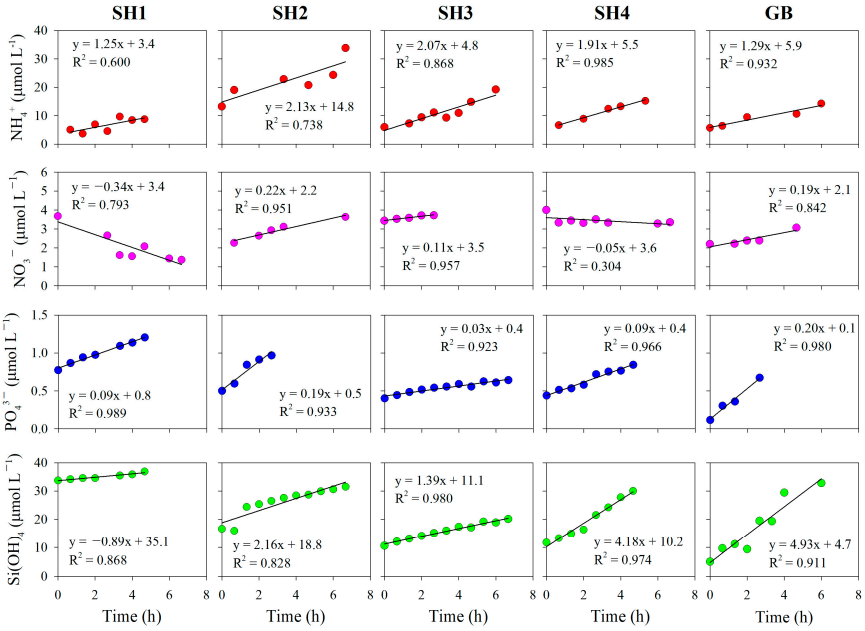

Figure 4. Time courses for the concentrations of the nutrients (NH_4^+, NO_3^-, PO_4^{3-}, $Si(OH)_4$) in the benthic chamber. The solid lines show the results of linear regressions.

Table 5. Sediment oxygen demand (SOD) and benthic nutrient flux (BNF) at the sediment–water interface (SWI).

Station	SOD	BNF			
	(mmol m^{-2} d^{-1})				
	O_2	NH_4^+	NO_3^-	PO_4^{3-}	$Si(OH)_4$
SH1	30.6 (±0.0)	7.36 (±2.69)	−1.99 (±0.45)	0.51 (±0.02)	3.56 (±0.36)
SH2	42.8 (±0.1)	12.50 (±3.72)	1.31 (±0.17)	1.11 (±0.17)	12.68 (±1.92)
SH3	42.9 (±0.1)	12.15 (±1.94)	0.66 (±0.08)	0.19 (±0.02)	8.17 (±0.39)
SH4	83.3 (±0.2)	11.21 (±0.80)	−0.32 (±0.20)	0.52 (±0.04)	24.59 (±1.65)
GB	-	7.59 (±1.18)	1.11 (±0.28)	1.18 (±0.12)	29.00 (±3.71)

Error denotes the uncertainty of each individual flux, estimated as the error of the slope of the concentrations versus time data; "-" denotes no data.

3.4. Heavy Metal Benthic Flux

Figure 5 shows the variation in dissolved heavy metals (Mn, Fe, Cr, Co, As, Cd, Pb, Ni, Cu, and Zn) during in situ incubation, and the fluxes of those are listed in Table 6. The initial concentrations of each heavy metal were comparable to previous results obtained at Shihwa Lake [41]. Nearly all heavy metal benthic fluxes were released via SWI. In particular, the benthic fluxes of Mn, Fe, Co, and Ni at SH4 were found to be 2–10, 1.4–13.6, 2–5, and 2–6 times higher, respectively, than those measured at other stations. On the other hand, the benthic fluxes of As and Pb at SH2 were 3–5 and 2–4 times higher, respectively. The benthic flux of Cu at SH2 showed the highest value, and it showed negative value at SH3. The benthic fluxes of Cr, Cd, and Zn at SH1 and SH2 were released via SWI, but they were sunk into other stations.

