Thesis for the Degree of Master of Environmental Engineering

Distribution and pollution assessment for heavy metals and polycyclic aromatic hydrocarbons in surface sediments from Gwangalli and Nakdong River, Busan, Korea

by

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August 2018

광안리와 낙동강의 표면 퇴적물에 존재하는 중금속과 다환 방향족 탄화 수소의 분포 및 오염도 평가

Advisor: Prof. Taeyoon Lee

By

Hong Kai

A thesis submitted in partial fulfillment of the requirements
for the degree of

Master of Engineering

in Department of Division of Earth Environment System Sciences, The Graduate School,

Pukyong National University

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August 24, 2018

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Abstract

The distribution and pollution assessment of heavy metals and 16 polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Gwangalli and Nakdong River in Busan, Korea were evaluated. The total concentrations of heavy metals and 16 PAHs in sediments collected from 14 sites were compared with sediment guidelines and assessed by multiple indices to determine their contamination degree and ecological risks. For heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn), enrichment factor (EF) values indicated that there were just minor enrichment or even no enrichment in studying areas. Both of the results of geoaccumulation index (l_{geo}) and potential ecological risk factor (PERF) showed Cd posed the highest contamination degree in Gwangalli and Nakdong River. Compared with sediment quality guidelines, the concentrations of Cd in all sampling sites exceeded contamination standards while Cu, Pb, Ni and Zn were below them (except Ni in sampling site G5 and Zn in G4 and G5). Meanwhile, PAHs were also given evaluated by mean effects range-median quotient and the results suggested low ecological risks in most of the studying areas. Concentrations of most PAHs in both Gwangalli and Nakdong River were all below the low effect range of guideline values. This study offered a guideline for protecting and promoting the sedimentary environment in Gwangalli and Nakdong River.

Acknowledgment

First of all, I would like to thank my Professor Taeyoon Lee at department of Earth Environment System Sciences in Pukyong National University. Professor Lee made instructive comments and recommendations on the research direction of my dissertation. In the process of writing the dissertation, he pointed out the difficulties and doubts I encountered, and put forward many useful suggestions for improvement. I want to expressed my sincere gratitude for his help and care. At the same time, I also thank all the students in the major of Environmental Engineering. Everyone learns from each other and helps each other during the project and all of us spent a perfect unforgettable time together.

In addition, I would also like to thank my friends and classmates for their great support and assistance in the preparation of the thesis, which gave me great inspiration. I would also like to thank the authors of the reference literature for their good research.

Finally, thanks for reviewing teachers' hard work. I sincerely thank my family, friends, and classmates for the successful completion of this thesis with their encouragement and support.

1. Introduction

1. 1. Background

Definition of heavy metals is as follows: Heavy metals have relatively high density (over 5 g/cm^3), poor natural degradation and could possibly cause chronic intoxication if reach a certain extent in human body [1,2]. Heavy metals are accumulated in the environment by natural and anthropogenic activities. Anthropogenic origins were mainly from the agricultural and industrial activities due to the rapid growth of world population and economy [3]. Sediments as one of the reservoirs for those heavy metals released by the anthropogenic activities were often detected and compared with background concentration for contamination regulations[4]. Therefore, it is of great significance to determine the concentrations of heavy metal ions in sediments.

PAHs that have two or more aromatic rings are a kind of persistent organic pollutants (POPs), which have the properties of bioaccumulative potential and carcinogenicity [5,6]. The sources of PAHs can be anthropogenic such as fuel combustion, vehicle exhausts, oil spills and some other industrial processes and also natural [7]. They can accumulate in bottom sediment due to their high hydrophobicity and released into the water under favorable conditions [8]. Meanwhile, PAHs with large molecular weights are easily absorbed on fine particles and eventually deposited into sediments [9]. Hence, PAHs in sediments are regarded as a standard to judge the potential risks of the aquatic system.

1. 2. Objectives and scope

The present study was designed to assess the contamination degree of heavy metals and PAHs in the sediments from Gwangalli and Nakdong River, Busan, Korea using different evaluating methods and compared with the baseline provided by the sediment quality guidelines. Meanwhile, the distribution of heavy metals and PAHs were also analyzed. Heavy metals and PAHs collected from two study sites were measured by standard methods, and then heavy metals were evaluated by I_{geo}, EF, PERF, and meanPELquotient indices, while PAHs were evaluated by M-ERM-Q index.

2. literature review

2. 1. Analytical technologies of heavy metals

In recent decades, with the widespread concerns of heavy metal pollution, numerous methods has applied in detecting the concentration of heavy metals. Those methods roughly categorized into traditional methods (such as spectroscopic and chromatography methods) and novel methods. In this paper, spectroscopic methods, chromatography, electrochemical approaches and some other technologies were listed to summarize their principles and performances.

2.1.1. Spectroscopic methods (AAS, GFAAS, ICP, ICP-MS and Molecular Spectroscopy)

Spectroscopic methods were traditional methods which mainly included Atomic Absorption Spectroscopy (AAS), Molecular Spectroscopy (MS), Inductive Coupled Plasma Mass Spectrometry (ICP-MS), Atomic Fluorescence Spectrometry (AFS) and so on. The details were listed below.

1. Atomic Absorption Spectroscopy (AAS)

AAS assesses the concentration of an analyte in a sample bases on the absorption degree of resonance radiation by the free radical atoms of the measured element. AAS has the advantages of low detection limit which reaches in ppb level, high precision, high sample throughput and high sensitivity. Meanwhile, AAS is widely used due to its low costs and the property of easy to operate. Compared with Graphite Furnace Atomic Absorption Spectrometry (GFASS), AAS can not measure multiple elements simultaneously which is a weakness to be improved.

2. Inductive Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS mainly consists of an ion source (ICP), a sampling interface, ion lens, a mass spectrophotometer and a detector. Sample is ionized in ICP and ions produced by ICP go through into the sampling surface, and finally transport to the mass analysis unit. Compared to AAS, ICP-MS has greater speed, precision, and sensitivity. The detection limit is between from 0.01 to 10 mg/L and simultaneous multi-element analysis is possible. Based on those benefits, our research chooses ICP-MS as our measurement method for heavy metal ions.

3. Molecular Spectroscopy (MS)

MS uses spectrophotometers to do colorimetric analysis. Sample reacts with chromogenic reagent to produce a certain chelate which can be detected in ultraviolet and visible light regions. This method has a good selectivity and sensitivity.

4. Atomic Fluorescence Spectrometry (AFS)

AFS analyzes fluorescence from a sample and typically for mercury, arsenic, antimony, bismuth, and selenium elements. This detecting approach possesses high sensitivity, low detection limit and costs, while its fluorescence quenching effect and the interference of scattered light restrict the scope of application.

2.1.2. Chromatography

Chromatography is also a traditional approach to measure the heavy metal ions and has the advantages of high separation efficiency, good selectivity, low sample consumption and high detection sensitivity. Therefore, High-Performance Liquid Chromatography (HPLC) has been rapidly developed in heavy metal ions measurement. In HPLC, the sample is react with organic compound to form a colour complex and based on the difference of polarity between the mobile and stationary phases, the compound are separated and then detected by a detector. Simultaneous multi-element analysis is available for HPLC but it is hard to pick a suitable complex.

2.1.3. Electrochemical approaches

Electrochemical approaches developed rapidly in recent decades. Electrochemistry provides technologies for the effluent treatment and make it possible to get the situ data even in Mars [10,11]. For the trace analysis of heavy metal ions, polarography, voltammetry which includes Anodic Stripping Voltammetry (ASV) and Cathodic Stripping Voltammetry (CSV), Potentiometric Stripping Analysis (PSA), Pseudo-polarography, Modulation Waveforms technologies were commonly employed [12]. Polarography was firstly proposed by J.Heyrovsk according to current-voltage curves derived from a dropping mercury [13] and blossomed into voltammetry. The voltammetry used solid electrodes or stationary electrodes such as platinum electrodes and chemically modified electrodes, which were less harmful than dropping mercury electrode used by polarography. ASV is a polarographic technique that combines potentiostatic electrolytic enrichment with voltammetric analysis and enable to detect several metals simultaneously. Electrochemical methods especially for ASV and CSV have been a powerful tool in metals measurement due to their low time-consuming, easy operation and low detection limits features.

2.1.4. Other technologies

In addition to those common approaches, there are other novel technologies (such as enzymatic analysis, biological sensor and immunoassay and so on) in heavy metal ions detection. For enzymatic methods, Enzyme urease, dehydrogenase and phosphatase are common indicators of soil heavy metal pollution [14]. According to the degree of reaction between metal ions and enzymes, we can obtain the concentration of heavy metal ions. Lately, Tahir Rasheed [15] found a real-time monitoring technology of toxic heavy metals using fluorescent sensor based models. Santanu Roy [16] used optical electrochemical probe in detection of heavy metal ions on a microspot electrode. There was a tendency in combining several approaches together to obtain more fast, accuracy, sensitive metal ions detection technologies. Therefore, further research are mainly based on these aspects.

2. 2. Analytical technologies of polycyclic aromatic hydrocarbons

By contrast with heavy metal ions detection methods, analytical technologies of PAHs is relatively a hard way. It mainly comprises of extraction, purification and analytical determination steps [17]. Currently, PAHs samples from the soils, sediments and solid wastes are extracted by soxhlet extraction, pressurized fluid extraction, microwave assisted extraction, ultrasonic extraction and supercritical fluid extraction methods according to USEPA [18]. After that, detection methods like chromatography and spectrophotometry are applied to measure the concentration of PAHs. In this paper, only GC-FID, GC-MS and HPLC-UV/FL are given details below.

2.2.1. GC-FID

Gas Chromatography-Flame Ionization Detector (GC-FID) regards FID as a detector and is widely used in the petrochemical, pharmaceutical and natural gas markets due to the advantages of high,sensitivity, wide linear range, simplicity of operation and predictable response [19]. Thus, GC-FID in signal detection aspect was predominant than other methods in gas chromatography [21]. Meanwhile, FID typically uses a Hydrogen/Air flame or coupled with makeup gas burning at the jet in a chamber and the sample components are ionized and produce electrically charged ions which are collected and produce an electrical signal for later measurement [20].

2.2.2. GC-MS

To fulfill a better separation, GC-MS separates complex components using capillary column.

Especially when use MS as a detector, simultaneous qualitative and quantitative analysis are possible. This method is available for the determination of polycyclic aromatic hydrocarbons in complex samples. On the other hand, GC-MS has trouble in detecting involatile and unstable compound.

2.2.3. HPLC-UV/FL

High performance liquid chromatography with UV or fluorescence detection method has the advantages of good selectivity, high sensitivity and is commonly used in analysis of the PAHs. HPLC was a technology developed from the column liquid chromatography and separated the samples due to their polarity. Then the detector such as UV detector and fluorescent detector calculated the concentration of samples based on the response signal obtained by the computers. This method also has a very high separation efficiency and extremely quick.

2. 3. Assessment methods for heavy metals and PAHs in sediments

With the rapid development of modern society, concentrations of the heavy metals and PAHs have increased considerably due to the emission of the processing industry, agriculture and wastewater runoff [22]. Sediments are used as standard to evaluate the risk degree of heavy metals and PAHs. In order to achieve the sustainable development, various assessment methods have been applied to determine marine sediment qualities. To evaluate the metal pollution degree and the ecological risks, the enrichment factor (EF), the geoaccumulation index (I_{geo}) and potential ecological risk factor (PERF) are often used [23,24,25]. As for PAHs, mean effects range-median quotient (M-ERM-Q) are popular in assessing the ecological risks caused by PAHs in the sediments [6]. Therefore, total four indices (EF, I_{geo}, PERF for heavy metals, and M-ERM-Q for PAHs) have applied in our research to evaluate the contamination degree and ecological risks of heavy metals and PAHs in Gwangalli and Nakdong River, Busan, Korea.

3. Materials and methods

3. 1. Study area

The Nakdong River (total watershed area: 24,000 km^2, length: 525 km) is the longest river in South Korea, which originates from the Taebaek Mountains in Gangwon Province and flows into the East China Sea. It passes through several metropolitan cities (Busan, Taegu, Ulsan, and so on) and serves as an important shipping, fishing, tourism, and mariculture area. During the past few decades, the water quality of Nakdong River became seriously deteriorated in midstream and downstream areas due to rapid population growth coupled with industrial and urban development, though some constructions and strategies were carried out to improve the environment of Nakdong River [26].

Gwangalli is located at Gwangan 2(i)-dong, Suyeong-gu, Busan Metropolitan City. It is a sanctuary for both dining and leisure. Each year thousands of people came here for traveling. Thus, it is necessary to analyse the distribution and potential risks of aquatic environment for both heavy metals and PAHs in sediments.

3. 2. Sampling

In our research, a total of 14 (6 samples from Gwangalli and 8 samples from Nakdong River) surface sediment samples were collected in September 2017. The locations of the sample station were shown in Fig. 1. Surface sediment samples were collected using a grab sampler and put it in acid-rinsed polyethylene bags. Then they were transferred into a box filled with ice and refrigerated at 4 ℃ in laboratory until further analysis.

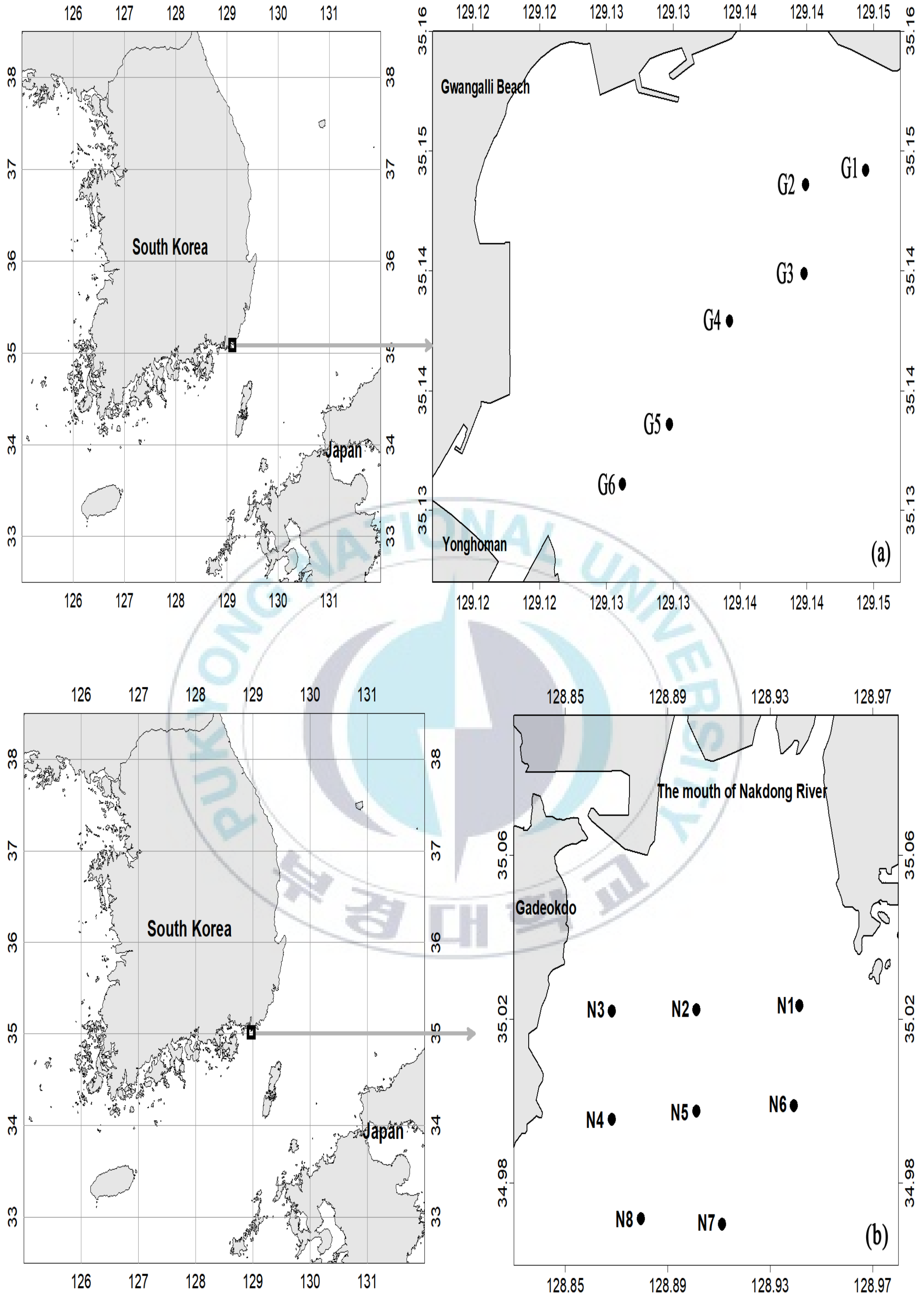


Fig. 1. Sampling locations at (a) Gwangalli (G1 to G6) and (b) Nakdong River (N1 to N8) in Busan, Korea.

3. 3. Sample pretreatment

3.3.1. Heavy metals

1 g of sample was dried out and ground before digestion. The condensed 20 ml of HNO_3 were used to digest samples and samples were heated until solution was evaporated in 100 ml beaker. Then, dilute the digested samples to 100 ml using 1N HNO_3 and wait for 5 min before transferring the samples into sampling bottles. Then, the processed samples were stored in refrigerator until further analysis.

3.3.2. PAHs

Soxhlet extraction method was used for extraction of the PAHs from sediments. Briefly, 10 g of wet sediment samples were put into the soxhlet extractor equipped with a thimble filter for approximately 16 hrs using toluene as the extractant. Soxhlet extractor which comprised of a flask, an extraction chamber, and a condenser was under continually heating. After that, the extracts were transferred and concentrated to 2-4 ml using a rotary evaporator at a temperature of 80 ℃ and a rpm of 50. Finally, the concentrated extracts were diluted with 5 ml hexane and stored in a refrigerator.

3. 4. Analytical methods for heavy metals and PAHs

In this study, a total of 11 heavy metal ions (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in sediments were quantified with inductively coupled plasma mass spectrometry (ICP-MS). The concentration of 16 PAHs were quantified by using a GC/MS (Agilent 7890A GC/5975C MSD) under selected ion monitoring mode (SIM) . Highly pure helium was used for carrier gas and introduced at a flow rate of 1 ml/min. The initial oven temperature was set at 70 ℃ and increased by 20 ℃/min to 280 ℃. The column was an Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm) silica-fused capillary column. Each PAH was calibrated using a standard solution before measurement.

3. 5. Assessment of sediment contamination and ecological risks for heavy metals

In this study, three different indices were used to evaluate the contamination degree and ecological risks for heavy metals in sediments obtained from Gwangalli and Nakdong River. For the comparison purpose, the upper continental crust (UCC) values [27] were used as the reference background for those three indices and two different metal guideline values (threshold effects level and potential effects level) were chosen as criteria for the determination of marine sediment quality. In addition, the heavy metal contamination degree was also assessed by USEPA sediment quality standards and Ontario sediment quality guidelines.

3.5.1. Enrichment factor (EF)

EF is used to evaluate the degree of heavy metal pollution caused by anthropogenic activities [28]. The EF for each element was computed using the relationship below:

$$EF = (C_{\mathrm{x}} - C_{back}) / C_{back}$$

where C_x and C_{back} indicate the level of trace metal in sample and in background, respectively. In this study, the background values of six heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) were obtained from other research [29]. The EF values generally are classified into seven grades such as EF<1, 1<EF<3, 3<EF<5, 5<EF<10, 10<EF<25, 25<EF<50 and EF>50, which indicate no enrichment, minor enrichment, moderate enrichment, moderately severe enrichment, severe enrichment, very severe enrichment, and extremely severe enrichment, respectively [30].

3.5.2. Geoaccumulation index (lgeo)

I_{geo} is a quantitative index which determine the degree of enrichment for exogenous heavy metals in sediment [31] and is defined by the following equation：

$$I_{\mathrm{geo}} = \log_2(\mathrm{C_i}/1.5\mathrm{B_i})$$

where C_i is the measured concentration of metal i in sediment samples and B_i is the geochemical background concentration of metal i. Conversion factor 1.5 is the background matrix correction factor due to lithospheric effects [32]. The geoaccumulation index is categorized into seven classes: $I_{geo} \leqslant 0$, $0<I_{geo}<1$, $1<I_{geo}<2$, $2<I_{geo}<3$, $3<I_{geo}<4$, $4<I_{geo}<5$, $5<I_{geo}$, which represent practically uncontaminated, uncontaminated to moderately contaminated, moderately contaminated, moderately to heavily contaminated, heavily contaminated, heavily to extremely contaminated and extremely contaminated, respectively [33].

3.5.3. Potential ecological risk factor (PERF)

PERF is widely used to assess environmental response and ecological risks for heavy metal contamination in terms of time change [34]. PERF ($E_{\mathrm{f}}^{\mathrm{i}}$) is defined as:

$$E_{\mathrm{f}}^{\mathrm{i}} = T_{\mathrm{r}}^{\mathrm{i}}\left(\frac{C_S^i}{C_{bkg}^i}\right)$$

where $E_{\mathrm{f}}^{\mathrm{i}}$ equals to potential ecological risk factor for element i; $T_{\mathrm{r}}^{\mathrm{i}}$ is the toxic-response factor for element i (e.g., Cd=30, Cu=Pb=Ni=5, Cr=2, Zn=1); C_{S}^{i} and $C_{\mathrm{bkg}}^{\mathrm{i}}$ equal to the concentration of metal element i in sediment sample and background, respectively. Hakanson [25] divided PERI values into five classes as $ER<40$, $40\leq ER<80$, $80\leq ER<160$, $160\leq ER<320$ and $320\leq ER$, which indicate low risk, moderate risk, considerable risk, high risk and very high risk, respectively.

3. 6. Sediment quality guidelines for heavy metals

Numerical sediment quality guidelines (SQGs) have been used based on a variety of approaches which can be mainly categorized into empirical, frequency-based approaches and theoretically based approaches [35]. In this study, two widely used SQGs were chosen to assess biological effects of Gwangalli and Nakdong River .

The sediment quality criteria of USEPA sediment quality standards (USA) [36] and Ontario sediment quality guidelines (Canada) [37] were applied and both of them regard five metals (Cd, Cu, Ni, Pb and Zn) as parameters to assess contamination extent of marine sediment quality. The two criteria are classified into three tiers (Table 1).

Threshold effects level (TEL) and probable effects level (PEL) were employed as sediment quality guidelines due to its extensive availability. The concentration of the samples (Cs) compare with SQGs showing the three toxic level: Cs<TEL, TEL<Cs<PEL and Cs>PEL, which indicate non-toxic, toxic occasionally and toxic [35, 38].

Heavy metals occur in saltwater sediments as complex mixtures. To provide a useful tool for evaluating the potential biological risks of the presence of heavy metals, the mean quotients of each contaminant has been widely used. The formula [39] is:

$$\text{meanPELquotient} = \sum (C_x/PEL_x)/n$$

where C_x is the metal concentration of component x, PEL_x is the PEL value for element x and n is the sum of components. According to the research of Long [40], the mean PEL quotient resulted in four categories of toxicity: the mean PEL quotients less than 0.1 have an 8 % probability of being toxic, the mean PEL quotients between 0.11 to 1.5 have a 21 % probability of being toxic, the mean PEL quotients between 1.51 to 2.3 have a 49 % probability of being toxic, and the mean PEL quotients bigger than 2.3 have a 73 % probability of being toxic.

3. 7. Assessment of ecological risks for PAHs

Mean effects range-median quotient (M-ERM-Q) which firstly proposed by Long and MacDonald was used to assess the potential ecological risk of PAHs in ocean sediments [41]. M-ERM-Q has the advantages for analyzing complex mixtures of substances and the quantity is calculated as follows:

$$\mathrm{M\text{-}ERM\text{-}Q} = \frac{\sum (C_i / ERM_i)}{n}$$

where C_i is the concentration of PAH i in the sample, ERM_i is the ERM values for PAH i, and n is the sum of compounds. The mean ERM quotients are categorized into four degrees as M-ERM-Q < 0.1, 0.11⩽M-ERM-Q<0.5, 0.51⩽M-ERM-Q<1.5 and M-ERM-Q> 1.5, which represent low, medium-low, medium-high and high-priority sites, respectively.

3. 8. Sediment quality guidelines for PAHs

In our study, we compared our concentrations of PAHs with SQGs provided by Long [41]. PAH concentration were below the effect range low (ERL) value implies that the sediment PAHs do not adversely affect organisms, whereas PAH concentration was higher than the effect range median (ERM) value could cause frequent damage to the environment.