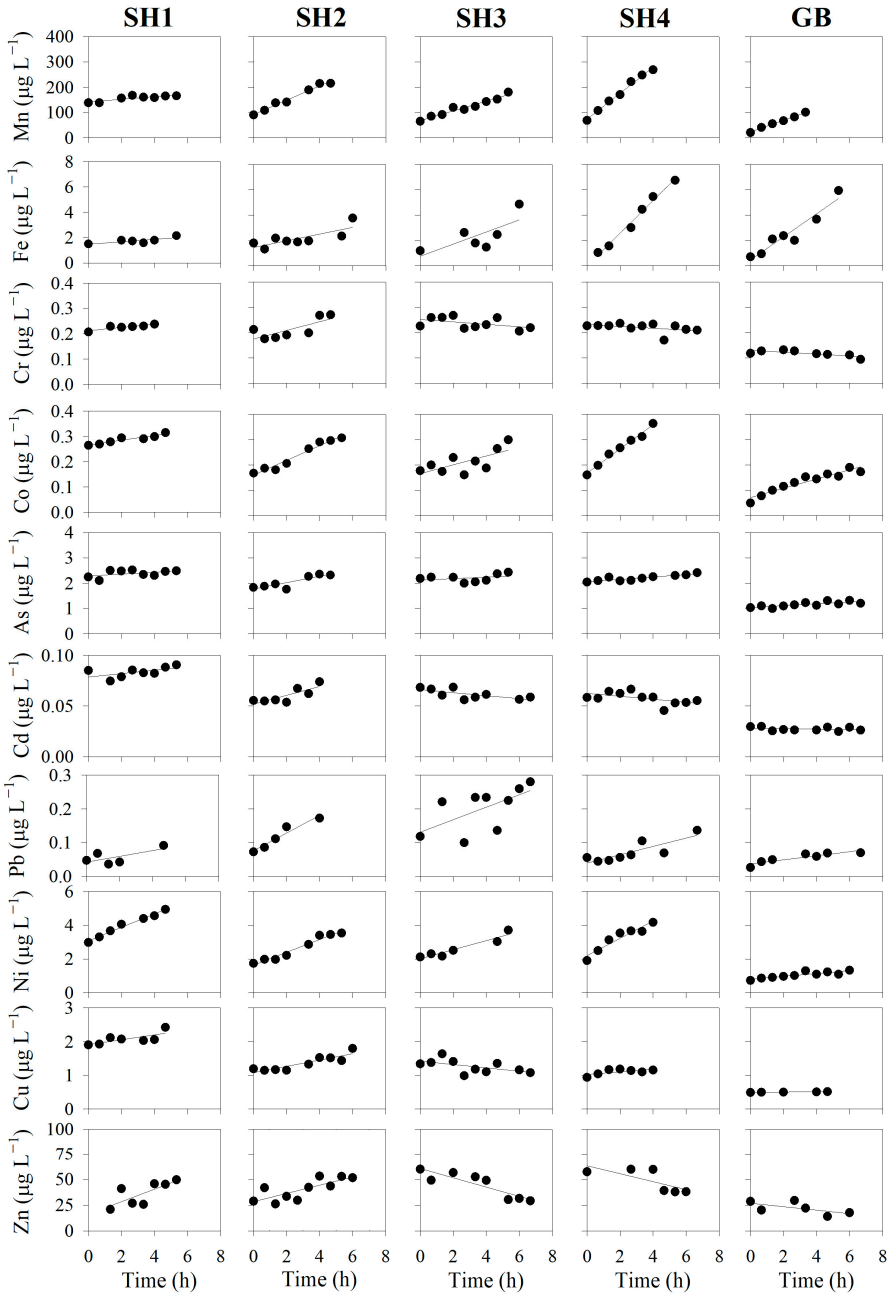

Figure 5. Time courses for the concentrations of dissolved heavy metals (Mn, Fe, Cr, Co, As, Cd, Pb, Ni, Cu, and Zn) in the benthic chamber. The solid lines show the simple linear regression results.