4. Results and discussion

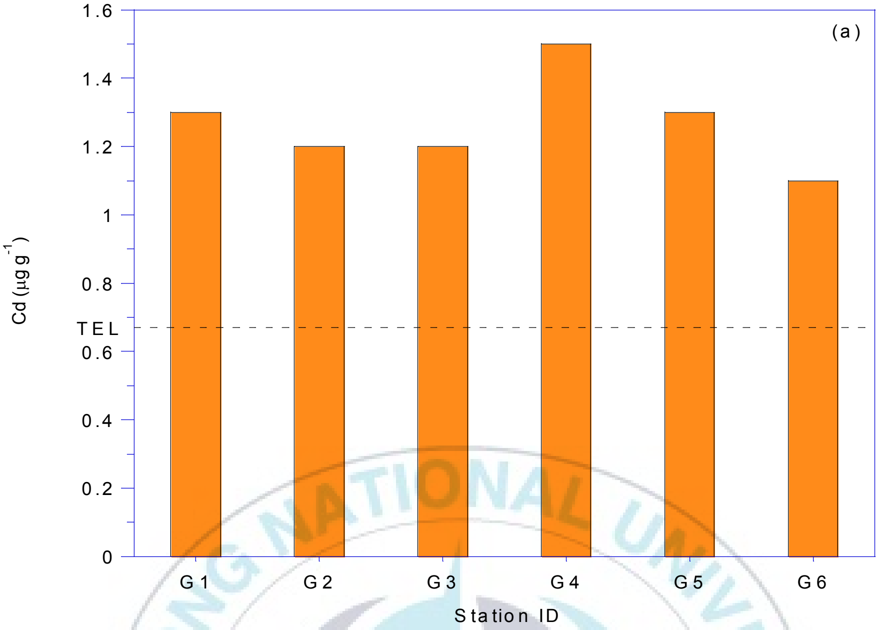
4. 1. Metal concentrations and compositions of Gwangalli sediments

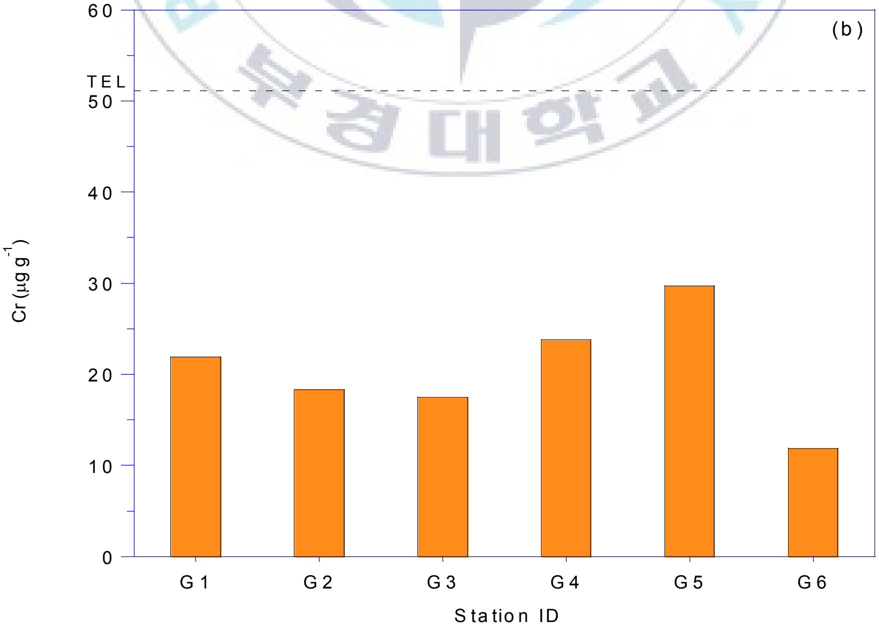
The 11 metal concentrations (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) from 14 sampling sites were measured and compared with values of the USEPA and Ontario sediment quality guidelines (Table 1). The range and mean concentrations (given in unit of mg/kg) of Cu, Pb, Ni, Mn, Zn, Cd, Co, Cr, As, Al and Fe in Gwangalli sediments were 7.9-20.8 (13.3), 15.3-31.6 (22.2), 10.2-21.3 (13.4), 194.5-407.6 (303.1), 57.1-154.4 (90.8), 1.1-1.5 (1.3), 4.6-9.3 (6.0), 11.9-29.7 (20.5), 3.1-6.7 (5.3), 6424.0-18390.0 (10780.2) and 9578.0-26790.0 (16294.7), respectively. Results indicated that greater fluctuation were found in Al, Fe, Mn and Zn, while other heavy metal ions showed a relatively stable trend among the different sampling sites. Same results also occurred in Nakdong river. Based on the mean concentration values, a desecending order can be found: Fe>Al>Mn>Zn>Pb>Cr>Ni>Cu>Co>As>Cd. In Gwangalli, the highest concentrations of Fe, Al, Mn, Cr, Ni, Cu, Co and As were all found in site G5, whereas site G6 showed the lowest concentrations of all metal ions except Mn.

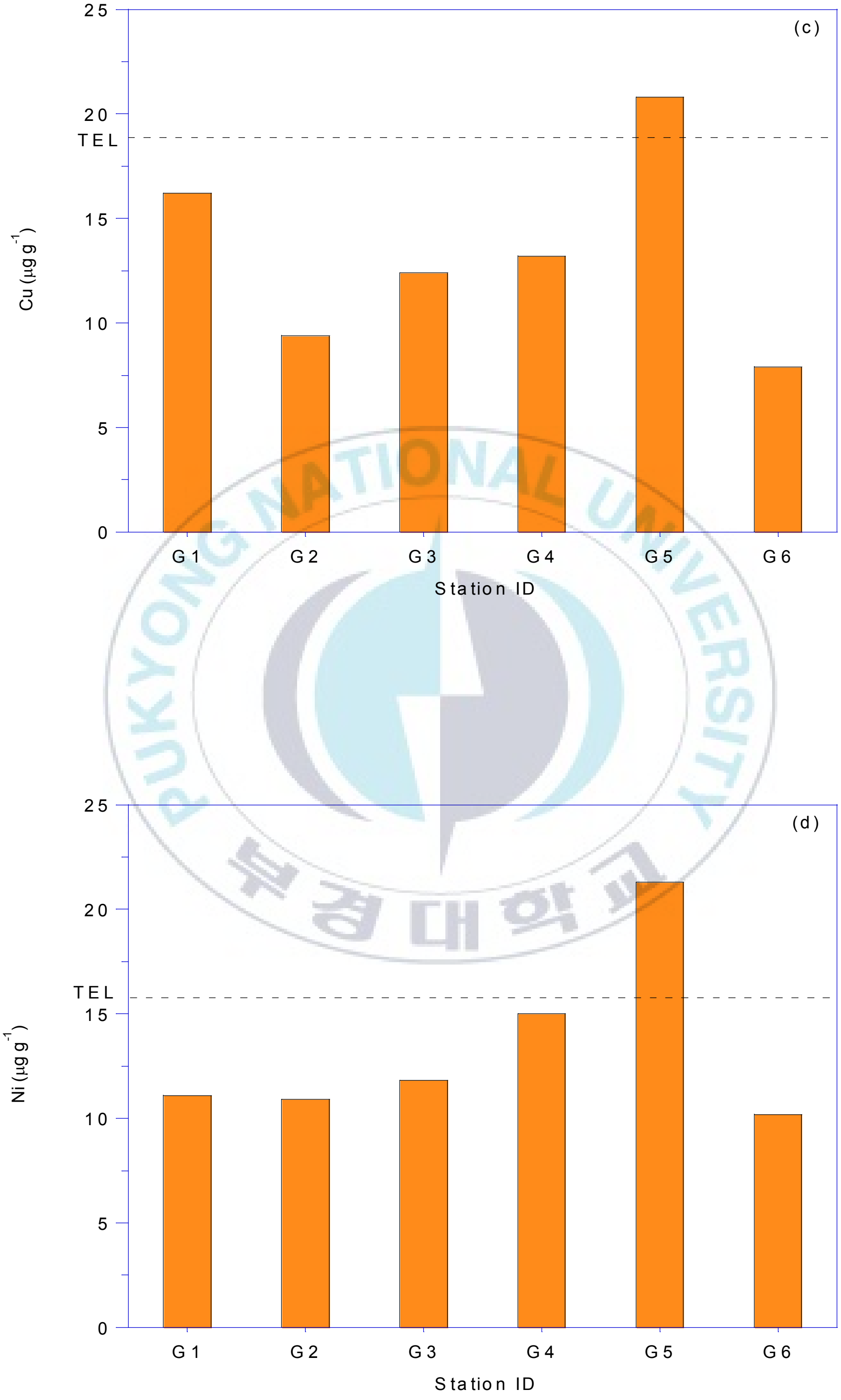
Table 1. Concentrations of heavy metals (mg/kg) in sediments and pollution criteria proposed by USEPA and Canada. G (1-6) and N (1-8) represent sampling sites in total of 14 in Gwangalli and Nakdong River, respectively.

		Cu	Pb	Ni	Mn	Zn	Cd	Co	Cr	As	Al	Fe	Ignition loss (wt,%)
USEPA sediment quality standards	Non polluted	<25	<40	<20	-	<90	-	-	-	-	-	-	<5
	Moderately polluted	25～50	40～60	20～50	-	90～200	-	-	-	-	-	-	5～8
	Heavily polluted	>50	>60	>50	-	>200	>8	-	-	-	-	-	>8
Ontario sediment quality guidelines	No effect level	-	-	-	-	-	-	-	-	-	-	-	-
	Lowest effect level	166	31	16	-	120	0.6	-	-	-	-	-	-
	Severe effect level	110	250	75	-	820	10	-	-	-	-	-	-
Sediment samples	N1	11.4	14.6	15.2	412.2	73.9	1.6	9.3	26.4	5.9	13520	23870	3.40
	N2	3.4	10.4	9.0	259.7	45.8	1.4	5.9	12.7	3.6	6616	10840	2.97
	N3	11.6	16.3	15.9	438.6	70.3	1.5	8.7	25.3	6.4	16030	23910	6.63
	N4	10.5	15.6	16.7	361.8	70.3	1.5	9.4	26.5	5.5	15880	23830	5.45
	N5	0.9	5.8	5.5	83.9	19.0	1.3	2.6	8.6	1.8	3560	5187	6.04
	N6	0.2	5.4	4.6	63.1	15.5	1.2	2.2	6.3	1.9	2616	3712	6.54
	N7	3.3	11.0	9.2	193.0	42.8	1.2	5.2	9.0	2.7	5220	6497	8.39
	N8	8.9	14.5	15.0	235.0	55.4	1.3	7.0	22.8	4.8	13260	18470	7.13
	G1	16.2	22.9	11.1	194.5	79.4	1.3	4.7	21.9	5.3	9344	13300	7.71
	G2	9.4	17.3	10.9	341.6	61.7	1.2	5.1	18.3	6.4	9086	14080	4.63
	G3	12.4	19.4	11.8	273.9	78.6	1.2	5.4	17.5	4.2	9327	14680	9.95
	G4	13.2	31.6	15.0	380.1	154.4	1.5	7.0	23.8	6.1	12110	19340	5.95
	G5	20.8	26.9	21.3	407.6	113.5	1.3	9.3	29.7	6.7	18390	26790	8.40
	G6	7.9	15.3	10.2	220.8	57.1	1.1	4.6	11.9	3.1	6424	9578	7.76

Compared with the USEPA and Ontario (Canada) sediment quality guidelines (Table 1), the concentrations of five heavy metal ions (Cd, Cu, Ni, Zn and Pb) were all below the third levels of standards. Meanwhile, Cu and Pb were non polluted in all sampling sites, whereas Ni in sampling site G5 and Zn in G4 and G5 were moderately polluted according to USEPA standard. The concentrations of Cd were between the lowest effect to severe effect level comparing with Ontario sediment quality guidelines. The data also compared with TEL and PEL sediment quality guidelines as illustrated in Fig 2. Six heavy metal ions (Cd, Cr, Cu, Ni, Pb and Zn) were all below corresponding PEL values which meant a good condition in Gwangalli sedimentary environment. Particularly, the concentration of Cr in all sites were also lower than TEL guideline. In case of other metals (Cu, Ni, Pb and Zn) in Gwangalli, 83.3% of sites were lower than TEL standard for them. Concentrations of Cd, however, exceeded the TEL guideline in all sites, which was in consistence with Ontario standard.


(a)
Cd (µg g^{-1})
1.6
1.4
1.2
1
0.8
TEL
0.6
0.4
0.2
0
G1
G2
G3
G4
G5
G6
Station ID


(b)
Cr (µg g^{-1})
60
TEL
50
40
30
20
10
0
G1
G2
G3
G4
G5
G6
Station ID


(c)
Cu (μg g^{-1})
25
20
TEL
15
10
5
0
G1
G2
G3
G4
G5
G6
Station ID
(d)
Ni (μg g^{-1})
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20
TEL
15
10
5
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G4
G5
G6
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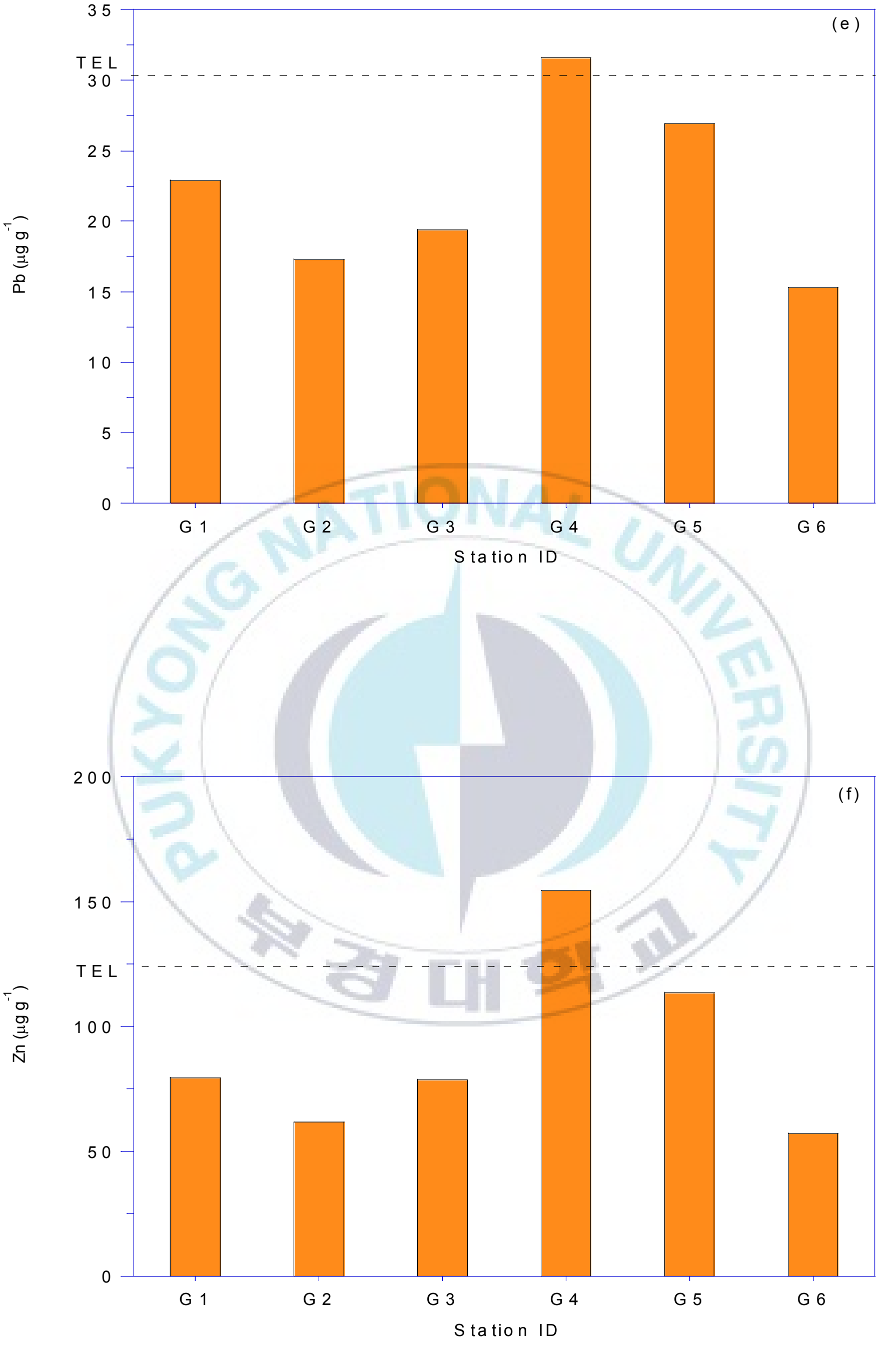


Fig. 2. The concentrations of heavy metals in sediments of Gwangalli for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f) (where G1~G6 denote sampling sites). The horizontal dash lines represent their corresponding TEL.

The related values for adjacent areas in Korea and other countries were shown in Table 4. The mean concentrations of Cd in Gwangalli were relatively higher than other studies listed. Other five metals of mean concentrations were all far below the values of South Busan Fishery Harbor and Red River in Vietnam. Compared with the average UCC values (Table 3), the mean concentrations of Cd, Pb and Zn were clearly higher than the related UCC values; the mean total content of Pb was close to it, whereas the mean concentrations of Cr and Cu were below the corresponding average UCC values.

The results of oxides and ignition loss of all sediments collected from studying areas were shown in Table 2. Based on that, the main composition of sediments in Gwangalli were SiO_2, Al_2O_3, CaO, Fe_2O_3,K_2O, MgO, Na_2O and Cl, which counted for more than 95%. As for ignition loss, only sampling site G2 was non polluted; half of the sampling sites were moderately polluted and sites (G3 and G5) were heavily polluted, which suggested much existence of organic compounds in surface sediments in Gwangalli.

Table 2. Results of oxides and ignition loss of sediments collected from Gwangalli and Nakdonggang Estuary (wt, %).

Sampling sites	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	Cl	SO_3	TiO_2	P_2O_5	MnO	SrO	Ignition loss
G-1	56.63	16.21	8.23	5.89	3.74	2.86	1.88	1.66	1.61	0.91	0.28	0.10	-	7.71
G-2	55.01	15.48	9.80	5.38	3.75	3.23	2.46	2.37	1.18	0.90	0.32	0.11	-	4.63
G-3	47.10	12.67	13.16	4.28	3.51	2.40	7.92	6.69	1.31	0.69	0.19	-	0.08	9.95
G-4	55.59	14.85	11.24	5.45	3.93	2.73	2.11	1.89	0.96	0.86	0.27	0.12	-	5.95
G-5	37.46	10.75	6.04	4.88	3.19	2.22	18.42	15.34	0.77	0.68	0.15	0.09	-	8.40
G-6	55.23	16.22	8.72	5.91	4.26	3.07	2.16	2.26	0.97	0.81	0.28	0.12	-	7.76
N-1	62.22	16.14	2.87	5.39	4.56	2.67	2.53	1.71	0.60	0.95	0.25	0.11	-	3.40
N-2	63.14	16.78	2.63	4.94	4.33	2.48	2.68	1.22	0.54	0.93	0.22	0.10	-	2.97
N-3	61.67	16.61	3.14	5.85	4.07	2.83	1.92	1.90	0.70	0.89	0.30	0.13	-	6.63
N-4	61.78	16.92	3.17	5.62	4.30	2.82	2.14	1.53	0.55	0.85	0.23	0.09	-	5.45
N-5	60.97	17.28	3.13	5.59	4.26	2.60	2.32	1.85	0.72	0.91	0.25	0.11	-	6.04
N-6	60.08	17.32	3.44	5.91	4.23	2.84	2.34	1.80	0.81	0.98	0.24	-	-	6.54
N-7	57.56	17.72	4.24	6.32	4.46	3.33	2.57	2.08	0.70	0.90	-	0.11	-	8.39
N-8	59.96	17.69	3.71	5.76	4.24	2.91	2.24	1.49	0.87	0.85	0.20	0.09	-	7.13

Table 3. Two different metal guideline values, the average upper continental crust (UCC) values and the results of indices of enrichment factor, geoaccumulation and potential ecological risk factor for samples obtained from Gwangalli and Nakdong River. Content unit is mg kg^{-1} for guideline values below.

Sediment quality guidelines		Cd			Cr			Cu			Ni			Pb			Zn			Reference
TEL guideline		0.68			52.3			18.7			15.9			30.2			124			[38]
PEL guideline		4.2			160			108			42.8			112			271			[38]
UCC		0.098			35			25			20			20			71			[27]
Index of I_{geo}, EF and PERF		I_{geo}	EF	PERF	I_{geo}	EF	PERF	I_{geo}	EF	PERF	I_{geo}	EF	PERF	I_{geo}	EF	PERF	I_{geo}	EF	PERF	Total enrichment factor(R)
Sediment samples	N1	1.30	2.69	110.77	0.58	1.25	4.50	-1.04	-0.27	3.64	-0.65	-0.04	4.78	-0.23	0.28	6.40	-0.01	0.49	1.49	4.40
	N2	1.11	2.23	96.92	-0.47	0.08	2.16	-2.79	-0.78	1.09	-1.41	-0.43	2.83	-0.72	-0.09	4.56	-0.70	-0.07	0.93	0.93
	N3	1.21	2.46	103.85	0.52	1.16	4.31	-1.02	-0.26	3.70	-0.58	0.00	5.00	-0.07	0.43	7.15	-0.08	0.42	1.42	4.21
	N4	1.21	2.46	103.85	0.59	1.26	4.52	-1.16	-0.33	3.35	-0.51	0.05	5.25	-0.13	0.37	6.84	-0.08	0.42	1.42	4.23
	N5	1.00	2.00	90.00	-1.03	-0.27	1.47	-4.71	-0.94	0.29	-2.12	-0.65	1.73	-1.56	-0.49	2.54	-1.97	-0.62	0.38	-0.97
	N6	0.88	1.77	83.08	-1.48	-0.46	1.07	-6.88	-0.99	0.06	-2.37	-0.71	1.45	-1.66	-0.53	2.37	-2.26	-0.69	0.31	-1.60
	N7	0.88	1.77	83.08	-0.97	-0.23	1.53	-2.83	-0.79	1.05	-1.37	-0.42	2.89	-0.64	-0.04	4.82	-0.79	-0.14	0.86	0.16
	N8	1.00	2.00	90.00	0.37	0.94	3.89	-1.40	-0.43	2.84	-0.67	-0.06	4.72	-0.24	0.27	6.36	-0.42	0.12	1.12	2.85
	G1	1.00	2.00	90.00	0.32	0.87	3.73	-0.54	0.03	5.17	-1.10	-0.30	3.49	0.42	1.01	10.04	0.10	0.60	1.60	4.21
	G2	0.88	1.77	83.08	0.06	0.56	3.12	-1.32	-0.40	3.00	-1.13	-0.31	3.43	0.02	0.52	7.59	-0.27	0.25	1.25	2.38
	G3	0.88	1.77	83.08	-0.01	0.49	2.98	-0.92	-0.21	3.96	-1.02	-0.26	3.71	0.18	0.70	8.51	0.08	0.59	1.59	3.08
	G4	1.21	2.46	103.85	0.44	1.03	4.06	-0.83	-0.16	4.21	-0.67	-0.06	4.72	0.89	1.77	13.86	1.06	2.12	3.12	7.17
	G5	1.00	2.00	90.00	0.75	1.53	5.06	-0.18	0.33	6.64	-0.16	0.34	6.70	0.65	1.36	11.80	0.61	1.29	2.29	6.85
	G6	0.76	1.54	76.15	-0.56	0.01	2.03	-1.57	-0.50	2.52	-1.23	-0.36	3.21	-0.16	0.34	6.71	-0.38	0.15	1.15	1.19

Table 4. The range and mean concentrations of heavy metals in surface sediments from Gwangalli and Nakdong River; and the related values (mg kg^{-1} d.w.) from adjacent areas in Korea and other countries.

Location	Sampling date		Cd	Cr	Cu	Ni	Pb	Zn	References
Gwangalli, Korea	Sep. 2017	Range	1.1-1.5	11.9-29.7	7.9-20.8	10.2-21.3	15.3-31.6	57.1-154.4	Present study
		Mean	1.3	20.5	13.3	13.4	22.2	90.8	
Nakdong River, Korea	Sep. 2017	Range	1.2-1.6	6.3-26.5	0.2-11.6	4.6-16.7	5.4-16.3	15.5-73.9	Present study
		Mean	1.4	17.2	6.3	11.4	11.7	49.1	
Masan Bay, Korea	Aug.2010- Aug. 2011		0.01-2.15	-	21.6-113.9	15.5-46.6	29.0-82.5	95.2-443.4	[46]
			0.66	-	53.3	32.4	48.4	218.3	
Nakdong River, Korea	Mar. 2013		-	14.7-62.2	3.6-20.3	4.0-19.1	11.7-24.7	44.4-182.6	[45]
			-	32.8	9.4	10.3	15.6	81.7	
South Busan fishery harbor, Korea	2004-2006		0.15-2.51	37.5-401.0	18-2360	16.4-82.2	26-374	117-1940	[47]
			1.33	124	629	35.2	180	788	
Central Bohai Sea, China	2006-2011		0.08–0.24	30.68–100.19	2.60–49.33	13.63–131.96	14.54–59.42	27.47–148.76	[48]
			0.14	61.45	24.34	35.88	30.69	79.91	
East China Sea	Nov. 2006		-	-	4.30–42.0	8.20–49.0	10.0–49.0	18.0–114	[49]
			-	-	15	26	27	60	
Jiaozhou Bay, China	May. 2015		0.24–0.43	51.36–107.00	13.42–54.08	17.01–44.94	26.60–44.83	44.53–131.76	[51]
			0.3	86.17	27.31	32.35	38.54	76	
Red River, Vietnam	2007-2015		0.06–1.40	23.88–113.08	20–332	12–122	27–188	40–287	[50]
			0.35	85.71	83	38	66	127	
Jade Bay, Germany	2009-2010		-	-	-	-	-	-	[52]
			0.25	49	7	10	16	43	

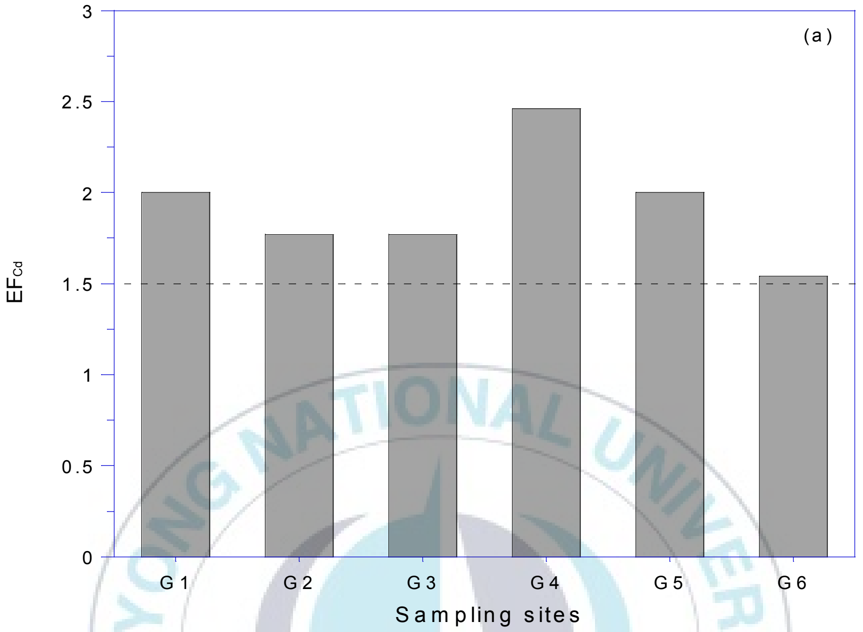
4. 2. Risk assessment according to multiple indices for metals in surface sediments of Gwangalli

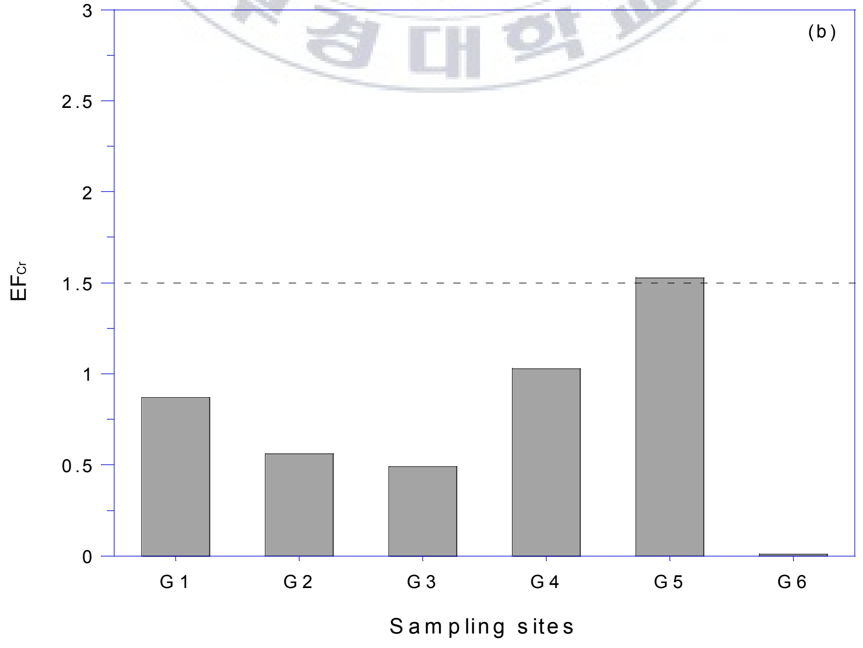
The spatial distribution of multiple indices were calculated and summarized in Table 3 and Fig 3-5. For EF values, the results suggested that Cu and Ni were no enrichment in Gwangalli area, whereas Cd indicated there was minor enrichment. Also, the highest EF value (2.46) occurred in site G4 for metal of Cd. EF values higher than 1.5 suggesting the source of the given metals were likely to be derived from human activities according to other study [42]. Generally, most of the stations were no metal enrichment or just slightly enrichment, which showed a good condition in sedimentary environment of Gwangalli.

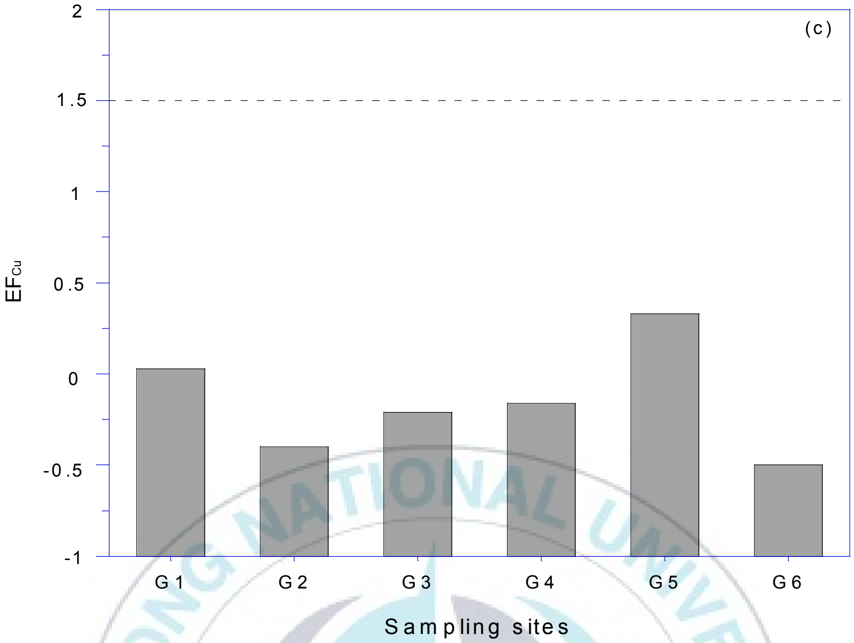
The calculated I_{geo} values for each site were shown in Fig 4. Most of the sampling sites in Gwangalli were practically uncontaminated and uncontaminated to moderately contaminated. Only stations of G4 for Cd (1.21) and Zn (1.06) reached moderately to heavily contaminated level. The results indicated that Cu and Ni were in uncontaminated level in Gwangalli area and more than half of the sampling sites of Cd, Cr and Pb were likely to be moderately polluted.

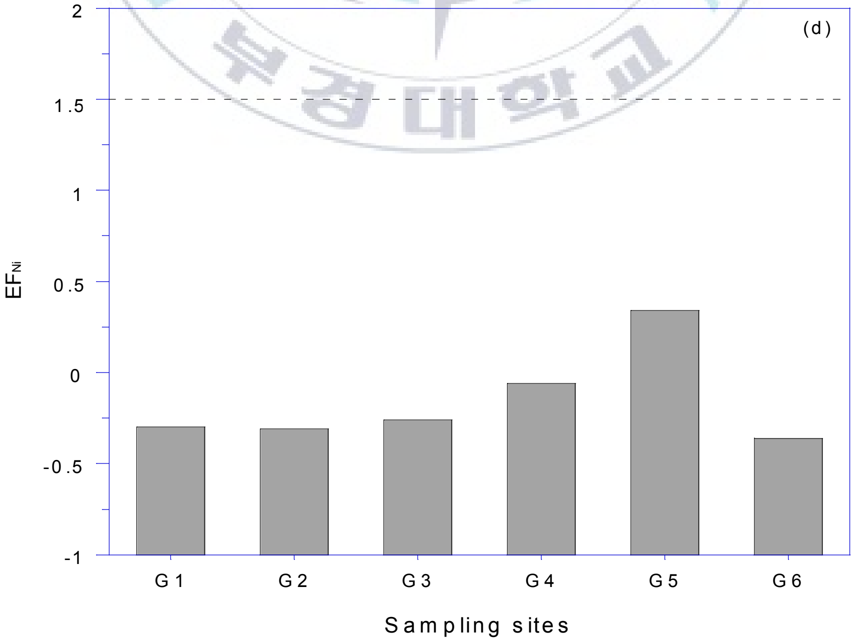
The PERF values in all sampling sites were shown in Fig 5. Compared with the referred PERF levels, the PERF values of all six metals were below 40 in Gwangalli area except metal of Cd, which means a low potential ecological risks. However, Cd posed a considerable risk in G1-G5 and moderate risk in G6.

The mean PEL quotient values from studying areas were listed in Fig 6. In the surface sediments of Gwangalli, the total content of six heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in all sites might have a 21 % probability of being toxic. The calculated mean values of EF, I_{geo}, PERF and metal concentrations in total for six metals were summarized in Fig 7. Based on that, it was clear that Cd posed the highest contamination degree in Gwangalli, whereas Cu and Ni were in good conditions comparing with other four metals. The mean values of EF followed the similar trend with I_{geo} and total metal concentrations, while the PERF values were inconsistent with them. The reasons might caused by calculation methods. For instance, the EF and I_{geo} values were calculated based on the background reference values; meanwhile for PERF, the toxic-response factor counted for a large proportion. Thus, not a single assessment method could sufficiently predict or analyze environmental risk in a certain area. A comprehensive combination methods and come with various tests are more precision and accurate.


(a)
EF$_{Cd}$
3
2.5
2
1.5
1
0.5
0
G1
G2
G3
G4
G5
G6
Sampling sites


(b)
EF$_{Cr}$
3
2.5
2
1.5
1
0.5
0
G1
G2
G3
G4
G5
G6
Sampling sites


(c)
EF$_{Cu}$
2
1.5
1
0.5
0
-0.5
-1
G1
G2
G3
G4
G5
G6
Sampling sites


(d)
EF$_{Ni}$
2
1.5
1
0.5
0
-0.5
-1
G1
G2
G3
G4
G5
G6
Sampling sites

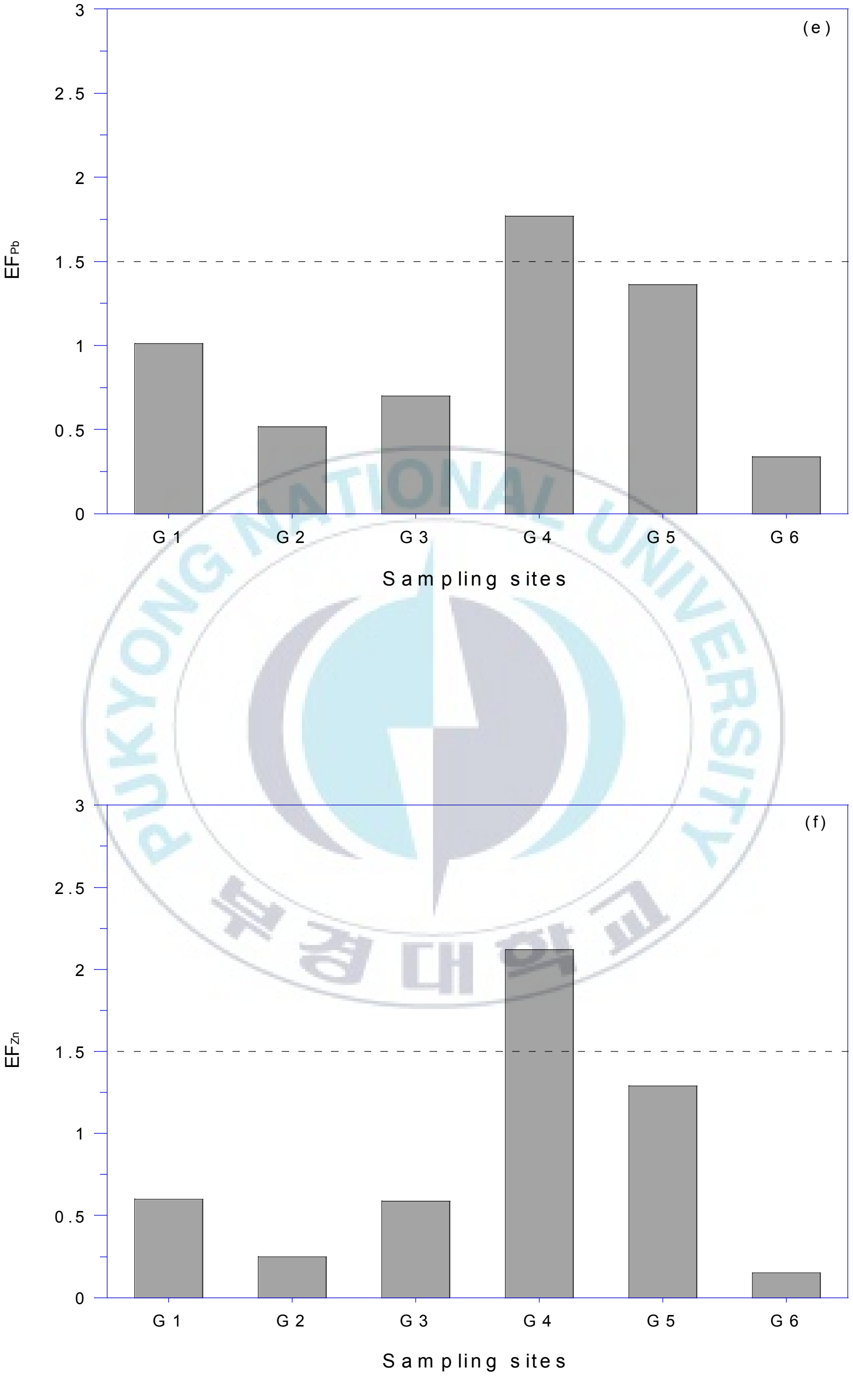
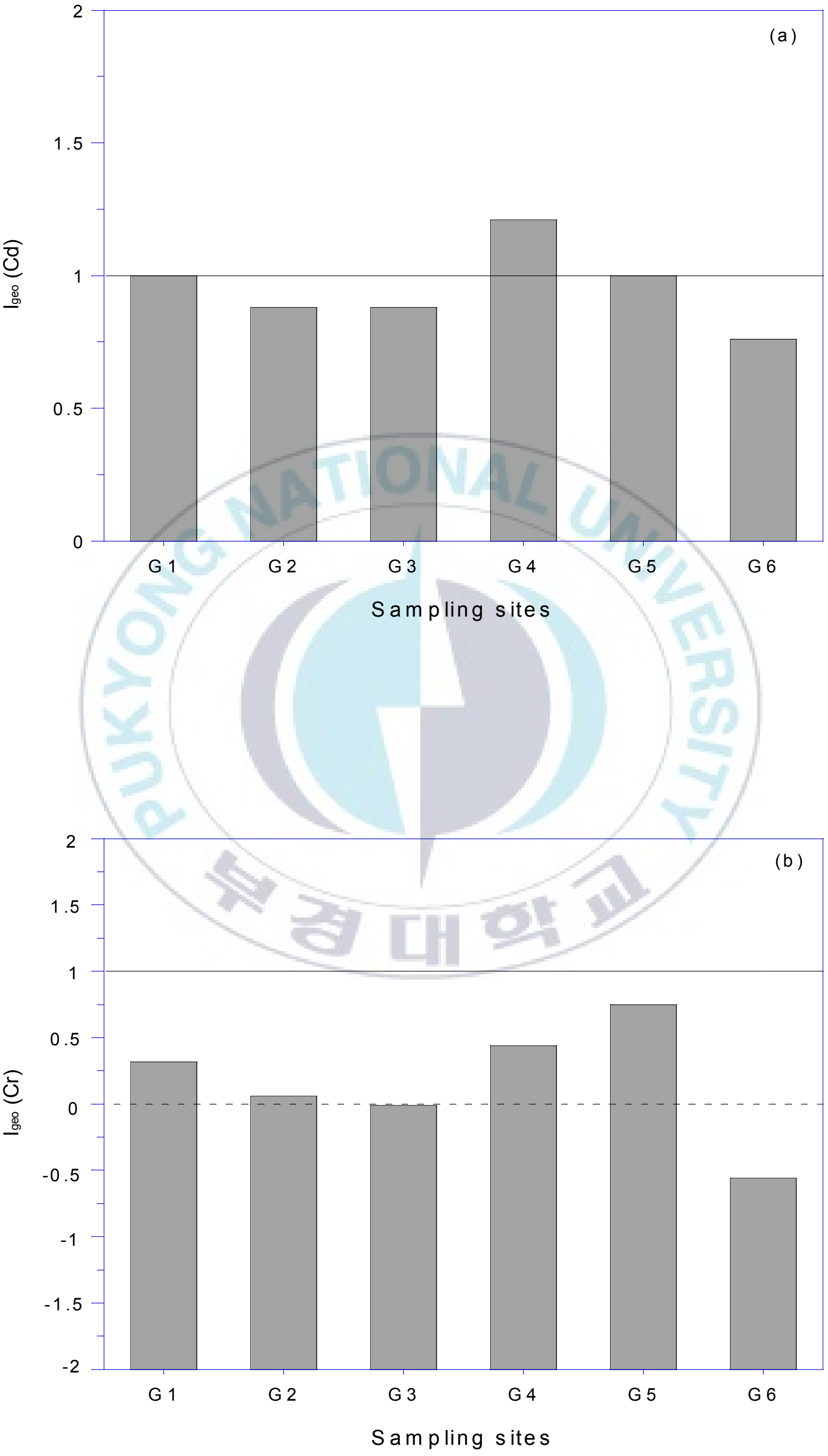
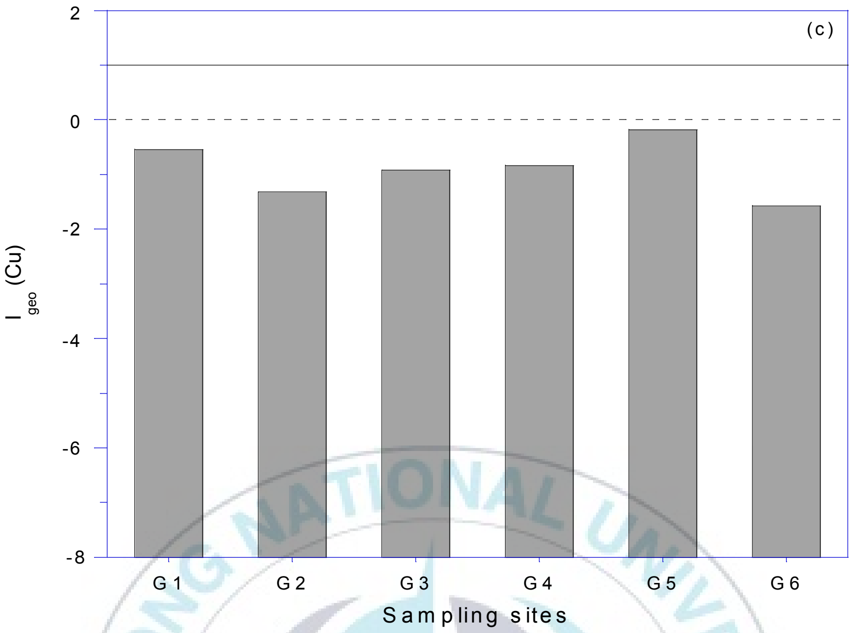
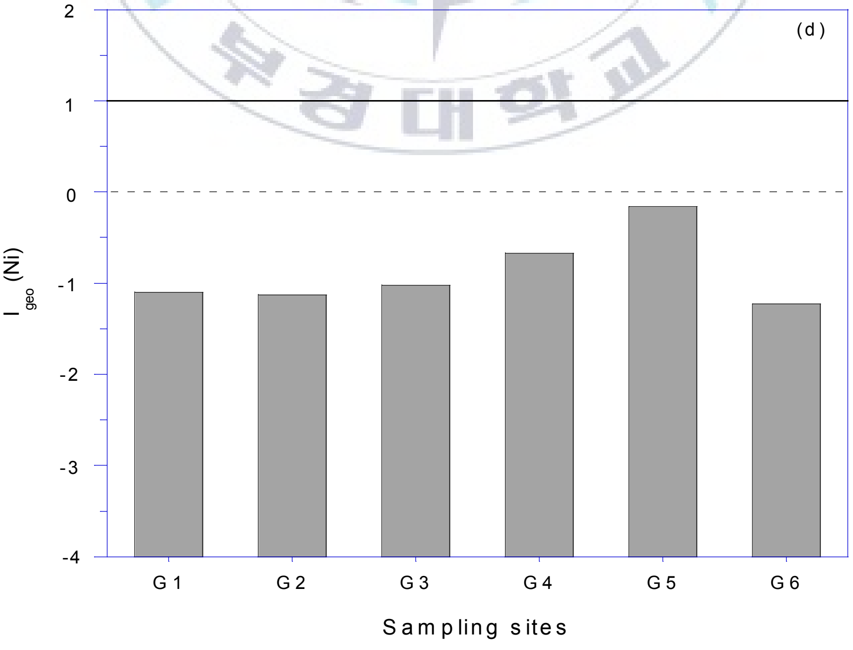


Fig. 3. The EF values of 6 sampling sites from Gwangalli for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f). The horizontal dash line represent 1.5 of EF value.


2
1.5
1
0.5
0
(a)
I_{geo} (Cd)
G1
G2
G3
G4
G5
G6
Sampling sites
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
(b)
I_{geo} (Cr)
G1
G2
G3
G4
G5
G6
Sampling sites