Table 6. The benthic fluxes of dissolved heavy metals (Mn, Fe, Cr, Co, As, Cd, Pb, Ni, Cu, and Zn).

Station	Mn	Fe	Cr	Co	As	Cd	Pb	Ni	Cu	Zn
	μmol m^{-2} d^{-1}									
SH1	573 (±139)	10 (±4)	0.72 (±0.18)	0.9 (±0.1)	3.0 (±2.0)	0.09 (±0.05)	0.24 (±0.15)	40 (±3)	6.7 (±2.7)	546 (±212)
SH2	3028 (±195)	28 (±9)	1.93 (±0.76)	2.9 (±0.2)	9.9 (±2.4)	0.23 (±0.07)	0.74 (±0.12)	38 (±3)	8.7 (±1.7)	359 (±101)
SH3	2060 (±169)	50 (±23)	−0.54 (±0.35)	1.7 (±0.7)	2.2 (±2.4)	−0.08 (±0.03)	0.53 (±0.25)	27 (±4)	−4.6 (±2.4)	−404 (±86)
SH4	5488 (±242)	136 (±8)	−0.41 (±0.28)	4.8 (±0.3)	3.7 (±0.6)	−0.08 (±0.04)	0.35 (±0.09)	51 (±7)	3.7 (±1.9)	−346 (±156)
GB	2473 (±95)	96 (±13)	−0.43 (±0.15)	1.8 (±0.2)	2.9 (±0.8)	−0.01 (±0.02)	0.17 (±0.04)	9 (±2)	0.4 (±0.0)	−151 (±92)

Error denotes the uncertainty of each individual flux, estimated as the error of the slope of the concentrations versus time data.

4. Discussion

4.1. Control Factors for Sediment Oxygen Demand

The benthic flux of oxygen has been used as a robust substitute for the OC oxidation rate and OM enrichment because microbial communities in the sediment use oxygen as an electron acceptor for OC degradation through complex respiration pathways [22]. SOD can be controlled by several factors, such as primary productivity in surface water, water depth, water temperature, oxygen concentration, vertical fluxes, and OM content [42–44]. As there were no significant differences in water depth, temperature, and DO concentration across the study area, the assessment of major control factors for SOD was not valid.

The SOD showed strong linear relationships with the POC content of settling particles (R^2 = 0.87) and vertical POC flux (R^2 = 0.99). In previous studies, the SOD showed a positive correlation with POC content in continental shelf sediment, but a negative correlation with the C/N ratio in OM-enriched fish farm sediment [44,45]. These results suggest that both OC quantity and quality in sediment are key to controlling the benthic mineralization of OM [46–48]. In the Shihwa Lake study area, however, the C/N and $\delta^{13}C$ values, which are proxies of OM quality, showed a relatively narrow range with spatial variations. Otherwise, the spatial differences in vertical fluxes of POC could be explained by a potential point source of OM, i.e., the significantly higher SOD and POC fluxes at SH4 may imply that benthic respiration is controlled by the quantity of OM supply from the water column to the sediment. Despite the highest SOD being recorded at SH4, the recorded accumulations of reduced products of metabolic activities (i.e., NH_4^+, PO_4^{3-}, Fe^{2+}, and TRS) in the porewater and solid phase at SH4 were lower than the values recorded at SH1 and SH2. This result indicates that the reduced inorganic metabolites produced via OM oxidation were, in fact, a result of reoxidation or flushing out produced by the strong current velocity (12–13 m s^{-1}) via the operation of the tidal power plant near SH4 [49].