(c)
2
0
-2
-4
-6
-8
I_geo (Cu)
G1
G2
G3
G4
G5
G6
Sampling sites


(d)
2
1
0
-1
-2
-3
-4
I_geo (Ni)
G1
G2
G3
G4
G5
G6
Sampling sites

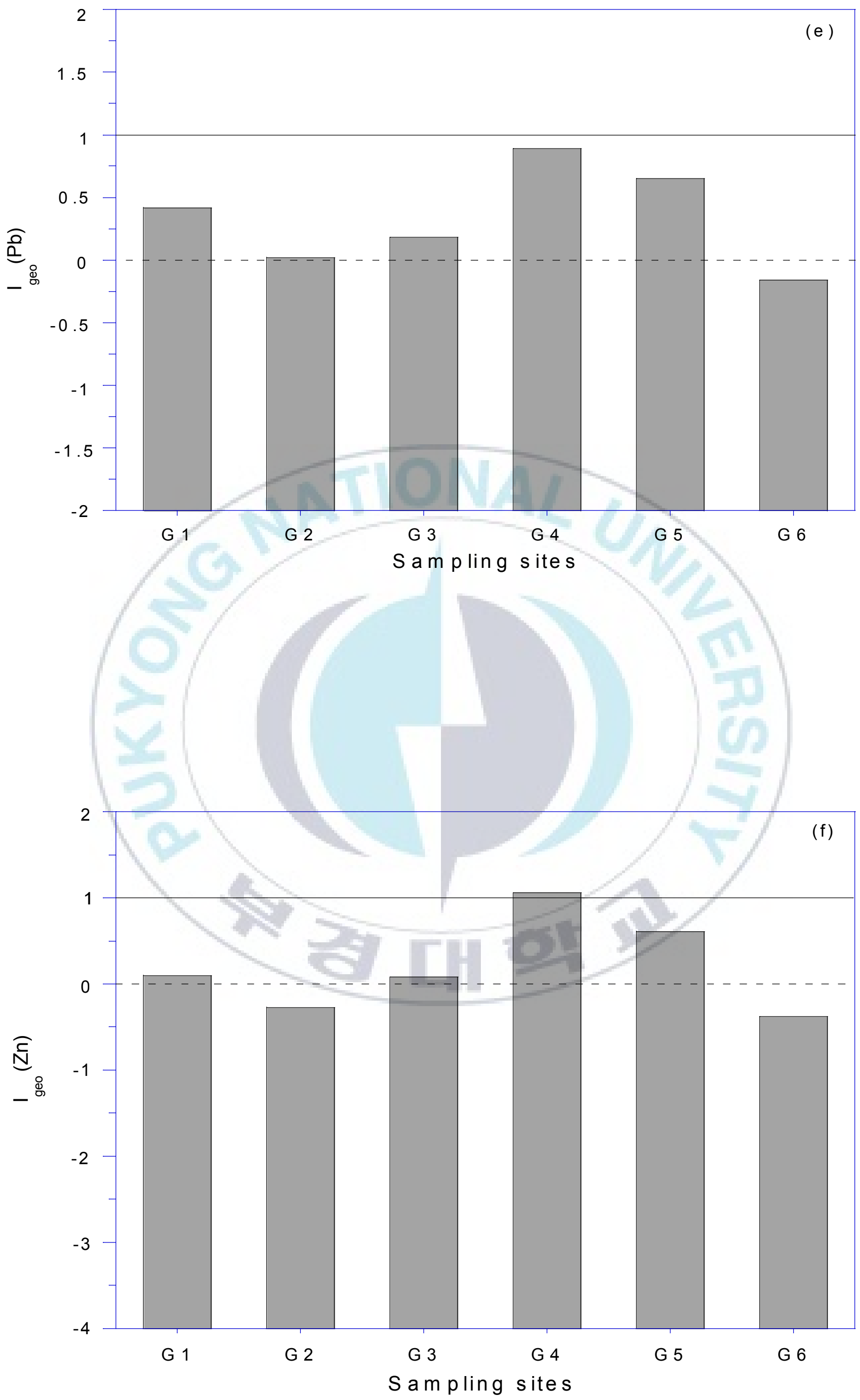
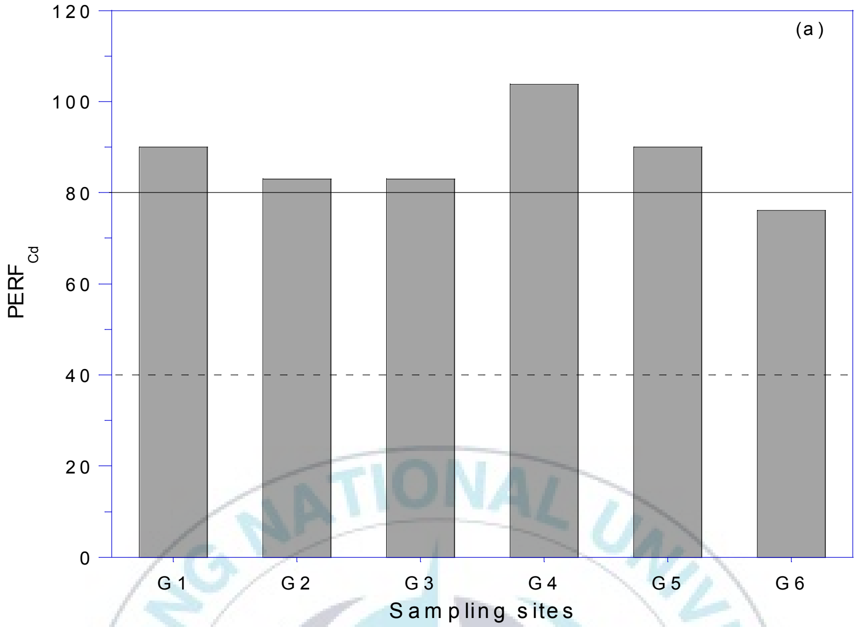
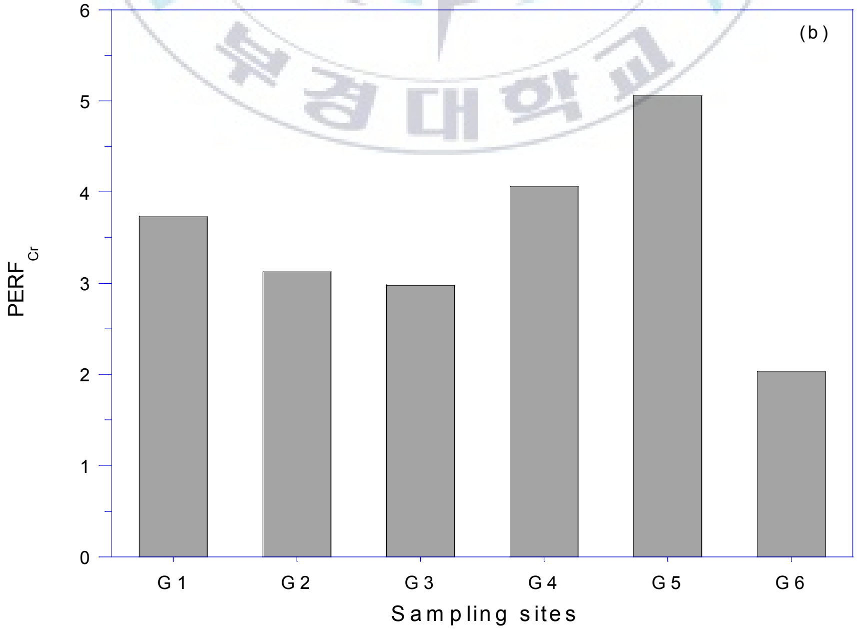
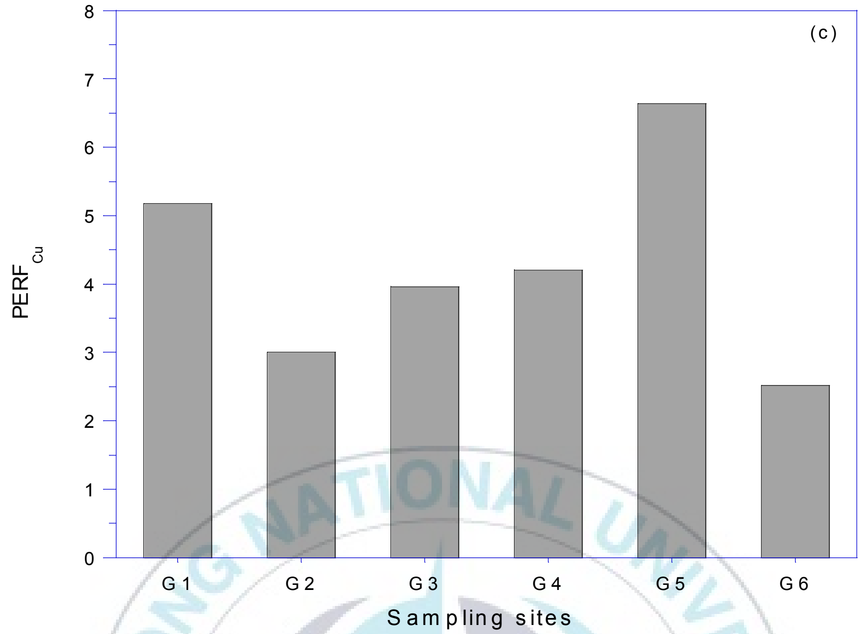
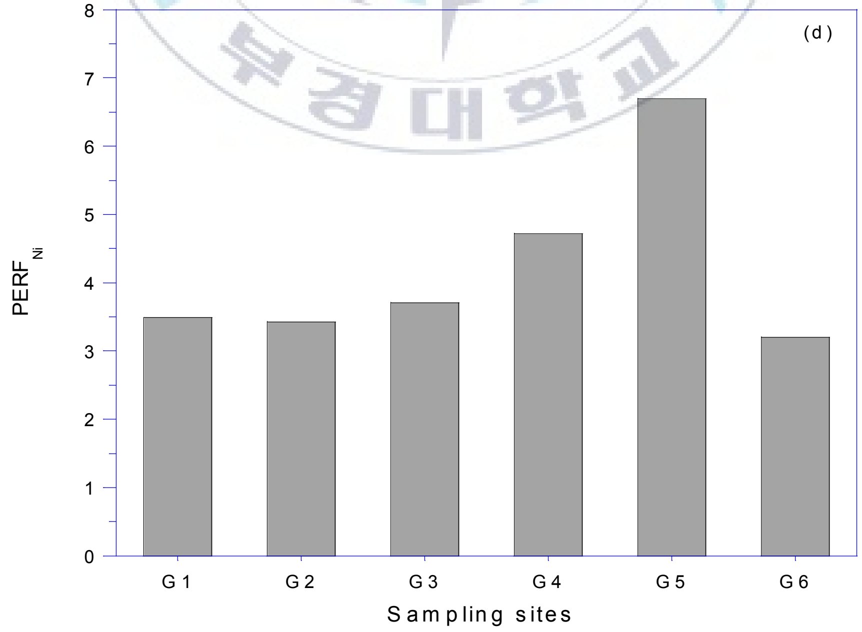


Fig. 4. The Igeo values of 6 sampling sites from Gwangalli for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f). The horizontal solid and dash line represent 1 and 0 of PERF values, respectively.


(a)
PERF$_{Cd}$
120
100
80
60
40
20
0
G1
G2
G3
G4
G5
G6
Sampling sites


(b)
PERF$_{Cr}$
6
5
4
3
2
1
0
G1
G2
G3
G4
G5
G6
Sampling sites


(c)
PERF$_{Cu}$
0
1
2
3
4
5
6
7
8
G 1
G 2
G 3
G 4
G 5
G 6
Sampling sites


(d)
PERF$_{Ni}$
0
1
2
3
4
5
6
7
8
G 1
G 2
G 3
G 4
G 5
G 6
Sampling sites

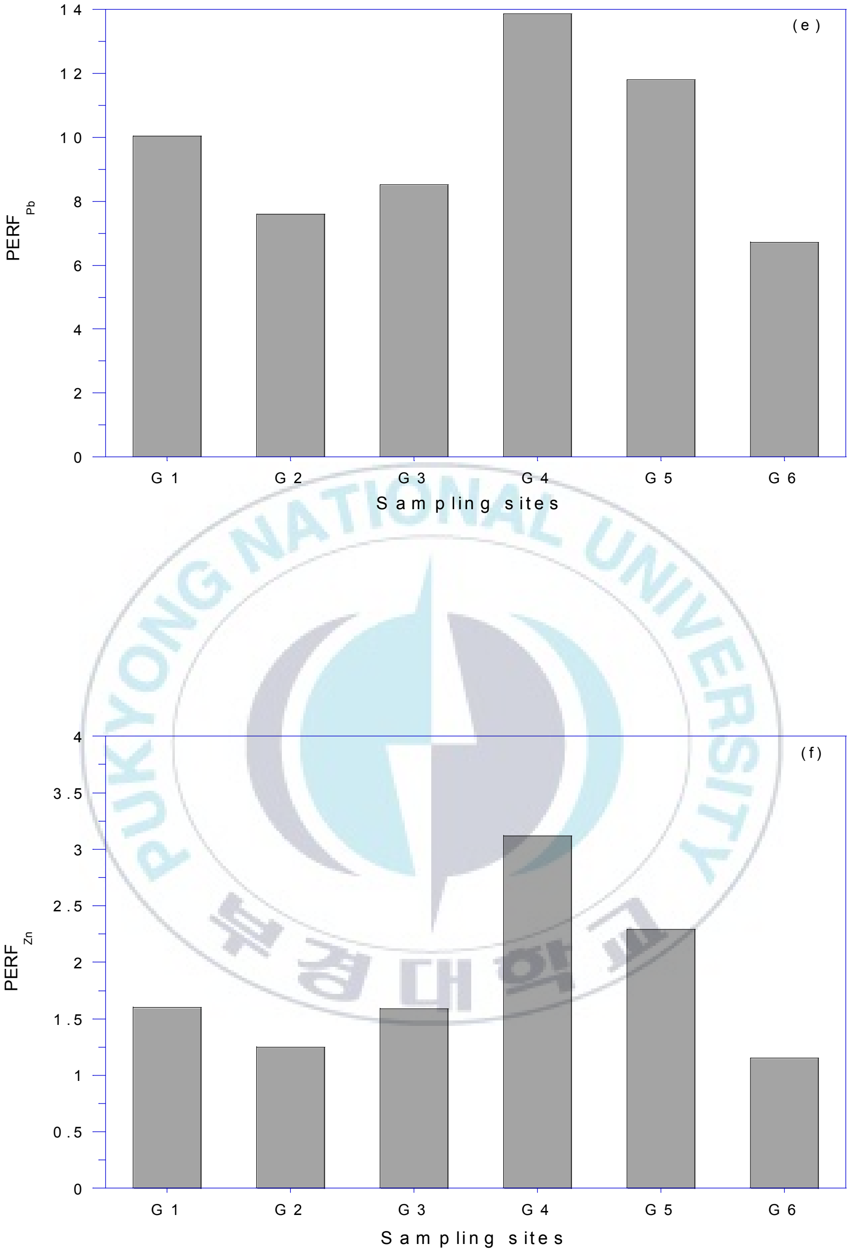


Fig. 5. The distribution of PERF values in Gwangalli sampling sites for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f). The histogram showed the PERF values for heavy metals in sediments of Gwangalli. The horizontal solid and dash line mean the PERF values of 40 and 80, respectively.

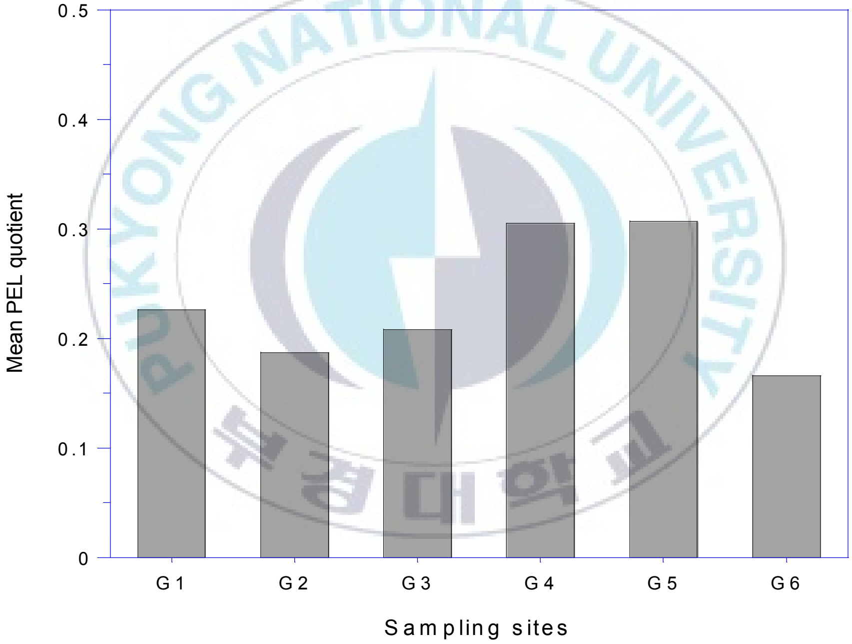


Fig. 6. The mean PEL quotient values in the surface sediments from Gwangalli.

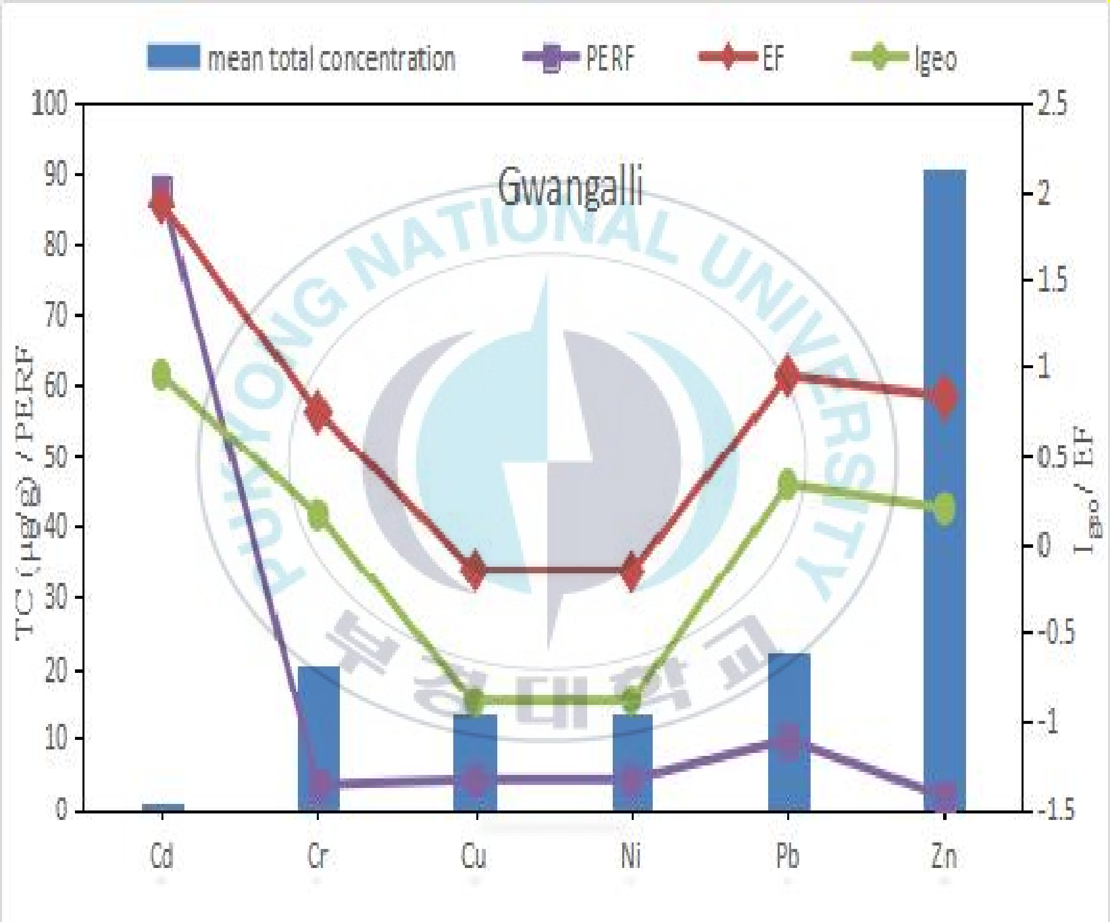


Fig. 7. The mean values of EF, Igeo, PERF and total concentration for metals in Gwangalli.

4. 3. The total concentrations of PAHs in Gwangalli

Total concentrations of 16 PAHs in surface sediments from Gwangalli were shown in Fig 8. The total concentrations ranged from 592.0 to 2570.3 ng g^{-1} dw with a mean value of 1213.1 ng g^{-1} dw. The highest values of total concentrations appeared in site G2 (2570.3 ng g^{-1} dw) followed by G1 (1272.3 ng g^{-1} dw) where only 7 PAH compounds were found, whereas the lowest one was shown in site G2 (592.0 ng g^{-1} dw). The sampling sites were near inshore area where anthropogenic activities may obviously influence the PAHs pollution. The total concentrations of 16 PAHs in Gwangalli followed in this descending order: G2>G1>G6>G5>G3>G4. Each concentration value of 16 PAHs in Gwangalli were shown in Table 5 and Fig 10. Based on that, Acys and Aces were not found in studying area, Baps were only found in site G2, Naps, Pyrs, BaAs, Chrs, BkFs, Dacs and BgPs were all present in the sediments. Mean values of 16 PAHs exhibited in following order: BaP>Dac>Nap>Inp>BgP>BbF>BaA>Chr>BkF>Pyr>Fla>Phe>Ant>Flu>Acy, Ace.

The ratio of ring size for 16 PAHs in surface sediments from Gwangalli were shown in Fig 9. The composition of PAHs in Gwangalli were mainly 2-ring and 5-ring compounds, which was similar as studies found by Liu [43]. 2-ring PAHs accounted for 52.51 % in site G6. 5-ring PAHs accounted for 51.20 %, 41.41 %, 37.90 %, 40.74 % and 35.58 % in sites G1 to G5, respectively. Meanwhile, 3-ring PAHs compounds contribute the lowest proportions in all sites, which were 0.00 %, 4.47 %, 8.23 %, 8.62 %, 7.35 % and 5.20 % in sites G1 to G6, respectively.

Compared with the sediment quality guidelines (Table 5), most of the concentrations of PAHs

(Fig 10) were below the median effect range except Dacs in sampling sites G1 and G2. Meanwhile, concentrations of Naps in G5 and G6, BaAs in G2 and Dacs in sites G3 to G6 were between effect range low to effect range median. Other PAHs showed a relatively low values in studying areas.

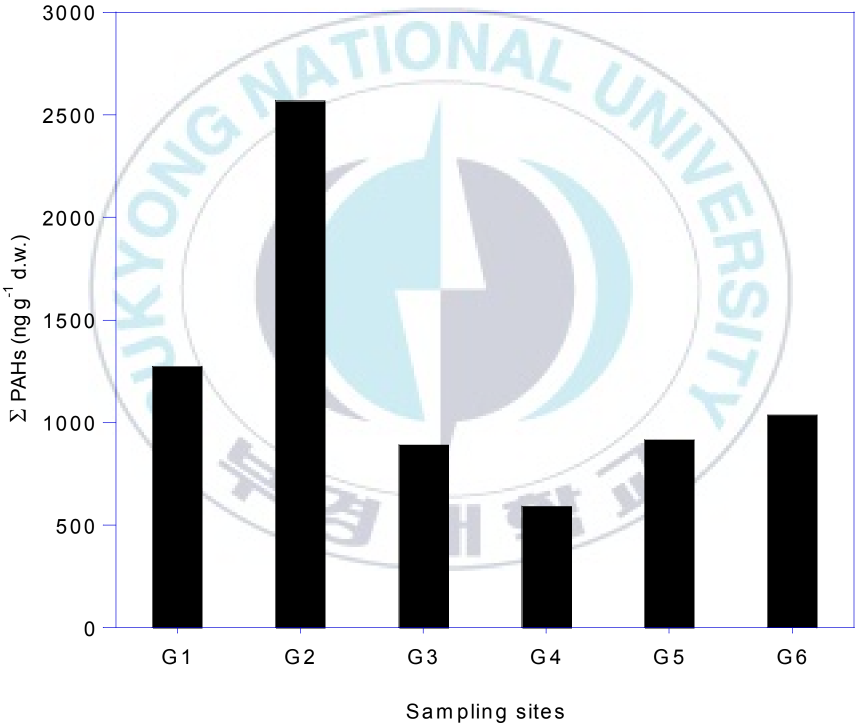


Fig. 8. Total 16 PAHs concentrations in the sediments from Gwangalli.

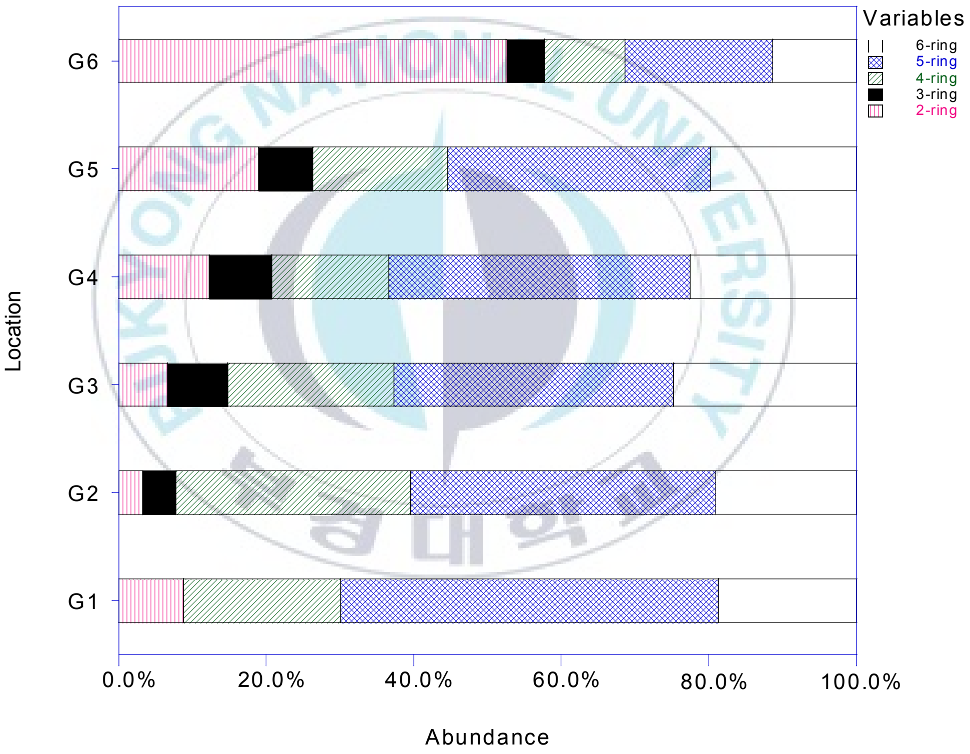
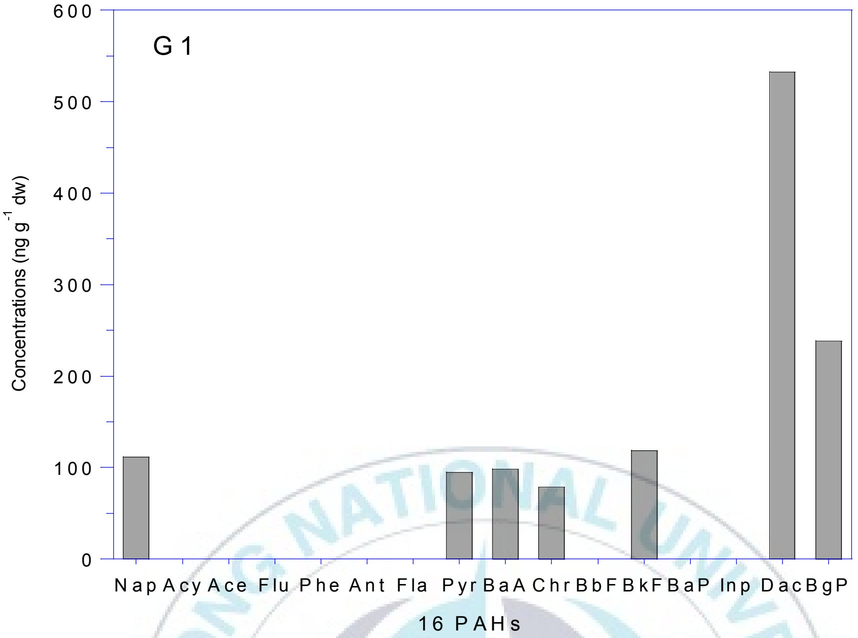
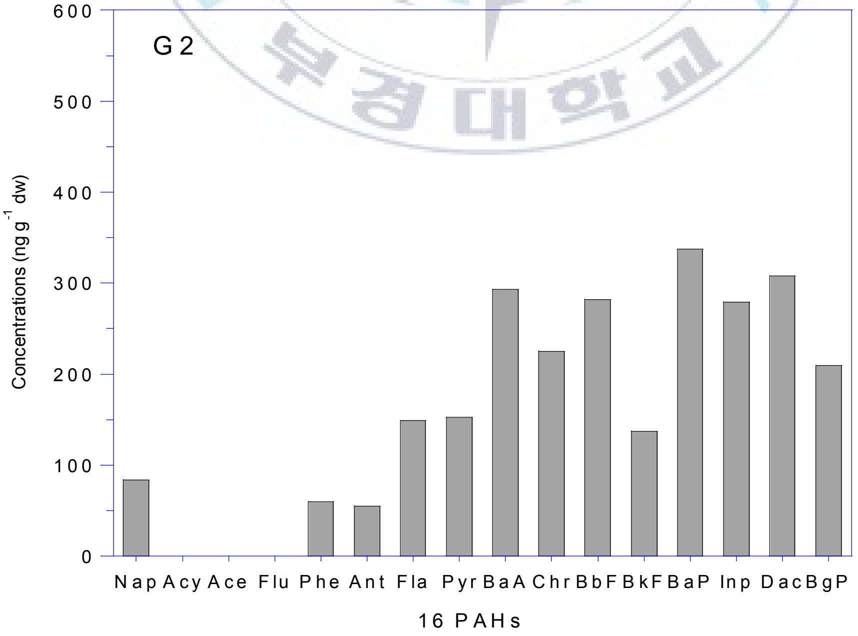
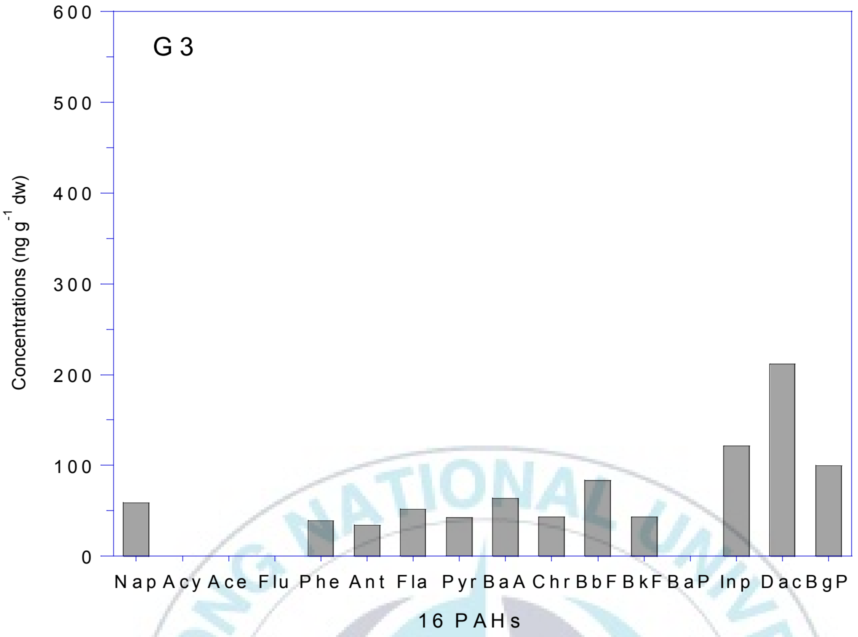
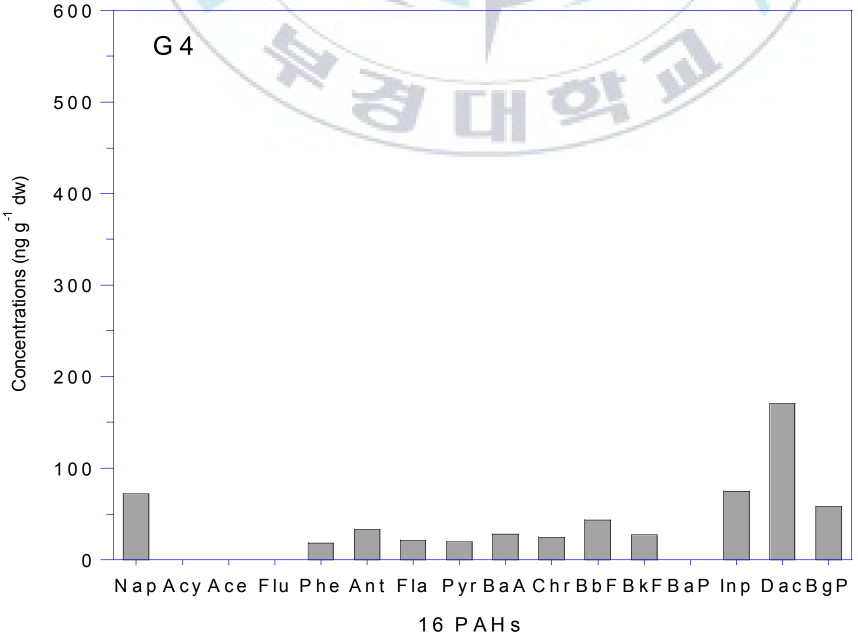