The averaged SOD inside of Shihwa Lake (49.9 ± 23.0 mmol m^{-2} d^{-1}) was significantly higher than the values obtained from other continental sediments, but it was comparable to values obtained from semi-enclosed and organically enriched coastal bay sediments elsewhere in South Korea (Table 7). However, our result was lower than that obtained from the aquaculture sediment deposited by excess OM from excess food and biodeposits (Table 7).

Table 7. Comparison between sediment oxygen demand (SOD) and associated environmental parameters measured in various environments.

Location	Environmental Description	Water Depth (m)	Temp (°C)	Salinity (psu)	SOD (mmol m^{-2} d^{-1})	Reference
Shihwa Lake, South Korea	Enclosed saline lake	4.4–7.1 (6.3 ± 1.3)	16.6–19.9 (14.7 ± 7.3)	31.2–31.3	30.6–83.3 (49.9 ± 23.0)	This study
Chonsu Bay, South Korea	Enclosed bay	12–17	20–21	31.5–31.7	25.6–50.4 (37.5 ± 12.4)	[9]
Namhae and Geoje Islands, South Korea	Coastal continental shelf	24–28	19.8–20.5	33.7–34.5	34.9–54.1 (46.3 ± 10.1)	[50]
Geoje-Tongyoung coastal, South Korea	Oyster farm	11	15.3–18.8	-	60–84 (73 ± 12)	[51]
	Finfish farm	19	15.9–19.1	-	77–157 (117 ± 40)	
Gulf of Cadiz, Iberian Peninsula	Near-shore continental shelf	8–34	12–24	35.3–36.7	9–27 (18 ± 5)	[45]
Northern East China Sea (ECS)	Continental shelf	83–93	13.4–14.1	32.0–33.9	2.7 and 8.4 (5.6 ± 4.1)	[14]

"-" denotes no data.

4.2. Benthic Nutrient Flux and Benthic–Pelagic Coupling

The mean BNF values were 10.7 ± 3.8 mmol N m^{-2} d^{-1} for dissolved inorganic nitrate (DIN; NH_4^+ + NO_3^-), 0.58 ± 0.4 mmol P m^{-2} d^{-1} for dissolved inorganic phosphate (DIP; PO_4^{3-}), and 10.05 ± 12.3 mmol m^{-2} d^{-1} for $Si(OH)_4$ (Table 8). The BNF values measured at Shihwa Lake were higher than those measured in other coastal environments, such as Namhae Island and the South Sea of South Korea (1.5–3.2 mmol N m^{-2} d^{-1} and 0.11–0.33 mmol P m^{-2} d^{-1}, respectively) [50] the Ria de Vigo of Galicia, Spain, and the wide Iberian Peninsula (1.1–5.4 mmol N m^{-2} d^{-1} and 0.08–0.34 mmol P m^{-2} d^{-1}, respectively) [15]; and the Mid-Atlantic Bight that extends from Cape Hatteras, NC, USA, to Cape Cod, MA, USA (−0.27–2.63 mmol N m^{-2} d^{-1} and 0.01–1.26 mmol P m^{-2} d^{-1}, respectively) [52]. Furthermore, those were comparable to that of the sediment at shellfish farms that received a tremendous amount of OM through biodeposition, an oyster farm in South Korea (9.30 mmol N m^{-2} d^{-1} and 0.46 mmol P m^{-2} d^{-1}) [44], and a mussel farm in Canada (1.1–8.2 mmol N m^{-2} d^{-1} and 0.36–1.20 mmol P m^{-2} d^{-1}) [53]. Additionally, outside of the Shihwa Lake dike, sampling station GB had a high efflux of dissolved inorganic nutrients, which were 8.7 mmol N m^{-2} d^{-1} for DIN, 1.18 mmol P m^{-2} d^{-1} for DIP, and 29.00 mmol m^{-2} d^{-1} for $Si(OH)_4$.

Table 8. Benthic nutrient flux (BNF) and contribution of BNF to primary production (PP) in Shihwa Lake.