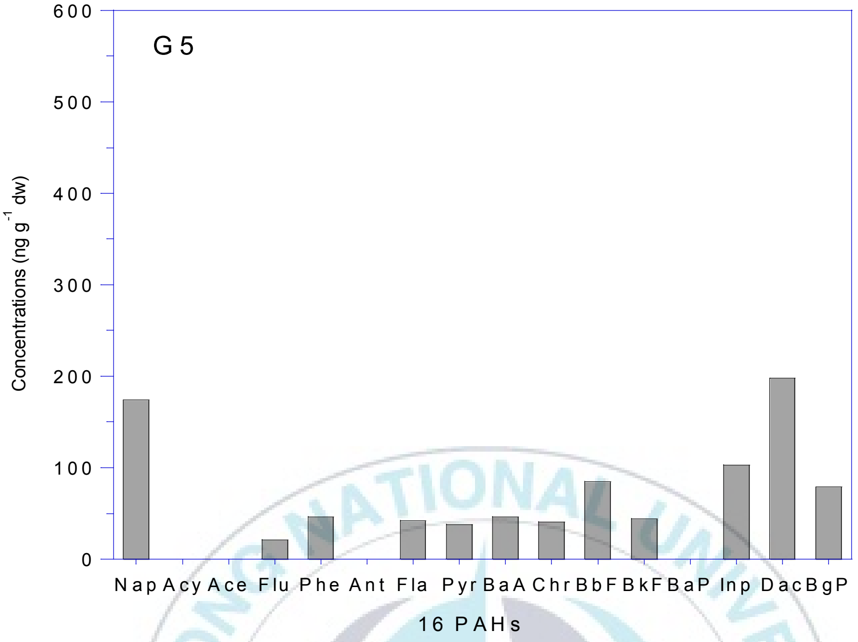
Fig. 9. The ratio of ring size for 16 PAHs in the surface sediments from Gwangalli.


G 1
Concentrations (ng g^{-1} dw)
0
100
200
300
400
500
600
Nap
Acy
Ace
Flu
Phe
Ant
Fla
Pyr
BaA
Chr
BbF
BkF
BaP
Inp
Dac
BgP
16 PAHs


G 2
Concentrations (ng g^{-1} dw)
0
100
200
300
400
500
600
Nap
Acy
Ace
Flu
Phe
Ant
Fla
Pyr
BaA
Chr
BbF
BkF
BaP
Inp
Dac
BgP
16 PAHs


G3
Concentrations (ng g^{-1} dw)
600
500
400
300
200
100
0
Nap Acy Ace Flu Phe Ant Fla Pyr BaA Chr BbF BkF BaP Inp Dac BgP
16 PAHs


G4
Concentrations (ng g^{-1} dw)
600
500
400
300
200
100
0
Nap Acy Ace Flu Phe Ant Fla Pyr BaA Chr BbF BkF BaP Inp Dac BgP
16 PAHs



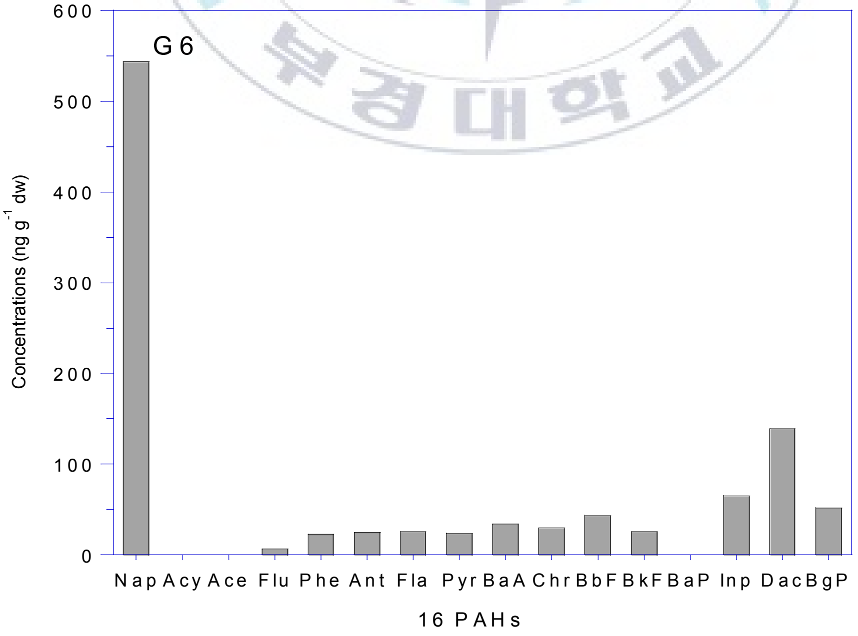


Fig. 10. The concentrations of each PAH in surface sediments from Gwangalli.

Table 5. Concentrations of 16 PAHs (ng g^{-1} d.w.) in the surface sediments from Gwangalli and Nakdong River, and some related toxicity guidelines.

PAHs	Abbreviation	Ring	G1	G2	G3	G4	G5	G6	N1	N2	N3	N4	N5	N6	N7	N8	ERL	ERM
Naphthalene	Nap	2	111.66	83.99	58.74	72.39	174.05	543.49	128.70	77.60	76.54	64.67	333.08	134.94	105.29	119.30	160	2100
Acenaphthalene	Acy	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	44	640
Acenaphthene	Ace	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16	500
Fluorene	Flu	3	ND	ND	ND	ND	21.27	6.45	ND	ND	ND	ND	ND	ND	ND	6.66	19	540
Phenanthrene	Phe	3	ND	59.71	39.17	18.27	46.07	22.51	18.59	17.68	23.76	29.28	36.83	28.14	40.61	26.85	240	1500
Anthracene	Ant	3	ND	55.20	34.22	32.74	ND	24.83	ND	ND	ND	ND	ND	ND	ND	ND	85.3	1100
Fluoranthene	Fla	4	ND	148.82	51.69	21.40	42.05	25.68	16.05	13.21	20.09	31.20	34.05	19.73	46.08	22.99	600	5100
Pyrene	Pyr	4	94.45	152.03	42.24	19.72	38.08	23.98	13.64	11.57	19.33	22.81	26.67	19.70	33.81	20.02	665	2600
Benzo(a)anthracene	BaA	4	98.23	292.84	63.72	28.01	46.46	33.84	ND	3.98	6.13	10.44	12.78	7.06	21.44	9.48	261	1600
Chrysene	Chr	4	78.28	224.89	43.04	24.77	40.78	29.40	22.43	4.31	6.59	13.29	12.78	6.25	22.93	8.83	384	2800
Benzo(b)fluoranthene	BbF	5	ND	282.29	83.67	43.26	84.41	43.34	10.48	ND	6.29	16.68	25.78	8.11	55.35	11.69	320	1880
Benzo(k)fluoranthene	BkF	5	118.83	137.15	43.13	27.25	44.22	25.71	6.11	ND	ND	5.54	9.33	5.43	25.89	8.94	280	1620
Benzo(a)pyrene	BaP	5	ND	337.09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	430	1600
Indeno(1,2,3-c,d)pyrene	Inp	6	ND	279.23	121.43	75.13	102.92	65.26	8.42	ND	ND	ND	7.94	7.31	23.54	ND	-	-
Dibenzo(a,h)anthracene	Dac	5	532.55	307.83	211.42	170.68	197.47	138.92	14.98	ND	ND	ND	ND	ND	ND	13.18	63.4	260
Benzo(g,h,i)perylene	BgP	6	238.25	209.24	99.84	58.39	78.67	51.65	5.00	ND	ND	ND	8.20	7.54	19.35	ND	430	1600

4. 4. Sources and ecological risk assessment of PAHs in Gwangalli

Source apportionment of PAHs in the surface sediments from Gwangalli were shown in Fig 12. The ratios of Fla/(Fla+Pyr), Ant/(Ant+Phe), BaA/(BaA+Chr) and Inp/(Inp+BgP) were used to identify the PAHs sources according to other studies [44]. The ratio of Ant/(Ant+Phe) in most of the sampling sites were higher than 0.2 indicating pyrogenic sources. Similarly, ratios of Fla/(Fla+Pyr) suggested a mixed sources. All sampling sites were defined as petroleum combustion sources according to ratios of BaA/(BaA+Chr). Most of the sites were identified as grass, wood and coal combustion sources due to Inp/(Inp+BgP).

In Gwangalli area, the values of M-ERM-Q were all below 0.5 (Fig 11). Only G1 and G2 were exceeded 0.1, which suggesting medium-low ecological risk. The results of M-ERM-Q in other sites from Gwangalli all showed a low ecological risk.

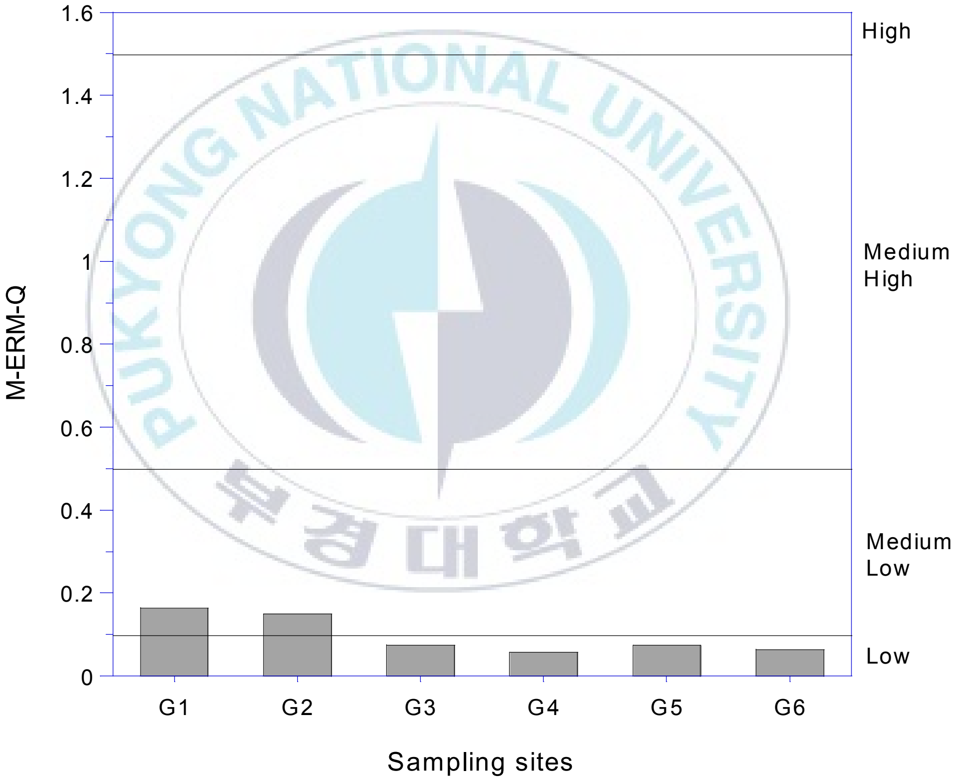


Fig. 11. Spatial distribution of M-ERM-Q in the surface sediments of Gwangalli.

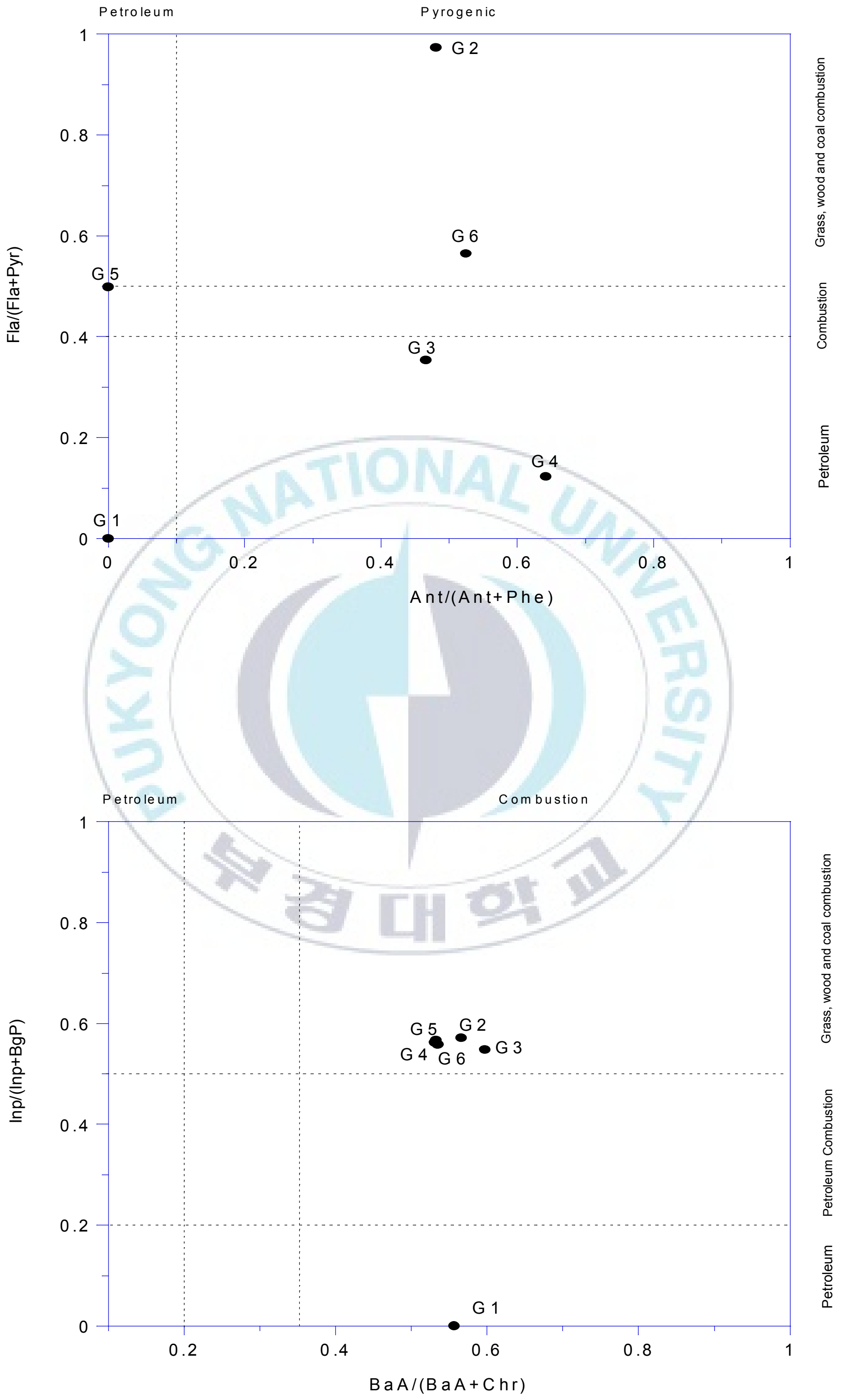
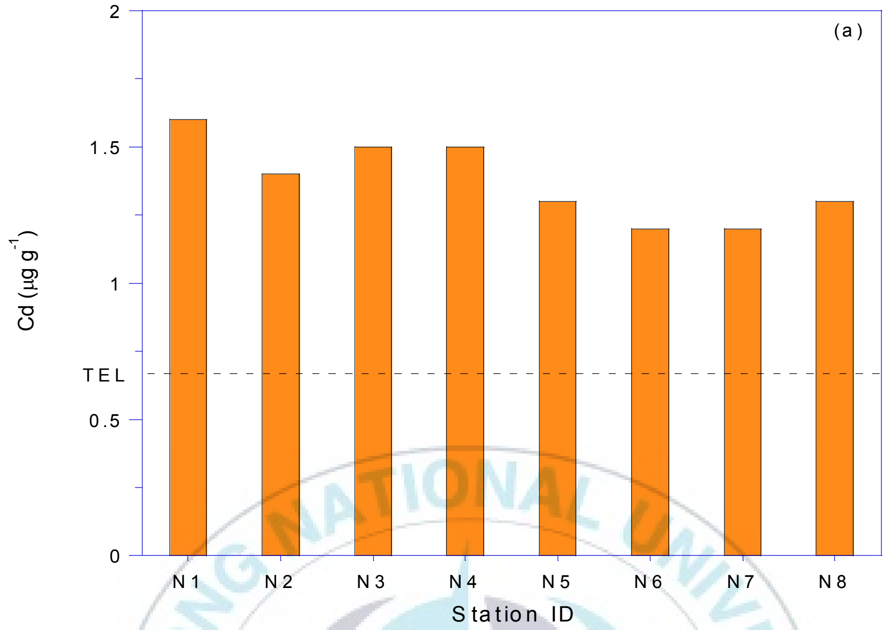
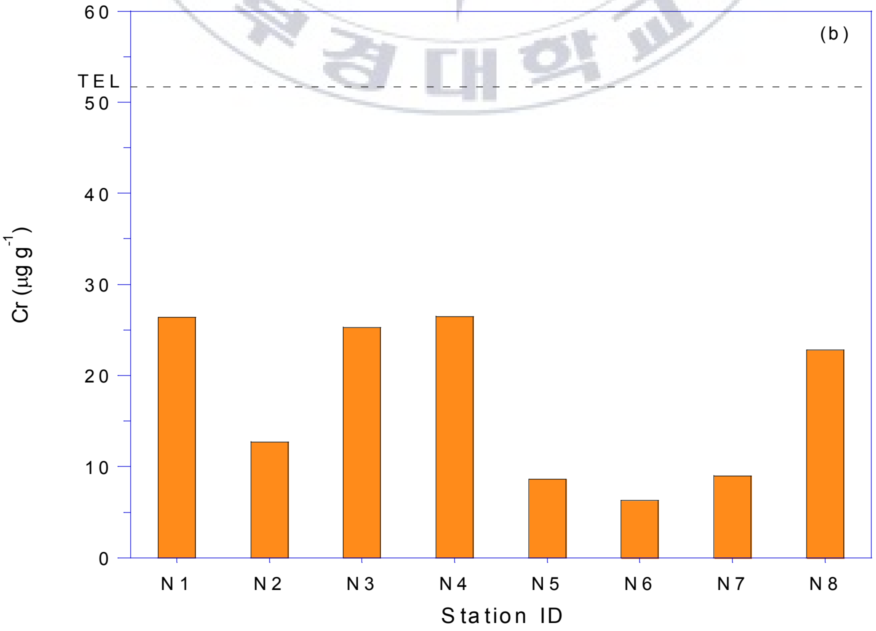


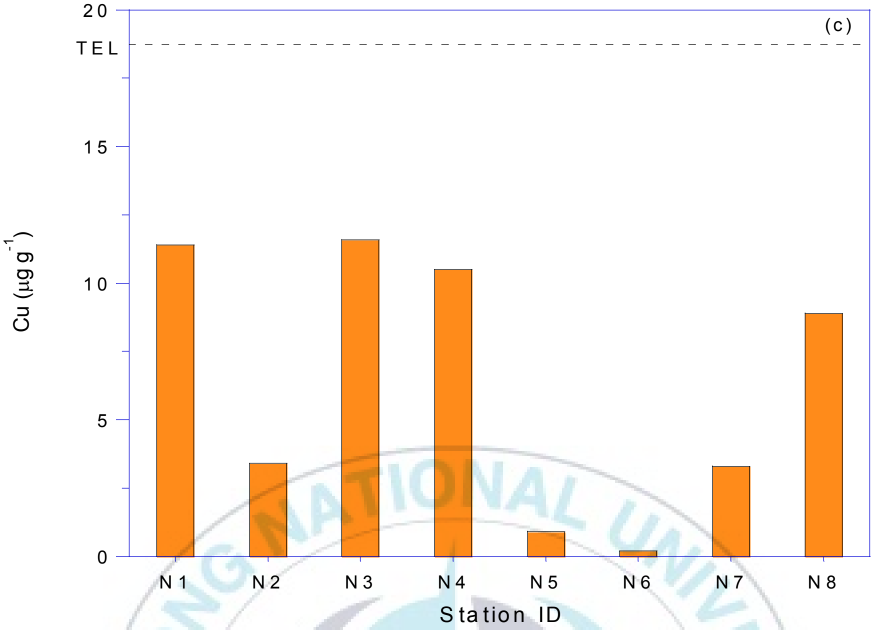
Fig. 12. Source apportionment of PAHs in Gwangalli.

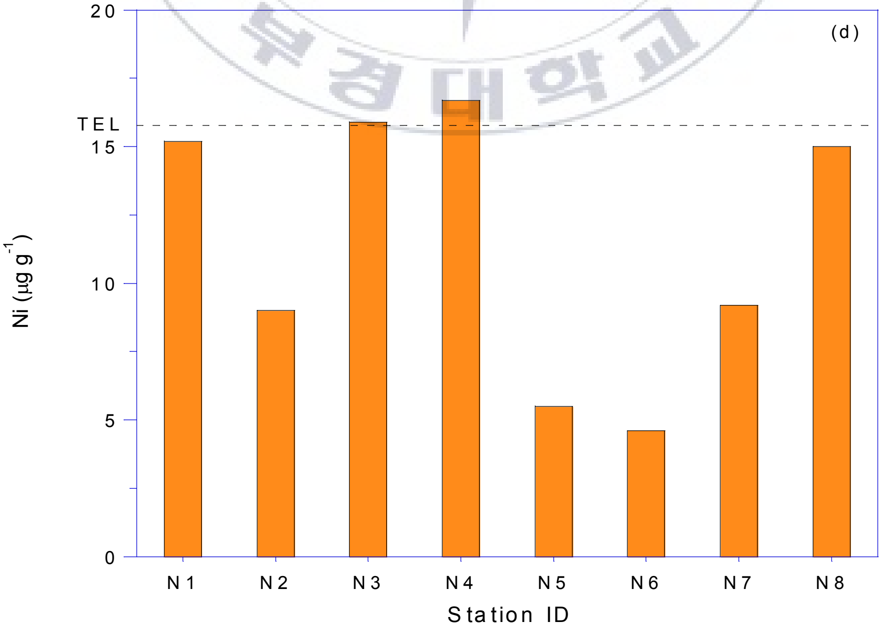
4. 5. Metal concentrations and compositions of sediments in Nakdong River

Based on the table 1, the range and mean concentrations (given in unit of mg/kg) of 11 heavy metal in Nakdong River were 0.2-11.6 (6.3) for Cu, 5.4-16.3 (11.7) for Pb, 4.6-16.7 (11.4) for Ni, 63.1-438.6 (255.9) for Mn, 15.5-73.9 (49.1) for Zn, 1.2-1.6 (1.4) for Cd, 2.2-9.4 (6.3) for Co, 6.3-26.5 (17.2) for Cr, 1.8-6.4 (4.1) for As, 2616.0-16030.0 (9587.8) for Al, 3712.0-23910.0 (14539.5) for Fe. Mean concentrations of 11 heavy metals followed in this sequence: Fe>Al>Mn>Zn>Cr>Pb>Ni>Co>Cu>As>Cd. The lowest concentrations of all metals occurred in sampling site N6 except As (Fig 13). The highest concentrations of metal Cu, Pb, Mn, As, Al and Fe located in site N3. Meanwhile, sampling site N1 suffered the highest concentrations of metal Zn, Cd and Cr.