Station	Benthic Nutrient Flux (mmol m^{-2} d^{-1})		Contribution of BNF to PP (%)	
	DIN	DIP	DIN	DIP
SH1	5.37 (±3.14)	0.51 (±0.02)	56	85
SH2	13.82 (±3.90)	1.11 (±0.17)	144	184
SH3	12.82 (±2.02)	0.19 (±0.02)	133	32
SH4	10.90 (±0.99)	0.52 (±0.04)	113	86
GB	8.70 (±1.46)	1.18 (±0.12)	35	75

In shallow coastal environments, the release of inorganic nutrients via SWI into the water column can sustainably support primary production (PP) [54–58]. To assess the

contribution of BNF to the requirements of PP, it was used to estimate the value by applying the Redfield ratio to the BNF. Heo [59] and Shin et al. [60] reported that PP inside of the Shihwa Lake dike ranged from 129 to 146 mmol C m^{-2} d^{-1} (average, 64 mmol C m^{-2} d^{-1}), and outside the Shihwa Lake dike, the value was 167 mmol C m^{-2} d^{-1}. Based on the Redfield ratio (C:N:P = 106:16:1) for phytoplankton growth, the DIN and DIP requirements for PP were estimated to be 9.6 mmol N m^{-2} d^{-1} and 0.6 mmol P m^{-2} d^{-1} inside of the Shihwa Lake dike and 25.2 mmol N m^{-2} d^{-1} and 1.58 mmol P m^{-2} d^{-1} outside of the Shihwa Lake dike. Therefore, the benthic fluxes of DIN and DIP accounted for 35–144% (average, 96 ± 39%) and 32–184% (average, 92 ± 63%) of the N and P requirements for PP, respectively (Table 7). These results suggest that high BNF values were comparable to those measured on other eutrophic coasts, e.g., at sea squirt farms (88 ± 90% for N, 64 ± 53% for P [31]) and oyster farms in South Korea (89% for N, 70% for P [44]). Consequently, the BNF of Shihwa Lake can act as an important point source of nutrients via tight benthic–pelagic coupling, which may promote unusual phytoplankton blooms.

4.3. Control Factors for Heavy Metal Benthic Flux

Heavy metal benthic fluxes in Shihwa Lake have revealed remarkable and outstanding results compared to other polluted coastal waters (Table 9). Our findings highlight the significant impacts of anthropogenic pollution sources, particularly from the steel-smelting, semiconductor, and machine manufacturing facilities that make up approximately 81% of the Shihwa industrial complex [61,62], on the heavy metal benthic fluxes in Shihwa Lake.

Table 9. Comparison of heavy metal benthic fluxes (μmol m^{-2} d^{-1}) measured in this study with in situ fluxes sourced from other locations.

Location	Shihwa Lake, South Korea	New Bedford Harbor, USA	Lagoon of Venice, Italy	Mar Piccolo, Italy	Galveston Bay, USA	Mejerda River Delta, Tunisia
Mn	573–5488 (2724 ± 1794)	-	2.9–4.6 (3.7 ± 1.2)	4.7–5.0 (4.9 ± 0.2)	450–2320 (1207 ± 792)	86–190 (130 ± 35)
Fe	10–136 (64 ± 51)	-	−1.5–0.8 (−1.2 ± −1.5)	3.9–8.7 (6.3 ± 3.4)	6.3–34 (18 ± 12)	-
Cr	−0.54–1.93 (0.3 ± 1.1)	-	-	−1.2–0.6 (−1.0 ± 0.4)	-	-
Co	0.9–4.8 (2.4 ± 1.5)	0.001–0.045 (0.02 ± 0.02)	-	-	-	−0.38–1.92 (0.67 ± 0.79)
As	2.2–9.9 (4.3 ± 3.2)	-	−0.04–0.06 (0.01 ± 0.07)	−0.15–0.83 (0.34 ± 0.69)	-	-
Cd	−0.08–0.23 (0.03 ± 1.13)	0.01–0.29 (0.12 ± 0.11)	0.04–0.05 (0.05 ± 0.01)	−0.04–0.00 (−0.02 ± 0.03)	-	−0.38–0.38 (−0.05 ± 0.32)
Pb	0.1–0.74 (0.41 ± 0.23)	−0.04–0.14 (0.03 ± 0.06)	-	0.12–0.27 (0.19 ± 0.11)	-	0.2–0.5 (0.41 ± 0.11)
Ni	9–51 (33 ± 16)	0.04–1.10 (0.5 ± 0.4)	-	0.32–0.37 (0.35 ± 0.04)	0.9–2.7 (1.6 ± 0.6)	-
Cu	−4.6–8.7 (3.0 ± 5.3)	1.3–11.0 (4.8 ± 3.1)	0.07–0.12 (0.09 ± 0.04)	−0.9–7.0 (3.1 ± 5.6)	-	0.1–0.4 (0.22 ± 0.09)
Zn	−404–546 (1 ± 428)	4–51 (20 ± 15)	15–16 (15 ± 1)	−0.4–6.9 (3.3 ± 5.2)	1.8–3.3 (2.3 ± 0.5)	27–270 (135 ± 86)
Reference	This study	[63]	[64]	[65]	[66]	[67]

"-" denotes no data.

Two principal components (PC) were identified that explained 82.4% of the total variance, with PC1 explaining 46.1% of the variance and PC2 explaining 36.3% of the variance (Table S2). The correlations between the measured fluxes and the two components

are shown in Figure 6. The loading plot reveals that PC1 is primarily driven by heavy metal fluxes that can be controlled by early diagenesis of sediment, while BNF has a weaker influence on this component. The high positive scores for Mn, Fe, Co, Ni, and SOD, as well as the high negative scores for nutrient variables (Table S2), indicate that Mn and Fe are released from sediments via Mn- and Fe-oxide reduction [68,69], accompanied by the remobilization of Co and Ni in the sediment [70]. Additionally, dissolved Co could be a source of bottom water during the diagenetic reduction of Mn and Fe oxides in the benthic chamber [22].

Similarly, PC2 showed the highest scores for Cr, As, Cd, Cu, and Zn, with relatively high scores for Pb compared to the other scores (Table S2). Ra et al. [25] reported that the enrichment factor (EF) of the metals indicated that metal pollution was mainly driven by the industrial complex, and concentrations of Cr, As, Pb, Cu, and Zn in the sediment exceeded the effects range low (ERL) provided for assessing sediment quality and adverse benthic biota. SH1 and SH2, located near the Shihwa industrial complex, exhibited the highest levels of metal pollution, with the average benthic fluxes for Cr (1.3 ± 0.9 μmol m^{-2} d^{-1}), As (6.4 ± 4.9 μmol m^{-2} d^{-1}), Cd (0.2 ± 0.1 μmol m^{-2} d^{-1}), Pb (0.5 ± 0.4 μmol m^{-2} d^{-1}), Cu (7.7 ± 1.4 μmol m^{-2} d^{-1}), and Zn (453 ± 132 μmol m^{-2} d^{-1}) being the highest (Figure 1, Table 6). The transport of contaminated sediment from upstream to downstream via water circulation effected by tidal plant operations [25,71] may have resulted in the accumulation of heavy metals in the sediment, leading to a lower benthic metal flux at SH1 compared to SH2. Ultimately, the discharge of pollutants from the Shihwa–Banweol industrial complex may lead to the significant accumulation of heavy metals in lake sediment, greatly impacting the benthic fluxes of toxic metals such as Cr, As, Cd, Pb, Cu, and Zn.