(a)
2
1.5
1
TEL
0.5
0
Cd (μg g-1)
N1
N2
N3
N4
N5
N6
N7
N8
Station ID


(b)
60
TEL
50
40
30
20
10
0
Cr (μg g-1)
N1
N2
N3
N4
N5
N6
N7
N8
Station ID


(c)
TEL
Cu (µg g^{-1})
20
15
10
5
0
N1
N2
N3
N4
N5
N6
N7
N8
Station ID


(d)
TEL
Ni (µg g^{-1})
20
15
10
5
0
N1
N2
N3
N4
N5
N6
N7
N8
Station ID

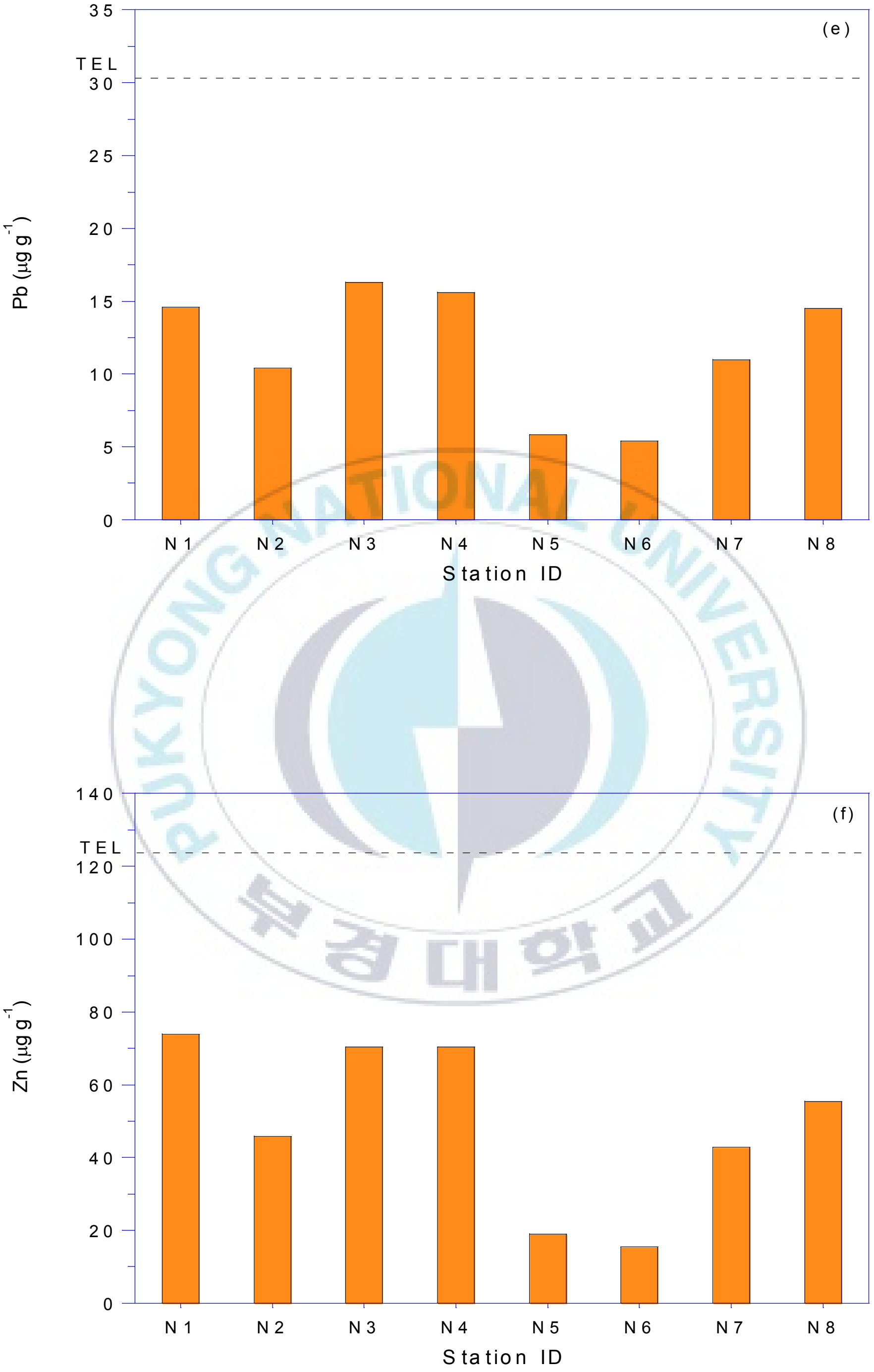


Fig. 13. The concentrations of heavy metals in sediments from Nakdong River for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f) (where N1~N8 denote sampling cites). The horizontal dash lines represent their corresponding TEL.

Several heavy metal ions were compared with related sediment quality guidelines to determine contamination level. According to USEPA and Ontario sediment standards, in Nakdong River, five metals (Cu, Pb, Ni, Zn and Cd) except Cd were all non polluted in all sampling sites which indicated a good condition of sedimentary environment. Compared with TEL and PEL sediment guidelines, metals of Cr, Cu, Pb and Zn in all sites were below TEL values, whereas Cd in all stations and Ni in sites N3 and N4 exceeded the TEL values. Mean concentrations for six metals (Cd, Cr, Cu, Ni, Pb and Zn) were all below average UCC values (Table 3) except Cd, which was in consistence with USEPA and Ontario sediment quality guidelines.

As is shown in Table 4, the average concentrations of metals Cr, Cu and Pb were all below the values according to other studies, whereas the mean concentration of Cd was higher than them. Compared the present data with former studies in Nakdong River [45], the mean concentrations of all six metals except Ni were lower than previous one, which indicated an improvement in sedimentary environment. Also, the mean total content of all metals in Nakdong River were similar with the results in Jade Bay where the sediment quality was in a good condition.

The composition of sediments in Nakdong River were almost the same as Gwangalli area. As for ignition loss, sites N1 and N2 were non polluted, whereas site N7 were heavily polluted; other sites were moderately polluted.

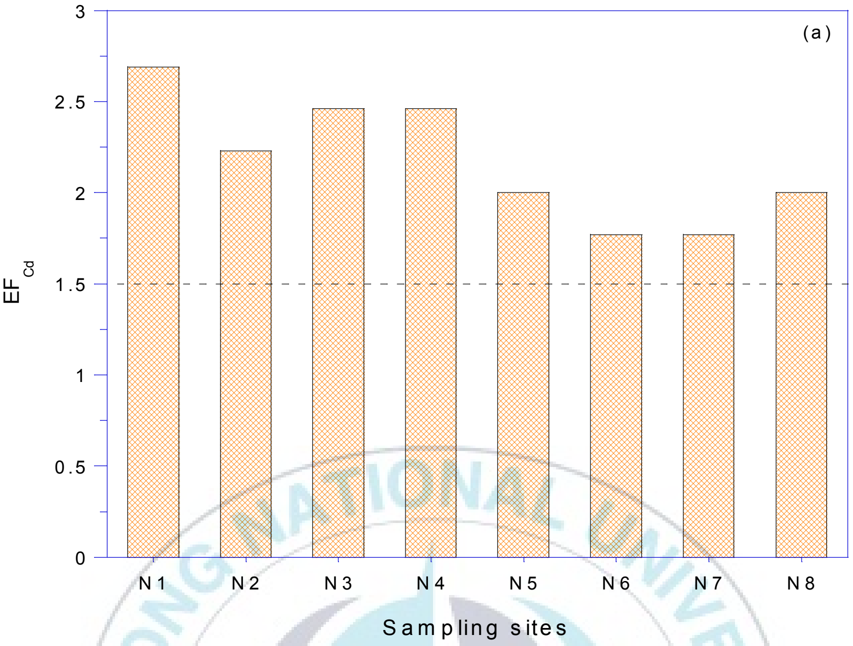
4. 6. Risk assessment according to multiple indices for metals in surface sediments of Nakdong River

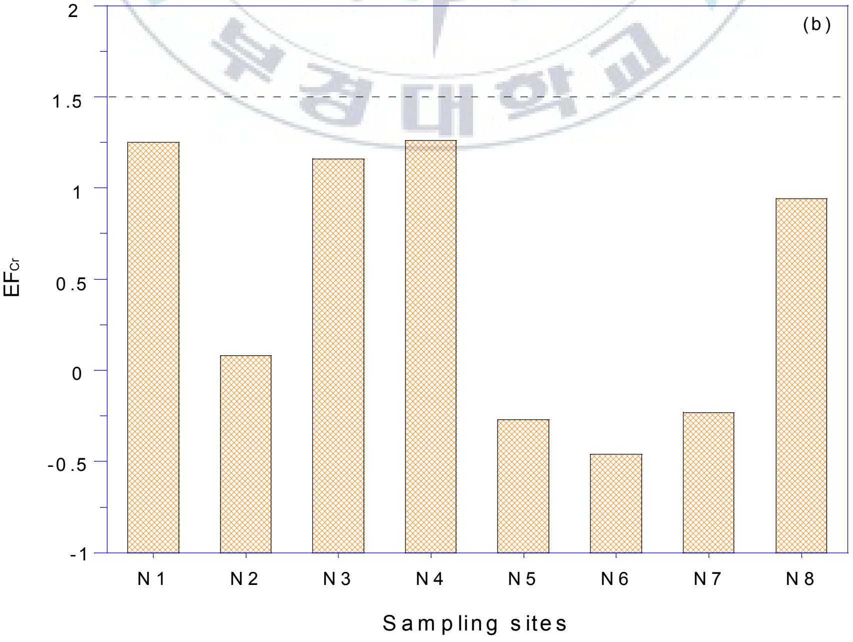
From Fig 14, the EF values of Cu, Ni, Pb and Zn were all below 1, which indicated that no enrichment of those metals in Nakdong River. Only the EF values of Cd and part of Cr (sites N1, N3 and N4) were between 1 to 3, resulted in minor enrichment in all sampling sites.

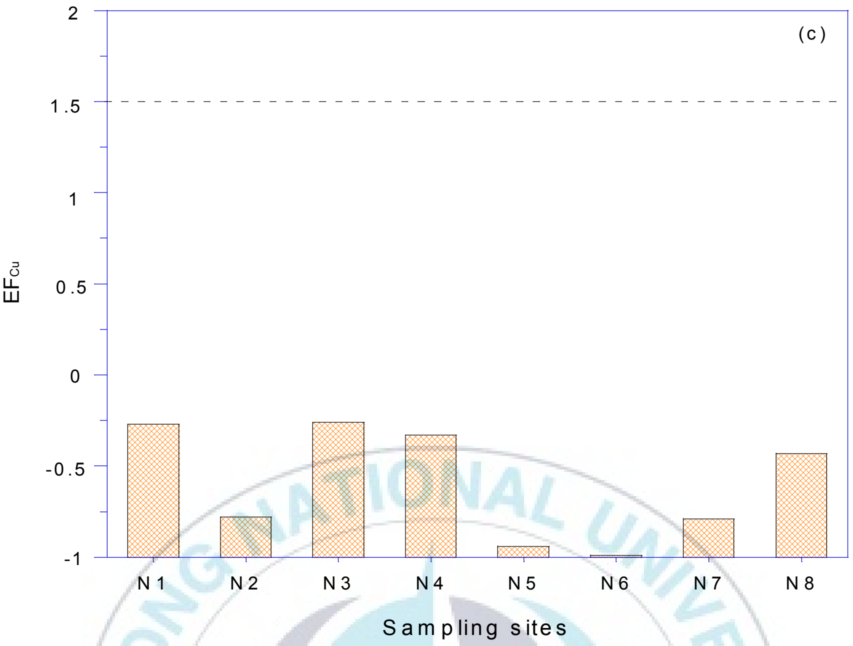
The I_{geo} values (Fig 15) of Cu, Ni, Pb and Zn were below 0, which meant there were practically uncontaminated by those metals. Meanwhile, half of sampling sites (N1, N3, N4 and N8) for metal Cr reached uncontaminated to moderately contaminated level. In the case of metal Cd, 50 % of sites (N1-N4) were under moderately contaminated level, other sites were all reached slightly contaminated.

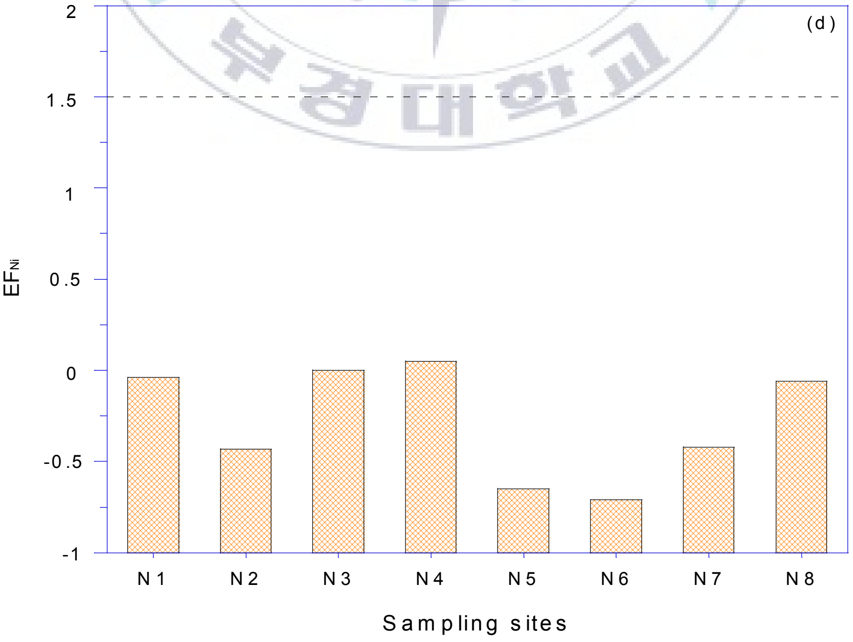
The PERF values (Fig 16) of six metals (Cd, Cr, Cu, Ni, Pb and Zn) were all below 40 except Cd, which suggested a low potential ecological risk in Nakdong River. However, PERF values of Cr fell into second tier, which represented a moderate risk in all sampling sites in Nakdong River. This conclusion was in consistence with the results derived by EF and I_{geo} indices.

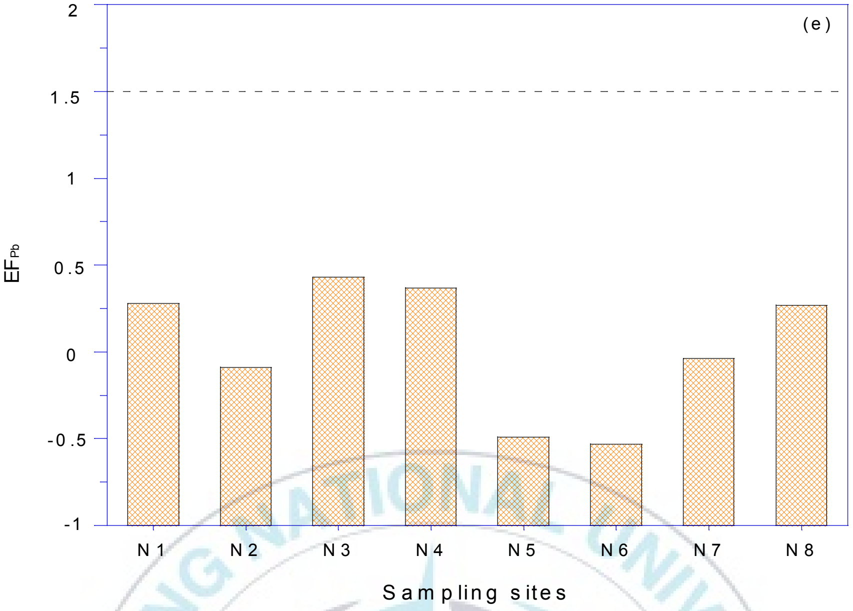
Most of the mean PEL quotient values (Fig 17) were between 0.11 to 1.5, which resulted in a 21 % probability of being toxic in Nakdong River, whereas only site N6 was below 0.1, showing an 8% probability of being toxic. As is shown in Fig 18, Cd showed the highest contamination degree comparing with other metals. Cu and Ni were in good conditions in Nakdong River. The trend of mean EF values were similar as the mean I_{geo} values while inconsistent with PERF values. Overall, sedimentary environment in Nakdong River was in a good condition.


(a)
EF$_{Cd}$
3
2.5
2
1.5
1
0.5
0
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(b)
EF$_{Cr}$
2
1.5
1
0.5
0
-0.5
-1
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(c)
EFCu
2
1.5
1
0.5
0
-0.5
-1
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(d)
EFNi
2
1.5
1
0.5
0
-0.5
-1
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites



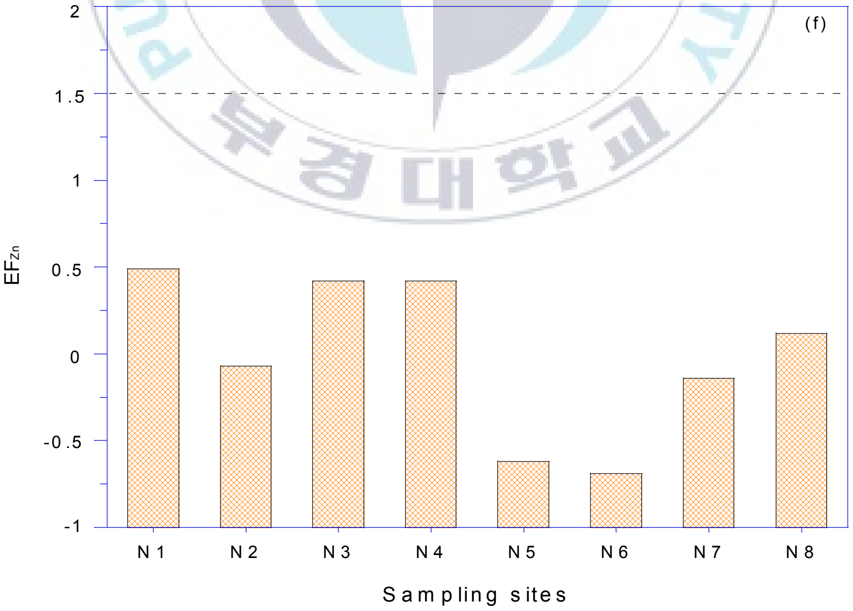
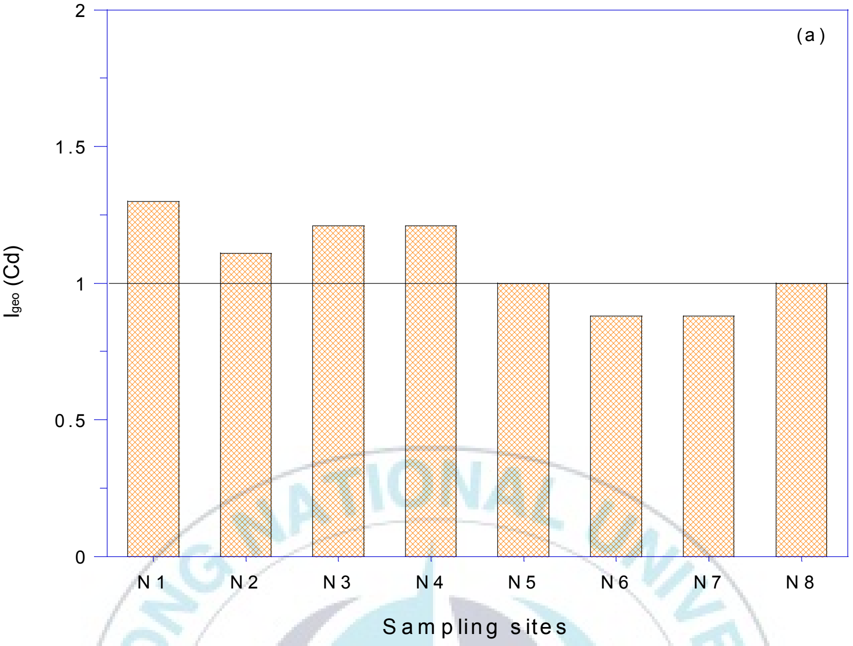
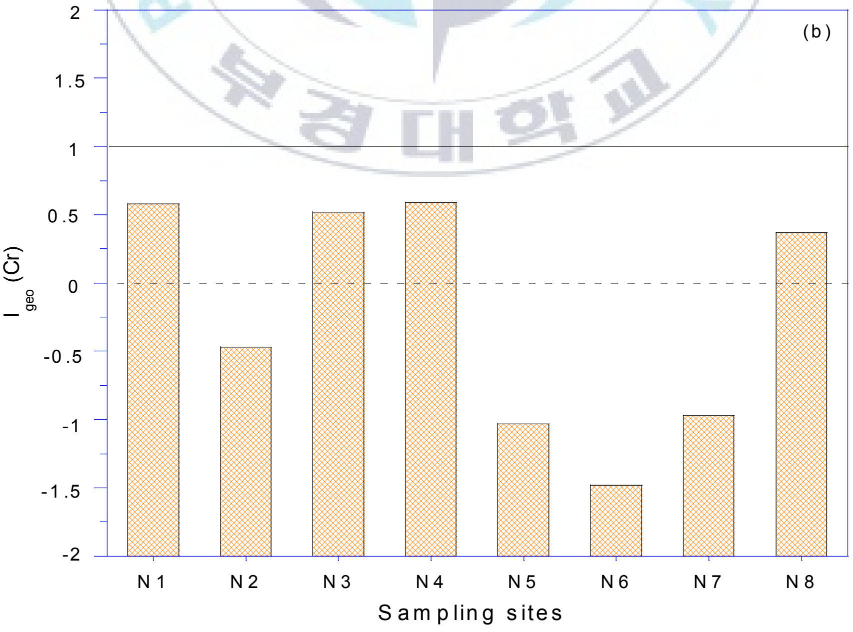
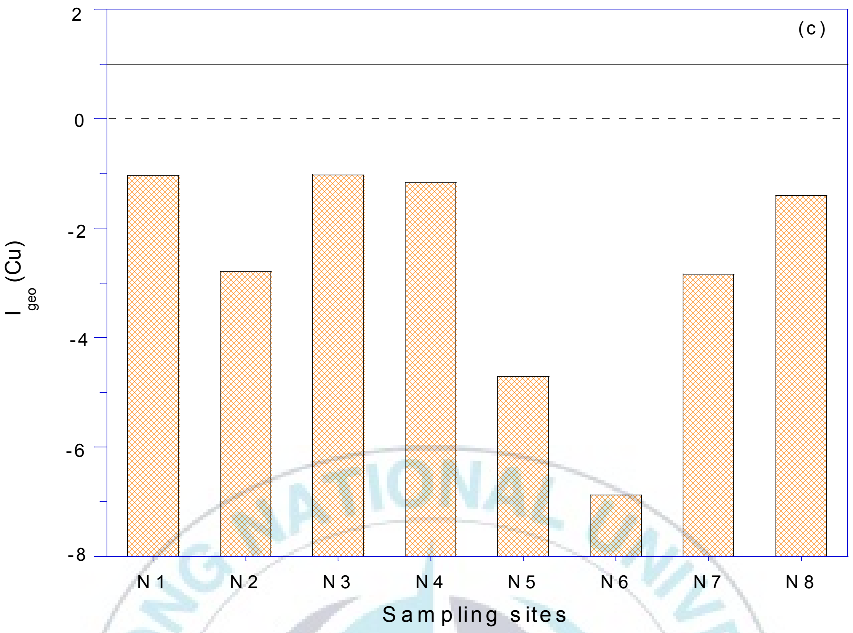
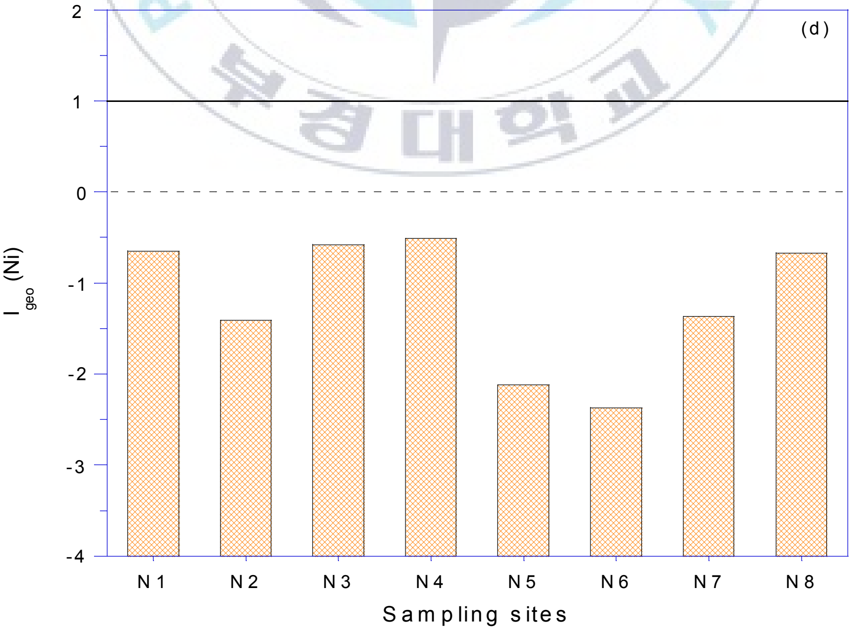


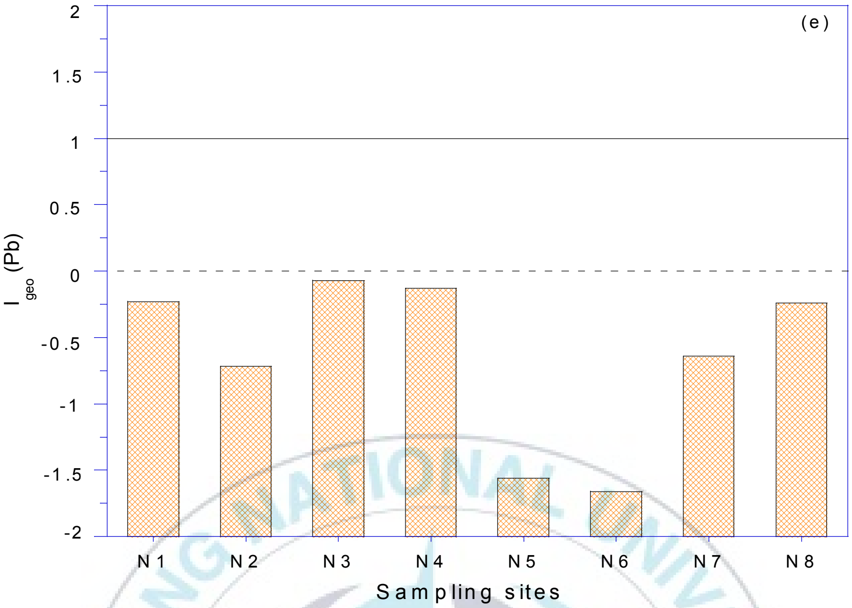
Fig. 14. The EF values of 8 sampling sites from Nakdong River for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f). The horizontal dash line represent 1.5 of EF value.