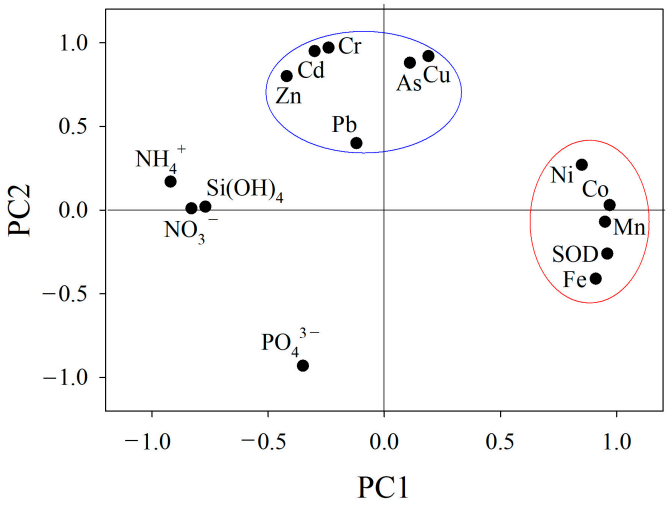

Figure 6. Principal component analysis (PCA) of benthic flux (oxygen, nutrients, and heavy metals). The red circle is related to PC1, and the blue circle is related to PC2.

4.4. Assessing the Contribution and Risk of Heavy Metal Benthic Fluxes in Shihwa Lake

To assess the significance of heavy metal flux as a source of the overlying water in Shihwa Lake, we applied our in situ measurements of heavy metal benthic fluxes to the inventories of each metal present in the lake. The residence time is estimated at 2 days [49], and the bottom concentration of metal is the average of the initial metal concentrations (t = 0) in the benthic chamber.

The release of heavy metals from sediment may have contributed to the current standing stock of dissolved Mn, Fe, Cr, Co, As, Cd, Pb, Ni, Cu, and Zn in Shihwa Lake, with contributions of 106%, 120%, 6%, 50%, 11%, 4%, 82%, 66%, 11%, and 3%, respectively, being recorded, which were significantly higher than those of the most contaminated harbors in China (Jinzhou Bay, the Bohai Sea [39]). The Cr, Cd, and Zn inputs into the Shihwa Lake water column are currently dominated by fluvial inputs containing industrial sewage, and

the benthic flux of Mn, Fe, Co, As, Pb, Ni, and Cu (with contributions greater than 10%) may be a crucial source in the water column. Consequently, the endogenous release of heavy metals may pose a potential and continual risk to Shihwa Lake's water quality. The benthic fluxes of heavy metals via SWI may significantly contribute to this issue.

5. Conclusions

The SOD in lake sediment was found to be regulated by vertical POC fluxes. The BNF accounted for more than 90% of N and P required for PP in the water column, indicating that it may act as a major source of nutrients in Shihwa Lake. Furthermore, the benthic fluxes of Fe, Mn, Co, and Ni were found to have strong correlations with OC oxidation rates, and these were associated with the reduction of Fe and Mn oxides. On the other hand, the benthic fluxes of Cr, As, Cd, Pb, Cu, and Zn were found to be highly dependent on the discharge of industrial wastewater from the steel-smelting, semiconductor, and machine manufacturing facilities, posing a potential risk to the marine environment and ecosystems. Although water exchange in Shihwa Lake was initiated in 2011 through the water gate of the tidal power plant to improve water quality, the contaminated sediment from industrial activities still releases heavy metals into the water, leading to metal contamination in the lake. The heavy metal-contaminated seawater flows outside of the Shihwa Lake dike through the water gate, posing a potential threat to coastal ecosystems. Therefore, the continuous monitoring of heavy metal fluxes and their sources in the SWI is necessary to prevent further contamination of the water and protect coastal ecosystems.

Supplementary Materials: The following supporting information can be downloaded via this link: https://www.mdpi.com/article/10.3390/jmse11112186/s1, Table S1: Comparison of the analytical results of heavy metals for nearshore Seawater Certified Reference Material (CASS-6; n = 3) from National Institute Standard and Technology of USA with certified value; Table S2: Factors loading for varimax-rotated PCA of benthic fluxes.

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