(a)
2
1.5
1
0.5
0
I_geo (Cd)
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(b)
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
I_geo (Cr)
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(c)
I_geo (Cu)
2
0
-2
-4
-6
-8
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(d)
I_geo (Ni)
2
1
0
-1
-2
-3
-4
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites



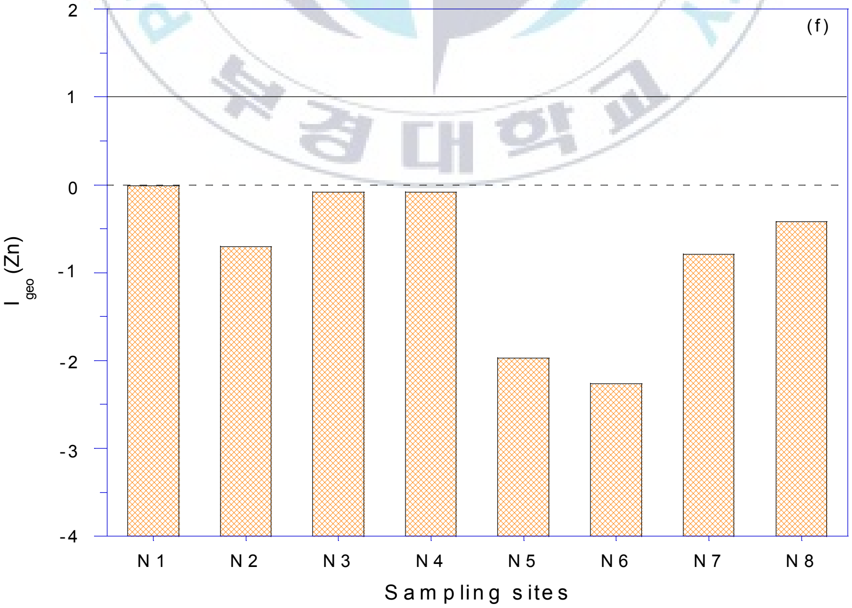
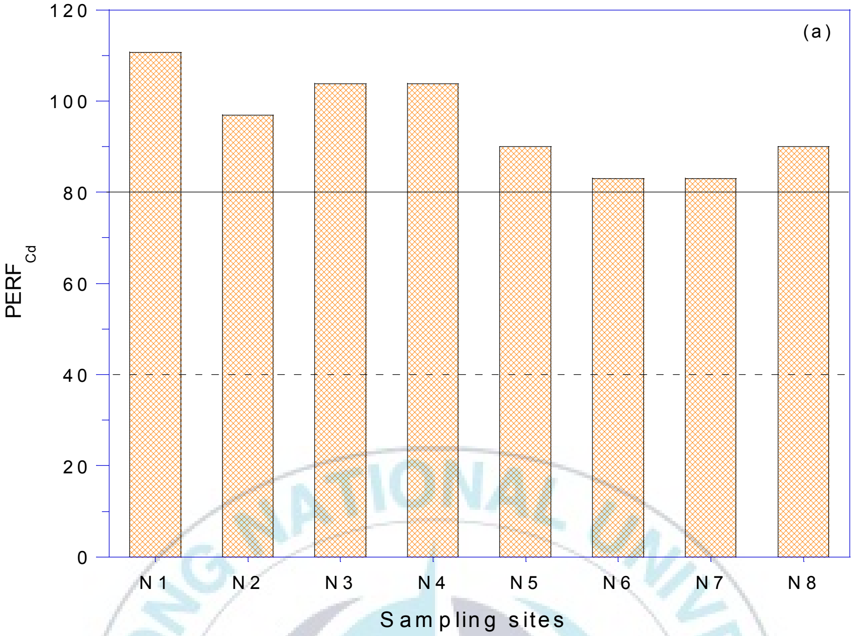
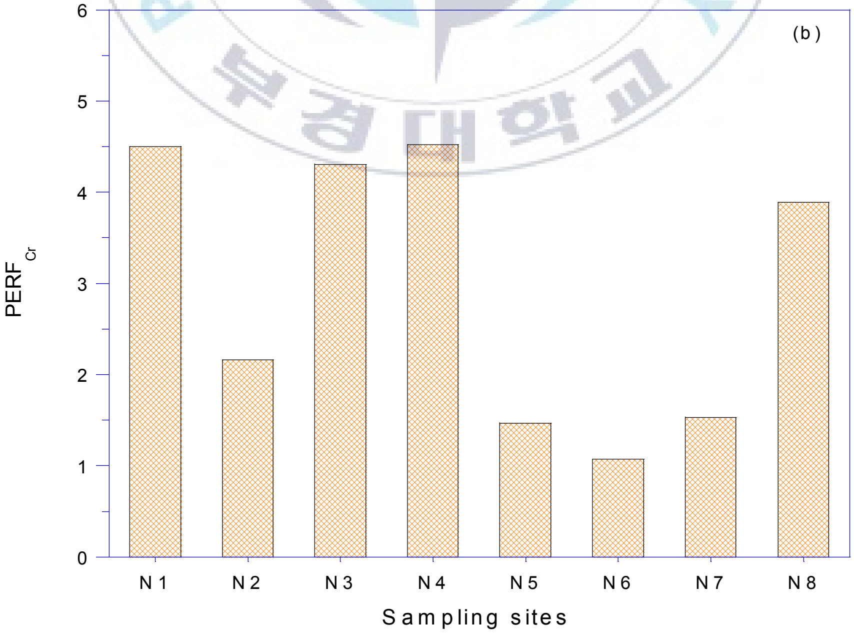
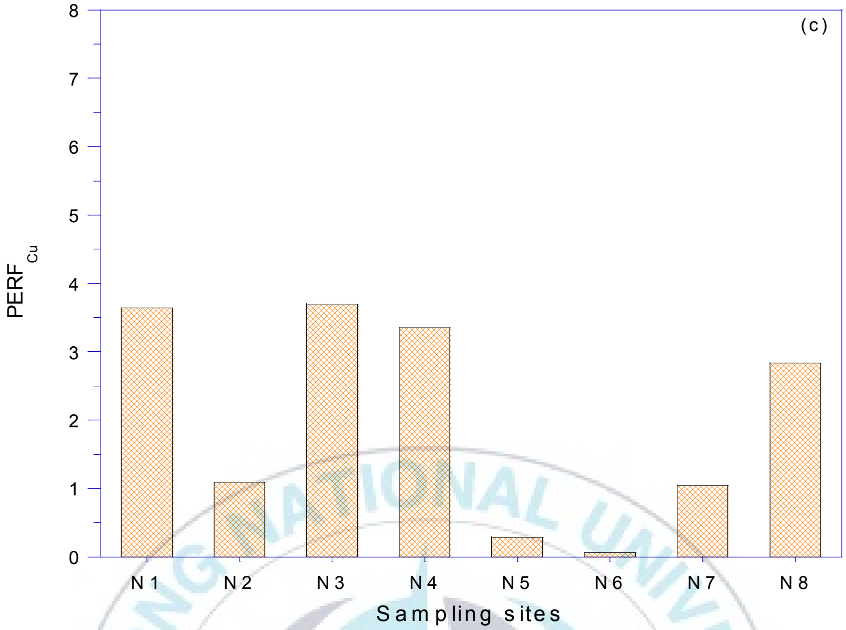
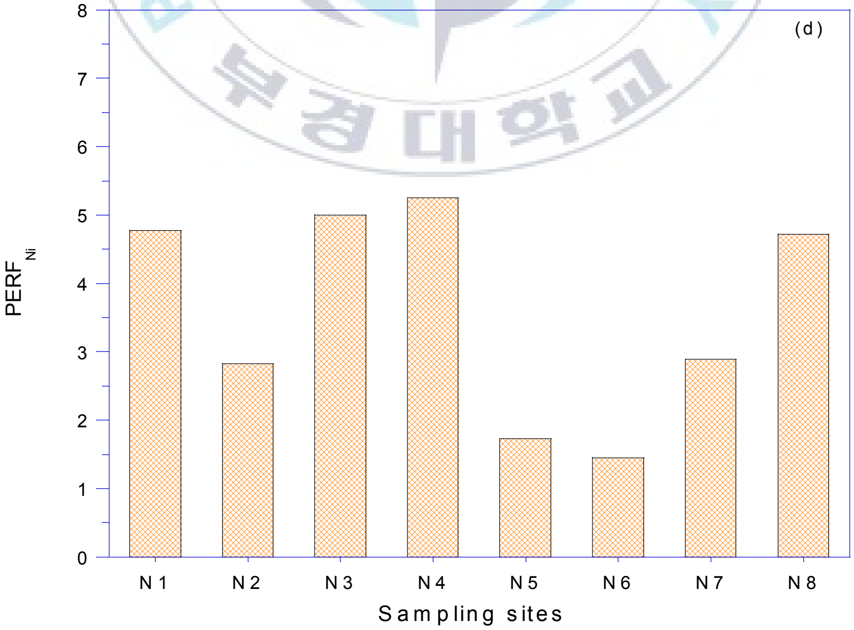


Fig. 15. The Igeo values of 8 sampling sites from Nakdong River for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f). The horizontal solid and dash line represent 1 and 0 of PERF values, respectively.


(a)
120
100
80
60
40
20
0
PERF$_{Cd}$
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(b)
6
5
4
3
2
1
0
PERF$_{Cr}$
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(c)
$PERF_{Cu}$
0
1
2
3
4
5
6
7
8
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites


(d)
$PERF_{Ni}$
0
1
2
3
4
5
6
7
8
N1
N2
N3
N4
N5
N6
N7
N8
Sampling sites

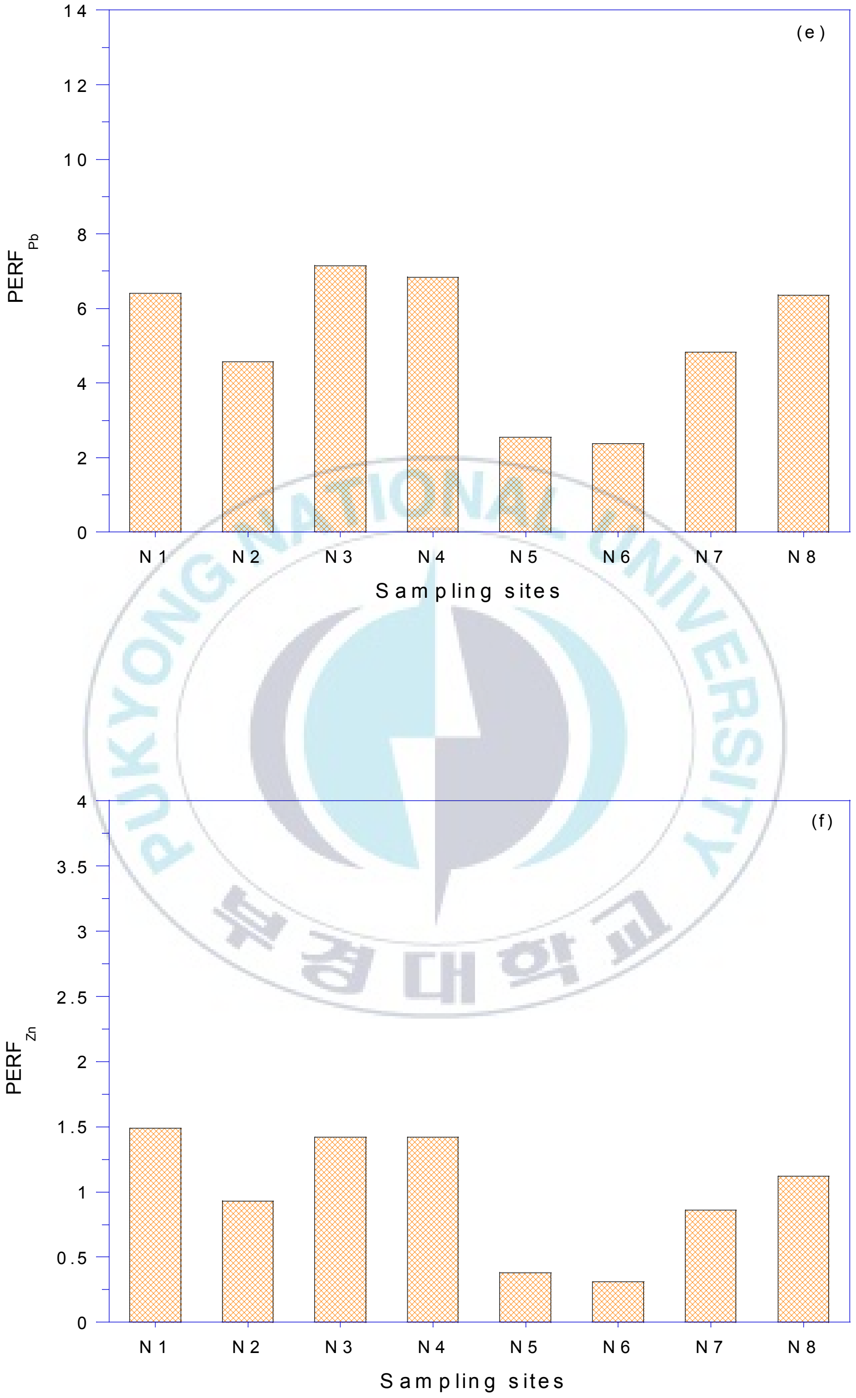


Fig. 16. The distribution of PERF values, the histogram showed the PERF values for heavy metals in sediments from Nakdong River for Cd (a), Cr (b), Cu (c), Ni (d), Pb (e), and Zn (f). The horizontal solid and dash line mean the PERF values of 40 and 80, respectively.

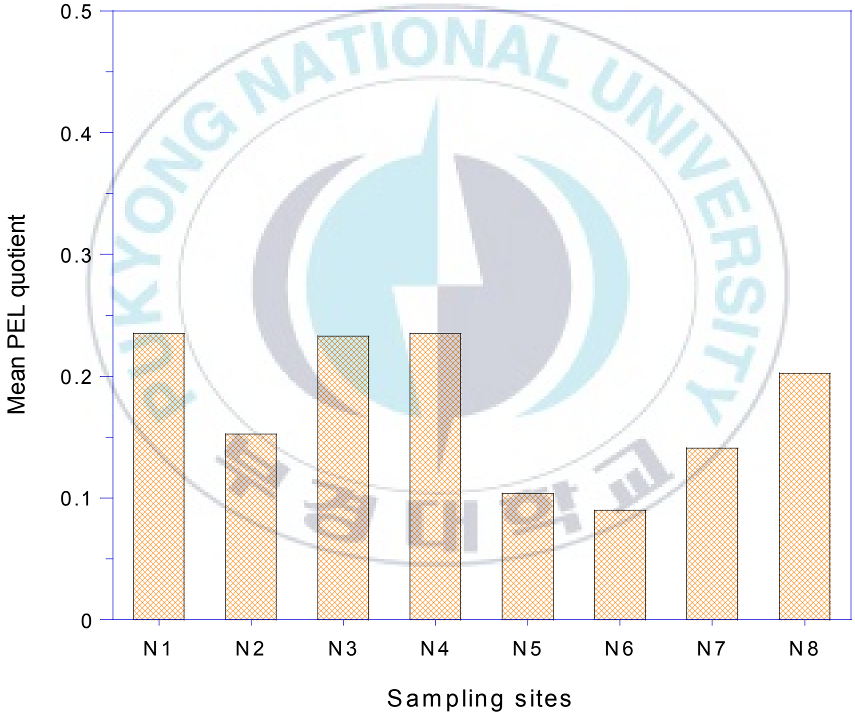


Fig. 17. The mean PEL quotient values from Nakdong River.

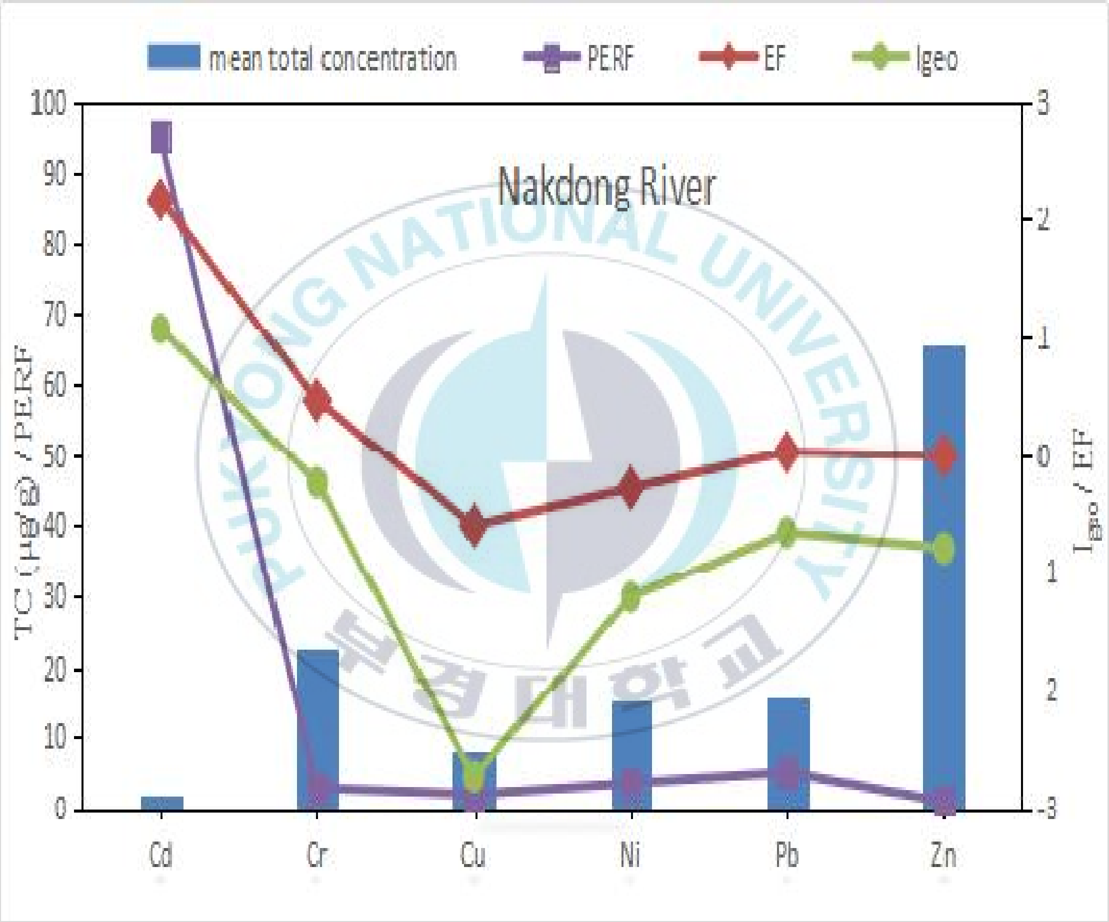


Fig. 18. The mean values of EF, Igeo, PERF and total concentration for metals in Nakdong River.

4. 7. The total concentrations of PAHs in Nakdong River

As is shown in Fig 19, total concentrations of PAHs in surface sediments of Nakdong River ranged from 128.4 (N2) to 507.4 (N5) ng g^{-1} dw with a mean concentrations of 264.9 ng g^{-1} dw. The total concentrations of 16 PAHs followed in this order: N5>N7>N8>N1>N6>N4>N3>N2. Acys, Aces, Ants and Baps were not found in Nakdong River. Flus, BkFs, Inps, Dacs and BgPs were detected at 12.5 %, 75 %, 50 %, 25 % and 50 % of the sampling sites. BaAs and BbFs were all found in 87.5 % of the sampling samples. The highest concentrations of 16 PAHs in each location appeared in Naps in N5, Flus in N8, Phes in N7, Flas in N7, Pyrs in N7, BaAs in N7, Chrs in N7, BbFs in N7, BkFs in N7, Inps in N7, Dacs in N1 and BgPs in N7 (Fig 21). And mean concentrations of 16 PAHs were shown in this descending order: Nap>Phe>Fla>Pyr>BbF>Dac>Chr>Inp>BkF>BaA>BgP>Flu>Acy, Ace, Ant and BaP.

From Fig 20 , the ring sizes of PAHs in Nakdong River were mainly consist of 2-ring and 4-ring compounds. 2-ring compounds were predominant in Nakdong River. Compared with risk assessment guidelines (Table 5), only Naps in sampling sites N5 exceeded the effect range low value, other PAHs were all below the threshold values indicating a good sedimentary quality in Nakdong River.

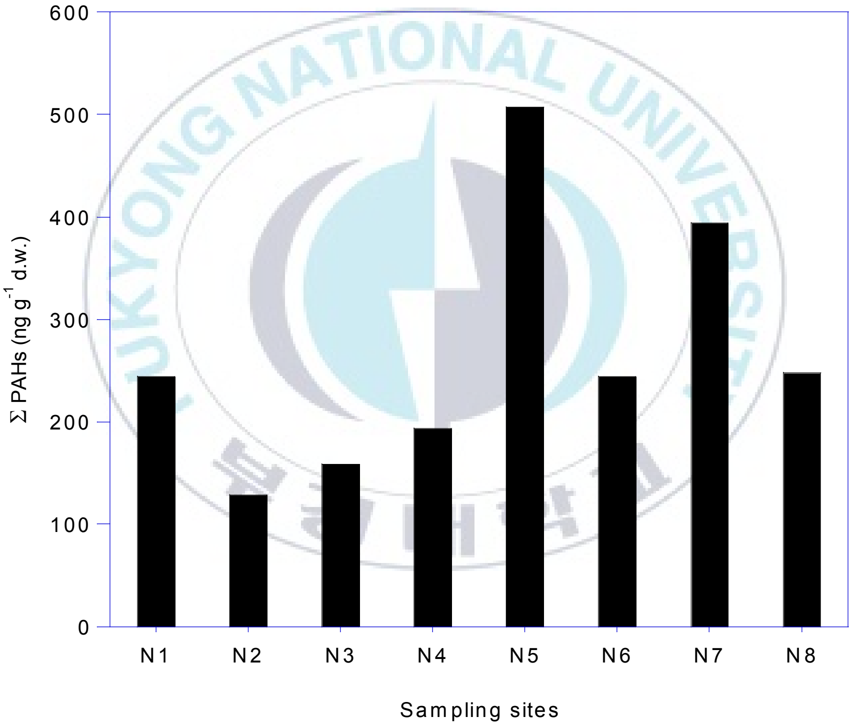


Fig. 19. Total 16 PAHs concentrations in the sediments from Nakdong River.

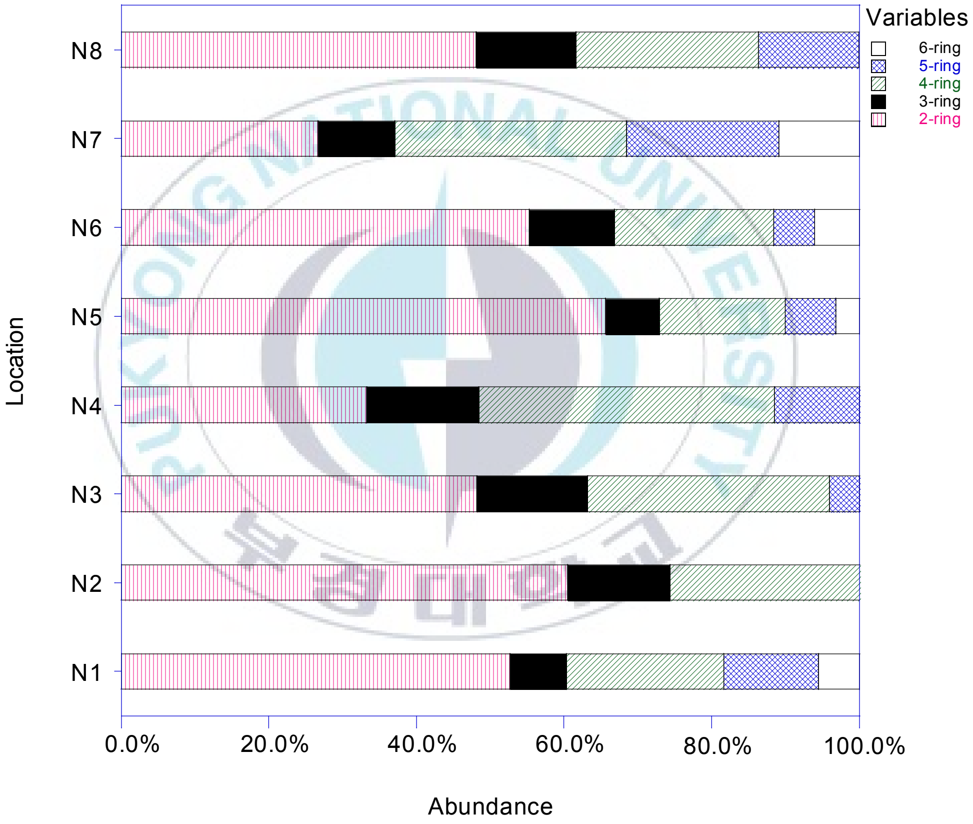
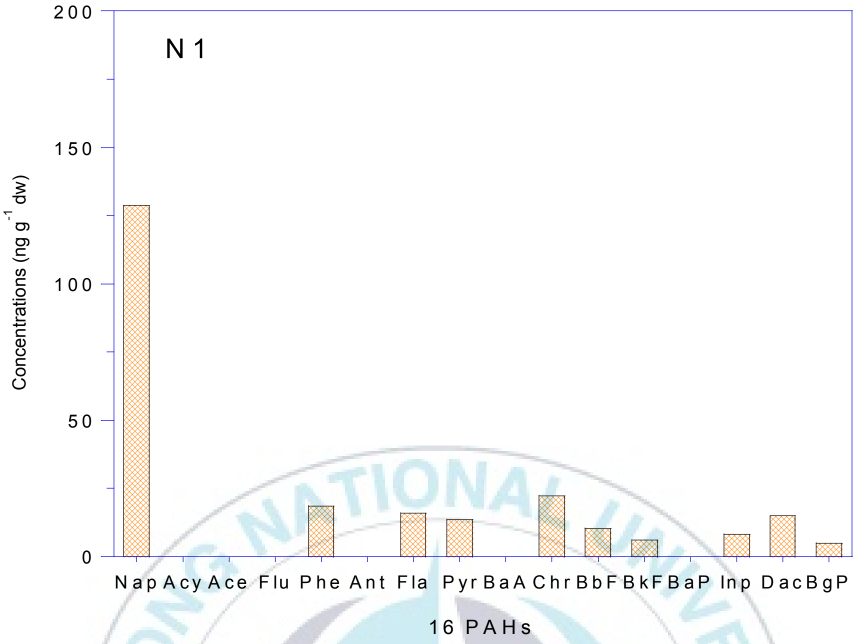
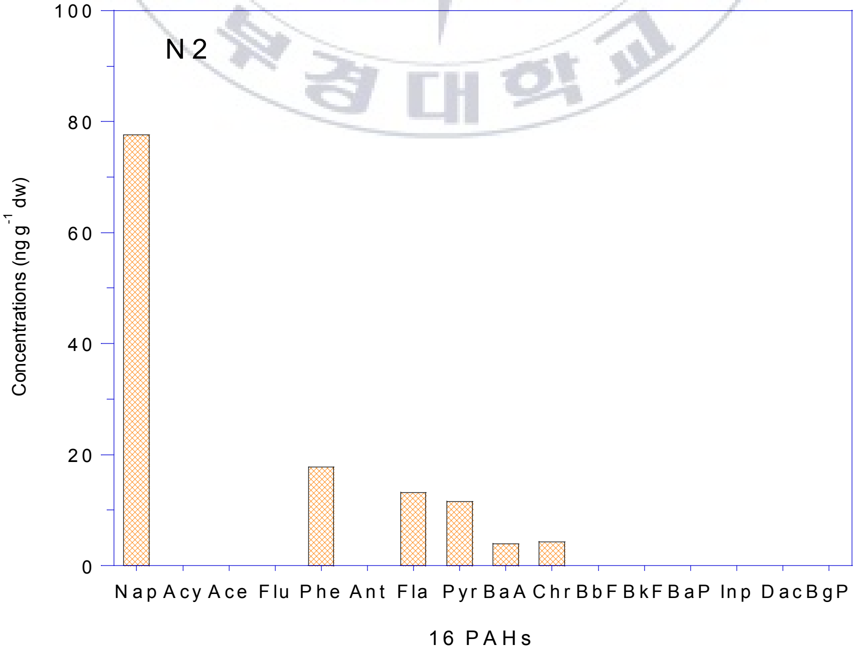
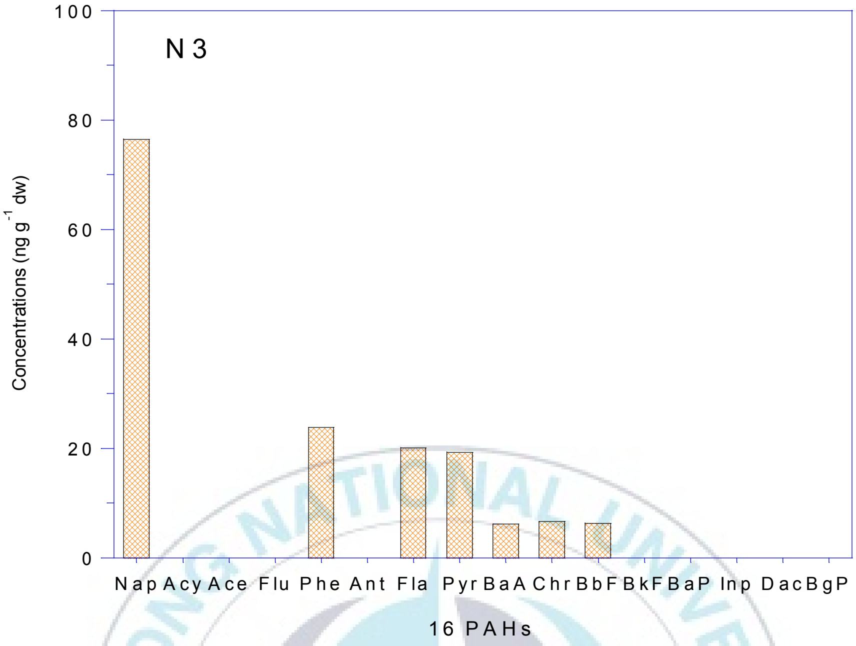
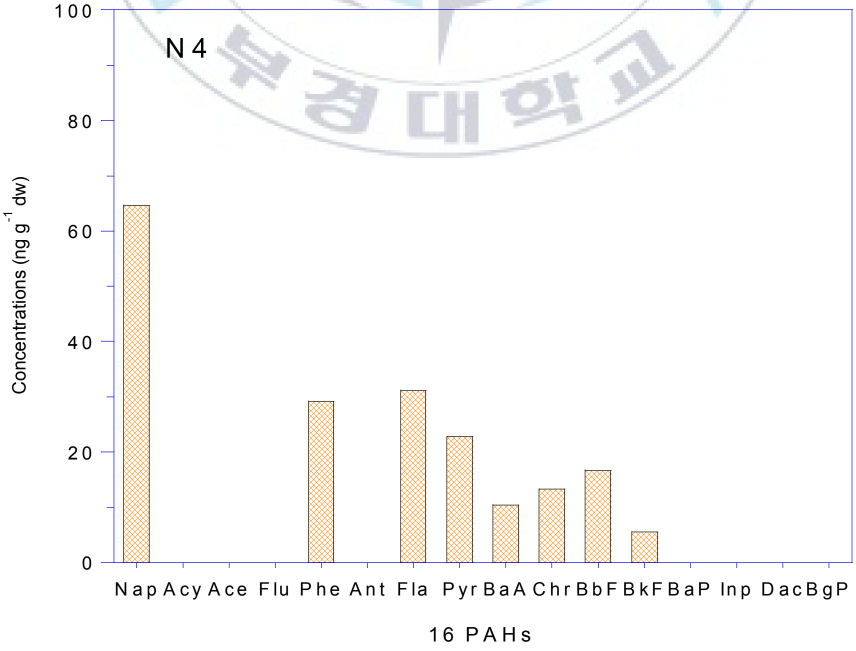


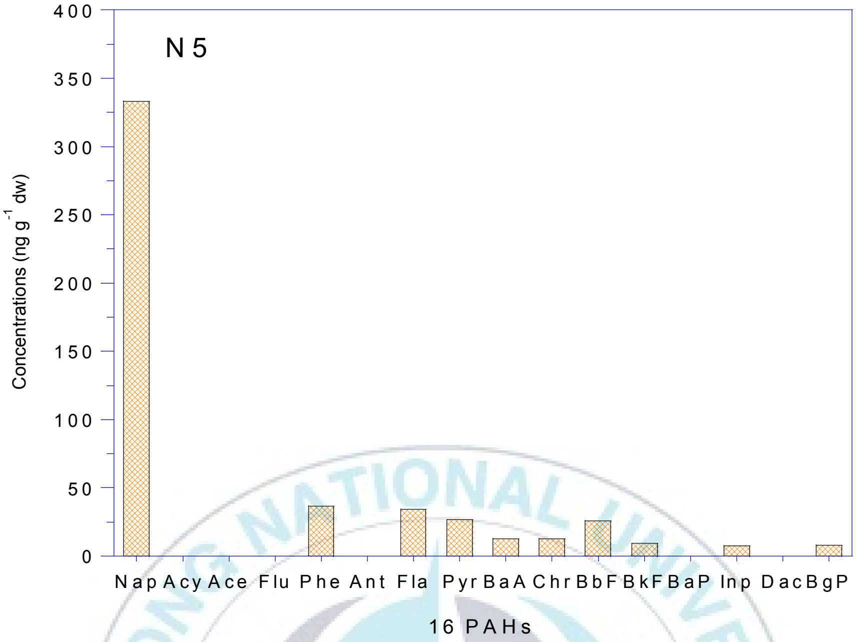
Fig. 20. The ratio of ring size for 16 PAHs in the surface sediments from Nakdong River.

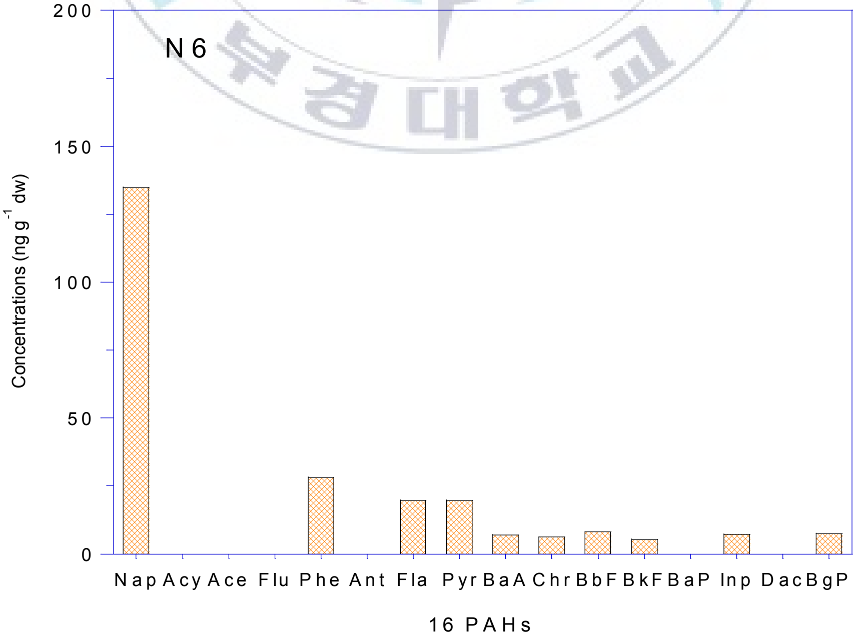

N1
Concentrations (ng g^{-1} dw)
200
150
100
50
0
Nap
Acy
Ace
Flu
Phe
Ant
Fla
Pyr
BaA
Chr
BbF
BkF
BaP
Inp
Dac
BgP
16 PAHs

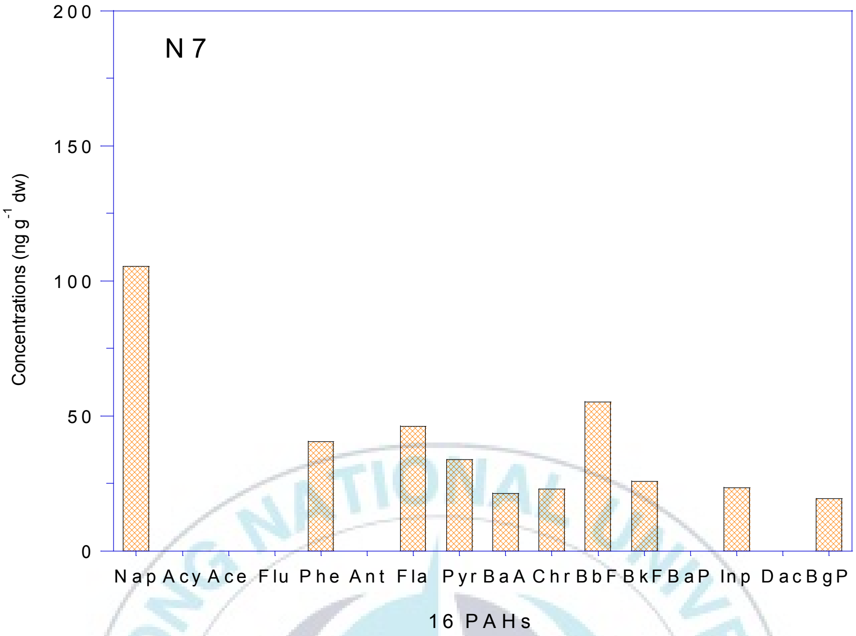

N2
Concentrations (ng g^{-1} dw)
100
80
60
40
20
0
Nap
Acy
Ace
Flu
Phe
Ant
Fla
Pyr
BaA
Chr
BbF
BkF
BaP
Inp
Dac
BgP
16 PAHs


N 3
100
80
60
40
20
0
Concentrations (ng g^{-1} dw)
Nap Acy Ace Flu Phe Ant Fla Pyr BaA Chr BbF BkF BaP Inp Dac BgP
16 PAHs


N 4
100
80
60
40
20
0
Concentrations (ng g^{-1} dw)
Nap Acy Ace Flu Phe Ant Fla Pyr BaA Chr BbF BkF BaP Inp Dac BgP
16 PAHs


N 5
Concentrations (ng g^{-1} dw)
400
350
300
250
200
150
100
50
0
Nap Acy Ace Flu Phe Ant Fla Pyr BaA Chr BbF BkF BaP Inp Dac BgP
16 PAHs


N 6
Concentrations (ng g^{-1} dw)
200
150
100
50
0
Nap Acy Ace Flu Phe Ant Fla Pyr BaA Chr BbF BkF BaP Inp Dac BgP
16 PAHs



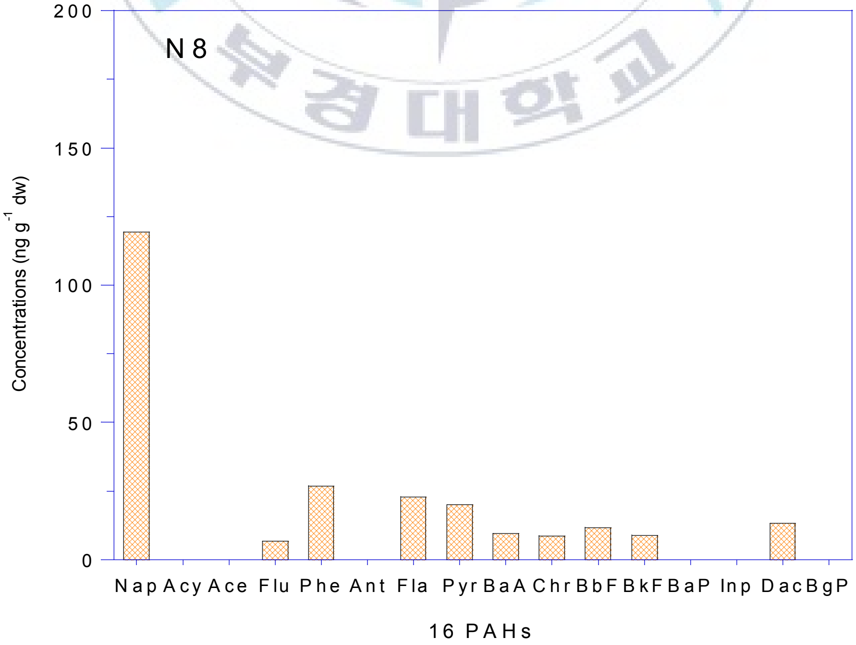


Fig. 21. The concentrations of each PAH in surface sediments from Nakdong River.

4. 8. Sources and ecological risk assessment of PAHs in Nakdong River

In Nakdong River, the ratios of Ant/(Ant+Phe) were all below 0.1 (Fig 23), representing petroleum sources. The ratios of Fla/(Fla+Pyr) suggested most of the PAHs were grass, wood and coal combustion sources. Meanwhile, most of stations were attribute to combustion sources based on the ratios of BaA/(BaA+Chr), whereas the ratios of Inp/(Inp+BgP) indicated sampling sites N1 and N7 for grass, wood and coal combustion sources, N5 and N6 for petroleum combustion sources and N2, N3, N4, N6 for petroleum sources,

In this study, the values of M-ERM-Q were all below 0.1 (Fig 22), resulting in a low ecological risk in Nakdong River.

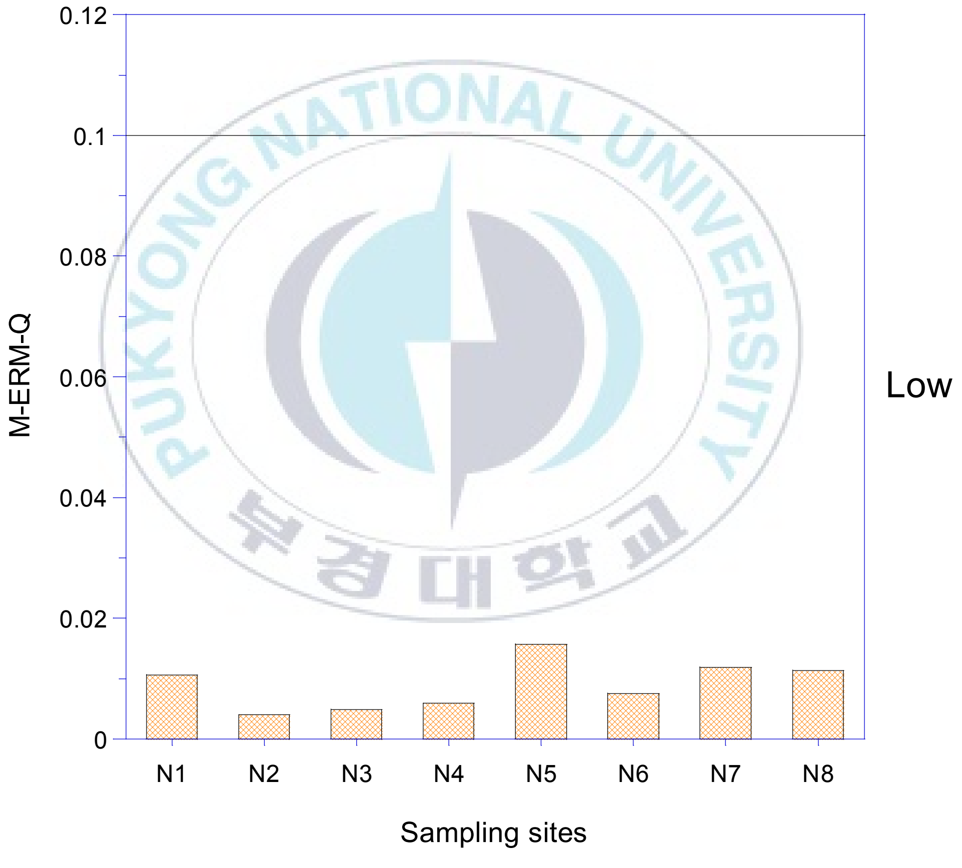


Fig. 22. Spatial distribution of M-ERM-Q in the surface sediments of Gwangalli.

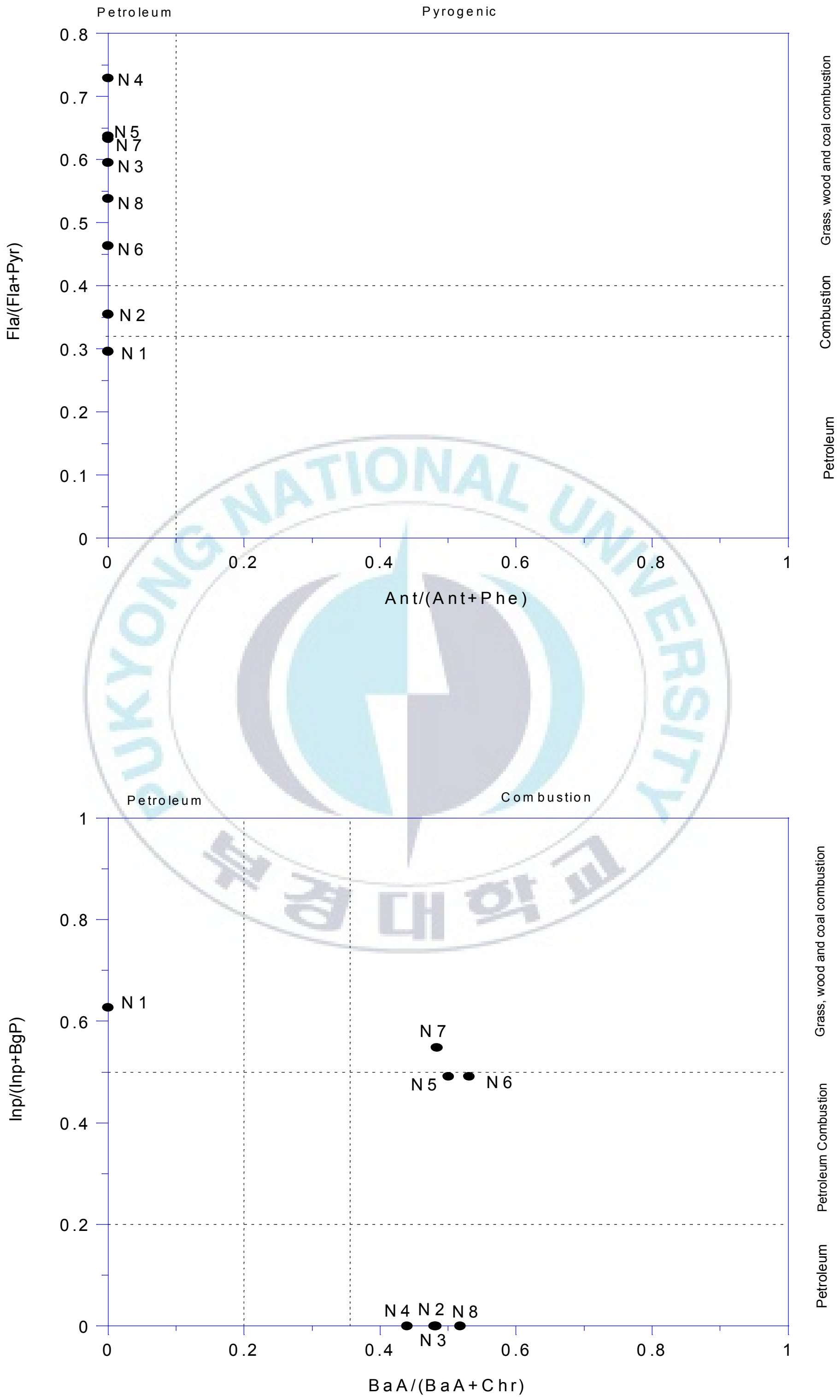


Fig. 23. Source apportionment of PAHs in Nakdong River.

5. Conclusions

This study investigated the total concentrations and the contamination degrees of heavy metals and 16 PAHs in the surface sediments from Gwangalli and Nakdong River. The various sediments quality guidelines showed the sedimentary environment was in good condition in Gwangalli area, whereas all of them indicated metal Cd might cause adverse ecological risks. Similarly, the four risk indices suggested an obvious pollution by Cd. According to mean PEL quotient, all sites in Gwangalli had a 21 % of probability of toxicity. As for PAHs in surface sediments from Gwangalli, the PAHs level were ranged from moderate to high [53]. The compositions of 16 PAHs were mainly 2-ring and 5-ring compounds. Meanwhile, the source apportionment indicated that combustion but grass, wood and coal combustion sources. Most PAHs were below the ERL values except Dac. Based on the values of M-ERM-Q, sites G3 to G6 presented low ecological risks, whereas site G1 and G2 had medium-low ecological risk level.

In Nakdong River, heavy metal of Cd posed a relatively higher risk among other five metals according to sediment quality guidelines and four risk assessment indices. The values of mean PEL quotient resulted in 21 % probability of being toxic at most of the sampling sites (except site N6) from Nakdong River. For PAHs, the PAHs level were moderate. Meanwhile, 2-ring compounds were predominant in 16 PAHs and sources apportionment indicated petroleum and combustion sources. All concentrations of PAHs in surface sediment of Nakdong River were below the ERL values except Nap in site N5 and the M-ERM-Q values indicated low ecological risks, which showed a good sedimentary condition. However, with rapid economical development coupled with anthropogenic activities, the Gwangalli and Nakdong River should be properly managed to protect the sedimentary environment.

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